Syntheses, Characterization, and Nucleophilic Substitution-Addition Reactions of Manganese-Oxapentadienyl **Compounds.** Structural Characterization of $(\eta^{5}-CH_{2}CHCHCOCH_{3})Mn(CO)_{2}L$ (L = CO, PPh₃) and the First Isolation of Novel η^5 -1-Azapentadienyl Complexes

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Manganese- η^5 -oxapentadienyl compounds (η^5 -CH₂CHCHCOR)Mn(CO)₃ (R = OCH₃ (3a), CH₃ (3b)) are produced from a refluxing cyclohexane solution of Mn(CO)₅(η^1 -CH₂CH=CHCOR) (R = OCH₃ (1a), CH₃ (1b)). In a heated cyclohexane solution, 3a and 3b react with 1 equiv of tertiary phosphine to afford $(\eta^5-CH_2CHCHCOR)Mn(CO)_2(PR_3)$ (PR₃ = PMe₃, PPh₃; R = OMe, Me). This phosphine substitution reaction proceeds via an η^3 -allyl species, and the intermediates (η^3 -CH₂CHCHCOOCH₃)Mn(CO)₃P (P = PMe₃, PPh₃) have been isolated and fully characterized. In polar solvents, **3a** takes up one solvent molecule to form (η^3 -CH₂CHCHCOOCH₃)Mn(CO)₃L (L = CH₃CN (**6a**), acetone (**6b**), THF (**6c**)). In CHCl₃ or CH₂Cl₂, **6b** and **6c** readily lose the ligating solvent and rearrange to **3a**. In the presence of BF₃·(C₂H₅)₂O, **3b** reacts with the primary amine RNH₂ at -78 °C to yield the first isolable 1-azapentadienyl complexes (η^5 -CH₂CHCHC(CH₃)NR)Mn(CO)₃ (R = (CH₃)₂CH (7a), (CH₃)₃C (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 ¹H, ¹³C, and ¹³R NMB expected. 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-metalacyclic 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-oxa-pentadienyl complex in 9% yield,^{1a,b} a rhenium complex (I) was obtained from the reaction between $(PPh_3)_2ReH_7$



and furan under reflux in THF in the presence of 3,3dimethyl-1-butene,^{1c} and a cationic iridium oxadienyl complex (II) was obtained from the reaction between $[Ir(\eta^5-C_5Me_5)(Me_2CO)](PF_6)_2$ 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-metalpentadienyl 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 metallabenzene,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

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Scheme I. Synthetic Route Leading to Manganese $-\eta^5$ -Oxapentadienyl Complexes



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- $(\eta^1-CH_2CH=CHCOR)$ (R = OCH₃ (1a), CH₃ (1b)). The two η^1 compounds were stable enough to isolate in ca. 60-70% yield and could be fully characterized. Their ¹H and ¹³C 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 $(syn-\eta^3$ -CH₂CHCHCOOCH₃)-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 ν (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 -CH₂CHCHCOR)Mn(CO)₃ (R = OCH₃ (3a), CH₃ (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 η^{5} **-Oxapentadienyl Complexes.** Compounds **3a** and **3b** are highly volatile and readily sublimable. The U-shaped configuration is shown by the coupling constant $J_{34} = 6.8$ Hz. The proton H⁴ 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 ν (CO) absorptions of the ketone group. In **3a**, ν (CO) appears as a weak absorption at 1556 cm⁻¹, whereas the corresponding ν (CO) absorption of **3b** is observed at 1506 cm⁻¹. The ν (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 (η^{5} -C₅H₇)Mn(CO)₃⁸



Figure 1. ORTEP drawing of $(\eta^5$ -CH₂CHCHCOCMe)Mn(CO)₃.

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

I UDIC II DOMU	DONBOND	(II) and Impics	(uog) tot ob
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)	0(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)	0(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)	3) 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)	B) 125.4 (4)
Mn-C(8)-C(7)	68.3(2)	1	

(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: η^{5} -CH₂CHCHCOCH₃ > η^{5} -CH₂CHCHCOOCH₃ > η^{5} -C₅H₇.

Crystal Structure of 3b. Previous structural characterization of metal-oxadienyl complexes is very scarce and is limited only to $(\eta^5$ -CH₂CHCHCOH)Re(CO)(PPh₃)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-

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dienyl ligand with respect to the $Mn(CO)_3$ fragment is identical with those observed for $(\eta^5-2, 4-\text{dien}-1-\text{yl})Mn(CO)_3$ 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==0 double bond (1.21 Å); this incresse reflects a significant degree of metal electron transfer into the empty ligand orbital including the ketonic $CO(\pi^*)$ 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 $(2.20 \pm 0.06 \text{ Å})$ for the related pentadienyl complex $(\eta^{5}-1-(C_{6}H_{5}O_{2})C_{5}H_{6})Mn(CO)_{3}$.¹¹

Reaction with Phosphine Ligands. One interesting feature in the chemistry of **3a** and **3b** is the facile $\eta^5 \rightleftharpoons \eta^3$ 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 $(\eta^{5}-CH_{2}CHCHCOR)Mn(CO)_{2}(PR_{3})$ (R = OCH₃, PR₃ = 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 ¹H and ³¹P NMR spectra. Spectroscopic data are consistent with the proposed structure. Interestingly, more than one conformer are recognizable for 4b and 4d. The ¹H and ³¹P NMR spectra in $\overline{CD}_3C_6D_5$ 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-



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 ¹H and ³¹P 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 $(\eta^3 - CH_2CHCHCOOCH_3)Mn(CO)_3(PR_3)$ (PR₃ = PMe₃ (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 $\nu(CO)$ 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 $(\eta^3$ -allyl)Mn(CO)₃(PR₃).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 ¹H 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 ¹H 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 PPh₃ 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 $(1.279 (4) \text{ \AA})$ of 3b. This condition reflects the degree of metal electron transfer into the ketonic $CO(\pi^*)$ empty orbital, more significant for 4d than for 3b. The oxapentadienyl ligands form a least-squares plane within 0.035 (8) Å. The methyl

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Figure 2. ORTEP drawings of the two racemers of 4d.

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 ¹³C NMR spectra of 3a and 3b are consistent with an asymmetric orientation of the three carbonyl groups observed in the solid-state structure. The ¹³C 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 met $al-\eta^5$ -oxadienyl oscillation either clockwise or counterclockwise. Calculation of ΔG^* based on the line-shape

