Di-rhodium(I) and tri-rhodium(I) complexes with bridging bis(dimethylphosphinomethyl)methylphosphine

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Abstract

The reaction between bis(dimethylphosphinomethyl)methylphosphine (dmmm) and rhodium dicarbonyl chloride dimer can be controlled by the order of addition to give the purple $[Rh_3(\mu\text{-dmmm})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$ or the yellow $[Rh_2(\mu\text{-dmmm})_2(CO)_2][BPh_4]_2$. $[Rh_3(\mu\text{-dmmm})_2(CO)_3(\mu\text{-Cl})Cl][B(C_6H_5)_4] \cdot 2CH_2Cl_2$ crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with a 9.688(2), b 13.571(2), c 21.303(3) Å, α 80.18(1), β 84.74(1), γ 83.99(1)°, $Z = 2$ at 130 K. Least-squares refinement of 424 parameters using 8164 reflections with $I > 3\sigma(I)$ yielded $R = 0.044$. The cation contains a bent (140.9(1)°) tri-rhodium chain with each rhodium having planar $P_2(CO)Cl$ coordination. Treatment of $[Rh_2(\mu\text{-dmmm})_2(CO)_2][BPh_4]_2$ with diiodomethane or sodium iodide yields $[Rh_2(\mu\text{-dmmm})_2(CO)I][BPh_4]$. Yellow crystals of $[Rh_2(\mu\text{-dmmm})_2(CO)I][B(C_6H_5)_4] \cdot (CH_3)_2C{=}O$ crystallize in the orthorhombic space group $P2_12_12_1$ (No. 19) with a 9.760(3), b 14.931(4), c 32.708(8) Å, $Z = 4$ at 130 K. Least-squares refinement of 386 parameters using 4244 reflections yield $R = 0.044$. The structure of the cation consists of a four-coordinate, planar rhodium (with bonds to the other rhodium, two PMe groups and the terminal carbonyl group) and a six-coordinate rhodium (with bonds to the four PMe_2 groups, the terminal iodide, and the other rhodium, at 2.735(1) Å).

Introduction

The small-bite, trifunctional ligands, bis(diphenylphosphinomethyl)phenylphosphine (dpmp), and bis(diphenylphosphinomethyl)phenylarsine (dpma), are useful building blocks for the construction of polynuclear complexes, particularly nearly linear trinuclear compounds. For example the trirhodium(I) cation **1** [1], which is formed from the reaction of dpmp with $[Rh(CO)_2(\mu\text{-Cl})]_2$, has a rich chemistry that involves reactions at the coordination sites that lie in a plane perpendicular to the Rh_3P_6 core [2–15]. These reactions involve ligand addition and loss, substitution, and oxidative-addition, and they may be accompanied by strengthening or weakening of the Rh–Rh bonding.
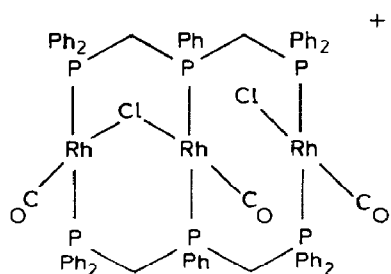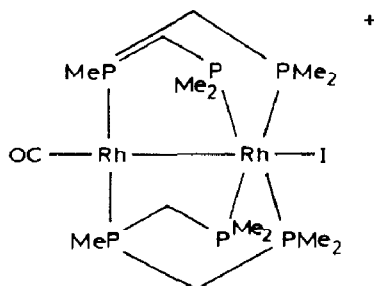
(1)
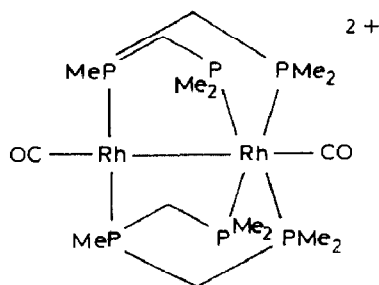
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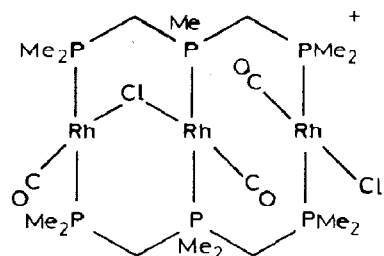
(3)

(4)

In considering modifications of the basic ligand design of dpmp and dpma, we turned our attention to the permethyl analog of dpmp, bis(dimethylphos-phinomethyl)methylphosphine (dmmm) [16]. This ligand possesses two desirable features. The increased basicity of the phosphine should render the coordinated metal ions more electron rich and hence reactive in oxidative-addition reactions. The reduced steric bulk, relative to dpmp, was expected to render the coordinated metal centers more accessible to external attack. However, the reduced steric constraints have also been found to allow folding of dmmm into a more compact form than possible with dpmp. Thus our initial examination of the reaction of dmmm with $[Rh(CO)_2(\mu-Cl)]_2$ led to the isolation of the remarkably crowded rhodium(I) dimer, $[Rh_2(\mu-dmmm)_2(CO)_2]^{2+}$ (2) [17].

