Effects of Ortho-Substituents in the Synthesis and Stability of Cyclomanganated Benzylamine Derivatives. X-ray Crystal Structure of $Mn\{C_6H_2(OCH_3)_2$-4,6-CH_2NMe_2-2$\}(CO)_4$†

Michel Pfeffer* and Esteban P. Urriolabeitia

Laboratoire de Synthèses Métallo-Induites (URA 416 du CNRS), Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex, France

Jean Fischer

Laboratoire de Cristallochimie (URA 424 du CNRS), Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex, France

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The reaction of $PhCH_2Mn(CO)_5$ with several tertiary amines such as 8-methylquinoline, *N,N*-dimethyl-1-naphthylamine, or mono- and disubstituted *N,N*-dimethylbenzylamine derivatives, in refluxing *n*-hexane, affords the corresponding neutral C,N-cyclometalated Mn(I) compounds of stoichiometry Mn(C-N)$(CO)_4$, **1**−**8** (C-N = cyclometalated ligand), in good yields. These new compounds have been characterized by their IR and ^1H and $^{13}C\{^1H\}$ NMR spectra. The crystal structure of $Mn(C_6H_2(OCH_3)_2$-4,6-CH_2NMe_2-2$)(CO)_4$, **4** (monoclinic, $P2_1/n$; $a = 13.644$ (4) Å, $b = 9.153$ (3) Å, $c = 14.432$ (4) Å, $\beta = 115.57$ (2)°, $Z = 4$), shows the *N,N*-dimethylbenzylamine derivative to be coordinated as a chelating ligand and that the distance between the oxygen atom of the ortho OMe group and the carbon atom of one carbonyl group is shorter than the sum of their van der Waals radii. The orientation in the cyclometalation of benzylamine derivatives, when two possibilities exist, tends to avoid the steric interaction between the R groups ortho to the Mn−C bond and a CO unit. However, when this R group is OMe, the latter compound isomerizes so that the interaction between the O atom of the methoxy unit and the C atom of the CO can take place.

Introduction

The chemistry of organometallic compounds containing cyclometalated ligands is an area that is still interesting for many research groups throughout the world.[1] This is partly due to the fact that they have already been shown to be useful starting materials for organic synthesis.[2] Important progress was recently made in this direction, and it was shown that, besides palladium, several other metals have useful applications. Recently it was shown that cyclomanganated compounds[3] derived from aromatic ketones could lead to carbocyclization reactions in the presence of internal alkynes.[4] This has prompted several research projects toward related organomanganese compounds containing C,O- or C,P-coordinated ligands.[5] We recently showed that cyclometalated dimethylbenzylamine derivatives of palladium[2b,c] or ruthenium[6] lead to the synthesis of heterocycles when reacted with alkynes. As a continuation of this project, we have been interested in investigating whether cyclomanganated compounds derived from the same N-containing ligands might display similar behavior. Hence a prerequisite was to synthesize the required starting materials.

In spite of the extensive development in the synthesis of C,N-cyclometalated azobenzenes or other N-containing ligands with manganese,[7] little attention has been directed toward the synthesis of compounds containing C,N-coordinated *N,N*-dimethylbenzylamine ligands and, with the exception of Mn-

† This paper is dedicated to Prof. E. Lindner in honor of his 60th birthday.

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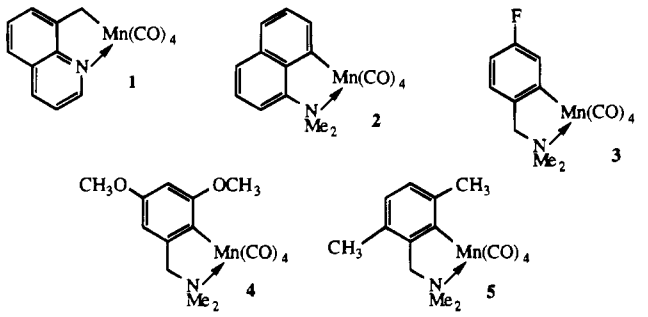
Chart 1



$(C_6H_4CH_2NMe_2\text{-}2)(CO)_4$,[7i,l] no other complexes containing *N,N*-dimethylbenzylamine have hitherto been reported.

Herein we present our results on the synthesis of a series of cyclomanganated compounds derived from N-ligands such as 8-methylquinoline, *N,N*-dimethyl-1-naphthylamine and *N,N*-dimethylbenzylamine derivatives.

Results

Among all the possible precursors for the cyclomanganation reaction, $PhCH_2Mn(CO)_5$ has proven to be the most efficient starting material in numerous reactions.[8] For this reason and due to its ready large-scale accessibility, we have found it to be an ideal precursor for our reaction.

Reactions with Tertiary Amines Containing One Potential Cyclometalation Site. The starting complex $PhCH_2Mn(CO)_5$ reacts in refluxing *n*-hexane with 8-methylquinoline or *N,N*-dimethyl-1-naphthylamine to give the corresponding neutral tetracarbonyl derivatives of stoichiometry $Mn(CH_2C_9H_6N)(CO)_4$, **1**, and $Mn(C_{10}H_6NMe_2)(CO)_4$, **2**, in good yields.

The reaction between $PhCH_2Mn(CO)_5$ and $4\text{-}FC_6H_4CH_2NMe_2$ is straightforward, leading to a yellow solid identified as $Mn(C_6H_3F\text{-}5\text{-}CH_2NMe_2\text{-}2)(CO)_4$, **3**. The reaction between $3,5\text{-}(MeO)_2C_6H_3CH_2NMe_2$ and $PhCH_2Mn(CO)_5$ gives the metallacycle $Mn(C_6H_2(MeO)_2\text{-}4,6\text{-}CH_2NMe_2\text{-}2)(CO)_4$, **4**. In both cases, the expected product results from the C−H activation at position 2. It is interesting to note that the presence of electron-withdrawing (F) or electron-donating (OMe) substituents does not have any significant effect upon the course of this reaction.

Both products can be obtained in similar yields under similar experimental conditions.

Reactions with Tertiary Amines Displaying Two Potential Cyclometalation Sites. In an attempt to examine a possible competition between activation of the C(aryl)−H bond and the C(alkyl)−H bond, we studied the reaction between $PhCH_2Mn(CO)_5$ and $2,5\text{-}Me_2C_6H_3CH_2NMe_2$. After the usual workup, the complex $Mn(C_6H_2Me_2\text{-}3,6\text{-}CH_2NMe_2\text{-}2)(CO)_4$, **5**, was isolated, showing that the C(aryl)−H bond alone has been activated. This result is in agreement with the general observations that the activation of a C(aryl)−H bond occurs more readily than that of a C(alkyl)−H bond, if both groups are present.[9] Furthermore this illustrates the higher relative stability of five-membered metallacycles.

At this point, we were interested in investigating the orientating effect of different substituents at the phenyl ring toward the ortho-metalation reaction. We therefore studied the metallation of other substituted *N,N*-dimethylbenzylamines such as $3,4\text{-}(OCH_2O)C_6H_3CH_2NMe_2$, $3,4\text{-}Me_2C_6H_3CH_2NMe_2$, and $3,4\text{-}(MeO)_2C_6H_3CH_2NMe_2$.

(8) Bennett, R. L.; Bruce, M. I.; Stone, F. G. A. *J. Organomet. Chem.* **1975**, *94*, 65.

(9) Note however that, rings being different, strict comparison is far from being straightforward.

