Syntheses, Characterization, and Nucleophilic Substitution–Addition Reactions of Manganese–Oxapentadienyl Compounds. Structural Characterization of (η^5-CH$_2$CHCHCOCH$_3$)Mn(CO)$_2$L (L = CO, PPh$_3$) and the First Isolation of Novel η^5-1-Azapentadienyl Complexes

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Manganese–η^5-oxapentadienyl compounds (η^5-CH$_2$CHCHCOR)Mn(CO)$_3$ (R = OCH$_3$ (**3a**), CH$_3$ (**3b**)) are produced from a refluxing cyclohexane solution of Mn(CO)$_5$(η^1-CH$_2$CH=CHCOR) (R = OCH$_3$ (**1a**), CH$_3$ (**1b**)). In a heated cyclohexane solution, **3a** and **3b** react with 1 equiv of tertiary phosphine to afford (η^5-CH$_2$CHCHCOR)Mn(CO)$_2$(PR$_3$) (PR$_3$ = PMe$_3$, PPh$_3$; R = OMe, Me). This phosphine substitution reaction proceeds via an η^3-allyl species, and the intermediates (η^3-CH$_2$CHCHCOOCH$_3$)Mn(CO)$_3$P (P = PMe$_3$, PPh$_3$) have been isolated and fully characterized. In polar solvents, **3a** takes up one solvent molecule to form (η^3-CH$_2$CHCHCOOCH$_3$)Mn(CO)$_3$L (L = CH$_3$CN (**6a**), acetone (**6b**), THF (**6c**)). In CHCl$_3$ or CH$_2$Cl$_2$, **6b** and **6c** readily lose the ligating solvent and rearrange to **3a**. In the presence of BF$_3$·(C$_2$H$_5$)$_2$O, **3b** reacts with the primary amine RNH$_2$ at -78 °C to yield the first isolable 1-azapentadienyl complexes (η^5-CH$_2$CHCHC(CH$_3$)NR)Mn(CO)$_3$ (R = (CH$_3$)$_2$CH (**7a**), (CH$_3$)$_3$C (**7b**)). For **7a** and **7b**, spectroscopic data in support of η^5 metal–ligand bonding are presented. For the manganese 1-oxa- and 1-azapentadienyl complexes above, oscillation of the metal–ligand bond has been observed by variable-temperature ^{1}H, ^{13}C, and ^{31}P NMR spectra. The molecular structures of **3b** and its PPh$_3$-substitution derivative (**4d**) have been determined by X-ray diffraction to have the following parameters: for **3b**, space group $P2_1/c$, $a = 9.378$ (6) Å, $b = 6.060$ (4) Å, $c = 16.244$ (9) Å, $\beta = 91.08$ (5)°, $Z = 4$, $R = 0.0326$, and $R_w = 0.0369$; for **4d**, space group $P2_1/c$, $a = 10.0814$ (11) Å, $b = 10.0560$ (11) Å, $c = 43.892$ (5) Å, $\beta = 93.182$ (9)°, $Z = 8$, $R = 0.045$, and $R_w = 0.031$.

Introduction

There have been a few reports of transition-metal-acyclic 1-oxapentadienyl compounds.[1] In previous work, it has been shown that compounds of this class were commonly obtained as unexpected products from various chemical reactions. For instance, 1-phenylpropanone condenses with MeMn(CO)$_5$ to give a manganese–oxapentadienyl complex in 9% yield,[1a,b] a rhenium complex (I) was obtained from the reaction between (PPh$_3$)$_2$ReH$_7$

I, L = PPh$_3$ II
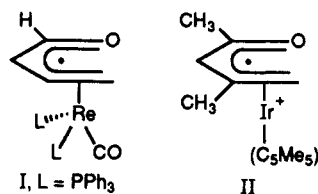
and furan under reflux in THF in the presence of 3,3-dimethyl-1-butene,[1c] and a cationic iridium oxadienyl complex (II) was obtained from the reaction between [Ir(η^5-C$_5$Me$_5$)(Me$_2$CO)](PF$_6$)$_2$ and mesityl oxide.[1d] Until the present, no general synthetic methods have been found applicable, and the chemistry of these complexes remains virtually unexplored. In recent years, there has been a rapid development in the chemistry of transition-metal-pentadienyl complexes. One interesting feature of compounds in this class is the variety of structural modes in the metal–ligand bonding, viz. η^1, η^3, and η^5 configurations.[2] More recent studies on metal–η^5-pentadienyl complexes have revealed an interesting reactivity pattern: the η^5-pentadienyl group is capable of undergoing a coupling reaction with metal or small molecules to form metalla-

benzene,[3] 1,3,7,9-decatetraene,[4] and [5 + 1] acetylation adducts.[5] It is of great interest to investigate the related chemistry of the oxapentadienyl group, particularly when one of the dienyl carbons is substituted with an oxygen atom, which may greatly influence the intrinsic nature of the ligand. In this paper, we report a convenient synthesis of manganese–oxapentadienyl complexes. The present studies center on (i) the structural characterization of the metal–oxapentadienyl bonding, (ii) two possible nucleophilic addition sites occurring at the manganese center as well as the metal-bound ketonic carbon, and (iii) the feasibility of the $\eta^5 \rightleftharpoons \eta^3$ interconversion of the ligand. In addition, isolation of the first 1-azapentadienyl complex and variable-temperature NMR data to illustrate oscillation of the metal–oxapentadienyl and metal–azapentadienyl bonds are also presented.

Results and Discussion

Synthesis of η^5-Oxapentadienyl Complexes. Previously, we have described the use of 1-halopenta-2,4-diene for the synthesis of manganese iron and molybdenum η^1-, η^3-, and η^5-dienyl compounds.[6] We therefore aim for a

(1) A few 1-oxapentadienyl complexes have been reported; see: (a) Bennett, R. L.; Bruce, R. L. *Aust. J. Chem.* **1978**, *28*, 1141. (b) Green, M.; Hancock, R. J. *J. Chem. Soc. A* **1968**, 109. (c) Baudry, D.; Daran, J. C.; Dromzee, Y.; Felkin, H.; Jeannin, Y.; Zakrzewski, J. *J. Chem. Soc., Chem. Commun.* **1983**, 813. (d) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Organomet. Chem.* **1977**, *134*, 319.

(2) For a leading review on transition-metal acyclic pentadienyl complexes, see: Ernst, R. D. *Chem. Rev.* **1988**, *88*, 1251 and references therein.

(3) Kralik, M. S.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1987**, *6*, 2612.

(4) (a) Bleeke, J. R.; Kotyk, J. J. *Organometallics* **1983**, *2*, 1263. (b) Geiger, W. E.; Bennett, T.; Lane, G. A.; Salzer, A.; Rheingold, A. L. *Organometallics* **1986**, *5*, 1352.

(5) Kralik, M. S.; Hutchinson, J. P.; Ernst, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 8296.

[†] National Tsing Hua University.
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Scheme I. Synthetic Route Leading to Manganese–η⁵-Oxapentadienyl Complexes

Figure 1. ORTEP drawing of $(\eta^5\text{-CH}_2\text{CHCHCOCMe})\text{Mn(CO)}_3$.
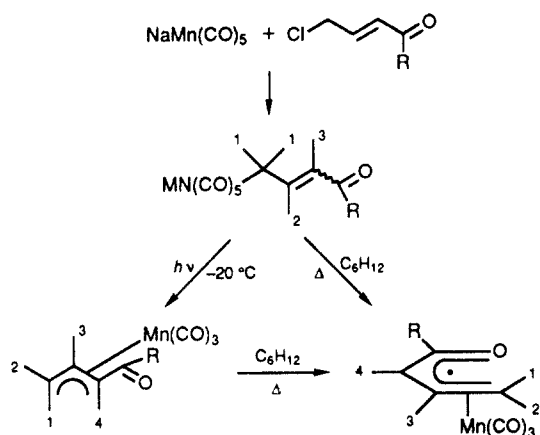
synthesis of metal–oxapentadienyl compounds involving methyl 4-chloro-2-butenoate and 5-chloro-3-penten-2-one. The two halides were prepared according to the reported procedures.[7] As depicted in Scheme I, the reactions between NaMn(CO)_5 and the halides produced Mn(CO)_5-$(\eta^1\text{-CH}_2\text{CH}=\text{CHCOR})$ (R = OCH_3 (1a), CH_3 (1b)). The two η^1 compounds were stable enough to isolate in ca. 60–70% yield and could be fully characterized. Their ^1H and ^{13}C NMR chemical shifts indicate that an η^1 structure is adopted. Both Z and E isomers were detectable for both 1a and 1b with E:Z ratios of ca. 65:35 and 70:30, respectively. The E isomer has the characteristic coupling constant J_{23} = 15.0–16.0 Hz, whereas the Z isomer has the corresponding coupling constant J_{23} = 10.5–11.0 Hz.
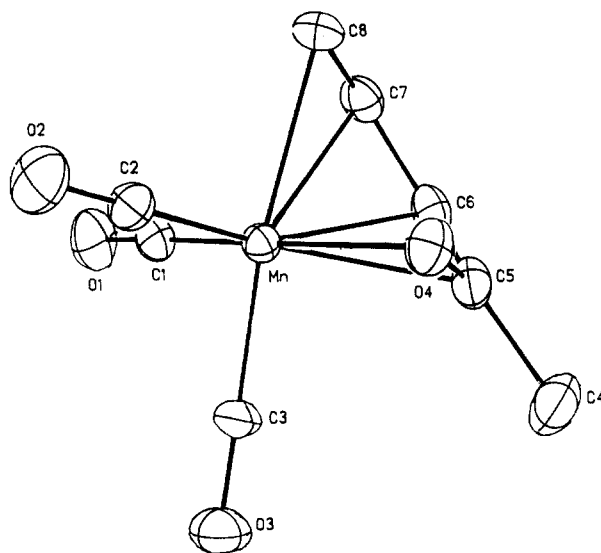
In the particular case of 1a, photolysis of its ether solution at –20 °C produced $(syn\text{-}\eta^3\text{-CH}_2\text{CHCHCOOCH}_3)$-$\text{Mn(CO)}_4$ (2a). No η^5-oxapentadienyl complexes were formed during prolonged irradiation. The ^1H NMR and IR spectra indicate that the ligand adopts an η^3-allyl configuration. The syn configuration was indicated by the coupling constants J_{13} = 13.0 Hz and J_{34} = 10.5 Hz. The $\nu(\text{CO})$ absorption of the unbound ester group of 2a is observed at 1705 (s) cm^{-1}.

