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Reaction of $Fe_2(CO)_9$ with Lithium: Preparation and Structures of Compounds with Strong Ion Pairing

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The reduction of $Fe_2(CO)_9$ with elemental lithium in THF solution at room temperature generates the dinuclear complex $[Li_2(THF)_6Fe_2(CO)_8]$ (**1**), in which the Li atoms are bonded to the oxygen atoms of bridging CO groups. Dissolution of **1** in toluene leads to loss of two THF molecules to give the polymeric complex $[Li_2(THF)_4Fe_2(CO)_8]_n$ (**2**); dimeric units ($n = 2$) are formed with the help of a planar Li_2O_2 ring, and these units are further linked by Li−O contacts to terminal carbonyl groups. Alkylation of **1** with $MeSO_3CF_3$ yields the known dinuclear compound $[(CO)_3Fe(\mu\text{-}C(Me)O)_2Fe(CO)_3]$ (**4**). Treatment of **1** with Me_3SnCl leads to splitting of the Fe−Fe bond, resulting in *cis*-$[CO)_4Fe(SnMe_3)_2]$ (**6**) as the main product. The X-ray structures of **1**, **2**, and **4** are presented along with the structure of the sodium salt $[Na_2(THF)_4Fe_2(CO)_8]_n$ (**5**), which has only terminal CO groups.

Introduction

The carbonyl ligand has the fascinating property of stabilizing low-valent transition metal compounds as well as a great number of anionic species. Thus, transition metal carbonylates of the type $[M_n(CO)_m]^{x-}$ are available from nearly every binary transition metal carbonyl compound by alkali metal reduction. In most cases the carbonylates are derived from a neutral carbonyl compound by replacement of one CO ligand by a pair of electrons. Carbonylates are highly reactive and are found to be useful precursors in organometallic synthesis. The dinuclear species $[Fe_2(CO)_8]^{2-}$ belongs to one of the first carbonyl anions reported by Hieber about 70 years ago[1] and can be considered as an important key compound in organometal chemistry. Salts of the dianion are known with various counterions,[2] and the most common sodium derivative is quantitatively obtained by reacting Collman's reagent with $Fe(CO)_5$.[3] The dianion also forms during many reactions in which the anion $[Fe(CO)_4]^{2-}$ has come into contact with potential oxidation agents. From X-ray diffraction studies on ammonium[4] or phosphonium[5] salts or others we know that $[Fe_2(CO)_8]^{2-}$ exhibits only terminal CO ligands, and no near contacts to the respective cations can be located. However, no structural data are available from corresponding salts with small counterions such as alkali ions, for which ion pairing is more common than for complex cations. Whereas the effect of ion pairing in transition metal carbonylates is well documented for mononuclear anions, only a few reports are available on ion pairing in dinuclear or polynuclear cluster anions.[6] Studies on the sodium salt of $[(\mu\text{-H})Fe(\mu\text{-CO})_2(CO)_6]^-$, which contains two bridging carbonyl groups, have shown the presence of various types of ion pairs in solution.[3]

The $[Fe_2(CO)_8]^{2-}$ moiety can act as a bidentate ligand to various main group elements[7−9] or transition metals,[10] and in all cases coordination occurs via the iron atoms. Upon coordinating to a metal M, the "ligand" $[Fe_2(CO)_8]^{2-}$ may be present with all terminal (mode **A**) or with two bridging CO groups (mode **B**) as depicted in Scheme 1. In no cases was coordination of a metal ion to one of the carbonyl oxygen atoms observed. Even protonation of $[Fe_2(CO)_8]^{2-}$ avoids carbonyl oxygen atoms and takes place at the Fe−Fe bond (the HOMO orbital) with formation of $[(\mu\text{-H})Fe_2(\mu\text{-CO})_2(CO)_6]^-$, related to the structural mode **B** ($M = H$).[3]

To our knowledge no lithium salt of $[Fe_2(CO)_8]^{2-}$ has been described in the literature. In this contribution we report on the results of the reduction of $Fe_2(CO)_9$ with elemental lithium in THF to produce a salt-like complex with strong ion pairing and its behavior in aromatic solvents. The structures of the resulting complexes in the solid state and the reaction products with electrophiles such as $MeSO_3CF_3$ and Me_3SnCl are also presented. For comparison and for better understanding of the bonding situation in the lithium complex the structure of the sodium salt has also been determined.

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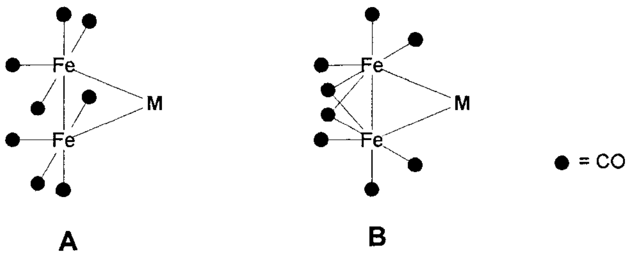
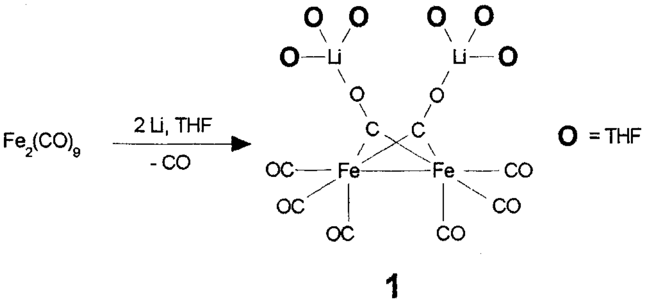
Scheme 1



Scheme 2



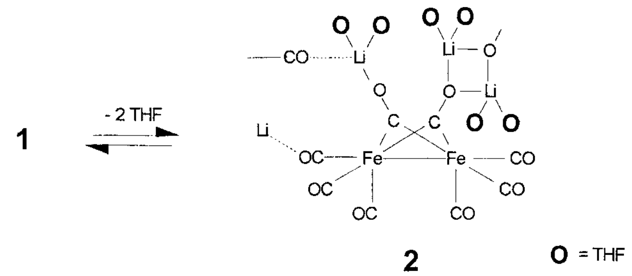
Results and Discussion

Synthesis and Spectra. Iron enneacarbonyl reacts with 2 equiv of metallic lithium in THF at room temperature to give a dark red-brown solution. After about 3 h all $Fe_2(CO)_9$ is consumed and dissolved. The reaction is exothermic, and water-cooling is required to keep the solution at room temperature. However, at lower temperature no reaction is observed; at about 20 °C on rapidly stirring the suspension, the reaction starts within a few minutes. Large yellow-orange crystals separate from the solution on layering with *n*-pentane and cooling to −20 °C. The crystals were identified by X-ray studies as the dinuclear complex **1**, containing two bridging CO groups with an oxygen to lithium coordination; three THF molecules complete the tetrahedral arrangement at the lithium atom. **1** is soluble in THF and toluene and only slightly soluble in *n*-pentane (Scheme 2).

The IR spectrum of **1** shows a very low lying ν(CO) stretching frequency at 1650 cm^{-1}, which can be attributed to the μ_3:η^2-CO groups. One sharp band at 1991 cm^{-1} and a broad unresolved band centered at 1900 cm^{-1} belong to stretching vibrations of the terminal CO ligands. Further strong bands at 1047, 916, and 839 cm^{-1} are assigned to vibrations of the coordinated THF ligands. Compared with the frequencies of the terminal CO groups of $Na_2[Fe_2(CO)_8]$, the related bands in **1** are slightly shifted to higher wavenumbers, indicating location of less electron density at the terminal CO groups of **1**.

