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Synthesis and Structure of the Diphenyl Binuclear Rhodium A-Frame Complex $Rh_2(\mu\text{-}CO)(Ph)_2(dmpm)_2$

D. Joe Anderson, Kurt W. Kramarz, and Richard Eisenberg*

Department of Chemistry, University of Rochester,
Rochester, New York 14627

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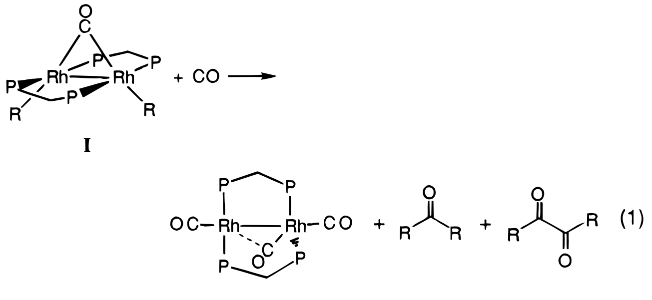
Introduction

Considerable effort has been brought to bear over the last several decades on the chemistry of binuclear complexes in which two transition metals are held in close proximity by bridging phosphine ligands.[1,2] The interest generated by these systems has focused on the search for novel structural features and reactivity not available to simpler but related mononuclear systems. Of particular interest has been the group of dppm-bridged (dppm = bis(diphenylphosphino)methane) binuclear complexes of the platinum group elements known as "A-frames".[1−10] In the context of unusual reactivity of these systems, we have previously reported the synthesis and *quantitative* carbonylation under mild conditions (eq 1) of the bis-



I

II

(1)

(alkyl) A-frame complexes $Rh_2(\mu\text{-}CO)R_2(dppm)_2$ (**I**, R = CH_3, $CH_2C_6H_5$) to produce the non-A-frame tricarbonyl complex $Rh_2(CO)_3(dppm)_2$ (**II**) and both singly and doubly carbonylated organic products RC(O)R and RC(O)C(O)R.[11−13]

The carbonylation reaction of eq 1 exhibits a number of intriguing mechanistic features. The distribution of organic carbonylated products is dependent on CO pressure, with monoketones predominating at low CO pressure (p_{CO} = 50 Torr) and diketones being the major or exclusive product at only slightly higher CO pressure (p_{CO} = 500 Torr). Crossover studies indicate an intramolecular mechanism for single carbonylation but an intermolecular mechanism for double carbonylation. The double carbonylation reaction in the presence of radical traps or H-atom donors gave products that were detectable respectively by ESR or NMR spectroscopy, thereby implicating the participation of radical species in this unusual transformation. In the course of studying the carbonylation chemistry of alkyl- and arylrhodium A-frame complexes, we synthesized a new rhodium complex which includes the diphosphine ligand dmpm (dmpm = bis(dimethylphosphino)methane). In this article, we present the synthesis and ^1H and ^{31}P NMR spectroscopic characterization of this new complex, $Rh_2(\mu\text{-}CO)(C_6H_5)_2(dmpm)_2$, as well as its X-ray crystallographic structure determination.

Experimental Section

General Considerations. All manipulations were performed under a nitrogen atmosphere using modified Schlenck techniques. All solvents were dried and distilled prior to use. Diethyl ether, THF, and benzene were distilled from dark blue or purple sodium−benzophenone ketyl solutions. Hexanes were distilled from a dark blue solution of sodium−benzophenone ketyl containing a few drops of diglyme. The ligand bis(dimethylphosphino)methane (dmpm) was used as received from Strem. $[RhCl(CO)(dmpm)]_2$ was prepared according to literature methods.[14] The Grignard reagent C_6H_5MgCl was used as received from Aldrich. NMR spectra were recorded of benzene-d_6 solutions on a Bruker AMX-400 spectrometer at 400.13 MHz (^1H) and 161.98 MHz (^{31}P). ^1H NMR chemical shifts (δ) are reported relative to TMS but were referenced to the residual proton impurity peak of benzene-d_6 at 7.15 ppm. ^{31}P chemical shifts are referenced to external 15% aqueous H_3PO_4.

