Table III. Metal Valence Populations[a] for $ScCp_2^+$ in Different Geometries[b]

∠CpScCp, deg	s	p_x	p_y	p_z	d_{xy}	d_{xz}	d_{yz}	$d_{x^2-y^2} + d_{z^2}$	d_{tot}
180	0.134	0.016	0.016	0.003	0.005	0.379	0.379	0.062	0.826
160	0.133	0.015	0.012	0.004	0.015	0.377	0.382	0.100	0.874

[a] Natural population analysis was employed.[11] [b] The *yz* plane contains the Cp ring midpoints and the metal.

ter-ring repulsion. This will also contribute to the more bent structures for the MCp_2^+ cations studied here compared to the neutral MCp_2 systems.

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Articles

Unusual Low-Valent Dirhodium Complexes Bridged by Bis(dimethylphosphino)methane Ligands

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The low-valent complex $[Rh_2(CO)_3(dmpm)_2]$ (1) (dmpm = $Me_2PCH_2PMe_2$) is prepared by the reaction of *trans*-$[RhCl(CO)(dmpm)]_2$ with aqueous NaOH and CO. Under a CO atmosphere 1 is in equilibrium with the labile tetracarbonyl species $[Rh(CO)(\mu\text{-}CO)(dmpm)]_2$ (2). The structure of 1 is believed to be unsymmetrical having a trans arrangement of diphosphine ligands at one metal and a cis arrangement at the other, and a mixed-valence Rh(1+)/Rh(1−) formulation, while 2 is symmetric having the bridging diphosphines cis at both metals, and a corresponding Rh(0)/Rh(0) formulation. Reduction of $[Rh_2Cl_2(CO)_2(\mu\text{-}RC{\equiv}CR)(dmpm)_2]$ (R = CO_2Me, CF_3) yields $[Rh_2(CO)_2(\mu\text{-}RC{\equiv}CR)(dmpm)_2]$ (**3**, **4**), which can also be obtained by alkyne addition to 1. The alkyne ligands are apparently bound perpendicular to the Rh–Rh axes in both species. Protonation of 1 with $HBF_4{\cdot}OEt_2$ yields $[Rh_2(CO)_3(\mu\text{-}H)(dmpm)_2][BF_4]$, and under carbon monoxide this yields $[Rh_2(CO)_4(\mu\text{-}H)(dmpm)_2][BF_4]$. Protonation of 3 yields $[Rh_2(CO)_2(\mu\text{-}DMAD)(\mu\text{-}H)(dmpm)_2][BF_4]$, whereas protonation of 4 yields $[Rh_2(CO)_2(CF_3C{=}C(H)CF_3)(dmpm)_2][BF_4]$, which apparently has a σ, π-vinylic moiety. Reaction of this vinyl complex with CO gives $[Rh_2(CO)_3(CF_3C{=}C(H)CF_3)(\mu\text{-}CO)(dmpm)_2][BF_4]$ in which the vinyl group is σ bound to only one metal.

Introduction

Oxidative-addition reactions are of fundamental importance in organometallic chemistry and are of enormous practical significance since oxidative addition represents one of the key steps in the mechanisms of most homogeneous catalysts.[1] As the term implies, the oxidative-addition reaction proceeds with an increase in coordination number and oxidation state of the metal center(s) involved. Coordinatively unsaturated, electron-rich metal complexes are therefore well suited to such processes. Our recent interest in oxidative-addition reactions[2-10] has centered around *dppm*-bridged complexes involving Rh or Ir (dppm = bis(diphenylphosphino)methane) in efforts to obtain an improved understanding about the functions of the adjacent metals in the oxidative-addition step(s), about the subsequent ligand rearrangements that occur, and about the possibility of coupling organic fragments on the adjacent metals. It was surmised that low-valent binuclear complexes of Rh(0) or Rh(I), bridged by the closely related

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dmpm ligand (dmpm = bis(dimethylphosphino)methane), would be excellent candidates for oxidative additions, owing to the smaller size and increased basicity of dmpm over dppm.[11]

Recent chemistry involving the low-valent species $[Rh_2(CO)_3(dppm)_2]$,[12-14] $[Ir_2(CO)_3(dppm)_2]$,[3,8,14] and $[RhIr(CO)_3(dppm)_2]$[6,14] had demonstrated a strong tendency of these complexes to oxidatively add substrates such as H_2, H_2S, thiols, silanes, and alkynes. We therefore undertook an extension of this chemistry to include related low-valent complexes of dirhodium, bridged by dmpm groups. The preparation and characterization of a series of unusual, low-valent binuclear complexes of Rh, utilizing *dmpm* as the bridging ligand, is reported herein. While this work was in progress, related chemistry involving dmpm-bridged, diiridium complexes was reported.[15,16]

Experimental Section

General Comments. General experimental conditions are as previously described.[17] Dimethyl acetylenedicarboxylate (DMAD), silver tetrafluoroborate, lithium triethylborohydride, acetyl chloride, thionyl chloride, and tetrafluoroboric acid etherate were purchased from the Aldrich Chemical Co. Concentrated hydrochloric acid was purchased from BDH Chemicals, and sodium borohydride, from Anachemia. Carbon monoxide (CP grade) and dihydrogen were purchased from Matheson, ^{13}CO (99%) from Isotec Inc., and hexafluoro-2-butyne (HFB) from SCM Speciality Chemicals. These and all other reagent grade chemicals were used as received. The compounds *trans*-$[RhCl(CO)(dmpm)]_2$, $[Rh_2Cl_2(CO)_2(\mu\text{-DMAD})(dmpm)_2]$, and $[Rh_2Cl_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ were prepared by the methods described.[17]

Preparation of Compounds. (a) $[Rh_2(CO)_3(dmpm)_2]$ (1). An atmosphere of CO was placed over 100 mg (0.165 mmol) of *trans*-$[RhCl(CO)(dmpm)]_2$ in THF (10 mL) and the resulting orange slurry stirred for 5 min. A 1 M solution of $NaOH/H_2O$ (0.33 mL, 0.33 mmol) was then added to the slurry. Complete reaction occurred within 10 to 15 min and was accompanied by dissolution of all solid. After an additional 20 min of stirring, the dark orange solution was placed under vacuum and all solvents were removed. The residue was extracted into benzene or toluene (10 mL) and filtered under dinitrogen through a pad of Celite to provide a clear orange solution. Once again, the solvent was removed under vacuum. At this point the product was recovered as an orange-brown solid or redissolved in THF and reacted further. The isolated yield varied between 65% and 75% (60–70 mg). This complex proved to be a nonelectrolyte in THF (Λ (10^{-3} M) = 0.67 Ω^{-1} cm^2 mol^{-1}).[18] Anal. Calcd for $C_{13}H_{28}O_3P_4Rh_2$: C, 27.8; H, 5.0. Found: C, 27.9; H, 4.8. Due to the extreme hygroscopic nature of compound 1, fresh samples were required for suitable elemental analyses.

