

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  $\text{H}_2\text{P}_2\text{Cr}(\text{CO})_5$  with structure A of Figure 1 as our model. This compound is analogous to the compound  $[\text{CH}(\text{SiMe}_3)_2]_2\text{P}_2\text{Cr}(\text{CO})_5$  prepared by Flynn, Hope, Murray, Olmstead, and Power.<sup>4</sup> 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  $\text{PR}_3\text{Cr}(\text{CO})_5$ , in which the phosphorus atom has been interpreted as a simple two-electron  $\sigma$  donor. Consequently, the doubly bonded group 15 ligands exhibiting the end-on mode of coordination have also been interpreted as simple two-electron  $\sigma$  donors.<sup>3-9</sup>

In our theoretical study on the idealized  $\text{H}_2\text{P}_2\text{Cr}(\text{CO})_5$  complex, we employed Fenske-Hall molecular orbital calculations<sup>11</sup> and partitioned the molecules into two parts: the  $\text{Cr}(\text{CO})_5$  metal moiety and the  $\text{P}_2\text{H}_2$  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  $\text{P}_2\text{H}_2$  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  $\text{Cr}(\text{CO})_5$  moiety, which have been described previously in great detail,<sup>12</sup> 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  $d_z$  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  $\text{P}_2\text{H}_2$  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  $d_z$  orbitals forming the lower  $a'$  level, a localized three-center two electron interaction. Transfer of electrons from the  $\text{H}_2\text{P}_2$  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  $\pi$  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  $\sigma$  and  $\pi$  interactions upon complexation to the metal, an electronic structure much more intricate than the pure  $\sigma$ -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.

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### Gas-Phase Reactions of the Acetyl Anion

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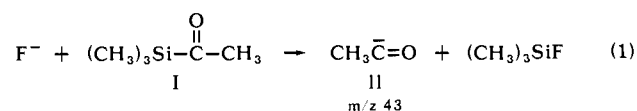
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Among the common types of carbanions acyl anions,  $\text{R}\bar{\text{C}}=\text{O}$ , are exceptional in that their chemical reactions have hardly been studied, either in solution or in the gas phase. This is so because aldehydes, their most obvious precursors, react most commonly by enolate formation or nucleophilic addition rather than by abstraction of the weakly acidic acyl hydrogen. Seyferth<sup>2</sup> 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.<sup>3,4</sup> In the gas phase the formyl anion arises by proton abstraction from formaldehyde,<sup>5</sup> but the resulting formyl anion is such a strong hydride donor<sup>6</sup> that its reactions cannot be considered typical. Nibbering<sup>7</sup> has recently prepared the benzoyl anion, but only a few of its reactions were noted. Schleyer<sup>8</sup> 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.<sup>9,10</sup>



Anion II is the major product of the reaction, but small amounts of  $M - 1$  and other high-mass ions are also produced.<sup>11</sup> 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.; Darenbourg, 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.

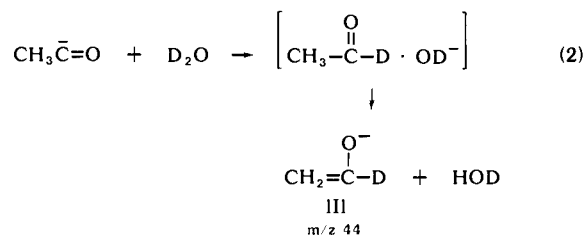
(11) The Fenske-Hall nonempirical molecular orbital method has been described elsewhere (Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768-775) and its uses reviewed (Fenske, R. F. *Pure Appl. Chem.* **1971**, *27*, 61-71). Fenske, R. F. *Prog. Inorg. Chem.* **1976**, *21*, 179-208. A method 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.

