Reactivity of Cyclomanganated 2-Phenylpyridine Derivatives toward Organolithium Reagents. Synthesis of Novel Chelated Tricarbonyl(η^3-benzyl)manganese(I) Complexes

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Ortho-manganated 2-arylpyridine and -quinoline derivatives were treated with aryllithium reagents and subsequently with alkyl triflates to yield air-stable chelated (η^3-benzyl)-tricarbonylmanganese complexes. Addition of PhLi to the cyclomanganated complex of 2-phenylpyridine [$NC_5H_4-C_6H_4-Mn(CO)_4$], **1**, followed by methylation with MeOTf afforded a red air-stable chelated η^3-benzyl, tricarbonyl{2-[(1,2-η^2),κC^{α}-2-(phenylmethoxymethylene)-phenyl]pyridine- κN}manganese(I), complex **4a**. The molecular structure of **4a** was established by single-crystal X-ray diffraction analysis. The study of this structure indicates a helical shape in which the manganese center adopts an octahedral configuration. Spectroscopic analysis indicates that the addition of the aryllithium reagent to **1** generates a new temperature- and air-sensitive benzoylmanganate species. The latter and other anionic acylmanganese species generated from different substrates readily decompose above a temperature of 0 °C to yield ketones and a formal $[Mn(CO)_3]^-$ species which is believed to remain coordinated to the ancilliary pyridinyl group. The latter anionic tricarbonylmanganese species was trapped by reaction with Me_3SnCl and 2 equiv of PPh_3 to yield a mixture of *mer* and *fac* isomers of $Me_3SnMn(CO)_3(PPh_3)_2$. The thermal decomposition of the benzoylmanganates into ketones *via* a reductive elimination step was exploited as a new synthetic route of aromatic ketones bearing a pyridyl, quinolinyl, or benzo[*h*]quinolinyl substitution pattern.

Introduction

The chemistry of cyclomanganated complexes has developed rapidly since the synthesis of the first examples of such complexes.[2] Many types of aromatic substrates are known to undergo a cyclometalation reaction when exposed to alkylpentacarbonylmanganese complexes under thermal conditions. For instance, aromatics derived from *N*,*N*-dimethylbenzylamine, alkyl benzyl thioether, 2-phenylpyridine, acetophenone, benzaldehyde, and diazobenzene may be readily transformed into the corresponding cyclomanganated products when treated with alkylpentacarbonylmanganese complexes.[3] However, one must point out that cyclomanganated aromatics display a smaller spectrum of reactivity than other families of cyclometalated arenes.[4] Indeed, most of the reactions reported to take place with cyclomanganated complexes deal with photolytically or thermally promoted insertion reactions of unsaturated hydrocarbons or inorganic molecules.[5] The latter insertion reactions are reported to occur mostly with chelates derived from aromatic ketones and aldehydes. In contrast, nitrogen-based $Mn(CO)_4$ chelates have never been reported to produce insertion reactions.[6] In some cases, however, cyclomanganated complexes have been reported to display a fluxional behavior producing,

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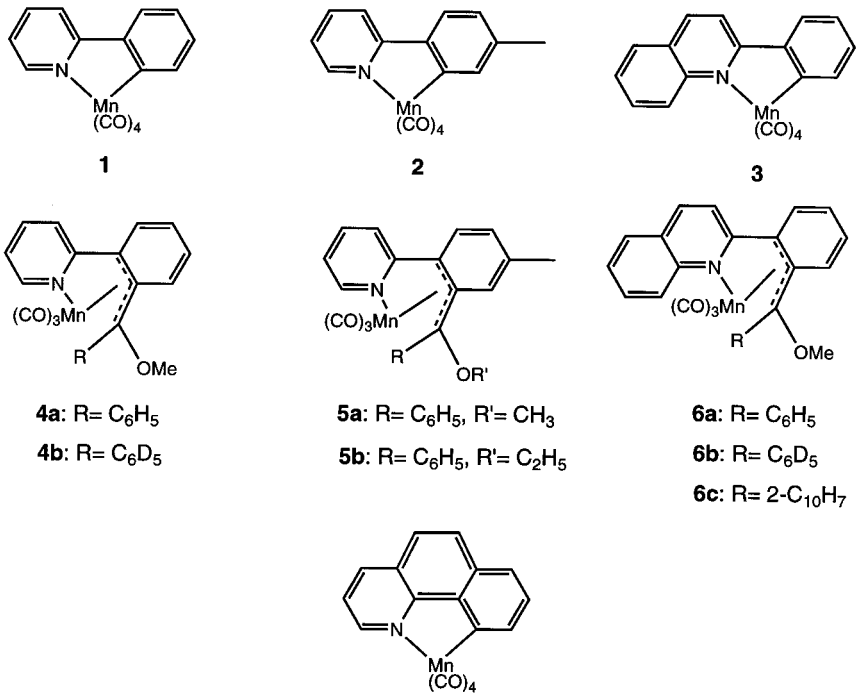
Chart 1



under thermal treatment, the formal transfer of the Mn-$(CO)_4$ moiety from one aromatic site or ligand to another.[7]

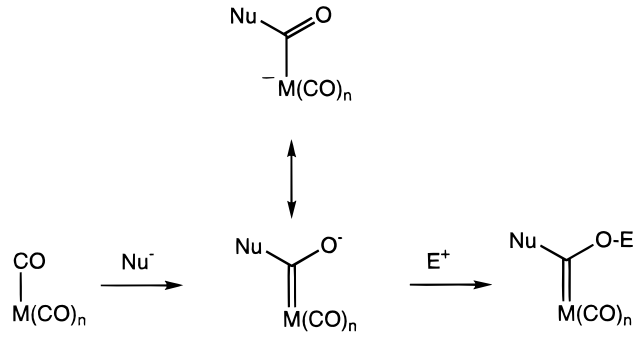
The behavior of cyclomanganated aromatic compounds toward carbanionic nucleophiles has not yet been addressed in a comprehensive way. We now present our first results on the study of the reactivity of carbonyl chelate manganese complexes derived from 2-arylpyridine and 2-arylquinoline toward aryllithium compounds, and we report on the unprecedented synthesis of chelated tricarbonyl(η^3-benzyl)manganese complexes.

Results

As established by the pioneering work of E. O. Fischer, the addition of alkyl- or aryllithium nucleophiles to metal carbonyl complexes leads in a first step to anionic acylmetalate complexes that may undergo alkylation at the oxygen atom to yield ultimately metal−carbene complexes (Scheme 1).[8]

At the begining of this study, our main aim was to check the possibility of metallocarbene formation. Several examples of manganese carbene complexes have been reported to form *via* the so-called "Fischer route" from substrates such as tricarbonyl(η^5-cyclopentadienyl or cyclohexadienyl)manganese[9] complexes, decacarbonyldimanganese(*Mn−Mn*),[10] and pentacarbonyl(η^1-alkyl

Scheme 1



or trialkylgermyl)manganese(I) complexes.[11] To our knowledge no other class of manganese carbonyl complexes has been reported to yield carbenes *via* the classical "Fischer route". We decided therefore to apply this methodology to a series of arylpyridine and -quinoline tetracarbonylmanganese derivatives (Chart 1) by reacting them with methyllithium and phenyllithium.[12]

Synthesis of Chelated Tricarbonyl(η^3-benzyl)-manganese Complexes. Our preliminary experiments showed that above −60 °C the addition of organolithium reagents to these compounds yields new air-sensitive organometallic anionic species. Our attempts to trap the intermediates resulting from the addition of MeLi by means of alkyl triflates or trialkyloxonium salts were unsuccessful (*vide infra*). However, the alkylation of the intermediates resulting from the addition of PhLi resulted in the formation of new neutral red or orange products, which were identified

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(12) List of abbreviations: phenyllithium, PhLi; methyllithium, MeLi; methyl trifluoromethane sulfonate, MeOTf; ethyl trifluoromethanesulfonate, EtOTf; tetrahydrofuran, THF; petroleum ether, PE; bis(triphenylphosphoranylidene)ammonium chloride, PPN^+Cl^-.

Scheme 2

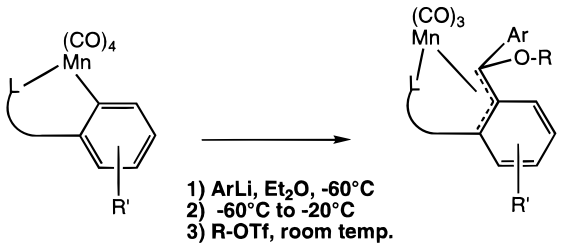

Table 1. Yields of Chelated (η^3-Benzyl)tricarbonylmanganese Complexes

comp	yield (%)	comp	yield (%)
4a	56	**6a**	22
4b	37	**6b**	20
5a	46	**6c**	56
5b	37		

subsequently as 18-electron chelated tricarbonyl(η^3-benzyl)manganese complexes. Consequently, we focused our efforts on the reaction of aryl lithium compounds with cyclomanganated substrates.

In general, the use of tetrahydrofuran as solvent was avoided due to its reactivity toward alkyl- and aryllithium reagents at room temperature. Diethyl ether was preferred, and the experiments were performed in a "one-pot" manner. The experiments proceeded in three steps: first, the addition of 2 equiv of aryllithium to a solution of the starting chelate at −60 °C; second, the reaction at a temperature below 0 °C; and third, the addition of an alkyl triflate at −20 °C ($CF_3SO_2OCH_3$ or $CF_3SO_2OCH_2CH_3$) followed by workup at room temperature (Scheme 2). It turned out that the mixture of ArLi and the starting complex had to be kept at temperatures below 0 °C in order to suppress the formation of brown decomposition products.

The alkylation was quite slow even when alkyl triflates were added at room temperature. The reaction was completed by warming the reaction medium to room temperature. The alkylation reaction could be monitored either by means of IR spectroscopy (*vide infra*) or visually by following the change in color of the reaction medium from a dark yellow-brown to an intense dark red. The starting materials and main products are displayed in Chart 1. All complexes were isolated as pure compounds after chromatography on deactivated silica gel[13] with yields ranging from 20% to 56% (Table 1). Analytical characterization, e.g., elemental analysis and/or high-resolution mass spectroscopy and ^{1}H and ^{13}C NMR and infrared spectroscopy, are in accord with the proposed structures (see the Experimental Section).