(b) $[Rh(CO)(\mu\text{-CO})(dmpm)]_2$ (2). A solution of compound 1 in THF (5 mL) was prepared in the manner described above using 50 mg (0.083 mmol) of *trans*-$[RhCl(CO)(dmpm)]_2$. Carbon monoxide was bubbled through the solution for 1 min at a rate of ca. 0.5 mL/s, resulting in a slight change in the orange color. Variable-temperature $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR studies in THF-d_8 solution showed the tetracarbonyl complex $[Rh(CO)(\mu\text{-CO})(dmpm)]_2$ (2) and a small amount of complex 1 to be the only species present.

(c) $[Rh_2(CO)_2(\mu\text{-DMAD})(dmpm)_2]$ (3). The compound $[Rh_2Cl_2(CO)_2(\mu\text{-DMAD})(dmpm)_2]$ (50 mg, 0.067 mmol) and $NaBH_4$ (10 mg, 0.27 mmol) were placed in an oven-dried Schlenk tube under a dinitrogen atmosphere. The addition of 98% EtOH (10 mL) produced a red solution which quickly turned to a deep purple color. After the solutions were stirred for 20 min, the solvents were removed under vacuum, the product was extracted into toluene (10 mL), and the solution was filtered under dinitrogen through a pad of Celite. Compound 3 was isolated in 60 to 70% yield (27–32 mg) as a deep purple solid upon removal of the solvent under vacuum. Storage of the solid overnight under an atmosphere of N_2 led to its decomposition to a dull metallic gray. Subsequent manipulation of the product was carried out in THF, THF-d_8, or toluene. Due to its extreme air sensitivity, suitable carbon and hydrogen elemental analysis results were not obtained. This complex proved to be a nonelectrolyte in THF (Λ (10^{-3} M) = 0.25 Ω^{-1} cm^2 mol^{-1}).

(d) $[Rh_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ (4). To $[Rh_2Cl_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ (50 mg, 0.065 mmol) in THF (10 mL) was added 2 molar equiv of $LiBEt_3H$ (0.13 mL of 1 M solution in THF). After the solution was stirred for 20 min, the solvent was removed under vacuum, the residue extracted into toluene (10 mL), and the deep purple solution filtered under dinitrogen through a pad of Celite. The product was isolated in ca. 70% yield (32 mg) as a purple powder upon removal of the toluene under vacuum. Prolonged storage of the solid under a dinitrogen atmosphere led to its decomposition. Subsequent manipulation of the product was carried out in THF or toluene solution. Due to the extreme air-sensitivity of the solid, reliable carbon and hydrogen elemental analysis results could not be obtained.

(e) $[Rh_2(CO)_3(\mu\text{-H})(dmpm)_2][BF_4]$ (5). A solution of $[Rh_2(CO)_3(dmpm)_2]$ (1) in THF (4 mL) was prepared in the manner described above using 50 mg (0.082 mmol) of *trans*-$[RhCl(CO)(dmpm)]_2$. A 1-equiv amount of $HBF_4\cdot OEt_2$ (8.3 μL, based on a 70% yield of 1) was added to the solution. The reaction was immediate, producing a color change from orange to red and some precipitation of product. Compound 5 was not isolated in solid form due to its facile decomposition. Subsequent characterization of the complex was undertaken spectroscopically in THF or THF-d_8 solution.

(f) $[Rh_2(CO)_4(\mu\text{-H})(dmpm)_2][BF_4]$ (6). A solution of $[Rh_2(CO)_3(\mu\text{-H})(dmpm)_2][BF_4]$ (5) in THF (4 mL) was prepared in the manner described above using 50 mg (0.082 mmol) of *trans*-$[RhCl(CO)(dmpm)]_2$. Carbon monoxide was slowly passed through the orange solution at a rate of ca. 0.5 mL/s for 1 min, resulting in a change in color to yellow-orange. Variable-temperature $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR spectroscopy in THF or THF-d_8 showed compound 6 to be the only species present after reaction. Passing dinitrogen through the solution regenerated the tricarbonyl complex 5, but the complex rapidly decomposed upon attempts to precipitate a solid.

(g) $[Rh_2(CO)_2(\mu\text{-DMAD})(\mu\text{-H})(dmpm)_2][BF_4]$ (7). A solution of $[Rh_2(CO)_2(\mu\text{-DMAD})(dmpm)_2]$ (3) in THF (5 mL) was prepared in the manner described above using 50 mg (0.067 mmol) of $[Rh_2Cl_2(CO)_2(\mu\text{-DMAD})(dmpm)_2]$. A 1-equiv amount of $HBF_4\cdot OEt_2$ (6.2 μL, 0.044 mmol based on a 65% yield of 3) was added to the solution. Reaction was immediate, producing a color change from purple to orange with the precipitation of a small amount of orange solid. $^{31}P\{^1H\}$, ^1H NMR, and infrared spectroscopy in THF or THF-d_8 revealed compound 7 to be the major product. Attempts to isolate the product in solid form resulted in its decomposition.

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(h) $[Rh_2(CO)_2(F_3CC{=}C(H)CF_3)(dmpm)_2][BF_4]$ (8). The compound $[Rh_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ (4) was prepared as described above (using 50 mg (0.065 mmol) of $[Rh_2Cl_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$) and dissolved in toluene (10 mL). To this was added 1 equiv of $HBF_4{\cdot}OEt_2$ (6.5 μL, 0.046 mmol based on 70% conversion of the starting material to complex 3). Upon stirring, the reaction mixture quickly changed color from purple to orange. After 15 min the product settled as an orange-brown oil on the side of the flask. The solvents were removed by cannula under positive N_2 pressure, and the oil was dried under vacuum for approximately 15 min. Subsequent manipulation and characterization of the complex was carried out in THF or THF-d_8 solution.

(i) $[Rh_2(CO)_3(F_3CC{=}C(H)CF_3)(\mu\text{-CO})(dmpm)_2][BF_4]$ (9). A THF solution (5 mL) of complex 8 was prepared as described above using $[Rh_2Cl_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ (50 mg, 0.067 mmol). A stream of CO was then passed through the solution at the rate of ca. 0.2 mL/s for 3 min, producing a color change from orange to yellow followed by the precipitation of a yellow solid. Complete precipitation of the compound was effected by the addition of CO-saturated diethyl ether (25 mL) and cooling of the mixture to 0 °C. The solvents were removed by cannula under positive N_2 pressure, and the product was dried under a slow stream of CO. Recrystallization of this solid from CO-saturated THF/diethyl ether yielded 37 mg (67%) of compound 9 as a yellow powder. This complex proved to be a 1:1 electrolyte in acetonitrile (Λ (10^{-3} M) = 164 Ω^{-1} cm^2 mol^{-1}).[18] Anal. Calcd for $BC_{18}F_{10}H_{29}O_4P_4Rh_2$: C, 25.7; H, 3.5. Found: C, 25.5; H, 3.5.

