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## Solution Infrared Study of Carbon- and Oxygen-Bonded Carbon Monoxide. The Interaction of Bridging Carbonyl Ligands with Aluminum Alkyls

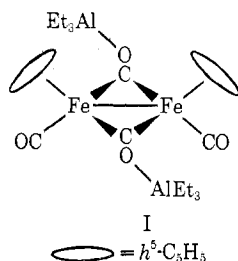
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As shown by the interaction of trialkylaluminum acceptors with polynuclear carbonyl derivatives, Lewis basicity is a fairly general property of bridging carbonyl groups. Diagnostic shifts in the  $\nu_{CO}$  region of the infrared spectra allow characterization of many complexes in solution which are not sufficiently stable to be isolated. Evidence is presented for the stepwise interaction of triethylaluminum or triisobutylaluminum with both of the bridging carbonyls in  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{CO})_2$  and with the four bridging carbonyls in  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$ . Under similar conditions only one of the two carbonyls in  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$  interacts with triisobutylaluminum. Compounds with the lowest bridging CO stretching frequencies appear to be the most basic. Adduct formation at a carbonyl ligand significantly increases the electron-acceptor character of the C- and O-bonded carbonyl.

### Introduction

In a previous paper,<sup>1</sup> describing the synthesis and crystal structure of a carbon- and oxygen-bonded carbonyl compound, I, it was shown that upon adduct



formation stretching frequencies of those carbonyls attached to triethylaluminum decrease by more than  $100\text{ cm}^{-1}$  while  $\nu_{CO}$  of the remaining carbonyls is increased by about  $40\text{ cm}^{-1}$ . Thus infrared spectroscopy in the CO stretch region affords a promising tool for the study of adduct formation by metal carbonyls. In the present work, solution infrared spectra were employed to demonstrate the stepwise addition of trialkylaluminum to bridging carbonyl groups. For a number of carbonyls it was possible to demonstrate adduct formation in solution at low temperatures, even though the adduct could not be isolated.

One objective of the present study was to test the generality of adduct formation between trialkylaluminum and bridging carbonyls. A second objective was to investigate the general physical and chemical consequences of C and O bonding, such as aluminum alkyl induced terminal-to-bridge CO shift.<sup>2</sup>

### Experimental Section

Trialkylaluminum solutions were handled by standard Schlenk and syringe inert atmosphere techniques.<sup>3</sup> Solid samples of some of the adducts were transferred for analyses and spectroscopy in a Vacuum Atmospheres glove box purged with boil-off high-purity liquid nitrogen. All solvents were distilled under a nitrogen atmosphere from calcium hydride or sodium benzophenone ketyl.

**Reagents.**—The carbonyl compounds  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2$  and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  were synthesized and purified according to

published procedures,<sup>4</sup> while other carbonyls were commercial samples which were purified before use. All of the carbonyl compounds were analyzed for C and H and satisfactory agreement with calculated values was obtained. Infrared spectra of the compounds agreed with the literature. Dicobalt octacarbonyl (Alfa) was sublimed before use. Infrared spectra indicated the presence of a significant tetracobalt dodecacarbonyl impurity which was advantageous for initial experiments because it allowed the reactivity of two carbonyls to be surveyed in one experiment. Triethylaluminum and triisobutylaluminum were used as obtained from Texas Alkyls Inc.

Elemental analyses on air-stable compounds were performed by Miss Hilda Beck of the Northwestern University Analytical Services Laboratory, and on air-sensitive compounds analyses were performed by Dornis and Kolbe, Mulheim (Ruhr), West Germany. Hydrolyzable ethyl groups were determined by fractionating hydrolysis products through traps cooled to  $-78^\circ$  and collecting the volatiles in a calibrated volume by a Toepler pump.

**Infrared Spectra.**—Reactions of the various metal carbonyls in dry, air-free hydrocarbon solution with added trialkylaluminum were monitored using matched NaCl windowed solution cells (0.750–0.914-mm path length). Several of the carbonyls underwent slow decomposition in the presence of aluminum alkyls. Therefore it became routine practice to mix solutions immediately prior to use and to cool the infrared cells by circulating a coolant ( $-3^\circ$ ) through the specially constructed cell face plates. Spectra were recorded on a Beckman IR9 spectrometer using an expanded scale to determine peak positions accurately. Each system was investigated at a series of trialkylaluminum concentrations to obtain evidence concerning successive equilibria. Also, an attempt was made to reverse the equilibrium by adding triethylamine to the adduct in solution. Under these conditions the reappearance of spectrum for the parent carbonyl constitutes good evidence for simple adduct formation rather than a more extensive reaction with the trialkylaluminum.

Nmr spectra were determined for deuteriotoluene solutions on a Bruker HFX-3 (90 MHz) and on a Varian A60 (60 MHz). Chemical shifts were accurately determined on the former instrument by reference to benzene. Peak areas were found by cutting and weighing the individual peaks from the 90-MHz spectra. In most cases, overlapping of these peaks limited the accuracy of the area determinations.

### Results and Discussion

$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ .—Interpretation of the spectra for aluminum alkyl adducts of this compound is aided by a variety of ancillary data such as the X-ray structure data for the bis(triethylaluminum) adduct,<sup>1</sup> and for the cis and trans isomers of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ .<sup>5</sup> Of particular importance are the recent detailed infra-

(1) N. J. Nelson, N. E. Kime, and D. F. Shriver, *J. Amer. Chem. Soc.*, **91**, 5173 (1969).

(2) A. Alich, N. J. Nelson, and D. F. Shriver, *Chem. Commun.*, 254 (1971).

(3) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

(4) E. O. Fischer and A. Vogler, *Z. Naturforsch.*, **B**, **17**, 421 (1962); R. B. King, *Inorg. Chem.*, **5**, 2227 (1966).

(5) R. F. Bryan and P. T. Greene, *J. Chem. Soc. A*, 3064 (1970); R. F. Bryan, P. T. Greene, M. J. Newlands, and D. S. Field, *ibid.*, 3068 (1970).

