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Preparation and Structure of Mono- and Binuclear Complexes of (Diphenylarsino)(diphenylphosphino)methane Including the X-ray Crystal Structure of *trans*-Rh(CO)Cl(μ-$Ph_2AsCH_2PPh_2$)$_2$-*cis*-$PtCl_2$

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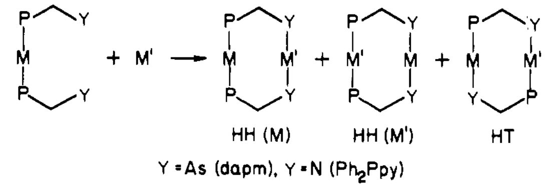
The reactions of (diphenylarsino)(diphenylphosphino)methane with (1,5-COD)PtX_2 (1,5-COD = 1,5-cyclooctadiene; X = Cl, Br, I) or with $Rh_2(CO)_4(\mu\text{-}Cl)_2$ to yield Pt(dapm)X_2 (chelating dapm), Pt(dapm)$_2X_2$, or *trans*-Rh(dapm)$_2$(CO)Cl (monodentate dapm) are reported. In solution Pt(dapm)$_2X_2$ can ionize to form [Pt(damp)$_2$X]X or [Pt(dapm)$_2$]X_2. The degree of ionization depends on X and on the solvent. *trans*-Rh(dapm)$_2$(CO)Cl reacts with $Rh_2(CO)_4(\mu\text{-}Cl)_2$ to yield the face-to-face dimer $Rh_2(\mu\text{-dapm})_2(CO)_2Cl_2$ as a mixture of head-to-head (P trans to P) and head-to-tail (P trans to As) isomers. Pt(dapm)$_2Cl_2$ reacts with Pt(dibenzylideneacetone)$_2$ to form head-to-head and head-to-tail isomers of $Pt_2(\mu\text{-dapm})_2Cl_2$. These react with carbon monoxide to form $Pt_2(\mu\text{-dapm})_2(\mu\text{-CO})Cl_2$. $Rh_2(CO)_4(\mu\text{-}Cl)_2$ reacts with Pt(dapm)$_2Cl_2$ to form *trans*-Rh(CO)Cl(μ-dapm)$_2$-*cis*-$PtCl_2$. This orange complex crystallizes in the space group $P2_1/c$ (No. 14) with a = 18.760 (3) Å, b = 11.610 (3) Å, c = 22.954 (6) Å, β = 92.81 (2)°, and Z = 4 at 140 K. The structure was refined to a conventional R value of 0.038 by using 6415 significant reflections and 572 parameters. The structure consists of face-to-face planar Rh(CO)ClAs_2 and PtP_2Cl_2 units. The nonbonded Pt···Rh distance is 3.043 (1) Å.

Introduction

Small-bite, bidentate ligands with dissimilar donor centers can be used to prepare dinuclear transition-metal complexes from mononuclear units in a rational, controlled fashion.[1] Here we present information on one such ligand, (diphenylarsino)(diphenylphosphino)methane (dapm), and compare it to another, 2-(diphenylphosphino)pyridine (Ph_2Ppy), which has been used to create new binuclear complexes.[2–9] Toward soft metal ions both ligands are expected to preferentially bind through phosphorus with the result that an uncoordinated arsenic atom, in the case of dapm, or nitrogen atom, for Ph_2Ppy, will be present. The presence of an uncoordinated donor in such molecules offers several possibilities for reaction. In an intramolecular reaction, the free end of the bidentate ligand can displace another ligand to form a somewhat strained, four-membered chelate ring. In intermolecular reactions, the free donor has the ability to coordinate to a second metal ion and form a binuclear species.

As with Ph_2Ppy, we have chosen to develop mononuclear complexes bearing two small-bite bidentate ligands as precursors to building binuclear complexes. In the resulting binuclear complexes, isomers arise because of the relative orientations of the two bridging ligands. As seen in eq 1 three orientational



(1)

isomers, two head-to-head (HH) and one head-to-tail (HT), are possible for heterobinuclear complexes while only two (one HH and one HT) are possible for homobinuclear complexes (where M = M').[8,10] Further isomeric complexities arise when one considers the possibility that the bridging ligands may be either cis or trans to one another at each metal center. Frequently however these bridging ligands take up trans orientations at both metals.

With two Ph_2Ppy ligands bridging a binuclear complex, there are severe geometric constraints that so far have limited the metal–metal separations to the range 2.2–2.8 Å.[2–9,11,12] Thus, metal–metal bonds appear to accompany the formation of $M_2(Ph_2Ppy)_2$ units, and these in general do not undergo reactions in which the metal–metal bonds break and the metal–metal separation needs to expand. In this regard dapm should form more flexible complexes that are capable of existing with a wider range of metal–metal separations. Consequently, dapm should resemble the much studied analogue bis(diphenylphosphino)methane (dpm), which can allow a wide range (2.1–4.4 Å) of metal–metal separations in complexes containing the $M_2(dpm)_2$ unit.[1]

Results and Discussion

Mononuclear Complexes. The reaction of (1,5-COD)PtX_2 (1,5-COD = 1,5-cyclooctadiene) with dapm yields either Pt(dapm)X_2 or Pt(dapm)$_2X_2$, with the stoichiometry of the reaction controlling the identity of the product. Phosphorus NMR data for these and other new compounds are collected in Table I along with information on other related species for comparison.[8,14] The complexes Pt(dapm)X_2 have a chelate structure. Their ^{31}P NMR spectra show the upfield shifts, relative to free dapm (−20.2 ppm), which are characteristic of chelation of group 8–10[31] metals by phosphines that form four-membered rings. The ^{31}P NMR spectra of Pt(dapm)$_2I_2$ at −80 and +25 °C in dichloromethane are shown in Figure 1. At −80 °C three species, two with monodentate dapm and one with both a chelating and a monodentate dapm, are present. Peaks due to *trans*-Pt(dapm)$_2I_2$ are labeled A. These are identified as the trans isomer on the basis of ^1J(PtP), which should be lower for mutually trans phosphorus atoms than for the cis isomer with phosphorus atoms trans to iodide.[8] Peaks due to *cis*-Pt(dapm)$_2I_2$ are labeled B. The salt [Pt(dapm)$_2$I]I gives rise to peaks labeled C and C′. The peaks due to the monodentate dapm ligand are labeled C and are assigned to the monodentate ligand on the basis of their downfield chemical shift. The chelated dapm produces the resonances labeled C′. These are identified

