Treatment of **3** with $M(CO)_3(CH_3CN)_3$ (M = Cr, Mo, W) and then with Diazald led to the isolated compounds **7a** (M = Cr), **7b** (M = Mo), and **7c** (M = W), respectively, in high yields. When the nitrosylation was performed by using $NOBF_4$, the yields were rather low. The red-orange chloroform solutions of compounds **7** were stable enough to record their IR and ^1H NMR spectra. The IR spectra of nitrosyl ligands in compounds **7a–c** display absorption frequencies at 1689, 1653, and 1646 cm^{-1}. As in the case of other cyclopentadienyl compounds, the stretching frequencies of nitrosyl ligands decrease as the central metal becomes heavier.[11] Compounds **7** are quite stable under N_2 and soluble in most organic solvents. This reaction demonstrates the incorporation of two transition metals (Mn and chromium triad metals) in a single molecule.

Treatment of **3** with $FeCl_3$ led to the isolation of compound **8**, a heterometallic derivative of ferrocene.[12] The orange crystalline compound **8** is air-stable and thermally decomposed at ca. 188 °C. The ^1H NMR spectrum of **8** in $CDCl_3$ shows the typical pattern for a 1,1′-disubstituted ferrocene system[13] and peaks typical of cyclohexadienyl ring protons. Two slightly deshielded triplets at δ 3.95 (t, J = 1.82 Hz) and 3.75 (t, J = 1.82 Hz) are observed for the cyclopentadienyl ring protons. This reaction demonstrates the incorporation of three transition metals in a single molecule.

Treatment of **2** with $Fe_2(CO)_9$ led to the isolation of compound **9**. Compound **9** is air-stable and thermally decomposed at ca. 217 °C. The IR spectrum of **9** displays a bridging carbonyl frequency at 1760 cm^{-1}. Compound **9** might be used as a useful precursor to a variety of substituted cyclopentadienyliron compounds. This reaction demonstrates the incorporation of four transition metals in a single molecule.

It has been demonstrated that exploring the use of compound **2** or the lithiated compound **3** as a π-coordinating ligand is a synthetically valuable procedure. With the appropriate organometallic reagents, bi- or polynuclear compounds can be easily obtained in reasonable yield.

Acknowledgment. We are grateful to the Korea National Science Foundation (Grant No. 90-03-00-18) for support of this research program. We are also grateful to Dr. Jeong of the KIST for assistance with the X-ray determination.

Registry No. 1, 38834-51-4; **2a**, 142159-64-6; **2b**, 142159-65-7; **4a**, 142159-66-8; **4b**, 142159-67-9; **5a**, 142159-68-0; **5b**, 142159-69-1; **5c**, 142159-70-4; **6a**, 142159-71-5; **6b**, 142159-72-6; **6c**, 142159-73-7; **7a**, 142159-74-8; **7b**, 142159-75-9; **7c**, 142159-76-0; 8, 142159-77-1; 9, 142159-78-2; $BrMn(CO)_5$, 14516-54-2; $BrRe(CO)_5$, 14220-21-4; $Cr(CO)_3(CH_3CN)_3$, 16800-46-7; $Mo(CO)_3(CH_3CN)_3$, 15038-48-9; $W(CO)_3(CH_3CN)_3$, 16800-47-8; $FeCl_3$, 7705-08-0; $HgCl_2$, 7487-94-7; $Fe_2(CO)_9$, 15321-51-4.

Supplementary Material Available: Tables of anisotropic thermal parameters for the non-hydrogen atoms and positional and isotropic thermal parameters for the hydrogen atoms of **5c** (2 pages). Ordering information is given on any current masthead page.

OM920091B

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Effect of an N–N Chelate Ligand on the Insertion Reactions of Carbon Monoxide into a Manganese–Alkyl Bond

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The reduction of *fac*-[Mn(N–N)$(CO)_3$Br] {N–N = 2,2′-bipyridine, bpy, **1a**; 1,10-phenanthroline, phen, **1b**; 1,4-di-*tert*-butyl-1,4-diaza-1,3-butadiene, ^{t}Bu-DAB, **1c**} with sodium amalgam followed by the addition of MeI affords the methyl tricarbonyl derivatives *fac*-[Mn(N–N)$(CO)_3$Me] (N–N = bpy, **2a**; phen, **2b**; ^{t}Bu-DAB, **2c**). Complexes of type **2** react with two-electron donor ligands L to yield the acyl complexes *cis,trans*-[Mn(N–N)$(CO)_2$(L)(COMe)] {N–N = bpy: L = CO, **3a**; CN-^{t}Bu, **3b**; CN-2,6-dimethylphenyl (CN-2,6-Xyl), **3c**; $P(OMe)_3$, **3d**; PEt_3, **3e**. N–N = phen: L = CO, **3f**; CN-^{t}Bu, **3g**. N–N = ^{t}Bu-DAB: L = CO, **3h**; CN-^{t}Bu, **3i**}. The reaction of *fac*-[Mn(bpy)$(CO)_3$Me] (**2a**) with *CO (CO 99% enriched in ^{13}C) affords *cis,trans*-[Mn(bpy)$(CO)_2$(*CO)(COMe)] (**4**), ruling out the formation of any intermediate [Mn(bpy)$(CO)_2$(*CO)(COMe)] (**5a–c**), in which the acyl and the *CO ligands were mutually cis and, therefore, supporting the hypothesis that the incoming ligands enter trans to the acyl group in the formation of complexes of type **3**. The structure of *cis,trans*-[Mn(phen)$(CO)_2$(CN-^{t}Bu)(COMe)] (**3g**) has been determined by X-ray diffraction methods. M = 417.3, orthorhombic, space group $Pn2_1a$ ($Pna2_1$ standard), a = 21.146 (8), b = 10.464 (5), c = 9.183 (5) Å, V = 2032 (2) Å^3, Z = 4, D_c = 1.36 g cm^{-3}. Mo Kα radiation (graphite crystal monochromator, λ = 0.71073 Å), μ = 6.5 cm^{-1}, $F(000)$ = 864, T = 293 K. Final conventional R factor 0.062 for 731 "observed" reflections and 148 parameters.