Reaction of Complexes with HCl, $SOCl_2$, and Acetyl Chloride. The appropriate reagent (up to 10 molar equiv) was added via syringe to a solution (THF or toluene) of the complexes, either $[Rh_2(CO)_3(dmpm)_2]$ (1), $[Rh_2(CO)_2(\mu\text{-DMAD})(dmpm)_2]$ (3), or $[Rh_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ (4), prepared as described above and allowed to stir under an atmosphere of dinitrogen for several hours. Subsequent characterization of the products was carried out by $^{31}P\{^1H\}$ NMR on the reaction mixture or by $^{31}P\{^1H\}$ NMR and infrared spectroscopic methods on THF or CH_2Cl_2 solutions (or their deuterated counterparts) of the residue.

The reaction of $[Rh_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ (4) with acetyl chloride entailed the addition of 2 equiv of the reagent (7.5 μL) to a purple toluene solution (8 mL) of 4 (0.052 mmol based on 80% conversion of $[Rh_2Cl_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$; 50 mg, 0.065 mmol). The solution color changed to orange-yellow within 15 min. Stirring was continued for an additional 15 min; the solvent was then removed under vacuum, the residue was washed with hexane (20 mL), and the products were dried under dinitrogen. The spectroscopic characterization of the products was carried out in THF or THF-d_8.

Results and Discussion

(a) Reduction Reactions. The reduction of *trans*-$[RhCl(CO)(dmpm)]_2$ is carried out under an atmosphere of CO using a 1 M solution of $NaOH/H_2O$ to yield $[Rh_2(CO)_3(dmpm)_2]$ (1), which is isolated in reasonable yield (65%) as an air-sensitive orange-brown residue. This species is highly reactive and must be kept out of contact with chlorinated solvents to prevent re-formation of the starting material, *trans*-$[RhCl(CO)(dmpm)]_2$. This chloro species is also obtained upon reaction of 1 with other chloro-containing reagents such as acetyl chloride, although HCl and $SOCl_2$ react with 1 to yield the tetrachloride $[RhCl_2(CO)(dmpm)]_2$. Both chloride-containing products were identified by comparison of their spectra with those of the previously characterized species.[17] Complex 1 can also be prepared from the reaction of sodium naphthalenide or sodium borohydride with *trans*-$[RhCl(CO)(dmpm)]_2$ under a CO atmosphere. However, due to impurities which are also formed in the latter two methods, the preparation from $NaOH/H_2O$ represents the most reliable procedure. The reaction with $NaOH/H_2O$ presumably involves the formation of an intermediate species containing an "–OHCl" moiety in which the coordinated hydroxide group is hydrogen-bonded to the chloride ion, much as that found in the dppm analogues $[Rh_2(CO)_2(\mu\text{-OH{\cdot}Cl})(dppm)_2]$[19] and $[Ir_2(CO)_2(\mu\text{-OH{\cdot}Cl})(dppm)_2]$.[20] The diiridium species was prepared under similar conditions, from the reaction of *trans*-$[IrCl(CO)(dppm)]_2$ with NaOH, and underwent an analogous transformation yielding $[Ir_2(CO)_3(dppm)_2]$ upon reaction with CO.[20] Attempts to characterize the hydroxide-bridged dmpm analogue of the above dppm species met with failure.

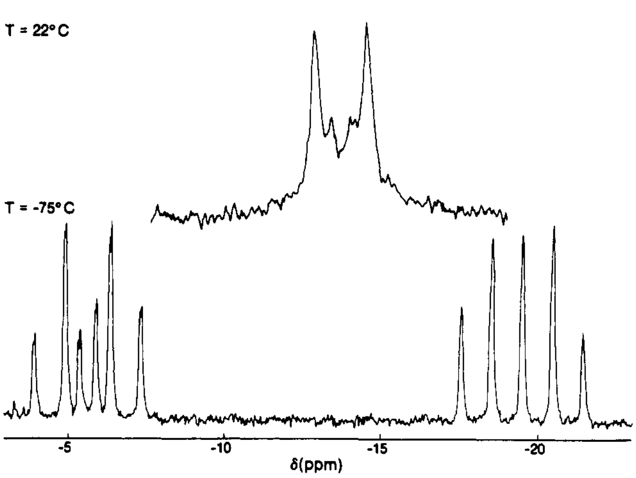
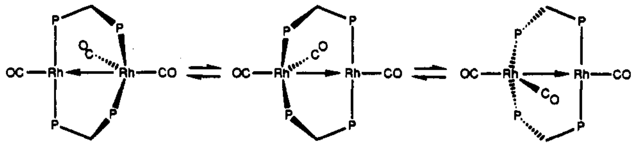


Figure 1. $^{31}P\{^1H\}$ NMR spectra of $[Rh_2(CO)_3(dmpm)_2]$ (1) at 22 and −75 °C.

The spectral data for 1 compare closely to that of the dppm analogues $[MM'(CO)_3(dppm)_2]$ (M, M′ = Rh, Ir; M = Rh, M′ = Co),[6,21-23] and in particular the carbonyl stretches for 1 (1953, 1912, and 1824 cm^{-1}) are very close to those for the above species. On this basis, 1 is assigned the structure, diagram below, that is as observed for the Rh_2, RhIr, and RhCo dppm analogues. In this formulation the metals have been assigned a mixed-valence formulation in which a pseudotetrahedral M′(1−) center forms a dative bond to the M(1+) center, giving the latter a square-planar geometry.

The NMR data for 1 indicate that it, like the dppm analogues, is fluxional at ambient temperature. At 22 °C the $^{31}P\{^1H\}$ NMR spectrum (Figure 1) is somewhat broad but nevertheless is typical of an AA′A″A‴XX′ spin system in which all four phosphorus nuclei are chemically equivalent. At −75 °C the $^{31}P\{^1H\}$ NMR spectrum is typical of an AA′BB′XY spin system, having two chemically inequivalent phosphorus environments. This suggests an equilibrium of the two metal centers via carbonyl transfer from one metal to the other, in which a simultaneous "merry-go-round" migration of the carbonyls around the Rh_2 framework also occurs.



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The observation of only one carbonyl resonance at 22 °C (δ 198.7) indicates that all carbonyls are exchanging at this

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Table I. Infrared Spectroscopic Data for the Compounds[a,b]

no.	compd	ν(CO)	others
1	$[Rh_2(CO)_3(dmpm)_2]$	1960 (m), 1925 (s), 1847 (m); 1953 (vs), 1912 (s), 1824 (m)[c]	
2	$[Rh(CO)(\mu\text{-}CO)(dmpm)]_2$	1962 (m), 1926 (m), 1914 (m, sh), 1847 (m)	
3	$[Rh_2(CO)_2(\mu\text{-}DMAD)(dmpm)_2]$	1956 (s), 1935 (m), 1685 (m)[d]	
4	$[Rh_2(CO)_2(\mu\text{-}HFB)(dmpm)_2]$	1963 (s), 1942 (m)	
5	$[Rh_2(CO)_3(\mu\text{-}H)(dmpm)_2][BF_4]$	1980 (m, sh), 1960 (vs), 1895 (w)	
6	$[Rh_2(CO)_4(\mu\text{-}H)(dmpm)_2][BF_4]$	1985 (s), 1958 (s)	
7	$[Rh_2(CO)_2(\mu\text{-}H)(\mu\text{-}DMAD)(dmpm)_2][BF_4]$	1988 (s), 1974 (m), 1743 (m)[d]	
8	$[Rh_2(CO)_2(F_3CC{=}C(H)CF_3)(dmpm)_2][BF_4]$	1995 (m), 1973 (m), 1964 (m), 1943 (w)	1608 (w)[e]
9	$[Rh_2(CO)_3(F_3CC{=}C(H)CF_3)(\mu\text{-}CO)(dmpm)_2][BF_4]$	2043 (m), 2020 (s), 1993 (m, br), 1792 (w, br); 2044 (vs), 2014 (vs), 1988 (vs), 1765 (vs)[c]	1600 (m)[c,e]

[a] Abbreviations used: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder. All values in cm^{-1}. [b] THF solution unless otherwise noted. [c] Nujol. [d] ν(CO) of CO_2Me. [e] ν(CC).