Molecular Structure of Complex 4a. Complex **4a** was synthesized by reaction of tetracarbonyl[2-(phenyl-κC^2)pyridine-κN)]manganese, **1**, with phenyllithium, followed by alkylation with methyl triflate. The pure compound was crystallized to give bright red air-stable crystals suitable for X-ray diffraction analysis. Acquisition parameters are displayed in Table 2. The main interatomic distances and bond angles are given in Tables 3 and Table 4. The molecular structure of complex **4a** indicates a particular bonding mode of the metal center to the benzyl fragment (Figure 1). In this complex the manganese atom meets the 18 valence electron requirement through coordination of the benzyl moiety in a trihapto fashion implying the contribution of π electrons from the arene ring, which therefore suffers from a partial loss of aromaticity.

The molecular structure of the complex indicates that the manganese center adopts an octahedral configuration. Atoms N, C4, C2, and C1 are regarded as being the equatorial components of an octahedron, while C3 and C6 occupy the axial positions. The octahedral coordination geometry is further corroborated by the corresponding interatomic bond angles given in Table 4.

Electronic peculiarities of the η^3-benzyl bonding mode in **4a** are suggested by the slight distortions of both the

(13) We observed that activated silica could induce a significant decomposition of the new complexes.

Table 2. Single-Crystal X-ray Diffraction Experimental Data for 4a

formula	$C_{22}H_{16}NO_4Mn$
mol wt	413.32
cryst syst	monoclinic
space group	$P2_1/n$
a (Å)	9.889(4)
b (Å)	15.776(6)
c (Å)	13.082(5)
β (deg)	110.68(2)
V (Å^3)	1909(2)
Z	4
color	red
cryst dimens (mm)	0.35 × 0.20 × 0.15
D_{calc} (g cm^{-3})	1.44
F_{000}	848
μ (mm^{-1})	5.878
transm min and max	0.58/1.00
temp (K)	273
wavelength (Å)	1.541 84
radiation	Cu Kα graphite monochromated
diffractometer	Philips PW1100
scan mode	$\theta/2\theta$
hkl limits	−10,9/0,16/0,13
Θ limits (deg)	3.0/54.06
no. of data measd	2512
no. of data with $I > 3\sigma(I)$	1545
weighting scheme	$4F_o^2/(\sigma^2(F_o^2) + 0.0064F_o^4)$
no. of variables	253
R	0.050
R_w	0.063
GOF	1.367
largest peak in final diff (e Å^{-3})	0.765

Table 3. Selected Interatomic Bond Lengths (Å) for 4a

Mn-C1	1.841(5)	C4−C5	1.467(5)
Mn−C2	1.786(5)	C4−O4	1.428(5)
Mn−C3	1.773(5)	C5−C6	1.428(5)
Mn−C4	2.104(4)	C5−C15	1.418(6)
Mn−C5	2.240(4)	C6−C7	1.479(6)
Mn−C6	2.438(4)	C6−C12	1.429(6)
Mn−N	2.018(3)	O4−C22	1.439(5)
C1−O1	1.133(5)	C12−C13	1.357(7)
C2−O2	1.164(5)	C13−C14	1.397(7)
C3−O3	1.143(5)	C14−C15	1.355(6)

Table 4. Selected Interatomic Bond Angles (deg) for 4a

C1−Mn−C2	88.4(2)	C4−C5−C6	123.0(4)
C1−Mn−C3	96.9(2)	C4−C5−C15	121.0(4)
C1−Mn−C4	168.4(2)	C6−C5−C15	115.6(4)
C1−Mn−C5	129.4(2)	C5−C6−C7	122.1(3)
C1−Mn−N	92.2(2)	C5−C6−C12	120.1(4)
C2−Mn−C3	89.0(2)	C7−C6−C12	117.6(4)
C2−Mn−C4	93.7(2)	C6−C12−C13	120.8(4)
C2−Mn−C5	90.8(2)	C12−C13−C14	119.8(4)
C2−Mn−N	175.0(2)	C13−C14−C15	120.4(4)
C3−Mn−C4	94.5(2)	C5−C15−C14	123.2(4)
C3−Mn−C5	133.7(2)	C5−C4−C16	123.3(3)
C3−Mn−N	95.9(2)	C5−C4−O4	112.6(3)
C4−Mn−C5	39.3(1)	C4−Mn−N	84.8(1)
C5−Mn−N	85.0(1)		

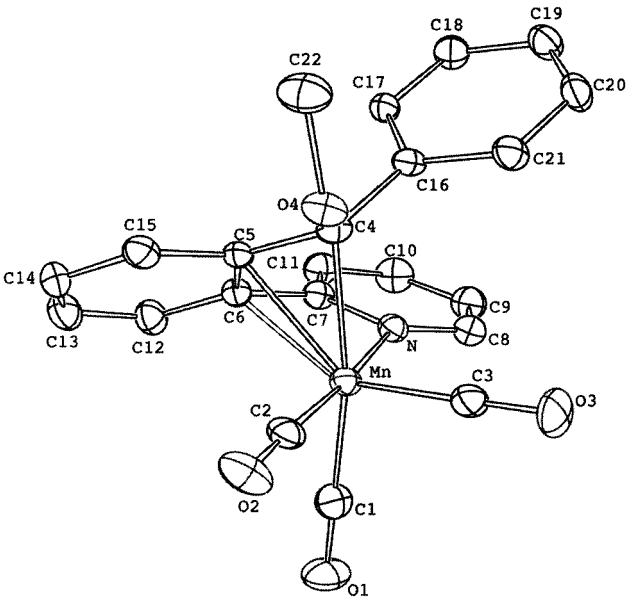

Figure 1. ORTEP view of the molecular structure of **4a**. Ellipsoids are scaled to enclose 30% of the electronic density. Hydrogen atoms are omitted.

benzylmetal and tricarbonylmetal substructures. However, as pointed out by one of the reviewers, in a molecule with such low symmetry, assigning bond parameter differences to $\sigma-\pi$ effects is difficult without more detailed theoretical analysis. For instance, the C4−Mn distance of 2.104(4) Å would suggest a σ-type bonding mode for the benzyl carbon C4 bound to the manganese atom.[14] However, a simple σ-type interaction between C4 and Mn is in contradiction with the fact that the bond distance Mn−C1 of 1.841(5) Å is longer than the distances measured for Mn−C2 and Mn−C3. Indeed a σ-donor ligand having weak or no π-accepting properties should induce a shortening of the bond between the metal and a trans CO ligand. For instance, the Mn−C2 bond distance has a value of 1.786(5) Å, which is consistent with those reported for Mn−CO bond distances of carbonyl carbon atoms located trans to strong σ-donor ligands of other analogous manganese carbonyl complexes.[14] The relatively short Mn−C2 bond distance as compared to Mn−C1 consistently reflects a strong σ donation of the pyridyl nitrogen atom. A similar conclusion cannot be drawn here for the electronic effect of the benzylic carbon C4 over the Mn−C1 bond distance.

The benzyl fragment is bound to manganese through C4, C5, and C6, and the corresponding carbon−manganese distances C4−Mn and C5−Mn are about 0.1 Å shorter than the analogous C−Re bond distances reported for a nonchelated rhenium complex.[15] It is noteworthy that the η^3-benzylic moiety is unsymmetrically bound to the metal; the carbon to manganese bond lengths decrease in the order C6−Mn > C5−Mn > C4−Mn (Table 3). The same trend has been observed for other ruthenium,[16] rhodium,[17] molybdenum,[18] and rhenium[15] (η^3-benzyl) complexes that have been characterized by X-ray diffraction analyses. This could be explained by a weaker bonding interaction between the aromatic carbon atoms (e.g., C6 and C5) and the metal center.[19] Therefore, it would seem more appropriate to consider the interaction between the manganese atom and C6, C5, and C4 in terms of a 6,5-η^2:4-η^1 rather than a 6,5,4-η^3 bonding mode.[20]

A partial loss of aromaticity of the coordinated arene ring can be deduced from the bond distances within the coordinated arene. For instance, the distances C12−C13 and C14−C15 are quite similar (mean value of 1.35 Å) but distinctly shorter than C6−C12, C13−C14, and C5−C15 (mean value of 1.41 Å) (Figure 1). This distortion is reminiscent of a cyclohexadiene-like ring system.[21]

The chelation of the manganese center by the nitrogen atom of the pyridyl group imposes an increased rigidity on the whole assembly and, thus, prevents the η^3-benzyl moiety from displaying any fluxional behavior that could be detected by NMR spectroscopy. We calculated that the pyridyl group and the coordinated arene ring are twisted around the C6−C7 axis by a torsion angle of 40.5°. The distortions are not limited to the twisting of the pyridylbenzyl system. The benzylic carbon C4 does not adopt a rigorously planar sp^2 configuration and seems to have some sp^3 character. The deviation of C4 from the mean plane formed by C16−O4−C5 is estimated to be 0.296 ± 0.005 Å toward the metal center. The phenyl ring attached to C4 originating from the organolithium nucleophile is tilted out of the mean plane formed by the benzyl moiety (Figure 1); it lies above the pyridyl unit and thus imposes a helical structure on the tricyclic ligand system. This molecular structure implies a restricted rotation of the phenyl group as a consequence of its crowded environment, as can be also established by temperature-dependent NMR spectroscopy (*vide infra*).

Spectroscopic Properties of the Novel Chelated Tricarbonyl(η^3-benzyl)manganese Complexes. The complexes described herein obey the general formula *fac*-LL′L″M(CO)$_3$. For a complex of the formula *fac*-L$_3$M(CO)$_3$ which possesses a C_{3v} symmetry the IR spectrum displays two intense bands (an A_1 and a degenerated E) for the vibrations of the CO ligands.[22] In the title complexes, however, the Mn(CO)$_3$ moiety is located in an asymmetric environment that causes the splitting of the E band into two separate absorptions. The intense carbonyl bands are detected for each complex at approximately 2000 (A_1), 1917, and 1898 cm^{-1} (split E).

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(20) Accordingly, complex **4a** may be named by following the "hapto" and "kappa" conventions established for chelates, e.g., tricarbonyl{2-[(1,2-η^2),κC^{α}-2-(phenylmethoxymethylene)phenyl]pyridine-κN}-manganese(I) or tricarbonyl{2-[(1,2,α-η^3)-phenylmethoxymethylene)-phenyl]pyridine-κN}manganese(I). Leigh, G. J., Ed. *IUPAC Nomenclature of Inorganic Chemistry, Recommendations, 1990*; Blackwell Scientific Publication: Oxford, 1991.

