A-Frame Complexes of Dirhodium Bridged by Dicarbene and Diphosphine Ligands

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The complexes [RhBr(COD)]$_2$(μ-di-NHC), in which di-NHC represents the di-N-heterocyclic carbenes ^{Me}CC^{meth} (1,1'-methylene-3,3'-dimethyldiimidazol-2,2'-diylidene), ^{tBu}CC^{meth} (1,1'-methylene-3,3'-di-*tert*-butyldiimidazol-2,2'-diylidene), and ^{Me}CC^{eth} (1,2-ethylene-3,3'-dimethyldiimidazol-2,2'-diylidene), have been prepared from the reactions of the corresponding diimidazolium bromide salts with the acetate-bridged complex [Rh(μ-OAc)(COD)]$_2$. The analogous complex containing the ^{tBu}CC^{eth} group (1,2-ethylene-3,3'-di-*tert*-butyldiimidazol-2,2'-diylidene) could not be prepared by this route, but the related chloro complex [RhCl(COD)]$_2$(μ-^{tBu}CC^{eth}) was prepared by prior double deprotonation of the corresponding diimidazolium salt and reaction of the resulting dicarbene with [RhCl(COD)]$_2$. Reaction of the above ^{Me}CC^{eth} and ^{tBu}CC^{eth} complexes with CO yields the corresponding dicarbene-bridged carbonyl products [RhX(CO)$_2$]$_2$(μ-di-NHC) (X = Cl, Br), while reaction of the ^{Me}CC^{meth} and ^{tBu}CC^{meth} complexes with CO instead yielded the products [Rh(CO)$_2$(η^1:η^1-di-NHC)]$^+$, containing chelating dicarbenes. The X-ray structure determinations of several of the above dicarbene-bridged species have been carried out and show metal−metal separations of greater than 6.6 Å in all cases. Reaction of all of the above COD complexes with dppm (Ph$_2$PCH$_2$PPh$_2$) followed by CO yields the dicarbene- and dppm-bridged A-frame species [Rh$_2$(CO)$_2$(μ-X)(μ-di-NHC)(dppm)]$^+$ (X = Cl, Br), in which the larger bite of the dicarbenes, compared to that of dppm, induces strain within the complexes. Introduction of the bridging dppm and bromide groups lowers the Rh−Rh separation to about 3.3 Å. Replacement of the bridging bromide by hydroxide in the ^{Me}CC^{eth} complex yields [Rh$_2$(CO)$_2$(μ-OH)(μ-^{Me}CC^{eth})(dppm)]$^+$, in which the bridging hydroxide can be used to deprotonate a monoimidazolium iodide to give [Rh$_2$Br(CO)$_2$(IMe)(μ-^{Me}CC^{eth})(dppm)][I] (IMe = 1,3-dimethylimidazol-2-ylidene). In this species the bromide is on one metal while the monocarbene occupies the other, opening up the dicarbene bite to 5.18 Å and the metal−metal separation to 4.07 Å. Attempts to better match the larger bite of the dicarbenes by substituting dppm with dppe (Ph$_2$PCH$_2$CH$_2$PPh$_2$) did not give a dppe-bridged product and, instead, yielded [(Rh(CO)(dppe))$_2$(μ-^{Me}CC^{eth})][CF$_3$SO$_3$]$_2$ in which the dppe groups are chelating.

Introduction

N-heterocyclic carbenes (NHC's)[1] have proven to be versatile ligands in organometallic chemistry and catalysis[2] and appear to offer a useful alternative to the ubiquitous phosphines. These carbene ligands are generally acknowledged to possess bonding properties like those of trialkylphosphines[3] and may actually be better donors than phosphines.[4] However, NHC's are not merely phosphine substitutes; they offer a useful steric alternative to phosphines in having a very different shape. While phosphines are often described as conical,[5] NHC ligands are more planar, having a slimmer, less sterically hindered axis orthogonal to the bulky imidazole ring plane.

The majority of NHC ligands used are monodentate,[1] and much fewer complexes are known that involve bidentate di-N-heterocyclic carbene (di-NHC) ligands,[2c,d,3a,6–8] in which pairs of NHC groups are joined by an appropriate linker group. Most of the complexes containing di-NHC's employ these groups as chelating ligands at a single metal,[3a,6,7] although some have been reported in which the di-NHC group bridges pairs of metals.[3a,7,8]

On the basis of an extensive chemistry of binuclear, late-metal complexes in which the pair of metals are bridged by diphosphine ligands,[9] we became interested in extending this chemistry to include bridging di-NHC ligands. In particular, we

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were interested in generating di-NHC analogues of the well-known "A-frame" complexes,[10] in which pairs of bidentate diphosphines (usually dppm) bridge a pair of metals. Owing to the rotational freedom in the linking groups between the diphosphine or dicarbene ends of these bidentate ligands, complexes bridged by only one of these groups tend to adopt a skewed arrangement[3a,7,11] in which the metals are quite widely spaced in order to minimize steric repulsions between the metal coordination spheres. Unfortunately, this arrangement, with its concomitant large metal−metal separation, is not entirely conducive to metal−metal cooperativity effects. In order to bring the metals together in a bid to optimize metal−metal interactions and their probability of interacting in a cooperative manner, a second bridging group is needed. This is exactly the strategy that has been utilized in "A-frame" complexes.

In this paper we describe our attempts to generate A-frame-like complexes of rhodium, in which a series of di-NHC ligands, diagrammed in Chart 1, are used as bridging groups. The abbreviations used for these di-NHC ligands, also shown in this chart, in which the substituent on the carbene rings appears first, followed by the dicarbene notation (CC) and finally an abbreviation designating a methylene or ethylene linker between the NHC rings, are those originally suggested by Green and co-workers.[6e] We are seeking to determine the influences of the different linker lengths and of the different steric factors of the NHC substituents.

Experimental Section

General Comments. All solvents were dried (using appropriate drying agents), distilled before use, and stored under a dinitrogen

Chart 1

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. Bis(diphenylphosphino)methane and bis(diphenylphosphino)ethane, sodium tetraphenylborate, sodium borohydride, potassium hydroxide, potassium bis(trimethylsilyl)amide, 1-methylimidazole, dibromomethane, and 1,2-dibromoethane were purchased from Aldrich and used without further purification. 1-*tert*-Butylimidazole was prepared using a published procedure and purified by vacuum distillation.[12] The preparations of diimidazolium salts used in this paper have been reported;[2g,3a,6b] however, a general synthetic approach has been outlined below. Bis(cycloocta-1,5-diene)(μ-dichloro)dirhodium was prepared using published procedures and used without further purification,[13] Bis(cycloocta-1,5-diene)(μ-diacetato)dirhodium was prepared as previously reported and recrystallized from ethyl acetate.[14]

The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a Varian iNova-400 spectrometer operating at 399.8 MHz for ^{1}H, 161.8 MHz for ^{31}P, and 100.6 MHz for ^{13}C. Elemental analyses were performed by the microanalytical service within the Department of Chemistry. Likewise, mass spectrometric analyses were performed by the Mass Spectrometry Laboratory using positive ion electrospray ionization on a Micromass ZabSpec Hybrid Sector-TOF. Infrared spectra were obtained using a Nicolet Avatar 370DTGS instrument or as solids using a Nicolet Magna 750 with a Nic-Plan infrared microscope. Carbonyl stretches reported are for non isotopically enriched samples. The ^{31}P chemical shifts are referenced to external 85% H$_3$PO$_4$, while ^{1}H and ^{13}C chemical shifts are referenced to TMS. The chemical shifts for the phenyl hydrogens and carbons are not given. Conductivity measurements on compound **5c** as both the BPh$_4^-$ and Br$^-$ salts were carried out on 1×10^{-3} M solutions of the compounds in nitromethane, using a Yellow Springs Instrument Model 31 conductivity bridge. For these species the conductivities obtained were $\Lambda = 59.3$ and 69.0 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 diluted with 200 mL of toluene. An excess (250 mmol) of the 1-alkylimidazole was then added and the solution refluxed for 24 h. The formed precipitate was collected by vacuum filtration and recrystallized from boiling methanol by cooling to −25 °C, whereupon colorless crystals were obtained with 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 usage. Compounds **1a−d** are the diprotonated versions of the respective carbenes ^{Me}CC^{meth} (**a**), ^{tBu}CC^{meth} (**b**), ^{Me}CC^{eth} (**c**), and ^{tBu}CC^{eth} (**d**) as dibromide salts, namely 1,1′-(methylene)-3,3′-dimethyldiimidazolium-2,2′-diylidene dibromide

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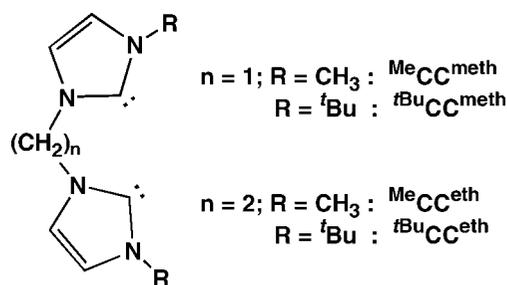
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(**1a**), 1,1′-(methylene)-3,3′-di-*tert*-butyldiimidazolium-2,2′-diylidene dibromide (**1b**), 1,1′-(1,2-ethylene)-3,3′-dimethyldiimidazolium-2,2′-diylidene dibromide (**1c**), and 1,1′-(1,2-ethylene)-3,3′-di-*tert*-butyldiimidazolium-2,2′-diylidene dibromide (**1d**).

(b) (μ-1,1′-Methylene-3,3′-dimethyldiimidazoline-2,2′-diylidene)-bis[bromo(η^2:η^2-1,5-cyclooctadiene)rhodium(I)] (2a). A 30 mL portion of THF was added to a equimolar mixture of compound **1a** (188 mg, 0.56 mmol) and [Rh$_2$(OAc)$_2$(C$_8$H$_{12}$)$_2$] (300 mg, 0.56 mmol). The resulting mixture was stirred under reflux for 4 h, after which the formation of a yellow precipitate was observed. Once it was cooled to room temperature, the vessel was charged with 60 mL of ether and the supernatant discarded. The remaining solid was redissolved in 15 mL of CH$_2$Cl$_2$, filtered through Celite, and precipitated using 40 mL of ether, yielding 0.34 g (80%) of a pale yellow powder. ^{1}H NMR (400.4 MHz, CD$_2$Cl$_2$, 27.0 °C): δ 7.80 (d, 2H, $^3J_{H-H}$ = 2.0 Hz), 6.84 (d, 2H, $^3J_{H-H}$ = 2.0 Hz, NCH); 7.41 (s, 2H, CH$_2$); 4.04 (s, 6H, NCH$_3$); 5.09 (m, 4H), 3.42 (m, 4H), 2.43 (m, 4H), 2.37 (m, 4H), 2.02 (m, 4H), 1.94 (m, 4H, COD). ^{13}C{^{1}H} NMR (100.7 MHz, CD$_2$Cl$_2$, 27.0 °C): δ 183.5 (d, 2C, $^1J_{C-Rh}$ = 50.3 Hz, C$_{carbene}$); 123.8 (s, 2C), 121.2 (s, 2C, NCH); 62.9 (s, 2C, CH$_2$); 38.0 (s, 2C, NCH$_3$); 99.2 (d, 2C, $^1J_{C-Rh}$ = 6.7 Hz), 98.7 (d, 2C, $^1J_{C-Rh}$ = 6.7 Hz), 70.3 (d, 2C, $^1J_{C-Rh}$ = 14.4 Hz), 69.7 (d, 2C, $^1J_{C-Rh}$ = 14.5 Hz), 33.3 (s, 2C), 32.6 (s, 2C), 29.4 (s, 2C), 29.1 (s, 2C, COD). Anal. Calcd for C$_{25}$H$_{36}$N$_4$Br$_2$Rh$_2$: C, 39.60; H, 4.79; N, 7.39. Found: C, 39.56; H, 4.77; N, 7.28.

