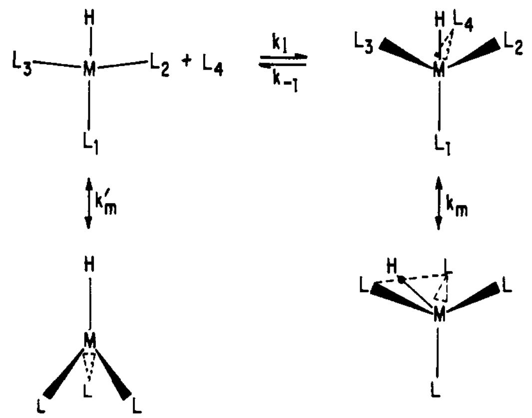

Figure 22. Schematic representation of overall reaction system. The k_m process is shown as going by the "tetrahedral jump" mechanism as opposed to the Berry mechanism since the HML_4^+ cation is expected to be distorted in the manner shown ($P(C_2H_5)_3$ is a bulky ligand). The k_m and k_{-1} processes are expected to be relatively insensitive to solvent. The k_m' and particularly the k_1 process are expected to show significant solvent effects due to weak inner sphere solvation.

ly that most of the phenomena can be encompassed mechanistically in sequences of four coordinate "planar" association, five-coordinate "trigonal bipyramidal" dissociation reactions, with competing intramolecular rearrangement in the five-coordinate complexes. In some cases, a solvent molecule may occupy one of the sites in the five-coordinate species. Many of the species could be present in very small concentrations and would escape detection in most classical approaches to planar substitution. The intermediate $HPtL_4^+$, clearly identified in the present work, is a case in point.

Acknowledgment. We would like to thank Mr. M. A. Cushing for preparation of some of the complexes and Messrs. G. Watunya and F. N. Schock for obtaining many of the NMR spectra.

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Site of Nucleophilic Attack on Acylpentacarbonylmanganese(I) Compounds

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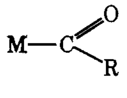
Abstract: Methyllithium reacts with benzoylpentacarbonylmanganese(I) at a coordinated CO to give lithium *cis*-acetylbenzoyltetracarbonylmangan(I)ate (**1b**) which was isolated as the tetramethylammonium salt **1a**. **1a** was characterized by ir, NMR, and x-ray crystallography. **1a** decomposes to acetophenone via preferential phenyl migration to manganese as determined by ^{13}C labeling studies.

Nucleophilic attack upon a carbon atom coordinated to a transition metal is an important process in the preparation of new organometallic complexes and in the generation of reactive intermediates useful for organic synthesis. While there is some information available concerning the relative reactivity of various ligands towards nucleophiles, it is not now possible to predict the site of nucleophilic attack in a polyfunctional organometallic compound.

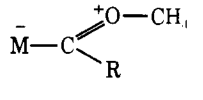
In the case of simple metal carbonyls, attack of organolithium reagents at a coordinated CO group is well known. The first synthesis of a stable transition metal carbene complex utilized the reaction of C_6H_5Li with $W(CO)_6$ to give an isolable acylpentacarbonyltungsten anion which was subsequently alkylated on oxygen to give $(CO)_5WC(OCH_3)C_6H_5$.[1] Reaction of organolithium reagents with $Fe(CO)_5$ led to acyl tetracarbonylferrates[2] which have proven to be extremely useful reagents for the synthesis of organic carbonyl compounds.[3] In the case of $LM(CO)_5$ where two sites of attack are possible, nucleophilic attack of $C_6H_5CH_2MgCl$[4] and CH_3Li[5] on $LM(CO)_5$ gives cis acyl anions.

For transition metal carbene complexes such as $(CO)_5WC(OCH_3)C_6H_5$, nucleophilic attack could in principle occur at either a coordinated CO or at the carbene carbon atom. However, only reaction at the carbene carbon atom is observed.[6] Reaction of amines and thiols with alkoxy substituted carbene complexes proceeds by attack at the carbene carbon atom and leads to amino and thiol substituted carbene complexes.[7,8] Stable addition products have been isolated in the case of diazabicyclo[2.2.2]octane[9] and trimethylphosphine.[10] While attack of amines at CO might be fast and reversible in these cases, the kinetically preferred site must also be the carbene carbon atom since C_6H_5Li reacts with $(CO)_5WC(OCH_3)C_6H_5$ at the carbene carbon atom to give an adduct which can be converted to $(CO)_5WC(C_6H_5)_2$ on treatment with HCl.[11]

The similarity between the structure of acyl metal compounds and of alkoxy carbene complexes makes a comparison of their relative reactivity interesting. Transesterifica-

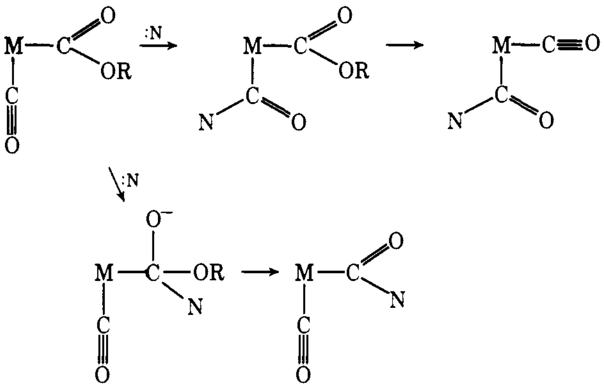


$$M-C(=O)R$$

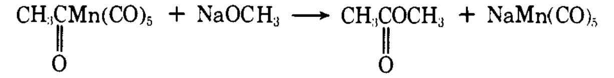


$$\overset{-}{M}-C(=\overset{+}{O}-CH_3)R$$

tion[12] and aminolysis[13] reactions of MCO_2R compounds are well known but the reactions can be explained either by nucleophilic attack at coordinated CO or at the ester carbon.