Thermolysis of 1a and 1b in refluxing cyclohexane formed the η^5-oxapentadienyl complexes (η^5-$\text{CH}_2\text{CHCHCOR})\text{Mn(CO)}_3$ (R = OCH_3 (3a), CH_3 (3b)), and the yield was quantitative. An alternative route for the synthesis of 3a is the thermolysis of its η^3-allyl complex in refluxing cyclohexane as depicted in Scheme I.

Characterization of η⁵-Oxapentadienyl Complexes. Compounds 3a and 3b are highly volatile and readily sublimable. The U-shaped configuration is shown by t he coupling constant J_{34} = 6.8 Hz. The proton H^4 resonates at δ 3.2–4.0 ppm, about 1.0–1.5 ppm downfield relative to that of 2a. The ketonic carbon atom of the η^5-oxadienyl ligand resonates at 170–180 ppm. The IR spectra show a drastic decrease in both the intensity and frequency of the $\nu(\text{CO})$ absorptions of the ketone group. In 3a, $\nu(\text{CO})$ appears as a weak absorption at 1556 cm^{-1}, whereas the corresponding $\nu(\text{CO})$ absorption of 3b is observed at 1506 cm^{-1}. The $\nu(\text{CO})$ absorption of the three carbonyl groups of 3a were observed at 2036 (vs), 1958 (vs), and 1933 (vs) cm^{-1}, and those of 3b were at 2041 (vs), 1968 (vs), and 1939 (vs) cm^{-1}. These values exceed those of $(\eta^5\text{-C}_5\text{H}_7)\text{Mn(CO)}_3$[8]

Table I. Bond Lengths (Å) and Angles (deg) for 3b

Mn–O(2)	2.075 (3)	Mn–C(1)	1.779 (4)
Mn–C(2)	1.803 (4)	Mn–C(3)	1.792 (4)
Mn–C(5)	2.213 (4)	Mn–C(6)	2.126 (4)
Mn–C(7)	2.124 (4)	Mn–C(8)	2.213 (4)
O(1)–C(1)	1.159 (5)	O(2)–C(2)	1.131 (5)
O(3)–C(3)	1.142 (5)	O(4)–C(5)	1.279 (4)
C(4)–C(5)	1.492 (6)	C(5)–C(6)	1.403 (5)
C(6)–C(7)	1.420 (5)	C(7)–C(8)	1.349 (5)
O(4)–Mn–C(1)	169.2 (1)	O(4)–Mn–C(2)	98.1 (1)
C(1)–Mn–C(2)	92.4 (2)	O(4)–Mn–C(3)	93.5 (1)
C(1)–Mn–C(3)	88.0 (2)	C(2)–Mn–C(3)	94.0 (2)
O(4)–Mn–C(5)	34.5 (1)	C(1)–Mn–C(5)	135.1 (2)
C(2)–Mn–C(5)	132.4 (2)	C(3)–Mn–C(5)	87.3 (1)
O(4)–Mn–C(6)	66.4 (1)	C(1)–Mn–C(6)	102.9 (2)
C(2)–Mn–C(6)	154.1 (2)	C(3)–Mn–C(6)	107.1 (1)
C(5)–Mn–C(6)	37.7 (1)	O(4)–Mn–C(7)	83.7 (1)
C(1)–Mn–C(7)	88.7 (2)	C(2)–Mn–C(7)	122.4 (2)
C(3)–Mn–C(7)	143.6 (1)	C(5)–Mn–C(7)	70.1 (1)
C(6)–Mn–C(7)	39.0 (1)	O(4)–Mn–C(8)	77.1 (1)
C(1)–Mn–C(8)	101.1 (2)	C(2)–Mn–C(8)	87.7 (2)
C(3)–Mn–C(8)	170.7 (2)	C(5)–Mn–C(8)	84.8 (1)
C(6)–Mn–C(8)	69.1 (1)	C(7)–Mn–C(8)	36.2 (1)
Mn–O(4)–C(5)	78.6 (2)	Mn–C(1)–O(1)	178.3 (3)
Mn–C(2)–O(2)	179.4 (3)	Mn–C(3)–O(3)	177.8 (3)
Mn–C(5)–O(4)	66.8 (2)	Mn–C(5)–C(4)	137.0 (3)
O(4)–C(5)–C(4)	119.4 (3)	Mn–C(5)–C(6)	67.8 (2)
O(4)–C(5)–C(6)	118.1 (3)	C(4)–C(5)–C(6)	122.5 (3)
Mn–C(6)–C(5)	74.5 (2)	Mn–C(6)–C(7)	70.4 (2)
C(5)–C(6)–C(7)	123.9 (3)	Mn–C(7)–C(6)	70.6 (2)
Mn–C(7)–C(8)	75.5 (2)	C(6)–C(7)–C(8)	125.4 (4)
Mn–C(8)–C(7)	68.3 (2)		

(2016 (vs), 1957 (s), 1937 (vs) cm^{-1}). These data are in accord with an electron-withdrawing power expected to be stronger for the oxapentadienyl group than for the pentadienyl group. According to the IR data above, the increasing trend in π-acidity can be arranged as follows: $\eta^5\text{-CH}_2\text{CHCHCOCH}_3 > \eta^5\text{-CH}_2\text{CHCHCOOCH}_3 > \eta^5\text{-C}_5\text{H}_7$.

Crystal Structure of 3b. Previous structural characterization of metal–oxadienyl complexes is very scarce and is limited only to $(\eta^5\text{-CH}_2\text{CHCHCOH})\text{Re(CO)(PPh}_3)_2$.[1c] In order to acquire more structural information, we have undertaken an X-ray diffraction study of 3b. Single crystals suitable for crystallographic study were grown from a saturated hexane solution at –40 °C. The ORTEP drawing (Figure 1) confirms that the molecule has an η^5-oxadienyl ligand. The relative orientation of the oxa-

(6) (a) Lee, G.-H.; Peng, S.-M.; Lush, S.-F.; Liao, M.-Y.; Liu, R.-S. *Organometallics* **1987**, *6*, 2094. (b) Lee, G.-H.; Peng, S.-M.; Lush, S.-F.; Muo, D.; Liu, R. S. *Ibid.* **1988**, *7*, 1155. (c) Lee, G.-H.; Peng, S.-M.; Liu, F.-C.; Mu, D.; Liu, R.-S. *Ibid.* **1989**, *8*, 402. (d) Lee, T.-W.; Liu, R.-S. *Ibid.* **1988**, *7*, 878.

(7) House, H. O.; John, V. K.; Frank, J. A. *J. Org. Chem.* **1964**, *29*, 3327.

(8) Seyferth, D.; Goldman, E. W.; Pornet, J. *J. Organomet. Chem.* **1981**, *208*, 189.

Scheme II

Chart I

endo-syn-η^3　　　exo-syn-η^3

endo-anti-η^3　　　exo-anti-η^3

ers. The conformers are distinguisable by their different phosphine orientations with respect to the oxapentadienyl fragment. At elevated temperatures, these conformers underwent mutual exchange and the dynamic process has been established by variable ^{1}H and ^{31}P NMR spectra (see Scheme II).

The phosphine substitution in Scheme II proceeds via η^3-allyl intermediates that are isolable and can be well characterized. In the particular case of **3a**, addition of 1 equiv of R_3P to a rapidly stirred cyclohexane solution gradually formed the yellow precipitates of (η^3-$CH_2CHCHCOOCH_3$)$Mn(CO)_3(PR_3)$ (PR$_3$ = PMe$_3$ (**5a**), PPh$_3$ (**5b**)). Rapid crystallization from hexane/ether at -20 °C afforded needlelike crystals. Compound **5a** exists as three isomers distinguished by their proton NMR spectra. The three isomers have identical ν(CO) absorptions, and likely their structural variations arise from the relative orientation of the allyl group (endo or exo) as well as the position (syn or anti) of the allyl ester substituent. The structures depicted in Chart I are proposed on the basis of the stereochemistry of complexes of the type (η^3-allyl)$Mn(CO)_3(PR_3)$.[12] In **5a**, the relative ratio of the three isomers is 45 (syn-η^3):32 (anti-η^3):22 (syn-η^3) as calculated from the ^{1}H NMR integrals. Assignments of the syn and anti isomers were determined from the magnitude of the coupling constant J_{34}, which is 6.5–7.0 Hz for the anti isomer and 9.0–10.0 Hz for the syn-η^3 isomer. Clarification of these conformational structures for the three observed species is not possible at present. In **5b**, only one anti isomer was detected by ^{1}H NMR spectra. The isomers observed for **5a** and **5b** appear to be in thermodynamic equilibrium, as no further change in the product distribution was observed over a prolonged period.

Molecular Structure of 4d. An X-ray diffraction study of single crystals of **4d** grown from a saturated hexane solution has been performed. The ORTEP drawing is shown in Figure 2; selected bond distances and angles are given in Table II. There are two independent molecules (racemers) in the unit cell. For each molecule, the PPh$_3$ group points toward the middle of the oxadienyl mouth whereas the two carbonyls point toward the two edges of the ligand. Notably, the alignment of C(3A-(3B))–Mn–P(1A(1B)) nearly bisects the oxadienyl group. Similar to **3b**, each racemer has C–C bond lengths of the oxadienyl group that range from 1.36 to 1.42 Å. In comparison with **3b**, the ketonic CO bond lengths C(4A)–O(1A) (1.319 (8) Å) and C(4B)–O(1B) (1.307 (9) Å) are significantly longer than the corresponding value (1.279 (4) Å) of **3b**. This condition reflects the degree of metal electron transfer into the ketonic CO(π^*) empty orbital, more significant for **4d** than for **3b**. The oxapentadienyl ligands form a least-squares plane within 0.035 (8) Å. The methyl

dienyl ligand with respect to the $Mn(CO)_3$ fragment is identical with those observed for (η^5-2,4-dien-1-yl)$Mn(CO)_3$ complexes,[9] in which one carbonyl points toward the open mouth of the oxadienyl group and the other two carbonyls point toward the two edges of the ligand. The bond lengths are given in Table I. Notably, the C(7)–C(8) bond (1.349 (5) Å) is shorter than the C(5)–C(6) (1.403 (5) Å) and C(6)–C(7) (1.420 (5) Å) bonds. The C(5)–O(4) bond (1.279 (4) Å) is significantly longer than a normal C=O double bond (1.21 Å); this increase reflects a significant degree of metal electron transfer into the empty ligand orbital including the ketonic CO(π^*) orbital. The oxapentadienyl ligand is quite planar to within 0.16 Å. The methyl group bends up (away from the metal) and deviates from the plane by 0.11 Å (4.54°). This feature is quite distinct from those commonly observed for the metalpentadienyl complexes;[2] in the latter, the methyl groups generally bend down so that the p orbitals of the dienyl carbons point directly toward the metal center to strengthen the bonding. In **3b**, the nonideal methyl orientation is imposed by the intrinsic short Mn–O(4) bond (2.073 (5) Å). This torsion angle somewhat weakens the metal–ketone bond, which probably contributes to the feasible $\eta^5 \rightarrow \eta^3$ ligand slippage (vide infra). Consequently, the O(4) atom tilts down toward the manganese atom with a deviation of 0.14 Å (6.45°) from the plane. The observed Mn–O(4) distance is comparable to the values commonly found for the Mn(1)–O(4) σ bond (1.95–2.10 Å) from several crystallographic data.[10] Within the metal–oxadienyl bonding, the average Mn–C distances 2.16 ± 0.04 Å are similar to the reported values (2.20 ± 0.06 Å) for the related pentadienyl complex (η^5-1-(C$_6$H$_5$O$_2$)C$_5$H$_6$)$Mn(CO)_3$.[11]

