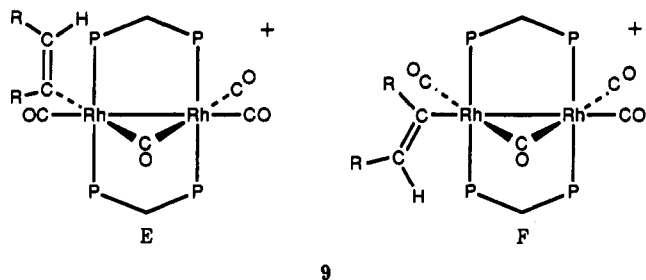


coupling interactions have therefore been difficult to interpret, and we were unable to distinguish between two isomers, E and F, in which the bridged carbonyl ligand is



trans or cis to the vinylic moiety, respectively. The highest-field ^{13}C resonance (δ 190.8) is the least complicated (appearing as a doublet of quartets, it is actually an overlapped doublet ($^1J_{\text{Rh-C}} = 69.1$ Hz) of doublet (12 Hz) of triplets ($^2J_{\text{P-C}} \sim 14$ 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 $[\text{Rh}_2(\text{CO})_3(\text{dmpm})_2]$ (1), $[\text{Rh}_2(\text{CO})_2(\mu\text{-DMAD})(\text{dmpm})_2]$ (3), or $[\text{Rh}_2(\text{CO})_2(\mu\text{-HFB})(\text{dmpm})_2]$ (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*- $[\text{RhCl}(\text{CO})(\text{dmpm})_2]$, 114445-93-1; $[\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-DMAD})(\text{dmpm})_2]$, 114445-99-7; $[\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-HFB})(\text{dmpm})_2]$, 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 $[\text{Rh}_2(\text{CO})_2(\mu\text{-RC}\equiv\text{CR})(\mu\text{-R}'\text{C}\equiv\text{CR}')(\text{dmpm})_2]$ ($\text{R} = \text{R}' = \text{CO}_2\text{Me}$ (1); $\text{R} = \text{CO}_2\text{Me}$, $\text{R}' = \text{CF}_3$ 9.833 $\text{dmpm} = \text{Me}_2\text{PCH}_2\text{PMe}_2$) are prepared by addition of dimethyl acetylenedicarboxylate to $[\text{Rh}_2(\text{CO})_2(\mu\text{-RC}\equiv\text{CR})(\text{dmpm})_2]$ ($\text{R} = \text{CO}_2\text{Me}$, CF_3). Addition of excess hexafluorobutyne (HFB) to $[\text{Rh}_2(\text{CO})_2(\mu\text{-HFB})(\text{dmpm})_2]$ yields $[\text{Rh}_2(\text{HFB})_2(\mu\text{-CO})(\mu\text{-HFB})(\text{dmpm})_2]$ (4), in which one alkyne is η^2 -bound to each rhodium while the third is bridging. Reaction of 4 with carbon monoxide yields $[\text{Rh}_2(\text{CO})_2(\eta^2\text{-HFB})(\mu\text{-HFB})(\text{dmpm})_2]$ (5), containing one terminal and one bridging HFB group, and this species rearranges to $[\text{Rh}_2(\text{CO})_2(\mu\text{-HFB})_2(\text{dmpm})_2]$ (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, $\alpha = 92.390$ (8)°, $\beta = 99.893$ (7)°, $\gamma = 118.180$ (8)°, $V = 775.5$ Å³, 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, $\beta = 95.34$ (1)°, $V = 1479.3$ Å³, 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 polym-

erization, and oxidative coupling.¹⁻⁶ Alkyne transformations on two adjacent metal centers are also of great in-

(1) Wielstra, Y.; Gambarotta, S.; Meetsma, A.; de Boer, J. L.; Chiang, M. Y. *Organometallics* 1989, 8, 2696 and references therein.

(2) Bouayad, A.; Dartiguenave, M.; Menu, M.-J.; Dartiguenave, Y.; Belanger-Gariepy, F.; Beauchamp, A. L. *Organometallics* 1989, 8, 629 and references therein.

Table I. Infrared Spectroscopic Data for the Compounds^a

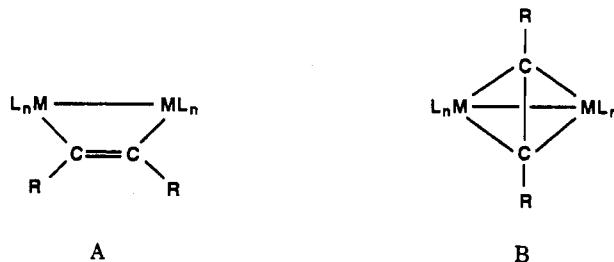
no.	compd	Nujol, cm ⁻¹		CH ₂ Cl ₂ solution, cm ⁻¹	
		$\nu(\text{CO})$	$\nu(\text{CC})$	$\nu(\text{CO})$	$\nu(\text{CC})$
1	[Rh ₂ (CO) ₂ (μ -DMAD) ₂ (dmpm) ₂]	1962 (s), 1670 (s), ^b 1649 (s) ^b	1526 (m)	1964 (s), 1670 (m) ^b	1525 (w)
2	[Rh ₂ (CO) ₂ (μ -DMAD)(μ -HFB)- (dmpm) ₂]	1967 (s), 1672 (m), ^b 1658 (m) ^b	1552 (w), 1528 (w)	1972 (s), 1675 (m) ^b	1560 (w), 1535 (w)
3	[Rh ₂ (CO) ₂ (μ -HFB) ₂ (dmpm) ₂]	1971 (s)	1559 (m)	1981 (w), 1978 (s); ^c 1933 (s) ^{c,d}	1559 (w), 1560 (w) ^c
4	[Rh ₂ (η^2 -HFB) ₂ (μ -CO)(μ -HFB)- (dmpm) ₂]	1867 (s)	1816 (m), 1773 (w), 1577 (m)	1879 (vs); ^c 1840 (s) ^{c,d}	1816 (s); ^c 1773 (m), ^c 1583 (m) ^c
5	[Rh ₂ (CO) ₂ (η^2 -HFB)(μ -HFB)(dmpm) ₂] ^e			2007 (s); ^c 2033 (s) ^c	1776 (w); ^c 1590 (w) ^c

^a Abbreviations used are as follows: vs, very strong; s, strong; m, medium; w, weak. ^b $\nu(\text{CO})$ of CO₂Me. ^c THF solution. ^d $\nu(^{13}\text{C})$. ^e Compound 5 was only observed in solution.

interest in light of suggestions made concerning the involvement of two metal atoms in catalytic alkyne-coupling reactions.⁷ Binuclear complexes have already proven useful in the formation of C-C bonds via the interaction of alkyne molecules with organic fragments, including other alkynes and alkylidenes.⁷⁻¹¹ It is anticipated that the further study of these systems may lead to forms of alkyne reactivity that have not been realized in mononuclear systems.

The reaction of alkyne molecules with binuclear transition-metal complexes which are bridged by diphosphine or related ligands (dppm,^{12,13a-d,14-17} dpam (bis(diphenylarsino)methane),^{13a} Ph₂Ppy (2-pyridyldiphenylphosphine),^{13e} ETM (bis(ethylthio)methane)¹⁰) usually results in the incorporation of the alkyne molecule in a bridged fashion between the two metals. Terminal coordination on the other hand is much less common.¹⁸ In the bridging mode the alkyne can bind in one of two ways,

either parallel to the metal-metal axis as a cis-dimetalated olefin (A) or perpendicular to the metal-metal axis as a



tetrahedral form (B).¹⁹ The former mode predominates in diphosphine-bridged complexes,^{12a-f,13a-d,14,15,17} although examples of type B have also been reported^{12g,h,16} and interconversion of A to B is known to take place.^{12g,h,16a} In general though, once coordinated in the bridging fashion, the alkyne unit in these complexes shows little tendency for bridge rearrangement or subsequent reaction with other ligands on the complex.^{12f,20} Exceptions to this trend include the complexes [Pd₂X₂(μ -DMAD)(dppm)₂] (X = Cl, I),¹⁵ both of which appear to behave as catalyst precursors for the cyclotrimerization of alkynes. On the basis of crossover experiments, intermediates in which alkyne molecules have been combined on the metal are implicated. However, apart from the cyclotrimerization product, only monoalkyne species have been recovered from these reactions.

Our interest in binuclear complexes containing more than one alkyne molecule led us to investigate chemistry involving bridging bis(dimethylphosphino)methane ligands (dmpm). This diphosphine is smaller than the more widely studied phenyl-substituted analogue bis(diphenylphosphino)methane (dppm) so the coordination of more than one alkyne molecule to the metals should be less sterically inhibited. In addition, the greater basicity of dmpm should also favor binding of multiple π -acid alkynes, such as dimethyl acetylenedicarboxylate (DMAD) and hexafluorobutene (HFB).

The electron-rich complexes [Rh₂(CO)₃(dmpm)₂], [Rh₂(CO)₂(μ -RC \equiv CR)(dmpm)₂] (R = CO₂Me, CF₃), described earlier,²¹ seemed like excellent candidates for this study. It has been noted, in the reactions of the tricarbonyl species with alkynes to yield the alkyne-bridged species, that addition of excess alkyne results in additional products.²¹ In this paper we describe the elucidation of these additional products, which are shown to contain multiple alkyne ligands.

(19) Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* 1982, 104, 3858.

(20) McKeer, I. R.; Sherlock, S. J.; Cowie, M. *J. Organomet. Chem.* 1988, 352, 205.

(21) Jenkins, J. A.; Cowie, M. *Organometallics*, preceding paper in this issue.

(3) Lindner, E.; Jansen, R.-M.; Mayer, H. A.; Hiller, W.; Fawzi, R. *Organometallics* 1989, 8, 2355 and references therein.