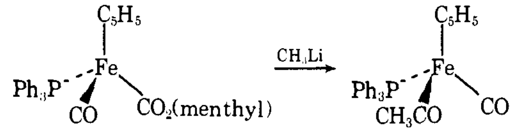


The cleavage of acyl derivatives by alkoxide gives esters[14] and demonstrates that attack at the acyl unit is feasible; however, reversible attack at coordinated CO may well be faster than acyl attack in these cases.



$$CH_3C(O)Mn(CO)_5 + NaOCH_3 \longrightarrow CH_3C(O)OCH_3 + NaMn(CO)_5$$

Bruner[15] has found that attack of CH_3Li upon an optically active carboalkoxy iron compound gives rise to a change in the circular dichroism spectrum. He has interpreted this result in terms of inversion of configuration at iron resulting from nucleophilic attack at coordinated CO.



To determine the kinetically controlled site of nucleophilic attack upon a metal complex bearing both acyl and CO ligands, we have studied the reaction of CH_3Li with $(CO)_5MnCOC_6H_5$.[16] Here we report that CH_3Li attacks $(CO)_5MnCOC_6H_5$ at a coordinated CO to give *cis*-acetylbenzoyltetracarbonylmanganese(I) anion and that $(CO)_4Mn(COCH_3)(^{13}COC_6H_5)^-$ decomposes via preferential phenyl migration to give unlabeled acetophenone. In the accompanying paper, we will report MO calculations which aid in the understanding of these results.[17]

Results and Discussion

Synthesis of Tetramethylammonium Acetylbenzoyltetracarbonylmangan(I)ate (1a). To determine the site of nucleophilic attack on acylpentacarbonylmanganese compounds, the reaction of $(CO)_5MnCOC_6H_5$ with CH_3Li in tetrahydrofuran at −78° was studied. Evaporation of THF at 0° and addition of aqueous $(CH_3)_4N^+Cl^-$ gave a yellow precipitate of $NMe_4^+[(CO)_4Mn(COCH_3)(COC_6H_5)]^-$ (**1a**) in 54% crude yield. Recrystallization from THF-ether at −25° gave bright yellow crystals of **1** in 29% yield. **1a** was also prepared in 46% yield from $(CO)_5MnCOCH_3$ and C_6H_5Li.

$$(CO)_5MnCOC_6H_5 \xrightarrow{CH_3Li}$$

$$\underset{\textbf{1b}}{Li^+[cis\text{-}(CO)_4Mn(COCH_3)(COC_6H_5)]^-} \xrightarrow{N(CH_3)_4{}^+Cl^-}$$

$$\underset{\textbf{1a}}{N(CH_3)_4{}^+[cis\text{-}(CO)_4Mn(COCH_3)(COC_6H_5)]^-}$$

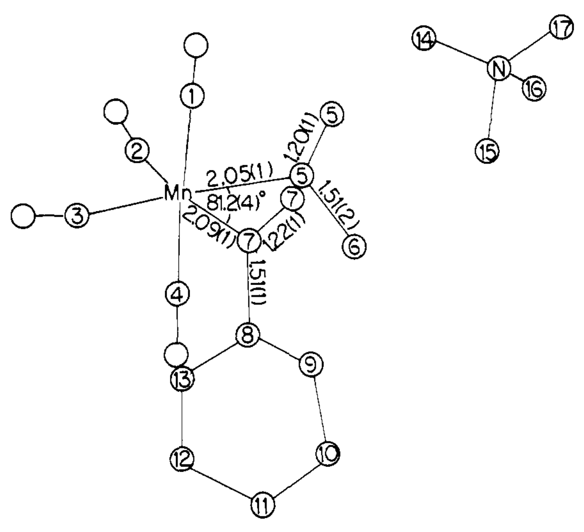


Figure 1. Structure of tetramethylammonium *cis*-acetylbenzoylmanganate(I) (**1a**) with selected bond distances.

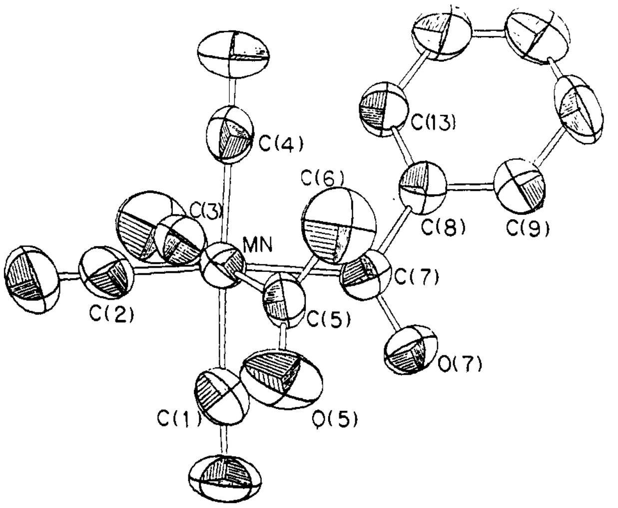


Figure 2. Structure of **1a** with thermal elipsoids of 50% probability.