(c) (μ-1,1′-Methylene-3,3′-di-*tert*-butyldiimidazoline-2,2′-diylidene)bis[bromo(η^2:η^2-1,5-cyclooctadiene)rhodium(I)] (2b). A 50 mL portion of THF was added to a mixture of compound **1b** (940 mg, 2.23 mmol) and excess [Rh$_2$(OAc)$_2$(C$_8$H$_{12}$)$_2$] (1.5 g, 2.78 mmol, 1.25 equiv). The slurry was stirred under reflux overnight, after which the formation of a yellow precipitate was observed. Once the mixture had cooled to room temperature, the vessel was charged with 40 mL of ether and the supernatant recycled. The remaining yellow solid was rinsed with 2 × 15 mL portions of ether and dried in vacuo, giving 1.2 g (64%) of product. ^{1}H NMR (399.8 MHz, CD$_2$Cl$_2$, 27.0 °C): δ 8.35 (s, 2H, CH$_2$); 7.81 (d, 2H, $^3J_{H-H}$ = 2.0 Hz), 7.05 (d, 2H, $^3J_{H-H}$ = 2.0 Hz, NCH); 1.97 (s, 18H, NC(CH$_3$)$_3$); 5.04 (m, 4H), 3.45 (m, 4H), 2.51 (m, 4H), 2.30 (m, 4H), 2.05 (m, 4H), 1.82 (m, 4H, COD). ^{13}C{^{1}H} NMR (100.5 MHz, CD$_2$Cl$_2$, 27.0 °C): δ 180.8 (d, 2C, $^1J_{C-Rh}$ = 49.8 Hz, C$_{carbene}$); 121.5 (s, 2C), 121.0 (s, 2C, NCH); 58.8 (s, 2C), 32.2 (s, 6C, NC(CH$_3$)$_3$); 67.5 (s,1C, CH$_2$); 96.8 (d, 2C, $^1J_{C-Rh}$ = 7.6 Hz), 95.0 (d, 2C, $^1J_{C-Rh}$ = 7.3 Hz), 72.4 (d, 2C, $^1J_{C-Rh}$ = 15.5 Hz), 68.7 (d, 2C, $^1J_{C-Rh}$ = 14.2 Hz), 34.2 (s, 2C), 31.4 (s, 2C), 30.2 (s, 2C), 28.7 (s, 2C, COD). HRMS: *m/z* calcd for C$_{31}$H$_{48}$N$_4$BrRh$_2$ (M$^+$ − Br), 761.1172; found, 761.1172 (M$^+$ − Br). Anal. Calcd for C$_{32}$H$_{50}$Br$_2$N$_4$Rh$_2$Cl$_2$ (**2b·CH$_2$Cl$_2$**): C, 41.45; H, 5.43; N, 6.04; Cl, 7.65. Found: C, 41.57; H, 5.49; N, 5.96; Cl, 7.56. The presence of 1 equiv of CH$_2$Cl$_2$ was confirmed by ^{1}H NMR spectroscopy in chloroform.

(d) (μ-1,1′-(1,2-Ethylene)-3,3′-dimethyldiimidazoline-2,2′-diylidene]bis[bromo(η^2:η^2-1,5-cyclooctadiene)rhodium(I))] (2c). A 50 mL portion of THF was added to a equimolar mixture of compound **1c** (0.8 g, 2.2 mmol) and [Rh$_2$(OAc)$_2$(C$_8$H$_{12}$)$_2$] (1.2 g, 2.2 mmol). The resulting mixture was stirred under reflux for 3 h, after which the formation of a yellow precipitate was observed. Once the mixture had cooled to room temperature, the vessel was charged with 60 mL of ether and the supernatant discarded. The remaining flocculent solid was redissolved in 30 mL of CH$_2$Cl$_2$, filtered through Celite, and precipitated using 40 mL of ether, leaving 1.47 g (86%) of a pale yellow powder. ^{1}H NMR (300.0 MHz, CD$_2$Cl$_2$, 27.0 °C): δ 6.89 (d, 2H, $^3J_{H-H}$ = 1.8 Hz), 6.59 (d, 2H, $^3J_{H-H}$ = 1.8 Hz, NCH); 5.11 (m, 4H, CH$_2$CH$_2$); 4.00 (s, 6H, NCH$_3$); 5.06 (m 4H), 3.38 (m, 4H), 2.46 (m, 4H), 2.34 (m, 4H), 2.06 (m, 4H), 1.93 (m, 4H, COD). ^{13}C{^{1}H} NMR (100.7 MHz, CD$_2$Cl$_2$, 27.0 °C): δ 181.7 (d, 2C, $^1J_{C-Rh}$ = 49.7 Hz, C$_{carbene}$); 123.8 (s, 2C), 121.1 (s, 2C, NCH); 50.5 (s, 2C, CH$_2$CH$_2$); 37.9 (s, 2C, NCH$_3$); 98.2 (d, 2C, $^1J_{C-Rh}$ = 6.7 Hz), 98.0 (d, 2C, $^1J_{C-Rh}$ = 6.7 Hz), 70.4 (d, 2C,

$^1J_{C-Rh}$ = 14.5 Hz), 69.1 (d, 2C, $^1J_{C-Rh}$ = 14.4 Hz), 33.5 (s, 2C), 32.4 (s, 2C), 30.0 (s, 2C), 28.7 (s, 2C, COD). HRMS: *m/z* calcd for C$_{26}$H$_{38}$N$_4$BrRh$_2$ (M$^+$ − Br), 691.0390; found:, 691.0385 (M$^+$ − Br). Anal. Calcd for C$_{27}$H$_{40}$Br$_2$N$_4$Rh$_2$Cl$_2$ (**2c·CH$_2$Cl$_2$**): C, 37.83; H, 4.70; N, 6.54; Cl, 8.27. Found: C, 37.87; H, 4.71; N, 7.08; Cl, 8.51. The presence of 1 equiv of CH$_2$Cl$_2$ was confirmed by ^{1}H NMR spectroscopy in chloroform.

(e) (μ-1,1′-(1,2-Ethylene)-3,3′-di-*tert*-butyldiimidazoline-2,2′-diylidene]bis[chloro(η^2:η^2-1,5-cyclooctadiene)rhodium(I)) (2d). Attempts to synthesize **2d** using the convenient approach outlined for compounds **2a**−**c** met with little success. Instead, a 50 mL portion of THF was added to a mixture of compound **1d** (1.33 g, 3.04 mmol, 1 equiv) and excess KN(Si(CH$_3$)$_3$)$_2$ (1.33 g, 6.67 mmol, 2.2 equiv) and the resulting mixture was stirred at room temperature for 16 h. The next day, a fine white precipitate was removed by passing the mixture through a bed of Celite contained within a porous frit. Without further purification, the deep yellow solution containing the dicarbene was added dropwise to a stirred orange solution of [Rh$_2$(Cl)$_2$(C$_8$H$_{12}$)$_2$] (1.5 g, 3.04 mmol, 1 equiv) in 30 mL of THF, resulting in the formation of a yellow precipitate. The mixture was stirred for 30 min before removal of the volatiles under reduced pressure afforded an oily residue. The crude product was extracted with 2 × 15 mL portions of CH$_2$Cl$_2$ and passed through a filter stick containing a bed of Celite before 50 mL of pentane was added to precipitate a yellow solid. The product was then dried in vacuo to yield 0.48 g (22%) of product. ^{1}H NMR (300.0 MHz, CD$_2$Cl$_2$, 27.0 °C): δ 6.95 (d, 2H, $^3J_{H-H}$ = 2.0 Hz), 6.69 (d, 2H, $^3J_{H-H}$ = 2.0 Hz, NCH); 5.50 (m, 4H, CH$_2$CH$_2$); 1.93 (s, 18H, NC(CH$_3$)$_3$); 4.92 (m, 4H), 3.26 (m, 4H), 2.52 (m, 4H), 2.40 (m, 4H), 1.98 (m, 4H), 1.88 (m, 4H, COD). ^{13}C{^{1}H} NMR (100.7 MHz, CD$_2$Cl$_2$, 27.0 °C): δ 179.6 (d, 2C, $^1J_{C-Rh}$ = 50.4 Hz, C$_{carbene}$); 123.1 (s, 2C), 118.5 (s, 2C, NCH); 51.9 (s, 2C, CH$_2$CH$_2$); 58.5 (s, 2C), 32.1 (s, 6C, NC(CH$_3$)$_3$); 96.7 (d, 2C, $^1J_{C-Rh}$ = 7.7 Hz), 94.1 (d, 2C, $^1J_{C-Rh}$ = 7.2 Hz), 70.5 (d, 2C, $^1J_{C-Rh}$ = 15.3 Hz), 68.9 (d, 2C, $^1J_{C-Rh}$ = 14.5 Hz), 33.0 (s, 2C), 32.5 (s, 2C), 29.4 (s, 2C), 28.8 (s, 2C, COD). HRMS: *m/z* Calcd for C$_{32}$H$_{50}$N$_4$ClRh$_2$ (M$^+$ − Cl), 731.1829; found, 731.1831 (M$^+$ − Cl). Anal. Calcd for C$_{32}$H$_{50}$Cl$_2$N$_4$Rh$_2$: C, 50.08; H, 6.57; N, 7.30. Found: C, 49.28; H, 6.55; N, 7.60. Repeated attempts were always low in the carbon analysis. A ^{1}H NMR spectrum of this compound is given in the Supporting Information.

(f) Methylene[(N-tert-butyl)imidazolium][(N-tert-butyl)imidazole-2-ylidene)]bromo(η^2:η^2-1,5-cyclooctadiene)rhodium(I) Bromide (3b). A 20 mL portion of CH$_3$CN was added to a solid mixture containing an excess of compound **1b** (582 mg, 1.38 mmol, 2.5 equiv) and [Rh$_2$(OAc)$_2$(C$_8$H$_{12}$)$_2$] (300 mg, 0.55 mmol, 1 equiv). The resulting slurry was stirred for 2 h under reflux conditions. The volatiles were then removed under reduced pressure to give a yellow solid. The crude product was redissolved in CH$_2$Cl$_2$, 20 mL of distilled water was added, and the resulting biphasic solution was stirred for 5 min. After settling, the aqueous phase was decanted to waste and the remaining organic layer precipitated with pentane. The light yellow powder was then washed with 2 × 10 mL portions of ether before being placed under vacuum for several days to ensure the removal of water: yield 0.62 g (89%). ^{1}H NMR (399.8 MHz, CD$_2$Cl$_2$, 27.0 °C): δ 10.68 (dd, 1H, $^4J_{H-H}$ = 1.6 Hz, $^4J_{H-H}$ = 1.6 Hz, NCHN); 8.84 (dd, 1H, $^3J_{H-H}$ = 1.6 Hz, $^4J_{H-H}$ = 1.6 Hz), 7.34 (dd, 1H, $^3J_{H-H}$ = 1.6 Hz, $^4J_{H-H}$ = 1.6 Hz, NCH$_{imid-H}$); 1.97 (s, 9H, N$_{imid-H}$C(CH$_3$)$_3$); 8.09 (d, 1H, $^2J_{H-H}$ = 12.0 Hz), 7.64 (d, 1H, $^2J_{H-H}$ = 12.0 Hz, NCH$_2$N); 8.04 (d, 1H, $^3J_{H-H}$ = 2.0 Hz), 7.16 (d, 1H, $^3J_{H-H}$ = 2.0 Hz, NCH$_{imid-Rh}$); 1.74 (s, 9H, N$_{imid-Rh}$C(CH$_3$)$_3$); 5.04 (m, 2H), 3.42 (m, 2H), 2.40 (m, 4H), 1.90 (m, 4H, COD). ^{13}C{^{1}H} NMR (100.5 MHz, CD$_2$Cl$_2$, 27.0 °C): δ 182.8 (d, 1C, $^1J_{C-Rh}$ = 49.9 Hz, C$_{carbene}$); 122.2 (s, 1C), 121.4 (s, 1C, NCH$_{imid-Rh}$); 59.3 (s, 1C), 30.0 (s, 3C, N$_{imid-Rh}$C(CH$_3$)$_3$); 136.5 (s, 1C, NCHN); 124.0 (s, 1C), 119.1 (s, 1C, NCH$_{imid-H}$); 61.0 (s, 1C), 32.0 (s, 3C, N$_{imid-H}$C(CH$_3$)$_3$); 63.0 (s, 1C, CH$_2$); 97.7 (d, 1C, $^1J_{C-Rh}$=

7.4 Hz), 95.5 (d, 1C, $^1J_{C-Rh}$ = 7.0 Hz), 73.1 (d, 1C, $^1J_{C-Rh}$ = 15.1 Hz), 70.0 (d, 1C, $^1J_{C-Rh}$ = 13.9 Hz), 33.5 (s, 1C), 31.6 (s, 1C), 29.5 (s, 1C), 28.9 (s, 1C, COD). HRMS: m/z calcd for $C_{23}H_{37}N_4BrRh$ (M$^+$), 551.1251; found, 551.1255 (M$^+$). Satisfactory analyses for this compound were not possible, owing to weight gain by the sample during analysis. A ^1H NMR spectrum is available in the Supporting Information.

(g) Conversion of Compound 3b to 2b. To a pale yellow solution containing **3b** (300 mg, 0.48 mmol, 1 equiv) in 20 mL of THF was added excess [Rh(μ-OAc)(COD)]$_2$ (154 mg, 0.29 mmol, 0.6 equiv) to give an orange solution. The resulting solution was refluxed overnight, resulting in the appearance of **2b** as a yellow precipitate. A 20 mL portion of ether was added, and the supernatant was discarded, giving a pale yellow solid, which afforded after rinsing with pentane and drying in vacuo 0.31 g (76%) of product **2b**.

(h) Reactions of 2c and 2d with Excess CO. A 30 min gentle purge of CO to a stirring solution of either compound **2c** or **2d** in THF yielded a pale yellow solution. The conversion to the respective *bis*-dicarbonyl complexes **4c** or **4d** was accompanied by the facile loss of 1,5-cyclooctadiene and was monitored to completion using ^1H NMR spectroscopy. Owing to their high solubility in nonpolar solvents the products were isolated by removal of volatiles under reduced pressure. For most reactions the compounds were used without further purification.

