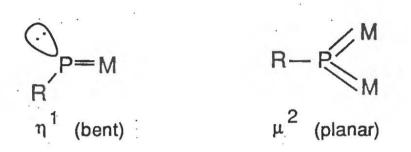
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Literature Seminar

Many new developments have occurred in recent years in the area of synthesis of transition metal phosphinidene complexes containing one or two metal atoms. These compounds contain the 6-electron phosphinidene fragment (RP) in a terminal or  $\mu^2$ -bridging mode for one and two metal complexes, respectively.



These compounds are of interest for several reasons: 1) The phosphinidene fragment has the potential for a large number of bonding modes as a ligand. 2) Transition metal phosphinidene complexes could provide a viable starting point for the synthesis of phosphorus containing species that would be difficult or impossible to reach by other methods. 3) The chemistry of multiple bonds between transition metals and heavier main group moieties is relatively underdeveloped.

Reagents commonly used as sources for phosphinidene ligands in the synthesis of transition metal phosphinidine complexes containing three or more metal atoms [1] have usually been ineffective in attaining lower nuclearity phosphinidene complexes. This is especially true in the case of terminal phosphinidene complexes. Difficulties with incomplete reactions [9] or subsequent side reactions [10] are common in attempts to synthesize terminal transition metal phosphinidene complexes. Thus, other methods [2,3] which are less direct have been developed to synthesize terminal and  $\mu^2$ -bridging transition metal phosphinidene complexes containing only one [2] or two [1] metal atoms, respectively.

Terminal phosphinidene complexes have been obtained by Mathey et al. [4] via thermolysis reactions of 7-phosphanorbornadienes which are complexed to transition metal pentacarbonyl fragments of the chromium triad. The terminal phosphinidene complexes which result are only transient but their existence has been proven through a rich reaction chemistry [2] in which these compounds react with unsaturated organic and organometallic species in a manner similar to electrophilic transition metal singlet carbene complexes [5]. In the absence of trapping agents such as unsaturated moleties, the formation of transition metal stabilized phcs-phorus-phosphorus double bond compounds results [11]. The only isolable terminal phosphinidene to date was recently obtained by Lappert et al. [6]. These compounds exhibit the shortest metal phosphorus bond length of any phosphorus containing transition metal complex of the chromium triad. The isolable terminal phosphinidene complexes exhibit some of the highest upfield <sup>31</sup>P NME shifts known [6].

The synthesis of binuclear transition metal phosphinidene complexes containing a  $\mu^2$ -bridging phosphinidene was first achieved by Huttner et al. [7]. These compounds also show a rich reaction chemistry and are in general more stable than terminal phosphinidine complexes. A characteristic feature of these compounds is that they are brightly colored due to a strong long wavelength absorption in the visible region which is a result of the 3-center-4m electronic structure [8]. These complexes show considerable Lewis acidity in their reactivity as demonstrated by the formation of several adducts which have tetrahedral phosphorus centers [12]. Substitution reactions can occur at the phosphorus center to give a substituted phosphinidene. The  $\mu^2$ -bridging phosphinidene compounds can also dimerize to give transition metal stabilized phosphorus-phosphorus double bond compounds [13]. These bridging phosphinidine complexes can react with organometallic nucleophiles to give higher nuclearity phosphinidene compounds. This suggests a possible intermediacy of the  $\mu^2$ -phosphinidene complex in the formation of higher nuclearity transition metal compounds.

## References

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- See for instance Cowley, A. H.; Champion, D. H., "Reaction of a Phosphaketene with Diiron Enneacarbonyl: Possible Intermediacy of a Terminal Phosphinidene Complex," Polyhedron 1985, 4, 1791. Gladysz, J. A.; Bertrand, G.; Buhro, W. E.; Nakazawa, H., "[(n<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>]: Spectroscopic Evidence for a Phosphinidine Complex," <u>Inorg. Chem.</u> 1984, 4, 3433.
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