Phosphinidenes [RP:] were first postulated to occur as reactive intermediates in the reactions of aryl- and alkyldichlorophosphines 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 phenyldichlorophosphine with zinc dust at 25°C or oxidizing phenylphosphine with iodine, by insertion into the double bond of diethyldisulfide [2]. Similarly, arsinidenes [RAs:] were postulated by Nefedow and Manakow [3] to act as intermediates during cyclooligoarsane (RAs)n formation.


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 dπ-pnicogen pπ 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 4π 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 \([\text{C}_5\text{H}_5\text{Mn(CO)}_2]_2\text{PC}_6\text{H}_5\) 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 \(\text{M}_3(\text{CO})_{12}\) where \(\text{M} = \text{Fe} [9], \text{Ru} [10], \text{Os} [11]\). Geoffroy et. al [12] recently reported the preparation of a \(\mu_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 Co$_4$(CO)$_6$-(µ$_4$-PC$_6$H$_5$)$_2$ and Cook and Evans [15] have examined the tethering of (µ-H)$_2$Ru$_3$(CO)$_4$(µ$_3$-PCH$_2$CH$_2$Si(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, (Cr(CO)$_5$)$_2$P(t-butyl), with a $^{31}$P-nmr chemical shift of 1362 ppm (rel. to H$_3$PO$_4$), 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 [Cp$_2$M(OCH$_3$)]$_2$PH, where Cp* = η$_5$-(CH$_3$)$_2$C$_5$ and M = Th, U. Jones and Whittlesey [19] reported, this year, the formation of a chromium arsinide 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


19. Jones, R. A.; Whittlesey, B. R., "Formation of an Arsinidene Complex of Chromium via Arsenic-Carbon Bond Cleavage. Further Reaction to Form a CrAs₄ Heterometallocycle. Synthesis and X-ray Structures of [Cr(CO)₅]₂(μ-t-butylAs) and (cyclo)-(CO)₄CrAs(t-butylAs)₂As(t-butyl)Cl", Organometallics 1984, 3, 469.