Introduction

The insertion of carbon monoxide into metal–alkyl bond has been extensively investigated, as acyl complexes are involved in many catalytic and stoichiometric carbonylation and decarbonylation reactions, both in the laboratory and in industry.[1] Thus, the stereochemistry at the metal

Table I. Spectroscopic Data for the New Compounds

compound	ν_{CO},[a] cm^{-1}	^1H NMR,[b] δ (J, Hz)	$^{13}C\{^1H\}$ NMR,[c] δ (J, Hz)
fac-[Mn(bpy)$(CO)_3$Me] (**2a**)	1988 s, 1889 s	9.1, 8.9, 8.0, 7.9 (m, bpy), –0.6 (s, CH_3)	228.9 (s, 2 CO, cis to CH_3),[d] 212.6 (s, CO, trans to CH_3), 153.9, 152.9, 136.7, 125.4, 122.7 (s, bpy)
fac-[Mn(phen)$(CO)_3$Me)] (**2b**)	1990 s, 1895 s	9.4, 8.5, 8.0, 7.4 (m, phen),[c] –0.6 (s, CH_3)	
fac-[Mn(^{t}Bu-DAB)$(CO)_3$Me] (**2c**)	1195 s, 1911 s	8.2 (s, N=CH), 1.6 (s, $C\{CH_3\}_3$), –0.5 (s, $MnCH_3$)	
fac-[Mn(bpy)$(CO)_3$(COMe)] (**3a**)	1999 s, 1910 s, 1889 s, 1598 w	8.5, 7.1, 6.7, 6.1 (m, bpy),[e] 2.8 (s, CH_3)	279.1 (s, $\mathit{C}OCH_3$), 225.1 (s, 2CO, cis to $COCH_3$), 212.6 (s, CO, trans to $COCH_3$), 155.4, 151.9, 136.6, 124.0, 121.9 (s, bpy), 46.6 (s, $CO\mathit{C}H_3$)
fac-[Mn(phen)$(CO)_3$-(COMe)] (**3f**)	2001 s, 1915 s, 1892 s, 1597 w	9.3, 8.3, 7.9, 7.6 (m, phen), 2.4 (s, CH_3)	
fac-[Mn(^{t}Bu-DAB)$(CO)_3$-(COMe)] (**3h**)	1999 s, 1911 s, 1889 s, 1599 w	8.2 (s, N=CH), 2.6 (s, $COCH_3$), 1.3 (s, $C\{CH_3\}_3$)	
cis,trans-[Mn(bpy)$(CO)_2$-(CN-^{t}Bu)(COMe)] (**3b**)	1912 s,[f] 1845 s, 1573 m	9.0, 8.1, 7.8, 7.2 (m, bpy),[c] 2.3 (s, $COCH_3$), 1.2 (s, $C\{CH_3\}_3$)	287.8 (s, $\mathit{C}OCH_3$), 229.9 (s, 2CO, cis to $COCH_3$), 170.5 (s, CN), 156.1, 151.8, 135.4, 123.6, 121.4 (s, bpy), 58.0 (s, $\mathit{C}\{CH_3\}_3$), 46.8 (s, $CO\mathit{C}H_3$), 31.2 (s, $C\{\mathit{C}H_3\}_3$)
cis,trans-[Mn(bpy)$(CO)_2$-(CN-2,6-Xyl)(COMe)] (**3c**)	1916 vs,[f] 1858 s, 1580 w	9.0, 8.1, 7.8, 7.2 (m, bpy),[c] 6.9 (m, $C_6\mathit{H}_3\{CH_3\}_2$), 2.4 (s, $COCH_3$), 2.1 (s, $C_6H_3\{C\mathit{H}_3\}_2$)	289.3 (s, $\mathit{C}OCH_3$),[b] 228.5 (s, 2CO, cis to $COCH_3$), 183.5 (s, CN), 155.7, 151.5, 135.2, 127.5, 123.2 (s, bpy), 133.8, 128.9, 126.5, 121.2 (s, $\mathit{C}_6H_3\{CH_3\}_2$), 47.5 (s, $CO\mathit{C}H_3$), 18.5 (s, $C_6H_3\{\mathit{C}H_3\}_2$)
cis,trans-[Mn(bpy)$(CO)_2$\{P-$(OMe)_3$\}(COMe)] (**3d**)	1912 s, 1844 s, 1582 w	9.0, 7.3, 6.8, 6.3 (m, bpy), 3.2 (d, J_{PH} = 10, $P\{OC\mathit{H}_3\}_3$),[g] 3.0 (s, $COCH_3$)	287.0 (s, $\mathit{C}OCH_3$),[b] 229.0 (s, 2CO, cis to $COCH_3$), 155.9, 152.0, 134.8, 122.7, 121.0 (s, bpy), 50.9 (s, $P\{O\mathit{C}H_3\}_3$), 46.8 (s, $CO\mathit{C}H_3$)
cis,trans-[Mn(bpy)$(CO)_2$-(PEt_3)(COMe)] (**3e**)	1897 s, 1824 s, 1571 w	8.9, 7.4, 6.8, 6.2 (m, bpy),[e] 3.1 (s, $COCH_3$), 1.2 (m, $P\{C\mathit{H}_2CH_3\}_3$), 0.5 (dt, J_{PH} = 13, J_{HH} = 8, $P\{CH_2C\mathit{H}_3\}_3$)[g]	286.4 (s, $\mathit{C}OCH_3$), 232.0 (s, 2CO, cis to $COCH_3$), 156.1, 151.9, 134.8, 123.2, 121.7 (s, bpy), 46.5 (s, $CO\mathit{C}H_3$), 18.1 (d, J_{PC} = 15, $P\{\mathit{C}H_2CH_3\}_3$), 7.4 (s, $P\{CH_2\mathit{C}H_3\}_3$)
cis,trans-[Mn(phen)$(CO)_2$-(CN-^{t}Bu)(COMe)] (**3g**)	1917 s,[f] 1849 s	9.4, 8.2, 7.9, 7.6 (m, phen), 2.4 (s, $COCH_3$), 1.1 (s, $C\{CH_3\}_3$)	288.4 (s, $\mathit{C}OCH_3$), 230.6 (s, 2CO, cis to $COCH_3$), 170.6 (s, CN), 151.5, 147.7, 134.2, 129.8, 127.0, 123.6 (s, phen), 57.5 (s, $\mathit{C}\{CH_3\}_3$), 46.7 (s, $CO\mathit{C}H_3$), 31.2 (s, $C\{\mathit{C}H_3\}_3$)
cis,trans-[Mn(^{t}Bu-DAB)-$(CO)_2$(CN-^{t}Bu)(COMe)] (**3i**)	1924 s,[f] 1866 s	8.3 (s, N=CH), 2.5 (s, $COCH_3$), 1.3 (s, $C\{CH_3\}_3$)	281.5 (s, $\mathit{C}OCH_3$), 234.1 (s, 2CO, cis to $COCH_3$), 172.0 (s, CN), 158.8 (s, N=CH), 61.5 (s, $\mathit{C}\{CH_3\}_3$), 50.1 (s, $CO\mathit{C}H_3$), 35.2 (s, $C\{\mathit{C}H_3\}_3$), 35.1 (s, $C\{CH_3\}_3$)

