Notes

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Synthesis and Crystal and Molecular Structure of the Dimetalated Olefin Complex $[Rh_2(H_3CN(P(OCH_3)_2)_2)_4(\mu\text{-}H_3CO_2CC{\equiv}CCO_2CH_3)](ClO_4)_2 \cdot CH_3OH$

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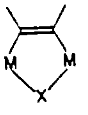
In recent years, considerable interest has been shown in the reactions of small molecules with binuclear complexes bridged by "short-bite" diphosphine ligands such as bis(diphenylphosphino)methane (DPPM)[1] and its permethyl analogue (dmpm).[2] Among the small molecules that can be bound to these complexes are electrophilic acetylenes. Frequently the attachment of these acetylenes occurs parallel to the metal–metal axis (A–C) rather than perpendicular to it (D) as has heretofore been more common. In our continuing studies on such systems we have begun an investigation of complexes of the related ligands $H_3CN(P(OR)_2)_2$ (R = CH_3, CH_2–, *i*-C_3H_7) and have recently described the synthesis of $[Rh_2(PNP)_2(\mu\text{-}PNP)_2]X_2$ (PNP = $H_3CN(P(OCH_3)_2)_2$; X = BPh_4, ClO_4, PF_6, O_3SCF_3), which has an unusual basket-shaped structure.[3] We report here on some chemistry of this complex and the structure of its adduct with dimethyl acetylenedicarboxylate.



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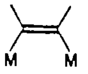

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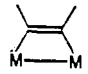

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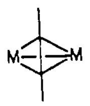


D

Experimental Section

All solvents were appropriately dried and distilled prior to use and were stored under dinitrogen. All operations were performed under a dinitrogen atmosphere although the products proved not to be noticeably sensitive to the ambient atmosphere. $[Rh_2(PNP)_2(\mu\text{-}PNP)_2]X_2$ (X = BPh_4, ClO_4) were prepared as previously described,[3] while dimethyl acetylenedicarboxylate (DMAD) was obtained from Aldrich. Proton NMR spectra were obtained on an IBM/Bruker instrument at 200.13 MHz (30 °C) and referenced to external tetramethylsilane (δ 0.0). Analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

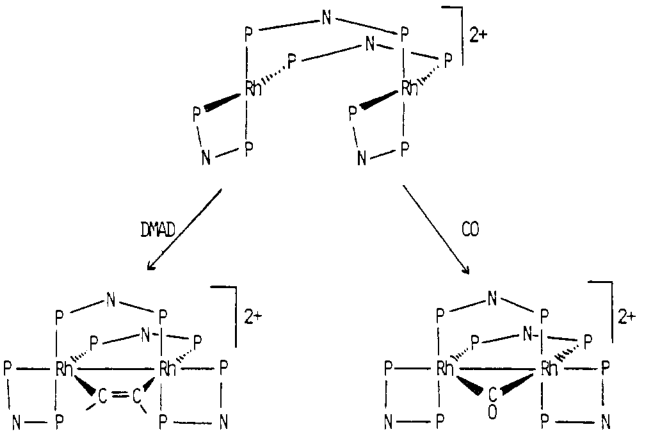
$[Rh_2(H_3CN(P(OCH_3)_2)_2)_2(\mu\text{-}H_3CN(P(OCH_3)_2)_2)_2(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)](B(C_6H_5)_4)_2$. To a solution of 0.2 g (0.12 mmol) of $[Rh_2(PNP)_2(\mu\text{-}PNP)_2](BPh_4)_2$ in 10 mL of acetone was added an excess of DMAD. After being stirred for ca. 48 h, the purple solution had become pale yellow, and addition of diethyl ether precipitated off-white crystals. These were recrystallized from acetone/diethyl ether to afford the product as pale yellow microcrystals in 90% yield: ^1H NMR ($(CD_3)_2CO$) δ 6.77–7.36 (m, 40 H, C_6H_5), 3.77–4.02 (m, 24 H, P–O–CH_3), 3.64 (s, 6 H, C–O–CH_3), 2.75–3.02 (m, 12 H, N–CH_3); IR 1555 (m) cm^{-1} ($\nu_{C{=}C}$). Anal. Calcd for $C_{74}H_{106}O_{20}P_8N_4B_2Rh_2$: C, 48.12; H, 5.80; N, 3.03. Found: C, 48.2; H, 5.8; N, 3.2.

