Å, which is consistent with all four peaks, b–e, originating from the heme methyls [calculated $\bar{r}$(Fe–CH$_3$) ~ 6.2 Å].

Conclusions

The present NMR study leads to the conclusions that the differences in ferricytochrome *c′* line widths of heme methyl resonances in I and II support a five-coordinate I and a II with a stronger axial ligand field which is consistent with six-coordination. The emergence of two new hyperfine shifted resonances during the I → II conversion confirms the six-coordinate nature of II, and qualitative analysis of their line widths favors their origin in the β-CH$_2$ of a glutamate ligand. The detection of an exchangeable resonance characteristic of an axial histidyl imidazole N$_1$H confirms the high-spin five-coordinate nature of ferrocytochrome *c′*.

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Stereochemistry at Manganese of the Carbon Monoxide Insertion in Pentacarbonylmethylmanganese(I). The Geometry of the Intermediate

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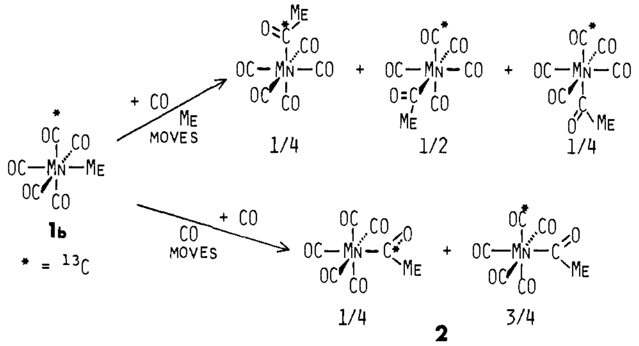
Abstract: The stereochemistry at manganese of the CO insertion into the Me–Mn bond of *cis*-MeMn(CO)$_4$(^{13}CO) has been examined by using ^{13}C NMR spectroscopy carried out at −115 °C to give sharp resonances. The insertion was induced by using both ^{12}CO and P(OCH$_2$)$_3$CMe, each in THF-acetone-d_6 and HMPA solvents. The positional ratios of isotopic label in the products are consistent only with methyl migration proceeding through a square-based pyramid with a basal acetyl group in all cases except the ^{12}CO-induced insertion in HMPA, in which case the product ratio is that resulting from complete label randomization in the intermediate. From known and estimated kinetic parameters, a ΔG_{298}^{*} for isomerization of (MeCO)Mn(CO)$_4$ of greater than 9 kcal/mol can be inferred.

A complete understanding of the "migratory insertion" of carbon monoxide into metal–carbon σ bonds requires detailed knowledge of a variety of issues, including the stereochemistry at both carbon and the metal, the geometry and stereochemical lability of any intermediates, the role of solvation of transition states and intermediates, and structure-reactivity relationships. Much of this information is currently available for a variety of molecular systems.[2,3] Nevertheless, reliable sterochemical information regarding the metal center is rather scarce.[3]

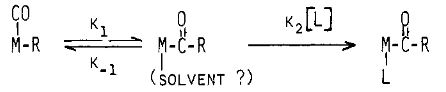
One extensively quoted set of experiments on this last issue dealt with the insertion of Scheme I.[4] It was argued that ^{12}CO-induced insertion of coordinated CO into the Mn–Me bond of *cis*-MeMn(CO)$_4$(^{13}CO) (**1b**)[5] would result in one of two site distributions of ^{13}CO in (MeCO)Mn(CO)$_5$ (**2**), depending on whether CO moves to Me or Me moves to CO. In the former case, only cis terminal CO would contain label, and in the latter case the cis/trans ^{13}CO label ratio would be 2/1. A ratio of 2/1 was reported on the basis of IR ^{13}CO stretching intensities.[4]

Other studies concerning the stereochemistry at the metal of CO insertion have appeared, including octahedral species such as PhCH$_2$CH$_2$RhCl$_2$(CO)(PPh$_3$)$_2$,[6] EtIrCl$_2$(CO)$_2$(AsMe$_2$Ph),[7] and MeFeX(CO)$_2$(PMe$_3$)$_2$ (X = I or Me),[8] square-planar species such as PhPtCl(CO)(PMePh$_2$),[9] and pseudooctahedral (or pseudotetrahedral) species such as η^5-C$_5$H$_5$Fe(CO)(PR$_3$)R.[10–12] These exhibit a variety of stereochemical paths including apparent CO migration to the alkyl site, apparent alkyl migration to the CO site, and more complicated geometrical reorganization not consistent with either simple CO or R migration.

Scheme I



Kinetics studies of coordinatively saturated complexes are consistent with the predominance of the path shown in eq 1.[2]



$$\text{M(CO)–R} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{M(solvent ?)–C(=O)–R} \xrightarrow{k_2[\text{L}]} \text{M(L)–C(=O)–R} \quad (1)$$

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[1] Alfred, P. Sloan Foundation Fellow, 1977–1981.

[2] (a) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87. (b) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299.

[3] Flood, T. C. *Top. Stereochem.* **1980**, *12*, 37.

