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DINUCLEAR RHODIUM COMPLEXES WITH THREE AND FOUR BRIDGING LIGANDS. THE PREPARATION AND CRYSTAL STRUCTURE OF $[Rh_2(Ph_2PCH_2PPh_2)_2(\mu\text{-Cl})(\mu\text{-CO})(CO)_2][Rh(CO)_2Cl_2] \cdot CH_2Cl_2$

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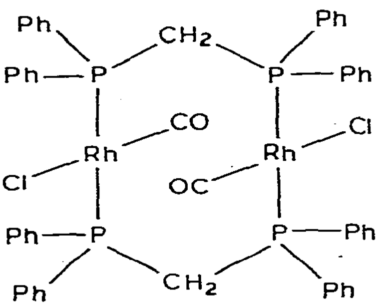
Summary

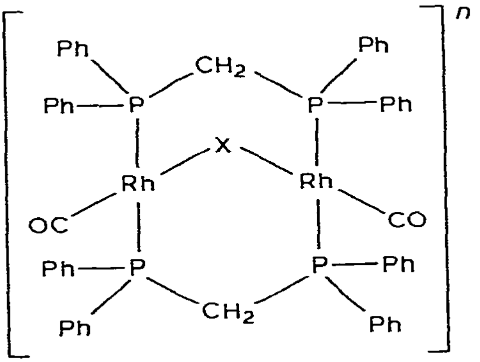
The reaction of four moles of bis(diphenylphosphino)methane (dpm) or bis(diphenylarsino)methane (dam) with three moles of $Rh_2(CO)_4Cl_2$ produces $[Rh_2(dpm)_2(\mu\text{-Cl})(CO)_2][Rh(CO)_2Cl_2]$ or $[Rh_2(dam)_2(\mu\text{-Cl})(CO)_2]$-$[Rh(CO)_2Cl_2]$. Reaction of $Rh_2(dam)_2(CO)_2Cl_2$ with $Rh_2(CO)_4Cl_2$ proceeds by halide ion abstraction to give $[Rh_2(dam)_2(\mu\text{-Cl})(CO)_2][Rh(CO)_2Cl_2]$. Carbon monoxide adds to $[Rh_2(dpm)_2(\mu\text{-Cl})(CO)_2][Rh(CO)_2Cl_2]$ to give $[Rh(dpm)_2$-$(\mu\text{-Cl})(\mu\text{-CO})(CO)_2][Rh(CO)_2Cl_2]$. The crystal structure of $[Rh_2(dpm)_2(\mu\text{-CO})$-$(\mu\text{-Cl})(CO)_2]$ $[Rh(CO)_2Cl_2] \cdot CH_2Cl_2$ has been determined by X-ray diffraction. The crystals are monoclinic, space group $P2_1/c$, with lattice constants: a 16.302(4) Å, b 18.370(3) Å, c 19.189(3) Å, β 91.11(2)°, $Z = 4$. Positional and isotropic thermal parameters of the non-hydrogen atoms were refined using a full-matrix least-squares method to a final R index of 0.085 for 6401 reflections with $I_{net} > 3\sigma(I_{net})$. Bond distances: Rh—Rh, 2.838(1) Å; Rh—C (bridged), 2.094(11), 2.051(11) Å; Rh—C (terminal), 1.813(1), 1.839(1) Å; P···P(av.), 3.055(6) Å. Correlations between P···P or As···As distances and M···M distances are noted for dpm or dam as bridging ligands.

Introduction

Bis(diphenylphosphino)methane (dpm) and its arsine analog, bis(diphenylarsino)methane (dam), can bridge two metal ions under a variety of circumstances. These include cases where the metals are connected by a single bond [1—3], by multiple bonds [4], by other bridging groups [5—7] and by no other formal connection at all [8]. The flexibility of these bidentate bridging ligands allows the two metal centers to engage in a variety of unusual reactions. A number of molecules, including carbon monoxide, isocyanides, and sulfur dioxide, insert into the metal—metal bond of $Pd_2(dpm)_2Cl_2$ [5—7]. Rhodium(I) compounds bridged by two *trans*-dpm ligands undergo *trans*-annular oxidative-addition to produce rhodium(II) compounds with direct Rh—Rh bonds [9]. The face-to-face rhodium(I) dimers I may be converted into anion bridged species II.



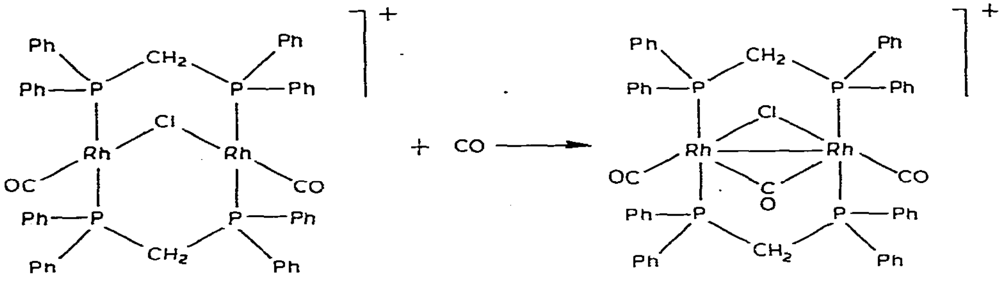
(I)



(II)

($x = s^{2-}$, $n = 0$; $x = PR_2^-$, $n = +1$; $x = Cl^-$, $n = +1$)

Carbon monoxide has been reported to add to II to produce a carbonyl bridged species III with the concomitant formation of a metal—metal bond [11].



