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Adduct Formation and Carbonyl Rearrangement of Polynuclear Carbonyls in the Presence of Group III Halides

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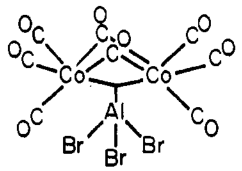
The chemistry of C- and O-bonded carbon monoxide has been significantly extended by the formation of: $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot BF_3$; $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot BBr_3$; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot xBF_3$, $x = 1, 2,$ or 4; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot xBCl_3$, $x = 1$ or 2; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot xBBr_3$, $x = 1$ or 2; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot xAlBr_3$, $x = 1, 2, 3,$ or 4; $(\pi\text{-}C_5H_5)_3Ni_3(CO)_2\cdot BF_3$; $Fe_2(CO)_9\cdot AlBr_3$; $Fe_3(CO)_{12}\cdot AlBr_3$; and $Ru_3(CO)_{12}\cdot AlBr_3$. All of these display one or more very low frequency carbonyl stretching absorptions characteristic of the Lewis acid coordinated bridging carbonyl stretch. Formation of the ruthenium compound involves a terminal-to-bridge CO shift. It is postulated that the formation of $Fe_2(CO)_9\cdot AlBr_3$ may involve the converse, a shift of two CO ligands from bridging to terminal positions. Detailed infrared and Raman investigation of $Co_2(CO)_8\cdot AlBr_3$ provides strong evidence for a structure involving $CO\text{–}AlBr_3$ linkages rather than the originally postulated three-center bond $Co_2\text{–}Al$.

Introduction

Until recently, metal carbonyls were only known in the C-bonded form. However, within the last few years extensive studies demonstrate the interaction of Lewis acids with metal carbonyl derivatives to form C- and O-bonded adducts.[1] Carbon monoxide basicity is particularly characteristic of the bridging ligand in polynuclear metal carbonyl derivatives.[1k] To date, the majority of this work has been conducted with aluminum alkyls as the Lewis acid. These have the advantage of forming soluble adducts, amenable to characterization in solution, but have the disadvantage of destroying many simple polynuclear carbonyls, which are interesting candidates for Lewis acid induced structural rearrangements.[1c] The use of group III halides in the present work was prompted by the thought that they might not participate in destructive side reactions, and being stronger electron pair acceptors than the alkyls,[2] they might exhibit a greater tendency for adduct formation. Group III halide reactions with simple polynuclear carbonyls present interesting structural problems, while interactions of group III halides with polynuclear cyclopentadienyl carbonyls allow comparison with similar studies in which aluminum alkyls were employed.[1c]

The only well-documented complex of a simple polynuclear carbonyl with a group III halide is $Co_2(CO)_8\cdot AlBr_3$, which was first isolated by Chini and Ercoli in 1958 and was thought to contain a three-center donor-acceptor bond, **1**.[3]



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This proposal remained reasonable for many years,[4] because the proton forms three-center, two-electron bonds with polynuclear carbonyls.[5] With the recent observations of bridging carbonyl basicity, a reinvestigation of the proposed $Co_2(CO)_8$ structure became desirable. Several preliminary investigations now favor a C- and O-bonded adduct rather than the originally proposed Co_2Al interaction.[6,7] A more thorough spectroscopic investigation involving both infrared and Raman spectra of this interesting system forms part of the present work.

Experimental Section

Materials. Commercial samples of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ and $(\pi\text{-}C_5H_5)_3Ni_3(CO)_2$ were purified by recrystallization before use, while $Co_2(CO)_8$, $Mn_2(CO)_{10}$, and $Fe_3(CO)_{12}$ were sublimed. $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ was synthesized by King's procedure.[8] $Ru_3(CO)_{12}$ and $Fe_2(CO)_9$ (Strem Chemicals) were used as received. All parent compounds were judged pure by C, H, and N analyses and infrared spectra.

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[4] (a) F. A. Cotton and R. R. Monchamp, *J. Chem. Soc.*, 1882 (1960); (b) D. F. Shriver, *Accounts Chem. Res.*, 3, 231 (1970).

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[7] J. S. Kristoff, N. J. Nelson, and D. F. Shriver, *J. Organometal. Chem.*, 49, C82 (1973).

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$AlBr_3$ (Fisher Chemicals) was twice sublimed before use. $(CH_3)_2O$, $N(CH_3)_3$, BF_3, BCl_3, and BBr_3 were purified by trap-to-trap distillations until their vapor pressures agreed with literature values.[9a] Hydrocarbon solvents were washed with concentrated H_2SO_4, distilled under a nitrogen atmosphere from calcium hydride or benzophenone ketyl, and stored over Linde 4A molecular sieves or comparable drying agents.

General Procedures. All compounds were manipulated on a preparative high vacuum line,[9] except as noted. Reactions of BF_3, BCl_3, and BBr_3 were conducted in grease-free O-ring sealed equipment. Stoichiometries of interaction with BF_3, BCl_3, $(CH_3)_2O$, and $N(CH_3)_3$ were followed by PVT measurements of initial and unused reagent. Complexes with $AlBr_3$ were synthesized utilizing a vacuum-tight grease-free H-type Schlenk tube,[9b] except for the $Fe_2(CO)_9$ system which was prepared in standard Schlenk equipment.[9] A nitrogen filled drybox was used for solids transfer. Analyses were performed by Dornis and Kolbe Micro-Analytical Laboratories, Mulheim (Ruhr), West Germany, Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and in some cases by the Northwestern Analytical Services Laboratory.

$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot BF_3$. A tensimetric titration by BF_3 of 0.333 mmol of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ suspended in *ca.* 1.5 ml of toluene at −78° demonstrates 1:1 interaction, 1.00:0.99 mol ratio of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2{:}BF_3$. This is confirmed by PVT measurement of initial and unused BF_3 for which the mole ratio was 1:1.07. Upon warming to room temperature, the blood red adduct reverted to the parent compound with stoichiometric release of BF_3.

A similar experiment, conducted at −78° using *n*-pentane as the solvent, produced a mole ratio of 1:1.00 as determined by PVT measurements. Removal of the solvent at −78° left the dark red adduct intact. At −2°, the compound exhibits a vapor pressure of 26 mm.

$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot BCl_3$. Formation of the BCl_3 adduct was hampered by a side reaction which produced $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ and other unidentified products. In one experiment employing BCl_3 as a solvent, partial formation occurred (*ca.* 75%) without cleavage. Exposure to air regenerated the parent compound and produced a small amount of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ as well.

