

thermal<sup>12</sup> and photochemical<sup>28</sup> reactions of  $(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  with diphenylacetylene. When the photolysis is performed at low temperatures,<sup>29</sup> the dinuclear compound  $(\eta\text{-C}_5\text{H}_5)_2\text{Co}_2(\mu\text{-CO})(\text{C}_2\text{Ph}_2)$  is also produced. The cyclobutadiene complex is also obtained in the thermal reaction of cyclopentadienylcobalt cyclooctadiene with diphenylacetylene.<sup>30</sup> Similar cyclopentadienylcobalt reactions with trifluoropropyne have not been reported, but thermal reaction<sup>21</sup> of this alkyne with cobalt octacarbonyl has been shown to yield the dinuclear complexes  $\text{Co}_2(\text{CO})_6(\text{CF}_3\text{C}_2\text{H})$  and  $\text{Co}_2(\text{CO})_4(\text{CF}_3\text{C}_2\text{H})_3$  as well as a three-metal system,  $\text{Co}_3(\text{CO})_9(\text{CF}_3\text{CH}_2\text{C})$ .

It is clear, then, that in general the products formed in the metal atom reactions of cobalt atoms, cyclopentadiene, and alkynes differ considerably from those produced in the analogous thermal and photochemical reactions. Evidently, the products found in each type of reaction are a function of the intermediate species produced in that reaction. For instance, in the photochemical reaction of  $(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  with diphenylacetylene, the primary intermediate has been postulated<sup>31</sup> to be the unsaturated monocarbonyl species  $(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CO})$  which can then coordinate two alkynes to yield the cyclopentadienone complex. Similar intermediates have also been suggested for the thermal reactions of  $(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ . It is apparent then that the presence of the carbonyl ligand has a large effect on both the intermediates and products formed in these thermal and photochemical reactions of cyclopentadienyl cobalt. In contrast, the analogous metal atom reactions which do not include the carbonyl ligands may proceed through a  $(\eta\text{-C}_5\text{H}_5)\text{CoH}$  reactive fragment as noted above. This different reactive species in conjunction with the unique synthetic conditions results in the production of a variety of compounds including both mono- and multimetal systems which are not found in the conventional reactions.

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## Lewis Basicity, Reactivity, and Bond Order of Metal Acetyls. Boron and Aluminum Halide Adducts of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)$

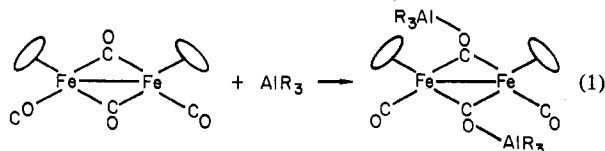
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The formation and characterization of the compounds  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)\cdot\text{MX}_3$  ( $\text{M} = \text{B}$ ,  $\text{X} = \text{F}$ ,  $\text{Cl}$ ,  $\text{Br}$ ;  $\text{M} = \text{Al}$ ,  $\text{X} = \text{Br}$ ,  $\text{CH}_3$ ) was undertaken to provide a comparison of basicities and reactivities of the carbonyl moiety in ketones, a metal acetyl, and polynuclear metal carbonyls. A quantitative equilibrium study, using FT-IR methods and qualitative  $\text{BF}_3$  dissociation pressure data, demonstrates the following order of basicity toward the reference acid  $\text{BF}_3$ :  $(\text{CH}_3)_2\text{C}=\text{O} < (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3) > (\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ . Upon interaction with a Lewis acid  $\nu(\text{CO})$  decreases for the basic CO in all three of the above-mentioned bases, with the order of decrease being  $(\text{CH}_3)_2\text{C}=\text{O} < (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3) < (\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ . This trend is attributed to the tendency of adduct formation to induce delocalization of electrons from d orbitals on the metal to the  $>\text{C}=\text{O}$  moiety, and such an interpretation is borne out by vibrational spectroscopic data. For example, a  $\nu(\text{CO})$  vs. bond order correlation demonstrates that metal acetyl adducts are analogues of Fischer-type metal carbene complexes. Reactions other than basicity are compared for ketonic, metal acetyl, and metal-bridging carbonyls.

