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Alan L. Balch,* Marilyn M. Olmstead
Department of Chemistry, University of California
Davis, California 95616

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Coordination Geometries and Bond Types in Three-Coordinate Phosphine Complexes of Copper(I), Silver(I), and Gold(I)

Sir:

It has recently been shown that the bidentate ligand 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (PP)[1] forms square planar complexes of the type $[MX_2(PP)]$ (M = Ni(II), Pd(II), and Pt(II), X = halide ion) in which the two phosphorus atoms span trans positions.[2] We report here the syntheses of complexes [MCl(PP)] (M = Cu(I), Ag(I), and Au(I)) and discuss their conductivities in solution in terms of their molecular geometries obtained from crystal structure determinations.

The complex [CuCl(PP)] was prepared by mixing acetone solutions of PP and $CuCl_2{\cdot}6H_2O$. The corresponding silver and gold complexes were obtained similarly starting from AgCl and $[AuCl(Ph_3P)]$, respectively. Pure crystals suitable for x-ray diffraction, were obtained by slow crystallization from benzonitrile (Cu and Au) and acetonitrile (Ag).

The structures of [CuCl(PP)]·PhCN, [AgCl(PP)], and [AuCl(PP)] have been determined from three-dimensional diffractometer data and refined to conventional *R* values of 7.4, 4.5, and 3.8%, respectively. The important parameters describing the coordination geometries are summarized in Table I. The metal atoms are coordinated to two phosphorus atoms and one chlorine atom. The deviations of M from the plane of the ligands are 0.012 Å (Cu), 0.066 Å (Ag), and 0.040 Å (Au).

The most striking feature of this set of structures is the change in P_1MP_2 bond angles which increase from 132° (Cu) to 141° (Ag) to 176° (Au). Thus, in the latter compound the donor atom geometry is practically T-shaped. The observed M-Cl bond lengths are all shorter than the corresponding sums of the ionic radii[3] (by 0.55 Å (Cu), 0.56 Å (Ag), and 0.36 Å (Au)), but they exceed the standard distances obtained by adding the covalent radius of chlorine[3] and the single-bond radii of the metals[6] (by 0.06 Å (Cu), 0.19 Å (Ag), and 0.49 Å (Au)). At the same time the average M-P distances become shorter than the corresponding sum of reference radii (by 0.04 Å (Cu), 0.01 Å (Ag), and 0.13 Å (Au)). Thus, the lengthening and weakening of the M-Cl bonds are compensated by a shortening and strengthening of the M-P bonds made possible, in part, by the concomitant opening of the P-M-P angles. This correlation of changes in bond lengths and angles may be used as a model of the minimum energy pathway[4] that leads from three-coordinate to two-coordinate complexes, or of the reverse process.

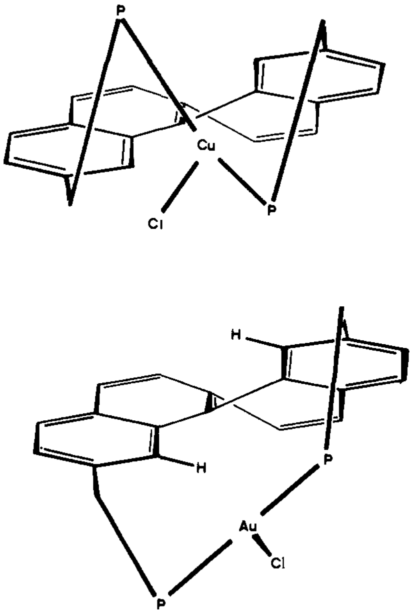

Figure 1. Schematic drawing of ligand conformations projected along the approximate twofold axis of the benzo[*c*]phenanthrene skeleton.

The ligand PP occurs in two different conformations, in the copper and silver complexes the $-CH_2PPh_2$ groups point in opposite directions while in the free ligand[5] and in the gold complex they point in the same direction (see Figure 1).

The complexes [MCl(PP)] represent the first complete set of compounds of Cu(I), Ag(I), and Au(I), of the type $[MXL_2]$ (L = tertiary phosphine), for which structural data have been obtained as no crystal structure determination of mononuclear complexes $[AgX(R_3P)_2]$ appears to have been reported.