(4) Herrmann, W. A.; Fischer, R. A.; Herdtweck, E. *Organometallics* 1989, 8, 2821 and references therein.

(5) Crook, J. R.; Chamberlain, B.; Mawby, R. *J. Chem. Soc., Dalton Trans.* 1989, 465.

(6) Rappoli, B. J.; Churchill, M. R.; Janik, T. S.; Rees, W. M.; Atwood, J. D. *J. Am. Chem. Soc.* 1987, 109, 5145.

(7) Green, M.; Kale, P. A.; Mercer, R. *J. Chem. Soc., Chem. Commun.* 1987, 375.

(8) (a) Dickson, R. S.; Fallon, G. D.; Nesbit, R. J.; Pain, G. N. *J. Organomet. Chem.* 1982, 236, C61. (b) Dickson, R. S.; Fallon, G. D.; Nesbit, R. J.; Pain, G. N. *Organometallics* 1985, 4, 355. (c) Dickson, R. S.; Fallon, G. D.; Jenkins, S. M.; Nesbit, R. J. *Organometallics* 1987, 6, 1240. (d) Dickson, R. S.; McLure, F. I.; Nesbit, R. J. *J. Organomet. Chem.* 1988, 349, 413.

(9) Knox, S. A. R. *Pure Appl. Chem.* 1984, 56, 81.

(10) Song, H.; Haltiwanger, R. C.; Rakowski Dubois, M. *Organometallics* 1987, 6, 2021.

(11) Baimbridge, C. W.; Dickson, R. S.; Fallon, G. D.; Grayson, I.; Nesbit, R. J.; Weigold, J. *Aust. J. Chem.* 1986, 39, 1187.

(12) (a) Cowie, M.; Southern, T. G. *J. Organomet. Chem.* 1980, 193, C46. (b) Cowie, M.; McKeer, I. R. *Inorg. Chim. Acta* 1982, 65, L107. (c) Cowie, M.; Dickson, R. S. *Inorg. Chem.* 1981, 20, 2682. (d) Cowie, M.; Southern, T. G. *Inorg. Chem.* 1982, 21, 246. (e) Sutherland, B. R.; Cowie, M. *Organometallics* 1984, 3, 1869. (f) Cowie, M.; Dickson, R. S.; Hames, B. W. *Organometallics* 1984, 3, 1879. (g) McDonald, R.; Cowie, M. Manuscript in preparation.

(13) (a) Mague, J. T.; DeVries, S. H. *Inorg. Chem.* 1982, 21, 1632. (b) Mague, J. T. *Inorg. Chem.* 1983, 22, 45. (c) Mague, J. T. *Inorg. Chem.* 1983, 22, 1158. (d) Mague, J. T.; Klein, C. L.; Majeste, R. J.; Stevens, E. D. *Organometallics* 1984, 3, 1860. (e) Mague, J. T. *Organometallics* 1986, 5, 918.

(14) (a) Puddephatt, R. J.; Thomson, M. A. *Inorg. Chem.* 1982, 21, 725. (b) Azam, K. A.; Puddephatt, R. J. *Organometallics* 1983, 2, 1396.

(15) (a) Balch, A. L.; Lee, C.-L.; Lindsay, C. H.; Olmstead, M. M. *J. Organomet. Chem.* 1979, 177, C22. (b) Lee, C.-L.; Hunt, C. T.; Balch, A. L. *Inorg. Chem.* 1981, 20, 2498.

(16) (a) Hommeltoft, S. I.; Berry, D. H.; Eisenberg, R. *J. Am. Chem. Soc.* 1986, 108, 5345. (b) Berry, D. H.; Eisenberg, R. *Organometallics* 1987, 6, 1796.

(17) (a) Higgins, S. J.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* 1986, 1629. (b) Higgins, S. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* 1988, 457.

(18) Vaartstra, B. A.; Cowie, M. *Organometallics* 1989, 8, 2388.

Table II. NMR Spectroscopic Data for the Compounds^{a,b}

compd	$\delta(^{31}\text{P}\{^1\text{H}\})^c$	$\delta(^{19}\text{F})$	$\delta(^1\text{H})$		
			P-CH ₃	-CH ₂ -	-OCH ₃
1	-4.66 (d, 91.7 Hz)		1.59 (s, 24 H)	2.80 (q, 4 H, $J = 5$ Hz)	3.65 (s, 12 H)
2	-5.67 (d, 91.1 Hz)	-54.7 (s, 6 F)	1.62 (m, 12 H), 1.56 (m, 12 H)	2.90 (m, 2 H), 2.61 (m, 2 H)	3.60 (s, 6 H)
3	-6.46 (d, 89.7 Hz)	-54.72 (s, 12 F)	1.60 (m, 24 H)	2.69 (q, 4 H, $J = 5$ Hz)	
4	1.38 (d, 98.0 Hz)	-52.27 (s, 6 F), -52.16 (s, 6 F), -53.16 (s, 6 F), -53.37 (s, 6 F) ^e	1.40 (s, 12 H), 1.29 (s, 12 H)	2.49 (dq, 2 H, $J = 13.9$, 5.5 Hz), 2.18 (dq, 2 H, $J = 13.8, 3.8$ Hz)	
5	-11.4 (m)	-47.08 (qr, 3 F, $J = 15.9$ Hz), $J = 12.9$ Hz), -53.64 (qr, 3 F, $J = 12.9$ Hz), -58.32 (q, 3 F, $J = 15.9$ Hz)			

^a Ambient temperature in CD₂Cl₂ except compounds 3 and 5 (THF-*d*₆). ^b Abbreviations used are as follows: s, singlet; d, doublet; t, triplet; qr, quartet; q, quintet; dq, doublet of quintets; m, multiplet. ^c Vs 85% H₃PO₄; numbers in parentheses represent the separation in hertz between the two major peaks in the second-order spectrum of the complex. ^d ¹³C{¹H} NMR of 4 (THF-*d*₆) at -40 °C: δ 201.56 (t, $J_{\text{C-Rh}} = 31.1$ Hz). ^e -70 °C.

Experimental Section

General Comments. Experimental conditions are as described previously.²² Dimethyl acetylenedicarboxylate (DMAD), diphenylacetylene, dimethylacetylene, and tetrafluoroboric acid etherate were obtained from the Aldrich Chemical Co. Carbon monoxide (CP grade) was purchased from Matheson, ¹³CO (99%) from Isotec Inc., and hexafluoro-2-butyne (HFB) from SCM Speciality Chemicals. These and all other reagent grade chemicals were used as received. [Rh₂(CO)₃(dmpm)₂], [Rh₂(CO)₂(μ -DMAD)(dmpm)₂], and [Rh₂(CO)₂(μ -HFB)(dmpm)₂] were prepared by the procedures reported.²¹ All physical measurements were carried out as described previously,²¹ and all spectroscopic data are recorded in Tables I and II.

Preparation of Compounds. (a) [Rh₂(CO)₂(μ -DMAD)₂(dmpm)₂] (1). **Method A.** A purple solution of [Rh₂(CO)₂(μ -DMAD)(dmpm)₂] (0.100 mmol based on 75% conversion of 100 mg, 0.134 mmol, of [Rh₂Cl₂(CO)₂(μ -DMAD)(dmpm)₂] in THF (8 mL) was prepared.²¹ A 1-equiv amount of DMAD (12.5 μ L, 0.100 mmol) was added and the mixture stirred for 1 h. The brown THF solution was removed by cannula under positive N₂ pressure. The resulting yellow solid was recrystallized from CH₂Cl₂/hexane and dried under vacuum. Compound 1 was obtained as a yellow powder in 38% yield (41 mg). The product was partially soluble in hexane, and the recrystallization solution had to be cooled to 0 °C to effect complete precipitation of the solid. Anal. Calcd for C₂₂H₄₀O₁₀P₄Rh₂: C, 35.2; H, 4.9. Found: C, 34.7; H, 4.9.

Method B. An orange solution of [Rh₂(CO)₃(dmpm)₂] in THF (5 mL) was prepared from *trans*-[RhCl(CO)(dmpm)₂] (50 mg, 0.083 mmol).²¹ A 3-equiv amount of DMAD (30 μ L, 0.25 mmol based on 100% conversion of the starting material) was added to the solution, producing an immediate color change from orange to purple and then brown. This was followed soon thereafter by the precipitation of a brown-yellow solid. After the solution was stirred for 10 min, the solvent was removed by cannula under positive N₂ pressure, and the yellow solid was recrystallized from CH₂Cl₂/hexane and dried under vacuum. Compound 1 was obtained as a yellow powder in 38% yield (26 mg).

(b) [Rh₂(CO)₂(μ -DMAD)(μ -HFB)(dmpm)₂] (2). A purple solution of [Rh₂(CO)₂(μ -HFB)(dmpm)₂] (0.104 mmol based on 80% conversion of 100 mg, 0.130 mmol, of [Rh₂Cl₂(CO)₂(μ -HFB)(dmpm)₂] in THF (8 mL) was prepared as reported.²¹ A 1-equiv amount of DMAD (13 μ L, 0.104 mmol) was added and the mixture stirred for 2 h. The solvent was removed under vacuum, the brown residue redissolved in a minimum volume of CH₂Cl₂ (ca. 6 mL), and the product precipitated with diethyl ether (20 mL). Upon cooling of the solution in an ice bath, the solvent was removed by cannula under positive N₂ pressure and the solid washed with diethyl ether. The orange-yellow product was dried under vacuum and isolated in 46% yield (50 mg). Anal. Calcd for C₂₂F₆H₃₄O₆P₄Rh₂: C, 31.5; H, 4.1. Found: C, 31.4; H, 4.0. This compound could also be obtained by exposing [Rh₂(CO)₂(μ -DMAD)(dmpm)₂] to an atmosphere of HFB; however, the route shown above is preferable.