[Rh$_2$(CO)$_4$Br$_2$(μ-C$_{10}$H$_{14}$N$_4$)] (4c). ^1H NMR (399.8 MHz, C$_4$D$_8$O, 27.0 °C): δ 7.06 (br s, 2H), 6.82 (br s, 2H, NCH); 4.96 (br m, 2H), 4.65 (br m, 2H, CH$_2$CH$_2$); 3.86 (s, 6H, NCH$_3$). ^{13}C{^{1}H} NMR (100.7 MHz, CD$_2$Cl$_2$, 27.0 °C): δ 186.6 (d, 2C, $^1J_{C-Rh}$ = 53.5 Hz), 182.5 (d, 2C, $^1J_{C-Rh}$ = 76.1 Hz, CO); 173.8 (d, 2C, $^1J_{C-Rh}$ = 42.9 Hz, C$_{carbene}$); 124.0 (s, 2C), 123.0 (s, 2C, NCH); 51.3 (s, 2C, CH$_2$CH$_2$); 39.0 (s, 2C, NCH$_3$). IR (solid, cm^{-1}): 2071 (CO), 2044 (CO), 2024 (CO), 1997 (CO). HRMS: m/z calcd for $C_{14}H_{14}N_4O_4BrRh_2$ (M$^+$ − Br): 586.8303; found, 586.8301 (M$^+$ − Br). Anal. Calcd for $C_{14}H_{14}N_4O_4Br_2Rh_2$: C, 25.18; H, 2.11; N, 8.39. Found: C, 25.31; H, 2.18; N, 8.22.

[Rh$_2$(CO)$_4$Cl$_2$(μ-C$_{16}$H$_{26}$N$_4$)] (4d). ^1H NMR (499.8 MHz, C$_4$D$_8$O, 27.0 °C): δ 7.05 (d, 2H, $^3J_{H-H}$ = 1.7 Hz), 7.01 (d, 2H, $^3J_{H-H}$ = 1.7 Hz, NCH); 5.25 (m, 2H), 4.99 (m, 2H, CH$_2$CH$_2$); 1.82 (s, 18H, NC(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (100.7 MHz, CD$_2$Cl$_2$, 27.0 °C): δ 186.2 (d, 2C, $^1J_{C-Rh}$ = 54.8 Hz), 182.9 (d, 2C, $^1J_{C-Rh}$ = 75.5 Hz, CO); 171.9 (d, 2C, $^1J_{C-Rh}$ = 42.6 Hz, C$_{carbene}$); 122.8 (s, 2C), 119.6 (s, 2C, NCH); 52.1 (s, 2C, CH$_2$CH$_2$); 59.1 (s, 2C), 32.2 (s, 6C, NC(CH$_3$)$_3$). IR (film cast, cm^{-1}): 2077 (CO), 1997 (CO). HRMS: m/z calcd for $C_{20}H_{26}N_4O_4ClRh_2$ (M$^+$ − Cl), 626.9747; found, 626.9753 (M$^+$ − Cl). Anal. Calcd for $C_{20}H_{26}Cl_2N_4O_4Rh_2$: C, 36.22; H, 3.95; N, 8.45. Found: C, 36.36; H, 4.08; N, 8.52.

(i) [(μ-1,1′-methylene-3,3′-dimethyldiimidazoline-2,2′-diylidene)-(μ-dppm)(μ-Br)bis((carbonyl)rhodium(I))][BPh$_4$] (5a). One equivalent of dppm (0.30 g, 0.78 mmol) was dissolved in 10 mL of THF, and the resulting solution added via cannula to a suspension containing **2a** (0.61 g, 0.78 mmol, 1 equiv) in 15 mL of THF. The mixture was stirred for 15 min before CO was added, resulting in a deep orange solution. After several minutes of CO purging, the formation of a yellow precipitate was observed and a 50 mL portion of ether was employed to isolate the product. An exchange of anions was achieved by redissolving the solid in a minimal volume of THF, followed by the addition of sodium tetraphenylborate (0.27 g, 0.78 mmol, 1 equiv) as a single portion. The immediate formation of a precipitate was observed and the resulting mixture filtered through a filter stick containing Celite. Excess pentane was then added, precipitating a yellow solid, which was dried in vacuo to give 7.61 g (80%) of product.

Attempts to synthesize **5a** via the addition of CO prior to dppm addition met with little success, leading only to the exclusive formation of [Rh$_2$(CO)$_2$(μ-Br)(μ-CO)(dppm)$_2$]$^+$. ^1H NMR (399.8 MHz, CD$_2$Cl$_2$, 27.0 °C): δ 7.80 (d, 1H, $^2J_{H-H}$ = 13.4 Hz), 5.61 (d,

1H, $^2J_{H-H}$ = 13.4 Hz, CH$_2$); 6.88 (d, 2H, $^3J_{H-H}$ = 2.0 Hz), 6.84 (d, 2H, $^3J_{H-H}$ = 2.0 Hz, NCH); 3.74 (s, 6H, NCH$_3$); 4.18 (dt, 1H, $^2J_{H-H}$ = 13.2 Hz, $^2J_{H-P}$ = 9.60 Hz), 3.39 (dt, 1H, $^2J_{H-H}$ = 13.2 Hz, $^2J_{H-P}$ = 12.8 Hz, PCH$_2$P). ^{13}C{^{1}H} NMR (100.6 MHz, CD$_2$Cl$_2$, 27.0 °C): δ 184.9 (dd, 2C, $^1J_{C-Rh}$ = 85.1 Hz, $^2J_{C-P}$ = 15.8 Hz, CO); 177.8 (dd, 2C, $^2J_{C-P}$ = 116.9 Hz, $^1J_{C-Rh}$ = 43.1 Hz, C$_{carbene}$); 125.1 (s, 2C), 121.3 (s, 2C, NCH); 64.0 (s, 1C, CH$_2$); 38.7 (s, 2C, CH$_3$); 24.3 (t, $^1J_{C-P}$ = 19.1 Hz, PCH$_2$P). ^{31}P NMR (161.8 MHz, CD$_2$Cl$_2$, 27.0 °C): δ 24.5 (symmetric multiplet with two principal lines separated by 107.8 Hz, dppm). IR (solid, cm^{-1}): 1969 broad (CO). HRMS: m/z calcd for $C_{36}H_{34}N_4O_2P_2BrRh_2$ (M$^+$ − BPh$_4$), 900.9445; found, 900.9443 (M$^+$ − BPh$_4$). Anal. Calcd for $C_{60}H_{54}BN_4O_2P_2BrRh_2$: C, 58.99; H, 4.46; N, 4.59. Found: C, 59.17; H, 4.61; N, 4.37.

(j) [(μ-1,1′-methylene-3,3′-di-*tert*-butyldiimidazoline-2,2′-diylidene)(μ-dppm)(μ-Br)(bis[((carbonyl)rhodium(I))][BPh$_4$] (5b). One equivalent of dppm (0.69 g, 1.78 mmol) was dissolved in 15 mL of THF and the resulting solution added via cannula to a solution containing **2b** (1.5 g, 1.78 mmol) in 15 mL of THF. The mixture was stirred for 15 min before CO was added, resulting in a deep orange solution. An anion exchange was formed by the addition of one equivalent of sodium tetraphenylborate (0.61 g, 1.78 mmol) dissolved in 15 mL of acetone. The mixture was then filtered through Celite and the volatiles removed under reduced pressure. The resulting oily residue was washed with 2 × 15 mL portions of ether, giving 1.7 g of the yellow solid **4b**, which was dried in vacuo (72%). ^1H NMR (399.8 MHz, CD$_2$Cl$_2$, 27.0 °C): δ 8.82 (d, 1H, $^2J_{H-H}$ = 13.2 Hz), 6.50 (d, 1H, $^2J_{H-H}$ = 13.2 Hz, CH$_2$); 7.96 (d, 2H, $^3J_{H-H}$ = 2.0 Hz), 7.32 (d, 2H, $^3J_{H-H}$ = 2.0 Hz, NCH); 1.61 (s, 18H, NC(CH$_3$)$_3$); 4.50 (dt, 1H, $^2J_{H-H}$ = 13.2 Hz, $^2J_{H-P}$ = 9.6 Hz), 3.28 (dt, 1H, $^2J_{H-H}$ = 13.2 Hz, $^2J_{H-P}$ = 9.6 Hz, PCH$_2$P). ^{13}C{^{1}H} NMR (100.6 MHz, CD$_2$Cl$_2$, 27.0 °C): δ 186.0 (dd, 2C, $^1J_{C-Rh}$ = 86.3 Hz, $^2J_{C-P}$ = 16.4 Hz, CO); 175.1 (dd, 2C, $^2J_{C-P}$ = 115.8 Hz, $^1J_{C-Rh}$ = 42.9 Hz, C$_{carbene}$); 122.4 (s, 2C), 121.4 (s, 2C, NCH); 67.5 (s, 1C, CH$_2$); 59.6 (s, 2C), 32.1 (s, 6C, NC(CH$_3$)$_3$); 24.0 (t, $^1J_{C-P}$ = 18.3 Hz, PCH$_2$P). ^{31}P NMR (161.8 MHz, CD$_2$Cl$_2$, 27.0 °C): δ 26.1 (symmetric multiplet with two principle lines separated by 109.7 Hz, dppm). IR (solid, cm^{-1}): 1974 (CO), 1962 (CO). Anal. Calcd for $C_{43}H_{46}N_4O_2P_2BrRh_2SO_3F_3$(elemental analyses carried out on the triflate salt of **5b**): C, 45.48; H, 4.08; N, 4.93. Found: C, 45.77; H, 4.24; N, 4.71. HRMS: m/z calcd for $C_{42}H_{46}N_4O_2P_2BrRh_2$ (M$^+$ − BPh$_4$), 985.0384; found, 985.0382 (M$^+$ − BPh$_4$).

(k) [(μ-1,1′-(1,2-ethylene)-3,3′-dimethyldiimidazoline-2,2′-diylidene)(μ-dppm)(μ-Br)bis[(carbonyl)rhodium(I)][BPh$_4$] (5c). A slurry of 30 mL of CH$_3$CN and **2c** (1.47 g, 1.94 mmol) was stirred under a gentle purge of CO. After 30 min, the formation of **4c** was observed as a pale yellow solution. A solution of dppm (0.75 g, 1.94 mmol, 1 equiv) in 20 mL of THF was added dropwise, via cannula, to the solution containing **4c**, giving a deep orange solution. Continued stirring under a CO atmosphere caused the formation of a yellow precipitate; addition of 50 mL of ether yielded **5c**, containing the bromide counterion. Alternatively, a THF solution containing equimolar amounts of dppm and **2c** followed by the addition of CO led to the formation of the desired product in similar yield. The tetraphenylborate salt of **5c** was obtained by redissolving the bromide product in a minimal amount of CH$_2$Cl$_2$ followed by the slow addition of a concentrated solution of sodium tetraphenylborate (0.66 g, 1.94 mmol, 1 equiv) in acetone. After it was stirred for 15 min, the mixture was filtered through Celite and 1.20 g of product **5c** was recovered by the addition of excess pentane and subsequent drying in vacuo (50%). ^1H NMR (399.8 MHz, CD$_2$Cl$_2$, 27.0 °C): δ 7.71 (d, 2H, $^3J_{H-H}$ = 1.6 Hz), 6.94 (d, 2H, $^3J_{H-H}$ = 1.6 Hz, NCH); 6.07 (m, 2H), 5.01 (m, 2H, CH$_2$CH$_2$); 3.71 (s, 6H, NCH$_3$); 4.22 (dt, 1H, $^2J_{H-H}$ = 13.2 Hz, $^2J_{H-P}$ = 9.6 Hz), 3.51 (dt, 1H, $^2J_{H-H}$ = 13.2 Hz, $^2J_{H-P}$ = 9.8 Hz, PCH$_2$P). ^{13}C{^{1}H} NMR (100.6 MHz, CD$_2$Cl$_2$, 27.0 °C): δ 185.6 (dd, 2C, $^1J_{C-Rh}$ = 86.0 Hz, $^2J_{C-P}$ = 15.7 Hz, CO); 175.1 (dd, 2C, $^2J_{C-P}$ = 117.1 Hz, $^1J_{C-Rh}$

= 43.1 Hz, $C_{carbene}$); 123.9 (s, 2C), 123.4 (s, 2C, NCH); 49.9 (s, 2C, CH_2CH_2); 39.1 (s, 2C, NCH_3); 26.8 (t, $^1J_{C-P}$ = 18.6 Hz, PCH_2P). ^{31}P NMR (161.8 MHz, CD_2Cl_2, 27.0 °C): δ 23.7 (symmetric multiplet with two principal lines separated by 107.8 Hz, dppm). IR (solid, cm^{-1}): 1986 (CO), 1974 (CO). Anal. Calcd for $C_{61}H_{56}N_4O_2P_2BrRh_2B$: C, 59.30; H, 4.57; N, 4.53. Found: C, 59.24; H, 4.62; N, 4.63. HRMS: *m/z* calcd for $C_{37}H_{36}N_4O_2P_2BrRh_2$ (M$^+$ − BPh$_4$), 914.9607; found, 914.9609 (M$^+$ − BPh$_4$). The ^1H and $^{31}P\{^1H\}$ NMR spectra of compound **5c** are available in the Supporting Information.

