Carbene-anchored/pendent-imidazolium species as precursors to di-*N*-heterocyclic carbene-bridged mixed-metal complexes†

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Reaction of a series of linked diimidazolium dibromide salts with one-half equivalent of $[Rh(\mu\text{-}OAc)(COD)]_2$ under reflux conditions generates a series of carbene-anchored/pendent-imidazolium complexes, $[RhBr(COD)(^{R}C(H)\text{-}\eta^1\text{-}C^{eth})][Br]$ ($^{Me}C(H)\text{-}\eta^1\text{-}C^{eth}$ = ethylene[(*N*-methyl)imidazolium][(*N*-methyl)imidazole-2-ylidene] and $^{tBu}C(H)\text{-}\eta^1\text{-}C^{eth}$ = ethylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene]) *via* deprotonation of one end of the diimidazolium salt and coordination of the resulting carbene to Rh. Reaction of these complexes with carbon monoxide or the appropriate diphosphine yields either $[RhBr(CO)_2(^{R}C(H)\text{-}\eta^1\text{-}C^{eth})][Br]$ (R = Me, ^{t}Bu) or $[RhBr(P^\frown P)(^{Me}C(H)\text{-}\eta^1\text{-}C^{eth})][Br]$ ($P^\frown P = Ph_2PCH_2PPh_2$, $Ph_2PCH_2CH_2PPh_2$, $Et_2PCH_2PEt_2$), respectively. The resulting diphosphine complexes readily decompose in solution. A series of palladium complexes $[PdI_{3\text{-}n}(PR_3)_n(L)][I]_n$ (n = 1,2) and $[PdI(P^\frown P)(L)][I]_2$ (L = $^{tBu}C(H)\text{-}\eta^1\text{-}C^{meth}$, $^{tBu}C(H)\text{-}\eta^1\text{-}C^{eth}$; $^{tBu}C(H)\text{-}\eta^1\text{-}C^{meth}$ = methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene]), containing the linked NHC-imidazolium moiety, have also been prepared by reacting the triiodo complexes, $[PdI_3(^{tBu}C(H)\text{-}\eta^1\text{-}C^{meth})]$ and $[PdI_3(^{tBu}C(H)\text{-}\eta^1\text{-}C^{eth})]$ with several mono- and diphosphines. Attempts to generate mixed Rh/Pd complexes using $Pd(OAc)_2$ to deprotonate the pendent arm of several of the above carbene-anchored/pendent-imidazolium complexes of Rh have proven unsuccessful. However, a targeted di-NHC-bridged heterobimetallic complex $[PdI_2(PEt_3)(\mu\text{-}^{tBu}CC^{meth})RhI(COD)]$ (^{tBu} CC^{meth} = 1,1′-methylene-3,3′-di-*tert*-butyldiimidazol-2,2′-diylidene) can be generated by deprotonation of the imidazolium group in $[PdI_2(PEt_3)(^{tBu}C(H)\text{-}\eta^1\text{-}C^{meth})][I]$ using half an equivalent of $[Rh(\mu\text{-}OAc)(COD)]_2$. The X-ray structure determination of this Pd/Rh complex confirms the dicarbene-bridged formulation and shows a metal-metal separation of approximately 6.2 Å. Reaction of this Rh/Pd complex with CO yields the corresponding dicarbonyl product $[PdI_2(PEt_3)(\mu\text{-}^{tBu}CC^{meth})RhI(CO)_2]$ *via* replacement of the COD ligand. The related dicarbene-bridged Ir/Rh complex $[IrBr(COD)(\mu\text{-}^{tBu}CC^{meth})RhBr(COD)]$ can be generated by reaction of $[IrBr(COD)(^{tBu}C(H)\text{-}\eta^1\text{-}C^{meth})][Br]$ with $[Rh(\mu\text{-}OAc)(COD)]_2$, while the Pd/Ir complexes $[PdI_2(PR_3)(\mu\text{-}^{tBu}CC^{meth})IrI(COD)]$ (PR_3 = PPh_3, PMe_2Ph) can be generated by reaction of the monometallic $[PdI_2(PR_3)(^{tBu}C(H)\text{-}\eta^1\text{-}C^{meth})][I]$ species with $K[N(SiMe_3)_2]$ in the presence of $[Ir(\mu\text{-}Cl)(COD)]_2$. The carbonyl analogues, $[PdI_2(PR_3)(\mu\text{-}^{tBu}CC^{meth})IrI(CO)_2]$, can be generated *via* a gentle purge of CO gas. These di-NHC-bridged heterobimetallic species represent some of the first examples of this class and are the first involving palladium.

Introduction

N-heterocyclic carbenes (NHCs)[1–4] have emerged as versatile ligands in organometallic chemistry, and offer a useful alternative to the ubiquitous phosphine ligands.[5–15] Although these carbene ligands are considered to have bonding properties similar to those of trialkylphosphines[16–19] their steric properties differ significantly; whereas phosphines are often described as conical,[20] NHC ligands having an unsaturated backbone are more planar, having a slimmer, less sterically hindered axis perpendicular to the carbene ring plane. This quasi two-dimensional shape is evident in square-planar complexes of NHCs in which the NHC plane is usually perpendicular to the metal coordination plane.[21–28]

Most reports on NHC complexes involve monocarbenes,[1–4] however there are a number of reports involving di-*N*-heterocyclic carbenes (di-NHCs), in which pairs of NHC groups are linked in a number of ways, as replacements for chelating[16,29–41] or bridging[7,8,16,29–32,34–45] diphosphines. Our initial study on binuclear di-NHC-bridged complexes concentrated on *homo*binuclear complexes of rhodium.[46] However our ongoing interest in mixed-metal systems,[47–56] and their use as mixed-metal catalysts[57–60] led us to extend our investigation to complexes in which di-NHC ligands could be used as bridging groups connecting *different* pairs of metals.

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† Electronic supplementary information (ESI) available: ^{1}H and $^{13}C\{^1H\}$ NMR spectra of **2c**, **8b**, **10b** and **23b**; decoupled spectra for **9b**; variable temperature spectral data for **18b**. CCDC reference numbers 726822–726827. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b906884h

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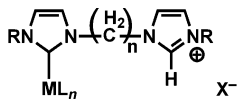
For the rational generation of mixed-metal species it appeared that stepwise incorporation of the different metals was the most straightforward strategy. A series of carbene-anchored/pendent-imidazolium salts of the type diagrammed in Chart 1,[11,37,42,43,46,61–69] appeared ideal for this purpose, through deprotonation of the pendent imidazolium salt in the presence of the second metal. We therefore set out to generate a more extensive series of such pendent species and to use them as synthons for a series of dicarbene-bridged mixed-metal complexes. The results of this study, in which the first series of di-NHC-bridged heterobinuclear compounds[69] are characterized, are reported herein.



$[ML_n(^{R}C(H)\text{-}\eta^1\text{-}C^{alk})][X]$

alk = meth (n = 1), eth (n = 2)

Chart 1

Experimental

General comments

All solvents were dried (using appropriate drying agents), distilled before use, and stored under a dinitrogen atmosphere. Deuterated solvents used for NMR experiments were freeze-pump-thaw degassed and stored under argon over appropriate molecular sieves. Reactions were performed under an inert argon atmosphere or the reactant gas using standard Schlenk techniques. Unless otherwise specified, reactions were carried out at ambient temperature. Ammonium carbonate, *tert*-butylamine, 1,5-cyclooctadiene, 1,2-dibromoethane, dibromomethane, bis(diphenylphosphino)methane (dppm), formaldehyde, glyoxal, 1-methylimidazole, palladium(II) acetate, potassium bis(trimethylsilyl)amide, triethylphosphine, triphenylphosphine and sodium iodide were purchased from Aldrich; diammonium hexachloroiridate(IV), 1,2-bis(diphenylphosphino)ethane (dppe), dimethylphenylphosphine, trimethylphosphine and rhodium(III) chloride hydrate were purchased from Strem; potassium bromide was purchased from BDH; and sodium acetate was purchased from Fischer Scientific. All chemicals were used without further purification, with the exception of sodium acetate, which was purified by repetitive melting under dynamic vacuum before use. 1-*tert*-Butylimidazole was prepared using a published procedure and purified by vacuum distillation.[70,71] The preparations of diimidazolium salts used in this paper have been reported;[11,16,30,72] however, a general synthetic approach has been outlined below. Bis(diethylphosphino)methane (depm) was prepared using published procedures and used without further purification,[73] as was bis(cycloocta-1,5-diene)(μ-dichloro)-dirhodium ($[Rh(\mu\text{-}Cl)(COD)]_2$) and bis(cycloocta-1,5-diene)-(μ-dichloro)diiridium ($[Ir(\mu\text{-}Cl)(COD)]_2$).[74,75] Bis(cycloocta-1,5-diene)(μ-diacetato)dirhodium ($[Rh(\mu\text{-}OAc)(COD)]_2$) was prepared as previously reported and recrystallized from ethyl acetate.[76] The pendent complex methylene[(*N*-*tert*-butyl)-imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene]bromo(η^2:η^2-1,5-cyclooctadiene)iridium(I) bromide was prepared similarly to the reported iodo analogue,[11] while methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene]triiodo-palladium(II) was prepared as previously reported.[63] The ^{1}H, ^{13}C and ^{31}P{^{1}H} NMR spectra were recorded on a Varian DirectDrive 500 MHz, iNova-500, or iNova-400 spectrometer operating at 499.82, 498.12, or 399.79 MHz for ^{1}H; 125.68, 125.26, or 100.53 MHz for ^{13}C; and 202.33, 201.64, or 161.8 MHz for ^{31}P, respectively; or on a Varian iNova-300 operating at 299.97 MHz for ^{1}H. The ^{1}H and ^{13}C{^{1}H} chemical shifts are referenced to TMS; whereas the ^{31}P{^{1}H} chemical shifts are referenced to 85% H_3PO_4. Elemental analyses were performed by the microanalytical service within this department. Likewise, mass spectrometric analyses were performed by the departmental Mass Spectrometry Laboratory using positive ion electrospray ionization on a Micromass ZabSpec Hybrid Sector-TOF or an Agilent Technologies 6220 Accurate-mass TOF LC/MS. Infrared spectra were obtained using a Nicolet Avatar 370DGTS instrument. Carbonyl stretches reported are for non-isotopically enriched samples. Conductivity measurements on compounds **10b** and **15b** as the iodide salts were carried out on 1×10^{-3} M solutions in nitromethane using a Yellow Springs Instruments Model 31 conductivity bridge. For these species the conductivities obtained were $\Lambda = 82.8$ and 135.2 Ω^{-1} cm^2 mol^{-1}, respectively.

Preparation of compounds

(a) General synthetic route to diimidazolium salts (1a–d). A 500 mL round-bottom flask was charged with 100 mmol of the dibromoalkane and dissolved in 200 mL of toluene. An excess (250 mmol) of the 1-alkylimidazole was then added and the solution refluxed for 24 h. The resulting precipitate was collected by vacuum filtration and recrystallized from boiling methanol by cooling to −25 °C, whereupon colourless crystals were obtained in yields ranging from 50 to 90%. The salts were then dried *in vacuo* for several days to remove residual solvent and stored in a desiccator before use. In this paper we use the abbreviations originally suggested by Green and coworkers,[42] with compounds **1a–d** as diprotonated versions of the respective dicarbenes $^{Me}CC^{meth}$ (**a**), $^{tBu}CC^{meth}$ (**b**), $^{Me}CC^{eth}$ (**c**), $^{tBu}CC^{eth}$ (**d**) as dibromide salts, namely 1,1′-(methylene)-3,3′-dimethyldiimidazolium-2,2′-diylidene dibromide **1a**), 1,1′-(methylene)-3,3′-di-*tert*-butyldiimidazolium-2,2′-diylidene dibromide (**1b**), 1,1′-(1,2-ethylene)-3,3′-dimethyldiimidazolium-2,2′-diylidene dibromide (**1c**) and 1,1′-(1,2-ethylene)-3,3′-di-*tert*-butyldiimidazolium-2,2′-diylidene dibromide (**1d**). As an adaptation of these abbreviations, the carbene-anchored/pendent-imidazolium ligands are designated as $^{Me}C(H)\text{-}\eta^1\text{-}C^{meth}$, $^{tBu}C(H)\text{-}\eta^1\text{-}C^{meth}$, $^{Me}C(H)\text{-}\eta^1\text{-}C^{eth}$ and $^{tBu}C(H)\text{-}\eta^1\text{-}C^{eth}$.

(b) Ethylene[(*N*-methyl)imidazolium][(*N*-methyl)imidazole-2-ylidene)bromo(η^2:η^2-cyclooctadiene)rhodium(I)] bromide, [RhBr(COD)($^{Me}C(H)\text{-}\eta^1\text{-}C^{eth}$)][Br] (2c). A 20 mL portion of CH_3CN was added to a solid mixture containing **1c** (422 mg, 1.17 mmol) and $[Rh(\mu\text{-}OAc)(COD)]_2$ (301 mg, 0.56 mmol). The resulting slurry was stirred for 18 h under reflux conditions and cooled to room temperature. The solvent was then removed under reduced pressure and the crude product redissolved in 10 mL of CH_2Cl_2. A 45 mL portion of diethyl ether was added to precipitate a white solid and the solution filtered *via* cannula. The solvent was removed under reduced pressure, giving 261 mg (83%).

^{1}H NMR (399.79 MHz, CD_2Cl_2, 27.0 °C): 10.18 (br dd, 1H, $^4J_{H\text{-}H}$ = 1.9 Hz, $^4J_{H\text{-}H}$ = 1.9 Hz, NCHN); 7.90 (dd, 1H, $^3J_{H\text{-}H}$ = 1.9 Hz, $^4J_{H\text{-}H}$ = 1.9 Hz), 7.15 (dd, 1H, $^3J_{H\text{-}H}$ = 1.9 Hz, $^4J_{H\text{-}H}$ = 1.9 Hz, $NCH_{imid\text{-}H}$); 4.03 (s, 3H, $N_{imid\text{-}H}CH_3$); 7.22 (d, 1H, $^3J_{H\text{-}H}$ = 1.9 Hz), 6.76 (d, 1H, $^3J_{H\text{-}H}$ = 1.9 Hz, $NCH_{imid\text{-}Rh}$); 3.96 (s, 3H, $N_{imid\text{-}Rh}CH_3$); 5.60 (m, 1H), 5.12 (m, 2H), 4.99 (m, 1H, NCH_2CH_2N); 5.09 (m, 1H), 4.99 (m, 1H), 3.48 (m, 1H), 3.30 (m, 1H), 2.41 (m, 4H), 1.97 (m, 4H, COD). $^{13}C\{^1H\}$ NMR (125.68 MHz, CD_2Cl_2, 27.0 °C): 182.8 (d, 1C, $^1J_{C\text{-}Rh}$ = 50.1 Hz, $C_{carbene}$); 124.1 (s, 1C, $NCH_{imid\text{-}Rh}$); 123.3 (s, 1C, $NCH_{imid\text{-}Rh}$); 36.9 (s, 1C, $N_{imid\text{-}Rh}CH_3$); 135.8 (s, 1C, $NCHN_{imid\text{-}H}$); 122.4 (s, 1C, $NCH_{imid\text{-}H}$); 122.3 (s, 1C, $NCH_{imid\text{-}H}$); 38.1 (s, 1C, $N_{imid\text{-}H}CH_3$); 50.0 (s, 1C), 49.6 (s, 1C, CH_2CH_2); 98.9 (d, 1C, $^1J_{C\text{-}Rh}$ = 7.0 Hz), 98.5 (d, 1C, $^1J_{C\text{-}Rh}$ = 7.0 Hz), 71.0 (d, 1C, $^1J_{C\text{-}Rh}$ = 15.0 Hz), 69.5 (d, 1C, $^1J_{C\text{-}Rh}$ = 15.0 Hz), 33.5 (s, 1C), 32.3 (s, 1C), 30.0 (s, 1C), 28.6 (s, 1C, COD). HRMS *m/z* Calcd for $C_{18}H_{27}BrN_4Rr$ (M^+ – Br): 481.0469. Found: 481.0470 (M^+ – Br). Anal. Calcd for $C_{18}H_{27}Br_2N_4Rh \cdot 0.17\ CH_2Cl_2$: C, 37.85; H, 4.8; N, 9.7. Found: C, 37.6; H, 4.8; N, 9.9. The presence of 0.17 equivalents of CH_2Cl_2 was confirmed by ^{1}H NMR spectroscopy in chloroform. The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of this compound are given in the electronic supplementary information, ESI (Fig. S1).†

(c) Ethylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)bromo-(η^2:η^2-cyclooctadiene)rhodium(I)] bromide, [RhBr(COD)(^{tBu}C(H)-η^1-C^{eth})][Br] (2d). The desired complex was prepared as described for **2c**, using **1d** (818 mg, 1.875 mmol) and [Rh(μ-OAc)(COD)]$_2$ (507 mg, 0.938 mmol) in 40 mL of CH_3CN, heated at reflux for 75 h. The crude product was purified as described for **2c**, and isolated using 10 mL of CH_2Cl_2 and 45 mL of diethyl ether, resulting in 835 mg (69%) of a yellow solid. ^{1}H NMR (399.79 MHz, CD_2Cl_2, 27.0 °C): 9.93 (dd, 1H, $^4J_{H\text{-}H}$ = 2.2 Hz, $^4J_{H\text{-}H}$ = 2.2 Hz, NCHN); 7.98 (dd, 1H, $^3J_{H\text{-}H}$ = 2.2 Hz, $^4J_{H\text{-}H}$ = 2.2 Hz), 7.29 (dd, 1H, $^3J_{H\text{-}H}$ = 2.2 Hz, $^4J_{H\text{-}H}$ = 2.2 Hz, $NCH_{imid\text{-}H}$); 1.94 (s, 3H, $N_{imid\text{-}H}C(CH_3)_3$); 7.16 (d, 1H, $^3J_{H\text{-}H}$ = 2.2 Hz), 6.96 (d, 1H, $^3J_{H\text{-}H}$ = 2.2 Hz, $NCH_{imid\text{-}Rh}$); 1.66 (s, 3H, $N_{imid\text{-}Rh}C(CH_3)_3$); 5.66 (m, 2H), 5.31 (m, 1H), 5.04 (m, 1H, NCH_2CH_2N); 5.07 (m, 1H), 4.94 (m, 1H), 3.42 (m, 1H), 3.30 (m, 1H), 2.39 (m, 4H), 1.89 (m, 2H), 1.65 (m, 2H, COD). $^{13}C\{^1H\}$ NMR (100.54 MHz, CD_2Cl_2, 27.0 °C): 180.5 (d, 1C, $^1J_{C\text{-}Rh}$ = 49.4 Hz, $C_{carbene}$); 120.0 (s, 1C, $NCH_{imid\text{-}Rh}$); 118.7 (s, 1C, $NCH_{imid\text{-}Rh}$); 59.0 (s, 1C), 32.1 (s, 3C, $N_{imid\text{-}Rh}C(CH_3)_3$); 135.8 (s, 1C, $NCHN_{imid\text{-}H}$); 122.8 (s, 1C, $NCH_{imid\text{-}H}$); 124.0 (s, 1C, $NCH_{imid\text{-}H}$); 60.4, (s, 1C), 30.0 (s, 3C, $N_{imid\text{-}H}C(CH_3)_3$); 51.6 (s, 1C), 48.9 (s, 1C, CH_2CH_2); 96.8 (d, 1C, $^1J_{C\text{-}Rh}$ = 7.5 Hz), 94.1 (d, 1C, $^1J_{C\text{-}Rh}$ = 6.9 Hz), 71.9 (d, 1C, $^1J_{C\text{-}Rh}$ = 15.4 Hz), 70.3 (d, 1C, $^1J_{C\text{-}Rh}$ = 14.1 Hz), 32.8 (s, 1C), 31.4 (s, 1C), 29.5 (s, 1C), 29.0 (s, 1C, COD). HRMS *m/z* Calcd for $C_{24}H_{39}BrN_4Rh$ (M^+ – Br): 565.1408. Found: 565.1410 (M^+ – Br). Anal. Calcd for $C_{24}H_{39}Br_2N_4Rh$: C, 44.6; H, 6.1; N, 8.7. Found: C, 44.95; H, 6.2; N, 8.6.

