Both compounds show deviation from tetrahedral angles about the amine nitrogens (N(3) and N(4)) with the external C–N–C angles opening to nearly 120° to facilitate the tetradentate coordination. In both cases the M–N–O angles are slightly larger (≈122°) than the "ideal" 120° $sp^2$ angle which tends to slightly lengthen the hydrogen bond. Other bond angles in the two cases are also very similar. The bond distances in the two compounds are generally in agreement except for the oxime N–O distances (average 1.383 Å in this complex and average 1.356 Å in the Ni complex) and the adjacent N(oxime)–C distances (average 1.271 Å in this complex and average 1.288 Å in the nickel complex). The apparent shift in the multiple bonding from the N–O toward C–N bond in this complex may be a result of the longer hydrogen bond (O···O, 2.698 Å) in this complex compared with the case of the nickel complex (2.474 Å). The longer N–O distance (1.398 Å) involves the oxygen to which the hydrogen atom is bonded in a nearly covalent fashion (O–H, 0.75 Å from difference Fourier position). The other O–H distance is 1.95 Å. The hydrogen bond in this complex is much longer than that in any other α-amine oxime complex we have studied. This may be partially due to the steric requirements of the ligand with the larger Cu(II) metal but is probably also partially a result of the dimerization which involves coordination of one of the hydrogen bond oxime oxygens with the copper. Attempts are under way to obtain single crystals with some other better coordinating anion replacing the perchlorate ion in hopes of obtaining a monomer.

**Acknowledgment.** Financial support of the National Science Foundation (Grant CHE77-08325) is gratefully acknowledged.

**Registry No.** $[Cu(EnAO\text{-}H)]_2(ClO_4)_2$, 68492-44-4.

**Supplementary Material Available:** Hydrogen atom positional parameters and a listing of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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# Structure of $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2][B(C_6H_5)_4]$: An "A-Frame" Complex Having a Carbonyl Ligand Coordinated in the Proposed Active Site

MARTIN COWIE

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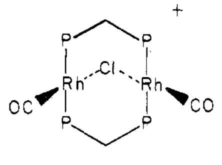
The facile, reversible reaction of the "A-frame" complex $[Rh_2(CO)_2(\mu\text{-}Cl)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]^+$ with carbon monoxide yields the tricarbonyl species $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]^+$. An X-ray crystallographic study on the tricarbonyl species indicates that one carbonyl ligand is coordinated in the proposed active site of the parent "A-frame" complex, bridging the two rhodium atoms, verifying that small unsaturated molecules can coordinate at this active site. The tricarbonyl species crystallizes in the space group $C_i^1$-$P\bar{1}$ in a cell of dimensions $a$ = 14.451 (2) Å, $b$ = 17.661 (2) Å, $c$ = 13.726 (1) Å, $\alpha$ = 102.06 (1)°, $\beta$ = 95.59 (1)°, and $\gamma$ = 75.56 (1)° with $Z$ = 2. On the basis of 8097 unique reflections, the structure was refined by full-matrix least-squares techniques to agreement indices of $R$ = 0.063 and $R_w$ = 0.099. Some relevant metrical parameters are Rh–P(av) = 2.333 (8) Å, Rh–C(terminal) = 1.831 (7) and 1.836 (7) Å, Rh–C(bridging) = 2.104 (7) and 2.034 (7) Å, Rh–Cl = 2.575 (2) and 2.607 (2) Å, C–O(terminal) = 1.139 (8) and 1.139 (8) Å, C–O(bridging) = 1.172 (8) Å, Rh–C–Rh = 86.7 (3)°, and Rh–Cl–Rh = 66.51 (4)°.

## Introduction

Binuclear metal complexes in which the metals are held in close proximity are of considerable interest owing, in part, to their potential utility as simple models for multicentered metal catalysts.[1] In these binuclear complexes the metals can act independently of each other, reacting essentially as two monomeric units, or one metal center can perturb the other, thereby altering its chemistry relative to the related mononuclear metal complex. Balch and co-workers[2] have carried out studies in this regard, relating the chemistry at the metal centers to the distances between the metals, utilizing diphosphine and other bidentate ligands of various bite sizes bridging two square-planar Rh(I) centers.

One particularly interesting class of binuclear metal complexes having the metals in close proximity are the so-called "A-frame" complexes.[3] Several such complexes have been reported,[3-7] one being $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2][BPh_4]$,[4] **1** (Ph = $C_6H_5$, DPM = $Ph_2PCH_2PPh_2$), the frame of which is diagrammed below:



In complexes of this type several coordination possibilities exist. Small molecules can coordinate in the proposed[3] active site, between the two metal atoms, opposite the bridging chloro ligand, or to either or both metals on the sides of the metals remote from the active site. In any case the proximity of the

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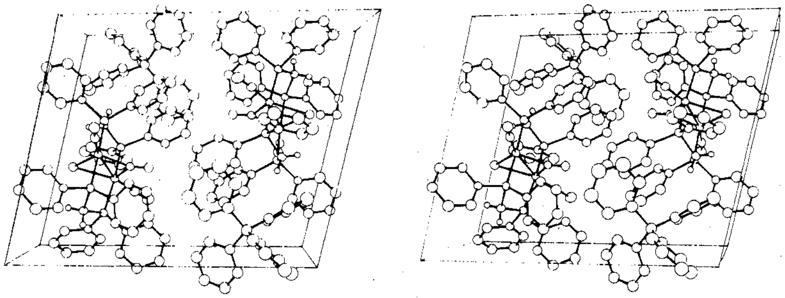

**Figure 1.** Stereoview of the cell of $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2][BPh_4]$. The *y* axis is horizontal to the right, the *x* axis runs from bottom to top and, the *z* axis goes into the page; 20% vibrational ellipsoids are used on all drawings for all atoms except methylene hydrogens which are drawn artificially small.

metal centers allows the possibility of chemistry significantly different from that of the analogous simple, four-coordinate Rh(I) monomeric species.

Reactions of **1** with small unsaturated molecules (CO,[4] NO,[8] $SO_2$,[9] $N_2Ph^+$[8]) yield products which seem to have these ligands coordinated in the active site, bridging the two metals. In support of this, the infrared spectrum of the tricarbonyl species obtained from the reaction of **1** and CO shows a new band at 1863 $cm^{-1}$ (Nujol), consistent with a bridging carbonyl ligand.[4] The X-ray structural determination of this tricarbonyl species was therefore undertaken to verify the proposed structure and to gain further structural information about this relatively new class of complexes. A preliminary report of this work has appeared.[4]

## Experimental Section

Orange crystals of the title compound, suitable for single-crystal X-ray diffraction studies, were supplied by Dr. A. R. Sanger of the Alberta Research Council. Preliminary film data showed $\bar{1}$ Lauë symmetry and no systematic absences, consistent with either of the space groups $P1$ or $P\bar{1}$. The centrosymmetric space group was chosen and later verified by (1) the successful refinement of the structure with acceptable positional parameters, thermal parameters, and agreement indices and (2) the location of all hydrogen atoms in difference Fourier syntheses. Accurate cell parameters were obtained by a least-squares analysis of 12 carefully centered reflections chosen from diverse regions of reciprocal space ($55° \leq 2\theta \leq 65°$, Cu K$\alpha$ radiation) and obtained using a narrow X-ray source. See Table I for pertinent crystal data. A cell reduction[10] failed to show the presence of higher symmetry. The reduced cell is reported.

