

Phosphinidene- and Arsinidene-Bridged Transition Metal Clusters

Kevin E. Howard

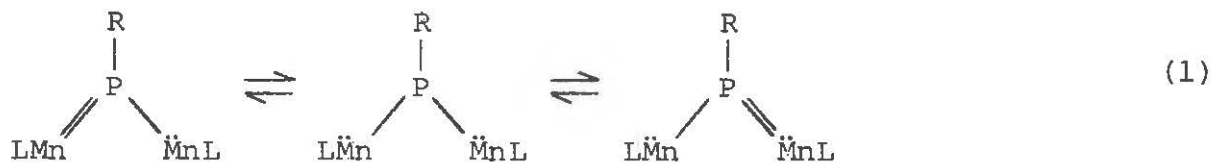
Literature Seminar

October 16, 1984

Phosphinidenes [RP:] were first postulated to occur as reactive intermediates in the reactions of aryl- and alkyl-dichlorophosphines with magnesium or lithium in tetrahydrofuran, yielding cyclic or linear oligomers [1]. Schmidt and Osterroht in 1965 successfully trapped phenylphosphinidene, generated by heating tetraphenylcyclo-tetraphosphine above 160°C or reacting phenyl-dichlorophosphine with zinc dust at 25°C or oxidizing phenylphosphine with iodine, by insertion into the double bond of diethyl-disulfide [2]. Similarly, arsinidenes [RAS:] were postulated by Nefedow and Manakow [3] to act as intermediates during cyclooligoarsane (RAS)_n formation.

Huttner *et. al* [4] first reported the stabilization of an arsinidene, phenylarsinidene, in a metal complex in 1975. Soon thereafter, Huttner and coworkers reported similar phenylphosphini-dene [5] and phenylstibinidene [6] complexes.

The unusual stability of these complexes arises from the nature of the arsinidene (or phosphinidene or stibinidene) ligand as a four-electron donor, as first described by Huttner [4]. The group VA atom completes its octet of electrons by metal d π -pnicogen p π back-bonding, while the ligand donates two electron pairs to the metal. The metal-group VA-metal bonding mode is most easily viewed as a 4 π electron-3 atom system.



These complexes were the first examples of trigonal planar As(I) and P(I) coordination geometries. The "allylic" nature of these complexes is reflected in unusually short P-metal and As-metal bond distances, as determined by x-ray crystallography [5,7]. Fenske and Kostić recently reported [8] molecular orbital studies on [C₅H₅Mn(CO)₂]₂PC₆H₅ which supported the three-center four electron bonding scheme in these complexes.

Inevitably, higher nuclearity phosphinidene, and to a lesser extent arsinidene, clusters have been prepared. Huttner and coworkers have prepared homometallic phosphinidene clusters from M₃(CO)₁₂ where M = Fe [9], Ru [10], Os [11]. Geoffroy *et. al* [12] recently reported the preparation of a μ_4 -phosphinidene complex which is chemically "attractive" as it contains a catalytically active metal-Rh, labile 1,5-cyclooctadiene ligands, and is coordinately unsaturated. Other researchers have begun investigating mixed-metal phosphinidene clusters containing catalytically active metals such as Ru/Rh [13] and Ru/Au [13].

Investigations into the catalytic behavior of phosphinidene-bridged transition metal clusters have been scarce. Pittman et. al [14] has studied the hydroformylation of pentenes by $\text{Co}_4(\text{CO})_8-(\mu_4-\text{PC}_6\text{H}_5)_2$ and Cook and Evans [15] have examined the tethering of $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_4\{\mu_3\text{-PCH}_2\text{CH}_2\text{Si}(\text{OEt})_3\}$ on oxide supports. The catalytic potential of phosphinidene-bridged transition metal clusters is an area still open to extensive research.