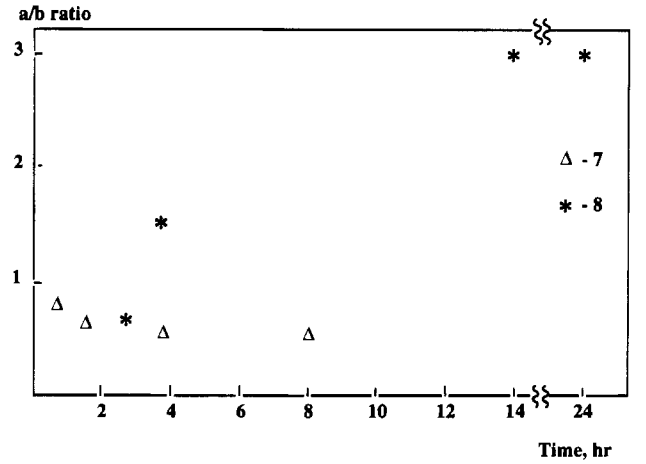
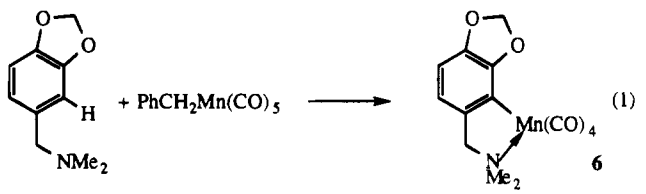


Figure 1. Plots of ratios of isomers of types **a** and **b** for compounds **7** and **8** versus reaction time.

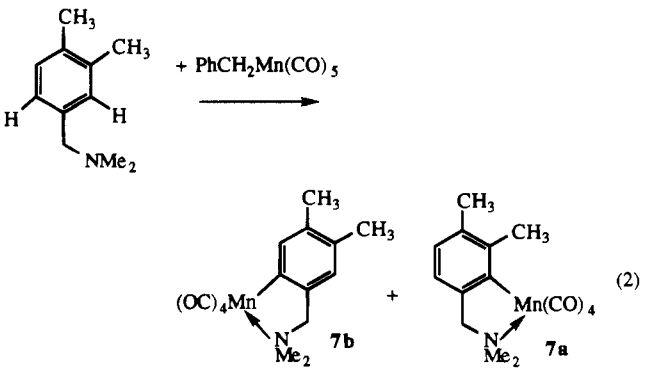
The reaction between $BzMn(CO)_5$ and $3,4\text{-}(OCH_2O)C_6H_3\text{-}CH_2NMe_2$ gives a deep yellow solid characterized as $Mn(C_6H_2(OCH_2O)\text{-}2,3\text{-}CH_2NMe_2\text{-}6)(CO)_4$, **6**. The structure depicted in eq 1 is in agreement with the experimental data,



(1)

indicating that exclusively the 2-position (i.e. between the $-CH_2NMe_2$ and the O_2CH_2 groups in the starting ligand) has been metalated. In order to detect whether other products or intermediates were produced, we examined the reaction products at earlier conversion times. When the reaction was stopped after 3 h reflux, only a mixture of **6** and $BzMn(CO)_5$ was found. Therefore, **6** is the only reaction product.

As in the preceding case, during the reaction between $PhCH_2Mn(CO)_5$ and $3,4\text{-}Me_2C_6H_3CH_2NMe_2$ two positions (2 and 6) are susceptible to C−H activation. When the reaction is carried out for 8 h in refluxing *n*-hexane, it is possible to isolate (after chromatographic purification; see Experimental Section) a yellow solid identified as a mixture of $Mn(C_6H_2\text{-}Me_2\text{-}2,3\text{-}CH_2NMe_2\text{-}6)(CO)_4$, **7a**, and $Mn(C_6H_2Me_2\text{-}4,5\text{-}CH_2NMe_2\text{-}2)(CO)_4$, **7b**. The net yield is 88%, and the relative **7a/7b** ratio is 1/2.

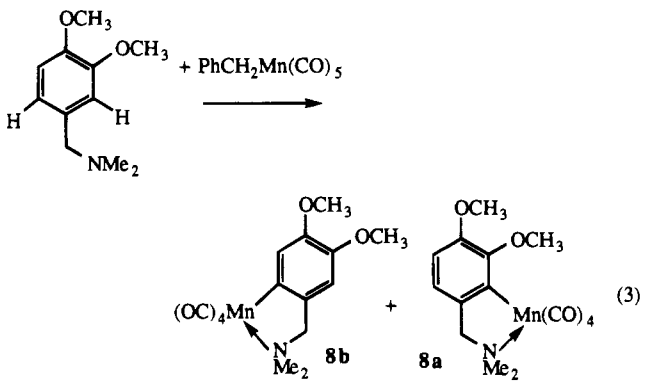


(2)

The same mixture of isomers is found when the reaction is stopped after 3.5 h in refluxing *n*-hexane (76% net yield); at shorter reaction times the conversion was not completed, and slightly different ratios of **7a/7b** were observed (see Figure 1).

Attempts to separate both products by chromatographic methods failed; however, by fractional crystallization in *n*-hexane, **7b** can be obtained in pure form (based on ^{1}H NMR), whereas **7a** is always contaminated with **7b** (a **7a/7b** ratio of 4/1 could be obtained; see Experimental Section). When both fractions were heated separately in C_6D_6 during 3 h at the nominal temperature (80 °C), some decomposition was evident (a brown precipitate appears). The ^{1}H NMR of the filtered solutions showed that no **7a** was present in the sample of pure **7b**, whereas for the enriched sample in **7a** the same **7a/7b** ratio was found. We can thus conclude that the formation of the products **7a** and **7b** is irreversible since this latter experiment shows that there is no interconversion between **7a** and **7b**.

The reaction between $PhCH_2Mn(CO)_5$ and 3,4-$(MeO)_2C_6H_3$-CH_2NMe_2 gives also more than one product. In refluxing *n*-hexane for 14 h, after chromatographic purification, a yellow solid of stoichiometry $Mn(C_6H_2(MeO)_2CH_2NMe_2)(CO)_4$, **8**, was obtained (69% net yield). The ^{1}H NMR of this solid shows a mixture of two products: one derived from the C−H activation at the 2-position (ortho to a 3-methoxy group and to the $-CH_2NMe_2$ group), **8a**, and the other one derived from the C−H activation at the 6-position (para to the 3-methoxy group and ortho to the $-CH_2NMe_2$ group), **8b**. The relative proportion of



(3)

each product **8a/8b** is 3/1. No other products were detected. No modification of this ratio was found when the reaction time was prolonged up to 24 h (70% net yield). Moreover, the observation of a constant overall yield (around 70%) shows that there is no decomposition.

When the reaction was stopped after shorter reaction times, we found mixtures with different proportions of each product (see Experimental Section). The results are also summarized in Figure 1.

These observations suggest that compound **8b** is a real *kinetic* isomer, as demonstrated by its presence in larger amounts than those of **8a** in syntheses performed with short reaction times. **8b** undergoes an isomerization process to give compound **8a**, which should thus be considered as the most thermodynamically stable isomer.

Compounds **8a** and **8b**, which were isolated in pure form (see Experimental Section), were refluxed separately in *n*-hexane for ca. 3 h. After removal of the solvent and without further chromatographic purification, the ^{1}H NMR spectra of the respective crude residues were recorded, showing in both cases the presence of a mixture of three products: **8a**, **8b**, and the free amine, in marked contrast to what we observed for **7a/7b**. The relative amount of each material was different, depending on the starting product. Thus for **8a** we found small quantities of both **8b** and free amine (9% and 4%, respectively); when **8b** was treated similarly, a more important quantity of **8a** was present (23%), together with larger amounts of the free amine (*ca.* 10%). From these data it is clear that the synthesis of compounds **8** leads to an equilibrium mixture between **8a** and **8b**. The ratio **8a/8b** changes with time because of the isomerization of **8b** to **8a** and not because of the decomposition of **8b**, as shown by the fact that the net yield of the reaction does not change with time.