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Table I. ^{31}P NMR Spectral Data from Dichloromethane Solutions of Platinum and Rhodium Complexes

compd	δ	J(M,P), Hz	compd	δ	J(M,P), Hz
$Pt(dapm)Cl_2$	−53.3	3129	$Pt(dpm)Cl_2$[c]	−64.3	3078
$Pt(dapm)Br_2$	−53.6	3083			
$Pt(dapm)I_2$	−57.3	2942			
cis-$Pt(dapm)_2Cl_2$	6.1	3875	*cis*-$Pt(Ph_2Ppy)_2Cl_2$[d]	11.6	3676
cis-$Pt(dapm)_2Br_2$	6.7	3644			
cis-$Pt(dapm)_2I_2$	7.1	3553	*cis*-$Pt(Ph_2Ppy)_2I_2$[d]	11.9	3453
trans-$Pt(dapm)_2I_2$	1.3	2380	*trans*-$Pt(Ph_2Ppy)_2I_2$[d]	9.8	2503
$[Pt(dapm)_2Br]Br$	10.0	2818	$[Pt(Ph_2Ppy)_2Cl]Cl$[d]	15.2	3704
	−39.8	3112		−50.03	3339
$[Pt(dapm)_2I]I$	9.7	2853	$[Pt(Ph_2Ppy)_2I]I$[d]	19.3	3637
	−45.8	3103		−61.2	3241
[*cis*-$Pt(dapm)_2][PF_6]_2$	−27.4	1992	*cis*-$Pt(PPh_3)_2Cl_2$[d]	14.7	3669
[*trans*-$Pt(dapm)_2][PF_6]_2$	−30.6	2481	*trans*-$Pt(PPh_3)_2Cl_2$[d]	20.6	2634
$Pt_2(\mu\text{-dapm})_2Cl_2$ (HH)	17.2	2977 (118)[a]			
$Pt_2(\mu\text{-dapm})_2Cl_2$ (HT)	8.1	3754 (106)[a]			
$Pt_2(\mu\text{-CO})Cl_2$	8.4	4777 (276)[a]			
$Pt_2(\mu\text{-dapm})_2(\mu\text{-CO})Cl_2$	10.9	3883 (265)[a]			
trans-$Rh(dapm)_2(CO)Cl$	25.1	124			
$Rh_2(\mu\text{-dapm})_2(CO)_2Cl_2$ (HH)[b]	23.3	127			
$Rh_2(\mu\text{-dapm})_2(CO)_2Cl_2$ (HT)[b]	28.1	149			
trans-$Rh(CO)Cl(\mu\text{-dapm})_2$-*cis*-$PtCl_2$	15.0	3826			

[a] ^2J(PtP). [b] Data from ref 10. [c] Data from ref 14. [d] Data from ref 8.

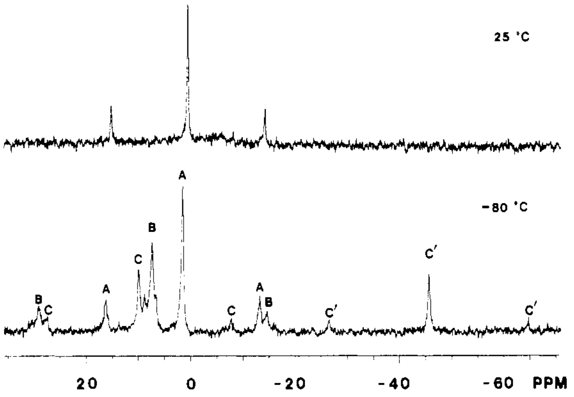
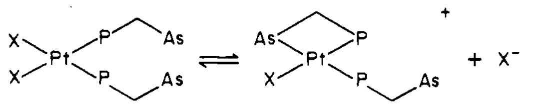


Figure 1. 81-MHz ^{31}P NMR spectrum of $Pt(dapm)_2I_2$ in dichloromethane solution at +25 and −80 °C. Resonance assignments are given in the text.

on the basis of their upfield chemical shift. On warming, the peaks labeled B, C, and C′ all broaden so that at 25 °C they are lost in the base line. However, the peaks labeled A remain unaffected by temperature. The broadening of some resonances is ascribed to rapid equilibration between the two species involved as shown in eq 2. This interconverts the salt and the cis isomer but leaves the trans isomer unaffected. The cis isomer is predicted to have the more labile Pt–I bond because of trans labilization from phosphorus. Hence, the iodide ligands are more readily displaced from this cis isomer than from the trans isomer. The pattern of J(PtP) values in the salt is consistent with this structure. The J(PtP) for the chelated dapm is larger in magnitude than is J(PtP) for the unidentate dapm because of the difference in the trans ligands. Because the two phosphorus atoms are cis, the coupling between them is expected to be small and in this case it is not observed. Very similar behavior has been reported for $Pt(Ph_2Ppy)_2I_2$ where *cis*-$Pt(Ph_2py)_2I_2$ and [*cis*-$Pt(Ph_2Ppy)_2I]I$ are in rapid equilibrium in the presence of the less easily ionized *trans*-$Pt(Ph_2Ppy)_2I_2$.[8] For $Pt(dapm)_2Br_2$ only two species, *cis*-$Pt(dapm)_2Br_2$ and [*cis*-$Pt(dapm)_2Br]Br$, are detected at −80 °C, and at 25 °C these are in rapid equilibrium. However, with $Pt(dapm)_2Cl_2$ only one species, *cis*-$Pt(dapm)_2Cl_2$, is present at all temperatures examined. For $Pt(dapm)_2X_2$ the degree of ionization of the cis isomer increases $Cl^- < Br^- < I^-$, probably as a result of solvation of the anion rather than metal–ligand bond strengths. For $Pt(Ph_2Ppy)_2X_2$ it was also noted that the degree of ionization of cis isomer increased from chloride to iodide.[8] For both $Pt(dapm)_2X_2$ and $Pt(Ph_2Ppy)_2X_2$[8] the trans isomer is present for X = I but nonexistent for X = Cl.



(2)

When $Pt(dapm)_2X_2$ is dissolved in methanol, however, both halide ions are ionized and the salt $[Pt(dapm)_2][PF_6]_2$ is isolated after the addition of ammonium hexafluorophosphate. The same product is obtained regardless of which halide is present in the starting material. As isolated, the salt is a mixture of about equal amounts of cis and trans isomers that have not been separated.