(d) Ethylene[(*N*-methyl)imidazolium][(*N*-methyl)imidazole-2-ylidene)bromo-dicarbonylrhodium(I)] bromide, [RhBr(CO)$_2$-(^{Me}C(H)-η^1-C^{eth})][Br] [3c]. A 10 mL portion of CH_2Cl_2 was added to a flask containing **2c** (175 mg, 0.311 mmol). A 15 min gentle purge of CO to a stirring solution yielded a more pale yellow solution. The conversion to the respective dicarbonyl complex **3c** was accompanied by the facile loss of 1,5-cyclooctadiene and was monitored to completion using ^{1}H NMR spectroscopy. The solvent was then removed under reduced pressure and the crude product redissolved in 10 mL of CH_2Cl_2. A 30 mL portion of diethyl ether was added to precipitate an oily pale yellow solid, which was washed with 3 × 25 mL portions of pentane before drying *in vacuo*, giving 157 mg (85%). ^{1}H NMR (399.79 MHz, CD_2Cl_2, 27.0 °C): 10.11 (br dd, 1H, NCHN); 7.62 (br dd, 1H), 7.15 (br dd, 1H, $NCH_{imid\text{-}H}$); 3.98 (s, 3H, $N_{imid\text{-}H}CH_3$); 7.72 (d, 1H, $^3J_{H\text{-}H}$ = 1.7 Hz), 6.96 (d, 1H, $^3J_{H\text{-}H}$ = 1.7 Hz, $NCH_{imid\text{-}Rh}$); 3.86 (s, 3H, $N_{imid\text{-}Rh}CH_3$); 5.56 (br m, 3H), 5.33 (br m, 1H, NCH_2CH_2N). $^{13}C\{^1H\}$ NMR (125.68 MHz, CD_2Cl_2, 27.0 °C): 186.2 (d, 1C, $^1J_{C\text{-}Rh}$ = 53.6 Hz), 182.1 (d, 1C, $^1J_{C\text{-}Rh}$ = 76.2 Hz, CO); 173.7 (d, 1C, $^1J_{C\text{-}Rh}$ = 42.6 Hz, $C_{carbene}$); 138.1 (s, 1C, NCHN); 124.2 (s, 1C), 123.6 (s, 1C), 123.4 (s, 1C), 122.7 (s, 1C, NCH); 50.3 (s, 1C), 49.6 (s, 1C, CH_2CH_2); 38.8 (s, 1C), 37.0 (s, 1C, NCH_3). IR (solution, cm^{-1}): 2083 (CO), 2007 (CO). HRMS *m/z* Calcd for $C_{12}H_{15}BrN_4O_2Rh$ (M^+ – Br): 428.9428. Found: 428.9427 (M^+ – Br). Compound **3c** could only be isolated as an oil so satisfactory elemental analyses could not be obtained.

(e) Ethylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)bromo-dicarbonylrhodium(I)] bromide, [RhBr(CO)$_2$-(^{tBu}C(H)-η^1-C^{eth})][Br] (3d). The desired complex was prepared as described for **3c** using **2d** (152 mg, 0.235 mmol), and the crude product purified using 10 mL of CH_2Cl_2 and 25 mL of diethyl ether, to precipitate an oily pale yellow solid, which was then washed with 2 × 25 mL portions of pentane before drying *in vacuo*, giving 104 mg (87%). ^{1}H NMR (299.97 MHz, CD_2Cl_2, 27.0 °C): 10.01 (dd, 1H, $^4J_{H\text{-}H}$ = 1.8 Hz, $^4J_{H\text{-}H}$ = 1.8 Hz NCHN); 7.90 (dd, 1H, $^3J_{H\text{-}H}$ = 1.8 Hz, $^4J_{H\text{-}H}$ = 1.8 Hz), 7.51 (dd, 1H, $^3J_{H\text{-}H}$ = 1.8 Hz, $^4J_{H\text{-}H}$ = 1.8 Hz, $NCH_{imid\text{-}H}$); 1.94 (s, 9H, $N_{imid\text{-}H}C(CH_3)_3$); 7.60 (d, 1H, $^3J_{H\text{-}H}$ = 2.0 Hz), 7.35 (d, 1H, $^3J_{H\text{-}H}$ = 2.0 Hz, $NCH_{imid\text{-}Rh}$); 1.82 (s, 9H, $N_{imid\text{-}Rh}C(CH_3)_3$); 5.70 (br m, 2H), 5.31 (br m, 2H, NCH_2CH_2N). $^{13}C\{^1H\}$ NMR (100.54 MHz, CD_2Cl_2, 27.0 °C): 186.2 (d, 1C, $^1J_{C\text{-}Rh}$ = 54.2 Hz), 182.3 (d, $^1J_{C\text{-}Rh}$ = 77.8 Hz, CO); 171.5 (d, 1C, $^1J_{C\text{-}Rh}$ = 42.1 Hz, $C_{carbene}$); 136.0 (s, 1C, NCHN); 124.7 (s, 1C), 122.9 (s, 1C), 120.7 (s, 1C), 118.8 (s, 1C, NCH); 59.3 (s, 1C), 30.0 (s, 3C, $N_{imid\text{-}Rh}C(CH_3)_3$); 60.8 (s, 1C), 32.1 (s, 3C, $N_{imid\text{-}H}C(CH_3)_3$); 51.7 (s, 1C), 48.4 (s, 1C, CH_2CH_2). IR (solution, cm^{-1}): 2081 (CO), 2005 (CO). HRMS *m/z* Calcd for $C_{18}H_{27}BrN_4O_2Rh$ (M^+ – Br): 513.0367. Found: 513.0366 (M^+ – Br). Compound **3d** could only be isolated as an oil so satisfactory elemental analyses could not be obtained.

(f) Ethylene[(*N*-methyl)imidazolium][(*N*-methyl)imidazole-2-ylidene)bromo(η^1:η^1-bis(diphenylphosphino)methane)rhodium(I)] bromide, [RhBr(dppm)(^{Me}C(H)-η^1-C^{eth})][Br] (4c). A 10 mL portion of CH_2Cl_2 was added to a solid mixture containing **2c** (49 mg, 0.087 mmol) and dppm (39 mg, 0.101 mmol). The resulting solution bleached to a paler yellow immediately. ^{1}H NMR (299.97 MHz, CD_2Cl_2, 27.5 °C): 10.15 (br s, 1H, NCHN); 7.21 (br s, 1H), 6.79 (br, 1H, $NCH_{imid\text{-}H}$); 3.95 (s, 3H, $N_{imid\text{-}H}CH_3$); 8.04 (d, 1H, $^3J_{H\text{-}H}$ = 1.8 Hz), 6.79 (br s, 1H, $NCH_{imid\text{-}Rh}$); 3.91 (s, 3H, $N_{imid\text{-}Rh}CH_3$); 4.44 (m, 2H), 4.09 (m, 2H, NCH_2CH_2N); 8.04 (m, 4H), 7.34 (m, 16H, Ph); 5.88 (ddd, 1H, $^2J_{H\text{-}H}$ = 13.7 Hz, $^2J_{H\text{-}P}$ = 9.7 Hz, $^2J_{H\text{-}P}$ = 6.5 Hz), 4.70 (ddd, 1H, $^2J_{H\text{-}H}$ = 13.7 Hz, $^2J_{H\text{-}P}$ = 3.6 Hz, $^2J_{H\text{-}P}$ = 3.6 Hz, PCH_2P). $^{31}P\{^1H\}$ NMR (161.84 MHz, CD_2Cl_2, 27.0 °C): –13.6 (dd, 1P, $^1J_{P\text{-}Rh}$ = 172.8 Hz, $^2J_{P\text{-}P}$ = 95.9 Hz), –36.0 (dd, 1P, $^1J_{P\text{-}Rh}$ = 103.9 Hz, $^2J_{P\text{-}P}$ = 95.9 Hz, dppm). The transient nature of the product precluded the acquisition of $^{13}C\{^1H\}$ NMR spectra and elemental analyses.

(g) Ethylene[(*N*-methyl)imidazolium][(*N*-methyl)imidazole-2-ylidene)bromo(η^1:η^1-bis(diphenylphosphino)ethane)rhodium(I)] bromide, [RhBr(dppe)(^{Me}C(H)-η^1-C^{eth})][Br] (5c). The desired complex was prepared as described for **4c** using **2c** (87 mg, 0.155 mmol) and dppe (62 mg, 0.156 mmol). The resulting solution bleached to a paler yellow immediately. ^{1}H NMR (299.97 MHz, CD_2Cl_2, 27.5 °C): 10.12 (br s, 1H, NCHN); 7.92 (br s, 1H), 7.07 (br s, 1H, $NCH_{imid\text{-}H}$); 3.92 (s, 3H, $N_{imid\text{-}H}CH_3$); 6.87 (br s, 1H), 6.65 (br s, 1H, $NCH_{imid\text{-}Rh}$); 3.72 (s, 3H, $N_{imid\text{-}Rh}CH_3$); 7.98 (m, 4H, NCH_2CH_2N); 7.33 (m, 20H, Ph); 2.02 (m, 4H, PCH_2CH_2P). ^{31}P{^{1}H} NMR (161.84 MHz, CD_2Cl_2, 27.0 °C): 72.9 (dd, 1P, $^1J_{P\text{-}Rh}$ = 197.6 Hz, $^2J_{P\text{-}P}$ = 33.4 Hz), 57.4 (dd, 1P, $^1J_{P\text{-}Rh}$ = 125.3 Hz, $^2J_{P\text{-}P}$ = 33.4 Hz, dppe). The transient nature of the product precluded the acquisition of ^{13}C{^{1}H} NMR spectra and elemental analyses.

(h) Ethylene[(*N*-methyl)imidazolium][(*N*-methyl)imidazole-2-ylidene)bromo(η^1:η^1-bis(diethylphosphino)methane)rhodium(I)] bromide, [RhBr(depm)(^{Me}C(H)-η^1-C^{eth})][Br] (6c). A 10 mL portion of CH_2Cl_2 was added to a flask containing 2c (50 mg, 0.089 mmol). The resulting solution was stirred for 10 min after which depm (30.2 μL, 0.134 mmol) was injected into the reaction vessel bleaching the solution to a paler yellow immediately. ^{1}H NMR (400.39 MHz, CD_2Cl_2, 27.0 °C): 10.29 (br s, 1H, NCHN); 7.90 (br s, 1H), 6.77 (br s, 1H, $NCH_{imid\text{-}H}$); 3.97 (s, 3H, $N_{imid\text{-}H}CH_3$); 8.16 (br s, 1H), 7.03 (br s, 1H, $NCH_{imid\text{-}Rh}$); 3.91 (s, 3H, $N_{imid\text{-}Rh}CH_3$); 5.10 (m, 4H, NCH_2CH_2N); 2.41 (m, 2H), 1.82 (m, 8H), 1.28 (m, 5H), 0.97 (m, 5H, PEt_2); 5.90 (ddd, 1H, $^2J_{H\text{-}H}$ = 14.2 Hz, $^2J_{H\text{-}P}$ = 11.9 Hz, $^2J_{H\text{-}P}$ = 6.9 Hz), 4.89 (ddd, 1H, $^2J_{H\text{-}H}$ = 14.2 Hz, $^2J_{H\text{-}P}$ = 14.2 Hz, $^2J_{H\text{-}P}$ = 4.1 Hz, PCH_2P). ^{31}P{^{1}H} NMR (161.08 MHz, CD_2Cl_2, 27.0 °C): −11.5 (dd, 1P, $^1J_{P\text{-}Rh}$ = 169.1 Hz, $^2J_{P\text{-}P}$ = 102.7 Hz), −30.2 (dd, 1P, $^1J_{P\text{-}Rh}$ = 102.7 Hz, $^2J_{P\text{-}P}$ = 102.7 Hz, depm). The transient nature of the product precluded the acquisition of ^{13}C{^{1}H} NMR spectra, as well as and elemental analyses.

(i) Methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)]-triiodopalladium(II), [PdI$_3$(^{tBu}C(H)-η^1-C^{eth})] (7d). A 20 mL portion of DMSO was added to a solid mixture containing **1d** (664 mg, 1.522 mmol) and $Pd(OAc)_2$ (343 mg, 1.526 mmol). The resulting solution was heated at 50 °C for exactly 4 hours, during which time the solution bleached to a paler orange. At this point an excess of KI (19.456 g, 117.203 mmol) was added along with 8 mL DMSO. The resulting dark purple solution was heated for another hour. DMSO was removed overnight *in vacuo* at 50 °C to give a dark purple solid, which was then dissolved in a 30 mL:30 mL acetonitrile/water mixture. The solution was heated at 80 °C for 10 min followed by the removal of the acetonitrile *in vacuo* and filtered to precipitate a dark brown solid which was washed with CH_2Cl_2 to give the product as a brick red solid which was then recrystallized from acetonitrile, giving 956 mg (82%). ^{1}H NMR (399.80 MHz, DMSO-d_6, 26.5 °C): 9.17 (br dd, 1H, NCHN); 7.95 (br s, 1H), 7.68 (br s, 1H), 7.66 (br s, 1H), 7.31 (br s, 1H, NCH); 1.84 (s, 9H), 1.53 (s, 9H, $NC(CH_3)_3$); 4.92 (br s, 4H, NCH_2CH_2N). ^{13}C{^{1}H} NMR (125.27 MHz, DMSO-d_6, 26.5 °C): $C_{carbene}$ not visible; 135.3 (s, 1C, NCHN); 123.7 (s, 1C), 123.5 (s, 1C), 123.1 (s, 1C), 121.0 (s, 1C, NCH); 60.4 (s, 1C), 32.1 (s, 3C), 59.5 (s, 1C), 29.6 (s, 3C, $NC(CH_3)_3$); 52.4 (s, 1C), 47.4 (s, 1C, NCH_2CH_2N). HRMS *m/z* Calcd for $C_{16}H_{27}I_2N_4Pd$ (M^+ − I): 634.9355. Found: 634.9353 (M^+ − I). Anal Calcd for $C_{16}H_{27}I_3N_4Pd$: C, 25.2; H, 3.6; N, 7.35. Found: C, 25.4; H, 3.75; N, 7.5.

(j) Methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)]-diiodotrimethylphosphinopalladium(II) iodide, [PdI$_2$(PMe$_3$)(^{tBu}C(H)-η^1-C^{meth})][I] (8b). A 10 mL portion of CH_3CN was added to a flask containing **7b** (106 mg, 0.133 mmol). The resulting slurry was stirred for 10 min, after which PMe_3 (14.7 μL, 0.143 mmol) was injected into the reaction vessel. The slurry changed from dark red to a pale green solution almost instantly, and was stirred for another 10 min. The solvent was reduced to 5 mL under reduced pressure and passed through a bed of Celite *via* cannula to remove small deposits of colloidal Pd. The rest of the solvent was then removed under reduced pressure and the crude product redissolved in 10 mL of CH_2Cl_2. A 20 mL portion of diethyl ether was added to precipitate a bright orange solid, which was then washed with 3 × 7 mL portions of diethylether and 3 × 7 mL portions of pentane before drying *in vacuo*, giving 84 mg (72%). ^{1}H NMR (399.80 MHz, CD_3CN, 26.5 °C): 9.11 (dd, 1H, NCHN, $^4J_{H\text{-}H}$ = 1.7 Hz, $^4J_{H\text{-}H}$ = 1.7 Hz); 7.73 (dd, 1H, $^3J_{H\text{-}H}$ = 1.7 Hz, $^4J_{H\text{-}H}$ = 1.7 Hz), 7.61 (dd, 1H, $^3J_{H\text{-}H}$ = 1.7 Hz, $^4J_{H\text{-}H}$ = 1.7 Hz $NCH_{imid\text{-}H}$); 1.81 (s, 9H, $N_{imid\text{-}H}C(CH_3)_3$); 7.72 (dd, 1H, $^3J_{H\text{-}H}$ = 2.3 Hz, $^5J_{H\text{-}P}$ = 1.4 Hz), 7.53 (dd, 1H, $^3J_{H\text{-}H}$ = 2.3 Hz, $^5J_{H\text{-}P}$ = 2.3 Hz $NCH_{imid\text{-}Pd}$); 1.63 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); 6.69 (s, 1H, NCH_2N); 1.76 (d, 9H, $^2J_{H\text{-}P}$ = 10.4 Hz $P(CH_3)_3$). ^{13}C{^{1}H} NMR (100.54 MHz, DMSO-d_6, 26.5 °C): 163.3 (d, 1C, $^2J_{C\text{-}P}$ = 194.3 Hz, $C_{carbene}$); 136.6 (s, 1C, NCHN); 122.6 (s, 1C), 122.8 (s, 1C, $NCH_{imid\text{-}H}$); 124.2 (d, 1C, $^4J_{C\text{-}P}$ = 6.1 Hz), 123.5 (d, 1C, $^4J_{C\text{-}P}$ = 6.5 Hz, $NCH_{imid\text{-}Pd}$); 60.6 (s, 1C, NCH_2N); 62.6 (s, 1C), 31.9 (s, 3C, $N_{imid\text{-}H}$ $C(CH_3)_3$); 59.8 (s, 1C), 29.5 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 18.6 (d, 3C, $^1J_{C\text{-}P}$ = 32.2 Hz, $P(CH_3)_3$). ^{31}P{^{1}H} NMR (161.84 MHz, CD_3CN, 27.0 °C): −25.2 (s, 1P, $P(CH_3)_3$). HRMS *m/z* Calcd for $C_{18}H_{34}I_2N_4PPd$ (M^+ − I): 696.9640. Found: 696.9644 (M^+ − I). Repeated attempts to separate this compound from minor amounts of the double-substituted **12b** failed (as observed in the ^{1}H NMR spectrum) so elemental analysis could not be obtained. The ^{1}H and ^{13}C{^{1}H} NMR spectra of this compound are given in the ESI (Fig. S2).†

(k) Methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)]-diiodotriethylphosphinopalladium(II) iodide, [PdI$_2$(PEt$_3$)(^{tBu}C(H)-η^1-C^{meth})][I] (9b). The desired complex was prepared as described for **8b**, using **7b** (136 mg, 0.182 mmol) and PEt_3 (65.7 μL, 0.441 mmol). The slurry changed from dark red to a pale green solution almost instantly, and was stirred for another 20 min. The crude product was purified as described for **8b**, and isolated using 10 mL of CH_2Cl_2, 20 mL of diethyl ether and 20 mL of pentane to precipitate a bright yellow solid, which was then washed with 3 × 10 mL of pentane before drying *in vacuo*, giving 130 mg (82%). ^{1}H NMR (399.80 MHz, DMSO-d_6, 26.5 °C): 9.24 (dd, 1H, NCHN, $^4J_{H\text{-}H}$ = 1.8 Hz, $^4J_{H\text{-}H}$ = 1.8 Hz); 8.12 (dd, 1H, $^3J_{H\text{-}H}$ = 1.8 Hz, $^4J_{H\text{-}H}$ = 1.8 Hz, ^{t}BuNC$H_{imid\text{-}H}$); 7.92 (dd, 1H, $^3J_{H\text{-}H}$ = 1.8 Hz, $^4J_{H\text{-}H}$ = 1.8 Hz $H_2CNCH_{imid\text{-}H}$); 1.58 (s, 9H, $N_{imid\text{-}H}C(CH_3)_3$); 7.90 (dd, 1H, $^3J_{H\text{-}H}$ = 1.9 Hz, $^5J_{H\text{-}P}$ = 1.9 Hz, ^{t}BuNC$H_{imid\text{-}Pd}$); 7.84 (dd, 1H, $^3J_{H\text{-}H}$ = 1.9 Hz, $^5J_{H\text{-}P}$ = 1.3 Hz $CH_2NCH_{imid\text{-}Pd}$); 1.77 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); 6.67 (s, 1H, NCH_2N); 2.09 (dq, 6H, $^2J_{H\text{-}P}$ = 9.5 Hz, $^3J_{H\text{-}H}$ = 7.5 Hz), 1.07 (dt, 9H, $^3J_{H\text{-}P}$ = 16.2 Hz, $^3J_{H\text{-}H}$ = 7.5 Hz, $P(CH_2CH_3)_3$). ^{13}C{^{1}H} NMR (125.69 MHz, DMSO-d_6, 26.1 °C): 162.2 (d, 1C, $^2J_{C\text{-}P}$ = 185.9 Hz, $C_{carbene}$); 136.2 (s, 1C,

NCHN); 121.9 (s, 1C, ^{t}BuN*C*H$_{imid\text{-}H}$); 122.6 (s, 1C, CH$_2$N*C*H$_{imid\text{-}H}$); 123.6 (d, 1C, $^4J_{C\text{-}P}$ = 4.7 Hz, ^{t}BuN*C*H$_{imid\text{-}Pd}$); 124.0 (d, 1C, $^4J_{C\text{-}P}$ = 6.3 Hz, CH$_2$N*C*H$_{imid\text{-}Pd}$); 62.8 (s, 1C, NCH$_2$N); 60.7 (s, 1C), 29.4 (s, 3C, N$_{imid\text{-}H}$ C(CH$_3$)$_3$); 60.0 (s, 1C), 32.0 (s, 3C, N$_{imid\text{-}Pd}$C(CH$_3$)$_3$); 18.8 (d, 3C, $^1J_{C\text{-}P}$ = 30.2 Hz), 9.23 (s, 3C, P(CH$_2$CH$_3$)$_3$). ^{31}P{^{1}H} NMR (161.84 MHz, CD$_3$CN, 27.0 °C): 10.0 (s, 1P, P(CH$_2$CH$_3$)$_3$). HRMS *m/z* Calcd for $C_{21}H_{40}I_2N_4PPd$ (M$^+$ – I): 739.0115. Found: 739.0109 (M$^+$ – I). Anal Calcd for $C_{21}H_{40}I_3N_4PPd$: C, 29.1; H, 4.65; N, 6.5. Found: C, 28.9; H, 4.7; N, 6.3.

