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# New Directions in the Chemistry of Dirhodium(II) Compounds

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**Abstract:** Three new complexes of the $Rh_2^{4+}$ unit, each containing phosphine and chloride ligands in addition to, or totally replacing, carboxylato ligands, are described. These have all been accessed by employing $Me_3SiCl$ to remove carboxyl groups from the starting materials, thus allowing each of them to be replaced by a combination of $Cl^-$ and a phosphorus atom. Compound **1**, $Rh_2Cl_2(O_2CCH_3)_2(dppm)_2{\cdot}2CH_3CN$, prepared by reaction of $Rh_2(O_2CCH_3)_4$ with 2 equiv of $Me_3SiCl$ in the presence of dppm, crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions $a$ = 14.599 (2) Å, $b$ = 15.395 (2) Å, $c$ = 24.614 (4) Å, $\beta$ = 103.63 (1)°, $V$ = 5376 (3) Å$^3$, and $Z$ = 4. The structure was refined to least-squares residuals of $R$ = 0.0443, $R_w$ = 0.0552, and quality-of-fit = 1.58. The molecules occupy general positions in the unit cell, and each one consists of a dirhodium unit bridged by two cisoid acetate groups and by two dppm ligands, with chloride ions in the axial positions. The asymmetric unit also contains two molecules of $CH_3CN$ as interstitial solvent. Compound **2**, $Rh_2Cl_4(dppm)_2{\cdot}3CH_3CN{\cdot}H_2O$, was prepared by the action of $Me_3SiCl$ on **1** or by the addition of 4 equiv of $Me_3SiCl$ to a mixture of $Rh_2(O_2CCH_3)_4$ and dppm in refluxing benzene. Orange-red crystals of **2** were isolated from a $CH_2Cl_2$–$CH_3CN$ solution and belong to the orthorhombic space group $Pc2_1n$ with $a$ = 9.379 (5) Å, $b$ = 22.65 (1) Å, $c$ = 27.31 (1) Å, $V$ = 5803 (4) Å$^3$, and $Z$ = 4. Molecules of **2** exhibit a novel geometry consisting of two square pyramids that share an edge. Two cis bridging chloride ligands occupy the positions of the shared basal edge, four phosphorus atoms of the cis dppm ligands define the additional edges of the square plane, and a terminal chloride ligand on each Rh atom occupies an apex position. This is an unprecendented arrangement of ligands for a $M_2X_4(L{-}L)_2$ compound; a possible reason for it will be discussed. The structure was refined to $R$ = 0.064, $R_w$ = 0.080, and quality-of-fit = 1.41. $Rh_2Cl_2(dmpm)_2[(C_6H_5)_2P(C_6H_4)]_2{\cdot}CH_2Cl_2$ (**3**) was isolated from the reaction of $Rh_2(O_2CCH_3)_2(Ph_2PC_6H_4)_2{\cdot}2CH_3COOH$, $Me_3SiCl$, and dmpm in THF. Red monoclinic crystals of **3** were grown from $CH_2Cl_2$–hexane, space group $P2_1/c$ with $a$ = 11.268 (2) Å, $b$ = 24.834 (3) Å, $c$ = 17.589 (5) Å, $\beta$ = 99.14 (2)°, $V$ = 4859 (3) Å$^3$, $Z$ = 4. The new compound is comprised of two cis bridging $o$-$(Ph_2P)C_6H_4^-$ groups in a head-to-tail arrangement and two cis dmpm ligands that also span the $Rh_2$ unit. The coordination sphere is completed by two axial chloride ligands. After final refinement the residuals were $R$ = 0.0641, $R_w$ = 0.0742, and the quality-of-fit = 1.43. The Rh–Rh distances in **1**, **2**, and **3** are 2.622 (1), 2.523 (2), and 2.770 (3) Å, respectively, values which are significantly longer than nearly all previously reported Rh–Rh single bond distances. This point is discussed along with other pertinent structural details. In addition to X-ray studies, the new compounds were characterized by elemental analysis, infrared and electronic spectroscopy, and cyclic voltammetry.

The chemistry of the $Rh_2^{4+}$ unit is extensive, but until now it has lacked variety. The many $Rh_2^{4+}$ compounds already known are virtually all of the type $Rh_2(O_2CR)_4$ or are closely analogous thereto.[1] This situation was in sharp contrast to that with other metals[1c] such as molybdenum, tungsten, and rhenium where in addition to $M_2(O_2CR)_4$ or $M_2(O_2CR)_4L_2$ species there were others, such as $M_2X_8^{n-}$ or $M_2X_4(PR_3)_4$. The dirhodium(II) unit might well be expected to be less robust than these other dimetal units, since they contain M–M multiple bonds while there is only a net single bond in $Rh_2^{4+}$. The possibility that only the buttressing effect of such rigid bridging ligands as $RCO_2^-$ or $RCONH^-$ would render the $Rh_2^{4+}$ unit stable therefore had to be recognized.

With these considerations in mind, we undertook to determine whether complexes of $Rh_2^{4+}$ containing ligands other than carboxyl groups (or similar ones) could be isolated and characterized. Our approach has been to employ the $(CH_3)_3SiCl$ reagent to remove carboxyl groups from $Rh_2(O_2CCH_3)_4$ in the presence of phosphine ligands. The objective of such a procedure would be to obtain a product in which the $Rh_2^{4+}$ unit would remain intact but be coordinated by $Cl^-$ ions and phosphine molecules in place of some or all of the carboxyl groups.

This approach has proven successful and we report here three new dirhodium(II) complexes that are significantly different from any that have been previously described. Each one has been fully identified and characterized by X-ray crystallography. Some of these results have been the subject of a preliminary communication.[2]

## Experimental Section

**Starting Materials.** Anhydrous $Rh_2(O_2CCH_3)_4$[3] and $Rh_2(O_2CCH_3)_2(Ph_2PC_6H_4)_2{\cdot}2CH_3COOH$[4] were prepared by the literature methods. Bis(diphenylphosphino)methane (dppm) and chlorotrimethylsilane ($Me_3SiCl$) were obtained from Aldrich Chemical Co. and used without further purification. Triphenylphosphine and bis(dimethylphosphino)methane (dmpm) were purchased from Strem Chemicals and were used as received. All solvents were dried and freshly distilled before use.

**Reaction Procedures.** Unless otherwise stated, all reactions were carried out in an argon atmosphere with use of standard vacuum line techniques.

**Reactions of $Rh_2(O_2CCH_3)_4$ with dppm.** (i) **$Rh_2(O_2CCH_3)_2(dppm)_2Cl_2$ (1).** $Rh_2(O_2CCH_3)_4$ (0.200 g, 0.453 mmol) was suspended in 15 mL of benzene and the mixture heated gently for 0.5 h in the presence of dppm (0.35 g, 0.905 mmol) and $Me_3SiCl$ (115 $\mu$L, 0.91 mmol). The solution was stirred at room temperature for an additional 3 h and then reduced in volume to ~5 mL. A salmon-colored precipitate was filtered off in air, washed with benzene followed by diethyl ether, and dried. Yield 0.40 g, 76%. The product is insoluble in all common solvents except dichloromethane, in which it is only sparingly soluble. Recrystallization from $CH_2Cl_2$–$CH_3CN$ afforded orange-brown crystals of $Rh_2(O_2CCH_3)_2(dppm)_2Cl_2{\cdot}2CH_3CN$: IR (Nujol mull, CsI) 1550 (m), 1485 (s), 1265 (w), 1195 (w), 1150 (m), 1100 (s), 1030 (m), 1005 (m), 760 (m), 740 (s), 730 (m), 700 (s), 545 (m), 530 (s), 520 (m), 500 (m).

(ii) **$Rh_2Cl_4(dppm)_2$ (2).** In a typical reaction, $Rh_2(O_2CCH_3)_4$ (0.150 g, 0.339 mmol) and dppm (0.26 g, 0.68 mmol) was refluxed in 20 mL of benzene with 4 equiv of $Me_3SiCl$ (172 $\mu$L, 1.36 mmol). After 12 h, the red-orange solution was cooled and reduced in volume to ~10 mL. The pale orange product was collected on a frit in air and washed with

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**Table I.** Crystal Data for **1**, **2**, and **3**

| | **1** | **2** | **3** |
|---|---|---|---|
| formula | $Rh_2Cl_2P_4O_4N_2C_{58}H_{56}$ | $Rh_2Cl_4P_4O_1N_3C_{56}H_{55}$ | $Rh_2Cl_4P_6C_{47}H_{58}$ |
| formula wt | 1245.69 | 1257.57 | 1156.45 |
| space group | $P2_1/c$ | $Pc2_1n$ | $P2_1/c$ |
| systematic absences | $00l$; $l \neq 2n$ | $0kl$; $l \neq 2n$, $h00$; $h \neq 2n$ | $00l$; $l \neq 2n$ |
| | $h0l$; $l \neq 2n$ | $0k0$; $k \neq 2n$, $00l$; $l \neq 2n$ | $h0l$; $l \neq 2n$ |
| | $0k0$; $k \neq 2n$ | $hk0$; $h + k \neq 2n$ | $0k0$; $k \neq 2n$ |
| $a$, Å | 14.599 (2) | 9.379 (5) | 11.268 (2) |
| $b$, Å | 15.395 (2) | 22.65 (1) | 24.834 (3) |
| $c$, Å | 24.614 (4) | 27.31 (1) | 17.589 (5) |
| $\alpha$, deg | 90 | 90 | 90 |
| $\beta$, deg | 103.63 (1) | 90 | 99.14 (2) |
| $\gamma$, deg | 90 | 90 | 90 |
| $V$, Å$^3$ | 5376 (3) | 5803 (4) | 4859 (3) |
| $Z$ | 4 | 4 | 4 |
| $d_{calcd}$, g/cm$^3$ | 1.527 | 1.437 | 1.581 |
| crystal size, mm | 0.30 × 0.30 × 0.05 | 0.40 × 0.30 × 0.15 | 0.30 × 0.25 × 0.20 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 8.685 | 8.928 | 11.181 |
| data collection instrument | Enraf-Nonius CAD-4 | Syntex P3 | Enraf-Nonius CAD-4 |
| radiation (monochromated in incident beam) | Mo K$\alpha$ ($\lambda\bar{\alpha}$ = 0.71073 Å); graphite monochromated | | |
| orientation reflctns, no., range ($2\theta$) | 25; $20 < 2\theta < 30°$ | 25; $20 < 2\theta < 30°$ | 25; $14 < 2\theta < 28°$ |
| temp, °C | 20 ± 1 | 22 ± 1 | −106 |
| scan method | $\omega$ scans | $\omega$–$2\theta$ scans | $\omega$–$2\theta$ scans |
| data col. range, $2\theta$, deg | $4 \leq 2\theta \leq 45$ | $4 \leq 2\theta \leq 45$ | $4 \leq 2\theta \leq 45$ |
| no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$ | 6701, 4822 | 3930, 2775 | 5194, 2473 |
| no. of parameters refined | 649 | 555 | 382 |
| trans, factors, max., min. | 99.9, 90.1 | 99.9, 91.14 | 99.65, 60.91 |
| $R^a$ | 0.0443 | 0.0645 | 0.0641 |
| $R_w{}^b$ | 0.0552 | 0.0806 | 0.0742 |
| quality-of-fit indicator$^c$ | 1.58 | 1.41 | 1.43 |
| largest shift/esd, final cycle | 0.18 | 0.18 | 0.17 |
| largest peak, e/Å$^3$ | 0.672 | 1.03 | 0.952 |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$.