Here we describe the preparation of $[Rh_3(\mu-dmmm)_2(CO)_3(\mu-Cl)Cl]^+$ (3) the dmmm of analog of 1, and a substitution reaction of 2 which yields $[Rh_2(\mu-dmmm)_2(CO)I]^+$ (4).

Results

Synthesis

Addition of a dichloromethane solution of dmmm to a dichloromethane solution of $[Rh(CO)_2(\mu-Cl)]_2$ produces a deep purple solution from which purple crystals of $[Rh_3(\mu-dmmm)_2(CO)_3(\mu-Cl)Cl][BPh_4]$ (3) can be isolated in 60% yield after the addition of a solution of sodium tetraphenylborate. On concentration of the mother liquor from this reaction, it is possible to isolate varying amounts (5–12%) of yellow $[Rh_2(\mu-dmmm)_2(CO)_2][BPh_4]$ (2). To maximize the yield of 3, the order of addition

is reversed. Adding a dichloromethane solution of dmmm to a solution of [Rh(CO)$_2$(μ-Cl)]$_2$ in methanol followed by the addition of sodium tetraphenyl-borate in methanol produces yellow **2** in 76% as described previously [17].

The infrared spectrum of [Rh$_3$(μ-dmmm)$_2$(CO)$_3$(μ-Cl)Cl][BPh$_4$] (**3**) exhibits a broad band at 1960 cm^{-1} indicative of the presence of terminal carbonyl groups. The electronic spectrum of **3** in dichloromethane solution shows a proximity shifted absorption [18] at 542 nm. The ^{1}H and ^{31}P NMR spectra of this complex are not informative because of serious overlapping of resonances. The ^{31}P NMR spectrum consists of a complex multiplet extending from 1 to -3.5 ppm. This does not change significantly on cooling. Analysis of the multiplet has not been possible. Apparently the three phosphorus environments are so similar that their chemical shifts are nearly identical. This lack of resolution has been seen in complexes of dpmp as well [14].

Treatment of an acetone solution of [Rh$_2$(μ-dmmm)$_2$(CO)$_2$][BPh$_4$]$_2$ (**2**) with a methanol solution of sodium iodide immediately produces a brown solution from which a brown precipitate can be isolated by addition of ethyl ether. Recrystallization from acetone gives yellow crystals of [Rh$_2$(μ-dmmm)$_2$(CO)I][BPh$_4$] · (C$_3$H$_6$O) (**4**) in 85% yield. This compound can also be prepared by treatment of an acetone solution of **2** with diiodomethane over a 3.5-h period at 60°C. By evaporation of the solvent, yellow crystals of **4** are formed in 73% yield. The infrared spectra of the products of each reaction are identical (ν(CO) 1971 cm^{-1}). The ^{31}P NMR spectrum of [Rh$_2$(μ-dmmm)$_2$(CO)I][BPh$_4$]$_2$ resembles that of [Rh$_2$(μ-dmmm)$_2$(CO)$_2$][BPh$_4$]$_2$ [17]. At -50°C in acetone solution, three multiplets at δ_1 -4.0 ppm, ^1J(Rh,P), 118 Hz; δ_2 -6.5 ppm, ^1J(Rh,P), 98 Hz; δ_3 -26.5 ppm, ^1J(Rh,P) 94 Hz are seen. Each contains further splitting due to P-P coupling. Thus three phosphorus environments are present in solution. This is consistent with the crystallographic results (vide infra). On warming to 23°C the resonances at -6.5 and -26.5 ppm broaden while the multiplet at -4 ppm remains sharp. We attribute this to exchange of the
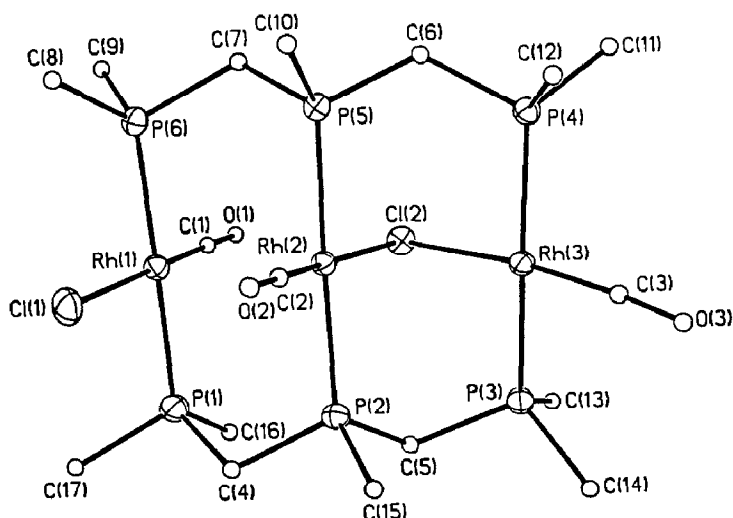

Fig. 1. A perspective view of [Rh$_3$(μ-dmmm)$_2$(CO)$_3$(μ-Cl)Cl]$^+$ (**3**) with 50% thermal contours for heavy atoms and arbitrarily sized circles for other atoms.