### Introduction

Ketones are well-known as mild Lewis bases, and the resulting complexes with boron and aluminum halides have been studied with respect to their physical properties and reactivity.<sup>1-5</sup> More recently, CO-bridged polynuclear metal complexes have been found to display Lewis basicity through the oxygen of the bridging carbonyls (e.g., reaction 1).<sup>6</sup> In the

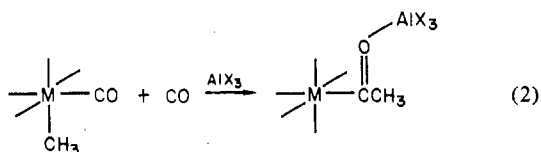


present work we have explored the Lewis basicity and reactivity of metal acyls, which at least in a structural sense, can be considered to be intermediate between ketones and CO-bridged polynuclear carbonyls. Lukehart and co-workers have studied extensively the chemistry of diacyl complexes,<sup>7-9</sup> but the basicity of neutral monoacyl metal complexes has received very little attention. Two noticeable exceptions are the observation of adduct formation between the NMR shift reagent  $\text{Eu}(\text{fod})_3$  with the acyl oxygen of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})[\text{P}(\eta\text{-C}_4\text{H}_9)_3](\text{C}(\text{=O})\text{CH}_3)$ <sup>10</sup> and protonation of the acyl oxygen in  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{L})(\text{C}(\text{=O})\text{CH}_3)$ .<sup>11</sup>

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Our interest in characterizing metal acetyl adducts stems in part from a desire to obtain a systematic picture of carbonyl basicity in a variety of environments. Of more immediate importance is the need for data on Lewis acid adducts of metal acyls in connection with work on Lewis acid promoted CO insertion reactions, in which metal acyl adducts are produced (eq 2).<sup>12</sup>



### Experimental Section

A commercial sample of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$  (Pressure Chemical Co.) was used as received to prepare  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)$  according to King's procedure.<sup>13,14</sup> The latter was judged pure by proton NMR and infrared spectra. The volatile reactants,  $\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{BBR}_3$ ,  $\text{AlMe}_3$ , and  $\text{NMe}_3$ , were purified by trap-to-trap distillation until their vapor pressures agreed with literature values.<sup>15</sup> Aluminum tribromide was purified by sublimation. All solvents were distilled under a nitrogen atmosphere from calcium hydride, sodium benzophenone ketyl, or Drierite and purged with nitrogen prior to use. Solvents which were manipulated in the vacuum line were degassed by freeze-pump-thaw cycles and stored over  $\text{P}_2\text{O}_5$ .

All samples were manipulated by vacuum-line or standard inert-atmosphere techniques. Reactions were carried out at room temperature (25–30 °C). All adducts decomposed upon exposure to air.

$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)\cdot\text{BF}_3$ . On the vacuum line an excess of  $\text{BF}_3$  (1.85 mmol) was trapped at liquid- $\text{N}_2$  temperature onto 0.568 mmol of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)$  in 6 mL of toluene. As the solution warmed to room temperature, the adduct precipitated as a light colored solid. The solution was stirred about 10 min at 25 °C, and unreacted  $\text{BF}_3$  was pulled away. The stoichiometry of the reaction was determined tensimetrically by measuring the initial and unreacted  $\text{BF}_3$ , yielding a 1.0:0.93 ratio of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)$  to  $\text{BF}_3$ . As a further check, all volatiles were removed from the reaction mixture,  $\text{BF}_3$  was separated by trap-to-trap distillation, and the excess was determined by *PVT* measurement, confirming a 1:1 interaction. The product, a light yellow, air-sensitive powder, was isolated by filtration and washed with toluene.

$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)\cdot\text{BCl}_3$ . To a solution of 0.737 mmol of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)$  in 5 mL of toluene was added 1.66 mmol of  $\text{BCl}_3$ . After a light beige solid had precipitated, the toluene and excess  $\text{BCl}_3$  were transferred to a separate trap. The stoichiometry of reaction, determined by weight gain of the adduct, established the interaction as 1.0:1.0, and the amount of excess  $\text{BCl}_3$  was determined by addition of pyridine to the previously separated  $\text{BCl}_3$ -toluene mixture to form the known  $\text{BCl}_3\cdot\text{NC}_5\text{H}_5$  adduct, which was weighed.<sup>16</sup> This measurement gives a ratio of adduct formation of (1.0:0.938)  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3):\text{BCl}_3$ .

$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)\cdot\text{BBR}_3$ . Addition of 1.98 mmol of  $\text{BBR}_3$  to 1.30 mmol of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)$  in 6 mL toluene resulted in the formation of a light yellow precipitate. The solvent and excess  $\text{BBR}_3$  were removed from the reaction flask. Weight gain of the product indicated a 1.0:1.0 stoichiometry which was confirmed by a "back-titration" of the excess  $\text{BBR}_3$  with  $\text{NMe}_3$ .