$[Rh_2(H_3CN(P(OCH_3)_2)_2)_2(\mu\text{-}H_3CH(P(OCH_3)_2)_2)_2(\mu\text{-}H_3CO_2CC{=}CCO_2CH_3)](ClO_4)_2 \cdot CH_3OH$. This was prepared from $[Rh_2(PNP)_2(\mu\text{-}PNP)_2](ClO_4)_2$ in a manner analogous to that for the previous complex. Following the color change to pale yellow, the reaction mixture was diluted with methanol and the solvent volume reduced with a slow stream of dinitrogen until crystals formed. These had virtually the same infrared and ^1H NMR spectra as the previous complex except for differences due to the different counterions.

Table I. Crystallographic Data for $[Rh_2(MeN(P(OMe)_2)_2)_4(\mu\text{-}DMAD)](ClO_4)_2 \cdot MeOH$

chem formula $C_{27}H_{70}O_{29}P_8N_4Cl_2Rh_2$	space group $P2_1$ (No. 4)
fw 1439.49	T = 298 K
a = 12.0981 (9) Å	λ = 0.71073 Å
b = 16.0366 (9) Å	ρ_{calc} = 1.678 g cm^{-3}
c = 15.5448 (12) Å	μ = 9.9 cm^{-1}
β = 112.040 (6)°	tranmissn coeff = 0.94–1.0
V = 2794 $Å^{+}$	$R(F_o)$ = 0.025
Z = 2	$R_w(F_o)$ = 0.033

Scheme I



Caution! Perchlorate salts are notoriously unpredictable with respect to shock and thermal instability. No problem was encountered here, but due care should always be exercised in handling them.

X-ray Crystallography. Pale yellow parallelpipeds of $[Rh_2(PNP)_2(\mu\text{-}PNP)_2(\mu\text{-}DMAD)](ClO_4)_2 \cdot MeOH$ were obtained directly from the reaction mixture as described above and proved to be of X-ray quality. A crystal approximately 0.3 mm on a side was sealed in a thin-walled glass capillary and mounted on an Enraf-Nonius CAD-4 diffractometer. General procedures for data collection and reduction and refinement of the structure have been published.[3] Parameters specific to the structure appear in Tables I and S10 (supplementary material). Systematic absences (0*k*0, $k = 2n + 1$) observed during the data collection were consistent with space groups $P2_1$ (No. 4) and $P2_1/m$ (No. 11). The choice of the former was suggested by the Wilson statistics and the fact that Z = 2. Confirmation was provided by the successful refinement when it soon became evident that the molecule did not possess crystallographic mirror symmetry.

The refinement proceeded smoothly, and the final cycles were performed with weights given by $w = 1/\sigma_F^2$ ($\sigma_F = \sigma_{F^2}/2F$; $\sigma_{F^2} = (\sigma_{I}^2 + (0.04F^2)^2)^{1/2}$). All hydrogen atoms could be seen in difference maps. These were included in idealized positions and allowed to ride on the attached carbon atoms with isotropic thermal parameters equal to 1.3 times those of the appropriate carbon atoms. Following refinement of the original model to convergence, its enantiomer was similarly refined to essentially the same values of R, R_w, and GOF. No clear choice between enantiomers could therefore be made, and the original one was retained, as it appeared to give slightly better values of these parameters. The final difference map was virtually featureless. Final positional parameters are given in Table II, while all other crystallographic information is included as supplementary material.

Results

Both dimethyl acetylenedicarboxylate and carbon monoxide react with purple $[Rh_2(PNP)_2(\mu\text{-}PNP)_2]^{2+}$ to yield pale yellow adducts (Scheme I). The rate of reaction is considerably slower with DMAD than with CO (2 days vs several minutes) presumably because access to the metal atoms is quite restricted.[3] There is some indication that the reaction is markedly slower when light is excluded, but attempts to quantify the extent (if any) of photoassistance were unsuccessful. The DMAD adduct has been

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(1) Mague, J. T. *Organometallics* **1986**, *5*, 918 and references therein.
(2) Jenkins, J. A.; Ennett, J. P.; Cowie, M. *Organometallics* **1988**, *7*, 1845 and references therein.
(3) Mague, J. T.; Lloyd, C. L. *Organometallics* **1988**, *7*, 983.