Table 1

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{Å}^2 \times 10^3$) for [Rh$_3$(μ-dmmm)$_2$(CO)$_3$(μ-Cl)Cl][BPh$_4$]

Atom	x	y	z	U ^{a}
Rh(1)	18(1)	5406(1)	1361(1)	17(1) *
Rh(2)	1931(1)	4670(1)	2424(1)	15(1) *
Rh(3)	1913(1)	4328(1)	3853(1)	15(1) *
P(1)	167(2)	7048(1)	1479(1)	24(1) *
P(2)	2284(1)	6313(1)	2491(1)	18(1) *
P(3)	1585(1)	6002(1)	3931(1)	19(1) *
P(4)	2066(1)	2610(1)	3823(1)	17(1) *
P(5)	1626(1)	3015(1)	2393(1)	16(1) *
P(6)	−154(1)	3770(1)	1227(1)	18(1) *
Cl(1)	2039(1)	5558(1)	641(1)	28(1) *
Cl(2)	−59(1)	4646(1)	3215(1)	19(1) *
Cl(3)	6073(2)	7040(2)	807(1)	55(1) *
Cl(4)	4954(2)	6985(2)	−390(1)	69(1) *
Cl(5)	3552(2)	9174(1)	468(1)	41(1) *
Cl(6)	1290(2)	10505(1)	935(1)	64(1) *
O(1)	−2645(4)	5383(3)	2147(2)	36(1)
O(2)	4661(4)	4480(3)	1686(2)	33(1)
O(3)	4411(4)	4217(3)	4568(2)	34(1)
B(1)	7878(6)	10061(4)	3145(3)	19(1)
C(1)	−1605(5)	5370(4)	1848(2)	25(1)
C(2)	3589(5)	4561(4)	1963(2)	21(1)
C(3)	3439(5)	4213(4)	4296(2)	24(1)
C(4)	1814(6)	7226(4)	1785(2)	24(2) *
C(5)	1281(5)	6800(4)	3158(2)	21(2) *
C(6)	1156(5)	2299(4)	3182(2)	18(2) *
C(7)	146(5)	2863(4)	1957(2)	20(2) *
C(8)	1001(6)	3303(4)	602(2)	27(2) *
C(9)	−1844(5)	3466(4)	1061(3)	28(2) *
C(10)	3047(5)	2236(4)	2055(2)	23(2) *
C(11)	1316(6)	1825(4)	4522(2)	25(2) *
C(12)	3798(5)	1992(4)	3721(3)	26(2) *
C(13)	31(6)	6335(4)	4421(3)	35(2) *
C(14)	2932(7)	6571(4)	4249(3)	33(2) *
C(15)	4061(5)	6576(4)	2570(3)	27(2) *
C(16)	−1174(6)	7628(4)	1991(3)	37(2) *
C(17)	137(8)	7944(4)	738(3)	42(2) *
C(18)	7335(5)	9982(4)	2449(2)	22(1)
C(19)	6243(5)	9411(4)	2379(3)	24(1)
C(20)	5781(6)	9356(4)	1788(3)	31(1)
C(21)	6385(6)	9853(4)	1239(3)	35(1)
C(22)	7457(6)	10453(4)	1271(3)	33(1)
C(23)	7912(5)	10507(4)	1865(2)	25(1)
C(24)	7583(5)	11237(4)	3284(2)	22(1)
C(25)	7825(6)	11481(4)	3876(3)	29(1)
C(26)	7572(7)	12458(5)	4012(3)	39(1)
C(27)	7072(7)	13220(5)	3566(3)	44(2)
C(28)	6796(7)	13024(5)	2972(3)	41(2)
C(29)	7044(6)	12046(4)	2838(3)	31(1)
C(30)	9573(5)	9734(4)	3190(2)	20(1)
C(31)	10103(5)	9489(4)	3798(3)	24(1)
C(32)	11521(6)	9299(4)	3880(3)	27(1)
C(33)	12485(6)	9333(4)	3351(3)	28(1)

Table 1 (continued)

Atom	x	y	z	U ^{a}
C(34)	11991(6)	9540(4)	2746(3)	25(1)
C(35)	10584(5)	9726(4)	2678(2)	21(1)
C(36)	7021(5)	9318(4)	3695(2)	19(1)
C(37)	7285(5)	8265(4)	3747(2)	24(1)
C(38)	6495(5)	7598(4)	4169(3)	26(1)
C(39)	5423(5)	7962(4)	4563(3)	24(1)
C(40)	5137(5)	8986(4)	4528(2)	23(1)
C(41)	5924(5)	9643(4)	4104(2)	19(1)
C(42)	5573(7)	6253(5)	309(3)	43(2)
C(43)	2985(8)	10425(6)	575(4)	61(2)

^{a} * Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

environments of the two types of PMe_2 groups between the bent and nearly linear groups in a process similar to that already described in detail for 2 [17].