$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)\cdot\text{AlMe}_3$ . To a hexane solution of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)$  (0.586 mmol) was added 4.16 mmol of  $\text{AlMe}_3$ . Some decomposition was evident as the resulting solution contained black solids, but the infrared spectrum showed a shift in the terminal CO stretches indicative of adduct formation. There were also weak bands due to free acetyl compound. Addition of 4.16 mmol of  $\text{NMe}_3$  regenerated  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)$  as detected

by IR methods. A solid adduct was not isolated.

$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)\cdot\text{AlBr}_3$ . A twofold excess of  $\text{AlBr}_3$  (1.8 mmol) was added to a  $\text{CH}_2\text{Cl}_2$  solution of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)$ . The initially yellow-orange solution became dark red, but no solids were formed. The infrared spectrum was taken as evidence for complete adduct formation. Addition of  $\text{NMe}_3$  to the adduct yielded the yellow-orange solution and an IR spectrum characteristic of the parent acyl compound. The adduct was not isolated as a solid.

$(\text{CH}_3)_2\text{CO}\cdot\text{BF}_3$ . On the vacuum line, 0.22 mmol of  $(\text{CH}_3)_2\text{CO}$  was distilled into 5 mL of  $\text{CH}_2\text{Cl}_2$ , forming a 0.44 M solution. After addition of 1 equiv of  $\text{BF}_3$ , the solution remained colorless, and the IR spectrum indicated complete adduct formation. The IR data are in agreement with literature values.<sup>1</sup>

$\text{Mn}(\text{CO})_5(\text{C}(\text{=O})\text{CF}_3) + \text{BF}_3$ . An excess of  $\text{BF}_3$  (1.32 mmol) was added to 0.820 mmol of  $\text{Mn}(\text{CO})_5(\text{C}(\text{=O})\text{CF}_3)$  in 10 mL of toluene. When the solution stood overnight, there was a 25% (based on  $\text{Mn}(\text{CO})_5(\text{C}(\text{=O})\text{CF}_3)$ ) uptake of  $\text{BF}_3$ , but removal of the solvent under vacuum reversed the reaction, and only solid  $\text{Mn}(\text{CO})_5(\text{C}(\text{=O})\text{CF}_3)$  remained.

**Infrared Spectra.** All infrared spectra were recorded on either a Perkin-Elmer 283 or a Nicolet 7199 FT-IR. Solid-state IR spectra were obtained as Nujol or Fluorolube mulls between KBr plates. Solution spectra were obtained from 0.04 M  $\text{CH}_2\text{Cl}_2$  solutions in an Irtran-2 windowed cell with a path length varying between 0.5 and 0.23 mm. Solvent reference spectra, obtained by using the sample cell, were digitally subtracted from the sample spectra, thus deleting solvent peaks.

Solution equilibria were studied by the determination of molar absorptivities for the  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)/\text{CH}_2\text{Cl}_2$  and  $(\text{CH}_3)_2\text{CO}/\text{CH}_2\text{Cl}_2$  systems. In a typical experiment, the spectrum of a known concentration of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)$  or  $(\text{CH}_3)_2\text{CO}$  in  $\text{CH}_2\text{Cl}_2$  was recorded and the solvent subtracted out. Absorbances were measured directly from this subtracted spectrum. The cell path length was determined on the empty or reference cell by the fringe method.<sup>17</sup>

In both systems the CO stretching frequencies are the most prominent bands and are used to monitor the equilibrium under investigation. Absorptivities for  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)$  were determined at 3 wavelengths: 2019, 1960, and 1647  $\text{cm}^{-1}$ . The high-frequency bands are assigned to terminal CO symmetric and asymmetric stretches and the lower frequency bands to the acyl moiety. For acetone, the molar absorptivity was determined for the  $\nu(\text{CO}) = 1712\text{-cm}^{-1}$  band. Molar absorptivity values were determined at several concentrations, and the values used in subsequent equilibrium calculations are the averages of three or four measurements.

<sup>1</sup>H NMR. Proton NMR spectra were recorded in methylene- $d_2$  chloride solutions on a CFT-20 90-MHz FT-NMR unit.

### Results and Discussion

**Formation and Characterization of Metal Acyl Adducts.** The interaction of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)$  with the boron halides was followed by the stoichiometry of Lewis acid uptake. In the case of  $\text{BF}_3$ , the formation of a 1:1 adduct was readily demonstrated by pressure measurements of initial and unreacted  $\text{BF}_3$ . With the less volatile Lewis acids  $\text{BCl}_3$  and  $\text{BBR}_3$  a measured excess of Lewis acid was employed for the reactions, and the unreacted boron halide was subsequently separated from the reaction mixture and measured. In both cases 1:1 adduct formation was found. Adduct formation also was observed spectroscopically with  $\text{Al}(\text{CH}_3)_3$  and  $\text{AlBr}_3$ , and back-reaction of these systems with trimethylamine followed by spectroscopic identification of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)$  demonstrated that the Lewis acid metal acyl compounds are simple adducts and not more complex products, which might, for example, result from addition across the C=O bond.