The ^{13}C NMR of **1** in THF-d_8 exhibits only one resonance for all carbonyl groups at 244 ppm at ambient temperature, typical for CO scrambling. Relative to $[PNP]_2[Fe_2(CO)_8]$ (230.7 ppm in CD_2Cl_2)[11] or $[MeP(NMe_2)_3]_2[Fe_2(CO)_8]$ (225.8 in CD_3CN),[12] which are compounds with terminal CO groups and no remarkable anion−cation interactions, the carbonyl signal of **1** is shifted significantly downfield, thus indicating a net drain of electron density from the $Fe_2(CO)_8$ unit. The lifetime of any COLi interaction is shorter than the time scale of the NMR experiment, and cooling to −40 °C does not result in signal broadening; lower temperatures could not be achieved because of crystallization of the product.

Scheme 3



The complex **1** dissolves readily in toluene, but the yellow crystals grown from this solution by layering with *n*-pentane are not identical with the starting material. As shown by an X-ray analysis and IR spectroscopic data, a new complex, **2**, has formed. The new species has two THF molecules less than **1** and is polymeric. Each Li atom has lost one THF molecule, and **2** can be reconverted into **1** on redissolving in THF. The reversible loss of THF molecules changes only the coordination mode at the Li atoms, generating two types of Li atoms and leaving the $Fe_2(CO)_8$ core untouched. As shown in Scheme 3, one Li atom of **2** is part of a four-membered ring which connects two units of **1** to a dimer. The second Li atom connects the dimeric unit with another unit via contact to an oxygen atom of a terminal CO group of the next $Fe_2(CO)_8$ core. The loss of two THF molecules transfers one of the μ_3:η^2-CO groups of **1** into a μ_4:η^2 coordination mode in **2**.

The IR spectrum of **2** is nearly identical with that of **1** with the exception of a new strong band at 1543 cm^{-1}, which is absent in **1**. This vibration may be attributed to the μ_4:η^2-CO group located between two Li and two Fe atoms. The CO distance of this group is about 2 pm longer than the distance found in the remaining μ_3:η^2-CO group and therefore is in the range of a ketonic double bond. These different types of bridging CO groups generate two absorptions at low frequencies.

We have evaporated the solvent THF/*n*-pentane from the solution obtained after removing the crystals of **1** and similarly from the toluene/*n*-pentane solution after filtering the crystals of **2**. The THF solution of **1** generates a brown material (**1a**) with μ-CO vibrations at 1626 and 1557 cm^{-1}, while the toluene solution from **2** gives a yellow pyrophoric powder (**2a**) which is identical with **2**, as shown by IR spectroscopy. The IR spectra of **1a** and **2a** are not identical and probably represent different condensation products on the way to losing THF molecules. From these steps only **2** could be obtained as crystals suitable for an X-ray diffraction study.

The presence of bridging carbonyl groups in **1**, **2**, and the intermediates **1a** and **2a** during loss of THF prompted us to study their reactivities toward electrophilic agents such as $MeSO_3CF_3$ and Me_3SnCl in order to replace the Li atom at the bridging carbonyl groups. However, the alkylation of **1** in toluene does not gener-

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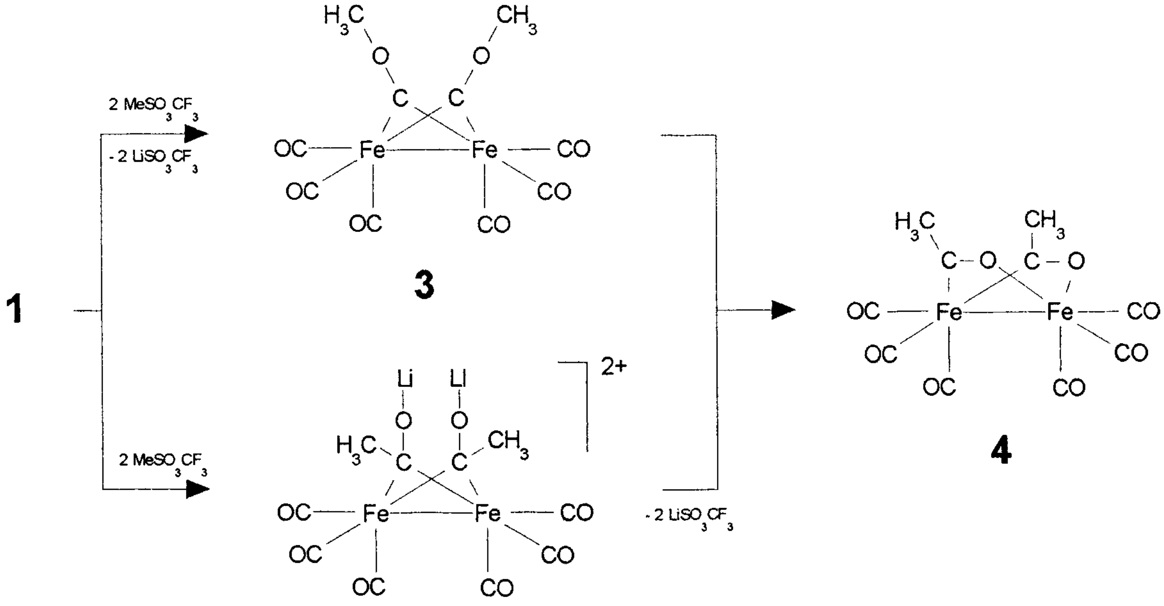
Scheme 4



ate the expected μ-carbyne complex **3**; instead of we isolated its asymmetric isomer **4** containing two bridging acyl ligands and two chemically different iron atoms as shown in Scheme 4. Compounds of the type $[(CO)_3Fe(\mu\text{-}RCO)_2Fe(CO)_3]$ including **4** have been known for more than 30 years, but their number is limited to three examples with R = Me, Ph,[13] and C_9H_{19}.[14] More common are the substituted compounds $[(CO)_3Fe(\mu\text{-}RCO)_2Fe(CO)_2D]$ with one donor ligand at the oxygen-coordinated iron atom and related compounds with R = carbamoyl, alkoxycarbonyl;[15] further examples have been obtained recently by the group of Hill[16] and Salaün[17] and in our group by reacting an iron carbamoyl complex with Lewis acids.[18] In all cases the compounds were obtained by oxidation of a mononuclear acyl anion $[(CO)_4FeC(O)R]^-$, and the mechanism of formation is still unclear. **4** also forms upon reaction of $[(CO)_4FeC(O)Me]^-$ with oxalyl chloride; the authors of this study propose a mechanism involving a thermal decomposition of a dinuclear bisacyl complex.[17]

The formation of **4** via alkylation of bridging carbonyl groups represents a new access to this class of compounds, and the question concerning the mechanism for this unusual intramolecular disproportionation arises again. We cannot exclude that first the carbyne complex **3** is formed, which rearranges to the thermodynamically more stable acyl complex **4**. Also alkylation at the bridging carbon atoms of **1** with formation of intermediate μ-carbene ligands and an electron-deficient dication (the carbene ligand acts as a two-electron donor) could be possible; loss of two Li^+ cations and concerted Fe–O bond formation than generates the three-electron-donating μ-acyl ligand.[19] The intermediacy of a μ-acyl ligand is also proposed by Salaün.[17]

Similarly, the reaction of Me_3SnCl with **1** does not generate an O-stannylated product. As the only identifiable compound we isolated $[(CO)_4Fe(SnMe_3)_2]$ (**6**) in about 50% yield along with tarry materials. The mechanism of this reaction is unclear; stannylation of **1** at the iron atoms followed by rearrangement and splitting off the thermodynamically more stable complex **6** may be operative. The isolation of **6** again demonstrates that tin is more ferrophilic than oxophilic. A similar Fe preference and formation of **6** was found by reacting $Fe(CO)_5$ with $N(SnMe_3)_3$[20] and by the reaction of $Li[(CO)_4FeC(O)NPr^i_2]$ with $ClSnPh_3$.[21] Studies of reactions of **1** with further electrophiles are in progress.