[4] Noack, K.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *10*, 101.

[5] Nomenclature and structures in this paper are designated as follows: **1** ≡ MeMn(CO)$_5$, ^{13}C label unspecified; **1a** ≡ randomly labeled MeMn(CO)$_4$(^{13}CO); **1b** ≡ *cis*-MeMn(CO)$_4$(^{13}CO); **2** ≡ (MeCO)Mn(CO)$_5$, ^{13}C label unspecified; **2a** ≡ (MeCO)Mn(CO)$_4$(^{13}CO), randomly labelled; mtpb ≡ P(OCH$_2$)$_3$CMe = 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane; **4** ≡ *cis*-(MeCO)Mn(mtpb)(CO)$_4$, ^{13}C label unspecified; **4a** ≡ *cis*-(MeCO)Mn(mtpb)(CO)$_3$(^{13}CO), randomly labelled.

[6] Slack, D. A.; Egglestone, D. L.; Baird, M. C. *J. Organomet. Chem.* **1978**, *146*, 71. Egglestone, D. L.; Baird, M. C.; Lock, J. C.; Turner, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1576.

[7] Glyde, R. W.; Mawby, R. J. *Inorg. Chim. Acta* **1971**, *5*, 317.

[8] Pankowski, M.; Bigorgne, M. *J. Organomet. Chem.* **1971**, *30*, 227. Pankowski, M.; Bigorgne, M. "Abstracts", The 8th International Conference on Organometallic Chemistry, Kyoto, Japan, 1977.

[9] Anderson, G. K.; Cross, R. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1246.

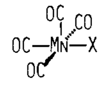
[10] Attig, T. G.; Wojcicki, A.; *J. Organomet., Chem.* **1974**, *82*, 397. Reich-Rohwig, P.; Wojcicki, A. *Inorg. Chem.* **1974**, *13*, 2457.

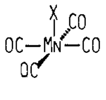
[11] Davison, A.; Martinez, N. *J. Organomet. Chem.* **1974**, *74*, C17.

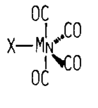
[12] Flood, T. C.; Campbell, K. D.; Downs, H. H.; Statler, J. A.; to be submitted for publication.

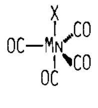
0002-7863/81/1503-4410$01.25/0

Whether the first transition state and/or the intermediate involves solvent coordination[2] and the geometry of the intermediate have been subjects of some concern. Although good evidence[13,14] suggests that group 6 d^6 metal species ML_5 are of C_{4v} geometry, there is little evidence which bears on this question for the corresponding manganese species. A recent matrix isolation study concludes that $MnX(CO)_4$ (X = halogen, Me, MeCO) is trigonal bipyramidal with an equatorial X group (C_{2v}, **3c**).[15] MO calculations also suggest that $MnBr(CO)_4$ is C_{2v},[16] although other calculations conclude that $(MeCO)Mn(CO)_4$ is of C_s symmetry (**3a**).[17]


3a


3b


3c


3d

Although the stereochemical studies mentioned above[6-12] indicate that a variety of stereochemical paths are available for the CO insertion in octahedral complexes and that energy differences between these paths are therefore small, $RMn(CO)_5$ may be regarded as a prototypic system because of its high symmetry and lack of trans effects etc. and so is of particular interest. While the study of Noack and Calderazzo[4] was elegantly conceived, there is always the concern of the quantitative interpretation of IR intensity data, and, also, given that their conclusions are correct (they are—see below), their intensity data are consistent with more than one possible geometry for the intermediate. Since solvents have recently been found to have a profound effect on the stereochemistry of the CO insertion in η^5-$C_5H_5Fe(CO)(L)Et$,[12] it is also of interest to examine the effect of solvent nucleophilicity on the insertion of **1**.

Consequently, we have further examined the stereochemistry of the CO insertion of **1**. In order to avoid any ambiguity arising from the interpretation of IR band intensities, we have employed ^{13}C NMR (CMR) spectroscopy for the determination of ^{13}C site labeling ratios.

Results

Preparation of ^{13}C-Labeled Materials. Since Fourier transform NMR was used to establish the ^{13}C site populations, it was of critical importance to establish the accuracy of the integrals. Randomly labeled samples of ca. 6% ^{13}CO-enriched **1a**, **2a**, and *cis*-$(MeCO)Mn(CO)_4$(mtpb) (**4a**)[5] were prepared by first enriching $Mn_2(CO)_{10}$ by photolysis under a ^{13}CO atmosphere. Then sodium amalgam reductive cleavage of $Mn_2(CO)_{10}$ in ether yielded $Na[Mn(CO)_5]$,[18] which in turn was treated with methyl iodide to form **1a** and acetyl chloride to form **2a**.[19] Reaction of **1a** with mtpb yielded **4a**.

Cis-labeled **1b** was prepared as previously described[4] by reaction of $Na[Mn(CO)_5]$ (unenriched) with $Me^{13}COCl$ (90% ^{13}C) to afford $(Me^{13}CO)Mn(CO)_5$, which was then thermally decarbonylated to **1b** in pentane at reflux. Only an enriched cis-CO resonance was visible in the CMR spectrum of **1b**, indicating that no site scrambling of CO ligands had occurred during decarbonylation.