The structure of $[Rh_3(\mu\text{-}dmmm)_2(CO)_3(\mu\text{-}Cl)Cl][BPh_4] \cdot 2CH_2Cl_2$

Atomic positional parameters are given in Table 1. Table 2 contains selected interatomic distances and angles. The salt crystallizes with one cation, a normal tetraphenylborate and two dichloromethane molecules in the asymmetric unit.

A perspective view of the cation is shown in Fig. 1. The structure of the cation is similar to that of the perphenyl analog 1 [1]. It consists of a bent chain of three rhodium atoms which are bridged by *trans* dmmm ligands, with an additional chloride bridge between two of the rhodium atoms.

There are, however, several significant differences between 1 and 3. Two of these regard relative positions of constituent groups. The orientation of the Cl(1)–Rh(1)–C(1)–O(1) group is reversed in the two cations. In 1 the terminal chloride ligand is adjacent to the bridging chloride while in 3 the carbonyl group, C(1)–O(1), occupies that position. This should have significant implications for the stereodynamic behavior of 3 relative to 1. In solution 1 undergoes rapid bridge terminal chloride ligand interchange via eq. 1 [1,11]. For 3 this should not be

(1)
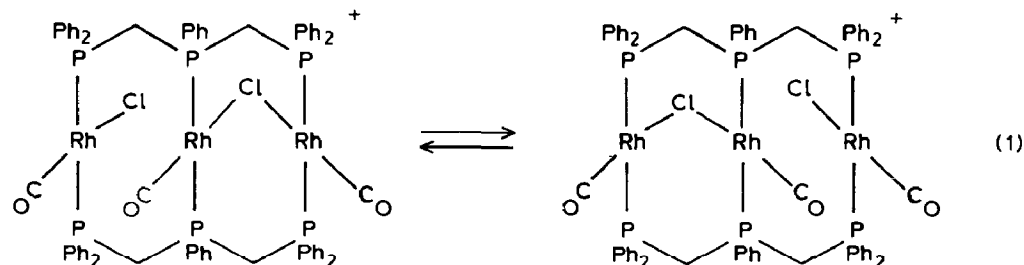
possible because of the relative locations of the ligands. Unfortunately, neither the ^{1}H nor the ^{31}P NMR spectrum of 3 has sufficient resolution to allow definitive characterization of 3 in solution. The other positional variation involves the location of the bridging methylene groups in the triphosphine ligands. In 1 all four methylene groups lie on one side of the P_6Rh_3 surface. In 3, however, only three methylene groups lie on the same side while the fourth, involving C(4), lies on the other side. This means that in 1, the pseudo six-membered ring formed by the P_4C_2 unit lacking

Table 2

Structural parameters for $[Rh_3(\mu\text{-dmmm})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]\cdot 2CH_2Cl_2$

Bond lengths (Å)

Rh(1) environment

Rh(1)–P(1)	2.304(2)	Rh(1)–C(1)	1.803(5)
Rh(1)–P(6)	2.311(2)	Rh(1) ··· Rh(2)	3.028(1)
Rh(1)–Cl(1)	2.378(1)		

Rh(2) environment

Rh(2)–P(2)	2.320(1)	Rh(2)–C(2)	1.810(5)
Rh(2)–P(5)	2.309(1)	Rh(2) ··· Rh(3)	2.999(1)
Rh(2)–Cl(2)	2.441(1)		

Rh(3) environment

Rh(3)–P(3)	2.292(1)	Rh(3)–Cl(2)	2.406(1)
Rh(3)–P(4)	2.332(1)	Rh(3)–C(3)	1.806(6)

Interatomic Angles (°)

At Rh(1)

P(1)–Rh(1)–P(6)	178.9(1)	C(1)–Rh(1)–Cl(1)	174 (2)
P(1)–Rh(1)–Cl(1)	87.2(1)	P(6)–Rh(1)–Cl(1)	92.7(1)
P(1)–Rh(1)–C(1)	91.0(2)	P(6)–Rh(1)–C(1)	89.0(2)

At Rh(2)

Rh(1) ··· Rh(2) ··· Rh(3)	140.9(1)	P(5)–Rh(2)–Cl(2)	86.9(1)
P(2)–Rh(2)–P(5)	177.8(1)	P(5)–Rh(2)–C(2)	90.7(2)
P(2)–Rh(2)–Cl(2)	92.8(1)	C(2)–Rh(2)–Cl(2)	169.1(2)
P(2)–Rh(2)–C(2)	89.2(2)		

At Rh(3)