Table 1. IR Data (ν, cm^{-1}; *n*-Hexane Solution) in the Carbonyl Region for Complexes **1**−**8b**

compd	ν(C≡O)				
1	2066	1979	1967		1925
2	2070	1982	1976		1940
3	2072	1980		$\Delta\nu = 0$	1946
4	2069	1983	1972	$\Delta\nu = 11$	1940
5	2065	1975	1971	$\Delta\nu = 4$	1937
6	2074	1988	1973	$\Delta\nu = 15$	1947
7	2067	1977	1972	$\Delta\nu = 5$	1939
8a	2070	1986	1972	$\Delta\nu = 14$	1942
8b	2068	1978	1973	$\Delta\nu = 5$	1939
$Mn(dmba)(CO)_4$	2069	1980	1975	$\Delta\nu = 5$	1941

Earlier examples of preference for isomers similar to **8a**, i.e., with $Mn(CO)_4$ adjacent to −OMe or −F, have been found in cyclomanganation of 3-substituted acetophenones.[4a,5a] Another report on cyclomanganation of acetophenones substituted at the 3- and 4-positions by 2-OMe groups[5c] seems to contradict our result. It was found in this latter case that the preferred isomer is the one having Mn at the least hindered position of the aryl ring. The authors, however, made this observation after a reaction time of 1.5 h in refluxing heptane. It would be very interesting to probe whether the compound obtained by Cooney et al.[5c] is stable in *n*-hexane at reflux temperature over the same period we have used (up to 8 h), in other words to check whether this compound is indeed the thermodynamic rather than the kinetic isomer of the reaction.

IR Spectra of Complexes 1−8b. The IR spectra of the complexes **1**−**8b** in *n*-hexane solution show the presence of four absorptions (see Table 1), as is expected for a cis configuration $ML_1L_2(CO)_4$,[10] except for complex **3**, in which only three absorptions were observed, the central one being very broad and showing a degeneracy for two of the four expected absorptions. These four absorptions correspond to the active normal modes $2a_1 + b_1 + b_2$, but the attribution of these normal modes is relatively uncertain: $a_1(1) > b_1$ and $a_1(2) > b_2$. However, whether or not $a_1(2)$ is greater or smaller than b_1 cannot be predicted, and examples of both orders are known.

The IR spectra of **4**, **6**, and **8a** show a remarkable splitting of the two central absorptions ($\Delta\nu$ = 11−15 cm^{-1}; see Table 1) which is not observed for other similar tetracarbonyl compounds in which either no substituents are present in the position ortho to the Mn−C bond or these substituents do not have an oxygen atom ($\Delta\nu$ = 5 or 6 cm^{-1}; Table 1). This splitting is such that one absorption is shifted to the higher energies, corresponding to a strengthening of the C≡O bond. As will be seen later, a real spatial interaction occurs between the oxygen atom of the ortho methoxy group and the carbon atom of the cis CO group (see the discussion of the X-ray structure of **4**), and this interaction may be electrostatic in nature[11] (the dipole C≡O has a certain $\delta+$ charge located in the carbon atom, and for the −OMe group the $\delta-$ charge resides on the oxygen atom). Such an electrostatic interaction should decrease the positive charge on the carbon atom. This in turn should raise the LUMO orbital of the CO unit involved.[12] As a result, the $d\pi \rightarrow p\pi^*$ backbonding from Mn to CO is less favorable and a strengthening of the C≡O bond is expected.

(10) Adams, D. M. In *Metal-Ligand and Related Vibrations*; Edward Arnold: London, 1967; pp 99−102.
(11) Darensbourg, D. J.; Wiegreffe, H. P. *Inorg. Chem.* **1990**, *29*, 592.

The observation of the $a_1(2)$ mode shifted by more than 10 cm^{-1} (the effect on the b_2 absorption is less clear) confirms these assumptions. Note that the assignment we have made for these three complexes, $a_1(1) > a_1(2) > b_1 > b_2$, follows the same order as that found by Cotton and Kraihanzel for W complexes.[13]

NMR Spectra of Compounds 1−8b. The ^1H NMR spectra of these compounds confirm the proposed structures. Thus, for compounds **1** and **2** we found the presence of six resonances in the low-field region corresponding to the six different arene protons. In the high-field region a singlet centered at 2.92 ppm ($-CH_2-Mn$) or 3.33 ppm (Me_2N-Mn) can be found for compound **1** or **2**, respectively, showing the equivalence of both H atoms of the CH_2 group or both Me groups of the NMe_2 unit; the last fact indicates the presence of a symmetry plane which contains the C-N ligand and the two equatorial carbonyl groups, in agreement with the proposed structure.

The ^1H NMR of **3** shows, in the low-field region, the presence of three sets of signals, of relative intensity 1/1/1, which appear as multiplets due to their coupling with the ^{19}F atom. In addition, we found two singlet resonances for the CH_2N group and for the NMe_2 group, respectively, showing, as in the case of complexes **1** and **2**, the presence of a symmetry plane which renders both H atoms of the CH_2N group and both Me groups of the NMe_2 unit equivalent. The latter observation is general for all the complexes **3**−**8b**. On the other hand, the ^{19}F NMR spectrum of **3** shows the presence of a triplet of doublets, centered at 117.75 ppm, due to its coupling with the H atoms H_4, H_6, and H_3. The coupling constants found in this spectrum are in good agreement with those found in its ^1H NMR spectrum.

For complexes **4**−**8b**, the ^1H NMR spectrum is also informative and permits the unambiguous assignment of the given structures for these products: in fact, only an AB spin system is observed in the 8.00−6.00 ppm region for complexes **4**, **5**, **6**, **7b**, and **8a** and two separated and well-defined singlet resonances of relative intensity 1/1 in the same region (8.00−6.00 ppm) were observed for compounds **7a** and **8b**.

The $^{13}C\{^1H\}$ NMR spectra of these complexes show the expected resonances for all the carbon atoms present in the molecule, except in the carbonyl region, where only a weak peak is observed. However, samples of compounds **1** and **8b** enriched with ^{13}CO show, as expected, three resonances corresponding to the two chemically inequivalent CO equatorial groups and the two chemically equivalent CO groups in the axial positions (see Experimental Section). One of these resonances is much more intense than the other two, showing a greater exchange of carbonyl ligands and is attributed to the more labile CO axial groups.[5f,14]

In order to obtain further information about the maverick behavior of the compounds having a methoxy substituent ortho to the Mn−C(ipso) bond, we determined the molecular structure of compound **4**.

Crystal and Molecular Structure of $Mn(C_6H_2(MeO)_2$-4,6-CH_2NMe_2-2)$(CO)_4$, 4. Suitable crystals of **4** were grown from saturated *n*-hexane solutions kept at −18 °C. The molecular structure involves the packing of four discrete monomeric molecules in the unit cell. An ORTEP drawing of **4**, along with the adopted numbering scheme, is shown in Figure 2. Selected bond distances and angles are given in Table 3. The manganese atom is coordinated in a distorted octahedral configuration to four terminal carbonyl groups and to the chelating ligand. The structure shows that the dimensions and conformation of this molecule are similar to those found in the complex $Mn(C_6H_4CH_2NMe_2$-2)$(CO)_4$ (abbreviated hereafter as Mn(dmba)$(CO)_4$).[7l] The more important differences arise from the presence of a methoxy group ortho to the metal−C(ipso) bond. Table 4 gives a comparison of metal−ligand distances and angles. From these data it appears that a slight steric interaction between the ortho methoxy group and the cis carbonyl unit takes place in complex **4**. This assumption is clearly reflected in the interatomic distance between O(1) and C(13), the found distance (2.73 Å) being notably smaller than the sum of their van der Waals radii (3.15 Å)[15] and indicating that the ortho methoxy substituent is in interaction with the Mn-