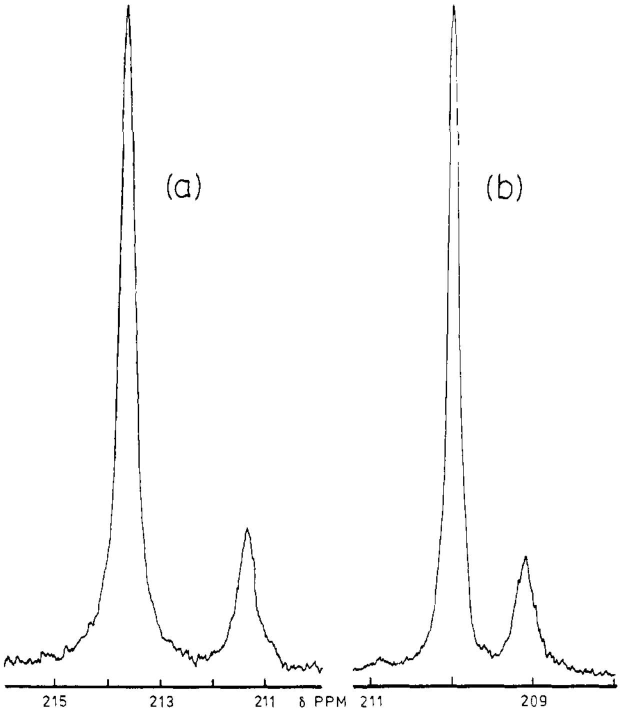


Figure 1. CMR spectra of the terminal CO resonances in (a) randomly ^{13}C-labeled $MeMn(CO)_5$ (**1a**) and (b) randomly labeled $(MeCO)Mn(CO)_5$ (**2a**), taken at −115 °C in 1/1 THF–acetone-d_6 at 25.2 MHz.

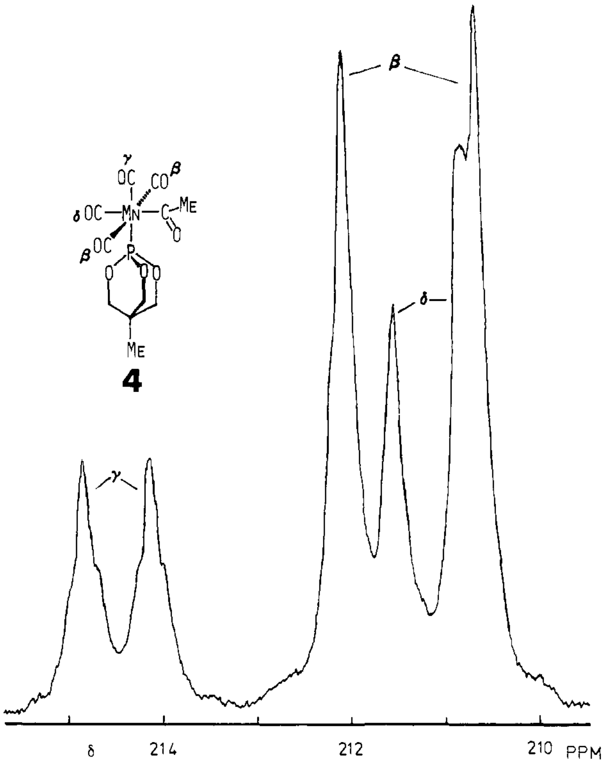


Figure 2. CMR spectrum of randomly ^{13}C-labeled $(MeCO)Mn(mtpb)(CO)_4$ (**4a**) taken at −115 °C in 1/1 THF–acetone-d_6 at 25.2 MHz.

CMR Spectra. The CMR spectra of all of these ^{13}C-enriched manganese compounds were, of course, severely broadened by the manganese nuclear quadrupole. Attempts were made to effect decoupling by using shiftless relaxation reagents,[20] viscous solvents,[21] and low temperature.[21,22] In our hands only the last

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(13) Dobson, G. R.; Asali, K. J. *J. Am. Chem. Soc.* **1979**, *101*, 5433 and references therein.

(14) Turner, J. J. et al. *J. Am. Chem. Soc.* **1975**, *97*, 4805 and references therein.

(15) McHugh, T. M.; Rest, A. J.; Taylor, D. J. "Abstracts," The 9th International Conference on Organometallic Chemistry, Dijon France, 1979. McHugh, T. M.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1980**, 2323.

(16) Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366.

(17) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224.

(18) Any isotope effect on the site distribution of ^{13}CO should be inconsequential. Regardless of any site preference for ^{13}CO incorporation into $Mn_2(CO)_{10}$, $[Mn(CO)_5]^-$ would be instantly randomized since the extremely rapid fluxional behavior of the isoelectronic $Fe(CO)_5$ is well documented: Sheline, R. K.; Mahnke, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 314.

(19) The acetyl group of **2a** prepared in this way is unenriched, of course, but only the terminal CO intensities are important.

