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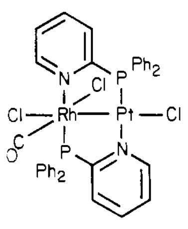
Factors Affecting Metal–Metal Interactions in Binuclear Complexes. Synthesis and Structure of the Face-to-Face Complex *trans*-Rh(CO)Cl(μ-$Ph_2AsCH_2PPh_2$)$_2$-*cis*-$PtCl_2$

Sir:

The formation of heterobinuclear transition-metal complexes and the nature of the metal–metal interactions present in these have received considerable attention in recent years.[1] Bifunctional ligands like 2-(diphenylphosphino)pyridine, Ph_2Ppy,[2] and (diphenylarsino)(diphenylphosphino)methane, dapm,[3] are particularly useful in constructing heterobinuclear species. For Ph_2Ppy the formation of such molecules has generally been accompanied by the oxidative addition of a metal–halogen bond to a second metal center as shown in reaction 1.[2e] It

cis-$(Ph_2Ppy)_2PtCl_2$ + $\frac{1}{2}Rh_2(\mu\text{-}Cl)_2(CO)_4$ ⟶



+ CO (1)

1

has been suggested[2] that the short bite of the Ph_2Ppy ligand favors the formation of the metal–metal bond in these reactions and that it cannot accommodate the larger nonbonded metal–metal separation that would be expected for a hypothetical structure with a face-to-face arrangement of planar Pt(II) and Rh(I) centers.

However, dapm should be more flexible and resemble bis(diphenylphosphino)methane (dpm), which has been demonstrated to be extremely versatile in the range of metal–metal separations (from 2.2 to 4.4 Å) that it can span.[4] Consequently it appeared that the reaction analogous to reaction **1** using dapm in place of Ph_2Ppy might yield a face-to-face species without causing oxidative addition.

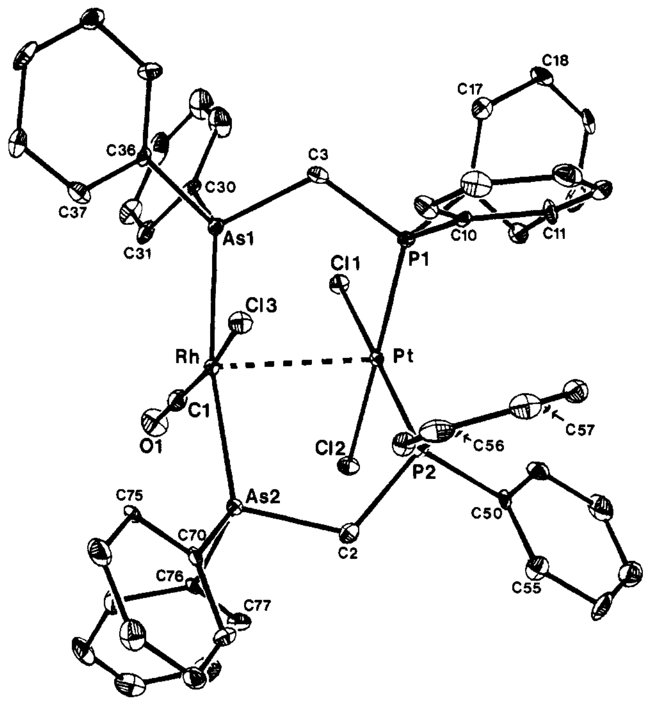


Figure 1. Perspective drawing showing the structure of *trans*-Rh(CO)Cl(μ-$Ph_2AsCH_2PPh_2$)$_2$-*cis*-$PtCl_2$. Interatomic distances and angles: Pt···Rh = 3.043 (1), Pt–P(1) = 2.237 (2), Pt–P(2) = 2.238(2), Pt–Cl(1) = 2.345 (2), Pt–Cl(2) = 2.356 (2), Rh–As(1) = 2.417 (1), Rh–As(2) = 2.400 (1), Rh–Cl(3) = 2.363 (2), Rh–C(1) = 1.818 (8) Å; P(1)–Pt–P(2) = 104.9 (1), P(1)–Pt–Cl(1) = 81.8 (1), P(2)–Pt–Cl(2) = 84.6 (1), Cl(1)–Pt–Cl(2) = 88.5 (1), As(1)–Rh–Cl(3) = 83.8(1), As(1)–Rh–C(1) = 98.3 (2), As(2)–Rh–C(1) = 87.9, As(2)–Rh–Cl(3) = 91.4(1)°.