**Spectroscopic Characterization.** Infrared spectra of the boron halide adducts reveal large decreases in  $\nu(\text{CO})$  for the acetyl carbonyl upon adduct formation. This decrease is in full accord with previous experience with ketones and poly-

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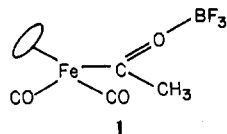
Table I. CO Stretching Frequencies (cm<sup>-1</sup>) in Organometallic and Organic Carbonyls and Their Adducts

| parent metal compd  | Lewis acid                         | $\nu(\text{CO})$                        |                          |                                | $\Delta\nu(\text{CO})$<br>>CO-M |
|---|------------------------------------|---|--------------------------|--------------------------------|---------------------------------|
|   |                                    | terminal                                | >CO-M                    | >CO                            |                                 |
| $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)$ | none                               | 2020 (2015) <sup>a</sup><br>1961 (1962) |                          | 1653 (1645)                    |                                 |
|   | BF <sub>3</sub>                    | 2054 (2052)<br>2004 (1999)              | 1492 <sup>b</sup> (1463) |                                | 161                             |
|   | BCl <sub>3</sub>                   | 2057 (2055)<br>2011 (2006)              | 1421 <sup>b</sup> (1360) |                                | 232                             |
|   | BBr <sub>3</sub>                   | 2060 (2055)<br>2014 (2006)              | 1389 <sup>b</sup> (1332) |                                | 264                             |
|   | AlBr <sub>3</sub>                  | 2060<br>2000                            | 1462 <sup>c</sup>        |                                |                                 |
|   | AlMe <sub>3</sub>                  | 2051<br>2000                            | <i>d</i>                 |                                |                                 |
|   | (CH <sub>3</sub> ) <sub>2</sub> CO | none                                    |                          |                                | 1712                            |
| $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2^e$                           | BF <sub>3</sub>                    |   | 1649                     |                                | 63                              |
|   | none                               | 1930<br>1971                            |                          | 1765, 1797                     |                                 |
|   | BCl <sub>3</sub>                   | 2038, 2020                              | 1463                     | 1845                           | ~317                            |
|   | BBr <sub>3</sub>                   | 2030, 2008 (sh)<br>2020, 1984 (sh)      | 1438                     | 1848                           | ~342                            |
| $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4^e$                             | none                               |   |                          | 1640                           |                                 |
|   | BF <sub>3</sub>                    |   | 1365                     | 1694, 1674, 1632<br>1689, 1671 | 275                             |
|   | BCl <sub>3</sub>                   |   | 1292                     | 1702, 1671                     | 348                             |
|   | BBr <sub>3</sub>                   |   | 1312, 1301               | 1705, 1672                     | ~334                            |
|   | AlBr <sub>3</sub>                  |   | 1392                     | 1700, 1673                     | 248                             |
|   |                                    |   |                          |                                |                                 |

<sup>a</sup> Values in parentheses were determined on solids. <sup>b</sup> Solution spectra in CD<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> Solution spectrum in toluene. <sup>d</sup> Obscured by solvent and aluminum alkyl. <sup>e</sup> Data in this table are for the 1:1 adduct only.

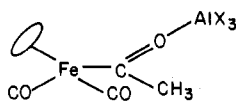
nuclear carbonyls. For example,  $\nu(\text{CO})$  is found to decrease by 63 cm<sup>-1</sup> when acetone interacts with BF<sub>3</sub> and by ~318 cm<sup>-1</sup> upon addition of BCl<sub>3</sub> to the bridging carbonyls of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ .<sup>18</sup> Other frequencies in the metal acyl are less affected by interaction with the Lewis acid. The most useful and diagnostic of these other shifts is the small but distinct increase in  $\nu(\text{CO})$  for terminal carbonyls (see Table I). This increase is analogous to the increases in terminal  $\nu(\text{CO})$  of polynuclear carbonyls and of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CN})$  upon adduct formation (at bridging carbonyls and cyanide, respectively).<sup>18,19</sup> The increase also is in harmony with the expectation that there is an electron demand placed on Fe by the formation of a FeC(=OBF<sub>3</sub>)CH<sub>3</sub> adduct, and this demand should decrease  $\pi$  back-bonding between Fe and the terminal carbonyls. An increase of ~50 cm<sup>-1</sup> in the frequency of the terminal CO's is observed when the acyl,  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{C}(\text{=O})\text{CH}_3)$ , is protonated to form a hydroxy methyl carbene  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{C}(\text{OH})\text{CH}_3)]^+$ .<sup>11</sup>