(20) Gansow, O. A.; Burke, A. R.; LaMar, G. N. *J. Chem. Soc., Chem. Commun.* **1972**, 456.

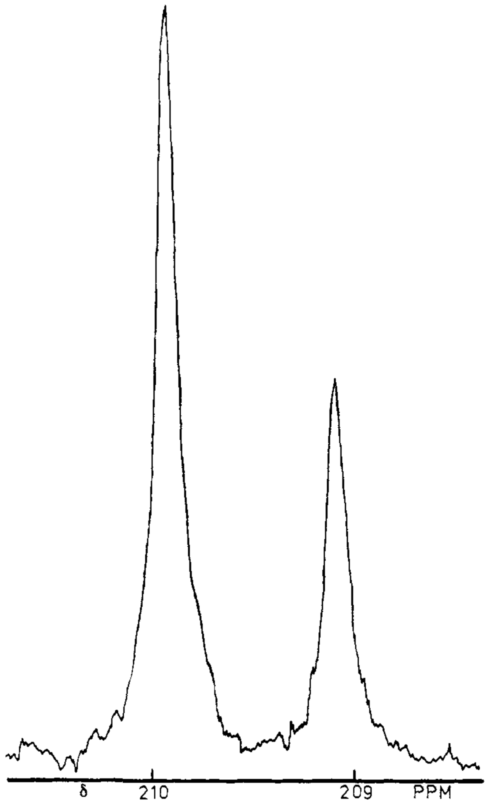


Figure 3. CMR spectrum of (MeCO)Mn(CO)$_5$ (**2**) from reaction of *cis*-MeMn(CO)$_4$(^{13}CO) (**1b**) and ^{12}CO in THF-acetone-d_6.

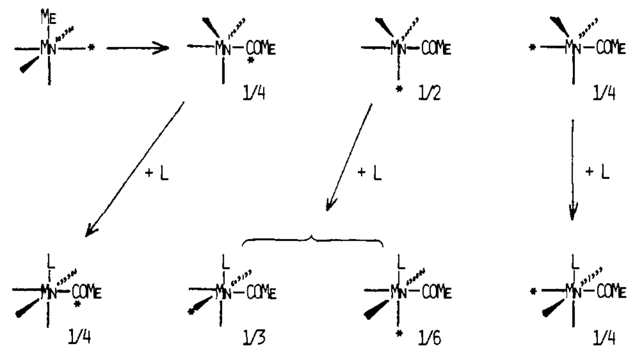
technique was satisfactory. High-quality CMR spectra were obtainable at ca. −115 °C in THF–acetone-d_6 solvent mixtures, with well-resolved resonances with band widths usually of less than 4 Hz.

Figure 1 shows the spectra of radomly labeled **1a** and **2a** wherein the cis and trans CO resonances are clearly well separated. The trans CO, whether trans to methyl or to acetyl, exhibits a resonance at higher field than does the cis CO, and the cis/trans integral ratios are 4.0 ± 0.1 for a number of spectra on each of several samples of both **1a** and **2a**. These integral ratios were quite reproducible, so that the integrals of specifically labeled samples can be interpreted accurately without the need for normalization.

The CMR spectrum of randomly labeled **4a** (Figure 2) contained the expected three doublets with an integral ratio of 2/1/1. A surprising feature is the $^2J_{PC}$ of 35 Hz for the facial CO resonances (sites β), while the two meridianal CO resonances (sites γ and δ) have $^2J_{PC}$ of 17 and 18 Hz (respectively). Ordinarily in octahedral complexes $^2J_{PC}(\text{trans}) > {}^2J_{PC}(\text{cis})$.[23] Nevertheless, assignments can be made for the two meridianal CO ligands since in **1** and **2** the CO ligand trans to the anionic ligand is distinctly at higher field, and furthermore, it is well documented that δ of CO trans to P is at lower field than δ of CO cis to P in octahedral complexes.[23] Thus, the doublet at δ 214.6 corresponds to the CO trans to the phosphite and cis to the acetyl group (site γ) and the doublet at δ 211.4 to the CO cis to the phosphite and trans to the acetyl group (site δ).

Insertion Reactions. Reaction of *cis*-MeMn(CO)$_4$(^{13}CO) (**1b**) with unlabeled CO in THF–acetone at 25 °C was carried out under 30, 60, and 275 psi of CO, with each reaction being thermally quenched at regular intervals to follow its progress by CMR. In each of these reactions after ca. 100 min (complete reaction) the ^{13}CO cis/trans label ratio was 2.0 ± 0.1. A typical CMR spectrum is shown in Figure 3. At very early conversion the ratio was always somewhat higher than 2.0, presumably owing to some short-lived mechanism resulting in CO site scrambling. Oxygen was ruled out as a cause of this phenomenon since incorporation of ca. 5% partial pressure of O$_2$ had no effect on the ratio at low or high conversion. Similarly, extra precautions to exclude light and repeated freeze–thaw degassing of the reaction solution before the admission of CO had no effect on the ratio. In any event, since the cis/trans ratio converged on 2.0 as conversion increased, the randomizing path must terminate very early in the reaction and account for only a very small percentage of the product.[24]