Reaction with Phosphine Ligands. One interesting feature in the chemistry of **3a** and **3b** is the facile $\eta^5 \rightleftarrows \eta^3$ ligand transformation. One representative case is the phosphine substitution reaction. In refluxing cyclohexane, **3a** and **3b** reacted with 1 equiv of tertiary phosphine to form (η^5-$CH_2CHCHCOR$)$Mn(CO)_2(PR_3)$ (R = OCH_3, PR$_3$ = PMe$_3$ (**4a**), PPh$_3$ (**4b**); R = CH_3, PR$_3$ = PMe$_3$ (**4c**), PPh$_3$ (**4d**)). The compounds were stable to air and were fully characterized by elemental analyses and IR and ^{1}H and ^{31}P NMR spectra. Spectroscopic data are consistent with the proposed structure. Interestingly, more than one conformer are recognizable for **4b** and **4d**. The ^{1}H and ^{31}P NMR spectra in $CD_3C_6D_5$ at -60 °C reveal that **4b** exists as two conformers whereas **4d** exists as three conformers. The remaining **4a** and **4c** were present as single conform-

(9) Ittel, S. D.; Whitney, J. F.; Chung, Y. K.; Williard, P. G.; Sweigart, D. A. *Organometallics* **1988**, 7, 1323.

(10) (a) Van der Veer, M. C.; Burlitch, J. M. *J. Organomet. Chem.* **1980**, *197*, 357. (b) Andrianov, V. G.; Struchkov, Y. T.; Pyshnoraeva, N. I.; Setkina, V. N.; Kursanov, D. N. *J. Organomet. Chem.* **1981**, *206*, 177.

(11) Barrow, M. J.; Mills, O. S.; Haque, F.; Pauson, P. L. *J. Chem. Soc., Chem. Commun.* **1971**, 1239.

(12) (a) Brisdon, B. H.; Edwards, D. A.; White, J. W.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* **1980**, 2219. (b) Gibson, D. H.; Hsu, W. L.; Ahmed, F. U. *J. Organomet. Chem.* **1981**, *215*, 379.
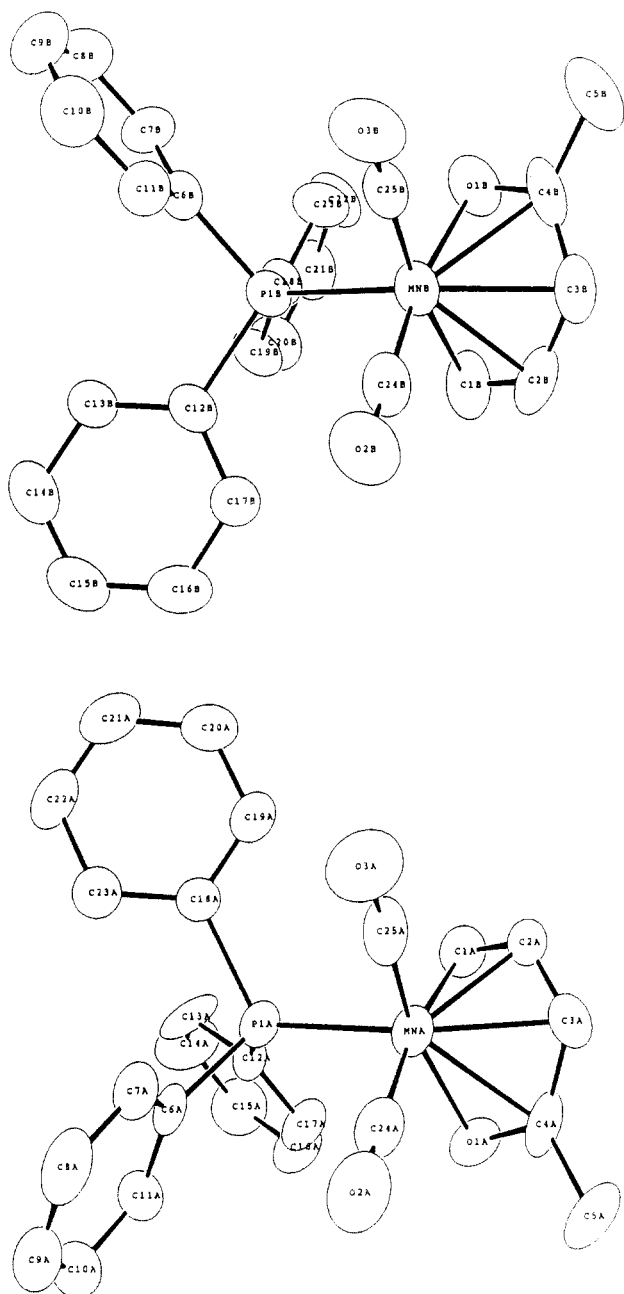
Figure 2. ORTEP drawings of the two racemers of **4d**.

Table II. Selected Bond Distances (Å) and Angles (deg) for 4d

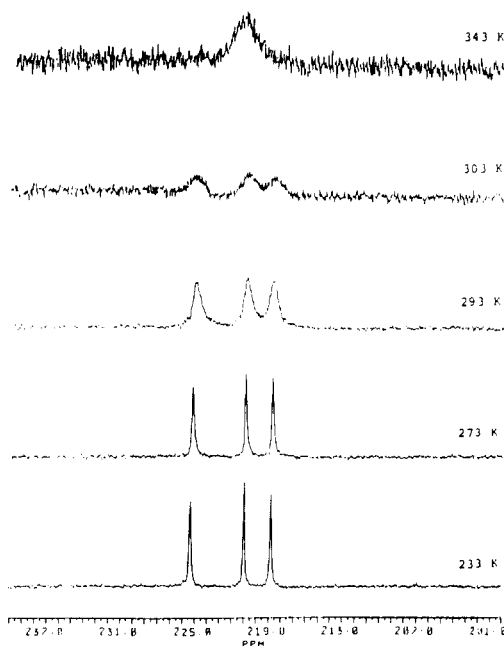| Mn(A)–P(1A)	2.2644 (23)	Mn(B)–P(1B)	2.2681 (23)
Mn(A)–C(1A)	2.265 (7)	Mn(B)–C(1B)	2.255 (8)
Mn(A)–C(2A)	2.129 (6)	Mn(B)–C(2B)	2.130 (7)
Mn(A)–C(3A)	2.134 (7)	Mn(B)–C(3B)	2.122 (7)
Mn(A)–C(4A)	2.189 (7)	Mn(B)–C(4B)	2.208 (7)
Mn(A)–C(24A)	1.803 (7)	Mn(B)–C(24B)	1.764 (7)
Mn(A)–C(25A)	1.748 (7)	Mn(B)–C(25B)	1.793 (7)
Mn(A)–O(1A)	2.107 (4)	Mn(B)–O(1B)	2.098 (5)
P(1A)–C(6A)	1.825 (7)	P(1B)–C(6B)	1.817 (7)
P(1A)–C(12A)	1.848 (7)	P(1B)–C(12B)	1.843 (7)
P(1A)–C(18A)	1.864 (7)	P(1B)–C(18B)	1.835 (7)
C(1A)–C(2A)	1.367 (10)	C(1B)–C(2B)	1.389 (11)
C(2A)–C(3A)	1.399 (10)	C(2B)–C(3B)	1.421 (12)
C(3A)–C(4A)	1.410 (10)	C(3B)–C(4B)	1.395 (11)
C(4A)–C(5A)	1.495 (10)	C(4B)–C(5B)	1.486 (11)
C(4A)–O(1A)	1.319 (8)	C(4B)–O(1B)	1.307 (9)
C(24A)–O(2A)	1.145 (8)	C(24B)–O(2B)	1.158 (9)
C(25A)–O(3A)	1.158 (8)	C(25B)–O(3B)	1.147 (9)
P(1A)–Mn(A)–C(1A)	89.68 (19)	P(1B)–Mn(B)–C(1B)	88.16 (20)
P(1A)–Mn(A)–C(2A)	123.05 (20)	P(1B)–Mn(B)–C(2B)	123.97 (24)
P(1A)–Mn(A)–C(3A)	157.93 (21)	P(1B)–Mn(B)–C(3B)	154.02 (22)
P(1A)–Mn(A)–C(4A)	138.92 (19)	P(1B)–Mn(B)–C(4B)	130.06 (21)
P(1A)–Mn(A)–C(24A)	93.20 (23)	P(1B)–Mn(B)–C(24B)	95.11 (23)
P(1A)–Mn(A)–C(25A)	90.76 (23)	P(1B)–Mn(B)–C(25B)	96.22 (22)
P(1A)–Mn(A)–O(1A)	103.63 (14)	P(1B)–Mn(B)–O(1B)	95.09 (14)
C(1A)–Mn(A)–C(2A)	36.1 (3)	C(1B)–Mn(B)–C(2B)	36.8 (3)
C(1A)–Mn(A)–C(3A)	68.8 (3)	C(1B)–Mn(B)–C(3B)	70.0 (3)
C(1A)–Mn(A)–C(4A)	84.9 (3)	C(1B)–Mn(B)–C(4B)	85.2 (3)
C(1A)–Mn(A)–C(24A)	167.0 (3)	C(1B)–Mn(B)–C(24B)	101.6 (3)
C(1A)–Mn(A)–C(25A)	106.0 (3)	C(1B)–Mn(B)–C(25B)	171.9 (3)
C(1A)–Mn(A)–O(1A)	75.85 (22)	C(1B)–Mn(B)–O(1B)	77.70 (25)
C(2A)–Mn(A)–C(3A)	38.3 (3)	C(2B)–Mn(B)–C(3B)	39.1 (3)
C(2A)–Mn(A)–C(4A)	69.5 (3)	C(2B)–Mn(B)–C(4B)	69.7 (3)
C(2A)–Mn(A)–C(24A)	143.7 (3)	C(2B)–Mn(B)–C(24B)	89.2 (3)
C(2A)–Mn(A)–C(25A)	90.8 (3)	C(2B)–Mn(B)–C(25B)	139.8 (3)
C(2A)–Mn(A)–O(1A)	82.55 (22)	C(2B)–Mn(B)–O(1B)	84.3 (3)
C(3A)–Mn(A)–C(4A)	38.0 (3)	C(3B)–Mn(B)–C(4B)	37.5 (3)
C(3A)–Mn(A)–C(24A)	106.7 (3)	C(3B)–Mn(B)–C(24B)	102.7 (3)
C(3A)–Mn(A)–C(25A)	99.8 (3)	C(3B)–Mn(B)–C(25B)	104.0 (3)
C(3A)–Mn(A)–O(1A)	67.20 (22)	C(3B)–Mn(B)–O(1)	67.32 (25)
C(4A)–Mn(A)–C(24A)	84.6 (3)	C(4B)–Mn(B)–C(24B)	134.7 (3)
C(4A)–Mn(A)–C(25A)	129.9 (3)	C(4B)–Mn(B)–C(25B)	86.8 (3)
C(4A)–Mn(A)–O(1A)	35.69 (21)	C(4B)–Mn(B)–O(1B)	35.22 (23)
C(24A)–Mn(A)–C(25A)	86.6 (3)	C(24B)–Mn(B)–C(25B)	84.8 (3)
C(24A)–Mn(A)–O(1A)	91.2 (3)	C(24B)–Mn(B)–O(1B)	169.7 (3)
C(25A)–Mn(A)–O(1A)	165.6 (3)	C(25B)–Mn(B)–O(1B)	95.1 (3)
Mn(A)–C(24A)–O(2A)	177.0 (6)	Mn(B)–C(24B)–O(2B)	176.0 (7)
Mn(A)–C(25A)–O(3A)	175.6 (7)	Mn(B)–C(25B)–O(3B)	172.2 (7)
Mn(A)–O(1A)–C(4A)	75.5 (3)	Mn(B)–O(1B)–C(4B)	77.0 (4)