**Table II.** Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å$^2$) and Their Estimated Standard Deviations for $Rh_2Cl_2(O_2CCH_3)_2(dppm)_2 \cdot 2CH_3CN$ (**1**)$^a$

| atom | $x$ | $y$ | $z$ | $B$ (Å$^2$) | atom | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|---|---|---|---|---|
| Rh(1) | 0.30608 (4) | 0.07050 (4) | 0.25447 (2) | 1.85 (1) | C(25) | −0.0476 (5) | 0.1114 (5) | 0.2732 (3) | 2.2 (2) |
| Rh(2) | 0.16755 (4) | −0.01025 (4) | 0.28427 (2) | 1.88 (1) | C(26) | −0.0762 (5) | 0.1944 (5) | 0.2833 (3) | 2.7 (2) |
| Cl(1) | 0.4356 (1) | 0.1121 (2) | 0.21044 (8) | 3.25 (5) | C(27) | −0.1633 (6) | 0.2058 (6) | 0.2977 (4) | 3.5 (2) |
| Cl(2) | 0.0512 (1) | −0.1207 (1) | 0.29928 (9) | 3.28 (5) | C(28) | −0.2201 (6) | 0.1353 (6) | 0.2993 (4) | 3.6 (2) |
| P(1) | 0.2342 (1) | 0.2007 (1) | 0.24062 (8) | 1.90 (4) | C(29) | −0.1935 (6) | 0.0518 (6) | 0.2879 (4) | 3.4 (2) |
| P(2) | 0.0608 (1) | 0.0934 (1) | 0.24806 (8) | 2.03 (4) | C(30) | −0.1064 (5) | 0.0387 (6) | 0.2742 (3) | 3.0 (2) |
| P(3) | 0.3851 (1) | 0.0975 (1) | 0.34322 (8) | 2.06 (4) | C(31) | 0.4615 (5) | 0.0075 (5) | 0.3745 (3) | 2.6 (2) |
| P(4) | 0.1981 (1) | 0.0431 (1) | 0.37158 (8) | 2.01 (4) | C(32) | 0.5323 (6) | −0.0191 (6) | 0.3478 (3) | 3.3 (2) |
| O(1) | 0.3649 (4) | −0.0564 (4) | 0.2596 (2) | 3.4 (1) | C(33) | 0.5914 (6) | −0.0874 (6) | 0.3708 (4) | 4.1 (2) |
| O(2) | 0.2720 (4) | −0.1075 (4) | 0.3106 (2) | 3.3 (1) | C(34) | 0.5815 (7) | −0.1301 (7) | 0.4199 (4) | 4.6 (2) |
| O(3) | 0.2343 (4) | 0.0301 (4) | 0.1738 (2) | 3.4 (1) | C(35) | 0.5120 (6) | −0.1017 (6) | 0.4460 (4) | 4.1 (2) |
| O(4) | 0.1510 (4) | −0.0688 (4) | 0.2050 (2) | 3.4 (1) | C(36) | 0.4528 (6) | −0.0326 (6) | 0.4240 (3) | 3.4 (2) |
| C(1) | 0.3005 (5) | 0.1161 (5) | 0.3870 (3) | 2.2 (2) | C(37) | 0.4668 (5) | 0.1893 (5) | 0.3629 (3) | 2.5 (2) |
| C(2) | 0.1160 (5) | 0.2001 (5) | 0.2581 (3) | 2.0 (2) | C(38) | 0.5393 (5) | 0.2018 (6) | 0.3356 (4) | 3.1 (2) |
| C(3) | 0.3326 (5) | −0.1092 (5) | 0.2860 (3) | 3.0 (2) | C(39) | 0.6047 (5) | 0.2690 (6) | 0.3530 (4) | 3.4 (2) |
| C(4) | 0.3931 (6) | −0.1987 (6) | 0.2942 (4) | 3.9 (2) | C(40) | 0.5993 (6) | 0.3213 (6) | 0.3977 (4) | 4.1 (2) |
| C(5) | 0.1842 (5) | −0.0328 (5) | 0.1711 (4) | 3.0 (2) | C(41) | 0.5286 (6) | 0.3094 (6) | 0.4260 (4) | 4.1 (2) |
| C(6) | 0.1574 (7) | −0.0770 (7) | 0.1086 (4) | 4.5 (2) | C(42) | 0.4606 (6) | 0.2430 (6) | 0.4077 (4) | 3.4 (2) |
| C(7) | 0.2904 (5) | 0.2963 (5) | 0.2787 (3) | 2.3 (2) | C(43) | 0.1095 (5) | 0.1077 (5) | 0.3956 (3) | 2.5 (2) |
| C(8) | 0.3739 (5) | 0.3242 (5) | 0.2641 (3) | 2.7 (2) | C(44) | 0.1172 (5) | 0.1966 (5) | 0.4084 (3) | 2.6 (2) |
| C(9) | 0.4185 (5) | 0.4001 (5) | 0.2877 (3) | 2.9 (2) | C(45) | 0.0469 (6) | 0.2374 (6) | 0.4292 (3) | 3.5 (2) |
| C(10) | 0.3818 (6) | 0.4485 (6) | 0.3253 (4) | 3.5 (2) | C(46) | −0.0300 (6) | 0.1912 (6) | 0.4371 (4) | 3.6 (2) |
| C(11) | 0.2987 (6) | 0.4213 (6) | 0.3399 (4) | 3.8 (2) | C(47) | −0.0379 (6) | 0.1028 (6) | 0.4247 (4) | 3.8 (2) |
| C(12) | 0.2540 (6) | 0.3439 (5) | 0.3167 (3) | 2.8 (2) | C(48) | 0.0317 (5) | 0.0605 (6) | 0.4036 (3) | 3.1 (2) |
| C(13) | 0.2077 (5) | 0.2470 (5) | 0.1701 (3) | 2.2 (2) | C(49) | 0.2239 (5) | −0.0348 (5) | 0.4291 (3) | 2.5 (2) |
| C(14) | 0.1630 (5) | 0.3271 (5) | 0.1640 (3) | 2.8 (2) | C(50) | 0.2485 (6) | 0.0001 (6) | 0.4841 (3) | 3.4 (2) |
| C(15) | 0.1355 (6) | 0.3654 (6) | 0.1108 (4) | 3.9 (2) | C(51) | 0.2690 (6) | −0.0577 (7) | 0.5300 (4) | 4.3 (2) |
| C(16) | 0.1530 (6) | 0.3237 (7) | 0.0649 (4) | 4.0 (2) | C(52) | 0.2653 (7) | −0.1474 (7) | 0.5217 (4) | 5.3 (3) |
| C(17) | 0.1995 (6) | 0.2455 (7) | 0.0714 (3) | 4.2 (2) | C(53) | 0.2382 (8) | −0.1806 (7) | 0.4685 (5) | 5.7 (3) |
| C(18) | 0.2286 (6) | 0.2049 (6) | 0.1238 (3) | 3.3 (2) | C(54) | 0.2185 (6) | −0.1253 (6) | 0.4197 (4) | 3.9 (2) |
| C(19) | 0.0065 (5) | 0.0785 (6) | 0.1736 (3) | 2.8 (2) | C(55) | 0.3086 (9) | 0.6313 (9) | 0.4022 (6) | 8.9 (4) |
| C(20) | −0.0374 (6) | −0.0014 (6) | 0.1564 (4) | 3.7 (2) | C(56) | 0.2414 (9) | 0.6596 (9) | 0.3519 (5) | 7.4 (4) |
| C(21) | −0.0877 (7) | −0.0125 (7) | 0.1009 (4) | 5.1 (3) | C(57) | 0.3445 (9) | 0.385 (1) | 0.5078 (5) | 8.2 (4) |
| C(22) | −0.0906 (7) | 0.0553 (9) | 0.0625 (4) | 6.1 (3) | C(58) | 0.3025 (9) | 0.346 (1) | 0.4733 (5) | 8.6 (4) |
| C(23) | −0.0483 (7) | 0.1354 (9) | 0.0797 (4) | 6.3 (3) | N(1) | 0.359 (1) | 0.6081 (9) | 0.4413 (6) | 14.9 (5) |
| C(24) | −0.0001 (6) | 0.1486 (7) | 0.1357 (4) | 4.5 (2) | N(2) | 0.404 (1) | 0.439 (1) | 0.5540 (6) | 14.3 (6) |

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

**Table III.** Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å$^2$) and Their Estimated Standard Deviations for $Rh_2Cl_4(dppm)_2 \cdot 3CH_3CN \cdot H_2O$ (**2**)[b]