The structure of **1a** was assigned on the basis of its ir spectrum, its NMR spectrum, and a single-crystal x-ray structure determination. The ir spectrum of **1a** in THF at 0° contains three strong bands at 1952, 1933, and 1906 cm^{-1} and a medium intensity band at 2038 cm^{-1} as expected for a cis disubstituted metal tetracarbonyl.[18] Two broad acyl absorptions were seen at 1550 and 1585 cm^{-1}. The proton NMR spectrum of **1a** has resonances for the phenyl group at δ 7.2 (5 H, m), for the tetramethylammonium ion at δ 3.24 (12 H, s), and for the acetyl group at δ 2.36 (3 H, s).

X-Ray Crystal Structure of 1a. The structure of **1** determined by x-ray crystallography is shown in Figures 1 and 2. The octahedrally coordinated manganese anion has acetyl and benzoyl ligands in a cis relationship with both acyl oxygens directed above the equatorial plane defined by the manganese atom and the two acyl carbon atoms. The tetramethylammonium cation is located above the equatorial plane of the anion in proximity to the acyl oxygen atoms (Figure 1). The ideal octahedral symmetry is distorted by the small angle between the acyl groups attached to the manganese atom (C(5)-Mn-C(7)), 81.2 (4)°, and an increase in the angle (C(2)-Mn-C(3)) between the equatorial carbonyl groups to 96.5 (5)°. The plane of the acetyl group is twisted 73.9° from the equatorial plane and the benzoyl group is twisted 66° from the equatorial plane. The oxygen atoms of the acyl groups are tilted away from each

Table I. Infrared Spectra of 1a and 1b in THF at 0°

Compd	CO stretching frequencies (cm^{-1})			
1a	2038	1952	1933	1906
1b	2045	1963	1946	1928
1b + 4HMPA	2038	1954	1934	1913

other. The phenyl ring is twisted 30.8° out of the plane defined by Mn and the carbon and oxygen atoms of the benzoyl carbonyl group.

Infrared Spectra of 1a and 1b. The isolation of **1a** in 54% yield demonstrated that attack of CH_3Li on $(CO)_5MnCOC_6H_5$ occurred predominately at coordinated CO. To determine whether attack of CH_3Li on $(CO)_5MnCOC_6H_5$ occurred only at coordinated CO, the infrared spectrum of the crude reaction mixture was examined in the metal-CO region and compared with that of the isolated $N(CH_3)_4^+$ salt **1a.** A 0.03 *M* solution of $(CO)_5MnCOC_6H_5$ was treated with a slight excess of CH_3Li in THF at −78°. The infrared spectrum of an aliquot of the solution was taken at 0°. The ir spectrum consisted of three intense bands at 1963, 1946, and 1928 cm^{-1} and a medium intensity band at 2045 cm^{-1} indicative of an anionic cis disubstituted tetracarbonyl manganese compound. While the ir spectrum of the lithium salt **1b** was qualitatively similar to that of the $N(CH_3)_4^+$ salt **1a,** all the bands of **1b** appeared at somewhat higher frequency than the bands of **1a** (Table I). This might be due to coordination of the ion to the acyl carbonyls of **1b** and removal of negative charge from manganese. To test for specific coordination of lithium to the acyl oxygens in **1b,** the ir spectrum of **1b** was taken in the presence of 4 equiv of hexamethylphosphoric triamide (HMPA) which is known to bind Li^+ strongly; the metal carbonyl bands shifted to lower frequency upon addition of HMPA and approached the frequencies observed for the $N(CH_3)_4^+$ salt **1a.** Thus the major species formed upon reaction of CH_3Li with $(CO)_5MnCOC_6H_5$ is the bisacyl anion. Attack of CH_3Li at the acyl group of $(CO)_5MnCOC_6H_5$ would lead to the formation either of $(CO)_5MnC(O^-)(C_6H_5)CH_3$, **2**, or its decomposition products, $(CO)_5Mn^-$ and acetophenone. The ir of $NaMn(CO)_5$ in THF has bands at 1898, 1862, and 1854 cm^{-1}. The ir of a pentacarbonylmanganese compound **2** would be expected to be similar to that of $(CO)_5MnR$ compounds and to have intense bands in the region of 2040–1980 cm^{-1}. The ir spectrum of the reaction mixture from the addition of CH_3Li to $(CO)_5MnCOC_6H_5$ did not contain bands attributable either to **2** or to $Mn(CO)_5^-$.

The nucleophilic attack upon $(CO)_5MnCOC_6H_5$ at coordinated CO is in marked contrast to the nucleophilic attack upon carbene complexes at the carbene carbon atom. Our molecular orbital calculations on the carbene complex, $(CO)_5CrC(OCH_3)CH_3$, and on the acyl complex, $(CO)_5MnCOCH_3$, reported in the accompanying paper,[17] provide an aid to understanding the contrasting reactivity of these two types of complexes in terms of the energy and localization of the LUMO of the complexes.

Thermal Decomposition of 1a and 1b. A THF solution of the $N(CH_3)_4^+$ salt was monitored by NMR at 25° and found to thermally decompose to acetophenone with a half-life of about 1 hr. The yield of acetophenone was 79%, and no other products were observed by gas chromatography. The lithium salt **1b** also thermally decomposes to give acetophenone in high yield.