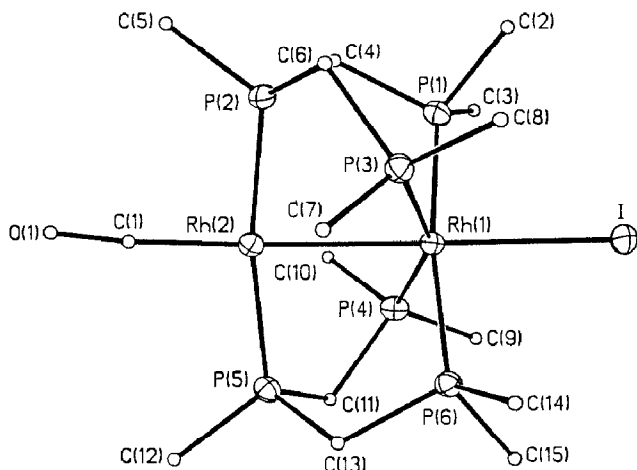|			
P(3)–Rh(3)–P(4)	175.2(1)	P(4)–Rh(3)–Cl(2)	92.1(1)
P(3)–Rh(3)–Cl(2)	86.0(1)	P(4)–Rh(3)–C(3)	92.8(2)
P(3)–Rh(3)–Cl(3)	89.4(2)	C(3)–Rh(3)–Cl(2)	174.3(2)

Fig. 2. A perspective view of $[Rh_2(\mu\text{-dmmm})_2(CO)I]^+$ (**4**) with 50% thermal contours for heavy atoms and arbitrarily sized circles for other atoms.

Table 3

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{Å}^2 \times 10^3$) for $[Rh_2(\mu\text{-dmmm})_2(CO)I]$ $[BPh_4]$

Atom	x	y	z	U^a
Rh(1)	5674(1)	3273(1)	6087(1)	14(1) *
Rh(2)	3396(1)	3079(1)	6566(1)	15(1) *
I	8128(1)	3440(1)	5622(1)	22(1) *
P(1)	5941(3)	4784(2)	6241(1)	21(1) *
P(2)	4354(2)	4170(2)	6959(1)	19(1) *
P(3)	6552(2)	2926(2)	6732(1)	18(1) *
P(4)	3904(2)	3538(2)	5628(1)	19(1) *
P(5)	2758(2)	2026(2)	6094(1)	17(1) *
P(6)	5669(2)	1782(2)	5872(1)	16(1) *
O(1)	1205(7)	2791(6)	7193(2)	36(2) *
O(2)	2054(14)	4235(8)	9660(5)	108(6) *
B	6636(11)	3455(7)	8514(3)	21(3) *
C(1)	1978(10)	2905(7)	6926(3)	24(3) *
C(2)	7616(10)	5118(8)	6436(3)	28(3) *
C(3)	5729(12)	5652(7)	5844(3)	30(3) *
C(4)	4815(11)	5140(7)	6654(3)	28(3) *
C(5)	3519(10)	4623(7)	7407(3)	24(3) *
C(6)	6025(10)	3745(7)	7126(3)	21(3) *
C(7)	5999(11)	1890(7)	6981(3)	24(3) *
C(8)	8393(10)	2850(8)	6811(3)	30(3) *
C(9)	4378(11)	3790(8)	5100(3)	28(3) *
C(10)	2650(10)	4416(7)	5741(3)	27(3) *
C(11)	2688(9)	2585(6)	5603(2)	14(2) *
C(12)	1174(9)	1408(7)	6132(3)	23(3) *
C(13)	4100(9)	1188(6)	6022(3)	18(2) *
C(14)	7115(10)	1073(7)	6008(3)	21(3) *
C(15)	5712(10)	1600(7)	5318(2)	22(3) *
C(16)	7506(9)	2524(6)	8440(3)	18(2)
C(17)	7836(10)	2242(7)	8043(3)	22(2)
C(18)	8585(10)	1474(7)	7965(3)	29(2)
C(19)	9086(12)	923(8)	8289(3)	34(2)
C(20)	8749(10)	1207(7)	8681(3)	27(2)
C(21)	7994(10)	1970(7)	8757(3)	22(2)
C(22)	7331(10)	4235(7)	8212(3)	21(2)
C(23)	8714(11)	4247(7)	8116(3)	30(2)
C(24)	9277(13)	4887(8)	7857(3)	39(3)
C(25)	8520(11)	5547(8)	7691(3)	33(2)
C(26)	7105(10)	5590(7)	7792(3)	27(2)
C(27)	6578(10)	4935(6)	8042(3)	20(2)
C(28)	6774(10)	3779(7)	8993(3)	24(2)
C(29)	8056(12)	4114(8)	9137(3)	33(3)
C(30)	8208(13)	4425(8)	9530(3)	41(3)
C(31)	7151(13)	4436(9)	9798(4)	44(3)
C(32)	5911(14)	4117(9)	9675(4)	43(3)
C(33)	5746(12)	3762(8)	9281(3)	33(2)
C(34)	5000(9)	3299(7)	8392(3)	22(2)
C(35)	4556(10)	2564(7)	8158(3)	22(2)
C(36)	3159(11)	2425(7)	8062(3)	28(2)
C(37)	2194(10)	3020(7)	8195(3)	25(2)
C(38)	2592(10)	3785(7)	8410(3)	22(2)
C(39)	3974(10)	3907(7)	8504(3)	23(2)
C(40)	1440(16)	2794(10)	9383(4)	65(4)
C(41)	2014	3439	9696	57(4)
C(42)	2568(21)	3079(13)	10065(5)	87(5)

^{a} * Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

a chloride bridge has a boat conformation while in **3**, that ring (C(4) P(1) P(2) P(5)-P(6) C(7)) has a chair conformation. Notice that these positional variations in methylene group location can be interchanged by simple bond rotations while the relative location of the Cl–Rh–C–O units cannot.