(l) [(μ-(1,1′-(1,2-ethylene)-3,3′-di-*tert*-butyldiimidazoline-2,2′-diylidene)(μ-dppm)(μ-Cl)bis((carbonyl)rhodium(I))][BPh$_4$] (5d). To a flask containing an equimolar mixture of **2d** (0.60 g, 0.78 mmol) and dppm (0.30 g, 0.78 mmol) was added 20 mL of THF, followed immediately by a CO purge through the slurry until the mixture dissolved, giving an orange solution. The reaction mixture was stirred for an additional 30 min before sodium tetraphenylborate (0.29 g, 0.86 mmol, 1.1 equiv) was added to the reaction vessel in a single portion. The mixture was filtered through a bed of Celite and the solvent evaporated under reduced pressure to give a dark oily solid. To extract the compound from a mixture containing various species, the crude product was redissolved in 15 mL of CH_2Cl_2 and 20 mL of ether was then added, causing an orange oil to settle. The remaining ethereal supernatant was transferred to a new flask, and the addition of 30 mL of pentane precipitated a bright yellow oil that was isolated and placed under vacuum to give 0.20 g (20%) of an oily solid product. ^1H NMR (399.8 MHz, CD_2Cl_2, 27.0 °C): δ 7.05 (d, 2H, $^3J_{H-H}$ = 2.0 Hz), 6.78 (d, 2H, $^3J_{H-H}$ = 2.0 Hz, NCH); 6.44 (m, 2H), 4.36 (m, 2H, CH_2CH_2); 1.61 (s, 18H, $NC(CH_3)_3$); 4.22 (dt, 1H, $^2J_{H-H}$ = 12.8 Hz, $^2J_{H-P}$ = 10.0 Hz), 3.20 (dt, 1H, $^2J_{H-H}$ = 12.8 Hz, $^2J_{H-P}$ = 10.0 Hz, PCH_2P). $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_2Cl_2, 27.0 °C): δ 185.5 (dd, 2C, $^1J_{C-Rh}$ = 84.6 Hz, $^2J_{C-P}$ = 16.4 Hz, CO); 175.0 (dd, 2C, $^2J_{C-P}$ = 116.4 Hz, $^1J_{C-Rh}$ = 43.5 Hz, $C_{carbene}$); 121.6 (s, 2C), 120.7 (s, 2C, NCH); 48.8 (s, 2C, CH_2CH_2); 59.0 (s, 2C), 32.2 (s, 6C, $NC(CH_3)_3$); 23.8 (t, $^1J_{C-P}$ = 16.8 Hz, PCH_2P). ^{31}P NMR (161.8 MHz, CD_2Cl_2, 27.0 °C): δ 26.4 (symmetric multiplet with two principal lines separated by 113.1 Hz, dppm). IR (solid, cm^{-1}): 1973 broad (CO). HRMS: *m/z* calcd for $C_{43}H_{48}N_4O_2P_2ClRh_2$ (M$^+$ − BPh$_4$), 955.1046; found, 955.1046 (M$^+$ − BPh$_4$). Anal. Calcd for $C_{67}H_{68}BN_4O_2P_2ClRh_2$: C, 63.10; H, 5.37; N, 4.39. Found: C, 63.39, H, 5.61; N, 4.55.

(m) [(μ-1,1′-(1,2-ethylene)-3,3′-dimethyldiimidazoline-2,2′-diylidene)(μ-dppm)(μ-OH)bis((carbonyl)rhodium(I))][BPh$_4$] (6c). To an orange solution containing **5c** (0.50 g, 0.41 mmol) in 15 mL of THF was added an excess of concentrated NaOH(aq) (2 mL, 6 M). After it was stirred for 1 h, the light yellow biphasic solution was brought to dryness in vacuo and the crude mixture dehydrated for 3 days under reduced pressure. Once dry, a 30 mL portion of THF was added and the resulting suspension filtered through Celite, from which 0.42 g of product **6c** was recovered by the addition of excess pentane and subsequent drying in vacuo (87%). ^1H NMR (400.4 MHz, OC_4D_8, 27.0 °C; the olefinic protons within the NHC rings were not located): δ 6.13 (m, 2H), 4.44 (m, 2H, CH_2CH_2); 3.62 (s, 6H, NCH_3); 3.81 (dt, 1H, $^2J_{H-H}$ = 12.8 Hz, $^2J_{H-P}$ = 10.8 Hz), 3.26 (dt, 1H, $^2J_{H-H}$ = 12.8 Hz, $^2J_{H-P}$ = 12.8 Hz, PCH_2P); 0.81 (t, 1H, $^2J_{H-Rh}$ = 4.4 Hz, OH). $^{13}C\{^1H\}$ NMR (100.7 MHz, OC_4D_8, 27.0 °C): δ 189.7 (dd, 2C, $^1J_{C-Rh}$ = 70 Hz, $^2J_{C-P}$ = 17 Hz, CO); 179.8 (dd, 2C, $^2J_{C-P}$ = 117 Hz, $^1J_{C-Rh}$ = 47 Hz, $C_{carbene}$); 123.0 (s, 2C), 122.2 (s, 2C, NCH); 49.8 (s, 2C, CH_2CH_2); 38.0 (s, 2C, NCH_3); 19.0 (t, $^1J_{C-P}$ = 15.1 Hz, PCH_2P). ^{31}P NMR (162.1 MHz, OC_4D_8, 27.0 °C): δ 28.9 (symmetric multiplet with two principal lines separated by 120.0 Hz, dppm). IR (film cast, cm^{-1}): 1958 (CO). HRMS: *m/z* calcd for $C_{37}H_{37}N_4O_3P_2Rh_2$ (M$^+$ − BPh$_4$), 853.0446; found, 853.0442 (M$^+$ − BPh$_4$). Anal. Calcd for $C_{61}H_{57}BN_4O_3P_2Rh_2$: C, 62.48; H, 4.90; N, 4.78. Found: C, 62.64, H, 5.19; N, 4.73.

(n) [(μ-1,1′-(1,2-ethylene)-3,3′-dimethyldiimidazoline-2,2′-diylidene)(μ-dppm)(1,3-dimethylimidazol-2-ylidene)(carbonyl)rhodium(I)(iodo)(carbonyl)rhodium(I)][BPh$_4$] (7c). To a yellow solution containing 1 equiv of **6c** (0.1 g, 0.085 mmol) in 10 mL of CH_2Cl_2 was added excess 1,3-dimethylimidazolium-2-ylidene iodide (38.1 mg, 0.17 mmol, 2 equiv). The resulting suspension was stirred overnight where ^{31}P NMR spectroscopy revealed a clean conversion to product **7c**. Solvent removal in vacuo gave a residue, and the addition of 15 mL of THF resulted in a suspension. Once this suspension was filtered through Celite, 0.098 g of product **6c** was recovered by the addition of excess ether and subsequent drying in vacuo (84%). Attempts to obtain crystals of compound **7c** suitable for an X-ray study failed. However, suitable crystals of the closely related [Rh$_2$Br(CO)$_2$(IMe)(μ-$^{Me}CC^{eth}$)(dppm)][I] (**7c′**; IMe = 1,3-dimethylimidazol-2-ylidene) were obtained by the reaction of **6c**, as the bromide salt, with excess 1,3-dimethylimidazolium-2-ylidene iodide. The structure determination was therefore carried out on **7c′** (vide infra). ^1H NMR (399.8 MHz, CD_2Cl_2, 27.0 °C): δ 8.20, 8.08, 7.20, 7.06 (d, 1H, $^3J_{H-H}$ = 1.6 Hz, NCH); 6.61, 6.19 (d, 1H, $^3J_{H-H}$ = 2.0 Hz, NCH); 6.56, 4.98, 4.79, 4.31 (ddd, 1H, $^2J_{H-H}$ = 14 Hz, $^3J_{H-H}$ = 12, 6 Hz, CH_2CH_2); 3.76, 3.69, 3.62, 3.21 (s, 3H, NCH_3); 4.68 (dt, 1H, $^2J_{H-H}$ = 13.6 Hz, $^2J_{H-P}$ = 9.6 Hz), 3.69 (dt, 1H, $^2J_{H-H}$ = 13.6 Hz, $^2J_{H-P}$ = 13.6 Hz, PCH_2P). $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_2Cl_2, 27.0 °C): δ 185.4 (dd, 1C, $^1J_{C-Rh}$ = 81.4 Hz, $^2J_{C-P}$ = 16.1 Hz), 181.1 (dd, 1C, $^1J_{C-Rh}$ = 45.2 Hz, $^2J_{C-P}$ = 16.1 Hz, CO); 177.7 (dd, 1C, $^2J_{C-P}$ = 114.6 Hz, $^1J_{C-Rh}$ = 43.2 Hz), 177.5 (dd, 1C, $^2J_{C-P}$ = 43.2 Hz, $^1J_{C-Rh}$ = 43.2 Hz) 176.7 (dd, 1C, $^2J_{C-P}$ = 99.5 Hz, $^1J_{C-Rh}$ = 46.2 Hz, $C_{carbene}$); 123.3 (s, 1C), 122.9 (s, 1C), 122.6 (s, 1C), 122.5 (s, 2C), 122.2 (s, 1C, NCH); 50.5, 49.8 (s, 1C, CH_2CH_2); 39.4, 39.3, 38.6, 38.5 (s, 1C, NCH_3); 34.5 (t, $^1J_{C-P}$ = 16.1 Hz, PCH_2P). ^{31}P NMR (161.8 MHz, CD_2Cl_2, 27.0 °C): 24.3 (dd, 1P, $^1J_{P-Rh}$ = 124.6 Hz, $^2J_{P-P}$ = 34.0 Hz), 21.8 (dd, 1P, $^1J_{P-Rh}$ = 113.3 Hz, $^2J_{P-P}$ = 34.0 Hz). IR (film cast, cm^{-1}): 1975 (CO). HRMS: *m/z* calcd for $C_{42}H_{44}N_6O_2P_2IRh_2$ (M$^+$ − BPh$_4$), 1059.0150; found, 1059.0154 (M$^+$ − BPh$_4$). Anal. Calcd for $C_{66}H_{64}BIN_6O_2P_2Rh_2$: C, 57.50; H, 4.68; N, 6.10. Found: C, 57.87, H, 4.92; N, 6.22.

(o) [(μ-1,1′-(1,2-ethylene)-3,3′-dimethyldiimidazoline-2,2′-diylidene)bis((carbonyl)(η^1:η^1-dppe)rhodium(I))][CF$_3$SO$_3$]$_2$ (8c). To a yellow solution containing **2c** (0.4 g, 0.60 mmol) in 15 mL of CH_2Cl_2 was added dropwise via cannula 15 mL of CH_2Cl_2 containing dppe (0.46 g, 1.20 mmol). The flask was then placed under a CO atmosphere, the mixture was stirred for 30 min, and then a 1.20 mol portion of sodium triflate was added, resulting in the formation of a white precipitate. The mixture was filtered through Celite before a 50 mL portion of pentane was added, giving a yellow precipitate. The solid was isolated, and ^{31}P NMR spectroscopy revealed a mixture of two species: **8c** and a doublet at 58.6 ($^1J_{P-Rh}$ = 133.0 Hz), assigned to [Rh(dppe)$_2$][CF$_3$SO$_3$]. The dicationic product was separated on the basis of its low solubility in THF. The addition of 20 mL of THF to the mixture resulted in a slurry, which was stirred for 2 h and then allowed to stand for several minutes, yielding a fine yellow precipitate. The yellow supernatant was discarded. The product was allowed to dry in vacuo, giving 0.11 g (14%) of product, and was shown by ^{31}P NMR spectroscopy to contain only compound **8c**. ^1H NMR (400.4 MHz, CD_2Cl_2, 27.0 °C): δ 6.83 (d, 2H, $^3J_{H-H}$ = 1.6 Hz), 6.15 (d, 2H, $^3J_{H-H}$ = 1.6 Hz, NCH); 3.95 (m, 2H), 2.67 (m, 2H, CH_2CH_2); 3.48 (s, 6H, NCH_3); 2.95 (m, 2H), 2.91 (m, 2H), 2.50 (m, 2H), 1.98 (m, 2H, dppe). $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_2Cl_2, 27.0 °C): δ 188.5 (ddd, 2C, $^1J_{C-Rh}$ = 65.4 Hz, $^2J_{C-P}$ = 100.5 Hz, $^2J_{C-P}$ = 14.1 Hz, CO); 175.7 (ddd, 2C, $^1J_{C-Rh}$ = 44.2 Hz, $^2J_{C-P}$ = 87.5 Hz, $^2J_{C-P}$ = 14.1 Hz, $C_{carbene}$); 124.5 (s, 2C), 123.1 (s, 2C, NCH); 50.8 (s, 2C, CH_2CH_2); 38.1 (s, 2C, NCH_3); 28.7 (dd, 2C, $^1J_{C-P}$ = 29.7 Hz, $^2J_{C-P}$ = 16.7 Hz), 27.1 (dd, 2C, $^1J_{C-P}$ = 29.7 Hz, $^2J_{C-P}$ = 15.6 Hz, PCH_2CH_2P). ^{31}P NMR (162.0 MHz, CD_2Cl_2, 27.0 °C): 62.4 (dd, 2P, $^1J_{P-Rh}$ = 110.7 Hz, $^2J_{P-P}$ = 29.7 Hz), 56.1 (dd, 2P, $^1J_{P-Rh}$

= 126.4 Hz, $^2J_{P-P}$ = 29.7 Hz, dppe). IR (solid, cm^{-1}): 2009.5 broad (CO). HRMS: *m/z* calcd for $C_{64}H_{62}N_4O_2P_4Rh_2$ (M^{2+}), 624.0961; found, 624.0957 (M^{2+}). We were unable to separate compound **8c** from a minor impurity; therefore, an elemental analysis was not possible. The ^{1}H and $^{31}P\{^1H\}$ NMR spectra of **8c** are given in the Supporting Information.