Scheme II



Hexamethylphosphoramide (HMPA) was also employed as solvent, in which case the reaction was carried out in an autoclave under 30 psi of CO at 25 °C. The CMR was again measured in THF–acetone whereupon the cis/trans ratio was found to be 3.05, corresponding to total site randomization of the label in intermediate **3**. This reaction had the curious property of generating a deep yellow solution, but careful examination of **1** and HMPA in CDCl$_3$ in the absence of CO by ^{1}H NMR revealed no evidence for a solvated intermediate. Labeled acyl **2** with an initial cis/trans ratio of 2.25 after dissolution in HMPA for 5 h under 30 psi of CO followed by the usual workup revealed a final ratio of 2.23, indicating that there is no randomization of product label under the insertion reaction conditions.

Insertion of CO was also induced by using mtpb for the express reason that this ligand has been reported to yield *cis*-**4** which is stable to cis/trans isomerization, unlike most other phosphines and phosphites which ultimately afford isomeric mixtures.[25] When being carried out on cis-labeled **1b** in THF–acetone, the reaction yielded labeled **4** wherein the site distribution was $\beta/\gamma/\delta = 2/0/1$. The yield was rather low when HMPA was employed as solvent, but the label ratio in isolated **4** was identical with that from reaction in THF–acetone. Typical CMR spectra are shown in Figure 4.

Discussion

There are several idealized limiting geometries which are available for the intermediate (MeCO)Mn(CO)$_4$ (**3**), namely, square pyramids **3a** and **3b** and trigonal bipyramids **3c** and **3d**. It is well established that leaving and/or entering of the sixth ligand to form and/or quench intermediate **3** is always kinetically cis.[26] Thus, while **3b** may play an important role in cis/trans isomerization of (MeCO)Mn(CO)$_4$L, it is unlikely to be present in significant quantity during the CO insertion. Intermediates **3c** and **3d** could be significant or predominant if, for example, they were attacked by incoming ligand only in the equatorial plane and were attacked only cis to X in that plane in the case of **3c**. Alternatively, rapid interconversion between **3a** and **3b** or between **3a** and **3c** would give a product ^{13}CO label distribution the same as though **3c** or **3d** were the only intermediate, even though all reaction might occur via **3a**.

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[21] Aime, S.; Gervasio, G.; Milone, L.; Rosenberg, E. *Transition Met. Chem.* **1976**, *1*, 177.

[22] Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *80*, C31.

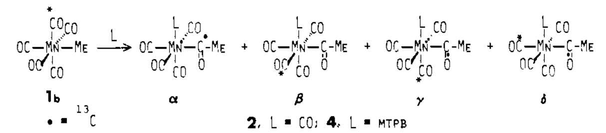
[23] Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1.

[24] It was not possible to follow the insertion rate quantitatively because MeMn(CO)$_5$ usually partially precipitated at the low temperature required to obtain good CMR spectra, and times required for heating and cooling the sample between −115 and 25 °C were of the same order as the half-life of the reaction.

[25] Green, M.; Wood D. C. *J. Am. Chem. Soc.* **1966**, *88*, 4106.

[26] Reference 16 and references therein.

Table I. Positions of ^{13}CO Label in Products of the Reaction



intermediate	L CO^a $(\beta + \gamma)/\delta$	 $P(OCH_2)_3CCH_3$ $(\beta + \gamma)/\delta$
alkyl migration		
square pyramid	2/1	2/0/1
trigonal bipyramid, axial acyl	2/1	2/1/1.5
trigonal bipyramid, radial acyl	5/1	2/0.5/0.5
CO migration		
square pyramid	all/0	2/1/0
trigonal bipyramid, axial acyl	all/0	2/1/0
trigonal bipyramid, radial acyl	5/1	2/0.5/0.5
stereorandom intermediate	3/1	2/1/1

[a] Normalized to $\delta = 1$. [b] Normalized to $\beta = 2$.

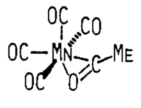
Each of the above structural possibilities, or combinations thereof, for the intermediate(s) leads to a particular ^{13}CO label distribution in product **2** or **4** when **1b** is employed as starting material. These distributions are listed in the Table I. For example, Scheme II shows the path for intermediate **3d** formed directly with methyl migration via a least motion path. When incoming ligand, L, is ^{12}CO, the result is indistinguishable from that of intermediate **3a** formed via methyl migration. This emphasizes the fact that the CO-induced insertion experiment is ambiguous concerning the geometry of the reaction intermediate. These possibilities may be differentiated, however, by the use of a suitable incoming ligand in place of ^{12}CO to trap **3**. This gives information on the location of the ^{13}CO in three rather than in just two sites. As stated above, the result of this experiment was a label ratio $\beta/\gamma/\delta$ of 2/0/1 consistent only with intermediate **3a**.