(c) [Rh₂(CO)₂(μ -HFB)₂(dmpm)₂] (3). Compound 4 was prepared as described below by using [Rh₂Cl₂(CO)₂(μ -HFB)(dmpm)₂] (100 mg, 0.130 mmol) and was redissolved in THF (10 mL). The mixture was allowed to react under a static atmosphere of CO for 48 h. The static CO atmosphere was replenished twice over this time period. Within 24 h a yellow solid had appeared. After 2 days the solvent was removed by evaporation under a stream of N₂ and the solid washed with two 10-mL aliquots of CH₂Cl₂. After the residue was dried under a dinitrogen atmosphere, the product was isolated as a bright yellow solid in 46% yield (52 mg). The bright yellow solid was sparingly soluble in THF and CH₂Cl₂. Recrystallization of the product was effected from a THF/diethyl ether mixture. Anal. Calcd for C₂₀F₁₂H₂₈O₂P₄Rh₂: C, 28.0; H, 3.3. Found: C, 27.9; H, 3.2.

(d) [Rh₂(π^2 -HFB)₂(μ -CO)(μ -HFB)(dmpm)₂] (4). A purple solution of [Rh₂(CO)₂(μ -HFB)(dmpm)₂] in THF (10 mL) was prepared from [Rh₂Cl₂(CO)₂(μ -HFB)(dmpm)₂] (100 mg, 0.130 mmol).²¹ The dinitrogen atmosphere in the flask was replaced with an atmosphere of HFB, and the solution was stirred for 1 h. The volume of the dark, brown-orange solution was reduced to ca. 5 mL under vacuum and the orange solid precipitated with hexane (25 mL). The solvents were removed by cannula under positive N₂ pressure, and the solid was washed with hexane and dried under vacuum. Compound 4 was isolated as an orange powder in 68% yield (95 mg). Anal. Calcd for C₂₇F₁₈H₃₆O₂P₄Rh₂: C, 30.5; H, 3.4. Found: C, 30.2; H, 2.9.

X-ray Data Collection. Yellow crystals of [Rh₂(CO)₂(μ -DMAD)(μ -HFB)(dmpm)₂] (2) were obtained by slow evaporation of an ethanol solution of [Rh₂(CO)₂(μ -DMAD)(dmpm)₂] which had been enriched with excess HFB. Yellow crystals of [Rh₂(CO)₂(μ -HFB)₂(dmpm)₂] (3) were obtained by slow diffusion of diethyl ether into a concentrated THF solution of the complex. In both cases, suitable crystals did not appear to be air-sensitive and were thus mounted on glass fibers. Data were collected on an Enraf-Nonius CAD4 diffractometer using Mo K α radiation. Unit-cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections in the range 22.0° \leq 2 θ \leq 28.0° for compound 2 and 18.0° \leq 2 θ \leq 32.0° for compound 3.

The diffraction symmetry and preliminary cell parameters for 2 suggested symmetry no higher than triclinic, and the lack of systematic absences led to the choice of space group as *P1* or *P1*. A cell reduction²² failed to detect a higher symmetry cell. Intensity data were collected at 22 °C using the $\theta/2\theta$ scan technique to a maximum 2 θ of 50.0°. For compound 3 the monoclinic diffraction symmetry and systematic absences (*h0l*, $h + l = \text{odd}$; $0k0$, $k = \text{odd}$) were consistent with the space group *P2*₁/*n*, a nonstandard setting of *P2*₁/*c*. Intensity data were collected as for 2 to a maximum 2 θ of 56.0°. In both cases, backgrounds were obtained by increasing the scan 25% on each side of the peak. Three reflections were chosen as intensity standards, being remeasured at 120-min intervals of X-ray exposure. There was no significant variation in the intensities of these standards, and thus no de-

(22) Jenkins, J. A.; Ennett, J. P.; Cowie, M. *Organometallics* 1988, 7, 1845.

(23) Programs used were those of the Enraf-Nonius Structure Determination Package by B. A. Frenz, in addition to local programs by R. G. Ball.

Table III. Crystallographic Data for Compounds 2 and 3

compd	[Rh ₂ (CO) ₂ (μ-DMAD)(μ-HFB)(dmpm) ₂] (2)	[Rh ₂ (CO) ₂ (μ-HFB) ₂ (dmpm) ₂] (3)
formula	C ₂₂ F ₆ H ₃₄ O ₆ P ₄ Rh ₂	C ₂₀ F ₁₂ H ₂₈ O ₂ P ₄ Rh ₂
fw	838.20	858.13
cryst shape	triclinic prism	monoclinic prism
cryst dimens, mm	0.109 × 0.253 × 0.447	0.090 × 0.106 × 0.115
space group	P $\bar{1}$ (No. 2)	P2 ₁ /n (No. 14, nonstandard setting)
temp, °C	22	22
radiation (λ, Å)	graphite-monochromated Mo Kα (0.71069)	graphite-monochromated Mo Kα (0.71069)
cell params		
a, Å	9.7825 (8)	9.474 (1)
b, Å	9.833 (1)	15.813 (2)
c, Å	9.3791 (9)	9.917 (1)
α, deg	92.390 (8)	90.0
β, deg	99.893 (7)	95.34 (1)
γ, deg	118.180 (8)	90.0
V, Å ³	775.5 (3)	1479.3 (6)
Z	1	2
ρ(calcd), g cm ⁻³	1.795	1.926
linear abs coeff μ, cm ⁻¹	13.196	14.043
range of transm factors	0.914–1.060	0.870–1.186
detector aperture, mm	(3.00 + tan θ) wide × 4.00 high	(3.00 + tan θ) wide × 4.00 high
takeoff angle, deg	3.0	3.0
maximum 2θ, deg	50.0	50.0
cryst-detector dist, mm	173	173
scan type	θ/2θ	θ/2θ
scan rate, deg/min	between 1.67 and 6.67	between 1.11 and 6.67
scan width, deg	0.80 + 0.347 tan θ	0.50 + 0.347 tan θ
tot. no. of unique reflcns	2711 (h,±k,±l)	3687 (h,k,±l)
tot. no. of observns (NO)	2486	1588
final no. of params varied (NV)	235	181
error in obs of unit wt (GOF) ^a	1.922	1.067
R ^b	0.030	0.040
R _w ^c	0.049	0.043

$$^a \text{GOF} = [\sum w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV})]^{1/2}. \quad ^b R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^c R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}.$$

composition correction was applied to either set of data. A total of 2711 reflections for compound 2 and 3687 reflections for compound 3 were measured and processed in the usual way, with use of a value of 0.04 for p^{24} to downweight intense reflections. Of the 2711 reflections collected, 2486 were considered to be observed for 2 and 1588 of 3687 were observed for 3 and were used in subsequent calculations. Absorption corrections were applied to the data by using the method of Walker and Stuart.²⁵ See Table III for a summary of crystal data and X-ray data collection information.

Structure Solution and Refinement. The structures of compounds 2 and 3 were solved in the space groups $P\bar{1}$ and $P2_1/n$, respectively. The metal atoms in each case were located by Patterson synthesis, and all other atoms were obtained by a sequence of full-matrix least-squares refinement and difference Fourier syntheses. All non-hydrogen atoms were ultimately located. Atomic scattering factors^{26,27} and anomalous dispersion terms²⁸ were taken from the usual tabulations. All hydrogen atoms were included as fixed contributions and not refined. Their idealized positions were generated from the geometries about the attached carbon atoms, and they were assigned thermal parameters 20% greater than the equivalent isotropic B's of their attached carbon atoms.

For compound 2 ($Z = 1$) the structure was refined in both $P1$ and $P\bar{1}$. For the latter, the structure was disordered about the alkyne ligand atoms with the subsequent CF₃ and CO₂Me groups superimposed. Substantially lower R and R_w values were obtained for the centrosymmetric case ($P1$, $R = 0.064$, $R_w = 0.097$; $P\bar{1}$, $R = 0.030$, $R_w = 0.049$), and further support for the centrosymmetric space group was obtained by location of all hydrogens on dmpm and by satisfactory refinement of all other atoms. The final model

Table IV. Positional and Thermal Parameters for [Rh₂(CO)₂(μ-DMAD)(μ-HFB)(dmpm)₂] (2)^a

atom	x	y	z	B, Å ²
Rh	-0.04955 (2)	-0.15392 (2)	-0.00502 (2)	2.256 (5)
P(1)	-0.2058 (1)	-0.1839 (1)	0.1624 (1)	3.33 (2)
P(2)	-0.0941 (1)	0.1532 (1)	0.1771 (1)	3.35 (2)
F(1)	-0.3914 (8)	-0.3900 (7)	-0.2536 (7)	9.5 (2)
F(2)	-0.3304 (9)	-0.2400 (9)	-0.4106 (6)	9.4 (3)
F(3)	-0.4842 (5)	-0.2544 (6)	-0.2784 (9)	8.2 (2)
F(4)	-0.3901 (6)	0.0368 (7)	-0.272 (1)	9.9 (2)
F(5)	-0.2432 (8)	0.0614 (7)	-0.4111 (7)	9.0 (2)
F(6)	-0.1697 (6)	0.2485 (5)	-0.2380 (7)	8.2 (2)
O(1)	-0.1715 (4)	-0.5008 (4)	-0.0236 (5)	7.8 (1)
O(2)	0.3292 (7)	-0.1272 (7)	0.2489 (8)	9.4 (2)
O(3)	0.1662 (8)	-0.1233 (8)	0.3918 (6)	6.4 (2)
O(4)	0.3634 (9)	0.3807 (8)	0.279 (1)	12.6 (3)
O(5)	0.4273 (8)	0.1964 (8)	0.3554 (9)	10.9 (2)
C(1)	-0.1237 (4)	-0.3695 (5)	-0.0144 (5)	4.2 (1)
C(2)	-0.3449 (4)	-0.2465 (4)	-0.2754 (4)	3.93 (9)
C(3)	-0.2065 (4)	-0.1215 (4)	-0.1703 (4)	2.82 (7)
C(4)	-0.1577 (3)	0.0301 (4)	-0.1671 (4)	2.69 (7)
C(5)	-0.2269 (5)	0.0991 (5)	-0.2721 (5)	5.7 (1)
C(6)	0.337 (1)	-0.234 (1)	0.383 (1)	9.0 (3)
C(7)	0.560 (1)	0.312 (1)	0.475 (1)	7.6 (3)
C(8)	-0.1405 (4)	-0.0076 (5)	0.2838 (4)	4.19 (9)
C(9)	-0.2123 (6)	-0.3211 (5)	0.2881 (5)	5.9 (1)
C(10)	-0.4162 (5)	-0.2551 (6)	0.0885 (6)	5.8 (1)
C(11)	-0.2821 (4)	0.1482 (5)	0.1117 (5)	5.3 (1)
C(12)	0.0051 (6)	0.3244 (6)	0.3176 (5)	6.1 (1)