Structures of 1, 2, 4, and 5. The structures of the compounds **1**, **2**, and **4** could be confirmed by single-crystal X-ray analyses. Suitable crystals of **1** were obtained by layering a THF solution with *n*-pentane and storage at −20 °C. **2** was similarly crystallized but from a toluene solution with *n*-pentane. Red crystals of **4** could be grown by slow sublimation of a crude material from room temperature to 0 °C at 10^{-4} Torr. ORTEP views of the molecules are depicted in Figures 1, 2, and 6; details of the structure determination are collected in Table 1; bond distances and angles are summarized in Tables 2 and 3. Additionally we have studied the structure of $[Na_2(THF)_4Fe_2(CO)_8]_n$ (**5**), which was prepared by reacting Collman's reagent with $Fe(CO)_5$ in THF. Small crystals were obtained by layering the filtered THF solution with *n*-pentane. The structure of

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Table 1. Experimental Data for the X-ray Diffraction Studies of Complexes 1, 2, 4, and 5

	1	**2**	**4**	**5**
formula	$C_{32}H_{48}Fe_2Li_2O_{14}$	$C_{24}H_{32}Fe_2Li_2O_{12}$	$C_{10}H_6Fe_2O_8$	$C_{24}H_{32}Fe_2Na_2O_{12}$
MW	782.29	638.08	365.84	670.18
cryst syst	orthorhombic	monoclinic	triclinic	orthorhombic
space group	*Pbca* (No. 61)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	*Cmca* (No. 64)
a (pm)	1925.7(1)	1100.0(1)	699.3(1)	998.2(1)
b (pm)	1847.9(1)	3031.2(3)	885.9(1)	1299.8(2)
c (pm)	2239.2(1)	983.3(1)	1150.3(1)	2386.2(3)
α (deg)			89.78(1)	
β (deg)		114.82(1)	81.45(1)	
γ (deg)			70.35(1)	
volume (pm^3)	7986.2(7) × 10^6	2975.8(5) × 10^6	662.8(1) × 10^6	3096.0(7) × 10^6
Z	8	4	2	4
d_{calcd} (g/cm^3)	1.304	1.424	1.883	1.438
temp (K)	193	183	193	193
$\mu_{Mo\ K\alpha}$ (cm^{-1})	9.7	10.2	22.2	10.2
$2\theta_{max}$ (deg)	52.2	51.99	51.86	51.99
radiation	Mo Kα, graphite monochromated	Mo Kα, graphite monochromated	Mo Kα, graphite monochromated	Mo Kα, graphite monochromated
diffractometer	IPDS (Stoe)	CAD4 (Enraf-Nonius)	IPDS	IPDS
cryst size (mm)	0.48 × 0.48 × 0.48	0.41 × 0.22 × 0.16	0.43 × 0.23 × 0.14	0.37 × 0.18 × 0.05
index range	$-23 \le h \le 23$;	$-11 \le h \le 12$;	$-8 \le h \le 8$;	$-12 \le h \le 12$;
	$-22 \le k \le 22$;	$-36 \le k \le 0$;	$-9 \le k \le 10$;	$-15 \le k \le 15$;
	$-27 \le l \le 27$	$-11 \le l \le 0$	$-14 \le l \le 14$	$-29 \le l \le 28$
no. of rflns collected	63 096	5550	5685	11 241
no. of indep rflns	7821 ($R_{int} = 0.1282$)	4994 ($R_{int} = 0.0513$)	2393 ($R_{int} = 0.0361$)	1596 ($R_{int} = 0.1675$)
no. of obsd rflns	2599 ($F_o > 4\sigma(F_o)$)	3444 ($F_o > 4\sigma(F_o)$)	1995 ($F_o > 4\sigma(F_o)$)	702 ($F_o > 4\sigma(F_o)$)
refinement	F^2 (SHELXL-97)[a]			
params	400	362	182	104
R_1 ($F_o > 4\sigma F_o$)	0.0645	0.0562	0.048	0.0439
wR_2 (all data)	0.2002	0.1707	0.139	0.0831
max/min rest electron density (e/pm^3) × 10^{-6}	0.5/−0.5	0.47/−0.51	1.23/−0.53	0.35/−0.35

[a] Sheldrick, G. M. *SHELXL-97*, A Program for the Refinement of Crystal Structures; Universität Göttingen, 1997.

5 is shown in Figure 4; a view of the polymeric network is shown in Figure 5.

The central $[Fe_2(CO)_8]^{2-}$ unit of **1** contains six terminal and two bridging carbonyl groups with an arrangement similar to that found in the isoelectronic $Co_2(CO)_8$ molecule in the solid state.[22] Each oxygen atom of the bridging CO groups interacts with a lithium atom with formation of μ_3:η^2-CO groups. The additional coordination of three THF molecules allows the Li atom to be in a tetrahedral environment of oxygen atoms. The Li−O bond distance to the bridging carbonyl group is 6 pm shorter than the average distances to the THF molecules. The Fe−Fe distance is closely related to the M−M distances in $Fe_2(CO)_9$ and $Co_2(CO)_8$ but is about 23 pm shorter than the Fe−Fe distance in “free” $[Fe_2(CO)_8]^{2-}$ without anion cation contacts and no bridging carbonyl groups.[4−6] The dihedral angle between the planes Fe1, Fe2, C1 and Fe1, Fe2, C2 is 121°. The C−O−Li angles are 169° and 173°, and the deviations from linearity are probably due to packing effects. The carbon atoms of the coordinated THF molecules are strongly disordered.

Large yellow crystals of the complex **2** were obtained by dissolving **1** in toluene and layering the filtered solution with *n*-pentane. The solid-state structure of **2** is governed by the loss of two THF molecules of **1**; the structure of **2** is depicted in Figure 2. The $Fe_2(CO)_8$ core with its bridging CO groups is maintained, but the environment at the Li atoms has completely changed. Whereas both Li atoms in **1** are equivalent, being connected to a bridging carbonyl group, the new complex **2** contains two types of lithium atoms, each in a tetrahedral coordination sphere of oxygen atoms. One Li atom (Li2) is part of the four-membered Li_2O_2 ring and is surrounded by two THF molecules and two μ-OC groups with Li−O distances of 199 pm to the bridging carbonyl oxygen atoms and 190 pm to the THF oxygen atoms. The other Li atom (Li1) has two THF molecules, one μ-OC group, and one terminal CO ligand (isocarbonyl) in its coordination sphere. The corresponding Li−O distances are 191 pm to THF, 188 pm to the bridging CO group, and 201 pm to the terminal CO group. The Li_2O_2 ring forms a nearly perfect square with Li−O−Li and O−Li−O angles of 89.4° and 90.6°, respectively. The $Fe_2(CO)_8$ fragment contains only five real terminal CO groups, while the sixth terminal group (trans to a bridging group) forms an isocarbonyl-like bond to the Li atom of another unit. The bridging CO groups at the $Fe_2(CO)_8$ fragment are different such that one is a μ_3:η^2-CO and the other one a μ_4:η^2-CO group.