Data were collected by the $\theta$–$2\theta$ scan method on a Picker four-circle automated diffractometer equipped with a scintillation counter and a pulse-height analyzer, tuned to accept 90% of the Cu K$\alpha$ peak. Background counts were measured at both ends of the scan range with stationary counter and crystal. Two crystals were used in the data collection. The intensities of three standard reflections were measured every 100 reflections. In addition four other standards were measured three times a day. All standards decreased by approximately 10% for the first crystal and 15% for the second crystal over the duration of the data collection. The observed intensities were corrected for this apparent decomposition.

The intensities of 9390 unique reflections ($2° \leq 2\theta \leq 120°$) were measured using Cu K$\alpha$ radiation. Data were processed in the usual manner using a value of 0.05 for $p$.[11] A total of 8097 reflections had $F_o^2 \geq 3\sigma(F_o^2)$ and were used in subsequent calculations. Absorption corrections were applied to the data using Gaussian integration.[12]

## Structure Solution and Refinement

The positions of the two independent Rh atoms were obtained from a sharpened Patterson synthesis. Subsequent refinements and difference Fourier calculations led to the location of all other atoms. Atomic scattering factors were taken from Cromer and Waber's tabulation[13] for all atoms except hydrogen for which the values of Stewart et al.[14] were used. Anomalous dispersion terms[15] for Rh, Cl, and P were included in $F_c$. All phenyl groups were refined as rigid groups having $D_{6h}$ symmetry and C–C distances of 1.392 Å. The carbon atoms in these groups were given independent, isotropic thermal parameters. The hydrogen atoms were included as fixed contributions and were not refined. Their idealized positions were calculated from the geometries about the attached carbon atoms using C–H distances of 0.95 Å. Hydrogen atoms were given isotropic thermal parameters of 1 $Å^2$ greater than their attached carbon atom. All other nongroup atoms were refined individually with anisotropic thermal parameters. The final model with 291 parameters varied converged to $R = 0.063$ and $R_w = 0.099$.[16] In a final difference Fourier map all of the highest 20 residuals were in the vicinity of the phenyl groups (0.83–0.41 e/$Å^3$). A typical carbon atom on earlier syntheses had an electron density of about 3.3 e/$Å^3$. On the basis of residuals about the phenyl groups and the high thermal parameters of some of these group atoms, it seems that an anisotropic refinement of the phenyl carbon atoms would have been more suitable. However, because of the very high cost and the feeling that no significant change in the parameters of interest would result, this was not attempted.

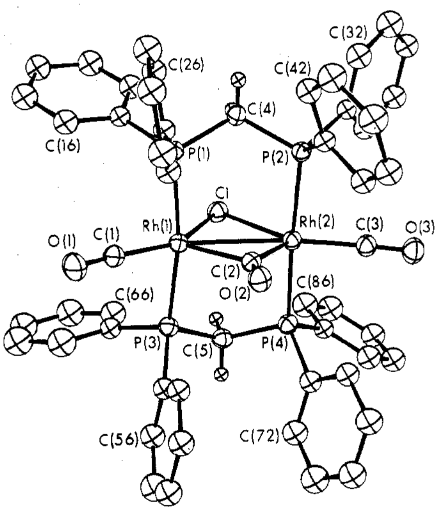

**Figure 2.** Perspective view of the $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]^+$ cation showing the numbering scheme. The numbering on phenyl carbon atoms starts at the carbon bonded to phosphorus and increases sequentially around the ring.

The final positional and thermal parameters of the groups and the nonhydrogen atoms are given in Tables II and III. The derived hydrogen positions and their thermal parameters, the root-mean-square amplitudes of vibration of the individual nonhydrogen atoms, and a listing of observed and calculated structure amplitudes used in the refinements are available.[17]

## Discussion

The unit cell of $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2][BPh_4]$, shown in Figure 1, contains discrete, well-separated anions and cations. Figure 2 presents a perspective view of the cation including the numbering scheme (phenyl hydrogen atoms have the same number as their attached carbon atom). The inner coordination sphere of the cation is shown in Figure 3 along with some relevant bond lengths.

The tetraphenylborate anion is not unusual, having a slightly distorted tetrahedral configuration about the boron atom. The B–C distances, shown in Table IV (average 1.695 (11) Å) agree with each other and with other determinations,[18] and

**Table I.** Summary of Crystal Data and Intensity Collection

| | |
|---|---|
| compound | $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2][BPh_4]$ |
| formula wt | 1413.3 |
| formula | $Rh_2P_4O_3ClBC_{77}H_{64}$ |
| reduced cell parameters | |
| *a* | 14.451 (2) Å |
| *b* | 17.661 (2) Å |
| *c* | 13.726 (1) Å |
| α | 102.06 (1)° |
| β | 95.59 (1)° |
| γ | 75.56 (1)° |
| *V* | 3313.8 Å$^3$ |
| *Z* | 2 |
| density | 1.416 (calcd), 1.40 (2) g/cm$^3$ (exptl by flotation) |
| space group | $C_i^1$–$P\bar{1}$ |
| crystal dimensions | (1) 0.154 × 0.485 × 0.308 mm<br>(2) 0.170 × 0.456 × 0.276 mm |
| crystal shape | triclinic prisms with faces of the forms {100}, {010}, {001}, {110}, {101}, {011} |
| crystal vol | (1) 0.0182 mm$^3$<br>(2) 0.0160 mm$^3$ |
| temp | 20 °C |
| radiation | Cu Kα (λ 1.540 562 Å) filtered with 0.5 mil thick nickel foil |
| μ | 57.982 cm$^{-1}$ |
| range in absorption corr factors (applied to $F_o$) | (1) 0.464–0.669<br>(2) 0.499–0.689 |
| receiving aperture | 4 × 4 mm, 30 cm from crystal |
| takeoff angle | 3.8° |
| scan speed | 2° in 2θ/min |
| scan range | 2θ < 99.50°, 0.95° below Kα, to 0.95° above Kα$_2$; 2θ > 99.50°, 1.00° below Kα, to 1.00° above Kα$_2$ |
| bkgd counts | 2θ ⩽ 83.00°, 20 s; 2θ > 83.00°, 40 s |
| 2θ limits | 2.0–120.0° |
| final no. of variables | 291 |
| unique data used ($F_o^2 \geqslant 3\sigma(F_o^2)$) | 8097 |
| error in observn of unit wt | 2.542 electrons |
| *R* | 0.063 |
| $R_w$ | 0.099 |

the C–B–C angles (Table V) are all close to the expected tetrahedral values. The small distortions present are no doubt a result of packing forces.