The reaction between $Rh_2(CO)_4(\mu\text{-}Cl)_2$ and 4 mol or more of dapm produces the yellow monomer *trans*-$Rh(dapm)_2(CO)Cl$. The yellow color, the magnitude of ^1J(RhP) (124 Hz), and the carbonyl stretching frequency (1980 cm^{-1}) are all similar to the case of other complexes containing the *trans*-$RhP_2Cl(CO)$ core.[15,16]

Preparation of Homobinuclear Complexes. Treatment of *trans*-$Rh(dapm)_2(CO)Cl$ with 0.5 mol of $Rh_2(CO)_4(\mu\text{-}Cl)_2$ yields orange $Rh_2(\mu\text{-dapm})_2(CO)_2Cl_2$. The ^{31}P NMR spectrum indicates that it is obtained as a 7:1 mixture of HT and HH isomers. The same material has been obtained previously from the reaction of equimolar amounts of $[Rh(CO)_2Cl_2]^-$ and dapm.[10,17] The formation of the face-to-face dimer, $Rh_2(\mu\text{-dapm})_2(CO)_2Cl_2$, by these methods is a good indication of the ability of dapm to span the relatively long metal–metal separation in a binuclear complex lacking a metal–metal bond. In contrast, the reaction of $Rh(Ph_2Ppy)_2(CO)Cl$ with $Rh_2(CO)_4(\mu\text{-}Cl)_2$ yields $Rh_2(\mu\text{-}Ph_2Ppy)_2(\mu\text{-CO})Cl_2$, which has a bridging carbonyl and a Rh–Rh bond distance of 2.612 (1) Å.[3]

The reaction between $Pt(dapm)_2Cl_2$ and $Pt(dba)_2$ (dba = dibenzylideneacetone), a source of zerovalent platinum, yields tan $Pt_2(\mu\text{-dapm})_2Cl_2$ in modest yield. The product occurs as a mixture of HH and HT isomers. The ^{31}P spectrum of the mixture is shown in the lower trace of Figure 2. Resonances due to the HT isomer are labeled T. T_a is the resonance of the isotopomer containing no ^{195}Pt (spin, $^1/_2$; natural abundance 33.8%) while resonances of the isotopomer with one ^{195}Pt are labeled T_b. The presence of PP coupling for this isotopomer is the evidence that allows us to identify it as the HT isomer. The resonances labeled H come from the HH isomer. The resonance H_a comes from the unlabeled isotopomer while the resonances labeled H_b come from the singly labeled isomer **1** with ^{195}Pt bound to phosphorus while those labeled $H_{b'}$ come from the other singly labeled isotopomer **2**. Since the phosphorus atoms in each isotopomer of the HH structure are identical and the lines labeled H_b and $H_{b'}$ result from separate

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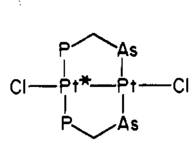

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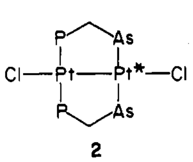
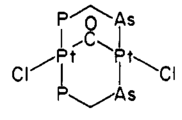


2

molecules, no PP coupling is observed in the spectrum of the HH isomers.

$Pt_2(\mu\text{-dapm})_2Cl_2$ reacts with carbon monoxide (1 atm for 5 min) to yield $Pt_2(\mu\text{-dapm})_2(\mu\text{-CO})Cl_2$ as a mixture of the HH and HT isomers **3** and **4**. The ^{31}P NMR spectrum of the product in



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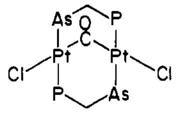

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dichloromethane is shown in the upper trace of Figure 2. Two species are present, their resonances are denoted by X and Y, and the subscript refers to the unlabeled isotopomer. Unfortunately, it is not possible to assign resonances X and Y to specific isomers. No PP coupling is present in either isomer. This is not unexpected since the carbon monoxide insertion breaks the Pt–Pt bond, which in turn disrupts the pathway of P–P coupling. The infrared spectrum of a dichloromethane solution of **3** and **4** shows a broad absorption at 1643 cm^{-1} which is due to the bridging carbonyl. For comparison $Pt_2(\mu\text{-dpm})_2(\mu\text{-CO})Cl_2$ has its carbonyl absorption at 1638 cm^{-1}.[18] For **3** and **4** the infrared spectrum is unable to resolve the separate absorptions of the two isomers present. This carbon monoxide insertion is a good indication of the flexibility of the dapm ligand since the reaction must accommodate a significant increase (>0.5 Å) in the distance between the two platinum atoms.

During the insertion some isomerization between the HH and HT structures occurs. The ratio of isomers in the lower trace of Figure 1 is 1:1 while after carbon monoxide insertion the ratio is 1:1.6. Other cases of HH/HT isomerization have been described.[6,8]

Heterobinuclear Complex Formation. Several routes appeared possible for the formation of a rhodium/platinum complex. However, many led to transfer of dapm from one metal to another. In particular the reaction between $Rh(dapm)_2(CO)Cl$ and platinum(II) complexes produces ligand exchange rather than binuclear complexes. The addition of (1,5-COD)$PtCl_2$ to $Rh(dapm)_2(CO)Cl$ in dichloromethane has been monitored by ^{31}P NMR spectroscopy. The reaction proceeds clearly according to eq 3. The dimer, $Rh_2(\mu\text{-dapm})_2(CO)_2Cl_2$, is formed as a mixture

$$2(1,5\text{-COD})PtCl_2 + 2Rh(dapm)_2(CO)Cl \rightarrow 2Pt(dapm)Cl_2 + 2(1,5\text{-COD}) + Rh_2(\mu\text{-dapm})_2(CO)_2Cl_2 \quad (3)$$

of HH and HT isomers. Similarly $Pt(dapm)Cl_2$ and $Rh(dapm)_2(CO)Cl$ react to transfer a dapm ligand according to eq 4. In both reactions the ligand transfer proceeds from rhodium

$$2Pt(dapm)Cl_2 + 2Rh(dapm)_2(CO)Cl \rightarrow 2Pt(dapm)_2Cl_2 + Rh_2(\mu\text{-dapm})_2(CO)_2Cl_2 \quad (4)$$

to platinum probably as a result of the greater metal–ligand bond strength associated with the third-transition-series metal. While binuclear complexes are likely to be involved as intermediates in these ligand-transfer reactions, they have not been detected during the reaction.

A binuclear platinum/rhodium complex is formed however in the reaction between $Pt(dapm)_2Cl_2$ and $Rh_2(CO)_4(\mu\text{-Cl})_2$. The product, *trans*-$Rh(CO)Cl(\mu\text{-dapm})_2$-*cis*-$PtCl_2$, is obtained as orange crystals in 70% yield. The infrared spectrum of the product shows the presence of a terminal carbonyl group (ν(CO) = 1986 cm^{-1}) in the region where Rh(I) carbonyl absorptions generally occur. The ^{31}P NMR spectrum shows satellites indicative of the presence of phosphorus–platinum bonds. In order to fully understand the geometry of this molecular, an X-ray diffraction study was undertaken.

