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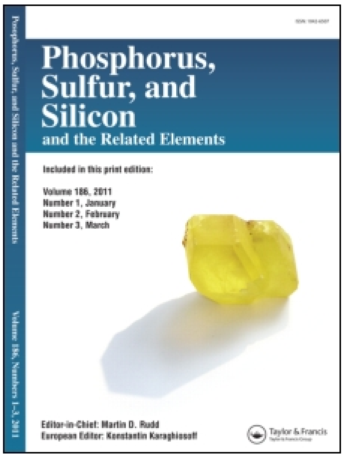

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Developments in the Coordination Chemistry of Dicoordinate Phosphenium Ion Ligands

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DEVELOPMENTS IN THE COORDINATION CHEMISTRY OF DICOORDINATE PHOSPHENIUM ION LIGANDS

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Abstract Phosphenium ion ligands display synergic σ-donor, π-acceptor properties which resemble other small molecules and the coordination chemistry of X_2P^+ ligands is compared here with NO and SO_2.

INTRODUCTION

Dicoordinate aminophosphenium ions[1] $(R_2N)_2P^+$, formed by heterolytic cleavage of a phosphorus-halogen bond in aminohalophosphines, have a number of interesting properties. In particular, molecular orbital analyses[2] indicate that $(R_2N)_2P^+$ should display amphoteric acid-base character as a consequence of an occupied, in-plane, lone pair (a_1) orbital localized on phosphorus and a vacant low lying, out-of-plane, antibonding (b_1^*) orbital delocalized over the N-P-N unit. These factors suggest a rich coordination chemistry with transition metals, and they also suggest a close resemblance to several "small-molecule" ligands including NO, SO_2, and carbenes. Some progress in developing parallels between $(R_2N)_2P^+$ reagents and NO and SO_2 are outlined here.

Six coordinate metal nitrosyl[3] and metal-SO_2[4] complexes containing six d electrons typically display linear M-N≡O and η^1-planar S-bonded M-SO_2 groups. The metal-nitrogen bond involves σ donation from nitrogen to the metal fragment and back donation from an occupied metal orbital to the π* MO on the nitrosyl. The

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metal-SO_2 interaction involves sulfur lone pair donation to the metal fragment and metal d orbital electron back donation to a π^* MO delocalized over the entire SO_2 molecule. Similarly, we find that combinations of $NaMCp(CO)_3$ (M=Cr, Mo, W) with a series of diaminohalophosphines and aminohalophosphites including $(Me_2N)_2$-PCl, $CH_3\overline{NCH_2CH_2N(CH_3)P}Cl$,[2] and $CH_3\overline{NCH_2CH_2OP}Cl$ result in the formation six coordinate six d-electron complexes of the general type $MCp(CO)_2[(R_2N)_2P]$. The diazadiphosphetidine $Cl\overline{PN(t\text{-}Bu)P(Cl)N}$-(t-Bu) also forms a monometallic complex $[MCp(CO)_2]\overline{PN(t\text{-}Bu)P(Cl)N}$-(t-Bu) as well as a bimetallic complex $[MCp(CO)_2]_2\overline{PN(t\text{-}Bu)PN}$-(t-Bu). Each complex displays two terminal carbonyl bands in the infrared spectrum, a low field ^{31}P NMR resonance (310-240 ppm) and tungsten complexes show large J_{WP} coupling constants (700-800 Hz). Single crystal X-ray diffraction structure determinations reveal an η^1-planar metal-$P(NR_2)_2$ coordination geometry with short M-P bond distances (2.10-2.25 Å) and P-N bond distances (1.64-1.71 Å) somewhat longer than that found in $[(i\text{-}Pr)_2N]_2P^+$ (1.613 Å).[5] We have described a bonding model for these complexes in which the X_2P^+ ligands undergo σ donation from the a_1 lone pair MO to an empty d_{z^2} orbital on the 16-electron $MCp(CO)_2^-$ fragment and π back-acceptance from an occupied d_{xz} HOMO on the metal to the b_1^* MO on the cation. This model is consistent with the observed planar $P(NR_2)_2$ geometry, the orientation of the $P(NR_2)_2$ plane with respect to the $M(CO)_2$ plane, the short M-P bond distances and elongated P-N bonds. It follows that these complexes are directly related to the known linear nitrosyl complexes $CpM(CO)_2NO$, M=Group VIB.[6] Complexes $CpMn(CO)_2[(R_2N)_2P]^+$ also have been prepared in our work, and these compare favorably to the η^1-planar SO_2 complex $CpMn(CO)_2SO_2$.[7]

Six coordinate metal nitrosyl and metal-SO_2 complexes with eight d-electrons often display bent MNO and η^1-pyramidal MSO_2 groups. Reactions of $NaFeCp(CO)_2$ with $(R_2N)_2PCl$ reagents produce metallophosphenium ion products $FeCp(CO)_2[(R_2N)_2P]$. The crystal structure determination for one of these molecules[8] reveals an η^1-pyramidal geometry for the phosphorus atom. Chemical properties and MO calculations suggest that the phosphenium ion base strength is not sufficient to displace a CO ligand from $FeCp(CO)_2^-$; therefore, the d_z^2 orbital is not available to accept electron density from the a_1 lone pair of $(R_2N)_2P^+$. As a result, the phosphorus atom is rehybridized and the Fe-P interaction only consists of electron donation from the occupied Fe d_{xz} orbital into the b_1^* MO on the $(R_2N)_2P^+$ ligand. A long Fe-P interaction would be expected and this is observed (Fe-P 2.340 Å). At the present time, an analogous $CpFe(CO)_2NO$ has not been isolated, and the corresponding SO_2 complex has only been mentioned as an unstable product in the reaction of SO_2 and $NaCpFe(CO)_2$.[9]

The above enumerated examples represent a few of the parallels which exist between X_2P^+ ligands and NO and SO_2. The nature of the electronic properties and orbital template of phosphenium ions allows them to participate in chemistry which is unique from known chemistry of NO and SO_2. In particular, phosphenium ions will act as both symmetrically bridging and semi-bridging ligands as evidenced by the formation $Mn_2(CO)_8(\overline{PN(CH_3)CH_2CH_2N}CH_3)_2$ and $Co_2(CO)_5(\overline{PN(CH_3)CH_2CH_2N}CH_3)_2$.[10] Phosphenium ion complexes also may undergo reductive coupling reactions as indicated by the formation of $Mn_2(CO)_8[\overline{PN(t\text{-}Bu)PN}(t\text{-}Bu)]_2$ from $Mn(CO)_5\overline{PN(t\text{-}Bu)P(Cl)N}\text{-}(t\text{-}Bu)$. Unlike NO and SO_2, phosphenium ions also provide an adjustable range of σ-donor and π-accepting ability, and a corresponding alteration in coordination chemistry. An example of this fact can be found in formation of metallophosphenium ion complexes from $R\overline{NCH_2CH_2N(R)P}Cl$, $R\overline{NCH_2CH_2OP}Cl$ and $\overline{OC(R)_2C(R)_2OP}Cl$ and $MoCp(CO)_3^-$. The first two phosphines form η^1-planar complexes $MoCp(CO)_2(PX_2)$ while the phosphite appears to form a seven coordinate η^1-pyramidal complex $MoCp(CO)_3(PX_2)$.[11] This chemistry

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is consistent with an increasing degree of π accepting ability in the ligands as N is replaced by O.

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