The kinetics of this insertion reaction studied in ether solvents have been reported to be first order in **1** and zero order in [CO] above 15 atm of CO pressure,[2b] consistent with $k_{-1} \ll k_2[CO]$ in eq 1. At this pressure, [CO] may be estimated in ether type solvents (essentially the same in ether–acetone) to be ca. 0.2 M,[27] which means that $k_{-1} \ll 0.2k_2$. Dobson and others[28] have reported that rates of ligation of $M^\circ L_5$ (M = Cr, Mo, W) species are surprisingly insensitive to the nature of the attacking ligand and that the bimolecular rate constants range from 3×10^6 to 2×10^8 L mol^{-1} s^{-1}. With the assumption of a value of 10^8 for our k_2 here, $k_{-1} < \sim 10^7$. Therefore the lifetime of intermediate **3** is $> 10^{-7}$ s and the ΔG for its disappearance is $> \sim 8$ kcal/mol. Since no isomerization of the square-pyramidal intermediate **3a** is detectable, $k_{isom} < \sim 10^{-1}\ k_{-1}$ and a reasonable lower limit for ΔG can be taken to be ~9 kcal/mol.

Since our results conclusively demonstrate that the thermally generated intermediate **3** at ambient temperature is of C_s symmetry (**3a**) with a $\Delta G^\ddagger \geq 9$ kcal/mol for rearrangement, it is interesting to note the recent report that **3**, when generated photochemically at 12 °K, is probably of quasi-C_{2v} symmetry (**3c**) and is "fluxional" at that temperature.[15] A C_{2v} d^6 species would probably be a triplet.[17] It could reasonably form via a photochemical path and could be trapped as a metastable species in the matrix. Our observation of a barrier to rearrangement of ca. 9 kcal/mol (the assumption is usually made that $\Delta S^\ddagger \approx 0$) would mean that any fluxionality at 12 K must be a photochemical reaction or that a C_{2v} triplet would have a $\Delta G^\ddagger <$ ca. 1 kcal/mol. Thus, while this work is interesting of itself, it probably has no relevance to ambient-temperature thermal processes.

It has been argued that, since the reaction of **1** with PPh_3 initially leads to *cis*-$(MeCO)Mn(PPh_3)(CO)_4$ with subsequent cis/trans isomerization, there must be two distinct intermediates which interconvert slowly during their lifetime and that the first probably has structure **3a**. This arguement is in error (although the conclusion probably is not) since the data may also be explained by any single intermediate or set of rapidly equilibrating intermediates with the requirements that E_a for trans product formation be greater than E_a for cis product formation, and that product formation be reversible (which it is—ref 2b).

In recent years a number of instances of η^2-acyl bonding have been demonstrated[29] or inferred.[12] The question arises as to whether intermediate **3** might satisfy its coordinative unsaturation by such bonding, as in **5**. Berke and Hoffmann[17] were not able to find any local energy minimum corresponding to **5** in their extended-Hückel calculations; however, our data neither require nor eliminate such a structure, and so in the absence of further information, we assume for now that **5** is not present on the basis of the calculations.



5

Whether intermediate **3** is solvent coordinated and, if so, whether coordination occurs in the insertion transition state or later have been long-standing questions. Certainly solvent effects on rates of insertion demonstrate important solvation in the transition states of most CO insertion reactions,[2] but more recent calculations[17] and experimental data[30] indicate that solvent coordination is probably not important in the transition state. The fact that random **2** is isolated from reaction of **1b** with CO in HMPA while unrandomized **4** is isolated from reaction of **1b** with mtpb in the same solvent indicates that sufficiently nucleophilic solvents[31] can have a profound stereochemical effect on intermediate **3** but that such effects may be circumvented by the use of a nucleophilic enough trapping ligand. We suspect that HMPA competes favorably with CO for coordination to **3** and lengthens the lifetime of **3**. Rapid solvent exchange and/or spin state/geometry interconversions may account for the randomization of ^{13}CO label in **3** under these conditions.

Experimental Section

General Data. Proton magnetic resonance spectra were recorded on Varian Instruments T-60 and XL-100 spectrometers. Carbon magnetic resonance spectra and variable-temperature studies were conducted on the latter instrument. Chemical shifts in ^{13}C spectra were measured relative to solvent peaks and corrected to δ (ppm) referenced to Me_4Si. Infrared spectra were recorded on a Perkin-Elmer 281 spectrometer, typically by using films or Nujol mulls on NaCl plates.

All reactions were carried out in flamed-out glassware under an atmosphere of prepurified nitrogen or in flamed-out, evacuated, and sealed NMR tubes. THF was distilled from a purple solution of benzophenone dianion just before use, and HMPA was distilled from CaH_2 under N_2 atmosphere. For NMR spectra, THF, purified as above, and acetone-d_6 were stored over activated molecular sieves under N_2 and were additionally freeze-thaw degassed just before distillation into the NMR tube on the vacuum line. Carbon monoxide was CP grade purchased from Amweld and was stated to have the following maximum impurities: N_2, 1500 ppm; O_2, 600 ppm; CO_2, 50 ppm; and H_2O, 4.5 ppm. Merck Sharp and Dome supplied 90% ^{13}C CO and 90% ^{13}C NaOAc.