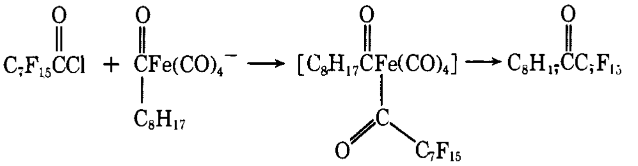
To determine whether the benzoyl or the acetyl carbonyl group was lost in the thermal decomposition of **1a** and **1b** to acetophenone, a ^{13}C labeling study was carried out. Reaction of $C_6H_5{}^{13}COCl$ (20% ^{13}C by MS) with $NaMn(CO)_5$ gave $(CO)_5Mn^{13}COC_6H_5$ (20% ^{13}C by MS). Treatment of $(CO)_5Mn^{13}COC_6H_5$ with CH_3Li at −78% followed by $NMe_4^+Cl^-$ gave $NMe_4^+[(CO)_4Mn(^{13}COC_6H_5)(COCH_3)]^-$, **1a**-$^{13}C$. Thermolysis of **1a**-$^{13}C$ in THF at 70° gave acetophenone with very low ^{13}C enrichment (Table II). This demonstrates the predominant loss of the benzoyl carbonyl group.

Table II. ^{13}C Enrichment

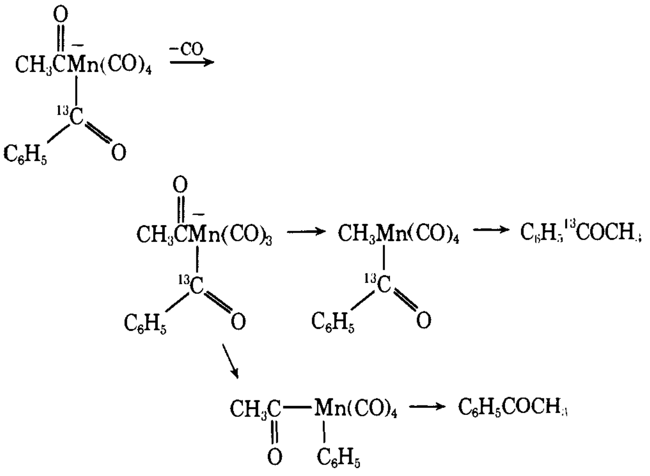
Compound	% ^{13}C enrichment	Ion used in MS analysis
$C_6H_5CO_2H$	19.5 ± 0.4	$[C_6H_5CO_2H]^+$
$(CO)_5Mn^{13}COC_6H_5$	19.9 ± 0.6	$[(CO)_4MnCOC_6H_5]^+$
$C_6H_5COCH_3$ from 1a-^{13}C	0.7 ± 0.4; 0.0 ± 0.4	$[C_6H_5COCH_3]^+$
$C_6H_5COCH_3$ from 1b-^{13}C	11.9 ± 0.5; 11.9 ± 0.5	$[C_6H_5COCH_3]^+$
$C_6H_5COCOCH_3$ from 1b-^{13}C	19.7 ± 0.3	$[C_6H_5COCOCH_3]^+$

In contrast to the results obtained for the NMe_4^+ salt, direct thermolysis at 70° of the Li^+ salt **1b**-^{13}C generated in situ from reaction of CH_3Li with $(CO)_5Mn^{13}COC_6H_5$ in THF gave acetophenone with 11.9% ^{13}C enrichment (Table II). Thus, either the benzoyl or the acetyl carbonyl group can be lost in decomposition of the lithium salt.

The thermal decomposition of **1a** and **1b** to acetophenone is interesting in relation to the synthesis of ketones from acyltetracarbonylferrates. Collman has reported that acyltetracarbonylferrates react with perfluorinated acyl chloride to give high yields of ketones.[19] A bis acyl iron compound is a possible intermediate in this reaction. A possible



mechanism for the thermolysis of **1a** is shown below. Loss of CO would generate a coordinately unsaturated manganese compound.[20] Migration of either phenyl or methyl to the coordinately unsaturated manganese atom would produce an alkyl acyl metal complex. Subsequent reductive elimination of acetophenone could then occur.



In the thermal decomposition of **1a**-^{13}C, the phenyl group migrates at least 20 times more rapidly than methyl. The favored phenyl migration to the electron deficient coordinately unsaturated manganese atom is similar to the preferential phenyl migration to the electron deficient carbon centers of carbonium ions and free radicals. Little is know about the relative ease of migration of various groups from an acyl group to a metal. This is due to the fact that the rate of conversion of an acyl metal complex to an alkyl metal complex does not involve alkyl migration as the rate determining step; the slow step is normally dissociation of a ligand to form a coordinately unsaturated complex which then undergoes rapid migratory rearrangement.[20] The only previous study which gave information concerning relative migration rates involved the rearrangement of five-coordinate acyliridium(III) complexes in which Kubota found that electron donor substituents on a benzyl group accelerated migration to iridium.[21]

Surprisingly, similar labeling studies on the lithium salt **1b**-^{13}C indicated that migration of phenyl and of methyl occurred at very similar rates. The effect of Li^+ on the relative migratory abilities of the phenyl and the methyl groups can only be explained by a specific interaction of Li^+ with the bisacylmanganese anion. In the infrared spectrum of Li^+ salt **1b** all the CO bands were shifted by ~15 cm^{-1} to higher frequency relative to the NMe_4^+ salt. This provides direct evidence for coordination of Li^+ to the anion and for electron withdrawal from manganese to lithium. Similar salt effects on the CO stretching frequencies of $CH_3COFe(CO)_4^-$ and $HCOFe(CO)_4^-$ have been observed by Collman.[22]

Coordination of Li^+ could occur at either the benzoyl oxygen or at the acetyl oxygen. Since phenyl substituted ketones are more basic than alkyl substituted ketones,[23] coordination of Li^+ to the benzoyl oxygen should be preferred. We propose that the preferential coordination of Li^+ to the benzoyl oxygen retards phenyl migration since the benzoyl oxygen would be converted to much less basic CO after phenyl migration. Effectively, Li^+ ion stabilizes the benzoyl group relative to phenyl and CO bonded to the metal. In related work, Li^+ ion was found to accelerate the transformation of an anionic alkyl iron complex to an anionic acyl iron complex by a factor of 10^3 relative to the $Ph_3P{=}NPPh_3^+$ ion.[24] This is another example of Li^+ stabilizing an acyl complex relative to an alkyl complex.