$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot BBr_3$. A 0.354-mmol sample of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ was suspended in $n\text{-}C_5H_{12}$ and a *ca.* tenfold excess of BBr_3 was added. After 12 hr at 0°, the solvent and excess BBr_3 were removed from the dark red complex. Exposure to air produced the parent compound and trace amounts of $(\pi\text{-}C_5H_5)Fe(CO)_2Br$. *Anal.* Calcd for $(C_5H_5)_2Fe_2(CO)_4BBr_3$: C, 27.80; H, 1.66; Fe, 18.47; B, 1.78. Found: C, 26.31; H, 2.09; Fe, 18.80; B, 1.78.

$[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot xBF_3$. $x = 1$. A 0.146-mmol sample of BF_3 was added to 0.138 mmol of $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ suspended in *ca.* 1.5 ml of toluene. After 24 hr at 0°, solvent and excess BF_3 were removed. Trap-to-trap distillation revealed that uptake of BF_3 was complete. $x = 2$. Over an 8-day period a tensimetric titration of 0.213 mmol of $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ suspended in *n*-pentane at −78° with BF_3 produced a break in the titration curve at a 1:1.98 mol ratio of $[(\pi\text{-}C_5H_5)Fe(CO)]_4{:}BF_3$. PVT measurement of initial and unreacted BF_3 produced a ratio of 1:2.10. $x = 4$. A tensimetric titration of 0.177 mmol of parent compound suspended in CH_2Cl_2 with BF_3 at −78° produced a 1:4.05 $[(\pi\text{-}C_5H_5)Fe(CO)]_4{:}BF_3$ mol ratio after 3 months. Measurements of the BF_3 evolved upon warming to room temperature revealed a mole ratio of 1:2.16 for the remaining solid.

$[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot xBCl_3$. $x = 1$. A 0.324-mmol sample of iron tetramer suspended in xylene was allowed to react at room temperature with 0.333 mmol of BCl_3 for 2 weeks. Trap-to-trap distillation revealed complete uptake of BCl_3. $x = 2$. To a suspension of 0.179 mmol of $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ in *ca.* 3 ml of xylene was added 0.609 mmol of BCl_3. After 2 weeks at room temperature excess BCl_3 and solvent were removed. PVT measurements of initial and unreacted BCl_3 produced a 1:1.91 mol ratio of $[(\pi\text{-}C_5H_5)Fe(CO)]_4{:}BCl_3$.

$[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot xBBr_3$. $x = 1$. To a 0.237-mmol sample of $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ in CH_2Cl_2 was added 0.024 ml of BBr_3. The reaction was allowed to proceed 1 week. *Anal.* Calcd for $(C_5H_5)_4Fe_4(CO)_4BBr_3$: C, 34.06; H, 2.38; B, 1.27. Found: C, 33.86; H, 2.78; B, 1.37. $x = 2$. To 0.8462 g (1.42 mmol) of $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ in *ca.* 15 ml of CH_2Cl_2 was added 1.8 ml of BBr_3 (*ca.* 18 mmol). The sample was stirred at room temperature for three weeks, whereupon excess BBr_3 and solvent were removed. Addition of excess $N(CH_3)_3$ followed by PVT measurement of the uncomplexed $N(CH_3)_3$ indicated a $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ to BBr_3 ratio of 1:2.07.

Table I

Carbonyl	Carbonyl: Lewis acid Ratio		
	BX_3[a]	$AlBr_3$[a]	AlR_3[b]
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$	1:1	1:2[c]	1:1, 1:2
$(\pi\text{-}C_5H_5)_3Ni_3(CO)_2$	1:1		1:1, 1:2
$[(\pi\text{-}C_5H_5)Fe(CO)]_4$	1:1, 1:2, 1:4	1:1, 1:2, 1:3, 1:4	1:4[d]
$Co_2(CO)_8$	*e*	1:1	Dec
$Fe_3(CO)_{12}$		1:1	Dec
$Fe_2(CO)_9$		1:1	Dec
$Ru_3(CO)_{12}$	*f*	1:1	

[a] Present work. [b] Reference 1c. [c] Identified by infrared spectrum. [d] Solution infrared data[1c] indicate a range of lower adducts also exist but these have never been characterized. [e] Evidence for weak interaction, see Experimental Section. [f] No evidence for interaction with BBr_3 or BI_3.

$[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot xAlBr_3$. $x = 1\text{–}4$. Stoichiometric quantities of $AlBr_3$ and $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ were allowed to react for prolonged periods at room temperature in aromatic solvents to produce 1:1, 1:2, and 1:3 $Fe_4{:}Al$ adducts. For $x = 4$, 3.0 mmol of $AlBr_3$ was allowed to react with 0.386 mmol of the iron tetramer at room temperature in toluene using the H apparatus. After 20 hr the resulting green adduct was washed with toluene and dried. When exposed to air, each of these adducts reverted to the parent carbonyl. *Anal.* Calcd for $(C_5H_5)_4Fe_4(CO)_4(AlBr_3)_4$: C, 17.38; H, 1.20; Fe, 13.43; Al, 6.49; Br, 57.67. Found: C, 17.69; H, 1.43; Fe, 12.79; Al, 7.21; Br, 58.60.

$(\pi\text{-}C_5H_5)_3Ni_3(CO)_2\cdot BF_3$. A 0.241-mmol sample of $(\pi\text{-}C_5H_5)_3Ni_3(CO)_2$ suspended in *ca.* 3 ml of toluene at −78° was tensimetrically titrated with BF_3 to yield a 1:1.0 mol ratio of $(\pi\text{-}C_5H_5)_3Ni_3(CO)_2{:}BF_3$. PVT measurement of initial and uncomplexed BF_3 gave a 1:0.93 $Ni_3{:}BF_3$ mol ratio at −78°. Upon warming to room temperature the yellow-brown suspension decomposed with stoichiometric loss of BF_3. Attempts to produce the respective BCl_3 and BBr_3 adducts were unsuccessful owing to decomposition of the parent compound in the presence of these halides.

$Co_2(CO)_8\cdot AlBr_3$. This compound was prepared according to the method of Chini and Ercoli.[3] To a suspension of $Co_2(CO)_8\cdot AlBr_3$ in heptane was added excess $(CH_3)_2O$ at −78°. Removal of uncomplexed $(CH_3)_2O$ at −78° indicated a 2.10:1 mol ratio of $(CH_3)_2O{:}Co_2(CO)_8\cdot AlBr_3$. Metal analysis produced a 2.03:1 mol ratio of Co:Al. As judged by infrared spectra, regeneration of the parent compound could be achieved by addition of excess $(CH_3)_2O$ at room temperature. Attempts to prepare a $Co_2(CO)_8\cdot 2AlBr_3$ complex by exposing $Co_2(CO)_8$ to a large excess of $AlBr_3$ for prolonged periods were unsuccessful. Infrared spectra revealed only the presence of a 1:1 species.

$Co_2(CO)_8\cdot BBr_3$. Addition of excess BBr_3 to a pentane solution containing $Co_2(CO)_8$ resulted in the formation of a yellow precipitate, resembling that of the $AlBr_3$ adduct. Removal of solvent and excess BBr_3 at room temperature regenerated the parent compound, demonstrating a finite vapor pressure of the adduct. Attempts to form adducts of BF_3 and BCl_3 at low temperatures were unsuccessful.