The systematics found in the various  $\nu(\text{CO})$  values clearly show that the boron halide adducts possess structure 1. The



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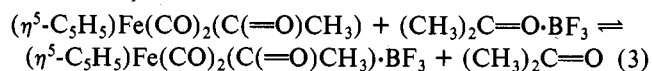
infrared spectroscopic experiments and regeneration of parent  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)$  by addition of base to the adducts also imply the formation of complexes 2a,b even though stoichiometry data are unavailable for their formation.



2a, X = Br  
b, X = CH<sub>3</sub>

Details of the shifts in  $\nu(\text{CO})$  upon adduct formation, which are collected in Table I, will be discussed further in connection with the chemistry of the metal acetyl adducts.

**Reactivity of Metal Acetyl Adducts.** The solid adducts hydrolyze rapidly upon exposure to air but are stable indefinitely under an inert atmosphere at room temperature. The surface of the BBr<sub>3</sub> adduct stored in the drybox darkens over a period of a few days, indicating that it might be slightly photosensitive. The solid adducts are stable toward loss of BX<sub>3</sub>. Under vacuum (10<sup>-3</sup> torr) at room temperature they display no measureable vapor pressure and show no signs of decomposition, indicating a strong donor-acceptor interaction. The basicities of the metal acetyls relative to ketones were determined by a series of quantitative FT-IR equilibrium studies in which  $K_{\text{eq}}$  was found for eq 3 at 25 °C. Molar absorptivities



were determined for the various CO bonds of the uncomplexed metal acetyl in CH<sub>2</sub>Cl<sub>2</sub> (2019 cm<sup>-1</sup>,  $\epsilon = 196$ ; 1960 cm<sup>-1</sup>,  $\epsilon = 214$ ; 1647 cm<sup>-1</sup>,  $\epsilon = 53$ ) and for acetone in CH<sub>2</sub>Cl<sub>2</sub> solution (1712 cm<sup>-1</sup>,  $\epsilon = 44$ ). The equilibrium was approached from both directions, i.e., either metal acetyl adduct plus acetone or acetone adduct plus metal acetyl, and a total of six measurements were made in the concentration range 0.037–0.049 M for  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)$  and 0.037–0.12 M for acetone, yielding  $K_{\text{eq}} = 51 \pm 9$  at 25 °C for equilibrium 3. Thus the metal acetyl is significantly more basic than acetone toward the hard acid BF<sub>3</sub>.

Adduct stabilities provide qualitative information on the relative basicities of bridging polynuclear metal carbonyls and metal acetyls. Even though  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2 \cdot \text{BF}_3$  can be prepared at -78 °C, it is unstable with respect to complete loss of BF<sub>3</sub> at room temperature.<sup>18</sup> In contrast, the acetyl complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3) \cdot \text{BF}_3$  is stable at room temperature and exhibits no measurable vapor pressure under high-vacuum conditions, indicating that it is the stronger base toward BF<sub>3</sub>. The trend in basicity  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2 < (\text{CH}_3)_2\text{CO} < (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)$  parallels the order of decreasing  $\nu(\text{CO})$  for the bridging carbonyls of the

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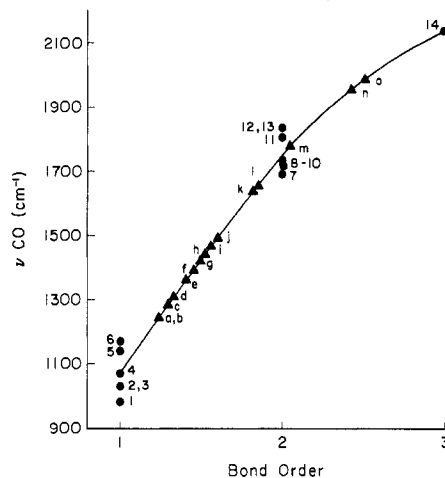
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parent bases  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2 > (\text{CH}_3)_2\text{CO} > (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)$ .