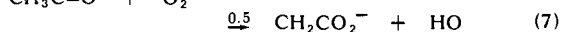
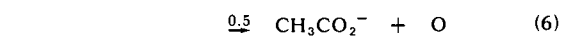
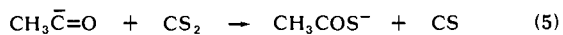
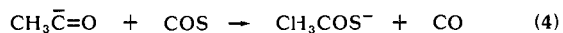
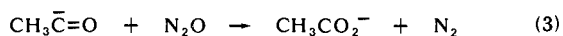
II is a strong base (vide infra) it reacts readily with I, so that maximum amounts of II arise at low conversions of reaction 1.

Ion II reacts in a completely different manner from its isomer, acetaldehyde enolate (III). It is a strong base, and  $m/z$  43 is converted completely into  $m/z$  44 by reaction with  $D_2O$  (eq 2).



No  $\text{DO}^-$  is produced in this reaction, which suggests that the first step is endothermic or thermoneutral and that II is less basic than hydroxide ion ( $\Delta H^\circ_{\text{acid}}(\text{H}_2\text{O}) = 391 \text{ kcal/mol}$ ).<sup>12</sup> This conclusion is strengthened by the observation of a small amount of allyl anion when II is allowed to react with a large excess of propylene ( $\Delta H^\circ_{\text{acid}} = 391 \text{ kcal/mol}$ ).<sup>12</sup> If we postulate  $\Delta H^\circ_{\text{acid}} = 390 \pm 2 \text{ kcal/mol}$  for the acyl hydrogen in acetaldehyde, the electron affinity of the acetyl radical  $\text{CH}_3\bar{\text{C}}=\text{O}$  can be calculated to be  $0.42 (\pm 0.10) \text{ eV}$  (10 kcal/mol), and indeed a small amount of  $\text{O}_2^-$  is formed when an excess of  $\text{O}_2$  ( $\text{EA} = 0.44 \text{ eV}$ )<sup>13</sup> reacts with II.<sup>14</sup> These conclusions are strongly supported by preliminary photodetachment data of Nimlos et al.,<sup>15</sup> which give  $\text{EA}(\text{CH}_3\bar{\text{C}}=\text{O}) = 0.438 (\pm 0.020) \text{ eV}$ .

The acetyl anion is highly reactive and atom transfer is observed with  $\text{N}_2\text{O}$ ,<sup>16</sup>  $\text{COS}$ ,<sup>17</sup> and  $\text{CS}_2$ .<sup>18</sup> The main products of its reaction with oxygen<sup>19</sup> also involve atom transfer.<sup>20</sup>



(11) The  $(M-1)$  ion from I is a minor product (<10%). Traces of ions corresponding to  $(M+F-\text{CH}_4)^-$  and  $(M+F-\text{C}_2\text{H}_4\text{O})^-$  are also detected.

(12) Bartmess, J. E.; McIver, R. T., Jr. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11. Stewart, J. H.; Shapiro, R. H.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* 1977, 99, 7650-7653.

(13) Celotta, R. J.; Bennett, R. A.; Hall, J. L.; Siegel, M. W.; Levine, J. *Phys. Rev. A* 1972, A6, 631.

(14) For this calculation we have used a value of 86 kcal/mol for the bond dissociation energy of the carbon-hydrogen bond (McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* 1982, 33, 493-532) and 313.6 kcal/mol for the ionization potential of the hydrogen atom (Stull, D. R.; Prophet, H. "JANAF Thermochemical Tables"; NSRDS-NBS-37, 2nd ed., National Bureau of Standards, Washington, DC, 1971). From this value for the electron affinity of the acetyl radical the heat of formation of acetyl anion can be calculated to be  $\Delta H_f^\circ_{298} = -17 \text{ kcal/mol}$ . These results are in perfect agreement with those calculated by Schleyer<sup>8</sup> when zero-point energy corrections are included in the latter.

(15) Nimlos, M. R.; Soderquist, J. A.; Ellison, G. B., private communication.

(16) Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H. *J. Am. Chem. Soc.* 1977, 99, 5800-5802.

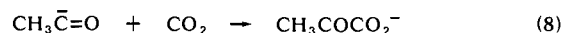
(17) DePuy, C. H.; Bierbaum, V. M. *Tetrahedron Lett.* 1981, 21, 5129-5130.