$Fe_2(CO)_9\cdot AlBr_3$. To a Schlenk flask containing 1.0 g of $Fe_2(CO)_9$ (2.75 mmol) and 3.4 g of $AlBr_3$ (12.70 mmol) was added 40 ml of heptane. After stirring 5 days at room temperature, the fine yellow precipitate was filtered, washed with heptane, and dried *in vacuo*. A 0.1100-g sample of the compound reacted with 0.190 mmol of $(CH_3)_2O$ at 0° indicating a 1:1.10 mol ratio of $Fe_2(CO)_9{:}AlBr_3$. The adduct upon reaction with $(CH_3)_2O$ was completely converted to the parent compound as judged by infrared spectra. *Anal.* Calcd for $(CO)_9Fe_2AlBr_3$: C, 17.01; Fe, 18.36; Al, 4.24; Br, 37.72. Found: C, 15.69; Fe, 18.03; Al, 4.46; Br, 39.97.

$Ru_3(CO)_{12}\cdot AlBr_3$. A 0.490-g sample of $Ru_3(CO)_{12}$ (0.767 mmol) and 1.0 g of $AlBr_3$ (3.7 mmol) were added to the chambers of the H apparatus. After evacuation, *ca.* 15 ml of toluene was distilled into the chamber containing the $AlBr_3$. The resulting $AlBr_3$–toluene solution was filtered into the chamber containing $Ru_3(CO)_{12}$, whereupon the orange-yellow of the parent changed to dark red. This suspension was stirred for 30 min at room temperature and cooled at −78° for 8 hr. Upon warming to room temperature, it was stirred for an additional 30 min and filtered. The product was washed twice using toluene which had been distilled from the filtrate arm. The red solid is diamagnetic at room temperature. It reverts to the parent carbonyl upon exposure to air or to $(CH_3)_2O$. *Anal.* Calcd for $(CO)_{12}Ru_3AlBr_3$: C, 15.90; Ru, 33.45; Al, 2.95. Found: C, 16.02; Ru, 33.48; Al, 2.76.

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(9) (a) D. F. Shriver, "Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969; (b) *ibid.*, p 153; this standard H-Schlenk tube was modified by the use of large Teflon-in-glass valves in place of ground glass joints.

Table II. Carbonyl Stretching Frequencies for Adducts of Cyclopentadienyl Metal Carbonyls[a,b]

Parent metal compd	Lewis acid	ν_{CO}(terminal)	ν_{CO}(>CO)	ν_{CO}(>CO-M)
cis-$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$[c]		1930 s	1765 s	
		1971 s	1797 sh	
	$Al(C_2H_5)_3$[d]	1985 s	1828 m	1682 s
		1993		
	BCl_3	2020 s	1845 s	1463 s
		2038 s		
	BBr_3	1984 s, sh	1848 s	1438 s
		2008 s, sh		
		2020 s		
		2030 s		
$[(\pi\text{-}C_5H_5)Fe(CO)]_4$			1640 s[e]	
	BF_3		1632 s, sh	1365 s
			1674 vs	
			1671 s, sh	
			1689 s	
			1694 s	
	BCl_3		1671 vs[f]	1292 s
			1702 s[f]	
	BBr_3		1672 vs[f]	1301 s
			1705 s[f]	1312 w, sh
	$AlBr_3$		1673 s[g]	1392 s
			1700 mw[g]	
$[(\pi\text{-}C_5H_5)Fe(CO)]_4$	$2BF_3$		1660 s, sh	1405 s
			1675 vs	1435 s
			1680 sh	
			1705 s	
	$2BCl_3$		1703 vs[h]	1327 s
			1722 m[h]	1360 s
	$2BBr_3$		1705 vs[h]	1320 s
			1722 m[h]	1365 s, sh
	$2AlBr_3$		1675 s[g]	{1368 sh
			1715 mw[g]	1395 vs
				1415 s, sh}
	$3AlBr_3$		1755 vs	{1439 vs
				1470 sh}
	$4AlBr_3$			1473 vs

[a] Features which are part of one broad absorption are enclosed in braces. [b] All data represent infrared spectra obtained on Nujol or Fluorolube mulls unless otherwise noted. [c] R. F. Bryan, D. S. Field, and M. J. Newlands, *Chem. Commun.*, 1477 (1969). [d] Heptane solution; see ref 1c. [e] CH_2Cl_2 solution. [f] 1.0 mm NaCl, saturated solution in CH_2Cl_2. [g] 1.0 mm NaCl, saturated solution in C_6H_6. [h] 1.0 mm NaCl, fivefold excess of Lewis acid in CH_2Cl_2.

$Fe_3(CO)_{12}\cdot AlBr_3$. The above procedures were employed with a 0.795-mmol sample of $Fe_3(CO)_{12}$ and 4.5 mmol of $AlBr_3$. The resulting green-black suspension was stirred 1 hr at room temperature, filtered, and washed. No gas evolution was detected. Addition of $(CH_3)_2O$ to the $AlBr_3$ adduct resulted in regeneration of the parent compound. *Anal.* Calcd for $(CO)_{12}Fe_3AlBr_3$: C, 18.70; Fe, 21.74; Al, 3.50. Found: C, 18.03; Fe, 22.52; Al, 3.60.

Spectra. All medium infrared spectra were obtained with a Beckman IR 9. Far infrared spectra were obtained with a Beckman IR 11 on Nujol mulls between polyethylene windows. Carbonyl band positions were determined with several slow scans on an expanded scale. Solution spectra of the halide adducts were obtained with saturated solutions in 1.0 mm NaCl or Irtran-2 windowed cells. Nmr spectra were obtained with a Bruker HFX-90 (90 MHz) spectrometer on toluene-d_8 solutions. Raman spectra were determined on rotating samples with a Spex 1401 spectrometer and a Spectra Physics 164 Kr^+ laser operating at 6471 Å with an estimated power at the sample of 0.2 W. The instrument band pass was *ca.* 2 cm^{-1}.

Discussion

Table I summarizes in general terms the observed stoichiometries for group III Lewis acids interacting with polynuclear carbonyls and carbonyl derivatives. An interesting feature in these data, which will be discussed later, is the observation of 1:1 adducts for $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ or $(\pi\text{-}C_5H_5)_3Ni_3(CO)_2$ interacting with boron halides, which contrasts with 1:2 interaction with the presumably weaker aluminum alkyl acids. Also notable is the fact that $AlBr_3$ adducts of several simple polynuclear carbonyls are isolable, while their aluminum alkyl analogs are not, owing to rapid side reactions.