Other differences between **1** and **3** involve some of the interatomic distances and angles. The Rh $\cdots$ Rh separations in **3** (3.028(1), 2.999(1) Å) are significantly shorter that those in **1** (3.164(3), 3.180(3) Å) [1]. While both sets are longer than the range found for Rh–Rh single bonds (2.5–2.8 Å), they fall in the range where significant overlap of out-of-plane Rh orbitals can occur. As a consequence of these shorter Rh $\cdots$ Rh separations the Rh–Cl(1)–Rh angle in **3** (76.4(1)°) is narrowed relative to that in **1** (82.8(2)°) [1]. Additionally, the Rh_3 chain is more severely bent in **3** (Rh $\cdots$ Rh $\cdots$ Rh angle, 140.9(1)°) than in **1** (Rh $\cdots$ Rh $\cdots$ Rh angle, 157.4(1)°) [1]. Otherwise the dimensions within the cation in **3** are normal.

The structure of $[Rh_2(\mu\text{-}dmmm)_2(CO)I][BPh_4] \cdot (CH_3)_2CO$

Atomic positional parameters are given in Table 3. Selected interatomic distances and angles are set out in Table 4. This salt crystallizes with one cation, one anion, and an acetone molecule in the asymmetric unit.

Figure 2 shows a perspective drawing of the cation of **4**. It is constructed about a nearly linear I–Rh–Rh–CO unit. The Rh–Rh separation (2.735(1) Å) within this unit is considerably shorter than those in **3** and is consistent with the presence of a Rh–Rh single bond.

Table 4

Structural parameters for $[Rh_2(\mu\text{-}dmmm)_2(CO)I][BPh_4]_2 \cdot (CH_3)_2CO$

Bond lengths (Å)			
At Rh(1)			
Rh(1)–Rh(2)	2.735(1)	Rh(1)–I	2.849(1)
Rh(1)–P(1)	2.326(3)	Rh(1)–P(3)	2.335(2)
Rh(1)–P(4)	2.322(2)	Rh(1)–P(6)	2.334(2)
At Rh(2)			
Rh(2)–P(2)	2.275(2)	Rh(2)Π(5)	2.291(2)
Rh(2)–C(1)	1.836(10)	Rh(2)–Rh(1)	2.735(1)
Bond angles (°)			
At Rh(1)			
Rh(2)–Rh(1)	177.1(1)	Rh(2)–Rh(1)–P(1)	94.0(1)
I–Rh(1)–P(1)	86.4(1)	Rh(2)–Rh(1)–P(3)	76.0(1)
I–Rh(1)–P(3)	101.1(1)	P(1)–Rh(1)–P(3)	88.8(1)
Rh(2)–Rh(1)–P(4)	77.5(1)	I–Rh(1)–P(4)	105.4(1)
P(1)–Rh(1)–P(4)	93.3(1)	P(3)–Rh(1)–P(4)	153.5(1)
Rh(2)–Rh(1)–P(6)	94.0(1)	I–Rh(1)–P(6)	85.7(1)
P(1)–Rh(1)–P(6)	172.0(1)	P(3)–Rh(1)–P(6)	93.5(1)
P(4)–Rh(1)–P(6)	88.1(1)		
At Rh(2)			
Rh(1)–Rh(2)–P(5)	84.7(1)	Rh(1)–Rh(2)–P(2)	85.1(1)
Rh(1)–Rh(2)–C(1)	174.4(3)	P(2)–Rh(2)–P(5)	169.7(1)
P(5)–Rh(2)–C(1)	97.5(3)	P(3)–Rh(2)–C(1)	92.8(3)

The arrangement of the bridging dmmm ligands is very similar to that in **2** [17]. Since there is no disorder in **4**, the similarity in these structures confirms the disordered model which was previously developed for **2** [17]. The four PMe_2 units bind to one rhodium which has six-coordinate geometry while the two PMe units are bound to the other rhodium, which has planar, four-coordinate geometry. This unusual mode of bridging has recently been seen in a dpmp complex, $[Re_2(\mu\text{-}dpmp)_2Cl_3]^+$, but there the two dpmp ligands were arranged in a head-to-tail fashion so that each Re atom was coordinated by two PPh_2 groups and one PPh unit [19]. In both **2** and **4** the dmmm ligands are arranged in a head-to-head fashion which gives one rhodium P_4 coordination and the other P_2 coordination.