Other Reactions of 1a and 1b. Oxidation of the bisacyl manganese anions leads to coupling of the acyl units. Reaction of **1a** with bromine in methanol at 0° gave a 67% yield of 1-phenyl-1,2-propanedione and about 17% each of acetophenone and methyl benzoate.

Treatment of either the NMe_4^+ salt **1a** or the Li^+ salt **1b** with HCl in ether led to a complex mixture of products which included 30% 1-phenyl-1,2-propanedione, 13% 1-phenyl-2-hydroxy-1-propanone, 3% acetophenone, and 4% benzaldehyde. When **1a**-^{13}C was treated with HCl at 0° in THF, the 1-phenyl-1,2-propanedione obtained had 19.6% ^{13}C enrichment at carbon-1 as determined by mass spectral analysis.

Experimental Section

General. Infrared spectra were recorded on a Perkin-Elmer 267 spectrophotometer. A low temperature ir cell was used for low temperature ir work. NMR spectra were determined on a JEOL MH100 spectrometer. ^{13}C NMR spectra were obtained on a Varian XL-100 spectrometer. Mass spectra were run on an AEI-MS9 spectrometer at 70 eV. GC-mass spectra were carried out on a Varian CH-7 spectrometer. All operations involving organometallics were carried out under a dry nitrogen atmosphere. $^{13}CO_2$ (20% enrichment) was obtained from Monsanto Research Corporation, Mound Laboratory, Miamisburgh, Ohio.

Tetramethylammonium *cis*-Acetylbenzoyltetracarbonylmanganate(I), 1a. Methyllithium in ether (1 ml, 1.95 *M*, 1.95 mmol) was added to $(CO)_5MnCOC_6H_5$ (450 mg, 1.50 mmol) in 10 ml of THF at −78°. After 15 min at −78°, solvent was removed at 0° under reduced pressure. Aqueous $N(CH_3)_4Cl$ (2 ml, 2 *M*) and 20 ml of water were added to the residue at 0°. The resulting yellow-brown precipitate was filtered, washed with water, and dried under a stream of nitrogen to give crude **1a** (316 mg, 54%) which was recrystallized from ether-THF at −25° to give bright yellow **1a** (170 mg, 29%), mp 87–89° dec.

Reaction of $(CO)_5MnCOCH_3$ (713 mg, 2.99 mmol) with C_6H_5Li (6.5 ml, 0.56 *M*, 3.64 mmol) in 25 ml of THF under similar conditions gave **1a** (540 mg, 46%), mp 83–85° dec.

Infrared Spectra of Lithium Acetylbenzoyltetracarbonylmanganate(I), 1b. Methyllithium (0.11 mmol) was added to $(CO)_5MnCOC_6H_5$ (0.09 mmol) in THF at −78°. The solution was stirred for 15 min at −78° and transferred by syringe to an ir cell at 0° (see Table II). In some cases, hexamethylphosphoric triamide (HMPA) was added to the reaction mixture prior to ir analysis.

Thermolysis of 1a and 1b. 1a (40 mg, 0.103 mmol) was refluxed in THF for 25 min. Gas chromatographic analysis (20% Carbowax 20M, 160°) using 1,3,5-triethylbenzene as an internal standard indicated that acetophenone was formed in 79% yield. Acetophenone was isolated by preparative gas chromatography and identified by comparison of its infrared and mass spectra with those of an authentic sample.

Lithium salt **1b** generated in situ from $(CO)_5MnCOC_6H_5$ and CH_3Li was refluxed for 25 min in THF. Gas chromatography indicated that acetophenone was formed in high yield and that no other volatile products were present.

Reaction of 1a and 1b with HCl. Lithium salt **1b** was generated in situ from $(CO)_5MnCOC_6H_5$ (82.8 mg, 0.28 mmol) and CH_3Li (0.36 mmol) in 4.6 ml of THF at −78°. After 25 min, HCl in ether (1 ml, 0.95 *M*, 0.95 mmol) was added. The solution was stirred for 15 min at −78°, warmed to room temperature and worked up with water and ether. Gas chromatographic analysis (10% UC-W98, 105–180°, *n*-$C_{14}H_{30}$ internal standard) of the dried ether extract indicated the formation of 4% benzaldehyde, 3% acetophenone, 3% 1-phenyl-2-propanone, 35% 1-phenyl-1,2-propanedione, and 14% of a mixture of 1-phenyl-2-hydroxy-1-propanone and 1-phenyl-1-hydroxy-2-propanone. Products were identified by comparison of GC retention times, of GC-mass spectra, and of NMR spectra with those of authentic samples.