A distinctive characteristic of metal carbonyl adduct formation is the large decrease observed for ν_{CO} of the carbonyl bridging to the Lewis acid and a small increase for ν_{CO} of all remaining carbonyls.[1c] This pattern is observed with all the group III halide adducts listed in Tables II and III, affording good evidence for adduct formation at the bridging carbonyl oxygen. By contrast, all the carbonyl frequencies would be expected to increase substantially if the Lewis acid addition occurred at the metal.[4b] In addition to these general features, detailed selection rules afford specific confirmation of the structures for certain of the adducts. The possibility of cleavage and other drastic reactions, rather than simple adduct formation, is ruled out by regeneration experiments with atmospheric moisture, ether, amine, or vacuum.

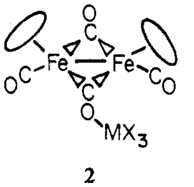
Cyclopentadienyl Metal Carbonyl-Lewis Acid Systems. These systems formed a logical starting point for work with group III halides, because their chemistry has been previously well developed with aluminum alkyls as Lewis acids.[1c] In contrast with the soluble aluminum alkyl systems, it was not possible to obtain complete solution spectra in the ν_{CO} region for most of the boron and aluminum halide adducts, because of low solubility in suitable solvents. Despite this complication, reasonably secure inferences can be drawn from vibrational spectra on solids. By confining our attention to the strong features in the $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot BCl_3$ and $\cdot BBr_3$ spectra (Table II), we see the strong pair of absorptions in the terminal ν_{CO} region, the single band due to an iron-bridging ν_{CO} in the region usually associated with the bridging carbonyl, and a very low frequency absorption attributed to ν_{CO} of $>COMX_3$. As we have described previously for the aluminum alkyl system, this pattern is con-

Table III. Carbonyl Stretching Frequencies for Adducts of Metal Carbonyls[a, b]

Parent carbonyl	Lewis acid	ν_{CO}(terminal)	ν_{CO}(>CO)	ν_{CO}-(>CO-M)
$Co_2(CO)_8$		2022 vs	1832 vs	
		2042 vs	1852 vs	
		2056 sh		
		2068 vs		
	$AlBr_3$	2025 ms	1867 s	1600 s
		2040 ms		
		2062 s		
		2070 s		
		2082 sh		
		2095 ms		
		2105 ms		
		2138 ms		
$Fe_3(CO)_{12}$		1955 sh	1821 m	
		2012 s, b	1852 sh	
		2054 vs		
	$AlBr_3$	2008-2070 s, b	1922 mw	1548 s
		2081 ms		
		2124 mw		
$Fe_2(CO)_9$		1986 sh	1828 s	
		2015 vs		
		2065 s		
	$AlBr_3$	2000 vs	1830 w?[c]	1523 w
		2024 vs		1557 s
		2030 sh		
		2048 s		
		2060 s		
		2070 s		
		2080 s		
		2135 m		
$Ru_3(CO)_{12}$		1978 s		
		1982 s		
		1987 vs		
		1998 vs		
		2017 s, b		
		2055 s		
		2062 s, b		
	$AlBr_3$	1987 s		1535 s
		2000 s		
		2024 vs, b		
		2040 m		
		2055 s, sh		
		2062 vs		
		2131 sh		

[a] Features which are part of a broad absorption are enclosed in braces. [b] All data represent solid state infrared spectra obtained on Nujol or Fluorolube mulls. [c] Feature sometimes observed. May be due to uncomplexed $Fe_2(CO)_9$.

sistent with a 1:1 bridging carbonyl adduct **2** or its trans counterpart.[1c]



2

1:1 adduct; ~C_s

ν_{CO} (–CO): a′, a″

ν_{CO} (>CO): a′

ν_{CO} (>CO-M): a′

⬭ = (π-C_5H_5)

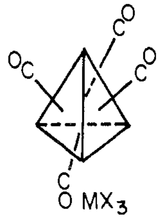
Variable temperature nmr spectra of [(π-C_5H_5)Fe(CO)$_2$]$_2$·BF_3 in toluene-d_8 reveal a high field peak assigned to the cis isomer and a much less intense low field feature due to the trans isomer, in agreement with previous [(π-C_5H_5)Fe(CO)$_2$]$_2$·AlR_3 investigations.[1c] Furthermore, the cis-trans exchange rate for the adduct is less than that of the parent compound, indicating stabilization of the bridged species.

As with the iron dimer, (π-C_5H_5)$_3$Ni$_3$(CO)$_2$ forms only a 1:1 adduct with BF_3 at −78°, which reverts to the parent at room temperature. The comparable basicity for these two carbonyls parallels the similarity in their bridging carbonyl stretching frequencies.

For [(π-C_5H_5)Fe(CO)]$_4$, infrared spectra were obtained on the whole series of adducts ranging from 1:1 to 1:4. Comparison of these data with selection rules for ν_{CO} provides a critical test of the structures, Table II and Figure 1. As expected, ν_{CO} for carbonyl groups not coordinated to the Lewis acid is generally split by solid state effects. Fortunately, solution infrared generally were obtainable in this region. Even though the solvents masked ν_{CO} of the

$$\overset{\backslash}{\underset{/}{-}}\mathrm{CO\text{-}MX_3}$$

groups, it was possible to employ solid state spectra for these absorptions because these modes appear not to be susceptible to splitting by interactions in the solid state, the single band of [(π-C_5H_5)Fe(CO)]$_4$·4$AlBr_3$ being a good case in point. Another potential complication which appears not to affect the vibrational data[1c] is lack of linearity of the CO-M linkages, which in available X-ray structural results are bent.[1a,g] Concentrating on the symmetry of the CO array, the selection rules for the successive adducts follow the pattern outlined in structures **3** through **6**. For each of the

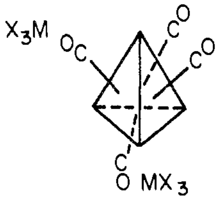


3

1:1 adduct; C_{3v}

ν_{CO}($\overset{\backslash}{\underset{/}{-}}$CO): a$_1$, e

ν_{CO}($\overset{\backslash}{\underset{/}{-}}$CO-M): a$_1$

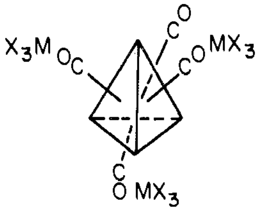


4

1:2 adduct; C_{2v}

ν_{CO} ($\overset{\backslash}{\underset{/}{-}}$CO): a$_1$, b$_1$

ν_{CO}($\overset{\backslash}{\underset{/}{-}}$CO-M): a$_1$, b$_2$

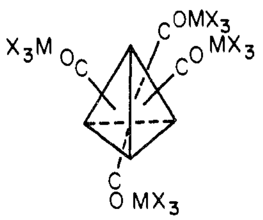


5

1:3 adduct; C_{3v}

ν_{CO} ($\overset{\backslash}{\underset{/}{-}}$CO): a$_1$

ν_{CO}($\overset{\backslash}{\underset{/}{-}}$CO-M): a$_1$, e



6

1:4 adduct; T_d

ν_{CO} ($\overset{\backslash}{\underset{/}{-}}$COM): t$_2$

adducts having solution infrared data, the expected numbers of CO stretching frequencies show perfect agreement with the observations recorded in Table II.