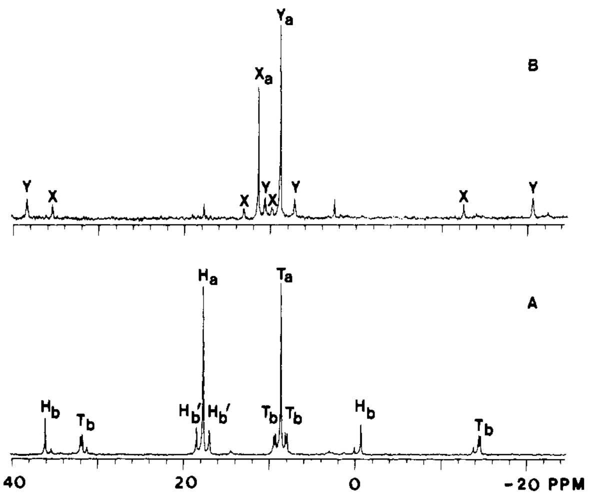

Figure 2. 81-MHz ^{31}P NMR spectrum of dichloromethane solutions: (A) a mixture of HH and HT isomers of $Pt_2(\mu\text{-dapm})_2Cl_2$; (B) the same mixture as in (A) after exposure to 1 atm of carbon monoxide.

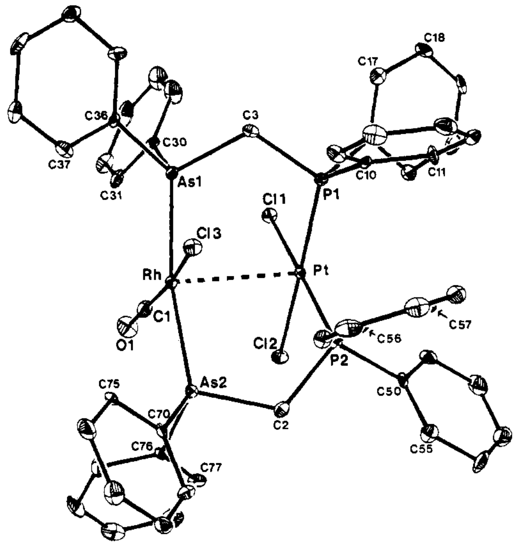

Figure 3. Perspective drawing of *trans*-$Rh(CO)Cl(\mu\text{-}Ph_2AsCH_2PPh_2)_2$-*cis*-$PtCl_2$.

X-ray Crystal Structure of *trans*-$Rh(CO)Cl(\mu\text{-dapm})_2$-*cis*-$PtCl_2$. The compound crystallizes with one molecule of the complex and one dichloromethane molecule in the asymmetric unit. There are no unusual intermolecular contacts. A perspective drawing of the complex molecule with the atomic labeling scheme is shown in Figure 3. Final atomic positional and thermal parameters are given in Table II. Table III contains selected interatomic distances, and Table IV contains relevant interatomic angles. There is no crystallographic symmetry imposed on the complex. However, it has approximate C_s symmetry, with an effective mirror plan passing through the Rh, Pt, Cl(3), C(1), and O(1) atoms.

The complex contains two planar, d^8 metal centers (one a *trans*-$Rh(CO)ClAs_2$ unit and the other a *cis*-$PtCl_2P_2$ unit) that are held together by the bridging dapm ligands. In electron-counting terms there is no need for a Rh–Pt bond. Each metal center has a normal 16-electron count for planar d^8 complexes. The Rh···Pt separation, 3.043 (1) Å, is longer than the value of 2.6 Å expected for a Rh–Pt single bond.[13] Nevertheless, the two metal centers are close enough to interact through their out-of-plane orbitals in the fashion shown by many planar d^8 complexes.[15]

The arrangement of the bridging ligands is unusual. Generally, bridging ligands of this type occupy trans coordination sites at both metals. In the present case, however, the bridging ligand takes up trans sites at rhodium but cis sites at platinum. Only

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Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for *trans*-Rh(CO)Cl(μ-dapm)$_2$-*cis*-PtCl$_2$