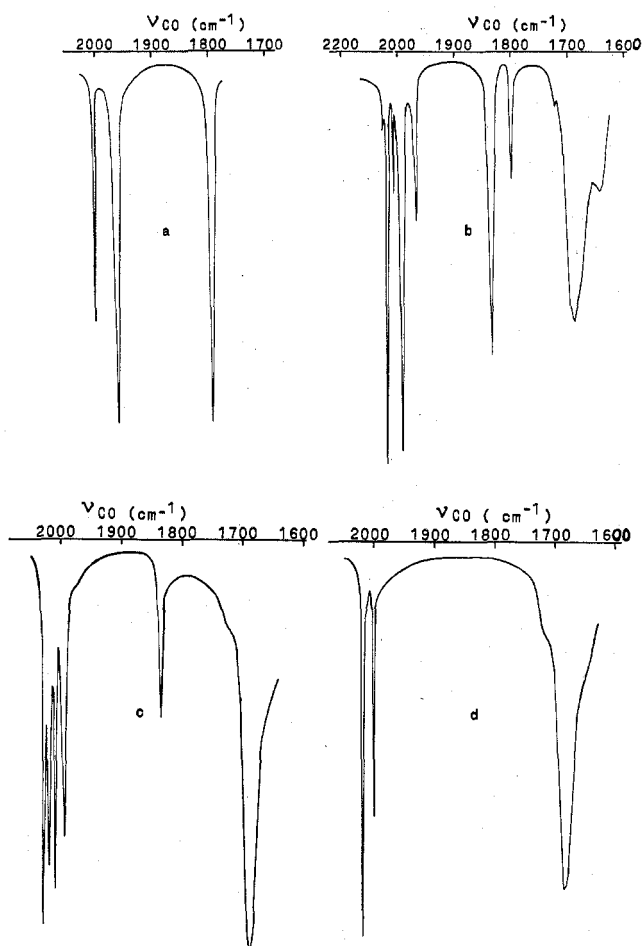


Figure 1.—Infrared spectra for the  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{-Al}(\text{i-C}_4\text{H}_9)_3$  system, in the  $\nu_{\text{CO}}$  region. Iron dimer concentration =  $2.34 \times 10^{-3} M$ : a, parent iron complex; b, Lewis acid added,  $6.45 \times 10^{-3} M$ , the primary species are  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  and its 1:1 adduct; c, Lewis acid increased to  $7.48 \times 10^{-3} M$ , the primary species are 1:1 and 1:2 adducts; d, Lewis acid increased further to  $1.46 \times 10^{-2} M$ , the primary species is the 1:2 adduct.

red studies of the parent iron complex in solution,<sup>6</sup> which demonstrate that the three prominent infrared absorptions in the CO stretch region are respectively symmetric terminal CO stretch ( $2006 \text{ cm}^{-1}$ ), asymmetric terminal CO stretch ( $1962 \text{ cm}^{-1}$ ), and asymmetric bridging stretch ( $1794 \text{ cm}^{-1}$ ). The symmetric bridging CO stretching absorption appears as a minor shoulder<sup>6</sup> because the nearly centrosymmetric arrangement of the bridging CO groups<sup>5</sup> leads to a low dipole moment derivative for this mode. While the most prominent features mentioned above arise from cis and trans isomers of the carbonyl-bridged compound, other weak features may be attributed to a small proportion of a nonbridged isomer in solution.<sup>7,8</sup> The presence of trialkylaluminum compounds causes a small degradation in quality of the spectra making unreliable the observation of the low intensity features. Therefore, attention is focused on the intense features which fortunately provide an accurate guide to the structures.

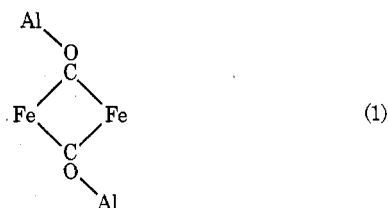
(6) (a) A. R. Manning, *J. Chem. Soc. A.*, 1319 (1968); (b) P. McArdle and A. R. Manning, *ibid.*, 2119 (1970); (c) P. McArdle and A. R. Manning, *ibid.*, 2133 (1970), and references therein.

(7) F. A. Cotton and G. Yagupsky, *Inorg. Chem.*, **6**, 15 (1967).

(8) R. D. Fischer, A. Vogler, and K. Noack, *J. Organometal. Chem.*, **7**, 135 (1967).

Addition of trialkylaluminum to a  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  solution causes lightening of the red color and the appearance of new CO stretching absorptions in the infrared, Figure 1. In the absence of air the solution is stable at room temperature. Variation of the spectrum as a function of trialkylaluminum concentration reveals three types of concentration-dependent bands, Figure 2. With increasing trialkylaluminum concentration the intensities of the three  $\nu_{\text{CO}}$  bands (Type I) of the parent iron complex decrease monotonically, another set (II) first increases in intensity and then decreases, and a third set (III) monotonically grows in intensity. By comparison with the spectrum of the solid, the last set can be identified with the adduct containing two  $\text{AlR}_3$  molecules. The concentration dependence of the second set of bands demonstrates 1:1 adduct formation. As described later in this discussion the number of observed type II bands establishes the structure of the 1:1 adduct.

As illustrated in Figure 3, the adduct containing two molecules of  $\text{AlR}_3$  displays a pattern of CO absorptions which is qualitatively similar to the parent compound, *viz.* two terminal and one bridging CO stretch. The lack of two strong bridging CO stretching frequencies may be due to the nearly centrosymmetric bridging array (1)



which results in negligible infrared absorption for the symmetric CO stretch. Quantitatively, there are differences between the parent and the 2:1 adduct, with the bridging CO stretching mode shifted  $113 \text{ cm}^{-1}$  to lower frequency and the terminal CO stretching frequencies increased by *ca.*  $40 \text{ cm}^{-1}$ . The decrease in  $\nu_{\text{CO}}$  of ketones upon adduct formation<sup>9</sup> provides some precedent for the decreases observed with the metal carbonyl adducts. This decrease upon oxygen coordination is a valuable diagnostic tool for C- and O-coordinated carbon monoxide. There is less precedent for the observed increase in the terminal CO stretching frequencies upon trialkylaluminum interaction with the bridging carbonyl ligands, but the result is easily explained by the inductive decrease in electron density on the iron atoms upon adduct formation. A similar increase in  $\nu_{\text{CO}}$  for terminal CO ligands has been observed when  $\text{Cr}(\text{CO})_5\text{CN}^-$  coordinates to Lewis acids through the CN group.<sup>10</sup>

The type II bands, characteristic of the 1:1 adduct, follow the pattern expected for coordination of an aluminum alkyl group to the oxygen of one bridging CO ligand. In agreement with the intermediate inductive effect expected for a single acceptor molecule, the two terminal CO stretching frequencies are between those of the parent and the 1:2 adduct. In contrast with the parent and the 1:2 adduct, the 1:1 adduct displays two strong bridging CO stretching frequencies (Figure 3). This result substantiates the nature of the

(9) I. Lindquist, "Inorganic Adduct Molecules of Oxo-Compounds," Academic Press, New York, N. Y., 1963, p 11.

(10) R. B. King, *Inorg. Chem.*, **6**, 25 (1967).