^a All atoms are refined anisotropically.

with 235 parameters refined, converged as shown in Table III. In the final difference Fourier map, the 10 highest peaks (0.8–0.3 e/Å³) were in the vicinity of the Rh, CF₃, and CO₂Me atoms.

For the structure of compound 3 the final model with 181 parameters refined, converged as shown in Table III. In the final difference Fourier map, the 10 highest peaks (0.6–0.4 e/Å³) were in the vicinity of the CF₃ atoms of HFB. The positional parameters of all non-hydrogen atoms for compounds 2 and 3 are listed in Table IV and V, respectively, and bond distances and angles for these compounds are listed in Tables VI–IX.

(24) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* 1967, 6, 204.

(25) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* 1983, A39, 1581.

(26) Cromer, D. T.; Waber, J. T. *International Tables for Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(27) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* 1965, 42, 3175.

(28) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* 1970, 53, 1891.

Table V. Positional and Thermal Parameters for $[\text{Rh}_2(\text{CO})_2(\mu\text{-HFB})_2(\text{dmpm})_2] (3)^a$

atom	x	y	z	B, Å ²
Rh	0.01230 (6)	0.05184 (4)	0.10839 (6)	2.110 (9)
P(1)	0.1661 (2)	-0.0388 (1)	0.2336 (2)	2.83 (4)
P(2)	0.1437 (2)	-0.1513 (1)	-0.0072 (2)	3.11 (5)
F(1)	-0.2732 (7)	-0.0999 (4)	0.3019 (6)	9.1 (2)
F(2)	-0.3914 (6)	-0.0066 (5)	0.1952 (6)	9.3 (2)
F(3)	-0.2230 (6)	0.0270 (4)	0.3332 (5)	7.3 (2)
F(4)	0.4111 (6)	0.1168 (5)	0.039 (1)	13.3 (3)
F(5)	0.2975 (8)	0.2033 (4)	-0.0791 (7)	13.9 (2)
F(6)	0.2720 (7)	0.1924 (4)	0.1177 (7)	9.5 (2)
O(1)	0.0483 (7)	0.1725 (4)	0.3466 (6)	6.1 (2)
C(1)	0.0332 (8)	0.1264 (5)	0.2573 (8)	3.4 (2)
C(2)	-0.2597 (9)	-0.0290 (6)	0.2360 (9)	4.4 (2)
C(3)	-0.1641 (7)	-0.0307 (4)	0.1257 (8)	2.6 (2)
C(4)	0.1770 (7)	0.0810 (5)	-0.0178 (8)	2.5 (2)
C(5)	0.2855 (9)	0.1470 (6)	0.0117 (9)	4.5 (2)
C(6)	0.088 (1)	-0.1064 (6)	0.3554 (9)	4.9 (2)
C(7)	0.3082 (9)	0.0115 (6)	0.3409 (9)	4.5 (2)
C(8)	0.2632 (8)	-0.1099 (5)	0.1311 (8)	3.2 (2)
C(9)	0.265 (1)	-0.1986 (6)	-0.117 (1)	4.8 (2)
C(10)	0.065 (1)	-0.2448 (6)	0.061 (1)	5.6 (3)

^a All atoms are refined anisotropically.

Table VI. Bond Distances (Å) for $[\text{Rh}_2(\text{CO})_2(\mu\text{-DMAD})(\mu\text{-HFB})(\text{dmpm})_2] (2)$

Rh-Rh'	2.6989 (4)	F(3)-C(2)	1.323 (6)
Rh-P(1)	2.3080 (8)	F(4)-C(5)	1.41 (1)
Rh-P(2)'	2.3132 (8)	F(5)-C(5)	1.30 (1)
Rh-C(1)	1.881 (3)	F(6)-C(5)	1.302 (7)
Rh-C(3)	2.133 (3)	O(1)-C(1)	1.140 (4)
Rh-C(4)'	2.140 (3)	O(2)-C(5)'	1.21 (1)
P(1)-C(8)	1.803 (4)	O(2)-C(6)	1.68 (1)
P(1)-C(9)	1.814 (4)	O(3)-C(5)'	1.34 (1)
P(1)-C(10)	1.820 (4)	O(4)-C(2)'	1.24 (1)
P(2)-C(8)	1.821 (4)	O(5)-C(2)'	1.286 (8)
P(2)-C(11)	1.813 (4)	O(5)-C(7)	1.50 (1)
P(2)-C(12)	1.829 (4)	C(2)-C(3)	1.478 (4)
F(1)-C(2)	1.300 (9)	C(3)-C(4)	1.331 (4)
F(2)-C(2)	1.301 (6)	C(4)-C(5)	1.465 (4)

Table VII. Bond Angles (deg) for $[\text{Rh}_2(\text{CO})_2(\mu\text{-DMAD})(\mu\text{-HFB})(\text{dmpm})_2] (2)$

Rh'-Rh-P(1)	93.13 (2)	C(2)'-O(5)-C(7)	116.8 (7)
Rh'-Rh-C(1)	178.6 (1)	Rh-C(1)-O(1)	178.1 (4)
Rh'-Rh-C(3)	71.17 (7)	F(1)-C(2)-F(2)	106.7 (7)
P(1)-Rh-P(2)'	173.75 (3)	F(1)-C(2)-F(3)	95.3 (7)
P(1)-Rh-C(1)	86.4 (1)	F(1)-C(2)-C(3)	118.2 (5)
P(1)-Rh-C(3)	92.30 (7)	F(2)-C(2)-F(3)	104.0 (6)
P(1)-Rh-C(4)'	89.38 (7)	F(2)-C(2)-C(3)	113.6 (4)
C(1)-Rh-C(3)	107.6 (1)	F(3)-C(2)-C(3)	116.9 (4)
C(3)-Rh-C(4)'	142.6 (1)	O(4)-C(2)'-O(5)	129.1 (8)
Rh-Rh'-P(2)	93.03 (2)	O(4)-C(2)'-C(3)'	117.8 (7)
Rh-Rh'-C(4)	71.46 (7)	O(5)-C(2)'-C(3)'	113.1 (4)
P(2)-Rh'-C(3)'	88.70 (7)	Rh'-C(3)'-C(2)'	125.8 (2)
P(2)-Rh'-C(4)	93.56 (7)	Rh-C(3)-C(4)	109.3 (2)
C(1)'-Rh'-C(4)	109.8 (1)	C(2)-C(3)-C(4)	125.0 (3)
Rh-P(1)-C(8)	113.6 (1)	Rh'-C(4)-C(3)	108.1 (2)
Rh-P(1)-C(9)	115.3 (1)	Rh'-C(4)-C(5)	126.4 (2)
Rh-P(1)-C(10)	116.6 (1)	C(3)-C(4)-C(5)	125.3 (3)
C(8)-P(1)-C(9)	102.6 (2)	F(4)-C(5)-F(5)	97.3 (7)
C(8)-P(1)-C(10)	105.3 (2)	F(4)-C(5)-F(6)	103.4 (6)
C(9)-P(1)-C(10)	101.7 (2)	F(4)-C(5)-C(4)	109.3 (5)
Rh'-P(2)-C(8)	113.6 (1)	F(5)-C(5)-F(6)	111.6 (6)
Rh'-P(2)-C(11)	117.3 (1)	F(5)-C(5)-C(4)	118.7 (6)
Rh'-P(2)-C(12)	115.3 (1)	F(6)-C(5)-C(4)	114.0 (3)
C(8)-P(2)-C(11)	105.0 (2)	O(2)-C(5)'-O(3)	125.7 (8)
C(8)-P(2)-C(12)	102.9 (2)	O(2)-C(5)'-C(4)'	121.3 (6)
C(11)-P(2)-C(12)	100.9 (2)	O(3)-C(5)'-C(4)'	112.9 (6)
C(5)'-O(2)-C(6)	101.2 (9)	P(1)-C(8)-P(2)	108.8 (2)

Results and Discussion

The bis(alkyne) complexes $[\text{Rh}_2(\text{CO})_2(\mu\text{-DMAD})_2(\text{dmpm})_2] (1)$ and $[\text{Rh}_2(\text{CO})_2(\mu\text{-DMAD})(\mu\text{-HFB})(\text{dmpm})_2] (2)$ are prepared via the addition of 1 equiv of DMAD to