(l) Ethylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)]diiodo-triethylphosphinopalladium(II) iodide, [PdI$_2$(PEt$_3$)(^{tBu}C(H)-η^1-C^{eth})][I] (9d). The desired complex was prepared as described for **8b**, using **7d** (151 mg, 0.198 mmol) and PEt$_3$ (58.3 μL, 0.396 mmol). The slurry changed from dark red to a pale yellow solution almost instantly, and was stirred for another 30 min. The crude product was purified as described for **8b**, and isolated using 10 mL of CH_2Cl_2, 10 mL of diethyl ether and 30 mL of pentane to precipitate a bright yellow solid, which was then washed with 3 × 10 mL of pentane before drying *in vacuo*, giving 215 mg (81%). ^{1}H NMR (399.80 MHz, DMSO-d_6, 26.5 °C): 9.13 (dd, 1H, NCHN, $^4J_{H\text{-}H}$ = 1.5 Hz, $^4J_{H\text{-}H}$ = 1.5 Hz); 8.02 (dd, 1H, $^3J_{H\text{-}H}$ = 1.5 Hz, $^4J_{H\text{-}H}$ = 1.5 Hz); 7.61 (dd, 1H, $^3J_{H\text{-}H}$ = 1.5 Hz, $^4J_{H\text{-}H}$ = 1.5 Hz, NCH$_{imid\text{-}H}$); 1.77 (s, 9H, N$_{imid\text{-}H}$C(CH$_3$)$_3$); 7.75 (dd, 1H, $^3J_{H\text{-}H}$ = 1.9 Hz, $^5J_{H\text{-}P}$ = 1.9 Hz); 7.37 (dd, 1H, $^3J_{H\text{-}H}$ = 1.9 Hz, $^5J_{H\text{-}P}$ = 1.3 Hz, NCH$_{imid\text{-}Pd}$); 1.57 (s, 9H, N$_{imid\text{-}Pd}$C(CH$_3$)$_3$); 4.88 (m, 2H), 4.80 (m, 2H, NCH$_2$CH$_2$N); 2.08 (dq, 6H, $^2J_{H\text{-}P}$ = 9.4 Hz, $^3J_{H\text{-}H}$ = 7.7 Hz), 1.07 (dt, 9H, $^3J_{H\text{-}P}$ = 15.5 Hz, $^3J_{H\text{-}H}$ = 7.5 Hz, P(CH$_2$CH$_3$)$_3$). ^{13}C{^{1}H} NMR (100.54 MHz, DMSO-d_6, 26.5 °C): 159.5 (d, 1C, $^2J_{C\text{-}P}$ = 186.1 Hz, C$_{carbene}$); 135.2 (s, 1C, NCHN); 123.5 (s, 1C), 121.2 (s, 1C, NCH$_{imid\text{-}H}$); 123.0 (d, 1C, $^4J_{C\text{-}P}$ = 5.8 Hz), 122.7 (d, 1C, $^4J_{C\text{-}P}$ = 5.2 Hz, NCH$_{imid\text{-}Pd}$); 51.9 (s, 1C), 47.7 (s, 1C, NCH$_2$CH$_2$N); 60.4 (s, 1C), 29.6 (s, 3C, N$_{imid\text{-}H}$ C(CH$_3$)$_3$); 59.3 (s, 1C), 32.1 (s, 3C, N$_{imid\text{-}Pd}$C(CH$_3$)$_3$); 18.6 (d, 3C, $^1J_{C\text{-}P}$ = 28.3 Hz), 9.20 (s, 3C, P(CH$_2$CH$_3$)$_3$). ^{31}P{^{1}H} NMR (161.84 MHz, CD$_3$CN, 27.0 °C): 9.3 (s, 1P, P(CH$_2$CH$_3$)$_3$). HRMS *m/z* Calcd for $C_{22}H_{42}I_2N_4PPd$ (M$^+$ – I): 753.0266. Found: 753.0266 (M$^+$ – I). Anal Calcd for $C_{22}H_{42}I_3N_4PPd$: C, 30.0; H, 4.8; N, 6.4. Found: C, 31.3; H, 4.9; N, 6.7.

(m) Methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)]diiodo-triphenylphosphinopalladium(II) iodide, [PdI$_2$(PPh$_3$)(^{tBu}C(H)-η^1-C^{meth})][I] (10b). A 20 mL portion of CH_3CN was added to a solid mixture of containing **7b** (139 mg, 0.186 mmol) and PPh$_3$ (49 mg, 0.153 mmol). The resulting slurry was stirred for 10 min, gradually changing from dark red to bright orange solution. The solvent was reduced to 5 mL under reduced pressure and passed through a bed of Celite *via* cannula to remove small deposits of colloidal Pd. The rest of the solvent was then removed under reduced pressure and the crude product redissolved in 10 mL of CH_2Cl_2. A 30 mL portion of diethyl ether was added to precipitate a bright orange solid, which was then washed with 3 × 7 mL portions of diethylether before drying *in vacuo*, giving 151 mg (80%). ^{1}H NMR (498.12 MHz, CD$_3$CN, 26.1 °C): 8.83 (dd, 1H, $^4J_{H\text{-}H}$ = 1.7 Hz, $^4J_{H\text{-}H}$ = 1.7 Hz, NCHN); 7.63 (dd, 1H, $^3J_{H\text{-}H}$ = 1.7 Hz, $^4J_{H\text{-}H}$ = 1.7 Hz), 7.56 (dd, 1H, $^3J_{H\text{-}H}$ = 1.7 Hz, $^4J_{H\text{-}H}$ = 1.7 Hz, NCH$_{imid\text{-}H}$); 1.56 (s, 9H, N$_{imid\text{-}H}$C(CH$_3$)$_3$); 7.63 (dd, 1H, $^3J_{H\text{-}H}$ = 1.7 Hz, $^5J_{H\text{-}P}$ = 1.7 Hz), 7.60 (dd, 1H, $^3J_{H\text{-}H}$ = 2.0 Hz, $^5J_{H\text{-}P}$ = 1.7 Hz NCH$_{imid\text{-}Pd}$); 1.91 (s, 9H, N$_{imid\text{-}Pd}$C(CH$_3$)$_3$); 6.71 (s, 2H, NCH$_2$N); 7.73 (m, 6H), 7.47 (m, 9H, PPh$_3$). ^{13}C{^{1}H} NMR (125.69 MHz, CD$_3$CN, 26.5 °C): 157.5 (d, 1C, $^2J_{C\text{-}P}$ = 194.3 Hz, C$_{carbene}$); 135.0 (s, 1C, NCHN); 122.7 (s, 1C), 120.7 (s, 1C, NCH$_{imid\text{-}H}$), 123.7 (d, 1C, $^4J_{C\text{-}P}$ = 6.7 Hz), 123.2 (d, 1C, $^4J_{C\text{-}P}$ = 4.9 Hz, NCH$_{imid\text{-}Pd}$); 63.5 (s, 1C, NCH$_2$N); 61.1 (s, 1C), 28.9 (s, 3C, N$_{imid\text{-}H}$ C(CH$_3$)$_3$); 60.2 (s, 1C), 31.3 (s, 3C, N$_{imid\text{-}Pd}$C(CH$_3$)$_3$); 132.6 (d, 3C, $^1J_{C\text{-}P}$ = 45.5 Hz), 128.4 (d, 6C, $^2J_{C\text{-}P}$ = 10.1 Hz), 130.7 (d, 6C, $^3J_{C\text{-}P}$ = 2.2 Hz), 134.9 (s, 3C, PPh$_3$). ^{31}P{^{1}H} NMR (202.33 MHz, CD$_3$CN, 27.0 °C): 17.5 (s, 1P, PPh$_3$). HRMS *m/z* Calcd for $C_{33}H_{40}I_2N_4P_2Pd$ (M$^+$ – I): 883.0109. Found: 883.0116 (M$^+$ – I). Repeated attempts to obtain satisfactory elemental analyses were always low in the carbon analysis. The ^{1}H and ^{13}C{^{1}H} NMR spectra of this compound are given in the ESI (Fig. S3).†

(n) Methylene[(*N*-*tert*-butyl)imidazolium]-[(*N*-*tert*-butyl)imidazole-2-ylidene)]diiodo-dimethylphenylphosphinopalladium(II) iodide, [PdI$_2$(PMe$_2$Ph)(^{tBu}C(H)-η^1-C^{meth})][I] (11b). The desired complex was prepared as described for **8b**, using **7b** (122 mg, 0.164 mmol) and PMe$_2$Ph (20.0 μL, 0.141 mmol). The slurry changed from dark red to a pale green solution almost instantly, and was stirred for another 10 min. The crude product was purified as described for **8b**, and isolated using 10 mL of CH_2Cl_2 and 20 mL of diethyl ether to precipitate a pale green solid, which was then washed with 2 × 5 mL portions of diethyl ether before drying *in vacuo*, giving 106 mg (85%). ^{1}H NMR (399.80 MHz, CD$_3$CN, 26.5 °C): 9.21 (dd, 1H, NCHN, $^4J_{H\text{-}H}$ = 1.6 Hz, $^4J_{H\text{-}H}$ = 1.6 Hz); 7.76 (dd, 1H, $^3J_{H\text{-}H}$ = 1.6 Hz, $^4J_{H\text{-}H}$ = 1.6 Hz), 7.59 (dd, 1H, $^3J_{H\text{-}H}$ = 1.6 Hz, $^4J_{H\text{-}H}$ = 1.6 Hz NCH$_{imid\text{-}H}$); 1.59 (s, 9H, N$_{imid\text{-}H}$C(CH$_3$)$_3$); 7.87 (dd, 1H, $^3J_{H\text{-}H}$ = 2.2 Hz, $^5J_{H\text{-}P}$ = 1.4 Hz), 7.54 (dd, 1H, $^3J_{H\text{-}H}$ = 2.2 Hz, $^5J_{H\text{-}P}$ = 1.8 Hz NCH$_{imid\text{-}Pd}$); 1.78 (s, 9H, N$_{imid\text{-}Pd}$C(CH$_3$)$_3$); 6.78 (s, 2H, NCH$_2$N); 7.73 (m, 2H), 7.47 (m, 3H), 2.13 (d, 6H, $^2J_{H\text{-}P}$ = 10.2 Hz, P(CH$_3$)$_2$Ph). ^{13}C{^{1}H} NMR (125.69 MHz, DMSO-d_6, 26.1 °C): 160.5 (d, 1C, $^2J_{C\text{-}P}$ = 197.8 Hz, C$_{carbene}$); 136.5 (s, 1C, NCHN); 122.6 (s, 1C), 121.8 (s, 1C, NCH$_{imid\text{-}H}$); 124.3 (d, 1C, $^4J_{C\text{-}P}$ = 4.5 Hz), 123.8 (d, 1C, $^4J_{C\text{-}P}$ = 5.9 Hz, NCH$_{imid\text{-}Pd}$); 62.7 (s, 1C, NCH$_2$N); 60.6 (s, 1C), 29.5 (s, 3C, N$_{imid\text{-}H}$C(CH$_3$)$_3$); 59.8 (s, 1C), 31.9 (s, 3C, N$_{imid\text{-}Pd}$C(CH$_3$)$_3$); 136.3 (d, 1C, $^1J_{C\text{-}P}$ = 44.0 Hz), 131.8 (d, 2C, $^2J_{C\text{-}P}$ = 10.5 Hz), 129.0 (d, 2C, $^3J_{C\text{-}P}$ = 9.8 Hz), 130.7 (s, 1C), 18.7 (d, 2C, $^1J_{C\text{-}P}$ = 32.9 Hz, P(CH$_3$)$_2$Ph). ^{31}P{^{1}H} NMR (161.84 MHz, CD$_3$CN, 27.0 °C): –16.9 (s, 1P, P(CH$_3$)$_2$Ph). HRMS *m/z* Calcd for $C_{23}H_{36}I_2N_4PPd$ (M$^+$ – I): 758.9796. Found: 758.9799 (M$^+$ – I). Anal Calcd for $C_{23}H_{36}I_3N_4PPd$: C, 31.2; H, 4.1; N, 6.3. Found: C, 31.2; H, 3.8; N, 6.4.

(o) Methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)]iodo-bis(trimethylphosphino)palladium(II) diiodide, [PdI(PMe$_3$)$_2$(^{tBu}C(H)-η^1-C^{meth})][I]$_2$ (12b). The desired complex was prepared as described for **8b**, using [Pd(^{tBu}C(H)-η^1-C^{meth})I$_3$] (143 mg, 0.191 mmol) and PMe$_3$ (47.5 μL, 0.461 mmol). The slurry changed from dark red to a pale green solution almost instantly, and was stirred for another 20 min. The crude product was purified as described for **8b**, and isolated using 7 mL of CH_2Cl_2, 20 mL of diethyl ether and 20 mL of pentane to precipitate a bright yellow solid, which was then washed with 3 × 7 mL portions of diethylether and 3 × 7 mL portions of pentane before drying *in vacuo*, giving 160 mg (93%). ^{1}H NMR (498.12 MHz, CD$_3$CN, 26.1 °C): 10.27 (dd, 1H, NCHN, $^4J_{H\text{-}H}$ = 1.8 Hz, $^4J_{H\text{-}H}$ = 1.8 Hz); 7.81 (dd, 1H, $^3J_{H\text{-}H}$ = 1.8 Hz, $^4J_{H\text{-}H}$ = 1.8 Hz), 7.65 (dd, 1H, $^3J_{H\text{-}H}$ = 1.8 Hz, $^4J_{H\text{-}H}$ = 1.8 Hz NCH$_{imid\text{-}H}$); 1.80 (s, 9H,

$N_{imid\text{-}H}C(CH_3)_3$); 8.02 (dd, 1H, $^3J_{H\text{-}H} = 2.2$ Hz, $^5J_{H\text{-}P} = 1.2$ Hz), 7.73 (dd, 1H, $^3J_{H\text{-}H} = 2.2$ Hz, $^5J_{H\text{-}P} = 2.2$ Hz $NCH_{imid\text{-}Pd}$); 1.70 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); 7.22 (d, 1H, $^2J_{H\text{-}H} = 14.0$ Hz), 6.78 (d, 1H, $^2J_{H\text{-}H} = 14.0$ Hz, NCH_2N); 1.91 (dd, 9H, $^2J_{H\text{-}P} = 10.4$ Hz, $^4J_{H\text{-}P} = 0.6$ Hz), 1.60 (dd, 9H, $^2J_{H\text{-}P} = 10.9$ Hz, $^4J_{H\text{-}P} = 0.7$ Hz, $P(CH_3)_3$). $^{13}C\{^1H\}$ NMR (125.27 MHz, DMSO-d_6, 26.1 °C): 165.3 (dd, 1C, $^2J_{C\text{-}P} = 158.7$ Hz, $^2J_{C\text{-}P} = 6.2$ Hz $C_{carbene}$); 137.1 (s, 1C, NCHN); 122.7 (s, 1C), 121.9 (s, 1C, $NCH_{imid\text{-}H}$); 124.9 (d, 1C, $^4J_{C\text{-}P} = 4.6$ Hz), 124.8 (d, 1C, $^4J_{C\text{-}P} = 3.6$ Hz, $NCH_{imid\text{-}Pd}$); 62.7 (s, 1C, NCH_2N); 60.9 (s, 1C), 30.9 (s, 3C, $N_{imid\text{-}H}$ $C(CH_3)_3$); 60.6 (s, 1C), 29.5 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 18.6 (d, 3C, $^1J_{C\text{-}P} = 32.3$ Hz), 17.2 (dd, 3C, $^1J_{C\text{-}P} = 33.1$ Hz, $^3J_{C\text{-}P} = 2.6$ Hz, $P(CH_3)_3$). $^{31}P\{^1H\}$ NMR (201.64 MHz, CD_3CN, 27.0 °C): −11.1 (d, 1P, $^2J_{P\text{-}P} = 27.3$ Hz), −19.4 (d, 1P, $^2J_{P\text{-}P} = 27.3$ Hz, $P(CH_3)_3$). HRMS *m/z* Calcd for $C_{18}H_{34}I_2N_4PPd$ ($M^{2+} - 2I$): 323.0516. Found: 323.0514 ($M^{2+} - 2I$). Anal Calcd for $C_{21}H_{43}I_3N_4P_2Pd$: C, 28.0; H, 4.8; N, 6.2. Found: C, 27.6; H, 4.8; N, 5.7.

(p) Methylene[(*N*-*tert*-butyl)imidazolium]-[(*N*-*tert*-butyl)imidazole-2-ylidene)]iodo-bis(dimethylphenylphosphino)palladium(II) diiodide, $[PdI(PMe_2Ph)_2(^{tBu}C(H)\text{-}\eta^1\text{-}C^{meth})][I]_2$ (13b). The desired complex was prepared as described for **8b**, using **7b** (142 mg, 0.190 mmol) and PMe_2Ph (81.5 μL, 0.570 mmol). The slurry changed from dark red to a bright yellow solution almost instantly, and was stirred for another 10 min. The crude product was purified as described for **8b**, and isolated using 10 mL of CH_2Cl_2, 20 mL of diethyl ether and 20 mL of pentane to precipitate a pale yellow solid, which was then washed with 3 × 10 mL portions of pentane before drying *in vacuo*, giving 126 mg (65%). ^1H NMR (498.12 MHz, CD_3CN, 26.1 °C): 10.18 (dd, 1H, NCHN, $^4J_{H\text{-}H} = 2.0$ Hz, $^4J_{H\text{-}H} = 2.0$ Hz); 7.90 (dd, 1H, $^3J_{H\text{-}H} = 2.0$ Hz, $^4J_{H\text{-}H} = 2.0$ Hz), 7.69 (dd, 1H, $^3J_{H\text{-}H} = 2.0$ Hz, $^4J_{H\text{-}H} = 2.0$ Hz $NCH_{imid\text{-}H}$); 1.82 (s, 9H, $N_{imid\text{-}H}C(CH_3)_3$); 7.86 (dd, 1H, $^3J_{H\text{-}H} = 2.4$ Hz, $^5J_{H\text{-}P} = 1.1$ Hz), 7.66 (dd, 1H, $^3J_{H\text{-}H} = 2.4$ Hz, $^5J_{H\text{-}P} = 2.4$ Hz $NCH_{imid\text{-}Pd}$); 1.70 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); 7.32 (d, 1H, $^2J_{H\text{-}H} = 13.6$ Hz), 6.78 (d, 1H, $^2J_{H\text{-}H} = 13.6$ Hz, NCH_2N); 2.15 (d, 3H, $^2J_{H\text{-}P} = 10.2$ Hz), 2.01 (d, 3H, $^2J_{H\text{-}P} = 10.2$ Hz), 1.70 (d, 3H, $^2J_{H\text{-}P} = 10.6$ Hz), 1.59 (d, 3H, $^2J_{H\text{-}P} = 10.6$ Hz, $P(CH_3)_2Ph$). $^{13}C\{^1H\}$ NMR (125.69 MHz, DMSO-d_6, 26.1 °C): 162.3 (dd, 1C, $^2J_{C\text{-}P} = 161.1$ Hz, $^2J_{C\text{-}P} = 7.0$ Hz, $C_{carbene}$); 137.1 (s, 1C, NCHN); 122.8 (s, 1C), 121.8 (s, 1C, $NCH_{imid\text{-}H}$); 125.5 (d, 1C, $^4J_{C\text{-}P} = 5.0$ Hz), 124.5 (d, 1C, $^4J_{C\text{-}P} = 4.1$ Hz, $NCH_{imid\text{-}Pd}$); 62.9 (s, 1C, NCH_2N); 61.0 (s, 1C), 29.5 (s, 3C, $N_{imid\text{-}H}$ $C(CH_3)_3$); 60.7 (s, 1C), 31.1 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 134.0 (d, 1C, $^1J_{C\text{-}P} = 48.0$ Hz), 132.7 (dd, 1C, $^1J_{C\text{-}P} = 50.2$ Hz, $^3J_{C\text{-}P} = 3.0$ Hz), 131.6 (d, 2C, $^2J_{C\text{-}P} = 11.4$ Hz), 130.1 (d, 2C, $^2J_{C\text{-}P} = 10.7$ Hz), 132.0 (d, 2C, $^3J_{C\text{-}P} = 10.3$ Hz), 129.3 (d, 2C, $^3J_{C\text{-}P} = 10.3$ Hz), 132.4 (d, 1C, $^4J_{C\text{-}P} = 1.8$ Hz), 131.3 (d, 1C, $^4J_{C\text{-}P} = 1.8$ Hz), 18.6 (d, 1C, $^1J_{C\text{-}P} = 33.0$ Hz), 16.8 (d, 1C, $^1J_{C\text{-}P} = 32.2$ Hz), 16.0 (d, 2C, $^1J_{C\text{-}P} = 31.3$ Hz, $P(CH_3)_2Ph$). $^{31}P\{^1H\}$ NMR (201.64 MHz, CD_3CN, 27.0 °C): −5.0 (d, 1P, $^2J_{P\text{-}P} = 25.6$ Hz), −11.7 (d, 1P, $^2J_{P\text{-}P} = 25.6$ Hz, $P(CH_3)_2Ph$). HRMS *m/z* Calcd for $C_{31}H_{47}IN_4P_2Pd$ ($M^{2+} - 2I$): 385.0672. Found: 385.0675 ($M^{2+} - 2I$). Anal Calcd for $C_{31}H_{47}I_3N_4P_2Pd$: C, 36.3; H, 4.6; N, 5.5. Found: C, 36.2; H, 4.9; N, 5.3.