$Rh_2(\mu\text{-}CO)(C_6H_5)_2(dmpm)_2$. A yellow-orange suspension of 117 mg (0.2 mmol) of $[RhCl(CO)(dmpm)]_2$ in 5 mL of benzene and 20 mL of THF in a Schlenk flask was cooled in a dry ice/acetone bath. To this suspension was added 200 μL of phenylmagnesium chloride (2 M, THF, 0.4 mmol) under N_2. Within 20 min, the orange suspension became a clear, deep orange-red solution with no visible sign of suspended matter. This solution was slowly warmed to room temperature over the course of 1 h, and then solvent was removed under vacuum. The residue was dissolved in *ca.* 20 mL of benzene, and upon addition of *ca.* 1 mL of 1,4-dioxane, a flocculent precipate formed, which was subsequently filtered out to afford a brown paste and a clear orange-red solution. Benzene was removed from this solution under vacuum, and the resulting residue was extracted with *ca.* 5 mL of 1:1 ether/hexanes solution. This solution was evaporated slowly at −30 °C to afford orange-red crystals. One of the crystals so obtained was used for the X-ray structure determination, while the rest were used for NMR measurements. ^1H NMR: 7.92, 7.40 (d, 4 H, 6.9 Hz, *o*-C_6H_5); 7.23 (t, 4 H, 7.7 Hz, *m*-C_6H_5); 7.05 (t, 2 H, 7.1 Hz, *p*-C_6H_5); 1.54 (d of virt quin, 2 H, $^2J_{HH}$ = 13.8 Hz, J_{PH} = 4.5 Hz, $(CH_3)_2PCH_2(CH_3)_2$); 1.13 (dm, 2 H, $^2J_{HH}$ = 13.8 Hz, $(CH_3)_2PCH_2(CH_3)_2$); 0.984, 0.961 (m, 24 H, $(CH_3)_2PCH_2(CH_3)_2$). ^{31}P NMR: 0.8535 (AA′A″A‴XX′, J_{RhP} = 143 Hz).

X-ray Data Collection. An orange-red prismatic crystal of molecular formula $Rh_2P_4C_{23}H_{38}O$ having approximate dimensions of 0.52 × 0.15 × 0.15 mm was mounted on a glass fiber. All measurements were made on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement of the setting angles of 25 carefully centered reflections in the range $4.00 < 2\theta < 44.00°$.

Intensity data were collected under the conditions specified in Table 1 using the $\omega/2\theta$ scan technique to a maximum 2θ value of 43.9°. ω

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Table 1. Crystallographic Data for $Rh_2(\mu\text{-}CO)(C_6H_5)_2(dmpm)_2$

chem formula	$C_{23}H_{38}OP_4Rh_2$	fw	660.26
a, Å	10.827(7)	space group	$P2_1/c$ (No. 14)
b, Å	21.047(9)	*T*, °C	−20 °C
c, Å	12.191(10)	$\lambda_{\text{Mo K}\alpha}$, Å	0.710 69 Å
β, deg	99.56(6)	ρ_{calc}, g cm^{-3}	1.601
V, Å^3	2739(2)	$R(F_o)^a$	0.026
Z	4	$R_w(F_o)^b$	0.031

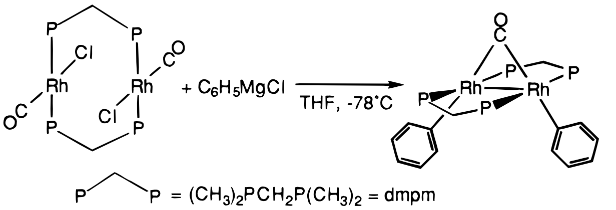
^{a} $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.29° with a take-off angle of 2.8°. Scans of (0.80 + 0.35 tan θ)° were made at speeds ranging from 2.4 to 16.5°/min (in ω). Moving-crystal/moving-counter background measurements were made by scanning an additional 25% above and below the scan range. For intense reflections an attenuator was automatically inserted in front of the detector. Of the 3683 measured reflections, 3468 were unique. The intensities of three representative reflections were measured after every 400 min of X-ray exposure time and showed no signs of decay. The data were corrected for Lorentz and polarization effects. The values for the mass attenuation coefficients are those of Creagh and Hubbel.[15] An empirical absorption correction using the program DIFABS[16] was applied which resulted in transmission factors ranging from 0.70 to 1.00.