atom	*x*	*y*	*z*	*U*
Pt	1611 (1)	1327 (1)	2243 (1)	9 (1)*
Rh	2749 (1)	3090 (1)	1975 (1)	10 (1)*
As(1)	1885 (1)	3627 (1)	1207 (1)	11 (1)*
As(2)	3518 (1)	2194 (1)	2708 (1)	11 (1)*
P(1)	1276 (1)	988 (2)	1310 (1)	10 (1)*
P(2)	2456 (1)	14 (2)	2460 (1)	11 (1)*
Cl(1)	688 (1)	2687 (2)	2147 (1)	15 (1)*
Cl(2)	1757 (1)	1830 (2)	3236 (1)	16 (1)*
Cl(3)	3261 (1)	2006 (2)	1230 (1)	16 (1)*
C(1)	2465 (4)	4073 (7)	2535 (3)	18 (3)*
O(1)	2323 (3)	4705 (5)	2897 (3)	28 (2)*
C(2)	3196 (4)	628 (6)	2902 (3)	14 (2)*
C(3)	1386 (4)	2276 (6)	847 (3)	14 (2)*
C(10)	1607 (4)	−210 (6)	879 (3)	10 (2)*
C(11)	1246 (4)	−1264 (7)	864 (3)	15 (2)*
C(12)	1453 (4)	−2158 (7)	518 (3)	18 (3)*
C(13)	2035 (4)	−2031 (7)	185 (4)	24 (3)*
C(14)	2417 (4)	−1009 (7)	193 (4)	22 (3)*
C(15)	2212 (4)	−101 (7)	542 (3)	19 (3)*
C(16)	324 (4)	627 (6)	1240 (3)	10 (2)*
C(17)	−43 (4)	641 (7)	698 (3)	16 (3)*
C(18)	−700 (4)	116 (7)	624 (4)	18 (3)*
C(19)	−997 (4)	−454 (7)	1074 (4)	17 (3)*
C(20)	−651 (4)	−449 (7)	1621 (4)	20 (3)*
C(21)	5 (4)	84 (7)	1707 (4)	17 (3)*
C(30)	1133 (4)	4753 (7)	1296 (3)	14 (2)*
C(31)	1243 (4)	5588 (7)	1733 (4)	20 (3)*
C(32)	720 (4)	6398 (7)	1843 (4)	23 (3)*
C(33)	83 (4)	6386 (8)	1512 (4)	30 (3)*
C(34)	−18 (4)	5584 (8)	1077 (4)	32 (3)*
C(35)	490 (4)	4757 (8)	975 (4)	28 (3)*
C(36)	2311 (4)	4262 (6)	518 (3)	11 (2)*
C(37)	3008 (4)	4666 (7)	566 (4)	18 (3)*
C(38)	3313 (4)	5208 (7)	106 (3)	18 (3)*
C(39)	2929 (4)	5312 (7)	−413 (3)	18 (3)*
C(40)	2225 (4)	4919 (7)	−482 (4)	18 (3)*
C(41)	1928 (4)	4389 (7)	−12 (3)	19 (3)*
C(50)	2117 (4)	−1049 (6)	2961 (3)	13 (2)*
C(51)	1405 (4)	−1104 (7)	3072 (3)	17 (3)*
C(52)	1160 (4)	−1953 (8)	3446 (4)	30 (3)*
C(53)	1629 (5)	−2718 (7)	3701 (4)	27 (3)*
C(54)	2337 (5)	−2689 (7)	3586 (4)	30 (3)*
C(55)	2588 (4)	−1851 (7)	3209 (3)	19 (3)*
C(56)	2907 (4)	−903 (6)	1946 (3)	12 (2)*
C(57)	2568 (4)	−1924 (7)	1772 (3)	17 (3)*
C(58)	2908 (4)	−2672 (7)	1395 (3)	18 (3)*
C(59)	3577 (4)	−2414 (7)	1209 (3)	21 (3)*
C(60)	3892 (4)	−1396 (8)	1374 (3)	23 (3)*
C(61)	3567 (4)	−635 (7)	1749 (3)	16 (3)*
C(70)	4507 (4)	1891 (6)	2542 (3)	12 (2)*
C(71)	4921 (4)	1142 (7)	2876 (3)	19 (3)*
C(72)	5626 (4)	931 (7)	2753 (4)	19 (3)*
C(73)	5910 (4)	1471 (7)	2295 (4)	22 (3)*
C(74)	5523 (4)	2248 (8)	1965 (4)	27 (3)*
C(75)	4810 (4)	2472 (7)	2085 (4)	17 (3)*
C(76)	3657 (4)	2921 (7)	3467 (3)	12 (2)*
C(77)	3320 (4)	2569 (7)	3970 (3)	18 (3)*
C(78)	3428 (5)	3159 (8)	4485 (4)	28 (3)*
C(79)	3869 (4)	4115 (8)	4514 (4)	29 (3)*
C(80)	4198 (4)	4485 (8)	4021 (4)	27 (3)*
C(81)	4094 (4)	3895 (7)	3503 (4)	21 (3)*
C(90)	5277 (4)	8173 (8)	4603 (4)	28 (3)*
Cl(91)	4969 (1)	9425 (2)	4211 (1)	30 (1)*
Cl(92)	4541 (1)	7311 (2)	4784 (1)	40 (1)*

* Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Selected Interatomic Distances (Å) for *trans*-Rh(CO)Cl(μ-dapm)$_2$-*cis*-PtCl$_2$

	At Rhodium		
Rh···Pt	3.043 (1)	Rh–C(1)	1.818 (8)
Rh–As(1)	2.417 (1)	Rh–As(2)	2.400 (1)
Rh–Cl(3)	2.363		
	At Platinum		
Pt···Rh	3.043 (1)		
Pt–P(1)	2.237 (2)	Pt–P(2)	2.238 (2)
Pt–Cl(1)	2.345 (2)	Pt–Cl(2)	2.356 (2)
	In Ligands		
As(1)–C(3)	1.986 (7)	As(1)–C(30)	1.942 (8)
As(1)–C(36)	1.952 (7)	As(2)–C(2)	1.973 (8)
As(2)–C(70)	1.945 (7)	As(2)–C(79)	1.942 (8)
P(1)–C(3)	1.851 (8)	P(1)–C(10)	1.833 (7)
P(1)–C(16)	1.833 (7)	P(2)–C(2)	1.825 (7)
P(2)–C(50)	1.822 (8)	P(2)–C(56)	1.828 (8)
C(1)–O(1)	1.150 (10)		
	Nonbonded Contacts		
P(1)···As(1)	3.283 (4)	P(2)···As(2)	3.254 (4)
Pt···Cl(3)	4.038 (2)	Rh···Cl(1)	3.934 (2)
Rh···Cl(2)	3.809 (2)	Pt···C(1)	3.616 (8)

Table IV. Selected Interatomic Angles (deg) for *trans*-Rh(CO)Cl(μ-dapm)$_2$-*cis*-PtCl$_2$

	At Platinum		
P(1)–Pt–P(2)	104.9 (1)	Pt(1)–Pt–Cl(1)	81.8 (1)
P(2)–Pt–Cl(1)	172.3 (1)	P(1)–Pt–Cl(2)	169.7 (1)
P(2)–Pt–Cl(2)	84.6 (1)	Cl(1)–Pt–Cl(2)	88.5 (1)
	At Rhodium		
As(1)–Rh–As(2)	169.0 (1)	As(1)–Rh–Cl(3)	83.8 (1)
As(2)–Rh–Cl(3)	91.4 (1)	As(1)–Rh–C(1)	98.3 (2)
As(2)–Rh–C(1)	87.9 (2)	Cl(3)–Rh–C(1)	171.5 (2)
	In Ligands		
Rh–As(1)–C(3)	112.7 (2)	Rh–As(2)–C(2)	112.2 (2)
Rh–As(1)–C(30)	124.2 (2)	Rh–As(2)–C(70)	119.1 (2)
Rh–As(1)–C(36)	113.7 (2)	Rh–As(2)–C(76)	119.4 (2)
Pt–P(2)–C(3)	111.9 (2)	Pt–P(2)–C(2)	111.7 (3)
Pt–P(1)–C(10)	124.3 (2)	Pt–P(2)–C(50)	109.7 (3)
Pt–P(1)–C(16)	110.5 (2)	Pt–P(2)–C(56)	126.7 (2)
As(1)–C(3)–P(1)	117.6 (4)	As(2)–C(2)–P(2)	117.9 (4)
Rh–C(1)–O(1)	176.3 (7)		

a relatively few cases of this trans/cis arrangement of bridging ligands have been found. The most relevant examples are PtMo(μ-Ph$_2$Ppy)$_2$(μ-CO)(CO)$_2$Cl[9] and Rh$_2$(μ-dpm)$_2$(CO)(*o*-O$_2$C$_6$Cl$_4$).[19] In order to accommodate this bridging geometry it appears that two types of distortions about the metals develop. The angle at the metal atom with trans bridging ligands may be bent toward the other metal so that the trans angle is less than 180°.[9] At the metal atom bearing cis bridging ligands the angle between these donors may open up wider than the anticipated 90°.[19] In the rhodium/platinum complex both of these distortions occur. The As–Rh–As angle is compressed to 169.0 (1)° while the P–Pt–P angle has opened up to 104.9 (1)°. The geometry of the bridging ligands appears normal. However, the As–C–P angles, 117.9 (4) and 117.6 (4)°, do fall at the wide end of the values found for the P–C–P or As–C–As angles for bridging dpm or bis(diphenylarsino)methane ligands.[1,20]