Most recently, Huttner and coworkers have reported the preparation of new stibinidene complexes of manganese and chromium [16] as well as a phosphinidene chromium complex, $(\text{Cr}(\text{CO})_5)_2\text{P}(\text{t-butyl})$, with a ^{31}P -nmr chemical shift of 1362 ppm (rel. to H_3PO_4), reported by the authors as the largest ^{31}P -nmr chemical shift documented to date [17]. Marks et. al [18] have recently prepared and characterized the phosphinidene-bridged actinide methoxy complexes $[\text{Cp}'_2\text{M}(\text{OCH}_3)]_2\text{PH}$, where $\text{Cp}' = \eta^5\text{-(CH}_3)_5\text{C}_5$ and $\text{M} = \text{Th, U}$. Jones and Whittlesey [19] reported, this year, the formation of a chromium arsinidene complex which reacts further to form the heterometallacycle CrAs_4 . Finally Mathey and Marinetti [20] examined the cycloaddition of alkenes to a phosphinidene complex.

Phosphinidene- and arsinidene-bridged transition metal clusters containing a variety of metals have been prepared and structurally characterized. However, the reactivity, both stoichiometric and catalytic, of these complexes has only begun to be investigated and may exhibit a rich and varied chemistry.

References

1. Henderson, Jr., W. A.; Epstein, M.; Seichter, F. S., "Some Aspects of the Chemistry of Cyclopolyphosphines", J. Am. Chem. Soc. 1963, 85, 2462.
2. Schmidt, U.; Osterroht, C., "Detection of Atomic Sulfur and Phenylphosphinidene ($\text{C}_6\text{H}_5\text{P:}$) in Solution", Angew. Chem. Internat. Ed. Engl. 1965, 4, 437.
3. Nefedow, O. M.; Manakow, M. N., "Inorganic, Organometallic, and Organic Analogues of Carbenes", Angew. Chem. Internat. Ed. Engl. 1966, 5, 1021.
4. Huttner, G.; Schmid, H.-G., "Arsinidene Complexes: Stabilization of Phenylarsanediyl, $\text{C}_6\text{H}_5\text{As}$, in $\text{C}_6\text{H}_5\text{As}[\text{Cr}(\text{CO})_5]_2$ ", Angew. Chem. Int. Ed. Engl. 1975, 14, 433.
5. Huttner, G.; Müller, H.-D.; Frank, A.; Lorenz, H., " $\text{C}_6\text{H}_5\text{P}[\text{Mn}(\text{CO})_2\text{C}_5\text{H}_5]_2$: A Phosphinidene Complex with Trigonal Planar Coordinated Phosphorous (I)", Angew. Chem. Int. Ed. Engl. 1975, 14, 705.