(II) (III)

Hieber and Kummer have reported that the reaction between equimolar amounts of dpm and $Rh_2(CO)_4Cl_2$ produces dpm$[Rh(CO)_2Cl]_2$, while, with a 2/1 ratio of dpm to $Rh_2(CO)_4Cl_2$, this reaction produces $[Rh(dpm)(CO)Cl]_n$ [12]. The greater flexibility and lower steric congestion of a compound such as dpm$[Rh(CO)_2Cl]_2$, with only a single bridging ligand, should confer novel potentials for reaction. We have previously demonstrated that some bidentate amines such as 1,8-naphthyridine can function as bridges between $Rh(CO)_2Cl$ units [13]. We anticipated that the presence of a soft phosphorus donor in the bridge would produce complexes with better stability and more extensive chemistry than the relatively unstable amine bridged complexes. On the other hand, a number of studies have demonstrated that compounds of the type $(R_3P)Rh(CO)_2Cl$ cannot be prepared by the reaction of monodentate phosphines with $Rh_2(CO)_4Cl_2$. Rather, substitution occurs to form $Rh_2(CO)_{4-x}$-$(PR_3)_xCl_2$ [14,15]. Consequently, we have undertaken a re-investigation of the reaction between $Rh_2(CO)_4Cl_2$ and dpm under conditions where the reactants are present in nearly equimolar quantities.

Experimental

Preparation of compounds

Dicarbonylrhodium chloride dimer, dpm and dam were obtained from Strem. $Rh_2(dpm)_2(CO)_2Cl_2$ and $Rh_2(dam)_2(CO)_2Cl_2$ were prepared by the previously reported routes [12,16].

$[Rh_2(dam)_2(\mu\text{-}Cl)(CO)_2][Rh(CO)_2Cl_2]$

Method 1. Under a nitrogen atmosphere a solution of 94.9 mg (0.20 mmol) of dam in 5 ml of benzene was added dropwise to a stirred solution of 79.5 mg (0.20 mmol) of $Rh_2(CO)_4Cl_2$ in 25 ml of pentane at −5° C. The yellow solid which precipitated from solution during the addition was collected by filtration and vacuum dried. The compound was purified by dissolving it in dichloromethane, filtering and crystallizing by the addition of ether; yield, 65%.

Method 2. Under an atmosphere of purified nitrogen a solution of 26 mg (0.067 mmol) of $Rh_2(CO)_4Cl_2$ in 5 ml of benzene was added to a solution of 69 mg (0.054 mmol) of $Rh_2(dam)_2(CO)_2Cl_2$ in 10 ml of benzene. The solution was cooled and the yellow-orange crystalline product which precipitated was collected and washed with cold benzene; yield 60 mg, 75%.

The products obtained by both routes had identical spectroscopic properties UV VIS (CH_2Cl_2) λ_{max}: 426 nm (7,800), 308(sh) (13,900), 249 (44,800); (acetone) Λ_M 107 $cm^2\ ohm^{-1}\ mol^{-1}$. Anal. Found: C, 44.15; H, 3.06; Cl, 7.73. $C_{54}H_{44}As_4Cl_3O_4Rh_3$ calcd.: C, 44.07; H, 3.06; Cl, 7.23%.

$[Rh_2(dpm)_2(\mu\text{-}Cl)(CO)_2][Rh(CO)_2Cl_2]$

A solution of 156 mg (0.40 mmol) of dpm in 10 ml of benzene was added to a solution of 117 mg (0.30 mmol) of $Rh_2(CO)_4Cl_2$ in benzene. The orange crystals, which precipitated from solution, were collected and washed with benzene; yield 230 mg, 89%. The complex salt may be recrystallized by dissolving it in dichloromethane and adding ether: UV VIS (CH_2Cl_2) λ_{max}: 442 nm (10,800), 312(sh) (10,800), 254 (42,000); Conductivity (acetone), Λ_M 116 $cm^2\ ohm^{-1}\ mol^{-1}$. Anal. Found: C, 50.00; H, 3.42. $C_{54}H_{44}Cl_3O_4P_4Rh_3$ calcd.: C, 50.05; H, 3.42%.

$[Rh_2(dpm)_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2][Rh(CO)_2Cl_2]$

$[Rh_2(dpm)_2(\mu\text{-}Cl)(CO)_2][Rh(CO)_2Cl_2]$ was placed under an atmosphere of carbon monoxide. Ether, which was previously purged with carbon monoxide, was allowed to slowly diffuse into this solution whereupon yellow prismatic crystals were deposited. The crystals were separated from the mother liquor by decantation; UV VIS (CO saturated CH_2Cl_2), λ_{max}: 433 nm (2,700), 342(sh) (15,000), 258(sh) (14,000). Conductivity (acetone), Λ_M 123 $cm^2\ ohm^{-1}\ mol^{-1}$. Further characterization was accomplished by the crystal structure determination.