A similar product distribution was obtained on HCl treatment of the lithium salt **1b** generated from $(CO)_5MnCOCH_3$ and C_6H_5Li. **1a** (33.6 mg, 0.09 mmol) in 1 ml of THF was treated with HCl in ether (0.1 ml, 1 *M*, 0.1 mmol) at 0° for 1 hr. Gas chromatographic analyses of the solution (20% Carbowax 20M, 140°, 1,3,5-triethylbenzene internal standard) indicated the formation of 2% benzaldehyde, 4% acetophenone, and 34% 1-phenyl-1,2-propanedione.

Bromination of 1a. A solution of **1a** (29.2 mg, 0.07 mmol) in 0.5 ml of THF was treated with bromine (4 μl, 0.08 mmol) at 0°. After 15 min 0.5 ml of methanol was added. Gas chromatographic analysis (20% Carbowax 20M, 160°, 1,3,5-triethylbenzene internal standard) indicated the formation of 1% acetophenone, 1% methyl benzoate, and 67% 1-phenyl-1,2-propanedione. The latter compound was identified by ir spectral comparison.

$C_6H_5{}^{13}CO_2H$ (19.4 ± 0.4% enrichment by MS) was prepared from phenylmagnesium bromide and $^{13}CO_2$ (20% enrichment). Treatment of $C_6H_5{}^{13}CO_2H$ with $SOCl_2$ gave $C_6H_5{}^{13}COCl$. $NaMn(CO)_5$ (85 ml, 0.19 *M*, 16.2 mmol) in THF was added to a solution of $C_6H_5{}^{13}COCl$ (2.2 g, 15.6 mmol) in 10 ml of THF at 0°. After 75 min at 0°, solvent was removed on a rotary evaporator. The residue was dissolved in CH_2Cl_2, filtered, and cooled to −20° to give yellow crystalline $(CO)_5Mn^{13}COC_6H_5$ (3.0 g, 64%). Mass spectral analysis of the M − 28 peak indicated 19.9 ± 0.6% ^{13}C enrichment.

$Li^+[cis\text{-}(CO)_4Mn(COCH_3)(^{13}COC_6H_5)]^-$, 1b-$^{13}C$. The ^{13}C labeled lithium salt **1b**-^{13}C was generated in situ from reaction of CH_3Li (0.3 ml, 1.93 *M*, 0.58 mmol) and $(CO)_5Mn^{13}COC_6H_5$ (153 mg, 0.51 mmol) in 5 ml of THF at −78°. After stirring for 15 min at −78°, the compound was thermally decomposed in refluxing THF. Acetophenone was isolated from the concentrated reaction mixture by preparative gas chromatography (25% Carbowax 20M, 200°). Analysis of the parent ion region in the mass spectrum indicated 11.9% ^{13}C enrichment in the acetophenone.

In another experiment, **1b**-^{13}C was generated in situ and treated with HCl in ether at −78°. 1-Phenyl-1,2-propanedione was isolated by gas chromatography (15% PMPE, 200°) and found to contain 19.7 ± 0.3% ^{13}C enrichment. The ^{13}C NMR of the labeled 1-phenyl-1,2-propanedione indicated that the label was located at the 1-carbonyl group. ^{13}C NMR δ^{TMS} (intensity of labeled ketone, intensity of unlabeled ketone, assignment): 200.5 (0.24, <0.8, 2-

Table III. Bonding Distances (Å) for 1a

Mn–C(1)	1.831 (13)	C(7)–O(7)	1.218 (13)
Mn–C(2)	1.785 (14)	C(7)–C(8)	1.510 (14)
Mn–C(3)	1.815 (13)	C(8)–C(9)	1.364 (14)
Mn–C(4)	1.843 (13)	C(8)–C(13)	1.397 (15)
Mn–C(5)	2.045 (11)	C(9)–C(10)	1.387 (16)
Mn–C(7)	2.091 (11)	C(10)–C(11)	1.347 (20)
C(1)–O(1)	1.144 (14)	C(11)–C(12)	1.348 (19)
C(2)–O(2)	1.172 (14)	C(12)–C(13)	1.383 (17)
C(3)–O(3)	1.148 (12)	N–C (14)	1.450 (13)
C(4)–O(4)	1.141 (14)	N–C (15)	1,472 (16)
C(5)–C(6)	1.512 (16)	N–C (16)	1.477 (15)
C(5)–O(5)	1.203 (13)	N–C (17)	1.458 (17)

Table IV. Intramolecular Angles (deg) for 1a

C(1)–Mn–C(2)	90.3 (5)	Mn–C(5)–O(5)	124.7 (8)
C(1)–Mn–C(3)	92.4 (5)	C(6)–C(5)–O(5)	114.4 (10)
C(1)–Mn–C(4)	175.3 (5)	Mn–C(7)–O(7)	121.3 (8)
C(1)–Mn–C(5)	84.9 (5)	Mn–C(7)–C(8)	123.6 (8)
C(1)–Mn–C(7)	84.9 (5)	O(7)–C(7)–C(8)	114.9 (9)
C(2)–Mn–C(3)	96.5 (5)	C(7)–C(8)–C(9)	119.0 (10)
C(2)–Mn–C(4)	90.5 (5)	C(7)–C(8)–C(13)	123.6 (9)
C(2)–Mn–C(5)	89.8 (5)	C(9)–C(8)–C(13)	117.3 (10)
C(2)–Mn–C(7)	170.1 (5)	C(8)–C(9)–C(10)	122.3 (11)
C(3)–Mn–C(4)	92.1 (5)	C(9)–C(10)–C(11)	118.3 (12)
C(3)–Mn–C(5)	173.2 (5)	C(10)–C(11)–C(12)	122.0 (12)
C(3)–Mn–C(7)	92.3 (5)	C(11)–C(12)–C(13)	119.8 (12)
C(4)–Mn–C(5)	90.4 (5)	C(8)–C(13)–C(12)	120.2 (11)
C(4)–Mn–C(7)	93.5 (5)	C(14)–N–C(15)	108.4 (9)
C(5)–Mn–C(7)	81.2 (4)	C(14)–N–C(16)	110.0 (9)
Mn–C(1)–O(1)	177.9 (11)	C(14)–N–C(17)	109.2 (9)
Mn–C(2)–O(2)	177.0 (11)	C(15)–N–C(16)	109.3 (9)
Mn–C(3)–O(3)	177.8 (10)	C(15)–N–C(17)	110.6 (10)
Mn–C(4)–O(4)	178.3 (12)	C(16)–N–C(17)	109.3 (10)
Mn–C(5)–C(6)	120.9 (9)		