[a] In CH_2Cl_2. [b] In $CDCl_3$. [c] In CD_2Cl_2. [d] At –30 °C. [e] In C_6D_6. [f] ν_{CN} (CH_2Cl_2): 2109 m, 2069 sh (**3b**); 2074 m (**3c**); 2106 m, 2070 sh (**3g**); 2102 m, 2069 m (**3i**). [g] ^{31}P NMR (C_6D_6): 176.8 (**3d**), 30.3 (**3e**).

and at the carbon atom, the structure of the intermediates, and the effect of the presence of Lewis acids or oxidants, as well as the nature of the solvent, the alkyl group, or the entering ligand, have been intensively studied.[1,2] The influence of the ancillary ligands, however, has received comparatively less attention.

We report here the reactions of alkyl tricarbonyl complexes of manganese containing N–N chelate ligands with two-electron donor ligands to afford acyl tri- or dicarbonyl derivatives. In these reactions, the incoming ligand enters trans to the acyl group, and not cis, as in the carbonylation reactions performed with other alkyl carbonyl complexes of manganese. This anomalous behavior should, therefore, be attributed to the presence of the N–N chelate ligands in the starting alkyl compounds. Although there exist in the literature[3] other cases in which the entering ligand occupies initially a trans position to the acyl group, the examples we present now are particularly noticeable, because the commonly accepted mechanism for carbonylation reactions, according to which the incoming ligand enters cis to the acyl group, is firmly supported by studies carried out with alkyl carbonyl complexes of manganese. A preliminary account of this work has been published.[4]

Results and Discussion

The reduction of *fac*-[Mn(N–N)$(CO)_3$Br] (N–N = bpy, **1a**; phen, **1b**; ^{t}Bu-DAB, **1c**) with Na/Hg in THF, followed by the addition of MeI, affords the alkyl tricarbonyl complexes *fac*-[Mn(N–N)$(CO)_3$Me] (N–N = bpy, **2a**; phen, **2b**; ^{t}Bu-DAB, **2c**), which can be isolated in good yields (Scheme I). Complexes **2** exhibit two ν_{CO} absorptions of

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(2) (a) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87. (b) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. (c) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195. (d) Treichel, P. M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 4, Chapter 29, pp 99–101. (e) Axe, F. U.; Marynick, D. S. *Organometallics* **1987**, *6*, 572. (f) Axe, F. U.; Marynick, D. S. *J. Am. Chem. Soc.* **1988**, *110*, 3728.

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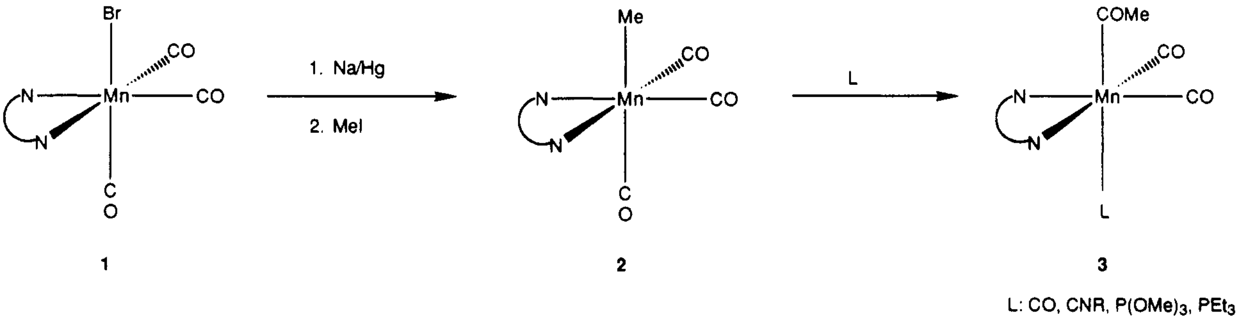
Scheme I. Formation of Alkyl and Acyl Carbonyl Complexes of Manganese(I) Containing N–N Chelate Ligands



similar intensity in their solution infrared spectra (Table I), indicating a fac disposition of the three CO ligands. Accordingly, their ^1H NMR spectra show four groups of signals for the bpy and phen protons and a single peak for the ^tBu-DAB imino protons. The $^{13}C\{^1H\}$ NMR spectrum of **2a** is also consistent with a *fac* geometry.

Monitoring the reduction of **1a** with sodium amalgam by IR spectroscopy reveals the formation of the dimer $[Mn_2(bpy)_2(CO)_6]$[5] (ν_{CO}, THF, cm^{-1} = 1980 m, 1963 w, 1936 s, 1886 m, 1866 m) as the first product, and the subsequent generation of a not well-characterized deep blue species, previously described as the 20-electron complex *fac*-$[Mn(bpy)(CO)_3(THF)]^-$[5] (ν_{CO}, THF, cm^{-1} = 1915 vs, 1824 s, 1784 m, br). In any case, this deep blue species seems to be a carbonylate complex, not only because it reacts with MeI to yield **2a** but also because it generates the hydrido complex *fac*-$[Mn(bpy)(CO)_3H]$ upon addition of NH_4PF_6.[6] A related rhenium hydrido complex, namely, *fac*-$[Re(bpy)(CO)_3H]$, has been obtained from $[Re(bpy)(CO)_3(H_2O)]^+$ by reaction with an excess of $NaBH_4$.[7]

If CO is bubbled through a CH_2Cl_2 solution of complexes **2**, the corresponding acyl derivatives, *fac*-[Mn(N–N)(CO)$_3$(COR)] (N–N = bpy, **3a**; phen, **3f**; ^tBu-DAB, **3h**), are obtained (Scheme I). The complex **3f** had been previously obtained starting from the metallo-β-diketonate complex $\{cis\text{-}[Mn(CO)_4(CH_3CO)_2]_3Al\}$.[8]

Complexes **3a,f,h** show three ν_{CO} bands in the 2000–1800-cm^{-1} range and a third weak absorption at about 1600 cm^{-1}, due to the acyl group. The ^1H NMR methyl resonances shift downfield significatively on going from the alkyl to the acyl derivatives, as they are located at about −0.6 ppm in alkyl tricarbonyl and at about 2.6 ppm in the acyl tricarbonyl complexes. The stereochemistry of the acyl derivatives is further supported by the $^{13}C\{^1H\}$ NMR spectrum of complex **3a**, which shows three carbonyl peaks at 280.9, 225.0, and 212.6 ppm, with a intensity ratio of 1:2:1, which should correspond to the acyl carbonyl and the two CO ligands cis and the CO trans to the acyl ligand, respectively.