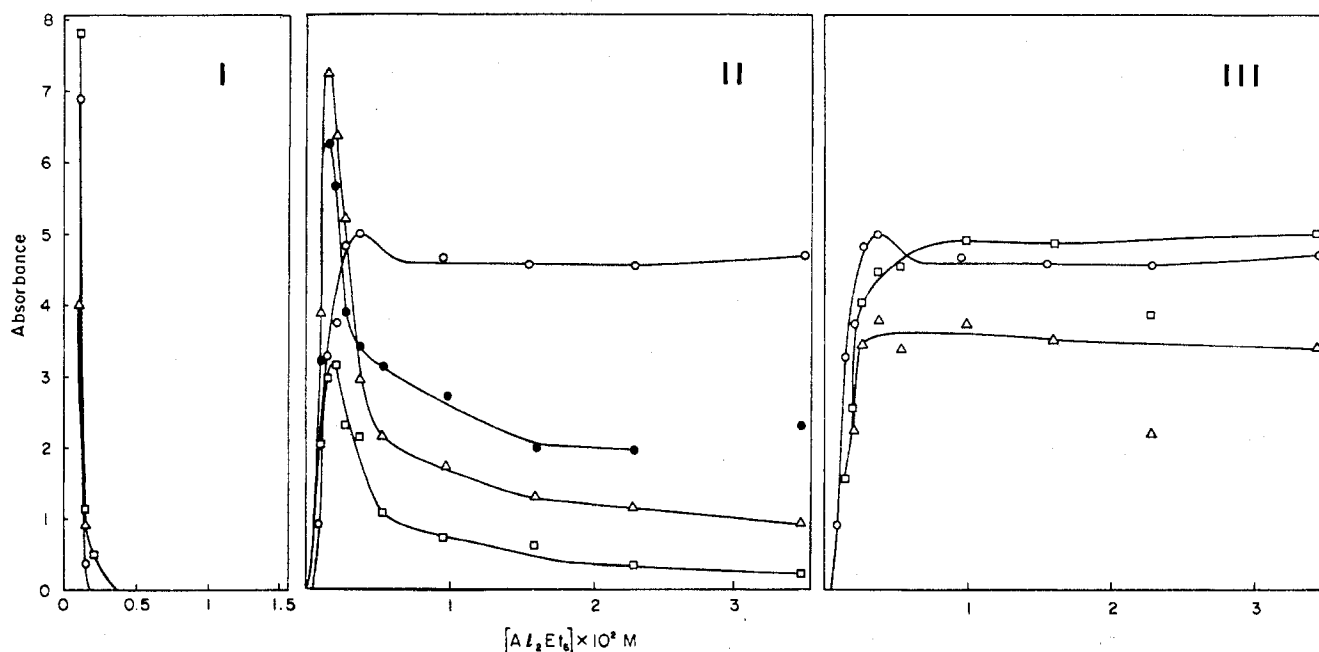


Figure 2.—Variation of intensities of carbonyl bands with increasing concentration of  $\text{Al}(\text{C}_2\text{H}_5)_3$ . Concentration  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2 = 2.54 \times 10^{-3} \text{ M}$ : (I) parent:  $\circ$ , 1794  $\text{cm}^{-1}$ ;  $\square$ , 1962  $\text{cm}^{-1}$ ;  $\Delta$ , 2005  $\text{cm}^{-1}$ ; (II) 1:1 adduct:  $\circ$ , 1682  $\text{cm}^{-1}$ ;  $\square$ , 1828  $\text{cm}^{-1}$ ;  $\Delta$ , 1985  $\text{cm}^{-1}$ ;  $\bullet$ , 2026  $\text{cm}^{-1}$ ; (III) 1:2 adduct:  $\circ$ , 1682  $\text{cm}^{-1}$ ;  $\Delta$ , 2004  $\text{cm}^{-1}$ ;  $\square$ , 2042  $\text{cm}^{-1}$ . The concentration dependent intensity variation is very similar for either  $\text{Al}(\text{C}_2\text{H}_5)_3$  or  $\text{Al}(i\text{-Bu})_3$  as the Lewis acid.

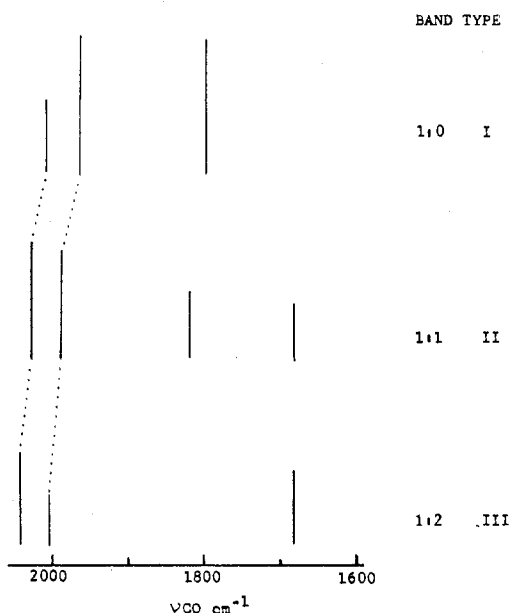
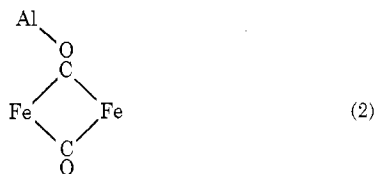


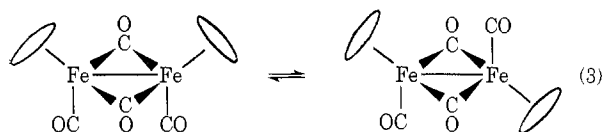
Figure 3.—Changes in intensities and positions of carbonyl frequencies upon adduct formation. Type I bands predominate at low  $\text{AlR}_3$  concentration, and type III at high  $\text{AlR}_3$  concentration (see Figure 2): (I)  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ ; (II)  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2(\text{Al}(i\text{-C}_4\text{H}_9)_3)$ ; and (III)  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2(\text{Al}(i\text{-C}_4\text{H}_9)_3)_2$ .

1:1 adduct since the expected structure (2) lacks a



center of symmetry and should therefore display two prominent CO stretching absorptions in the infrared.

An interesting intensity variation occurs for the terminal CO stretching frequencies upon adduct formation. Manning has shown that the ratio of the intensity for the high-frequency terminal CO stretch,  $\nu_{\text{sym}}$ , to that of the low-frequency terminal CO stretch,  $\nu_{\text{asym}}$ , reflects the cis-trans ratio (eq 3).<sup>5</sup> It will be



noted in Figure 3 that the intensities follow the order,  $I_{\text{sym}} < I_{\text{asym}}$ ,  $I_{\text{sym}} \approx I_{\text{asym}}$ , and  $I_{\text{sym}} > I_{\text{asym}}$ , for the parent, 1:1, and 1:2 adducts, respectively. Judging from the crystal structure of the 1:2 adduct,<sup>1</sup> the aluminum alkyl group has little effect on bond distances and angles within the  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  moiety. Therefore, Manning's line of reasoning may be carried over to the adduct system. Apparently, both cis and trans adducts are present in solution and the proportion of cis adduct increases from parent to 1:1 to 1:2 adduct.