(p) Attempted Reduction of Compounds 4a−d. An NMR tube containing 20 mg of **4(a-d)** dissolved in 0.7 mL of *d*^{8}-THF was charged with either an excess of NaBH$_4$ or concentrated KOH (aq) followed by a gentle CO purge. The reaction was then monitored using ^{31}P NMR spectroscopy; in all cases, reduction attempts let to the formation of [Rh$_2$(CO)$_3$(dppm)$_2$] as indicated by the rise of a symmetric multiplet at 19.4 with two principle lines separated by 144.3 Hz.

X-ray Structure Determinations. (a) General Considerations. Crystals were grown via slow diffusion of diethyl ether (**2b,d**, **4c**, **5c**, **7c′**, **8c**) or pentane (**5b**) into a CH$_2$Cl$_2$ solution of the compound. Data were collected using a Bruker SMART 1000 CCD detector/ PLATFORM diffractometer[15] using Mo Kα radiation, with the crystals cooled to −80 °C. The data were corrected for absorption through use of a multiscan model (SADABS (**2a,d**, **4c**, **8c**) or TWINABS (**5b**)) or through Gaussian integration from indexing of the crystal faces (**5c**, **7c′**). Structures were solved using the direct methods program SHELXS-97[16] (**2b,d**, **4c**, **5c**, **8c**) or using the Patterson search/structure expansion facilities within the DIRDIF-99[17] program system (**5b**, **7c′**). Refinements were completed using the program SHELXL-97.[18] Hydrogen atoms were assigned positions on the basis of the geometries of their attached carbon atoms and were given thermal parameters 20% greater than those of the attached carbons. See the CIF files, given as Supporting Information, for the crystallographic experimental data.

(b) Special Refinement Conditions. (i) 2d. The C(11A)−C(12A) distance was restrained to be 1.400(2) Å. The geometry of the minor (40%) forms of the disordered *tert*-butyl group and the disordered cyclooctadiene group were restrained to be the same as that of the major (60%) form by use of the SHELXL-97 SAME instruction during refinement.

(ii) 6b. The crystal used for data collection was found to display nonmerohedral twinning. Both components of the twin were indexed with the program CELL_NOW. The first twin component can be related to the second component by 180° rotation about the [−^{1}/$_4$ −^{1}/$_4$ 1] axis in real space and about the [0 0 1] axis in reciprocal space. Integrated intensities for the reflections from the two components were written into a SHELXL-97 HKLF 5 reflection file with the data integration program SAINT (version 7.06A), using all reflection data (exactly overlapped, partially overlapped and nonoverlapped). Distances within the solvent dichloromethane molecule were given fixed idealized values: *d*(Cl(S)−C(1S)) = *d*(C1(1S)−C(1S)) = 1.80 Å; *d*(Cl(1S)···Cl(2S)) = 2.95 Å. .

(iii) 7c′. The P−C distances involving the ipso carbons of the disordered dppm phenyl ring were constrained to be equal (within 0.001 Å): *d*(P(2)−C(51A)) = *d*(P(2)−C(51B)).

Results and Compound Characterization

The methylene- or ethylene-linked diimidazolium salts (**1a−d**) that were subsequently used to generate the series of dicarbene-bridged binuclear complexes were synthesized, as

(15) Programs for diffractometer operation, unit cell indexing, data collection, data reduction, and absorption correction were those supplied by Bruker.

(16) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.

(17) Sheldrick, G. M. *SHELXL-97. Program for Crystal Structure Determination*; University of Göttingen, Gottingen, Germany, 1997.

(18) Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granada, S.; Israel, R.; Gould, R. O.; Smits, J. M. M. *The DIRDIF-99 program system*; Crystallography Laboratory, University of Nijmegen, Nijmegen, The Netherlands, 1999.
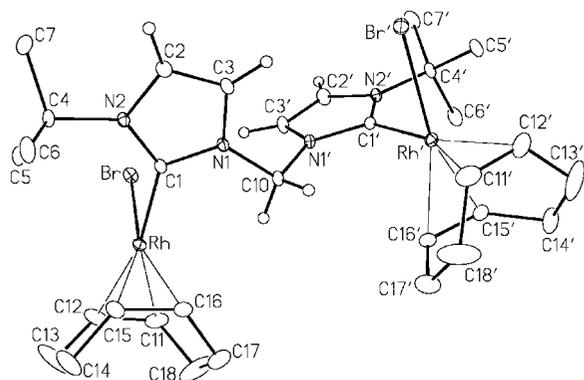
Scheme 1
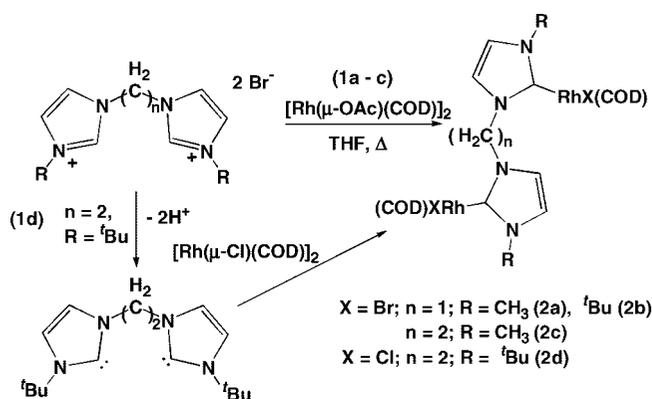
previously reported,[2g,3a,6b] by the reaction of the appropriate 1-alkylimidazole with either methylene dibromide or 1,2-dibromoethane. Two methods were used to generate the di-N-heterocyclic carbene-bridged dirhodium complexes from these diimidazolium salts, as outlined in Scheme 1. In the first method, the diimidazolium bromide salts **1a−c** were reacted with the acetate-bridged species [Rh(*µ*-OAc)(COD)]$_2$ in refluxing THF to yield the respective di-N-heterocyclic carbene-bridged species [RhBr(COD)]$_2$(*µ*-di-NHC) (**2a−c**). All attempts to obtain the corresponding product by this method using the diimidazolium salt **1d** failed; only starting materials were observed after refluxing in a number of solvents for periods of up to 2 days. The missing member of this series, as the chloro complex (**2d**) was instead synthesized through initial double deprotonation of the diimidazolium salt **1d** using K[N(SiMe$_3$)$_2$], followed by reaction of the resulting dicarbene with [Rh(*µ*-Cl)(COD)]$_2$. This product had been previously synthesized by a transmetalation reaction, using the appropriate Ag$_2$(di-NHC)Br$_2$ species as the carbene-transfer agent.[7d]

Although a number of analogous dirhodium complexes have been reported incorporating the ^{Me}CC^{meth}, ^{Me}CC^{eth}, and ^{tBu}CC^{eth} bridging dicarbenes used in this paper (see Chart 1 for the abbreviations used), compound **2b** appears to represent the first report of a species containing the bridging ^{tBu}CC^{meth} dicarbene. In a previous study Crabtree and co-workers had generated a series of binuclear species incorporating C$_2$-, C$_3$-, and C$_4$-linked, *tert*-butyl-substituted di-NHC ligands, using the above trans-metalation route,[7d] but had not observed the CH$_2$-linked analogue, instead obtaining only a mononuclear species in which the ^{tBu}CC^{meth} group functioned as a chelating ligand. Very analogous species incorporating the ^{nBu}CC^{meth} and ^{nBu}CC^{eth} groups,[7b] as well as C$_2$-, C$_3$-, and C$_4$-linked dicarbenes having isopropyl substituents,[7d] have also been reported.

The spectral parameters for compounds **2a,c,d** are closely comparable to those of related species which have previously been reported,[2a,3a,7a,d] and so will not be discussed here. However, since compound **2b** has not previously been reported, its spectral parameters are briefly discussed here. The ^{1}H NMR spectrum of **2b** shows the typical resonances for the coordinated COD ligands (between δ 1.82 and 5.04) as given in the Experimental Section. In addition, a single resonance appears at δ 1.97 for all 18 protons of the two *tert*-butyl groups. The inequivalent vinylic protons within the unsaturated carbene rings appear as two doublets at δ 7.81 and 7.05, displaying mutual coupling of 2.0 Hz, while the protons in the linking methylene group appear as a singlet at δ 8.35. In the $^{13}C\{^1H\}$ NMR spectrum the carbene carbons appear as a doublet at δ 180.8, displaying 49.8 Hz coupling to Rh; both the chemical shift and the coupling constant are typical for related NHC complexes.
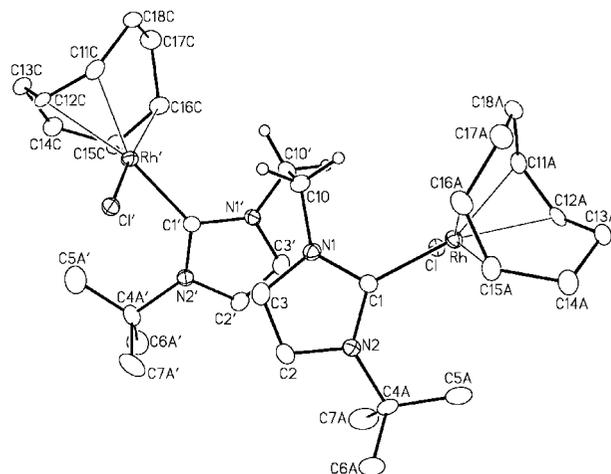
Figure 1. Three-dimensional representation of [Rh$_2$Br$_2$(COD)$_2$(μ-^{t}BuCC^{meth})] (**2b**) showing the numbering scheme. Primed atoms are related to unprimed ones by a crystallographic C_2 axis passing through C(10). Thermal ellipsoids are shown at the 20% probability level, except for the linker CH$_2$ and the olefinic protons, which are shown artificially small. Hydrogen atoms on the COD and ^{t}Bu groups are not shown. Relevant parameters (distances in Å and angles in deg): Rh−Rh′ = 6.6575(5), Rh−Br = 2.5158(3), Rh−C(1) = 2.051(2), Rh−C(11) = 2.207(3), Rh−C(12) = 2.205(3), Rh−C(15) = Rh−C(16) = 2.115(3); N(1)−C(10)−N(1)′ = 112.5(3)°.

The ^{13}C resonance for the methylene linker appears at δ 67.5, while the olefinic carbons of the NHC groups appear at δ 121.5 and 121.0, and the quaternary carbon and the methyl carbons of the *tert*-butyl groups appear at δ 58.8 and 32.2, respectively.

As has previously been noted for related species,[7b] two diastereomers of compound **2b** are possible—the *meso* form, in which the two RhBr(COD) units are related by mirror symmetry, and the *dl* form, in which these units are related by a C_2 rotation axis. The appearance of only one set of resonances for the complex indicates that only one diastereomer is present, and the appearance of the resonance for the protons of the methylene linker as a singlet indicates that the *dl* form is present; the *meso* form would be expected to display an AB quartet for these protons. This is also the diastereomer found in the solid state by X-ray crystallography, in which each molecule has crystallographically imposed C_2 symmetry. A representation of complex **2b** is shown in Figure 1. A comparison of this structure with that of the closely related [RhI(COD)]$_2$(μ-^{Me}CC^{meth})[7a] species shows that the two have very similar geometries. The Rh−Rh separation in **2b** (6.6575(5) Å) is somewhat longer than that observed in the iodo analogue (6.6376 Å), presumably as a consequence of the bulkier *tert*-butyl substituents in our case. Similarly, the Rh−carbene distance in **2b** (2.051(2) Å) is only slightly longer than the related distances (2.023, 2.014 Å) in the iodo species. A glance at Figure 1 shows that this latter elongation in **2b** may also result from repulsions between the *tert*-butyl substituents on the dicarbene and the COD ligands. Further indications of the steric repulsions involving the bulky *tert*-butyl substituents are the unsymmetrical angles at the carbene carbon (Rh−C(1)−N(1) = 122.3(2)° and Rh−C(1)−N(2) = 133.8(2)°), with the larger angle corresponding to that adjacent to the *tert*-butyl group.

Interestingly, the Rh−C(11) and Rh−C(12) separations (2.207(3), 2.205(3) Å) involving the COD ligand are longer than those to the other olefin moiety (Rh−C(15) = Rh−C(16) = 2.115(3) Å). This difference is probably a consequence of both steric repulsions between half of the COD ligand and the adjacent bromo ligand and the larger trans influence of the carbene ligand.[3a,6c,f,7b] The weaker Rh−olefin interaction is paralleled by a shorter C(11)−C(12) distance (1.360(5) Å)
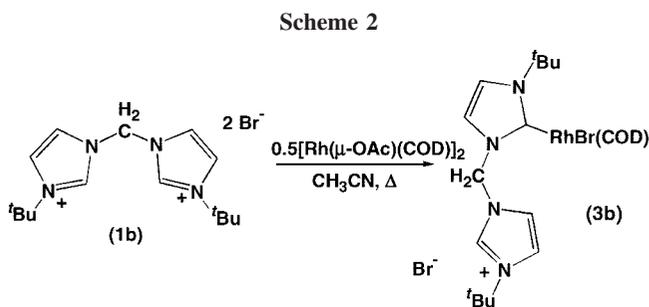
compared to C(15)−C(16) (1.399(4) Å), consistent with less π back-donation in this case.