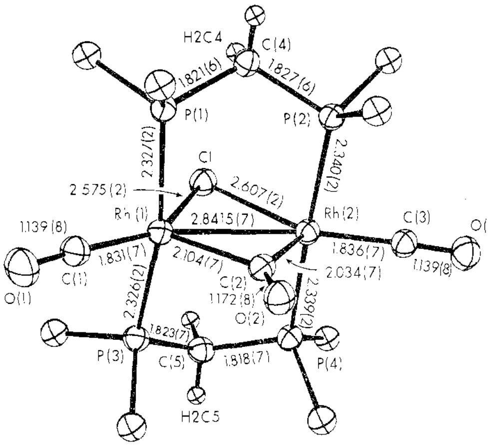

**Figure 3.** Inner coordination sphere of the $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]^+$ cation showing some relevant bond lengths. Only the first carbon atom of each phenyl ring is shown.

In the $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]^+$ cation the two Rh(I) centers are bridged by two bis(diphenylphosphino)methane ligands (DPM) which are opposite each other (transoid). The metal coordinations are completed, in the equatorial plane, approximately perpendicular to the metal–phosphorus vectors, by a bridging chloro and a bridging carbonyl ligand and by one terminal carbonyl ligand on each metal. In addition there is a Rh–Rh single bond. Excluding this Rh–Rh bond, the coordination geometries of the Rh atoms are best described as distorted trigonal bipyramids sharing a common edge (at C(2) and Cl). The metal–metal bond bisects the Cl–Rh–C(2) angles. The terminal carbonyl ligands are almost trans to the Rh–Rh bond but are bent toward the bridging CO and away from the bridging Cl by about 18°.

The Rh–Rh distance (2.8415 (7) Å) is consistent with a Rh–Rh single bond, although it is slightly longer than typical Rh–Rh single-bond distances which range from 2.617 (3) to 2.796 (8) Å.[19–23] However, weak Rh–Rh interactions have been postulated in dimeric systems in which the Rh–Rh separation is as high as 3.167 (1) Å.[24–26] The presence of a Rh–Rh bond is further substantiated by several other structural parameters: (1) the acute Rh(1)–Cl–Rh(2) angle of 66.51 (4)° is significantly less than the values of ca. 80–95° which are typically observed when no formal Rh–Rh bond is present;[24,25,27,28] (2) the acute Rh(1)–C(2)–Rh(2) angle of 86.7 (3)° compares well with other values reported for carbonyls bridging Rh–Rh bonds[20–23] and is in contrast to the only example reported[6] where a carbonyl ligand bridges two metals which are not bonded in which the Pd–C–Pd angle is 119 (3)°; (3) the Rh–Rh separation is significantly less than the intraligand P–P separations of 3.068 (2) and 3.056 (2) Å, whereas in $Rh_2Cl_2(CO)_2(DAM)_2$[29] (DAM = bis(diphenylarsino)methane), where the metals are not bonded, the reverse is true (Rh–Rh = 3.396 (1) Å and As–As = 3.288 Å). In

**Table II.** Positional and Thermal Parameters for Nongroup Atoms of $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2][BPh_4]$

| atom | $x^a$ | $y$ | $z$ | $U_{11}{}^b$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Rh(1) | 0.33627 (3) | 0.26288 (3) | 0.49057 (3) | 5.46 (4) | 5.85 (5) | 5.66 (4) | −1.80 (2) | 0.43 (2) | 0.78 (2) |
| Rh(2) | 0.44357 (3) | 0.19884 (3) | 0.31708 (3) | 5.35 (4) | 5.92 (4) | 5.86 (4) | −1.81 (2) | 0.65 (2) | 0.93 (2) |
| P(1) | 0.1906 (1) | 0.2578 (1) | 0.4039 (1) | 5.59 (9) | 6.09 (10) | 5.98 (10) | −1.75 (7) | 0.84 (7) | 0.74 (7) |
| P(2) | 0.3040 (1) | 0.2060 (1) | 0.2140 (1) | 5.90 (10) | 5.68 (10) | 5.74 (9) | −1.66 (7) | 0.69 (7) | 0.80 (7) |
| P(3) | 0.4711 (1) | 0.2523 (1) | 0.5989 (1) | 6.48 (10) | 6.16 (10) | 6.05 (10) | −2.02 (8) | 0.16 (8) | 1.38 (8) |
| P(4) | 0.5877 (1) | 0.1862 (1) | 0.4128 (1) | 5.58 (10) | 6.35 (11) | 7.10 (11) | −1.94 (8) | 0.41 (8) | 1.36 (8) |
| Cl | 0.3879 (1) | 0.1122 (1) | 0.4215 (1) | 7.20 (10) | 6.77 (11) | 7.92 (11) | −2.49 (8) | 0.40 (8) | 1.68 (8) |
| C(1) | 0.2735 (5) | 0.3384 (5) | 0.5904 (6) | 6.3 (4) | 9.0 (5) | 7.5 (5) | −1.3 (4) | 1.2 (4) | −0.8 (4) |
| C(2) | 0.3893 (5) | 0.3126 (4) | 0.3875 (5) | 6.0 (4) | 7.0 (5) | 5.6 (4) | −2.1 (3) | 0.4 (3) | 0.8 (3) |
| C(3) | 0.5127 (5) | 0.1831 (4) | 0.2062 (5) | 6.7 (4) | 7.5 (5) | 7.1 (4) | −2.8 (3) | 1.1 (4) | 0.6 (3) |
| C(4) | 0.2063 (5) | 0.1949 (4) | 0.2806 (5) | 6.1 (4) | 6.7 (4) | 5.8 (4) | −1.3 (3) | 0.9 (3) | 1.1 (3) |
| C(5) | 0.5714 (4) | 0.1780 (4) | 0.5395 (5) | 5.6 (4) | 6.6 (4) | 7.5 (4) | −1.7 (3) | −0.5 (3) | 1.8 (3) |
| O(1) | 0.2376 (5) | 0.3911 (4) | 0.6483 (5) | 9.4 (4) | 14.3 (6) | 9.3 (4) | −0.7 (4) | 1.4 (3) | −3.7 (4) |
| O(2) | 0.3846 (4) | 0.3781 (3) | 0.3788 (3) | 9.6 (4) | 5.9 (3) | 7.7 (3) | −2.7 (3) | 1.2 (3) | 1.5 (2) |
| O(3) | 0.5547 (4) | 0.1791 (3) | 0.1385 (4) | 10.0 (4) | 10.1 (4) | 8.6 (4) | −2.9 (3) | 3.8 (3) | 0.2 (3) |
| B | 0.8567 (7) | 0.2482 (6) | 0.9503 (7) | 8.6 (6) | 8.8 (6) | 9.0 (6) | −1.8 (5) | 0.4 (5) | 3.3 (5) |

[a] Estimated standard deviations in the least significant figures are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$. The quantities given in the table are the thermal coefficients ×10$^2$.