Reversible adduct formation characteristic of these metal carbonyls is not always observed for organic analogues. In organic chemistry further reaction beyond simple adduct formation is common, giving the reduced species as products. Under conditions similar to those employed in the present work, aluminum alkyls add across the C=O bond of ketones, yielding the corresponding alcohols on hydrolysis.<sup>20-22</sup> Addition across the double bond also is suspected in the reaction of benzophenone with  $\text{BCl}_3$ .<sup>23</sup> The acetone  $\text{BF}_3$  adduct has been prepared, isolated, and characterized,<sup>1</sup> but acetone and  $\text{BCl}_3$  produce HCl and a polymeric material.<sup>24</sup> In contrast to the simple 1:1 adducts reported in this work, when the Lewis acid employed is  $\text{BH}_3$ , a more extensive reaction occurs, resulting in formation of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CH}_2\text{CH}_3)$ . Presumably this reduction proceeds through adduct formation at the acyl oxygen, followed by addition of  $\text{BH}_3$  across the CO double bond which eventually leads to the ethyl complex.<sup>25</sup>

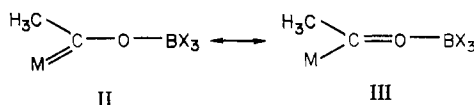
The generally lower reactivity toward addition across the C=O bond of the iron acyl complex than of simple ketones probably stems from the greater electron density on the C atom in the iron acetyl compound, arising from delocalization of electron density from the metal. Physical evidence for this hypothesis is developed in the next section.

**Shifts in  $\nu(\text{CO})$ .** The C–O stretching frequency is strongly influenced by the C–O bond order, but similar effects in  $\nu(\text{CO})$  may arise from coupling between the C–O stretching coordinate with other internal displacement coordinates<sup>26,27</sup> and the influence of ionic terms in the C–O potential. To provide a basis for comparison of the metal acetyl compounds, we constructed a bond order vs. frequency plot (Figure 1) from available data on carbon monoxide, ketones, ethers, and alcohols. The CO bond orders for these compounds were taken from their formal valencies, viz., 3 for CO, 2 for ketones, and 1 for ethers and alcohols. For compounds such as ethers where two  $\nu(\text{CO})$  values are observed, the average value is used in the plot. The rather wide spread in frequencies, which is evident for the ethers and alcohols, probably arises from the strong coupling between C–C and C–O coordinates in these molecules.<sup>26</sup> Coupling also is likely to be a significant factor for the ketones. Despite the approximate nature of this frequency vs. bond order plot, it provides useful insight into gross changes in CO bond orders for the organometallic carbonyls. We have drawn a curve through the data for the organic systems and then matched the frequencies of the organometallic systems to this curve to deduce relative bond orders. (On the basis of the results of vibrational calculations for ethyl acetate adducts,<sup>28</sup> coupling between the CO coordinates and O– $\text{MX}_3$  coordinates is thought to be small.) The resulting correlation (Figure 1) makes good chemical sense. The terminal carbonyl frequencies for neutral metal carbonyls fall around bond order 2.5, which agrees with the general interpretation that M–CO  $\pi$  back-bonding in these compounds lowers the bond order somewhat below 3. Similarly, metal acyls fall somewhat below bond order 2, indicating that the presence of the metal lowers the CO bond order below that in ketones. The influence of a metal center is again evident



**Figure 1.** CO stretching frequency vs. bond order. The curve was drawn through points for CO and organic carbonyl compounds which are labeled by numbers. Organometallics, indicated by letters, were placed on the curve according to their observed values of  $\nu(\text{CO})$ : 1,  $(\text{C}_2\text{H}_5)_2\text{O}$ ;<sup>26</sup> 2,  $(\text{CH}_3)_2\text{O}$ ;<sup>30</sup> 3,  $\text{CH}_3\text{OH}$ ;<sup>31</sup> 4,  $\text{C}_2\text{H}_5\text{OH}$ ;<sup>32</sup> 5,  $p\text{-ClC}_6\text{H}_4\text{OCH}_3$ ;<sup>33</sup> 6,  $\text{C}_6\text{H}_5\text{OCH}_3$ ;<sup>34</sup> 7,  $\text{C}_6\text{H}_5\text{C}(\text{=O})\text{CH}_3$ ;<sup>35</sup> 8,  $(\text{C}_6\text{H}_5)_2\text{CO}$ ;<sup>35</sup> 9,  $\text{C}_2\text{H}_5\text{C}(\text{=O})\text{CH}_3$ ;<sup>35</sup> 10,  $\text{C}_6\text{H}_5\text{C}(\text{=O})\text{H}$ ;<sup>35</sup> 11,  $\text{ClC}(\text{=O})\text{CH}_3$ ;<sup>35</sup> 12,  $\text{Cl}_2\text{CO}$ ;<sup>36</sup> 13,  $\text{Br}_2\text{CO}$ ;<sup>36</sup> 14, CO;<sup>37</sup> a,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{P}(\text{Hx})_3](\text{C}(\text{OCH}_3)\text{CH}_3)^+$ ;<sup>38</sup> b,  $(\text{CO})_5\text{W}(\text{C}(\text{OCH}_3)\text{CH}_3)$ ;<sup>39</sup> c,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4\text{BCl}_3$ ;<sup>18</sup> d,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4\text{BBr}_3$ ;<sup>18</sup> e,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4\text{BF}_3$ ;<sup>18</sup> f,  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)\cdot\text{BBr}_3$  (present work); g,  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)\cdot\text{BCl}_3$  (present work); h,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\cdot\text{BBr}_3$ ;<sup>18</sup> i,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\cdot\text{BCl}_3$ ;<sup>18</sup> j,  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)\cdot\text{BF}_3$  (present work); k,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$ ;<sup>18</sup> l,  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)$  (present work); m,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ ;<sup>18</sup> n,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  terminal  $\nu(\text{CO})$ ;<sup>18</sup> o,  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)$  terminal  $\nu(\text{CO})$  (present work).