Mn(A)-P(1A) 2284 (23) Mn(B)-C(1B) 2285 (3) Mn(A)-C(2A) 2.129 (6) Mn(B)-C(2B) 2.130 (7) Mn(A)-C(2A) 2.138 (7) Mn(B)-C(2B) 2.122 (7) Mn(A)-C(2A) 2.138 (7) Mn(B)-C(2B) 2.208 (7) Mn(A)-C(2A) 1.238 (7) Mn(B)-C(2B) 1.748 (7) Mn(A)-C(1A) 2.105 (7) Mn(B)-C(1B) 2.088 (5) P(1A)-C(2A) 1.748 (7) Mn(B)-C(1B) 2.088 (5) P(1A)-C(1A) 2.105 (7) P(1B)-C(1B) 1.843 (7) P(1A)-C(2A) 1.387 (10) C(1B)-C(2B) 1.383 (7) C(2A)-C(2A) 1.397 (10) C(1B)-C(2B) 1.389 (11) C(2A)-C(A) 1.39 (8) C(2B)-C(2B) 1.389 (11) C(2A)-C(A) 1.319 (8) C(2B)-C(2B) 1.385 (11) C(2A)-C(A) 1.358 (8) C(2B)-C(2B) 1.385 (8) C(2A)-C(A) 1.358 (2) P(1B)-Mn(B)-C(2B) 1.358 (9) C(1A)-Mn(A)-C(2A) 3.83 (2) P(1B)-Mn(B)-C(2B) 1.421 (12) C(2A)-Mn(A)-C(2A) 1.368	Table II.	Selected	Bond Distan	ces (Å) and Angle	es (deg) for 4d
Mn(A)-C(1A) 2.226 (7) Mn(B)-C(1B) 2.235 (8) Mn(A)-C(3A) 2.134 (7) Mn(B)-C(2B) 2.136 (7) Mn(A)-C(2A) 1.896 (7) Mn(B)-C(2B) 1.764 (7) Mn(A)-C(2A) 1.896 (7) Mn(B)-C(2B) 1.764 (7) Mn(A)-C(2A) 1.895 (7) P(1B)-C(1B) 2.098 (6) P(1A)-C(1A) 1.848 (7) P(1B)-C(1B) 1.843 (7) P(1A)-C(1A) 1.848 (7) P(1B)-C(1B) 1.843 (7) P(1A)-C(1A) 1.846 (7) P(1B)-C(1B) 1.843 (7) P(1A)-C(1A) 1.846 (7) P(1B)-C(1B) 1.848 (7) P(1A)-C(1A) 1.846 (7) P(1B)-C(1B) 1.848 (1) C(2A)-C(3A) 1.495 (10) C(2B)-C(3B) 1.448 (1) C(2A)-C(2A) 1.345 (10) C(2B)-C(2B) 1.858 (1) P(1A)-Mn(A)-C(1A) 1.858 (1) P(1B)-Mn(B)-C(2B) 88.16 (20) P(1A)-Mn(A)-C(2A) 1.320 5 (20) P(1B)-Mn(B)-C(2B) 88.16 (20) P(1A)-Mn(A)-C(2A) 1.83.20 (23) P(1B)-Mn(B)-C(2B) 88.16 (20) P(1A)-Mn(A	Mn(A)-H	P(1A)	2.2644 (23)	Mn(B)-P(1B)	2.2681 (23)
Mn(A)-C(2A) 21.29 (f) Mn(B)-C(2B) 21.20 (f) Mn(A)-C(2A) 1.280 (f) Mn(B)-C(4B) 2.208 (f) Mn(A)-C(2A) 1.380 (f) Mn(B)-C(2B) 1.783 (f) Mn(A)-C(1A) 2.107 (f) Mn(B)-C(1B) 2.983 (f) Mn(A)-C(1A) 1.784 (f) P(1B)-C(1B) 1.843 (f) P(1A)-C(1A) 1.848 (f) P(1B)-C(1B) 1.843 (f) P(1A)-C(1A) 1.848 (f) P(1B)-C(1B) 1.835 (f) C(1A)-C(2A) 1.387 (10) C(1B)-C(2B) 1.389 (11) C(2A)-C(3A) 1.439 (10) C(2B)-C(2B) 1.421 (12) C(2A)-C(2A) 1.435 (10) C(2B)-C(2B) 1.428 (11) C(4A)-C(1A) 1.458 (10) C(2B)-C(2B) 1.429 (12) C(2A)-C(2A) 1.458 (10) C(2B)-C(2B) 1.421 (12) C(2A)-C(2A) 1.458 (10) C(2B)-C(2B) 1.421 (12) C(2A)-C(2A) 1.458 (10) C(2B)-C(2B) 1.428 (13) C(2A)-Mn(A)-C(2A) 1.538 (20) C(1B)-Mn(B)-C(2B) 1.539 (21) P(1A)-Mn(A)-C(2A)	Mn(A) - C	C(1A)	2.265 (7)	Mn(B)-C(1B)	2.255 (8)
Min(A)-C(AA) 1.898 (7) Min(B)-C(AB) 2.208 (7) Min(A)-C(BA) 1.686 (7) Min(B)-C(2BS) 1.798 (7) Min(A)-C(CA) 2.107 (4) Min(B)-C(2BS) 1.798 (7) Min(A)-C(IA) 2.107 (4) Min(B)-C(2BS) 1.798 (7) P(IA)-C(IA) 1.248 (7) P(IB)-C(IBS) 1.383 (7) C(IA)-C(IA) 1.364 (7) P(IB)-C(IBS) 1.383 (11) C(IA)-C(IA) 1.367 (10) C(IB)-C(IB) 1.383 (11) C(IA)-C(IA) 1.367 (10) C(IB)-C(IB) 1.383 (11) C(IA)-C(IA) 1.367 (10) C(IB)-C(IB) 1.385 (11) C(IA)-C(IA) 1.319 (8) C(IB)-C(IB) 1.385 (11) C(IA)-C(IA) 1.319 (8) C(IB)-C(IB) 1.307 (9) C(IA)-C(IA) 1.319 (8) C(IB)-C(IB) 1.308 (12) P(IA)-Min(A)-C(IA) 38.86 (19) P(IB)-Min(B)-C(IB) 38.16 (20) P(IA)-Min(A)-C(IA) 38.92 (19) P(IB)-Min(B)-C(2B) 38.16 (20) P(IA)-Min(A)-C(IA) 38.92 (19) P(IB)-Min(B)-C(2B) 38.16 (20) P(IA)-Min(A)-C(IA) 38.33 (3) C(IB)-Min(B)-C(2B) 38.16 (Mn(A) = 0 Mn(A) = 0	$\mathcal{L}(\mathbf{2A})$	2.129 (6)	Mn(B) - C(2B) Mn(B) - C(3B)	2.130 (7)
Mn(A)-C(24A) 1.403 (7) Mn(B)-C(24B) 1.764 (7) Mn(A)-O(1A) 2.107 (4) Mn(B)-C(2BS) 1.798 (7) P(1A)-C(1A) 1.248 (7) P(1B)-C(12B) 1.243 (7) P(1A)-C(1A) 1.248 (7) P(1B)-C(12B) 1.843 (7) P(1A)-C(12A) 1.248 (7) P(1B)-C(12B) 1.383 (7) C(1A)-C(2A) 1.397 (10) C(2B)-C(2B) 1.389 (11) C(2A)-C(2A) 1.399 (10) C(2B)-C(2B) 1.385 (11) C(4A)-C(1A) 1.399 (8) C(2B)-C(2B) 1.421 (12) C(2A)-C(2A) 1.456 (8) C(2B)-C(2B) 1.358 (9) C(2A)-O(2A) 1.145 (8) C(2B)-O(2B) 1.147 (9) C(2A)-O(2A) 1.145 (8) C(2B)-O(2B) 1.383 (12) P(1A)-Mn(A)-C(2A) 35.20 (12) P(1B)-Mn(B)-C(2B) 38.16 (20) P(1A)-Mn(A)-C(2A) 35.20 (2) P(1B)-Mn(B)-C(2B) 36.62 (22) P(1A)-Mn(A)-C(2A) 35.20 (2) P(1B)-Mn(B)-C(2B) 36.81 (2) P(1A)-Mn(A)-C(2A) 35.20 (2) P(1B)-Mn(B)-C(2B) 36.83 (3)	Mn(A) - C	C(4A)	2.189 (7)	Mn(B) - C(4B)	2.208 (7)