(q) Methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)iodo-(η¹:η¹-bis(diphenylphosphino)methane)palladium(II)] diiodide, $[PdI(dppm)(^{tBu}C(H)\text{-}\eta^1\text{-}C^{meth})][I]_2$ (14b). The desired complex was prepared as described for **10b**, using **7b** (114 mg, 0.152 mmol) and dppm (59 mg, 0.153 mmol). The slurry changed from dark red to a bright orange, and was stirred for another 20 min. The crude product was purified as described for **10b**, and isolated using 10 mL of CH_2Cl_2 and 30 mL of diethyl ether to precipitate a bright orange solid, which was then washed with 3 × 7 mL portions of pentane before drying *in vacuo*, giving 155 mg (90%). ^1H NMR (399.79 MHz, DMSO-d_6, 26.5 °C): 9.14 (dd, 1H, $^4J_{H\text{-}H} = 1.6$ Hz, $^4J_{H\text{-}H} = 1.6$ Hz NCHN); 8.09 (dd, 1H, $^3J_{H\text{-}H} = 1.6$ Hz, $^4J_{H\text{-}H} = 1.6$ Hz), 7.84 (dd, 1H, $^3J_{H\text{-}H} = 1.6$ Hz, $^4J_{H\text{-}H} = 1.6$ Hz, $NCH_{imid\text{-}H}$); 1.40 (s, 9H, $N_{imid\text{-}H}C(CH_3)_3$); both $NCH_{imid\text{-}Pd}$ peaks disguised by phenyl multiplets; 1.51 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); 6.76 (d, 1H, $^2J_{H\text{-}H} = 13.8$ Hz), 6.23 (d, 1H, $^2J_{H\text{-}H} = 13.8$ Hz NCH_2N); 8.05 (m, 6H), 7.63 (m, 8H), 7.48 (m, 1H), 7.30 (m, 3H), 7.00 (m, 2H, PPh_2); 5.44 (dm, 1H, $^2J_{H\text{-}H} = 16.7$ Hz), 5.34 (dm, 1H, $^2J_{H\text{-}H} = 16.7$ Hz, PCH_2P). $^{13}C\{^1H\}$ NMR (100.54 MHz, DMSO-d_6, 26.5 °C): 164.1 (dd, 1C, $^2J_{C\text{-}P} = 172.2$ Hz, $^2J_{C\text{-}P} = 2.8$ Hz, $C_{carbene}$); 136.3 (s, 1C, NCHN); 122.5 (s, 1C), 122.2 (s, 1C, $NCH_{imid\text{-}H}$); 125.4 (d, 1C, $^4J_{C\text{-}P} = 4.4$ Hz), 125.1 (d, 1C, $^4J_{C\text{-}P} = 2.9$ Hz, $NCH_{imid\text{-}Pd}$); 62.2 (s, 1C, NCH_2N); 60.7 (s, 1C), 29.3 (s, 3C, $N_{imid\text{-}H}C(CH_3)_3$); 60.5 (s, 1C), 31.3 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 137.0–121.8 (24C, PPh_2); 36.8 (dd, $^1J_{C\text{-}P} = 27.5$ Hz, $^1J_{C\text{-}P} = 27.5$ Hz), PCH_2P). $^{31}P\{^1H\}$ NMR (162.08 MHz, DMSO-d_6, 27.0 °C): −47.3 (d, $^2J_{P\text{-}P} = 77.0$ Hz, 1P), −55.7 (d, $^2J_{P\text{-}P} = 77.0$ Hz, 1P, dppm). HRMS *m/z* Calcd for $C_{40}H_{47}IN_4P_2Pd$ ($M^{2+} - 2I$): 439.0672. Found: 439.0670 ($M^{2+} - 2I$). Anal Calcd for $C_{40}H_{47}I_3N_4P_2Pd$: C, 42.4; H, 4.2; N, 4.95. Found: C, 42.0; H, 4.2; N, 5.0.

(r) Ethylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)iodo-(η¹:η¹-bis(diphenylphosphino)methane)palladium(II)] diiodide, $[PdI(dppm)(^{tBu}C(H)\text{-}\eta^1\text{-}C^{eth})][I]_2$ (14d). The desired complex was prepared as described for **10b**, using **7d** (275 mg, 0.361 mmol) and dppm (140 mg, 0.364 mmol). The slurry changed from dark red to a bright orange, and was stirred for another 20 min. The crude product was purified as described for **10b**, and isolated using 15 mL of CH_2Cl_2, 30 mL of diethyl ether, and 25 mL of pentane to precipitate a bright yellow solid, which was then washed with 3 × 15 mL portions of pentane before drying *in vacuo*, giving 310 mg (75%). ^1H NMR (399.80 MHz, DMSO-d_6, 26.5 °C): 9.19 (br dd, 1H, $^4J_{H\text{-}H} = 2.1$ Hz, $^4J_{H\text{-}H} = 2.1$ Hz NCHN); 7.99 (dd, 1H, $^3J_{H\text{-}H} = 2.1$ Hz, $^4J_{H\text{-}H} = 2.1$ Hz), 7.45 (dd, 1H, $^3J_{H\text{-}H} = 2.1$ Hz, $^4J_{H\text{-}H} = 2.1$ Hz, $NCH_{imid\text{-}H}$); 1.48 (s, 9H, $N_{imid\text{-}H}C(CH_3)_3$); 7.90 (br dd, 1H, $^3J_{H\text{-}H} = 2.1$ Hz, $^5J_{H\text{-}P} = 2.1$ Hz), 7.56 (br dd, 1H, $^3J_{H\text{-}H} = 2.1$ Hz, $^4J_{H\text{-}H} = 2.1$ Hz, $NCH_{imid\text{-}Pd}$); 1.55 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); 4.86 (m, 2H), 4.73 (m, 1H), 4.17 (m, 1H, NCH_2CH_2N); 7.94 (m, 6H), 7.59 (m, 9H), 7.42 (m, 5H), 7.29 (m, 3H), 7.16 (m, 2H, PPh_2); 5.36 (ddd, 1H, $^2J_{H\text{-}H} = 16.1$ Hz, $^2J_{H\text{-}P} = 11.3$ Hz, $^2J_{H\text{-}P} = 10.6$ Hz), 5.12 (ddd, 1H, $^2J_{H\text{-}H} = 16.1$ Hz, $^2J_{H\text{-}P} = 11.7$ Hz, $^2J_{H\text{-}P} = 10.1$ Hz, PCH_2P). $^{13}C\{^1H\}$ NMR (125.17 MHz, DMSO-d_6, 26.1 °C): 162.2 (dd, 1C, $^2J_{C\text{-}P} = 173.7$ Hz, $^2J_{C\text{-}P} = 5.9$ Hz, $C_{carbene}$); 135.4 (s, 1C, NCHN); 123.5 (s, 1C), 121.2 (s, 1C, $NCH_{imid\text{-}H}$); 133.2 (d, 1C, $^4J_{C\text{-}P} = 5.2$ Hz), 124.4 (d, 1C, $^4J_{C\text{-}P} = 4.9$ Hz, $NCH_{imid\text{-}Pd}$); 51.7 (s, 1C), 47.9 (s, 1C, NCH_2CH_2N); 60.5 (s, 1C), 29.6 (s, 3C, $N_{imid\text{-}H}C(CH_3)_3$); 59.8 (s, 1C), 31.2 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 134.2–126.5 (24C, PPh_2); 37.5 (dd, $^1J_{C\text{-}P} = 26.7$ Hz, $^1J_{C\text{-}P} = 26.7$ Hz), PCH_2P). $^{31}P\{^1H\}$ NMR (161.84 MHz, DMSO-d_6, 27.0 °C): −45.3 (d, $^2J_{P\text{-}P} = 79.6$ Hz, 1P), −54.5 (d, $^2J_{P\text{-}P} = 79.6$ Hz, 1P, dppm). HRMS *m/z* Calcd for $C_{41}H_{49}IN_4P_2Pd$ ($M^{2+} - 2I$): 446.0751. Found: 446.0750 ($M^{2+} - 2I$). Anal Calcd for $C_{41}H_{49}I_3N_4P_2Pd$: C, 42.9; H, 4.3; N, 4.9. Found: C, 43.2; H, 4.45; N, 4.95.

(s) Methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)iodo-(η^1:η^1-bis(diphenylphosphino)ethane)palladium(II)] diiodide, [PdI(dppe)($^{t\text{Bu}}$C(H)-η^1-C$^{\text{meth}}$)][I]$_2$ (15b). The desired complex was prepared as described for **10b**, using **7b** (103 mg, 0.138 mmol) and dppe (51 mg, 0.128 mmol). The slurry changed from dark red to a pale green, and was stirred for another 10 min. The crude product was purified as described for **10b**, and isolated using 20 mL of CH_2Cl_2 and 20 mL of diethyl ether to precipitate a pale green solid, which was then washed with 2 × 5 mL portions of pentane before drying *in vacuo*, giving 101 mg (69%). ^{1}H NMR (498.12 MHz, DMSO-d_6, 26.1 °C): 9.19 (dd, 1H, NCHN, $^4J_{H\text{-}H}$ = 1.7 Hz, $^4J_{H\text{-}H}$ = 1.7 Hz); 8.13 (dd, 1H, $^3J_{H\text{-}H}$ = 1.7 Hz, $^4J_{H\text{-}H}$ = 1.7 Hz), 7.79 (dd, 1H, $^3J_{H\text{-}H}$ = 1.7 Hz, $^4J_{H\text{-}H}$ = 1.7 Hz NCH$_{imid\text{-}H}$); 1.29 (s, 9H, N$_{imid\text{-}H}$C(CH$_3$)$_3$); 7.86 (dd, 1H, $^3J_{H\text{-}H}$ = 2.2 Hz, $^5J_{H\text{-}P}$ = 2.2 Hz), 7.72 (dd, 1H, $^3J_{H\text{-}H}$ = 2.2 Hz, $^5J_{H\text{-}P}$ = 1.0 Hz, NCH$_{imid\text{-}Pd}$); 1.55 (s, 9H, N$_{imid\text{-}Pd}$C(CH$_3$)$_3$); 6.62 (d, 1H, $^2J_{H\text{-}H}$ = 14.1 Hz), 6.06 (d, 1H, $^2J_{H\text{-}H}$ = 14.1 Hz, NCH$_2$N); 7.95 (m, 2H), 7.87 (m, 2H), 7.69 (m, 2H), 7.59 (m, 10H), 7.41 (m, 2H) 7.23 (m, 2H, PPh$_2$); 3.20 (m, 2H), 3.02 (m, 1H), 2.15 (m, 1H, PCH$_2$CH$_2$P). ^{13}C{^{1}H} NMR (125.69 MHz, DMSO-d_6, 26.1 °C): 163.8 (dd, 1C, $^2J_{C\text{-}P}$ = 152.5 Hz, $^2J_{C\text{-}P}$ = 5.0 Hz, C$_{carbene}$); 136.4 (s, 1C, NCHN); 122.7 (s, 1C), 122.2 (s, 1C, NCH$_{imid\text{-}H}$); 126.0 (d, 1C, $^4J_{C\text{-}P}$ = 4.2 Hz), 123.8 (d, 1C, $^4J_{C\text{-}P}$ = 3.5 Hz, NCH$_{imid\text{-}Pd}$); 62.6 (s, 1C, NCH$_2$N); 61.1 (s, 1C), 29.4 (s, 3C, N$_{imid\text{-}H}$C(CH$_3$)$_3$); 60.0 (s, 1C), 30.7 (s, 3C, N$_{imid\text{-}Pd}$C(CH$_3$)$_3$); 134.4–129.0 (24C, PPh$_2$); 31.3 (dd, 1C, $^1J_{C\text{-}P}$ = 33.5 Hz, $^2J_{C\text{-}P}$ = 13.2 Hz), 23.8 (dd, 1C, $^1J_{C\text{-}P}$ = 31.8 Hz, $^2J_{C\text{-}P}$ = 12.4 Hz, PCH$_2$CH$_2$P). ^{31}P{^{1}H} NMR (162.08 MHz, DMSO-d_6, 27.0 °C): 57.8 (d, 1P, $^2J_{P\text{-}P}$ = 11.5 Hz), 53.7 (d, 1P, $^2J_{P\text{-}P}$ = 11.5 Hz, dppe). HRMS *m*/*z* Calcd for $C_{41}H_{49}IN_4P_2Pd$ (M^{2+} – 2I): 446.0751. Found: 446.0749 (M^{2+} – 2I). Anal Calcd for $C_{41}H_{49}I_3N_4P_2Pd$: C, 42.9; H, 4.3; N, 4.9. Found: C, 42.5; H, 4.5; N, 4.7.

(t) Ethylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)iodo-(η^1:η^1-bis(diphenylphosphino)ethane)palladium(II)] diiodide, [PdI(dppe)($^{t\text{Bu}}$C(H)-η^1-C$^{\text{eth}}$)][I]$_2$ (15d). The desired complex was prepared as described for **10b**, using **10d** (447 mg, 0.586 mmol) and dppe (234 mg, 0.587 mmol). The slurry changed from dark red to a pale green, and was stirred for another 10 min. The crude product was purified as described for **10b**, and isolated using 10 mL of CH_2Cl_2, 20 mL of diethyl ether, and 30 mL of pentane to precipitate a pale green solid, which was then washed with 3 × 10 mL portions of pentane before drying *in vacuo*, giving 453 mg (67%). ^{1}H NMR (399.80 MHz, DMSO-d_6, 26.5 °C): 9.41 (br dd, 1H, NCHN, $^4J_{H\text{-}H}$ = 2.3 Hz, $^4J_{H\text{-}H}$ = 2.3 Hz); 7.93 (dd, 1H, $^3J_{H\text{-}H}$ = 2.3 Hz, $^4J_{H\text{-}H}$ = 2.3 Hz), 7.50 (dd, 1H, $^3J_{H\text{-}H}$ = 2.3 Hz, $^4J_{H\text{-}H}$ = 2.3 Hz, NCH$_{imid\text{-}H}$); 1.15 (s, 9H, N$_{imid\text{-}H}$C(CH$_3$)$_3$); 7.67 (dd, 1H, $^3J_{H\text{-}H}$ = 2.1 Hz, $^5J_{H\text{-}P}$ = 2.1 Hz), 7.65 (dd, 1H, $^3J_{H\text{-}H}$ = 2.1 Hz, $^5J_{H\text{-}P}$ = 2.1 Hz, NCH$_{imid\text{-}Pd}$); 1.54 (s, 9H, N$_{imid\text{-}Pd}$C(CH$_3$)$_3$); 4.83 (m, 3H), 4.11 (m, 1H, NCH$_2$CH$_2$N); 7.94 (m, 3H), 7.82 (m, 2H), 7.55 (m, 15H), 7.39 (m, 2H), 7.21 (m, 2H, PPh$_2$); 3.04 (m, 3H), 1.84 (m, 1H, PCH$_2$CH$_2$P). ^{13}C{^{1}H} NMR (100.54 MHz, DMSO-d_6, 26.5 °C): 162.0 (dd, 1C, $^2J_{C\text{-}P}$ = 154.0 Hz, $^2J_{C\text{-}P}$ = 4.6 Hz, C$_{carbene}$); 135.6 (s, 1C, NCHN); 123.9 (s, 1C), 120.9 (s, 1C, NCH$_{imid\text{-}H}$); 124.7 (d, 1C, $^4J_{C\text{-}P}$ = 4.2 Hz), 123.1 (d, 1C, $^4J_{C\text{-}P}$ = 4.2 Hz, NCH$_{imid\text{-}Pd}$); 55.6 (s, 1C), 52.4 (s, 1C, NCH$_2$CH$_2$N); 60.4 (s, 1C), 30.5 (s, 3C, N$_{imid\text{-}H}$C(CH$_3$)$_3$); 59.2 (s, 1C), 29.6 (s, 3C, N$_{imid\text{-}Pd}$C(CH$_3$)$_3$); 135.0–128.6 (24C, PPh$_2$); 31.4 (dd, 1C, $^1J_{C\text{-}P}$ = 33.5 Hz, $^2J_{C\text{-}P}$ = 13.0 Hz), 25.7 (dd, 1C, $^1J_{C\text{-}P}$ = 33.5 Hz, $^2J_{C\text{-}P}$ = 11.9 Hz, PCH$_2$CH$_2$P). ^{31}P{^{1}H} NMR (161.84 MHz, DMSO-d_6, 27.0 °C): 57.6 (d, 1P, $^2J_{P\text{-}P}$ = 11.8 Hz), 52.9 (d, 1P, $^2J_{P\text{-}P}$ = 11.8 Hz, dppe). HRMS *m*/*z* Calcd for $C_{42}H_{51}IN_4P_2Pd$ (M^{2+} – 2I): 453.0829. Found: 453.0833 (M^{2+} – 2I). Anal Calcd for $C_{42}H_{51}I_3N_4P_2Pd$: C, 43.45; H, 4.4; N, 4.8. Found: C, 43.45; H, 4.5; N, 4.7.

(u) Methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene)iodo-(η^1:η^1-bis(diethylphosphino)methane)palladium(II)] diiodide, [PdI(depm)($^{t\text{Bu}}$C(H)-η^1-C$^{\text{meth}}$)][I]$_2$ (16b). The desired complex was prepared as described for **8b**, using **7b** (109 mg, 0.146 mmol) and depm (32.8 μL, 0.145 mmol). The slurry changed from dark red to a pale green solution almost instantly, and was stirred for another 10 min. The crude product was purified as described for **8b**, and isolated using 10 mL of CH_2Cl_2, and 20 mL of diethyl ether to precipitate a pale yellow solid, which was then washed with 2 × 5 mL portions of pentane before drying *in vacuo*, giving 125 mg (92%). ^{1}H NMR (399.80 MHz, CD_3CN, 26.5 °C): 10.24 (dd, 1H, $^3J_{H\text{-}H}$ = 1.7 Hz, $^4J_{H\text{-}H}$ = 1.7 Hz NCHN); 7.78 (dd, $^3J_{H\text{-}H}$ = 1.7 Hz, $^3J_{H\text{-}H}$ = 1.7 Hz 1H), 7.63 (dd, $^3J_{H\text{-}H}$ = 1.7 Hz, $^3J_{H\text{-}H}$ = 1.7 Hz 1H, NCH$_{imid\text{-}H}$); 1.66 (s, 9H, N$_{imid\text{-}H}$C(CH$_3$)$_3$); 8.00 (dd, 1H, $^3J_{H\text{-}H}$ = 2.2 Hz, $^5J_{H\text{-}P}$ = 1.1 Hz), 7.65 (dd, 1H, $^3J_{H\text{-}H}$ = 1.1 Hz, $^5J_{H\text{-}H}$ = 1.1 Hz, NCH$_{imid\text{-}Pd}$); 1.77 (s, 9H, N$_{imid\text{-}Pd}$C(CH$_3$)$_3$); 7.42 (d, 1H, $^2J_{H\text{-}H}$ = 13.9 Hz), 6.68 (d, 1H, $^2J_{H\text{-}H}$ = 13.9 Hz NCH$_2$N); 2.89 (dm, 1H, $^2J_{H\text{-}P}$ = 11.4 Hz), 2.67 (m, 2H), 2.46 (m, 1H), 2.11 (m, 2H), 1.65 (m, 2H), 1.27 (dt, 3H, $^3J_{H\text{-}P}$ = 20.0 Hz, $^3J_{H\text{-}H}$ = 7.4 Hz), 1.17 (dt, 3H, $^3J_{H\text{-}P}$ = 18.7 Hz, $^3J_{H\text{-}H}$ = 7.7 Hz), 1.03 (dt, 3H, $^3J_{H\text{-}P}$ = 19.1 Hz, $^3J_{H\text{-}H}$ = 7.4 Hz), 0.88 (dt, 3H, $^3J_{H\text{-}P}$ = 20.0 Hz, $^3J_{H\text{-}H}$ = 7.4 Hz, PEt$_2$); 4.16 (ddd, 1H, $^2J_{H\text{-}H}$ = 16.6 Hz, $^2J_{H\text{-}P}$ = 12.4 Hz, $^2J_{H\text{-}P}$ = 12.4 Hz) 3.43 (ddd, 1H, $^2J_{H\text{-}H}$ = 16.6 Hz, $^2J_{H\text{-}P}$ = 10.8 Hz, $^2J_{H\text{-}P}$ = 9.7 Hz, PCH$_2$P). ^{13}C{^{1}H} NMR (125.69 MHz, DMSO-d_6, 26.1 °C): 169.6 (d, 1C, $^2J_{C\text{-}P}$ = 158.5 Hz, C$_{carbene}$); 136.4 (s, 1C, NCHN); 122.5 (s, 1C), 122.1 (s, 1C, NCH$_{imid\text{-}H}$); 124.4 (d, 1C, $^4J_{C\text{-}P}$ = 4.3 Hz), 124.1 (d, 1C, $^4J_{C\text{-}P}$ = 3.4 Hz, NCH$_{imid\text{-}Pd}$); 62.6 (s, 1C, NCH$_2$N); 60.9 (s, 1C), 29.4 (s, 3C, N$_{imid\text{-}H}$C(CH$_3$)$_3$); 61.0 (s, 1C), 31.1 (s, 3C, N$_{imid\text{-}Pd}$C(CH$_3$)$_3$); 20.8 (dd, 1C, $^1J_{C\text{-}P}$ = 13.6 Hz, $^3J_{C\text{-}P}$ = 13.6 Hz), 19.5 (d, 1C, $^1J_{C\text{-}P}$ = 22.7 Hz), 18.0 (d, 1C, $^1J_{C\text{-}P}$ = 23.4 Hz), 17.5 (dd, 1C, $^1J_{C\text{-}P}$ = 19.5 Hz, $^3J_{C\text{-}P}$ = 19.5 Hz), 9.0 (s, 1C), 8.0 (d, 1C, $^2J_{C\text{-}P}$ = 5.8 Hz), 6.8 (d, 1C, $^2J_{C\text{-}P}$ = 4.9 Hz), 6.4 (d, 1C, $^2J_{C\text{-}P}$ = 5.3 Hz, PEt$_2$); 27.7 (dd, 1C, $^1J_{C\text{-}P}$ = 27.2 Hz, $^1J_{C\text{-}P}$ = 27.2 Hz, PCH$_2$P). ^{31}P{^{1}H} NMR (161.84 MHz, DMSO-d_6, 27.0 °C): –46.6 (d, 1P, $^2J_{P\text{-}P}$ = 81.1 Hz), –51.2 (d, 1P, $^2J_{P\text{-}P}$ = 81.1 Hz, depm). HRMS *m*/*z* Calcd for $C_{24}H_{47}IN_4P_2Pd$ (M^{2+} – 2I): 343.0672. Found: 343.0675 (M^{2+} – 2I). Anal Calcd for $C_{24}H_{47}I_3N_4P_2Pd$: C, 30.6; H, 5.0; N, 6.0. Found: C, 30.4; H, 5.0; N, 6.0.