As is typical for square-planar NHC complexes, the carbene plane lies essentially perpendicular to the metal coordination plane. Thus, for **2b** the dihedral angle between the five-membered carbene ring and the plane defined by Rh, Br, and C(1) is 87.75(8)°.

We have also carried out an X-ray structural study of the C$_2$H$_4$-linked analogue [RhCl(COD)]$_2$(μ-^{t}BuCC^{eth}) (**2d**) as a comparison, and a representation of this species is given in Figure 2. This structure compares very well with that previously determined for [RhCl(COD)]$_2$(μ-^{Me}CC^{eth}),[3a] with both adopting a synclinal conformation about the H$_2$C−CH$_2$ bond of the linker; in compound **2d** the torsion angle about this C−C bond is 36.7(10)°, compared to 55.3 and 57.6° in the two independent molecules of the related ^{Me}CC^{eth} complex. Both species have similar Rh−Rh separations (7.2627(9) Å in **2d** and 7.221, 7.258 Å in the ^{Me}CC^{eth} complex), which are significantly larger than the values for **2b** (6.658 Å) and a related CH$_2$-linked species (6.638 Å),[7a] consistent with the additional methylene group linking the two carbene units in **2d**. Again, the Rh−carbene distance (2.048(5) Å) is close to those in previous determinations and the carbene plane is close to orthogonal to the metal coordination plane (dihedral angle 85.3(2)°).

On one occasion, the overnight reflux in THF, required to generate **2b**, was interrupted after only 4 h. The resulting solution was found to contain a number of products, one of which was isolated in low yield and found to correspond to the mononuclear species **3b**, shown in Scheme 2, in which deprotonation of only one end of the diimidazolium salt has occurred to give a monocarbene complex having a pendant imidazolium group. This species was subsequently obtained in high yield after 3 h of reflux in acetonitrile of a 1:0.5 mixture of **1b** and the acetate-bridged [Rh(μ-OAc)(COD)]$_2$. This product, [RhBr(^{t}BuC(H)-η^1-C^{meth})(COD)][Br] (**3b**), is analogous to an iridium complex, reported by Albrecht et al.,[2g] and is found to have spectral parameters very comparable to those of this species. In particular, the acidic proton of the pendant imidazolium group appears in the ^{1}H NMR spectrum at δ 10.68 in **3b**, compared to δ 10.44 in the Ir analogue, and the protons of

Figure 2. Representation of [Rh$_2$Cl$_2$(COD)$_2$(μ-^{t}BuCC^{eth})] (**2d**) showing the numbering scheme. Primed atoms are related to unprimed ones by a crystallographic C_2 axis bisecting the C(10)−C(10)′ bond. Thermal parameters for the hydrogens of the C$_2$H$_4$ linker are shown artificially small; all others are as described in Figure 1. Relevant parameters (distances in Å): Rh−Rh′ = 7.2627(9), Rh−C(1) = 2.048(5).

Scheme 2

Figure 3. Representation of $[Rh_2Br_2(CO)_4(\mu\text{-}^{Me}CC^{eth})]$ (**4c**). Thermal ellipsoids are as in Figure 1. All hydrogens are shown artificially small. Relevant parameters (distances in Å): Rh(1)−Rh(2) = 7.0052(8), Rh(1)−C(12) = 2.054(3), Rh(2)−C(22) = 2.055(3).

the methylene linker appear as an AB quartet at δ 8.09 and 7.64 ($^2J_{H-H}$ = 12.0 Hz) compared to the resonances at δ 7.80 and 7.41 ($^2J_{H-H}$ = 12.9 Hz) for the Ir species. The appearance of the methylene protons as an AB quartet suggests that the plane of the NHC unit is bound perpendicular to the square plane of the metal, as has been observed in all such cases. In agreement with our formulation, four separate resonances appear for the vinylic protons within the NHC and the imidazolium rings, appearing at δ 8.04 and 7.16 ($^3J_{H-H}$ = 2.0 Hz) for the former and at δ 8.84 and 7.34 ($^3J_{H-H}$ = 1.6 Hz) for the latter. These latter resonances also display a coincidental 1.6 Hz coupling to the acidic hydrogen of this imidazolium group and so appear as pseudotriplets. In the $^{13}C\{^1H\}$ NMR spectrum the carbene carbon appears at δ 182.8 and displays 49.9 Hz coupling to Rh, while the carbonium carbon of the imidazolium group appears at δ 136.5; by comparison, the carbene carbon in the Ir analogue was reported at δ 180.5. The other spectral parameters, given in the Experimental Section, offer additional support for this formulation, including the mass spectral data, which show the incorporation of only a single RhBr(COD) unit. Two related monocarbene complexes of Pd, having a pendant imidazolium group, have also been reported.[6e,19]

Not surprisingly, compound **3b** can be deprotonated by additional $[Rh(\mu\text{-}OAc)(COD)]_2$, adding a second RhBr(COD) unit to give the originally targeted **2b**. No analogous intermediate was observed at intermediate times in any of the other reactions generating compounds **2a,c,d**, even when attempted under conditions that successfully yielded **3b**.

Compounds **2a−d** react readily with CO with displacement of the COD ligands. However only **2c,d** give the clean generation of the binuclear products $[RhBr(CO)_2]_2(\mu\text{-}^{Me}CC^{eth})$ (**4c**) and $[RhCl(CO)_2]_2(\mu\text{-}^{tBu}CC^{eth})$ (**4d**), respectively, and the structure of the former is shown in Figure 3. Under CO, compounds **2a,b** yield the mononuclear products $[Rh(CO)_2\eta^1:\eta^1\text{-}di\text{-}NHC)][Br]$, containing chelating dicarbenes, together with $[Rh(\mu\text{-}Br)(CO)_2]_2$. The former species were identified by their mass spectra, which showed mononuclear species, and by a comparison of their NMR data with the known compounds,[7b,20] while the latter product was identified by its reaction with dppm to give the known species $[Rh_2(CO)_2(\mu\text{-}Br)(\mu\text{-}CO)(dppm)_2][Br]$.[21]

As has been the case for the other binuclear, C_2H_4-linked compounds, the *dl* diastereomer is observed in the crystal of **4c**, in which the synclinal conformation is again observed, displaying a N(11)−C(10)−C(20)−N(21) torsion angle of 61.9(3)° about the $H_2C−CH_2$ bond of the linking group. All structural parameters within this product are basically as anticipated, in which the Rh−Rh separation of 7.0052(8) Å is
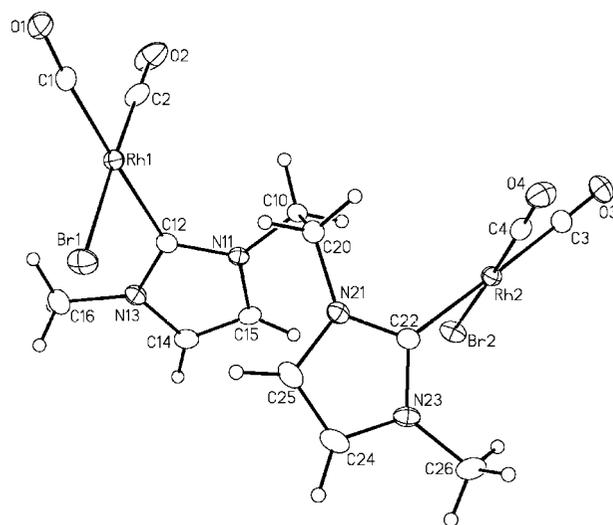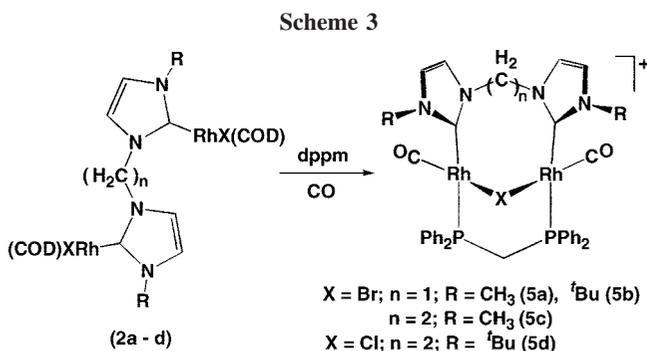
shorter than for the COD complex **2d** (vide infra), for which the larger COD and *tert*-butyl groups presumably force the metals further apart. The Rh−carbene bonds (2.054(3), 2.055(3) Å) are also as expected. There is a significant shortening of the Rh−carbonyl bonds opposite the bromo ligands (1.832(3), 1.836(3) Å) compared to those opposite the carbenes (1.906(3), 1.898(3) Å), resulting from the π-donor properties of the former and the trans influence of the latter. This shortening is accompanied by a slight but noticeable lengthening of the corresponding C−O bonds (1.137(3), 1.134(3) Å compared to 1.124(3), 1.129(3) Å).

Reaction of compounds **2a−d** with 1 equiv of dppm $(Ph_2PCH_2PPh_2)$, followed by the addition of CO and $NaBPh_4$, yields the dicarbene- and diphosphine-bridged products $[Rh_2(CO)_2(\mu\text{-}Br)(\mu\text{-}di\text{-}NHC)(\mu\text{-}dppm)][BPh_4]$ (**5a−d**), shown in Scheme 3. Compound **5c** (di-NHC = $^{Me}CC^{eth}$) can also be generated from the reaction of **4c** with 1 equiv of dppm or by reacting **2c** with CO and dppm in the reverse order to that given above. However, reaction of compounds **2a** or **2b** first with CO then with dppm does not give the targeted dppm-bridged products but instead gives mixtures of products, presumably related to their reactions with CO noted earlier, in which fragmentation of the binuclear framework occurred. In the case of **2d**, reaction with CO, followed by addition of dppm, or alternatively by reaction of **4d** with dppm does yield **5d**, but only in very low yield, together with a complex mixture of products which appear to be oligomeric in which dppm groups presumably connect adjacent dicarbene-bridged Rh_2 fragments.

Scheme 3

X = Br; n = 1; R = CH_3 (**5a**), ^tBu (**5b**)
n = 2; R = CH_3 (**5c**)
X = Cl; n = 2; R = ^tBu (**5d**)

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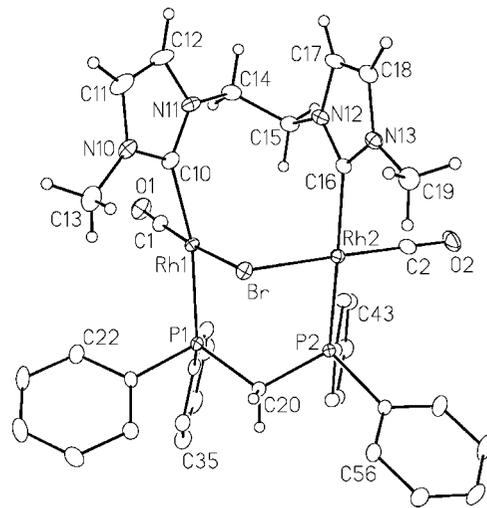(21) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2500.
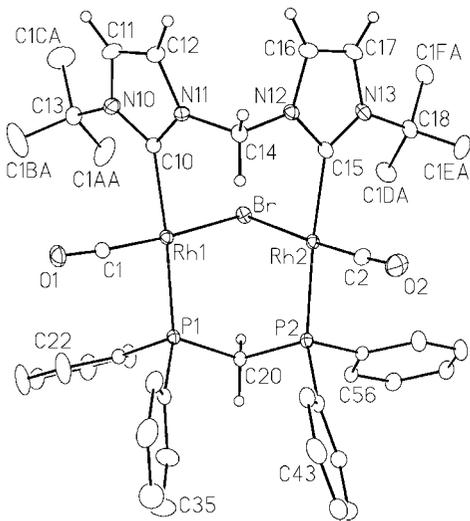
Figure 4. Representation of the complex cation of [Rh$_2$(CO)$_2$(μ-Br)(μ-$^{t\text{Bu}}$CC$^{\text{meth}}$)(dppm)][BPh$_4$] (**5b**). Thermal parameters are as described in Figure 1. Hydrogen atoms on the phenyl and *tert*-butyl groups are not shown. Relevant parameters (distances in Å and angles in deg): Rh(1)−Rh(2) = 3.3022(5), Rh(1)−C(10) = 2.083(3), Rh(2)−C(15) = 2.057(4), P(1)−P(2) = 3.048(1), C(10)−C(15) = 3.838(5); Rh(1)−Br−Rh(2) = 80.94(2).

Figure 5. Representation of the complex cation of [Rh$_2$(CO)$_2$(μ-Br)(μ-$^{\text{Me}}$CC$^{\text{eth}}$)(dppm)][BPh$_4$] (**5c**). Thermal parameters are as described in Figure 1. Phenyl hydrogens are not shown. Relevant parameters (distances in Å and angles in deg): Rh(1)−Rh(2) = 3.3370(4), Rh(1)−C(10) = 2.048(4), Rh(2)−C(16) = 2.051(3), P(1)−P(2) = 3.041(1), C(10)−C(16) = 3.845(5); Rh(1)−Br−Rh(2) = 82.28(1), P(1)−Rh(1)−C(10) = 165.9(1), P(2)−Rh(2)−C(16) = 176.3(1).