Mn(A)-C(25A) 1.748 (7) Mn(B)-C(25B) 1.793 (7) Mn(A)-C(2A) 1.425 (7) P(1B)-C(12B) 1.643 (7) P(1B)-C(12B) 1.643 (7) P(1A)-C(12A) 1.846 (7) P(1B)-C(12B) 1.643 (7) P(1B)-C(12B) 1.643 (7) C(1A)-C(2A) 1.364 (7) P(1B)-C(12B) 1.643 (7) P(1B)-C(12B) 1.643 (7) C(2A)-C(2A) 1.367 (10) C(1B)-C(2B) 1.388 (11) C(2A)-C(2A) 1.368 (11) C(2A)-C(2A) 1.368 (11) C(2B)-C(2B) 1.358 (6) C(22B)-C(2B) 1.358 (6) C(2A)-O(2A) 1.158 (8) C(2AB)-O(2B) 1.135 (8) C(2AB)-O(2B) 1.358 (6) P(1A)-Mn(A)-C(2A) 38.64 (20) P(1B)-Mn(B)-C(2B) 38.16 (20) 662 (21) P(1A)-Mn(A)-C(2A) 38.26 (23) P(1B)-Mn(B)-C(2B) 38.16 (20) 661 (21) P(1A)-Mn(A)-C(2A) 38.23 (21) P(1B)-Mn(B)-C(2B) 38.16 (20) 661 (21) P(1A)-Mn(A)-C(2A) 38.23 (21) P(1B)-Mn(B)-C(2B) 38.16 (20) 38.16 (20) 38.16 (20) P(1A)-Mn(A)-C(2A) 39.2 (23) P(1B)-Mn(B)-C(2B) 38.16 (20) 38.16 (20) 38.16 (20	Mn(A)-O	C(24A)	1.803 (7)	Mn(B)-C(24B)	1.764 (7)
PI(A)-O(IA) 2.107 (4) PI(B)-C(B) 1.317 (7) PI(A)-C(I2A) 1.348 (7) PI(B)-C(I2B) 1.343 (7) PI(A)-C(I2A) 1.346 (7) P(IB)-C(I2B) 1.385 (1) C(IA)-C(2A) 1.367 (10) C(IB)-C(IB) 1.385 (1) C(2A)-C(IA) 1.367 (10) C(IB)-C(IB) 1.385 (1) C(2A)-C(IA) 1.410 (10) C(2B)-C(IB) 1.385 (1) C(4A)-C(IA) 1.318 (8) C(2AB)-O(IB) 1.318 (9) C(2A)-O(IA) 1.145 (8) C(2AB)-O(IB) 1.147 (9) P(IA)-Mn(A)-C(IA) 38.96 (19) P(IB)-Mn(B)-C(2B) 1.328 (9) C(IA)-Mn(A)-C(IA) 38.92 (19) P(IB)-Mn(B)-C(2B) 1.328 (9) P(IA)-Mn(A)-C(IA) 38.92 (19) P(IB)-Mn(B)-C(2B) 38.91 (20) P(IA)-Mn(A)-C(ZA) 39.20 (23) P(IB)-Mn(B)-C(2B) 95.11 (23) P(IA)-Mn(A)-C(ZA) 39.20 (23) P(IB)-Mn(B)-C(2B) 95.01 (23) P(IA)-Mn(A)-C(ZA) 39.07 (62) P(IB)-Mn(B)-C(2B) 95.01 (23) P(IA)-Mn(A)-C(ZA) 96.03 (1B) 96.01 (2B) 96.1 (2B) P(IA)-Mn(A)-C(ZA) 96.63 (3) C(IB)-Mn(B)-C(2B	Mn(A) - C	C(25A)	1.748 (7)	Mn(B)-C(25B)	1.793 (7)
P(1A)-C(12A) 1.244 (7) P(1B)-C(12B) 1.244 (7) P(1A)-C(12A) 1.246 (7) P(1B)-C(12B) 1.238 (7) C(1A)-C(2A) 1.397 (10) C(2B)-C(3B) 1.421 (12) C(3A)-C(4A) 1.410 (10) C(2B)-C(3B) 1.421 (12) C(3A)-C(4A) 1.410 (10) C(2B)-C(3B) 1.421 (12) C(4A)-C(5A) 1.495 (10) C(4B)-C(5B) 1.486 (11) C(4A)-C(5A) 1.495 (10) C(4B)-C(2B) 1.158 (6) C(22A)-O(2A) 1.145 (8) C(2B)-O(2B) 1.158 (6) C(22A)-O(2A) 1.158 (8) C(2B)-O(2B) 1.158 (6) C(22A)-O(2A) 1.158 (8) C(2B)-O(2B) 1.158 (6) C(2CA)-Mn(A)-C(2A) 13.92 (19) P(1B)-Mn(B)-C(2B) 123.97 (24) P(1A)-Mn(A)-C(2A) 13.92 (19) P(1B)-Mn(B)-C(2B) 123.97 (24) P(1A)-Mn(A)-C(2A) 13.92 (12) P(1B)-Mn(B)-C(2B) 13.93 (12) P(1A)-Mn(A)-C(2A) 35.0 (23) P(1B)-Mn(B)-C(2B) 15.0 (6) C(1A)-Mn(A)-C(2A) 35.0 (23) P(1B)-Mn(B)-C(2B) 15.0 (6) C(1A)-Mn(A)-C(2A) 35.1 (3) C(1B)-Mn(B)-C(2B) 16.6 (3) C(1A)-Mn(A)-C(2A) 35.1 (3) C(1B)-Mn(B)-C(2B) 16.6 (3) C(1A)-Mn(A)-C(2A) 35.1 (3) C(1B)-Mn(B)-C(2B) 16.6 (3) C(1A)-Mn(A)-C(2A) 35.3 (3) C(2B)-Mn(B)-C(2B) 11.6 (3) C(1A)-Mn(A)-C(2A) 38.3 (3) C(2B)-Mn(B)-C(2B) 11.6 (3) C(2A)-Mn(A)-C(2A) 38.6 (3) C(2B)-Mn(B)-C(2B) 11.6 (3) C(2A)-Mn(A)-C(2A) 38.6 (3) C(2B)-Mn(B)-C(2B) 11.6 (3) C(2A)-Mn(A)-C(2A) 13.5 (2) C(2B)-Mn(B)-C(2B) 11.6 (3) C(2A)-Mn(A)-C(2A) 13.5 (2) C(2B)-Mn(B)-C(2B) 11.6 (3) C(2A)-Mn(A)-C(2A) 13.5 (2) C(2B)-Mn(B)-C(2B) 11.6	Mn(A)-C	J(1A) (6A)	2.107 (4)	Mn(B) = O(1B) P(1B) = C(6B)	2.098 (5)
P(1A)-C(1A) 1.864 (7) P(1B)-C(1BB) 1.835 (7) C(1A)-C(2A) 1.367 (10) C(1B)-C(2B) 1.839 (11) C(2A)-C(4A) 1.410 (10) C(3B)-C(4B) 1.396 (11) C(4A)-O(1A) 1.319 (8) C(4B)-C(4B) 1.396 (11) C(2A)-O(2A) 1.145 (8) C(2AB)-O(2B) 1.158 (9) C(22A)-O(2A) 1.158 (8) C(2AB)-O(2B) 1.158 (9) C(22A)-O(2A) 1.158 (8) C(2AB)-O(2B) 1.158 (9) C(2A)-M(A)-C(2A) 123.05 (20) P(1B)-Mn(B)-C(2B) 183.07 (9) P(1A)-Mn(A)-C(2A) 123.05 (20) P(1B)-Mn(B)-C(2B) 13.07 (9) P(1A)-Mn(A)-C(2A) 123.05 (20) P(1B)-Mn(B)-C(2B) 13.07 (9) P(1A)-Mn(A)-C(2A) 123.05 (20) P(1B)-Mn(B)-C(2B) 13.00 (6) (21) P(1A)-Mn(A)-C(2A) 138.92 (12) P(1B)-Mn(B)-C(2B) 130.06 (21) P(1A)-Mn(A)-C(2A) 38.1 (3) C(1B)-Mn(B)-C(2B) 130.06 (21) P(1A)-Mn(A)-C(2A) 38.1 (3) C(1B)-Mn(B)-C(2B) 130.06 (21) P(1A)-Mn(A)-C(2A) 38.1 (3) C(1B)-Mn(B)-C(2B) 130.06 (21) P(1A)-Mn(A)-C(2A) 88.1 (3) C(1B)-Mn(B)-C(2B) 130.06 (21) C(1A)-Mn(A)-C(2A) 88.1 (3) C(1B)-Mn(B)-C(2B) 130.06 (21) C(1A)-Mn(A)-C(2A) 88.1 (3) C(1B)-Mn(B)-C(2B) 130.06 (21) C(1A)-Mn(A)-C(2A) 88.3 (3) C(1B)-Mn(B)-C(2B) 130.06 (21) C(1A)-Mn(A)-C(2A) 88.3 (3) C(1B)-Mn(B)-C(2B) 130.8 (3) C(1A)-Mn(A)-C(2A) 88.3 (3) C(1B)-Mn(B)-C(2B) 130.8 (28) (3) C(2A)-Mn(A)-C(2A) 143.7 (3) C(2B)-Mn(B)-C(2B) 119.8 (3) C(2A)-Mn(A)-C(2A) 143.7 (3) C(2B)-Mn(B)-C(2B) 119.8 (3) C(2A)-Mn(A)-C(2A) 143.7 (3) C(2B)-Mn(B)-C(2B) 159.1 (3) C(2A)-Mn(A)-C(2A) 105.7 (3) C(3B)-Mn(B)-C(2B) 199.8 (3) C(2A)-Mn(A)-C(2A) 175.0 (C) Mn(A)-C(2A)-O(2A) 175.0 (C) Mn(B)-C(2B)-Mn(B)-C(2B) 199.7 (3) C(2A)-Mn(A)-C(2A) 175.6 (7) Mn(B)-C(2B) 172.2 (7) Mn(A)-O(1A) -C(2A) 175.6 (7) Mn(B)-C(2B) 172.2 (7) Mn(A)-O(1A)-C(2A) 175.6 (7) Mn(B)-C(2B) 199.7 (3) C(2A)-Mn(A)-C(2A) 175.6 (7) Mn(B)-C(2B)	P(1A)-C	(12A)	1.848 (7)	P(1B)-C(12B)	1.843 (7)