Structure Solution and Refinement. The structure was solved by direct methods[17] and expanded using Fourier techniques.[18] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the final model but were not refined. The final cycle of full-matrix least-squares refinement[19] was based on 2710 observed reflections ($I > 3.00\sigma(I)$) and 271 variable parameters. Neutral atom scattering factors were taken from Cromer and Waber.[20] Anomalous dispersion effects were included in F_c;[21] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[22] The weighting scheme was based on counting statistics and included a factor ($p = 0.016$) to downweight the intense reflections. Plots of $\Sigma w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.40 and −0.34 e/Å^3, respectively. All calculations were performed using the teXsan[23] crystallographic software package of Molecular Structure Corp.

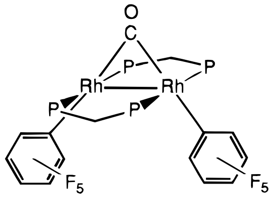
Results and Discussion

Addition of phenylmagnesium chloride to a yellow-orange suspension of $[RhCl(CO)(dmpm)]_2$ in benzene/THF at −78° C produces a bright orange-red solution (eq 2). Workup followed by crystallization from diethyl ether/hexanes affords deep orange red prismatic crystals.

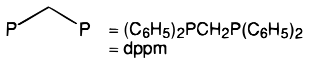


(2)

A ^1H NMR spectrum of these crystals dissolved in C_6D_6 reveals two unresolved multiplets at δ 0.98 and 0.96 ppm (24 H) for the dmpm methyl groups as well as a doublet of virtual quintets at δ 1.54 (2 H, $^2J_{HH} = 13.8$ Hz, $J_{PH} = 4.5$ Hz) and a doublet of multiplets at δ 1.13 ppm (2 H, $^2J_{HH} = 13.8$ Hz). Both sets of multiplets collapse to clean doublets upon ^{31}P decoupling. The remaining resonances in the ^1H NMR spectrum at δ 7.92 and 7.40 (d, 4 H, 6.9 Hz), 7.23 (t, 4 H, 7.7 Hz), and 7.05 (t, 2 H, 7.1 Hz) indicate the successful introduction of phenyl ligands into the metal complex. The signals at δ 7.92 and 7.40 ppm are assigned to *ortho* protons on rhodium-bound phenyl rings which are *not* free to rotate about the Rh−C bond. This assignment is supported by ^{19}F NMR spectroscopy of the bis((perfluorophenyl)rhodium) A-frame complex $Rh_2(\mu\text{-}CO)(C_6F_5)_2(dppm)_2$ (**III**) reported by Garcia *et al.*, in which the *ortho* and *meta* fluorines each exhibit two resonances.[24] Examination of the ^{31}P NMR spectrum revealed only a single resonance which displays a complex AA′A″A‴XX′ pattern consistent with an A-frame geometry.[10,25,26]



III



On the basis of the similarity of the ^1H and ^{31}P NMR spectra to those spectra of the A-frame rhodium complexes $Rh_2(\mu\text{-}CO)R_2(dppm)_2$ (R = methyl, benzyl, phenyl, *o*-tolyl) reported previously,[11−13] this product was identified as the diphenyl A-frame complex $Rh_2(\mu\text{-}CO)(C_6H_5)_2(dmpm)_2$. This assignment was confirmed by a crystal structure analysis, details of which are summarized in Table 1. An ORTEP plot of the resulting molecular structure (Figure 1) shows the A-frame geometry of the complex, in which each Rh occupies a five-coordinate environment consisting of another Rh atom, the C atom of the carbonyl bridge, the *ipso* C of a phenyl ring, and two *trans* diphosphine P atoms. Important bond distances are given in Table 2, and important bond angles are listed in Table 3.