Table 2. Positional Parameters and Esd's[a]

atom	*x*	*y*	*z*	*B*, Å²
Mn	0.62537(3)	0.02723(6)	0.81036(3)	2.34(1)
C(1)	0.4574(2)	0.0154(3)	0.7373(2)	2.37(7)
C(2)	0.3908(2)	−0.0905(4)	0.6695(2)	2.47(7)
C(3)	0.2792(2)	−0.0795(4)	0.6255(2)	2.40(7)
C(4)	0.2303(2)	0.0420(4)	0.6475(2)	2.65(8)
C(5)	0.2928(2)	0.1500(4)	0.7118(2)	2.63(8)
C(6)	0.4056(2)	0.1344(3)	0.7555(2)	2.45(7)
O(1)	0.4440(2)	−0.2057(2)	0.6504(2)	3.05(5)
C(7)	0.3823(2)	−0.3096(4)	0.5764(2)	3.72(9)
O(2)	0.1184(2)	0.0426(2)	0.5971(2)	3.18(6)
C(8)	0.0646(2)	0.1602(4)	0.6196(3)	3.72(9)
C(9)	0.4781(2)	0.2482(4)	0.8256(2)	3.21(8)
N	0.5823(2)	0.2519(3)	0.8152(2)	2.72(6)
C(10)	0.6635(3)	0.3369(4)	0.9018(3)	3.92(9)
C(11)	0.5631(3)	0.3325(4)	0.7196(3)	4.03(9)
C(12)	0.6132(2)	0.0367(4)	0.6781(2)	2.92(8)
O(3)	0.6035(2)	0.0322(3)	0.5954(2)	4.54(7)
C(13)	0.6490(2)	−0.1640(4)	0.8070(2)	2.72(8)
O(4)	0.6688(2)	−0.2876(3)	0.8100(2)	4.15(6)
C(14)	0.7703(2)	0.0653(4)	0.8731(2)	2.86(8)
O(5)	0.8625(2)	0.0856(3)	0.9140(2)	4.02(6)
C(15)	0.6160(2)	−0.0089(4)	0.9310(2)	2.77(8)
O(6)	0.6121(2)	−0.0442(3)	1.0058(2)	4.28(6)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

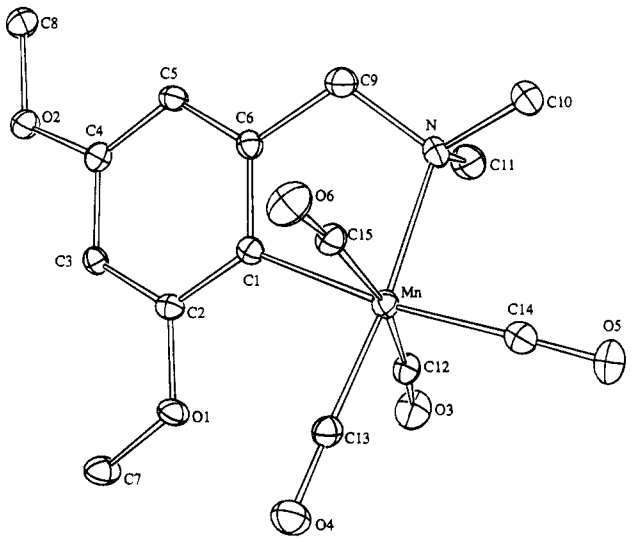


Figure 2. ORTEP drawing of **4** showing the atom-numbering scheme.

(12) Similar arguments have been put forth to explain the lowering of the LUMO of C_2H_4 which is also a π-acceptor when interacting with the cation Ag^+. We therefore expect here the opposite behavior: Mingos, M. *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, U.K., 1982; Vol. 3, pp 1−88.

(13) (a) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432. (b) Kraihanzel, C. S.; Cotton, F. A. *Inorg. Chem.* **1963**, *2*, 533.

(14) Parker, P. J.; Wojcickci, A. *Inorg. Chim. Acta* **1974**, *11*, 17.

(15) (a) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. (b) Allinger, N. L.; et al. *J. Am. Chem. Soc.* **1968**, *90*, 1199.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **4**

	Bond Distances (Å)		
Mn−C(1)	2.071(3)	Mn−N	2.149(3)
Mn−C(12)	1.846(4)	Mn−C(13)	1.785(4)
Mn−C(14)	1.818(4)	Mn−C(15)	1.831(4)
C(2)−O(1)	1.374(4)	C(4)−O(2)	1.379(4)
O(1)−C(7)	1.406(4)	O(2)−C(8)	1.418(4)
C(12)−O(3)	1.143(4)	C(13)−O(4)	1.159(4)
C(14)−O(5)	1.151(4)	C(15)−O(6)	1.149(4)
	Bond Angles		
C(1)−Mn−N	78.9(1)	C(1)−Mn−C(12)	83.7(1)
C(1)−Mn−C(13)	96.2(1)	C(1)−Mn−C(14)	171.9(1)
C(1)−Mn−C(15)	87.6(1)	N−Mn−C(12)	94.9(1)
N−Mn−C(13)	174.4(1)	N−Mn−C(14)	93.1(1)
N−Mn−C(15)	90.5(1)	C(12)−Mn−C(13)	87.4(2)
C(12)−Mn−C(14)	95.7(1)	C(12)−Mn−C(15)	168.7(2)
C(13)−Mn−C(14)	91.8(2)	C(13)−Mn−C(15)	86.3(2)
C(14)−Mn−C(15)	93.9(2)	C(1)−C(2)−C(3)	121.8(3)
C(1)−C(2)−O(1)	115.6(3)	C(3)−C(2)−O(1)	122.6(3)
C(3)−C(4)−C(5)	120.4(3)	C(3)−C(4)−O(2)	114.2(3)
C(5)−C(4)−O(2)	125.3(3)	C(2)−O(1)−C(7)	118.4(3)
C(4)−O(2)−C(8)	116.6(3)	Mn−C(12)−O(3)	175.1(3)
Mn−C(13)−O(4)	176.4(3)	Mn−C(14)−O(5)	178.1(3)
Mn−C(15)−O(6)	174.0(3)		

Table 4. Comparison of Metal−Ligand Distances and Angles (deg) in Complexes **4** and Mn(dmba)

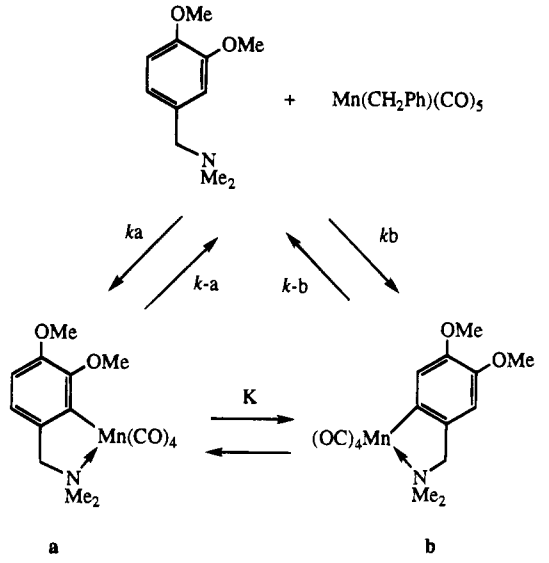
	4	(dmba)Mn(CO)$_4$, from ref 41
Mn−C(CO)$_{ax}$	1.831(4)	1.839(5)
Mn−C(CO)$_{ax}$	1.846(4)	1.857(5)
Mn−C(CO)$_{eqtransN}$	1.785(4)	1.781(5)
Mn−C(CO)$_{eqtransC}$	1.818(4)	1.827(4)
Mn−C(ipso)	2.071(3)	2.055(4)
Mn−N	2.149(3)	2.139(3)
C(1)−Mn−C(13)	96.2(1)	92.6(1)
C(13)−Mn−C(14)	91.8(2)	93.1(2)
C(1)−Mn−N	78.9(1)	80.2(2)

(CO)$_4$ group. This interaction is very likely responsible for the absorption splitting observed in the IR spectra. However, this interaction is sufficiently weak so as not to modify to any great extent the structural parameters of other nonimplied groups.