C(1A)-C(2A) 1.367 (10) C(1B)-C(2B) 1.389 (11) C(2A)-C(3A) 1.499 (10) C(2B)-C(3B) 1.421 (12) C(3A)-C(4A) 1.410 (10) C(3B)-C(4B) 1.335 (11) C(4A)-C(1A) 1.319 (8) C(4B)-C(1B) 1.337 (9) C(22A)-O(2A) 1.145 (8) C(24B)-O(2B) 1.158 (9) C(22A)-O(2A) 1.158 (8) C(22B)-O(2B) 1.158 (9) C(2A)-Mn(A)-C(2A) 123.05 (20) P(1B)-Mn(B)-C(2B) 183.97 (24) P(1A)-Mn(A)-C(2A) 123.05 (20) P(1B)-Mn(B)-C(2B) 183.06 (21) P(1A)-Mn(A)-C(2A) 33.20 (22) P(1B)-Mn(B)-C(2B) 196.02 (22) P(1A)-Mn(A)-C(2A) 33.1 (3) C(1B)-Mn(B)-C(2B) 96.22 (22) P(1A)-Mn(A)-C(2A) 83.1 (3) C(1B)-Mn(B)-C(2B) 96.22 (22) P(1A)-Mn(A)-C(2A) 83.1 (3) C(1B)-Mn(B)-C(2B) 196.63 (3) C(1A)-Mn(A)-C(2A) 84.9 (3) C(1B)-Mn(B)-C(2B) 196.63 (3) C(1A)-Mn(A)-C(2A) 84.9 (3) C(1B)-Mn(B)-C(2B) 196.85 (2) C(2A)-Mn(A)-C(2A) 106.0 (3) C(1B)-Mn(B)-C(2B) 111.9 (3) C(2A)-Mn(A)-C(2A) 106.0 (3) C(1B)-Mn(B)-C(2B) 111.9 (3) C(2A)-Mn(A)-C(2A) 106.0 (3) C(1B)-Mn(B)-C(2B) 111.9 (3) C(2A)-Mn(A)-C(2A) 138.3 (3) C(2B)-Mn(B)-C(2B) 111.9 (3) C(2A)-Mn(A)-C(2A) 137.0 (3) C(2B)-Mn(B)-C(2B) 111.9 (3) C(2A)-Mn(A)-C(2A) 137.0 (2B)-Mn(B)-C(2B) 139.8 (3) C(2A)-Mn(A)-C(2A) 143.7 (3) C(2B)-Mn(B)-C(2B) 139.8 (3) C(2A)-Mn(A)-C(2A) 143.7 (3) C(2B)-Mn(B)-C(2B) 139.8 (3) C(2A)-Mn(A)-C(2A) 167.0 (3) C(3B)-Mn(B)-C(2B) 139.8 (3) C(2A)-Mn(A)-C(2A) 167.0 (3) C(3B)-Mn(B)-C(2B) 139.7 (3) C(3A)-Mn(A)-C(2A) 167.0 (3) C(3B)-Mn(B)-C(2B) 139.7 (3) C(3A)-Mn(A)-C(2A) 177.0 (4) C(3A)-Mn(A)-C(2A) 177.0 (5) C(3B)-Mn(B)-C(2B) 148.7 (3) C(2A)-Mn(A)-C(2A) 177.0 (4) C(3A)-Mn(A)-C(2A) 177.0 (5) Mn(B)-C(2B) 84.8 (3) C(2A)-Mn(A)-C(2A) 177.0 (5) Mn(B)-C(2B) 84.8 (3) C(2A)-Mn(A)-C(2A) 175.6 (7) Mn(B)-C(2B) 84.8 (3) C(2A)-Mn(A)-C(2A) 175.6 (7) Mn(B)-C(2B) 84.8 (3) C(2A)-Mn(A)-C(2A) 175.6 (7) Mn(B)-C(2B) 196.0 (P(1A)-C	(18A)	1.864 (7)	P(1B)-C(18B)	1.835 (7)
C(2A)-C(3A) 1.399 (10) C(2B)-C(3B) 1.421 (12) 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(22A)-O(2A) 1.158 (8) C(24B)-O(2B) 1.158 (9) C(22A)-O(3A) 1.158 (8) C(24B)-O(2B) 1.158 (9) C(22A)-O(3A) 1.158 (8) C(24B)-O(2B) 1.147 (9) P(1A)-Mn(A)-C(2A) 123.05 (20) P(1B)-Mn(B)-C(2B) 123.97 (24) P(1A)-Mn(A)-C(2A) 123.05 (20) P(1B)-Mn(B)-C(4B) 130.06 (21) P(1A)-Mn(A)-C(2A) 138.92 (19) P(1B)-Mn(B)-C(2B) 123.97 (24) P(1A)-Mn(A)-C(2A) 138.92 (19) P(1B)-Mn(B)-C(2B) 154.02 (22) P(1A)-Mn(A)-C(2A) 138.92 (19) P(1B)-Mn(B)-C(4B) 130.06 (21) P(1A)-Mn(A)-C(2A) 38.1 (3) C(1B)-Mn(B)-C(2B) 150.06 (14) C(1A)-Mn(A)-C(2A) 38.1 (3) C(1B)-Mn(B)-C(2B) 166.8 (3) C(1A)-Mn(A)-C(2A) 38.1 (3) C(1B)-Mn(B)-C(2B) 166.8 (3) C(1A)-Mn(A)-C(2A) 84.9 (3) C(1B)-Mn(B)-C(2B) 110.6 (3) C(1A)-Mn(A)-C(2A) 84.9 (3) C(1B)-Mn(B)-C(2B) 111.9 (3) C(1A)-Mn(A)-C(2A) 83.3 (3) C(2B)-Mn(B)-C(2B) 111.9 (3) C(1A)-Mn(A)-C(2A) 143.7 (3) C(2B)-Mn(B)-C(2B) 111.9 (3) C(2A)-Mn(A)-C(2A) 143.7 (3) C(2B)-Mn(B)-C(2B) 89.1 (3) C(2A)-Mn(A)-C(2A) 143.7 (3) C(2B)-Mn(B)-C(2B) 89.1 (3) C(2A)-Mn(A)-C(2A) 143.7 (3) C(2B)-Mn(B)-C(2B) 89.1 (3) C(2A)-Mn(A)-C(2A) 143.7 (3) C(2B)-Mn(B)-C(2B) 89.2 (3) C(2A)-Mn(A)-C(2A) 143.7 (3) C(2B)-Mn(B)-C(2B) 199.4 (3) C(2A)-Mn(A)-C(2A) 143.7 (3) C(2B)-Mn(B)-C(2B) 199.4 (3) C(2A)-Mn(A)-C(2A) 143.7 (3) C(2B)-Mn(B)-C(2B) 199.4 (3) C(2A)-Mn(A)-C(2A) 98.8 (3) C(2B)-Mn(B)-C(2B) 199.4 (3) C(2A)-Mn(A)-C(2A) 98.8 (3) C(2B)-Mn(B)-C(2B) 199.4 (3) C(2A)-Mn(A)-C(2A) 99.8 (3) C(2B)-Mn(B)-C(2B) 139.8 (3) C(2A)-Mn(A)-C(2A) 35.69 (21) C(4B)-Mn(B)-C(2B) 139.4 (3) C(2A)-Mn(A)-C(2A) 35.69 (21) C(4B)-Mn(B)-C(2B) 139.4 (3) C(2A)-Mn(A)-C(2A) 35.69 (21) C(4B)-Mn(B)-C(2B) 139.4 (3) C(2A)-Mn(A)-C(2A) 75.5 (3) Mn(B)-C(1B) 5.1 (3) Mn(A)-C(2A)-O(3) 175.6 (7) Mn(B)-C(2B)-O(3B) 172.2 (7) Mn(A)-C(2A)-O(3) 175.6 (7) Mn(B)-C(2B)-O(2B) 172.2 (7) Mn(A)-C(2A)-O(2A) 175.6 (7) Mn(B)-C(2B) 193.5 (3) C(2A)-Mn(A)-C(2A) 75.5 (3) Mn(B)-C(1B) 70.0 (4)	C(1A)-C	(2A)	1.367 (10)	C(1B)-C(2B)	1.389 (11)