The molecular structure of **2** contains an interesting detail of CO coordination not yet reported before. In Scheme 5 the bonding situation at the μ_4:η^2-CO group is shown being surrounded by four metal atoms. The CO bond length is very long at 122 pm. The carbon and oxygen atoms are each in a planar environment of three atoms. The sum of the bond angles at the C and O atoms are 359.7° and 358.9°, respectively. The Li_2OC plane is perpendicular to the Fe_2CO plane.

Figure 3 gives an impression how the $LiFe_2Li_2Fe_2Li$ units of **2** are linked together with formation of a three-dimensional network by Li−O contacts to terminal CO groups of the $Fe_2(CO)_8$ fragments. Compounds in which terminal or bridging CO ligands coordinate to Lewis

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(22) Leung, P. C.; Coppens, P. *Acta Crystallogr.* **1983,** *B39*, 535.

Table 2. Selected Bond Lengths (pm)

Compound **1**			
Fe(1)−Fe(2)	255.1(1)	O(2)−C(2)	121.6(7)
Fe(1)−C(1)	192.8(7)	O(3)−C(3)	118.2(9)
Fe(1)−C(2)	191.9(7)	O(4)−C(4)	119.0(8)
Fe(2)−C(1)	192.3(7)	O(5)−C(5)	116.9(9)
Fe(2)−C(2)	192.9(7)	O(6)−C(6)	116.4(9)
Fe(1)−C(3)	175.9(8)	O(7)−C(7)	116.9(8)
Fe(1)−C(4)	173.2(8)	O(8)−C(8)	119.1(9)
Fe(1)−C(5)	176.9(9)	O(9)−Li(1)	194(1)
Fe(2)−C(6)	176.5(9)	O(10)−Li(1)	194(1)
Fe(2)−C(7)	174.9(8)	O(11)−Li(1)	192(1)
Fe(2)−C(8)	173.9(8)	O(12)−Li(2)	192(1)
O(1)−Li(1)	187(1)	O(13)−Li(2)	188(1)
O(2)−Li(2)	187(1)	O(14)−Li(2)	194(1)
O(1)−C(1)	120.7(7)		
Compound **2**			
Fe(1)−Fe(2)	256.5(1)	O(1)−C(1)	120.3(6)
Fe(1)−C(1)	197.2(5)	O(2)−C(2)	122.2(5)
Fe(1)−C(2)	190.6(5)	O(3)−C(3)	116.2(7)
Fe(2)−C(1)	189.8(5)	O(4)−C(4)	115.6(6)
Fe(2)−C(2)	194.5(5)	O(5)−C(5)	115.0(7)
Fe(1)−C(3)	175.4(6)	O(6)−C(6)	115.2(6)
Fe(1)−C(4)	177.0(5)	O(7)−C(7)	114.0(7)
Fe(1)−C(5)	179.4(6)	O(8)−C(8)	115.1(7)
Fe(2)−C(6)	175.6(6)	O(4)−Li(1)d	201(1)
Fe(2)−C(7)	179.9(6)	O(9)−Li(1)	190(1)
Fe(2)−C(8)	178.8(6)	O(10)−Li(1)	191(1)
O(1)−Li(1)	188(1)	O(11)−Li(2)	191.1(9)
O(2)−Li(2)	199.2(9)	O(12)−Li(2)	189.8(9)
O(2)−Li(2A)	198.8(9)		
Compound **4**			
Fe(1)−Fe(2)	257.48(9)	O(1)−C(1)	114.0(7)
Fe(1)−C(1)	181.6(6)	O(2)−C(2)	113.4(7)
Fe(1)−C(2)	182.6(5)	O(3)−C(3)	113.6(7)
Fe(1)−C(3)	179.4(5)	O(4)−C(4)	124.6(6)
Fe(1)−C(4)	193.1(5)	O(5)−C(5)	124.4(6)
Fe(1)−C(5)	195.4(5)	O(6)−C(6)	113.8(7)
Fe(2)−C(6)	179.5(6)	O(7)−C(7)	114.0(7)
Fe(2)−C(7)	178.2(6)	O(8)−C(8)	113.3(7)
Fe(2)−C(8)	186.8(5)	C(4)−C(41)	150.7(7)
Fe(2)−O(4)	199.3(3)	C(5)−C(51)	150.0(7)
Fe(2)−O(5)	197.8(4)		
Compound **5**			
Fe(1)−Fe(1A)	278.5(2)	O(3)−C(3)	118.3(5)
Fe(1)−C(1)	175.6(6)	Na(1)−O(2)	238.2(5)
Fe(1)−C(2)	177.2(6)	Na(1)−O(4)	245.1(4)
Fe(1)−C(3)	175.9(4)	Na(1)−O(5)	234.9(5)
O(1)−C(1)	117.1(7)	Na(1)−O(4A)	247.0(5)
O(2)−C(2)	115.8(7)		

acids via the oxygen atom are known for a variety of transition metal carbonyl and acid combinations.[23]

For comparison, selected bond distances and angles of related $M_2(CO)_8$ derivatives with bridging CO groups are collected in Table 4.

We have also determined the molecular structure of the sodium salt **5**, obtained as $[Na_2(THF)_4Fe_2(CO)_8]_n$ from the reaction of $Fe(CO)_5$ with Collman's reagent in THF. Crystals were obtained by layering the red THF solution with *n*-pentane. The IR spectrum does not indicate the presence of bridging CO ligands, which is confirmed by the X-ray structure determination. The molecular structure of **5** differs markedly from the structure of **1**, where no near contacts to other molecules are found. The $Fe_2(CO)_8$ core of **5** is closely related to that in salts with noncoordinating cations. The iron atoms are each coordinated to four CO groups and are arranged in a trigonal bipyramidal fashion. The six equatorial CO groups are staggered but form contacts to Na^+ ions, whereas the apical CO ligands do not further coordinate. However, the Fe−C and C−O bond distances are not affected during Na coordination, as shown by comparison of the related distances with those

Table 3. Selected Bond Angles (deg)