Table III

Derived Parameters for the Rigid Group Atoms of $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2][BPh_4]$

| atom | x | y | z | B, Å$^2$ | atom | x | y | z | B, Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| C(11) | 0.1166 (4) | 0.2122 (3) | 0.4629 (3) | 4.97 (13) | C(71) | 0.6496 (4) | 0.2659 (3) | 0.4215 (5) | 5.51 (14) |
| C(12) | 0.1089 (4) | 0.1340 (3) | 0.4285 (3) | 6.79 (17) | C(72) | 0.7181 (4) | 0.2777 (3) | 0.4981 (4) | 7.68 (20) |
| C(13) | 0.0520 (4) | 0.1017 (2) | 0.4767 (4) | 7.93 (21) | C(73) | 0.7680 (4) | 0.3363 (3) | 0.5019 (3) | 9.01 (24) |
| C(14) | 0.0027 (4) | 0.1477 (3) | 0.5593 (3) | 7.83 (20) | C(74) | 0.7494 (4) | 0.3832 (3) | 0.4291 (5) | 8.26 (21) |
| C(15) | 0.0103 (4) | 0.2259 (3) | 0.5937 (3) | 7.81 (20) | C(75) | 0.6809 (4) | 0.3714 (3) | 0.3525 (4) | 7.97 (20) |
| C(16) | 0.0673 (4) | 0.2582 (2) | 0.5455 (4) | 7.07 (18) | C(76) | 0.6310 (4) | 0.3127 (3) | 0.3487 (3) | 6.35 (16) |
| C(21) | 0.1113 (3) | 0.3512 (2) | 0.3836 (3) | 5.03 (13) | C(81) | 0.6769 (4) | 0.0951 (3) | 0.3725 (4) | 4.96 (13) |
| C(22) | 0.1429 (2) | 0.4214 (3) | 0.4041 (2) | 6.02 (15) | C(82) | 0.7579 (4) | 0.0964 (3) | 0.3261 (4) | 7.05 (18) |
| C(23) | 0.0824 (3) | 0.4917 (2) | 0.3837 (4) | 7.74 (20) | C(83) | 0.8253 (3) | 0.0258 (4) | 0.2952 (3) | 8.10 (21) |
| C(24) | −0.0096 (3) | 0.4916 (2) | 0.3427 (3) | 7.24 (18) | C(84) | 0.8119 (4) | −0.0461 (3) | 0.3106 (4) | 7.80 (20) |
| C(25) | −0.0411 (2) | 0.4214 (3) | 0.3222 (2) | 7.35 (19) | C(85) | 0.7309 (4) | −0.0474 (3) | 0.3570 (4) | 9.21 (25) |
| C(26) | 0.0193 (3) | 0.3512 (2) | 0.3427 (4) | 6.25 (16) | C(86) | 0.6635 (3) | 0.0232 (4) | 0.3879 (3) | 8.71 (23) |
| C(31) | 0.3079 (4) | 0.1249 (3) | 0.1071 (4) | 4.55 (12) | C(91) | 0.8163 (5) | 0.1829 (3) | 0.8587 (6) | 6.79 (17) |
| C(32) | 0.2313 (4) | 0.1284 (2) | 0.0371 (3) | 7.25 (19) | C(92) | 0.8305 (5) | 0.1808 (3) | 0.7592 (5) | 6.93 (18) |
| C(33) | 0.2301 (5) | 0.0646 (3) | −0.0417 (3) | 8.29 (22) | C(93) | 0.7988 (6) | 0.1253 (4) | 0.6844 (3) | 7.77 (20) |
| C(34) | 0.3056 (4) | −0.0028 (3) | −0.0505 (4) | 6.71 (17) | C(94) | 0.7528 (5) | 0.0719 (3) | 0.7092 (6) | 8.77 (23) |
| C(35) | 0.3823 (4) | −0.0063 (2) | 0.0195 (3) | 7.16 (18) | C(95) | 0.7386 (5) | 0.0740 (3) | 0.8087 (5) | 11.64 (34) |
| C(36) | 0.3834 (5) | 0.0576 (3) | 0.0983 (3) | 6.09 (15) | C(96) | 0.7703 (6) | 0.1295 (4) | 0.8834 (3) | 10.61 (30) |
| C(41) | 0.2600 (4) | 0.2963 (2) | 0.1623 (3) | 5.05 (13) | C(101) | 0.9389 (4) | 0.2841 (4) | 0.9046 (3) | 6.24 (16) |
| C(42) | 0.1631 (4) | 0.3222 (3) | 0.1380 (3) | 6.24 (16) | C(102) | 0.9104 (3) | 0.3562 (3) | 0.8717 (3) | 7.50 (19) |
| C(43) | 0.1314 (4) | 0.3877 (3) | 0.0917 (3) | 7.45 (19) | C(103) | 0.9766 (5) | 0.3853 (3) | 0.8321 (4) | 8.37 (22) |
| C(44) | 0.1966 (4) | 0.4272 (2) | 0.0697 (3) | 7.63 (20) | C(104) | 1.0714 (4) | 0.3422 (4) | 0.8254 (3) | 7.93 (25) |
| C(45) | 0.2936 (4) | 0.4012 (3) | 0.0940 (3) | 7.01 (18) | C(105) | 1.0999 (3) | 0.2701 (3) | 0.8583 (3) | 8.03 (21) |
| C(46) | 0.3253 (4) | 0.3358 (3) | 0.1403 (3) | 6.01 (15) | C(106) | 1.0337 (5) | 0.2411 (3) | 0.8979 (4) | 7.18 (18) |
| C(51) | 0.5191 (4) | 0.3389 (3) | 0.6482 (4) | 5.36 (13) | C(111) | 0.9051 (7) | 0.1977 (5) | 1.0428 (5) | 7.60 (19) |
| C(52) | 0.4881 (4) | 0.4076 (3) | 0.6080 (3) | 5.86 (15) | C(112) | 0.9711 (7) | 0.1256 (5) | 1.0152 (5) | 8.40 (22) |
| C(53) | 0.5322 (4) | 0.4708 (3) | 0.6396 (4) | 6.92 (17) | C(113) | 1.0146 (5) | 0.0813 (3) | 1.0870 (8) | 10.38 (29) |
| C(54) | 0.6073 (4) | 0.4652 (3) | 0.7113 (4) | 7.99 (21) | C(114) | 0.9920 (7) | 0.1090 (5) | 1.1865 (5) | 10.49 (30) |
| C(55) | 0.6383 (4) | 0.3965 (3) | 0.7515 (3) | 9.31 (25) | C(115) | 0.9259 (7) | 0.1810 (5) | 1.2141 (5) | 9.92 (28) |
| C(56) | 0.5942 (4) | 0.3334 (3) | 0.7199 (4) | 7.33 (19) | C(116) | 0.8825 (5) | 0.2254 (3) | 1.1422 (8) | 9.21 (25) |
| C(61) | 0.4535 (5) | 0.2169 (4) | 0.7078 (4) | 5.46 (14) | C(121) | 0.7665 (6) | 0.3244 (4) | 0.9990 (6) | 8.23 (21) |
| C(62) | 0.4126 (5) | 0.2727 (3) | 0.7888 (5) | 10.11 (28) | C(122) | 0.6712 (7) | 0.3198 (4) | 0.9841 (6) | 10.30 (29) |
| C(63) | 0.3918 (5) | 0.2474 (4) | 0.8720 (4) | 11.14 (32) | C(123) | 0.5997 (5) | 0.3827 (5) | 1.0285 (5) | 13.56 (43) |
| C(64) | 0.4119 (5) | 0.1665 (4) | 0.8741 (4) | 9.31 (25) | C(124) | 0.6235 (6) | 0.4500 (4) | 1.0877 (6) | 12.96 (39) |
| C(65) | 0.4528 (5) | 0.1107 (3) | 0.7930 (5) | 9.93 (28) | C(125) | 0.7188 (7) | 0.4545 (4) | 1.1026 (6) | 11.76 (34) |
| C(66) | 0.4736 (5) | 0.1360 (4) | 0.7098 (4) | 8.41 (22) | C(126) | 0.7903 (5) | 0.3917 (5) | 1.0582 (5) | 9.30 (25) |