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The intrinsic steric hindrance encountered in this type of chelated tricarbonyl(η^3-benzyl)manganese complex has been corroborated by ^{1}H NMR spectroscopy. Indeed, the proton NMR spectra of complexes **4a**, **5a**, **5b**, **6a**, and **6c** recorded at room temperature contain two types of signals in the aromatic region. In addition to well-resolved signals, broad peaks are observed, indicating a fluxional behavior within the aromatic fragment. The well-resolved part of the spectra generally displays a deshielded signal at around 8.3 ppm (benzyl H_2) in C_6D_6 that is related to the proton located ortho to the benzylic carbon on the coordinated arene. The rest of the signals related to the benzyl group appear for **4a** at 7.35 (triplet, benzyl H_3) and at 7.05 (multiplet, benzyl H_4, and H_5) ppm in C_6D_6. The signals that belong to the pyridyl group are usually observed in the range 6.0−5.7 ppm in C_6D_6. For **4a**, the pyridyl proton signals appear at 7.23 (H_6 vicinal to the nitrogen atom), 6.40 (triplet, H_4), 5.85 (doublet, H_3), and 5.80 (doublet, H_5) ppm. In the case of quinoline derivatives **6a**−**c** the spectra are more complex in the aromatic region. However, the signals of the benzyl fragment appear at values similar to those obtained for **4a**. For the ethoxy analogue **5b**, the asymmetry of the molecule is characterized by the signals of the $-OCH_2-$ diastereotopic protons of the ethoxy group, which are detected as two multiplets at 3.86 and 4.05 ppm, respectively. The corresponding CH_3 proton resonance appears as a single triplet at 1.39 ppm. For the phenyl complexes **4a**, **5a**, **5b**, and **6a** a broad peak is observed at an approximate value of 6.6 ppm at room temperature and can be reasonably attributed to the protons of the phenyl group bound to the benzylic carbon. In order to ascertain its origin we undertook the preparation of the deuterium-labeled analogues of **4a** and **6a**. We first prepared a stock solution of d_5-PhLi from pentadeuteriobromobenzene and lithium. This reagent was then reacted with the corresponding complexes **1** and **3** under conditions similar to those used for the synthesis of **4a** and **6a**. The ^{1}H NMR spectra of the pure products **4b** and **6b** revealed the absence of the broad peak.

The ^{13}C NMR spectra inform also on the asymmetry at the metal atom and denote a marked magnetic difference of the three carbonyl carbons for **4a**, **5a**, and **6a**. They appear as three distinct peaks at 220, 221, and 230 ppm (for the carbonyl ligand trans to the pyridyl nitrogen atom). The benzylic carbon substituted by alkoxy groups and coordinated to manganese resonates at around 100 ppm.

Low-Temperature NMR Experiments with 4a. Low-temperature NMR experiments ascertained our assignments for **4a**. For instance, a ^{1}H NMR experiment carried out at 253 K with a solution of **4a** in deuterated acetone revealed four broadened but well-defined peaks at 8.00 (doublet, H_{ortho}), 7.26 (triplet, H_{meta}), 6.61 (triplet, H_{meta}), and 6.05 ppm (doublet, H_{ortho}), each integrating for one proton. These four signals can be assigned to the diastereotopic ortho and meta protons of the phenyl group bound to the benzylic carbon (Figure 2).

Warming the NMR probe caused further broadening of the latter signals at 273 K and their disappearance at 298 K.[23] Due to the large separation in frequency between related peaks, the signals resulting from the coalescence of two signals were not detected in deuterated acetone. The proton para at the arene ring, which is not expected to undergo any line broadening, was located in an intense multiplet at 7.80 ppm. Complementary ^{13}C NMR measurements on this sample of **4a** were carried out at 213, 243, 273, and 298 K. At 243 K, five signals related to the phenyl group observed at values of 140.7 (para), 132.3, 128.2, 127.6, and 127.1 ppm could be attributed to tertiary aromatic carbon atoms. Four out of these five signals underwent broadening upon warming of the NMR probe to 273 K. Three broad and unresolved signals consequently appeared at 132.5, 128.0, and 127.2 ppm (Figure 3).

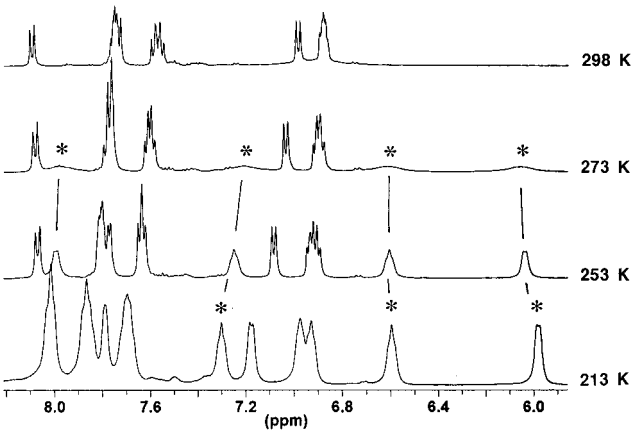


Figure 2. Temperature dependence of the ^{1}H NMR spectrum of compound **4a**. Signals bearing an asterisk correspond to the resonances of the protons located at the meta and ortho positions of the phenyl ring attached to the benzylic carbon atom.

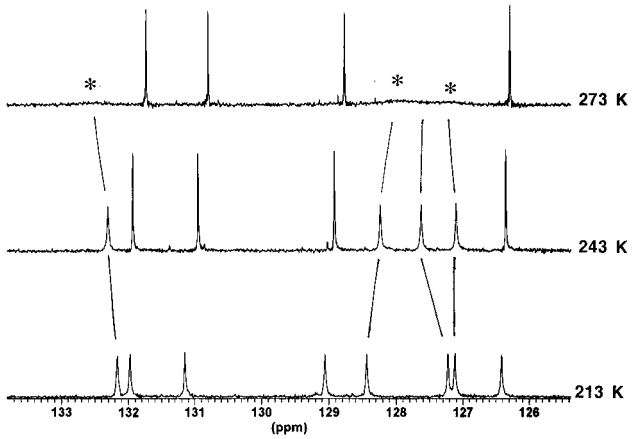


Figure 3. Temperature dependence of the ^{13}C NMR spectrum of compound **4a**. Signals bearing an asterisk correspond to resonances of the ortho and meta carbon atoms of the phenyl ring attached to the benzylic carbon atom.

We attribute the dynamic behavior described above to a restrained rotation of the phenyl group around the $C_{ipso}-C_{benzyl}$ bond axis. Given the large separation in frequency between the ^{1}H or ^{13}C signals described here it was difficult to establish the exact coalescence temperature for a pair of structurally related NMR signals. However, if one considers that the coalescence occurs at a temperature of ca. 298 K, the barrier of rotation for the phenyl moiety can be estimated to be approximately 14 kJ·mol^{-1}.

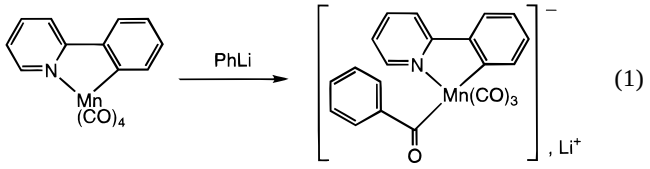
Investigations on the Mechanism of Formation of (η^3-Benzyl)tricarbonylmanganese Complexes.

(23) A similar NMR dynamic effect has been reported for a strained (porphyrinato)osmium(II) ylide; Djukic, J. P.; Young, V. G.; Woo, L. K. *Organometallics* **1994**, *13*, 3995.

The addition of organolithium reagents such as MeLi or PhLi to cyclomanganated complexes is expected to yield acyltricarbonylmanganates $[RC(O)Mn(CO)_3L_2]^-$ that should be detectable by various spectroscopic methods. We monitored the reaction mixture resulting from the action of PhLi with **1** by means of infrared spectroscopy at 253 K using the method described by Gladysz and co-workers.[24] We noticed that shortly after the addition of 2 equiv of PhLi to a solution of **1** in THF ($c = 0.031$ M) the color of the solution changed from pale yellow to orange-brown. The IR spectrum of the resulting mixture displayed after 1 min of reaction only three separated intense bands in the carbonyl ligand region at 1975, 1885, and 1856 cm^{-1} and the absence of any signal related to **1** (note that a THF solution of **1** gives four bands in the IR spectrum at 2073 (w), 1988.3 (vs), 1974.6 (s), and 1933.4 (m) cm^{-1}).

This experiment indicated the quantitative conversion of the starting tetracarbonyl complex into an anionic asymmetric tricarbonylmanganese complex. The anionic nature of the intermediate may be deduced from the decrease in wavenumbers for the CO vibration relative to those of the substrate **1** in the same solvent. A buildup of negative charge at the metal center lowers the bond order of the carbonyl ligand C−O bond and thus induces a bathochromic shift of the IR absorption bands.

Only weak signals were detected around 1600 cm^{-1}. Line rolling prevented us from ascertaining the presence of any signal that could have been related to a benzoyl PhCO-Mn group of a plausible benzoylmanganate intermediate **7** (eq 1). In the literature related to manganese carbonyl complexes the CO stretching band of a benzoyl moiety has been detected by Casey and coworkers at around 1570 cm^{-1} for a compound formulated as $Li[cis\text{-}(CO)_4Mn(COCH_3)(COC_6H_5)]$ and at 1525 cm^{-1} for $N(CH_3)_4[cis\text{-}(CO)_4Re(CH_3)(COC_6H_5)]$.[25]



(1)

1 Li-**7**

In order to either ascertain or rule out the transitory formation of the benzoyl tricarbonylmanganate intermediate **7** in the process leading to chelated (η^3-benzyl)-tricarbonylmanganese complexes, we attempted to isolate the anionic intermediate described above at −30 °C. We decided first to isolate the putative lithium salt formulated as Li-**7** and then concentrated on the influence of the countercation on the IR spectrum of the anionic intermediate. We reacted 1 equiv of PhLi with a solution of **1** in THF at −70 °C. The temperature was allowed to rise to −30 °C, and the solvent was removed under reduced pressure. The IR spectrum of the resulting residue, dissolved in CH_2Cl_2, showed three bands at 1983.2 (strong, A), 1861 (broad and very strong, E), and 1597.6 (weak) cm^{-1}. The last band can plausibly be assigned to the C═O stretching vibration of a benzoylmanganese moiety of a molecule such as Li-**7**. It is important to note that this absorption band was observable only in highly concentrated solutions of the lithium salt.