Compounds **5a**−**d** all display very similar spectral parameters, particularly for ligands that all products have in common. For example, all display ^{31}P{^{1}H} NMR spectra in which the dppm resonance appears at ca. δ 25 as a second-order pattern, characteristic of an AA′XX′ spin system, in which the separation between the two major peaks is ca. 110 Hz. The methylene protons of the dppm group appear as two doublets of triplets at ca. δ 4.2 and 3.3, having approximately 10 Hz coupling to both ^{31}P nuclei and 13 Hz coupling to each other. Sample ^{1}H and ^{31}P{^{1}H} NMR spectra for compound **5c** are shown in the Supporting Information.

The IR spectra for all species are consistent with the presence of terminal carbonyls and display either a single broad carbonyl stretch at ca. 1970 cm^{-1} (**5a,d**) or two closely spaced stretches (1974, 1963 cm^{-1} (**5b**); 1986, 1974 cm^{-1} (**5c**)). Furthermore, all display a single carbonyl resonance at ca. δ 185 in their ^{13}C{^{1}H} NMR spectra. The carbonyl resonances for these compounds display approximately 85 Hz coupling to Rh and 16 Hz coupling to a single adjacent ^{31}P nucleus. Also in the ^{13}C{^{1}H} NMR spectra, the carbene carbons appear as doublets of doublets at ca. δ 175; in this case, however, the coupling to phosphorus (ca. 116 Hz) is larger than that to Rh (ca. 43 Hz), indicating that the carbene and phosphine groups are mutually trans at each metal. The larger Rh coupling involving the carbonyl ligands is consistent with the carbonyl carbon having greater "s" character than the carbene carbon.

In the ^{1}H NMR spectra the methylene protons of the $^{\text{R}}$CC$^{\text{meth}}$ ligands appear as a pair of doublets, displaying mutual coupling of about 13 Hz, while the resonances for the ethylene linker in the $^{\text{R}}$CC$^{\text{eth}}$ ligands appear as two multiplets. The methyl and *tert*-butyl resonances (R = Me, ^{t}Bu) appear as expected.

An X-ray structure determination for [Rh$_2$(CO)$_2$(μ-Br)(μ-$^{t\text{Bu}}$CC$^{\text{meth}}$)(dppm)][BPh$_4$] (**5b**) confirms the tribridged geometry (bridging dicarbene, diphosphine, and bromide), as shown for the complex cation in Figure 4. The most notable effect of adding the diphosphine is the dramatic compression of the metal−metal separation from 6.66 Å in **2b** to 3.3022(5) Å in **5b**. This latter metal−metal separation is still well beyond what one would usually consider appropriate for a Rh−Rh bond, and

certainly no bond is expected on the basis of electron counting, in which both metals have a favorable square-planar geometry, typical of Rh(I). The geometry observed for **5b** is very reminiscent of the classical "A-frame" complexes involving two mutually trans dppm groups,[10] with one of the dppm groups being replaced by the di-NHC ligand. Clearly, the larger bite of the dicarbene ligand compared to dppm gives rise to some distortion within the complex in which the C(10)−C(15) separation of the two carbene centers (3.838(5) Å) is much greater than the P(1)−P(2) separation (3.048(1) Å), with the Rh−Rh separation being intermediate.

The Rh−carbene bonds (2.057(4), 2.083(3) Å) are normal and are significantly longer than the metal–carbonyl distances (1.799(4), 1.802(4) Å), consistent with the accepted notion that there is little π-back-donation to these carbenes. As is also typical for square-planar complexes, involving NHCs, the carbene planes lie essentially perpendicular to the coordination planes of the metals (dihedral angles at Rh(1) and Rh(2): 85.9(1), 87.8(1)°). One consequence of this arrangement is that the *tert*-butyl groups are directed into the open sites above the Rh square planes, remote from the adjacent metal and away from the A-frame pocket. In concert with this dicarbene arrangement, one phenyl group on each dppm ligand (rings containing C(22) and C(56)), on the sides adjacent to the *tert*-butyl groups, lie close to horizontal, thereby minimizing nonbonded contacts between the phenyl and *tert*-butyl groups, while on the opposite face the phenyl rings take a close-to-vertical arrangement, aiming into the relatively open pocket between the metals.

We have also carried out an X-ray structural determination of the $^{\text{Me}}$CC$^{\text{eth}}$-bridged species **5c**, in which the two NHC rings are linked by a longer C$_2$H$_4$ unit. Although the overall geometry of **5c** is very similar to that of **5b** (see Figure 5), the additional CH$_2$ group in the linker has resulted in some noticeable distortions in the latter compound. These distortions result from the relatively fixed geometry of the dppm fragment in which the P−P separation (3.041(1) Å) remains essentially unchanged from that in **5b**, while the separation between the pair of NHC rings has increased by the addition of a CH$_2$ group. Surprisingly

perhaps, the increased length of the linker unit has given rise to only a very slight increase in carbene−carbene separation from the 3.838(5) Å noted above in **5b** to 3.845(5) Å in **5c**; at the same time, the metal−metal separation has increased by only 0.035 Å to 3.3370(4) Å in **5c**. Although the additional CH_2 group in the linker has not given rise to the expected increase in carbene−carbene separation, it is instead manifest in a bending back of the carbene unit at Rh(1) (C(10)−Rh(1)−P(1) = 165.9(1)°), significantly distorting this square plane (compare C(16)−Rh(2)−P(2) = 176.3(1)°), and a skewing of this carbene plane with regard to the Rh(1) coordination plane. The dihedral angle between this carbene plane and the Rh(1) coordination plane (68.8(1)°) is twisted significantly from the favored orthogonal arrangement, as observed at Rh(2) (87.2(1)°). It appears that both of these distortions could be avoided by a slight increase in the Rh(1)−Rh(2) separation. However, it also appears that the bridging bromo ligand plays a role in inhibiting the necessary expansion of the metal−metal separation that would minimize the distortions noted above (more about this later). As was the case for compound **5b**, the orientation of the NHC planes is such that the substituents on the NHC rings are aimed on the opposite faces from the A-frame pocket. As with the other NHC complexes, reported herein, the Rh−carbene distances (2.048(4), 2.051(3) Å) are normal, as are most other parameters in the complex.

In all cases, the complexes **5a−d** were ultimately prepared as the BPh_4^- salts, owing to their superior crystallinity. These salts were derived from the original products, having bromide counterions, by anion exchange. Although we have not extensively characterized these bromide salts, their $^{31}P\{^1H\}$ NMR spectra are almost superimposable on those of the BPh_4^- salts. Furthermore, we have ruled out bromide ion coordination to give neutral dibromo compounds, through conductivity studies which show both **5c** (BPh_4^- anion) and its bromo salt have conductivities characteristic of 1:1 electrolytes (see the Experimental Section).

In attempts to generate the dicarbene-bridged analogues of the formally M(0)/M′(0) or $M_2(0)$ complexes [MM′(CO)₃-(dppm)₂] (M, M′ = Rh, Ir)[22−24] or [$M_2(CO)_3$(dmpm)₂] (M = Rh, Ir; dmpm = $Me_2PCH_2PMe_2$),[25] respectively, compounds **5b,c** were reacted with either $NaBH_4$ or NaOH under an atmosphere of carbon monoxide—conditions that had previously been used for the reduction of the bis-diphosphine-bridged halide precursors. Although compounds **5b,c** both react instantly under these conditions, the dicarbene- and disphosphine-bridged cores do not remain intact and instead disproportionate, generating the known bis-dppm species [$Rh_2(CO)_3$(dppm)₂][22] as the only phosphorus-containing product. The fates of the dicarbene ligands and the other 1 equiv of "Rh₂" in these reactions were not determined, although presumably mononuclear species containing chelating dicarbenes were obtained as described earlier.

Reaction of the bromo-bridged A-frame **5c** with excess NaOH in the absence of CO results in replacement of the bromide ligand by hydroxide, yielding the hydroxide-bridged analogue, which was isolated as the BPh_4^- salt [$Rh_2(CO)_2$(μ-OH)(μ-$^{Me}CC^{eth}$)(dppm)][BPh_4] (**6c**). The hydroxide proton appears as a triplet in the ^1H NMR spectrum at δ 0.81, displaying 4.4 Hz

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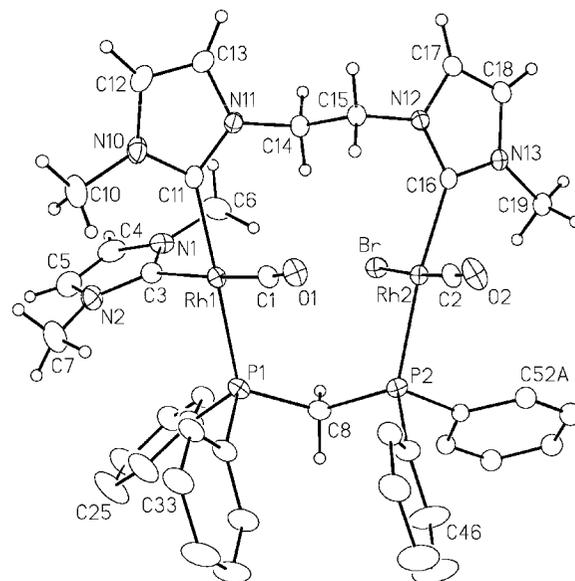
Figure 6. Representation of the complex cation of [$Rh_2Br(CO)_2$-(IMe)(μ-$^{Me}CC^{eth}$)(dppm)][I] (**7c′**). Thermal parameters are as in Figure 1. Phenyl hydrogens are not shown. Relevant parameters (distances in Å and angles in deg): Rh(1)−Rh(2) = 4.0745(3), Rh(1)−C(11) = 2.063(3), Rh(1)−C(3) = 2.091(3), Rh(2)−C(16) = 2.042(3), P(1)−P(2) = 3.202(1), C(11)−C(16) = 5.180(4); Rh(1)−P(1)−C(8) = 119.5(1), Rh(2)−P(2)−C(8) = 117.3(1), P(1)−C(8)−P(2) = 120.9(2).

coupling to the pair of Rh atoms. Otherwise, the spectral parameters resemble those of the other A-frame species (**5a−d**). We had anticipated that reaction of **6c** with carbon monoxide would yield a hydride-bridged product through elimination of CO_2, mimicking water-gas-shift chemistry; however, as with the other dicarbene-bridged A-frames, compound **6c** is unreactive to CO at atmospheric pressure and its reactivity under higher pressures was not investigated. An X-ray structural determination of **6c** was carried out, but this structure could not be refined well, owing to disorder, and so is not reported here. Nevertheless, the A-frame core structure is obvious, confirming our formulation.

Having synthesized the hydroxide-bridged complex [Rh_2-(CO)₂(μ-OH)(μ-$^{Me}CC^{eth}$)(dppm)][BPh_4] (**6c**), we questioned whether the hydroxide ligand could function as a base in the deprotonation of additional imidazolium salts, much as was accomplished earlier in the use of the acetate-bridged dimer [Rh(μ-OAc)(COD)]₂ for generating compounds **2a−c**. Reacting **6c** with the imidazolium salt 1,3-dimethylimidazolium iodide instantly yields [$Rh_2I(CO)_2$(IMe)(μ-$^{Me}CC^{eth}$)(dppm)][BPh_4] (**7c**; IMe = 1,3-dimethylimidazol-2-ylidene). Attempts to obtain suitable crystals of **7c** failed. However, we did obtain crystals of the closely related [$Rh_2Br(CO)_2$(IMe)(μ-$^{Me}CC^{eth}$)(dppm)][I] (**7c′**) by the analogous reaction of the bromide salt of **6c**, namely [$Rh_2(CO)_3$(μ-OH)(μ-$^{Me}CC^{eth}$)(dppm)][Br], with the imidazolium iodide. This compound (**7c′**), containing a bromo ligand, was actually of more interest to us, since a more direct structural comparison to the bromide-bridged **5c** could be made. The ORTEP diagram of the complex cation of **7c′** is shown in Figure 6. A glance at this figure confirms that the dicarbene- and diphosphine-bridged framework has remained intact, but now this pair of bidentate ligands are the only bridging groups; the anionic bromo ligand, which was bridging for compounds **5a−d**, is now terminally bound to one Rh center while the new monocarbene unit is bound to the other, giving two independent square-planar Rh centers. Also obvious from Figure 6, is the

substantial opening up of the dicarbene part of the complex, in which the separation between the carbene centers (C(11)−C(16)) has widened to 5.180(4) Å—an increase of more than 1.3 Å from that observed in the C_2H_4-linked **5c**. Two factors appear to be responsible for this opening up of the A-frame structure: (1) the absence of the bridging bromo ligand allows the metals to increase their separation from that observed in **5c** (to 4.0745(3) from 3.3370(4) Å), and (2) the large monocarbene unit on Rh(1) and adjacent bromo ligand on Rh(2) appear to force the metal centers apart even further than what might have been achieved in **5c**, even in the absence of the bridging bromide. The strain within complex **7c′**, resulting from the increased bite of the dicarbene, is evident in the geometry within the dppm group. First, the P(1)−P(2) separation (3.202(1) Å) is much larger than is usually observed, where values near 3.05 Å, as observed for **5b,c**, are more typical. This larger P−P separation also gives rise to significantly enlarged angles at phosphorus (Rh(1)−P(1)−C(8) = 119.5(1), Rh(2)−P(2)−C(8) = 117.3(1)°) and at C(8) (P(1)−C(8)−P(2) = 120.9(2)°). By comparison, in compounds **5b,c**, the former angles range from 114.4 to 116.9° while the latter are approximately 112°.