| atom | *x* | *y* | *z* | *B* (Å$^2$) |
|---|---|---|---|---|
| Rh(1) | 0.2963 (2) | 0.235 | 0.09119 (6) | 1.92 (3) |
| Rh(2) | 0.3406 (2) | 0.24980 (9) | 0.18143 (6) | 1.85 (3) |
| Cl(1) | 0.2729 (7) | 0.2664 (3) | 0.2672 (2) | 3.7 (1) |
| Cl(2) | 0.1424 (7) | 0.2238 (3) | 0.0186 (2) | 3.7 (1) |
| Cl(3) | 0.1675 (7) | 0.1753 (3) | 0.1527 (2) | 2.9 (1) |
| Cl(4) | 0.1726 (6) | 0.3127 (3) | 0.1365 (2) | 2.7 (1) |
| P(1) | 0.4968 (7) | 0.1754 (3) | 0.1905 (2) | 2.0 (1) |
| P(2) | 0.4950 (7) | 0.3250 (3) | 0.1748 (2) | 2.1 (1) |
| P(3) | 0.4377 (7) | 0.1567 (3) | 0.0796 (2) | 2.1 (1) |
| P(4) | 0.4471 (7) | 0.3047 (3) | 0.0646 (2) | 2.0 (1) |
| C(1) | 0.570 (3) | 0.155 (1) | 0.1282 (8) | 2.9 (5) |
| C(2) | 0.573 (3) | 0.3253 (9) | 0.1144 (7) | 2.2 (5) |
| C(3) | 0.654 (2) | 0.180 (1) | 0.2322 (7) | 2.1 (4)[a] |
| C(4) | 0.790 (3) | 0.169 (1) | 0.2141 (9) | 3.7 (6) |
| C(5) | 0.901 (2) | 0.170 (1) | 0.2464 (8) | 3.3 (6) |
| C(6) | 0.882 (3) | 0.179 (1) | 0.2921 (9) | 3.8 (6) |
| C(7) | 0.745 (3) | 0.192 (1) | 0.312 (1) | 5.3 (7) |
| C(8) | 0.627 (3) | 0.195 (1) | 0.2764 (9) | 3.9 (6) |
| C(9) | 0.411 (3) | 0.110 (1) | 0.2184 (8) | 2.5 (5)[a] |
| C(10) | 0.318 (2) | 0.113 (1) | 0.2536 (8) | 2.9 (5) |
| C(11) | 0.262 (3) | 0.064 (1) | 0.275 (1) | 4.6 (7) |
| C(12) | 0.310 (3) | 0.008 (1) | 0.261 (1) | 5.6 (7) |
| C(13) | 0.407 (3) | 0.004 (1) | 0.227 (1) | 4.8 (7) |
| C(14) | 0.464 (3) | 0.055 (1) | 0.2044 (9) | 3.3 (6) |
| C(15) | 0.648 (2) | 0.3299 (9) | 0.2156 (8) | 2.1 (5) |
| C(16) | 0.791 (3) | 0.322 (1) | 0.2005 (9) | 3.7 (6)[a] |
| C(17) | 0.912 (4) | 0.326 (1) | 0.2325 (9) | 5.4 (8) |
| C(18) | 0.882 (3) | 0.342 (1) | 0.281 (1) | 4.6 (7) |
| C(19) | 0.740 (3) | 0.352 (1) | 0.2962 (9) | 3.7 (6) |
| C(20) | 0.623 (2) | 0.347 (1) | 0.2625 (9) | 3.1 (5) |
| C(21) | 0.423 (2) | 0.398 (1) | 0.1820 (9) | 2.9 (5) |
| C(22) | 0.486 (3) | 0.448 (1) | 0.160 (1) | 4.3 (6) |
| C(23) | 0.432 (3) | 0.506 (1) | 0.169 (1) | 5.4 (7) |
| C(24) | 0.316 (3) | 0.510 (1) | 0.205 (1) | 6.7 (9) |
| C(25) | 0.249 (3) | 0.464 (1) | 0.226 (1) | 5.9 (8) |
| C(26) | 0.300 (3) | 0.408 (1) | 0.217 (1) | 4.1 (6) |
| C(27) | 0.546 (3) | 0.149 (1) | 0.0235 (9) | 3.8 (6) |
| C(28) | 0.700 (4) | 0.147 (1) | 0.026 (1) | 5.3 (7) |
| C(29) | 0.773 (3) | 0.139 (1) | −0.018 (1) | 5.1 (7) |
| C(30) | 0.699 (4) | 0.128 (1) | −0.058 (1) | 7.1 (8) |
| C(31) | 0.545 (4) | 0.125 (1) | −0.0606 (8) | 5.1 (8) |
| C(32) | 0.472 (4) | 0.137 (1) | −0.019 (1) | 4.9 (7) |
| C(33) | 0.346 (3) | 0.0863 (9) | 0.0781 (9) | 2.9 (5) |
| C(34) | 0.202 (2) | 0.083 (1) | 0.0639 (9) | 3.7 (5)[a] |
| C(35) | 0.144 (3) | 0.027 (1) | 0.054 (1) | 6.3 (9) |
| C(36) | 0.223 (3) | −0.025 (1) | 0.063 (1) | 5.2 (8) |
| C(37) | 0.365 (4) | −0.021 (1) | 0.079 (1) | 6.3 (9) |
| C(38) | 0.435 (3) | 0.035 (1) | 0.0845 (9) | 4.0 (6) |
| C(39) | 0.559 (3) | 0.295 (1) | 0.0120 (8) | 3.0 (5) |
| C(40) | 0.705 (2) | 0.307 (1) | 0.0123 (8) | 2.4 (4)[a] |
| C(41) | 0.789 (3) | 0.305 (1) | −0.0286 (9) | 3.9 (6) |
| C(42) | 0.736 (3) | 0.294 (1) | −0.074 (1) | 4.8 (7) |
| C(43) | 0.596 (3) | 0.278 (1) | −0.075 (1) | 5.7 (7) |
| C(44) | 0.490 (4) | 0.282 (1) | −0.0305 (9) | 5.6 (8) |
| C(45) | 0.358 (3) | 0.375 (1) | 0.0457 (8) | 3.0 (5) |
| C(46) | 0.448 (3) | 0.424 (1) | 0.040 (1) | 4.4 (7) |
| C(47) | 0.386 (4) | 0.474 (1) | 0.019 (1) | 7.2 (9) |
| C(48) | 0.229 (3) | 0.474 (1) | 0.004 (1) | 5.5 (8) |
| C(49) | 0.151 (4) | 0.421 (1) | 0.006 (1) | 6.5 (8) |
| C(50) | 0.220 (3) | 0.376 (1) | 0.0285 (9) | 3.4 (6) |
| N(1) | 0.305 (3) | 0.535 (1) | 0.371 (1) | 7.3 (8)[a] |
| C(51) | 0.547 (4) | 0.513 (2) | 0.321 (1) | 6.8 (9)[a] |
| C(52) | 0.404 (4) | 0.528 (2) | 0.349 (1) | 6.5 (9)[a] |
| N(2) | 0.468 (3) | 0.371 (1) | 0.384 (1) | 6.9 (7)[a] |
| C(53) | 0.217 (5) | 0.380 (2) | 0.376 (2) | 10 (1)[a] |
| C(54) | 0.364 (3) | 0.379 (1) | 0.383 (1) | 4.9 (7)[a] |
| N(3) | 0.695 (4) | 0.438 (2) | 0.587 (1) | 11 (1)[a] |
| C(55) | 0.459 (5) | 0.479 (2) | 0.623 (2) | 11 (1)[a] |
| C(56) | 0.597 (4) | 0.456 (2) | 0.604 (1) | 6.2 (8)[a] |
| O(1) | 0.623 (2) | 0.2350 (9) | 0.6021 (6) | 4.3 (4)[a] |

[a] Atoms refined isotropically. [b] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

**Table IV.** Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å$^2$) and Their Estimated Standard Deviations for $Rh_2Cl_2(dmpm)_2[(C_6H_5)_2P(C_6H_4)]_2 \cdot CH_2Cl_2$ (**3**)[b]

| atom | *x* | *y* | *z* | *B* (Å$^2$) |
|---|---|---|---|---|
| Rh(1) | 0.6701 (2) | 0.17340 (7) | 0.7898 (1) | 1.02 (3) |
| Rh(2) | 0.7061 (1) | 0.09181 (7) | 0.6885 (1) | 0.85 (3) |
| Cl(1) | 0.6384 (5) | 0.2574 (2) | 0.8687 (3) | 2.1 (1) |
| Cl(2) | 0.7722 (5) | 0.0200 (2) | 0.6025 (3) | 1.7 (1) |
| P(1) | 0.4625 (5) | 0.1579 (2) | 0.7606 (3) | 1.3 (1) |
| P(2) | 0.6936 (5) | 0.0284 (2) | 0.7845 (3) | 1.3 (1) |
| P(3) | 0.9171 (5) | 0.1069 (2) | 0.7077 (4) | 1.5 (1) |
| P(4) | 0.8718 (5) | 0.1749 (3) | 0.8394 (4) | 1.6 (1) |
| P(5) | 0.6720 (5) | 0.1498 (2) | 0.5841 (4) | 1.4 (1) |
| P(6) | 0.6908 (6) | 0.2408 (2) | 0.6959 (4) | 1.9 (1) |
| C(1) | 0.430 (2) | 0.1003 (9) | 0.699 (1) | 1.4 (5) |
| C(2) | 0.521 (2) | 0.0780 (8) | 0.662 (1) | 1.2 (4)[a] |
| C(3) | 0.487 (2) | 0.0385 (8) | 0.606 (1) | 1.0 (4)[a] |
| C(4) | 0.365 (2) | 0.0208 (8) | 0.584 (1) | 1.1 (4)[a] |
| C(5) | 0.279 (2) | 0.0430 (8) | 0.623 (1) | 1.1 (4)[a] |
| C(6) | 0.305 (2) | 0.0832 (9) | 0.680 (1) | 2.2 (6) |
| C(7) | 0.386 (2) | 0.1449 (9) | 0.847 (1) | 1.8 (5)[a] |
| C(8) | 0.332 (2) | 0.095 (1) | 0.857 (1) | 2.9 (6) |
| C(9) | 0.281 (2) | 0.086 (1) | 0.923 (1) | 3.6 (6) |
| C(10) | 0.280 (2) | 0.127 (1) | 0.978 (1) | 2.6 (6) |
| C(11) | 0.334 (2) | 0.178 (1) | 0.966 (1) | 3.8 (7) |
| C(12) | 0.386 (2) | 0.1873 (9) | 0.900 (1) | 2.0 (5)[a] |
| C(13) | 0.356 (2) | 0.2093 (8) | 0.713 (1) | 1.4 (4)[a] |
| C(14) | 0.283 (2) | 0.2012 (8) | 0.643 (1) | 0.9 (4)[a] |
| C(15) | 0.198 (2) | 0.242 (1) | 0.611 (1) | 2.7 (5)[a] |
| C(16) | 0.190 (2) | 0.2893 (9) | 0.648 (1) | 2.2 (5)[a] |
| C(17) | 0.272 (2) | 0.302 (1) | 0.722 (1) | 3.5 (7) |
| C(18) | 0.347 (2) | 0.2605 (9) | 0.752 (1) | 2.7 (6) |
| C(19) | 0.654 (2) | 0.0589 (8) | 0.870 (1) | 1.1 (4)[a] |
| C(20) | 0.654 (2) | 0.1168 (8) | 0.874 (1) | 1.1 (4)[a] |
| C(21) | 0.643 (2) | 0.1372 (8) | 0.950 (1) | 1.4 (4)[a] |
| C(22) | 0.626 (2) | 0.103 (1) | 1.012 (1) | 2.8 (6) |
| C(23) | 0.621 (2) | 0.045 (1) | 1.003 (1) | 2.6 (6) |
| C(24) | 0.632 (2) | 0.0244 (9) | 0.930 (1) | 1.5 (5)[a] |
| C(25) | 0.579 (2) | −0.0235 (8) | 0.757 (1) | 1.0 (4)[a] |
| C(26) | 0.470 (2) | −0.0224 (9) | 0.788 (1) | 1.7 (5)[a] |
| C(27) | 0.380 (2) | −0.0611 (9) | 0.765 (1) | 2.4 (5)[a] |
| C(28) | 0.396 (2) | −0.100 (1) | 0.709 (1) | 3.0 (5)[a] |
| C(29) | 0.504 (2) | −0.1006 (9) | 0.678 (1) | 2.0 (5)[a] |
| C(30) | 0.594 (2) | −0.0635 (8) | 0.700 (1) | 1.3 (4)[a] |
| C(31) | 0.822 (2) | −0.0180 (9) | 0.820 (1) | 1.7 (5)[a] |
| C(32) | 0.872 (2) | −0.0169 (8) | 0.899 (1) | 1.5 (4)[a] |
| C(33) | 0.974 (2) | −0.0477 (9) | 0.929 (1) | 3.0 (7) |
| C(34) | 1.021 (2) | −0.084 (1) | 0.875 (1) | 2.7 (6) |
| C(35) | 0.966 (2) | −0.0845 (9) | 0.796 (1) | 2.1 (5) |
| C(36) | 0.871 (2) | −0.0501 (9) | 0.766 (1) | 2.4 (5)[a] |
| C(37) | 0.973 (2) | 0.166 (1) | 0.763 (1) | 2.8 (6) |
| C(38) | 1.021 (2) | 0.0534 (9) | 0.752 (1) | 2.2 (6) |
| C(39) | 0.987 (2) | 0.1190 (8) | 0.620 (1) | 1.5 (5)[a] |
| C(40) | 0.933 (2) | 0.2336 (9) | 0.895 (1) | 2.1 (5)[a] |
| C(41) | 0.930 (2) | 0.123 (1) | 0.908 (1) | 2.4 (5)[a] |
| C(42) | 0.740 (2) | 0.2174 (9) | 0.604 (1) | 1.9 (5) |
| C(43) | 0.518 (2) | 0.1671 (9) | 0.544 (1) | 1.9 (5)[a] |
| C(44) | 0.724 (2) | 0.1294 (9) | 0.496 (1) | 1.9 (5)[a] |
| C(45) | 0.805 (2) | 0.2927 (9) | 0.721 (1) | 2.0 (5)[a] |
| C(46) | 0.563 (2) | 0.2845 (9) | 0.660 (1) | 1.7 (5)[a] |
| C(47) | 0.851 (3) | −0.103 (1) | 0.553 (2) | 5.0 (8) |
| Cl(3) | 0.7884 (8) | −0.1643 (4) | 0.5862 (5) | 7.0 (3) |
| Cl(4) | 1.0058 (7) | −0.1017 (4) | 0.5899 (5) | 7.1 (3) |