Rigid Group Parameters

| group | $X_c$[a] | $Y_c$ | $Z_c$ | $\delta$[b] | $\epsilon$ | $\eta$ |
|---|---|---|---|---|---|---|
| ring 1 | 0.0596 (3) | 0.1800 (2) | 0.5111 (3) | 3.279 (3) | 0.913 (3) | 5.708 (3) |
| ring 2 | 0.0509 (2) | 0.4214 (2) | 0.3632 (2) | 3.273 (3) | 2.787 (3) | 2.322 (3) |
| ring 3 | 0.3068 (2) | 0.0611 (2) | 0.0283 (2) | 2.582 (3) | 2.553 (4) | 4.359 (3) |
| ring 4 | 0.2283 (2) | 0.3617 (2) | 0.1160 (2) | 2.504 (3) | −0.149 (4) | 1.155 (4) |
| ring 5 | 0.5632 (2) | 0.4021 (2) | 0.6798 (2) | 0.247 (3) | 2.404 (4) | 5.118 (3) |
| ring 6 | 0.4327 (3) | 0.1917 (3) | 0.7909 (3) | −0.267 (4) | 1.238 (4) | 0.386 (4) |
| ring 7 | 0.6995 (3) | 0.3245 (3) | 0.4253 (3) | 3.680 (3) | 2.183 (4) | 1.420 (4) |
| ring 8 | 0.7444 (3) | 0.0245 (2) | 0.3415 (3) | 2.889 (3) | 0.532 (4) | 3.967 (3) |
| ring 9 | 0.7846 (3) | 0.1274 (3) | 0.7839 (3) | 3.616 (4) | 1.432 (5) | 4.179 (4) |
| ring 10 | 1.0051 (3) | 0.3132 (2) | 0.8650 (3) | 2.558 (3) | 0.262 (4) | 2.467 (4) |
| ring 11 | 0.9485 (3) | 0.1533 (3) | 1.1146 (3) | 2.402 (4) | 1.610 (6) | 5.638 (6) |
| ring 12 | 0.6950 (4) | 0.3872 (3) | 1.0434 (4) | 3.565 (5) | 0.096 (5) | 0.726 (6) |

[a] $X_c$, $Y_c$, and $Z_c$ are the fractional coordinates of the centroid of the rigid group. [b] The rigid group orientation angles, $\delta$, $\epsilon$, and $\eta$ (radians), are the angles by which the rigid body is rotated with respect to a set of axes $X$, $Y$, and $Z$. The origin is the center of the ring; $X$ is parallel to $a^*$, $Z$ is parallel to $c$, and $Y$ is parallel to the line defined by the intersection of the plane containing $a^*$ and $b^*$ with the plane containing $b$ and $c$.

addition, the proximity shifted band at 443 nm in the electronic spectrum[4] is characteristic of significant Rh–Rh interaction.[2,30] Furthermore, the presence of a metal–metal bond is required to explain the observed diamagnetism and to give each metal an 18-electron configuration.

The Rh–Cl distances (2.575 (2) and 2.607 (2) Å) are significantly longer than those observed in some typical Rh(I) complexes in which the chloro ligands are either terminal or bridging. For example, in the red and orange forms of Wilkinson's catalyst[31] the Rh–Cl distances are 2.376 (4) and 2.404 (4) Å, respectively. In RhCl(PPP)[32] and $RhCl(N_2Ph)(PPP)^{+}$[33] (PPP = $PhP((CH_2)_3PPh_2)_2$) the Rh–Cl distances (2.381 (2) and 2.403 (2) Å, respectively) are again considerably less than in the present case. Similarly in some Cl-bridged dimeric systems a range of ca. 2.30–2.45 Å seems typical.[24,25,27,28]

The bridging and terminal carbonyl ligands show the expected structural differences, i.e., the bridging ligand has longer Rh–C and C–O distances. These distances in the present compound are comparable to other reported values.[19-23] Both terminal carbonyl ligands are bent slightly (Rh–C–O angles of 172.7 (8) and 175.1 (7)°), presumably as a result of packing forces.

The bridging carbonyl and chloro ligands are asymmetrically bonded in a compensating fashion. In other words C(2) is closer to Rh(2) and Cl is closer to Rh(1). Since chemically there is no a priori reason to expect a difference in the two rhodium atoms, the observed asymmetry is probably steric in origin, resulting from nonbonded contacts. In support of this, the only significant nonbonded contacts involving these bridging ligands involve H(22)–O(2) and H(52)–O(2), both of these occurring such as to cause lengthening of the

**Table IV.** Selected Distances (Å) in $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2][BPh_4]$

| | | | | | |
|---|---|---|---|---|---|
| Bond Distances | | | | | |
| Rh(1)-Rh(2) | 2.8415 (7) | | P(1)-C(4) | 1.821 (6) | 1.822 (7) |
| Rh(1)-C(1) | 1.831 (7) | | P(2)-C(4) | 1.827 (6) | |
| Rh(2)-C(3) | 1.836 (7) | | P(3)-C(5) | 1.823 (7) | |
| Rh(1)-C(2) | 2.104 (7) | | P(4)-C(5) | 1.818 (7) | |
| Rh(2)-C(2) | 2.034 (7) | | P(1)-C(11) | 1.821 (4) | 1.816 (9) |
| Rh(1)-Cl | 2.575 (2) | | P(1)-C(21) | 1.815 (4) | |
| Rh(2)-Cl | 2.607 (2) | | P(2)-C(31) | 1.819 (4) | |
| Rh(1)-P(1) | 2.327 (2) | 2.333 (8)[a] | P(2)-C(41) | 1.823 (4) | |
| Rh(1)-P(3) | 2.326 (2) | | P(3)-C(51) | 1.812 (4) | |
| Rh(2)-P(2) | 2.340 (2) | | P(3)-C(61) | 1.798 (5) | |
| Rh(2)-P(4) | 2.339 (2) | | P(4)-C(71) | 1.825 (4) | |
| C(1)-O(1) | 1.139 (8) | | P(4)-C(81) | 1.814 (4) | |
| C(2)-O(2) | 1.172 (8) | | B-C(91) | 1.685 (11) | 1.695 (11) |
| C(3)-O(3) | 1.139 (8) | | B-C(101) | 1.701 (10) | |
| | | | B-C(111) | 1.698 (10) | |
| | | | B-C(121) | 1.696 (11) | |
| Nonbonded Distances | | | | | |
| P(1)-P(2) | 3.068 (2) | | C(3)-H(76) | 2.64 | |
| P(3)-P(4) | 3.056 (2) | | C(4)-H(12) | 2.62 | |
| Cl-C(2) | 3.670 (8) | | O(2)-H(52) | 2.50 | |
| P(1)-H1C4 | 2.31 | | O(2)-H(22) | 2.63 | |
| P(1)-H2C4 | 2.31 | | H1C4-H(42) | 2.09 | |
| P(2)-H1C4 | 2.30 | | H2C4-H(12) | 1.98 | |
| P(2)-H2C4 | 2.30 | | H2C4-C(12) | 2.66 | |
| P(3)-H1C5 | 2.32 | | H1C5-H(66) | 2.10 | |
| P(3)-H2C5 | 2.32 | | H1C5-H(86) | 2.19 | |
| P(4)-H1C5 | 2.30 | | H2C5-H(72) | 2.16 | |
| P(4)-H2C5 | 2.30 | | | | |
| C(3)-H(36) | 2.70 | | | | |