0020-1669/89/1328-2215$01.50/0

Table II. Positional Parameters with Esd's for $[Rh_2(MeN(P(OMe)_2)_2)_4(\mu\text{-}MeO_2CC{=}CCO_2Me)](ClO_4)_2\cdot MeOH$

atom	*x*	*y*	*z*	*B*,[a] Å^2	atom	*x*	*y*	*z*	*B*,[a] Å^2
Rh1	0.81315 (3)	0.236	0.81980 (2)	1.919 (6)	C61	1.0852 (6)	0.3316 (6)	0.6402 (6)	7.5 (2)
Rh2	0.80275 (3)	0.14914 (3)	0.66370 (2)	1.846 (6)	C62	0.8633 (7)	0.2807 (6)	0.4354 (4)	6.9 (2)
P1	1.0120 (1)	0.20975 (8)	0.87658 (8)	2.43 (2)	C71	0.7678 (6)	0.0694 (6)	0.3641 (4)	5.8 (2)
P2	0.8291 (1)	0.36395 (8)	0.75389 (8)	2.58 (3)	C72	0.7884 (6)	−0.0846 (4)	0.5365 (5)	4.9 (2)
P3	0.8049 (1)	0.28712 (9)	0.95512 (8)	2.68 (3)	C81	0.4445 (6)	0.0881 (5)	0.6025 (5)	4.9 (2)
P4	0.6145 (1)	0.26594 (9)	0.80583 (8)	2.63 (3)	C82	0.4918 (6)	0.3028 (5)	0.4545 (5)	5.8 (2)
P5	0.9861 (1)	0.09026 (8)	0.73528 (8)	2.37 (2)	N1	1.0586 (3)	0.1200 (3)	0.8460 (3)	2.67 (8)
P6	0.8657 (1)	0.26634 (8)	0.60842 (8)	2.59 (2)	N2	0.8389 (4)	0.3594 (3)	0.6485 (3)	3.18 (9)
P7	0.7367 (1)	0.07576 (9)	0.52618 (8)	2.58 (2)	N3	0.6574 (4)	0.3012 (3)	0.9155 (3)	3.4 (1)
P8	0.6093 (1)	0.18322 (9)	0.57326 (8)	2.49 (2)	N4	0.6012 (4)	0.1207 (3)	0.4858 (3)	3.15 (9)
O11	1.0863 (3)	0.2810 (3)	0.8516 (3)	3.87 (9)	C1	1.1830 (5)	0.0890 (4)	0.8983 (4)	3.9 (1)
O12	1.0785 (3)	0.2118 (3)	0.9861 (2)	3.40 (8)	C2	0.8059 (7)	0.4337 (4)	0.5870 (4)	5.2 (2)
O21	0.9379 (3)	0.4181 (2)	0.8211 (3)	3.58 (8)	C3	0.5887 (5)	0.3526 (5)	0.9574 (4)	5.3 (2)
O22	0.7191 (3)	0.4271 (3)	0.7267 (3)	3.67 (9)	C4	0.4970 (5)	0.0976 (5)	0.4016 (4)	4.9 (2)
O31	0.8450 (3)	0.2279 (3)	1.0417 (3)	4.33 (9)	C5	0.7755 (4)	0.1092 (3)	0.8336 (3)	2.21 (9)
O32	0.8492 (3)	0.3773 (3)	0.9964 (3)	3.72 (9)	C6	0.7613 (4)	0.0709 (3)	0.7555 (3)	2.14 (8)
O41	0.5281 (3)	0.1889 (3)	0.7903 (3)	3.45 (8)	C7	0.7627 (5)	0.0675 (4)	0.9152 (3)	3.1 (1)