Data for the  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{-Al}(\text{C}_2\text{H}_5)_3$  and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{-Al}(i\text{-C}_4\text{H}_9)_3$  systems are collected in Table I. The general concentration dependence of spectra and CO stretching frequencies are very similar for the two systems. Consistent with the formulation of these compounds as simple adducts is the abstraction of trialkylaluminum by triethylamine. Thus, quantitative infrared experiments show that a slight molar excess of triethylamine over triethylaluminum leads to complete regeneration of the parent  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ .

Proton nmr results confirm the presence of both cis and trans adducts in solution. For free  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  a single proton nmr line is observed at room temperature, owing to rapid interconversion of the cis

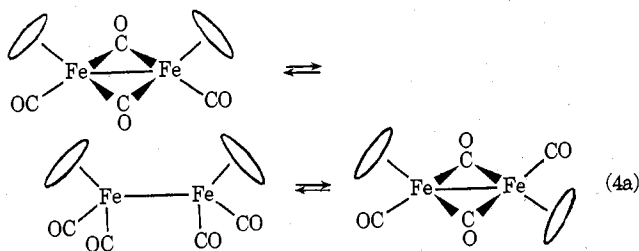
TABLE I

INFRARED BANDS IN THE CARBONYL REGION FOR  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  AND ITS ADDUCTS. SPECTRA ARE OF  $2 \times 10^{-3} M$  HEPTANE SOLUTIONS OF  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$

| Lewis base                                                | Lewis acid                          | $\nu_{\text{CO}}$ , $\text{cm}^{-1}$ | Key  |
|-----------------------------------------------------------|-------------------------------------|--------------------------------------|------|
| $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ |                                     | 1794 s                               |      |
|                                                           |                                     | 1962 s                               |      |
|                                                           |                                     | 2005 s                               |      |
| $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ | $\text{Al}(\text{C}_2\text{H}_5)_3$ | 1682 s                               | a, b |
|                                                           |                                     | 1828 m                               | a    |
|                                                           |                                     | 1985 s                               | a    |
|                                                           |                                     | 1993                                 | a, c |
|                                                           |                                     | 2004 s                               | b    |
|                                                           |                                     | 2009                                 | b, c |
|                                                           |                                     | 2026 s, sh                           | a    |
|                                                           |                                     | 2031                                 | c    |
| $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ | $\text{Al}(i\text{-Bu})_3$          | 1680 s                               | a, b |
|                                                           |                                     | 1827 m                               | a    |
|                                                           |                                     | 1984 s, sh                           | a    |
|                                                           |                                     | 2003 s, sh                           | b    |
|                                                           |                                     | 2026 s, sh                           | a    |
|                                                           |                                     | 2041 s                               | b    |

<sup>a</sup> 1:1 adduct bands (see Figure 2 for concentration dependence). <sup>b</sup> 1:2 adduct bands (see Figure 2 for concentration dependence). <sup>c</sup> These features probably arise from the trans form of the 1:2 adduct. In some spectra they are not resolved from stronger adjacent features.

and trans isomers.<sup>11</sup> Similarly, in the presence of moderate trialkylaluminum concentrations, a single  $\text{C}_5\text{H}_5$  resonance is observed, however when the Lewis acid concentration is increased, two peaks appear, a large one at 2.81 and a weaker one at 2.72 ppm upfield from benzene. In agreement with the infrared spectra of the adduct and low-temperature nmr of the parent iron compound,<sup>11</sup> the high field peak is assigned to cyclopentadienyl protons for the cis isomer while the less intense low field feature is assigned to the lower concentration trans isomer. The much slower cis-trans exchange rate for the adduct than the parent iron complex is consistent with the proposal<sup>11</sup> that isomerization proceeds through the nonbridged form, eq 4, because adduct formation should stabilize the bridged form relative to the transition state, which



presumably involves CO-bridge breaking.

For  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2 \cdot 2\text{Al}(\text{C}_2\text{H}_5)_3$  the equilibrium constant,  $K = [\text{trans}]/[\text{cis}]$ , determined from nmr area ratios has the value 0.15 at 30° (0.04 M nominal parent iron complex, and 0.85 M nominal  $\text{AlEt}_3$  in deuterio-toluene). With this triisobutylaluminum complex, the corresponding equilibrium constant is 0.2. Peak area measurements for the triethylaluminum adduct, over the range 175–303°K, yield  $\Delta G^\circ_{303} = 1 \pm 0.2$  kcal/mol,  $\Delta H^\circ = -0.7 \pm 0.2$  kcal/mol, and  $\Delta S^\circ_{303} = -6 \pm 2$  cal/deg mol. These quantities may be compared with the results of Bullitt, Cotton, and Marks on the parent

(11) (a) J. G. Bullitt, F. A. Cotton, and T. J. Marks, *Inorg. Chem.*, **11**, 879 (1972); (b) J. G. Bullitt, F. A. Cotton, and T. J. Marks, *J. Amer. Chem. Soc.*, **92**, 2155 (1970).

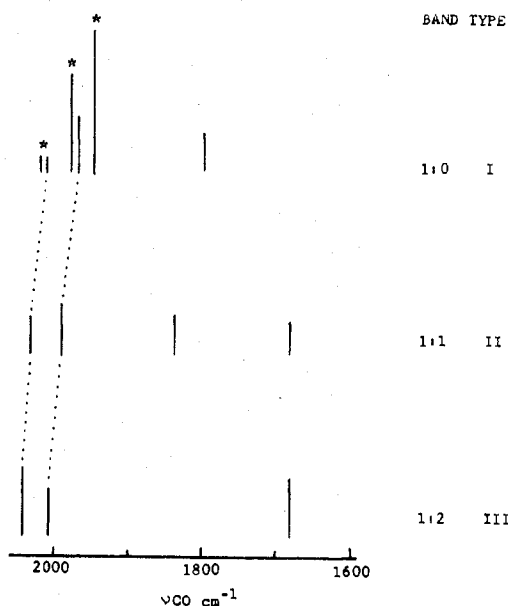
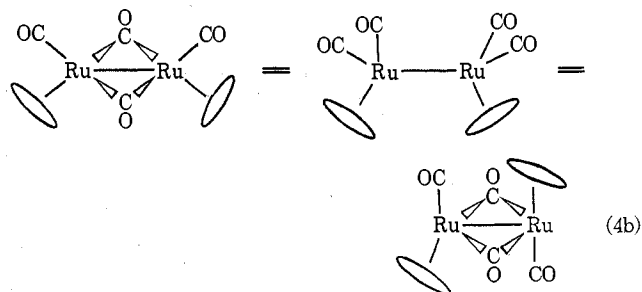


Figure 4.—Changes in intensities and positions of carbonyl frequencies upon adduct formation. These diagrams are derived from the plots of the type shown in Figure 2: (I)  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2$ ; (II)  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2(\text{Al}(\text{C}_2\text{H}_5)_3)_2$ , and (III)  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2(\text{Al}(\text{C}_2\text{H}_5)_3)_2$ .

iron compound;  $\Delta H^\circ = 0.90 \pm 0.1$  kcal/mol and  $\Delta S^\circ = 3.5 \pm 0.7$  cal/deg mol.