Figure 3. Variable-temperature ^{13}C NMR spectra of **3b**.

groups bend up (away from the manganese center) by 0.106 (12) Å (1.1 (9)°) and 0.112 (13) Å (3.6 (10)°) for racemers A and B, respectively. The observed Mn–C(4A) and Mn–C(4B) distances are 2.189 (7) and 2.208 (7) Å, whereas those of Mn–O(1A) and Mn–O(1B) are 2.107 (4) and 2.098 (5) Å, respectively.

Dynamic NMR Studies. One common feature in the metal–pentadienyl complexes is the small barrier in oscillation of the metal–dienyl bond.[2] The process of the metal–oxapentadienyl oscillation has been examined by variable-temperature NMR spectra. At –60 °C, the ^{13}C NMR spectra of **3a** and **3b** are consistent with an asymmetric orientation of the three carbonyl groups observed in the solid-state structure. The ^{13}C NMR spectra of **3b** are depicted in Figure 3. However, with increasing temperatures, the rate of metal–oxadienyl oscillation with respect to the Mn(CO)$_3$ fragment increases. The three nonequivalent CO resonances begin to broaden and coalesce at 70 °C. This process is consistent with a metal–η^5-oxadienyl oscillation either clockwise or counterclockwise. Calculation of $\Delta G^{\ddagger}$ based on the line-shape analysis leads to a value of 15.6 ± 0.4 kcal mol^{-1} for **3a** and 15.8 ± 0.4 kcal mol^{-1} for **3b**.

A similar oscillation process has been observed for **4b** and **4d**. Two conformers in a 92:8 molar ratio were ob-

Scheme III. Interconversion of the Three Conformers of 4d in a Clockwise or Counterclockwise Rotation
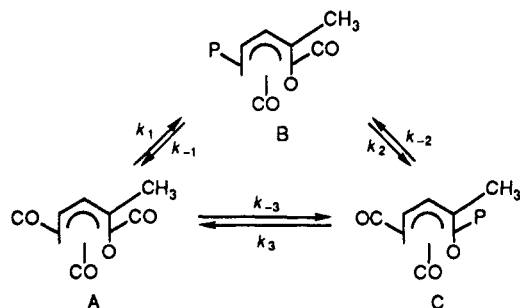
served for **4b**, whereas three conformers (82:16.5:1.5) were observed for **4d** (Figure 4). For **4d**, 2% of the third isomer is detectable only by ^{31}P NMR spectra and its ^{1}H NMR resonances are probably masked by resonances of the other major isomers. For **4b** and **4d**, the most abundant isomer is assignable to A because of its most upfield resonance (Scheme IV). This structural assignment stems from the stereochemistry of $(\eta^5\text{-dienyl})\text{Mn(CO)}_2(\text{P(OCH}_2)_3\text{CEt})$ as well as the ^{31}P NMR assignment.[13] The phosphine situated beneath the open mouth of the dienyl group is expected to encounter the shielding effect of the pentadienyl electrons. The other isomers cannot be assigned at present. Figure 4 shows variable-temperature ^{1}H and ^{31}P NMR spectra for **4d**. With increasing temperatures, owing to the increasing rates, the three phosphine signals (δ 74.1, 63.0, 61.2 ppm) begin to broaden and are averaged to one resonance at 60 °C. Similar behavior is observed in the temperature-dependent ^{1}H NMR spectra of the oxadienyl hydrogens of the two major isomers (Figure 4), which coalesce at 40 °C. The process shows a 180° metal-η^5-ligand rotation either clockwise or counterclockwise. In theory, the average process of the three isomers should involve the three stepwise barriers k_1 (k_{-1}), k_2 (k_{-2}), and k_3 (k_{-3}) and the dynamic process is expected to comprise a two-stage coalescence. The latter is not observable in the present case, owing to the very close chemical shifts at δ 61.2 and 63.0 ppm. However, the observation that the three isomers are averaged to one form in the narrow temperature range 293–333 K implies that the three barriers in interconversion of the three isomers are likely to have comparable magnitudes. Line-shape analysis of the ^{31}P NMR spectra of the two major isomers yields $\Delta G^* =$ 15.6 ± 0.8 kcal mol^{-1} for **4d**. For **4b**, the phosphine ligands of the two isomers resonate at δ 75.2 and 63.88 ppm, respectively, which coalesce at 70 °C. Line-shape analysis of the spectrum yields $\Delta G^* =$ 15.7 ± 0.4 kcal mol^{-1}.

It is of interest to compare the rotational barriers between oxapentadienyl complexes and their pentadienyl analogues. The observed barriers of 15–16 kcal mol^{-1} for $(\eta^5\text{-CH}_2\text{CHCHCOR})\text{Mn(CO)}_2\text{L}$ (L = CO, PPh$_3$; R = OCH$_3$, CH$_3$) are considered significantly high with respect to the normal ranges of 10–14 kcal mol^{-1} common for most metal-pentadienyl complexes containing small ligands.[2] For close relatives of **4b** and **4d**, previous studies have shown that $(\eta^5\text{-dienyl})\text{Mn(CO)}_2(\text{P(OCH}_2)_3\text{CEt})$[13] exists as two conformers:
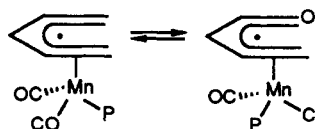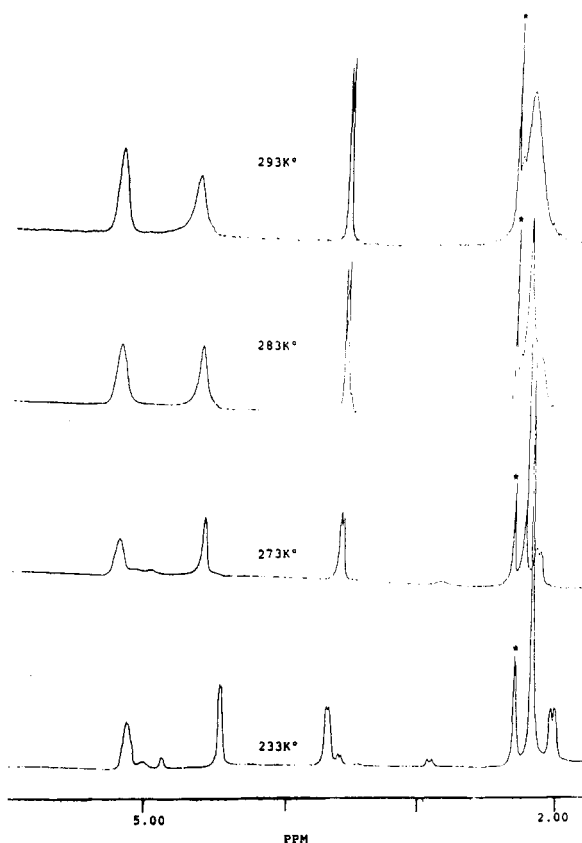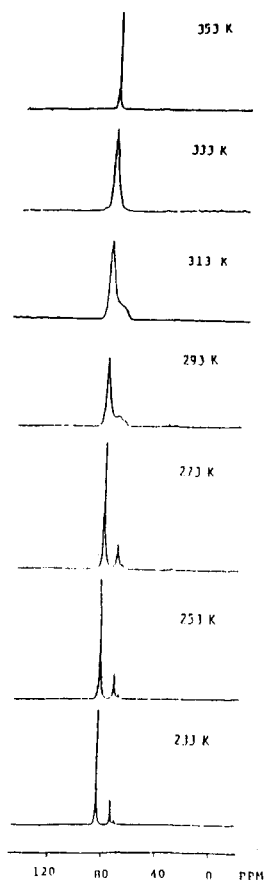

The barriers of interconversion between these two con-

(13) Whitesides, T. H.; Budnik, R. A. *Inorg. Chem.* **1975**, *14*, 664.