(v) Diiodotriethylphosphinopalladium(II)-μ-(1,1′-methylene-3,3′-di-*tert*-butyldiimidazoline-2,2′-diylidene)iodo(η^2:η^2-cyclooctadiene)rhodium(I), [PdI$_2$(PEt$_3$)(μ-$^{t\text{Bu}}$CC$^{\text{meth}}$)RhI(COD)] (17b). A 10 mL portion of CH_3CN was added to a solid mixture containing **9b** (79 mg, 0.091 mmol) and [Rh(μ-OAc)(COD)]$_2$ (25 mg, 0.046 mmol). The resulting slurry was stirred for 36 h under reflux conditions and allowed to cool to room temperature. After settling, the mother liquor was decanted to waste *via* cannula and the resulting dark green product was dissolved in 10 mL of CH_2Cl_2. The green solution was passed through a bed of Celite *via* cannula to remove small deposits of colloidal Pd resulting in a bright yellow solution. The solvent was then removed under reduced pressure resulting in a bright yellow powder. The crude product washed with 3 × 20 mL portions of

acetone before drying *in vacuo*, giving 64 mg (65%). ^{1}H NMR (399.95 MHz, CD_2Cl_2, 26.5 °C): 7.63 (d, 1H, $^3J_{H\text{-}H}$ = 2.2 Hz), 7.12 (d, 1H, $^3J_{H\text{-}H}$ = 2.2 Hz, $NCH_{imid\text{-}Rh}$); 1.95(s, 9H, $N_{imid\text{-}Rh}C(CH_3)_3$); 7.77 (br dd, 1H), 7.21 (dd, 1H, $^3J_{H\text{-}H}$ = 1.8 Hz, $^5J_{H\text{-}P}$ = 1.8 Hz, $NCH_{imid\text{-}Pd}$); 1.88(s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); 8.08 (d, 1H, $^2J_{H\text{-}H}$ = 13.2 Hz), 7.40 (d, 1H, $^2J_{H\text{-}H}$ = 13.2 Hz NCH_2N); 5.26 (m, 1H), 5.07 (m, 1H), 3.49 (m, 1H), 3.39 (m, 1H), 2.57 (m, 1H), 2.27 (m, 3H), 1.88 (m, 4H, COD); 2.19 (dq, 6H, $^2J_{H\text{-}P}$ = 9.5 Hz, $^3J_{H\text{-}H}$ = 7.6 Hz), 1.15 (dt, 9H, $^3J_{H\text{-}P}$ = 16.3 Hz, $^3J_{H\text{-}H}$ = 7.6 Hz, $P(CH_2CH_3)_3$). $^{13}C\{^1H\}$ NMR (125.69 MHz, CD_2Cl_2, 26.1 °C): 180.9 (d, 1C, $^1J_{C\text{-}Rh}$ = 49.3 Hz, $C_{carbene\text{-}Rh}$); 160.8 (d, 1C, $^2J_{C\text{-}P}$ = 187.7 Hz, $C_{carbene\text{-}Pd}$); 121.4 (s, 1C), 120.7 (s, 1C, $NCH_{imid\text{-}Rh}$); 121.8 (d, 1C, $^4J_{C\text{-}P}$ = 4.1 Hz), 121.7 (d, 1C, $^4J_{C\text{-}P}$ = 6.1 Hz, $NCH_{imid\text{-}Pd}$); 66.9 (s, 1C, NCH_2N); 58.8 (s, 1C), 32.0 (s, 3C, $N_{imid\text{-}Rh}C(CH_3)_3$); 59.2 (s, 1C), 31.8 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 18.7 (d, 3C, $^1J_{C\text{-}P}$ = 28.3 Hz), 8.8 (s, 3C, $P(CH_2CH_3)_3$); 95.9 (d, 1C, $^1J_{C\text{-}Rh}$ = 7.8 Hz), 92.9 (d, 1C, $^1J_{C\text{-}Rh}$ = 7.1 Hz), 74.3 (d, 1C, $^1J_{C\text{-}Rh}$ = 15.7 Hz), 71.9 (d, 1C, $^1J_{C\text{-}Rh}$ = 14.2 Hz), 33.1 (s, 1C), 31.2 (s, 1C), 30.2 (s, 1C), 29.2 (s, 1C, COD). $^{31}P\{^1H\}$ NMR (161.84 MHz, CD_2Cl_2, 27.0 °C): 10.0 (s, 1P, $P(CH_2CH_3)_3$). HRMS *m/z* Calcd for $C_{29}H_{51}I_2N_4PPdRh$ ($M^+ - I$): 949.0025. Found: 949.0021 ($M^+ - I$). Anal Calcd for $C_{29}H_{51}I_3N_4PPdRh$: C, 32.4; H, 4.8; N, 5.2. Found: C, 32.7; H, 4.9; N, 5.1.

(w) Diiodotriethylphosphinopalladium(II)-μ-(1,1′-methylene-3,3′-di-*tert*-butyldiimidazoline-2,2′-diylidene)iododicarbonylrhodium(I), [$PdI_2(PEt_3)(\mu$-$^{rBu}CC^{meth})RhI(CO)_2$] (18b). The desired complex was prepared as described for complexes **3** using **17b** (238 mg, 0.221 mmol), and the crude product purified using 4 mL of CH_2Cl_2 and 40 mL of diethyl ether, to precipitate a pale yellow solid at 4°C, which was then washed with 3 × 20 mL portions of pentane before drying *in vacuo*, giving 215 mg (85%). ^{1}H NMR (399.80 MHz, CD_2Cl_2, 50.0 °C, see Fig. S6, ESI†): 7.92 (d, $^3J_{H\text{-}H}$ = 2.1 Hz, 1H), 7.30 (d, 1H, $^3J_{H\text{-}H}$ = 2.1 Hz, $NCH_{imid\text{-}Rh}$); 1.82 (s, 9H, $N_{imid\text{-}Rh}C(CH_3)_3$); 7.49 (br dd, 1H, $^3J_{H\text{-}H}$ = 2.1 Hz), 7.22 (dd, 1H, $^3J_{H\text{-}H}$ = 2.1 Hz, $^5J_{H\text{-}P}$ = 2.1 Hz, $NCH_{imid\text{-}Pd}$); 1.87 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); 7.12 (d, 1H, $^2J_{H\text{-}H}$ = 13.2 Hz), 7.08 (d, 1H, $^2J_{H\text{-}H}$ = 13.2 Hz NCH_2N); 2.17 (dq, 6H, $^2J_{H\text{-}P}$ = 9.4 Hz, $^3J_{H\text{-}H}$ = 7.6 Hz), 1.14 (dt, 9H, $^3J_{H\text{-}P}$ = 16.3 Hz, $^3J_{H\text{-}H}$ = 7.5 Hz, $P(CH_2CH_3)_3$). $^{13}C\{^1H\}$ NMR (125.69 MHz, CD_2Cl_2, 26.1 °C): 187.2 (d, 1C, $^1J_{C\text{-}Rh}$ = 54.6 Hz), 181.6 (d, 1C, $^1J_{C\text{-}Rh}$ = 76.3 Hz, CO); 171.0 (d, 1C, $^1J_{C\text{-}Rh}$ = 42.3 Hz, $C_{carbene\text{-}Rh}$); 162.2 (d, 1C, $^2J_{C\text{-}P}$ = 184.9 Hz, $C_{carbene\text{-}Pd}$); 122.0 (s, 1C), 121.8 (s, 1C, $NCH_{imid\text{-}Rh}$); 121.1 (br d, 1C), 122.0 (br d, 1C, $NCH_{imid\text{-}Pd}$); 66.4 (s, 1C, NCH_2N); 59.4 (s, 1C), 31.9 (s, 3C, $N_{imid\text{-}Rh}C(CH_3)_3$); 59.5 (s, 1C), 32.0 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 18.7 (d, 3C, $^1J_{C\text{-}P}$ = 30.3 Hz), 8.8 (s, 3C, $P(CH_2CH_3)_3$). $^{31}P\{^1H\}$ NMR (161.84 MHz, CD_2Cl_2, 27.0 °C): 9.7 (s, 1P, $P(CH_2CH_3)_3$). IR (solution, cm^{-1}): 2076, 2004 (CO). HRMS *m/z* Calcd for $C_{22}H_{39}I_2N_4O_2PPdRh$ (M^+ – CO, I): 868.9036. Found: 868.9035 (M^+ – CO, I). Anal Calcd for $C_{23}H_{39}I_3N_4O_2PPdRh$: C, 27.0; H, 3.8; N, 5.5. Found: C, 27.3; H, 4.0; N, 5.6.

(x) Bromo(η²:η²-cyclooctadiene)iridium(I)-μ-(1,1′-methylene-3,3′-di-*tert*-butyldiimidazoline-2,2′-diylidene)bromo(η²:η²-cyclooctadiene)rhodium(I), [IrBr(COD)(μ-$^{rBu}CC^{meth}$)RhBr(COD)] (19b). A 40 mL portion of THF was added to a solid mixture containing Ir(COD)Br(^{rBu}C(H)-η¹-C^{eth})][Br] (504 mg, 0.70 mmol) and [Rh(μ-OAc)(COD)]$_2$ (187 mg, 0.35 mmol). The resulting slurry was stirred for 2.5 h under reflux conditions. The solvent was then removed under reduced pressure and the crude product redissolved in 10 mL of hot CH_2Cl_2 and allowed to cool to room temperature, precipitating a dark orange crystalline solid. After settling, the mother liquor was decanted to waste *via* cannula and the resulting product was dried *in vacuo*, giving 300 mg (46%). ^{1}H NMR (399.95 MHz, CD_2Cl_2, 27.0 °C): 7.89 (d, 1H, $^3J_{H\text{-}H}$ = 2.3 Hz), 7.73 (d, 1H, $^3J_{H\text{-}H}$ = 2.3 Hz), 7.07 (d, 1H, $^3J_{H\text{-}H}$ = 2.3 Hz), 7.06 (d, 1H, $^3J_{H\text{-}H}$ = 2.3 Hz, NCH_{imid}); 8.24 (d, 1H, $^2J_{H\text{-}H}$ = 11.5 Hz), 8.06 (d, 1H, $^2J_{H\text{-}H}$ = 11.5 Hz, NCH_2N); 1.97 (s, 9H), 1.89 (s, 9H, $N_{imid}C(CH_3)_3$); 5.03 (m, 2H), 3.38 (m, 2H), 4.61 (m, 1H), 4.52 (m, 1H), 3.03 (m, 1H), 2.99 (m, 1H), 2.63 (m, 4H), 2.48 (m, 4H), 1.78 (m, 4H), 1.64 (m, 4H, COD). $^{13}C\{^1H\}$ NMR(100.58 MHz, CD_2Cl_2, 27.0 °C): 180.5 (d, 1C, $^1J_{C\text{-}Rh}$ = 50.1 Hz, $C_{carbene\text{-}Rh}$), 179.2 (s, 1C, $C_{carbene\text{-}Ir}$); 121.4 (s, 1C), 121.2 (s, 1C), 120.4 (s, 1C), 120.4 (s, 1C, NCH_{imid}); 68.0 (s, 1C, CH_2), 59.0 (s, 1C), 58.7 (s, 1C, $N_{imid}C(CH_3)_3$); 32.4 (s, 3C), 32.0 (s, 3C, $N_{imid}C(CH_3)_3$); 96.7 (d, 1C, $^1J_{C\text{-}Rh}$ = 7.3 Hz), 94.8 (d, 1C, $^1J_{C\text{-}Rh}$ = 7.0 Hz), 72.3 (d, 1C, $^1J_{C\text{-}Rh}$ = 15.7 Hz), 68.6 (d, 1C, $^1J_{C\text{-}Rh}$ = 14.0 Hz), 82.3 (s, 1C), 80.7 (s, 1C), 55.4 (s, 1C), 52.4 (s, 1C), 32.3 (s, 1C), 30.3 (s, 1C), 29.5 (s, 1C), 28.5 (s, 1C), 34.3 (s, 1C), 34.1 (s, 1C), 30.1 (s, 1C), 25.8 (s, 1C, COD). HRMS *m/z* Calcd for $C_{31}H_{48}BrN_4IrRh$ (M^+ – Br): 851.1741. Found: 851.1741 (M^+ –Br).

(y) Diiodotriphenylphosphinopalladium(II)-μ-(1,1′-methylene-3,3′-di-*tert*-butyldiimidazoline-2,2′-diylidene)iodo(η²:η²-cyclooctadiene)iridium(I), [$PdI_2(PPh_3)(\mu$-$^{rBu}CC^{meth})IrI(COD)$] (20b). A 5 mL portion of CH_3CN was added to **10b** (70 mg, 0.069 mmol), and the resulting orange solution was added slowly to a 10 mL CH_3CN solution containing K[$N(SiMe_3)_2$] (34 mg, 0.170 mmol) and [Ir(μ-Cl)(COD)]$_2$ (23 mg, 0.034 mmol). The solution was stirred for 24 h, and the solvent removed under reduced pressure. The resulting solid was dissolved in 15 mL of CH_2Cl_2 and passed through a bed of Celite *via* cannula to remove suspended white salts. The solvent was removed under reduced pressure and the product extracted with 40 mL of pentane. The solvent was removed and the deep red solid dried *in vacuo*, giving 14 mg (15%). ^{1}H NMR (498.12 MHz, CD_2Cl_2, 26.1 °C): 7.74 (dd, 1H, $^3J_{H\text{-}H}$ = 2.4 Hz, $^5J_{H\text{-}P}$ = 1.7 Hz, $NCH_{imid\text{-}Pd}$), other $NCH_{imid\text{-}Pd}$ peak disguised by phenyl multiplets; 1.99 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); $NCH_{imid\text{-}Ir}$ peaks disguised by phenyl multiplets; 1.90 (s, 9H, $N_{imid\text{-}Ir}C(CH_3)_3$); 7.01 (d, 1H, $^2J_{H\text{-}H}$ = 11.5 Hz), 6.96 (d, 1H, $^2J_{H\text{-}H}$ = 11.5 Hz NCH_2N); 5.58 (m, 2H), 4.85 (m, 2H), 3.11–0.06 (m, 8H, COD). $^{13}C\{^1H\}$ NMR (100.54 MHz, CD_2Cl_2, 26.5 °C): 176.6 (s, 1C, $C_{carbene\text{-}Ir}$); 164.4 (d, 1C, $^2J_{C\text{-}P}$ = 217.1 Hz, $C_{carbene\text{-}Pd}$); 128.7 (s, 1C), 128.6 (s, 1C, $NCH_{imid\text{-}Ir}$); 128.1 (d, 1C, $^4J_{C\text{-}P}$ = 8.1 Hz), 128.0 (d, 1C, $^4J_{C\text{-}P}$ = 7.1 Hz, $NCH_{imid\text{-}Pd}$); 75.3 (s, 1C, NCH_2N); 69.6 (s, 1C), 22.5 (s, 3C, $N_{imid\text{-}Ir}C(CH_3)_3$); 67.9 (s, 1C), 14.0 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 131.0 (d, 3C, $^1J_{C\text{-}P}$ = 49.6 Hz), 132.1 (d, 6C, $^2J_{C\text{-}P}$ = 9.6 Hz), 132.0 (d, 6C, $^3J_{C\text{-}P}$ = 3.0 Hz), 135.4 (s, 3C, PPh_3); 92.2 (s, 1C), 92.0 (s, 1C), 57.0 (s, 1C), 52.7 (s, 1C), 34.8 (s, 1C), 34.3 (s, 1C), 34.2 (s, 1C), 31.7 (s, 1C, COD). $^{31}P\{^1H\}$ NMR (201.64 MHz, CD_2Cl_2, 27.0 °C): 28.3 (s, 1P, PPh_3). HRMS *m/z* Calcd for $C_{41}H_{51}I_2N_4PPdIr$ (M^+ – I): 1183.0600. Found: 1183.0610 (M^+ – I). Anal Calcd for $C_{41}H_{51}I_3IrN_4PPd$: C, 37.6; H, 3.9; N, 4.3. Found: C, 37.9; H, 4.1; N, 4.2.

(z) Diiododimethylphenylphosphinopalladium(II)-μ-(1,1′-methylene-3,3′-di-*tert*-butyldiimidazoline-2,2′-diylidene)iodo(η²:η²-cyclooctadiene)iridium(I), [$PdI_2(PMe_2Ph)(\mu$-$^{rBu}CC^{meth})IrI(COD)$] (21b). The desired complex was prepared as described for

20b, using 11b (64 mg, 0.072 mmol), K[N(SiMe$_3$)$_2$] (36 mg, 0.180 mmol), and [Ir(μ-Cl)(COD)]$_2$ (24 mg, 0.036 mmol). The crude product was purified as described for 20b, resulting in 17 mg (20%) of a yellow solid. ^{1}H NMR (498.12 MHz, CD_2Cl_2, 26.1 °C): 7.77 (d, 1H, $^3J_{H\text{-}H}$ = 2.2 Hz), 7.14 (d, 1H, $^3J_{H\text{-}H}$ = 2.2 Hz, $NCH_{imid\text{-}Ir}$); 1.89(s, 9H, $N_{imid\text{-}Ir}C(CH_3)_3$); 7.78 (dd, 1H, $^3J_{H\text{-}H}$ = 1.9 Hz, $^5J_{H\text{-}P}$ = 1.9 Hz), 7.23 (dd, 1H, $^3J_{H\text{-}H}$ = 1.9 Hz, $^5J_{H\text{-}P}$ = 1.9 Hz, $NCH_{imid\text{-}Pd}$); 1.87 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); both NCH_2N peaks disguised by phenyl multiplets; 7.88–7.16 (m, 5H), 2.16 (d, 3H, $^2J_{H\text{-}P}$ = 9.8 Hz), 2.15 (d, 3H, $^2J_{H\text{-}P}$ = 9.8 Hz, PMe_2Ph); 4.87 (m, 1H), 4.65 (m, 1H), 3.06 (m, 1H), 3.90 (m, 1H), 2.30–1.23 (m, 8H, COD).^{13}C{^{1}H} NMR (125.26 MHz, CD_2Cl_2, 26.1 °C): 179.2 (s, 1C, $C_{carbene\text{-}Ir}$); 171.9 (d, 1C, $^2J_{C\text{-}P}$ = 207.5 Hz, $C_{carbene\text{-}Pd}$); 121.7 (s, 1C), 120.3 (s, 1C, $NCH_{imid\text{-}Ir}$); 128.9 (d, 1C, $^4J_{C\text{-}P}$ = 6.7 Hz), 121.6 (d, 1C, $^4J_{C\text{-}P}$ = 6.6 Hz, $NCH_{imid\text{-}Pd}$); 66.7 (s, 1C, NCH_2N); 59.1 (s, 1C), 32.2 (s, 3C, $N_{imid\text{-}Ir}C(CH_3)_3$); 57.3 (s, 1C), 32.0 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 136.3 (d, 1C, $^1J_{C\text{-}P}$ = 44.7 Hz), 131.3 (d, 2C, $^2J_{C\text{-}P}$ = 10.6 Hz), 128.4 (d, 2C, $^3J_{C\text{-}P}$ = 10.0 Hz), 130.1 (s, 1C), 18.8 (d, 1C, $^1J_{C\text{-}P}$ = 32.6 Hz), 18.7 (d, 1C, $^1J_{C\text{-}P}$ = 33.0 Hz, PMe_2Ph); 82.0 (s, 1C), 79.3 (s, 1C), 59.1 (s, 1C), 55.5 (s, 1C), 33.4 (s, 1C), 31.8 (s, 1C), 30.6 (s, 1C), 30.1 (s, 1C, COD). ^{31}P{^{1}H} NMR (201.64 MHz, CD_2Cl_2, 26.1 °C): 17.0 (s, 1P, PMe_2Ph). HRMS *m/z* Calcd for $C_{31}H_{47}I_2IrN_4PPd$ (M^+ – I): 1059.0286. Found: 1059.0276 (M^+ – I). Anal Calcd for $C_{31}H_{47}I_3IrN_4PPd$: C, 31.4; H, 4.0; N, 4.7. Found: C, 31.7; H, 4.3; N, 4.9.