$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2$ .—From infrared spectra of this complex in hydrocarbon solution it is known that both bridged and nonbridged isomers (4) are present in comparable amounts.<sup>7,12</sup> Therefore the interaction of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2$  with aluminum alkyls affords a convenient system to study the influence of adduct formation on the bridged-nonbridged equilibrium.

Unlike the iron analog, the ruthenium compound decomposes slowly at room temperature in the presence of aluminum alkyls. This decomposition was negligible at  $-3^\circ$  in the time interval of the infrared experiments (ca. 2 hr). Upon adduct formation the solution lightens slightly. As with the  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{-AlR}_3$  system, three types of concentration-dependent bands are observed, Figure 4. The type I bands characteristic of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2$  are fairly



complex owing to the presence of absorptions at 2021 w, 1976 s, and 1945  $\text{cm}^{-1}$  which arise from the nonbridged form, plus bands at 2011 w, 1967 m, and 1795  $\text{cm}^{-1}$  of the cis and trans bridged species.<sup>7,12</sup> Type II bands (2030 s, 2024 sh, 1993 sh, 1988 s, 1834 m, 1679  $\text{cm}^{-1}$ ), which first increase and then decrease in intensity with added  $\text{AlR}_3$ , are nearly identical in frequency and

(12) P. McArdle and A. R. Manning, *J. Chem. Soc. A*, 2128 (1970).

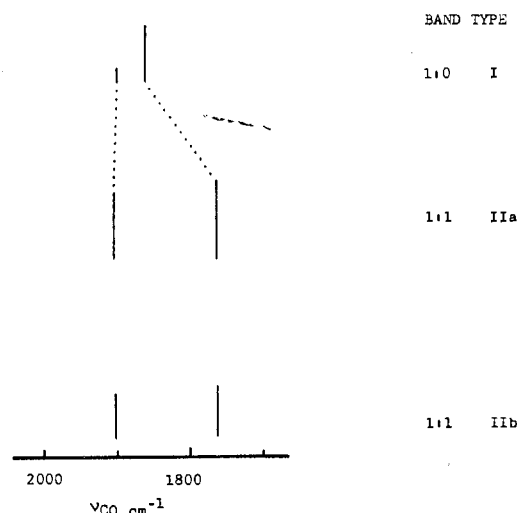
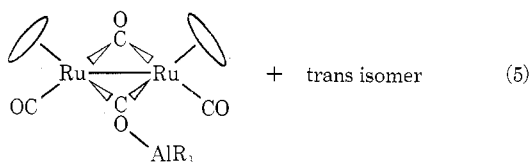
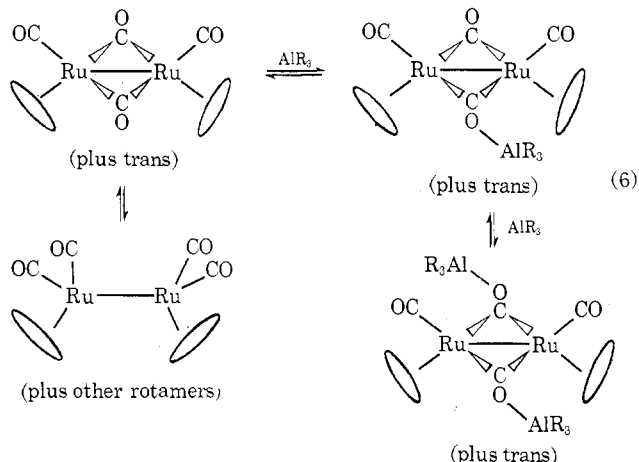


Figure 5.—Changes in positions and intensities of carbonyl frequencies upon adduct formation. These diagrams were derived from dependence of the spectra on  $\text{AlR}_3$  concentration: (I)  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$ , (IIa) 1:1 adduct of  $\text{Al}(\text{C}_2\text{H}_5)_3$ , and (IIb) 1:1 adduct of  $\text{Al}(i\text{-Bu})_3$ .

relative intensity with those of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2 \cdot \text{AlR}_3$ ; therefore, the detailed arguments presented for the iron adduct apply here. As with the iron system, type II bands demonstrate the presence of singly coordinated bridging-CO species in the cis and trans forms (5).



Type III bands (2046 s, 2011 sh, 2006 s, 1679 s  $\text{cm}^{-1}$ ) monotonically increase in intensity with  $\text{AlR}_3$  concentration and at high  $\text{AlR}_3$  concentration dominate the spectrum. Again the frequencies and relative intensities are quite similar (Table I) to those of the iron system and it is concluded that as with the iron system two aluminum alkyl groups are attached to the two bridging carbonyls. Clearly, the coordination of  $\text{AlR}_3$  to bridging carbonyls serves as a driving force for the isomerization of nonbridged  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2$  to the bridged 1:1 and 1:2 adducts according to eq 6.



At concentrations of  $2.2 \times 10^{-3} M$   $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2$

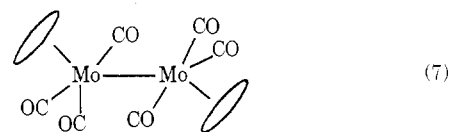
and  $1.8 \times 10^{-2} M$  triisobutylaluminum the primary species present in solution is the bridged 1:2 complex along with a minor amount of the 1:1 complex and no observable parent. These results demonstrate that the basicity of the bridging CO group provides a rational means of producing a terminal-to-bridge CO shift.

$[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$ .—The structure of this compound has not been described in detail although a few of the bond distances were mentioned in the publication of another structure.<sup>13</sup> In solution, the compound is thought to have the two carbonyl bridges folded slightly away from the cyclopentadienyl groups, because the symmetric carbonyl stretch is infrared active.<sup>14</sup> However, the deviation from planarity for the  $\text{Ni}_2(\text{CO})_2$  moiety cannot be great since the dipole moment in benzene solution is small (0.38 D), and only the asymmetric CO stretch is observed in the gas phase.<sup>15</sup>

Upon adduct formation with either triethyl- or triisobutylaluminum the solution color changes from red to brown and the two CO stretching frequencies of the parent, 1857 s and 1897 w  $\text{cm}^{-1}$ , are shifted to 1761 s and 1902 m s  $\text{cm}^{-1}$ , Figure 5. This pattern, which is characteristic of a 1:1 complex, only develops at relatively high trialkylaluminum concentration. There is no indication in the infrared of 1:2 adduct formation. Whereas in the iron and ruthenium systems the relative concentrations of carbonyl and Lewis acid were  $2.5 \times 10^{-3}$  and  $6.1 \times 10^{-3} M$ , respectively, to bring type II bands to a maximum, this nickel system required a Lewis acid concentration of  $21.4 \times 10^{-3} M$  (nickel dimer  $2.7 \times 10^{-3} M$ ). Thus, the nickel dimer is much less basic than the iron and ruthenium dimers which have asymmetric bridging CO stretching frequencies, ca. 60  $\text{cm}^{-1}$  lower than that of the nickel compound.