Figure 4. Variable-temperature ^{31}P and ^{1}H NMR spectra of **4d**. The peak marked by an asterisk is due to the resonance of toluene-d_8.

formers were ca. 10–11 kcal mol^{-1}. A low barrier is also noted for the related complex $(\eta^5\text{-C}_5\text{H}_7)\text{Mn(CO)}_3$,[8] which exhibits only one carbonyl resonance at 23 °C. These

Scheme IV. Solution Chemistry of 3a in Ligating Solvents

Scheme V. Two Possible Nucleophilic Addition Sites for η⁵-Oxadienyl Compounds
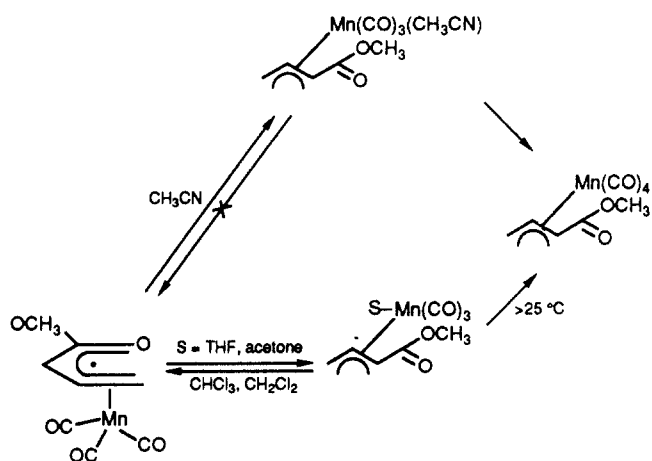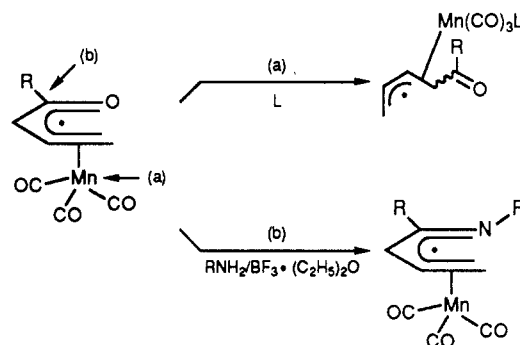

results prove that rotational barriers in manganese-oxapentadienyl complexes are significantly higher than those of their pentadienyl analogues.

Facile $\eta^5 \rightleftarrows \eta^3$ Interconversion. As indicated by the molecular structure of **3b** above, the ketone group of the ligand is not situated in an ideal position for metal-ligand bonding. If this condition represents a general feature of metal-oxadienyl bonding, the $\eta^5 \rightarrow \eta^3$ ligand slippage that yields η^3-allyl derivatives can be regarded as energetically favorable in comparison with that for their pentadienyl analogues.

In CHCl$_3$ and CH$_2$Cl$_2$, complexes **3a** and **3b** retain their η^5-bonding mode. Nevertheless, in acetonitrile, tetrahydrofuran, and acetone at 15 °C, IR spectra of **3a** showed an increasing absorption at 1720 cm^{-1} while the absorption at 1556 (w) cm^{-1} was slowly diminishing. These results suggest that **3a** takes up one solvent molecule to form an η^3-allyl ester complex. In contrast, **3b** still retains its η^5 configuration in these solvents after standing for 24 h. Isolation of these η^3-allyl adducts is readily achieved by removal of solvents to dryness at 0 °C, followed by addition of hexane, to afford yellow crystalline (η^3-CH$_2$CHCHCOOCH$_3$)Mn(CO)$_3$L (L = CH$_3$CN (**6a**), acetone (**6b**), THF (**6c**)). The analytic purity of crystalline **6a–c** is indicated by elemental analyses. Compounds **6a–c** exist in a syn-η^3 geometry as shown from the proton coupling constants. An interesting observation of the syn-η^3 forms of **6b** and **6c** is that in CH$_2$Cl$_2$ or CHCl$_3$ below 15 °C the complexes re-form **3a** nearly quantitatively, whereas **6a** still retains its η^3-CH$_3$CN configuration under these conditions. **6a–c** are thermally unstable, and above 25 °C they slowly decompose to **2a** in mother solvents. Passing CO gas through mother solutions of **6a–c** affords a quantitative yield of **2a**.

3b tends to be more stable as η^5 forms in weakly ligating solvents such as CH$_3$CN, acetone, and THF. This trend is similar to that for the reported metal-oxaallyl complexes CpM(CO)$_3$(η^3-CH$_2$CHRO) (R = OR, R, NR$_2$; M = Mo, W).[14] In the latter, the trend in allyl stability is observed as follows: R = NR$_2$ > alkyl > OR. As discussed in a previous section, the π-acidity of the oxapentadienyl ligand of **3b** is superior to that of **3a** on the basis of a comparison of their infrared data. For **3b**, the efficient metal electron transfer into the vacant π^* orbital of the ketone group tends to stabilize its η^5 structure.

Nucleophilic Addition at the Ketonic Carbon. The reaction chemistry of **3a** and **3b** above, in the kinetic as-

pect, represents a facile nucleophilic addition at the manganese center (Scheme V, path a). Previous studies of the (η^5-NC$_4$H$_4$)Mn(CO)$_3$[15] system revealed that the pyrrolyl group withdraws electrons more powerfully than its cyclopentadienyl analogues. It is rationally expected that the η^5-oxadienyl group probably exerts a similar effect, and this results in increasing acidity at the manganese center. This argument, however, does not preclude an addition site occurring at the ketonic carbon (Scheme V, path b). A representative case is the imination of **3b** in the presence of BF$_3$·(C$_2$H$_5$)$_2$O, which allows isolation of the first 1-azapentadienyl complexes. Until the present, the metal-heteropentadienyl compounds have been limited to only 1-oxa- and 3-boradienyl[16] analogues.

Treatment of a dichloromethane solution of **3b** with 2.3 equiv of BF$_3$·(C$_2$H$_5$)$_2$O at -78 °C, followed by addition of 2.4 equiv of RNH$_2$, affords (η^5-CH$_2$CHCHC(CH$_3$)NR)-Mn(CO)$_3$ (R = (CH$_3$)$_2$CH (**7a**), (CH$_3$)$_3$C (**7b**)) in high yields. In a blank test, BF$_3$·(C$_2$H$_5$)$_2$O is indispensable for initiation of the reaction. An X-ray diffraction study of **7a** and **7b** is hampered by their oily nature. Structural characterization is achievable through elemental analysis and spectroscopic evidence. In mass spectra of **7a** (m/e), the key feature in support of the proposed formula is the presence of the parent ion 263 (M$^+$) and the fragment ions 235 (M$^+$ - CO), 207 (M$^+$ - 2CO), 179 (M$^+$ - 3CO), and 124 (C$_8$H$_{14}$N$^+$). The iminic carbons of **7a** and **7b** resonate in the region δ 169–171 ppm, similar to **3a** and **3b**, which are close to those of the free imine and ketone counterparts.

The ^{1}H NMR and IR spectra are informative in structural interpretations. The U-shaped configuration is indicated by the coupling constant J_{34} = 6–7 Hz. The iminic methyl (N=CCH$_3$) of **7a** and **7b** resonates at δ 0.8–0.9 ppm, nearly 1.20 ppm upfield relative to those of free iminic methyl. In the 1480–1650-cm^{-1} region, IR spectra do not show any absorption assignable to a ν(C=N) band. Indeed, several absorptions appear at 1400–1470 cm^{-1}, which may be due to the coordinated ν(C=N) vibration. This information precludes the metal-(η^3,η^1-azadienyl) structure represented by III. Additional evidence in

III, η^3, η^1 IV, η^5
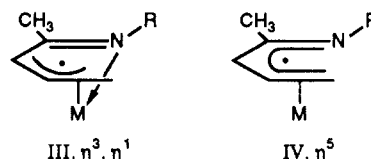
support of the η^5-azadienyl structure IV is provided by the

(14) Burkhardt, E. R.; Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 2022.

(15) (a) Toshi, K. K.; Pauson, P. L.; Qazi, A. R.; Stubbs, W. H. *J. Organomet. Chem.* **1964**, *1*, 471. (b) Pauson, P. L.; Qazi, A. R.; Rockett, B. W. *J. Organomet. Chem.* **1964**, *1*, 477.

(16) Mintz, E. A. *Organometallics* **1988**, *7*, 1788 and references therein.

variable-temperature ^{13}C NMR spectra. At 23 °C, three distinct carbonyl resonances appear in the δ 200–220 ppm region. As the temperature is increased, the three CO signals begin to broaden and coalesce at 85 °C. This dynamic process reveals oscillation of the η^5-azapentadienyl group with respect to the $Mn(CO)_3$ fragment. The calculation of ΔG^* from line-shape analysis gives 16.9 ± 0.4 kcal mol^{-1} for **7a** and 17.3 ± 0.4 kcal mol^{-1} for **7b**. These values are greater than those of oxapentadienyl and pentadienyl complexes.

Attempts to perform imination of **4b** and **4d** were not successful. The electron-donating capability of the tertiary phosphine effectively deactivates the ketonic carbon toward amine attack.

Azapentadienyl complexes **7a** and **7b** are inert to phosphine substitution even under reflux in cyclohexane. This observation is in sharp contrast with the case for their pentadienyl[17] and oxadienyl analogues, in which the phosphine ligand readily promotes $\eta^5 \rightarrow \eta^3$ ligand slippage to initiate ligand substitution. Studies of metal electron density revealed by IR spectra of **7a** and **7b** show $\nu(CO)$ bands of the three carbonyl groups appearing at smaller wavenumbers ($\sim$2010, $\sim$1925, $\sim$1915 cm^{-1}) than those of the pentadienyl and oxadienyl analogues. This observation indicates that the azapentadienyl ligand acts as a π-acceptor as well as a good electron donor. The synergistic effect of these two contributions is expected to strengthen metal–ligand bonding.

Concluding Remarks. Previously there has been little study of metal–oxapentadienyl complexes. The present study is the most extensive examination of metal–oxapentadienyl complexes conducted to date. In the reaction chemistry, we have shown two interesting characteristics of complexes in this class: (i) a feasible $\eta^5 \rightleftarrows \eta^3$ interconversion that is initiated by nucleophilic addition at the manganese center and (ii) nucleophilic attack at the η^5-ketonic carbon that has allowed the first isolation of an 1-azapentadienyl complex. In (i), the scope of the chemistry is more extensive than that of $(\eta^5$-$C_5H_7)Mn(CO)_3$.[17] In the kinetic aspects, we believe that the chemical reactivity in the nucleophilic addition is facilitated by enhancement of the positive charge of manganese contributed by the electronegativity of the oxygen atom.