The methyl complexes **2** also react at room temperature with isocyanides, phosphites, and phosphines, generating the acyl dicarbonyl complexes *cis,trans*-[Mn(N–N)(CO)$_2$(L)(COMe)] (N–N = bpy: L = CN-^{t}Bu, **3b**; CN-2,6-Xyl, **3c**; P(OMe)$_3$, **3d**; PEt$_3$, **3e**. N–N = phen: L = CN-^{t}Bu, **3g**. N–N = ^{t}Bu-DAB: L = CN-^{t}Bu, **3i**).

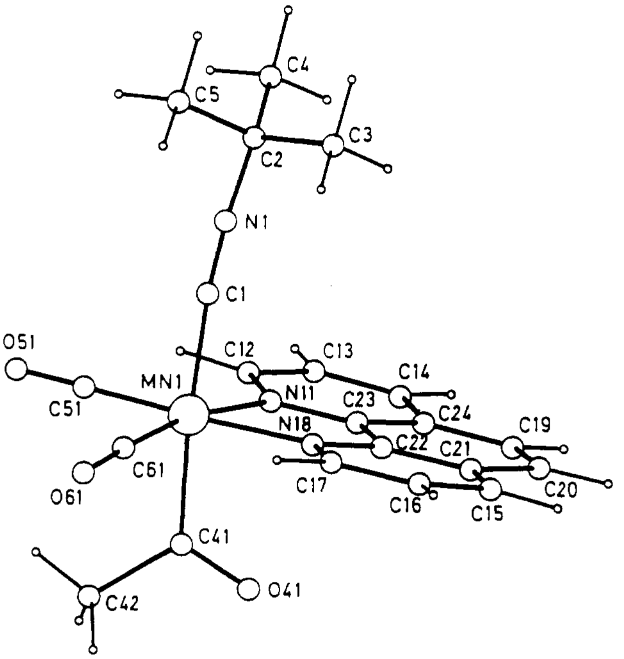


Figure 1. Perspective view of the structure of *cis,trans*-[Mn(phen)(CO)$_2$(CN-^{t}Bu)(COMe)] (**3g**). Selected bond lengths (Å) and angles (deg): Mn–N11 2.07 (2), Mn–N18 2.03 (2), Mn–C1 1.90 (2), Mn–C41 2.05 (2), Mn–C51 1.75 (2), Mn–C61 1.73 (2); N11–Mn–C1 92.0 (8), N18–Mn–C1 87.4 (7), N11–Mn–C41 83.9 (7), N18–Mn–C41 88.7 (7), C1–Mn–C41 174.7 (8), N11–Mn–C61 170.1 (7), N18–Mn–C51 174.8 (8), Mn–C1–N1 175 (2), C2–N1–C1 176 (2).

The proposed stereochemistry for complexes **3b–e,g,i** is in accordance with their spectroscopic data, which are collected in Table I. In particular, the two ν(CO) absorptions in the 2000–1800-cm^{-1} range together with the single $^{13}C\{^1H\}$ NMR resonance at about 230 ppm indicate the existence of two equivalent CO ligands mutually cis, which is only compatible with the proposed cis,trans geometry.

The complexes **3b,g,i** exhibit two ν_{CN} absorptions in their solution infrared spectra, their relative intensities being solvent dependent. Although unusual, there are several precedents of isocyanide complexes that give rise to more IR ν_{CN} bands than expected.[9] This fact can normally be attributed to the existence of two or more isomers or to the presence of several conformers arising from the nonlinearity of the isocyanide ligand; however, it could not always be satisfactorily explained.[9b]

In our case, it seems very improbable the existence of more than one isomer taking into account the following

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[6] The hydride *fac*-[Mn(bpy)(CO)$_3$H] could not be isolated pure, because it is thermally unstable, even in solid state, decomposing to the dimer [Mn$_2$(bpy)$_2$(CO)$_6$]. However, it was spectroscopically characterized: ν_{CO} (THF, cm^{-1}) = 1989 s, 1892 s. ^1H NMR (THF-d_8, −30 °C, δ in ppm) = 9.1, 8.3, 7.9, 7.4 (m, bpy); −3.0 (s, MnH).

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[8] Darst, K. P.; Lukehart, C. M. *Inorg. Chim. Acta* **1978**, *27*, 219.

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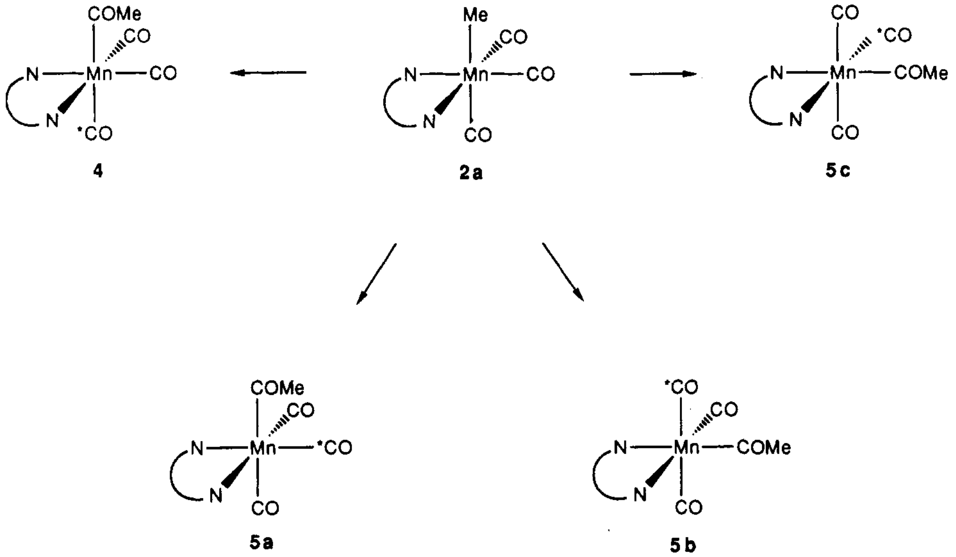
Scheme II. Reaction of [Mn(bpy)(CO)$_3$Me] with *CO. Possible Direct Isomers of [Mn(bpy)(CO)$_2$(*CO)(COMe)]



facts; no any ^{1}H NMR signal of **3b** collapses or splits in deuterated toluene even down to −80 °C; the complex **3i** shows two ν_{CN} bands but only two very sharp ν_{CO} absorptions in hexane; and the closely related complex **3c** exhibits only a single ν_{CN} band.