Comparison of structural data for $[CuBr(Ph_3P)_2]$[6] ($Cu-P_1$ = 2.282 (3) Å, $Cu-P_2$ = 2.263 (3) Å, P_1-Cu-P_2 = 126.0 (1) Å) and for the PP complex shows that the donor atom geometries in the two complexes are very similar. On the other hand, the P_1-Au-P_2 bond angle in [AuCl(PP)] differs considerably from that found in $[AuCl(Ph_3P)_2]$[7] ($Au-P_1$ = 2.323 (4) Å, $Au-P_2$ = 2.339 (4) Å, P_1-Au-P_2 = 132.1 (1) °). A direct inference from these comparisons is that while the ligand PP can adopt coordination geometries similar to those of the corresponding complexes with monodentate tertiary phosphines, its steric requirements are such that it imparts some preference for linear P-M-P bonds and thus it provides a useful probe for assessing the relative tendencies of metal ions to form trigonal vs. digonal complexes.

The different nature of the M-Cl bonds in the [MCl(PP)] complexes is also reflected by their molar conductances. These were determined in nitromethane and acetonitrile over a range of concentrations[8] and some of the data are given in Table I.

Table I. Molar Conductances (in $ohm^{-1}\ cm^2\ mol^{-1}$ for 10^{-3} M solutions at 25°) and Coordination Geometries (with esd's) for Complexes [MCl(PP)]

M	$\Lambda(CH_3NO_2)^a$	$\Lambda(CH_3CN)^a$	$d(P_1-M)$	$d(P_2-M)$	d(M-Cl), Å	$\alpha(P_1MP_2)$	$\alpha(P_1MCl)$	$\alpha(P_2MCl)$, deg
Cu	7.2	insol.	2.258(2)	2.217(4)	2.222(2)	131.9(1)	104.8(1)	123.3(1)
Ag	18.3	18.6	2.458(3)	2.411(3)	2.514(4)	140.7(1)	98.2(1)	120.9(1)
Au	65.5	83.0	2.307(2)	2.310(2)	2.818(3)	175.7(1)	90.4(1)	93.4(1)

[a] Values quoted for solutions of 1:1 electrolytes range from 75 to 95 $ohm^{-1}\ cm^2\ mol^{-1}$ in CH_3NO_2 and from 120 to 160 $ohm^{-1}\ cm^2\ mol^{-1}$ in CH_3CN.[9]

While the interpretation of conductivity data for complexes of the type $[MX(R_3P)_2]$ is complicated by a variety of competing equilibria,[10] our data are likely to depend mainly on the equilibrium:[11]

$$[MCl(PP)] \rightleftharpoons [M(PP)]^+ + Cl^-$$

indicating that the degree of dissociation increases in the series. Cu(I) < Ag(I) < Au(I). It should be noted, however, that even for [AuCl(PP)], ionization is not complete since plots of Λ vs. $\sqrt{c}$ are nonlinear,[8] i.e., the corresponding solutions do not obey Onsager's law for 1:1 electrolytes.[12] Thus, conductivity data and solid-state structures of Cu(I), Ag(I), and Au(I) PP complexes yield complementary information about the relative degrees of covalency in the metal–ligand bonds of their complexes.[13]

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(11) Processes involving phosphine dissociation are expected to be negligible because PP is a rather stiff bidentate ligand and the formation of species containing more than two coordinated phosphorus atoms from a ligand such as PP is unlikely for reasons of steric overcrowding.
(12) Solutions of complexes $[Ag(BF_4)(PP)]$ and $[Au(NO_3)(PP)]$ in CH_3NO_2 do obey this law;[8] e.g., 10^{-3} M solutions of the latter compound have Λ_M (25°) values of about 83 (CH_3NO_2) and 129 $ohm^{-1}\ cm^2\ mol^{-1}$ (CH_3CN).
(13) We wish to thank the "Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung" and the "Zentenarfonds der ETH" for support of this work.

M. Barrow, H. B. Bürgi,* D. K. Johnson, L. M. Venanzi
Laboratorium für anorganische Chemie
ETH Zürich, 8006-Zürich, Switzerland

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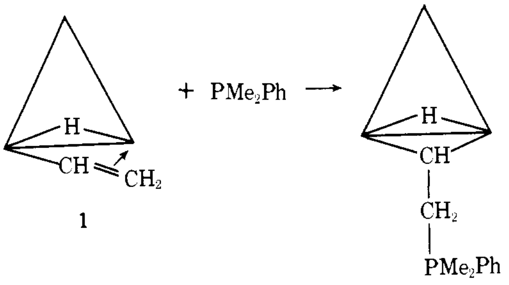
Attack by Phosphorus Nucleophiles on a Cluster-Bound Vinyl Group. The Crystal Structure of $HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$

Sir:

Coordination of the carbon–carbon double bond is known to activate it toward nucleophilic attack, although experience with mononuclear complexes suggests that a positive charge on the complex or a strong nucleophile is required.[1] We now wish to report attack by relatively weak trivalent phosphorus nucleophiles on a double bond coordinated in a metal cluster, wherein the resulting products are stabilized by virtue of multicenter bonding.