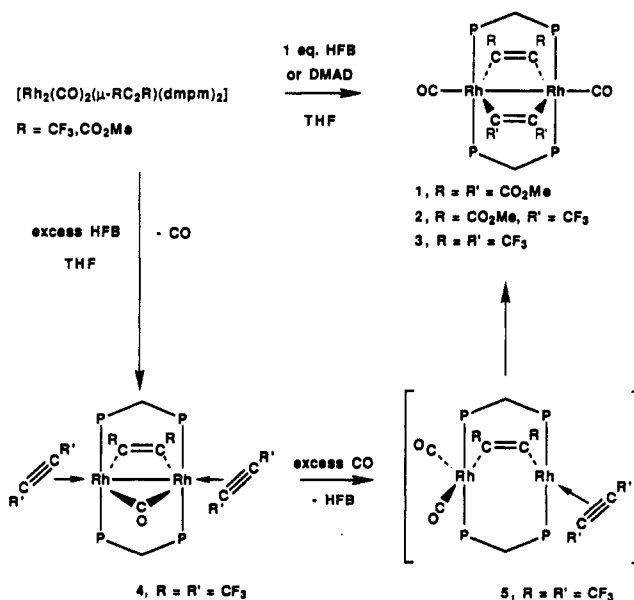
Table VIII. Bond Distances (Å) for $[\text{Rh}_2(\text{CO})_2(\mu\text{-HFB})_2(\text{dmpm})_2] (3)$

Rh-Rh'	2.696 (1)	P(2)-C(10)	1.82 (1)
Rh-P(1)	2.320 (2)	F(1)-C(2)	1.31 (1)
Rh'-P(2)	2.322 (2)	F(2)-C(2)	1.32 (1)
Rh-C(1)	1.886 (9)	F(3)-C(2)	1.33 (1)
Rh-C(3)	2.140 (7)	F(4)-C(5)	1.29 (1)
Rh-C(4)	2.139 (8)	F(5)-C(5)	1.28 (1)
P(1)-C(6)	1.821 (9)	F(6)-F(5)	1.30 (1)
P(1)-C(7)	1.820 (9)	O(1)-C(1)	1.146 (9)
P(1)-C(8)	1.821 (8)	C(2)-C(3)	1.48 (1)
P(2)-C(8)	1.818 (8)	C(3)-C(4)'	1.33 (1)
P(2)-C(9)	1.816 (9)	C(4)-C(5)	1.47 (1)

Table IX. Bond Angles (deg) for $[\text{Rh}_2(\text{CO})_2(\mu\text{-HFB})_2(\text{dmpm})_2] (3)$

Rh'-Rh-P(1)	93.13 (6)	C(8)-P(2)-C(9)	102.5 (4)
Rh'-Rh-C(1)	178.4 (3)	C(8)-P(2)-C(10)	105.1 (4)
Rh'-Rh-C(3)	71.5 (2)	C(9)-P(2)-C(10)	101.2 (5)
Rh'-Rh-C(4)	71.2 (2)	Rh-C(1)-O(1)	178.6 (8)
Rh-Rh'-P(2)	93.61 (6)	F(1)-C(2)-F(2)	104.5 (8)
P(1)-Rh-P(2)'	173.11 (8)	F(1)-C(2)-F(3)	103.8 (8)
P(1)-Rh-C(1)	87.2 (2)	F(1)-C(2)-C(3)	116.6 (8)
P(1)-Rh-C(3)	92.1 (2)	F(2)-C(2)-F(3)	102.6 (8)
P(1)-Rh-C(4)	89.4 (2)	F(2)-C(2)-C(3)	113.7 (8)
P(2)'-Rh-C(1)	86.1 (2)	F(3)-C(2)-C(3)	114.2 (8)
P(2)'-Rh-C(3)	88.7 (2)	Rh-C(3)-C(2)	125.7 (6)
P(2)'-Rh-C(4)	94.1 (2)	Rh-C(3)-C(4)'	108.4 (5)
C(1)-Rh-C(3)	110.1 (3)	C(2)-C(3)-C(4)'	126.0 (7)
C(1)-Rh-C(4)	107.1 (3)	Rh-C(4)-C(3)'	108.9 (5)
C(3)-Rh-C(4)	142.7 (3)	Rh-C(4)-C(5)	124.8 (6)
Rh-P(1)-C(6)	116.3 (3)	C(3)'-C(4)-C(5)	126.4 (8)
Rh-P(1)-C(7)	115.9 (3)	F(4)-C(5)-F(5)	105 (1)
Rh-P(1)-C(8)	114.0 (3)	F(4)-C(5)-F(6)	101.3 (9)
C(6)-P(1)-C(7)	101.1 (5)	F(4)-C(5)-C(4)	113.2 (9)
C(6)-P(1)-C(8)	105.4 (4)	F(5)-C(5)-F(6)	102 (1)
C(7)-P(1)-C(8)	102.3 (4)	F(5)-C(5)-C(4)	117.4 (8)
Rh'-P(2)-C(8)	114.1 (3)	F(6)-C(5)-C(4)	115.8 (8)
Rh'-P(2)-C(9)	115.7 (3)	P(1)-C(8)-P(2)	109.4 (4)
Rh'-P(2)-C(10)	116.5 (3)		

Scheme I



a solution of the mono(alkyne) complexes $[\text{Rh}_2(\text{CO})_2(\mu\text{-DMAD})(\text{dmpm})_2] (1)$ or $[\text{Rh}_2(\text{CO})_2(\mu\text{-HFB})(\text{dmpm})_2] (2)$, respectively. The preparation of complex 1 can also be achieved from the addition of 2 equiv of DMAD to $[\text{Rh}_2(\text{CO})_3(\text{dmpm})_2]$. The third member in this series, $[\text{Rh}_2(\text{CO})_2(\mu\text{-HFB})_2(\text{dmpm})_2] (3)$, is obtained upon long-term reaction of CO with the complex $[\text{Rh}_2(\eta^2\text{-HFB})_2(\mu\text{-CO})(\mu\text{-HFB})(\text{dmpm})_2] (4)$, which is in turn prepared from the reaction of excess HFB with $[\text{Rh}_2(\text{CO})_2(\mu\text{-HFB})_2(\text{dmpm})_2] (3)$.

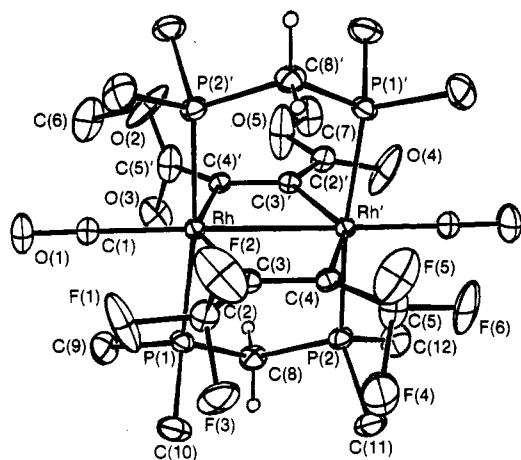


Figure 1. Perspective view of $[\text{Rh}_2(\text{CO})_2(\mu\text{-DMAD})(\mu\text{-HFB})(\text{dmpm})_2]$ (**2**), showing the numbering scheme. Thermal parameters are shown at the 20% level except for methylene hydrogens which are shown artificially small. Hydrogen atoms on the methyl groups are omitted for the sake of clarity. Primed atoms are related by inversion symmetry. Only one of the disordered sets of alkyne substituents is shown. See Experimental Section for details.

(dmpm)₂) (vide infra). These reactions are summarized in Scheme I. All species are coordinatively-saturated metal-metal-bonded 18-electron complexes which exhibit a much greater degree of air-stability than their unsaturated precursors. No subsequent reaction of the three bis(alkyne) complexes with excess CO, DMAD, HFB, or $\text{HBF}_4\cdot\text{OEt}_2$ was found to take place.

The X-ray structures of two of these bis(alkyne) complexes, $[\text{Rh}_2(\text{CO})_2(\mu\text{-DMAD})(\mu\text{-HFB})(\text{dmpm})_2]$ (**2**) and $[\text{Rh}_2(\text{CO})_2(\mu\text{-HFB})_2(\text{dmpm})_2]$ (**3**), have been determined, and perspective views of these species are shown in Figures 1 and 2. In both cases the asymmetric unit represents half of the molecule with the other half being related by an inversion center situated midway between the two metals. As suggested by the spectroscopic data (vide infra) and as shown in Figures 1 and 2, both structures are symmetric. In each, the metal centers are held together by the two bridging diphosphine ligands and two alkyne ligands. The dmpm ligands have the classical trans arrangement found in many dppm -bridged^{12-15,29,30} and dmpm -bridged binuclear species,³¹⁻³⁴ and the two alkyne ligands occupy equatorial positions on opposite faces of the " $\text{Rh}_2(\text{dmpm})_2$ " core. Both alkynes are coordinated in a cis-dimetalated fashion with the two rhodium atoms and all four unsaturated carbon atoms of the two alkynes essentially in the same plane to give a 1,4-dimetallacyclohexadiene-type unit. Each metal has a terminal carbonyl attached to it which is also in the equatorial plane and along the metal-metal axis. In both complexes the rhodium atoms are regarded as Rh(II) centers, viewing the bridging alkyne ligands as dianionic. If the single metal-metal bond is taken into account, each metal atom has a coordination number of 6 with a geometry resembling that of a distorted octahedron. As noted, the diphosphines have a trans arrangement at each metal ($\text{P}(1)\text{-Rh-P}(2)'$ = 173.75 (3)° for