C(4A)-C(1A) 1.319 (8) C(4B)-C(1B) 1.338 (11) C(4A)-C(1A) 1.319 (8) C(4B)-C(1B) 1.307 (9) C(24A)-O(2A) 1.145 (8) C(24B)-O(2B) 1.155 (9) C(25A)-O(3A) 1.158 (8) C(24B)-O(2B) 1.155 (9) C(25A)-O(3A) 1.158 (8) C(25B)-O(3B) 1.147 (9) P(1A)-Mn(A)-C(2A) 123.05 (20) P(1B)-Mn(B)-C(2B) 123.97 (24) P(1A)-Mn(A)-C(2A) 133.92 (1) P(1B)-Mn(B)-C(2B) 154.02 (22) P(1A)-Mn(A)-C(2A) 93.20 (23) P(1B)-Mn(B)-C(2B) 96.22 (22) P(1A)-Mn(A)-C(2A) 90.76 (23) P(1B)-Mn(B)-C(2B) 96.22 (22) P(1A)-Mn(A)-C(2A) 103.63 (14) P(1B)-Mn(B)-C(2B) 36.8 (3) C(1A)-Mn(A)-C(2A) 103.63 (14) P(1B)-Mn(B)-C(2B) 36.8 (3) C(1A)-Mn(A)-C(2A) 105.63 (14) P(1B)-Mn(B)-C(2B) 36.8 (3) C(1A)-Mn(A)-C(2A) 106.0 (3) C(1B)-Mn(B)-C(2B) 36.8 (3) C(1A)-Mn(A)-C(2A) 106.0 (3) C(1B)-Mn(B)-C(2B) 101.6 (3) C(1A)-Mn(A)-C(2A) 106.0 (3) C(1B)-Mn(B)-C(2B) 171.9 (3) C(1A)-Mn(A)-C(2A) 106.0 (3) C(1B)-Mn(B)-C(2B) 171.9 (3) C(1A)-Mn(A)-C(2A) 38.3 (3) C(2B)-Mn(B)-C(1B) 77.70 (25) C(2A)-Mn(A)-C(2A) 106.0 (3) C(2B)-Mn(B)-C(1B) 77.70 (25) C(2A)-Mn(A)-C(2A) 183.3 (3) C(2B)-Mn(B)-C(1B) 77.70 (25) C(2A)-Mn(A)-C(2A) 183.3 (3) C(2B)-Mn(B)-C(1B) 89.1 (3) C(2A)-Mn(A)-C(2A) 183.3 (3) C(2B)-Mn(B)-C(1B) 89.1 (3) C(2A)-Mn(A)-C(2A) 38.0 (3) C(2B)-Mn(B)-C(1B) 89.1 (3) C(2A)-Mn(A)-C(2A) 38.0 (3) C(2B)-Mn(B)-C(2B) 199.1 (3) C(2A)-Mn(A)-C(2A) 185.7 (2) C(2B)-Mn(B)-C(1B) 89.1 (3) C(2A)-Mn(A)-C(2A) 38.0 (3) C(2B)-Mn(B)-C(1B) 89.1 (3) C(3A)-Mn(A)-C(2A) 185.7 (3) C(3B)-Mn(B)-C(1B) 84.3 (3) C(3A)-Mn(A)-C(2A) 185.6 (2) C(2B)-Mn(B)-C(1B) 189.7 (3) C(3A)-Mn(A)-C(2A) 38.6 (3) C(2B)-Mn(B)-C(2B) 84.8 (3) C(2A)-Mn(A)-C(2A) 38.6 (3) C(2B)-Mn(B)-C(1B) 189.7 (3) C(3A)-Mn(A)-C(2A) 38.6 (3) C(2B)-Mn(B)-C(2B) 189.7 (3) C(2A)-Mn(A)-C(2A) 38.6 (3) C(2B)-Mn(B)-C(2B) 189.7	C(2A) - C	(3A) (4A)	1.399 (10)	C(2B) = C(3B)	1.421 (12)
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 (8) C(25A)-O(3A) 1.155 (8) C(25B)-O(2B) 1.1758 (9) P(1A)-Mn(A)-C(2A) 123.05 (20) P(1B)-Mn(B)-C(2B) 123.97 (24) P(1A)-Mn(A)-C(2A) 137.93 (21) P(1B)-Mn(B)-C(2B) 130.06 (21) P(1A)-Mn(A)-C(2A) 137.93 (21) P(1B)-Mn(B)-C(2B) 130.06 (21) P(1A)-Mn(A)-C(2A) 90.76 (23) P(1B)-Mn(B)-C(2B) 96.22 (22) P(1A)-Mn(A)-C(2A) 90.76 (23) P(1B)-Mn(B)-C(2B) 96.22 (22) P(1A)-Mn(A)-C(2A) 86.1 (3) C(1B)-Mn(B)-C(2B) 70.0 (3) C(1A)-Mn(A)-C(2A) 86.1 (3) C(1B)-Mn(B)-C(2B) 70.0 (3) C(1A)-Mn(A)-C(2A) 86.1 (3) C(1B)-Mn(B)-C(2B) 70.0 (3) C(1A)-Mn(A)-C(2A) 167.0 (3) C(1B)-Mn(B)-C(2B) 71.0 (3) C(1A)-Mn(A)-C(2A) 167.0 (3) C(1B)-Mn(B)-C(2B) 171.9 (3) C(1A)-Mn(A)-C(2A) 167.0 (3) C(1B)-Mn(B)-C(2B) 171.9 (3) C(1A)-Mn(A)-C(2A) 38.3 (3) C(2B)-Mn(B)-C(2B) 191.9 (3) C(2A)-Mn(A)-C(2A) 90.8 (3) C(2B)-Mn(B)-C(2B) 139.8 (3) C(2A)-Mn(A)-C(2A) 90.8 (3) C(2B)-Mn(B)-C(2B) 84.8 (3) C(3A)-Mn(A)-C(2A) 99.8 (3) C(2B)-Mn(B)-C(2B) 84.8 (3) C(3A)-Mn(A)-C(2A) 99.8 (3) C(2B)-Mn(B)-C(2B) 84.8 (3) C(3A)-Mn(A)-C(2A) 106.7 (3) C(3B)-Mn(B)-C(2B) 84.8 (3) C(3A)-Mn(A)-C(2A) 106.7 (3) C(3B)-Mn(B)-C(2B) 84.8 (3) C(3A)-Mn(A)-C(2A) 175.6 (7) Mn(B)-C(2B) 84.8 (3) C(2A)-Mn(A)-C(2A) 75.5 (3) Mn(B)-O(1B) 77.0 (4) 433.8 447.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4 457.4	C(4A)-C	(5A)	1.495 (10)	C(4B) - C(5B)	1.486 (11)
C(24A)-O(2A) 1.145 (8) C(24B)-O(2B) 1.158 (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(2A) 138.92 (19) P(1B)-Mn(B)-C(2B) 130.06 (21) P(1A)-Mn(A)-C(2A) 33.02 (23) P(1B)-Mn(B)-C(2B) 96.22 (22) P(1A)-Mn(A)-C(2A) 30.76 (23) P(1B)-Mn(B)-C(2B) 96.22 (22) P(1A)-Mn(A)-C(2A) 36.1 (3) C(1B)-Mn(B)-C(2B) 96.22 (22) P(1A)-Mn(A)-C(2A) 36.1 (3) C(1B)-Mn(B)-C(2B) 96.22 (22) P(1A)-Mn(A)-C(2A) 103.63 (14) P(1B)-Mn(B)-C(2B) 96.22 (22) P(1A)-Mn(A)-C(2A) 36.1 (3) C(1B)-Mn(B)-C(2B) 96.22 (22) C(1A)-Mn(A)-C(2A) 106.0 (3) C(1B)-Mn(B)-C(2B) 101.6 (3) C(1A)-Mn(A)-C(2A) 106.0 (3) C(1B)-Mn(B)-C(2B) 171.9 (3) C(2A)-Mn(A)-C(2A) 38.3 (3) C(2B)-Mn(B)-C(2B) 171.9 (3) C(2A)-Mn(A)-C(2A) 69.5 (3) C(2B)-Mn(B)-C(2B) 192.1 (3) C(2A)-Mn(A)-C(2A) 108.7 (3) C(2B)-Mn(B)-C(2B) 192.1 (3) C(2A)-Mn(A)-C(2A) 108.7 (3) C(2B)-Mn(B)-C(2B) 193.8 (3) C(3A)-Mn(A)-C(2A) 106.7 (3) C(2B)-Mn(B)-C(2B) 193.8 (3) C(3A)-Mn(A)-C(2A) 106.7 (3) C(2B)-Mn(B)-C(2B) 102.1 (3) C(3A)-Mn(A)-C(2A) 106.7 (3) C(3B)-Mn(B)-C(2B) 102.1 (3) C(3A)-Mn(A)-C(2A) 135.69 (21) C(3B)-Mn(B)-C(2B) 103.0 (3) C(3A)-Mn(A)-C(2A) 129.9 (3) C(3B)-Mn(B)-C(2B) 104.0 (3) C(3A)-Mn(A)-C(2A) 170.0 (6) Mn(B)-C(2B) 84.8 (3) C(2A)-Mn(A)-O(1A) 15.66 (3) C(2B)-Mn(B)-O(1B) 35.22 (23) C(2A)-Mn(A)-O(1A) 15.66 (3) C(24B)-Mn(B)-O(1B) 35.22 (24) Mn(A)-C(25A) 03.8 (6) C(24B)-Mn(B)-O(25B) 84.8 (3) C(24A)-Mn(A)-O(1A) 15.66 (3) C(24B)-Mn(B)-O(2B) 84.8 (3) C(24A)-Mn(A)-O(1A) 15.6 (3) C(24B)-Mn(B)-O(2B) 84.8 (3) C(24A)-Mn(A)-O(1A) 15.6 (3) C(24B)-Mn(B)-O(2B) 84.8 (3) C(24A)-Mn(A)-O(1A) 15.6 (3) C(24B)-Mn(B)-O(2B) 84.8 (3) C(24A)-Mn(A)-O(2A) 177.0 (6) Mn(B)-O(2B) 0.35.22 (23) 84.8 (3) C(24A)-Mn(A)-O(2A) 177.0 (6) Mn(B)-O(2B) 0.35.22 (23) 84.8 (3) C(24A)-Mn(A)-O(2A) 175.6 (7) Mn(B)-O(2B) 0.35.2 (23) 84.8 (3) C(24A)-Mn(A)-O(2A) 175.6 (7) Mn(C(4A)-O	(1A)	1.319 (8)	C(4B)-O(1B)	1.307 (9)