in the comparison of  $\Delta\nu(\text{CO})$  of the organic adducts with the metal carbonyl adducts. The low value of  $\nu(\text{CO})$  for metal acetyl adducts (e.g., 1492  $\text{cm}^{-1}$  for  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)\cdot\text{BF}_3$  vs. 1649  $\text{cm}^{-1}$  for  $\text{CH}_3\text{COCH}_3\cdot\text{BF}_3$ ) suggests that the metal carbene resonance form II is a significant



contributor for the metal acyl adducts but is not a significant contributor for the aliphatic ketones. In keeping with this interpretation the metal acyl adducts are found in the bond order 1.5 range, which is close to the  $\sim 1.3$  bond order of the Fischer-type carbene complexes.<sup>29</sup> As judged by the shifts in  $\nu(\text{CO})$ , the carbene resonance form, II, becomes increasingly important in the series  $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$ . This trend parallels the order of acidity:  $\text{BF}_3 < \text{BCl}_3 \lesssim \text{BBr}_3$ . Thus it is seen that, physically as well as structurally, these Lewis acid

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adducts of metal acetyls are close analogues of Fischer-type carbenes.

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**Registry No.**  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)\cdot\text{BF}_3$ , 73104-94-6;  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)\cdot\text{BCl}_3$ , 73104-95-7;  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}$

$(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)\cdot\text{BBr}_3$ , 73104-96-8;  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)\cdot\text{AlMe}_3$ , 73104-97-9;  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)\cdot\text{AlBr}_3$ , 73104-98-0;  $(\text{CH}_3)_2\text{CO}\cdot\text{BF}_3$ , 661-27-8;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ , 12154-95-9;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\cdot\text{BCl}_3$ , 43198-12-5;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\cdot\text{BBr}_3$ , 41666-89-1;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_4]$ , 12203-87-1;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_4]\cdot\text{BF}_3$ , 39466-88-1;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_4]\cdot\text{BCl}_3$ , 39334-00-4;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_4]\cdot\text{BBr}_3$ , 39333-98-7;  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_4]\cdot\text{AlBr}_3$ , 39466-84-7;  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}(\text{=O})\text{CH}_3)$ , 12108-22-4;  $(\text{CH}_3)_2\text{CO}$ , 67-64-1.

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## Novel Bonding Modes of $\alpha$ -Diimines. Synthesis and Characterization of $[\text{MCl}_2\text{L}(\alpha\text{-diimine})]$ and $[\text{MCl}_2(\alpha\text{-diimine})_n]$ ( $\text{M} = \text{Pd}, \text{Pt}$ ; $\text{L} = \text{Phosphine}, \text{Arsine}$ ; $n = 1, 2$ ) Containing $\sigma, \sigma\text{-N}, \text{N}'$ , $\sigma\text{-N}$ , or $\sigma\text{-N} \leftrightarrow \sigma\text{-N}'$ Bonded $\alpha$ -Diimines