Data collection

A crystal of dimensions 0.20 × 0.45 × 0.325 mm was selected for data collection. Data were collected on a Syntex P2$_1$ diffractometer at 150 K using Mo-K_α radiation and a graphite monochromator. The orientation matrix and cell dimensions were obtained from a least-squares fit of 18 well-centered reflections having h, $k > 0$ and $30° < 2\theta < 40°$. Intensity data were collected using a variable speed ω scan from 3 to 60° min^{-1} of an 0.8° range in ω and using a 1° offset for stationary background counts. A total of 7523 reflections were measured with $0° < 2\theta < 45°$. Two check reflections monitored throughout showed a random fluctuation <1%. Crystal data: $P2_1/c$, a 16.302(4) Å, b 18.370(3) Å, c 19.189(3) Å; β 91.11(2)°; μ 11.8 cm^{-1}; V 574.5 Å^3, ρ_{expt} (298 K), 1.50 g cm^{-3}; ρ_{calc} (150 K) for Z of 4, 1.63 g cm^{-3}.

Solution and refinement of structure

The usual Lorentz and polarization corrections were applied to the intensity data. Based on crystal dimensions and an absorption coefficient of 11.8 cm^{-1}, absorption correction factors range from 1.22 to 1.38. Consequently the maximum effect of absorption is expected to be approximately ±3.5% and no correction for absorption was applied. Form factor tables were those of Cromer and Waber [17a] and the correction for the real and imaginary components of anomalous dispersion [17b] was applied to Rh, Cl, and P. The two rhodium atoms of the cation were located from a Patterson map; the third rhodium atom of the anion revealed its presence in the first Fourier map. Three chlorine atoms and four phosphorus atoms were also located from this Fourier map. Two cycles of full-matrix least-squares refinement of these ten atoms brought the R index to 0.28. A second Fourier map was sufficient to locate all except five of the remaining atoms. Following two more cycles of full-matrix least-squares refinement, a difference Fourier map was calculated and the five remaining atoms were located. These atoms are part of a phenyl ring defined by carbon atoms C(36) through C(41). This ring is somewhat disordered or undergoes large thermal motion. The molecule of dichloromethane also displays fairly large thermal motion, but nevertheless was easily identified. Three more cycles of least-squares refinement brought R to 0.085 and the last shift in any parameter was less than 1/6 the e.s.d. except for the four carbons with large B_{iso} in the ill-behaved phenyl ring. For these carbons a few of the parameters shifted ca. one e.s.d. We felt that the expense of anisotropic refinement was not warranted and ended our refinement at this stage, having all 73 atoms with isotropic B's. A total of 6401 reflections having $I_{\text{net}} > 3\sigma(I_{\text{net}})$ were used in all stages of refinement. Final atomic fractional coordinates and isotropic thermal parameters together with estimated standard deviations are given in Table 1. A table of observed and calculated structure factors is available as supplementary material *.

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* The table of structure factors has been deposited as NAPS Document No. 03493 (35 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting \$ 8.75 for photocopies or \$ 3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

TABLE 1

FINAL ATOMIC FRACTIONAL COORDINATES AND ISOTROPIC THERMAL PARAMETERS FOR $[Rh_2(dpm)_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2][Rh(CO)_2Cl_2]\cdot CH_2Cl_2$ [a]