One notable aspect of the chemistry of these oxapentadienyl ligands is their capability of withdrawing metal electrons. Accordingly, the oxapentadienyl ligand possibly possesses potential in the stabilization of novel low-valent metal species. The use of such ligands to prepare highly reactive low-valent complexes will be further explored.

Summary. A general synthesis of manganese η^5-oxapentadienyl complexes has been described. The crystal structure of compounds of this class reveals a nonideal position of the keton group bonding to the metal because of the steric effect of the intrinsic Mn$_1$–O short bond. The oxapentadienyl compounds undergo phosphine substitution reactions through η^3-allyl intermediates, which are isolable. The oxapentadienyl ligand of **3a** is prone to $\eta^5 \rightarrow \eta^3$ ligand slippage, which is promoted even by weakly ligating solvents. An interesting observation of the monophosphine complex **4d** is the presence of three isomers that are mutually exchangeable. The oxapentadienyl ligand facilitates nucleophilic addition at the metal center in both kinetic and thermodynamic ways. However, in the presence of a strong Lewis acid, nucleophilic addition at the ketonic carbon is operative. The first isolation of a 1-azapentadienyl complex has been reported and a com-

pound fully characterized. For 1-aza-[18] and 1-oxadienyl complexes, oscillation of the η^5 ligand has been established. Measurement of their activation energies in comparison with those of metal–pentadienyl complexes follows the trend 1-aza-pentadienyl > 1-oxa-pentadienyl > 1-pentadienyl complexes.

Experimental Section

All operations were carried out under argon or in a Schlenk apparatus. The solvents benzene, diethyl ether, tetrahydrofuran, and pentane were dried with sodium/benzophenone and distilled before use. Dichloromethane and chloroform were dried over P_2O_5 and distilled. $Mn_2(CO)_{10}$, trimethylphosphine, and triphenylphosphine were obtained from Strem Chemicals and used without further purification. $NaMn(CO)_5$,[19] 5-chloro-3-penten-2-one, and methyl 4-chloro-2-butenoate[7] were prepared according to the procedures in the literature.

All ^1H (400-MHz), ^{13}C (100-MHz), and ^{31}P (40.2-MHz) NMR spectra were obtained on either a JEOL FX-100 or a Bruker AM-400 spectrometer; the ^1H and ^{13}C NMR spectra were referenced to tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer. Microanalyses were performed by the Microanalytic Laboratory at National Taiwan University.

(a) Synthesis of $Mn(CO)_5(\eta^1$-CH_2CH=$CHCOOCH_3)$ (1a). A tetrahydrofuran solution (50 mL) of $NaMn(CO)_5$ (1.67 g, 7.70 mmol) was stirred with methyl 4-chloro-2-butenoate (1.05 g, 7.81 mmol) at –78 °C for 4 h. The solvent was removed under reduced pressure, leaving a red residue. Purification of this residue by two vacuum distillations (4 × 10^{-3} Torr) at 23 °C into a 0 °C cold trap afforded a yellow oil (1.62 g, 5.50 mmol). IR (in CH_2Cl_2): $\nu(CO)$ 2111 (vs), 2056 (vs), 2019 (vs), 1984 (vs), 1965 (vs), 1704 (s) cm^{-1}; $\nu(C$=$C)$ 1593 cm^{-1}. ^1H NMR (CDCl$_3$, 400 MHz): trans isomer (65%), δ 1.61 (d, 2 H, H^1), 3.64 (s, 3 H, OCH$_3$), 5.60 (d, 1 H, H^3), 7.42 (dt, 1 H, H^2), J_{12} = 9.5 Hz, J_{23} = 15.0 Hz; cis isomer (35%), δ 2.31 (d, 2 H, H^1), 3.65 (s, 3 H, OCH$_3$), 5.40 (d, 1 H, H^3), 6.70 (dt, 1 H, H^2), J_{12} = 9.5 Hz, J_{23} = 10.8 Hz. Mass spectrum (12 eV): m/e 294 (M$^+$). Anal. Calcd for $C_{10}H_7MnO_7$: C, 40.82; H, 2.38. Found: C, 40.93; H, 2.37.

(b) Synthesis of $Mn(CO)_5(\eta^1$-CH_2CH=$CHCOCH_3)$ (1b). This complex is prepared similarly by the reaction between $NaMn(CO)_5$ and 5-chloro-3-penten-2-one. The yield is 56%. IR (in CH_2Cl_2): $\nu(CO)$ 2110 (vs), 2015 (vs), 1992 (vs), 1980 (vs), 1688 (s) cm^{-1}. Mass spectrum (12 eV): m/e 278 (M$^+$). ^1H NMR (400 MHz, CDCl$_3$): trans isomer (70%), δ 1.98 (d, 2 H, H^1), 2.05 (s, 3 H, CH$_3$), 5.70 (d, 1 H, H^3), 7.20 (dt, 1 H, H^2), J_{12} = 8.2 Hz, J_{23} = 15.5 Hz; cis isomer (30%), δ 2.10 (s, 3 H, CH$_3$), 2.20 (d, 2 H, H^1), 5.40 (d, 1 H, H^3), 6.50 (d, 1 H, H^2), J_{12} = 9.0 Hz, J_{23} = 10.5 Hz. Anal. Calcd for $C_{10}H_7MnO_6$: C, 43.34; H, 3.15. Found: C, 43.42; H, 3.25.

(c) Synthesis of $Mn(CO)_4(\eta^3$-$CH_2CHCHCOOCH_3)$ (2a). A vacuum-sealed Pyrex tube containing 20 mL of an ether solution of **1a** (0.50 g, 1.70 mmol) was irradiated with a 400-W mercury lamp for 5 h. The solvent was removed in vacuo at 0 °C, leaving an oil. Further vacuum distillation of the oil at 23 °C into a –25 °C cold trap gave the yellow oil of **2a** (0.36 g, 1.36 mmol). IR (in CH_2Cl_2): $\nu(CO)$ 2082 (vs), 2065 (vs), 1992 (vs), 1965 (vs), 1705 (s) cm^{-1}. ^1H NMR (400 MHz, CDCl$_3$): δ 2.22 (d, 1 H, H^1), 2.49 (d, 1 H, H^4), 2.98 (d, 1 H, H^2), 3.74 (s, 3 H, OCH$_3$), 5.64 (ddd, 1 H, H^3), J_{12} = 13.0 Hz, J_{23} = 7.5 Hz, J_{34} = 10.3 Hz. Mass spectrum (12 eV): m/e 266. Anal. Calcd for $C_9H_7MnO_6$: C, 40.60; H, 2.53. Found: C, 40.82; H, 2.74.

(d) Synthesis of $(\eta^5$-$CH_2CHCHCOOCH_3)Mn(CO)_3$ (3a). A cyclohexane solution (30 mL) of **1a** (0.50 g, 1.70 mmol) was heated under reflux for 24 h. The solvent was removed in vacuo and to 0 °C to give a yellow residue. Sublimation of the residue at 40 °C gave yellow crystals of **3a** (0.34 g, 1.45 mmol). IR (cyclohexane): $\nu(CO)$ 2036 (s), 1958 (s), 1933 (s), 1556 (w) cm^{-1}. ^1H NMR (400

(17) Powell, P.; Paz-Sandoval, M. D.; Drew, M. G. B.; Perutz, R. N. *Organometallics* **1984**, *3*, 1026.

(18) For 1-aza- and 2-azallyl complexes, quite a few compounds have been reported; see: Green, M.; Mercer, R. J.; Merton, C. E.; Orpen, A. G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 422 and references therein.
(19) Eisch, J. J.; King, R. B., Eds. *Organometallic Synthesis*; Academic Press: New York, 1965; Vol. 1, p 114.

MHz, CDCl$_3$): δ 1.95 (d, 1 H, H^1), 3.52 (s, 3 H, OCH$_3$), 3.55 (d, 1 H, H^4), 4.92 (d, 1 H, H^2), 5.47 (ddd, 1 H, H^3), J_{12} = 13.5 Hz, J_{23} = 6.0 Hz, J_{34} = 7.4 Hz. ^{13}C NMR (100 MHz, CDCl$_3$): δ 52.45 (OCH$_3$), 57.01 (CH^3), 60.67 (CH^{1}H^2), 105.54 (CH^4), 165.45 (CO-OCH$_3$), 217.1, 221.9, 223.5 (M–CO). Mass spectrum (12 eV): m/e 238 (M$^+$). Anal. Calcd for C$_8$H$_7$MnO$_5$: C, 40.34; H, 2.94. Found: C, 40.72; H, 2.70.

(e) Synthesis of (η^5-CH$_2$CHCHCOCH$_3$)Mn(CO)$_3$ (3b). A cyclohexane solution (30 mL) of **1b** (0.25 g, 0.89 mmol) was heated under reflux for 3 h. The resulting orange suspension was evaporated to dryness, and the residue was chromatographed through a silica column with hexane as the eluting solvent. The first yellow band off the column was identified as Mn$_2$(CO)$_{10}$. The orange residue on the top of the column was eluted with ether, and an orange band was developed and collected. After removal of the solvent, the residues were recrystallized from a saturated hexane solution at -40 °C to afford orange block-shaped crystals (0.16 g, 0.71 mmol). IR (cyclohexane): ν(CO) 2041 (s), 1968 (s), 1939 (s), 1506 (s) cm^{-1}. ^{1}H NMR (benzene-d_6): δ 1.75 (s, 3 H, CH$_3$), 2.50 (d, 1 H, H^1), 3.25 (d, 1 H, H^4), 4.43 (d, 1 H, H^2), 4.64 (ddd, 1 H, H^3), J_{12} = 13.5 Hz, J_{23} = 5.10 Hz, J_{34} = 7.0 Hz. ^{13}C NMR (100 MHz, toluene-d_8, 25 °C): δ 23.9 (CH$_3$), 69.9 (CH^{1}H^2), 76.60 (CH^3), 105.8 (CH^4), 170 (COCH$_3$), 218.9, 221.0, 225.1 (M–CO). Mass spectrum (12 eV): m/e 222 (M$^+$), 194 (M$^+$ – CO), 166 (M$^+$ – 2CO), 138 (M$^+$ – 3CO). Anal. Calcd for C$_8$H$_7$MnO$_4$: C, 43.24; H, 3.15. Found: C, 43.50; H, 3.20.