As with **2** the geometry about the six-coordinate rhodium in **4** is irregular with a nearly linear P(1)–Rh(1)–P(6) angle (172.0(1)°) but a decidedly bent P(3)–Rh(1)–P(4) angle (153.5(1)°). This reflects the difficulty of packing the six methyl groups and three methylene groups that surround Rh(1). In **4** as in **2**, these are arranged into two nearly hexagonal layers. Thus the structural considerations that were set out in detail for **2** hold for **4** as well [17].

The structural parameters within **2** and **4** are also similar. The Rh–Rh bond length in **4** (2.735(1) Å) is slightly shorter than that in **2** (2.777(1) Å). This shortening can be ascribed to the reduced *trans* influence of iodide relative to carbon monoxide. As with **2**, the P–Rh distances at the six-coordinate rhodium in **4** are slightly longer than at the four coordinate rhodium.

Conclusion

Comparison of the structures of **3** and **4** shows that dmmm is capable of engaging in at least two modes of bridging. The compact, crowded structure of **2** and **4** contrasts markedly with the open structure of the trinuclear **3**, which should have as rich a chemistry as **1**, with additional reactivity promoted by the more basic phosphine ligands.

Experimental

Materials

Both dmmm [16] and **2** [17] were prepared as described previously. The ligand dmmm was handled under a nitrogen atmosphere by standard Schlenk techniques. Solvents were purged of oxygen before use.

Physical measurements

The ^{31}P (^1H] NMR spectra were recorded on a Nicolet NT-360 Fourier transform spectrometer operating at 145.8 MHz. The spectra were obtained using 10 mm tubes and broad-band proton decoupling. An external 85% phosphoric acid reference and high frequency positive convention was used in reporting all chemical shifts.

X-ray data were collected using a Syntex $P2_1$ diffractometer equipped with a locally modified LT-1 low temperature device. The SHELXTL version 4 software package installed in a Data General Eclipse S/230 computer was used for the analysis of the X-ray data.

Infrared spectra were recorded in acetone solution using an IBM IR32 Fourier transform infrared spectrometer.

Preparation of compounds

[Rh₂(μ-dmmm)₂(CO)I][BPh₄] (4)

[Rh$_2$(μ-dmmm)$_2$(CO)I][BPh$_4$] (4)

Method 1. Methylene iodide (100 mg, 0.370 mmol) was added to a yellow solution of **2** (150 mg, 0.113 mmol) in 10 ml of acetone. The solution was stirred at 60 °C for 3.5 h during which time it turned red. The solution was evaporated to a volume of 1 ml under a stream of nitrogen during which time yellow crystals were formed. The product was collected by filtration and washed with ethyl ether; yield 88.4 mg, 73%. *Note*: occasionally under identical conditions an isomer of **3** is formed. Based on the IR of the reaction solution (ν(CO) 2016 cm^{-1}) it appears that the positions of iodine and carbon monoxide have interchanged positions as compared with **3**.

Method 2. A solution of sodium iodide (150 mg, 1.00 mmol) in 5 ml of methanol was added while stirring to a solution of **2** (150 mg, 0.113 mmol) in 10 ml of acetone. The reaction mixture changed color rapidly from yellow to brown and was allowed to stir for 2 h. The solution was evaporated to a volume of 5 ml under a stream of nitrogen and ethyl ether was added to precipitate a brown solid. Recrystallization from acetone gave yellow crystals; yield 103 mg, 85%.

[Rh₃(μ-dmmm)₂(CO)₃(μ-Cl)Cl][BPh₄] (3)

[Rh$_3$(μ-dmmm)$_2$(CO)$_3$(μ-Cl)Cl][BPh$_4$] (3)

Under a dioxygen-free environment a solution of dmmm (202 mg, 1.03 mmol) in 15 ml of dichloromethane was rapidly added to a stirred solution of [Rh(CO)$_2$Cl]$_2$ (300 mg, 0.772 mmol) in 20 ml of dichloromethane. The solution immediately turned deep purple, and the liberation of carbon monoxide was observed. A solution of sodium tetraphenylborate (400 mg, 1.17 mmol) in methanol was added dropwise over a period of 20 min. After the mixture was stirred for an additional 1 h, **2** was removed from the purple solution by filtration. Addition of ethyl ether to the solution gave deep purple crystals: yield; 362 mg, 60%.

X-ray data collection

[Rh₂(μ-dmmm)₂(CO)I][BPh₄] (4). Well-formed yellow crystals were grown by slow diffusion of diethyl ether into an acetone solution of the compound. The crystals were removed from the diffusion tube and immediately coated with a light hydrocarbon oil to reduce loss of solvent from the crystal. Accurate unit cell parameters were obtained from a least-squares fit of 24 reflections with $25° \leq 2\theta \leq 30°$. The non-centrosymmetric, orthorhombic space group $P2_12_12_1$ (No. 19) was uniquely determined by the observed conditions $h00$, $h = 2n$; $0k0$, $k = 2n$ and $00l$, $l = 2n$. No decay in the intensities of two standard reflections occurred. Data collection parameters are summarized in Table 5. The data were corrected for Lorentz and polarization effects.