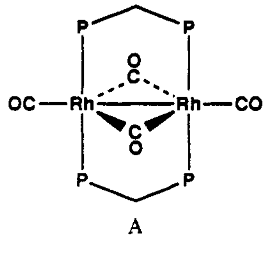
Table II. NMR Spectroscopic Data for the Compounds[a,b]

compd	$\delta(^{31}P\{^1H\})$[c]	$\delta(^{13}C\{^1H\})$[d]	$\delta(^{19}F)$	$\delta(^1H)$		
				P–CH_3	–CH_2–	others
1	−13.55 (137 Hz); −5.71 (dt, 117.3, 78.8 Hz),[e] −19.62 (dt, 155.7, 78.8 Hz)[e]	198.7 (s, br); 184.4 (d, br, $^1J_{Rh-C}$ = 72 Hz),[f] 205.4 (d, br, $^1J_{Rh-C}$ = 69 Hz),[f] 207.7 (m, $^1J_{Rh-C}$ = 76 Hz),[f]		1.54 (s, 24 H), 1.61 (s, 12 H),[e] 1.47 (s, 12 H)[e]	2.75 (m, 4 H), 2.79 (m, 4 H)[e]	
2	14.38 (99.8 Hz)[e]	198.4 (dd, $^1J_{Rh-C}$ = 90.6 Hz, $^2J_{Rh-c}$ = 3 Hz),[f] 245.3 (sp, $^1J_{Rh-C}$ = 28 Hz, $^2J_{P-C}$ ~ 28 Hz)[f]		1.52 (s, 24 H)[e]	3.06 (m, 4 H)[e]	
3	−7.17 (144 Hz)			1.56 (s, 12 H), 1.53 (s, 12 H)	2.68 (m, 4 H)	3.41 (s, 6 H)[g]
4	−9.30 (142 Hz)	197.54 (dm, $^1J_{Rh-C}$ = 58.4 Hz)	−48.8 (s)	1.61 (s, 12 H), 1.50 (s, 12 H)	2.45 (m, 4 H)	
5	6.49 (98 Hz)	194.1 (s); 188.3 (m),[f] 196.4 (tq, $^1J_{Rh-C}$ = 34.1 Hz, $^2J_{P-C}$ = 7.4 Hz)[f]		1.76 (s, 24 H)	2.87 (m 4 H)	−9.33 (m, 1 H, $^1J_{Rh-C}$ = 25.2 Hz, $^2J_{P-H}$ = 11.5 Hz)[h]
6	1.19 (83.2 Hz), 1.93 (81.5 Hz)[i]	199.4 (dm, J = 67 Hz)[f]		1.78 (s, 24 H)[i]	3.32 (m, 4 H)[i]	−7.65 (m, 1 H, $^1J_{Rh-H}$ = 21.9 Hz, $^2J_{P-H}$ = 11.5 Hz)[h,i]
7	−4.2 (104 Hz)			1.68 (s, 12 H), 1.63 (s, 12 H)	3.1 (m, 4 H)	−11.53 (m, 1 H, $^1J_{Rh-H}$ = 22.5 Hz)[h]
8	−0.5 (m), −1.0 (m)[i]	196.14 (d, $^1J_{Rh-C}$ = 50 Hz),[f] 179.03 (d, $^1J_{Rh-C}$ = 74 Hz)[f]	−51.8 (m, 3 F),[i] −59.9 (m, 3 F),[i] −149.5 (s br, 4 F)[i]	1.77 (m, 12 H), 1.67 (m, 12 H)	2.92 (m, 2 H), 2.74 (m, 2 H)	5.85 (m, br, 1 H)[j]
9	4.66 (m, unresolved), 2.60 (dt, 87.7, 43 Hz); 6.12 (dt, 76, 40 Hz),[i] 3.50 (dt, 84, 40 Hz)[i]	234.6 (m, five-line m upon $\{^{31}P\}$),[f] 199.0 (m),[f] 198.1 (m),[f] 190.8 (ddt, $^1J_{Rh-C}$ = 69.1 Hz, J_{P-C} = 14 Hz, J = 12 Hz)[f]	−51.48 (qr, 3 F, $^5J_{F-F}$ = 12.2 Hz),[i] −59.36 (dqr, 3 F, $^5J_{F-F}$ = 12.2 Hz, $^3J_{F-H}$ = 10 Hz),[i] 149.5 (s, br, 4 F)[i]	1.88 (t, 6 H),[i] 1.82 (t, 6 H, $^2J_{P-H}$ = 3.0 Hz),[i] 1.67 (t, 6 H),[i] 1.38 (t, 6 H, $^2J_{H-P}$ = 3.8 Hz)[i]	3.2 (m, 2 H),[i] 2.9 (m, 2 H)[i]	6.10 (qr, 1 H, $^3J_{F-H}$ = 10 Hz)[i,j]

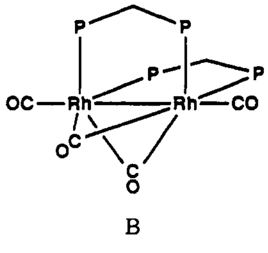
[a] Ambient temperature in THF-d_8 unless otherwise noted. [b] Abbreviations used: s, singlet; d, doublet; t, triplet; qr, quartet; q, quintet; sp, septet; m, multiplet; dd, doublet of doublets; dt, doublet of triplets; dqr, doublet of quartets; dm, doublet of multiplets; ddt, doublet of doublet of triplets; tq, triplet of quintets; br, broad. [c] Vs 85% H_3PO_4; numbers in parentheses represent the separation in hertz between the major peaks in the second-order spectrum of the complex. [d] ^{13}CO-enriched samples. [e] −75 °C. [f] −85 °C. [g] CO_2Me. [h] M–H. [i] −40 °C. [j] $C(H)CF_3$.

temperature. At −75 °C the three equal-intensity carbonyl resonances expected for the static structure are observed at δ 184.4 ($^1J_{Rh-C}$ = 72 Hz), δ 205.4 ($^1J_{Rh-C}$ = 69 Hz), and δ 207.7 ($^1J_{Rh-C}$ = 76 Hz).