C(22A)-O(3A) 1.156 (8) C(22B)-O(3B) 1.147 (9) P(1A)-Mn(A)-C(2A) 32.05 (20) P(1B)-Mn(B)-C(2B) 123.97 (24) P(1A)-Mn(A)-C(2A) 132.05 (20) P(1B)-Mn(B)-C(2B) 130.06 (21) P(1A)-Mn(A)-C(2A) 33.20 (22) P(1B)-Mn(B)-C(2B) 96.12 (22) P(1A)-Mn(A)-C(2A) 30.76 (23) P(1B)-Mn(B)-C(2B) 36.8 (3) P(1A)-Mn(A)-C(2A) 30.53 (14) P(1B)-Mn(B)-C(2B) 36.8 (3) C(1A)-Mn(A)-C(2A) 36.1 (3) C(1B)-Mn(B)-C(2B) 36.8 (3) C(1A)-Mn(A)-C(2A) 107.0 (3) C(1B)-Mn(B)-C(2B) 171.9 (3) C(1A)-Mn(A)-C(2A) 160.0 (3) C(1B)-Mn(B)-C(2B) 171.9 (3) C(1A)-Mn(A)-C(2A) 160.0 (3) C(1B)-Mn(B)-C(2B) 171.9 (3) C(1A)-Mn(A)-C(2A) 38.3 (3) C(2B)-Mn(B)-C(1B) 77.70 (25) C(2A)-Mn(A)-C(2A) 38.3 (3) C(2B)-Mn(B)-C(2B) 139.8 (3) C(2A)-Mn(A)-C(2A) 90.8 (3) C(2B)-Mn(B)-C(2B) 139.8 (3) C(2A)-Mn(A)-C(2A) 90.8 (3) C(2B)-Mn(B)-C(2B) 139.8 (3) C(2A)-Mn(A)-C(2A) 99.8 (3) C(2B)-Mn(B)-C(2B) 139.7 (3) C(3A)-Mn(A)-C(2A) 99.8 (3) C(2B)-Mn(B)-C(2B) 139.7 (3) C(3A)-Mn(A)-C(2A) 167.3 (C2B)-Mn(B)-O(1B) 84.8 (3) C(2A)-Mn(A)-C(2A) 85.6 (2) C(2B)-Mn(B)-O(1B) 85.22 (25) C(2A)-Mn(A)-C(2A) 167.3 (C2B)-Mn(B)-O(1B) 169.7 (3) C(2A)-Mn(A)-C(2A) 85.6 (3) C(2B)-Mn(B)-O(1B) 169.7 (3) C(2A)-Mn(A)-C(2A) 70.0 (6) Mn(B)-C(2B) 84.8 (3) C(2A)-Mn(A)-C(2A) 70.6 (7) Mn(B)-C(2B) 84.8 (3) C(2A)-Mn(A)-C(2A) 75.5 (3) Mn(B)-O(1B) 169.7 (3) C(2A)-Mn(A)-C(4A) 75.5 (3) Mn(B)-O(1B)-C(4B) 77.0 (4) 343 K 4074-404-404-404-404-404-404-404-404-404	C(24A)-(D(2A)	1.145 (8)	C(24B)-O(2B)	1.158 (9)
P(1A)-Mn(A)-C(1A) 99.68 (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(2A) 133.92 (19) P(1B)-Mn(B)-C(2B) 1130.06 (21) P(1A)-Mn(A)-C(2A) 93.20 (23) P(1B)-Mn(B)-C(2B) 96.22 (22) P(1A)-Mn(A)-C(2A) 93.20 (23) P(1B)-Mn(B)-C(2B) 96.22 (22) P(1A)-Mn(A)-C(2A) 90.76 (23) P(1B)-Mn(B)-C(2B) 96.22 (22) P(1A)-Mn(A)-C(2A) 86.8 (3) C(1B)-Mn(B)-C(2B) 96.22 (22) P(1A)-Mn(A)-C(2A) 88.8 (3) C(1B)-Mn(B)-C(2B) 96.22 (22) P(1A)-Mn(A)-C(2A) 103.63 (14) P(1B)-Mn(B)-C(2B) 101.6 (3) C(1A)-Mn(A)-C(2A) 165.1 (3) C(1B)-Mn(B)-C(2B) 101.6 (3) C(1A)-Mn(A)-C(2A) 165.0 (3) C(1B)-Mn(B)-C(2B) 171.9 (3) C(1A)-Mn(A)-C(2A) 165.6 (22) C(1B)-Mn(B)-C(2B) 191.9 (3) C(2A)-Mn(A)-C(2A) 163.7 (3) C(2B)-Mn(B)-C(2B) 139.8 (3) C(2A)-Mn(A)-C(2A) 90.8 (3) C(2B)-Mn(B)-C(2B) 139.7 (3) C(3A)-Mn(A)-C(2A) 84.6 (3) C(3B)-Mn(B)-C(2B) 102.7 (3) C(3A)-Mn(A)-C(2A) 84.6 (3) C(2B)-Mn(B)-C(1B) 84.3 (3) C(2A)-Mn(A)-C(2A) 84.6 (3) C(2B)-Mn(B)-C(1B) 135.2 (25) C(2A)-Mn(A)-C(2A) 84.6 (3) C(2B)-Mn(B)-C(1B) 135.2 (25) C(2A)-Mn(A)-C(2A) 84.6 (3) C(2B)-Mn(B)-C(1B) 135.2 (25) C(2A)-Mn(A)-C(2A) 95.6 (3) C(2B)-Mn(B)-C(1B) 135.2 (25) C(2A)-Mn(A)-C(2A) 84.6 (3) C(2B)-Mn(B)-C(1B) 135.2 (25) C(2A)-Mn(A)-C(2A) 95.6 (3) C(2B)-Mn(B)-C(1B) 135.2 (7) Mn(A)-C(2A)-O(2A) 175.6 (7) Mn(B)-C(2B)-O(2B) 176.0 (7) Mn(A)-C(2A)-O(2A) 175.6 (7) Mn(B)-O(1B) 169.7 (3) C(2A)-Mn(A)-C(2A) 75.5 (3) Mn(B)-O(1B) 169.7 (3) C(2A)-Mn(A)-C(2A) 75.5 (3) Mn(B)-O(1B) 77.0 (4) 233.8 241.2 241.2 241.2 241.2 242.2 241.2 241.2 241.2 241.2 241.2 241.2 241.2 241.2 241.2 241.2 24	C(25A)-(J(3A)	1.158 (8)	C(25B)O(3B)	1.147 (9)
P(1A)-Mn(A)-C(2A) 123.05 (20) P(1B)-Mn(B)-C(2B) 123.97 (24) P(1A)-Mn(A)-C(3A) 138.92 (19) P(1B)-Mn(B)-C(2B) 130.06 (21) P(1A)-Mn(A)-C(2A) 93.20 (23) P(1B)-Mn(B)-C(2B) 96.22 (22) P(1A)-Mn(A)-C(2A) 90.76 (23) P(1B)-Mn(B)-C(2B) 96.22 (22) P(1A)-Mn(A)-C(2A) 36.1 (3) C(1B)-Mn(B)-C(2B) 96.22 (22) P(1A)-Mn(A)-C(2A) 68.8 (3) C(1B)-Mn(B)-C(2B) 101.6 (3) C(1A)-Mn(A)-C(2A) 167.0 (3) C(1B)-Mn(B)-C(2B) 101.6 (3) C(1A)-Mn(A)-C(2A) 166.0 (3) C(2B)-Mn(B)-C(2B) 131.6 (3) C(2A)-Mn(A)-C(2A) 143.7 (3) C(2B)-Mn(B)-C(2B) 139.1 (3) C(2A)-Mn(A)-C(2A) 90.8 (3) C(2B)-Mn(B)-C(2B) 139.8 (3) C(2A)-Mn(A)-C(2A) 106.7 (3) C(3B)-Mn(B)-C(2B) 139.8 (3) C(3A)-Mn(A)-C(2A) 106.7 (3) C(3B)-Mn(B)-C(2B) 139.8 (3) C(4A)-Mn(A)-C(2A) 84.6 (3) C(4B)-Mn(B)-C(2B) 139.8 (3) C(4A)-Mn(A)-C(1A) 15.5 (3) C(2B)-Mn(B)-C(2B) 188.8 (3) C(2A)-Mn(A)-O(1A) 165.6 (3) C(2B)-Mn(B)-O(1B) 35.22 (23) C(2A)-Mn(A)-O(1A) 15.5 (3) Mn(B)-O(1B) 169.7 (3) C(2A)-Mn(A)-O(1A) 15.6 (3) C(2B)-Mn(B)-O(1B) 169.7 (3) C(2A)-Mn(A)-O(1A) 75.5 (3) Mn(B)-O(1B) 95.1 (3) Mn(A)-C(25A)-O(3A) 175.6 (7) Mn(B)-O(1B) 95.1 (3) Mn(A)-C(25A)-O(3A) 175.6 (7) Mn(B)-O(2B) 172.0 (7) Mn(A)-O(1A)-C(4A) 75.5 (3) Mn(B)-O(1B) 95.1 (3) Mn(A)-C(25A)-O(3A) 175.6 (7)	P(1A)-Mn(A)	-C(1A)	89.68 (19)	P(1B)-Mn(B)-C(1	B) 88.16 (20)