Atom	*x/a*	*y/b*	*z/c*	B_{iso}, Å^2
Rh(1)	0.33781 (5)	0.10310 (5)	0.40759 (4)	1.37 (3)
Rh(2)	0.16387 (5)	0.10775 (5)	0.40914 (4)	1.45 (3)
Rh(3)	0.2659 (1)	—0.0232 (1)	0.0187 (1)	2.89 (3)
Cl(1)	0.2471 (2)	0.1871 (1)	0.3298 (1)	1.7 (1)
Cl(2)	0.2421 (2)	—0.0992 (2)	0.1159 (2)	3.1 (1)
Cl(3)	0.2831 (2)	0.0787 (2)	0.0907 (2)	3.3 (1)
Cl(4)	0.1735 (4)	—0.1482 (4)	0.6123 (4)	8.4 (2)
Cl(5)	0.3380 (4)	—0.1418 (4)	0.6733 (4)	8.2 (1)
P(1)	0.3503 (2)	0.1981 (2)	0.4873 (1)	1.5 (1)
P(2)	0.3372 (2)	0.0181 (2)	0.3179 (1)	1.5 (1)
P(3)	0.1629 (2)	0.2076 (2)	0.4844 (1)	1.6 (1)
P(4)	0.1504 (2)	0.0269 (2)	0.3154 (1)	1.6 (1)
O(1)	0.2523 (5)	0.0028 (5)	0.5086 (4)	2.4 (2)
O(2)	0.5139 (5)	0.0668 (5)	0.4347 (4)	2.4 (2)
O(3)	—0.0028 (6)	0.0668 (6)	0.4576 (5)	3.7 (2)
O(4)	0.3002 (8)	0.0737 (7)	—0.1027 (7)	5.4 (3)
O(5)	0.2426 (9)	—0.1505 (8)	—0.0745 (8)	6.5 (3)
C(1)	0.2529 (7)	0.0484 (6)	0.4652 (6)	1.6 (2)
C(2)	0.4472 (7)	0.0823 (6)	0.4223 (6)	2.0 (2)
C(3)	0.0619 (8)	0.0831 (7)	0.4370 (6)	2.4 (2)
C(4)	0.2597 (7)	0.2566 (6)	0.4845 (6)	1.7 (2)
C(5)	0.2447 (7)	0.0234 (6)	0.2641 (6)	1.7 (2)
C(6)	0.3630 (6)	0.1725 (6)	0.5782 (5)	1.4 (2)
C(7)	0.3422 (7)	0.2195 (6)	0.6324 (6)	2.0 (2)
C(8)	0.3500 (8)	0.1966 (7)	0.7021 (7)	2.6 (2)
C(9)	0.3762 (8)	0.1271 (8)	0.7178 (7)	3.0 (2)
C(10)	0.3967 (8)	0.0788 (8)	0.6635 (7)	2.9 (2)
C(11)	0.3903 (7)	0.1019 (6)	0.5941 (6)	1.9 (2)
C(12)	0.4308 (7)	0.2636 (6)	0.4659 (6)	1.7 (2)
C(13)	0.4480 (8)	0.3226 (7)	0.5086 (7)	2.8 (2)
C(14)	0.5070 (10)	0.3742 (9)	0.4877 (8)	3.8 (3)
C(15)	0.5452 (9)	0.3665 (8)	0.4267 (8)	3.5 (3)
C(16)	0.5297 (9)	0.3066 (8)	0.3841 (7)	3.1 (3)
C(17)	0.4707 (8)	0.2570 (7)	0.4030 (7)	2.8 (2)
C(18)	0.4160 (7)	0.0407 (6)	0.2563 (6)	1.8 (2)
C(19)	0.4332 (8)	0.1145 (7)	0.2441 (6)	2.2 (2)
C(20)	0.4943 (8)	0.1344 (8)	0.1995 (7)	2.9 (2)
C(21)	0.5407 (8)	0.0812 (8)	0.1649 (7)	2.9 (2)
C(22)	0.5236 (9)	0.0092 (8)	0.1756 (7)	3.1 (3)
C(23)	0.4622 (7)	—0.0124 (7)	0.2200 (6)	2.2 (2)
C(24)	0.3510 (7)	—0.0765 (6)	0.3424 (6)	1.7 (2)
C(25)	0.3838 (3)	—0.0929 (7)	0.4084 (6)	2.2 (2)
C(26)	0.3952 (7)	—0.1650 (7)	0.4273 (6)	2.3 (2)
C(27)	0.3745 (8)	—0.2209 (7)	0.3831 (7)	2.9 (2)
C(28)	0.3399 (9)	—0.2051 (8)	0.3178 (7)	3.0 (3)
C(29)	0.3287 (8)	—0.1335 (7)	0.2967 (6)	2.4 (2)
C(30)	0.1429 (7)	0.1926 (6)	0.5763 (6)	2.0 (2)
C(31)	0.1335 (8)	0.2519 (7)	0.6207 (6)	2.4 (2)
C(32)	0.1198 (8)	0.2426 (7)	0.6906 (7)	2.6 (2)
C(33)	0.1141 (9)	0.1718 (8)	0.7157 (7)	3.2 (3)
C(34)	0.1209 (9)	0.1112 (8)	0.6745 (8)	3.5 (3)
C(35)	0.1353 (8)	0.1227 (7)	0.6027 (7)	2.4 (2)
C(36)	0.0898 (7)	0.2780 (6)	0.4585 (6)	1.6 (2)
C(37)	0.0140 (14)	0.2588 (13)	0.4320 (12)	7.2 (5)
C(38)	—0.0460 (15)	0.3145 (13)	0.4162 (12)	7.4 (5)
C(39)	—0.0269 (8)	0.3825 (7)	0.4194 (7)	2.7 (2)
C(40)	0.0529 (13)	0.4045 (11)	0.4342 (11)	6.2 (4)

TABLE 1 (continued)

Atom	x/a	y/b	z/c	B_{iso}, Å^2
C(41)	0.1109 (13)	0.3472 (12)	0.4533 (11)	6.3 (4)
C(42)	0.0727 (7)	0.0534 (7)	0.2503 (6)	2.3 (2)
C(43)	0.0897 (7)	0.0574 (7)	0.1784 (6)	2.3 (2)
C(44)	0.0311 (9)	0.0738 (8)	0.1293 (7)	3.1 (3)
C(45)	−0.0510 (9)	0.0875 (8)	0.1522 (8)	3.4 (3)
C(46)	−0.0676 (11)	0.0862 (10)	0.2227 (9)	4.6 (3)
C(47)	−0.0053 (9)	0.0698 (8)	0.2700 (7)	3.3 (3)
C(48)	0.1275 (7)	−0.0694 (6)	0.3322 (6)	1.9 (2)
C(49)	0.1273 (9)	−0.0937 (8)	0.4004 (7)	3.2 (3)
C(50)	0.1135 (11)	−0.1669 (10)	0.4134 (9)	4.8 (4)
C(51)	0.1008 (9)	−0.2146 (8)	0.3578 (8)	3.8 (3)
C(52)	0.1005 (9)	−0.1883 (8)	0.2883 (8)	3.4 (3)
C(53)	0.1125 (8)	−0.1158 (7)	0.2770 (6)	2.3 (2)
C(54)	0.2867 (10)	0.0336 (9)	−0.0553 (8)	3.9 (3)
C(55)	0.2522 (10)	−0.1011 (8)	−0.0352 (8)	3.8 (3)
C(56)	0.2786 (17)	−0.1676 (15)	0.5999 (14)	8.2 (6)

[a] Estimated standard deviations are given in parentheses.