In solution, under excess CO, compound 1 is found to be in equilibrium with a small amount of the labile tetracarbonyl species $[Rh(CO)(\mu\text{-}CO)(dmpm)]_2$ (2). Replacement of the CO atmosphere with dinitrogen regenerates the starting material 1. The ease with which the fourth carbonyl ligand is removed from 2 is reminiscent of the behavior observed for the *dppm* complex, $[Ir(CO)_2(dppm)]_2$, which also loses CO when placed under an atmosphere of N_2.[20] In contrast to compound 2, however, removal of CO from the diiridium *dmpm* analogue, $[Ir(CO)_2(dmpm)]_2$, is reported to be more difficult, requiring heating in the presence of Me_3NO.[16] Due to the equilibrium between compounds 1 and 2 under excess CO, the room-temperature spectra of the latter are somewhat deceiving and the presence of the new species 2 is hard to discern. Only slight changes occur in the solution-infrared spectrum with the appearance of a new shoulder at 1914 cm^{-1}, in addition to the original three bands of 1 (see Table I). In the $^{31}P\{^1H\}$ NMR spectrum, a broad, unresolved resonance, appearing to be that of $[Rh_2(CO)_3(dmpm)_2]$ (1), appears at δ −15.5. At −75 °C, however, one major resonance appears in the $^{31}P\{^1H\}$ NMR spectrum at δ 14.4 (assigned to compound 2) having an AA′A″A‴XX′ pattern typical of a symmetrical "Rh_2(diphosphine)$_2$" complex. A much smaller amount of compound 1 is also present, indicating that the equilibrium between 1 and 2 has been shifted toward a higher concentration of 2 under these conditions. The change is also evident in the carbonyl region of the $^{13}C\{^1H\}$ NMR spectrum (−85 °C) in which resonances due to 1 are of very low intensity. New resonances appearing at δ 245.3 and 198.4 in a 1:1 ratio have been assigned to compound 2. Their chemical shifts indicate the presence of both bridging and terminal CO ligands, respectively. These data are consistent with either a trans–trans diphosphine geometry (A) or a cis–cis ge-



A



B

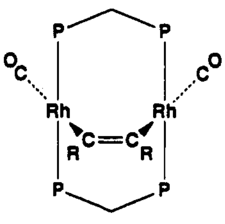
ometry (B). We favor geometry B on the basis of the interpretation of the low-temperature $^{13}C\{^{1}H\}$ and $^{13}C\{^{31}P\}\{^{1}H\}$ NMR data and note that this geometry was observed for the dicobalt analogues of 2, $[Co(CO)(\mu\text{-}CO)(dppm)]_2$[24] and $[Co(CO)(\mu\text{-}CO)(dmpm)]_2$,[24b] and the isoelectronic diiridium complexes $[Ir(CNR)(\mu\text{-}CNR)(dmpm)]_2$ and $[Ir(CNR)(\mu\text{-}CN(BH_3)R)(dmpm)]_2$ (R = 2,6-$Me_2C_6H_3$).[15] In the $^{13}C\{^{1}H\}$ NMR spectrum of 2, the signal at δ 245.3 is assigned to the bridged carbonyl ligands and appears as a multiplet containing five lines in the proton-decoupled spectrum. This pattern is rationalized in terms of an overlapped triplet of triplets due to coupling with the two Rh nuclei and with the two phosphorus nuclei which are almost trans to these bridging carbonyls ($^{1}J_{Rh-C} \cong {}^{2}J_{P-C} \cong 28$ Hz). The lack of coupling to the cis phosphorus nuclei is not surprising, typically being less than 17 Hz in related compounds and frequently being too weak to be resolved.[6,17,25] The coupling of the bridging carbonyls to both rhodium nuclei is clearly seen when the phosphorus nuclei are decoupled, giving rise to a triplet pattern. The carbon atoms of the terminal carbonyl ligands are strongly coupled to a single rhodium atom and appear as a doublet at δ 198.4 ($^{1}J_{Rh-C} = 90.6$ Hz). Two-bond P–C coupling and the C–C coupling between the carbonyls are apparently too weak to be resolved. In the phosphorus-decoupled spectrum the signal, now a doublet of doublets, is much sharper, and we are able to observe the weaker two-bond coupling of carbon to the second rhodium as well ($^{2}J_{Rh-C} = 3$ Hz). This two-bond interaction is usually too small to be observed except in cases where the carbonyl ligand is colinear with the metal–metal bond.[17,26–28] The structure B proposed for 2 is in contrast to that observed for the diiridium analogue $[Ir_2(CO)_4(dmpm)_2]$,[29] which retains the mixed-valence formulation like the tricarbonyl species of both dmpm and dppm, having a cis arrangement of diphosphine ligands at one metal and a trans arrangement at the other. This unsymmetrical geometry was also observed for the closely related dicobalt complexes $[Co_2(CO)_4((CH_2O)_2PN(Et)P(OCH_2)_2)_2]$[30] and $[Co_2(CO)_4((CH_3O)_2PN(CH_3)P(OCH_3)_2)_2]$,[31] suggesting that they too be formulated as mixed-valent Co(1+)Co(1−) species. It is not clear why these three species should favor the mixed-valence formulation while our Rh_2 species and the previously noted Co_2 and diiridium isocyanide systems appear better described as M(0) complexes.

Due to the equilibrium between compounds 1 and 2 and to the predominance of 1 in solution at room temperature, we have been unable to determine whether the bridged CO ligands of compound 2 remain so at higher temperature or whether, as seen for the cobalt analogues, they become terminally coordinated.[24b]

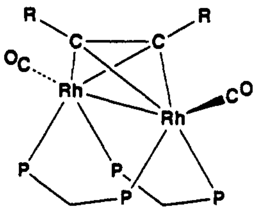
Low-valent species involving bridging alkyne ligands can also be prepared. The $NaBH_4$/EtOH reduction of $[Rh_2Cl_2(CO)_2(\mu\text{-}DMAD)(dmpm)_2]$ and the $LiBEt_3H$/THF reduction of $[Rh_2Cl_2(CO)_2(\mu\text{-}HFB)(dmpm)_2]$ result in the removal of the chloride ligands and formation of symmetrical alkyne-bridged complexes with the formula $[Rh_2(CO)_2(\mu\text{-}alkyne)(dmpm)_2]$ (alkyne = DMAD (3), HFB (4)). The same species may be obtained from the addition of 1 equiv of DMAD or HFB to $[Rh_2(CO)_3(dmpm)_2]$ (1); however, this method requires strict control of the stoichiometry in order to avoid reaction of the products with a second equivalent of alkyne, as discussed in the following paper.[32] The two new alkyne species 3 and 4 are stable in THF under dinitrogen for extended periods of time but are readily reoxidized to their respective starting materials in the presence of chlorinated solvents or hydrochloric acid. In addition, attempts to recrystallize either compound from THF/pentane or THF/hexane resulted in their decomposition. This behavior, in addition to their extreme air-sensitivity, has limited their characterization to solution spectroscopy.