P(1A)-Mn(A)-C(3A) 13.8.92 (12) P(1B)-Mn(B)-C(3B) 130.06 (21) P(1A)-Mn(A)-C(24A) 93.20 (23) P(1B)-Mn(B)-C(24B) 96.21 (23) P(1A)-Mn(A)-C(25A) 90.76 (23) P(1B)-Mn(B)-C(25B) 96.22 (22) C(1A)-Mn(A)-C(2A) 36.1 (3) C(1B)-Mn(B)-C(2B) 36.8 (3) C(1A)-Mn(A)-C(2A) 68.8 (3) C(1B)-Mn(B)-C(2B) 36.8 (3) C(1A)-Mn(A)-C(24A) 167.0 (3) C(1B)-Mn(B)-C(24B) 101.6 (3) C(1A)-Mn(A)-C(24A) 167.0 (3) C(1B)-Mn(B)-C(24B) 101.6 (3) C(1A)-Mn(A)-C(24A) 167.0 (3) C(1B)-Mn(B)-C(24B) 101.6 (3) C(2A)-Mn(A)-C(24A) 167.0 (3) C(2B)-Mn(B)-C(24B) 193.1 (3) C(2A)-Mn(A)-C(24A) 163.7 (3) C(2B)-Mn(B)-C(24B) 189.7 (3) C(2A)-Mn(A)-C(24A) 163.7 (3) C(2B)-Mn(B)-C(24B) 189.7 (3) C(2A)-Mn(A)-C(24A) 163.7 (3) C(2B)-Mn(B)-C(24B) 189.8 (3) C(2A)-Mn(A)-C(24A) 165.7 (3) C(2B)-Mn(B)-C(24B) 198.8 (3) C(2A)-Mn(A)-C(24A) 166.7 (3) C(2B)-Mn(B)-C(24B) 198.8 (3) C(2A)-Mn(A)-C(24A) 166.7 (3) C(2B)-Mn(B)-C(24B) 198.7 (3) C(3A)-Mn(A)-C(24A) 166.7 (3) C(2B)-Mn(B)-C(24B) 198.7 (3) C(3A)-Mn(A)-C(24A) 166.7 (3) C(2B)-Mn(B)-C(24B) 198.2 (3) C(3A)-Mn(A)-C(25A) 99.8 (3) C(2B)-Mn(B)-C(24B) 192.7 (3) C(3A)-Mn(A)-C(25A) 199.9 (3) C(4B)-Mn(B)-C(24B) 194.7 (3) C(3A)-Mn(A)-C(25A) 129.9 (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) 84.8 (3) C(24A)-Mn(A)-C(1A) 155.6 (3) C(24B)-Mn(B)-C(25B) 84.8 (3) C(24A)-Mn(A)-C(1A) 155.6 (3) C(24B)-Mn(B)-C(25B) 84.8 (3) C(24A)-Mn(A)-C(1A) 175.5 (3) Mn(B)-C(24B) 176.0 (7) Mn(A)-C(25A)-C(3A) 175.6 (7) Mn(B)-C(25B) 76.0 (7) Mn(A)-C(25A)-C(3A) 175.5 (3) Mn(B)-C(25B) 77.0 (4)	P(1A)-Mn(A)	-C(2A)	123.05 (20)	P(1B)-Mn(B)-C(2)	B) 123.97 (24)
1 (1A) - MI(A) - C(2A) 133.20 (23) P(1B) - Mn(B) - C(24B) 98.21 (22) P(1A) - Mn(A) - C(2A) 93.20 (23) P(1B) - Mn(B) - C(24B) 98.22 (22) P(1A) - Mn(A) - C(2A) 36.1 (3) C(1B) - Mn(B) - C(2B) 38.8 (3) C(1A) - Mn(A) - C(2A) 84.8 (3) C(1B) - Mn(B) - C(2B) 38.8 (3) C(1A) - Mn(A) - C(2A) 68.8 (3) C(1B) - Mn(B) - C(2B) 106. (3) C(1A) - Mn(A) - C(2A) 167.0 (3) C(1B) - Mn(B) - C(2B) 101.6 (3) C(1A) - Mn(A) - C(2A) 167.0 (3) C(1B) - Mn(B) - C(2B) 101.6 (3) C(1A) - Mn(A) - C(2A) 165.3 (22) C(B) - Mn(B) - C(2B) 101.6 (3) C(1A) - Mn(A) - C(2A) 165.3 (22) C(B) - Mn(B) - C(2B) 108.2 (23) C(2A) - Mn(A) - C(2A) 143.7 (3) C(2B) - Mn(B) - C(2B) 189.2 (3) C(2A) - Mn(A) - C(2A) 90.8 (3) C(2B) - Mn(B) - C(2B) 189.2 (3) C(2A) - Mn(A) - C(2A) 90.8 (3) C(2B) - Mn(B) - C(2B) 189.2 (3) C(2A) - Mn(A) - C(2A) 90.8 (3) C(2B) - Mn(B) - C(2B) 189.2 (3) C(3A) - Mn(A) - C(2A) 90.8 (3) C(2B) - Mn(B) - C(1B) 13.2 (23) C(3A) - Mn(A)	P(1A)-Mn(A) P(1A)-Mn(A)	-C(3A)	157.93 (21)	P(1B)-Mn(B)-C(3) P(1B)-Mn(B)-C(4)	B) 154.02 (22) B) 190.06 (91)
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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)-C(3A) 38.3 (3) C(2B)-Mn(B)-C(2B) 39.1 (3) C(2A)-Mn(A)-C(4A) 69.5 (3) C(2B)-Mn(B)-C(2B) 69.7 (3) C(2A)-Mn(A)-C(2A) 143.7 (3) C(2B)-Mn(B)-C(2B) 139.8 (3) C(2A)-Mn(A)-C(2A) 143.7 (3) C(2B)-Mn(B)-C(2B) 139.8 (3) C(2A)-Mn(A)-C(2A) 38.0 (3) C(2B)-Mn(B)-C(2B) 139.8 (3) C(3A)-Mn(A)-C(2A) 106.7 (3) C(3B)-Mn(B)-C(2B) 104.0 (3) C(3A)-Mn(A)-C(25A) 99.8 (3) C(3B)-Mn(B)-C(24B) 102.7 (3) C(3A)-Mn(A)-C(25A) 99.8 (3) C(3B)-Mn(B)-C(24B) 102.7 (3) C(3A)-Mn(A)-C(25A) 129.9 (3) C(4B)-Mn(B)-C(24B) 104.0 (3) C(3A)-Mn(A)-C(25A) 129.9 (3) C(4B)-Mn(B)-C(24B) 104.7 (3) C(4A)-Mn(A)-C(25A) 129.9 (3) C(4B)-Mn(B)-C(24B) 104.7 (3) C(4A)-Mn(A)-C(25A) 129.9 (3) C(4B)-Mn(B)-C(24B) 104.7 (3) C(24A)-Mn(A)-C(25A) 129.9 (3) C(24B)-Mn(B)-C(24B) 135.22 (23) C(24A)-Mn(A)-C(25A) 129.9 (3) C(24B)-Mn(B)-C(25B) 86.8 (3) C(24A)-Mn(A)-C(25A) 129.9 (3) C(24B)-Mn(B)-C(21B) 136.8 (3) C(24A)-Mn(A)-C(25A) 129.9 (3) C(24B)-Mn(B)-C(25B) 86.8 (3) C(24A)-Mn(A)-C(25A) 177.0 (6) Mn(B)-C(25B)-O(2B) 176.6 (7) Mn(A)-C(25A)-O(3A) 175.6 (7) Mn(B)-C(24B) 104.7 (3) C(25A)-Mn(A)-O(1A) 165.6 (3) C(24B)-Mn(B)-O(1B) 169.7 (3) C(25A)-O(3A) 175.6 (7) Mn(B)-C(24B) 77.0 (4)	C(1A) - Mn(A) C(1A) - Mn(A)	-C(3A)	84.9 (3)	C(1B)-Mn(B)-C(3) C(1B)-Mn(B)-C(4)	B) 85.2 (3)