Results and discussion

Synthetic studies

In our hands the reaction of nearly equimolar amounts of either dpm or dam with $Rh_2(CO)_4Cl_2$ does not yield dpm$[Rh(CO)_2Cl]_2$ or its arsenic analog; rather these reactions produce the salts $[Rh_2(dpm)_2(\mu\text{-}Cl)(CO)_2][Rh(CO)_2Cl_2]$ (IV) and $[Rh_2(dam)_2(\mu\text{-}Cl)(CO)_2][Rh(CO)_2Cl_2]$ (V). The net reaction is shown in eq. 2, and this may be broken down into the two stages represented by eq. 3 and 4. Reaction 3 has been previously reported.

$$3\,Rh_2(CO)_4Cl_2 + 4\,L \rightarrow 2\,Rh_2(L)_2(\mu\text{-}Cl)(CO)_2^- + 2\,Rh(CO)_2Cl_2^- + 4\,CO \qquad (2)$$

$$Rh_2(CO)_4Cl_2 + 2\,L \rightarrow Rh_2(L)_2(CO)_2Cl_2 + 2\,CO \qquad (3)$$

$$2\,Rh_2(L)_2(CO)_2Cl_2 + Rh_2(CO)_4Cl_2 \rightleftharpoons 2\,Rh_2(L)_2(\mu\text{-}Cl)(CO)_2^- + 2\,Rh(CO)_2Cl_2^- \qquad (4)$$

(L = dpm or dam)

The independent occurrence of reaction 4 in which $Rh_2(CO)_4Cl_2$ acts to abstract halide ion is reported later in this article for the first time. It should be noted that the 3 to 4 stoichiometry of eq. 2 approximates the stoichiometry used originally by Hieber and Kummer to prepare "dpm$[Rh(CO)_2Cl]_2$".

Infrared spectral data for the new compounds are reported in Table 2. The data for IV and V in the carbonyl stretching region indicate that only terminal carbonyl groups are present. In comparison, Hieber and Kummer report carbonyl stretching frequencies for "dpm$[Rh(CO)_2Cl]_2$" of 2085w(sh); 2068s, and 1990vs [12] so that they may have isolated an impure specimen of this salt. The bands at ca. 2060 and 1975 cm^{-1} are characteristics of $Rh(CO)_2Cl_2^-$ as are the Rh—Cl stretching frequencies at ca. 318 and 290 cm^{-1}. The remaining carbonyl stretching frequency at 1960 cm^{-1} in IV as well as the presence of a proximity shifted electronic absorption in the visible spectrum at 442 nm agree

TABLE 2

INFRARED SPECTRA [a]

	ν(CO)(cm^{-1})	ν(Rh—Cl)(cm^{-1})
$[Rh_2(dpm)_2(\mu\text{-}Cl)(CO)_2][Rh(CO)_2Cl_2]$	2056, 1976, 1960	316, 288
$[Rh_2(dpm)_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2][Rh(CO)_2Cl_2]$	2060, 1980, 1962, 1865	316, 285
$[Rh_2(dam)_2(\mu\text{-}Cl)(CO)_2][Rh(CO)_2Cl_2]$	2057, 1995(sh), 1982(sh), 1972	321, 290
$[Rh_2(dam)_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2][Rh(CO)_2Cl_2]$	2074, 1990, 1883 [b]	
$[Rh_2(dpm)_2(CO)_2Cl_2]$	1976, 1937(sh) [c]	298, 284 [c]
$[Rh_2(dam)_2(CO)_2Cl_2]$	1965, 1929(sh) [c]	302, 285 [c]
$[Ph_4As][Rh(CO)_2Cl_2]$	2060vs, 1975vs [d]	318s, (br); 290s, (br) [d]

[a] Nujol mull unless otherwise indicated. [b] In CH_2Cl_2 solution. [c] Ref. 16. [d] Ref. 34.

with the data reported for $[Rh_2(dpm)_2(\mu\text{-}Cl)(CO)_2][BPh_4]$. Both IV and V have conductivities in acetone solution which are typical for 1/1 electrolytes. Further characterization of IV is provided by its conversion, under a carbon monoxide atmosphere, into $[Rh_2(dpm)_2(\mu\text{-}CO)(\mu\text{-}Cl)(CO)_2][Rh(CO)_2Cl_2]$.

The ability of $Rh_2(CO)_4(Cl)_2$ to act as a halide abstracting agent and the separate occurrence of reaction 4 has been investigated using the readily soluble $Rh_2(dam)_2(CO)_2Cl_2$ rather than the less tractable diphosphine analog. In benzene solution, V readily precipitates as orange crystals when solutions of $Rh_2(dam)_2(CO)_2Cl_2$ and $Rh_2(CO)_4Cl_2$ are mixed. This reaction is reversible. Slow diffusion of ether into an acetonitrile solution of V yields crystals of $Rh_2(dam)_2(CO)_2Cl_2$.

Carbon monoxide adds readily to the cation of the salt IV as shown by the growth of a bridging carbonyl absorption in the infrared spectrum at 1865 cm^{-1}. The product of this reaction has been characterized by X-ray crystallography.

Description of the structure of $[Rh_2(dpm)_2(\mu\text{-}CO)(\mu\text{-}Cl)(CO)_2][Rh(CO)_2Cl_2] \cdot CH_2Cl_2$

The salt V crystallized with one cation, one anion, and one molecule of dichloromethane in the asymmetric unit or four of each in the unit cell. (There are no unusually short contacts between the cation, anion, or dichloromethane.) Interatomic distances and angles for the cation are listed in Table 3. An ORTEP drawing of $[Rh_2(Ph_2PCH_2PPh_2)_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2]^+$ is shown in Fig. 1.