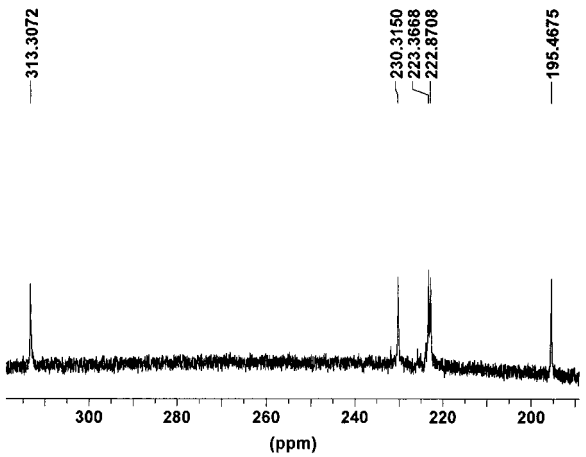


Figure 4. ^{13}C NMR spectrum of Li-**7** at 253 K in d_8-THF. The typical resonance of the acyl carbon appears at 313 ppm. The resonances at 222, 223, and 230 ppm are related to the $Mn(CO)_3$ moiety.

Addition of HMPA to a solution of the lithium salt induced a bathochromic shift to give absorptions bands at 1951.4 (strong, A), 1847.1 (strong), 1833.2 (strong), and 1593.8 (weak) cm^{-1}. This reflects the chelation of the lithium cation and can be rationalized in terms of a weaker coordination of the lithium cation to the benzoylmanganate anion **7** resulting in a higher delocalization of the negative charge within the tricarbonyl manganese fragment.[26] We similarly prepared the PPN^+ salt. PPN-**7** was obtained as a dark red compound after metathesis reaction of Li-**7** with PPN^+Cl^-. Its IR spectrum in CH_2Cl_2 at room temperature displays bands at 1941.3 (strong, A), 1836.5 (very strong), and 1593.3 (weak) cm^{-1}, indicating an even more pronounced bathochromic shift in comparison to Li-**7** due to the pronounced ionic character of the PPN salt.

The lithium salt Li-**7** was also characterized by ^{13}C NMR at 253 K. At this temperature the spectrum displayed five signals above 190 ppm (Figure 4). The first one at 195.5 ppm is attributed to benzaldehyde, which is likely to be a decomposition product of the reaction between the anionic intermediate **7** and the residual water present in d_8-THF. This interpretation was corroborated by reacting a solution of PPN-**7** in CH_2Cl_2 with a slight amount of water. A GC−MS analysis of the mixture indicated the presence of significant amounts of benzaldehyde.

The other low-field signals appear at 222.9, 223.3, 230.3, and 313.3 ppm. The first group of three signals can reasonably be assigned to the $Mn(CO)_3$ moiety (Figure 4). The more deshielded ^{13}C NMR signal at 313.3 ppm was identified as that arising from the carbonyl carbon of the benzoyl moiety.

Although a few data are available on the ^{13}C NMR spectroscopic properties of neutral or anionic acylmanganese complexes, our results are in accord with those reported for acetyl-, benzoyl-, and formylmanganese complexes. For instance, the carbonyl ^{13}C resonances of benzoyl fragments have been detected at ca. 270 ppm

(24) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553.

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(26) (a) Fischer, E. O.; Offhaus, E.; Müller, J.; Nothe, D. *Chem. Ber.* **1972**, *105*, 3027. (b) Casey, C. P.; Cyr, C. R.; Anderson, R. L.; Marten, D. F. *J. Am. Chem. Soc.* **1975**, *97*, 3053.

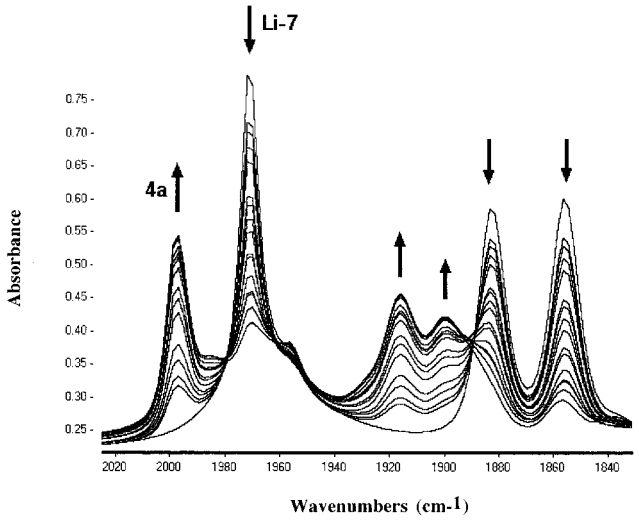


Figure 5. IR monitoring of the reaction of Li-**7** with MeOTf in THF at −20 °C: formation of **4a**.

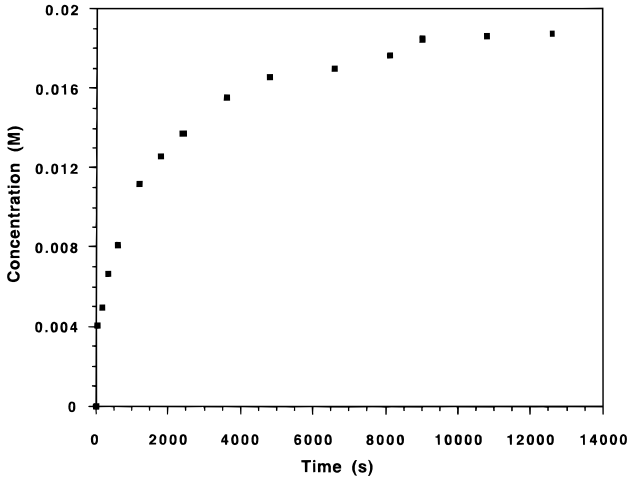


Figure 6. Alkylation of Li-**7** by MeOTf at −20 °C and formation of **4a**. Plot of the concentration in **4a** (M) *versus* time (s).

for $[(\eta^6\text{-}\{(CO)_5Mn\}C(O)C_6H_5)Cr(CO)_3]$[27] and at ca. 250 ppm for 4-$CH_3C_6H_4C(O)$-$Mn(CO)_5$.[28] Signals at approximately 284 ppm were reported by Gladysz and coworkers for homobimetallic anionic formylmanganese and -rhenium complexes of the formula $Li[(CO)_5MM(CO)_4\{C(O)H\}]$ (M= Mn, Re).[29] In addition, the ^{13}C NMR resonance of the acyl moiety in $[NMe_4]^+[(CO)_5Cr(^{13}C(O)Ph)]^-$ has been detected at 306 ppm.[30]

In summary, IR and NMR data clearly indicate that the reaction between PhLi and **1** at −30 °C leads to the anionic benzoylmanganese intermediate Li-**7**.

Reaction of the Anionic Intermediate with MeOTf. A solution of Li-**7** was prepared as described above and treated with a slight excess of methyl triflate at 253 K. This was carried out in order to obtain a qualitative estimation of the rate of alkylation of the putative anionic benzoylmanganese complex prepared above. The reaction was monitored over 3 h by IR spectroscopy. Figure 5 demonstrates the formation of a new species whose IR absorptions at 2000, 1918, and 1900 cm^{-1} are consistent with the structure of a tricarbonylmanganese complex **4a**. Compared with the generation of the benzoylmanganate intermediate, the methylation step seems much slower. The plot of the concentration in complex **4a** *versus* time indicates that the alkylation reaction requires approximately 2.5 h to reach completion at 253 K (Figure 6).

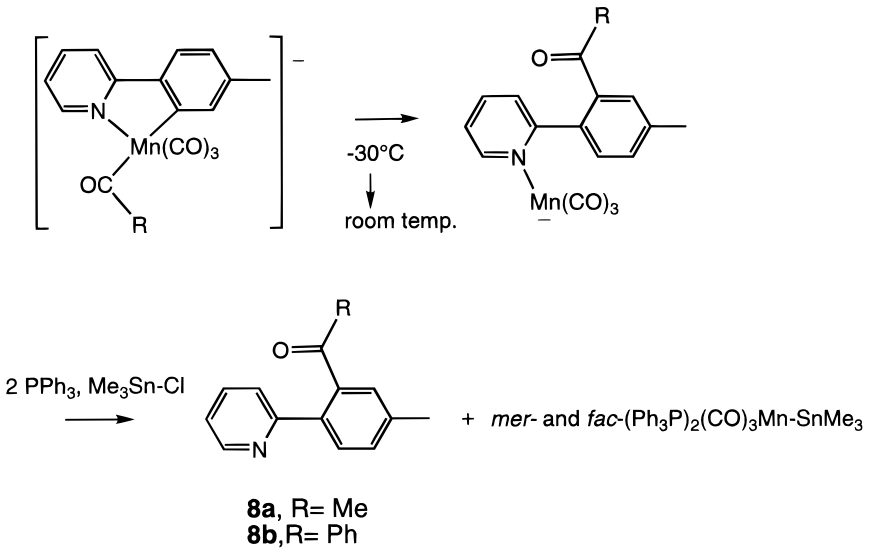
Trapping of the Anionic Tricarbonylmanganese Species $[Mn(CO)_3]^-$. In our preliminary studies we noticed that MeLi and PhLi exhibited distinctly different behavior when reacted with **2**. All of our attempts to isolate neutral (η^3-benzyl)manganese compounds from reactions with MeLi led to very air sensitive brownish solutions. Variation of the temperature, the concentration of the reactants, and the nature of the alkylating agent did not provide any stable neutral organometallic species. We speculated whether this might be a consequence of the propensity of acylmanganate anions toward reductive elimination of a ketone and the subsequent generation of an electron deficient tricarbonylmanganese anion which supposedly remains coordinated to the ancilliary pyridyl nitrogen atom.

This particular process has been already established for the thermal decomposition of acyl manganate and -rhenate anions such as Li[*cis*-$(CO)_4Mn(COCH_3)(CO\text{-}C_6H_5)$] and $N(CH_3)_4$[*cis*-$(CO)_4Re(CH_3)(COC_6H_5)$].[25] In order to obtain evidence for the formation of a $[Mn(CO)_3]^-$ species, we treated **2** with 1 equiv of MeLi at −30 °C during 0.5 h in Et_2O, and we injected the resulting mixture into a solution containing 2 equiv of triphenylphosphine and 1 equiv of trimethyltin chloride at −30 °C. The temperature of the solution was allowed to rise to room temperature in order to assist the reductive elimination process of the benzoylmanganate species. An abundant pale yellow precipitate was produced within 1 h in over 91% yield. This compound was separated from the mother liquor, purified by chromatography on silica gel, and finally identified as a mixture of *mer*- and *fac*-$(Ph_3P)_2(CO)_3MnSnMe_3$ (Scheme 3). Spectroscopic characterization was in good agreement with published data.[31] A GC−MS analysis of the liquor revealed the presence of considerable amounts of a compound which has a relative molecular mass of 196 *m/e* and which we identified as the ketone **8a**. In addition, an experiment was carried out with PhLi under identical conditions, and the same bimetallic tin−manganese complex was isolated in only 26% yield. The GC−MS analysis of the supernatant indicated, apart from the presence of triphenylphosphine, major amounts of a compound having a relative molecular mass of 273 *m/e*; it was identified as the ketone **8b**.