Infrared data reveal the presence of two terminal carbonyl bands for each of 3 and 4 in the range 1963–1935 cm^{-1} (Table I) and an additional band for 3 at 1685 cm^{-1} due to the carboxylate group of DMAD. The symmetrical nature of 3 and 4 is evident from the appearance of a second-order resonance with an AA′A″A‴XX′ pattern in the respective $^{31}P\{^{1}H\}$ NMR spectra. Complex 4 also exhibits a singlet in the ^{19}F NMR spectrum due to the six chemically equivalent fluorine atoms of the HFB ligand.

Unfortunately, the actual configuration of the alkyne ligands in 3 and 4 could not be determined from the available spectroscopic data. The two possible geometric forms are as illustrated:



C



D

Structure C contains a formally dianionic, four-electron-donor alkyne coordinated parallel to the metal–metal vector, implying two Rh(1+) centers. In structure D, in which the metal centers are considered to be Rh(0), the alkyne functions as a neutral, four-electron donor and is coordinated perpendicular to the metal–metal vector. Although the vast majority of "$Rh_2(diphosphine)_2$" complexes have the alkyne coordinated parallel to the metals, as in C,[17,25b,33] the closely related complexes $[Rh_2(CO)_2(\mu\text{-}PhC_2Ph)(dppm)_2]$[34] and $[Ir_2(CO)_2(\mu\text{-}DMAD)(dppm)_2]$[35] have been shown to have the alkynes bound perpendicular to the metals, as in D. A structure C for compounds 3 and 4 would make them analogous to the isoelectronic Pd and Pt complexes $[MM'Cl_2(\mu\text{-}RC{\equiv}CR)(dppm)_2]$ (M, M′ = Pd, Pt; R = CF_3, CO_2Me)[36–38] and would mean that no alkyne

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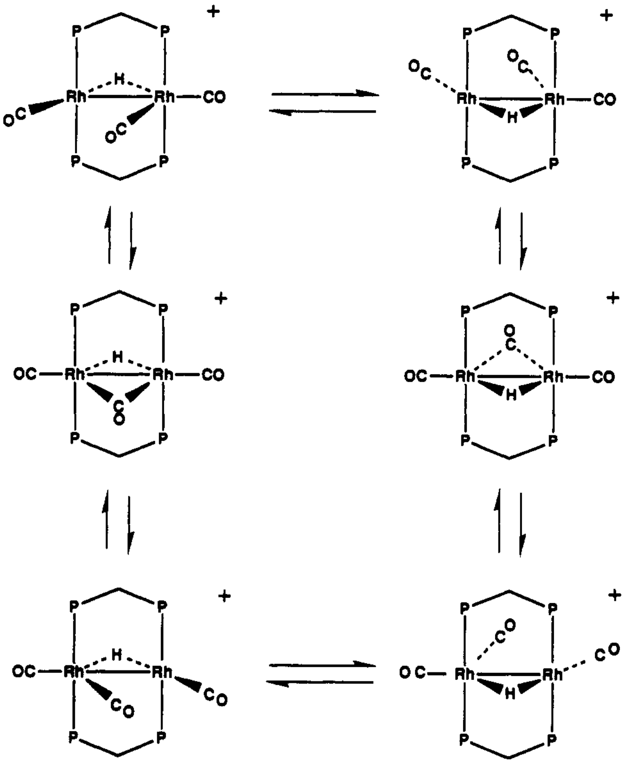
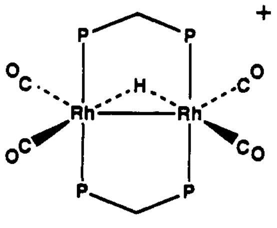
reorientation had occurred upon reduction of the precursors, since both reactants and products would have the alkynes bound parallel to the two metals. Clearly geometry D requires alkyne reorientation. In the above dppm complexes, alkyne reorientation from the parallel to perpendicular binding modes had been shown to be quite slow,[34,35] suggesting that if it occurred in the formation of 3 and 4, intermediates having structure C might be observed. Our failure to detect intermediates, even at −80 °C, suggests that either no reorientation has occurred or it is too facile to allow detection. The small bulk of the dmpm ligands compared to dppm makes a facile transformation feasible. In spite of our failure to observe intermediates in the proposed transformation, structure D is favored since the ^1H and $^{31}P\{^1H\}$ NMR spectra for 3 and 4 closely resemble those of $[Rh_2(CO)_2(\mu\text{-}PhC_2Ph)(dppm)_2]$, for which the perpendicular alkyne binding mode was established.[34] We had hoped to be able to establish the geometries of 3 and 4 on the basis of the IR spectra, since it had been shown that the (trans, trans) or (cis, cis) "$M_2(dmpm)_2$" geometries could be distinguished on the basis of an examination of the P–C stretching region between 910 and 970 cm^{-1}.[15b] In our compounds the appropriate bands were not observed in this region. Carbon-13 NMR spectroscopy has also been used to differentiate the two alkyne binding modes;[39–43] however using the alkyne having natural-abundance ^{13}C, we were unable to identify the alkyne resonances even after overnight data acquisition.

(b) Protonation Reactions. The compound $[Rh_2(CO)_3(dmpm)_2]$ (1) adds 1 equiv of $HBF_4{\cdot}OEt_2$ to yield the hydride-bridged species $[Rh_2(CO)_3(\mu\text{-}H)(dmpm)_2][BF_4]$ (5), which displays three carbonyl stretches in the IR spectrum at 1980, 1960, and 1895 cm^{-1} (THF). The $^{31}P\{^1H\}$ and ^1H NMR spectra, both at ambient temperature and −85 °C, are consistent with a symmetrical hydride-bridged species. With phosphorus decoupling, the triplet of quintets in the ^1H NMR spectrum for the hydride ligand transforms to a triplet, displaying coupling to both Rh nuclei of 25.2 Hz. This resonance changes very little over the temperature range studied suggesting that the hydride remains bridging. However at ambient temperature the $^{13}C\{^1H\}$ NMR spectrum displays only a single carbonyl resonance at δ 194.1, indicating equilibration of the three carbonyl groups. At −85 °C two carbonyl resonances appear, at δ 196.4 (triplet of quintets, $^1J_{Rh-C}$ = 34.1 Hz, $^2J_{P-C}$ = 7.4 Hz) and δ 188.3 (unresolved multiplet), in a 1:2 intensity ratio. A fluxional process is proposed for 5, as shown in Scheme I, in which tunneling of the hydride between the metals interchanges two carbonyls on one rhodium while exchange of carbonyls between metals occurs via a carbonyl-bridged species. The hydride tunneling proposed has been observed in several related systems[6,21,22,44] and requires a species having no bridging carbonyl group. Such an intermediate, in which all carbonyls are terminal and inequivalent, was not observed at low temperature; instead the carbonyl-bridged species is the only observed species.