In order to ascertain the possible existence of conformers, the structure of *cis,trans*-[Mn(phen)(CO)$_2$(CN-^{t}Bu)(COMe)] (**3g**) has been determined by X-ray diffraction methods and it is shown in Figure 1. Although the low quality of the crystal and the disorder found on the *tert*-butyl group limited the number of "observed" reflections, and therefore the standard deviations of angles and bond distances are greater than usual, the obtained data are good enough for our purposes.

According to the spectroscopic data, the coordination around the manganese atom displays a distorted octahedral geometry, with the two CO ligands mutually cis and with the isocyanide ligand occupying a position trans to the acyl group. The coordinated isocyanide ligand C(1)–N(1)–C(2) angle is 176 (2)°, not far from the linearity. Moreover, the corresponding C(1)–N(1)–C(2) angle of the coordinated 2,6-xylyl isocyanide in the closely related complex *cis,trans*-[Mn(bpy)(CO)$_2$(CN-2,6-Xyl)(COMe)] (**3c**) is 172.9 (3)°,[4] but **3c** presents only a single ν_{CN} infrared absorption. Therefore, this seems to be another example in which the origin of the anomalous IR (ν_{CN} region) spectra observed remains obscure.

On the other hand, the formation of complexes *cis,trans*-[Mn(N-N)(CO)$_2$(L)(COMe)] (**3b–e,g,i**) is somewhat unexpected, since, according to the proposed mechanism for the insertion reactions of CO into a metal–alkyl bond,[1] the reaction of *fac*-[Mn(N-N)(CO)$_3$Me] (**2**) with L should give rise to *cis,cis*-[Mn(N-N)(CO)$_2$(L)(COMe)] instead of the observed cis,trans isomers **3b–e,g,i**.

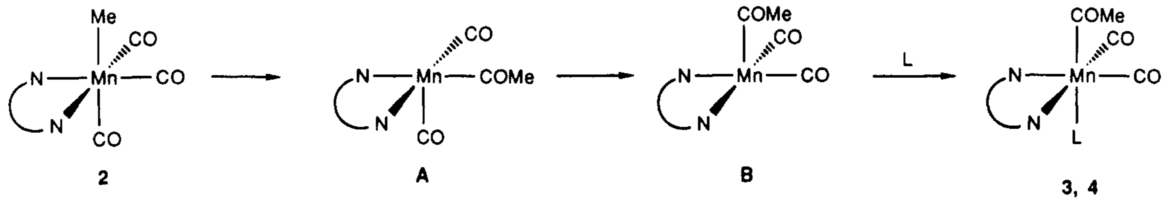
The formation of **3b–e,g,i** could be eventually explained if it is assumed that complexes *cis,cis*-[Mn(N-N)(CO)$_2$(L)(COMe)] are formed in the first reaction step and then they isomerize to the more stable compounds **3b–e,g,i**. In order to verify this hypothesis, the reaction of *fac*-[Mn(bpy)(CO)$_3$Me] (**2a**) with 4-fold excess of P(OMe)$_3$ was carried out at −40 °C in an NMR tube, but *cis,trans*-[Mn(bpy)(CO)$_2${P(OMe)$_3$}(COMe)] (**3d**) was the only complex containing P(OMe)$_3$ detected by ^{31}P{^{1}H} NMR spectroscopy.

Moreover, **2a** reacts with *CO (CO 99% enriched in ^{13}C) to give *cis,trans*-[Mn(bpy)(CO)$_2$(*CO)(COMe)] (**4**), as is evidenced by its ^{13}C{^{1}H} NMR spectrum (Figure 2). The obtainment of **4** rules out the formation of any possible intermediate [Mn(bpy)(CO)$_2$(*CO)(COMe)] (**5a–c** in Scheme II), in which the *CO and the acyl ligands were mutually cis. In fact, since the complexes **5a–c** are not observed, they should isomerize into **4**; however, if the isomerization mechanism were intramolecular, they would give rise to **4** but also to **5a**, which is not detected. On the other hand, if the isomerization mechanism were intermolecular, as the reaction that takes place under *CO atmosphere, **5a–c** would originate considerable amounts of [Mn(bpy)(CO)(*CO)$_2$(COMe)], which is not the case.

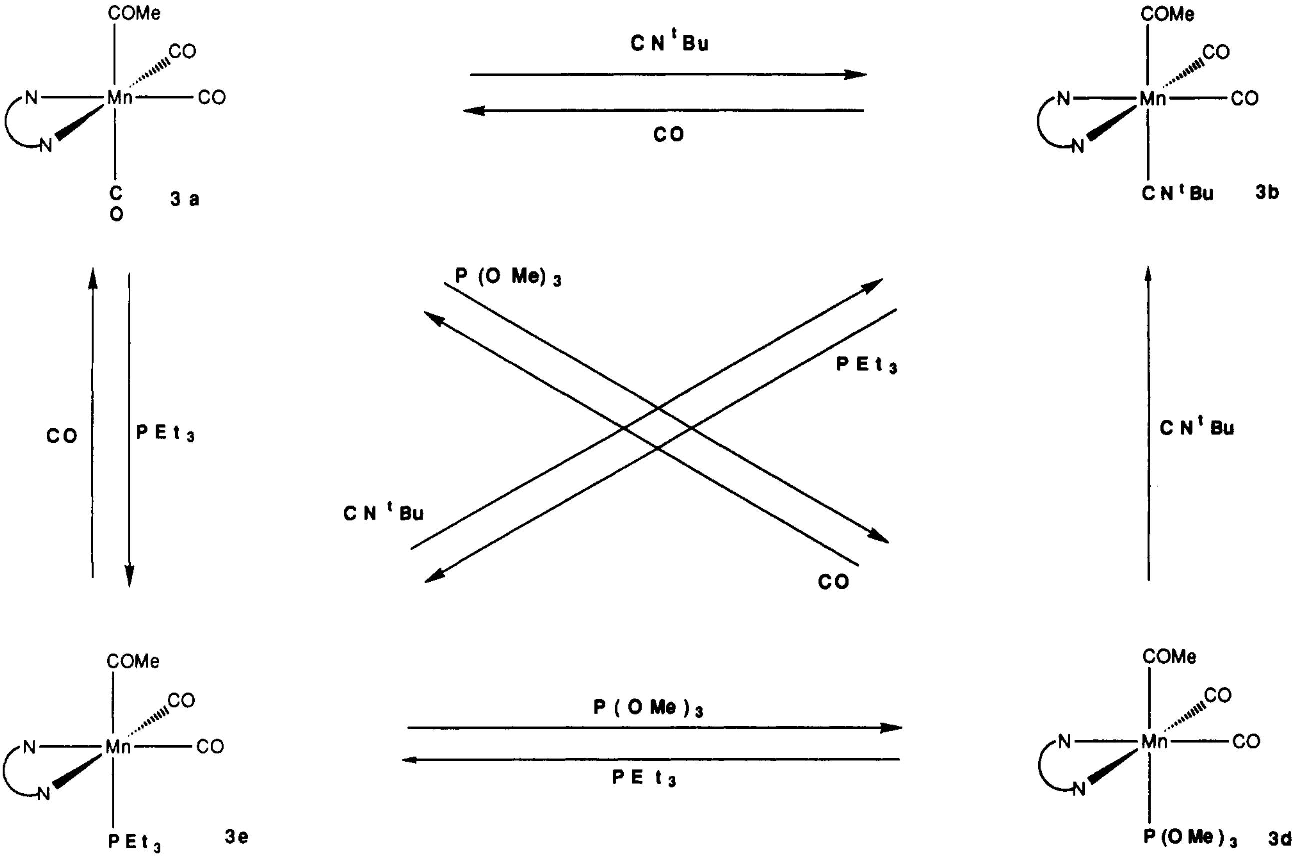
Figure 2. ^{13}C NMR spectrum of [Mn(bpy)(CO)$_2$(*CO)(COMe)] (**4**) in the CO range (CD$_2$Cl$_2$, −30 °C): δ 279.1 (s, COCH$_3$), 225.2 (s, 2CO, cis to COCH$_3$), 213.0 (s, *CO, trans to COCH$_3$).