Discussion

It has previously been suggested that $MnCH_2Ph(CO)_5$ displays weak nucleophilic properties in the cyclometalation reaction.[4j] However, the presence of the benzyl ligand in $MnCH_2Ph(CO)_5$ might be diagnostic of the fact that the complex can also react via a multicentered pathway[1] in this *reversible* cyclometalation reaction. A typical feature of such pathways is a relatively low sensitivity of the C−H breaking process to electronic effects.[1] The data obtained in this work suggest that this may be true. In fact, similar high yields of **3** and **4** in the cases 3,5-$(OMe)_2C_6H_3$-NMe_2 and 4-$FC_6H_4CH_2NMe_2$, respectively, support this suggestion. It is interesting to note here that formation of compound **1** proceeds very cleanly in excellent yield, showing that $PhCH_2$-$Mn(CO)_5$ is able to readily activate not only the C(aryl)−H bonds but also less acidic C(alkyl)−H bonds. In the synthesis of complexes **2**−**4**, only one product is expected due to the equivalence of the two possible cyclometalation sites. These complexes are obtained with good yields and show that, in these cases, the presence of an electron-withdrawing (F) or electron-donating (OMe) substituent does not significantly alter the course of the reaction. The formation of complex **5** was also expected, due to the relative ease of activation of a C(aromatic)−H bond when compared to that of a C(alkyl)−H bond. However, in the synthesis of complex **6**, two products were expected but only one was observed, even at short reaction times. The presence of an oxygen ortho to the metal−carbon (ipso) bond does not prevent the C−H activation at this position, and furthermore, it would stabilize the cyclometalated final product.

Scheme 1



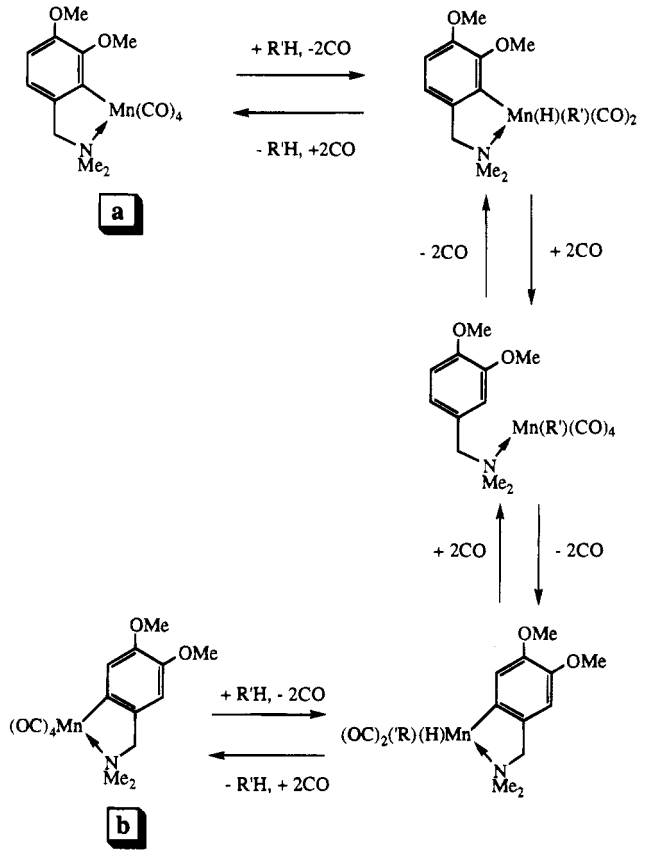
On the other hand, a comparison of the different relative amounts of each product **7a/7b** allows us to propose that there is a slight preference between the two possible sites of metalation: the higher amount of complex **7b** could be explained by a lower steric hindrance between the Me substituents of the cyclometalated amine and the $Mn(CO)_4$ unit.

It is seen from Figure 1 that the amounts of the reaction products **8a** and **8b** are close to each other at a low reaction time when the conversion is low or, in other words, when the contribution from the reverse reaction can be neglected. When the reaction reaches near-completion, the **a/b** ratio increases, and this behavior may be accounted for by taking into consideration the reversible nature of the cyclometalation with $MnCH_2Ph(CO)_5$. Scheme 1 is useful for visualization of this process.

If the reactions that lead to isomers **a** and **b** occur at similar rates (i.e., the rate constants k_a and k_b are close to each other), the isomeric distribution must be driven by the rate constants of the reverse process, i.e. k_{-a} and k_{-b}. These can differ significantly, and we have substantial evidence for this. It has been demonstrated by the examples of **8a** and **8b** that the cyclometalation reaction is reversible and that **8b** is thermodynamically less stable than **8a**. The crystal structure data for **4** provide a clue for the understanding of this phenomenon. In fact, there is an intramolecular stabilization via the O···CO−Mn bonding in such compounds that possess the $-OCH_2$ or $-OCH_3$ moiety ortho to the Mn−C bond. If the reverse reaction starts with the oxidative addition of the C−H bond of a solvent to the metal center, as shown in Scheme 2, a dissociation of at least one CO ligand from Mn(I) is needed for creating a vacant coordination site. It seems likely that the CO ligands in structures similar to those of **4**, **6**, or **8a** should have a decreased tendency to dissociate because of the intramolecular bonding. If so, these compounds should be less reactive in the reverse process compared to their positional isomers such as **8b** and the other complexes where the methoxy group ortho to the metal is absent.

We also wished to investigate the intimate mechanism of the isomerization process of **8b** → **8a**. As has been discussed, in all the experiments performed, the starting and isomerized compounds were obtained, together with significant amounts

Scheme 2



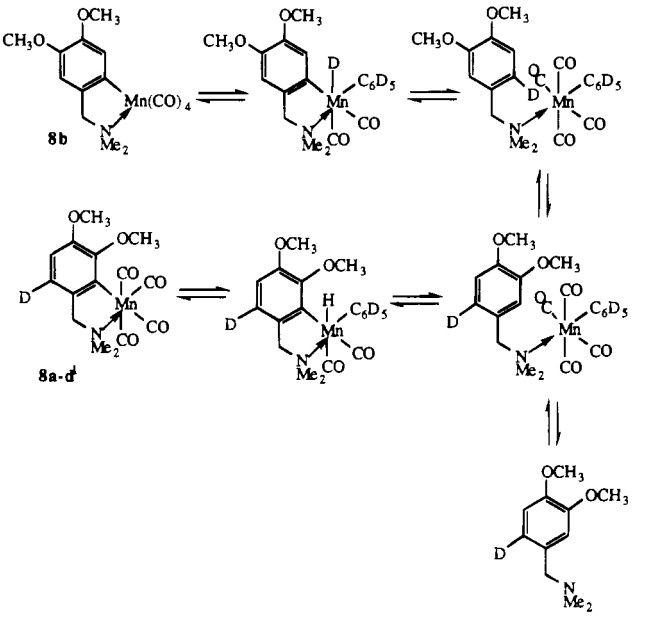
of the free amine. No other species were detected, including hypothetical products derived from the degradation of the amine. Very small amounts of an insoluble orange-brown solid (not enough for a complete characterization) precipitated during heating, and they were only detected in experiments performed in sealed tubes (see below). Given that there is no degradation process during which protons could be generated as a result of bond-breaking and -forming reactions, the presence of free amine could be explained by a participation of the solvent in the isomerization process. Searching in this direction, we performed isomerization experiments in a deuterated solvent: the reaction was thus carried out in C_6D_6 in a sealed tube, and this was heated for 24 h at the nominal temperature (refluxing hexane) to obtain the highest conversion (see Experimental Section). At the end of the reaction, the NMR measurements afforded some important observations:

(1) The ^1H NMR spectrum of this sample shows the presence of aromatic resonances corresponding to **8b**, **8a**, and the free amine, the pattern of these resonances being almost identical to those observed for the same mixtures coming from reactions performed in a nondeuterated solvent.