O42	0.5277 (3)	0.3420 (3)	0.7602 (3)	4.3 (1)	C8	0.7210 (4)	−0.0175 (3)	0.7367 (3)	2.44 (9)
O51	1.0942 (3)	0.1031 (3)	0.7006 (2)	3.41 (8)	C9	0.7305 (6)	−0.1544 (4)	0.7977 (5)	5.1 (2)
O52	0.9722 (3)	−0.0087 (2)	0.7339 (3)	3.24 (8)	C10	0.6264 (7)	0.0094 (7)	0.9747 (6)	10.2 (2)
O61	1.0051 (3)	0.2637 (3)	0.6317 (3)	4.7 (1)	O1	0.8425 (4)	0.0469 (3)	0.9836 (3)	5.4 (1)
O62	0.8068 (4)	0.2851 (3)	0.5003 (2)	4.09 (9)	O2	0.6478 (3)	0.0523 (4)	0.8998 (3)	6.3 (1)
O71	0.8070 (3)	0.0955 (3)	0.4600 (2)	3.49 (8)	O3	0.7711 (4)	−0.0681 (2)	0.8098 (3)	3.69 (9)
O72	0.6996 (3)	−0.0196 (2)	0.5030 (3)	3.65 (9)	O4	0.6498 (4)	−0.0422 (3)	0.6657 (3)	4.2 (1)
O81	0.4893 (3)	0.1685 (3)	0.5894 (3)	3.45 (8)	Cl1	0.1275 (1)	0.1843 (1)	0.3796 (1)	4.31 (3)
O82	0.5891 (3)	0.2766 (3)	0.5396 (3)	3.49 (8)	O1A	0.0451 (5)	0.1237 (4)	0.3797 (5)	9.7 (2)
C11	1.1978 (6)	0.3128 (6)	0.9049 (6)	7.3 (2)	O2A	0.1909 (8)	0.2130 (5)	0.4720 (5)	11.0 (3)
C12	1.0815 (5)	0.1471 (5)	1.0517 (4)	4.4 (1)	O3A	0.2075 (5)	0.1520 (6)	0.3448 (5)	11.2 (2)
C21	0.9872 (6)	0.4922 (4)	0.7979 (5)	5.0 (2)	O4A	0.0682 (7)	0.2538 (6)	0.3366 (7)	12.5 (3)
C22	0.7042 (6)	0.4886 (4)	0.7901 (5)	4.7 (2)	Cl2	0.4796 (1)	0.1698 (2)	0.1328 (1)	5.81 (5)
C31	0.8090 (7)	0.2294 (6)	1.1171 (4)	5.8 (2)	O5A	0.3751 (6)	0.1640 (8)	0.1461 (6)	13.6 (3)
C32	0.9775 (6)	0.3943 (5)	1.0391 (4)	4.8 (2)	O6A	0.4619 (9)	0.200 (1)	0.0506 (6)	20.7 (4)
C41	0.4294 (5)	0.1836 (6)	0.8194 (5)	6.4 (2)	O7A	0.5643 (9)	0.2092 (8)	0.2010 (7)	16.2 (4)
C42	0.4418 (6)	0.3453 (5)	0.6666 (5)	5.6 (2)	O8A	0.527 (1)	0.0891 (9)	0.1486 (8)	18.9 (4)
C51	1.0835 (5)	0.0861 (5)	0.6073 (4)	4.9 (2)	O1S	0.3409 (7)	0.8750 (6)	0.7909 (6)	10.2 (2)*
C52	1.0658 (5)	−0.0688 (4)	0.7482 (5)	4.5 (1)	C1S	0.385 (1)	0.928 (1)	0.7396 (9)	10.9 (4)*