The vinyl group in the cluster complex $HOs_3(CO)_{10}(CH{=}CH_2)$ (**1**) has been characterized as bridging an edge of the Os_3 triangle in an unsymmetrical σ,π fashion.[2] In order to determine whether the coordinated double bond could be displaced, the interaction of **1** with phosphorus donors was examined. Addition of PMe_2Ph to a concentrated pentane solution of **1** at room temperature immediately produced a bright yellow precipitate. This material has been characterized as $HOs_3(CO)_{10}(^-CHCH_2P^+Me_2Ph)$ (**2**), resulting from an unexpected attack of the nucleophile at the vinyl group rather than at an osmium atom.



1

2

The mass spectrum of **2** shows only ions arising from **1** and PMe_2Ph. However, the infrared spectrum of the complex in solution is quite distinct from that of a mixture of **1** and PMe_2Ph, since the carbonyl stretching modes for **2** appear at significantly lower frequencies.[3] The hydride NMR resonance appears at τ 26.33 (consistent with a bridging position[4]) and is coupled to both the methine proton (J = 3.4 Hz) and the methylene protons (J = 0.5 Hz) as well as to the phosphorus nucleus (J = 1.8 Hz).[5] The methylene protons (τ 6.83) and the methine proton (τ 4.54, $J_{CH_2\text{-}CH}$ = 7.6 Hz) are also coupled to phosphorus, but by much larger values ($J_{P\text{-}H}$ = 11.0 and 16.5 Hz, respectively).[6] The methyl groups give rise to one doublet at τ 7.70 ($J_{P\text{-}H}$ = 12 Hz). A single ^{31}P NMR signal is found at 20.86 ppm downfield from 85% H_3PO_4, in the region expected for a phosphonium ion.[7] Refluxing the complex in acidic(HCl) methanol for 16 h gave PMe_2PhEt^+ as the only observed phosphorus-containing product. These data support the conclusion that attack at the vinyl β-carbon has resulted in the formal 1,3-dipolar moiety $^-CHCH_2P^+Me_2Ph$. However, in order to establish unambiguously the molecular structure of **2**, a single-crystal x-ray study has been carried out.

The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/n$, unit cell parameters at 21.4 (3) °C being a = 11.3389 (18) Å, b = 16.4265 (25) Å, c = 13.8840 (20) Å, and β = 100.64 (1) °. The observed density, ρ(obsd) = 2.66 (1) g cm^{-3}, is in good agreement with the value calculated for V = 2541.5 (7) $Å^3$, Z = 4 and mol wt = 1016.91 (ρ(calcd) = 2.657 g cm^{-3}). X-Ray diffraction data were collected with a Picker FACS-1 automated diffractometer using Nb-filtered Mo Kα radiation and a coupled θ (crystal)–2θ (counter) scan technique. The structure was solved by the Patterson method and optimized via difference-Fourier and least-squares refinement techniques. All data were corrected for absorption (μ = 150.9 cm^{-1}; T = 0.147 – 0.287), the final discrepancy indices being R_F = 3.61 and R_{wF} = 3.31% for 3342 reflections with $2\theta < 45°$. All atoms other than the methyl hydrogens have been located unambiguously. The molecular geometry is illustrated in Figure 1. Four terminal carbonyl ligands are associated with Os(3) while Os(1) and Os(2) are each linked to three such ligands. In addition, Os(1) and Os(2) are mutually bridged by a hydride ligand (which was located and refined in the structural analysis) and by a $^-CHCH_2P^+Me_2Ph$ ligand. The triosmium cluster defines an isosceles triangle in which Os(1)-Os(2) = 2.8002 (6) Å vs. Os(1)-Os(3) = 2.8688 (6) Å and Os(2)-Os(3) = 2.8729 (10) Å. Since a single *unsupported* bridging hydride ligand usually causes a lengthening of a metal–metal bond in a triangulated metal cluster complex[4,8] it appears that this effect is counterbalanced in the present molecule by a bond-shortening influence of the $^-CHCH_2P^+Me_2Ph$ ligand. (A similar situation was recently encountered in a structural analysis of $HRu_3(C$-$_{10}(C{=}NMe_2)$.[9] The osmium-hydrogen distances are Os(1)-H = 1.95 (7) Å and Os(2)-H = 1.80 (8) Å (average = 1.88 ± 0.11 Å), while ∠Os(1)-H-Os(2) = 97(3)°. The