[a] Atoms refined isotropically. [b] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

benzene followed by diethyl ether. The IR spectrum of the crude solid was complicated, indicating a mixture of compounds. This was substantiated by our observation that two different kinds of crystals were formed when a $CH_3CN$ solution of the impure solid was allowed to slowly evaporate. A red crystal of **2** and a yellow crystal of $RhCl_3(dppm)(CH_3CN)$ was selected and identified by X-ray procedures. The Rh(III) mononuclear complex will be discussed in another paper.[5]

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(5) Cotton, F. A.; Dunbar, K. R., manuscript in preparation.

**Table V.** Selected Bond Distances (Å) and Bond Angles (deg) for $Rh_2Cl_2(O_2CCH_3)_2(dppm)_2 \cdot 2CH_3CN$ (**1**)

Bond Distances

| atom 1 | atom 2 | distance | atom 1 | atom 2 | distance | atom 1 | atom 2 | distance |
|---|---|---|---|---|---|---|---|---|
| Rh(1) | Rh(2) | 2.622 (1) | Rh(2) | O(4) | 2.110 (5) | P(4) | C(1) | 1.837 (7) |
| Rh(1) | Cl(1) | 2.475 (2) | P(1) | C(2) | 1.873 (8) | P(4) | C(43) | 1.836 (8) |
| Rh(1) | P(1) | 2.251 (2) | P(1) | C(7) | 1.833 (7) | P(4) | C(49) | 1.825 (8) |
| Rh(1) | P(3) | 2.256 (2) | P(1) | C(13) | 1.830 (7) | O(1) | C(3) | 1.203 (10) |
| Rh(1) | O(1) | 2.125 (6) | P(2) | C(2) | 1.822 (8) | O(2) | C(3) | 1.184 (10) |
| Rh(1) | O(3) | 2.108 (5) | P(2) | C(19) | 1.831 (7) | O(3) | C(5) | 1.206 (10) |
| Rh(2) | Cl(2) | 2.492 (2) | P(2) | C(25) | 1.850 (8) | O(4) | C(5) | 1.197 (11) |
| Rh(2) | P(2) | 2.261 (2) | P(3) | C(1) | 1.844 (8) | C(3) | C(4) | 1.623 (12) |
| Rh(2) | P(4) | 2.245 (2) | P(3) | C(31) | 1.831 (8) | C(5) | C(6) | 1.643 (12) |
| Rh(2) | O(2) | 2.126 (5) | P(3) | C(37) | 1.840 (8) | | | |

Bond Angles

| atom 1 | atom 2 | atom 3 | angle | atom 1 | atom 2 | atom 3 | angle | atom 1 | atom 2 | atom 3 | angle |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Rh(2) | Rh(1) | Cl(1) | 164.70 (6) | O(1) | Rh(1) | O(3) | 83.6 (2) | P(4) | Rh(2) | O(4) | 174.1 (2) |
| Rh(2) | Rh(1) | P(1) | 95.85 (6) | Rh(1) | Rh(2) | Cl(2) | 164.33 (6) | O(2) | Rh(2) | O(4) | 84.2 (2) |
| Rh(2) | Rh(1) | P(3) | 93.95 (6) | Rh(1) | Rh(2) | P(2) | 93.48 (6) | Rh(1) | P(1) | C(2) | 112.5 (3) |
| Rh(2) | Rh(1) | O(1) | 82.8 (2) | Rh(1) | Rh(2) | P(4) | 95.84 (6) | Rh(2) | P(2) | C(2) | 109.9 (2) |
| Rh(2) | Rh(1) | O(3) | 83.0 (2) | Rh(1) | Rh(2) | O(2) | 82.8 (2) | Rh(1) | P(3) | C(1) | 109.6 (2) |
| Cl(1) | Rh(1) | P(1) | 94.60 (8) | Rh(1) | Rh(2) | O(4) | 82.7 (2) | Rh(2) | P(4) | C(1) | 113.0 (3) |
| Cl(1) | Rh(1) | P(3) | 96.15 (7) | Cl(2) | Rh(2) | P(2) | 96.27 (7) | Rh(1) | O(1) | C(3) | 116.7 (5) |
| Cl(1) | Rh(1) | O(1) | 85.7 (2) | Cl(2) | Rh(2) | P(4) | 95.55 (8) | Rh(2) | O(2) | C(3) | 115.4 (5) |
| Cl(1) | Rh(1) | O(3) | 85.7 (2) | Cl(2) | Rh(2) | O(2) | 86.5 (2) | Rh(1) | O(3) | C(5) | 116.8 (5) |
| P(1) | Rh(1) | P(3) | 95.49 (7) | Cl(2) | Rh(2) | O(4) | 84.9 (2) | Rh(2) | O(4) | C(5) | 118.1 (5) |
| P(1) | Rh(1) | O(1) | 174.2 (1) | P(2) | Rh(2) | P(4) | 94.72 (7) | P(3) | C(1) | P(4) | 114.1 (4) |
| P(1) | Rh(1) | O(3) | 90.6 (2) | P(2) | Rh(2) | O(2) | 174.3 (2) | P(1) | C(2) | P(2) | 112.1 (4) |
| P(3) | Rh(1) | O(1) | 90.3 (2) | P(2) | Rh(2) | O(4) | 91.1 (2) | O(1) | C(3) | O(2) | 134.1 (8) |
| P(3) | Rh(1) | O(3) | 173.5 (2) | P(4) | Rh(2) | O(2) | 90.0 (2) | O(3) | C(5) | O(4) | 132.2 (8) |

The two products were separated in bulk by washing the total precipitate with methanol which dissolves the yellow monomer and leaves behind the red-brown binuclear product as a pure powder. Yield 0.42 g, 53%. Anal. Calcd for $C_{50}H_{44}Cl_4P_4Rh_2$: C, 53.79; H, 3.97. Found: C, 53.67; H, 3.45. IR (Nujol mull, CsI) 1590 (w), 1575 (m), 1485 (m), 1435 (s), 1280 (w), 1195 (m), 1260 (m), 1250 (m), 1100 (s), 1030 (m), 1005 (m), 850 (w), 770 (s), 740 (s), 730 (s), 695 (s), 620 (w), 555 (m), 545 (m), 530 (s), 520 (s), 495 (m), 425 (w), 295 (m).

**Reaction of $Rh_2(O_2CCH_3)_2[(C_6H_5)_2P(C_6H_4)]_2$ with dmpm.** (i) **$Rh_2Cl_2(dmpm)_2[(C_6H_5)_2P(C_6H_4)]_2 \cdot CH_2Cl_2$.** Purple $Rh_2(O_2CCH_3)_2(Ph_2PC_6H_4)_2 \cdot 2CH_3COOH$ (0.200 g, 0.207 mmol) was dissolved in THF to yield a dark blue solution of the bis-THF adduct. The solution was heated and 106 μL (0.84 mmol) of $Me_3SiCl$ was introduced, whereupon the color immediately turned green. dmpm (80 μL, 0.53 mmol) was added with stirring and the color changed to cherry red. The reaction was refluxed for 0.5 h and then stirred at room temperature for 5 h. Reduction of the volume to ~3 mL produced a crop of pink microcrystals which were filtered off, washed with diethyl ether, and dried in vacuo. Yield 0.21 g, 95%.

The compound was recrystallized by slow evaporation of a $CH_2Cl_2$ solution in air. Calcd for $C_{47}H_{58}Cl_4P_6Rh_2$: C, 48.81; H, 5.06; Cl, 12.26. Found: C, 48.42; H, 5.72; Cl, 12.65. The formula used for the calculated percentages includes a molecule of dichloromethane, shown by X-ray data to be present in crystals of **3**; the experimental values are in good agreement with this. IR (Nujol mull, CsI) 1585 (w), 1570 (m), 1540 (w), 1480 (m), 1445 (s), 1410 (m), 1300 (m), 1282 (m), 1200 (w), 1160 (w), 1125 (m), 1090 (m), 1070 (m), 1032 (w), 1010 (w), 945 (s), 900 (m), 805 (m), 825 (w), 755 (s), 740 (s), 715 (s), 695 (s), 685 (m), 665 (m), 542 (s), 525 (m), 500 (s), 480 (m), 440 (m), 420 (w).

**Preparation of Single Crystals.** Orange-brown crystals of $Rh_2Cl_2(O_2CCH_3)_2(dppm)_2 \cdot 2CH_3CN$ (**1**) and orange-red crystals of $Rh_2Cl_4(dppm)_2 \cdot 3CH_3CN \cdot H_2O$ (**2**) were each prepared by slow evaporation of a $CH_2Cl_2$–$CH_3CN$ solution of the compound. Dark red rhombohedral crystals of $Rh_2Cl_2(dmpm)_2(Ph_2PC_6H_4)_2 \cdot CH_2Cl_2$ (**3**) were obtained by carefully placing a layer of hexane over a $CH_2Cl_2$ solution of the complex under argon.