[a] Starred values indicate atoms were refined isotropically. *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)\mathrm{B}(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

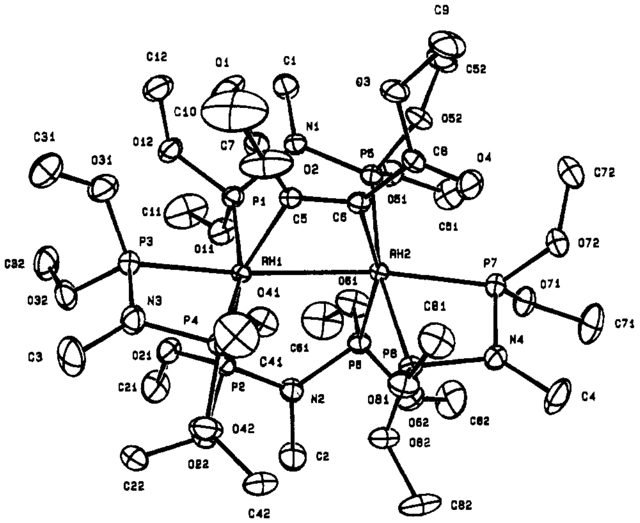

Figure 1. Perspective view of the $[Rh_2(MeN(P(OMe)_2)_2)_2(\mu\text{-}MeN(P(OMe)_2)_2)_2(\mu\text{-}MeO_2CC{=}CCO_2Me)]^{2+}$ cation. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms have been omitted for clarity.

obtained as both perchlorate and tetraphenylborate salts, and a perspective view of the cation from the former is shown in Figure 1, while the inner coordination sphere is shown in Figure 2. The structure of the tetraphenylborate salt has also been solved,[4] and the cation appears virtually the same there, but with two independent molecules in that crystal, it was not feasible to complete the refinement.

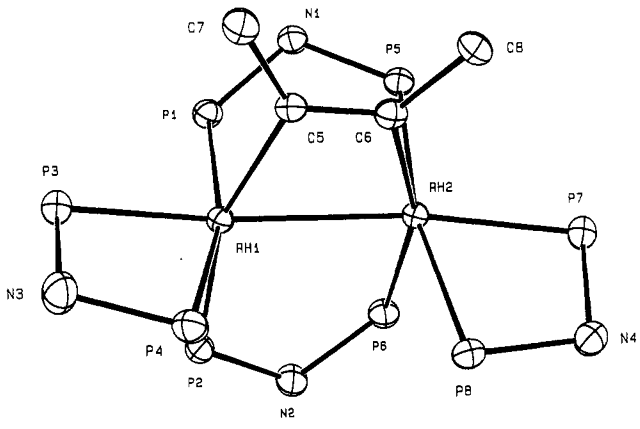

Figure 2. View of the inner coordination sphere of the $[Rh_2(MeN(P(OMe)_2)_2)_2(\mu\text{-}MeN(P(OMe)_2)_2)_2(\mu\text{-}MeO_2CC{=}CCO_2Me)]^{2+}$ cation. Thermal ellipsoids are drawn at the 30% probability level.

Table III. Selected Bond Distances (Å) for $[Rh_2(MeN(P(OMe)_2)_2)_4(\mu\text{-}MeO_2CC{=}CCO_2Me)](ClO_4)_2\cdot MeOH$[a]

Rh1–Rh2	2.7595 (5)	C5–C6	1.313 (7)
Rh1–P1	2.269 (1)	Rh2–C6	2.097 (5)
Rh1–P2	2.334 (1)	P1–N1	1.677 (4)
Rh1–P3	2.294 (1)	P2–N2	1.687 (5)
Rh1–P4	2.378 (1)	P3–N3	1.670 (5)
Rh2–P5	2.278 (1)	P4–N3	1.683 (5)
Rh2–P6	2.311 (1)	P5–N1	1.681 (4)
Rh2–P7	2.305 (1)	P6–N2	1.695 (5)
Rh2–P8	2.298 (1)	P7–N4	1.680 (4)
Rh1–C5	2.112 (5)	P8–N4	1.663 (5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

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(4) Mague, J. T. Unpublished observations.

Table IV. Selected Interbond Angles (deg) for $[Rh_2(MeN(P(OMe)_2)_2)_4(\mu\text{-}MeO_2CC{=}CCO_2Me)](ClO_4)_2 \cdot MeOH$[a]