(za) Diiododimethylphenylphosphinopalladium(II)-μ-(1,1′-methylene-3,3′-di-*tert*-butyldiimidazoline-2,2′-diylidene)iododicarbonyliridium(I), [PdI$_2$(PPh$_3$)(μ-^{rBu}CC^{meth})IrI(CO)$_2$] (21b). The desired complex was prepared as described for complexes 3 using 20b (10 mg, 0.008 mmol), 10 mL THF, and the crude product purified by filtration after washing with 1 mL of pentane before drying *in vacuo*, giving 7 mg (80%). ^{1}H NMR (498.12 MHz, CD_2Cl_2, 26.1 °C): $NCH_{imid\text{-}Ir}$ peaks disguised by phenyl multiplets; 1.87 (s, 9H, $N_{imid\text{-}Ir}C(CH_3)_3$); $NCH_{imid\text{-}Pd}$ peaks disguised by phenyl multiplets; 1.83 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); 7.26 (d, 1H, $^2J_{H\text{-}P}$ = 16.1 Hz), 6.98 (d, 1H, $^2J_{H\text{-}P}$ = 16.1 Hz, NCH_2N); 7.77–7.31 (m, 15H, PPh_3). ^{13}C{^{1}H} NMR (125.26 MHz, CD_2Cl_2, 26.1 °C): 169.7 (s, 1C), 167.1 (s, 1C, CO); 180.1 (s, 1C, $C_{carbene\text{-}Ir}$); 164.1 (d, 1C, $^2J_{C\text{-}P}$ = 214.5 Hz, $C_{carbene\text{-}Pd}$); 128.7 (s, 1C), 128.7 (s, 1C, $NCH_{imid\text{-}Ir}$); 129.8 (d, 1C, $^4J_{C\text{-}P}$ = 9.1 Hz), 128.8 (d, 1C, $^4J_{C\text{-}P}$ = 10.3 Hz, $NCH_{imid\text{-}Pd}$); 75.3 (s, 1C, NCH_2N); 69.6 (s, 1C), 34.8 (s, 3C, $N_{imid\text{-}Ir}C(CH_3)_3$); 68.0 (s, 1C), 34.2 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 131.5 (d, 3C, $^1J_{C\text{-}P}$ = 38.7 Hz), 132.2 (d, 6C, $^2J_{C\text{-}P}$ = 9.7 Hz), 132.1 (d, 6C, $^3J_{C\text{-}P}$ = 3.0 Hz), 133.6 (s, 3C, PPh_3). ^{31}P{^{1}H} NMR (201.64 MHz, CD_2Cl_2, 26.1 °C): 28.4 (s, 1P, PPh_3). IR (solution, cm^{-1}): 2065, 1987 (CO). Anal Calcd for $C_{35}H_{39}I_3IrN_4O_2PPd$: C, 33.4; H, 3.1; N, 4.45. Found: C, 33.5; H, 3.3; N, 4.6.

(zb) Diiododimethylphenylphosphinopalladium(II)-μ-(1,1′-methylene-3,3′-di-*tert*-butyldiimidazoline-2,2′-diylidene)iododicarbonyliridium(I), [PdI$_2$(PMe$_2$Ph)(μ-^{rBu}CC^{meth})IrI(CO)$_2$] (23b). The desired complex was prepared as described for complexes **3** using **20b** (15 mg, 0.013 mmol), and the crude product purified by filtration after washing with 1 mL of pentane before drying *in vacuo*, giving 12 mg (84%). ^{1}H NMR (299.97 MHz, CD_3CN, 27.5 °C): 7.73 (d, 1H, $^3J_{H\text{-}H}$ = 2.2 Hz), 7.45 (d, 1H, $^3J_{H\text{-}H}$ = 2.2 Hz, $NCH_{imid\text{-}Ir}$); 1.85 (s, 9H, $N_{imid\text{-}Ir}C(CH_3)_3$); 7.42 (dd, 1H, $^3J_{H\text{-}H}$ = 2.1 Hz, $^5J_{H\text{-}P}$ = 1.4 Hz, $NCH_{imid\text{-}Pd}$), other $NCH_{imid\text{-}Pd}$ peak disguised by phenyl multiplets; 1.81 (s, 9H, $N_{imid\text{-}Pd}C(CH_3)_3$); 7.04 (d, 1H, $^2J_{H\text{-}H}$ = 13.2 Hz), 6.91 (d, 2H, $^2J_{H\text{-}H}$ = 13.2 Hz, NCH_2N); 7.82–7.41 (m, 5H), 2.13 (d, 3H, $^2J_{H\text{-}P}$ = 9.8 Hz), 2.13 (d, 3H, $^2J_{H\text{-}P}$ = 9.8 Hz, PMe_2Ph).^{13}C{^{1}H} NMR (125.27 MHz, CD_3CN, 26.1 °C): 169.6 (s, 1C), 167.5 (s, 1C, CO); 180.6 (s, 1C, $C_{carbene\text{-}Ir}$); 159.6 (d, 1C, $^2J_{C\text{-}P}$ = 194.1 Hz, $C_{carbene\text{-}Pd}$); 122.4 (s, 1C), 121.9 (s, 1C, $NCH_{imid\text{-}Ir}$); 122.6 (d, 1C, $^4J_{C\text{-}P}$ = 6.5 Hz), 121.5 (d, 1C, $^4J_{C\text{-}P}$ = 5.2 Hz, $NCH_{imid\text{-}Pd}$); 66.6 (s, 1C, NCH_2N); 59.9 (s, 1C), 31.6 (s, 3C, $N_{imid\text{-}Ir}C(CH_3)_3$); 59.4 (s, 1C), 31.4 (s, 3C, $N_{imid\text{-}Pd}C(CH_3)_3$); 136.3 (d, 1C, $^1J_{C\text{-}P}$ = 46.1 Hz), 131.5 (d, 2C, $^2J_{C\text{-}P}$ = 10.9 Hz), 128.6 (d, 2C, $^3J_{C\text{-}P}$ = 10.2 Hz), 130.2 (d, 1C, $^4J_{C\text{-}P}$ = 2.5 Hz), 18.2 (d, 1C, $^1J_{C\text{-}P}$ = 33.6 Hz), 17.9 (d, 1C, $^1J_{C\text{-}P}$ = 33.6 Hz, PMe_2Ph). ^{31}P{^{1}H} NMR (161.84 MHz, CD_3CN, 26.5 °C): –17.1 (s, 1P, PMe_2Ph). IR (solution, cm^{-1}): 2065, 1986 (CO). HRMS *m/z* Calcd for $C_{25}H_{35}I_2IrN_4O_2PPd$ (M^+–I): 1006.9246. Found: 1006.9234 (M^+ – I). The ^{1}H and ^{13}C{^{1}H} NMR spectra of this compound are given in the ESI (Fig. S4).†

X-Ray structure determinations

(a) General considerations. Crystals were grown either from concentrated CH_3CN solutions of the compound (**11b**, **13b**), *via* slow diffusion of ether and pentane into a CH_2Cl_2 solution of the compound (**2c**, **2d**, **17b**), or *via* slow diffusion of ether and pentane into an acetone solution of compound (**16b**). Data were collected[77] using either a Bruker SMART 1000 CCD detector/PLATFORM diffractometer with the crystals cooled to –80 °C (**2c**, **2d**) or using a Bruker APEX II detector/D8 diffractometer with the crystals cooled to –100 °C (**11b**, **13b**, **16b**, **17b**); in all cases Mo Kα radiation was used. The data were corrected for absorption through use of a multiscan model (*SADABS*) (**2c**, **2d**, **11b**, **13b**) or through use of Gaussian integration (using the indexed faces and measured dimensions of the crystal (**16b**, **17b**). Structures were solved using direct methods (*SHELXS-97*[78] (**2c**, **11b**, **13b**) or *SIR97*[79] (**2d**, **17b**)) or through Patterson location of heavy atom positions followed by structure expansion (*DIRDIF-2008*[80] (**16b**)). The program *SHELXL-97*[78] was used for structure refinements. Hydrogen atoms (including those involved in hydrogen bonds) were assigned positions on the basis of the geometries of their attached carbon atoms and were given thermal parameters 120% of their parent carbons. See Table 1 for a listing of crystallographic experimental data.

(b) Special refinement conditions. (i) Despite crystallizing in a chiral space group ($P2_1$), the crystal of **2d** was found to be racemically twinned. This was accommodated during refinement through use of the *SHELXL-97*[78] TWIN instruction, and the Flack parameter refined to a value of 0.364(6). (ii) For **13b**, a half-occupancy molecule of solvent acetonitrile was found to be disordered about the inversion center (1/2, 0, 1/2). Distances within this molecule were constrained during refinement to be equal (within 0.01 Å) to the corresponding distances within the other (full-occupancy, non-disordered) cocrystallized solvent CH_3CN molecule: d(N(1S)–C(1S)) = d(N(2S)–C(3S)); d(C(1S)–C(2S)) = d(C(3S)–C(4S)); d(N(1S)···C(2S)) = d(N(2S)···C(4S)).

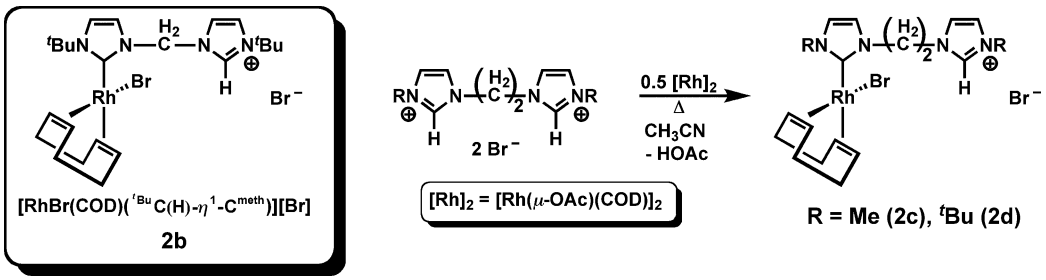
Results and compound characterization

As noted earlier, it appeared that di-*N*-heterocyclic carbene-bridged complexes involving two *different* metals could be

Table 1 Crystallographic experimental details

Compound	**2c**	**2d**·2CH_2Cl_2	**11b**	**13b**·1.5CH_3CN	**16b**·$(CH_3)_2CO$	**17b**
Formula	$C_{18}H_{27}Br_2N_4Rh$	$C_{26}H_{43}Br_2Cl_4N_4Rh$	$C_{23}H_{36}I_3N_4PPd$	$C_{34}H_{51.50}I_3N_{5.50}P_2Pd$	$C_{27}H_{53}I_3N_4OP_2Pd$	$C_{29}H_{51}I_3N_4PPdRh$
Formula weight	562.17	816.17	886.63	1086.35	998.77	1076.72
Crystal dimens (mm)	0.37 × 0.10 × 0.05	0.45 × 0.17 × 0.15	0.47 × 0.27 × 0.12	0.45 × 0.27 × 0.23	0.47 × 0.36 × 0.27	0.58 × 0.41 × 0.18
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$ (No. 14)	$P2_1$ (No. 4)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$Pbca$ (No. 61)
Unit cell parameters						
a/Å	23.748 (2)	8.5243 (10)	9.4861 (11)	15.060 (2)	14.2452 (6)	15.4844 (14)
b/Å	6.9405 (7)	13.8891 (16)	12.0320 (13)	13.1140 (17)	21.1101 (8)	11.9963 (11)
c/Å	12.3794 (12)	14.5876 (17)	14.0083 (16)	22.022 (3)	12.9669 (5)	40.421 (4)
α/°			91.9746 (12)			
β/°	91.4800 (10)	101.093 (2)	100.9332 (12)	96.159 (2)	94.9031 (4)	
γ/°			103.9630 (12)			
V/Å^3	2039.7 (3)	1694.8 (3)	1518.0 (3)	4324.4 (10)	3885.1 (3)	7508.3 (12)
Z	4	2	2	4	4	8
ρ_{calcd}/g cm^{-3}	1.831	1.599	1.940	1.669	1.708	1.905
μ/mm^{-1}	4.764	3.199	3.732	2.673	2.968	3.451
Diffractometer	Bruker PLATFORM/SMART 1000 CCD (compnds **2c**, **2d**)[a]		Bruker D8/APEX II CCD (compnds **11b**–**17b**)[a]			
Radiation λ/Å	graphite-monochromated Mo Kα (0.71073)					
Temperature/°C	–80	–80	–100	–100	–100	–100
Scan type	ω scans (0.3 °) (25 s exposures)	ω scans (0.3 °) (20 s exposures)	ω scans (0.3 °) (20 s exposures)	ω scans (0.3 °) (20 s exposures)	ω scans (0.3 °) (20 s exposures)	ω scans (0.4 °) (10 s exposures)
$2\theta_{max}$/°	55.06	54.88	52.80	55.00	55.00	55.04
Total data collected	16813 ($-30 \le h \le 30$, $-9 \le k \le 8$, $-15 \le l \le 16$)	14567 ($-11 \le h \le 11$, $-18 \le k \le 17$, $-18 \le l \le 18$)	11967 ($-11 \le h \le 11$, $-15 \le k \le 15$, $-17 \le l \le 17$)	36366 ($-19 \le h \le 19$, $-17 \le k \le 16$, $-28 \le l \le 28$)	33796 ($-18 \le h \le 18$, $-27 \le k \le 27$, $-16 \le l \le 16$)	59218 ($-20 \le h \le 20$, $-15 \le k \le 15$, $-52 \le l \le 52$)
Independ reflns (R_{int})	4660 (0.0370)	7648 (0.0163)	6159 (0.0148)	9905 (0.0309)	8906 (0.0162)	8629 (0.0256)
Obsd reflns [$I \ge 2\sigma(I)$]	3703	7288	5815	8875	8022	8116
Restraints/params	0/228	0/335	0/290	3[b]/426	0/345	0/352
Flack abs struct parameter		0.364(6)				
Goodness-of-fit (S)[c]	1.051	1.071	1.157	1.030	1.038	1.208
Final R indices[d]						
R_1 [I ≥ 2σ(I)]	0.0314	0.0294	0.0251	0.0241	0.0284	0.0250
wR_2 [all data]	0.0753	0.0755	0.0764	0.0595	0.0760	0.0560
Largest diff peak, hole/e Å^{-3}	1.227, –0.331	1.989, –0.525	1.306, –0.697	1.093, –0.924	2.290, –0.970	0.924, –0.924

[a] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker. [b] The distances and angles of the inversion-disordered acetonitrile solvent molecule (N2S, C3S, C4S) were restrained to be the same as those of the ordered acetonitrile solvent molecule (N1S, C1S, C2S) by use of the *SHELXL* SAME instruction. [c] $S = [\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (a_0P)^2 + a_1P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$; for **2c**, $a_0 = 0.0421$, $a_1 = 0$; for **2d**, $a_0 = 0.0504$, $a_1 = 0.2277$; for **11b**, $a_0 = 0.0310$, $a_1 = 4.1569$; for **13b**, $a_0 = 0.0281$, $a_1 = 2.5400$; for **16b**, $a_0 = 0.0380$, $a_1 = 5.5389$; for **17b**, $a_0 = 0.0143$, $a_1 = 16.7787$). [d] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$.



Scheme 1

accessed *via* deprotonation of a carbene-anchored/pendent-imidazolium complex, of the type shown earlier in Chart 1, in the presence of a second metal. We had already shown that such a strategy could be employed to generate dicarbene-bridged Rh_2 complexes *via* deprotonation of the mononuclear species, [RhBr(COD)($^{t\mathrm{Bu}}$C(H)-η^1-C$^{\mathrm{meth}}$)][Br] ($^{t\mathrm{Bu}}$C(H)-η^1-C$^{\mathrm{meth}}$ = methylene[(*N*-*tert*-butyl)imidazolium][(*N*-*tert*-butyl)imidazole-2-ylidene]), by [Rh(μ-OAc)(COD)]$_2$. A number of carbene-anchored/pendent-imidazolium species of Rh,[18,31] Ir,[18,68,69,81] Pd,[82–86] Ni,[81,87,88] Fe,[89] and Ru,[67] which seemed appropriate for generation of binuclear species, were already known and in this paper we sought to extend the number of these complexes of Rh and Pd to serve as potential synthons for a range of dicarbene-bridged mixed-metal complexes involving these metals.

In this paper we use the abbreviations, $^{\mathrm{R}}$C(H)-η^1-C$^{\mathrm{alk}}$ for the monodentate pendent species and μ-$^{\mathrm{R}}$CC$^{\mathrm{alk}}$ for bidentate dicarbene systems, as originally suggested by Green, *et al.* and as shown in Chart 2.[42] In these abbreviations the substituent (R) on the carbene or imidazolium rings appears first, followed by the pendent/anchored (C(H)-η^1-C) or dicarbene notation (CC) and finally an abbreviation (alk = meth, eth) designating a methylene or ethylene linker between the NHC/NHC or NHC/imidazolium rings. We will additionally use the label **a** in the numbering scheme to indicate the Me/meth combination, the label **b** to indicate ^{t}Bu/meth, the label **c** to indicate Me/eth, and **d** for the ^{t}Bu/eth combination.

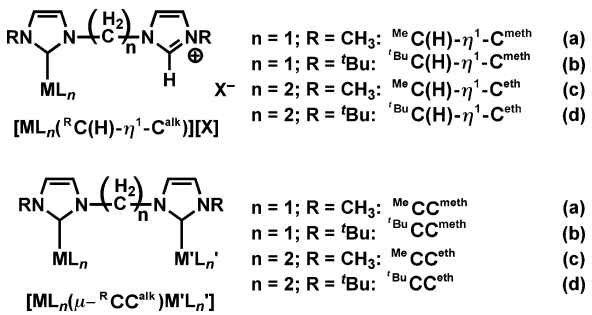


Chart 2

(a) Carbene-anchored/pendent-imidazolium complexes of Rh. Although there are a few examples in which an external base can be used to deprotonate only one end of a diimidazolium salt to generate pendent-imidazolium species, they are usually specific to diimidazolium salts terminated by bulky *N*-substituents such as ^{t}Bu and Mes[11,43,66,67] and therefore limit the scope of carbene-anchored complexes possible. Most often, single deprotonation of the diimidazolium salts is carried out using complexes containing basic ligands such as acetate or methoxide groups, which serve to deprotonate these salts. This is the method used with some success in this report, and in previous reports by us[46] and others.[18,31,46,81–84,86–88,90–93] In a previous study we had shown that the acetate-bridged complex, [Rh(μ-OAc)(COD)]$_2$, was effective in the deprotonation of a number of diimidazolium salts generating the corresponding series of di-NHC-bridged dirhodium products.[46] In one case the mononuclear carbene-anchored/pendent-imidazolium complex [RhBr(COD)($^{t\mathrm{Bu}}$C(H)-η^1-C$^{\mathrm{meth}}$)][Br] (**2b**, Scheme 1) was generated and found to be a probable intermediate in the formation of the di-NHC-bridged target. Although our initial attempts to prepare the other members of this series, namely, [RhBr(COD)L][Br] (L = $^{\mathrm{Me}}$C(H)-η^1-C$^{\mathrm{meth}}$, $^{\mathrm{Me}}$C(H)-η^1-C$^{\mathrm{eth}}$, $^{t\mathrm{Bu}}$C(H)-η^1-C$^{\mathrm{eth}}$), from the corresponding diimidazolium salts were unsuccessful, we have subsequently been able to generate both the methyl- and *tert*-butyl-substituted *ethylene*-linked systems (**2c**,**d**, Scheme 1) by using longer reaction times (see Experimental section). Attempts to generate the fourth member of the series, [RhBr(COD)($^{\mathrm{Me}}$C(H)-η^1-C$^{\mathrm{meth}}$)][Br] (**2a**), using a similar procedure gave only a mixture of unidentified products, under a variety of conditions.

The ^{1}H NMR spectral parameters for the series of complexes (**2c** and **2d**) are closely comparable to those described for **2b**[46] and also to those of previously reported pendent complexes involving other metals.[18,31,67,81–89] Complexes **2b-2d** show typical resonances for the coordinated COD ligands (between δ 1.7 and δ 5.7) as given in the Experimental section. The acidic proton of the pendent imidazolium group appears characteristically downfield at *ca.* δ 10 as a pseudotriplet, displaying approximately equal coupling to the pair of inequivalent olefinic protons, while these olefinic protons on the imidazolium group display mutual coupling ($^3J_{\mathrm{H\text{-}H}} \approx 2$ Hz) in addition to coupling ($^4J_{\mathrm{H\text{-}H}} \approx 2$ Hz) to the acidic proton and therefore also appear as pseudotriplets. The appearance of two different resonances for the *N*-bound substituents (at *ca.* δ 4.0 for the methyl groups in **2c**; and at *ca.* δ 1.8 for the *tert*-butyl groups in **2b**,**d**) is as expected for an unsymmetrical, carbene/imidazolium system, and the four separate resonances for the olefinic protons within the NHC and imidazolium rings offer further support for the pendent species. The AB quartet observed for the methylene linker in **2b** rather than a singlet suggests that the NHC unit adopts the usual orientation in which it is bound perpendicular to the square plane of the metal. In this orientation, the plane bisecting the linking CH_2 group is unsymmetrical on each side, having a bromo ligand on one side and one half of the COD ligand on the other. The ^{13}C{^{1}H} NMR data offer additional support for the

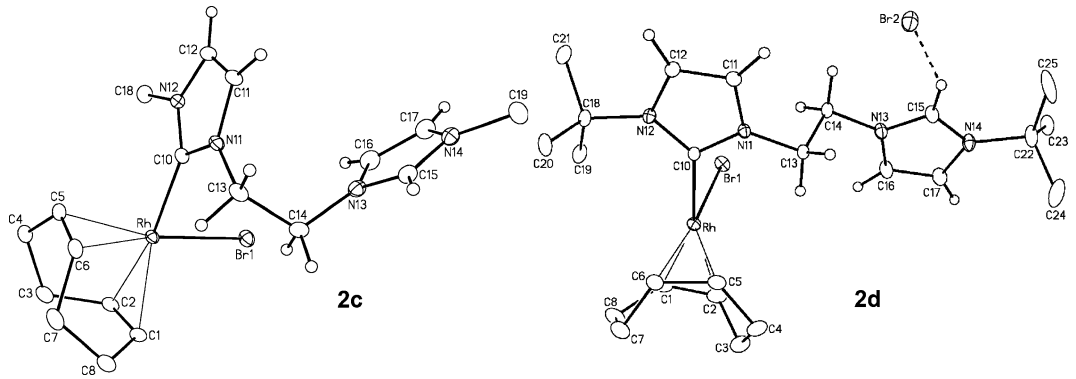


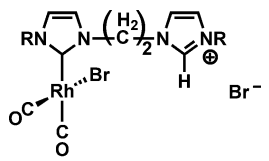
Fig. 1 Three-dimensional representations of the complex cation of [RhBr(COD)(^{Me}C(H)-η^1-C^{eth})][Br] (**2c**) and both the anion and cation of [RhBr(COD)(^{tBu}C(H)-η^1-C^{eth})][Br] (**2d**) showing the numbering schemes. Thermal ellipsoids are shown at the 20% probability level. Hydrogen atoms are shown only on the linked carbene/imidazolium group. Relevant parameters for **2c** (distances in Å and angles in °): Rh–Br(1) = 2.5054(4), Rh–C(1) = 2.205(3), Rh–C(2) = 2.226(3), Rh–C(5) = 2.102(3), Rh–C(6) = 2.123(3), Rh–C(10) = 2.022(3); Br(1)–Rh–C(10)–N(12) = 83.2(3)°, N(11)–C(13)–C(14)–N(13) = 61.7(4)°. Relevant parameters for **2d** (distances in Å and angles in °.): Rh–Br(1) = 2.5338(4), Rh–C(1) = 2.190(4), Rh–C(2) = 2.229(3), Rh–C(5) = 2.101(3), Rh–C(6) = 2.127(3), Rh–C(10) = 2.053(3); Br(1)–Rh–C(10)–N(12) = 98.5(3)°, N(11)–C(13)–C(14)–N(13) = −176.6(2)°.

pendent structure, displaying two different signals for the *N*-bound substituents on the carbene and imidazolium rings, and four different olefinic carbons. More significantly, the carbene carbon in these complexes appears at *ca.* δ 181.7 with typical coupling to Rh[39,46,94–96] of approximately 50 Hz, while the protonated carbon of the imidazolium group appears as a singlet at *ca.* δ 122.0. This imidazolium carbon resonance appears as a doublet in the proton-coupled ^{13}C NMR spectrum having $^1J_{C\text{-}H} \approx 220$ Hz coupling to the acidic proton (as confirmed by 2D Heteronuclear Single Quantum Coherence (HSQC) and Heteronuclear Multiple Quantum Coherence (HMQC) NMR experiments).