Synthesis of Aromatic Ketones from Ortho-Manganated Pyridine Derivatives. The latter series of experiments provide relevant information regarding the thermal stability of the anionic intermediate **7**. Formation of the ketones **8a** and **8b** occurs at temperatures above −30 °C via a process that generates a very sensitive and electron deficient tricarbonylmanganese anion. We decided to apply this property to the synthesis of polycyclic aromatic ketones. For this purpose we reacted compounds **1**, **3**, and **9** with PhLi at low temperature (−60 °C) in Et_2O and allowed the reaction mixture to reach room temperature in order to promote reductive elimination to afford the corresponding ke-

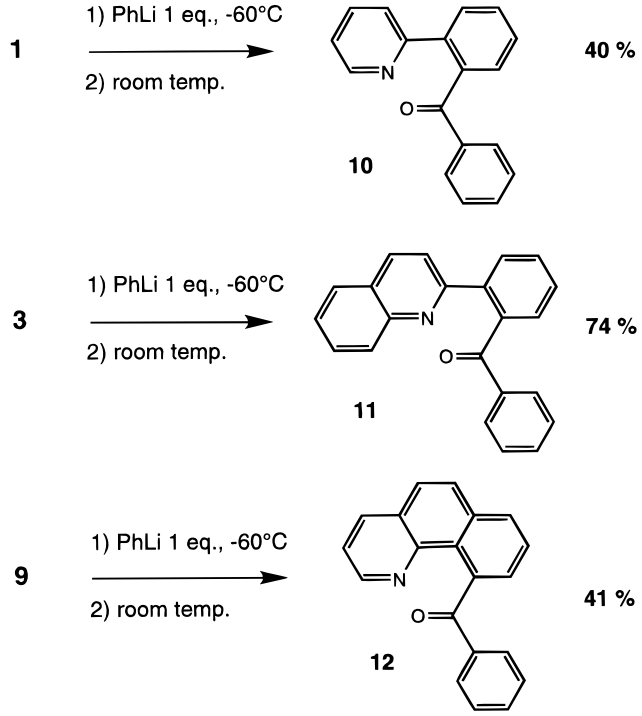
(27) Lotz, S.; Schindehutte, M.; van Rooyen, P. H. *Organometallics* **1992**, *11*, 629.
(28) Sheeran, D. J.; Arenivar, J. D.; Orchin, M. *J. Organomet. Chem.* **1986**, *316*, 139.
(29) Tam, W.; Marsi, M.; Gladysz, J. A. *Inorg. Chem.* **1983**, *22*, 1413.
(30) Lee, I.; Cooper, N. J. *J. Am. Chem. Soc.* **1993**, *115*, 4389.
(31) Onaka, S.; Yoshikawa, Y.; Yamatera, H. *J. Organomet. Chem.* **1978**, *157*, 187.

Scheme 3



8a, R= Me
8b,R= Ph

Scheme 4



tone. After the end of the reaction the workup was performed in air using water to neutralize unreacted amounts of organolithium reagent and to induce the oxidation of the sensitive Mn(I) species into the metal oxide easily separable by filtration through Celite. Following this procedure, three different aromatic ketones, **10**, **11**, and **12**, were synthesized in isolated yields of 40%, 74%, and 41% after chromatographic purification (Scheme 4). A similar experiment carried out with **3** and 2-lithionaphthalene afforded less than 5% of the corresponding crowded aromatic ketone.

Discussion. The formation of the chelated (η^3-benzyl)tricarbonyl species is not a straightforward process. As evidenced above, the first step, which involves the addition of the aryl lithium to the tetracarbonylmanganese substrate, yields an anionic benzoylmanganate Ar−CO−Mn intermediate. Previous work has demonstrated that the addition of organolithium reagents to metal carbonyl complexes of the formula $(CO)_nML$ preferentially occurs at the carbonyl ligand located cis with respect to the better donor ligand L.[32] In our case, it is not clear yet whether the nucleophilic ArLi reagent attacks only the axial carbonyl ligand of the starting tetracarbonylmanganese chelate or adds also to one of the other two equatorial CO ligands, affording therefore a mixture of three anionic benzoylmanganate species. To address this question one must be able to isolate temperature-stable intermediates that might be characterized by X-ray diffraction analysis. Unfortunately, all of our attempts to crystallize the manganese anions failed to produce good quality crystals, and so far only decomposition products have been obtained. At this moment, we focus our efforts on the isolation of more stable rhenium analogues, which will be described elsewhere.

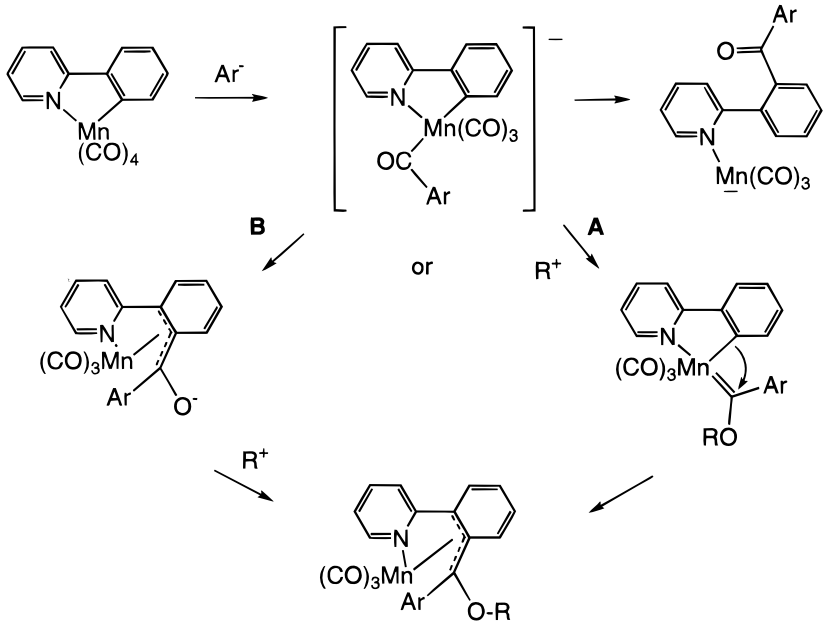
From our investigations we know that the anionic benzoyl- or acetylmanganate anions may undergo reductive elimination following a process similar to that described by Casey and co-workers for the decomposition of Li[*cis*-$(CO)_4Mn(COCH_3)(COC_6H_5)$] into $[Mn(CO)_4]^-$ and acetophenone.[25a] The intermediate proposed by these authors, e.g., $[(CO)_4Mn(C(O)Me)(Ph)]^-$, closely resembles the anion **7**. Related anionic rhenium species, $[(CO)_4Re(C(O)Me)(Ph)]^-$ and $[(CO)_4Re(C(O)Ph)(Me)]^-$,[33] have been reported to yield acetophenone when heated to 120 °C.[25b]

The alkylation of intermediates such as Li-**7** may be challenged by the competing reductive elimination path. The latter process, which produces an aromatic ketone, may in some respects lower the efficiency of the process that yields the new (η^3-benzyl)tricarbonylmanganese complex. We speculate whether in the reaction with MeLi a fast reductive elimination reaction prevents the anionic acetyl intermediate from giving a (η^3-benzyl)-manganese complex. This difference of reactivity between acetyl- and benzoylmanganates has been previously addressed in part by Casey and co-workers.[25a] However, in the cases presented herein a more thorough discussion requires reliable kinetic data, which are not available so far.

(32) (a) Darensbourg, M. Y.; Conder, D. J.; Darensbourg, D. J.; Hasday, C. *J. Am. Chem. Soc.* **1973**, *95*, 5919. (b) Dobson, G. R.; Paxson, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 5925. (c) Casey, C. P.; Bunnell, C. A. *J. Am. Chem. Soc.* **1976**, *98*, 436.

(33) Casey, C. P.; Scheck, D. M. *J. Organomet. Chem.* **1977**, *142*, C12.

Scheme 5



4a, R= Me, Ar= Ph

The detailed mechanism of the formation of the (η^3-benzyl)tricarbonylmanganese complexes is still unknown. However, we can propose two reasonable paths that are consistent with our experimental observations (Scheme 5) .

First, the alkylating agent may add to the oxygen atom of the aroyl fragment to afford a reactive manganese arylmethoxymethylidene species, which may undergo a nucleophilic migration of the phenyl moiety of the 2-phenylpyridine chelate from the manganese center to the electrophilic carbene carbon atom and yield the chelated (η^3-benzyl)tricarbonylmanganese complex as the final stable product (path A).

Alternatively, a reductive elimination pathway starting from the anionic benzoylmanganate could afford an alcoholate precursor of the neutral (η^3-benzyl)tricarbonyl manganese complex (path B). This intermediate could also be seen as the precursor of the aromatic ketones that we detected and isolated throughout this work.

However, one might argue that the reductive elimination step yielding an aromatic ketone is a prerequisite for the further formation of a (η^3-benzyl)manganese complex. In this context, an anionic $(S)_nMn(CO)_3^-$ species (S = solvent, n = 1 or 2) could act as a strong nucleophile that adds to the carbon of the endogenous aryl ketone. To some extent, this would be consistent with other reports that confer to the $[Mn(CO)_3]^-$ species in the gas phase a high reactivity toward the C−H bond activation of hydrocarbons.[34,35]

At this point in our studies we may rule out none of these proposals. Qualitative experiments performed with PPN-**7** suggest that the oxygen atom of the benzoyl group is not the only nucleophilic center. As reported above, the treatment of PPN-**7** with H_2O yields considerable amounts of benzaldehyde that could be considered as the product of the decomposition either of a manganese hydroxycarbene[36] or of a hydridomanganese(III) acyl intermediate. This latter possibility, a known process in iron and nickel carbonyl chemistry, implies a localization of the negative charge at the metal center.[37] In most of the cases where the yields of (η^3-benzyl)tricarbonylmanganese complexes are high after alkylation, we observe low yields of aromatic ketones resulting from the reductive elimination step. This suggests that in some cases the competing reductive elimination might be more disfavored than the formation of the η^3 manganese complex arising from the same anionic intermediate.

