occurs. On this basis a unique EPR spectrum is not surprising.[18]

Finally, we note that {FeNO}[7] complexes having a bent FeNO geometry are often formulated as $Fe^{III}NO^-$.[19] On the basis of crystallographic results[2] for binding of N_3^- and O_2 in metHr and oxyHr, respectively, a bent FeNO geometry is quite likely for deoxyNO. Thus, $[Fe^{II},Fe^{III}NO^-]$ would seem to be a reasonable formalism for the iron site. If deoxyNO represents an analogue of the proposed intermediate, $[Fe^{II},Fe^{III}O_2^-]$, then our data suggest either that the iron atoms in deoxyHr are antiferromagnetically coupled (presumably through one or more bridging ligands) or that the originally uncoupled iron atoms in deoxyHr become coupled after binding of O_2 to the exposed iron but prior to formal oxidation of the second iron. An EPR signature exists which could distinguish between these possibilites during earlier stages of the deoxyHr plus NO reaction, namely, the $S = {}^3/_2$ type with $g \sim 4.0$ and 2.0.

Note Added in Proof. Recently, Reem and Solomon (*J. Am. Chem. Soc.* **1984**, *106*, 8323–8325) have presented evidence of weak antiferromagnetic exchange coupling $(-J \sim 13 \text{ cm}^{-1})$ for the iron site in deoxyHr.

Registry No. N_3^-, 14343-69-2; CNO^-, 661-20-1; Fe, 7439-89-6.

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(17) Nocek, J. M.; Kurtz, D. M., Jr.; Pickering, R. A.; Doyle, M. P. *J. Biol. Chem.* **1984**, *259*, 12334–12338.

(18) A model calculation assuming isotropic exchange $J\vec{S}\cdot\vec{S}'$ between spins $S = {}^3/_2$ and $S' = 2$ and including zero-field splitting for both sites allows one to produce a lowest doublet with effective g values close to the measured ones.

(19) McCleverty, J. A. *Chem. Rev.* **1979**, *79*, 53–76.

Electronic Structure of a Metalated Doubly Bonded Group 15 Complex[†]

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The unusual linkage of one or more transition-metal moieties to two doubly bonded group 15 atoms places such compounds among the structural exotica of inorganic complexes. A recent flurry of synthetic activity in this area has generated a wealth of these complexes[1] whose modes of bonding have far exceeded early workers' expectations.[2] Figure 1 illustrates some metal coordination modes thus far encountered, and Table I gives a partial listing of compounds whose structures have been verified by X-ray crystallography. Figure 1 schematically depicts two possible modes of coordination for transition-metal moieties to doubly bonded group 15 elements. Structures A and C involve end-on coordination alone while B and D exhibit simultaneous end-on and side-on coordination. Side-on coordination has been interpreted

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(1) For a recent review of the synthetic progress in this area, see: Cowley, A. H. *Polyhedron* **1984**, *3*, 389–432.