No significant differences were observed between the infrared spectra of the nickel compound in the presence of triethylaluminum or triisobutylaluminum. Under some conditions, a small splitting (7–9  $\text{cm}^{-1}$ ) was observed for the higher frequency carbonyl band. The aluminum alkyl solutions do not destroy the nickel dimer at room temperature.

$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ .—An X-ray structure determination of this compound<sup>16</sup> shows a nonbridged nearly centrosymmetric configuration (7). Similarly,



solution infrared spectra do not contain absorptions in the bridging  $\nu_{\text{CO}}$  region<sup>17,18</sup> and have been interpreted in terms of structure 7 even though the compound displays a significant dipole moment in benzene solution.<sup>18</sup>

The spectral changes of this molybdenum dimer in the presence of a trialkylaluminum are fairly complex, however study of the spectra as a function of concentration, time, and temperature reveals two general types of products—equilibrium and kinetic. The

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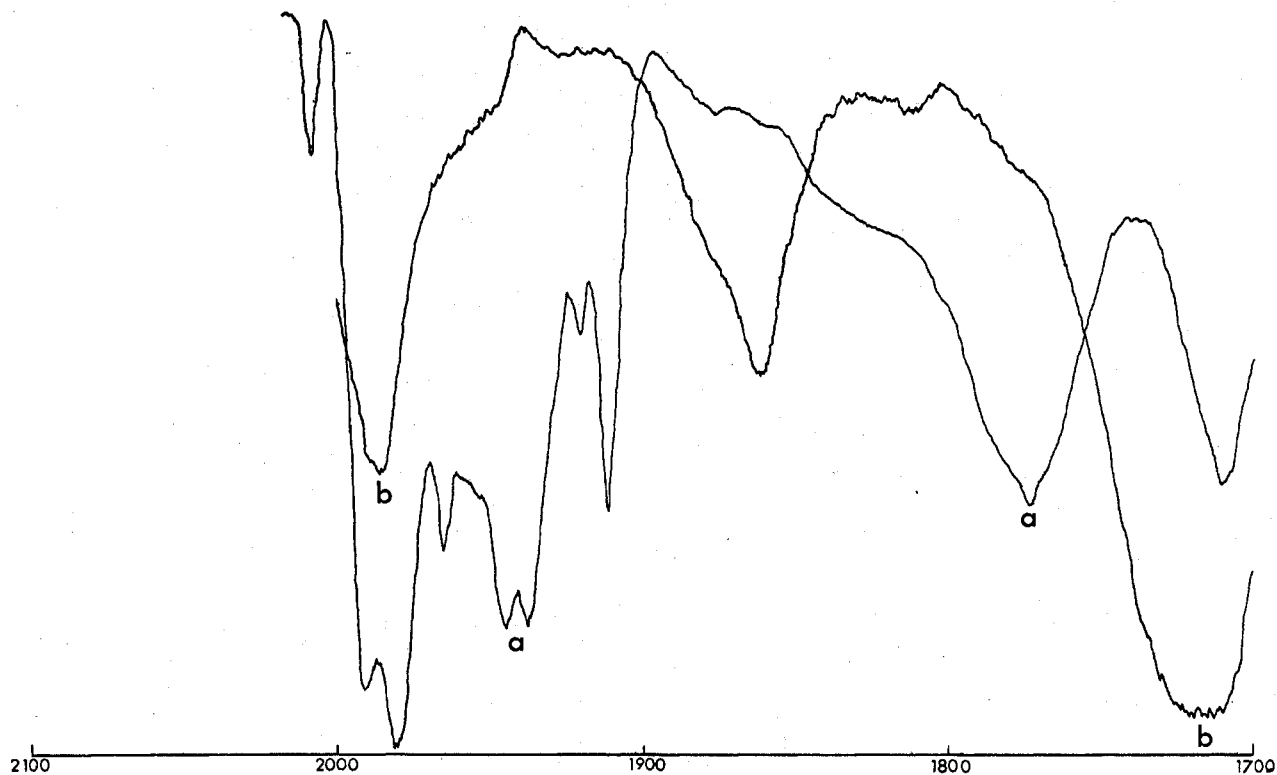


Figure 6.—Infrared spectra of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2\text{-Al}(i\text{-Bu})_3$  system: a, "equilibrium product" at  $-3^\circ$ ; b, "kinetic product" at room temperature. (The  $1620\text{-cm}^{-1}$  band is not shown.)

purple parent dimer displays three CO stretching frequencies in heptane,  $1964\text{ s}$ ,  $1920\text{ m}$ , and  $1911\text{ w cm}^{-1}$ , which decrease in intensity as the triisobutylaluminum concentration is increased. At  $-3^\circ$  new bands are observed upon mixing (the maximum delay between mixing and the spectral determination was 10 min) at  $2020\text{ w}$ ,  $1990\text{ ms}$ ,  $1979\text{ vs}$ ,  $1944\text{ m}$ ,  $1936\text{ m}$ ,  $1911$  (this band appears to overlap the parent),  $1774\text{ m}$ , and  $1710\text{ m cm}^{-1}$ , and the solution turns red. The species responsible for this spectrum is termed the "equilibrium product" because all these bands increase relative to the parent as the  $\text{AlR}_3$  concentration is increased and revert to the parent spectrum upon addition of triethylamine. At a concentration of  $9.9 \times 10^{-3}\text{ M}$   $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$  and  $0.4\text{ M}$   $\text{Al}(i\text{-C}_4\text{H}_9)_3$  the spectrum is predominantly that of the equilibrium product(s), Figure 6a. When the above mixture stands for a matter of hours at  $-3^\circ$  the  $1990$  and  $1710\text{ cm}^{-1}$  absorptions increase and the color darkens, and bands appear at  $1860$  and  $1620\text{ cm}^{-1}$ . These are the only CO stretching absorptions remaining in the brown solution after 8 days at room temperature, Figure 6b. The variation in intensity of these "kinetic product" bands upon addition of triethylamine is not entirely clear, because the  $1860\text{-cm}^{-1}$  band is the only one for which there is no possible confusion with triethylamine or triethylamine-triisobutylaluminum. The  $1860\text{-cm}^{-1}$  band continues to grow stronger when the solution containing added triethylamine stands at room temperature. The nature of the kinetic product(s) is still under investigation. However, the equilibrium product(s) display the behavior expected for trialkylaluminum adduct formation with bridging CO groups. Specifically, the two new bands in the bridging CO region ( $1710$  and  $1774\text{ cm}^{-1}$ ) and increased frequency of the terminal

carbonyl stretches fall into the pattern observed for other bridging carbonyl adducts in the present study. A structure involving two  $\text{AlR}_3$ -coordinated carbonyls and four terminal carbonyls would be consistent with the observed spectrum but certainly cannot be considered to be proven.