The results we have obtained are compatible with any proposed mechanism for CO insertion, namely, methyl migration, actual carbonyl group insertion, or a concerted pathway. Thus, for instance, assuming methyl migration

Scheme III. Possible Mechanism for the Reaction of *fac*-[Mn(N-N)(CO)$_3$Me] (2) with L



Scheme IV. Interconversion of Complexes *cis,trans*-[Mn(bpy)(CO)$_2$(L)(COMe)] (L = CO, 3a; CN-^{t}Bu, 3b; P(OMe)$_3$, 3d; PEt$_3$, 3e)



and square pyramidal intermediates, the incoming ligand L could enter trans to the acyl group as a consequent of isomerization of the initially formed five-coordinate [Mn(N-N)(CO)$_2$(COMe)] (**A** to **B** in Scheme III). In a similar way the other mechanisms could be properly modified to take into account that L enters trans to the acyl group.

Although there exists in the literature other examples in which the entering ligand L occupies initially a trans position to the acyl group,[3] these are the first examples in alkyl complexes of manganese. This is to be emphasized because the proposed mechanism for CO insertion in the metal-alkyl bond, in which it is assumed that L enters cis to the acyl group, is firmly supported by studies carried out mainly in manganese carbonyl complexes.

On the other hand, the complexes *cis,trans*-[Mn(bpy)(CO)$_2$(L)(COMe)] {L = CO, **3a**; CN-^{t}Bu, **3b**; P(OMe)$_3$, **3d**; PEt$_3$, **3e**} can be interconverted into each other under very mild conditions, indicating that in these compounds the acyl group acts as it had a strong trans-labilizing influence. Thus, when the complexes **3a,b,d,e** are allowed to react, in CH_2Cl_2 at room temperature and atmospheric pressure, with a 4-fold excess of a two-electron donor ligand L′ {L′ = CO, CN-^{t}Bu, P(OMe)$_3$, or PEt$_3$; L′ = L}, the ligand L trans to the acyl group is substituted by L′ (see Scheme IV). An exception is [Mn(bpy)(CO)$_2$(CN-^{t}Bu)(COMe)] (**3b**), which does not react with P(OMe)$_3$ even after 5 days (see Scheme IV).

The relationship between an acyl trans-labiling influence (the facility in the replacement of a ligand trans to an acyl group) and a trans-directing effect (according to which the entering ligand occupies a position trans to the acyl group) has been pointed out previously.[10]

It should be pointed out that, although N-N chelates have a strong cis-labilizing effect, only the presence of the bpy ligand does not explain the very mild conditions under which these interconvertions take place. For example, we do not know any example in manganese chemistry in which an isocyanide ligand is replaced by CO at room temperature at atmospheric pressure. Moreover, the substitution of a CO cis to the bpy or phen ligands in fac-tricarbonyl complexes of manganese(I) requires more forcing conditions[11] or the use of a decarbonilating agent such as $ONMe_3$.[12]

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The anomalous behavior we have observed in the reactivity of complexes **2** and **3** should be attributable to a synergic effect between the N–N chelate ligands and the acyl group, since no acyl trans-directing or trans-labilizing influence has been detected in other manganese complexes.

Experimental Section

All reactions were performed under nitrogen atmosphere by using standard schlenk techniques. Solvents were dried and distilled under nitrogen. Petroleum ether was a fraction with bp 62–66 °C. Complexes *fac*-[Mn(N-N)(CO)$_3$Br] (N-N = bpy, phen, ^{t}Bu-DAB; **1a–c**) were prepared as described in the literature.[13] The reactants were obtained from commercial sources and used without further purification. Alumina for column chromatography was deactivated by appropriate addition under nitrogen of deoxigenated water to the commercial material (neutral, activity I). Infrared spectra were recorded on a Perkin-Elmer 1720-X infrared spectrophotometer. For spectral intensities, the abbreviations w, m, s, and vs refer to weak, medium, strong, and very strong, respectively. Proton, carbon, and phosphorus magnetic resonance spectra (NMR) were measured in a Bruker AC-300 instrument at 300.13, 75.47, and 121.49 MHz, respectively. Chemical shifts are referred to internal TMS (^{1}H, ^{13}C) or external 85% H_3PO_4 (^{31}P). Spectral multiplicities are reported as follows: s, singlet; d, doublet; dt, doublet of triplets; m, multiplet. Elemental C, H, N analyses were obtained with a Perkin-Elmer 240-B microanalyzer.