[a] For averaged quantities the estimated standard deviation is the larger of an individual standard deviation or the standard deviation of a single observation as calculated from the mean.

**Table V.** Selected Angles (deg) in $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2][BPh_4]$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Bond Angles | | | | | | | |
| Rh(2)-Rh(1)-Cl | 57.28 (4) | Cl-Rh(2)-C(3) | 137.8 (2) | Rh(2)-P(2)-C(31) | 115.6 (2) | P(1)-C(11)-C(16) | 117.7 (3) |
| Rh(2)-Rh(1)-C(1) | 158.4 (3) | C(2)-Rh(2)-C(3) | 118.3 (3) | Rh(2)-P(2)-C(41) | 116.9 (2) | P(1)-C(21)-C(22) | 120.9 (3) |
| Rh(2)-Rh(1)-C(2) | 45.6 (2) | P(2)-Rh(2)-P(4) | 176.71 (6) | Rh(1)-P(3)-C(51) | 120.0 (2) | P(1)-C(21)-C(26) | 119.0 (3) |
| Rh(2)-Rh(1)-P(1) | 93.53 (4) | C(2)-Rh(2)-P(2) | 89.0 (2) | Rh(1)-P(3)-C(61) | 111.8 (2) | P(2)-C(31)-C(32) | 119.2 (3) |
| Rh(2)-Rh(1)-P(3) | 93.85 (5) | C(2)-Rh(2)-P(4) | 93.9 (2) | Rh(2)-P(4)-C(71) | 116.0 (2) | P(2)-C(31)-C(36) | 120.7 (3) |
| Cl-Rh(1)-C(1) | 144.4 (3) | C(3)-Rh(2)-P(2) | 89.1 (2) | Rh(2)-P(4)-C(81) | 114.7 (2) | P(2)-C(41)-C(42) | 120.6 (3) |
| Cl-Rh(1)-C(2) | 102.9 (2) | C(3)-Rh(2)-P(4) | 88.2 (2) | C(4)-P(1)-C(11) | 103.2 (3) | P(2)-C(41)-C(46) | 119.2 (3) |
| C(1)-Rh(1)-C(2) | 112.8 (3) | Cl-Rh(2)-P(2) | 91.65 (6) | C(4)-P(1)-C(21) | 105.4 (3) | P(3)-C(51)-C(52) | 120.6 (3) |
| P(1)-Rh(1)-P(3) | 167.56 (6) | Cl-Rh(2)-P(4) | 89.10 (6) | C(4)-P(2)-C(31) | 100.9 (3) | P(3)-C(51)-C(56) | 119.1 (3) |
| C(1)-Rh(1)-P(1) | 89.8 (2) | Rh(1)-Cl-Rh(2) | 66.51 (4) | C(4)-P(2)-C(41) | 106.9 (3) | P(3)-C(61)-C(62) | 118.1 (4) |
| C(1)-Rh(1)-P(3) | 87.0 (2) | Rh(1)-C(2)-Rh(2) | 86.7 (3) | C(5)-P(3)-C(51) | 104.4 (3) | P(3)-C(61)-C(66) | 121.7 (4) |
| C(2)-Rh(1)-P(1) | 95.8 (2) | Rh(1)-C(1)-O(1) | 172.7 (8) | C(5)-P(3)-C(61) | 104.8 (3) | P(4)-C(71)-C(72) | 120.3 (3) |
| C(2)-Rh(1)-P(3) | 96.5 (2) | Rh(2)-C(3)-O(3) | 175.1 (7) | C(5)-P(4)-C(71) | 107.1 (3) | P(4)-C(71)-C(76) | 119.6 (3) |
| Cl-Rh(1)-P(1) | 86.29 (6) | Rh(1)-C(2)-O(2) | 133.6 (5) | C(5)-P(4)-C(81) | 101.4 (3) | P(4)-C(81)-C(82) | 120.8 (3) |
| Cl-Rh(1)-P(3) | 89.30 (6) | Rh(2)-C(2)-O(2) | 139.6 (5) | C(11)-P(1)-C(21) | 104.1 (2) | P(4)-C(81)-C(86) | 119.2 (3) |
| Rh(1)-Rh(2)-Cl | 56.21 (4) | Rh(1)-P(1)-C(4) | 111.9 (2) | C(31)-P(2)-C(41) | 104.6 (2) | C(91)-B-C(101) | 109.2 (6) |
| Rh(1)-Rh(2)-C(2) | 47.7 (2) | Rh(2)-P(2)-C(4) | 110.3 (2) | C(51)-P(3)-C(61) | 104.2 (3) | C(91)-B-C(111) | 106.6 (6) |
| Rh(1)-Rh(2)-C(3) | 165.9 (2) | Rh(1)-P(3)-C(5) | 110.3 (2) | C(71)-P(4)-C(81) | 104.9 (2) | C(91)-B-C(121) | 111.8 (6) |
| Rh(1)-Rh(2)-P(2) | 91.66 (4) | Rh(2)-P(4)-C(5) | 111.5 (2) | P(1)-C(4)-P(2) | 114.5 (4) | C(101)-B-C(111) | 111.8 (6) |
| Rh(1)-Rh(2)-P(4) | 91.43 (5) | Rh(1)-P(1)-C(11) | 113.1 (2) | P(3)-C(5)-P(4) | 114.2 (3) | C(101)-B-C(121) | 110.1 (6) |
| Cl-Rh(2)-C(2) | 103.9 (2) | Rh(1)-P(1)-C(21) | 117.8 (2) | P(1)-C(11)-C(12) | 122.3 (3) | C(111)-B-C(121) | 107.2 (6) |
| Torsion Angles | | | | | | | |
| P(1)-Rh(1)-Rh(2)-P(2) | 7.59 (6) | C(5)-P(4)-P(2)-C(4) | 5.0 (3) | C(61)-P(3)-P(4)-C(81) | 6.1 (4) | C(3)-Rh(2)-P(2)-C(31) | 50.6 (3) |
| P(3)-Rh(1)-Rh(2)-P(4) | 1.28 (6) | C(5)-P(3)-P(1)-C(4) | 6.7 (3) | C(1)-Rh(1)-P(1)-C(11) | 70.1 (3) | C(3)-Rh(2)-P(2)-C(41) | 73.3 (3) |
| P(1)-Rh(1)-Rh(2)-P(4) | 171.26 (6) | C(11)-P(1)-P(3)-C(61) | 6.7 (3) | C(1)-Rh(1)-P(1)-C(21) | 51.5 (3) | C(3)-Rh(2)-P(4)-C(71) | 67.8 (3) |
| P(3)-Rh(1)-Rh(2)-P(2) | 177.57 (6) | C(21)-P(1)-P(3)-C(51) | 7.9 (3) | C(1)-Rh(1)-P(3)-C(51) | 59.0 (3) | C(3)-Rh(2)-P(4)-C(81) | 54.8 (3) |
| C(1)-Rh(1)-Rh(2)-C(3) | 1.9 (11) | C(31)-P(2)-P(4)-C(81) | 4.1 (3) | C(1)-Rh(1)-P(3)-C(61) | 63.4 (3) | Cl-Rh(1)-P(1)-C(11) | 74.5 (2) |
| Rh(1)-P(1)-C(4)-P(2) | 41.4 (4) | C(41)-P(2)-P(4)-C(71) | 5.5 (3) | C(2)-Rh(1)-P(1)-C(21) | 61.4 (3) | Cl-Rh(1)-P(3)-C(61) | 81.1 (2) |
| Rh(2)-P(2)-C(4)-P(1) | 48.9 (4) | C(11)-P(1)-P(2)-C(31) | 11.6 (3) | C(2)-Rh(1)-P(3)-C(51) | 53.6 (3) | Cl-Rh(2)-P(2)-C(31) | 87.3 (2) |
| Rh(1)-P(3)-C(5)-P(4) | 46.0 (4) | C(21)-P(1)-P(2)-C(41) | 7.8 (2) | C(2)-Rh(2)-P(2)-C(41) | 45.0 (3) | Cl-Rh(2)-P(4)-C(81) | 83.1 (2) |
| Rh(2)-P(4)-C(5)-P(3) | 48.0 (4) | C(51)-P(3)-P(4)-C(71) | 5.0 (2) | C(2)-Rh(2)-P(4)-C(71) | 50.5 (3) | | |