Compound **1**			
Fe(2)−Fe(1)−C(1)	48.4(2)	C(2)−Fe(1)−C(5)	155.4(3)
Fe(2)−Fe(1)−C(2)	48.7(2)	C(1)−Fe(2)−C(6)	154.8(3)
Fe(1)−Fe(2)−C(2)	48.3(2)	C(1)−Fe(2)−C(7)	99.0(3)
Fe(1)−Fe(2)−C(1)	48.6(2)	C(1)−Fe(2)−C(8)	87.6(3)
Fe(1)−C(1)−Fe(2)	83.0(2)	C(2)−Fe(2)−C(6)	87.0(3)
Fe(1)−C(2)−Fe(2)	83.0(3)	C(2)−Fe(2)−C(7)	98.4(3)
C(1)−O(1)−Li(1)	169.4(6)	C(2)−Fe(2)−C(8)	155.1(3)
C(2)−O(2)−Li(2)	173.1(7)	C(3)−Fe(1)−C(4)	108.1(4)
Fe(2)−Fe(1)−C(4)	127.2(3)	C(3)−Fe(1)−C(5)	93.8(4)
Fe(1)−Fe(2)−C(7)	130.7(3)	C(4)−Fe(1)−C(5)	107.1(4)
Fe(2)−Fe(1)−C(3)	107.1(3)	C(6)−Fe(2)−C(7)	104.6(4)
Fe(2)−Fe(1)−C(5)	108.4(3)	C(6)−Fe(2)−C(8)	94.3(4)
Fe(1)−Fe(2)−C(6)	107.7(3)	C(7)−Fe(2)−C(8)	105.2(4)
Fe(1)−Fe(2)−C(8)	108.4(3)	O(1)−Li(1)−O(9)	106.9(7)
Fe(1)−C(1)−O(1)	138.4(5)	O(1)−Li(1)−O(10)	108.3(6)
Fe(2)−C(1)−O(1)	138.5(5)	O(1)−Li(1)−O(11)	118.9(7)
Fe(1)−C(2)−O(2)	138.4(5)	O(2)−Li(2)−O(12)	105.0(6)
Fe(2)−C(2)−O(2)	138.4(6)	O(2)−Li(2)−O(13)	111.5(7)
C(1)−Fe(1)−C(2)	81.2(3)	O(2)−Li(2)−O(14)	116.6(7)
C(1)−Fe(2)−C(2)	81.1(3)	O(9)−Li(1)−O(10)	108.3(6)
C(1)−Fe(1)−C(3)	154.0(3)	O(9)−Li(1)−O(11)	104.4(6)
C(1)−Fe(1)−C(4)	96.0(3)	O(10)−Li(1)−O(11)	109.4(7)
C(1)−Fe(1)−C(5)	87.9(3)	O(12)−Li(2)−O(13)	108.3(7)
C(2)−Fe(1)−C(3)	86.8(3)	O(12)−Li(2)−O(14)	109.0(7)
C(2)−Fe(1)−C(4)	96.0(3)	O(13)−Li(2)−O(14)	106.3(6)
Compound **2**			
Fe(2)−Fe(1)−C(1)	47.3(2)	C(2)−Fe(1)−C(5)	87.9(2)
Fe(2)−Fe(1)−C(2)	48.9(2)	C(1)−Fe(2)−C(6)	99.2(2)
Fe(1)−Fe(2)−C(2)	47.6(2)	C(1)−Fe(2)−C(7)	86.1(3)
Fe(1)−Fe(2)−C(1)	49.7(2)	C(1)−Fe(2)−C(8)	153.4(3)
Fe(1)−C(1)−Fe(2)	83.0(2)	C(2)−Fe(2)−C(6)	94.3(2)
Fe(1)−C(2)−Fe(2)	83.5(2)	C(2)−Fe(2)−C(7)	161.8(2)
C(1)−O(1)−Li(1)	155.7(6)	C(2)−Fe(2)−C(8)	89.3(2)
C(2)−O(2)−Li(2)	127.2(4)	C(3)−Fe(1)−C(4)	107.9(3)
C(2)−O(2)−Li(2)a	142.3(4)	C(3)−Fe(1)−C(5)	103.6(3)
C(4)−O(4)−Li(1)d	146.9(6)	C(4)−Fe(1)−C(5)	94.7(3)
Fe(2)−Fe(1)−C(4)	102.7(2)	C(6)−Fe(2)−C(7)	102.0(3)
Fe(1)−Fe(2)−C(7)	114.8(2)	C(6)−Fe(2)−C(8)	106.8(3)
Fe(2)−Fe(1)−C(3)	125.0(2)	C(7)−Fe(2)−C(8)	93.5(3)
Fe(2)−Fe(1)−C(5)	118.2(2)	O(1)−Li(1)−O(9)	105.9(6)
Fe(1)−Fe(2)−C(6)	126.6(2)	O(1)−Li(1)−O(10)	119.6(6)
Fe(1)−Fe(2)−C(8)	107.9(3)	O(1)−Li(1)−O(4)c	108.6(6)
Fe(1)−C(1)−O(1)	136.3(5)	O(2)−Li(2)−O(11)	107.6(5)
Fe(2)−C(1)−O(1)	140.5(5)	O(2)−Li(2)−O(12)	109.1(4)
Fe(1)−C(2)−O(2)	140.1(5)	O(2)−Li(2)−O(2)b	90.6(4)
Fe(2)−C(2)−O(2)	136.1(4)	O(11)−Li(2)−O(12)	128.5(5)
C(1)−Fe(1)−C(2)	82.5(2)	O(9)−Li(1)−O(10)	117.9(6)
C(1)−Fe(2)−C(2)	83.5(2)	O(9)−Li(1)−O(4)c	102.3(5)
C(1)−Fe(1)−C(3)	89.5(3)	O(10)−Li(1)−O(4)c	100.7(5)
C(1)−Fe(1)−C(4)	87.3(2)	O(11)−Li(2)−O(2)b	108.0(5)
C(1)−Fe(1)−C(5)	165.2(3)	O(12)−Li(2)−O(2)b	106.4(4)
C(2)−Fe(1)−C(3)	103.4(2)	Li(2)−O(2)−Li(2)a	89.4(4)
C(2)−Fe(1)−C(4)	147.0(3)		
Compound **4**			
Fe(2)−Fe(1)−C(1)	98.3(2)	Fe(1)−Fe(2)−C(8)	161.9(2)
Fe(2)−Fe(1)−C(2)	97.0(2)	O(4)−Fe(2)−O(5)	85.2(2)
Fe(2)−Fe(1)−C(3)	158.4(2)	O(4)−Fe(2)−C(6)	167.1(2)
Fe(2)−Fe(1)−C(4)	67.9(1)	O(4)−Fe(2)−C(7)	90.8(2)
Fe(2)−Fe(1)−C(5)	68.3(1)	O(4)−Fe(2)−C(8)	95.6(2)
C(1)−Fe(1)−C(2)	94.1(3)	O(5)−Fe(2)−C(6)	91.5(2)
C(1)−Fe(1)−C(3)	96.9(3)	O(5)−Fe(2)−C(7)	169.4(2)
C(1)−Fe(1)−C(4)	165.9(2)	O(5)−Fe(2)−C(8)	94.0(2)
C(1)−Fe(1)−C(5)	90.6(2)	C(6)−Fe(2)−C(7)	90.3(3)
C(2)−Fe(1)−C(3)	97.2(2)	C(6)−Fe(2)−C(8)	97.0(2)
C(2)−Fe(1)−C(4)	90.5(2)	C(7)−Fe(2)−C(8)	96.1(2)
C(2)−Fe(1)−C(5)	165.0(2)	Fe(2)−O(4)−C(4)	102.8(3)
C(3)−Fe(1)−C(4)	95.8(3)	Fe(2)−O(5)−C(5)	104.8(3)
C(3)−Fe(1)−C(5)	96.3(2)	Fe(1)−C(4)−O(4)	117.1(4)
C(4)−Fe(1)−C(5)	81.8(2)	Fe(1)−C(5)−O(5)	114.8(4)
Fe(1)−Fe(2)−O(4)	72.2(1)	Fe(1)−C(4)−C(41)	127.5(4)
Fe(1)−Fe(2)−O(5)	72.1(1)	Fe(1)−C(5)−C(51)	128.4(4)
Fe(1)−Fe(2)−C(6)	94.9(2)	O(4)−C(4)−C(41)	115.4(5)
Fe(1)−Fe(2)−C(7)	97.3(2)	O(5)−C(5)−C(51)	116.8(4)
Compound **5**			
C(1)−Fe(1)−C(2)	96.8(5)	O(5)−Na(1)−O(4)a	177.9(2)
C(1)−Fe(1)−C(3)	95.3(2)	O(5)−Na(1)−O(3)e	92.4(1)
C(2)−Fe(1)−C(3)	116.8(1)	O(5)−Na(1)−O(3)h	92.4(1)
C(3)−Fe(1)−C(3)c	123.5(2)	O(4)a−Na(1)−O(3)e	87.5(1)
O(2)−Na(1)−O(4)	178.5(2)	O(3)e−Na(1)−O(3)h	172.2(2)
O(2)−Na(1)−O(5)	89.2(2)	Na(1)−O(2)−C(2)	176.7(5)
O(2)−Na(1)−O(4)a	88.7(2)	C(3)−O(3)−Na(1)d	150.9(3)
O(2)−Na(1)−O(3)e	86.94(9)	Na(1)−O(4)−Na(1)f	90.2(2)
O(4)−Na(1)−O(5)	92.3(2)	Fe(1)−C(1)−O(1)	179.(1)
O(4)−Na(1)−O(4)a	89.8(2)	Fe(1)−C(2)−O(2)	177.0(6)
O(4)−Na(1)−O(3)e	92.99(9)	Fe(1)−C(3)−O(3)	176.5(4)