Preparation of *fac*-[Mn(bpy)(CO)$_3$Me] (2a). A solution of *fac*-[Mn(bpy)(CO)$_3$Br] (**1a**) (0.20 g, 0.53 mmol), in THF (30 mL), was stirred with sodium amalgam (12.2 g, 0.5%) for 1 h at room temperature. The resulting blue-violet solution was transferred to a schlenk flask containing an excess of MeI (1 mL, 16 mmol), turning the mixture red and cloudy (because of the precipitation of NaI). After evaporation of the solvent and the excess of MeI, the product was extracted from the residue with CH_2Cl_2. After filtration of the resulting solution, addition of petroleum ether, and concentration, the product was obtained as a red solid (0.10 g, 61%). Anal. Calcd for $C_{14}H_{11}MnN_2O_3$ (**2a**): C, 54.21; H, 3.57; N, 9.03. Found: C, 54.37; H, 3.72; N, 9.10.

The complexes **2b,c** were prepared in a similar way. Anal. Calcd for $C_{16}H_{11}MnN_2O_3$ (**2b**, red solid, 55%): C, 57.50; H, 3.32; N, 8.38. Found: C, 57.29; H, 3.22; N, 8.35.

Anal. Calcd for $C_{14}H_{23}MnN_2O_3$ (**2c**, red solid, 56%): C, 52.18; H, 7.19; N, 8.69. Found: C, 52.34; H, 7.28; N, 8.75.

Preparation of *fac*-[Mn(bpy)(CO)$_3$(COMe)] (3a). Carbon monoxide was bubbled through a solution of *fac*-[Mn(bpy)-(CO)$_3$Me] (**2a**) (0.10 g, 0.32 mmol) in CH_2Cl_2 (30 mL) until the IR spectrum of the mixture evidenced the disappearance of the starting complex (about 30 min). After addition of petroleum ether the solvents were evaporated to afford the acyl compound as a red garnet solid (95 mg, 87%). Anal. Calcd for $C_{15}H_{11}MnN_2O_4$ (**3a**): C, 53.27; H, 3.28; N, 8.28. Found: C, 53.45; H, 3.26; N, 8.18.

The complexes **3f,h** were obtained following a similar procedure. Anal. Calcd for $C_{17}H_{11}MnN_2O_4$ (**3f**, red solid, 80%): C, 56.37; H, 3.06; N, 7.73. Found: C, 56.59; H, 3.12; N, 7.65.

Anal. Calcd for $C_{15}H_{23}MnN_2O_4$ (**3h**, red solid, 65%): C, 51.43; H, 6.62; N, 8.00. Found: C, 51.22; H, 6.58; N, 7.94.

Preparation of *cis,trans*-[Mn(bpy)(CO)$_2$(CN-^{t}Bu)-(COMe)] (3b). CN-^{t}Bu (0.11 mL, 0.96 mmol, d = 0.736 g/mL) was added to a solution of *fac*-[Mn(bipy)(CO)$_3$Me] (**2a**) (0.10 g, 0.32 mmol) in CH_2Cl_2 (30 mL) and the resulting mixture was stirred at room temperature for 2 h. After removing the solvent, the residue was washed with petroleum ether (3 × 5 mL) to eliminate the excess of isocyanide. Recrystallization from CH_2Cl_2/petroleum ether at -20 °C gave **3b** as violet crystals (87 mg, 75%). Anal. Calcd for $C_{19}H_{20}MnN_3O_3$ (**3b**): C, 58.02; H, 5.12; N, 10.68. Found: C, 57.81; H, 5.08; N, 10.63.

The other acyl dicarbonyl complexes, **3c–e,g,i**, were synthesized by following the same procedure described for **3b**. Complexes **3c–e** required, however, that the CH_2Cl_2 solutions containing the products were filtered through an alumina column (neutral, Brockman activity IV, 2,5 × 8 cm) before the recrystallization.

Anal. Calcd for $C_{23}H_{20}MnN_3O_3$ (**3c**, violet solid, 69%): C, 62.59; H, 4.57; N, 9.52. Found: C, 62.79; H, 4.49; N, 9.46.

Anal. Calcd for $C_{17}H_{20}MnN_2O_6P$ (**3d**, violet solid, 62%): C, 47.02; H, 4.64; N, 6.45. Found: C, 46.85; H, 4.63; N, 6.51.

Anal. Calcd for $C_{20}H_{26}MnN_2O_3P$ (**3e**, violet solid, 64%): C, 56.08; H, 6.12; N, 6.54. Found: C, 56.11; H, 6.08; N, 6.48.

Anal. Calcd for $C_{21}H_{20}MnN_3O_3$ (**3g**, violet solid, 68%): C, 60.44; H, 4.83; N, 10.07. Found: C, 60.21; H, 4.80; N, 9.99.

Anal. Calcd for $C_{19}H_{32}MnN_3O_3$ (**3i**, violet solid, 70%): C, 56.29; H, 7.95; N, 10.36. Found: C, 56.51; H, 8.03; N, 10.26.

X-ray Data Collection, Structure Determination, and Refinement for the Complex *cis,trans*-[Mn(phen)(CO)$_2$-(CN-^{t}Bu)(COMe)] (3g). Violet crystal were obtained: 0.20 × 0.16 × 0.06 mm size; Mo Kα graphite monochromated radiation, Enraf-nonius CAD-4 single-crystal diffractometer. Unit cell dimensions were determined from the angular settings of 25 reflections, 5° < θ <10°. Space group $Pn2_1a$ ($Pna2_1$ Standard) from systematic absences and structure determination. 4143 reflections were measured within the hkl range (−25,0,0) to (25,12,10) and 0° < θ < 25°. ω–2θ scan technique with a variable scan speed and maximum scan time of 60 s per reflection was used. The intensity was checked by monitoring three standard reflections every 60 min. Final drift corrections were between 1.00 and 1.02. On all reflections profile analyses were performed.[14,15] Empirical absorption corection was applied, using ψ scans,[16] with correction factors from 0.96 to 1.00. Symmetry equivalent reflections were averaged, $R_{int} = \sum(I - \langle I \rangle)/\sum I = 0.11$, resulting in 1889 *unique* reflections of which only 731 were observed with $I > 1.5\sigma(I)$. Lorentz and polarization corections were applied and data reduced to $|F_o|$ values. The structure was solved by Patterson using the program SHELX86[17] and Fourier synthesis. Isotropic least-squares refinement, using SHELX76,[18] converged to $R = 0.086$. At this stage additional empirical absorption correction was applied using DIFABS,[19] resulting in a further decrease of R to 0.073 and with correction factors from 0.45 to 1.00. Anisotropic refinements followed by a difference Fourier synthesis allowed the location of some hydrogen atoms, the rest were geometrically placed, and all were refined riding on their parent atoms. Some non-hydrogen atoms, namely, Mn, N(1), N(11), N(18), and C(3–5), were anisotropically refined.