Table VI. Least-Squares-Plane Calculations[a]

(A) Atoms Defining Plane: Rh(1), Rh(2), P(1), P(2)

Equation of Plane: $0.2134X + 0.9697Y - 0.1189Z - 3.4645 = 0.0$

| | | | |
|---|---|---|---|
| Rh(1) | 0.0124 (5) | P(2) | 0.139 (2) |
| Rh(2) | −0.0125 (5) | C(4) | −0.652 (7) |
| P(1) | −0.143 (2) | | |

(B) Atoms Defining Plane: Rh(1), Rh(2), P(3), P(4)

Equation of Plane: $0.2952X + 0.9528Y - 0.0706Z - 4.1765 = 0.0$

| | | | |
|---|---|---|---|
| Rh(1) | 0.0019 (5) | P(4) | 0.024 (2) |
| Rh(2) | −0.0019 (5) | C(5) | −0.677 (7) |
| P(3) | −0.024 (2) | | |

(C) Atoms Defining Plane: Rh(1), Rh(2), Cl, C(2)

Equation of Plane: $-0.8092X + 0.1586Y - 0.5657Z + 7.5497 = 0.0$

| | | | |
|---|---|---|---|
| Rh(1) | −0.0002 (5) | O(2) | 0.109 (5) |
| Rh(2) | −0.0002 (5) | C(1) | −0.021 (8) |
| Cl | 0.002 (2) | C(3) | −0.028 (7) |
| C(2) | 0.051 (7) | | |

[a] $X$, $Y$, and $Z$ are orthogonal coordinates (Å) with $X$ along the $a$ axis, $Y$ in the $a,b$ plane, and $Z$ along the $c^*$ axis.

Rh(1)–C(2) bond (see Table IV and Figure 2). In unsymmetrical, bridging carbonyl ligands the M–C–O angle involving the metal, to which the carbonyl ligand is more tightly bound, is more nearly linear.[34] Thus, in the present structure the Rh(2)–C(2)–O(2) angle (139.6 (5)°) is more nearly linear than the Rh(1)–C(2)–O(2) angle (133.6 (5)°). It is significant that this distortion is the opposite to that expected based solely on steric effects since the previously mentioned contacts involving O(2) would tend to increase the Rh(1)–C(2)–O(2) angle. Therefore these steric interactions force C(2)O(2) away from Rh(1) slightly, with a concomitant increase in the Rh(2)–C(2)–O(2) angle owing to the stronger interaction of this carbonyl ligand with Rh(2).

The DPM ligand is capable of functioning as either a chelating[35–37] or a bridging[3,5,6,9,38–41] group. In the former case the $\overline{\text{M–P–C–P}}$ chelate moiety is essentially planar,[35–37] whereas in the bridging situation the methylene carbon atom is significantly displaced from the best M–P–P–M plane[3,5,6,9,38–41] (0.76 Å in $Fe_2(DPM)(CO)_7$[41]). In the present structure the cation contains two bridging DPM ligands with the methylene carbon atoms significantly displaced from their respective Rh–P–P–Rh planes. Although the rhodium and phosphorus atoms are not strictly planar, the distances of the methylene carbon atoms from these best least-squares planes, shown in Table VI, are nevertheless useful indications of the fold about the intraligand P–P axes. Thus C(4) is 0.653 (7) Å out of the Rh(1)–P(1)–P(2)–Rh(2) plane and C(5) is 0.677 (7) Å out of the Rh(1)–P(3)–P(4)–Rh(2) plane. Another indication of this distortion is the four individual Rh–P–C–P torsion angles about the P–C methylene bonds, shown in Table V; these average 46.1°.