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[23] Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219.

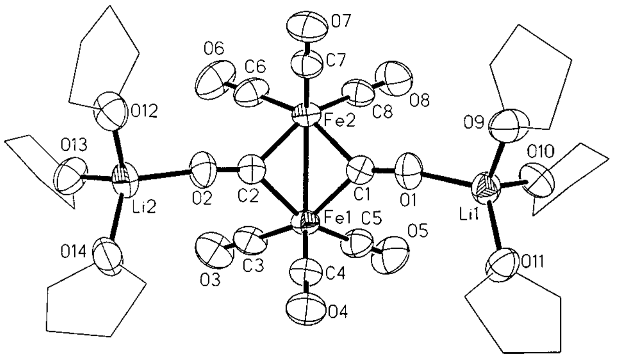

Figure 1. Projection view of $[Li_2(THF)_6Fe_2(CO)_8]$ (**1**) showing the atom-numbering scheme. The ellipsoids are drawn at the 40% probability level. For clarity the CH_2 groups of the THF ligands are given schematically.

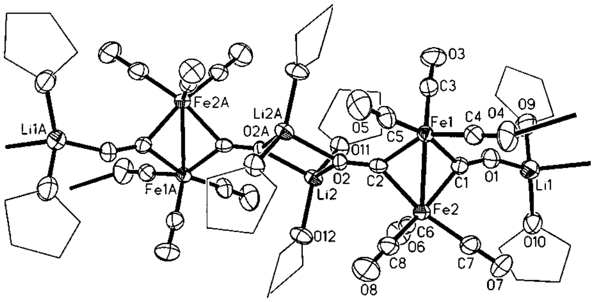

Figure 2. Projection view of $[Li_2(THF)_4Fe_2(CO)_8]_n$ (**2**) showing the atom-numbering scheme. The ellipsoids are drawn at the 40% probability level. For clarity the CH_2 groups of the THF ligands are given schematically.

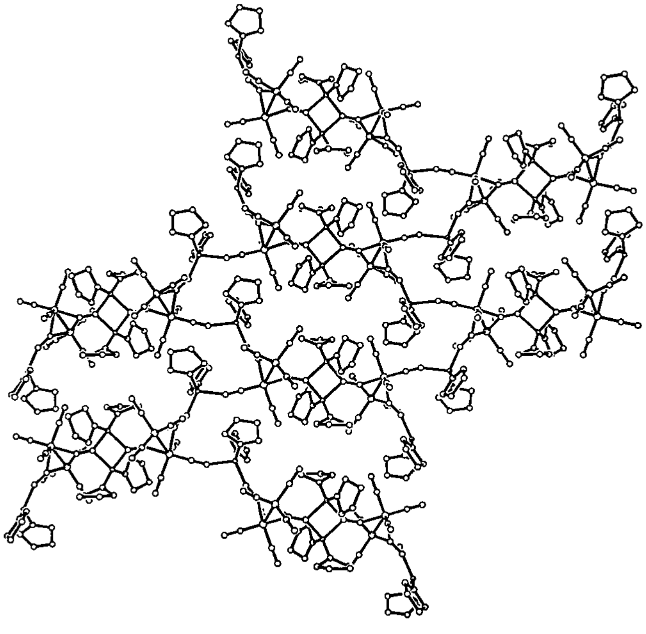

Figure 3. Ball and stick view of three-dimensional network of $[Li_2(THF)_4Fe_2(CO)_8]_n$ (**2**).

in compounds with no contacts to the cations. The $Fe_2(CO)_8$ groups are linked through centrosymmetric planar Na_2O_2 rings, and all Na atoms are equivalent. Three equatorial arranged terminal CO ligands from $Fe_2(CO)_8$ fragments contact each Na^+ cation, and one terminal and two bridging THF groups complete the octahedral environment of oxygen atoms in the coordination sphere of Na^+. Despite the lack of μ-CO groups, there are some structural aspects that also appear in **2**. Thus, a planar Na_2O_2 ring similar to the Li_2O_2 ring is formed, but the bridging oxygen atoms belong to a THF groups and not to bridging carbonyl ligands as in **2**. Contacts of the alkali metal to the oxygen atoms of terminal CO groups exist in both compounds, but in **5** to the unique ring Na atom. The distances of sodium to iron or carbon atoms are too long to be considered as bonding interactions. The molecular structure of **5** is shown in Figure 4.

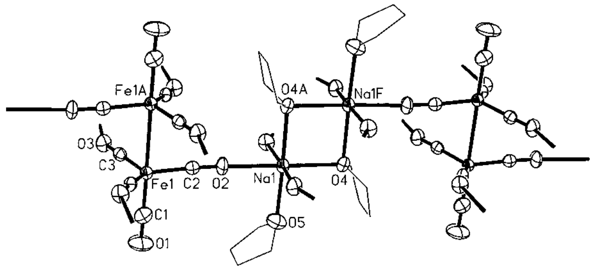

Figure 4. Projection view of $[Na_2(THF)_4Fe_2(CO)_8]_n$ (**5**) showing the atom-numbering scheme. The ellipsoids are drawn at the 40% probability level. For clarity the CH_2 groups of the THF ligands are given schematically.

The lack of bridging CO groups leads to long Fe−Fe bond distances of 278.5 pm, identical to those reported for the "free" $[Fe_2(CO)_8]^{2-}$ anions.[4,5] Two equatorial CO groups of each iron atom of one $Fe_2(CO)_8$ unit are linked to the Na atoms of the Na_2O_2 ring. The participation of six terminal CO groups contacting sodium cations leads to the formation of layers parallel to (001), and the stacking proceeds therefore along [001], as depicted in Figure 5.

The coordination of oxygen atoms from different sources leads to three different Na···O contacts. The longest contacts of 245 and 247 pm are formed to the bridging THF molecules, and the shortest distances are those to the terminal THF molecule at 235 pm. Between are the Na···O(carbonyl) contacts, which are 238 pm. These contacts are similar to those found in Collman's reagent, $Na_2Fe(CO)_4$·1.5 dioxane, to one of the two different Na^+ ions.[23,24] In the dimeric [Na(15-crown-5)]-$[Mn(CO)_5]$ similar Na···O(carbonyl) distances are recorded, but they are appreciably longer, being 241 and 256 pm .[25] A schematic presentation of the structure is shown in Scheme 6.