Each rhodium in the cation is bonded to two *trans*-phosphine ligands, a terminal carbonyl ligand, a bridging chloride ligand, and a bridging carbonyl ligand. Additionally, the Rh—Rh distance of 2.838 Å is indicative of the presence of a single bond between the two metals. While the Rh—Rh distance is comparable to bond distances of unbridged Rh—Rh single bonds (2.785 Å in $[(p\text{-}CH_3C_6H_4NC)_8Rh_2I_2]^+$ [1] and 2.936 Å in $(Ph_3P)_2Rh_2$(dimethylglyoximate)$_4$ [19]) it is longer than other bridged Rh—Rh bonds (2.614 Å in $(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CH_3C_2(CH_3)CO(CF_3)C_2CF_3)$ [20], 2.665 Å in $(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CH_2)$ [21], 2.630 Å in $(Ph_3P)_4Rh_2(\mu\text{-}CO)_2$ [22], 2.681 Å in $(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(CO)_2$ [23], 2.62 Å in $(\eta^5\text{-}C_5H_5)_3Rh_3(\mu\text{-}CO)_3$ [24] and 2.620 Å in $(\eta^5\text{-}C_5H_5)_3Rh_3(\mu\text{-}CO)_2(CO)$ [25]).

TABLE 3.

INTRAMOLECULAR DISTANCES (IN Å) AND ANGLES (IN DEG) FOR $[Rh_2(dpm)_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2]^+$

Rh(1) — Rh(2)	2.838 (1)
Rh(1) — Cl(1)	2.591 (3)
Rh(2) — Cl(1)	2.522 (3)
Rh(1) — C(1)	2.05 (1)
Rh(2) — C(1)	2.09 (1)
Rh(1) — C(2)	1.84 (1)
Rh(2) — C(3)	1.81 (1)
Rh(1) — P(1)	2.326 (3)
Rh(1) — P(2)	2.324 (3)
Rh(2) — P(3)	2.335 (3)
Rh(2) — P(4)	2.339 (3)
C(1) — O(1)	1.18 (1)
C(2) — O(2)	1.14 (1)
C(3) — O(3)	1.17 (2)
P(1) — C(6)	1.82 (1)
P(1) — C(12)	1.83 (1)
P(1) — C(4)	1.83 (1)
P(2) — C(18)	1.81 (1)
P(2) — C(24)	1.81 (1)
P(2) — C(5)	1.81 (1)
P(3) — C(30)	1.82 (1)
P(3) — C(36)	1.82 (1)
P(3) — C(4)	1.82 (1)
P(4) — C(42)	1.83 (1)
P(4) — C(48)	1.84 (1)
P(4) — C(5)	1.84 (1)
P(1) ··· P(3)	3.060 (4)
P(2) ··· P(4)	3.049 (4)
Cl(1) ··· C(1)	3.64 (1)

Rh(1) — Cl(1) — Rh(2)	67.4 (1)
Rh(1) — C(1) — Rh(2)	86.4 (1)
C(1) — Rh(1) — Cl(1)	102.6 (3)
C(1) — Rh(2) — Cl(1)	103.6 (3)
Rh(1) — C(1) — O(1)	137.9 (9)
Rh(2) — C(1) — O(1)	135.7 (9)
Rh(1) — C(2) — O(2)	175.8 (10)
Rh(2) — C(3) — O(3)	177.4 (11)
Cl(1) — Rh(1) — C(2)	138.8 (4)
Cl(1) — Rh(2) — C(3)	146.0 (4)
C(1) — Rh(1) — C(2)	118.6 (5)
C(1) — Rh(2) — C(3)	110.4 (5)
P(1) — C(4) — P(3)	114.2 (6)
P(2) — C(5) — P(4)	113.0 (6)

As usual the Rh—C distances to the bridging carbonyl are longer than those to the terminal carbonyl groups. These distances are quite similar to the comparable distances found in $(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(CO)_2$ [23]. On the other hand, as a result of the presence of a Rh—Rh bond, the Rh—Cl distances are unusually long. For a number of chloro-bridged rhodium(I) dimers, all of which lack direct Rh—Rh bonds, the Rh—Cl distances fall in the range 2.35—2.43 Å [26], whereas in the present structure the two distances are 2.591(3) and 2.522(3) Å. The Rh—Cl—Rh angle of 67.4(1)° also falls outside the range of 81.0—85.0° found for chloro-bridged rhodium(I) dimers lacking Rh—Rh bonds [26].