Structural data are available for two non-A-frame binuclear Rh complexes containing a Rh−Rh bond and the dmpm ligand, $[RhCl(dmpm)((C_5H_6)_2P(C_6H_4))]_2$ (**IV**)[27] and $[RhCl_2(CO)(dmpm)]_2$ (**V**)[14] (Chart 1). Structural data are also available for five A-frame complexes of the general type **A** (M = Rh), in which two Rh centers are joined by a metal−metal bond (**VI**−**X**, Table 4).[10,14,26,28,29] While the Rh−Rh bond length of 2.8254 Å in

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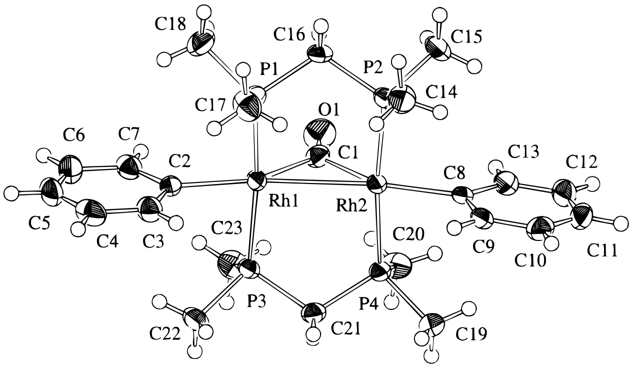


Figure 1. ORTEP view of $Rh_2(\mu\text{-}CO)(C_6H_5)_2(dmpm)_2$. Thermal ellipsoids for non-hydrogen atoms are shown at the 50% probability level.

Table 2. Selected Bond Lengths (Å) for $Rh_2(\mu\text{-}CO)(C_6H_5)_2(dmpm)_2$

Rh(1)−Rh(2)	2.8254(5)	Rh(1)−P(1)	2.285(1)
Rh(1)−P(3)	2.293(1)	Rh(1)−C(1)	1.969(5)
Rh(1)−C(2)	2.066(5)	Rh(2)−P(2)	2.279(1)
Rh(2)−P(4)	2.291(1)	Rh(2)−C(1)	1.987(5)
Rh(2)−C(8)	2.072(5)	P(1)−C(16)	1.833(5)
P(4)−C(21)	1.841(5)	O(1)−C(1)	1.188(6)
C(2)−C(3)	1.424(7)	C(2)−C(7)	1.380(7)
C(3)−C(4)	1.397(7)	C(4)−C(5)	1.385(8)
C(5)−C(6)	1.369(8)	C(6)−C(7)	1.393(7)
C(8)−C(9)	1.406(7)	C(8)−C(13)	1.396(6)
C(9)−C(10)	1.404(7)	C(10)−C(11)	1.372(7)
C(11)−C(12)	1.384(8)	C(12)−C(13)	1.391(7)

Table 3. Selected Bond Angles (deg) for $Rh_2(\mu\text{-}CO)(C_6H_5)_2(dmpm)_2$

Rh(2)−Rh(1)−P(1)	92.03(4)	Rh(2)−Rh(1)−P(3)	93.35(4)
Rh(2)−Rh(1)−C(1)	44.7(1)	Rh(2)−Rh(1)−C(2)	166.2(1)
P(1)−Rh(1)−P(3)	172.97(5)	P(1)−Rh(1)−C(1)	95.1(1)
P(1)−Rh(1)−C(2)	86.1(1)	P(3)−Rh(1)−C(1)	91.9(1)
P(3)−Rh(1)−C(2)	87.6(1)	C(1)−Rh(1)−C(2)	149.1(2)
Rh(1)−Rh(2)−P(2)	93.35(4)	Rh(1)−Rh(2)−P(4)	92.97(3)
Rh(1)−Rh(2)−C(1)	44.2(1)	Rh(1)−Rh(2)−C(8)	166.6(1)
P(2)−Rh(2)−P(4)	173.68(5)	P(2)−Rh(2)−C(1)	93.7(1)
P(2)−Rh(2)−C(8)	86.2(1)	P(4)−Rh(2)−C(1)	90.7(1)
P(4)−Rh(2)−C(8)	87.6(1)	C(1)−Rh(2)−C(8)	149.2(2)
Rh(1)−P(1)−C(16)	114.5(2)	Rh(2)−P(2)−C(16)	114.5(2)
Rh(1)−P(3)−C(21)	115.2(2)	Rh(2)−P(4)−C(21)	115.3(2)
Rh(1)−C(1)−Rh(2)	91.2(2)	Rh(1)−C(1)−O(1)	135.6(4)
Rh(2)−C(1)−O(1)	133.2(4)	Rh(1)−C(2)−C(3)	122.7(4)
Rh(1)−C(2)−C(7)	122.3(4)	C(3)−C(2)−C(7)	115.0(4)
C(2)−C(3)−C(4)	122.1(5)	C(3)−C(4)−C(5)	119.8(5)
C(4)−C(5)−C(6)	119.4(5)	C(5)−C(6)−C(7)	120.2(5)
C(2)−C(7)−C(6)	123.5(5)	Rh(2)−C(8)−C(9)	123.4(3)
Rh(2)−C(8)−C(13)	122.1(4)	C(9)−C(8)−C(13)	114.4(4)
C(8)−C(9)−C(10)	122.9(5)	C(9)−C(10)−C(11)	120.1(5)
C(10)−C(11)−C(12)	119.0(5)	C(11)−C(12)−C(13)	120.2(5)
C(8)−C(13)−C(12)	123.4(5)		