**X-ray Crystallography.** The structures of **1**, **2**, and **3** were determined by general procedures that have been fully described elsewhere.[6] The diffraction data for **1** and **3** were collected on an Enraf-Nonius CAD-4 diffractometer and the data for **2** were obtained with a Syntex P3 autodiffractometer; both are equipped with graphite monochromated Mo Kα ($\bar{\alpha}$ = 0.71073 Å) radiation. Data reduction was carried out by standard methods with use of well-established computational procedures.[7] The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I. Tables II, III, and IV list the positional parameters for structures **1**, **2**, and **3**, respectively. Complete tables of bond distances and angles as well as anisotropic thermal parameters and structure factors are available as supplementary meaterial.

**$Rh_2Cl_2(O_2CCH_3)_2(dppm)_2$ (1).** An orange-brown platelet of **1** (approximate dimensions 0.30 × 0.30 × 0.05 mm) was mounted on a glass fiber. A rotation photograph indicated that the crystal diffracted well. An automatic search routine was used to locate 25 reflections in the range $12 < 2\theta < 25°$. The reduced cell dimensions indicated that the crystal belonged to the monoclinic crystal system, which we verified by axial photography. Systematic absences from the data led to the choice of $P2_1/c$ as the space group.

An ω-scan motion was used to scan 7681 possible data points in a range of $4 < 2\theta < 45°$. The structure factors were obtained after a Lorentz and polarization correction. Three standard reflections measured following every 2 h of X-ray exposure decreased in intensity by an average of 4.1% over the 128.5 h of beam exposure; a decay correction was applied to account for this. Azimuthal scans of 9 reflections with Eulerian angle χ near 90° were used as the basis for an empirical absorption correction.[8] After averaging the equivalent reflections, there remained 6701 unique data and 4822 reflections with $F_o^2 \geq 3\sigma(F_o)^2$.

Both the Patterson peak search and the direct-methods program MULTAN 11/82 led to location of the two independent Rh atoms. A sequence of successive difference Fourier maps and least-squares cycles led to full development of the coordination sphere. Two molecules of interstitial $CH_3CN$ were also located. After isotropic convergence was achieved an additional absorption correction DIFABS was applied.[9] Subsequent anisotropic refinement was successfully completed to give $R$ = 0.0443 and $R_w$ = 0.0552, using 4822 reflections to fit 649 variables. A final difference Fourier map had a maximum peak of density 0.67 e/Å$^3$. The last cycle did not shift any parameter by more than 0.18 times its estimated standard deviation.

**$Rh_2Cl_4(dppm)_2 \cdot 3CH_3CN \cdot H_2O$ (2).** A red-brown rectangular shaped crystal of **2** (approximate dimensions 0.40 × 0.30 × 0.15 mm) was mounted inside a capillary surrounded by the mother liquid. The crystal was found to be orthorhombic and the cell parameters and orientation

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(6) (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.

(7) Crystallographic computing was done on a PDP-11/60 (RSX-11 MV4.1) with PDP-11 simulated VAXSDP and on a VAX-11/780 (VMS V4.1). In the case of **1**, refinement was done on a cluster with VAX 8650 and VAX 8800 computers.

(8) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys. Diffr., Theor. Gen. Crystallogr.* **1968**, *24*, 351.

(9) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *39*, 158.

**Table VI.** Selected Bond Distances (Å) and Bond Angles (deg) for $Rh_2Cl_4(dppm)_2{\cdot}3CH_3CN{\cdot}H_2O$ (**2**)

Bond Distances

| atom 1 | atom 2 | distance | atom 1 | atom 2 | distance | atom 1 | atom 2 | distance |
|---|---|---|---|---|---|---|---|---|
| Rh(1) | Rh(2) | 2.523 (2) | Rh(2) | P(1) | 2.247 (7) | P(4) | C(2) | 1.86 (2) |
| Rh(1) | Cl(2) | 2.466 (6) | Rh(2) | P(2) | 2.244 (7) | C(3) | C(4) | 1.39 (3) |
| Rh(1) | Cl(3) | 2.466 (6) | P(1) | C(1) | 1.89 (2) | C(3) | C(8) | 1.28 (3) |
| Rh(1) | Cl(4) | 2.451 (6) | P(1) | C(3) | 1.87 (2) | C(4) | C(5) | 1.37 (4) |
| Rh(1) | P(3) | 2.229 (6) | P(1) | C(9) | 1.85 (2) | C(5) | C(6) | 1.28 (3) |
| Rh(1) | P(4) | 2.247 (6) | P(2) | C(2) | 1.80 (2) | C(6) | C(7) | 1.42 (4) |
| Rh(2) | Cl(1) | 2.457 (6) | P(2) | C(15) | 1.82 (2) | C(7) | C(8) | 1.48 (3) |
| Rh(2) | Cl(3) | 2.470 (6) | P(2) | C(21) | 1.80 (2) | | | |
| Rh(2) | Cl(4) | 2.454 (6) | P(3) | C(1) | 1.82 (3) | | | |

Bond Angles

| atom 1 | atom 2 | atom 3 | angle | atom 1 | atom 2 | atom 3 | angle | atom 1 | atom 2 | atom 3 | angle |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Rh(2) | Rh(1) | Cl(2) | 153.6 (2) | Rh(1) | Rh(2) | Cl(3) | 59.2 (1) | Rh(2) | P(1) | C(1) | 108.6 (8) |
| Rh(2) | Rh(1) | Cl(3) | 59.3 (2) | Rh(1) | Rh(2) | Cl(4) | 59.0 (1) | Rh(2) | P(2) | C(2) | 109.8 (7) |
| Rh(2) | Rh(1) | Cl(4) | 59.1 (2) | Rh(1) | Rh(2) | P(1) | 96.5 (2) | Rh(1) | P(3) | C(1) | 108.6 (8) |
| Rh(2) | Rh(1) | P(3) | 98.5 (2) | Rh(1) | Rh(2) | P(2) | 97.5 (2) | Rh(1) | P(4) | C(2) | 109.9 (7) |
| Rh(2) | Rh(1) | P(4) | 96.6 (2) | Cl(1) | Rh(2) | P(1) | 100.3 (2) | P(1) | C(1) | P(3) | 114 (2) |
| Cl(2) | Rh(1) | P(3) | 99.0 (2) | Cl(1) | Rh(2) | P(2) | 97.3 (2) | P(2) | C(2) | P(4) | 114 (1) |
| Cl(2) | Rh(1) | P(4) | 100.3 (2) | Cl(3) | Rh(2) | Cl(4) | 79.4 (2) | | | | |
| Cl(3) | Rh(1) | Cl(4) | 79.5 (2) | P(1) | Rh(2) | P(2) | 99.1 (2) | | | | |
| P(3) | Rh(1) | P(4) | 98.0 (2) | Rh(1) | Cl(3) | Rh(2) | 61.5 (2) | | | | |
| Rh(1) | Rh(2) | Cl(2) | 155.5 (2) | Rh(1) | Cl(4) | Rh(2) | 61.9 (1) | | | | |

**Table VII.** Selected Bond Distances (Å) and Bond Angles (deg) for $Rh_2Cl_2(dmpm)_2[(C_6H_5)_2P(C_6H_4)]_2{\cdot}CH_2Cl_2$ (**3**)

Bond Distances

| atom 1 | atom 2 | distance | atom 1 | atom 2 | distance | atom 1 | atom 2 | distance |
|---|---|---|---|---|---|---|---|---|
| Rh(1) | Rh(2) | 2.770 (3) | Rh(2) | P(5) | 2.317 (6) | P(4) | C(37) | 1.91 (3) |
| Rh(1) | Cl(1) | 2.561 (6) | Rh(2) | C(2) | 2.09 (2) | C(1) | C(2) | 1.41 (3) |
| Rh(1) | P(1) | 2.345 (6) | P(1) | C(1) | 1.80 (2) | C(1) | C(6) | 1.46 (3) |
| Rh(1) | P(4) | 2.302 (6) | P(1) | C(7) | 1.89 (2) | C(2) | C(3) | 1.40 (3) |
| Rh(1) | P(6) | 2.388 (7) | P(1) | C(13) | 1.86 (2) | C(3) | C(4) | 1.43 (3) |
| Rh(1) | C(20) | 2.07 (2) | P(2) | C(19) | 1.80 (2) | C(4) | C(5) | 1.40 (3) |
| Rh(2) | Cl(2) | 2.527 (6) | P(2) | C(25) | 1.84 (2) | C(5) | C(6) | 1.40 (3) |
| Rh(2) | P(2) | 2.329 (6) | P(2) | C(31) | 1.88 (2) | C(19) | C(20) | 1.44 (3) |
| Rh(2) | P(3) | 2.377 (6) | P(3) | C(37) | 1.82 (2) | C(20) | C(21) | 1.45 (3) |

Bond Angles

| atom 1 | atom 2 | atom 3 | angle | atom 1 | atom 2 | atom 3 | angle | atom 1 | atom 2 | atom 3 | angle |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Rh(2) | Rh(1) | Cl(1) | 172.5 (2) | P(6) | Rh(1) | C(20) | 178.0 (6) | P(3) | Rh(2) | C(2) | 175.5 (6) |
| Rh(2) | Rh(1) | P(1) | 89.0 (2) | Rh(1) | Rh(2) | Cl(2) | 171.4 (1) | P(5) | Rh(2) | C(2) | 83.9 (6) |
| Rh(2) | Rh(1) | P(4) | 91.1 (2) | Rh(1) | Rh(2) | P(2) | 89.8 (2) | Rh(1) | P(1) | C(1) | 111.2 (7) |
| Rh(2) | Rh(1) | P(6) | 91.6 (2) | Rh(1) | Rh(2) | P(3) | 92.2 (2) | Rh(2) | P(2) | C(19) | 111.8 (7) |
| Rh(2) | Rh(1) | C(20) | 90.1 (6) | Rh(1) | Rh(2) | P(5) | 91.8 (2) | Rh(2) | C(2) | C(1) | 127 (1) |
| Cl(1) | Rh(1) | P(1) | 91.8 (2) | Rh(1) | Rh(2) | C(2) | 91.1 (6) | Rh(2) | C(2) | C(3) | 115 (1) |
| Cl(1) | Rh(1) | P(4) | 89.7 (2) | Cl(2) | Rh(2) | P(2) | 90.9 (2) | C(1) | C(2) | C(3) | 117 (2) |
| Cl(1) | Rh(1) | P(6) | 80.9 (2) | Cl(2) | Rh(2) | P(3) | 79.3 (2) | C(2) | C(3) | C(4) | 124 (2) |
| Cl(1) | Rh(1) | C(20) | 97.4 (6) | Cl(2) | Rh(2) | P(5) | 89.5 (2) | C(3) | C(4) | C(5) | 117 (2) |
| P(1) | Rh(1) | P(4) | 167.4 (2) | Cl(2) | Rh(2) | C(2) | 97.5 (6) | C(4) | C(5) | C(6) | 123 (2) |
| P(1) | Rh(1) | P(6) | 99.6 (2) | P(2) | Rh(2) | P(3) | 100.3 (2) | C(1) | C(6) | C(5) | 118 (2) |
| P(1) | Rh(1) | C(20) | 81.3 (5) | P(2) | Rh(2) | P(5) | 166.7 (2) | P(2) | C(19) | C(20) | 118 (2) |
| P(4) | Rh(1) | P(6) | 93.0 (2) | P(2) | Rh(2) | C(2) | 82.8 (6) | P(2) | C(19) | C(24) | 118 (2) |

matrix were refined by a least-squares fit to the positions of 25 intense reflections in the range $20 < 2\theta < 30°$. Axial photography was used to verify the lattice dimensions and symmetry.