Conclusion

In this paper we have reported the unprecedented synthesis of chelated (η^3-benzyl)tricarbonylmanganate complexes starting from tetracarbonylmanganese cyclometalated arylpyridines and aryllithium nucleophiles followed by alkylation. The molecular structure of complex **4a** reveals a sterically congested helical-type assembly of aromatic rings which reveals peculiar temperature dependent NMR properties. We have demonstrated that the reaction of PhLi with the starting tetracarbonylmanganese complexes generates anionic benzoylmanganates. We have shown that one of the side reactions that compete with the formation of the novel benzylic η^3 species is a reductive elimination process yielding the corresponding aromatic ketones from the anionic benzoylmanganate intermediate. We have shown, in three cases, that this reaction path could be exploited for the synthesis of extended aromatic

(34) (a) McDonald, R. N.; Jones, M. T.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1992**, *114*, 71. (b) McDonald, R. N.; Jones, M. T.; Chowdhury, A. K. *Organometallics* **1992**, *11*, 392. (c) McDonald, R. N.; Jones, M. T.; Chowdhury, A. K. *Organometallics* **1992**, *11*, 356.

(35) McDonald, R. N.; Jones, M. T.; Chowdhury, A. K. *Organometallics* **1991**, *113*, 476.

(36) Fischer, E. O.; Riedel, A. *Chem. Ber.* **1968**, *101*, 156.

(37) (a) Bates, R. W. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 12, pp 349−355. (b) Alper, H.; Fabre, J. L. *Organometallics* **1982**, *1*, 1037. (c) Corey, E. J.; Hegedus, L. S. *J. Am. Chem. Soc.* **1969**, *91*, 4926. (d) Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 4099.

ketones containing pyridyl-type moieties.[38] Several questions concerning the mechanism of the formation of the (η^3-benzyl)manganese species remain unanswered, and we intend to focus our attention on these issues in our subsequent work. We also intend to apply the novel synthetic access to aromatic ketones to other types of manganese chelates.

Experimental Section

All reactions were carried out under a dry argon atmosphere. 2-Phenylpyridine, 2-(4-tolyl)pyridine, 2-phenylquinoline, methyl and ethyl trifluoromethanesulfonate, phenyllithium, and methyllithium were purchased from Aldrich and Fluka Companies. 2-Lithionaphthalene and pentadeuteriolithiobenzene solutions were obtained from the reactions of 2-bromonaphthalene and pentadeuteriobromobenzene, respectively, with lithium metal in dry diethyl ether. Pentacarbonyl(α-η^1-benzyl)manganese was prepared following a literature procedure.[39] All reactions involving manganese complexes were always protected from exposure to oxygen even though most of the isolated compounds withstood an oxygen atmosphere for days without undergoing decomposition. Tetrahydrofuran and diethyl ether were dried over sodium benzophenone ketyl under a dry argon atmosphere and distilled prior to use. Hexane and petroleum ether were distilled over CaH_2 prior to use. Before NMR experiments were performed, deuterated solvents were filtered through a column of activated basic alumina, and sample tubes were purged with dry argon to remove oxygen. Products were separated by flash chromatography using deactivated silica gel (60 μm) under a dry atmosphere of argon gas. ^{1}H and ^{13}C NMR spectra were acquired on Bruker WR 250, AC 400, and DRX 500 equipment, and chemical shifts are reported in parts per million (δ in ppm) downfield of Me_4Si. ^{1}H NMR spectra were referenced against the residual ^{1}H impurity of the deuterated solvent (δ (ppm) 7.15 (C_6D_6); 7.24 ($CDCl_3$); 2.05 ($(CD_3)_2CO$)), and ^{13}C NMR spectra were referenced against the ^{13}C resonance of the solvent (δ 128.0 (C_6D_6); 77.1 ($CDCl_3$); 29.8, 206.0 ($(CD_3)_2CO$)). Infrared spectra (reported in cm^{-1}) were performed on a FT-IR Nicolet Magna 550 spectrometer. Kinetic measurements were done by using the method of Gladysz and co-workers.[24] The ϵl factor of the Beer−Lambert formula $A = \epsilon cl$ was calculated for complex **4a** at a frequency of 1998.3 cm^{-1}. Mass spectra and high-resolution mass determination were performed at the Analytical Center of the Chemical Institutes of the University of Bonn by using the electron impact method. Elemental analyses (reported in % mass) were performed at the Kekulé-Institut für Organische Chemie und Biochemie der Universität Bonn, Germany, and at the Faculté de Chimie de l'Université Louis Pasteur, Strasbourg, France. Complex **1**, tetracarbonyl[2-(phenyl-κC^2)pyridine-κN]manganese(I),[40] complex **9**,[41] and complexes **2** and **3** were prepared according to literature methods from the uncoordinated pyridine, benzo[*h*]quinoline, and quinoline derivatives and from pentacarbonyl(α-η^1-benzyl)manganese.

Pentadeuteriobromobenzene. This compound was prepared starting from hexadeuteriobenzene by using an adapted literature procedure.[42] Elemental anal. Calcd for C_6D_5Br : C, 44.47; H + $^1/_2$D, 3.11. Found: C, 43.45; H + $^1/_2$D, 3.05. High-resolution MS (EI) calcd for C_6D_5Br: 160.9883. Found (intensity (%)): 160.9889 (83.39). MS (EI): 82, 161 *m/e*. ^{13}C NMR (neat): δ 122.4, 126.3 (t, $J_{C-D} = 50$ Hz), 129.6 (t), 131.1 (t).

Tetracarbonyl[2-(4-methylphenyl-κC^2)pyridine-κN]manganese(I), Complex 2. Elemental anal. Calcd for $C_{16}H_{10}NO_4Mn$: C, 57.33; H, 3.01; N, 4.18. Found: C, 57.53; H, 3.02; N, 4.07. MS (EI): 169, 223, 251, 279, 335. High-resolution MS (EI) calcd for $C_{16}H_{10}NO_4Mn$: 334.9990. Found (intensity (%)): 334.9999 (2.44). IR (CH_2Cl_2) ν(CO): 2074 (w), 1989 (s), 1976 (s), 1932 (m). ^{1}H NMR (C_6D_6): δ 8.16 (d, 1H), 8.03 (s, 1H), 7.36 (d, 1H), 7.02 (d, 1H), 6.87 (d, 1H), 6.74 (t, 1H), 6.06 (t, 1H), 2.18 (s, 3H). ^{13}C NMR (C_6D_6): δ 21.7, 118.8, 121.6, 124.5, 125.5, 137.2, 140.8, 142.6, 143.8, 153.5, 166.3, 174.1, 214.0, 215.0 (2CO), 220.8.

Tetracarbonyl[2-(phenyl-κC^2)quinoline-κN]manganese-(I), Complex 3. Elemental anal. Calcd for $C_{19}H_{10}NO_4Mn$: C, 61.47; H, 2.72; N, 3.77. Found: C, 61.48; H, 2.74; N, 3.68. MS (EI): 204, 259, 200, 315, 371 *m/e*. IR (CH_2Cl_2) ν(CO): 2075 (w), 1993 (s), 1973 (s), 1930 (m) cm^{-1}. ^{1}H NMR (C_6D_6): δ 8.65 (d, 1H), 8.29 (dd, 1H), 7.46 (dd, 1H), 7.40−7.05 (m, 7H). ^{13}C NMR (C_6D_6): δ 117.3, 124.4, 126.4, 126.7, 128.1, 128.6, 130.7, 131.1, 148.4, 150.1, 169.3, 176.7, 214.5, 215.1, 221.7.

General Procedure for the Synthesis of Chelated Tricarbonyl(η^3-benzyl)manganese(I) Complexes. To a solution of the starting manganese chelate in dry diethyl ether was added an excess of a solution of aryllithium reagent at −60 °C. A slight change in color from pale yellow to reddish occurred. The resulting solution was then warmed to −30 °C, stirred and maintained during ca. 30 min between −30 and −20 °C. The brownish mixture was cooled down to −60 °C, a slight excess of alkyl triflate was added to it, and the resulting mixture was warmed slowly to room temperature. At this stage, the reaction could be considered complete only when the color of the solution turned to an intense dark red or orange. The solvent was removed under reduced pressure and the residue further dried under vacuum. The latter was redissolved in Et_2O, and deactivated silica was added to the solution. The solvent was removed *in vacuo* and the coated silica loaded on the top of a column of deactivated silica gel. A first band of the starting manganese complex was eluted (from 30% to 50% Et_2O in petroleum ether) followed by a red or orange band of the corresponding chelated tricarbonyl(η^3-benzyl)manganese (Et_2O, 100%). The solution of the latter complex was stripped of solvent and the solid recrystallized from hexane.

Tricarbonyl{2-[(1,2-η^2),κC^α-2-(phenylmethoxymethylene)phenyl]pyridine-κN}manganese(I), Complex 4a. Complex **1** (349 mg, 1.09 mmol), PhLi (1.8 M, 1.5 mL, 2.5 mmol), and MeOTf (0.4 mL, 3.62 mmol) were used to prepare complex **4a** (230 mg, 0.557 mmol). Fp: 148 °C dec. Elemental anal. Calcd for $C_{22}H_{16}NO_4Mn$: C, 63.92; H, 3.89; N, 3.38. Found: C, 63.89; H, 3.88; N, 3.27. IR (CH_2Cl_2) ν(CO): 2000 (s), 1916 (s), 1899 (s) cm^{-1}. MS (EI): 289, 244, 299, 329 (M − 3CO), 357 (M − 2CO), 385 (M − CO), 413 (M) *m/e*. High-resolution MS (EI) calcd for $C_{22}H_{16}NO_4Mn$: 413.0460. Found (intensity (%)): 413.0456 (1.62). ^{1}H NMR (C_6D_6, 298 K): δ 8.27 (d, 1H), 7.29 (t, 1H), 7.17 (m, 1H), 7.01 (m, 2H), 6.70 (m), 6.36 (t, 1H), 5.80 (d, 1H), 5.74 (t, 1H), 3.58 (s, 3H). ^{1}H NMR (C_3D_6O, 253 K): δ 8.08 (d, 1H), 8.00 (d, 1H), 7.80 (m, 3H), 7.65 (t, 2H), 7.26 (t, 1H), 7.09 (1H), 6.93 (m, 2H), 6.61 (t, 1H), 6.05 (d, 1H), 3.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 298 K): δ 57.7, 102.2, 110.4, 121.3, 123.2, 125.9, 127.4 (broad), 128.0, 129.9, 131.3, 134.8, 136.9, 140.5, 151.0, 220.2, 220.6, 232.0. ^{13}C NMR (C_3D_6O, 243 K): δ 57.3, 103.6, 109.7, 110.2, 122.8, 124.6, 126.4, 127.1, 127.6, 128.2, 128.9, 130.9, 131.9, 132.3, 134.7, 138.5, 140.7, 151.5, 157.9, 221.0, 221.2, 232.5.