Other aspects of the coordination of each metal ion are unexceptional. Many platinum complexes with *cis*-PtP$_2$Cl$_2$ environments are known, and the Pt–Cl and Pt–P bond lengths are normal.[21-23] Likewise, the geometric details of the rhodium environment are consistent with prior characterization of compounds containing the *trans*-Rh(CO)ClAs$_2$ unit.[24,25] The Rh–C, Rh–Cl, and Rh–As distances fall within known values.

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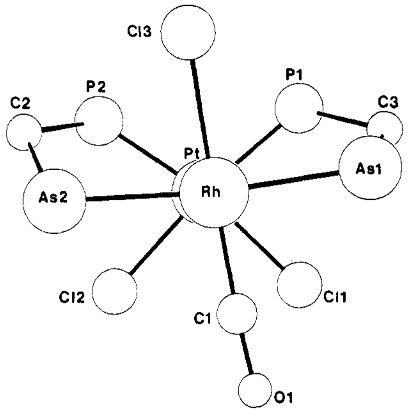

Figure 4. View of the inner coordination of *trans*-Rh(CO)Cl(μ-$Ph_2AsCH_2PPh_2)_2$-*cis*-$PtCl_2$ down the Rh–Pt axis.

The two coordination planes are arranged in almost perfectly staggered orientation. This is shown in Figure 4, which shows a view of the inner coordination sphere looking almost parallel to the Pt···Rh line. The carbonyl group lies over the $PtCl_2$ portion of the molecule. Interestingly, although trans carbonyl and chloro ligands can be disordered,[25,26] there is no evidence for disorder in this structure. Consequently, the molecule exists as this one isomer. There is no evidence, particularly from ^{31}P NMR, for the presence of any other isomer in solution either. The observed orientation is probably favored because it results in opposite alignment of the local dipoles that arise from the polarization present in the M–Cl bonds.

Experimental Section

Synthesis of Compounds. (Diphenylarsino)(diphenylphosphino)methane,[28] (1,5-COD)PtX_2,[29] and $Pt(dba)_2$[30] were prepared by standard routes.

Pt(dapm)Cl_2. A solution of 89.6 mg (0.209 mmol) of dapm in 5 mL of dichloromethane was added to a solution of 77.8 mg (0.248 mmol) of (1,5-COD)$PtCl_2$ in 10 mL of dichloromethane. The mixture was stirred for 1 h and then filtered. Ethyl ether (15 mL) was added to the filtrate slowly. The white crystalline product was collected by filtration, washed with ethyl ether, and vacuum dried; yield 60%. Anal. Calcd for $C_{25}H_{22}AsCl_2PPt$: C, 43.24; H, 3.17. Found: C, 42.45; H, 3.27.

Pt(dapm)Br_2. This yellow crystalline complex was prepared from (1,5-COD)$PtBr_2$ by the procedure described for Pt(dapm)Cl_2; yield 64%. Anal. Calcd for $C_{25}H_{22}AsBr_2PPt$: C, 38.33; H, 2.83; Br, 20.40. Found: C, 38.45; H, 2.84; Br, 20.77.

Pt(dapm)I_2. This bright yellow solid was obtained from (1,5-COD)PtI_2 by the method described for Pt(dapm)Cl_2; yield 70%. Anal. Calcd for $C_{25}H_{22}AsI_2PPt$: C, 34.23; H, 2.53. Found: C, 34.68; H, 2.68.

Pt(damp)$_2Cl_2$. A solution of 200 mg (0.637 mmol) of (1,5-COD)$PtCl_2$ in 20 mL of dichloromethane was added dropwise to a solution of 545 mg (1.27 mmol) of dapm in 10 mL of dichloromethane. After the solution was stirred for 5 min, its volume was reduced to 10 mL through the use of a rotary evaporator. The solution was filtered, and ether was added slowly to the filtrate. The ivory crystals that formed were collected by filtration, washed with ethyl ether, and vacuum dried; yield 71%. Anal. Calcd for $C_{50}H_{44}As_2Cl_2P_2Pt$: C, 53.49; H, 3.95; Cl, 6.32. Found: C, 54.11; H, 3.90; Cl, 6.28.

Pt(dapm)$_2Br_2$. This yellow crystalline material was obtained from (1,5-COD)$PtBr_2$ by the method described for Pt(dapm)$_2Cl_2$; yield 67%. Anal. Calcd for $C_{50}H_{44}As_2Br_2P_2Pt$: C, 49.56; H, 3.66; Br, 13.19. Found: C, 49.28; H, 3.67; Br, 13.58.

Pt(dapm)$_2I_2$. This yellow complex was prepared from (1,5-COD)PtI_2 by the route used to make Pt(dapm)$_2Cl_2$; yield 63%. Anal. Calcd for $C_{50}H_{44}As_2I_2P_2Pt$: C, 46.00; H, 3.40; I, 19.44. Found: C, 46.37; H, 3.51; I, 19.34.

Table V. Crystal Data for *trans*-Rh(CO)Cl(μ-dapm)$_2$-*cis*-$PtCl_2\cdot CH_2Cl_2$

formula	$C_{52}H_{46}As_2Cl_5OPPtRh$
fw (dimer + solvent)	1374
diffractometer	Syntex $P2_1$
cryst dimens, mm	0.45 × 0.50 × 0.50
color	orange
unit cells dimens (140 K)[a]	
a, Å	18.760 (3)
b, Å	11.610 (3)
c, Å	22.954 (6)
β, deg	92.81 (2)
V, Å^3	4993.5
space gp	$P2_1/c$
obsd density (20 °C), mg m^{-3}	1.75
calcd density (140 K), mg m^{-3}	1.83
Z	4
radiatn; λ, Å (graphite monochromator)	Mo; 0.71069
μ(Mo Kα), cm^{-1}	49.4
range of transmissn factors	0.187–0.204
scan type ($2\theta_{max}$, deg)	ω, 50
no. of reflcns measd	9281
no. of unique data ($F > 6\sigma(F)$)	6415
R	0.0382
R_w	0.0354
no. of parameters	572

[a] Routine data collection at 140 K in our laboratory reduces thermal motion and allows for speed up of data collection.