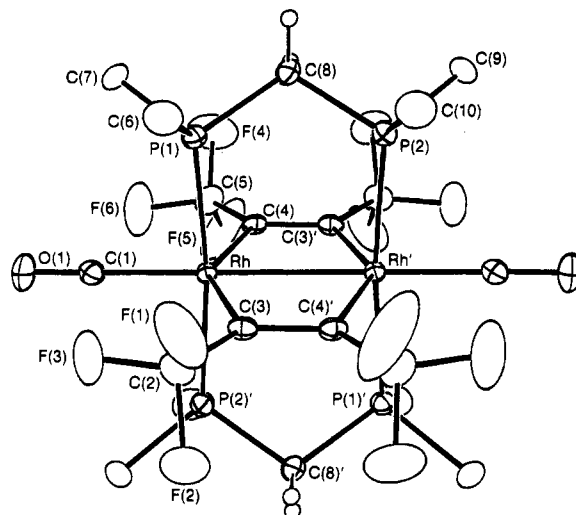


Figure 2. Perspective view $[\text{Rh}_2(\text{CO})_2(\mu\text{-HFB})_2(\text{dmpm})_2]$ (**3**). Thermal parameters are as described in Figure 1. Primed atoms are related by inversion symmetry.

compound **2** and 173.11 (8)° for compound **3**) and are eclipsed about the Rh-Rh bond with a torsion angle ($\text{P}(1)\text{-Rh-Rh'-P}(2)$) of 1.04 (4)° for **2** and 1.42 (8)° for **3**. The Rh-P distances (2.3080 (8), 2.3132 (8) Å for **2** and 2.320 (2), 2.322 (2) Å for **3**) are similar to values in related Rh(II) complexes bridged by dmpm ²² and dppm ^{12c,f,13c} (range 2.301 (2)– 2.384 (2) Å).

In both compounds distortion from octahedral geometry results from the restrictions imposed by the two bridging alkyne groups. Therefore, C(alkyne)-Rh-Rh' angles (ca. 71°) and C(alkyne)-Rh-CO angles (ca. 109°) are significantly different from 90° . These distortions are representative of those found in other metal-metal-bonded complexes which are bridged by a single cis-dimetalated olefin.^{12c,e,f,35,36} Alternatively, the geometry could be discussed as trigonal bipyramidal by ignoring the Rh-Rh' bond.

Although the Rh-Rh' separations of 2.6989 (4) Å in **2** and 2.696 (1) Å in **3** fall within the range of normal Rh-Rh single bonds in related diphosphine systems (2.682 (1)– 2.9653 (6) Å),^{12c,e,f,35,37,38} they are clearly on the short end of the range observed in other binuclear Rh(II) compounds in which the Rh atoms are bridged by cis-dimetalated olefins.^{12c,f,13c,35} Compression along the Rh-Rh' axis, through mutual attraction of the metals, is apparent upon comparison of the Rh-Rh' distances with the intraligand P...P separations (nonbonded intraligand P-P separation = 2.947 (1) Å for **2** and 2.969 (3) Å for **3**).

The Rh-C(alkyne) distances (2.133 (3), 2.140 (3) Å for **2**; 2.139 (8), 2.140 (7) Å for **3**) are noticeably longer than those in " $\text{Rh}_2(\text{diphosphine})_2$ " compounds containing only one bridged alkyne unit (range 1.994 (9)– 2.089 (4) Å).^{12c,f,13c,35} Presumably this is a reflection of the strain imposed on the unsaturated carbon atoms by the relatively short Rh-Rh' distances of compounds **2** and **3**. Indeed, distortion from the idealized sp^2 hybridization of these carbon atoms is evident in the compressed Rh-C(alkyne)-C(alkyne) angles (109.3 (2) and 108.1 (2)° for **2** and

(29) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99.

(30) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191.

(31) Cotton, F. A.; Eglin, J. L.; Luck, R. L.; Son, K. *Inorg. Chem.* **1990**, *29*, 1802.

(32) Wu, J.; Reinking, M. K.; Fanwick, P. E.; Kubiak, C. P. *Inorg. Chem.* **1987**, *26*, 247.

(33) Ge, Y.-W.; Peng, F.; Sharp, P. R. *J. Am. Chem. Soc.* **1990**, *112*, 2632.

(34) Johnson, K. A.; Gladfelter, W. L. *Organometallics* **1989**, *8*, 2866.

(35) Dickson, R. S.; Johnson, S. H.; Kirsch, H. P.; Lloyd, D. J. *Acta Crystallogr.* **1977**, *B33*, 2057.

(36) Koie, Y.; Shinoda, S.; Saito, Y.; Fitzgerald, B. J.; Pierpont, C. G. *Inorg. Chem.* **1980**, *19*, 770.

(37) (a) Kubiak, C. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 3637. (b) Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1982**, *21*, 2119. (c) Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1985**, *24*, 1285.

(38) Haines, R. J.; Meintjies, E.; Laing, M.; Sommerville, P. J. *Organomet. Chem.* **1981**, *216*, C19.

108.4 (5) and 108.9 (5)° for 3). Apart from the Rh–C(alkyne) separation, the bond distances about the unsaturated carbon atoms of each alkyne ligand correspond to those of the “M₂(μ-alkyne)” unit in mono(alkyne), metal–metal-bonded complexes.^{12c,f,13c,19,35,36} The C(alkyne)–C(alkyne)–R angles C(2)–C(3)–C(4) = 125.0 (3), C(3)–C(4)–C(5) = 125.3 (3)° for 2; C(2)–C(3)–C(4) = 126.0 (7), C(3)–C(4)–C(5) = 126.4 (8)° for 3 are similar to the appropriate values in the above mono(alkyne) species. The C(3)–C(4) or C(3)–C(4)′ distances within the acetylenic unit (1.331 (4) Å for 2; 1.33 (1) Å for 3) are close to those of olefinic double bonds³⁹ and are the same as values observed for “M₂(μ-alkyne)” systems with and without metal–metal bonds.^{12,13b,c,19,29,30,36}

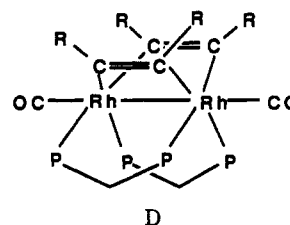
The presence of the crystallographic inversion center between the metal atoms requires that the alkyne substituents of compound 2 be disordered with respect to each other, so the CO₂Me and CF₃ groups are superimposed on electron density maps. Despite this disorder, the substituents are rather well defined and have their expected geometries. Furthermore it is clear that the two carboxylate groups of DMAD are perpendicular to each other (interplanar angle 97.4 (1)°) with one in the equatorial plane of the molecule and the other out of the plane (Figure 1). This represents the typical arrangement observed in related binuclear complexes bridged by a DMAD group,^{12d,e,g,13b,d,40,41} and is one which clearly minimizes the contact between the alkyne and diphosphine substituents.

Binuclear diphosphine-bridged compounds containing a bridging alkyne molecule are quite common,^{12–17,40,41} but compounds 1–3 are the first such species in which two alkyne ligands have been successfully coordinated at the metal centers as cis-dimetalated olefins. They also represent the first examples of binuclear bis(alkyne) complexes in which the two metal atoms and the two unsaturated carbon atoms of each alkyne unit lie in a single plane. Other examples of bimetallic bis(alkyne) species^{42–49} form either a boat conformation without a metal–metal bond as in [Ir(μ-HFB)(NO)(PPh₃)₂]₂⁴² or have the alkyne ligands perpendicular to the metal–metal bond, as in [CpNb(CO)(μ-PhC₂Ph)]₂.⁴⁵ In contrast to complexes 1–3, these other binuclear bis(alkyne) species have been prepared via the reaction of a mononuclear starting material with an alkyne. The only exception to this is [Fe(CO)₂(μ-η²-(^tBuC≡C^tBu))]₂, which is obtained from the reaction of Fe₃(CO)₁₂ with di-*tert*-butylacetylene.⁴⁶

It seems apparent that the low oxidation state of the metals and the basic nature of the dmpm ligands are important factors in the coordination of a second electrophilic alkyne ligand. Not surprisingly, the unactivated alkynes

diphenylacetylene and 2-butyne (which are better electron donors but poorer π-acceptors than either of DMAD and HFB) are unreactive toward the starting materials [Rh₂(CO)₂(μ-alkyne)(dmpm)₂] (alkyne = DMAD, HFB). In addition, the reduced steric bulk of the dmpm ligand is also a factor in the reactivity, allowing the second alkyne ligand room to coordinate with a minimum of steric interference from the diphosphine substituents. By comparison, we note that the related species [Ir₂(CO)₂(μ-η²-DMAD)(dppm)₂], which contains the more bulky dppm ligands, does not react with a second equivalent of DMAD.^{12g}

Other possible structures, in which one or both alkyne molecules are perpendicular to the two metals, do not seem possible owing to the severe steric interactions that would result between the alkynes and the dmpm ligands. The only related structures involving diphosphine ligands and a perpendicular alkyne bonding are the mono(alkyne) complexes [Rh₂(CO)₂(μ-PhC≡CPh)(dppm)₂]¹⁶ and [Ir₂(CO)₂(μ-DMAD)(dppm)₂],^{12h} in which the phosphines are folded away from the alkyne in a cis arrangement at each metal. It would appear, with such an arrangement, that there is no room for an additional alkyne between these “cis” phosphines. One geometry that does appear possible is that shown (D) in which the alkynes are parallel to the



metals in a boat arrangement as previously noted for a diiridium triphenylphosphine species.⁴² Such an arrangement does not appear to be unfavorable since a cis,cis-diphosphine arrangement has been observed with the much bulkier dppm ligand.^{12h,16b,50,51} The observed structure, with alkynes on each face of the complex, may be dictated by the site of attack of the second alkyne.