(18) DePuy, C. H. *Org. Mass Spectrom.*, in press.

(19) Bierbaum, V. M.; Schmitt, R. J.; DePuy, C. H. *EHP Environ. Health Perspect.* 1980, 36, 119-124.

(20) A referee has noted that atom transfer from  $\text{N}_2\text{O}$  or  $\text{COS}$  to the acetyl anion cannot be distinguished by mass from methide ion transfer from the acetyl anion to these reagents. However, we do not believe that methide ion transfer occurs based on the fact that this process is not observed with  $\text{CS}_2$  nor with hexafluoroacetone. The decomposition of the acetyl anion to methide and CO is endothermic by 24 kcal/mol. We hope to find alkide ion-transfer reactions with substituted acetyl anions for which the analogous decomposition is less endothermic.

It also undergoes addition reactions, for example with  $\text{CO}_2$ .<sup>16</sup>



It seems likely that this method will prove general for the formation of acyl anions in the gas phase, and further investigations are currently in progress.

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**Registry No.**  $\text{CH}_3\text{CO}^-$ , 64723-93-9;  $(\text{CH}_3)_3\text{SiCOCH}_3$ , 13411-48-8; F-, 16984-48-8;  $\text{CH}_3\bar{\text{C}}\text{O}$ , 3170-69-2.

### Energetics of a Homogeneous Gas-Phase Photocatalytic System: The Hydrogenation of Ethylene by $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$

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An interesting class of photochemical reactions consists of those processes in which photofragmentation generates an active thermal catalyst. Particularly important examples exist for which the catalyst and its precursor are organometallic complexes. In such cases, when the photochemical initiation step is reversible, photocatalytic activity can be maintained almost indefinitely, and the overall conversion process is highly efficient in its use of photons. The kinetics of the reversion step are critical; its rate regulates the turnover number and irreversible loss of photoprepared catalysts.<sup>1,2</sup>

Recent work in our laboratory has concentrated on the elementary kinetics of photoinitiated homogeneous catalytic processes of organometallic complexes in the *gas phase*.<sup>1,2</sup> There the distinction between various competing *molecular* interactions is particularly sharp, and the importance of reversion becomes a natural focus.

Our system of principal interest has been the iron carbonyl photocatalyzed hydrogenation of ethylene, Scheme I.

We have recently measured<sup>2</sup> the rate constant for catalyst,  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)$ , recombination with CO to be nearly 3 orders of magnitude smaller than that determined elsewhere for  $\text{Fe}(\text{C}-\text{O})_4$ .<sup>3</sup> The present paper traces the source of this kinetically important difference to a substantial activation energy for the reaction of CO with the ethylene-substituted complex.

Figure 1 shows quantum yields for  $\text{C}_2\text{H}_4$  hydrogenation measured<sup>1,2</sup> as function of laser repetition rate at three temperatures. The yield per photon declines at high repetition rates because successive laser pulses perturb catalytic cycles still working from previous pulses. The point at which this perturbation becomes significant allows us to estimate the lifetime of the catalyst,  $\tau = (k_R[\text{CO}])^{-1}$ . Taken together with a knowledge of the low repetition rate, maximum quantum yield,  $\Phi_{\text{max}}$ , this lifetime information gives the turnover rate (TOR) of the catalyst:

$$\text{TOR} = \Phi_{\text{max}}/\tau \quad (1)$$

The results are summarized in Table I. We obtain an Arrhenius temperature dependence for TOR yielding an activation energy for the substrate-saturated cycle of  $9.4 \pm 1.3 \text{ kcal/mol}$ .

(1) Whetten, R. L.; Fu, K.-J.; Grant, E. R. *J. Chem. Phys.* 1982, 77, 3769-3770.

(2) Miller, M. E.; Grant, E. R. *J. Am. Chem. Soc.* 1984, 106, 4635-4636.

(3) Ouderkirk, A. J.; Weitz, E. *J. Chem. Phys.* 1983, 79, 1089-1091.