Structural details of compounds of the type $[(CO)_3Fe(\mu\text{-}RCO)_2Fe(CO)_3]$ have been restricted until the present time to the example with R = Ph obtained earlier by Fischer in 1968.[13] Now we are able to present the molecular structure of **4**, the simplest organic derivative in these series of compounds with R = Me. Compared with the structural parameters of the phenyl derivative, no dramatic changes in bond distances and angles are observed. The $C-C_{CO}$ distance to the sp^3 carbon atom of the Me group in **4** is somewhat longer than the corresponding distance to the sp^2 carbon atom of the phenyl group; this is compensated by reverse trends in the acyl C−O distances, but the effects are only marginal. The Fe−C distances of carbonyl groups opposite to oxygen atoms are shorter than those opposite to

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(24) Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1976**, *98*, 2434.

(25) Alvanipour, A.; Zhang H.; Atwood J. L. *J. Organomet. Chem.* **1988**, *358*, 295.

(26) Cotton, F. A.; Troup, J. M. *J. Chem. Soc.* **1974**, 800.

(27) Chin, H. B.; Bau, R. *Inorg. Chem.* **1978**, *17*, 2314.

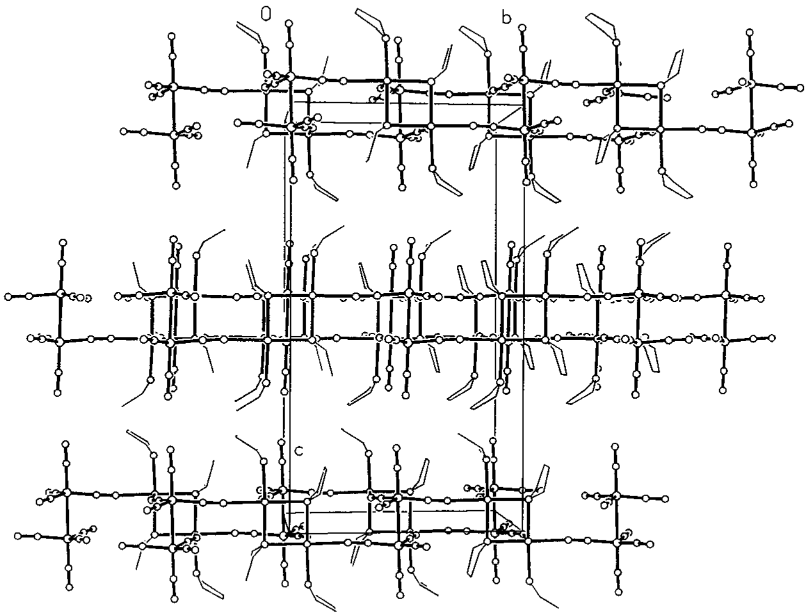
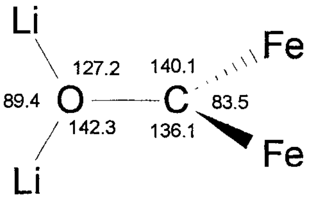


Figure 5. Ball and stick view of the layer structure of $[Na_2(THF)_4Fe_2(CO)_8]_n$ (**5**).

Scheme 5



carbon atoms; both iron atoms attain coordination number 6. The two planes defined by the atoms Fe−C−O−Fe form an angle of 90°. The molecular structure of **4** is shown in Figure 6.

The μ-acyl compounds may be described by the resonance forms **I**, **II**, and **III** shown in Scheme 7. The contribution of **I** and **II** with a “soft” iron atom containing carbenoid bonds and a “hard” iron atom with bonds to oxygen presumably dominate, but the real situation is somewhat in between.[16] Also the possible contribution **III** with reversed formal oxidation states of the two iron atoms can probably be neglected.

Conclusion

We have shown that the presence of the Li^+ cations in $[Fe_2(CO)_8]^{2-}$ forces two of the terminal ligands into a bridging position, giving with **1** an unprecedented example of ion pair interaction in iron carbonyl chemistry. Removal of coordinated solvent molecules either by dissolving **1** in an nonpolar solvent or evaporation in a vacuum leads to condensation of the $Li_2[Fe_2(CO)_8]$ units via coordination of Li to oxygen atoms of terminal CO groups; the reversible loss of THF molecules leaves the $Li_2[Fe_2(CO)_8]$ core untouched. Coordination number 6 at the Na^+ ion in **5** leads to a situation where these contacts to terminal CO groups predominate in the solvated sodium complex $Na_2[Fe_2(CO)_8]$, generating a highly polymeric structure in the solid state. The excellent solubility of **1** in THF and even in nonpolar organic solvents such as toluene indicates that the Li to O bond is more covalent in nature than similar contacts in other alkali metal carbonylates. The structural data of **1** allow different interpretations of the nature of the complex. The compound can be considered either as a $[Fe_2(CO)_8]^{2-}$ anion with short contacts of the counterion to the bridging CO oxygen atom (strong ion pairing) or as a carbyne complex with two μ-COLi(THF)$_3$ bridging carbyne ligands or finally as the result of coordination of two cationic isocarbonyl complexes $[COLi(THF)_3]^+$ at the 30-electron fragment $[Fe_2(CO)_6]^{2-}$. As yet, we have not been able to create μ-carbyne complexes by reacting **1** with electrophiles replacing the $Li(THF)_3$ group.

Experimental Section

General Considerations. All operations were carried out under an argon atmosphere in dried and degassed solvents using Schlenk techniques. IR spectra were run on a Nicolet spectrometer. ^{13}C NMR spectra were recorded on a Bruker AC 300 instrument using $SiMe_4$ ($\delta = 0.00$ ppm) as the external standard. Elemental analyses were performed by the analytical service of the Fachbereich Chemie der Universität Marburg (Germany). $Fe_2(CO)_9$ has been prepared according to a published procedure.[9] $Na_2[Fe_2(CO)_8]$ was prepared by addition of $Fe(CO)_5$ to a suspension of Collman’s reagent in THF.[3] Lithium powder was a gift from the Metallgesellschaft Frankfurt. Commercially available $MeSO_3CF_3$ and Me_3SnCl (Aldrich) were used without further purification.

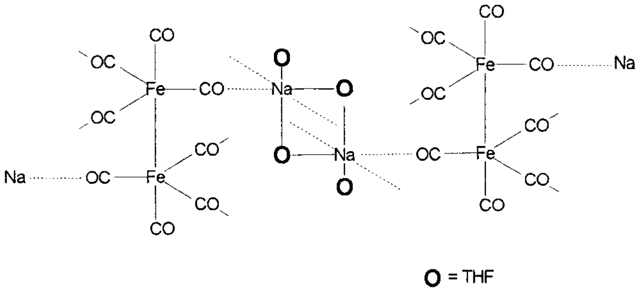
Preparation of $[Li_2(THF)_6Fe_2(CO)_8]$ (1). To a suspension of $Fe_2(CO)_9$ (6.06 g, 16.6 mmol) in THF (50 mL) with continuous stirring under argon was added lithium powder (0.27 g, 38.9 mmol). The temperature was kept at about 20 °C by cooling the mixture with a water bath. Within 5−10 min $Fe_2(CO)_9$ began to dissolve under evolution of CO, and after about 2 h a dark brown homogeneous solution resulted. The mixture was stirred for about 10 h at room temperature. The solution was filtered through a G3 glass filter equipped with 4 cm dried and degassed diatomaceous earth. The resulting clear orange-brown solution was then layered with *n*-pentane and stored for several days in a refrigerator at −20 °C. Large orange-yellow crystals of **1** (2.09 g, 2.67 mmol) separated, which were removed by filtration and washed with about 3 mL of *n*-pentane, yield 16.1%. During several runs this procedure gave crystals between 6 and 20% yield. ^{13}C NMR (THF-d_8): 244.15 ppm (CO). IR (Nujol): 1991 (s), 1937 (vs), 1925 (sh), 1885 (vs), 1855 (vs), 1651 (s), 1645 (s), 1179 (w), 1047 (s), 916 (m), 893