(f) Synthesis of (η^5-CH$_2$CHCHCOOCH$_3$)Mn(CO)$_2$(PMe$_3$) (4a). PMe$_3$ (0.16 g, 2.1 mmol) and **3a** (0.50 g, 2.1 mmol) were refluxed in 30 mL of cyclohexane for 24 h. After removal of the solvent, the residues were chromatographed through a silica column. An orange band was developed, collected, and evaporated to dryness. Recrystallization from CH$_2$Cl$_2$–hexane gave orange plates (0.42 g, 1.47 mmol). IR (in CH$_2$Cl$_2$): ν(CO) 1944 (vs), 1873 (vs) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.74 (dd, 1 H, H^1), 1.12 (9 H, d, PCH$_3$), 2.98 (d, 1 H, H^2), 3.33 (s, 3 H, OCH$_3$), 3.62 (d, 1 H, H^4), 5.20 (m, 1 H, H^3), J_{13} = 9.2 Hz, J_{1-P} = 6.7 Hz, J_{23} = 6.4 Hz, J_{34} = 6.0 Hz. ^{31}P NMR (40.25 MHz, CDCl$_3$): δ 33.2. Anal. Calcd for C$_{10}$H$_{16}$MnO$_4$P: C, 41.96; H, 5.59. Found: C, 42.14; H, 5.45.

(g) Synthesis of (η^5-CH$_2$CHCHCOOCH$_3$)Mn(CO)$_2$(PPh$_3$) (4b). This complex was prepared similarly from the thermal reaction between PPh$_3$ (0.55 g, 2.10 mmol) and **3a** (0.46 g, 1.95 mmol); the yield was 85% (0.85 g, 1.70 mmol). IR (in CH$_2$Cl$_2$): ν(CO) 1951 (vs), 1878 (vs) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): major isomer, δ 2.20 (d, 1 H, H^2), 3.26 (d, 1 H, H^1), 3.55 (s, 3 H, OCH$_3$), 4.48 (d, 1 H, H^4), 5.27 (complex m, 1 H, H^3), 7.06–7.40 (complex m, 15 H, PC$_6$H$_5$), J_{13} = 10.5 Hz, J_{23} = 7.0 Hz, J_{34} = 6.4 Hz, J_{3-P} = 2.0 Hz; minor isomer, δ 2.75 (d, 1 H, H^1), 3.40 (d, 1 H, H^2), 4.60 (m, 1 H, H^4), 5.20 (m, 1 H, H^3), J_{13} = 10.5 Hz, J_{23} = 6.4 Hz, J_{34} = 5.4 Hz, J_{P-4} = 2.2 Hz. ^{31}P NMR (40.25 MHz, CDCl$_3$): 75.2 (major isomer), 63.88 (minor isomer). Anal. Calcd for C$_{25}$H$_{22}$MnO$_4$P: C, 63.56; H, 4.66. Found: C, 63.50; H, 4.87.

(h) Synthesis of (η^5-CH$_2$CHCHCOCH$_3$)Mn(CO)$_2$(PMe$_3$) (4c). This complex was similarly prepared from a boiling cyclohexane solution (30 mL) of PMe$_3$ (0.07 g, 0.92 mmol) and **3b** (0.21 g, 0.95 mmol); the yield was 80% (0.21 g, 0.76 mmol). IR (in cyclohexane): ν(CO) 1948 (vs), 1879 (vs) cm^{-1}. ^{1}H NMR (400 MHz, benzene-d_6): δ 1.89 (dd, 1 H, H^1), 2.01 (s, 3 H, OCH$_3$), 3.01 (d, 1 H, H^2), 4.48 (d, 1 H, H^4), 4.91 (m, 1 H, H^3), J_{13} = 12.0 Hz, J_{23} = 6.4 Hz, J_{34} = 6.6 Hz. ^{31}P NMR (40.25 MHz, benzene-d_6): δ 32.1. Anal. Calcd for C$_{10}$H$_{16}$MnO$_3$P: C, 44.44; H, 5.93. Found: C, 44.65; H, 6.14.

(i) Synthesis of (η^5-CH$_2$CHCHCOCH$_3$)Mn(CO)$_2$(PPh$_3$) (4d). This complex was prepared similarly from a refluxing cyclohexane solution (30 mL) of PPh$_3$ (0.26 g, 1.02 mmol) and **3b** (0.22 g, 1.00 mmol), and the yield was 77% (0.35 g, 0.78 mmol). IR (in cyclohexane): ν(CO) 1957 (s), 1887 (s) cm^{-1}. ^{1}H NMR (400 MHz, -40 °C, toluene-d_8): isomer A (82%), 2.02 (dd, 1 H, H^1), 2.05 (s, 3 H, CH$_3$), 3.65 (d, 1 H, H^2), 4.45 (d, 1 H, H^4), 5.05 (m, 1 H, H^3), J_{13} = 10.8 Hz, J_{23} = 7.0 Hz, J_{34} = 5.6 Hz, J_{P-1} = 2.3 Hz; isomer B (16.5%), 2.90 (d, 1 H, H^1), 3.58 (d, 1 H, H^2), 4.88 (m, 1 H, H^4), 5.00 (m, 1 H, H^3), J_{13} = 10.4 Hz, J_{23} = 6.5 Hz, J_{34} = 5.2 Hz, J_{P-4} = 2.0 Hz. The third isomer (1.5%) is not detectable by ^{1}H NMR spectroscopy because it is probably masked by resonances of other isomers. ^{31}P NMR (40.25 MHz): δ 74.1 (82%), 63.0 (16.5%), 61.2 (1.5%). Anal. Calcd for C$_{10}$H$_{16}$MnO$_3$P: C,

44.44; H, 5.93. Found: C, 44.70; H, 6.10.

(j) Synthesis of Mn(CO)$_3$(PMe$_3$)(η^3-CH$_2$CHCHCOOCH$_3$) (5a). PMe$_3$ (0.16 g, 2.1 mmol) was added dropwise to a rapidly stirred cyclohexane solution (20 mL) of **3a** (0.50 g, 2.1 mmol) at 0 °C, which immediately yielded yellow crystalline **5a** (0.99 g, 1.98 mmol). Recrystallization from CH$_2$Cl$_2$–hexane gave yellow platelike crystals. IR (CH$_2$Cl$_2$): ν(CO) 2014 (vs), 1933 (vs), 1914 (vs), 1713 (s) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): syn isomer (45%), δ 0.75 (d, 9 H, PCH$_3$), 0.81 (d, 1 H, H^1), 1.77 (d, 1 H, H^4), 2.34 (dd, 1 H, H^2), 3.62 (s, 3 H, OCH$_3$), 5.92 (ddd, 1 H, H^3), J_{13} = 11.9 Hz, J_{23} = 7.7 Hz, J_{34} = 14.7 Hz, J_{2-P} = 2.4 Hz, J_{P-CH_3} = 6.0 Hz; anti isomer (32%), δ 0.48 (d, 1 H, H^2), 1.16 (9 H, d, PCH$_3$), 1.91 (d, 1 H, H^1), 2.44 (d, 1 H, H^4), 3.40 (s, 3 H, OCH$_3$), 5.58 (m, 1 H, H^3), J_{13} = 12.0 Hz, J_{23} = 7.4 Hz, J_{34} = 7.0 Hz, J_{3-P} = 2.0 Hz, J_{P-CH_3} = 8.0 Hz; syn isomer (22%), δ 0.83 (9 H, d, PCH$_3$), 1.81 (d, 1 H, H^1), 2.13 (d, 1 H, H^4), 2.81 (dd, 1 H, H^2), 3.53 (s, 3 H, OCH$_3$), 4.98 (m, 1 H, H^3), J_{13} = 10.0 Hz, J_{23} = 7.5 Hz, J_{34} = 10.9 Hz, J_{4-P} = 3.3 Hz, J_{P-CH_3} = 8.2 Hz. Anal. Calcd for C$_{11}$H$_{16}$MnO$_5$P: C, 42.04; H, 5.10. Found: C, 42.14; H, 5.03.

(k) Synthesis of Mn(CO)$_3$(PPh$_3$)(η^3-CH$_2$CHCHCOOCH$_3$) (5b). This complex was prepared similarly from the reaction between PPh$_3$ (0.55 g, 2.1 mmol) and **3a** (0.46 g, 2.1 mmol); the yield was 95% (0.99 g, 1.98 mmol). IR (in CH$_2$Cl$_2$): ν(CO) 2015 (vs), 1948 (vs), 1917 (vs), 1710 (s) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): anti isomer, δ 2.80 (d, 1 H, H^2), 3.01 (d, 1 H, H^4), 3.35 (d, 1 H, H^1), 3.51 (s, 3 H, OCH$_3$), 4.13 (m, 1 H, H^3), 7.02–7.45 (15 H, m, PC$_6$H$_5$), J_{13} = 13.4 Hz, J_{23} = 7.1 Hz, J_{34} = 7.1 Hz. Anal. Calcd for C$_{26}$H$_{22}$MnO$_5$P: C, 62.40; H, 4.40. Found: C, 62.19; H, 4.31.

(l) Synthesis of (η^3-CH$_2$CHCHCOOCH$_3$)Mn(CO)$_3$(CH$_3$CN) (6a). Compound **3a** (0.25 g, 1.05 mmol) was dissolved in 20 mL of CH$_3$CN, and the mixture was stirred at 15 °C for 1 h, followed by removal of solvent at 0 °C to leave a light yellow oil. Upon addition of hexane, this light oil quickly turned into light yellow crystalline **8** (0.22 g, 0.80 mmol). IR (in CH$_3$CN): ν(CO) 2022 (vs), 1929 (vs), 1712 (s) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.01 (s, 3 H, CH$_3$CN), 2.07 (d, 1 H, H^1), 2.42 (d, 1 H, H^4), 3.58 (d, 1 H, H^2), 3.75 (s, 3 H, OCH$_3$), 5.68 (m, 1 H, H^3). Anal. Calcd for C$_{10}$H$_{10}$MnO$_5$N: C, 43.01; H, 3.58. Found: C, 43.12; H, 3.42.