(2) The ^2H NMR spectrum of this sample displays a resonance at δ 6.42 ppm, showing the incorporation of a deuterium atom in the aromatic ring of the cyclometalated benzylamine. It is most likely that this deuterium atom is located for the isomerized product at the 5-position. No other peaks were found, but this does not exclude the presence of deuterium in the free amine.

These data mean that partial deuteration of the cyclometalated position in **8b** has occurred. It is clear that the solvent participates in the mechanism of the isomerization. Due to the nucleophilic nature of Mn(I), we propose the mechanism shown in the Scheme 3. The oxidative addition of C_6D_6 to the Mn(I) center and reductive elimination of deuterated amine give an

Scheme 3



intermediate from which (i) a new C−H activation can take place, giving, after reductive elimination of C_6D_5H, the isomerized product, and (ii) alternatively, the amine can be lost (this explains the presence of free amine in solution); this should also lead to some degradation of the carbonylmanganese moiety that probably precipitates as a nondefinable carbonyl cluster. However, we have no evidence to ascertain this last point.

Since it is clear from the ^1H NMR data that only a very minor amount of deuterium has been incorporated on the aryl ring, the isomerization mechanism proposed in Scheme 3 cannot be the only operative process. We can also invoke an intramolecular mechanism which would involve the activation of C−H bonds of the $-CH_2N-$ or $-NMe_2$ groups. Indeed, it was shown previously that Mn(I) derivatives are able to activate these bonds, for instance in ((dimethylamino)methyl)ferrocene.[16b]

Conclusion

The efficient behavior of the complex $PhCH_2Mn(CO)_5$ leading to high-yield synthesis of C,N-cyclometalated complexes by the C−H activation reaction of substituted tertiary amines has been confirmed. The orientation of the C−H activation and the stability of the cyclometalated product are substituent-dependent. Through an appropriate choice of substituent, it is possible to direct the orientation of the metalation to a determined position. This fact could have an important influence in the hypothetical applications of these cyclometalated products as starting materials in organic synthesis.

Experimental Section

General Comments. All reactions were performed in Schlenk-type flasks under oxygen-free and water-free nitrogen. Solvents were dried and distilled under nitrogen prior to use: diethyl ether and tetrahydrofuran over benzophenone ketyl, *n*-hexane over sodium, and dichloromethane over P_2O_5. Elemental analyses were performed by the Service Central d'Analyse du CNRS (Lyon). The IR spectra were recorded in *n*-hexane solution on a Bruker IFS 66. The ^1H NMR spectra were recorded at 300.13 MHz and ^{13}C NMR spectra at 75.47 MHz on an FT-Bruker instrument (AC-300) at room temperature and externally referenced to TMS. The ^{19}F NMR spectrum was recorded at 376.5

(16) (a) Abel, E. W.; Rowley, R. J.; Mason, R.; Thomas, K. M. *J. Chem. Soc., Chem. Commun.* **1974**, 72. (b) Crawford, S. S.; Firestein, G.; Kaesz, H. D. *J. Organomet. Chem.* **1975**, *91*, C57.

MHz on an AM-400 FT-Bruker instrument and externally referenced to $CFCl_3$. The ^2H NMR spectra were recorded at 61.44 MHz on an AM-400 FT-Bruker instrument. Column chromatography was performed under nitrogen by using Al_2O_3 as support (Aluminiumoxid 90, Merck). Samples of compounds **1** and **8b** were enriched in ^{13}CO by stirring a solution of the compound in $CDCl_3$ under an atmosphere of ^{13}CO (99% ^{13}C, Aldrich) for 2 h. $PhCH_2Mn(CO)_5$ was prepared according to published methods.[17]

Mn(8-$CH_2C_9H_6N$-C,N)$(CO)_4$, 1. A solution of $PhCH_2Mn(CO)_5$ (3.50 g, 12.23 mmol) and 8-methylquinoline (1.73 mL, 13.0 mmol) in *n*-hexane (100 mL) was refluxed for 8 h. During this time, a deep yellow solid precipitated. The resulting suspension was cooled in an ice bath and filtered. The crude product obtained was redissolved in a minimum amount of CH_2Cl_2, and the solution was subjected to flash chromatography over Al_2O_3 using a mixture of Et_2O/*n*-hexane (1/1) as eluent. The yellow fraction was collected and the solvent removed *in vacuo*, leaving a yellow powder, **1**. Yield: 3.56 g, 94%.

Anal. Calc for $MnC_{14}H_8NO_4$: C, 54.39; H, 2.61; N, 4.53. Found: C, 54.47; H, 2.67; N, 4.61. IR (*n*-hexane solution): 2066 (s), 1979 (vs), 1967 (vs), 1925 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.97 (d, H_2, Ar, $^3J_{H_2-H_3}$ = 4.1 Hz), 8.15 (d, H_7, Ar, $^3J_{H_6-H_7}$ = 8.2 Hz), 7.79 (d, H_5, Ar, $^3J_{H_5-H_6}$ = 8.0 Hz), 7.54 (d, H_4, Ar, $^3J_{H_3-H_4}$ = 8.2 Hz), 7.51 (t, H_6, Ar), 7.28 (dd, H_3, Ar), 2.92 (s, 2H, CH_2Mn). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 221.24, 213.64 (CO equatorial), 217.98 (CO axial), 154.22, 153.97, 151.47, 135.15, 128.58, 127.67, 125.45, 123.36, 121.45 (C_9H_6N), 16.21 (CH_2Mn).

Mn($C_{10}H_6NMe_2$-1-C^8,N)$(CO)_4$, 2. A solution of $PhCH_2Mn(CO)_5$ (1.70 g, 5.94 mmol) and *N*,*N*-dimethyl-1-naphthylamine (0.98 mL, 6.0 mmol) in *n*-hexane (60 mL) was refluxed for 8 h. After cooling, the resulting yellow solution was evaporated to dryness. The residue was redissolved in a minimum amount of CH_2Cl_2, and the solution was subjected to flash chromatography over Al_2O_3 using a mixture of Et_2O/*n*-hexane (1/1). The yellow fraction was collected and the solvent removed *in vacuo* until crystals began to form. Subsequent crystallization at −18 °C afforded 1.30 g (65%) of the yellow product **2**.

Anal. Calc for $MnC_{16}H_{12}NO_4$: C, 56.99; H, 3.58; N, 4.15. Found: C, 56.20; H, 3.83; N, 4.21. IR (*n*-hexane solution): 2070 (s), 1982 (vs), 1976 (vs), 1940 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.85 (d, 1H, Ar, $^3J_{H-H}$ = 6.58 Hz), 7.71 (d, 1H, Ar, $^3J_{H-H}$ = 7.87 Hz), 7.55 (d, 1H, Ar, $^3J_{H-H}$ = 8.05 Hz), 7.43 (t, 1H, Ar), 7.37 (t, 1H, Ar), 7.30 (d, 1H, Ar, $^3J_{H-H}$ = 7.47 Hz), 3.23 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 214.02 (CO), 164.42, 155.84, 140.91, 137.90, 134.42, 128.22, 127.73, 124.49, 122.40, 114.88 ($C_{10}H_6$), 60.61 (NMe_2).

Mn(C_6H_3-F-5-CH_2NMe_2-2)$(CO)_4$, 3. A solution of $PhCH_2Mn(CO)_5$ (1.80 g, 6.29 mmol) and 4-$FC_6H_4CH_2NMe_2$ (1.07 mL, 6.30 mmol) in *n*-hexane (60 mL) was refluxed for 8 h. After cooling, the yellow solution was evaporated to dryness, the residue was dissolved in 5 mL of Et_2O, and the resulting solution was subjected to flash chromatography over Al_2O_3 using Et_2O/*n*-hexane (1/1) as eluent. The yellow fraction was collected and the solvent removed under reduced pressure until a red oil was obtained, which was dried *in vacuo* for 6 h at 60 °C, affording **3** (1.45 g, 73%) as deep yellow crystals.