The reaction between (1,5-cyclooctadiene)$PtCl_2$ and 2 mol of dapm in dichloromethane solution followed by precipitation with ether yields ivory crystals of *cis*-(dapm)$_2PtCl_2$ whose $^{31}P\{^1H\}$ NMR spectrum (δ 6.1, ^1J(Pt,P) = 3675 Hz) indicates that a *cis*-P_2PtCl_2 group is present. Mixing 0.5 mol of $Rh_2(\mu\text{-}Cl)_2(CO)_4$ with *cis*-(dapm)$_2PtCl_2$ in dichloromethane solution at −5 °C produces orange Rh(CO)Cl(μ-dapm)$_2PtCl_2$ (**2**) ($^{31}P\{^1H\}$ NMR: δ 15.0, ^1J(Pt,P) = 3826 Hz. IR: ν(CO) 1986 cm^{-1}), which forms orange crystals upon the addition of methanol. In the presence of a small amount of dapm, **2**

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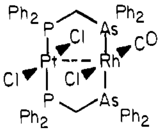
undergoes isomerization to **3** ($^{31}P\{^1H\}$ NMR: δ 16.4, $^1J(Pt,P)$ = 2880 Hz. IR: $\nu(CO)$ = 1965 cm^{-1}). The spectroscopic properties, particularly the carbonyl stretching frequencies, indicate that oxidative addition of Pt–Cl bond to the rhodium center has not occurred during these reactions.



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The details of the structure **2** have been obtained by X-ray diffraction study.[5] A perspective drawing of the molecule is shown in Figure 1. Although the molecule has no crystallographically imposed symmetry, there is a virtual mirror plane passing through Pt, Rh, Cl(1) and the carbonyl group. The coordination about rhodium consists of a *trans*-Rh(CO)ClAs$_2$ group while at platinum it involves a *cis*-PtP$_2$Cl$_2$ unit. The Pt···Rh separation is 3.043 (1) Å, a value that is significantly longer than that expected for a Pt–Rh single bond.[6] Other interatomic distances for bonded atoms fall within the normal ranges.

A number of features of this structure are noteworthy. The metal–metal separation, 3.043 (1) Å, is comparable to those in other face-to-face dimers where a metal–metal single bond is absent.[4] Thus, the face-to-face structure seems to require a larger metal–metal separation than is apparently possible with a small-bite ligand like Ph$_2$Ppy. The arrangement of the bridging dapm ligands is unique for a face-to-face dimer. The trans/trans arrangement, as shown for **3**, is quite common for binuclear complexes,[4] and examples of a cis/cis unit are known.[7] The only cases where a cis/trans bridging arrangement has been seen previously are binuclear complexes where a five-coordinate metal center is bonded to a four-coordinate metal atom.[8] The complex as prepared appears to be isomerically pure with regard to the relative orientation of the rhodium carbonyl and chloride ligands toward the *cis*-PtP$_2$Cl$_2$ group. There is no evidence in the crystal structure for disorder of these groups, and in solution the spectroscopic properties do not indicate the presence of another isomer. Additionally there is no evidence for the formation of any head-to-tail isomers under the comparatively mild condition of our reactions. We have previously noted several examples of the formation of head-to-head/head-to-tail isomers with dapm as the bridging ligands.[9] The lack of isomerization of this type in the present case probably is a reflection of the relative inertness of the Pt(II)–P bond. It is unlikely that the relative orientation of these bridging ligands (i.e., head-to-head/head-to-tail isomerization) will have a marked effect on the metal–metal separation.

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Registry No. 2·CH$_2$Cl$_2$, 88867-60-1; 3, 88928-90-9; *cis*-(dapm)$_2$PtCl$_2$, 88867-61-2; Rh$_2$(μ-Cl)$_2$(CO)$_4$, 14523-22-9; LPtCl$_2$ (L = 1,5-cyclooctadiene), 12080-32-9.