Table 4. Collection of Parameters of Related Compounds with μ-CO Groups Including the Isoelectronic $Co_2(CO)_8$

compound	M−M (pm)	μ-C−O (pm)	O−M′ (pm)	M−C (pm)	M−C−M (deg)	dihedral angle[a] (deg)	ref
1	255.1	121.1	187	192.5	83.0	121	this work
2	256.5	120.3	188	189.8	83.5	125	this work
		122.2	199.2	190.6			
			198.8	194.5			
				197.2			
$Fe_2(CO)_9$	252.3	116.0		201.6	77.6	120	26
$\{Cd[Fe_2(CO)_8]_2\}^{2-}$	261.8	118.5		197.5			10
$Co_2(CO)_8$	253	116.5		183.3	n.r.	n.r.	22
$[(\mu\text{-H})Fe_2(CO)_8]^-$	252.1	116		197.0	79.6	n.r.	27

[a] Dihedral angle between the Fe_2C planes.

Scheme 6



5

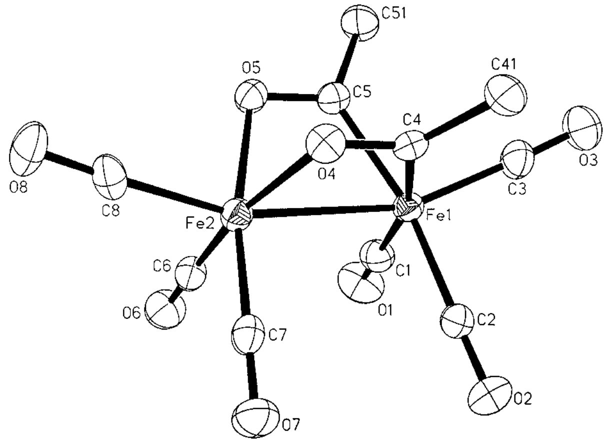
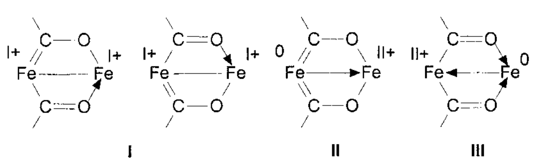


Figure 6. Projection view of $[(CO)_3Fe(\mu\text{-MeCO})_2Fe(CO)_3]$ (**4**) showing the atom-numbering scheme. The ellipsoids are drawn at the 40% probability level. The H atoms are omitted for clarity.

Scheme 7



(m), 685 (s), 646 (m), 619 (m), 598 (m), 581 (m) cm^{-1}. Anal. Calcd for $C_{32}H_{48}Fe_2Li_2O_{14}$: C 49.13, H 6.19. Found: C 49.32, H 5.89. Evaporation of the solvent from the THF solution gave the brown material **1a**. The combined yields of **1** and **1a** are 90−95%. **1a** was not identical with **1** by its IR spectrum but could be converted into crystals of **1** when dissolved in THF and layered again with *n*-pentane. IR (Nujol): 1958 (vs), 1935 (vs), 1915 (vs), 1902 (vs), 1865 (vs), 1701 (w), 1626 (s), 1557 (s), 1047 (s), 918 (m), 893 (m), 665 (s), 644 (m), 625 (m), 611 (m), 586 (s) cm^{-1}.

Preparation of $[Li_2(THF)_4Fe_2(CO)_8]$ (2). The solid material **1a** obtained by evaporation of the THF/*n*-pentane solvent from the solution after separation of the crystals of **1** was extracted with toluene. After layering the filtered solution with *n*-pentane, yellow crystals of **2** separated. **2** was similarly obtained from **1**. IR (Nujol): 2020 (sh), 2000 (s), 1939 (vs), 1894 (vs), 1854 (s), 1653 (s), 1545 (s), 1045 (s), 916 (m), 893 (m), 702 (s), 650 (m), 621 (m), 600 (m), 588 (m) cm^{-1}. **2** is very air sensitive, and no C, H analyses could be obtained. Evaporation of the toluene solvent from the solution after filtration of **2** gave the yellow-brown pyrophoric material **2a**. IR (Nujol): 2000 (s), 1941 (vs), 1883 (vs), 1852 (vs), 1657 (sh), 1651 (s), 1545 (s), 1045 (s), 916 (m), 893 (m), 700 (m), 673 (m), 650 (m), 621 (m), 599 (sh), 600 (s) cm^{-1}.

Reaction of 1a, 2a, or 2 with THF. **1a**, **2a**, or **2** dissolves completely in THF; layering solutions of these materials with *n*-pentane produced crystals, the IR spectra of which were identical with those of **1**.

Reaction of 1 with $MeSO_3CF_3$. A solution of **1** (2.09 g, 2.67 mmol) in 20 mL toluene was cooled to −78 °C. Under continuous stirring an excess of $Me_3SO_3CF_3$ (1.0 mL) was added in portions and the mixture stirred at this temperature for 2 h. Then the mixture was allowed to warm to room temperature and stirred for an additional hour. Addition of *n*-pentane precipitated a red-brown material. The precipitate was filtered and the solvent evaporated to dryness. Sublimation of the residue at 10^{-4} Torr from room temperature to −20 °C gave red crystals of **4** (160 mg, 0.44 mmol), yield 16%. Anal. Calcd for $C_{10}H_6Fe_2O_8$: C 32.83, H 1.65. Found: C 30.62, H 1.87. IR (Nujol): 1960 (s), 1969 (vs), 2002 (vs), 2035 (s), 2081 (s), 1541 (m), 1497 (w), 1431 (w), 1343 (w), 1119 (m), 1105 (m), 980 (w), 952 (w), 627 (w), 606 (m), 594 (m), 577 (m), 546 (m) cm^{-1}.

Reaction of 1 with Me_3SnCl. To a solution of **1** (1.28 g, 1.64 mmol) in about 8 mL of THF was added under continuous stirring and at ambient temperature solid Me_3SnCl (655 mg, 3.28 mmol). The color of the brown solution immediately turned dark green. The solvent was evaporated and the oily residue extracted with toluene. Evaporation of the solvent gave a brown liquid, which was purified by distillation. The volatile colorless liquid was identified as *cis*-$[(CO)_4Fe(SnMe_3)_2]$ (**6**) by comparison of its IR spectrum with that of an authentic sample. IR (neat): 2056 (vs), 1985 (vs), 1964 (vs), 1736 (w), 1719 (w), 770 (s), 706 (m), 671(w), 610 (vs), 540 (w), 517 (m), 502 (m) cm^{-1}.

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Supporting Information Available: Tables of atomic positions, equivalent isotropic thermal parameters, and anisotropic thermal displacement coefficients. This material is available free of charge via the Internet at http://pubs.acs.org.

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