Anal. Calc for $MnC_{13}H_{11}NFO_4$: C, 48.92; H, 3.47; N, 4.38. Found: C, 48.83; H, 3.51; N, 4.24. IR (*n*-hexane solution): 2072 (s), 1980 (vs, br), 1946 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.46 (dd, H_6, Ar, $^3J_{H_6-F}$ = 8.64 Hz, $^4J_{H_6-H_4}$ = 2.59 Hz), 7.02 (dd, H_3, Ar, $^3J_{H_3-H_4}$ = 8.20 Hz, $^4J_{H_3-F}$ = 5.23 Hz), 6.67 (ddd, H_4, Ar, $^3J_{H_4-F}$ = 8.98 Hz), 3.64 (s, 2H, CH_2N), 2.66 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 219.25, 213.70 (CO), 172.22, 162.01 ($^1J_{C-F}$ = 248.6 Hz), 142.73, 126.92 ($^2J_{C-F}$ = 15.62 Hz), 123.40 ($^3J_{C-F}$ = 6.33 Hz), 110.31 ($^2J_{C-F}$ = 22.11 Hz) (C_6H_3), 75.12 (CH_2N), 56.95 (NMe_2). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ -117.75 (dt).

Mn($C_6H_2(MeO)_2CH_2$-4,6-NMe_2-2)$(CO)_4$, 4. $PhCH_2Mn(CO)_5$ (0.40 g, 1.40 mmol) and 3,5-$(MeO)_2C_6H_3CH_2NMe_2$ (0.27 g, 1.40 mmol) were dissolved in *n*-hexane (50 mL), and the solution was refluxed for 8 h. The yellow solution was cooled and evaporated to dryness, and the oily residue was redissolved in 10 mL of Et_2O. Subsequent chromatography of the ethereal solution over Al_2O_3 using *n*-hexane as eluent and evaporation to dryness of the collected fraction afforded **4** (0.33 g, 65%) as a lemon-yellow solid.

(17) Bruce, M. I.; Liddell, M. I.; Pain, G. N. *Inorg. Synth.* **1989**, *26*, 172.

Anal. Calc for $MnC_{15}H_{16}NO_6$: C, 49.87; H, 4.46; N, 3.87. Found: C, 49.73; H, 4.51; N, 4.00. IR (*n*-hexane solution): 2069 (s), 1983 (vs), 1972 (vs), 1940 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.41, 6.36 (AB system, H_3 and H_5, Ar, $^4J_{H_3-H_5}$ = 2.14 Hz), 3.81 (s, 3H, OMe), 3.78 (s, 3H, OMe), 3.61 (s, 2H, CH_2N), 2.62 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 214.11 (CO), 167.21, 147.96 (two signals collapsed), 102.04 (two signals collapsed), 96.62 (C_6H_2), 76.63 (CH_2N), 56.66 (NMe_2), 55.35 (OMe, two signals collapsed).

Mn($C_6H_2Me_2$-3,6-CH_2NMe_2-2)$(CO)_4$, 5. A solution of $PhCH_2Mn(CO)_5$ (0.20 g, 0.72 mmol) and 2,5-$Me_2C_6H_3CH_2NMe_2$ (0.12 g, 0.72 mmol) in 20 mL of *n*-hexane was refluxed for 8 h. The solvent was evaporated from the resulting solution under reduced pressure, the residue was dissolved in 5 mL of Et_2O, and the solution was chromatographed over Al_2O_3 using a mixture of Et_2O/*n*-hexane (1/1) as eluent. The yellow fraction was collected and the solvent evaporated to dryness, giving **5** (0.075 g, 31%) as a yellow solid.

Anal. Calc for $MnC_{15}H_{16}NO_4$: C, 54.72; H, 4.90; N, 4.25. Found: C, 54.54; H, 5.05; N, 4.16. IR (*n*-hexane solution): 2065 (s), 1975 (vs), 1971 (vs), 1937 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.96, 6.76 (AB system, H_4 and H_5, Ar, $^3J_{H_4-H_5}$ = 7.49 Hz), 3.70 (s, 2H, CH_2N), 2.66 (s, 6H, NMe_2), 2.51 (s, 3H, Me), 2.17 (s, 3H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 214.49 (CO), 166.74, 147.04, 145.42, 129.56, 128.11, 126.04 (C_6H_2), 73.85 (CH_2N), 57.27 (NMe_2), 27.69 (Me), 20.75 (Me).

Mn($C_6H_2(OCH_2O)$-2,3-CH_2NMe_2-6)$(CO)_4$, 6. $PhCH_2Mn(CO)_5$ (0.40 g, 1.40 mmol) and 3,4-$(OCH_2O)C_6H_3CH_2NMe_2$ (0.25 g, 1.40 mmol) were dissolved in 40 mL of *n*-hexane, and the resulting solution was refluxed for 8 h. During this time, a small quantity of a yellow solid precipitated. After cooling, the suspension was evaporated to dryness and the residue redissolved in 5 mL of CH_2Cl_2. Flash chromatography of this CH_2Cl_2 solution over Al_2O_3 using a mixture Et_2O/*n*-hexane (1/1) and subsequent evaporation to dryness of the yellow fraction collected yielded 0.30 g (62%) of **6** as a yellow solid.

Anal. Calc for $MnC_{14}H_{12}NO_6$: C, 48.71; H, 3.50; N, 4.05. Found: C, 48.13; H, 3.49; N, 3.65. IR (*n*-hexane solution): 2074 (s), 1988 (vs), 1973 (vs), 1947 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.64, 6.51 (AB system, H_4 and H_5, Ar, $^3J_{H_4-H_5}$ = 7.31 Hz), 5.93 (s, 2H, O_2CH_2), 3.58 (s, 2H, CH_2N), 2.64 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 212.98 (CO), 156.79, 143.76, 142.41, 141.61, 116.50, 104.05 (C_6H_2), 99.42 (O_2CH_2), 75.68 (CH_2N), 56.64 (NMe_2).

Mn($C_6H_2Me_2$-2,3-CH_2NMe_2-6)$(CO)_4$, 7a, and Mn($C_6H_2Me_2$-4,5-CH_2NMe_2-2)$(CO)_4$, 7b. A solution of $PhCH_2Mn(CO)_5$ (0.30 g, 1.05 mmol) and 3,4-$Me_2C_6H_3CH_2NMe_2$ (0.17 g, 1.05 mmol) in *n*-hexane (20 mL) was refluxed for 8 h. After cooling and evaporation of the solvent *in vacuo*, the yellow oily residue was redissolved in 10 mL of Et_2O, and the solution was chromatographed over Al_2O_3 using a mixture of Et_2O/*n*-hexane (1/1) as eluent. The yellow fraction was collected and the solvent was evaporated to dryness, affording 0.30 g (87%) of a yellow solid which was a mixture of **7a** and **7b** in a 1/2 ratio.

Anal. Calc for $MnC_{15}H_{16}NO_4$: C, 54.72; H, 4.90; N, 4.25. Found: C, 54.65; H, 4.74; N, 4.28.

Compound **7b** could be obtained from this mixture in pure form by fractional crystallization: The mixture was dissolved in 15 mL of warm *n*-hexane, and the solution was kept at −18 °C for 18 h. Yellow crystals of **7b** were formed (0.18 g, 52%). The hexane solution was evaporated to dryness, giving a mixture of **7a/7b** in a 4/1 ratio (0.11 g, 32%).