A striking difference between the aluminum alkyls and the group III halides is the much greater shift in ν_{CO} upon adduct formation with the latter acids. The increase in frequency

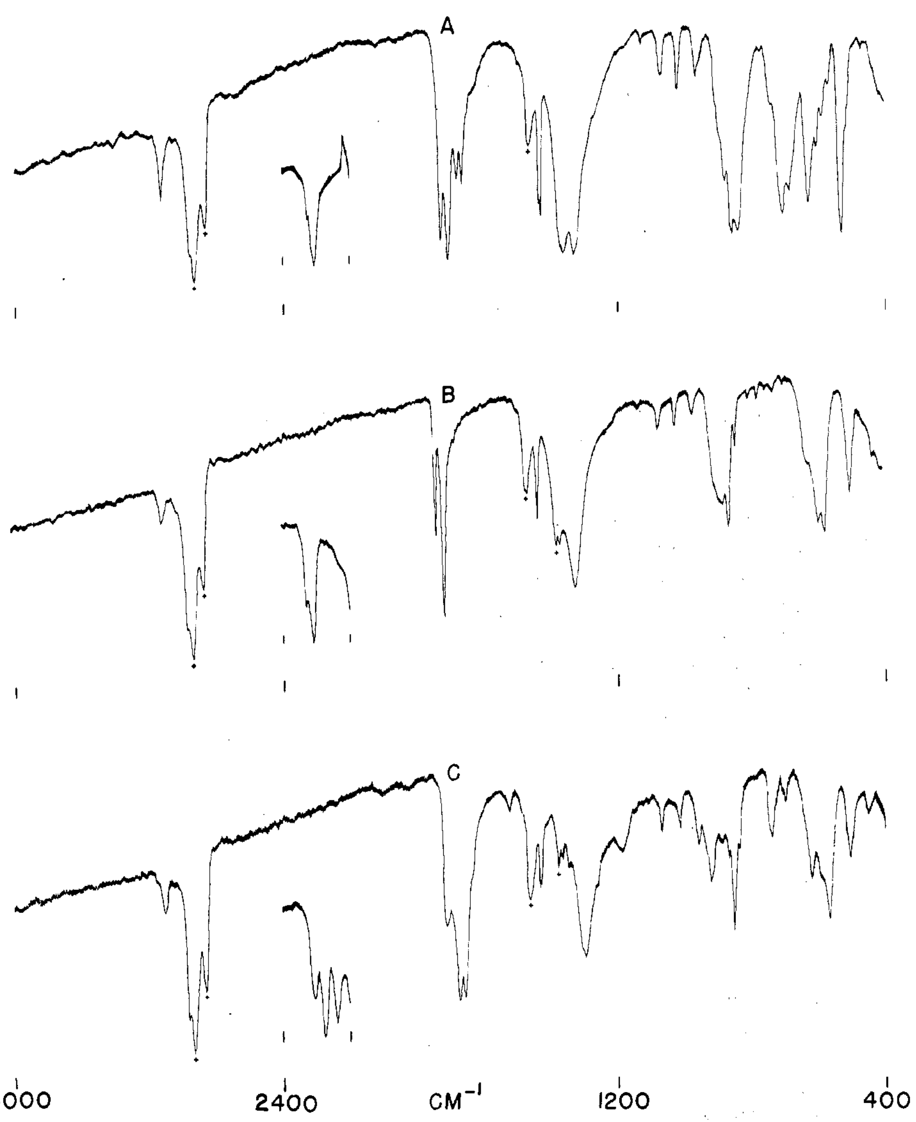


Figure 1. Infrared spectra of: A, $[(\pi\text{-}C_5H_5)Fe(CO)]_4 \cdot 2BCl_3$; B, $[(\pi\text{-}C_5H_5)Fe(CO)]_4 \cdot 2BBr_3$; C, $[(\pi\text{-}C_5H_5)Fe(CO)]_4 \cdot BBr_3$. For each compound the upper tracing was obtained on a mull. Nujol peaks are marked by +. The lower tracing in each case is a CH_2Cl_2 solution spectrum for ν_{CO} of CO ligands which are not coordinated at oxygen, the 1600 and 1800 cm^{-1} positions being indicated by vertical lines. The low frequency peak of insert to C arises from the rapid decomposition of the 1:1 adduct to produce the parent.

for ν_{CO} of carbonyl groups not coordinated to the Lewis acid has been attributed to a lowering of electron density on the metal atoms *via* increased back π bonding with the Lewis acid coordinated carbonyls.[1b,c] Detailed analysis of this type of phenomenon has been presented recently for the formation of $(\pi\text{-}C_5H_5)Fe(CO)_2(CNMX_3)$ adducts, where it was shown that the degree of increase in $\nu_{CO}{}^{asym}$ is related to the electron pair acceptor strength of the acid, MX_3.[2] The observed increases listed in Table II are in harmony with a larger electron pair acceptor strength for the boron halides and $AlBr_3$ than for the aluminum alkyls.

The very large decreases in ν_{CO} for the C- and O-bonded carbonyls in these group III halide adducts must in part reflect a decrease in CO bond order upon adduct formation, some of which may be attributed to increased π acceptor character for the MX_3-coordinated carbonyl. In addition, kinematic coupling with MX_3 and a variety of electronic effects may influence these particular modes, so little significance can be attached to trends among the various MX_3 adducts.

As mentioned earlier, one remarkable feature of the group III halide adducts is the tendency toward lower stoichiometries than found with the aluminum alkyls, Table I. The iron dimer, $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, provides a good example since 1:2 adducts were readily isolated when an excess of aluminum alkyl was employed in the synthesis but only 1:1 adducts were detected with BF_3 and BCl_3. Similarly the iron tetramer, $[(\pi\text{-}C_5H_5)Fe(CO)]_4$, forms a 1:4 aluminum alkyl adduct, but the only BF_3 and BCl_3 adducts isolated at room temperature have 1:2 stoichiometry. Some of these differences may be attributable to the greater volatility of the boron halides which leads to low concentration of the halide in solution during adduct isolation and consequently an unfavorable adduct equilibrium. This cannot be a complete explanation because infrared spectra of saturated methylene chloride solutions of $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ containing a five-fold excess of either BCl_3 or BBr_3 show only the 1:2 adduct. The present results, however, leave no doubt that $AlBr_3$ is a stronger acid than AlR_3 toward the iron tetramer, $[(\pi\text{-}C_5H_5)Fe(CO)]_4$, since it was possible to prepare 1:1, 1:2, 1:3, and 1:4 adducts by mixing the tetramer with $AlBr_3$ in the exact ratio required for each of these stoichiometries. In each case the infrared spectra verify that a unique compound and not a mixture is produced. By contrast, an