(m) Synthesis of (η^3-CH$_2$CHCHCOOCH$_3$)Mn(CO)$_3$(acetone) (6b). Complex **3** (0.25 g, 1.05 mmol) was dissolved in 10 mL of acetone, and the mixture was stirred for 4 h at 15 °C, followed by removal of solvent at 0 °C to leave a light yellow oil. Upon addition of hexane, this oil immediately turned into light yellow crystalline **9** (0.24 g, 0.81 mmol). IR (Nujol): ν(CO) 2030 (vs), 1947 (vs), 1925 (vs), 1716 (s) cm^{-1}. ^{1}H NMR (400 MHz, CD$_3$COCD$_3$): δ 1.64 (d, 1 H, H^1), 2.04 (s, 6 H, (CH$_3$)$_2$CO), 3.50 (s, 3 H, OCH$_3$), 3.58 (d, 1 H, H^2), 5.09 (d, 1 H, H^4), 5.69 (ddd, 1 H, H^3), J_{13} = 13.4 Hz, J_{23} = 7.0 Hz, J_{34} = 10.9 Hz. Anal. Calcd for C$_{11}$H$_{13}$MnO$_6$: C, 44.59; H, 4.39. Found: C, 44.80; H, 4.21.

(n) Synthesis of (η^3-CH$_2$CHCHCOOCH$_3$)Mn(CO)$_3$(THF) (6c). Complex **3a** (0.25 g, 1.05 mmol) was dissolved in 20 mL of tetrahydrofuran, and the mixture was stirred for 18 h, followed by removal of solvent at 0 °C to leave a pale yellow oil. Upon addition of hexane, the pale yellow oil quickly turned into crystalline **6c** (0.26 g, 0.88 mmol). IR (in THF): ν(CO) 2028 (vs), 1944 (vs), 1923 (vs), 1711 (vs) cm^{-1}. ^{1}H NMR (400 MHz, THF-d_8): δ 1.60 (t, 4 H, J = 8.0 Hz), 1.84 (d, 1 H, H^1), 3.46 (s, 3 H, OCH$_3$), 3.50 (d, 1 H, H^2), 3.54 (t, 4 H, J = 8.0 Hz), 5.00 (d, 1 H, H^4), 5.58 (ddd, 1 H, H^3), J_{13} = 13.3 Hz, J_{23} = 7.6 Hz, J_{34} = 11.8 Hz. Anal. Calcd for C$_{12}$H$_{15}$MnO$_6$: C, 46.45; H, 4.84. Found: C, 46.27; H, 4.92.

(o) Synthesis of (η^5-CH$_2$CHCHC(CH$_3$)NCH(CH$_3$)$_2$)Mn-(CO)$_3$ (7a). Complex **3b** (0.14 g, 0.63 mmol) in 15 mL of CH$_2$Cl$_2$ was treated with 0.18 mL of BF$_3$·Et$_2$O (0.23 g, 1.70 mmol) at -78 °C, and the mixture was stirred for 0.5 h. After slow addition of (CH$_3$)$_2$CHNH$_2$ (0.10 g, 1.65 mmol) the mixture was stirred for 2 h, followed by removal of solvent. The resulting residues were extracted with hexane and chromatographed through silica gel with CH$_2$Cl$_2$ as eluting solvent. A yellow band was developed, collected, and evaporated to dryness to yield a yellow oil (0.11 g, 0.42 mmole). IR (in CH$_2$Cl$_2$): ν(CO) 2005 (vs), 1924 (vs), 1912 (vs) cm^{-1}. ^{1}H NMR (400 MHz, benzene-d_6): δ 0.73 (d, 3 H, CHCH$_3$), 0.76 (d, 3 H, CHCH$_3$'), 0.82 (s, 3 H, NC(CH$_3$)), 1.84 (d, 1 H, H^1), 2.64 (m, 1 H, NCH), 2.66 (d, 1 H, H^2), 3.49 (d, 1 H, H^4), 4.69 (ddd, 1 H, H^3), J_{13} = 12.5 Hz, J_{23} = 7.4 Hz, J_{34} = 6.0 Hz. ^{13}C

Table III. Summary of Crystal and Diffraction Data

	3b	4d
formula	$MnC_8H_7O_4$	$MnPC_{25}H_{22}O_3$
color habit	red chunk	yellow chunk
cryst dimens, mm	0.28 × 0.60 × 0.60	0.20 × 0.25 × 0.35
space group	$P2_1/c$	$P2_1/c$
a, Å	9.378 (6)	10.081 (1)
b, Å	6.060 (4)	10.056 (1)
c, Å	16.244 (9)	43.892 (5)
β, deg	91.08 (5)	93.182 (9)
Z	4	8
fw	222.1	456.36
density, Mg/m^3	1.598	1.365
abs coeff, mm^{-1}	1.351	5.73
$F(000)$	448	1888
diffractometer used	Nicolet R3m/V	Nonius CAD4
radiation	Mo Kα (λ = 0.71073 Å)	Cu Kα (λ = 1.5405 Å)
2θ range, deg	2–45	2–100
scan type	$\theta/2\theta$	$\theta/2\theta$
scan speed (variable), deg/min	4.19–114.65	1.648–8.24
scan param (ω)	1.28 + (Kα separation)	0.70 + 0.14 tan θ
no. of rflns collected	2499 (2032 > 3$\sigma(I)$)	4539 (2728 > 2$\sigma(I)$)
no. of indep rflns	1209 (1103 > 3$\sigma(I)$)	4539 (2728 > 2$\sigma(I)$)
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0006F^2$	$w^{-1} = \sigma^2(F)$
final R, R_w, %	3.26, 3.69	4.5, 3.1
goodness of fit	1.93	1.85
largest Δ/σ	0.024	0.156
data to param ratio	9.3:1	5.03:1
final D-map max, $e/Å^3$	0.32	0.34

NMR (100 MHz, toluene-d_8): δ 21.8, 19.4 (CH(CH$_3$)$_2$), 24.9 (NCCH$_3$), 45.9 (CH^{1}H^2), 51.3 (CH(CH$_3$)$_2$), 59.3 (CH^3), 105.1 (CH^4), 171.2 (NC(CH$_3$)), 227.7, 224.3, 223.6 (3 CO). Mass spectrum (12 eV): m/e 263 (M$^+$), 235 (M$^+$ − CO), 207 (M$^+$ − 2CO), 179 (M$^+$ − 3CO), 124 (C$_8$H$_{14}$N$^+$). Anal. Calcd for C$_{11}$H$_{14}$MnNO$_3$: C, 50.19; H, 5.32; N, 5.32. Found: C, 50.20; H, 5.44; N, 5.42.

(p) Synthesis of (η^5-CH$_2$CHCHC(CH$_3$)NC(CH$_3$)$_3$)Mn(CO)$_3$ (7b). Complex **2** (0.22 g, 1.0 mmol) in 20 mL of CH$_2$Cl$_2$ was treated with 0.18 mL of BF·Et$_2$O (0.23 g, 1.70 mmol) at −78 °C and the mixture was stirred for 0.5 h. After slow addition of (CH$_3$)$_3$CNH$_2$ (0.10 g, 1.30 mmol), the resulting yellow suspension was stirred for 2 h and evaporated to dryness. The residues were extracted with hexane and chromatographed through silica gel with hexane as the eluting solvent. A yellow band was developed, collected, and evaporated to dryness to yield a yellow oil (0.16 g, 0.58 mmol). IR (in CH$_2$Cl$_2$): ν(CO) 2014 (vs), 1928 (vs), 1917 (vs). ^{1}H NMR

(400 MHz, benzene-d_6): δ 0.84 (s, 9 H, (CH$_3$)$_3$C), 1.13 (s, 3 H, NCCH$_3$), 2.06 (d, 1 H, H^1), 2.69 (d, 1 H, H^2), 3.48 (d, 1 H, H^4), 4.73 (m, 1 H, H^3), J_{13} = 12.4 Hz, J_{23} = 6.4 Hz, J_{34} = 6.7 Hz. ^{13}C NMR (100 MHz, benzene-d_6): 23.05 (NC$_3$CH$_3$), 30.13 (−C(CH$_3$)$_3$), 47.31 (CH^{1}H^2), 56.4 (−C(CH$_3$)$_3$), 58.1 (CH^4), 103.4 (CH^3), 169.9 (C═N), 215.7, 216.1, 223.2 (3 CO). Mass spectrum (12 eV): m/e 277 (M$^+$), 249 (M$^+$ − CO), 221 (M$^+$ − 2CO), 193 (M$^+$ − 3CO), 138 (C$_7$H$_{13}$N$^+$). Anal. Calcd for C$_{12}$H$_{16}$MnNO$_3$: C, 51.99; H, 5.78; N, 5.05. Found: C, 52.14; H, 5.92; N, 5.15.

(q) Solution Dynamics. Samples were prepared in CD$_3$C$_6$D$_5$, and NMR spectra were recorded over the temperature range −60 to 100 °C. Probe temperatures were calibrated by using the temperature dependence of the differences in chemical shift between the ^{1}H resonances of the methyl and hydroxyl groups of methanol below ambient temperature and between the ^{1}H resonances of the methylene and hydroxyl groups of ethylene glycol above ambient temperature. Theoretical line shapes were calculated for a series of rates by using the method of Johnson.[20] Exchange rate constants for each temperature were determined by matching the theoretical spectra to experimental spectra. The rate constants k were then used to calculate the free energy of activation $\Delta G^{\ddagger}$ at each temperature T, by using the Eyring equation:

$$k_c = (k'/\hbar)Te^{-\Delta G^{\ddagger}/RT}$$

where k' = Boltzmann constant, $\hbar$ = Planck constant divided by π, and R = ideal gas constant.

(r) X-ray Diffraction Study of 3b and 4d. Single crystals of **3b** and **4d** were sealed in glass capillaries under an inert atmosphere. Data for **3b** were collected at room temperature on a Nicolet R3m/V diffractometer, using graphite-monochromated Mo Kα radiation. The structure of **3b** was solved by direct methods; all data reduction and structural refinement were performed by means of the SHELXTL PLUS package. Data for **4d** were collected on a Nonius CAD4 diffractometer, using graphite-monochromated Cu Kα radiation, and the structure was solved by the heavy-atom method; all data reduction and structure refinement were performed with the NRCCSDP package. Two independent molecules were found, and there was no crystallographic symmetry between them. Crystal data and details of the data collection and structure analysis are summarized in Table III. For both structures, all non-hydrogen atoms were refined with anisotropic parameters. All hydrogen atoms included in the structure factor calculation were placed in idealized positions.

Supplementary Material Available: Listings of atomic coordinates and thermal parameters for **3b** and **4d** (6 pages); listings of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

(20) Johnson, C. S. *Am. J. Phys.* **1967**, *35*, 929.