Tricarbonyl{2-[(1,2-η^2),κC^α-2-(pentadeuteriophenyl)-methoxymethylene]phenyl]pyridine-κN}manganese-(I), Complex 4b. Complex **1** (263 mg, 0.82 mmol), d_5-PhLi (1 M, 1.3 mL, 1.3 mmol), MeOTf (0.22 mL, 2 mmol), and Et_2O (15 mL) were used to prepare complex **4b** (126.4 mg). Fp: 148 °C dec. Elemental anal. Calcd for $C_{22}H_{11}D_5NO_4Mn$: C, 63.16; H + $^1/_2$D, 3.86; N, 3.35. Found: C, 63.03; H + $^1/_2$D, 3.87; N, 3.14. MS (EI): 209, 249, 291, 304, 334, 362, 390, 418 *m/e*. High-resolution MS (EI) calcd for $C_{22}H_{11}D_5NO_4Mn$: 418.0768. Found (intensity (%)): 418.0772 (1.18). ^{1}H NMR (C_6D_6, 298

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K): δ 8.29 (d, 1H), 7.29 (t, 1H), 7.17 (m, 1H), 7.01 (m, 2H), 6.36 (t, 1H), 5.80 (d, 1H), 5.74 (t, 1H), 3.58 (s, 3H). ^{13}C NMR ($CDCl_3$, 298 K): δ 57.7, 102.2, 110.4, 121.3, 123.2, 125.5 (t, $J_{C-D} = 27$ Hz), 128.0, 129.9, 131.3, 134.8, 136.9, 140.5, 151.0, 220.2, 220.6, 232.0.

Tricarbonyl{2-[(1,2-η^2),κC^{α}-4-methyl-2-(phenylmethoxymethylene)phenyl]pyridine-κN}manganese(I), Complex 5a. Complex **2** (340 mg, 1.01 mmol), PhLi (1.8 M, 1.11 mL, 2 mmol), MeOTf (0.5 mL, 4.56 mmol), and Et_2O (20 mL) were used to prepare complex **5a** (199.6 mg). Fp: 145−151 °C dec. Elemental anal. Calcd for $C_{23}H_{18}NO_4Mn$: C, 64.65; H, 4.25; N, 3.28. Found: C, 64.57; H, 4.24; N, 2.98. MS (EI): 223, 258, 313, 343, 371, 399, 427 *m/e*. High-resolution MS (EI) calcd for $C_{23}H_{18}NO_4$ Mn: 427.0616. Found (intensity (%)): 427.0608 (1.68). IR (CH_2Cl_2) ν(CO): 1999 (s), 1915 (s), 1896 (s) cm^{-1}. ^{1}H NMR (C_6D_6): δ 8.29 (s, 1H), 7.31 (d, 1H), 7.26 (m, 1H), 7.13 (m, 1H), 7.02 (m, 1H), 6.83 (m, 4H), 6.50 (t, 1H), 5.95 (d, 1H), 5.88 (t, 1H), 3.78 (s, 3H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 298 K): δ 22.1, 57.7, 100.3, 110.0, 110.9, 121.1, 123.0, 125.8, 127.2 (broad), 129.9, 130.1, 133.2, 136.8, 140.7, 141.7, 150.9, 158.3, 221.0, 220.6, 232.0.

Tricarbonyl{2-[(1,2-η^2),κC^{α}-4-methyl-2-(phenylethoxymethylene)phenyl]pyridine-κN}manganese(I), Complex 5b. Complex **2** (344 mg, 1.02 mmol), PhLi (1.8 M, 1.13 mL, 2 mmol), and EtOTf (0.6 mL, 4.65 mmol), and Et_2O (20 mL) were used to prepare complex **5b** (158 mg). Fp: 149−152 °C dec. Elemental anal. Calcd for $C_{24}H_{20}NO_4Mn$: C, 65.31; H, 4.57; N, 3.17. Found: C, 65.02; H, 4.65; N, 2.91. MS (EI): 223, 258, 313, 357, 385, 413, 441 *m/e*. High-resolution MS (EI) calcd for $C_{24}H_{20}NO_4Mn$: 441.0773. Found (intensity (%)): 441.0774 (0.75). IR (CH_2Cl_2) ν(CO): 1998(s), 1916 (s), 1895 (s) cm^{-1}. ^{1}H NMR (C_6D_6): δ 8.26 (s, 1H), 7.26−6.91 (m, 4H), 6.24 (m), 6.39 (t, 1H), 5.84 (d, 1H), 5.78 (t, 1H), 4.05 (q, 1H), 3.86 (q, 1H), 2.22 (s, 3H), 1.39 (t, 3H). ^{13}C NMR (C_6D_6): δ 15.9, 21.4, 65.7, 100.6, 109.5, 111.8, 120.7, 122.7, 125.9, 129.9, 130.0, 133.9, 136.3, 141.6, 141.8, 151.0, 158.3, 221.1, 233.0.

Tricarbonyl{2-[(1,2-η^2),κC^{α}-2-(phenylmethoxymethylene)phenyl]quinoline-κN}manganese(I), Complex 6a. Complex **3** (371 mg, 1 mmol), PhLi (1.8 M, 1.1 mL, 2 mmol), MeOTf (0.5 mL, 4.56 mmol), and Et_2O (20 mL) were used to prepare complex **6a** (103.7 mg). Fp: 190 °C. Elemental anal. Calcd for $C_{26}H_{18}NO_4Mn$: C, 67.39; H, 3.92; N, 3.02. Found: C, 67.12; H, 3.90; N, 2.82. MS (EI): 217, 259, 294, 324, 349, 379, 407, 435, 463 *m/e*. High-resolution MS (EI) calcd for $C_{26}H_{18}NO_4Mn$: 463.0616. Found (intensity (%)): 463.0616 (1.59). IR (CH_2Cl_2) ν(CO): 2000 (s), 1919 (s), 1895 (s) cm^{-1}. ^{1}H NMR (C_6D_6): δ 8.22 (m, 2H), 7.38 (t, 1H), 7.25 (d, 1H), 7.15−6.75 (m, 5H), 6.31 (m, 5H, broad $C_{benzyl}-Ph$), 6.08 (d, 1H), 3.58 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 57.7, 94.4, 109.0, 110.9, 119.6, 124.4, 125.4, 126.4 (broad), 126.9, 127.2, 127.3, 128.4, 131.1, 131.3, 131.7, 133.0, 138.3, 139.7, 146.2, 158.8, 220.0, 221.2, 232.0.

Tricarbonyl{2-[(1,2-η^2),κC^{α}-2-[(pentadeuteriophenyl)-methoxymethylene]phenyl]quinoline-κN}manganese-(I), Complex 6b. Complex **3** (382 mg, 1.03 mmol), d_5-PhLi (1 M, 2 mL, 2 mmol), MeOTf (0.22 mL, 2 mmol), and Et_2O (15 mL) were used to prepare complex **6b** (97.9 mg). Fp: 190 °C. MS (EI): 259, 299, 354, 304, 412, 468 *m/e*. High-resolution MS (EI) calcd for $C_{26}H_{13}D_5NO_4Mn$: 468.0925. Found (intensity (%)): 468.0926 (1.29). ^{1}H NMR (C_6D_6): δ 8.22 (m, 2H), 7.38 (t, 1H), 7.25 (d, 1H), 7.15−6.75 (m, 5H), 6.08 (d, 1H), 3.58 (s, 3H).

Tricarbonyl{2-[(1,2-η^2),κC^{α}-2-(β-naphthylmethoxymethylene)phenyl]quinoline-κN}manganese(I), Complex 6c. Complex **3** (398 mg, 1.07 mmol), 2-lithionaphthalene (0.48 M, 4.45 mL, 2.14 mmol), MeOTf (0.5 mL, 4.56 mmol), and Et_2O (20 mL) were used to prepare complex **6c** (308.8 mg). Fp: 168 °C. Elemental anal. Calcd for $C_{30}H_{22}NO_4Mn$: C, 70.18; H, 3.93; N, 2.73. Found: C, 70.71; H, 4.09; N, 2.49. MS (EI): 259, 344, 399, 429, 457, 469, 513 *m/e*. High-resolution MS (EI) calcd for $C_{30}H_{20}NO_4Mn$: 513.0773. Found (intensity (%)): 513.0782 (0.36). IR (CH_2Cl_2) ν(CO): 2001 (s), 1919 (s), 1897 (s) cm^{-1}. ^{1}H NMR (C_6D_6, 298 K): δ 8.60 (m, broad), 8.19 (m, broad), 7.39 (t, 1H), 7.26 (d, 1H), 7.08−6.84 (m, 5H), 6.73 (d, 1H), 6.61 (t, 1H), 6.48 (d, 1H), 6.12 (m, broad), 3.58 (s, 3H). ^{1}H NMR (C_3D_6O, 253 K): δ 8.20 (d, 1H), 8.04−8.01 (m, 3H), 7.89 (t, 1H), 7.83 (d, 1H), 7.71 (t, 1H), 7.67 (t, 1H), 7.35 (m, 5H), 7.21 (m, 2H), 7.15 (t, 1H), 6.42 (s, 1H), 3.48 (s, 3H). ^{13}C NMR ($CDCl_3$, 298 K): δ 58.3 (broad), 119.5, 124.1, 124.7, 125.4, 126.4, 127.1 (broad), 127.9, 129.7 (broad), 130.9, 131.4, 131.5, 131.8, 132.8, 136.9, 138.3, 146.1, 158.7, 221.1, 232.0.