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Compounds of the type  $[\text{PdX}_2(\text{RN}=\text{CHCH}=\text{NR})_n]$  ( $n = 1, 2$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) and  $[\text{M}^{\text{II}}\text{Cl}_2\text{L}(\text{RN}=\text{CHCH}=\text{NR})]$  ( $\text{L} = \text{monodentate phosphine or arsine}$ ;  $\text{M} = \text{Pd}, \text{Pt}$ ;  $\text{R} = \text{alkyl}$ ) have been synthesized starting from the  $\alpha$ -diimine (R-dim) and  $[\text{PdCl}_2(\text{PhCN})_2]$  or  $[(\text{M}^{\text{II}}\text{Cl}_2\text{L})_2]$ , respectively. Three types of metal- $\alpha$ -diimine interactions have been established: (i)  $\sigma, \sigma\text{-N}, \text{N}'$  chelate bonded R-dim in  $[\text{PdX}_2(\text{R-dim})]$ ; (ii)  $\sigma\text{-N}$  monodentate bonded R-dim in monomeric *trans*- $[\text{PdX}_2(\text{R-dim})_2]$  ( $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy reveals that the R-dim ligand has the anti conformation with the C-C and Pd-N bonds of the coordinated part of the ligand in the cis configuration. This brings the  $\beta$ -imine proton ( $\delta(\text{CH})$  9.70) in the proximity of the palladium atom.); (iii)  $\sigma\text{-N} \leftrightarrow \sigma\text{-N}'$  bonded R-dim in the monomeric complexes, *trans*- $[\text{M}^{\text{II}}\text{Cl}_2\text{L}(\text{R-dim})]$ , which contain monodentate ( $\sigma\text{-N}$ ) bonded R-dim in the slow-exchange limit ( $-55^\circ\text{C}$ ). At  $120^\circ\text{C}$  (fast-exchange limit) the complexes are fluxional by an intramolecular process which involves a pentacoordinate intermediate containing  $\sigma, \sigma\text{-N}, \text{N}'$  bonded R-dim. These novel bonding modes for the R-dim ligand in these palladium and platinum complexes are a clear indication of the versatile coordination properties of the R-dim ligand compared with ligands such as bpy and phen, which also contain the  $\text{N}=\text{CC}=\text{N}$  skeleton.

A large number of metal- $\alpha$ -diimine complexes have been reported in which the  $\alpha$ -diimine (R-dim) ligand acts as a  $\sigma, \sigma$ -chelating ligand.<sup>1-4</sup> To date only a limited number of complexes of R-dim ligands with Pt, Pd, or Rh have been described. Maresca, Natile, and Cattalini<sup>5</sup> reported the isolation of  $[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{R-dim})]$  (R-dim = *N,N'*-di(cyclopropyl- or *p*-tolyl)biacetyl diimine) while Brodie and Otsuka<sup>6</sup> recently described the synthesis of palladium complexes with *N,N'*-(1,7,7-trimethylbicyclo[2.2.1]heptane-2,3-diyliidene)di-aniline ligands. In these complexes the R-dim ligand is also  $\sigma, \sigma$ -chelating.

These observations seem to be consistent with the  $\sigma, \sigma$ -bonding mode found for the related bipyridine (bpy) and phenanthroline (phen) ligands which like the R-dim ligand have two N lone pairs suitably positioned for symmetric coordination. Recently, Dixon<sup>7</sup> showed that the solid-state structure of  $[\text{PtCl}(\text{PEt}_3)_2(\text{phen})]\text{BF}_4$  contained two different Pt-N distances, pointing to a monodentate coordinated phen ligand. However, in solution no evidence for such monodentate behavior of the phen or bpy ligand in related  $[\text{PtCl}(\text{PEt}_3)_2(\text{bpy})]\text{BF}_4$  was found. This was explained by a fluxional process involving a simple oscillatory motion of the bpy and

phen ligands via a trigonal-bipyramidal transition state. It is important to note that this is a low-energy process due to the favorable orientation of the N lone pairs. In the phen ligand this lone-pair orientation is locked because of the rigid phen ring system. Apparently the bpy ligand also contains extra rigidity leading to high preference for the  $\sigma, \sigma$ -chelating bonding mode.<sup>8-10</sup> It can be anticipated that the monodentate bonding mode would be stabilized when conformations of the coordinating ligand having the coordinated and noncoordinated N atoms in trans positions would become more favorable. Comparison of the molecular skeleton of the R-dim and bpy ligands reveals that rotation around the NC-CN bond is less hindered in the R-dim ligand, both in the free molecule and in the monodentate bonded form.

In this paper we report the isolation and characterization of the first examples of stable metal-R-dim complexes in which the R-dim molecule is monodentate bonded.<sup>11</sup> Moreover, complexes will be described in which at low temperatures the R-dim molecule is bonded to the metal atom via one N atom while at higher temperatures the R-dim molecule rapidly exchanges its point of attachment to the metal from one N to the other. It will be shown that in particular the degree of flexibility of the R-dim skeleton plays an important role in the bonding mode of the R-dim ligand in these complexes.

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