The final agreement factors were $R = 0.062$ and $R_w = 0.068$ for the 731 *observed* reflections and 148 parameters; this low reflection/parameter ratio ~5, in part due to the disorder found on the *tert*-butyl group, led to rather high standard deviations on the structural calculations. The minimized function was $\sum w(F_o - F_c)^2$, with $w = 1/[\sigma^2(F_o) + 0.00025F_o^2]$ and $\sigma(F_o)$ from counting statistics. The maximum shift in esd ratio in the last full-matrix least-squares cycle was less than 0.02. The final difference Fourier map showed no peaks higher than 0.43 e/Å^3 or deeper than −0.55 e/Å^3. Atomic scattering factors were taken from Internatinal Tables for X-Ray Crystallography.[20] The plot was made with PLUTO.[21] Geometrical calculations were made with PARST.[22] All calculations were made on a MicroVax 3300 computer at the Scientific Computer Center of the University of Oviedo.

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Registry No. **1a**, 38173-71-6; **1b**, 56811-95-1; **1c**, 70749-13-2; **2a**, 136182-90-6; **2b**, 141753-30-2; **2c**, 141753-31-3; **3a**, 136182-94-0; **3b**, 141753-35-7; **3c**, 136182-93-9; **3d**, 136182-91-7; **3e**, 136182-92-8; **3f**, 141753-33-5; **3g**, 141753-36-8; **3h**, 141753-34-6; **3i**, 141753-37-9; **4**, 136182-95-1; $[Mn_2(bpy)_2(CO)_6]$, 128927-36-6; *fac*-$[Mn(bpy)(CO)_3(THF)]^-$, 141753-32-4; CN-^{t}Bu, 7188-38-7; CN-2,6-Xyl, 2769-71-3; $P(OMe)_3$, 121-45-9; PEt_3, 554-70-1; *fac*-$[Mn(bpy)(CO)_3H]$, 141753-38-0.

Supplementary Material Available: Tables of structural data, positional and thermal parameters, bond lengths and bond angles, anisotropic temperature factors, hydrogen atom parameters, torsion angles, and least-squares planes (9 pages). Ordering information is given on any current masthead page.

OM910657G

Palladium(II)-Catalyzed Exchange and Isomerization Reactions. 15.[1] Kinetics and Stereochemistry of the Isomerization of 2-(Methyl-d_3)-4-methyl-1,1,1,5,5,5-hexafluoro-3-penten-2-ol in Aqueous Solution Catalyzed by $PdCl_4^{2-}$ at High Chloride Concentrations

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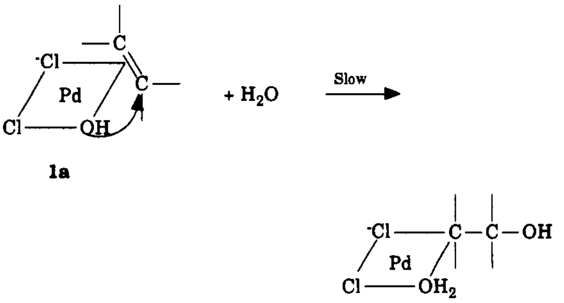
The isomerization of 2-(methyl-d_3)-4-methyl-1,1,1,5,5,5-hexafluoro-3-penten-2-ol (**2a**) into an equilibrium mixture of **2a** and 2-methyl-4-(methyl-d_3)-1,1,1,5,5,5-hexafluoro-3-penten-2-ol (**2b**) in aqueous solution was studied by ^1H and ^2H NMR spectroscopy under conditions of high chloride (>2.0 M) concentration used previously in the presence of $CuCl_2$ to determine the stereochemistry of hydroxypalladation. The rate expression under these conditions is rate = $k_i[PdCl_4^{2-}][\mathbf{2a}]/[Cl^-]$, with $k_i = 1.1 \times 10^{-3}\ s^{-1}$. This rate expression at high chloride concentrations is identical to the rate expression found for the nonoxidative isomerization of allyl alcohol under the same reaction conditions and is consistent with an equilibrium π-complex formation followed by trans attack of water to give the oxypalladation intermediate, which reverses the process to give exchange. The fact that the attack is from outside the coordination sphere of the palladium(II) explains the single-chloride inhibition. Stereochemical studies were conducted with chiral (*E*)-**2a**. The observed result was the formation of chiral **2b** with the same configuration as the initial **2a** but with the *Z* geometric configuration. This result is also consistent only with trans hydroxypalladation; thus, both the kinetic and stereochemical studies give the same result. This result also agrees with earlier stereochemical studies at high chloride concentrations which used quite a different technique. The important point is that since the exchange stereochemical studies carried out in the previous paper of this series showed the hydroxypalladation to have stereochemistry opposite from that at high chloride concentrations, the previous stereochemical studies at high [Cl$^-$] are *not* a valid indication of the stereochemistry at low [Cl$^-$].

Introduction

The fact that most catalytic reactions involve several steps makes the interpretation of kinetic data in terms of mechanisms ambiguous in such complicated systems. For instance, in the Wacker process for the oxidation of olefins to aldehydes and ketones in aqueous solution by $PdCl_4^{2-}$, the kinetic rate expression, given by eq 1, can be interpreted in several ways.

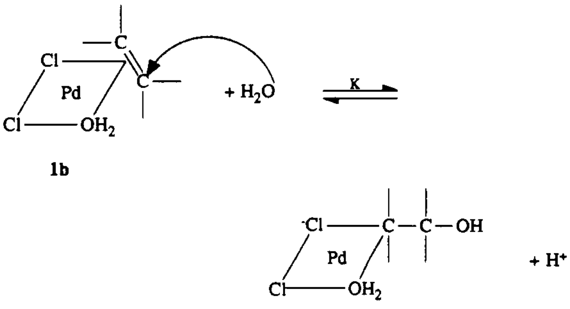
$$\text{rate} = \frac{k[PdCl_4^{2-}][\text{olefin}]}{[H^+][Cl^-]^2} \qquad (1)$$

Although most workers agree the $[Cl^-]^2$ inhibition results from displacement of two chlorides by olefin and water in the Pd(II) coordination sphere in rapid preequilibria, there is considerable disagreement as to the source of the proton inhibition. The kinetics are consistent with (a) cis addition by coordinated hydroxyl in the slow step (eq 2) or (b) trans attack by external water in an equilibrium step (eq 3).[2] In the second mechanism, decomposition of the adduct is rate-determining.



1a

(2)



1b

(3)

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[1] Part 14: Francis, J. W.; Henry, P. M. *Organometallics* **1991**, *10*, 3498.