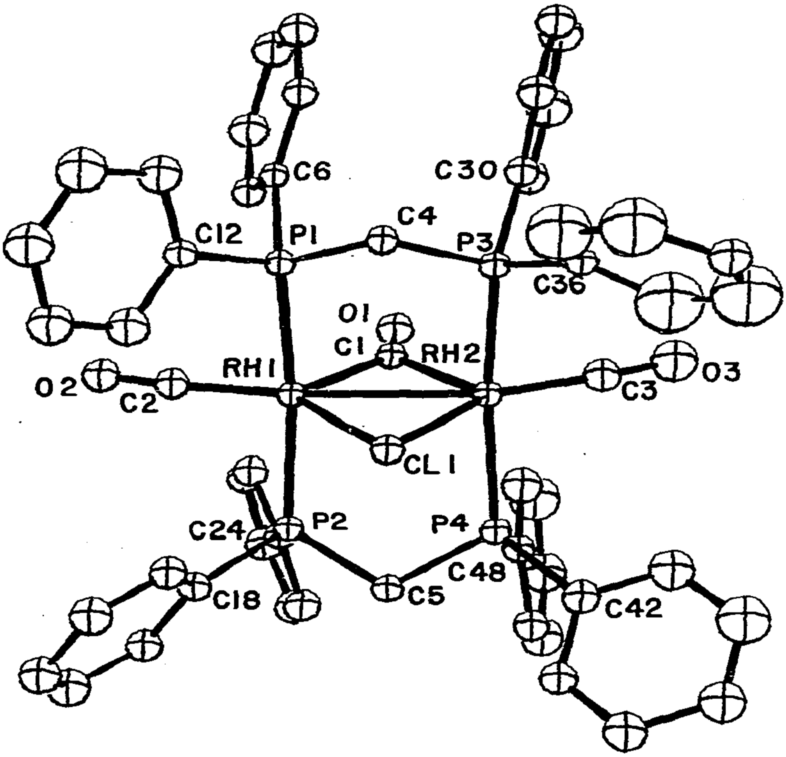

Fig. 1. An ORTEP drawing of $[Rh_2(Ph_2PCH_2PPh_2)_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2]^+$ showing 50% thermal ellipsoids.

In general the structural parameters reported for this salt agree well with those recently reported for $[Rh_2(dpm)_2(\mu\text{-}CO)(\mu\text{-}Cl)(CO)_2][BPh_4]$ [27]. Initially, however, very different non-bonded P···P separations were reported for the tetraphenylborate salt [11], and we pursued our studies because these differences suggested major differences between the two salts. The corrected parameters [27] for the tetraphenylborate salt show that the cations in both salts have similar geometry.

The structural parameters found for $Rh(CO)_2Cl_2^-$ agree with those determined previously [28].

Structural correlations for bis(diphenylphosphino)methane and bis(diphenylarsino)methane as bridging ligands

The remarkable flexibility of dpm and dam is manifest in their ability to act as monodentate ligands (in $W(CO)_3(NO)$dam [29] for example), to act as chelating ligands (in dpmPd$(SCN)_2$ [30] for example), and to bridge two metal ions under the variety of circumstances noted in the introduction. Of particular interest is the range of metal—metal distances spanned by these ligands. For metals bridged by dpm ligands the range of metal—metal distances is 2.46 to 3.38 Å while the range for dam bridged metals is 2.52 to 3.81 Å. The range of non-bonded P···P separations for dpm complexes is more restricted, ranging from 2.88 to 3.43 Å, but as shown in Fig. 2 these distances are correlated with