An intriguing problem with this interpretation is the possibility that the Mo-Mo bond is too long to accommodate a CO bridge. Bridging carbonyls are thought to exist where the metal-metal bond is less than  $2.8\text{ \AA}$ ,<sup>19</sup> and it would therefore seem that the Mo-Mo bond distance in the present compound,  $3.22\text{ \AA}$ , is prohibitively long for the formation of carbonyl bridges. However, molybdenum covalent radii, which are variously estimated at  $1.30\text{--}1.5\text{ \AA}$ ,<sup>20,21</sup> do not appear prohibitive. Similarly, Mo-Mo bonded compounds are known with Mo-Mo distances in the range  $2.89\text{--}3.09\text{ \AA}$ .<sup>22,23</sup> It is thus conceivable that bridging carbonyl formation in the  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$  moiety could occur with a simultaneous shortening of the Mo-Mo bond.

$[\text{Co}(\text{CO})_4]_2$ ,  $[\text{Co}(\text{CO})_3]_4$ , and  $[\text{Co}(\text{CO})_3(\text{P}(\text{C}_6\text{H}_5)_3)]_2$ .— Judging from infrared spectra<sup>24</sup> dicobalt octacarbonyl exists in solution in both  $>\text{CO}$  bridged and nonbridged

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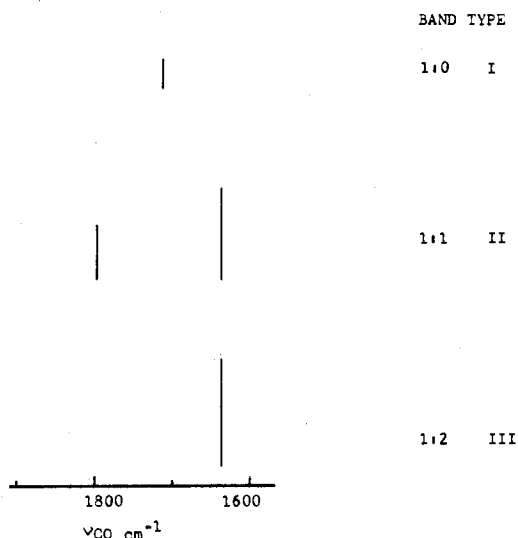


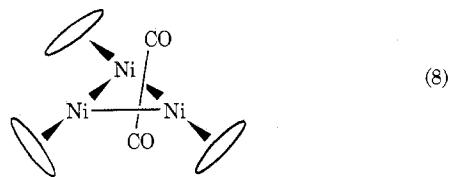
Figure 7.—Changes in positions and intensities of carbonyl frequencies upon adduct formation. These diagrams were derived from dependence of the spectra on  $\text{AlR}_3$  concentration: (I)  $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2$ , (II)  $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2(\text{Al}(i\text{-Bu})_3)$ , (III)  $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2(\text{Al}(i\text{-Bu})_3)_2$ .

forms. Therefore, the interaction of this compound with aluminum alkyls is of interest from the standpoint of possible displacement of the nonbridged-bridged equilibrium. Unfortunately a dark sludge devoid of carbonyl absorptions in the infrared forms upon mixing a  $\text{Co}_2(\text{CO})_8$  solution with  $\text{Al}(\text{C}_2\text{H}_5)_3$  solution. Tetracobalt dodecacarbonyl, which occurred as an impurity in the dicobaltoctacarbonyl, also was destroyed by triethylaluminum. With the compound  $[\text{Co}(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2]$ , which exists in solution primarily in the nonbridged form,<sup>24</sup> a large excess of triisobutylaluminum ( $6.3 \times 10^{-2} M$  with the CO compound  $3.4 \times 10^{-3} M$ ) does not destroy the cobalt compound, but judging from infrared spectra an adduct is not formed.

**$\text{Fe}_2(\text{CO})_9$ .**—Addition of trimethylaluminum to a suspension of  $\text{Fe}_2(\text{CO})_9$  in benzene followed by stirring for 3 hr yielded an unpromising black tar and a noncondensable gas, presumed to be CO.  $\text{Fe}(\text{CO})_5$  was detected in the volatile and condensable fraction.

**$\text{Mn}_2(\text{CO})_{10}$ .**—An attempt to induce CO bridging in this compound was made by preparing solutions  $2 \times 10^{-2} M$  in  $\text{Mn}_2(\text{CO})_{10}$  and up to  $1.5 M$  in triisobutylaluminum. Infrared spectra of these solutions showed no significant changes in the terminal CO stretch region and no new bands attributable to CO bridges; thus, a CO bridged adduct is not formed.

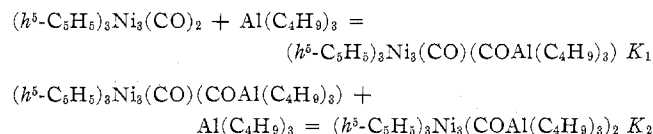
**$(\eta^5\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2$ .**—This paramagnetic trinuclear compound contains triply bridging CO groups (8).<sup>25</sup> A single CO stretching frequency ( $1761 \text{ cm}^{-1}$ —heptane



solution) is observed in keeping with the centrosymmetric disposition of the two CO groups which should

give rise to a single asymmetric infrared active stretching frequency.<sup>26</sup> As indicated in Figure 7,  $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2$  forms both a 1:1 and 1:2 adduct in solution. At concentrations around  $2.8 \times 10^{-3} M$  nickel trimer and  $5.4 \times 10^{-3} M$  Lewis acid the bridging carbonyl frequency is shifted to  $1637 \text{ cm}^{-1}$  which represents a decrease of  $124 \text{ cm}^{-1}$ , and a second frequency appears at  $1795 \text{ cm}^{-1}$ . This pattern of CO stretching frequencies indicates a noncentric 1:1 adduct which displays one low-frequency band due to  $>\text{CO}-\text{Al}$  and a higher frequency absorption due to  $>\text{CO}$ . As the aluminum alkyl concentration is increased the intensity of the  $1795\text{-cm}^{-1}$  band decreases while that of the  $1637\text{-cm}^{-1}$  band increases, indicating the formation of a 1:2 adduct, which is the sole species at  $8.5 \times 10^{-3} M \text{ Al}(i\text{-Bu})_3$ . The trimer is significantly more basic than the dimer, since the concentration of Lewis acid required to form the 1:1 dimer adduct is nearly four times that for the 1:1 trimer adduct, indicating that the carbonyl oxygen is better able to act as donor in the trimer. Again a correlation between basicity and low values of  $\nu_{\text{CO}}$  is evident since the parent trimer has an asymmetric CO stretching frequency which is  $96 \text{ cm}^{-1}$  lower than  $\nu_{\text{CO}}(\text{asym})$  for the dimer.