(2) Purcell, K. F.; Kotz, J. C. "Inorganic Chemistry"; W. B. Saunders: Philadelphia, 1977; Chapter 6, p 318.
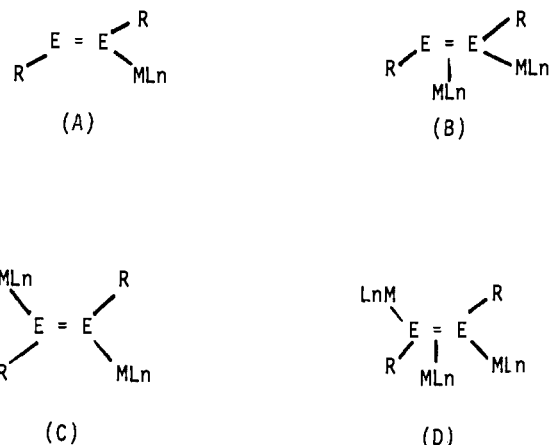
Figure 1. Illustrations of some encountered coordination modes for transition-metal moieties to two doubly bonded group 15 elements.
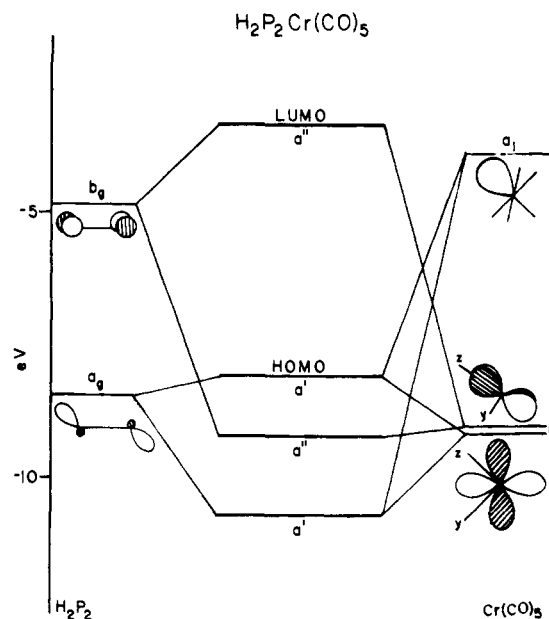

Figure 2. Molecular orbital scheme for $H_2P_2Cr(CO)_5$. Only molecular orbitals containing interactions of the H_2P_2 fragment and the $Cr(CO)_5$ moiety are depicted.

Table I

complex	type of bond (as shown in Figure 1)	ref
$(2,4,6\text{-}t\text{-}Bu_3C_6H_2)_2P_2Fe(CO)_4$	A	3
$[CH(SiMe_3)_2]_2P_2Cr(CO)_5$	A	4
$(2,4,6\text{-}t\text{-}Bu_3C_6H_2O_2)_2P_2[\mu\text{-}Fe(CO)_4]Fe(CO)_4$	B	5
$H_2N_2[Cr(CO)_5]$	C	5
$[CH(SiMe_3)_2]_2P_2[Fe(CO)_4]^2$	C	6
$(C_6H_5)_2As_2[\mu\text{-}Cr(CO)_5(Cr(CO)_5)]_2$	D	10

as a π interaction between metal and ligand orbitals, while end-on bonding has been construed as a purely σ interaction.[3-7] To ascertain the validity of these concepts, we have undertaken theoretical studies of the various modes of coordination. In this

(3) Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Norman, N. C., Pakulski, M.; Ando, F.; Wright, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 7751–7752.

(4) Flynn, K. M.; Hope, H.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 7750–7751.

(5) Huttner, G.; Gartzke, W.; Allinger, K. *J. Organomet. Chem.* **1975**, *91*, 47–56.

(6) Flynn, K. M.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 2085–2086.

(7) Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Norman, N. C.; Pakulski, M.; Ando, F.; Wright, T. C. *Organometallics* **1984**, *3*, 1044–1050.

paper we address the nature of the end-on bond. We defer a discussion of other modes of coordination between transition metals and multiply bonded complexes from groups 14–16 to a later paper.

To elucidate the electronic structure of the M–E end-on interaction, we chose $H_2P_2Cr(CO)_5$ with structure A of Figure 1 as our model. This compound is analogous to the compound $[CH(SiMe_3)_2]_2P_2Cr(CO)_5$ prepared by Flynn, Hope, Murray, Olmstead, and Power.[4] Substitution of hydrogen for the fragment attached to the phosphorous atom simplifies the calculational procedure and does not detract from the overall bonding picture. On the basis of the crystallographic results of the compound synthesized by Flynn et al., the Cr–P bond length in this complex was assigned a value of 2.36 Å. This value is similar to that found in a trialkylphosphine complex such as $PR_3Cr(CO)_5$, in which the phosphorus atom has been interpreted as a simple two-electron σ donor. Consequently, the doubly bonded group 15 ligands exhibiting the end-on mode of coordination have also been interpreted as simple two-electron σ donors.[3–9]