It has been assumed that the structures of the mono(alkyne) precursors have a cis-diphosphine arrangement at the two metals and a perpendicular alkyne binding mode,²¹ as observed in two closely related species.^{12h,16a} Reaction of such a species with additional alkyne, to yield the bis(alkyne) complexes 1–3, would require alkyne attack between the phosphines, accompanied by rotation of the originally bound alkyne. Owing to the crowding between the phosphines in this geometry and the saturation of both metals, reaction of such a species with additional alkyne does not seem likely. Alternatively, it may be that the structure containing the perpendicular alkyne is in equilibrium with a small amount of the “parallel” cis-dimetalated form having a trans arrangement of the diphosphine ligands. Such a structure has unsaturated metals and a diphosphine arrangement which is more conducive to attack by the second alkyne. In this species attack at the “open” side opposite the bridging alkyne would lead to the bis(alkyne) products.

The spectroscopic characterization of the bis(alkyne) compounds 1–3 is straightforward. Each exhibits a second-order resonance in the ³¹P{¹H} NMR spectrum comprised of two principal peaks, consistent with an

(39) MacGillavry, C. H.; Rieck, G. D., Ed. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1968; Vol. III, Table 4.2.2.

(40) Balch, A. L.; Fossett, L. A.; Linehan, J.; Olmstead, M. M. *Organometallics* 1986, 5, 691.

(41) Cowie, M.; Vasapollo, G.; Sutherland, B. R.; Ennett, J. P. *Inorg. Chem.* 1986, 25, 2648.

(42) Clemens, J.; Green, M.; Kuo, M.-C.; Fritchie, C. J., Jr.; Mague, J. T.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* 1972, 53.

(43) Clemens, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1973, 375.

(44) Smart, L. E.; Browning, J.; Green, M.; Laguna, A.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1977, 1777.

(45) Nesmeyanov, A. N.; Gusev, A. I.; Pasyonskii, A. A.; Anisimov, K. N.; Kolobova, N. E.; Struchkov, Y. T. *J. Chem. Soc., Chem. Commun.* 1968, 1365.

(46) Nicholas, K.; Bray, L. S.; Davis, R. E.; Pettit, R. *J. Chem. Soc., Chem. Commun.* 1971, 608.

(47) Schmitt, H.-J.; Ziegler, M. L. *Z. Naturforsch.* 1973, 28b, 508.

(48) Davidson, J. L. *J. Chem. Soc., Chem. Commun.* 1980, 749.

(49) Schauffele, H.; Pritzkow, H.; Zenneck, U. *Angew. Chem., Int. Ed. Engl.* 1988, 27, 1519.

(50) DeLaet, D. L.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* 1986, 5, 1807.

(51) Elliot, D. J.; Ferguson, G.; Holah, D. G.; Hughes, A. N.; Jennings, M. C.; Magnuson, V. R.; Potter, D.; Puddephatt, R. *J. Organometallics* 1990, 9, 1336.

AA'A''XX' spin system. This pattern is typical of those observed for symmetrical $[\text{Rh}_2(\text{dmpm})_2]^{33,34}$ and $[\text{Rh}_2(\text{dppm})_2]^{29,30}$ complexes. The methyl protons (ca. δ 1.6) and methylene protons (ca. δ 2.8) of the dmpm ligands appear in the ^1H NMR spectra as either one or two resonances depending on whether each side of the plane defined by the Rh_2P_4 framework of the complex is the same as in 1 and 3 (one resonance) or different as in 2 (two resonances). The methyl protons belonging to the carboxylate group in 1 and 2 are present as additional resonances at ca. δ 3.60 (singlets). Complexes 2 and 3 exhibit a single resonance each for the requisite fluorine atoms of coordinated hexafluoro-2-butyne at ca. δ -55.0 in the ^{19}F NMR spectra. A single terminal CO stretch is observed in the infrared spectra for each of 1-3, and a general increase in frequency of this band (ca. 9 cm^{-1} in THF solution) is noted as each DMAD ligand is replaced by HFB. This trend reflects the greater group electronegativity of the CF_3 group relative to CO_2Me ⁵² and the greater electron-withdrawing ability of HFB over DMAD. Additional bands of note in the infrared region include those due to the carboxylate moiety of 1 and 2, ranging from 1675 to 1650 cm^{-1} . Weak bands appearing in the vicinity of 1525 to 1560 cm^{-1} have been assigned to the unsaturated carbon-carbon stretching vibrations of the alkyne ligands.

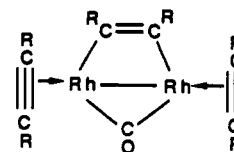
The addition of excess HFB to $[\text{Rh}_2(\text{CO})_2(\mu\text{-HFB})(\text{dmpm})_2]$ was originally investigated as a means of preparing the bis(alkyne) complex 4 and in an attempt to induce the coupling of alkyne molecules. Neither of these objectives was initially achieved. The reaction instead involves the coordination of two additional alkyne units and loss of CO from the starting material to yield the unusual species $[\text{Rh}_2(\eta^2\text{-HFB})_2(\mu\text{-CO})(\mu\text{-HFB})(\text{dmpm})_2]$ (4), which contains three alkyne groups (see Scheme I). The preparation of complex 4 represents one of only a few examples of a binuclear diphosphine complexes in which an alkyne molecule is terminally bonded to one metal center in an η^2 fashion¹⁸ and appears to be the only one in which three independent alkyne ligands are incorporated into a binuclear complex. The reaction appears to be quantitative, and we see no spectroscopic evidence to suggest the presence of alkyne-condensation products.

Each of the two new HFB ligands in compound 4 is coordinated to a single metal atom as a terminal, π -bound alkyne and is formally counted as a neutral 2-electron donor. In the infrared spectrum two C-C stretches for the terminally coordinated alkyne ligands appear at 1816 and 1773 cm^{-1} , approximately midway between that observed for free HFB ($\nu(\text{CC}) = 2300\text{ cm}^{-1}$, Raman)⁵³ and that of cis-dimetalated HFB (see Table I for compounds 2 and 3). These values for the η^2 -alkyne groups are also significantly higher than the value of 1577 cm^{-1} observed for the bridging HFB group in 4. Similar values have been found for the η^2 -coordinated HFB ligand in the dinuclear species $[\text{Ir}_2(\text{CO})(\eta^2\text{-HFB})(\mu\text{-S})(\mu\text{-CO})(\text{dppm})_2]$ ($\nu(\text{CC}) = 1747\text{ cm}^{-1}$)¹⁸ and $[\text{Ir}_2(\text{CO})_2(\eta^2\text{-HFB})(\text{P}(\text{O}-t\text{-Bu})_3)(\mu\text{-S}-t\text{-Bu})_2]$ ($\nu(\text{CC}) = 1765\text{ cm}^{-1}$).⁵⁴ The higher frequency C-C stretches indicate that the carbon-carbon bonds of the newly coordinated η^2 -HFB moieties retain more multiple-bond character and therefore have a much weaker interaction with the Rh centers than cis-dimetalated HFB. Consequently, compound 4 is found to undergo loss of one η^2 -HFB ligand and migration of the second η^2 -HFB into a cis-dimetalated position, yielding the bis(alkyne) complex

3 upon reaction with CO. It is clear that the tris(alkyne) species $[\text{Rh}_2(\eta^2\text{-HFB})_2(\mu\text{-CO})(\mu\text{-HFB})(\text{dmpm})_2]$ (4) is not formed from the dibridged species $[\text{Rh}_2(\text{CO})_2(\mu\text{-HFB})_2(\text{dmpm})_2]$ (3) since the reaction is not reversible. These results are consistent with the inability of the bis(alkyne) species 1-3 to react with CO once both alkyne ligands become coordinated as cis-dimetalated olefins.

Other prominent infrared vibrations of compound 4 include the bridging CO stretch at 1879 cm^{-1} (THF). An isotopic shift of this band to 1840 cm^{-1} for the ^{13}CO -enriched sample confirms the assignment. The same sample produces a single resonance in the CO region of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at δ 201.56 (triplet). The chemical shift and one-bond C-Rh coupling value of 31.1 Hz is typical of those observed for other CO-bridged dirhodium complexes.²¹

The presence of three resonances, all of equal intensity, in the ^{19}F NMR spectrum of 4 implies a lack of rotation of the two new HFB ligands about the alkyne-metal vector and defines the orientation of the two η^2 -HFB ligands as perpendicular to the P-Rh-P vector.



Thus, each CF_3 group on the two terminally bound HFB ligands remains in a distinct environment, one being on the same side of the complex as the bridging CO and the other on the same side as the cis-dimetalated olefin, giving rise to a total of two resonances. The fact that these two resonances appear as broad singlets and not resolved quartets (even at $-70\text{ }^\circ\text{C}$) implies that the intraligand F-F coupling is too small to be resolved. The third resonance is assigned to the two CF_3 groups on the cis-dimetalated HFB ligand. These data are consistent with the hypothesis that the two η^2 -HFB ligands adopt a configuration which is perpendicular to the " Rh_2P_4 " plane in order to minimize contact with the dmpm ligands.