CO), 191.4 (11.9, 0.16, 1-CO), 134.5 (2.6, 1.1), 131.9 (<0.8, 0.4), 130.3 (4.3, 1.9), 128.9 (4.3, 2.0), 26.2 (1.0, 1.0, CH_3).

$N(CH_3)_4{}^+$[*cis*-$(CO)_4Mn(COCH_3)(^{13}COC_6H_5)$], 1a-$^{13}C$. **1a-$^{13}C$** was prepared by the same method used to obtain **1a. 1a-^{13}C** (40 mg, 0.10 mmol) in 1 ml of THF was thermally decomposed by heating to reflux for 15 min. Acetophenone was isolated by preparative gas chromatography (20% Carbowax 20M, 200°) and found to contain 0.0 ± 0.4% and 0.7 ± 0.4% ^{13}C enrichment in two separate experiments.

X-Ray Crystal Structure of 1a. Yellow crystals of **1a** were obtained by crystallization from dichloromethane at −25°. A needlelike crystal of irregular octagonal cross section[25] was wedged in a glass capillary, sealed in air, and placed on a Syntex $P\bar{1}$ computer controlled diffractometer equipped with a graphite monochromated Mo Kα radiation source. The preliminary Syntex routines[26] indicated a primitive monoclinical cell with dimensions a = 10.346 (5) Å, b = 15.578 (7) Å, c = 12.094 (3) Å, β = 100.99 (3)°, and V = 1913 (1) Å^3. The experimental density of 1.36 g cm^{-3}, determined by flotation in a chloroform-heptane mixture, agrees with the 1.35 g cm^{-3} calculated for $Z = 4$.

A total of 2771 diffraction maxima were collected from $3° \leq 2\theta \leq 45°$ through three octants (h, k, $\pm l$) by the variable 2θ-ω scan speed technique. The intensities of two standard peaks monitored every 48 reflections fluctuated less than 5%. The intensities were corrected accordingly, reduced, and merged in the usual manner[27] to yield 1249 independent reflections for which $I > 2\sigma(I)$. Later the data were corrected for crystal absorption effects. With the linear absorption coefficient, μ = 7.53 cm^{-1}, the transmission factors varied from 0.89 to 0.96. The observed systematic absences for $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$) uniquely define the space group as $P2_1/c$ (no. 14 C^5_{2h}).[28]

The structure was determined using the standard heavy atom method.[29] Full-matrix isotropic least-squares refinement converged at R_1 = 10.6% and R_2 = 11.6%.[30] At this stage, the hydrogen atom coordinates were calculated using idealized geometry and a bonding distance of 1.0 Å. These were included as fixed-atom contributions (β = 7.0 Å^2) in the final anisotropic refinement series (the nitrogen atom and four bonded carbon atoms were varied isotropically) to yield R_1 = 6.9% and R_2 = 7.0%. In the last cycle the maximum shift in any anisotropic or isotropic atom parameter was $<0.10\sigma$. The final error-of-fit was 1.43.

Table V. Least-Squares Planes and Deviations (Å)

1. Mn, C(5), C(6), O(5)
   −0.0001, −0.0002, 0.0001, 0.0001
2. Mn, C(7), O(7), C(8)
   −0.0074, 0.0286, −0.0116, −0.0096
3. C(7), C(8), C(9), C(10), C(11), C(12), C(13)
   0.0084, −0.0190, 0.0106, −0,0084, 0.0059, 0.0034, −0.0009
4. Mn, C(2), C(3), C(5), C(7)
   0.0435, −0.0275, 0.0022, 0.0058, −0.0275
5. Mn, C(1), C(3), C(4), C(5)
   0.0493, 0.0335, −0.0588, 0.0305, −0.0545
6. Mn, C(1), C(2), C(4), C(7)
   0.0885, 0.0174, −0.0637, 0.0126, −0 0548

Selected Dihedral Angles (deg)

1–2	104.8	2–3	30.8
1–4	73.9	2–4	66.1
1–5	18.7	2–5	22.7

Bond distances and angles and selected nonbonding intramolecular distances are given in Tables III and IV, respectively. Table V shows selected least-squares planes. The final atomic coordinates and thermal parameters and their associated standard deviations are given in Tables VI–VIII and tables of observed and calculated structure factor amplitudes are shown in Table IX.

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Supplementary Material Available: Tables VI–IX, final atomic coordinates, thermal parameters, and structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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background counts, B_R is the ratio of background time to scan time ($B_R = 0.67$ for this data set), and T_R is the 2θ scan rate in degrees per minute. The standard deviation of I was calculated as $\sigma(I) = T_R\{S + (B_1 + B_2)/B_R^2 + q(I)^2\}^{1/2}$ where q in this case was set equal to 0.003.