Rh2-Rh1-P1	86.58 (3)	P6-Rh2-P7	96.79 (5)
Rh2-Rh1-P2	92.39 (3)	P6-Rh2-P8	88.90 (5)
Rh2-Rh1-P3	169.49 (4)	P6-Rh2-C6	159.3 (1)
Rh2-Rh1-P4	108.09 (3)	P7-Rh2-P8	68.58 (5)
Rh2-Rh1-C5	70.30 (8)	P7-Rh2-C6	103.7 (1)
P1-Rh1-P2	94.80 (5)	P8-Rh2-C6	96.3 (1)
P1-Rh1-P3	96.54 (5)	Rh1-P1-N1	117.9 (2)
P1-Rh1-P4	163.71 (5)	Rh1-P2-N2	115.8 (2)
P1-Rh1-C5	91.1 (1)	Rh1-P3-N3	96.8 (2)
P2-Rh1-P3	97.33 (5)	Rh1-P4-N3	93.4 (2)
P2-Rh1-P4	91.70 (5)	Rh2-P5-N1	114.9 (2)
P2-Rh1-C5	161.4 (1)	Rh2-P6-N2	116.4 (2)
P3-Rh1-P4	67.78 (5)	Rh2-P7-N4	94.5 (2)
P3-Rh1-C5	99.6 (1)	Rh2-P8-N4	95.2 (2)
P4-Rh1-C5	87.4 (1)	P1-N1-P5	115.6 (2)
Rh1-Rh2-P5	93.71 (3)	P2-N2-P6	119.2 (3)
Rh1-Rh2-P6	90.21 (4)	P3-N3-P4	102.1 (2)
Rh1-Rh2-P7	163.52 (4)	P7-N4-P8	101.7 (2)
Rh1-Rh2-P8	96.77 (4)	Rh1-C5-C6	108.4 (3)
Rh1-Rh2-C6	69.34 (8)	Rh1-C5-C7	127.8 (4)
P5-Rh2-P6	97.06 (5)	C6-C5-C7	123.8 (5)
P5-Rh2-P7	100.17 (5)	Rh2-C6-C5	111.6 (3)
P5-Rh2-P8	167.92 (5)	Rh2-C6-C8	125.4 (3)
P5-Rh2-C6	81.8 (1)	C5-C6-C8	123.0 (4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

The crystal structure of $[Rh_2(PNP)_2(\mu\text{-}PNP)_2(\mu\text{-}DMAD)](ClO_4)_2 \cdot MeOH$ consists of discrete bimetallic cations interspersed with perchlorate anions and solvent methanol molecules. There are no unusually short intermolecular contacts. Selected bond distances and interbond angles are presented in Table III and IV, respectively, while additional metrical parameters are included as supplementary material.

Discussion

As can be seen from the figures and the scheme, the binding of DMAD to $[Rh(PNP)_2(\mu\text{-}PNP)_2]^{2+}$ to form the title compound causes one end of each chelating ligand (here P3 and P7) to swing away from the center of the cation by ca. 90°[5] and the metal–metal distance to decrease from 3.2727 (5) Å in the parent to 2.7595 (5) Å in the adduct. The latter distance compares well with that found in $[Rh_2Cl_2(\mu\text{-}HFB)(DPPM)_2]$ (2.7447 (9) Å),[6] and as it is also shorter than the P--P contacts within each of the two bridging ligands (P1--P5 = 2.842 (2), P2--P6 = 2.917 (2) Å), the presence of a Rh–Rh single bond is indicated. The coordination about each metal can be roughly described as octahedral if the position of the second metal is included, but as can be seen from Figure 2 and Table IV, there are significant distortions. The coordination sphere about Rh1 is somewhat more regular than that about Rh2, but in neither instance is any set of three ligating atoms coplanar with the attached metal (Table S8, supplementary material). The major distortions in the coordination spheres of the metals result from constraints imposed by the short "bite" of the chelating ligands and the binding of the olefinic moiety. Smaller distortions are a rotation of the chelating ligand on Rh2 away from P5 so that the Rh1–Rh2–P7 angle is significantly less than the Rh2–Rh1–P3 angle and an opening of the P5–Rh2–P6 angle as compared with P1–Rh1–P2. These latter distortions can be attributed to nonbonded contacts. Because of the different rotational orientations of the carbomethoxy groups, O4 makes contacts of 2.52 and 2.60 Å, respectively, with H813 and H722,[7] but the closest approach of the other with the chelating ligand on Rh1 is 2.88 Å (O2--H411). Also, one perchlorate ion is situated close to the methoxy groups on P5, P6, and P7 (O1A--H623 = 2.86 Å, O1A--H712 = 2.55 Å, O2A--H511 = 2.62 Å), but the corresponding site on the other side of the cation is not similarly occupied.