The intensity data, gathered by the $\omega$–$2\theta$ scan technique, were reduced by routine procedures. Three check reflections monitored throughout data collection did not show any significant gain or loss in intensity. Absorption corrections were applied on the basis of azimuthal scans of 9 reflections with diffractometer angle $\chi$ near 90°. After equivalent data had been averaged, there remained 2775 data with $F_o^2 \geq 3\sigma(F_o)^2$. These were used in the subsequent development and refinement of the structure.

Systematic absences from the data led to two possibilities for a space group. The Rh atoms were located by application of direct methods (MULTAN 11/82). We began the refinement in the centrosymmetric space group *Pcmn*, which requires that each molecule reside on a mirror plane containing the Rh atoms and the two terminal Cl ligands. It became obvious early in the development of the structure that the crystallographically imposed symmetry required a disordered model with respect to the terminal chlorine atoms. By switching to a refinement in the acentric group $Pc2_1n$ we were able to abandon the mirror plane in favor of a model that showed no sign of disorder or high correlation. A careful checking of the atomic coordinates of the atoms in question revealed an absence of mirror symmetry. The structure developed normally in the acentric group, and all nonhydrogen atoms were located with use of alternating least-squares refinement and Fourier maps. Toward the end of the refinement, several peaks appeared in intersitial positions and were identified as three $CH_3CN$ molecules and one $H_2O$ molecule. The $H_2O$ molecule does not appear to be hydrogen bonded to anything, but its presence in the sample was confirmed by IR spectroscopy of the crystals: the spectrum exhibits bands that are characteristic of an OH stretch (3500 cm$^{-1}$, br) and an OH bend (1630 cm$^{-1}$).

In the end, 2775 data were used to fit 555 variables giving $R = 0.0645$, $R_w = 0.0806$, and goodness-of-fit = 1.41. Both enantiomorphs were refined, and the correct one was established at the 99% confidence level by application of the Hamilton significance test. The highest remaining peak in the difference Fourier map is 1.03 e/Å$^3$ and the final cycle did not shift any parameter by more than 0.18 times its estimated deviation.

**$Rh_2Cl_2(dmpm)_2[(C_6H_5)_2P(C_6H_4)]_2{\cdot}CH_2Cl_2$ (3).** A red crystal of **3** (0.30 × 0.25 × 0.20 mm) was mounted on the end of a glass fiber with use of vacuum grease. A stream of cold air (−106 °C) was directed at the crystal during data collection. The lattice dimensions and orientation matrix were determined by routine search and indexing routines. The crystal was found to be monoclinic (Laue class 2/m).

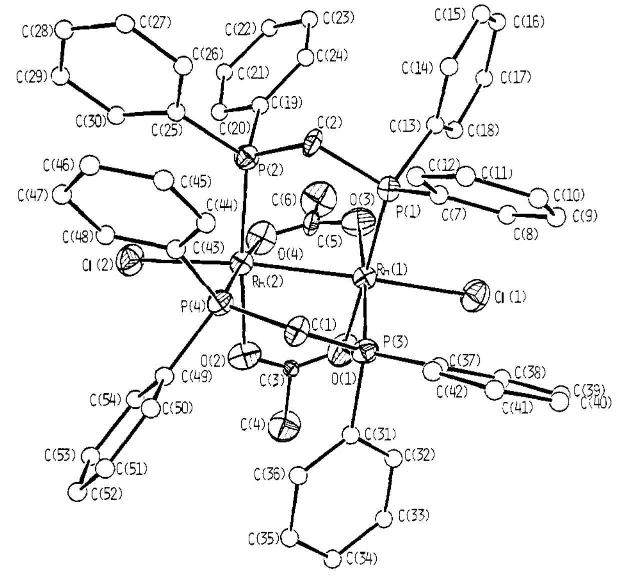

**Figure 1.** ORTEP view of $Rh_2Cl_2(O_2CCH_3)_2(dppm)_2$. Phenyl group carbon atoms are shown as small circles for clarity. All other atoms are represented by their 50% probability ellipsoids.

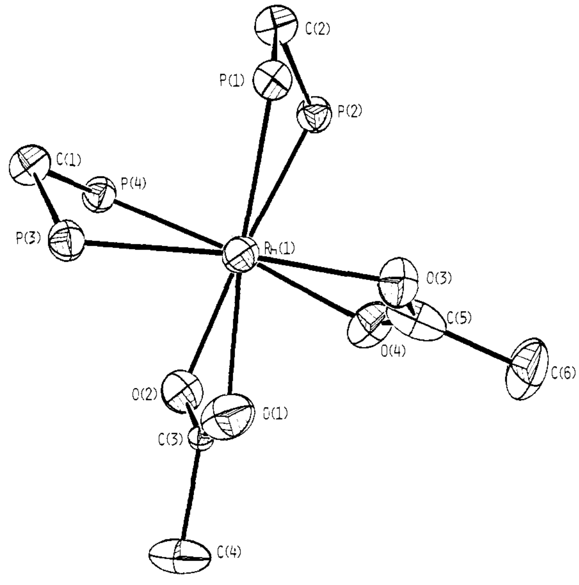

**Figure 2.** Central portion of $Rh_2Cl_2(O_2CCH_3)_2(dppm)_2$ viewed along the Rh(1)–Rh(2) axis. The chlorine and phenyl group carbon atoms were omitted.

During intensity-data collection ($\omega$–$2\theta$) check reflections were measured at regular intervals; no average gain or loss in intensity was observed. Data reduction included absorption corrections by the $\psi$-scan method (4 curves). Averaging of equivalent reflections was done, leaving 2473 reflections with $F_o^2 \geq 3\sigma(F_o)^2$ for use in data refinement.

The space group was determined to be $P2_1/c$ based upon systematic absences. The positions of the unique Rh atoms were located by direct methods. The coordination sphere was developed and refined in a series of alternating difference Fourier maps and full-matrix least-squares refinements. Anisotropic convergence was reached with $R = 0.0641$ and $R_w = 0.0742$, using 2473 data for 382 parameters. The largest shift/esd for the final cycle is 0.17 and the highest peak in the last difference Fourier map is 0.952 e/Å$^3$.

**Physical Measurements.** Infrared spectra were recorded by using Nujol mulls between CsI plates on a Perkin-Elmer 785 spectrophotometer. The electronic spectra were measured on dichloromethane solutions (HPLC grade) with a Cary 17D spectrophotometer. Electrochemical measurements were performed with a Bioanalytical Systems, Inc., Model BAS 100 electrochemical analyzer in conjunction with a Houston Instruments Model DMP 40 digital plotter. Experiments were carried out in dichloromethane containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as a supporting electrolyte. A three-electrode cell configuration was used, with a platinum disk, Model BAS MF 2032, and a platinum wire as working and auxiliary electrodes, respectively. A BAS MF 2020 Ag/AgCl cell was used as a reference electrode (against which ferrocene is oxidized at $E_{1/2} = +0.48$ V). All potentials were referenced to the Ag/AgCl electrode at 22 ± 2 °C with a full positive feedback resistance compensation and are uncorrected for junction potentials. $E_{1/2}$ values were determined as $(E_{p,a} + E_{p,c})/2$. Microanalyses were performed by Galbraith Laboratories of Knoxville, TN.

## Results and Discussion

**Synthetic Methods.** The preparations of the new compounds entail the use of the $(CH_3)_3SiCl$ reagent both to remove carboxylate ligands and to introduce chloride ligands into the coordination sphere. This synthetic procedure has proved very effective in the synthesis of $Mo_2X_4(PR_3)_4$ and $Mo_2X_4(P{-}P)_2$ compounds directly from $Mo_2(O_2CCH_3)_4$,[10–16] and we have recently been able to extend this chemistry to the late transition elements thus allowing the isolation of some unusual binuclear compounds of Os[17,18] and Rh[2].

In the present study, two different carboxylato starting materials were used to prepare dirhodium(II) complexes that contain $\mu$-$R_2PCH_2PR_2$ (R = Me, Ph) groups. These results constitute the first report in the literature of mixed phosphine–carboxylate or phosphine–halide $Rh_2^{4+}$ compounds.

The reaction of $Rh_2(O_2CCH_3)_4$ with dppm in the presence of 2 or 4 equiv of $Me_3SiCl$ leads to the formation of **1** and **2**, respectively. Suspensions of green anhydrous dirhodium(II) tetraacetate in warm benzene react immediately with dppm to give an orange precipitate, presumably an axial phosphine adduct. Upon introduction of $Me_3SiCl$ into the refluxing solution, the color quickly changes to pale salmon, signaling the formation of $Rh_2Cl_2(O_2CCH_3)_2(dppm)_2$. This partially substituted compound reacts slowly with additional $Me_3SiCl$ to yield the insoluble orange-red complex $Rh_2Cl_4(dppm)_2$, which is invariably contaminated with a yellow Rh(III) monomeric species.[5] Extended reflux times should be avoided since a greater degree of decomposition of **2** has been observed to occur under these conditions. We have also noted that the use of solvents other than benzene, e.g., $CH_3CN$, $CH_2Cl_2$, THF, and toluene, leads to lower yields of the desired dimeric product.

As a further demonstration of the general nature of the above approach, we studied the reaction of $(CH_3)_3SiCl$ with the ortho-metalated compound $Rh_2(O_2CCH_3)_2(Ph_2PC_6H_4)_2\cdot 2CH_3COOH$. A bright cherry red product, $Rh_2Cl_2(dmpm)_2(Ph_2PC_6H_4)_2$, is formed when the reaction is carried out in refluxing THF in the presence of 2 equiv of dmpm. When the amount of added dmpm is reduced to 1 equiv, a deep orange product, the nature of which is still under investigation, can be isolated.

**Structural Results and Interpretation. $Rh_2Cl_2(O_2CCH_3)_2(dppm)_2\cdot 2CH_3CN$ (1) and $Rh_2Cl_2(dmpm)_2[(C_6H_5)_2P(C_6H_4)]_2\cdot CH_2Cl_2$ (3).** Compounds **1** and **3** have the same basic coordination geometry and will therefore be discussed together. The principal interatomic distances and angles are listed in Tables V and VII for **1** and **3**, respectively.