the present structure is significantly longer than that for other A-frame complexes tabulated in Table 4, it nonetheless represents a Rh−Rh single-bond distance. A-Frame structures of Rh(I) in which a metal−metal bond does not exist have significantly longer Rh···Rh separations: 3.155(4) Å for $Rh_2(\mu\text{-}S)(CO)_2(dppm)_2$,[9] 3.011(1) Å for $Rh_2(\mu\text{-}CC(C_6H_5))(CO)_2(dppm)_2$,[31] 3.0637(3) Å for $Rh_2(\mu\text{-}N(p\text{-}NO_2C_6H_4))(CO)_2(dppm)_2$,[3] and 3.082(1) Å for $Rh_2(\mu\text{-}O)(CO)_2(dppm)_2$.[3]

The phenyl ligand Rh−C bond lengths for $Rh_2(\mu\text{-}CO)(C_6H_5)_2(dmpm)_2$ are essentially identical to those in $[RhCl(dmpm)((C_5H_6)_2P(C_6H_4))]_2$. The phenyl rings are also coplanar with the rhodium atoms and carbonyl bridge, with torsion angles between the Rh−C bonds of the carbonyl bridge and the phenyl rings of 1.5(6)° (C(1)−Rh(1)−C(2)−C(7)) and −6.2(6)° (C(1)−Rh(2)−C(8)−C(13)).

Chart 1

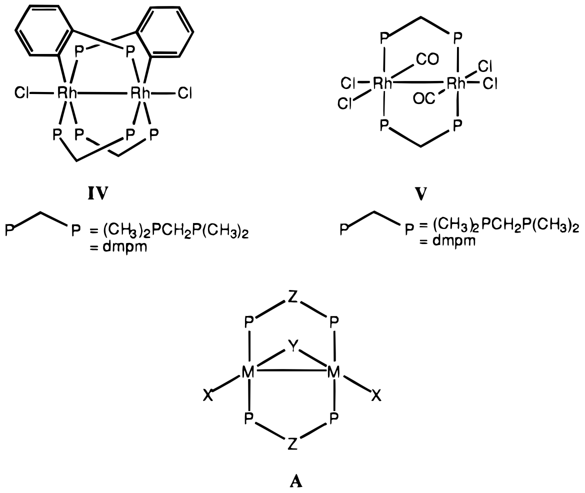
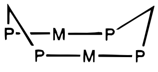


Table 5 lists several important bond angles for the A-frame "skeleton" of $Rh_2(\mu\text{-}CO)(C_6H_5)_2(dmpm)_2$ and compares them with the same angles in the closely related dihalide A-frames $Rh_2(\mu\text{-}CO)(X)_2(dppm)_2$ (X = Br, Cl).[26,30] Although a slight asymmetry in the carbonyl bridge can be seen in the Rh−C−O angles for $Rh_2(\mu\text{-}CO)(C_6H_5)_2(dmpm)_2$, nearly all the angles compare favorably with those in the dihalide A-frame structures. Of particular note are the Rh−Rh−C(phenyl) angles 166.6(1) and 166.2(1)°, which are very similar to the corresponding Rh−Rh−X angles for the dihalide A-frames, demonstrating the lack of steric interaction between the phenyl ligands of the complex. This lack of interaction between the phenyl groups is apparent in Figure 1 and suggests that the hindered phenyl rotation that manifests itself as separate *ortho* ^1H NMR resonances results from interaction between the phenyl groups and the methyls of the dmpm ligands.