Scheme I



Complex 5 adds 1 equiv of CO to yield the tetracarbonyl species $[Rh_2(CO)_4(\mu\text{-}H)(dmpm)_2][BF_4]$ (6). On the basis of spectroscopic evidence we propose the geometry for compound 6, which is analogous to that proposed for the related diiridium species $[Ir_2(CO)_4(\mu\text{-}H)(dppm)_2][BF_4]$.[3] The preparation of compound 6 follows the trend of "$Rh_2(dmpm)_2$" complexes in forming products containing a higher number of CO ligands than their "$Rh_2(dppm)_2$" counterparts.[17] Like these other "$Rh_2(dmpm)_2$" complexes, compound 6 is quite labile and readily loses CO under N_2 to provide the tricarbonyl starting material 5. Consistent with the proposed geometry, only terminal CO stretches are revealed in the solution infrared spectrum. The $^{31}P\{^1H\}$ NMR spectrum resembles the typical second-order AA′A″A‴XX′ pattern of a symmetrical complex both at ambient and low temperature, and the ^1H NMR spectrum (−40 °C) displays a complex nine-line pattern (δ −7.65) for the hydride ligand, which is transformed into a triplet with broad-band phosphorus-decoupling. The appearance of only one resonance each for the methylene (δ 3.32) and methyl (δ 1.78) protons in the ^1H NMR and a single carbonyl resonance (δ 199.4, −40 °C) in the $^{13}C\{^1H\}$ NMR points to a fluxional process whereby the bridging hydride ligand is again passing between the metals from one face of the complex to the other.



6

Protonation of the alkyne-bridged complex 3 also occurs yielding the unstable species $[Rh_2(CO)_2(\mu\text{-}DMAD)(\mu\text{-}H)(dmpm)_2][BF_4]$ (7) as the major product. Spectroscopic investigations of the reaction mixture indicate that compound 7 has the structure shown in which protonation at

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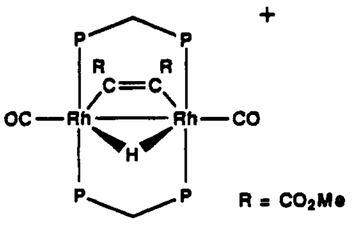
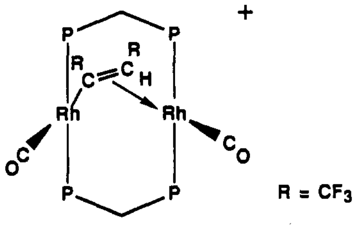


7

the metals has again occurred. The complex is symmetrical about the two rhodium atoms as evidenced by the AA'A''A'''XX' resonance observed in the $^{31}P\{^1H\}$ NMR spectrum and the IR spectrum which shows only terminal carbonyls and the carboxylate CO group of DMAD. A hydride resonance consisting of nine lines appears in the ^1H NMR spectrum at δ -11.53 ppm, and again phosphorus-decoupling transforms this signal into a triplet ($^1J_{Rh-H}$ = 22.5 Hz). Like the other hydride complexes (**5** and **6**) reported herein, compound **7** was found to decompose in solution with time or upon addition of hexane or diethyl ether and was not successfully isolated as a solid.

Protonation of $[Rh_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ (**4**) with 1 equiv of $HBF_4{\cdot}OEt_2$ also occurs, yielding the unstable species $[Rh_2(CO)_2(F_3CC{=}C(H)CF_3)(dmpm)_2][BF_4]$ (**8**).



8

This species differs from **7** in that protonation appears to have occurred at the alkyne, forming a vinylic ligand. The lack of resolution in all NMR spectra of complex **8** suggests that the molecule is fluxional. At room temperature the vinylic proton is apparent in the ^1H NMR spectrum as a broad resonance at δ 5.85, and the fluorine atoms of the two CF_3 groups appear at δ -51.8 and -59.9 in the ^{19}F NMR spectrum. Neither spectra provide H–F or F–F coupling data; however, we know from the subsequent reaction of compound **8** with CO and characterization of the tetracarbonyl product $[Rh_2(CO)_3(F_3CC{=}C(H)CF_3)(\mu\text{-CO})(dmpm)_2][BF_4]$ (**9**), discussed below, that the two CF_3 groups occupy cis positions across the double bond of the vinylic moiety. Studies of the carbonyl region of the $^{13}C\{^1H\}$ NMR spectrum reveal that both carbonyl ligands of **8** remain terminally bound (δ 196.14, $^1J_{Rh-C}$ = 50 Hz; δ 179.03, $^1J_{Rh-C}$ = 74 Hz at -85 °C). The proposed geometry of **8** requires a σ, π interaction of the vinylic ligand as shown, to maintain a 16-electron configuration at the metal centers. This proposed interaction is not unlike that which is observed in the acetylide-bridged species $[Rh_2(CO)_2(\mu\text{-}C_2\text{-}t\text{-Bu})(dppm)_2][ClO_4]$[45] and that which is reported for $[Pt_2(F_3CC{=}C(H)CF_3)(cod)_2][BF_4]$[46] and suggested for $[(\eta^5\text{-}C_5H_5)_2Rh_2(F_3CC{=}C(H)CF_3)(CO)_2][BF_4]$.[47]

As in most examples of protic-acid addition to HFB complexes, it is not clear whether protonation occurs initially at a metal center or directly at the alkyne ligand.[47-50] On the basis of the analogy with compound **7**, it is proposed that protonation of $[Rh_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ (**4**) yields a metal–hydride species which subsequently rearranges to the vinylic product **8**. A similar reaction sequence involving the addition of $HBF_4{\cdot}OEt_2$ to the diplatinum complexes $[Pt_2(\mu\text{-alkyne})(cod)_2]$ has been reported by Stone and co-workers;[46] it was found that when the alkyne was HFB, only a cationic vinyl-bridged complex was detected, but when the alkyne was $C_2(4\text{-MeOC}_6F_4)_2$, an initial hydride-bridged, alkyne-bridged species, similar to complex **7**, was formed which subsequently rearranged to a vinyl compound. Direct protonation of the alkyne in **4** also cannot be ruled out since $M_{\delta+}$–$C_{\delta-}$ bond polarization,[51] brought about by electron-withdrawing groups on the alkyne,[48,49] may make the alkyne carbon atom the most likely site of electrophilic H^+ attack. The differences in electron-withdrawing ability between HFB and DMAD[52] may explain why the reactions of complexes **3** and **4** with acid produce different results.