X-ray Determination and Processing for 4a. Crystal data and details of data collection for **4a** are given in Table 2. Data for **4a** were collected in the $\omega/2\theta$ flying step-scan mode using Cu Kα graphite-monochromated radiation ($\lambda = 1.5418$ Å) on a red crystal of dimensions $0.15 \times 0.20 \times 0.35$ mm^3 with a Philips PW1100/16 automatic diffractometer at room temperature. Three standard reflections measured every 1 h during the entire data collection period showed no significant trend. The raw data were converted to intensities and corrected for Lorentz polarization and absorption factors. The structure was solved by the heavy atom method. After refinement of the non-hydrogen atoms, Fourier difference maps revealed maxima of residual electron density close to positions expected for hydrogen atoms. Hydrogen atoms were refined at calculated positions with a riding model in which the C−H vector was fixed at 0.95 Å with isotropic temperature factors such as $B(H) = 1.3B_{eqv}(C)$ Å^2. A final Fourier difference map revealed no significant maxima. All calculations were performed on a DEC Alpha 3000 computer using the Nonius OpenMoleN package.[43] Neutral atom scattering factor coefficients and anomalous dispersion coefficients were taken from a standard source.[44]

IR Monitoring of the Reaction of PhLi with 1, Followed by Alkylation with MeOTf. To a solution of complex **1** (200 mg, 0.623 mmol, 0.031 M) in THF (20 mL) was added a solution of PhLi in a 30:70 diethyl ether−cyclohexane mixture (2 equiv, 1.246 mmol, 0.7 mL, 1.8 M) at 253 K. The solution was immediately monitored by IR spectroscopy. The solution was stirred for 30 min and a slight excess of MeOTf (0.136 mL, 1.240 mmol) was added. The plot of the concentration in **4a** versus time was obtained from the CO vibration band at 1998.3 cm^{-1}.

^{13}C NMR Study of the Intermediate. To a solution of complex **1** in Et_2O was added a solution of PhLi at −60 °C. The solution was warmed to −30 °C and kept at this temperature for 30 min. At this stage the solvent was removed *in vacuo* and the resulting residue washed with dry hexane and redissolved in a commercial sample of d_8-THF. At this stage unavoidable decomposition of a part of the solution prevented us from acquiring resolved ^{1}H NMR spectra. The solution was kept at 213 K and introduced in the probe at 243 K. Measurements allowed the detection of benzaldehyde main signals at 195.5, 135.3, 128.7, and 126.9 ppm. Other signals were attributed to the benzoylmanganate intermediate Li-**7**: δ 313.3 (CO−Ph), 230.3 (CO), 223.3 (CO), 222.9 (CO), 166.1, 157.5, 153.4, 145.8, 141.3, 140.1, 129.2, 127.7, 127.3, 125.3, 122.7, 121.9, 120.4, 117.9.

Metathesis Reaction of Li-7 and PPN$^+$Cl$^-$. Complex **1** was reacted with 1 equiv of PhLi in dry Et_2O at −60 °C. The temperature of the cooling bath was raised slowly to −30 °C and the solvent removed under reduced pressure. The residue was washed with hexane, and solid PPN$^+$Cl$^-$ was added. The solid mixture containing Li-**7** was dissolved in dichloromethane at −30 °C and stirred for a while. After filtration of the crimson solution over Celite and evaporation of the solvent under vacuum, PPN-**7** was isolated as a dark red compound, insoluble in diethyl ether.

Addition of MeLi to 2. Trapping of "[Mn(CO)$_3$]$^-$". A

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solution of **2** (405.2 mg, 1.22 mmol) in Et_2O (15 mL) was treated with MeLi (1.6 M, 0.76 mL, 1.21 mmol) at −78 °C and the resulting mixture warmed to −30 °C. The solution was stirred at the same temperature for 20 min and injected *via* a syringe into a solution containing triphenylphosphine (641 mg, 2.44 mmol) and trimethylstannyl chloride (244 mg, 1.23 mmol) in Et_2O (10 mL) at −30 °C. The resulting mixture was allowed to warm slowly to room temperature. After 2 h of reaction at room temperature an abundant precipitate formed, which was filtered off and purified further by chromatography on silica gel (eluent: CH_2Cl_2). The filtrate was analyzed by the GC−MS technique to contain ketone **8a**. The yellow flaky solid isolated after chromatographic purification was identified as being a mixture of the *mer* and *fac* stereoisomers of $(PPh_3)_2(CO)_3MnSnMe_3$ (920 mg, 1.11 mmol, 91% yield). ^{1}H NMR indicates two singlets at 0.23 and 0.53 ppm, a broad multiplet centered at 6.97 ppm, a signal at 7.38 ppm, and a triplet at 7.85 ppm. The ^{13}C NMR spectrum displays two peaks at −3.42 and −2.97 ppm and a series of peaks at 128.4, 129.8, 129.9, 133.4 (multiplet), 134.2, 136.6 (triplet), 137.7, and 138.4 ppm and relatively weak signals at 224.8, 226.5, 226.9, and 227.1 ppm assigned as the signals of the carbonyl ligands of the two species. IR (CH_2Cl_2) ν(CO): 1981 (s), 1908 (s), 1895 (s).

Addition of PhLi to 2. Trapping of "$[Mn(CO)_3]^-$". A similar procedure was used for the experiment with PhLi: complex **2** (518 mg, 1.56 mmol) in 15 mL of Et_2O, PhLi (1.8 M, 0.95 mL, 1.7 mmol); Me_3SnCl (342 mg, 1.71 mmol), PPh_3 (820 mg, 3.12 mmol) in 15 mL of Et_2O. *mer*- and *fac*-$(PPh_3)_2(CO)_3MnSnMe_3$: 340 mg, 0.41 mmol, 26% yield.

General Procedure for the Synthesis of Functionalized Aromatic Ketones. To a solution of the starting complex in dry Et_2O was added 1 equiv of PhLi at −60 °C. The temperature was slowly raised to 20 °C during 2 or 3 h. The color of the mixture changed from bright yellow to deep orange-brown. The reaction mixture was stirred for approximately 1 h at room temperature, the vessel opened to air, and ca. 0.5 mL of water added. The brownish suspension that formed rapidly was filtered through a plug of Celite and the filtrate dried over Na_2SO_4 and stripped of solvents. The crude residue was then separated by silica gel chromatography. A strong band corresponding to the organometallic substrate was eluted with a CH_2Cl_2−hexane (30:70) mixture. The organic products, e.g., the aromatic ketones, were eluted with pure CH_2Cl_2, and the eluate was stripped of solvent. The resulting oil was recrystallized from a hexane−CH_2Cl_2 mixture and the purity of the solid compound checked by GC−MS.

2-Pyridin-6-ylbenzophenone, 10. Compound **1** (424 mg, 1.31 mmol), PhLi (1.8 M, 0.73 mL, 1.30 mmol), and Et_2O (20 mL) were used to prepare compound **10** (136 mg, 40% yield). Fp: 109 °C. Elemental anal. Calcd for $C_{22}H_{15}NO$: C, 83.37; H, 5.05; N, 5.40. Found: C, 83.37; H, 5.10; N, 5.38. IR (CH_2Cl_2) ν(ArCOAr′): 1668.2. MS (EI): 259.0 (M^+), 230.1, 182.0, 154.0, 127.0, 105.0, 77.0 *m/e*. High-resolution MS (EI) calcd for $C_{18}H_{13}NO$: 259.0997. Found (intensity (%)): 259.0998 (11.41). ^{1}H NMR ($CDCl_3$): δ 8.38 (d, 1H), 7.80 (d, 1H), 7.70 (dd, 2H), 7.63 (t, 1H), 7.57 (m, 4H), 7.40 (t, 1H), 7.29 (t, 2H), 7.02 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 121.9, 122.7, 128.1, 128.5, 128.8, 129.1, 129.5, 130.3, 132.4, 136.3, 137.9, 139.5, 139.7, 149.1, 156.8, 198.3.

2-Quinolin-6-ylbenzophenone, 11. Compound **3** (371 mg, 1 mmol), PhLi (1.8 M, 0.55 mL, 1 mmol), and Et_2O (15 mL) were used to prepare compound **11** (230 mg, 74% yield). Fp: 119−120 °C. IR (neat) ν(ArCOAr′): 1666.2. MS (EI): 311 (M^+), 288, 232, 204 *m/e*. High-resolution MS (EI) calcd for $C_{22}H_{16}NO$: 310.1232. Found (intensity (%)): 310.1235 (5.72). Elemental anal. Calcd for $C_{22}H_{16}NO$: C, 85.41; H, 4.89; N, 4.53. Found: C, 85.21; H, 4.95; N, 4.62. ^{1}H NMR ($CDCl_3$): δ 8.04 (d, 1H), 7.91 (d, 1H), 7.72−7.61 (m, 5H), 7.62 (t, 1H), 7.54 (m, 3H), 7.40 (t, 1H), 7.28 (t, 1H), 7.19 (t, 2H). ^{13}C NMR ($CDCl_3$): δ 119.9, 126.5, 127.3, 128.0, 128.8, 128.9, 129.0, 129.1, 129.2, 129.7, 130.2, 132.2, 136.7, 138.3, 139.5, 140.4, 147.4, 156.2, 198.4.

10-Benzo[*h*]quinolin-6-ylbenzophenone, 12. Compound **9** (500 mg, 1.35 mmol), PhLi (1.8 M, 0.8 mL, 1.44 mmol), and Et_2O (20 mL) were used to prepare compound **12** (160 mg, 41%). Fp: 148 °C. Elemental anal. Calcd for $C_{20}H_{13}NO$: C, 84.78; H, 4.62; N, 4.94. Found: C, 84.58; H, 4.68; N, 5.01. IR (CH_2Cl_2) ν(ArCOAr′): 1670.4. MS (EI): 283.1 (M^+), 254.1, 206.1, 178.1. High-resolution MS (EI) calcd for $C_{20}H_{13}NO$: 283.0997. Found (intensity (%)): 283.1002 (40.35). ^{1}H NMR ($CDCl_3$): δ 8.48 (dd, 1H), 8.07 (dd, 1H), 8.03 (dd, 1H), 7.88 (d, 1H), 7.75 (m, 4H), 7.61 (dd, 1H), 7.40 (t, 1H), 7.30 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 121.7, 126.2, 126.4, 127.0, 127.8, 127.9, 128.3, 128.8, 129.0, 129.2, 131.8, 133.9, 135.4, 139.0, 139.3, 144.7, 147.2, 198.7.

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Supporting Information Available: Listings of atomic coordinates and isotropic displacement parameters, H atom coordinates and isotropic displacement parameters, anisotropic displacement parameters (U values), and bond distances and angles for **4a** and IR spectra of **1** (7 pages). Ordering information is given on any current masthead page.

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