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(27) References 16 and 17 in Casey, C. P.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 1166.

(28) Dobson, G. R.; Rousche, J.-C. *J. Organomet. Chem.* **1979**, *179*, C42 and references therein.

(29) (a) Fachinetti, G.; Floriani, C.; Roselli, A.; Pucci, S. *J. Chem. Soc., Chem. Commun.* **1978**, 269, and references therein. (b) Alt, H. G. *J. Organomet. Chem.* **1977**, *127*, 349. (c) Fagan, J. et al. *J. Am. Chem. Soc.* **1980**, *102*, 5393.

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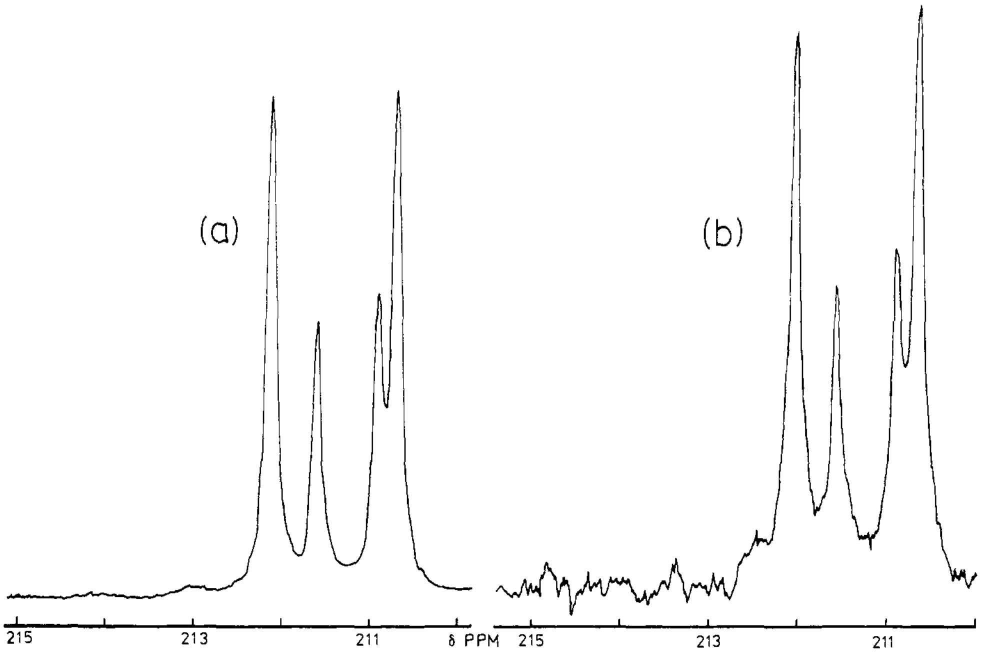

Figure 4. CMR spectra taken at 25.2 MHz in 1/1 THF–acetone-d_6 of (MeCO)Mn(mtpb)(CO)$_4$ (**4**) from reaction of *cis*-MeMn(CO)$_4$(^{13}CO) (**1b**) and mtpb in (a) THF–acetone and (b) HMPA.

The ligand mtpb[32] and standard samples of (Me)Mn(CO)$_5$ (**1**)[33] (MeCO)Mn(CO)$_5$(**2**)[34] and (MeCO)Mn(CO)$_4$(mtpb) (**4**)[25] were all prepared by literature methods.

Preparation of Randomly ^{13}CO-Enriched Materials. A vigorously stirred solution of freshly sublimed Mn$_2$(CO)$_{10}$ (2.0 g, 8.3 mmol) in freeze–thaw degassed toluene (60 mL) under ca. 200 torr of 90% ^{13}C-enriched CO (6 mmol) in a Pyrex flask was irradiated for 5 h with a 275-W sunlamp. Solvent removal left Mn$_2$(CO)$_{10}$ with a maximum of 6% ^{13}C enrichment which was pure enough for subsequent use.

This Mn$_2$(CO)$_{10}$ was used to prepare MeMn(CO)$_5$ (**1a**)[33] and (Me^{12}CO)Mn(CO)$_5$ (**2a**)[34] by published proceedures. In the latter case, diethyl ether was used in place of THF. The CMR spectra of these materials, recorded in 1/1 THF-acetone-d_6 at −115 °C, are shown in parts a and b of Figure 1, respectively.