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(29) All crystallographic programs used in structural determination and least-squares refinement were written by J. C. Calabrese. The absorption correction program DEAR (J. F. Blount) uses the Gaussian integration method of Busing and Levy. Plots were made using ORTEP (C. K. Johnson).

(30) $R_1 = [\sum||F_o| - |F_c||/\sum|F_o|] \times 100\%$ and $R_2 = [\sum w||F_o| - |F_c||^2/w|F_o|^2] \times 100\%$.

MO Calculations on Metal Carbene Complexes and Metal Acyl Complexes. The Importance of the LUMO in Determining the Site of Nucleophilic Attack

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Abstract: Molecular orbital calculations have been performed on $(CO)_5CrC(OCH_3)CH_3$ and $(CO)_5MnCOCH_3$ in order to discover which factors determine the site of nucleophilic attack in metal carbene complexes and metal acyl complexes. The reaction of a nucleophile with either $(CO)_5CrC(OCH_3)CH_3$ or $(CO)_5MnCOCH_3$ is frontier, rather than charge, controlled. The differences in the energies and localization properties of the LUMO's of the two compounds indicate that attack of nucleophiles at coordinated CO is much more likely for the acyl species than for the carbene complex.

The factors which determine the site of nucleophilic attack on a polyfunctional organometallic compound are not well understood. The kinetically controlled site of nucleophilic attack of CH_3Li on $(CO)_5MnCOCH_3$ was found to be the cis CO ligand and not the acyl carbon.[1] In contrast, the kinetically controlled site of nucleophilic attack upon metal-carbene complexes, such as $(CO)_5WC(OCH_3)C_6H_5$, is the carbene carbon atom[2-4] and not the CO ligand. To gain an understanding of the differing reactivities of these structurally related compounds, we have carried out molecular orbital (MO) calculations on $(CO)_5MnCOCH_3$ and $(CO)_5CrC(OCH_3)CH_3$. The results of our calculations indicate that charge is not the factor determining the site of nucleophilic attack in the acyl and carbene complexes.[5a] Rather, the calculations indicate that there is a correlation between the site of nucleophilic attack and the location of the lowest unoccupied molecular orbital (LUMO) in the metal complexes.

Experimental Section

Parameter-free molecular orbital calculations, which have been described elsewhere,[6] were carried out on $(CO)_5CrC(OCH_3)CH_3$ and $(CO)_5MnCOCH_3$.

Clementi's double $-\zeta$ functions for neutral atoms were used as basis functions for carbon and oxygen.[7] The 1s and 2s functions were curve-fit to single $-\zeta$ form using the maximum overlap criterion.[8] For hydrogen, a 1s exponent of 1.16 was chosen, as this is the minimum energy exponent for hydrogen in methane.[9]

For the metal basis functions, the 1s-3d atomic orbitals given by Richardson et al.[10] for Cr(+) and Mn(+) were used. A 4s exponent of 2.0, and a 4p exponent of 1.6, were used for each of the metals.[11] One calculation in which a 4d orbital, with exponent 1.6, was placed on chromium was also performed. This latter expansion of the basis set had the effect of stabilizing all molecular orbitals by roughly the same amount. Since it is the separation of the energy levels (and not the actual magnitude of the eigenvalues) which is important in predicting the reactivity of the compounds, it was concluded that it was unnecessary to include the 4d orbital in the rest of the calculations.

Although the calculations were carried out in the atomic orbital basis set, it is easier to discuss the results in terms of appropriate molecular and hybrid atomic orbitals. Therefore, after self-consistency had been reached, the results were transformed to an MO basis derived from the eigenvectors of the free CO group and sp^2 or sp^3 hybrids on the carbon and oxygen atoms of the acyl and carbene ligands.

The bond distances and angles employed are shown in Table I. The carbonyl C-O distance was kept constant at 1.128 Å, the distance observed in free CO.[12] This was done so that a single set of ligand basis functions could be used for all carbonyls and is in accord with the insensitivity of the carbon-oxygen bond length for the bond order range 2-3.[13] The other bond lengths for $(CO)_5CrC(OCH_3)CH_3$ represent a synthesis of the crystal structure data for $(CO)_5CrC(OCH_3)C_6H_5$ and $[(C_6H_5)_3P]-(CO)_4CrC(OCH_3)CH_3$.[2] The bond distances for $(CO)_5MnCOCH_3$ are in agreement with those found for *cis*-$[(CH_3CO)(C_6H_5CO)Mn(CO)_4]^-$.[1]

Results

The possibility that nucleophilic attack on $CH_3COMn(CO)_5$ and $(CO)_5CrC(OCH_3)CH_3$ might be charge controlled was considered first. Examination of the resonance forms for $(CO)_5MnCOCH_3$ and $(CO)_5CrC(OCH_3)CH_3$ does not allow an estimation of the relative positive charge on the acyl and the carbene carbon atoms. Both the acyl carbon and the carbene carbon have π electron density donated from an oxygen atom and from a metal atom. While the oxygen atom of the acyl complex is a better π-donor to carbon than the methoxy oxygen of the carbene complex, the manganese atom of the acyl complex is a poorer π-donor to carbon than the chromium atom of the carbene complex. Since the relative magnitude of these opposing effects is not readily evaluated, resonance theory cannot be used to determine the relative positive charges on