[Pt(dapm)$_2$][PF_6]$_2$. A 5-mL portion of a saturated methanol solution of ammonium hexafluorophosphate was added to a solution of 50 mg of Pt(dapm)$_2Cl_2$ in 40 mL of methanol. After stirring for 5 min, the volume of the solution was reduced to 20 mL by rotary evaporation. The solution was filtered, and the filtrate was stored at −5 °C for 12 h. The white crystalline product was collected by filtration, washed with cold methanol, and vacuum dried: yield 83%. Anal. Calcd for $C_{50}H_{44}As_2F_{12}P_4Pt$: C, 44.76; H, 3.31. Found: C, 44.67; H, 3.59.

Rh(dapm)$_2$(CO)Cl. A solution of 22 mg (0.057 mmol) of rhodium carbonyl chloride dimer in 5 mL of ethyl ether was added to a stirred solution of 101 mg (0.233 mmol) of dapm in 1 mL of dichloromethane. Ethyl ether was added dropwise to the yellow solution until precipitation of the yellow plates of the product was complete. These were collected by filtration, washed with ethyl ether, and vacuum dried; yield 72%. Anal. Calcd for $C_{51}H_{44}As_2ClOPRh$: C, 59.87; H, 4.34; Cl, 3.30. Found: C, 59.86; H, 4.35; Cl, 3.47.

***trans*-Rh(CO)Cl(μ-dapm)$_2$-*cis*-$PtCl_2$.** A solution of 53.4 mg (0.137 mmol) of rhodium dicarbonyl chloride dimer in 3 mL of dichloromethane was added to a solution of 308 mg (0.274 mmol) of Pt(dapm)$_2Cl_2$ in a minimum volume of dichloromethane at −5 °C. After stirring the resulting mixture for 10 min, the volume was reduced by two-thirds by use of a rotary evaporator at room temperature. The solution was filtered, and the filtrate was cooled in a dry ice/acetone bath. Methanol was slowly added to the solution to precipitate the orange product. The solid was removed by filtration, washed with methanol and diethyl ether, and vacuum dried at room temperature; yield 70%. Anal. Calcd for $C_{51}H_{44}As_2Cl_3OP_3PtRh$: C, 47.52; H, 3.44; Cl, 8.25. Found: C, 47.72; H, 3.75; Cl, 8.48.

Pt_2(μ-dapm)$_2Cl_2\cdot 0.5CH_2Cl_2$. A solution of 231 mg (0.348 mmol) of $Pt(dba)_2$ in 40 mL of dioxygen-free dichloromethane was added dropwise under a dinitrogen atmosphere to a solution of 300 mg (0.267 mmol) of Pt(dapm)$_2Cl_2$ in 20 mL of dioxygen-free dichloromethane. The mixture was heated under reflux for 24 h. After cooling to room temperature, the brown solution was filtered to remove a black solid. The volume of the filtrate was reduced to two-thirds of the original volume by evaporation. Ethyl ether was added to this solution until precipitation of the brown product was complete. This solid was removed by filtration and purified by recrystallization from dichloromethane/diethyl ether. The yield of the tan, crystalline product was 33%. Anal. Calcd for $C_{50}H_{44}As_2Cl_2P_2Pt_2\cdot 0.5CH_2Cl_2$: C, 44.59; H, 3.33; Cl, 7.82. Found: C, 44.58; H, 3.47; Cl, 8.02.

X-ray Crystallography. Orange crystals of *trans*-Rh(CO)Cl(μ-dapm)$_2$-*cis*-$PtCl_2$ were obtained by diffusion of ethyl ether into a dichloromethane solution of the complex. Crystal data and data collection procedure and refinement data are summarized in Table V. The data were corrected for Lorentz, polarization, and absorption effects. No decay was noted in the two check reflections that were examined at intervals after collecting 198 reflections. Computer programs used were

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(31) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

from the SHELXTL version 4 package (Nicolet Instruments, Madison, WI). The lattice was found to be monoclinic *P* by standard procedures using the $P2_1$ software. Quick scan of the reflections for space group determination gave the conditions $0k0$ ($k = 2n$) and $h0l$ ($l = 2n$), which are consistent with the space group $P2_1/c$ (No. 14). The positions of the platinum and rhodium atoms were determined from a Patterson map. The remaining non-hydrogen atoms were found on successive Fourier maps. Final refinement included all hydrogen atoms of the phenyl rings in calculated positions and fixed by a riding model in which the C–H distance is fixed at 0.96 Å and the *U* value for hydrogen is tied to 1.2 times the *U* value for the carbon atom to which it is bonded. Final refinement, which used anisotropic thermal motion for all atoms except hydrogen, resulted in a conventional *R* value of 0.0382. A final difference map was devoid of chemically significant features.

Physical Measurements. The ^{31}P NMR spectra were recorded at 81 MHz on a Nicolet NT-200 Fourier transform spectrometer. The ^{31}P NMR spectra were proton decoupled and referenced to external 85% phosphoric acid. The high-frequency-positive convention recommended by IUPAC was used to report chemical shifts. Infrared spectra were recorded from mineral oil mulls or dichloromethane solutions on a Perkin-Elmer 180 spectrometer.

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Registry No. Pt(dapm)Cl_2, 88867-61-2; Pt(dapm)Br_2, 96211-61-9; Pt(dapm)I_2, 96211-62-0; *cis*-Pt(dapm)$_2Cl_2$, 89144-43-4; *cis*-Pt(dapm)$_2Br_2$, 96211-63-1; *cis*-Pt(dapm)$_2I_2$, 96227-23-5; *trans*-Pt(dapm)$_2I_2$, 96290-72-1; [Pt(dapm)$_2$Br]Br, 96227-24-6; [Pt(dapm)$_2$I]I, 96227-25-7; [*cis*-Pt(dapm)$_2$][PF_6]$_2$, 96211-65-3; [*trans*-Pt(dapm)$_2$][PF_6]$_2$, 96290-34-5; Pt_2(μ-dapm)$_2Cl_2$ (HH), 89153-36-6; Pt_2(μ-dapm)$_2Cl_2$ (HT), 89153-37-7; Pt_2(μ-dapm)$_2$(μ-CO)Cl_2 (HH), 96211-66-4; Pt_2(μ-dapm)$_2$(μ-CO)Cl_2 (HT), 96211-67-5; *trans*-Rh(dapm)$_2$(CO)Cl, 96211-68-6; Rh_2(μ-dapm)$_2$(CO)$_2Cl_2$ (HH), 89144-46-7; Rh_2(μ-dapm)$_2$(CO)$_2Cl_2$ (HT), 83153-27-9; *trans*-Rh(CO)Cl(μ-dapm)$_2$-*cis*-PtCl_2, 88867-59-8; (1,5-COD)PtCl_2, 12080-32-9; (1,5-COD)PtBr_2, 12145-48-1; (1,5-COD)PtI_2, 12266-72-7; Rh_2(CO)$_4$(μ-Cl)$_2$, 14523-22-9; Pt_2(dba)$_2$, 35915-79-8.