In our theoretical study on the idealized $H_2P_2Cr(CO)_5$ complex, we employed Fenske–Hall molecular orbital calculations[11] and partitioned the molecules into two parts: the $Cr(CO)_5$ metal moiety and the P_2H_2 ligand fragment. The results are given in Figure 2. The left-hand side of Figure 2 schematically describes the two significant frontier molecular orbitals of the trans P_2H_2 ligand fragment labeled according to the fragment's C_{2h} symmetry. Only the filled a_g and unfilled b_g combinations are high enough in energy relative to the metal fragment to participate in frontier level interactions of the full molecule. The right-hand side of Figure 2 depicts the significant orbitals of the $Cr(CO)_5$ moiety, which have been described previously in great detail,[12] labeled according to the C_{4v} symmetry of this entity. These normally consist of a filled e level containing d_{xz} and d_{yz} orbitals and an empty a_1 lobe primarily d_{z^2} in character which serves as the metal moiety's LUMO. However, since the symmetry of the full molecule is not C_{4v}, the e level splits into two levels, one primarily d_{xz} and the other primarily d_{yz} in character.

The center of Figure 2 depicts the molecular orbital scheme for the interaction of the metal moiety and ligand fragment. Omission of the hydrogen atoms of the P_2H_2 fragment allows the assignment of C_s symmetry to the full molecule. The mirror plane then contains the two phosphorus atoms, the carbonyl group trans to them, and two nonadjacent cis carbonyls.

The molecular orbital scheme indicates that the simple two-electron donor ligand model is an inadequate description of the interactions. The fragment's filled a_g level finds its symmetric complement in the linear combination of metal filled d_{yz} and empty d_{z^2} orbitals forming the lower a′ level, a localized three center two electron interaction. Transfer of electrons from the H_2P_2 fragment to the metal moiety also results in a filled destabilized interaction, the upper a′ level which serves as the HOMO of the complex. The filled metal d_{xz} orbital becomes stabilized by interacting with the empty b_g of the ligand fragment, resulting in the a″ level of the complex, again a delocalized three-center two-electron interaction. Here the metal moiety π back-donates from a filled metal orbital into an empty ligand level. The extent of back-donation is quite

large, 0.30 electrons are accepted by the formerly empty ligand level.

In conclusion, the doubly bonded main group ligand invokes delocalized σ and π interactions upon complexation to the metal, an electronic structure much more intricate than the pure σ-donor structure originally assigned to it. Bond length comparisons, while a facile method for analysis of electronic structures, can occasionally result in insufficient descriptions of bonding interactions.

Gas-Phase Reactions of the Acetyl Anion

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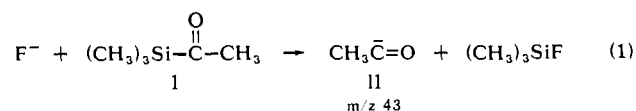
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Among the common types of carbanions acyl anions, $R\bar{C}{=}O$, are exceptional in that their chemical reactions have hardly been studied, either in solution or in the gas phase. This is so because aldehydes, their most obvious precursors, react most commonly by enolate formation or nucleophilic addition rather than by abstraction of the weakly acidic acyl hydrogen. Seyferth[2] has recently shown how acyl anions, prepared by the addition of alkyllithium reagents to carbon monoxide, can be trapped in situ at low temperature in useful yields, and others have suggested that aroyl anions might be involved in the fluoride-catalyzed reactions of aroyl trimethylsilanes.[3,4] In the gas phase the formyl anion arises by proton abstraction from formaldehyde,[5] but the resulting formyl anion is such a strong hydride donor[6] that its reactions cannot be considered typical. Nibbering[7] has recently prepared the benzoyl anion, but only a few of its reactions were noted. Schleyer[8] has carried out MNDO and ab initio molecular orbital calculations on acyl anions and made predictions about their basicity and heats of formation.