6. Seyerl, J. von; Huttner, G.; "C₆H₅Sb[Mn(CO)₂C₅H₅]₂-The First Compound Containing Trigonal-Planar Coordinate Antimony(I)", Angew. Chem. Int. Ed. Engl. 1978, 17, 843.
7. Huttner, G.; Seyerl, J. von; Marsili, M.; Schmid, H.-G., "Arsinidene Complexes: Structure and Electronic Spectrum of C₆H₅As[Cr(CO)₅]₂", Angew. Chem. Int. Ed. Engl. 1975, 14, 434.
8. Kostić, N. M.; Fenske, R. F., "Molecular Orbital Study of Bonding and Conformations in Dinuclear Cyclopentadienyldicarbonyl Complexes of Manganese and Chromium Containing Germanium, Sulfide, Dinitrogen, or Phosphinidene Bridges", J. Organomet. Chem. 1982, 233, 337.
9. Huttner, G.; Schneider, J.; Mohr, G.; Seyerl, J. von, "R-P Bridged Iron-Cluster-Hydride", J. Organomet. Chem. 1980, 191, 161.
10. Natarajan, K.; Scheidsteger, O.; Huttner, G., "R-P and R-As Bridged Ruthenium Carbonyl Hydrides and Related Clusters. Crystal and Molecular Structure of [(μ₂-H)₂Ru₃(CO)₉(μ₃-P-(p-CH₃OC₆H₄))]", J. Organomet. Chem. 1981, 221, 301.
11. Natarajan, K.; Zsolnai, L.; Huttner, G., "Syntheses and Characterization of [Os₃(CO)₁₁(PRH₂)], [(μ₂-H)Os₃(CO)₁₀(μ₂-PRH)] (R = C₆H₅, p-CH₃OC₆H₄, C₆H₁₁) and [(μ₂-H)₂Os₃(CO)₉-(μ₃-PR)] (R = C₆H₅, C₆H₁₁). Interconversion of Cluster-Bound Phosphine and Phosphido Ligands. Crystal and Molecular Structures of [(μ₂-H)Os₃(CO)₁₀(μ₂-P(C₆H₅)H)] and [(μ₂-H)₂Os₃(CO)₉(μ₃-PC₆H₅)]", J. Organomet. Chem. 1981, 220, 365.
12. Burkhardt, E. W.; Mercer, W. C.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C., "Rh₄(μ₄-PPh)₂(cyclo-octa-1,5-diene)₄. A Doubly Co-ordinatively Unsaturated Phosphinidene-bridged Cluster without Carbonyl Ligands", J. Chem. Soc., Chem. Commun. 1983, 1251.
13. Mays, M. J.; Raithby, P. R.; Taylor, P. L., "Synthesis of a μ₄-PPh Mixed Metal Cluster: The X-ray Structures of [Ru₃Rh₂(CO)₁₃(PEt₃)(μ₄-PPh)] and [Ru₃Au(μ₂-H)(CO)₉(PMe₂Ph)(μ₃-PPh)]", J. Organomet. Chem. 1982, 224, C45.
14. Ryan, R. C.; Pittman Jr., C. V.; O'Connor, J. P., "Metal Cluster Catalysis. 1. Hydroformylations of 1- and 2-Pentene Catalyzed by Two Cobalt Carbonyl Clusters: Co₃(CO)₉(μ₃-CC₆H₅) and Co₄(CO)₈(μ₂-CO)₂(μ₄-PC₆H₅)₂", J. Am. Chem. Soc. 1977, 99, 1986.
15. Cook, S. L.; Evans, J., "Tethering of a Phosphinidene Stabilized Cluster to Oxide Supports", J. Chem. Soc., Chem. Commun. 1983, 713.

16. Weber, U.; Zsolnai, L.; Huttner, G., "Stibinidene Complexes: Compounds with Trigonal Planar Coordinated Antimony", J. Organomet. Chem. 1984, 260, 281.
17. Huttner, G.; Borm, J.; Zsolnai, L., " $(Cr(CO)_5)_2PCMe_3$, a Phosphinidene Complex with an Extreme Phosphorous-31 Down Field Shift", J. Organomet. Chem. 1984, 263, C33.
18. Duttera, M. R.; Day, V. W.; Marks, T. J., "Organoactinide Phosphine/Phosphite Coordination Chemistry. Facile Hydride-Induced Dealkoxylation and the Formation of Actinide Phosphinidene Complexes", J. Am. Chem. Soc. 1984, 106, 2907.
19. Jones, R. A.; Whittlesey, B. R., "Formation of an Arsinidene Complex of Chromium via Arsenic-Carbon Bond Cleavage. Further Reaction to Form a $CrAs_4$ Heterometallic Cycle. Synthesis and X-ray Structures of $[Cr(CO)_5]_2(\mu-t-butylAs)$ and $(cyclo)-(CO)_4CrAs(t-butylAs)_2As(t-butyl)Cl$ ", Organometallics 1984, 3, 469.
20. Marinetti, A.; Mathey, F., "The Carbene-Like Behavior of Terminal Phosphinidene Complexes Toward Olefins. A New Access to the Phosphirane Ring", Organometallics 1984, 3, 456.