Exposure of compound **8** to CO in THF solution affords the tetracarbonyl species $[Rh_2(CO)_3(F_3CC{=}C(H)CF_3)(\mu\text{-CO})(dmpm)_2][BF_4]$ (**9**) as a bright yellow precipitate. The product is stable both in solution and solid form only when under an atmosphere of CO. No evidence of an intermediate tricarbonyl species was ever observed. The $^{31}P\{^1H\}$ NMR spectrum of complex **9** at room temperature is partially unresolved, but at -40 °C a pattern consisting of two sets of multiplets (δ 6.12, 3.50), typical of an AA'BB'XY spin system, is observed. In the ^1H NMR spectrum the vinylic proton resonance now appears as a quartet (δ 6.10 ppm, $^3J_{H-F}$ = 10 Hz) due to coupling with the three fluorine atoms of the geminal CF_3 group.[53-59] At -40 °C the two CF_3 resonances appear in the ^{19}F NMR spectrum at δ -51.48 (quartet, $^5J_{F-F}$ = 12.2 Hz) and δ -59.36 (a doublet of quartets, $^5J_{F-F}$ = 12.2 Hz, $^3J_{F-H}$ = 10 Hz). The second resonance has a more complex splitting pattern due to F–H coupling and therefore is assigned to the CF_3 group located geminal to the proton. Upon proton decoupling, this resonance becomes a quartet as only the F–F interaction remains. The magnitude of $^5J_{F-F}$ indicates a relative cis disposition of the CF_3 groups,[53-59] consistent with all other reported protonations of metal-coordinated HFB.[46-49,51]

Evidence for the four carbonyl ligands of compound **9** is found in the infrared spectrum, which contains three terminal bands at 2044, 2014, and 1988 cm^{-1} and a single bridging carbonyl band at 1765 cm^{-1}, and in the carbonyl region of the $^{13}C\{^1H\}$ NMR spectrum with resonances appearing at δ 234.6, 199.0, 198.1, and 190.8 ppm (-40 °C in THF-d_8). We had hoped to use $^{13}C\{^1H\}$ NMR data to assign the configuration of the CO ligands in the molecule, but due to numerous spin–spin coupling sources all resonances in this region appear as complex multiplets. The

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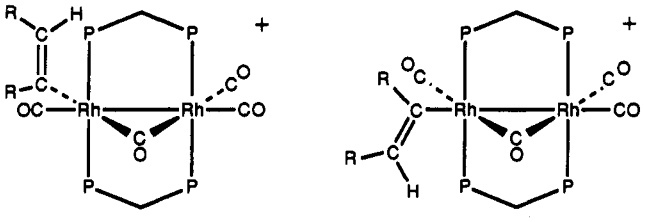
coupling interactions have therefore been difficult to interpret, and we were unable to distinguish between two isomers, E and F, in which the bridged carbonyl ligand is



E

F

9

trans or cis to the vinylic moiety, respectively. The highest-field ^{13}CO resonance (δ 190.8) is the least complicated (appearing as a doublet of quartets, it is actually an overlapped doublet ($^1J_{Rh-C}$ = 69.1 Hz) of doublet (12 Hz) of triplets ($^2J_{P-C} \sim$ 14 Hz)) and can be assigned to the lone terminal carbonyl adjacent to the vinyl group. Upon broad-band phosphorus-decoupling, the pattern is simplified into a doublet of doublets. It is not clear from the decoupling experiments whether the coupling of 12 Hz arises from a two-bond C–C interaction with a trans-oriented, bridged-CO ligand as in F or from a two-bond interaction with the second rhodium via the metal–metal bond as in E. The complex lowfield resonance (δ 234.6) is assigned to the carbon atom of the bridging carbonyl ligand. It is simplified into a five-line pattern resembling an overlapped doublet of doublet of doublets (in the phosphorus-decoupled spectrum), but no coupling information was obtained; in particular it was not possible to confirm or reject the earlier proposal of 12 Hz coupling between trans carbonyl ligands. Although the remaining two resonances (δ 199.0, 198.1) have been assigned to the carbon atoms of the terminally coordinated CO ligands, the complex nature of the signals has made individual assignments impossible.

Attempts to oxidatively add organic fragments (acetyl chloride) to the reduced species $[Rh_2(CO)_3(dmpm)_2]$ (**1**), $[Rh_2(CO)_2(\mu\text{-DMAD})(dmpm)_2]$ (**3**), or $[Rh_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ (**4**) has, for the most part, resulted in the re-formation of the chloride precursors.

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Registry No. 1, 141439-06-7; 2, 141613-93-6; 3, 141613-94-7; 4, 141613-95-8; 5, 141585-01-5; 6, 141585-03-7; 7, 141585-05-9; 8, 141585-07-1; 9, 141613-97-0; *trans*-$[RhCl(CO)(dmpm)]_2$, 114445-93-1; $[Rh_2Cl_2(CO)_2(\mu\text{-DMAD})(dmpm)_2]$, 114445-99-7; $[Rh_2Cl_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$, 114446-00-3.

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Novel Binuclear Bis(dimethylphosphino)methane-Bridged Complexes of Rhodium Containing Two and Three Alkyne Molecules

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The bis(alkyne) complexes $[Rh_2(CO)_2(\mu\text{-RC}{\equiv}\text{CR})(\mu\text{-R}'\text{C}{\equiv}\text{CR}')(dmpm)_2]$ (R = R′ = CO_2Me (**1**); R = CO_2Me, R′ = CF_3 9.833 dmpm = $Me_2PCH_2PMe_2$) are prepared by addition of dimethyl acetylenedicarboxylate to $[Rh_2(CO)_2(\mu\text{-RC}{\equiv}\text{CR})(dmpm)_2]$ (R = CO_2Me, CF_3). Addition of excess hexafluorobutyne (HFB) to $[Rh_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ yields $[Rh_2(HFB)_2(\mu\text{-CO})(\mu\text{-HFB})(dmpm)_2]$ (**4**), in which one alkyne is η^2-bound to each rhodium while the third is bridging. Reaction of **4** with carbon monoxide yields $[Rh_2(CO)_2(\eta^2\text{-HFB})(\mu\text{-HFB})(dmpm)_2]$ (**5**), containing one terminal and one bridging HFB group, and this species rearranges to $[Rh_2(CO)_2(\mu\text{-HFB})_2(dmpm)_2]$ (**3**), analogous to species **1** and **2**. All bis(alkyne) complexes **1**–**3** are unreactive and do not react with CO or with additional alkyne. The structures of **2** and **3** have been determined. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with a = 9.7825 (8) Å, b = 9.833 (1) Å, c = 9.3791 (9) Å, α = 92.390 (8)°, β = 99.893 (7)°, γ = 118.180 (8)°, V = 775.5 Å^3, and Z = 1, while **3** crystallizes in the monoclinic space group $P2_1/n$ with a = 9.474 (1) Å, b = 15.813 (2) Å, c = 9.917 (1) Å, β = 95.34 (1)°, V = 1479.3 Å^3, and Z = 2. For compound **2** the disorder present affects only the substituents on the alkynes (CO_2Me, CF_3); all other atoms are well behaved. In spite of this disorder in **2** all atoms refined well, converging to R = 0.030 and R_w = 0.049 based on 2486 observations. Compound **3** refined to R = 0.040 and R_w = 0.043 based on 1588 observations. Both compounds have a trans arrangement of diphosphines with the alkynes bound on opposite faces of the complex as cis–dimetalated olefins. The Rh–Rh separations of 2.6989 (4) Å (**2**) and 2.696 (1) Å (**3**) are quite short; however, all parameters associated with the alkyne ligands are as expected for this binding mode.

Introduction

Interest in metal–alkyne complexes stems from the desire to modify the reactivity of alkynes by complexation with a metal center thereby providing new synthetic routes to organic products. A variety of alkyne transformations on mononuclear metal complexes is possible, including alkyne dimerization, trimerization, higher order polymerization, and oxidative coupling.[1-6] Alkyne transformations on two adjacent metal centers are also of great in-

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