We wish to report that in our flowing afterglow apparatus the acetyl anion can readily be prepared by the reaction shown in eq 1.[9,10]

$$F^- + (CH_3)_3Si\overset{\overset{\displaystyle O}{\displaystyle \|}}{-}C-CH_3 \longrightarrow CH_3\bar{C}{=}O + (CH_3)_3SiF \quad (1)$$

$$\underset{\textbf{1}}{} \qquad \underset{\substack{\textbf{II}\\m/z\ 43}}{}$$

Anion II is the major product of the reaction, but small amounts of M − 1 and other high-mass ions are also produced.[11] Since

(8) Flynn, K. M.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983,** *105,* 7460–7461.

(9) For an interesting analysis of the relative donor and acceptor abilities of some trialkylphosphine complexes, see: Bursten, B. E.; Darensbourg, D. J.; Kellogg, G. E.; Lichtenberger, D. L. *Inorg. Chem.* **1984,** *23,* 4361–4365.

(10) Hutter, G.; Schmid, H.-G.; Frank, A.; Orama, O. *Angew. Chem., Int. Ed. Engl.* **1976,** *15,* 234.

(11) The Fenske–Hall nonempirical molecular orbital method has been described elsewhere (Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972,** *11,* 768–775) and its uses reviewed (Fenske, R. F. *Pure Appl. Chem.* **1971,** *27,* 61–71. Fenske, R. F. *Prog. Inorg. Chem.* **1976,** *21,* 179–208). A method devoid of adjustable parameters, the results depend only upon the internuclear distances and atomic basis sets. In our calculation, the geometries have been idealized while retaining the integrity of the crystal structure data. Bond lengths and angles used are P–H 1.40 Å, P–P 2.02 Å, C–O 1.15 Å, Cr–P 2.36 Å, Cr—P≕P 120°, and H—P≕P 120°.

(12) (a) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975,** *14,* 1058–1076. (b) Hoffmann, R.; Albright, T. A.; Thorn, D. L. *Pure Appl. Chem.* **1978,** *50,* 1–9.

(1) (a) Boulder. (b) Denver. (c) University of Puerto Rico.

(2) Seyferth, D.; Hui, R. C. *Organometallics* **1984,** *3,* 327–329.

(3) (a) Degl'Innocenti, A.; Pike, S.; Walton, D. R. M.; Seconi, G.; Ricci, A.; Fiorenza, M. *J. Chem. Soc., Chem. Commun.* **1980,** 1201–1202. (b) Ricci, A.; Degl'Innocenti, A.; Chimichi, S.; Fiorenza, M.; Rossini, G.; Bestmann, H. J. *J. Org. Chem.* **1985,** *50,* 130–133.

(4) Schinzer, D.; Heathcock, C. H. *Tetrahedron Lett.* **1981,** *22,* 1881–1884. In ref 12 the authors note that an aliphatic acylsilane can be protodesilylated to an aldehyde in the presence of fluoride ion.

(5) Karpas, Z.; Klein, F. S. *Int. J. Mass Spectrom. Ion Phys.* **1975,** *18,* 65–68.

(6) Kleingeld, J. C.; Ingemann, S.; Jalonen, J. E.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1983,** *105,* 2474–2475.

(7) Kleingeld, J. C.; Nibbering, N. M. M. *Tetrahedron* **1984,** *40,* 2789–2794.

(8) Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981,** *103,* 5612–5613.

(9) The acetyltrimethylsilane was prepared by the method of: Soderquist, J. A.; Hsu, G. J.-H. *Organometallics* **1982,** *1,* 830–833.

(10) The generation of gas-phase anions from trimethylsilyl compounds is reported by: DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A. Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1980,** *102,* 5012–5015.