The opening up of the carbene−carbene separation has relieved some of the strain that was evident in **5c**, so that now both NHC planes of the dicarbene are symmetrically oriented with respect to the metal coordination planes, being skewed from these planes by similar amounts (76.8(1), 75.48(8)°), although both still deviate from the favored 90°. Similarly, the monocarbene unit is also skewed from the Rh(1) plane by 74.0(1)°. All Rh−carbene distances (2.063(3), 2.091(3), 2.042(3) Å) are again typical for such species.

In an attempt to decrease the strain within these mixed-bridge, A-frame species that has resulted from the differing bite distances of the dicarbene and dppm ligands (particularly for the C_2H_4-linked $^RCC^{eth}$ groups), we attempted to generate the bis(diphenylphosphino)ethane (dppe) analogue of **5c**, in which dppe bridged the metals instead of dppm. The bite of dppe, having the additional CH_2 group linking the two ends of the diphosphine, should be a better match to the longer separation between the carbene centers. Although dppe is commonly used as a chelating group, it is also known to bridge pairs of metals.[27]

Using reaction conditions similar to those used to generate the dppm-bridged **5c** did not give the targeted dppe-bridged analogue but instead yielded a 2:1 mixture (from $^{31}P\{^1H\}$ NMR) of the known species [Rh(dppe)$_2$]$^{+28}$ and the new product [Rh$_2$(CO)$_2$(dppe)$_2$(μ-$^{Me}CC^{eth}$)]$^{2+}$ (**8c**), together with unreacted starting material. The yield of both dppe products could be increased, accompanied by the disappearance of **2c**, by the addition of excess dppe. Attempts to generate a dppe-bridged analogue of **5c** by slow addition of dppe, even at low temperatures, only yielded the chelated product **8c**, which was subsequently isolated as the triflate salt after ion replacement.

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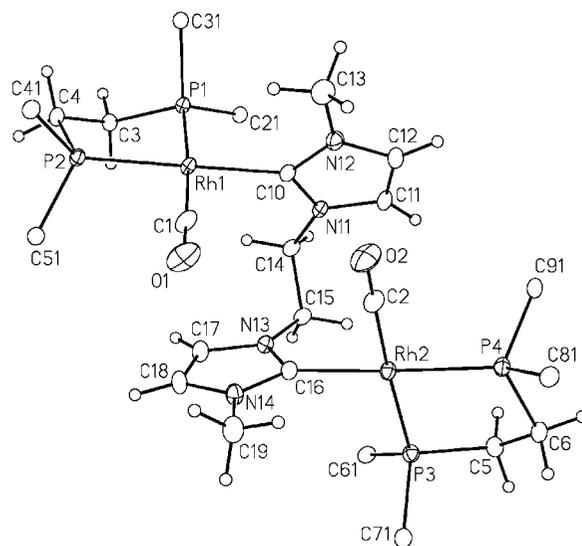
Figure 7. Representation of the complex dication of [Rh$_2$(CO)$_2$(dppe)$_2$(μ-$^{Me}CC^{eth}$)][CF$_2$SO$_3$]$_2$ (**8c**). Only the ipso carbons of the dppe phenyl rings are shown. Relevant parameters (distances in Å): Rh(1)−Rh(2) = 5.8605(6), Rh(1)−C(10) = 2.053(3), Rh(2)−C(16) = 2.069(3), Rh(1)−P(1) = 2.3185(7), Rh(1)−P(2) = 2.2796(7), Rh(2)−P(3) = 2.3246(7), Rh(2)−P(4) = 2.2763(7).

The fate of the dicarbene unit lost in the formation of [Rh(dppe)$_2$]$^+$ was not established.

The $^{31}P\{^1H\}$ NMR spectrum of **8c** (as the triflate salt), which is given in the Supporting Information, displays two doublets of doublets at δ 62.4 and 56.1; the former resonance shows 110.7 Hz coupling to Rh and 56.1 Hz coupling to the other P nucleus, while the Rh coupling in the latter is 126.4 Hz. In the $^{13}C\{^1H\}$ NMR spectrum the carbonyl resonance appears as a doublet of doublets of doublets at δ 188.5, displaying coupling to the trans phosphine (100.5 Hz), Rh (65.4 Hz), and the cis phosphine (14.1 Hz). The carbene carbon at δ 175.7 shows a similar pattern, also having coupling to the trans phosphine (87.5 Hz), rhodium (44.2 Hz), and the cis phosphine (14.1 Hz).

Crystals of **8c** were obtained by recrystallization, and an X-ray structural determination was carried out. Figure 7 gives a representation of the complex dication, which clearly shows that the dppe groups have adopted a chelating arrangement at both metals (only the ipso carbons of the dppe phenyl rings are shown). The resulting Rh(1)−Rh(2) separation (5.8605(6) Å) is significantly shorter than the 7 Å or greater that is observed in the COD and dicarbonyl precursors **2c** and **4c**, respectively, but is still indicative of two independent, noninteracting Rh centers. For the most part, the structural parameters are as expected for a di-NHC-bridged species. Both Rh−carbene bonds (2.053(3), 2.069(3) Å) are normal, and the NHC planes are twisted out of the coordination planes of the respective metals (dihedral angles 76.62(9) and 75.76(9)°), although still deviating significantly from the idealized orientation perpindicular to the metal plane. The dicarbene unit again adopts a synclinal arrangement about the C(14)−C(15) bond of the ethylene linker, such that the N(11)−C(14)−C(15)−N(13) torsion angle is 72.9(3)°. Binding of each end of the diphosphine ligands opposite either the carbene or the carbonyl units results in inequivalent sets of Rh−P distances; the distances opposite the carbonyls (Rh(1)−P(1) = 2.3185(7), Rh(2)−P(3) = 2.3246(7) Å) are longer than those opposite the carbenes (Rh(1)−P(2) = 2.2796(7), Rh(2)−P(4) = 2.2763(7) Å), demonstrating a larger trans influence of the former.

Discussion

A number of strategies have been reported for the generation of NHC complexes, the most common of which are (1) prior deprotonation of the imidazolium ion precursor, using a variety of bases, and subsequent direct reaction of the carbene with an appropriate metal complex, (2) transmetalation, in which the carbene is transferred from a metal−carbene precursor (usually silver) to the metal complex of choice, (3) direct metalation in which the complex and the imidazolium salt are reacted in the presence of a weak base (in this case a transition state in which simultaneous coordination of the base and the imidazolium salt to the metal has been proposed[2g]), and (4) deprotonation of the imidazolium salt by a basic ligand bound to the precursor complex. In this last route the basic ligands used include acetate, acetylacetonate, and alkoxide ions. This route has been the method of choice in much of the chemistry reported herein, yielding the dicarbene-bridged complexes [RhBr(COD)]$_2$(μ-di-NHC) (**2a−c**) from the acetate-bridged dimer [Rh(μ-OAc)-(COD)]$_2$ and the bromo salts of the appropriate imidazolium ions. One advantage of this route is that the stoichiometry is limited by the number of basic ligands in the precursor; thus, the use of the above diacetate dimer results in the double deprotonation of only one diimidazolium dication to yield a single dicarbene unit.

We have also demonstrated in one case that the deprotonation can proceed stepwise at a rate such that the monocarbene product [RhBr(COD)(^{Me}C(H)-η^1-C^{eth})][Br] (**3c**), resulting from deprotonation of one end of the diimidazolium salt, can be isolated, as shown earlier in Scheme 2. The pendant imidazolium functionality that remains can be subsequently deprotonated by additional [Rh(μ-OAc)(COD)]$_2$ to yield the dicarbene-bridged dirhodium species (**2c**), suggesting the potential for this and related pendant compounds to be used for the generation of dicarbene-bridged, mixed-metal complexes via reaction of the pendant intermediate with an appropriate metal source. Such studies are currently underway in our group.

Although the reactions of the methyl-substituted imidazolium salts **1a,c** with the acetate-bridged dimer occur readily (in 3–4 h), that of the *tert*-butyl-substituted **1b** is very sluggish, requiring overnight reflux. Therefore, it is possibly not surprising that no reaction is observed with the *tert*-butyl-substituted **1d** and the acetate-bridged dimer, even after prolonged reflux. Nevertheless, the targeted dicarbene-bridged product **2d** (as the chloride) was readily obtained by prior deprotonation of **1d** and reaction of the resulting dicarbene with [RhCl(COD)]$_2$.

Although it would appear to be a trivial transformation to convert compounds **2a−d** into the tetracarbonyl analogues [RhX(CO)$_2$]$_2$(μ-di-NHC) via COD displacement by CO, this reaction only worked cleanly for compounds **2c,d**. The reactions of **2a,b** gave rise to the mononuclear products [Rh(CO)$_2$(η^1:η^1-di-NHC)][Br], containing chelating di-NHC groups, and [Rh(CO)$_2$(μ-Br)]$_2$. The bridging dicarbenes in these latter precursors were surprisingly labile, converting to chelating at ambient temperature. It is noteworthy that the CH$_2$-bridged dicarbenes ^{R}CC^{meth} (R = Me, ^{t}Bu) are less prone to remain bridging than the C$_2$H$_4$-linked analogues ^{R}CC^{eth}. This is in keeping with a previous conclusion[6b] that the C$_2$H$_4$-linked dicarbenes are under a greater degree of steric strain than the CH$_2$-linked analogues when chelating. An extension of this argument would suggest that the C$_2$H$_4$-linked dicarbenes prefer a bridging coordination mode.

In all of the above compounds, bridged by a single dicarbene unit, the skewing of the two carbene rings about the CH$_2$ or C$_2$H$_4$ linkers gives rise to large Rh−Rh separations

of greater than 6.5 Å. However, taking a page out of A-frame chemistry, the addition of 1 equiv of dppm brings the metals to within 3.34 Å apart through the generation of new A-frame species in which the metals are simultaneously bridged by mutually trans dicarbene and diphosphine groups and by a halide ligand (see Scheme 3). Although the differing bites of these dicarbene and diphosphine groups, in which the carbene−carbene separation is greater than the phosphine−phosphine separation, results in some distortions within the A-frame, there is surprisingly little difference in metal−metal and carbene−carbene separations on proceeding from a CH$_2$ to a C$_2$H$_4$ linker between the carbenes. It appears that in these A-frame species the bridging halide plays a strong role in defining the metal−metal separation and appears unable to accommodate additional separation. The addition of a mono-carbene unit, which forces the bromide ligand from its bridging site to a terminal site, clearly demonstrates the restrictive role played by the bridging bromide through a substantial opening up of the metal−metal separation from ca. 3.34 to 4.07 Å, accompanied by an even greater increase in carbene−carbene separation from 3.85 to 5.18 Å.

On the basis of the strain inherent in this system, we were surprised that the products [Rh$_2$(CO)$_2$(μ-Br)(μ-di-NHC)(dpp-m)][Br], having a bromide counterion, were ionic rather than having both bromide ions coordinated, one to each metal, much as was observed for the monocarbene and bromide ligands in compound **7c′**. In such an arrangement the metals would have been able to separate, allowing the bridging dicarbene to achieve a less strained arrangement. We assume that the bromide-bridged geometries observed for **5b,c** are a compromise in which the strain within the dicarbene unit is tolerated, owing to the absence of such strain within the dppm framework. Furthermore, the basic dicarbene ligands may also play a role in favoring the cationic complex obtained upon bromide loss.

An additional consequence of the above-noted strain appears to be the inability of compounds **5a−d** to react with CO. We had anticipated that the uptake of 1 equiv of CO would yield the carbonyl-bridged adducts [Rh$_2$(CO)$_2$(μ-Br)(μ-CO)(μ-di-NHC)(dppm)]$^+$, much as is well-known in bis-dppm-bridged A-frames. We assume that the inability of our dicarbene-bridged species to react with CO results from their inability to form these carbonyl-bridged adducts with an accompanying metal−metal bond, owing to the increased strain within the dicarbene framework that would result by facing the metals closer together. Similarly, attempts to reduce the Rh(I) A-frames **5a−d**, to formally Rh(0), metal−metal-bonded species, as has been achieved for the bis-dppm and bis-dmpm analogues, failed for our dicarbenes. Again we assume that such products cannot be attained, owing to the contraction in metal−metal separation that would be required with concomitant Rh−Rh bond formation.

Conclusions

Although the targeted A-frame complexes [Rh$_2$(CO)$_2$(μ-Br)(μ-di-NHC)(dppm)]$^+$ have been successfully prepared, their apparent inability to support metal−metal bonds, owing to the strain imposed by the relatively large bite within the dicarbenes, threatens to limit the scope of reactivity for these species; many of the transformations usually observed in binuclear species are accompanied by metal−metal bond making and breaking. Nevertheless, the reactivity of the monobridged ([RhXL$_2$]$_2$(μ-di-NHC)) and tribridged ([Rh$_2$(CO)$_2$(μ-X)(μ-di-NHC)(dppm)]$^+$) compounds will be investigated and compared to that of related

mononuclear analogues to probe whether such systems can display metal−metal cooperativity.

Supporting Information Available: Figures giving ^{1}H NMR spectra for compounds **2d** and **3b**, and ^{1}H and ^{31}P{^{1}H} NMR spectra for compounds **5c** and **8c** and CIF files giving crystal data for compounds **2b,d**, **4c**, **5b,c**, **7c′**, and **8c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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