Supplementary Material Available: Listings of atomic fractional coordinates and temperature factors, bond lengths, bond angles, and crystallographic data for Rh(CO)Cl(μ-dapm)$_2$PtCl$_2$·CH$_2$Cl$_2$ (6 pages). Ordering information is given on any current masthead page.

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(5) Single crystals of *trans*-Rh(CO)Cl(μ-Ph$_2$AsCH$_2$PPh$_2$)$_2$-*cis*-PtCl$_2$·CH$_2$Cl$_2$ were grown by diffusion of diethyl ether into a dichloromethane solution of the complex. They belong to 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. Refinement yielded R = 3.8% for 6415 reflections with $F > 6\sigma(F)$ and 572 parameters.

(6) A value of ca. 2.6 Å is to be expected on the basis of the Pd–Rh distance of 2.594 (1) Å found for RhPd(μ-Ph$_2$Ppy)$_2$(CO)Cl$_3$.[2f]

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Ambient- and Low-Temperature Crystal Structure of Vanadyl Hydrogen Phosphate, (VO)$_2$H$_4$P$_2$O$_9$

Sir:

Vanadium phosphorus oxides are known to act as heterogeneous catalysts in the oxidation of *n*-butane and *n*-butene to maleic anhydride.[1] A study of the crystal structures of these phosphates is valuable in understanding the mechanisms of the catalytic process. Recently, the crystal structure of the catalytically important compound (VO)$_2$P$_2$O$_7$ was reported.[2] This structure is built of double chains of VO$_6$ octahedra that share opposite corners along the chain and share edges across the chain. Pyrophosphate groups link the double chains into a three-dimensional network by sharing oxygen corners with vanadium.

The vanadyl pyrophosphate is formed from its precursor, (VO)$_2$H$_4$P$_2$O$_9$, by heating at 400 °C. A study of the precursor is important because it apparently controls the microstructure of the final catalyst. Recently, this precursor has been formulated as a hydrated pyrophosphate, i.e., (VO)$_2$P$_2$O$_7$·2H$_2$O, on the basis of thermogravimetric and infrared data.[3] Described here is the crystal growth and ambient- and low-temperature X-ray structure determinations of (VO)$_2$H$_4$P$_2$O$_9$. Although structurally related to (VO)$_2$P$_2$O$_7$, the precursor is composed of vanadyl hydrogen phosphate layers.

Crystals of (VO)$_2$H$_4$P$_2$O$_9$ were grown hydrothermally in a sealed gold tube under 3 kbar pressure by slowly cooling from 500 °C a mixture of VO$_2$ and 85% H$_3$PO$_4$ in mole ratio 1:1.2. X-ray powder diffraction, thermogravimetric analyses, and infrared data confirmed the material as the desired phase.

The crystal structure[4,5] consists of vanadyl hydrogen

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(4) Room-temperature crystal structure information: orthorhombic, space group *Pmmn*, a = 7.416 (1) Å, b = 9.592 (2) Å, c = 5.689 (1) Å, V = 404.7 Å^3, Z = 2; CAD4 diffractometer, graphite monochromator, Mo Kα radiation, λ = 0.71069 Å, θ–2θ scans, $2 < \theta < 30°$, 2501 reflections. An analytical absorption correction was applied with use of a Gaussian grid of 8 × 8 × 8; transmission factors ranged from 0.68 to 0.93. The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques: 605 reflections with $I > 2\sigma(I)$, 58 variables (V, P, and O with anisotropic thermal parameters; H with isotropic parameters), anomalous dispersion correction for V and P, R = 0.022, R_w = 0.023. The hydrogen atom that forms the water molecule (H1) was refined reasonably well; parameters for the other hydrogen atom (H2) had higher standard deviations because of half-occupancy due to statistical disorder. An average isotropic thermal parameter was used for the hydrogen atoms in Figure 1. Oxygen atoms O2 and O3 initially exhibited relatively large B_{11} and B_{22} terms, respectively, when positioned on mirror planes (as shown in Figure 1). When these atoms were finally refined with half-occupancy in a position just off of their respective mirror planes, the thermal ellipsoids were reasonable and standard deviations and R factor were lowered. An ordered structure was not found with use of the room-temperature data in the lower symmetry space group $P2_12_12$.