A more subtle structural difference between $Rh_2(\mu\text{-}CO)(C_6H_5)_2(dmpm)_2$ and the majority of binuclear bis(diphosphine) A-frame complexes lies in the conformation of the eight-membered $M_2P_4C_2$ ring. Nearly all binuclear bis(diphosphine) A-frame complexes with or without M−M bonds exhibit a boatlike structure (**B**), in which methylene carbons of the diphosphine ligands both point in the same direction as the A-frame bridgehead ligand.[32,33] In contrast, a chairlike structure is seen for the $Rh_2P_4C_2$ ring in $Rh_2(\mu\text{-}CO)(C_6H_5)_2(dmpm)_2$ (Figure 2). A similar conformation is seen only in the palladium A-frames $Pd_2Cl_2(\mu\text{-}CO)(dmpm)_2$[34] and $Pd_2(\mu\text{-}CO)(OC(O)CF_3)_2$-



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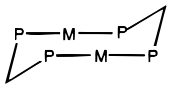

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(32) For purposes of comparison, the Cambridge Crystal Structure Database (see ref 33) was searched for complexes of the general type **A** (see text) in which M = a metal from group 8, 9, or 10. A-frames with multiple atoms in the bridge position Y (*e.g.*, 1,2-alkynyl but not 1,1-carbonyl) were somewhat arbitrarily excluded, as were complexes in which the coordination number about the metal was greater than 5. Phosphine substituents (*e.g.*, methyl, phenyl, or fluoro), the bis(phosphine) bridge Z, and the ligands X were left unspecified. With these criteria, 51 structures were found to have a boat configuration, while only 3 were found with a chairlike configuration.

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Table 4. Comparative Bond Lengths for Rh_2(diphosphine)$_2$ Complexes[a]

			Rh−C			
	Rh−Rh	Rh−P	phenyl	carbonyl	C−O	ref
$Rh_2(\mu\text{-CO})Ph_2(dmpm)_2$	2.8245(4)	2.287(6)	2.069(5)	1.98(1)	1.188(6)	this work
$[RhCl(dmpm)((C_6H_5)_2P(C_6H_4))]_2$ (**IV**)	2.770(3)	2.34(3)[b]	2.08(2)			27
$Rh_2(\mu\text{-CO})(Cl)_2(dppm)_2$ (**V**)	2.724(3)	2.306(9)		1.90(3)	1.22(3)	30
$Rh_2(\mu\text{-CO})(Br)_2(dppm)_2$ (**VI**)	2.7566(8)	2.317(11)		1.960(8)	1.167(9)	26
$[RhCl_2(CO)(dmpm)]_2$ (**VII**)	2.759(5)	2.345(9)				14
$Rh_2(\mu\text{-SO}_2)(Cl)_2(dppm)_2$ (**VIII**)	2.7838(8)	2.331(9)				28
$Rh_2(\mu\text{-CO})(Cl)_2(dppee)_2$ (**IX**)	2.651(14)	2.28(6)		1.77(9)	nr	29
$[Rh(CO)RhMe(\mu\text{-CO})(dppm)_2]^+$ (**X**)	2.821(2)	2.316(5)		1.9(1)	1.13(1)	10

[a] dmpm = bis(dimethylphosphino)methane, dppm = bis(diphenylphosphino)methane, dppee = 1,1-bis(diphenylphosphino)ethene; nr = not reported. Values for Rh−P and Rh−C bonds are averages, the uncertainty in which is given as the largest among the individual bond lengths reported or the estimated standard deviation for the mean bond length. [b] These bonds are grouped into three distinct types for two dmpm P atoms *trans* to tris(aryl)phosphine P atoms (2.310(11) Å), two dmpm P atoms *trans* to phenyl C atoms (2.383(8) Å), and two tris(aryl)phosphine P atoms *trans* to dmpm P atoms (2.337(11) Å).