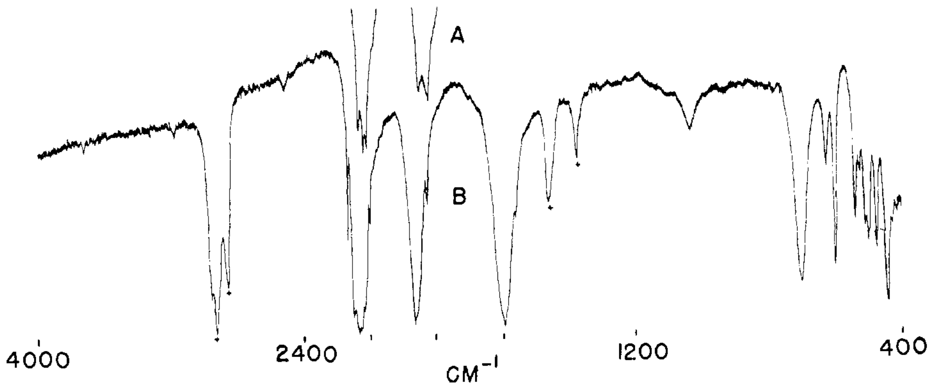
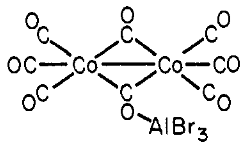


Figure 2. Infrared spectra of (A) $Co_2(CO)_8$ and (B) $Co_2(CO)_8 \cdot AlBr_3$. Peaks due to the mulling agent, Nujol, are indicated by +. The *ca.* 1000 cm^{-1} band is not seen in all spectra and therefore may be spurious.

excess of aluminum alkyl is required to produce a 1:4 adduct.

Polynuclear Carbonyl-Lewis Acid Systems. The yellow, extremely air-sensitive $Co_2(CO)_8 \cdot AlBr_3$ system is very insoluble in nonreacting solvents and was therefore characterized by solid state infrared and Raman spectroscopy. The structure originally proposed for this compound, **1**, involving a three-center donor-acceptor bond, requires two bridging CO stretching modes increased in frequency from the parent. For adduct formation on a bridging carbonyl, structure **7**, two ν_{CO} are expected, one at higher frequency from either of the parent bands and one much lower. Precisely this pattern is evident in the infrared spectra, Table III and Figure 2, which exhibits a strong band at 1867 cm^{-1}, 15 cm^{-1} above the highest frequency bridging mode in the parent, and a strong 1600 cm^{-1} band, which is 232 cm^{-1} below the lowest frequency mode of the parent. The magnitude of this frequency decrease is similar to that found with the aluminum bromide adducts of bridging carbonyls in cyclopentadienyl metal carbonyls, Table II. Far infrared data also support a C- and O-bonded structure. A strong feature at 280 cm^{-1} is similar to a band found in organic carbonyl-aluminum halide adducts,[10] and an absorption at 448 cm^{-1} is similar to that of the asymmetric $AlBr_3$ stretch in $AlBr_3N(CH_3)_3$.[11]



7

The Raman spectra for $Co_2(CO)_8$ and its $AlBr_3$ adduct are much better resolved than the infrared, owing to the usual narrow line width of Raman bands for solid samples. While shifted to higher frequency in the adduct, the terminal CO stretch region of both the parent and adduct are quite similar in pattern, Figure 3. Also, only one feature is observed in the bridging carbonyl region at 1863 cm^{-1}, which further substantiates the correctness of structure **7** for the adduct. The 1600-cm^{-1} infrared band of the oxygen-coordinated bridging carbonyl does not have a Raman counterpart presumably because bridging $\nu(>COAlBr_3)$ are very weak in Raman. (A medium weak feature is observed at 1544 cm^{-1}, which may correspond to an instrumental artifact as it is often seen under very high gain conditions with a variety of samples.)

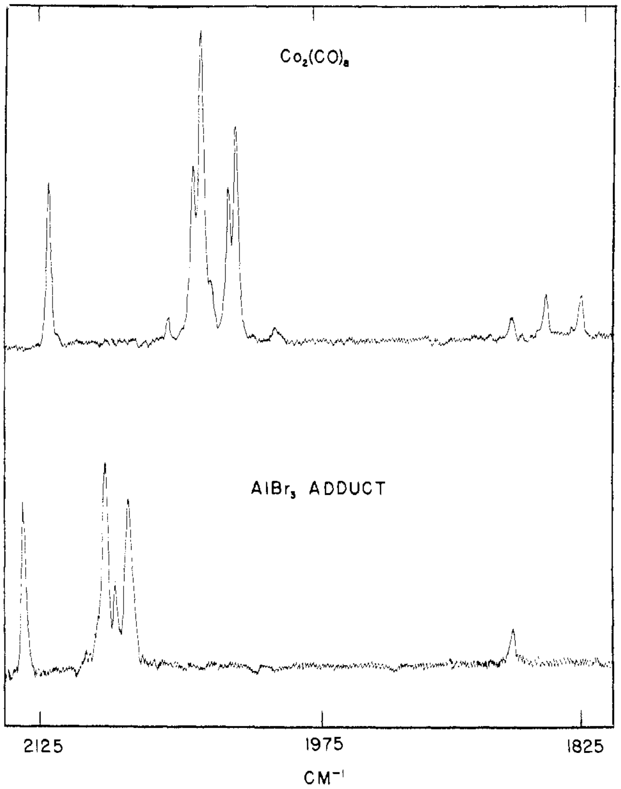
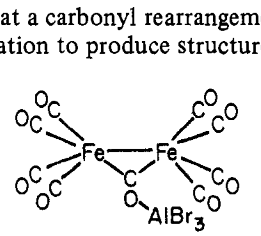


Figure 3. Raman spectra of $Co_2(CO)_8$ and $Co_2(CO)_8 \cdot AlBr_3$.

The infrared spectrum of $Fe_2(CO)_9 \cdot AlBr_3$, Table II and Figure 4, is quite interesting because only one CO stretch is observed in the bridging carbonyl stretch region and this is at a low frequency characteristic of $>CO\text{-}AlBr_3$. This spectral datum indicates that a carbonyl rearrangement may occur upon adduct formation to produce structure **8**, in which the



8

disposition of CO ligands is similar to that proposed for $Os_2(CO)_{12}$.[12] Such a structure would require the migration of two carbonyls from their bridging positions in the parent

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(10) D. E. H. Jones and J. W. Wood, *J. Chem. Soc. A*, 1140 (1967).