Supplementary Material Available: Tables of structure factors, bond lengths, bond angles, anisotropic temperature factors, and hydrogen atom positions (42 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, Victoria University of Wellington, Wellington, New Zealand,
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Structural and Magnetic Studies of Bis(μ-olato) Dinuclear Compounds of Copper(II) with Bicyclic Amine Alcohols

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Reaction of partially hydrolyzed quaternary hydroxyalkyl "hexaminium" salts with copper(II) results in the formation of compounds of bicyclic tetraamine alcohols coordinated as tridentate diamine olato ligands. X-ray structural studies for four compounds with the ligands (1,3,5,7-tetraazabicyclo[3.3.1]nonan-3-yl)ethanolato (eta), the 3-propanolato analogue (pta), and the 7-(methoxymethyl) derivative of the first compound (etam) are reported: [{Cu(eta)(ClO_4)}$_2$]·2CH_3OH, triclinic, $P\bar{1}$, $a = 8.970$ (4) Å, $b = 9.974$ (3) Å, $c = 10.123$ (5) Å, $\alpha = 101.09$ (3)°, $\beta = 128.57$ (3)°, $\gamma = 93.93$ (3)°, $Z = 2$ for $C_8H_{19}ClCuN_4O_6$, $R = 0.053$ for 2153 reflections; [{Cu(eta)(dmso)}$_2$](ClO_4)$_2$, monoclinic, $P2_1/c$, $a = 9.175$ (2) Å, $b = 13.511$ (3) Å, $c = 12.934$ (2) Å, $\beta = 99.86$ (1)°, $Z = 4$ for $C_9H_{21}ClCuN_4O_6S$, $R = 0.046$ for 1642 reflections; [{Cu(etam)(dmso)}$_2$](ClO_4)$_2$, monoclinic, $P2_1/n$, $a = 12.431$ (2) Å, $b = 14.251$ (3) Å, $c = 11.132$ (2) Å, $\beta = 108.01$ (2)° Å, $Z = 4$ for $C_{11}H_{25}ClCuN_4O_7S$, $R = 0.033$ for 2148 reflections; [{Cu(pta)(ClO_4)}$_2$], triclinic, $P\bar{1}$, $a = 9.074$ (1) Å, $b = 9.971$ (1) Å, $c = 7.708$ (1) Å, $\alpha = 82.39$ (1)°, $\beta = 104.77$ (1)°, $\gamma = 107.02$ (1)°, $Z = 2$ for $C_8H_{17}ClCuN_4O_5$, $R = 0.025$ for 2135 reflections. These compounds have centrosymmetric dinuclear, bis(μ-olato)-bridged structures, with nitrogen atoms 3 and 7 and the deprotonated alcohol oxygen atoms approximately coplanar with the Cu(II) and with an oxygen atom of a perchlorate ion or of dimethyl sulfoxide weakly coordinated axially. Magnetic susceptibilities, 95–330 K, indicate no appreciable spin coupling for the eta compounds or for [{Cu(etam)(dmso)}$_2$] and appreciable spin coupling ($J = -72$ cm^{-1}) for [{Cu(etam)(ClO_4)}$_2$], while the pta compounds are highly spin coupled (J = ca. -400 cm^{-1}).

Introduction

Preparations of quaternary "hexaminium" salts (salts of 1-alkyl-3,5,7-triaza-1-azoniatricyclo[3.3.1.1^{3,7}]decane cations) by reaction of the substituted ammonium salt, formaldehyde, and ammonia have been described.[2] Hydroxyalkyl perchlorate salts of this type are formed by 2-aminoethanol,[2] [etad]ClO_4, and the analogue derived from 3-aminopropan-1-ol, [ptad]ClO_4 is now reported (Scheme I) (etad = 1-(2-hydroxyethyl)-3,5,7-triaza-1-azoniatricyclo[3.3.1.1^{3,7}]decane; ptad = 1-(3-hydroxypropyl)-3,5,7-triaza-1-azoniatricyclo[3.3.1.1^{3,7}]decane).

The partially hydrolyzed compounds coordinate to copper(II) as tridentate diamine alcohols. Compounds of copper(II) with a variety of amine alcohols have been described,[3] including a number of diamine alcohols, which form compounds structurally similar to those reported here. These commonly have dinuclear structures, with the deprotonated alcohol (olato) oxygen atoms acting as bridging groups and with other donor atoms completing square-planar coordination about the copper ions. One, or less commonly two, additional donor atoms are often weakly coordinated axially to give tetragonal coordination environments. These additional donor atoms are often the bridging oxygens of other dinuclear groups to form tetranuclear (cubanelike) clusters, or higher order polymers. Aggregation of the dinuclear units is uncommon for bulkier amine alcohol ligands, including in general those with 3-(amino olato) bridging groups. Spin coupling between the copper(II) ions, mediated by the bridging oxygen atoms, is usually present; antiferromagnetic coupling within the basic dinuclear unit and weaker antiferromagnetic, or occasionally ferromagnetic, coupling between the dinuclear units may occur. Many attempts have been made to establish correlations between magnetic coupling and structural parameters, but these are generally valid only within groups of compounds that are structurally closely related.

In this paper the preparations and magnetic and spectroscopic properties of some copper(II) compounds with tridentate bicyclic ligands formed by partial hydrolysis of the 1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane (hexamine) cage of etad and ptad are reported. The structures of four of the compounds, with three different amine alcohol ligands, have been determined by X-ray diffraction. Magnetic susceptibilities (95–330 K) have been determined, and the relationship between the spin coupling pa-

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(1) (a) Victoria University of Wellington. (b) Simon Fraser University.
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(3) Melnik, M. *Coord. Chem. Rev.* **1982**, *42*, 259.

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