The known (MeCO)Mn(CO)$_4$(mtpb) (**4**)[25] was prepared in randomly enriched form, **4a**, as follows: freeze–thaw degassed acetone-d_6 (2 mL) and THF (2 mL) were distilled on a vacuum line onto randomly ^{13}CO-enriched **1a** (115 mg, 0.55 mmol) and mtpb (81 mg, 0.55 mmol) in a 12-mm NMR tube. After being sealed, the tube was allowed to warm to ambient temperature, and reaction was complete in ca. 20 min. The NMR spectrum, taken at −115 °C, is shown in Figure 2. ^{1}H NMR and IR spectra corresponded to those published.[25]

Preparation of *cis*-MeMn(CO)$_4$(^{13}CO) (1b). Acetyl chloride was prepared from 90% enriched sodium acetate-1-^{13}C by a standard proceedure,[35] and this was converted to (Me^{13}CO)Mn(CO)$_5$ by a published proceedure,[34] except that ether was used in place of THF. Then (Me^{13}CO)Mn(CO)$_5$ (100 mg, 0.42 mmol) was heated in pentane (10 mL) at reflux for 2 h under an acetone–dry ice condenser. Careful solvent removal at the aspirator pump and sublimation of the residue yielded 65 mg (0.31 mmol) of **1b**: IR (Nujol mull) 2012 (s), 1995 (s), 1978 (s, cis-^{13}CO) cm^{-1}; no band at 1950 cm^{-1} (trans-^{13}CO). The CMR spectrum, taken at −115 °C in THF-acetone-d_6, showed only one peak at δ 213.7, with none visible at all at δ 211.4 (trans-CO).

Carbonylation of *cis*-MeMn(CO)$_4$(^{13}CO) (1b). (a) **In THF–Acetone.** Typically, THF (2 mL) and acetone-d_6 (2 mL) were distilled via a vacuum line onto 80–100 mg (0.38–0.47 mmol) of **1b** in a 12-mm NMR tube. With use of liquid N$_2$, ^{12}CO was condensed into the NMR tube which was then sealed. An estimate of the quantity of CO used was made by simple *PV* calculations. For calculated pressures of up to 100 psi, 1-mm walled tubes were used, while 2-mm walled tubes were used for pressures above this. The sealed NMR tube was placed in a steel pipe which was attached to mechanical rocker, and the sample was allowed to warm to ambient temperature. Progress of the reaction was followed by CMR.[24] A typical CMR spectrum of the (MeCO)Mn(CO)$_5$ product from this reaction is shown in Figure 3. All integrals were checked by repeated calculations of areas using triangulation, a planimeter, and cutting and weighing of the spectral print-out from several different data collections. The ratios were all 2.0 and are believed to be accurate to ±5%.

(b) **In HMPA.** A steel bomb was equipped with a three-way ball joint which allowed access to the interior via a rubber septum. A magnetic stirrer was found to operate through the base of the bomb. A 25-mL flask inside the bomb was charged with **1b** (120 mg, 0.57 mmol), and the vessel was purged by pressuring to 30 psi of CO and then venting, this cycle being executed six times. HMPA (5 mL) was added by syringe via the septum and then 30 psi of CO pressure was maintained for 4 h. Removal of the sample, addition of hexane (10 mL), diethyl ether (5 mL), and water (5 mL), subsequent additional washing of the organic layer by water (3 × 5 mL), drying (Na$_2$SO$_4$), and careful solvent removal at reduced pressure afforded pale yellow solid (MeCO)Mn(CO)$_5$ (87 mg, 0.36 mmol) for which CMR revealed a cis/trans ^{13}CO ratio of 3.05/1.

A control experiment was performed as follows. In exactly the same way as just described, the bomb was charged with a sample of (MeCO)Mn(CO)$_5$ with a cis/trans ^{13}CO ratio of 2.25/1 and 2 mL of HMPA. After 5 h under 30 psi of CO and then workup as above, CMR spectroscopy revealed a cis/trans ^{13}CO ratio for the recovered (MeCO)Mn(CO)$_5$ of 2.23/1.

(c) In **the Presence of O$_2$** in **THF–Acetone.** THF (1.2 mL) and acetone-d_6 (1.2 mL) were distilled onto **1b** (77 mg, 0.36 mmol) in a 12-mm NMR tube with 2-mm walls. Then CO (5.01 mmol) and O$_2$ (0.68 mmol) were condensed into the tube as described under part a, and the tube was sealed. The total internal pressure was calculated to be ~350 psi. The reaction was followed as usual by CMR spectroscopy. At completion, the cis/trans ^{13}CO ratio was 2.00/1.

Reaction of *cis*-MeMn(CO)$_4$(^{13}CO) (1b) with mtpb. (a) **In THF–Acetone-d_6.** Using a proceedure identical with that described above for the randomly labeled material, 0.5 mmol of each **1b** and mtpb in 2 mL of THF and 2 mL of acetone-d_6 formed (MeCO)Mn(mtpb)(CO)$_4$ (**4**) whose CMR specrum is shown in Figure 4a.

(b) **In HMPA.** HMPA (5.0 mL) was distilled on a vacuum line onto **1b** (114 mg, 0.54 mmol) and mtpb (86 mg, 0.58 mmol). After 2.5 h at ambient temperature 5 mL of water was added to this solution and this was extracted (3 × 15 mL) with 1/2 ether–hexane. The combined organic layers were washed (3 × 10-mL) with water, dried (Na$_2$SO$_4$), and evaporated to a white powder. The CMR of this sample in 1/1 THF–acetone-d_6 is shown in Figure 4b.

In both parts a and b the products exhibited CMR peak ratios (as labeled in eq 2) β/γ/δ of 2/0/1.

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