(11) I. R. Beattie and G. A. Ozin, *J. Chem. Soc. A*, 2373 (1968).

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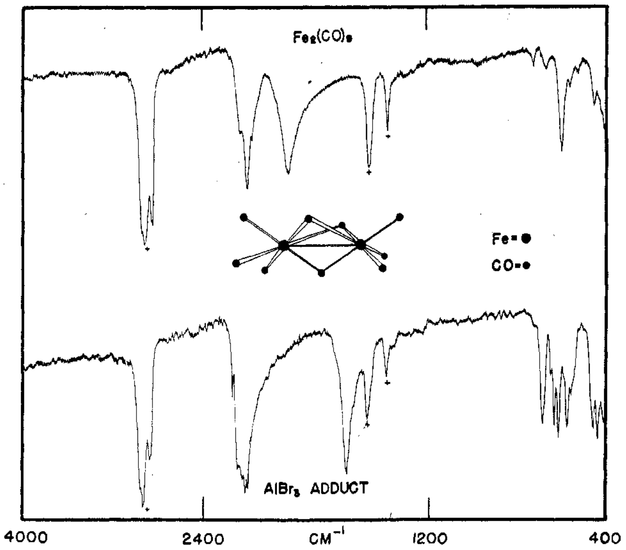
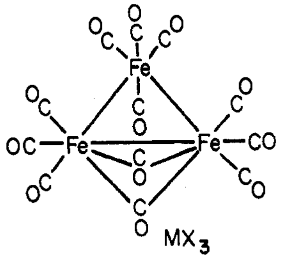


Figure 4. Infrared spectra of $Fe_2(CO)_9$ and $Fe_2(CO)_9 \cdot AlBr_3$. Nujol peaks are indicated by +.

compound[13] to terminal positions in the adduct. The very broad low frequency wing of the terminal ν_{CO} band for the adduct does, however, leave open the possibility that weak bridging carbonyl absorptions are buried. Therefore, the possibility of simple adduct formation without carbonyl rearrangement cannot definitely be ruled out. The Raman spectrum of the adduct is very complex in the terminal CO stretch region, showing a total of 11 bands between 2000 and 2135 cm^{-1}. No Raman peaks in the bridging carbonyl region are detected except a weak feature attributed to $>CO{:}AlBr_3$, which is consistent with **8**.

The 1:1 adduct $Fe_3(CO)_{12} \cdot AlBr_3$ probably has either structure **9** or **10**. The first, **9**, involves addition to one of the bridging carbonyls in the known $Fe_3(CO)_{12}$ structure,[14] and the second, **10**, represents an adduct in which CO rearrangement has occurred. Both structures would give rise to one low frequency CO-Al carbonyl stretch, such as that observed at 1548 cm^{-1}. Structure **9** should display a single $>CO$ carbonyl stretch, while **10** should have two such absorptions. As may be seen in Figure 5, only one distinct band is observed (at 1922 cm^{-1}) which would favor structure **9**, but there also is a hint of a weak feature in this region, which if present indicates structure **10**. The disposition of carbonyls in the latter structure is the same as that proposed for $Fe_3(CO)_{12}$ in solution.[14,15]



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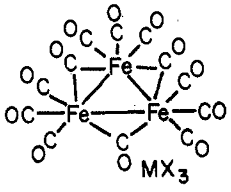

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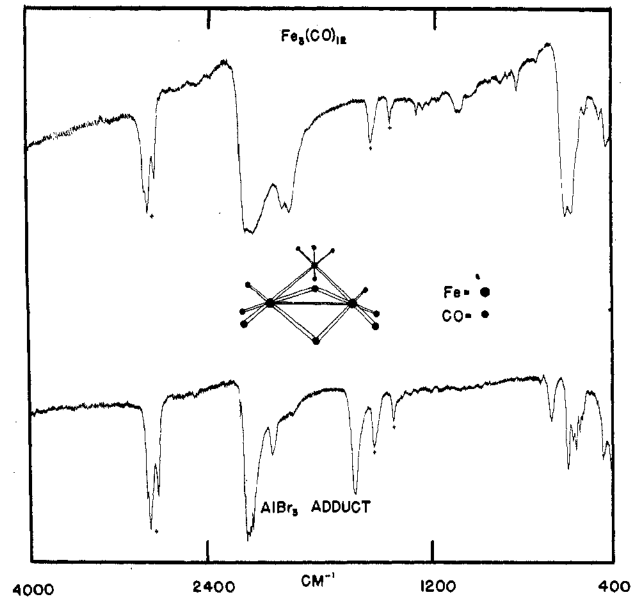


Figure 5. Infrared spectra of $Fe_3(CO)_{12}$ and $Fe_3(CO)_{12} \cdot AlBr_3$. Nujol peaks are indicated by +.

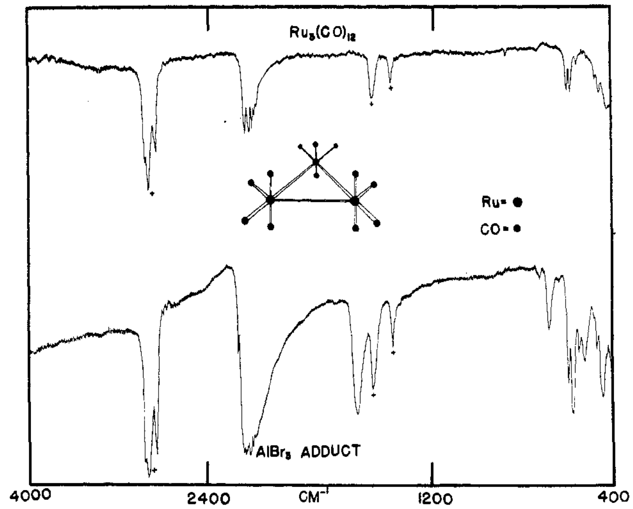
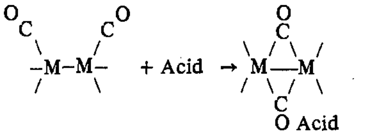


Figure 6. Infrared spectra of $Ru_3(CO)_{12}$ and $Ru_3(CO)_{12} \cdot AlBr_3$. Nujol peaks are indicated by +.



$$-\overset{\overset{O}{C}}{M}-\overset{\overset{O}{C}}{M}- \ + \text{Acid} \rightarrow \ M\underset{\underset{\text{O Acid}}{C}}{\overset{\overset{O}{C}}{-}}M \qquad (1)$$

In previous work it has been shown that the affinity of Lewis acids for bridging carbonyls may induce a terminal-to-bridge CO shift schematically shown in (1).[1c,d] The $Ru_3(CO)_{12}$ molecule was chosen as a likely candidate for this type of rearrangement since the structure of the parent involves only terminal carbonyls,[16] but analogy with $Fe_3(CO)_{12}$ suggests that bridging CO groups may be energetically accessible. As described in the Experimental Section, a 1:1 adduct, $Ru_3(CO)_{12} \cdot AlBr_3$, does form. The infrared spectrum, Figure 6 and Table III, displays the characteristic low frequency CO-$AlBr_3$ ν_{CO} at 1535 cm^{-1} and an increase in the terminal stretch region. However, no absorptions are found in the $>CO$ stretch regions as would be required for structures analogous to **9** or **10**. It will be noted in Figure 6 that the terminal CO stretch absorption, which is usually broad on

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[13] H. M. Powell and R. V. G. Ewens, *J. Chem. Soc.*, 286 (1939).