Table 5. Comparative Bond Angles (deg) for the A-Frame Complexes $Rh_2(\mu\text{-CO})X_2$(diphosphine)$_2$ (X = C_6H_5, Cl, Br)

	$Rh_2(\mu\text{-CO})Ph_2(dmpm)_2$[a]	$Rh_2(\mu\text{-CO})Cl_2(dppm)_2$[b] (**V**)	$Rh_2(\mu\text{-CO})Br_2(dppm)_2$[c] (**VI**)
Rh(2)−Rh(1)−C(1)	44.7(1)	44.1(9)	45.3(2)
X(1)−Rh(1)−Rh(2)	166.2(1)	162.3(3)	167.06(4)
X(1)−Rh(1)−C(1)	149.1(2)	154(1)	147.6(2)
Rh(1)−C(1)−O	135.6(4)	136(2)	135.3(6)
Rh(1)−Rh(2)−C(1)	44.2(1)	44(1)	45.2(2)
X(2)−Rh(2)−Rh(1)	166.6(1)	160.6(3)	165.45(5)
X(2)−Rh(2)−C(1)[c]	149.2(2)	155(1)	149..2(2)
Rh(2)−C(1)−O	133.2(4)	133(2)	135.3(6)
Rh(1)−C(1)−Rh(2)	91.2(2)	92(1)	89.4(4)

[a] dmpm = bis(dimethylphosphino)methane. For angle measurements in $Rh_2(\mu\text{-CO})Ph_2(dmpm)_2$, atoms X(1) and X(2) are the *ipso* carbons of each of the two phenyl rings. [b] dppm = bis(diphenylphosphino)methane. From reference 30. [c] From reference 26.

$(dppm)_2$[35] and in the A-framelike portion of the trinuclear complex $[Rh_3(\mu^3\text{-dmmmm})_2(\mu\text{-Cl})(CO)_3Cl][BPh_4]$ (dmmmm = bis(dimethylphosphinomethyl)methylphosphine).[36] For dppm-bridged systems, the overwhelmingly favored conformation is the boat (**B**). The existence of the boatlike conformation for the dmpm A-frame $[Ir_2(\mu^2\text{-CH}_3)(CO)_2(dmpm)_2][CF_3SO_3]$[37] and the chairlike conformation of the dppm A-frame $Pd_2(\mu\text{-CO})(OC(O)CF_3)_2(dppm)_2$ makes it difficult to unconditionally ascribe these conformational variations to electronic or steric effects from the diphosphine ligand substituents. However, given the rarity of chairlike conformations in the many dppm-bridged A-frame structures known, it can be concluded that steric demands of phenyl substituents on dppm ligands disfavor the chairlike conformation of the $M_2P_4C_2$ ring in contrast to what is observed for the title complex.

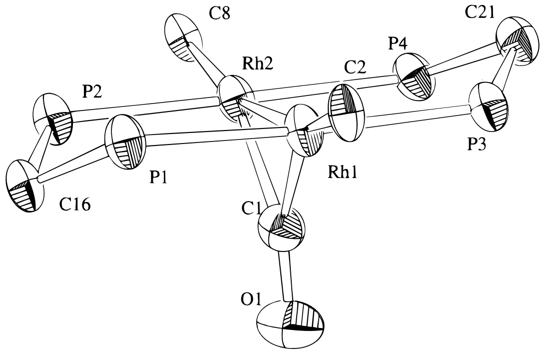

Figure 2. ORTEP view of $Rh_2(\mu\text{-CO})(C_6H_5)_2(dmpm)_2$ showing the chairlike conformation of the eight-membered $Rh_2P_4C_2$ ring. Thermal ellipsoids are shown at the 50% probability level. Methyl groups, hydrogen atoms, and all but one carbon atom for each of the phenyl rings have been omitted for clarity.

Despite the slight differences in Rh−Rh bond length and diphosphine conformation between $Rh_2(\mu\text{-CO})(C_6H_5)_2(dmpm)_2$ and structurally similar compounds, the overall geometry of $Rh_2(\mu\text{-CO})(C_6H_5)_2(dmpm)_2$ is unquestionably that of an A-frame. The structural and spectroscopic data presented above provide good evidence in support of the same structural assignments for the complexes $Rh_2(\mu\text{-CO})(R)_2(dppm)_2$ (R = CH_3, $CH_2C_6H_5$, C_6H_5, $o\text{-}C_6H_4CH_3$),[11−13] which were based previously on spectroscopic evidence alone.

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Supporting Information Available: Tables of crystal data, positional and thermal parameters, anisotropic displacement parameters, complete bond distances and angles, and selected torsion angles and least-squares planes (12 pages). Ordering information is given on any current masthead page.

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