As was found for $[Rh_2(CNCMe_3)_4(\mu\text{-}HFB)(DPPM)_2](PF_6)_2$,[8] one side of the cation is twisted relative to the other by ca. 15.51 (5)°[10] although interestingly the angle between the Rh1–Rh2 and C5–C6 vectors is only 6.5 (1)°. Here also it appears likely that the twist is to minimize nonbonded contacts (e.g. O41--H813 = 2.47 (Å), O82--H423 = 2.41 Å),[7] as is the case in $[Rh_2(PNP)_2(\mu\text{-}PNP)_2]^{2+}$.

The C5–C6, Rh1–C5, and Rh2–C6 distances (Table III) compare favorably with the corresponding values found in $[Rh_2(CNCMe_3)_4(\mu\text{-}HFB)(DPPM)_2](PF_6)_2$ (1.318 (9), 2.089 (4) Å).[8] The difference in the two Rh–C distances is of only marginal significance ($\Delta/\sigma = 3$). The Rh–P distances vary considerably although all are in the range found previously for the $[Rh_2(PNP)_2(\mu\text{-}PNP)_2]^{2+}$ cation.[3,9] Comparison of corresponding pairs between the two sides of the cation shows close agreement except for Rh1–P4 vs Rh2–P8. The possibility that this arises from an incorrect choice of enantiomer was checked by calculating all Rh–P distances and P–Rh–P angles in the enantiomer that had been rejected. Essentially the same values were found, and we therefore have no obvious explanation for the difference. Within the dimeric cation, all other metrical parameters are unexceptional although there is considerable congestion (Table S7, supplementary material). The perchlorate ions also have normal geometries although showing considerable thermal motion.

The carbonyl adduct of $[Rh_2(PNP)_2(\mu\text{-}PNP)_2]^{2+}$ proved too labile to be isolated. However, the observation of a strong absorption at 1864 cm^{-1} in a CO-saturated solution indicated the presence of a bridging carbonyl. This together with the pale yellow color strongly suggests the carbonyl adduct has a structure similar to that of $[Rh_2(PNP)_2(\mu\text{-}PNP)_2(\mu\text{-}DMAD)]^{2+}$ with a metal–metal bond.

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Supplementary Material Available: Tables S1–S9, listing bond distances, interbond angles, anisotropic thermal parameters, amplitudes of anisotropic thermal displacement, calculated hydrogen atom positions, torsion angles, selected nonbonded contacts, results of least-squares plane calculations, and full details of data collection and refinement (25 pages); Table S10, listing observed and calculated structure factors (50 pages). Ordering information is given on any current masthead page.

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(5) In $[Rh_2(PNP)_2(\mu\text{-}PNP)_2]^{2+}$, with reference to the numbering scheme of Figure 2, P3 and P7 are approximately trans respectively to P2 and P6.

(6) Cowie, M.; Dickson, R. S. *Inorg. Chem.* **1981**, *20*, 2682.

(7) The hydrogen atoms are numbered such that the first digit or digits refer to the number of the attached carbon atom, while the final digit identifies the particular hydrogen atom of that methyl group.

(8) Mague, J. T. *Inorg. Chem.* **1983**, *22*, 1158.

(9) Blakely, R. L.; Yin, Y.; Lloyd, C. L.; Mague, J. T.; McPherson, G. L. Manuscript in preparation.

(10) This is the average of the torsional angles P1–Rh1–Rh2–P5 (15.91 (5)°), P2–Rh1–Rh2–P6 (13.49 (5)°), and P4–Rh1–Rh2–P8 (17.14 (5)°).

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Evidence for the Existence of the $[MgCl(THF)_5]^+$ Cation. Crystal Structures of $[MgCl(THF)_5][FeCl_4] \cdot THF$ and $[MgCl(THF)_5][AlCl_4] \cdot THF$

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The formation of $[Mg(THF)_6]^{2+}$, $[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+$, and $[MgCl_4]^{2-}$ ions from $[MgCl_2(THF)_2]$ in tetrahydrofuran (THF) is well documented.[1-3] The conductivity of $[MgCl_2(THF)_2]$ in

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(1) Sobota, P.; Utko, J.; Lis, T. *J. Chem. Soc. Dalton Trans.* **1984**, 2077.

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