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the low frequency side, could easily mask a weak bridging CO stretch. In any case, the data clearly indicate a terminal-to-bridge CO rearrangement.[17]

Acknowledgments. We appreciate the support of this research by the NSF through Grant GP-28878. J. S. Kristoff acknowledges an NDEA Fellowship.

[17] As an incidental point, we note that $Mn_2(CO)_{10}$ does not form an adduct under similar conditions.

Registry No. $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot BF_3$, 41666-88-0; $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot BCl_3$, 43198-12-5; $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot BBr_3$, 41666-89-1; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot BF_3$, 39466-88-1; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot 2BF_3$, 39334-03-7; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot BCl_3$, 39334-00-4; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot 2BCl_3$, 39334-01-5; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot BBr_3$, 39333-98-7; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot 2BBr_3$, 39333-99-8; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot AlBr_3$, 39466-84-7; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot 2AlBr_3$, 39466-85-8; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot 3AlBr_3$, 39466-86-9; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot 4AlBr_3$, 39466-87-0; $Co_2(CO)_8\cdot AlBr_3$, 40964-38-3; $Fe_2(CO)_9\cdot AlBr_3$, 49564-14-9; $Ru_3(CO)_{12}\cdot AlBr_3$, 39466-83-6; $Fe_3(CO)_{12}\cdot AlBr_3$, 39466-82-5.

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Alkylation and Substitution Reactions of Metal Carbonyl Acylate and Carbene Complexes

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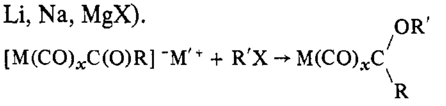
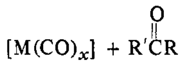
Alkylation reactions of *trans*-$LFe(CO)_3C(O)R^-Li^+$, where L = CO, PPh_3, $P(n\text{-}Bu)_3$, $P(OMe)_3$, and $P(OPh)_3$ and R = Ph, Me, and benzyl, employing as alkylating agents MeI, $MeOSO_2F$, $THFMe^+SO_3F^-$, and $Et_3O^+BF_4^-$, have been investigated. Alkoxonium salts react exclusively at the acyl oxygen yielding carbene complexes; ketones and products of $[LFe(CO)_3]$ are obtained from reaction of the acylate with MeI and $MeOSO_2F$. The rate of MeI reaction with $LFe(CO)_3C(O)R^-Li^+$ is ligand dependent with $P(n\text{-}Bu)_3 > PPh_3 > P(OPh)_3$. MeI is found to react with metal carbonyl carbene complexes also to yield ketone, however too slowly to suggest intermediacy of carbene complex in the ketone synthesis directly from the acylate complex. Alkoxycarbene ligands as well as the acyl ligand (lithiooxycarbene) were found to labilize ligands trans to themselves, *i.e.*, for X = Li or Et, the reaction is $LFe(CO)_3C(OX)R + L' \rightarrow L + L'Fe(CO)_3C(OX)R$. Mechanistic implications for the ketone synthesis based on the observation of ligand-exchange processes at both L and acyl sites ($LFe(CO)_3C(O)R^-Li^+ + L' \rightarrow LFe(CO)_3L' + [Li^+C(O)R^-]$) are discussed.

Introduction

Alkylation reactions of metal carbonyl acylates yield products according to eq 1 and 2 (M = transition metal; M′ = Li, Na, MgX).



$$[\mathrm{M(CO)}_x\mathrm{C(O)R}]^-\mathrm{M'}^+ + \mathrm{R'X} \rightarrow \mathrm{M(CO)}_x\mathrm{C}\begin{smallmatrix}\diagup\mathrm{OR'}\\ \diagdown\mathrm{R}\end{smallmatrix} \qquad (1)$$



$$\rightarrow [\mathrm{M(CO)}_x] + \mathrm{R'}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R} \qquad (2)$$

Equation 1 represents the basis of Fischer's *in situ* preparation of the novel carbene ligand and is most successful with group VIb transition metal carbonyl complexes.[1] On the other hand Fischer and others have had difficulty alkylating analogous iron acylates.[2] Attempted methylation of $Fe(CO)_4[C(O)Ph]^-Li^+$ with $Me_3O^+BF_4^-$ in CH_2Cl_2 led to formation of $Fe_3(CO)_{12}$ and $Fe_2(CO)_9$ as major reaction products with μ-diphenylmethylene-octacarbonyldiiron in <0.5% yield; $Fe(CO)_4C(OMe)Ph$ was not observed. Alkylation of iron tetracarbonyl acylates by $Et_3O^+BF_4^-$ according to eq 1 in CH_2Cl_2 at −60° was observed only when R was a very electron-withdrawing group such as C_6F_5, C_6Cl_5, or $N(CH_3)_2$.[3]

The anionic acylates generated either by reaction of organolithium reagents with $Fe(CO)_5$[4,5] or by reaction of alkyl halides with $Na_2Fe(CO)_4$[6,7] have received much attention due to their usefulness in organic synthesis. Initial investigations into the mechanism of (2) and the isolation of alkyliron carbonylates prompts Collman and coworkers[8-10] to suggest a reductive elimination of the proposed (alkylacyl)iron carbonyl intermediate (formed by two successive oxidative additions of R^+ to $Fe(CO)_4^{2-}$) rather than a nucleophilic reaction by the acyl carbon on the alkyl halide as is most likely the case with main group metal acylates.[11,12]

We have recently completed a kinetic study of the reaction of benzylmagnesium chloride with monosubstituted iron carbonyl derivatives to give chloromagnesium salts of the metal carbonyl acylate.[13] These acylates may be readily characterized by reaction with Meerwein's salt, triethoxonium tetrafluoroborate, in tetrahydrofuran (THF) at room temperature to form the carbene derivative (eq 1). Characteristic CO stretching frequencies for the isolated carbene derivatives may be found in Table I.

Since methyl iodide alkylates at the acyl oxygen in group VIb metal carbonyl acylates[14] but yields ketones with iron carbonyl acylates, further studies on the dependence of site of alkylation on the metal carbonyl residue were undertaken. In particular, we were interested in examining (1) the possible intermediacy of a metal carbene complex in the ketone preparation according to eq 2, (2) the fate of the

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