The proposed pendent structures for complexes **2c**,**d** are confirmed by X-ray crystallography and their structures are shown in Fig. 1. Consistent with the NMR data, the NHC plane lies close to perpendicular to the metal coordination plane in both cases (dihedral angles = 83.2(3)° and 98.5(3)° respectively); and the Rh–$C_{carbene}$ distances are normal, suggesting a metal–carbon single bond. The Rh–C(1) and Rh–C(2) separations (2.205(3), 2.226(3) Å in **2c**; 2.190(4), 2.229(3) Å in **2d**) involving the olefinic moiety of the COD ligand *trans* to the NHC are longer than those of Rh–C(5) and Rh–C(6) to the other olefin moiety (2.102(3), 2.123(3) Å in **2c**; 2.101(3), 2.127(3) Å in **2b**). This difference can be rationalized either on the basis of steric repulsions between half of the COD ligand and the adjacent bromo ligand or the larger *trans* influence of the carbene ligand.[16,31,34,39] The weaker Rh–olefin interaction is paralleled by a shorter C(1)–C(2) distance (1.382(4) Å in **2c**; 1.383(6) Å in **2d**) compared to C(5)–C(6) (1.404(5) Å in **2c**; 1.403(5) Å in **2d**), consistent with less π back-donation in this case. The major difference between the two structures involves the different torsion angles around the C_2H_4 linker as shown in Fig. 1. These differences are presumably a consequence of packing effects and are unlikely to be of chemical significance.

The close separation (2.67 Å) between the acidic proton of the imidazolium group and the bromide counterion in **2d**, which is significantly shorter than the sum of their van der Waals radii (3.05 Å),[97] indicates hydrogen bonding between the two whereas for **2c** the closest H–Br distance (3.12 Å) is normal and does not suggest such an interaction.

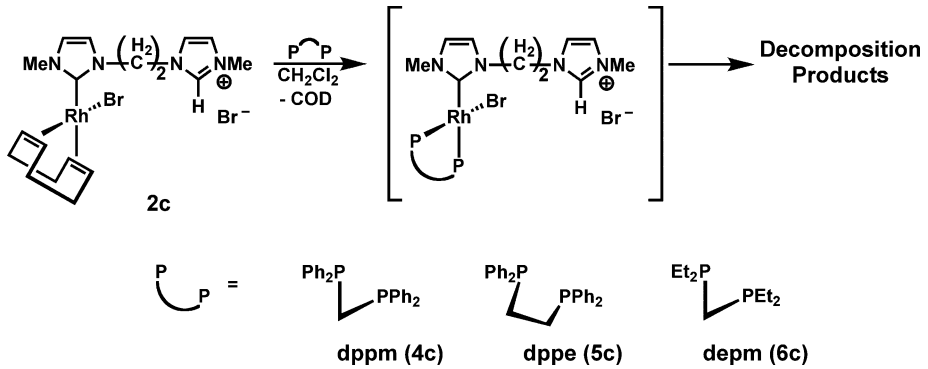
Although replacement of the COD ligands by CO in compounds **2c** and **2d** proceeds as expected to yield the analogous dicarbonyl complexes [RhBr(CO)$_2$(^{Me}C(H)-η^1-C^{eth})][Br] (**3c**) and [RhBr(CO)$_2$(^{tBu}C(H)-η^1-C^{eth})][Br] (**3d**), shown in Chart 3, CO addition to the C_1-linked complex **2b** does not proceed as expected, but instead yields a number of unidentified decomposition products. This result parallels the previously observed differences with the C_1- and C_2-linked dicarbene ligands ^{R}CC^{meth} and ^{R}CC^{eth} (R = Me, ^{t}Bu), respectively, in which the C_2-linked dicarbene-bridged complexes [RhX(COD)]$_2$(μ-^{R}CC^{eth}) underwent facile COD replacement by CO to give the anticipated products, [RhX(CO)$_2$]$_2$(μ-^{R}CC^{eth}), while the related C_1-linked species [RhBr(COD)]$_2$(μ-^{R}CC^{meth}) did not undergo simple substitution, instead yielding the unexpected mononuclear products [RhBr(CO)(η^1:η^1-^{R}CC^{meth})] together with [Rh(μ-Br)(CO)$_2$]$_2$,[46] through fragmentation of the dicarbene-bridged precursors.



R = Me (3c), ^{t}Bu (3d)

Chart 3

Although single crystals of **3c**,**d** suitable for an X-ray diffraction study could not be obtained (the Br^-, BF_4^- and OTf^- salts could only be obtained as oils), the spectral data leave little doubt about their formulations. In addition to the downfield pseudotriplet at *ca.* δ 10.1 in the ^{1}H NMR spectrum for the imidazolium proton, a downfield peak for the carbene carbon appears as a doublet ($^1J_{C\text{-}Rh} \approx 42$ Hz) in the ^{13}C{^{1}H} NMR at *ca.* δ 172.6 together with a singlet at *ca.* δ 137.1, corresponding to the imidazolium carbon. Furthermore, the carbonyl stretches of **3c**,**d** appear at *ca.* 2006 and 2082 cm^{-1} in the IR spectra, with these carbons appearing at *ca.* δ 186.2 and 182.2 in the ^{13}C{^{1}H} NMR spectra showing typical coupling to rhodium. The carbonyl *trans* to the carbene displays approximately 54 Hz coupling to Rh while the



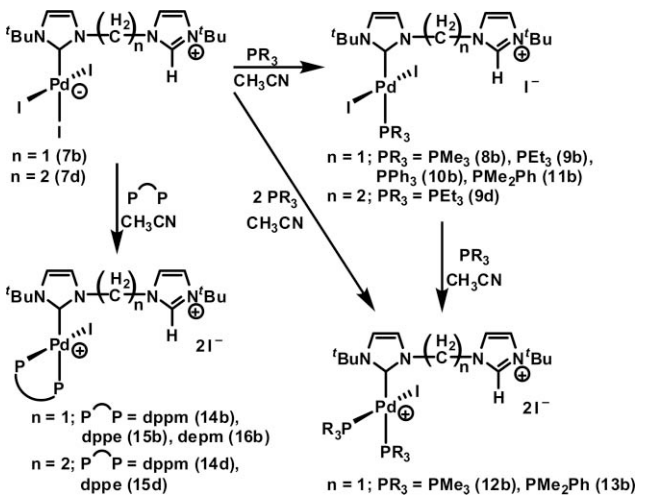
Scheme 2

carbonyl group *trans* to the bromide shows approximately 77 Hz coupling, as is seen in similar systems.[39] The larger $^{1}J_{Rh\text{-}C}$ and smaller ν_{CO} is consistent with this carbonyl, opposite the bromo ligand, being more strongly bound—presumably a consequence of both the lower *trans* influence of the bromo ligand compared to the NHC group[16,31,34,39] and its greater π donor ability.

Reaction of the COD complex (**2c**) with a series of diphosphine ligands generates the diphosphine-chelated products [RhBr(P⌒P)(^{Me}C(H)-η^{1}-C^{eth})][Br] (**4c-6c**), as shown in Scheme 2. The ^{31}P{^{1}H} NMR spectra of these products display two sets of doublets of doublets; both resonances display coupling to Rh (ranging from 102.7 to 197.6 Hz) and to the other ^{31}P nucleus (33.4 to 102.7 Hz). Additionally, these peaks are located more upfield when methylene-linked diphosphines (**4c**, **6c**) are used (both peaks centred about δ –25, –21, respectively) whereas a more downfield set of peaks is observed in the ethylene-linked case of **5c** (centred about δ 65), consistent with the large deshielding reported for five-membered diphosphine rings,[98] confirming the chelating formulation above. As observed in the parent complex **2c**, the acidic proton of the pendent imidazolium group in these pendent species appears downfield at *ca.* δ 10.2 in the ^{1}H NMR spectrum. The pendent nature is also evident by the four different peaks for the olefinic protons, as well as two different peaks for the methyl substituents in the ^{1}H NMR spectra. Surprisingly perhaps, the other COD precursors **2b**,**d** fail to react with these diphosphines, even after prolonged reflux. In addition, all complexes (**2a-d**) are inert to a number of monophosphines, even under forcing conditions.

The resulting diphosphine complexes (**4c-6c**) are unstable and decompose over the course of 1 h to form undesired complexes lacking the acidic proton. On the basis of ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, the resulting species most likely contain chelating diphosphine and dicarbene groups, and are themselves unstable, decomposing to a mixture of unidentified products over the course of 1–1.5 h, even in the presence of coordinating solvents such as THF or CH_3CN. These transient intermediates were not of interest, and were not characterized further.

(b) Carbene-anchored/pendent-imidazolium complexes of Pd. An analogous series of carbene-anchored/pendent-imidazolium complexes of palladium can be generated by substitution of the iodo ligands in [PdI$_3$(^{tBu}C(H)-η^{1}-C^{meth})] (**7b**),[63] by a number of mono- and diphosphine ligands as outlined in Scheme 3. Unlike the previously described Rh species that were unreactive to monophosphines, the triiodide C_1-linked Pd precursor (**7b**)



Scheme 3

reacts with monophosphines in a stepwise manner yielding first the monophosphine products (**8b-11b**) which subsequently, in the presence of additional PR_3, result in a second iodide substitution to give the bis(phosphine) species **12b** and **13b**. With a number of diphosphines, the diphosphine-substituted products (**14b-16b**) are produced. The analogous methyl-substituted species, [PdI$_3$(^{Me}C(H)-η^{1}-C^{meth})] and [PdI$_3$(^{Me}C(H)-η^{1}-C^{eth})], were not investigated since Herrmann, *et al.* have reported that only di-NHC-chelated dicarbene products [PdX$_2$(η^{1}:η^{1}-^{Me}CC^{meth})] and [PdX$_2$(η^{1}:η^{1}-^{Me}CC^{eth})] were obtained.[83]

The spectral parameters for the carbene/imidazolium groups of complexes **8b-16b** are closely comparable to those in related pendent species which have previously been reported,[11,37,42,43,61–65,67–69,99] and again confirm the carbene-anchored/pendent-imidazolium formulation. The methylene protons of the C_1-linker in the pendent group show up as a singlet at *ca.* δ 6.71 in the monophosphine complexes, reflecting the symmetry on either side of the NHC plane, whereas for the bis(phosphine) species (**12b**, **13b**) and the chelated diphosphine complexes (**14b-16b**) the protons of the methylene linker appear as an AB quartet, ($^{2}J_{H\text{-}H}$ ≈ 14 Hz, Δδ ≈ 0.4–0.7 ppm) consistent with the lack of symmetry on either side of the carbene plane for these products. As was observed with **4c-6c**, complexes **15** exhibit a similar downfield shift in their ^{31}P{^{1}H} NMR resonances (centred at *ca.* δ 56) compared to the four-membered ring-containing analogues **14** and **16b** (centred

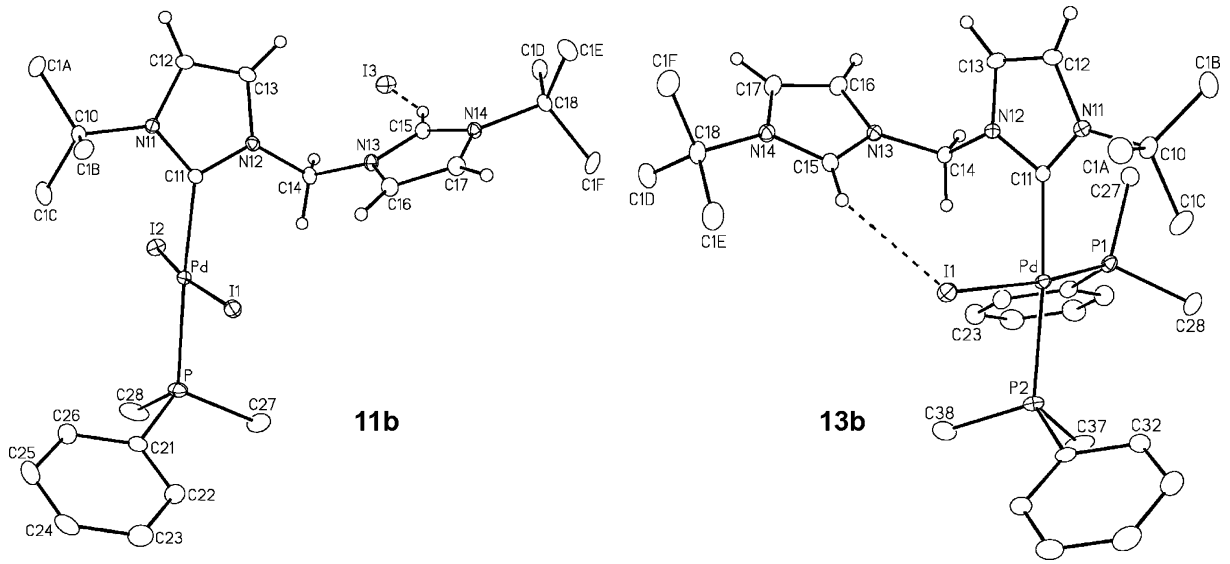


Fig. 2 Three-dimensional representations of $[PdI_2(PMe_2Ph)(^{tBu}C(H)\text{-}\eta^1\text{-}C^{meth})][I]$, **11b** and the dication complex $[PdI(PMe_2Ph)_2(^{tBu}C(H)\text{-}\eta^1\text{-}C^{meth})][I]_2$, **13b** showing the numbering scheme. Thermal ellipsoids are as described in Fig. 1. Hydrogen atoms are shown only on the linked carbene/imidazolium group. Relevant parameters for **11b** (distances in Å and angles in °): Pd–C(11) = 2.049(4); N(12)–C(14)–N(13) = 110.6(3)°. Relevant parameters for **13b** (distances in Å and angles in °): Pd–C(11) = 2.052(2); N(12)–C(14)–N(13) = 110.98(19)°.

at *ca.* δ −51 and δ −49, respectively), consistent with the ring contribution effect[98] noted earlier. As an interesting contrast to this chelating diphosphine phenomenon, the midpoint of the two doublets in the bis(phosphine) complex **13b** is located at about δ −8.

All olefinic protons, for the carbene and imidazolium moieties appear as pseudotriplets; for the imidazolium groups these olefinic protons again display mutual coupling as well as coupling to the acidic proton, whereas for the carbene groups the olefinic protons show essentially equal coupling to each other and to the ^{31}P nucleus in the position opposite the carbene ligand. These resonances are readily differentiated by appropriate $^1H\{^{31}P\}$ and $^1H\{^1H\}$ NMR experiments (Fig. S5, ESI).† Identification of individual ^1H and ^{13}C resonances is also aided by ^1H Nuclear Overhauser Effect (NOE), HSQC, HMQC and Heteronuclear Multiple Bond Correlation (HMBC) NMR experiments (assignments are outlined in the Experimental section).

The carbene carbon in each case appears at *ca.* δ 160.0 in the $^{13}C\{^1H\}$ NMR spectrum. In the case of the monophosphine complexes (**8b-11b**) this carbene resonance displays coupling ($^2J_{C\text{-}P}$ ≈ 190 Hz) to the *trans*-phosphine; while in the bis(phosphine) (**12b**, **13b**) or diphosphine (**14b-16b**) complexes, additional coupling to the *cis*-phosphorus nucleus ($^2J_{C\text{-}P}$ ≈ 3–7 Hz) can also be observed for some species. However, in the case of **16b** only the large *trans*-phosphine coupling is resolvable. Coupling of the pair of olefinic carbons in the carbene moiety to the *trans*-phosphine can also be observed ($^4J_{C\text{-}P}$ ≈ 5 Hz). In the proton-coupled ^{13}C NMR spectrum, the resonance for the pendent protonated carbon appears as a doublet displaying approximately 220 Hz coupling to the attached acidic proton, as noted above for the Rh species **2**.

Although all reactions involving monophosphines were carried out with an excess of phosphine, only in the cases of PMe_3 and PMe_2Ph did I^- substitution by a second phosphine occur (Scheme 3). This is presumably a result of steric repulsion between the phosphine and the nearby *tert*-butyl group since the somewhat larger, yet strongly basic triethylphosphine does not substitute a second iodide ion, even in the presence of a tenfold excess of phosphine. The only phosphines to give the double-substitution products were the two smallest studied.[20] For the three diphosphines studied, all have cone angles less than that of PEt_3,[20] and coordination of both ends of these diphosphines is additionally favoured entropically by the chelate effect.

The X-ray structure determinations for compounds **11b** and **13b**, shown in Fig. 2, and of **16b**, shown in Fig. 3 confirm the

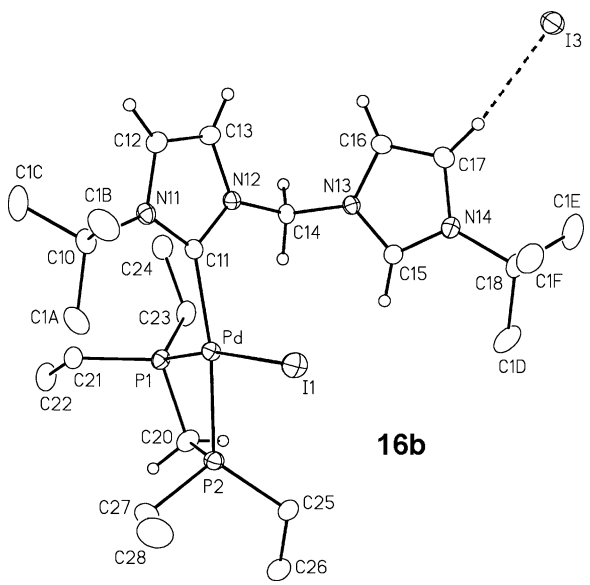
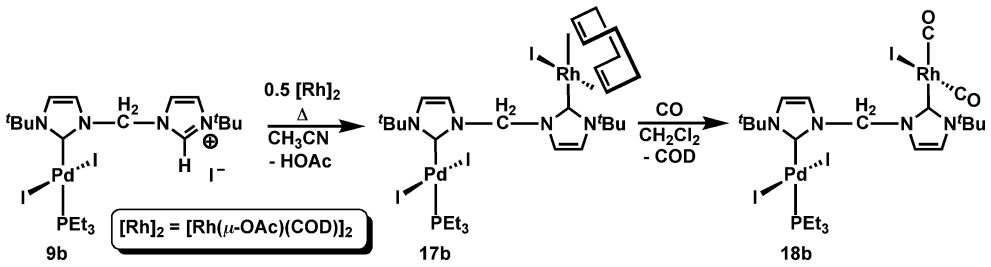


Fig. 3 Three-dimensional representation of the cation complex $[PdI(depm)(^{tBu}C(H)\text{-}\eta^1\text{-}C^{meth})][I]_2$, **16b** showing the numbering scheme. Thermal ellipsoids are as described in Fig. 1. Hydrogen atoms are shown only on the linked carbene/imidazolium group. Relevant parameters (distances in Å and angles in °): Pd–C(11) = 2.062(3); N(12)–C(14)–N(13) = 111.5(2)°, P(1)–C(20)–P(2) = 94.71(15)°, P(2)–Pd–C(11) = 170.58(8)°, I(1)–Pd–P(1) = 167.14(2)°.