From the concentration dependence of the  $1795\text{-cm}^{-1}$  CO stretching band the ratio of the formation constants  $K_1/K_2$  was estimated to be 4 at  $-3^\circ$  in heptane solution.



Steric interaction between the two triisobutylaluminum groups is precluded by the geometry of the molecule. The agreement between the observed ratio and the  $K_1/K_2$  ratio of 4 expected on statistical grounds demonstrates that the electronic interaction between the two CO groups is too small to be reflected in the chemistry.

While a buff-brown solid adduct may be isolated, infrared spectra of the solid always indicate the presence of weak peaks due to a 1:1 adduct impurity in the 1:2 compound. The infrared spectra also showed a curious phenomenon not observed with any other adducts. Generally a Nujol spectrum of a solid adduct has bands  $10\text{--}20 \text{ cm}^{-1}$  lower in frequency than the same compound in hydrocarbon solution. However, for this adduct, the infrared peaks for the solid were at  $1570 \text{ m}$  and  $1759 \text{ w cm}^{-1}$  (the latter varies in intensity and is assigned to the C-bonded carbonyl of a 1:1 impurity) which represent shifts of  $-67$  and  $-36 \text{ cm}^{-1}$  from the corresponding vibrations for heptane solutions. The remainder of the spectrum of the solid is very similar to that of the parent nickel trimer except for three bands at  $626 \text{ m}$ ,  $657 \text{ m}$ , and  $1198 \text{ vw cm}^{-1}$ , which are characteristic of coordinated trialkylaluminum.<sup>27</sup>

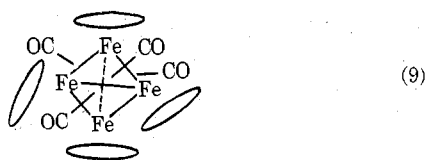
**$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$ .**—As with the carbonyl derivative in the previous section, this compound involves face bridging carbonyl groups (9).<sup>28</sup> Attempts to follow the successive formation of triethylaluminum adducts in solution were not promising; however, there is no

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doubt that intermediate species are formed. For example, a solution of  $5 \times 10^{-4} M$  iron tetramer and  $2 \times 10^{-3} M$  triethylaluminum has a strong absorbance due to the parent at  $1649 \text{ cm}^{-1}$  and broad features about  $1699$ ,  $1606$ , and  $1547 \text{ cm}^{-1}$  which are about  $1/3$  the intensity of the parent. For concentrations of tetramer of  $5.0 \times 10^{-4} M$ , and of Lewis acid of  $6.7 \times 10^{-3} M$ , the major product is the 1:4 adduct with a strong band at  $1547 \text{ cm}^{-1}$ . At larger concentrations, the 1:4 adduct is the only species present in solution, as identified by a single infrared active band. Solutions of the 1:4 adduct have a lighter green color than those of the parent.

The 1:4 adduct was isolated by adding 1.5 ml of triethylaluminum to 0.75 g of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  in 200 ml of benzene. The mixture was stirred for 2 hr, 200 ml of heptane was added, and solvent was reduced under vacuum to *ca.* 20 ml. The black product was filtered off, washed with several portions of degassed heptane, and dried under vacuum. *Anal.* Calcd for  $\text{C}_{48}\text{H}_{80}\text{Al}_4\text{Fe}_4\text{O}_4$ : C, 31.14; Al, 10.25; Fe, 21.22; Found: C, 32.30; Al, 10.68; Fe, 20.64;  $\text{Fe}_4(\text{C}_5\text{H}_5)_4(\text{CO})_4$  (after hydrolysis), 57.26; mol wt, 1056 (benzene).

**Conclusions.**—As summarized in Table II, the present work demonstrates that Lewis basicity is a general phenomenon among bridging carbonyl groups. The compounds with the lowest bridging CO stretching frequencies appear to be the most basic as shown by the following relative affinities for  $\text{AlR}_3$ :  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_2 > [(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2, (\eta^5\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2 >$

TABLE II

## SUMMARY OF LEWIS ACID-BASE ADDUCTS FORMED

| Lewis base                                                | Lewis acid                            | Stoichiometry  | Characterization      |
|-----------------------------------------------------------|---------------------------------------|----------------|-----------------------|
| $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_2$   | $\text{Al}(\text{C}_2\text{H}_5)_3$   | 1:1, 1:2       | Solid,<br>solution ir |
| $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$   | $\text{Al}(i\text{-C}_4\text{H}_9)_3$ | 1:1, 1:2       | Solution ir           |
|                                                           | $\text{Al}(\text{C}_2\text{H}_5)_3$   | 1:4            | Solid,<br>solution ir |
| $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})]_2$   | $\text{Al}(i\text{-C}_4\text{H}_9)_3$ | 1:4            | Solid,<br>solution ir |
|                                                           | $\text{Al}(\text{C}_2\text{H}_5)_3$   | 1:1, 1:2       | Solution ir           |
| $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$   | $\text{Al}(\text{C}_2\text{H}_5)_3$   | 1:1, 1:2       | Solution ir           |
|                                                           | $\text{Al}(i\text{-C}_4\text{H}_9)_3$ | 1:1            | Solution ir           |
| $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2$ | $\text{Al}(\text{C}_2\text{H}_5)_3$   | 1:1, 1:2       | Solid,<br>solution ir |
|                                                           | $\text{Al}(i\text{-C}_4\text{H}_9)_3$ | 1:1, 1:2       | Solution ir           |
| $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})]_2$   | $\text{Al}(\text{C}_2\text{H}_5)_3$   | Not determined | Solution ir           |
|                                                           | $\text{Al}(i\text{-C}_4\text{H}_9)_3$ |                |                       |

$[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$ , and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4 > [(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_2$  for which the most basic compound in each pair has the lowest bridging CO stretching frequencies. This observation is in harmony with the idea that low CO stretching frequencies correspond to high electron density on the carbonyl ligand.

While  $\nu_{\text{CO}}$  decreases for all the C- and O-bonded carbonyls, an increase in  $\nu_{\text{CO}}$  is noted for all remaining CO groups. This increase indicates that upon adduct formation significant electron density has been removed from the metal. However the ratio of successive formation constants for the triisobutylaluminum adducts of  $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2$  shows no inductive effect of the first acid on the basicity of the remaining carbonyl.

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