[Rh₃(μ-dmmm)₂(CO)₃(μ-Cl)Cl][BPh₄] (3). Deep purple parallelepipeds were formed by vapor diffusion of diethyl ether into a dichloromethane solution of the compound. The air-sensitive crystals were taken from the Schlenk tube under a stream of nitrogen and immediately covered with epoxy resin to retard deterioration. The crystal was found to be triclinic by a least-squares refinement of 25 reflections with $35° \leq 2\theta \leq 40°$. The procedure for data collection and reduction

Table 5

Crystal and data collection parameters

	[Rh$_2$(μ-dmmm)$_2$(CO)-I][BPh$_4$]·(C$_3$H$_6$O) (4)	[Rh$_3$$\mu$-dmmm)$_2(CO)_3$($\mu$-Cl)-Cl][BPh$_4$]·2(CH$_2Cl_2$) (3)
formula	C$_{42}$H$_{64}$BIO$_2$P$_6$Rh$_2$	C$_{43}$H$_{62}$BCl$_6$O$_3$P$_6$Rh$_3$
fw	113028	1345.06
crystal system	orthorhombic	triclinic
space group	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)
cryst dimens (mm)	0.17×0.20×0.21	0.15×0.18×0.20
color and habit	yellow rectangular prisms	deep-purple parallelepipeds
unit cell dimens (130 K)		
a (Å)	9.760(3)	9.688(2)
b (Å)	14.931(4)	13.571(2)
c (Å)	32.708(8)	21.303(3)
α (°)		80.18(1)
β (°)		84.74(1)
γ (°)		83.99(1)
V (Å^3)	47668(2)	2737 (1)
D_{calc} (g/cm^3)	1.58	1.63
Z	4	2
radiation, λ (Å) (graph. monochr.)	Mo-K_α, 0.71069	Mo-k_α, 0.71069
μ(Mo-K_α) (cm^{-1})	12.11	12.66
transm. factors	0.763–0.847	0.775–0.682
octants	+ h, + k, + l	+ h, ± k, ± l
scan type, $2\theta_{max}$(°)	ω, 50	ω, 50
scan range (°)	1.3	1.4
scan speed (° min^{-1})	60	60
no. unique data	4707	9652
no. data $I > 3\sigma(I)$	4244	8164
data/parameter	10.99	19.25
R	0.044	0.044
R_w	0.049	0.048

was as described for compound **4**. Data collection parameters are summarized in Table 5.

Solution of refinement of structures

[Rh$_2$(μ-dmmm)$_2$(CO)I][BPh$_4$] (4). The positions of the two rhodium atoms were found from the Patterson map. The remaining non-hydrogen atoms were located from subsequent difference Fourier maps. An absorption correction using the programs XABS [20*] was applied to the data. The handedness of the crystal was determined by use of a SHELXTL routine. This indicated that the coordinates originally chosen were correct and no inversion of coordinates was necessary. Hydrogen atoms were placed at idealized positions (d(C–H) 0.96 Å) and assigned isotropic thermal parameters 20% greater than the carbon atom to which they were attached. A riding model was utilized to continuously update hydrogen atom positions during each refinement cycle. All non-hydrogen atoms were refined with anisotropic thermal parameters except the carbons of tetraphenylborate and the

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* Reference number with asterisk indicates a note in the list of references.

acetone molecule. The final $R = 0.044$ was computed from 388 least-squares parameters and 4244 reflections. This yielded a goodness-of-fit of 1.002 and a maximum shift/esd of 0.007 for the z coordinate of O(2) during the last cycle of refinement. A value of 1.6 e Å^{-3} was found as the largest feature on the final difference Fourier map. This was 1.00 Å from C(40) of the acetone molecule. The weighting scheme used was $w = [\sigma^2(F_o)]^{-1}$. Correction for anomalous dispersion was applied to all atoms [21]. Neutral-atom scattering factors were those of Cromer and Waber [21].

[Rh$_3$(μ-dmmm)$_2$(CO)$_3$(μ-Cl)Cl][BPh$_4$] (3). The structure was solved in the centrosymmetric space group $P\bar{1}$. The positions of the three rhodium atoms were generated from FMAP 8, the Patterson solving routine of SHELXTL. The remaining atoms were located from different maps. Anisotropic thermal parameters were assigned to rhodium, phosphorus, chlorine, and the carbon atoms of the phosphorus ligands. Isotropic thermal parameters were assigned to the remaining atoms. The final $R = 0.044$ was computed from 424 least-squares parameters and 8146 reflections. This yielded a goodness-of-fit of 1.849 and a maximum shift/esd of 0.011 for U_{33} of Rh(1) during the last cycle of refinement. A value of 0.60 e Å^{-3}, 12.02 Å from Rh(3), was found as the largest feature on the final difference Fourier map. The weighting scheme used was $w = [\sigma^2(F_o) + 0.00041F_o^2]^{-1}$. All other details of the refinement was identical to those of **4**.

Copies of tables of all bond lengths and angles, anisotropic thermal parameters, calculated hydrogen coordinates and structure factors are available from the authors.

Acknowledgements

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