Scheme 4

structural assignments determined on the basis of spectral data. In all three structures the geometry is typical of square-planar NHC complexes in which the carbene plane lies essentially perpendicular to the metal coordination plane, having a dihedral angle with the plane defined by I(1), Pd, C(11) and N(11) of −93.1(3)° for **11b**; 86.1(2)° for **13b**; and −86.0(3)° for **16b**. The Pd–$C_{carbene}$ distances are also typical of such systems, suggesting a metal–carbon single bond. All three complexes display some degree of hydrogen bonding involving the imidazolium proton and a nearby iodide ion, having H(15)–I contacts of 2.75 Å, 2.95 Å and 2.94 Å for **11b**, **13b** and **16b**, respectively, which are less than the sum of their van der Waals radii of 3.18 Å.[97] In the case of compounds **11b** and **16b**, this hydrogen bond involves an iodide counterion, while for **13b** this is an inner-sphere interaction with the coordinated iodo ligand, forming an 8-membered pseudometallocycle (both interactions are diagrammed in Fig. 2 and 3). For compound **13b** an additional hydrogen bond of 2.87 Å appears between one of the outer-sphere iodide ions (I(2)) and one of the methylene hydrogens on the linker carbon C(14), while a similar interaction (I(3)–H(17) = 2.85 Å) involves a olefinic hydrogen of **16b**.

The strain within complex **16b**, resulting from diphosphine chelation to a square-planar centre, is evident in the geometry within the depm group as well as in the angles about Pd. Within the diphosphine the P(1)–P(2) separation (2.6907(11) Å) is much smaller than is usually observed in an unstrained depm moiety, where values near 3.05 Å are more typical,[46] and is accompanied by an acute P(1)–C(20)–P(2) angle (94.71(15)°) which is significantly less than the idealized 109.5°. Accompanying this strain, the P(1)–Pd–P(2) angle (72.29(3)°) is also compressed from the idealized 90°.

The C_2-linked analogue, [PdI_3(^{tBu}C(H)-η^1-C^{eth})] (**7d**), in which the carbene is connected to the imidazolium ring by a C_2H_4 linker was also successfully prepared using a similar procedure to that used by Herrmann, *et al.* to generate [PdI_3(^{tBu}C(H)-η^1-C^{meth})] (**7b**),[63] and a number of mono- (**9d**) and diphosphine (**14d**, **15d**) derivatives involving this C_2-linked carbene/imidazolium species have also been generated as described for the C_1-linked products (Scheme 3). These species display NMR spectra very similar to those described for compounds **8b-11b** and **14b-15b**, respectively, as documented in the Experimental section. Interestingly, the peak corresponding to the carbene carbon in **7d** could not be observed in the $^{13}C\{^1H\}$ NMR spectrum, as also reported by Herrmann, *et al.* for the C_1-linked system.[63]

(c) Mixed-metal, di-NHC-bridged heterobimetallic complexes. In our initial study,[46] we were able to prepare a binuclear dicarbene-bridged complex from a mononuclear, carbene-anchored/pendent-imidazolium precursor by deprotonating the pendent acidic imidazolium hydrogen of **2b** using one-half-equivalent of [Rh(μ-OAc)(COD)]$_2$ yielding the dirhodium target. Attempts to extend this strategy to generate mixed-metal complexes of rhodium using **2b-2d** as precursors and using the complexes [Ir(μ-OAc)(COD)]$_2$, or [$Pd(OAc)_2$], containing the basic acetate ligands, all failed. Although the ^{1}H NMR spectra indicate that deprotonation of the acidic proton on the imidazolium group has occurred (as evident from the absence of a downfield pseudotriplet), no evidence of a binuclear Rh/Ir or Rh/Pd product could be detected by NMR or HRMS.

However, using the reverse strategy, starting with carbene-anchored/pendent-imidazolium complexes of other metals and using [Rh(μ-OAc)(COD)]$_2$ to perform the deprotonation, has allowed us to successfully prepare dicarbene-bridged products of both Pd/Rh and Ir/Rh. Additionally, a number of related Pd/Ir systems can be generated by deprotonation of the pendent-imidazolium group by an external base in the presence of [Ir(μ-Cl)(COD)]$_2$.

Using the first approach, the heterobimetallic Pd/Rh complex [$PdI_2(PEt_3)$(μ-^{tBu}CC^{meth})RhI(COD)] (**17b**), can successfully be generated by reacting the carbene-anchored/pendent-imidazolium complex **9b** and half an equivalent of [Rh(μ-OAc)(COD)]$_2$, as shown in Scheme 4. Deprotonation of the imidazolium moiety of **9b** and concomitant incorporation of Rh, yielding **17b**, is obvious in the spectral data. The low-field acidic proton of **9b** is conspicuously absent in the ^{1}H NMR spectrum and the olefinic protons remote from Pd no longer display coupling to this acidic proton, and now appear as doublets, whereas the olefinic protons on the NHC ring bound to palladium still appear as pseudotriplets due to coupling to the *trans*-phosphorus nucleus of the PEt_3 group. In addition, the loss of symmetry upon incorporation of the "RhI(COD)" moiety transforms the singlet resonance for the methylene protons of the linker in **9b** into an AB quartet in **17b**. The rhodium-coordinated COD protons display similar NMR properties to those of the pendent Rh complexes noted earlier, displaying two resonance signals at *ca.* δ 5.2, and another set of multiplets at *ca.* δ 3.4, representing the protons on the olefinic moiety *trans* to the carbene and the iodide, respectively. One multiplet from each set of resonances displays a through-space interaction (monitored *via* NOE experiments) with one of the ^{t}Bu signals, further confirming the perpendicular arrangement of the NHC ring to the Rh coordination plane.

In the $^{13}C\{^1H\}$ NMR spectra, two carbene moieties can now be observed; a doublet at δ 160.8 ($^2J_{C\text{-}P}$ = 187.7 Hz) compares closely to that of the precursor **9b** (and other phosphine-containing Pd-carbenes) and again shows strong coupling to the

trans-phosphine while the other is significantly downfield at δ 180.9 appearing in the region of other Rh-carbene species with typical coupling to Rh ($^1J_{C\text{-}Rh}$ = 49.3 Hz).[39,46,94–96] The remaining peaks display typical resonances for an unsymmetric di-NHC-bridging backbone, a Pd-coordinated PEt_3 ligand, and a Rh-coordinated COD ligand.

The X-ray structure determination for compound **17b**, shown in Fig. 4 confirms the above assignment in which the two different metals are bridged by a di-NHC ligand. All parameters associated with this structure are typical of such NHC complexes. At each metal the NHC plane lies essentially perpendicular to the metal coordination plane and the metal-carbene distances are consistent with single bonds (Pd–C(11) = 2.045(3) Å, Rh–C(15) = 2.037(3) Å). The slightly larger Pd–C(11) distance may result from the larger *trans* influence of the PEt_3 group. Consistent with such a proposal, this Pd–C(11) distance is very close to those in the phosphine compounds **11b** and **13b** (*vide infra*) and is substantially longer than the Pd-carbene distances in **7b**[63] and [PdI_2(OAc)($^{t\text{Bu}}$C(H)-η^1-C^{meth})][63] (1.990(9) and 1.953(5) Å, respectively) in which iodo and acetate ligands, having a low *trans* influence, are opposite the carbene. As is also typical of binuclear species bridged by only a di-NHC ligand, the dicarbene framework is twisted in such a way to allow the metal coordination planes to avoid each other. As a result the Pd–Rh separation is quite large, at 6.2054(5) Å. This skewing about the dicarbene methylene linker is shown clearly in Fig. 4 and is evident by the dihedral angle of 71.43(12)° between the two NHC planes. Interestingly, the close contacts between part of the COD ligand on Rh and the PEt_3 group on Pd, observed in the solid state, are also present in solution as shown by the NOE experiment noted above.

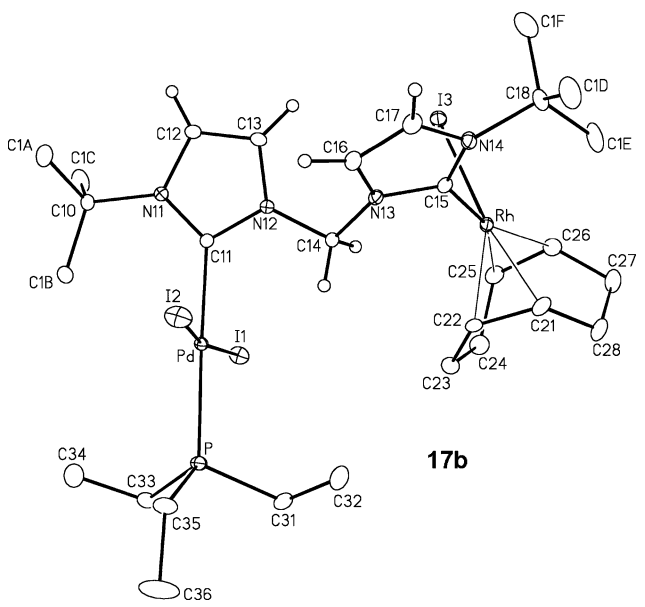
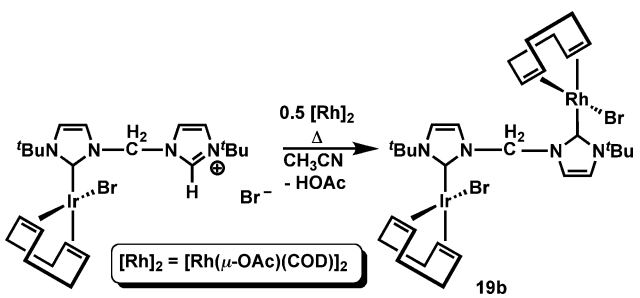


Fig. 4 Three-dimensional representation of [PdI_2(PEt_3)(μ-$^{t\text{Bu}}$CC^{meth})RhI(COD)], **17b** showing the numbering scheme. Thermal ellipsoids are as described in Fig. 1. Hydrogen atoms are shown only on the dicarbene backbone. Relevant parameters (distances in Å and angles in °): Pd–C(11) = 2.045(3), Rh–C(15) = 2.037(3), Rh–C(21) = 2.137(3), Rh–C(22) = 2.137(3), Rh–C(25) = 2.211(3), Rh–C(26) = 2.194(3); N(12)–C(14)–N(13) = 110.6(2)°, I(1)–Pd–I(2) = 170.078(12)°, I(1)–Pd–C(11)–N(11) = 93.3(3)°, I(3)–Rh–C(15)–N(14) = –91.9(3)°.

A gentle purge of carbon monoxide gas through a solution of **17b** readily results in substitution of COD and generation of the less sterically hindered carbonyl analogue [PdI_2(PEt_3)(μ-$^{t\text{Bu}}$CC^{meth})RhI($CO)_2$] (**18b**, Scheme 4), as seen by the appearance of two carbonyl stretches at 2004 and 2076 cm^{-1} in the IR spectrum, along with two carbonyl peaks in the $^{13}C\{^1H\}$ NMR spectrum (δ 187.2, δ 181.6) alongside the carbenes. The carbonyl resonance show coupling to rhodium ($^1J_{C\text{-}Rh}$ = 54.6 Hz; $^1J_{C\text{-}Rh}$ = 76.3 Hz), representing the carbonyl ligands *trans* to the carbene and iodo ligands respectively, much as described earlier for **3c** and **3d**.

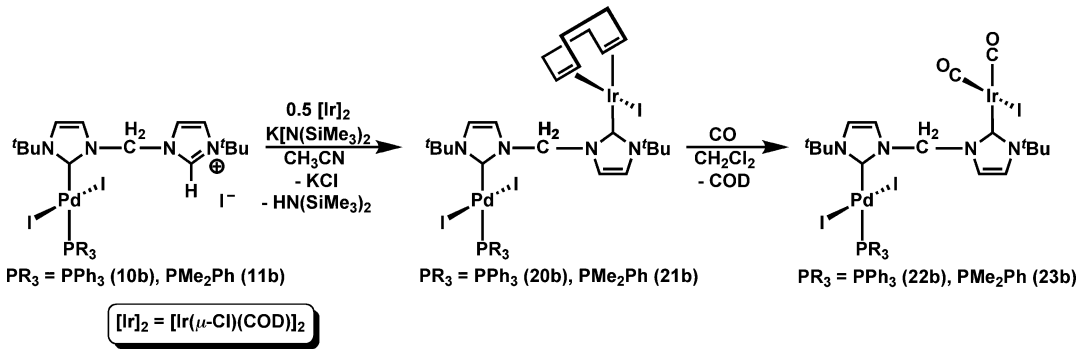
Attempts to generate di-NHC-bridged Pd/Rh complexes *via* deprotonation of the carbene-anchored/pendent-imidazolium Pd species **8–16** using [Rh(μ-OAc)(COD)]$_2$ has only succeeded with **9b**, as noted above; all other attempts failed. Even the other very similar monophosphine complexes, **8b**, **9d**, **10b** and **11b** did not generate the targeted Pd/Rh species using the conditions used to generate **17b**. In the reaction of compounds **14** and **15** (using both the C_1- and C_2-linked dicarbenes) trace amounts of the mixed-metal products could be detected by HRMS but these species were not detectable by NMR techniques.

Using an identical strategy, deprotonation of the pendent imidazolium species, [IrBr(COD)($^{t\text{Bu}}$C(H)-η^1-C^{meth})][Br] (the iodo analogue of which is known)[11] by [Rh(μ-OAc)(COD)]$_2$ successfully yielded the mixed Ir/Rh product, [IrBr(COD)(μ-$^{t\text{Bu}}$CC^{meth})-RhBr(COD)] (**19b**) as outlined in Scheme 5. The carbene carbons of the di-NHC groups are surprisingly close in the $^{13}C\{^1H\}$ NMR spectrum, at δ 180.5 and 179.2, with the former being readily identified as being Rh-bound by the 50.1 Hz coupling to this metal.[39,46,94–96] Additionally, the appearance of two different resonances for the *N*-bound *tert*-butyl groups in the ^1H and $^{13}C\{^1H\}$ NMR spectra, combined with the absence of the low-field acidic proton in the ^1H NMR spectrum further support our formulation. Interestingly, reaction of **19b** with dppm or carbon monoxide did not yield the desired substituted products, but rather gave a mix of unidentified products. The instability of complex **19b** towards CO substitution parallels that of the analogous COD-substituted di-NHC-linked dirhodium complex mentioned earlier.[46]



Scheme 5

Although the conditions employed to generate complex **17b** failed when extended to other Pd pendent species, related mixed-metal species involving Pd can be obtained using milder conditions and an *external* base. In the presence of half an equivalent of a suitable Ir precursor, such as [Ir(μ-Cl)(COD)]$_2$, the pendent-imidazolium arm of the monophosphine-containing **10b** and **11b** can be deprotonated using K[N($SiMe_3$)$_2$], presumably generating a transient Pd carbene-anchored/pendent-carbene



Scheme 6

intermediate which subsequently attacks the Ir dimer, forming the desired di-NHC-bridged mixed-metal species $[PdI_2(PR_3)(\mu\text{-}^{tBu}CC^{meth})IrI(COD)]$ ($PR_3 = PPh_3$ (**20b**); PMe_2Ph (**21b**), Scheme 6). Although the high solubility of both complexes in most solvents did not allow us to obtain single crystals, the spectral data leave little doubt about their formulations. The carbene carbons of the di-NHC groups in the $^{13}C\{^1H\}$ NMR spectrum appear at *ca.* δ 177.9 and *ca.* 168.2, with the latter being readily identified as Pd-bound by the *ca.* 212 Hz coupling to the *trans* phosphorus nucleus. As was observed in the Pd/Rh and Ir/Rh complexes, the appearance of two different resonances for the *N*-bound *tert*-butyl groups in the ^1H and $^{13}C\{^1H\}$ NMR spectra combined with the absence of the low-field acidic proton in the ^1H NMR spectrum further support our formulation. Additionally, the AB quartet observed for the protons of the C_1 linker suggest the plane bisecting the linking CH_2 group is now unsymmetrical on each side, confirming the replacement of a pendent proton with an "IrBr(COD)" moiety. As a result, the methyl protons of the PMe_2Ph moiety in **21b** have become atropisotopic which gives rise to a set of two doublets in the ^1H NMR spectrum ($^2J_{H\text{-}P} \approx 10$ Hz), as well as a corresponding pair in the $^{13}C\{^1H\}$ NMR spectrum ($^1J_{C\text{-}P} \approx 33$ Hz).

A gentle purge of carbon monoxide gas through a CH_2Cl_2 solution of both **20b** and **21b** readily results in substitution of COD generating the carbonyl analogues $[PdI_2(PPh_3)(\mu\text{-}^{tBu}CC^{meth})IrI(CO)_2]$ (**22b**) and $[PdI_2(PMe_2Ph)(\mu\text{-}^{tBu}CC^{meth})IrI(CO)_2]$ (**23b**), respectively, as seen by the appearance of two carbonyl stretches in the IR spectra (1987 and 2065 cm^{-1} (**22b**); 1986 and 2065 cm^{-1} (**23b**)) along with two carbonyl resonances in the $^{13}C\{^1H\}$ NMR spectrum (δ 169.7, 167.1 (**22b**); δ 169.6, 167.5 (**23b**)) alongside the carbene peaks. The AB quartet resonances representing the protons of the methylene linker, previously buried under the multiplets of the aromatic region in **21b**, shift upfield in **23b** to *ca.* δ 6.98 upon replacement of COD by two carbonyl ligands, distancing themselves from the phenyl resonances.

Discussion

Our strategy of using carbene-anchored/pendent-imidazolium complexes as precursors for di-NHC-bridged, mixed-metal complexes *via* deprotonation of the pendent imidazolium salt through an internal base route has succeeded in two cases, but has to date been surprisingly unproductive with the majority of closely related mononuclear precursors studied. On the basis of our successful syntheses of di-NHC-bridged complexes of dirhodium using the basic acetate ligands of $[Rh(\mu\text{-}OAc)(COD)]_2$ to deprotonate the imidazolium salts, we had anticipated that this approach should be quite general for the generation of mixed-metal analogues. However, one problem with this method appears to be the rather harsh conditions necessary for deprotonation of the imidazolium group, requiring extended reflux in acetonitrile. Even for the first deprotonation, to give the carbene-anchored/pendent-imidazolium precursors, conditions need to be carefully controlled for imidazolium deprotonation and successful incorporation of the metal. So although we have successfully generated three of four members of a series of carbene-anchored/pendent-imidazolium precursors of Rh, the fourth member, $[RhBr(COD)(^{Me}C(H)\text{-}\eta^1\text{-}C^{meth})][Br]$ has remained elusive. It appears that successful deprotonation of the pendent imidazolium group and incorporation of the second metal, using the same strategy, is equally sensitive to reaction conditions, and is additionally plagued by the tendency of the dicarbenes to chelate rather than bridge. We are also investigating whether the acetic acid produced in the deprotonation by acetate complexes is interfering with the generation of the desired bimetallic species.

The lack of success in generating the di-NHC-bridged Pd/Rh species utilizing the zwitterionic $[PdI_3(^{tBu}C(H)\text{-}\eta^1\text{-}C^{meth})]$ (**7b**) and $[PdI_3(^{tBu}C(H)\text{-}\eta^1\text{-}C^{eth})]$ (**7d**) is probably not surprising, since deprotonation of the imidazolium group by the Rh-bound acetate group leaves a three-coordinate Rh centre after carbene incorporation. Although such a three-coordinate Rh centre should be stabilized through binding of CH_3CN solvent, generation of binuclear species using this stepwise strategy has only been successful when replacement of the acetate group by a halide occurs. No free halide is available in **7b** and **7d**, and the sharing of a Pd-bound iodo ligand in a bridging arrangement may not be favourable. However, the lack of success in the case of the monophosphine (**8–13**) and diphosphine (**14–16**) complexes, in which iodo counterions are available, remains puzzling. It was expected that upon generation of the targeted Pd/Rh complex, using the diphosphine-chelated Pd complexes **14–16**, the diphosphine could easily unwind to bridge the metals, thereby locking the metals into close proximity. However, it appears that these systems are not well suited for the harsh conditions required for deprotonation of the weakly acidic imidazolium group. It is especially surprising that the monophosphine complexes **8**, **9d**, **10** and **11** did not yield di-NHC-bridged Pd/Rh complexes, while the closely analogous $[PdI_2(PEt_3)(^{tBu}C(H)\text{-}\eta^1\text{-}C^{eth})][I]$ (**9b**) did yield the mixed-metal target.

In spite of the convenience in using a metal-coordinated base to effect the deprotonation of pendent imidazolium groups, we sought to avoid the harsh conditions noted above by using an external strong base to bring about this deprotonation under milder conditions, in the presence of a complex containing the second metal. Using this strategy, we have been able to successfully prepare the first examples of a di-NHC-bridged Pd/Ir system using potassium bis(trimethylsilyl)amide as an external base. Although this method generates a substantial number of unwanted byproducts (including di-NHC-chelated species), the desired products are indeed observable *via* NMR and can be isolated from the crude mixture. Various Pd/Rh combinations (not yet accessible using $[Rh(\mu\text{-}OAc)(COD)]_2$) also seem possible, although not pursued in this report. The importance of choice of base for deprotonating the imidazolium group in pendent imidazolium complexes has previously been noted.[69]

In any case, these strategies have been successful in generating the first unambiguously characterized examples of di-NHC-bridged heterobinuclear complexes,[69] and studies are underway investigating the reactivity of these new species. Future work will also focus on other ways of converting the pendent imidazolium group to a metal-bound carbene, such as the use of Ag_2O in order to generate dicarbene-bridged M/Ag species as carbene-transfer agents for accessing other M/M′ combinations, or through the oxidative addition of the imidazolium C–H bond to a suitable electron-rich metal precursor (*ie*, $Ni(COD)_2$, $Pd(PPh_3)_4$, *etc.*).[100]

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