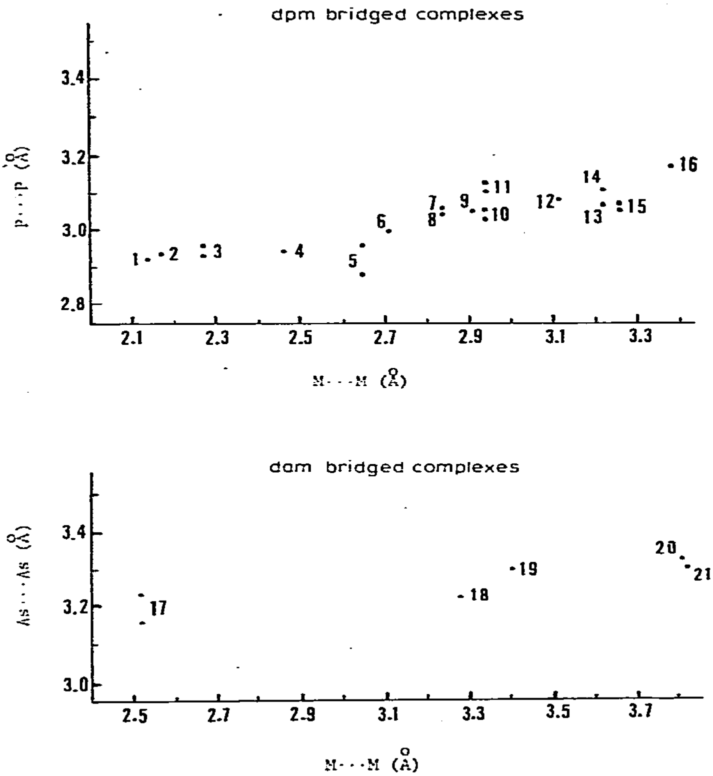

Fig. 2. A correlation of phosphorus—phosphorus and arsenic—arsenic distances to metal—metal distances in dpm and dam bridged dinuclear complexes. (1) $Mo_2(dpm)_2Cl_2$, E.H. Abbott, K.S. Bose, F.A. Cotton, W.T. Hall and J.C. Sekutowski, Inorg. Chem., 17 (1978) 3240; (2) $Mo_2(dpm)_2(NCS)_2$, ref. 1; (3) $Re_2(dpm)_2Cl_5$, F.A. Cotton, L.W. Shive and B.R. Stults, Inorg. Chem., 15 (1976) 2239; (4) $Co_2(dpm)(CO)_4(C_2Ph_2)$, P.H. Bird, A.R. Fraser and D.N. Hall, Inorg. Chem., 16 (1977) 1923; (5) $Pd_2(dpm)_2(SnCl_3)Cl$, M.M. Olmstead, L.S. Benner, H. Hope and A.L. Balch, Inorg. Chim. Acta, in press; (6) $Fe_2(dpm)(CO)_7$, F.A. Cotton and J.M. Troup, J. Amer. Chem. Soc., 96 (1974) 4422; (7) $Rh_2(dpm)_2(CO)_3Cl^+$, this work; (8) $Rh_2(dpm)_2(CO)_3Cl^+$, M. Cowie, Inorg. Chem., 18 (1979) 268. (9) $Cu_2(dpm)Cl_2$, G. Nardin and L. Randaccio, Acta. Crystallogr. B., 30 (1974) 1377; (10) $Mn_2(dpm)_2(CO)_5$, C. Commons and B. Hoskins, Aust. J. Chem., 28 (1975) 1663; (11) $Mn_2(dpm)_2(CO)_4(CNC_6H_4CH_3)$, L.S. Benner, M.M. Olmstead and A.L. Balch, J. Organometal. Chem., 159 (1978) 289; (12) $Cu_2(dpm)I_2$, A. Camus, G. Nardin and L. Randaccio, Inorg. Chim. Acta, 12 (1975) 23; (13) $Pd_2(dpm)_2(CNCH_3)_3{}^{2+}$, M.M. Olmstead, H. Hope, L.S. Benner and A.L. Balch, J. Amer. Chem. Soc., 99 (1977) 5502; (14) $Pd_2(dpm)_2Cl_2(SO_2)$, molecule B, L.S. Benner, M.M. Olmstead, H. Hope and A.L. Balch, J. Organometal. Chem., 153 (1978) C31; (15) $Pd_2(dpm)_2Cl_2(S)$, A.L. Balch, L.S. Benner and M.M. Olmstead, submitted for publication; (16) $Pd_2(dpm)_2Cl_2(SO_2)$, molecule A, ref. 14; (17) $Co_2(dam)_2(CO)_2(C_2Ph_2)$, ref. 4; (18) $Pd_2(dam)_2Cl_2(CO)$, R. Colton, M. McCormick and C. Pannan, Aust. J. Chem., 31 (1978) 1425; (19) $Rh_2(dam)_2Cl_2(CO)_2$, J.T. Mague, Inorg. Chem., 8 (1969) 1975; (20) $Re_2(dam)_2Cl_2(CO)_6$, molecule A, C. Commons and B. Hoskins, Aust. J. Chem., 28 (1975) 1201; (21) $Re_2(dam)_2Cl_2(CO)_6$, molecule B, ref. 20.

the metal—metal distances. It should be noted that the minimum P···P separations observed for these bridged complexes are significantly larger than the P···P separations found for chelating dpm ligands. Representative non-bonded P···P separations in chelating dpm ligands are 2.74 Å in $Pt(dpm)Ph_2$ [31], 2.792(3) Å in $Mo(dpm)(CO)_4$ [32] and 2.658 Å in $Pd(dpm)Cl_2$ [33]. A similar correlation between the As···As separation in dam complexes and the metal—metal distances is also apparent from this figure. However, with dam the range

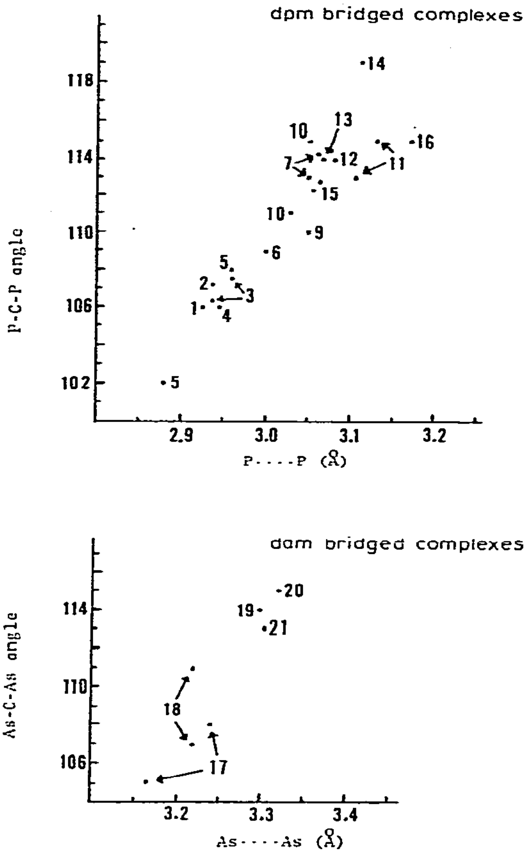

Fig. 3. Correlation between P—C—P angle (or As—C—As angle) and P···P (or As···As) non-bonded distances in dpm (or dam) bridged complexes. The numbering scheme follows that of Fig. 2.

of As···As separations is smaller, ranging from 3.16 to 3.32 Å. The inability of dam to close its bite as effectively as dpm is due to the larger Van der Waals radius of arsenic. As the P···P or As···As separations increase, the P—C—P or As—C—As angles open up as shown in Fig. 3. The variation in P···P or As···As distances can be entirely accounted for by the bond angle changes at the methylene carbon, no significant variation in the C—P or C—As distances is observed for these complexes.

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