The methylene groups are cis, i.e., they are folded in the same direction, toward the Cl ligand. In DPM complexes this is typical,[3,5,6,9,40] namely, that the methylene group bends toward the larger ligand or the more sterically encumbered position, thereby minimizing the repulsive contacts involving the more bulky phenyl groups. One exception to this is $Fe_2(DPM)(CO)_7$[41] in which the methylene ligand is folded away from the bridging carbonyl ligand and toward the open site opposite this ligand. Undoubtedly, here again the major contributing factor is the minimizing of nonbonded repulsions between the phenyl groups and the ligands in the equatorial plane. Methylene groups in the trans configuration (i.e., folding of these groups in opposite directions) have also been observed.[29,42] The relative orientations of the DPM ligands (cis or trans methylene groups) are governed, it seems, primarily by the nonbonded contacts involving the phenyl groups and the equatorial ligands. In $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]^+$, in which the methylene groups are cis, the phenyl rings on transoid phosphorus atoms are essentially eclipsed, as can be seen from the Ph–P–P–Ph torsion angles (e.g., C(11)–P(1)–P(3)–C(61)), which average 6.1°. In this orientation these phenyl rings are staggered with respect to the equatorial ligands. This can be seen clearly in Figures 2 and 3 and is also evident from the CO–Rh–P–Ph and Cl–Rh–P–Ph torsion angles, which range from 45.0 (3) to 87.3 (2)°. The reason for the cis methylene arrangement in the present structure is quite clear. If one visualizes the effect of a trans methylene arrangement with C(5) bent toward the bridging CO ligand, rings 5 and 7 would then almost exactly eclipse C(1)O(1) and C(3)O(3), respectively, with resulting unfavorable contacts. In addition, short contacts involving the bridging Cl ligand and rings 6 and 8 would probably result.

The Rh–P vectors on each metal are slightly staggered when viewed down the Rh–Rh axis, as is shown by the P(1)–Rh(1)–Rh(2)–P(2) and P(3)–Rh(1)–Rh(2)–P(4) torsion angles of 7.59 (6) and 1.28 (6)°, respectively. This slight twisting about the metal–metal axis has been observed in several DPM complexes.[5,6,41] $Pd_2Cl_2(DPM)_2$,[42] on the other hand, is severely twisted with an average torsion angle about the Pd–Pd axis of 39°. Similarly, $Rh_2(CO)_2(\mu\text{-}S)(DPM)_2$[3] seems severely twisted although no value for this is reported.

Within the rhodium–DPM frame, all parameters are usual. The Rh–P distances (average 2.333 (8) Å) are typical for rhodium(I)–phosphine distances when trans to another phosphine ligand (e.g., 2.334 (4) and 2.338 (4) Å in red and orange Wilkinson's catalyst[31]) and can be compared to the 2.305 (4) Å distance observed in $Rh_2(CO)_2(\mu\text{-}S)(DPM)_2$[3] and the 2.365 (5) Å distance in $[RhCl(CO)\{t\text{-}Bu_2P(CH_2)_{10}P\text{-}t\text{-}Bu_2\}]_2$[43] ($t$-Bu = *tert*-butyl). The P–C distances (both methylene and phenyl) are not unusual and compare well with other determinations. The P–C–P angles (average 114.4 (4)°) are close to the tetrahedral value as is typical when the steric strain within the ligand is minimal. In comparison, when the DPM ligand is chelating, P–C–P angles near 90° are observed.[35–37]

The chemical significance of the present structure is that it conclusively establishes that small unsaturated molecules can coordinate in the "active site" of the parent "A-frame" complex and hence suggests the possibility of interesting chemistry involving small unsaturated molecules and both metal atoms in the complex. The reactivity of "A-frame" complexes at both metal centers was first suggested by Kubiak and Eisenberg,[3] who observed reaction of $SO_2$ with the related "A-frame" complex $[Rh_2(CO)_2(\mu\text{-}S)(DPM)_2]$. We have subsequently studied the reaction of **1** with $SO_2$[9] and seem to obtain, as the initial product, a species analogous to the carbonyl-bridged species described herein but having an $SO_2$ ligand bridging the two metals. Furthermore, NO and $N_2Ph^+$ also react with **1** yielding species which we believe have these ligands bridging the metal atoms[8] (the results of these studies will be reported presently).

A naïve assumption, based on the present structure and the above reactions with $SO_2$, NO, and $N_2Ph^+$, would be that the small molecules attack **1** at the active site. However, $^{13}CO$ labeling studies[4,44] have shown that, in fact, $^{13}CO$ attack seems to occur between the bridging Cl and the terminal CO ligands, at the site remote from the active site. One of the originally terminal CO ligands then swings into the bridge. This seems to be in contrast to the reactions of **1** with $SO_2$, NO, and $N_2Ph^+$ where these molecules *do* seem to attack at the "active site", since spectroscopic evidence indicates that the products have these ligands bridging the metals, yet no evidence of bridging carbonyl ligands is observed. This aspect is being investigated further.

It is anticipated that the study of "A-frame" complexes and their chemistries with small unsaturated molecules will, in addition to yielding a great deal of interesting and varied chemistry, be of tremendous value in furthering the understanding of catalytic processes involving multicentered metal catalysts.

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**Registry No.** $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2][BPh_4]$, 67235-83-0.

**Supplementary Material Available:** Tables VII and VIII, showing the idealized hydrogen parameters and the root-mean-square amplitudes of vibration of the individual atoms, respectively, and a listing of the observed and calculated structure amplitudes (39 pages). Ordering information is given on any current masthead page.

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# Nitrosylmetalloporphyrins. 5. Molecular Stereochemistry of Nitrosyl(5,10,15,20-tetratolylporphinato)manganese(II) and Nitrosyl(4-methylpiperidine)(5,10,15,20-tetraphenylporphinato)manganese(II)

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The molecular stereochemistries of five-coordinate nitrosyl(5,10,15,20-tetratolylporphinato)manganese(II) (I) and six-coordinate nitrosyl(4-methylpiperidine)(5,10,15,20-tetraphenylporphinato)manganese(II) (II) have been determined by X-ray diffraction methods. I crystallizes as the benzene solvate in the monoclinic system, space group $P2_1/a$. The unit cell has $a = 15.755$ (6) Å, $b = 16.979$ (4) Å, $c = 17.389$ (3) Å, $\beta = 112.43$ (2)°, and $Z = 4$. II crystallizes as a chloroform solvate in the orthorhombic system, space group $P2_12_12_1$. The unit cell constants are $a = 17.561$ (6) Å, $b = 25.580$ (13) Å, and $c = 10.175$ (6) Å for $Z = 4$. Both complexes have essentially linear Mn–N–O groups. The Mn–N(NO) bond distances [1.641 (2) Å (I) and 1.644 (5) Å (II)] are not affected by the increase in coordination number, but the Mn–N(porphinato) bond distances [2.004 (5) Å (I) and 2.027 (3) Å (II)] are affected. The data for I along with the results for Fe(TPP)(NO) and Co(TPP)(NO) permit an assessment of the effects of nonbonded repulsion between the axial ligand and porphinato ligand on the displacements of the respective metal atoms.

The interaction of diatomic ligands with metalloporphyrins has been intensively investigated in recent years.[2-14] Much of our work in this area has dealt with the interaction of nitric oxide with metalloporphyrins. Our earlier reports of the preparations and stereochemistry of nitrosylmetalloporphyrins emphasized the iron[11-13] and cobalt[14] derivatives. Herein we report the characterization of two $\{MnNO\}^6$ derivatives:[15] five-coordinate nitrosyl(5,10,15,20-tetra-*p*-tolylporphinato)manganese(II), written as Mn(TTP)(NO), and six-coordinate nitrosyl(4-methylpiperidine)(5,10,15,20-tetraphenylporphi-

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