Mn($C_6H_2Me_2$-4,5-CH_2NMe_2-2)$(CO)_4$, 7b. IR (*n*-hexane solution): 2067 (s), 1977 (vs), 1972 (vs), 1939 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.50 (s, H_6, Ar), 6.89 (s, H_3, Ar), 3.62 (s, 2H, CH_2N), 2.67 (s, 6H, NMe_2), 2.28 (s, 3H, Me), 2.22 (s, 3H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 214.54 (CO), 163.17, 145.05, 142.52, 135.38, 131.72, 124.35 (C_6H_2), 75.58 (CH_2N), 56.95 (NMe_2), 19.55 (Me), 19.36 (Me).

Mn($C_6H_2Me_2$-2,3-CH_2NMe_2-6)$(CO)_4$, 7a. ^1H NMR ($CDCl_3$): δ 7.47, 6.97 (AX system, H_4 and H_5, Ar, $^3J_{H_4-H_5}$ = 7.50 Hz), 3.73 (s, 2H, CH_2N), 2.69 (s, 6H, NMe_2), 2.25 (s, 3H, Me), 2.14 (s, 3H, Me).

When the reaction was stopped after 3.5 h of reflux and a workup similar to that for the preceding case was carried out, a yellow solid was obtained in 76% yield which was a mixture of **7a** and **7b** in a 1/2 ratio. When the reaction was stopped at shorter reaction times (0.75 or 1.5 h) and the same workup was carried out, an uncrystallizable oil was obtained, due to the presence of free amine. In the first case (0.75 h) a 1/1.3 ratio (**7a/7b**) was found, while in the second one (1.5 h) the found ratio (**7a/7b**) was 1/1.7.

$Mn(C_6H_2(MeO)_2$-2,3-CH_2NMe_2-6)$(CO)_4$, 8a, and $Mn(C_6H_2(MeO)_2$-4,5-CH_2NMe_2-2)$(CO)_4$, 8b. A solution of $PhCH_2Mn(CO)_5$ (0.40 g, 1.40 mmol) and 3,4-$(MeO)_2C_6H_3CH_2NMe_2$ (0.27 g, 1.40 mmol) in *n*-hexane (40 mL) was refluxed for 14 h. After cooling of the solution, the solvent was evaporated to dryness and the remaining residue dissolved in 10 mL of Et_2O. Subsequent chromatography over Al_2O_3 using Et_2O as eluent and evaporation of the solvent from the collected yellow fraction gave a mixture of the products **8a** and **8b** in a 3/1 ratio (**8a/8b**). The overall yield was 0.35 g (69%).

Anal. Calc for $MnC_{15}H_{16}NO_6$: C, 49.87; H, 4.46; N, 3.87. Found: C, 49.29; H, 4.50; N, 4.00.

This mixture could be separated by column chromatography. The obtained solid was dissolved in 5 mL of CH_2Cl_2, and the solution was placed at the top of a column (22 cm, o.d. = 4 cm) charged with Al_2O_3. First elution with a mixture of Et_2O/*n*-hexane (500 mL) resulted in the migration of a yellow band from which $Mn(C_6H_2(MeO)_2$-2,3-CH_2NMe_2-6)$(CO)_4$, **8a** (0.183 g), was obtained after evaporation of the solvent to dryness. Subsequent elution with Et_2O (250 mL) and evaporation of the solvent afforded $Mn(C_6H_2(MeO)_2$-4,5-CH_2NMe_2-2)$(CO)_4$, **8b** (0.05 g).

$Mn(C_6H_2(MeO)_2$-2,3-CH_2NMe_2-6)$(CO)_4$, 8a. IR (*n*-hexane solution): 2070 (s), 1986 (vs), 1972 (vs), 1942 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.85, 6.63 (AB system, H_4 and H_5, Ar, $^3J_{H_4-H_5}$ = 7.91 Hz), 3.88 (s, 3H, OMe), 3.86 (s, 3H, OMe), 3.62 (s, 2H, CH_2N), 2.63 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 218.64, 214.07 (CO), 160.17, 156.18, 151.47, 140.37, 118.89, 108.80 (C_6H_2), 75.68 (CH_2N), 60.08 (OMe), 56.66 (NMe_2), 55.47 (OMe).

$Mn(C_6H_2(MeO)_2$-4,5-CH_2NMe_2-2)$(CO)_4$, 8b. IR (*n*-hexane solution): 2068 (s), 1978 (vs), 1973 (vs), 1939 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.20 (s, H_6, Ar), 6.71 (s, H_3, Ar), 3.93 (s, 3H, OMe), 3.81 (s, 3H, OMe), 3.60 (s, 2H, CH_2N), 2.66 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 219.98, 213.50 (CO equatorial), 214.30 (CO axial), 156.17, 148.52, 146.62, 138.61, 123.21, 107.89 (C_6H_2), 75.60 (CH_2N), 56.94 (NMe_2), 56.09 (OMe, two signals collapsed).

When the reaction was left stirring for 24 h in refluxing *n*-hexane and a similar workup was carried out, a yellow solid was obtained, which was a mixture of **8a/8b** in a 3/1 ratio (yield 70%). If the reaction was stopped after 3.5 h of reflux and the usual workup was carried out, a yellow solid was obtained in 55% yield, which was a mixture of **8a/8b** in a 1.5/1 ratio. Finally, when the reaction was stopped after 2.5 h of reflux and the usual workup was carried out, an uncrystallizable oil was obtained, due to the presence of free amine. The ^1H NMR spectrum reveals the presence of an **8a/8b** mixture in a 1/1.4 ratio, together with the starting compounds.

Deuteration Experiments. A sample of compound **8b** (typically 30−50 mg) was dissolved in 0.3 mL of C_6D_6 under N_2 in an NMR tube which was subsequently sealed *in vacuo*. The tube was heated at 80 °C in an oil bath, and the ^1H NMR spectra of its contents were recorded several times over a period of 24 h. After 24 h of heating, the ^1H NMR reveals the presence of only free amine (27%), **8a** (52%), and **8b** (21%) with the exclusion of any other organic or organometallic compounds. The ^2H NMR experiment was performed after removal of C_6D_6 in vacuo and redissolution of the residue in C_6H_6. We could only detect a singlet signal at 6.42 ppm, in addition to the C_6D_6 resonance.

Table 5. Crystallographic Data for **4**

$C_{15}H_{16}NO_6Mn$	fw = 361.2
a = 13.644(4) Å	space group $P2_1/n$
b = 9.153(3) Å	T = −100 °C
c = 14.432(4) Å	λ = 1.5418 Å
β = 115.57(2)°	ϱ_{calc} = 1.476 g cm^{-3}
V = 1625.8 $Å^3$	μ = 69.03 cm^{-1}
Z = 4	$R_F{}^a$ = 0.027
$R_{wF}{}^b$ = 0.042	

$^a R_F = \sum(|F_o| - |F_c|)/\sum|F_o|$. $^b R_{wF} = [\sum(w(|F_o| - |F_c|)^2)/\sum(wF_o^2)]^{1/2}$.

Structure Determination and Refinement of Compound 4. Crystal data and numerical details of the structure determination are given in Table 5. The crystal was mounted on a rotation-free goniometer head and transferred to a Philips PW1100/16 automatic diffractometer for data collection at 173 K. The resulting data set was transferred to a VAX computer, and for all subsequent calculations the MOLEN/VAX package was used.[18] Three standard reflections measured every 1 h during the entire data collection period showed no significant decay. The raw data were converted to intensities and corrected for Lorentz, polarization, and absorption factors, the last computed using the empirical method. The structure was solved using the heavy atom method. Refinement was carried out by full least-squares techniques; $\sigma^2(F^2) = \sigma_{counts}{}^2 + (pI)^2$. A final difference map revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients were taken from refs 19a and 19b, respectively.

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Supplementary Material Available: Tables giving summaries of data collection and refinement parameters, anisotropic displacement coefficients of the non-hydrogen atoms, hydrogen atom parameters, and full bond distances and angles (5 pages). Ordering information is given on any current masthead page.

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(19) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV: (a) Table 2.2b. (b) Table 2.3.1.