In both **1** and **3** the molecules reside on general positions in the unit cell. The salient features of both structures are the presence of two different types of $\mu$-bidentate groups and two axial chloride ligands, arranged in a distorted octahedral geometry about

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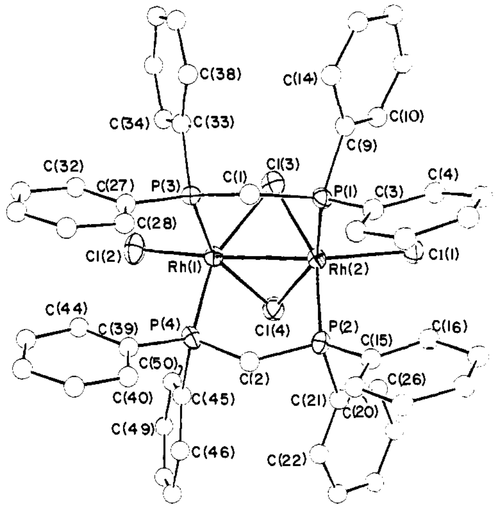

Figure 3. Structure and labeling scheme for $Rh_2Cl_4(dppm)_2$. The thermal ellipsoids are at the 50% probability level and the phenyl carbons are represented by circles.

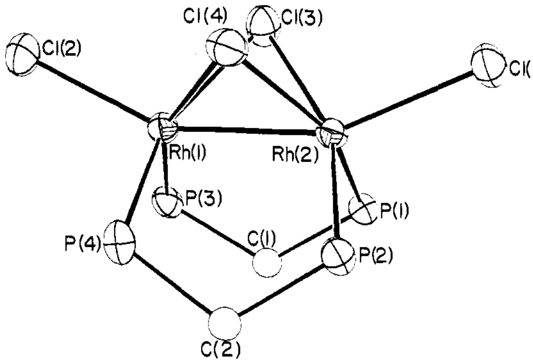

Figure 4. A skeletal view of $Rh_2Cl_4(dppm)_2$ without the phenyl groups on the phosphorus atom.

each Rh atom (see Figures 1 and 5).

In $Rh_2Cl_2(O_2CCH_3)_2(dppm)_2{\cdot}2CH_3CN$ (**1**) all the ligands are rotated considerably from an eclipsed conformation with an average torsion angle $\chi = 18°$. The ORTEP diagram in Figure 2 giving a view of **1** along the Rh–Rh bond axis depicts clearly the twisting exhibited by the $\mu$-acetato and $\mu$-dppm groups. The symmetry of this skeletal set of atoms is $C_2$. While the molecule shown has a counterclockwise twist it must be remembered that in each unit cell there are four twisted molecules, two of each chirality.

The situation is somewhat different in $Rh_2Cl_2(dmpm)_2(Ph_2PC_6H_4)_2{\cdot}CH_2Cl_2$ (**3**) where only the *cis* dmpm ligands are twisted ($\chi_{av} = 16°$) because the $o$-$(C_6H_5)_2PC_6H_4^-$ ligands in the five-membered ring Rh–C–C–P–Rh must maintain a strict planarity. The result is an unusual molecule with two twisted ligands on one side and two eclipsed ligands on the other side. The molecular symmetry is $C_2$.

Bond distances and angles in **1** and **3** are within the expected ranges. The Rh–P distances are short (Rh–$P_{av}$ = 2.253 [2] Å, **1**; 2.241 [6] Å, **3**), which is apparently not unusual for $Rh_2^{4+}$ complexes.[19] The average Rh–Cl (axial) distances of 2.475 (2) Å in **1** and 2.561 [6] Å in **3** are normal. The Rh–Rh–Cl(axial) angles are quite different in the two structures; the average angle in **1** is 164.5 (6)° and in **3** the value is 171.9°. The deviation from linearity in **1** is not surprising considering the overall distortion of the molecule (vide supra).

As a final point of discussion, we turn to a comparison of the Rh–Rh bond distances in **1** and **3** with Rh–Rh separations found in other Rh(II,II) compounds. The distances of 2.622 (1) Å in **1** and 2.770 (3) Å in **3** are considerably longer than the values for nearly all other singly bonded dirhodium complexes.[1] The (tetracarboxylato)dirhodium(II) compounds typically have Rh–Rh separations in the range 2.35 to 2.50 Å. The loss of the small-bite carboxylato groups which act to hold the $Rh_2$ unit together along with the addition of the axial chloride ligands are presumably the two most important factors contributing to the lengthening of the M–M bond.

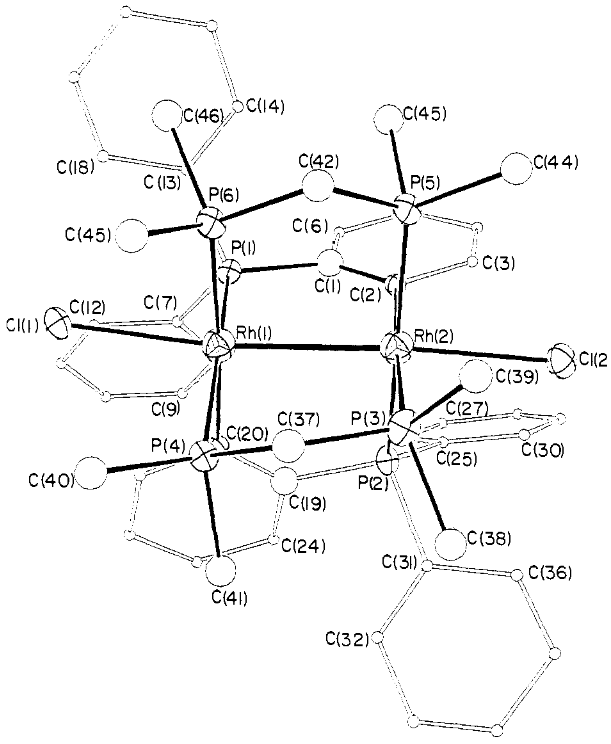

Figure 5. Drawing of the $Rh_2Cl_2(dppm)_2[(C_6H_5)_2P(C_6H_4)]_2$ molecule emphasizing the immediate coordination sphere of the Rh atoms. Phenyl carbon atoms are represented by small circles; all other atoms are at the 50% probability level.

**$Rh_2Cl_4(dppm)_2{\cdot}3CH_3CN{\cdot}H_2O$ (2).** Molecules of **2** occupy general positions in the acentric space group $Pc2_1n$. The asymmetric unit consists of one $Rh_2Cl_4(dppm)_2$ molecule, three $CH_3CN$ molecules, and one $H_2O$ molecule. A labeled ORTEP diagram of the $Rh_2Cl_4(dppm)_2$ molecule is shown in Figure 3. Important distances and angles are listed in Table VI. $Rh_2Cl_4(dppm)_2$ consists of two *cis*-$\mu$-dppm ligands (∠P–Rh–P(av) = 98.5 [2]°) and four chloride ligands, two of which occupy cis bridging positions. This arrangement of ligands is best described as a pair of distorted square pyramids sharing one edge. The skeletal view in Figure 4 shows this quite clearly. The molecular symmetry of **2** is $C_{2v}$, due to the presence of mirror planes, one of which lies perpendicular to the Rh–Rh vector and contains the bridging chlorine atoms and the methylene carbons of the dppm groups, the other containing the Rh atoms and the terminal Cl atoms.

As in **1** and **3**, the Rh–P bonds are on the short end of the range of expected M–P distances (Rh–P(av) = 2.242 [6] Å). The Rh–Cl(terminal) distances (av = 2.461 [6] Å) are the same as the Rh–Cl(bridge) distances (av = 2.460 [6] Å). The Rh–Rh bond distance of 2.523 (2) Å in **2** is shorter than the corresponding distances in **1** and **3** but it is still longer than the values of ~2.4 Å reported for various $Rh_2(O_2CCH_3)_4L_2$ compounds.[1]

The type of structure we have for compound **2** is unusual but not entirely unprecedented. The structure of the complex $Ir_2(\mu\text{-}CNAr)_2(CNAr)_2(dmpm)_2$[20] is essentially the same and there are two other structures that differ in having only one bridging group,

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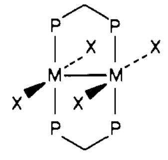
[19] Tortorelli, L. J.; Tucker, C. A.; Woods, C.; Bordner. J. *Inorg. Chem.* **1986**, *25*, 3534.

[20] Wu, J.; Kubiak, C. P. Presented at the 192nd National Meeting of the American Chemical Society, Anaheim, CA, September 1986; paper INOR 305.

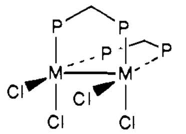
but are similar in having the cis pair of bridging diphosphine ligands: $Co_2(\mu\text{-}PMe_2)(dmpm)_2(PMe_3)_2$[21] and $Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2$.[22] Such structures have been described as cradles[20] and W-frames.[21]

The most important fact about the structure of compound **2** from our point of view is that it is *not* the one we had expected to find for a compound having the constitution $M_2X_4(P\text{-}P)_2$, namely, the type **4** found in compounds of Mo, W, and Re.[23] We do not rule out the possibility that an isomer of $Rh_2Cl_4(dppm)_2$ having a structure of type **4** can be obtained, and, in fact, efforts are being made to do this. We can, however, rationalize the structure that has been found with a combination of both kinetic and thermodynamic factors.



**4**

From the kinetic, or mechanistic, point of view, one can easily envisage that when the two acetate groups of $Rh_2Cl_2(O_2CCH_3)_2(dppm)_2$ are replaced by chlorine atoms, the dppm ligands retain their cisoid relationship, thus affording as the immediate product a cis structure of type **5**. This could easily rearrange to the actual bridged structure and would have a thermodynamic incentive to do so: the actual structure has two more Rh–Cl bonds while retaining, qualitatively speaking, all the other bonds present in **5**.



**5**

It must be noted that no similar rearrangement would be expected in other cases where there are M–M multiple bonds, even if it were mechanistically possible. A structure of the type displayed by compound **2** is entirely compatible with the retention of a *single bond* between the metal atoms, and for M = Rh, this is the highest bond order to be expected in any of the alternative structures (i.e., **4** or **5**). For metal atoms that would form triple or quadruple bonds (Re and Mo, respectively) when in molecules having structures **4** or **5**, the change to the Cl-bridged structure would presumably interfere seriously with maintaining the high M–M bond order. The consequent loss of M–M bond energy would presumably not be compensated by the two additional M–Cl bonds arising when two of the chlorine atoms become bridges.

**Electronic Spectroscopy and Electrochemistry.** Solutions of **1**, **2**, and **3** were exposed to air for prolonged periods of time without any apparent decomposition as evidenced by electronic spectroscopy and cyclic voltammetry. Consequently, no special precautions were taken during these studies.