As noted, $[\text{Rh}_2(\eta^2\text{-HFB})_2(\mu\text{-CO})(\mu\text{-HFB})(\text{dmpm})_2]$ (4) loses 1 equiv of HFB slowly under a CO atmosphere yielding the bis(alkyne) product 3, as shown in Scheme I. There is no spectroscopic evidence to suggest the loss of two HFB ligands from compound 4 to yield the original starting material, $[\text{Rh}_2(\text{CO})_2(\mu\text{-HFB})(\text{dmpm})_2]$, during the reaction. The mild conditions under which HFB is lost is reminiscent of the behavior exhibited by the related species $[\text{Ir}_2(\text{CO})_2(\eta^2\text{-HFB})(\mu\text{-S})(\mu\text{-CO})(\text{dppm})_2]$, which loses HFB upon reflux in CH_2Cl_2 .¹⁸ This lability appears to be restricted to η^2 -alkynes since the removal of cis-dimetalated olefin ligands in general has not been observed for binuclear diphosphine complexes.^{12f,20} In fact, the reaction of $[\text{Rh}_2\text{Cl}_2(\mu\text{-CH}_2)(\mu\text{-HFB})(\text{dppm})_2]$ with PMe_3 resulted in the loss of dppm but not the alkyne ligand, yielding the alkyne-bridged species $[\text{Rh}_2\text{Cl}(\mu\text{-Cl})(\mu\text{-CH}_2)(\mu\text{-HFB})(\text{PMe}_3)_3]$.²⁰

Since both metal centers of compound 4 formally have an 18-electron count, reaction with CO to yield complex 3 requires the generation of a site of unsaturation. This can result either by the dissociation of a terminal HFB ligand from 4 or by an intramolecular rearrangement. Spectroscopically monitoring the reaction mixture shows only two main products of CO addition to 4. One of these is the final product 3, which is ultimately obtained together with very minor quantities of unidentified species. The

(52) Kosower, E. M. *An Introduction to Physical Organic Chemistry*; Wiley: New York, 1968; p 49.

(53) Masklowsky, E. *Vibrational Spectra of Organometallic Compounds*; Wiley: New York, 1977; p 262 and references therein.

other is an unsymmetrical species observed at intermediate times in the reaction. This second product is tentatively assigned the formula $[\text{Rh}_2(\text{CO})_2(\eta^2\text{-HFB})(\mu\text{-HFB})(\text{dmpm})_2]$ (5) and the geometry shown in Scheme I. The $^{31}\text{P}\{^1\text{H}\}$ NMR resonance assigned to the new species ($\delta -11.4$) is a complex multiplet indicating an unsymmetrical configuration. Also consistent with the proposed geometry is the appearance of four separate resonances in the ^{19}F NMR spectrum. All are quartets of equal intensity suggesting that each end of the two HFB ligands are in different environments. On the basis of the appearance of the resonances and the magnitude of the F-F coupling values, the two at $\delta -47.08$ and -58.32 ($J_{\text{F-F}} = 15.9$ Hz) have been assigned to the CF_3 groups of the same HFB ligand. Likewise, the two resonances at $\delta -51.15$ and -53.64 ($J_{\text{F-F}} = 12.9$ Hz) belong to the second HFB ligand. The infrared spectrum of the reaction mixture reveals two intense terminal CO stretches at 2033 and 2007 cm^{-1} and two weak bands at 1776 and 1590 cm^{-1} which are attributed to C-C stretches of the coordinated alkynes. The frequencies of the latter two bands are consistent with one terminally bound HFB and one bridging HFB ligand, the former having more multiple-bond character than the latter. Complex 5 rearranges to the symmetrical product 3 as shown by the final spectra in which no signals due to the intermediate are observed. Alternate structures for 5, involving a terminal alkyne and a terminal carbonyl ligand on the same metal, are ruled out by steric considerations.

Migration of an $\eta^2\text{-HFB}$ ligand in complex 5 to a bridged position in complex 3 is interesting from the point of view that $\eta^2\text{-alkyne}$ intermediates have been proposed but never observed for the addition of alkynes to complexes such as $[\text{Ir}_2(\text{CO})_2(\mu\text{-Cl})(\text{dppm})_2][\text{BF}_4]$, which immediately generates the cis-dimetalated olefin species $[\text{Ir}_2\text{Cl}(\text{CO})_2(\mu\text{-alkyne})(\text{dppm})_2][\text{BF}_4]$ (alkyne = DMAD, HFB).^{12a} This type of rearrangement has also been reported for the binuclear iridium system involving $[\text{Ir}_2(\text{CO})_2(\eta^2\text{-HFB})(\text{P}(\text{O}-t\text{-Bu})_3)_2(\mu\text{-S}-t\text{-Bu})_2]$.⁵⁴ In contrast, attempts to induce the rearrangement of HFB in $[\text{Ir}_2(\text{CO})_2(\eta^2\text{-HFB})(\mu\text{-S})(\mu\text{-CO})(\text{dppm})_2]$,¹⁸ from terminal to bridging coordination, were unsuccessful, presumably owing to the inflexibility inherent in the system in which the bridging sulfide and diphosphine ligands do not readily move from their bridging positions. The conversion of compound 5 to complex 3 confirms that this type of rearrangement is possible in diphosphine-bridged dimers.

As yet the DMAD analogue of 4, $[\text{Rh}(\eta^2\text{-DMAD})_2(\mu\text{-CO})(\mu\text{-DMAD})(\text{dmpm})_2]$, has not been prepared. The addition of excess DMAD (ca. 30 molar equiv) to an ethanol solution of $[\text{Rh}_2(\text{CO})_2(\mu\text{-DMAD})(\text{dmpm})_2]$ leads only to the bis(alkyne) species 1. We interpret these results to mean that DMAD does not interact strongly enough with the rhodium atoms in the starting complex to displace a CO ligand, as in the reaction with HFB. This can be rationalized in terms of a less electronegative DMAD ligand (relative to HFB),⁵² which induces less π -back-bonding and therefore a weaker interaction from the rhodium atoms. Similar arguments have been used to explain the

trend in reactivity of the A-frame complexes $[\text{Rh}_2\text{X}_2(\mu\text{-L})(\mu\text{-alkyne})(\text{dppm})_2]$ (X = Cl; L = CO and SO_2 , alkyne = DMAD and HFB; X = I, L = CO and SO_2 , and alkyne = HFB)^{12f} and the facile loss of DMAD from $[\text{Ir}_2(\text{CO})_2(\eta^2\text{-DMAD})(\mu\text{-S})(\mu\text{-CO})(\text{dppm})_2]$.¹⁸

Conclusions

The utility of " $\text{Rh}_2(\text{dmpm})_2$ " chemistry in providing new types of binuclear diphosphine complexes has been realized in the preparation of the bis(alkyne) species $[\text{Rh}_2(\text{CO})_2(\mu\text{-DMAD})_2(\text{dmpm})_2]$ (1), $[\text{Rh}_2(\text{CO})_2(\mu\text{-DMAD})(\mu\text{-HFB})(\text{dmpm})_2]$ (2), and $[\text{Rh}_2(\text{CO})_2(\mu\text{-HFB})_2(\text{dmpm})_2]$ (3) and the tris(alkyne) species $[\text{Rh}(\eta^2\text{-HFB})_2(\mu\text{-CO})(\mu\text{-HFB})(\text{dmpm})_2]$ (4). In comparison, the related " $\text{Rh}_2(\text{dppm})_2$ " and " $\text{Ir}_2(\text{dppm})_2$ " systems prepared so far have shown no tendency to form such species. The variation in reactivity between dmpm and dppm systems is attributed to the difference in ligand basicity, which produces a buildup of electron density at the metal centers, and to the small steric bulk of dmpm, which allows more room for rearrangement and ligand coordination at the metal centers. Like the mono(alkyne) dppm species, the bridged alkyne moieties in the newly prepared bis(alkyne) complexes are not labile toward substitution or subsequent rearrangement, reflecting the inherent stability of the cis-dimetalated olefin form of alkyne coordination.

The structural curiosity of these bis(alkyne) compounds stems from the incorporation of two alkyne molecules and the two Rh atoms into an equatorial plane. The trans geometry of the alkyne ligands is presumably related to the site of alkyne attack at the starting material $[\text{Rh}_2(\text{CO})_2(\mu\text{-alkyne})(\text{dmpm})_2]$ (alkyne = DMAD, HFB). Other examples of bis(alkyne) species such as $[\text{Ir}(\mu\text{-HFB})(\text{NO})(\text{PPh}_3)_2]$ ⁴² contain alkynes as the only bridging ligands and appear to be much less rigid.

Like the related complex $[\text{Ir}_2(\text{CO})(\eta^2\text{-HFB})(\mu\text{-S})(\mu\text{-CO})(\text{dppm})_2]$,¹⁸ the preparation of $[\text{Rh}(\eta^2\text{-HFB})_2(\mu\text{-CO})(\mu\text{-HFB})(\text{dmpm})_2]$ (4) provides evidence for the initial terminal coordination of alkyne ligands to a metal center in their reaction with binuclear diphosphine complexes. The subsequent migration of a terminal $\eta^2\text{-HFB}$ ligand in $[\text{Rh}_2(\text{CO})_2(\eta^2\text{-HFB})(\mu\text{-HFB})(\text{dmpm})_2]$ (5) into a bridge configuration to yield $[\text{Rh}_2(\text{CO})_2(\mu\text{-HFB})_2(\text{dmpm})_2]$ (3) confirms that such rearrangements are possible about a diphosphine-bridged binuclear framework.

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Registry No. 1, 141439-01-2; 2, 141439-02-3; 3, 141439-03-4; 4, 141483-89-8; 5, 141439-04-5; DMAD, 762-42-5; HFB, 692-50-2; $[\text{Rh}_2(\text{CO})_3(\mu\text{-DMAD})(\text{dmpm})_2]$, 141439-05-6; $[\text{Rh}_2(\text{CO})_3(\text{dmpm})_2]$, 141439-06-7; $[\text{Rh}_2(\text{CO})_2(\mu\text{-HFB})(\text{dmpm})_2]$, 141439-07-8.

Supplementary Material Available: Tables of anisotropic thermal parameters and idealized hydrogen parameters (5 pages). Ordering information is given on any current masthead page.

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(54) Guilmet, E.; Maisonnat, A.; Poilblanc, R. *Organometallics* 1983, 2, 1123.