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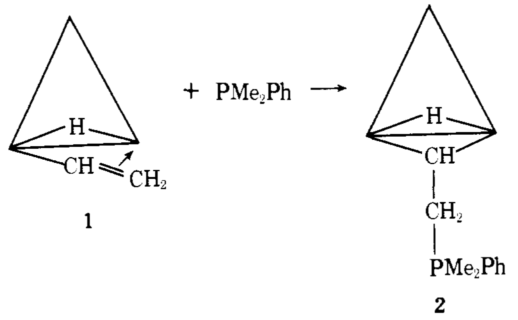
Attack by Phosphorus Nucleophiles on a Cluster-Bound Vinyl Group. The Crystal Structure of $HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$

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.



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

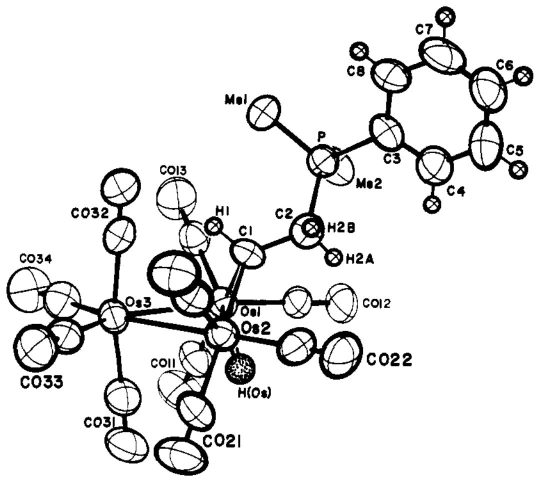


Figure 1. Structure of HOs$_3$(CO)$_{10}$($^-$CHCH$_2$P$^+$Me$_2$Ph) determined by x-ray crystallography.

Os(1)-H-Os(2) system makes an angle of 110.25° with the Os$_3$ plane.

The dipolar >$^-$CHCH$_2$P$^+$Me$_2$Ph ligand is in a symmetrical bridging mode with $\angle$Os(1)-C(1)-Os(2) = 80.8(3)°, Os(1)-C(1) = 2.148 (9) Å, and Os(2)-C(1) = 2.173 (8) Å and takes up an all-staggered conformation. Bond lengths within this moiety are as follows: C(1)-C(2) = 1.514 (12), C(2)-P = 1.823 (9), P-Me(1) = 1.813 (9), P-Me(2) = 1.816 (10), and P-Ph = 1.784 (9) Å. The Os(1)-C(1)-Os(2) bridge makes an angle of 108.97° with the Os$_3$ plane and an angle of 140.78° with Os(1)-H-Os(2) system.

Preliminary results indicate that among group 5 ligands the reaction exemplified by the formation of **2** is specific to phosphorus donors. Thus, compounds analogous to **2** were formed under similar conditions from treatment of **1** with P(n-Bu)$_3$ and P(OMe)$_3$, but no reaction was observed with AsMe$_2$Ph, NC$_5$H$_5$, NEt$_3$, or NHEt$_2$. Steric as well as electronic effects at the reacting center must be important, since PPh$_3$ also did not react with vinylic complex **1**. However, kinetic factors may determine whether a reaction is observed in a particular case. After 8 h in chloroform solution HOs$_3$(CO)$_{10}$(CH-CH$_2$P(OMe)$_3$) is almost completely dissociated to **1** and P(OMe)$_3$. In contrast, **2** is only a few percent dissociated after 48 h.

Carty and co-workers[10] recently reported attack by phosphite ligands on the σ,π-bridged alkynyl ligand in a dimeric iron complex, Fe$_2$(CO)$_6$(μ-C$_2$Ph)(μ-PPh$_2$). Although the bridging moiety formed differs in detail from that found for **2**, these two examples suggest unusual reactivity for polynuclear compounds.[11] We are currently investigating the interaction of **1** and related compounds with a wider variety of nucleophiles in order to assess the potential for elaboration of cluster-bound hydrocarbon groups.

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Melvyn Rowen Churchill*
Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

Barry G. DeBoer
Department of Chemistry
University of Illinois at Chicago Circle
Chicago, Illinois 60680

John R. Shapley,* Jerome B. Keister
Department of Chemistry
University of Illinois at Urbana-Champaign
Urbana, Illinois 61801

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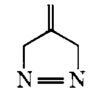
Kinetic Confirmation and Synthetic Circumvention of the Cascade Mechanism for Population of the Triplet Ground State of a Trimethylenemethane[1]

Sir:

The transformation of singlet reactant molecules by thermal (nonphotochemical) excitation into triplet intermediates or products continues to attract interest because the details of the change of multiplicity are not well understood. We recognize two broad mechanistic categories: type I, a "direct" mechanism, in which passage from the singlet to the triplet energy surface occurs without intervention of a discrete intermediate,[2] and type II, a "cascade" mechanism, reactant → singlet intermediate → ground state triplet.[3,4]

The thermal decomposition of azo compound **1** has a low entropy of activation, which is attributed to a requirement for a spin-forbidden process in the type I direct generation of N$_2$ and the triplet ground state of trimethylenemethane (**2**).[5] On the other hand, in the case of the thermal decomposition of the related azo compound **3** to N$_2$ and the diyl **4**, we interpret the chemical evidence[6,7] as strongly suggestive of a type II mechanism. The apparent paradox makes the application of the kinetic criterion to that case imperative. The present paper reports the confirmation of the type II mechanism for **3** by such experiments and also describes two methods for the generation and reaction of triplet **4** free of the singlet species that necessarily precedes it in the cascade.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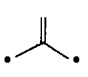
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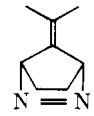
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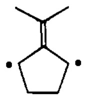
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The decomposition of **3** at several temperatures between 40 and 80 °C can be monitored by analysis for unreacted **3**, which