UV–visible spectroscopic measurements of the new compounds were carried out in dichloromethane giving the following results, $\lambda_{max}$, nm ($\epsilon$): **1**, 357 (15000), 485 (800), 520 sh; **2**, 365 (43000), 440 sh, 530 (740); **3** 300 (9370), 368 (16400), 520 sh, 550 (740). The close electronic relationship among the three complexes indicated by these measurements is further supported by the electrochemical data (vide infra). The spectral properties of the new compounds may be compared to those exhibited by $Rh_2(O_2CR)_4L_2$, complexes whose spectra consist of two distinct absorptions around 600 and 450 nm, with the low-energy band being quite sensitive to the identity of the axial ligand.[1] The assignment of these transitions in dirhodium(II) singly bonded species has been a topic of interest in recent years.[24] A detailed discussion of the visible spectra for the new $Rh_2^{4+}$ compounds will have to await further studies.

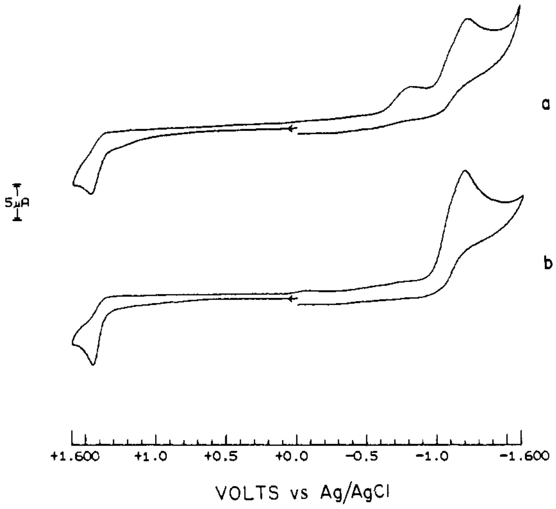


**Figure 6.** Cyclic voltammograms (scan rate 200 mV/s at a Pt disk electrode vs. Ag/AgCl in 0.2 M TBAH–$CH_2Cl_2$): (a) $Rh_2Cl_2(O_2CCH_3)_2(dppm)_2\cdot 2CH_3CN$; (b) $Rh_2Cl_4(dppm)_2$.

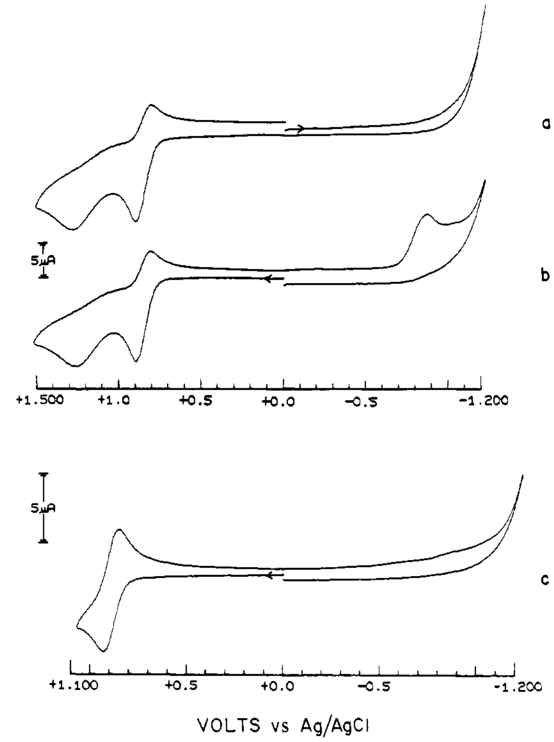


**Figure 7.** Cyclic voltammograms of $Rh_2Cl_2(dmpm)_2(Ph_2PC_6H_4)_2$: (a) scan range +1.5 to −1.2 V, negative scan direction; (b) scan range +1.5 to −1.2 V, positive scan direction; (c) scan range +1.1 to −1.2 V, positive scan direction. Experiments were done in 0.2 M TBAH–$CH_2Cl_2$ at a Pt disk electrode referenced to Ag/AgCl at room temperature.

The electrochemical properties of **1** and **2**, as determined by cyclic voltammetry, are characterized by an oxidation and a reduction process—both irreversible. It is interesting that the two compounds exhibit strikingly similar redox behavior, even though the molecules are not structurally related (vide supra). Compound **1** (Figure 6a) possesses an oxidation wave at $E_{p,a}$ = 1.47 V and

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a reduction at $E_{p,c} = -1.23$ V vs. Ag/AgCl. An additional minor feature is present at $E_{p,c} = 0.69$ V. The corresponding potentials for **2** (Figure 6b) occur at values of +1.44 and −1.18 V. The relative inaccessibility of $Rh_2^{3+}$ or $Rh_2^{5+}$ core valencies in **1** and **2**, as evidenced by the high values of the redox potentials required to access them, implies that dppm and chloride ligands are quite effective in stabilizing the $Rh_2^{4+}$ unit in the absence of $\mu$-$O_2CCH_3^-$ groups.

Figure 7 shows three separate cyclic voltammograms of **3**. The initial scan direction is negative in Figure 7a, leading to the detection of two processes, both oxidations, at $E_{1/2} = 0.86$ V and $E_{p,a} = +1.24$ V vs. Ag/AgCl. In Figure 7b, the measurement was recorded in the same solution but with a reversal of scan direction. In this case there is an additional irreversible feature at $E_{p,c}$ −0.85 V due to a chemical product formed after compound **3** has been oxidized. The quasireversible couple at $E_{1/2} = +0.85$ V becomes more reversible and the product wave at −0.85 V disappears (Figure 7c) when the highest positive scan potential applied to the electrode is +1.10 V (instead of +1.50 V as in parts a and b). The accessibility of the reversible couple representing the process

$$Rh_2^{4+} \xrightarrow{-e^-} Rh_2^{5+}$$

suggests the feasibility of chemically isolating the cationic complex $[Rh_2Cl_2(dmpm)_2(Ph_2PC_6H_4)_2]^+$. Reactivity studies indicate that $NO^+$ is a suitable oxidizing agent for this purpose; further work is underway.

**Conclusion.** This work provides the basis for future investigations into dirhodium(II) chemistry with ligands other than small bidentate groups containing O–O or O–N donor atoms. The three new compounds reported here are significantly different than any previously known $Rh_2^{4+}$ complexes. Furthermore, the geometry of the $Rh_2Cl_4(dppm)_2$ molecule constitutes a new structural type for $M_2X_4(L-L)_2$ species. Preliminary investigations into the reactivity of **1** and **3** imply that a rich chemistry is associated with chemical oxidation and removal of the axial chloride ligands. Compound **2**, although much more stable than **1** or **3**, appears to react with bases such as pyridine, but the products have not yet been identified.

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**Supplementary Material Available:** Full tables of bond distances, bond angles, and anisotropic displacement parameters for the crystal structures of **1**, **2**, and **3** (18 pages); tables of observed and calculated structure factors (52 pages). Ordering information is given on any current masthead page.

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# Synthesis and Characterization of Niobium(II) and Tantalum(II) Compounds Containing Triple M–M Bonds

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**Abstract:** Convenient preparative methods for confacial bioctahedral dimers of Nb(II) and Ta(II) with a triple M–M bond of the formula $M_2X_6(THT)_3^{2-}$, where X = Cl or Br and THT = tetrahydrothiophene, have been developed. They involve reduction of $M_2X_6(THT)_3$ or $MCl_5$ with sodium amalgam in appropriate environments. Depending on the method of isolation, salts of different composition can be obtained and several of them have been characterized structurally. The following crystallographic data were obtained. $(NEt_4)_2[Nb_2Cl_6(THT)_3]\cdot CH_3CN$ (**1c**): space group $P\bar{1}$ with $a = 11.618$ (4) Å, $b = 19.226$ (4) Å, $c = 10.845$ (3) Å, $\alpha = 93.17$ (2), $\beta = 103.39$ (2)°, $\gamma = 107.70$ (3)°, $V = 2224$ (3) Å$^3$, and $Z = 2$; 324 parameters were refined to $R = 0.052$ and $R_w = 0.068$ with 5529 observables. $[Na(THF)_3]_2[Nb_2Cl_5(THT)_3]_2$ (**3**): space group $P2_1/n$ with $a = 13.649$ (4) Å, $b = 19.261$ (7) Å, $c = 14.112$ (4) Å, $\beta = 99.49$ (3)°, $V = 3659$ (2) Å$^3$, and $Z = 4$; 223 parameters were refined to $R = 0.0597$ and $R_w = 0.0702$ with 1582 observables. $[Na(THF)_3]_2[Nb_2Br_5(THT)_3]_2$ (**4**): space group $P\bar{1}$ with $a = 12.156$ (3) Å, $b = 16.098$ (7) Å, $c = 11.268$ (4) Å, $\alpha = 105.97$ (3)°, $\beta = 112.23$ (2)°, $\gamma = 95.68$ (3)°, $V = 1910$ (1) Å$^3$, and $Z = 2$; 343 parameters were refined to $R = 0.045$ and $R_w = 0.0566$ with 2360 observables. $[Li(THF)_2]_2[Ta_2Cl_6(THT)_3]$ (**5a**): space group $P\bar{1}$ with $a = 10.622$ (1) Å, $b = 22.468$ (3) Å, $c = 10.581$ (2) Å, $\alpha = 103.37$ (2)°, $\beta = 119.28$ (2)°, $\gamma = 83.31$ (2)°, $V = 2141$ (2) Å$^3$, and $Z = 2$; 236 parameters were refined to $R = 0.0612$ and $R_w = 0.0763$ with 3053 observables. $Na_2[Ta_2Cl_6(THT)_3]\cdot{}^3/_2THF$ (**5b**): space group $P2_1/n$ with $a = 11.044$ (2) Å, $b = 18.734$ (5) Å, $c = 16.019$ (5) Å, $\beta = 105.56$ (2)°, $V = 3193$ (1) Å$^3$, and $Z = 4$; 283 parameters were refined to $R = 0.0323$ and $R_w = 0.0457$ with 4019 observables. Spectroscopic characterization (UV–vis and proton NMR) has been carried out. MO calculations confirm the presence of a triple M–M bond and allow assignment of the electronic spectrum.

The field of metal–metal bonded complexes of the group 5 metals is rapidly growing. Many complexes containing single and double metal–metal bonds have been reported over the last few years. Complexes with double M–M bonds (M = Nb, Ta) have been synthesized by reduction of the pentahalides in the presence of donor ligands such as $SMe_2$,[1] THT (THT = tetrahydrothiophene),[2] $PMe_3$,[3] and $PMe_2Ph$.[4] The sulfur ligands give face-sharing bioctahedral complexes of the type $M_2X_6L_3$ whereas the phosphine ligands give edge-sharing bioctahedral species of the kind $M_2X_6L_4$. Both types of compounds have an extensive chemistry associated with them and have been used to form other

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