C(1A)-Mn(A)-C(25A) 106.0 (3) C(1B)-Mn(B)-C(2EB) 171.9 (3) C(1A)-Mn(A)-C(1A) 75.85 (22) C(1B)-Mn(B)-C(1B) 77.70 (25) C(2A)-Mn(A)-C(4A) 69.5 (3) C(2B)-Mn(B)-C(4B) 68.7 (3) C(2A)-Mn(A)-C(2A) 143.7 (3) C(2B)-Mn(B)-C(2EB) 198.9 (3) C(2A)-Mn(A)-C(2A) 143.7 (3) C(2B)-Mn(B)-C(2EB) 198.8 (3) C(2A)-Mn(A)-C(2A) 90.8 (3) C(2B)-Mn(B)-C(1B) 84.3 (3) C(3A)-Mn(A)-C(2A) 106.7 (3) C(3B)-Mn(B)-C(2B) 138.8 (3) C(3A)-Mn(A)-C(25A) 99.8 (3) C(3B)-Mn(B)-C(2EB) 104.0 (3) C(3A)-Mn(A)-C(25A) 99.8 (3) C(3B)-Mn(B)-C(2EB) 104.0 (3) C(3A)-Mn(A)-C(25A) 129.9 (3) C(3B)-Mn(B)-C(2EB) 104.0 (3) C(3A)-Mn(A)-C(25A) 129.9 (3) C(4B)-Mn(B)-C(2EB) 104.0 (3) C(4A)-Mn(A)-C(25A) 129.9 (3) C(4B)-Mn(B)-C(2EB) 86.8 (3) C(2A)-Mn(A)-C(25A) 86.6 (3) C(24B)-Mn(B)-C(2EB) 86.8 (3) C(24A)-Mn(A)-C(1A) 35.69 (21) C(4B)-Mn(B)-C(1B) 135.22 (23) Mn(A)-C(25A)-O(1A) 165.6 (3) C(22B)-Mn(B)-O(1B) 169.7 (3) C(25A)-Mn(A)-O(1A) 165.6 (3) C(22B)-Mn(B)-O(1B) 169.7 (3) C(25A)-Mn(A)-O(1A) 165.6 (3) C(22B)-Mn(B)-O(1B) 169.7 (3) C(25A)-Mn(A)-O(1A) 170.6 (6) Mn(B)-C(2B) O(2B) 176.0 (7) Mn(A)-C(25A)-O(3A) 175.6 (7) Mn(B)-C(2B) -O(2B) 176.0 (7) Mn(A)-C(25A)-O(3A) 175.6 (7) Mn(B)-C(2B) -O(2B) 176.0 (7) Mn(A)-O(1A)-C(4A) 75.5 (3) Mn(B)-O(1B) 77.0 (4)	C(1A)-Mn(A)	-C(24A)	167.0 (3)	C(1B)-Mn(B)-C(2	4B) 101.6 (3)
C(1A)-Mn(A)-C(3A) 75.85 (22) C(1B)-Mn(B)-C(1B) 77.70 (25) C(2A)-Mn(A)-C(3A) 38.3 (3) C(2B)-Mn(B)-C(2B) 39.1 (3) C(2A)-Mn(A)-C(2A) 143.7 (3) C(2B)-Mn(B)-C(2AB) 89.2 (3) C(2A)-Mn(A)-C(2A) 143.7 (3) C(2B)-Mn(B)-C(2B) 139.8 (3) C(2A)-Mn(A)-C(1A) 82.55 (22) C(2B)-Mn(B)-C(1B) 84.3 (3) C(3A)-Mn(A)-C(2A) 106.7 (3) C(3B)-Mn(B)-C(4B) 37.5 (3) C(3A)-Mn(A)-C(2A) 106.7 (3) C(3B)-Mn(B)-C(2B) 102.7 (3) C(3A)-Mn(A)-C(2A) 99.8 (3) C(3B)-Mn(B)-C(2B) 104.0 (3) C(3A)-Mn(A)-C(2A) 106.7 (3) C(3B)-Mn(B)-C(2B) 104.0 (3) C(3A)-Mn(A)-C(2A) 129.9 (3) C(4B)-Mn(B)-C(2B) 104.7 (3) C(4A)-Mn(A)-C(2A) 129.9 (3) C(4B)-Mn(B)-C(2B) 86.8 (3) C(4A)-Mn(A)-C(2A) 86.6 (3) C(2AB)-Mn(B)-C(2B) 86.8 (3) C(2AA)-Mn(A)-C(2A) 86.6 (3) C(2AB)-Mn(B)-C(2B) 86.8 (3) C(2AA)-Mn(A)-C(2A) 129.9 (3) C(4B)-Mn(B)-C(2B) 86.8 (3) C(2AA)-Mn(A)-C(2A) 129.9 (3) C(4B)-Mn(B)-C(2B) 86.8 (3) C(2AA)-Mn(A)-C(2A) 129.9 (3) C(2AB)-Mn(B)-C(2B) 86.8 (3) C(2AA)-Mn(A)-C(2A) 129.0 (3) C(2AB)-Mn(B)-C(2B) 86.8 (3) C(2AA)-Mn(A)-C(2A) 129.0 (3) C(2AB)-Mn(B)-C(2B) 86.8 (3) C(2AA)-Mn(A)-C(2A) 177.0 (6) Mn(B)-C(2B)-0(1B) 166.7 (3) C(25A)-Mn(A)-C(2A) 177.0 (6) Mn(B)-C(2B)-0(2B) 176.0 (7) Mn(A)-C(25A)-O(3A) 175.6 (7) Mn(B)-C(2B)-O(2B) 176.0 (7) Mn(A)-C(2A)-O(2A) 177.0 (6) Mn(B)-C(2B)-O(2B) 176.0 (7) Mn(A)-C(2A)-O(3A) 175.6 (7) Mn(B)-C(2B)-O(2B) 177.0 (4)	C(1A)-Mn(A)	-C(25A)	106.0 (3)	C(1B)-Mn(B)-C(2)	5B) 171.9 (3)
C(2A) - Mn(A) - C(2A) = Mn(B) - C(2B) = Mn(B) - C(2B) = Mn(B) - C(2B) = Mn(A) - C(2A) = Mn(A) - C(2A) = Mn(B) - C(2B) = Mn(B) - C(2B) = Mn(B) - C(2B) = Mn(A) - C(2A) - Mn(A) - C(2A) = Mn(B) - C(2B) = Mn(B) - C(2B) = Mn(B) - C(2B) = Mn(B) - C(2A) = Mn(A) - C(2A) = Mn(A) - C(2A) = Mn(B) - C(2B) = Mn(B) - C(2B) = Mn(B) - C(2B) = Mn(B) - C(2A) = Mn(A) - C(2A) = Mn(B) - C(2B) = Mn(B) - C(2B) = Mn(B) - C(2A) = Mn(A) - C(2A) - Mn(A) - C(2A) = Mn(B) - C(2B) = Mn(B) - C(2B) = Mn(B) - C(2B) = Mn(B) - C(2A) = Mn(A) - C(2A) - Mn(A) - C(2A) = Mn(B) - C(2B) - Mn(B) - C(2B) = Mn(B) - C(2A) = Mn(A) - C(2A) - Mn(A) - C(2A) = Mn(B) - C(2B) - Mn(B) - C(2B) = Mn(B) - C(2B) = Mn(B) - C(2B) = Mn(B) - C(2A) = Mn(A) - C(2A) - Mn(A) - C(2A) = Mn(B) - C(2B) - Mn(B) - C(2B) = Mn(B) - C(2A) = Mn(A) - C(2A) - Mn(A) - C(2A) = Mn(B) - C(2B) - Mn(B) - C(2B) = Mn(B	C(1A) - Mn(A)	-0(1A)	75.85 (22)	C(1B)-Mn(B)-O(1)	.B) 77.70 (25)
C(2A)-Mn(A)-C(2A) 143.7 (3) C(2B)-Mn(B)-C(2AB) 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)-C(1A) 82.55 (22) C(2B)-Mn(B)-C(1B) 84.3 (3) C(3A)-Mn(A)-C(2A) 106.7 (3) C(3B)-Mn(B)-C(2AB) 102.7 (3) C(3A)-Mn(A)-C(25A) 99.8 (3) C(3B)-Mn(B)-C(24B) 102.7 (3) C(3A)-Mn(A)-C(25A) 129.9 (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(24A)-Mn(A)-C(25A) 129.9 (3) C(4B)-Mn(B)-C(25B) 86.8 (3) C(24A)-Mn(A)-C(25A) 129.9 (3) C(24B)-Mn(B)-C(25B) 86.8 (3) C(24A)-Mn(A)-C(1A) 91.2 (3) C(24B)-Mn(B)-C(25B) 86.8 (3) C(24A)-Mn(A)-O(1A) 91.2 (3) C(24B)-Mn(B)-C(25B) 86.8 (3) C(24A)-Mn(A)-O(1A) 91.2 (3) C(24B)-Mn(B)-C(25B) 84.8 (3) C(24A)-Mn(A)-O(1A) 165.6 (3) C(24B)-Mn(B)-C(1B) 95.1 (3) Mn(A)-C(25A)-O(3A) 175.6 (7) Mn(B)-C(25B)-O(3B) 176.0 (7) Mn(A)-O(1A)-C(4A) 75.5 (3) Mn(B)-O(1B) 77.0 (4)	C(2A)-Mn(A) C(2A)-Mn(A)	-C(3A)	69.5 (3)	C(2B)-Mn(B)-C(3)	B) 69.7 (3)
$C(2A)-Mn(A)-C(25A) = 90.8 (3) = C(2B)-Mn(B)-C(25B) = 139.8 (3) \\ C(2A)-Mn(A)-C(1A) = 82.55 (22) = C(2B)-Mn(B)-C(4B) = 37.5 (3) \\ C(3A)-Mn(A)-C(2A) = 106.7 (3) = C(3B)-Mn(B)-C(2B) = 104.0 (3) \\ C(3A)-Mn(A)-C(25A) = 99.8 (3) = C(3B)-Mn(B)-C(25B) = 104.0 (3) \\ C(3A)-Mn(A)-C(25A) = 48.6 (3) = C(4B)-Mn(B)-C(25B) = 104.7 (3) \\ C(4A)-Mn(A)-C(25A) = 129.9 (3) = C(4B)-Mn(B)-C(25B) = 86.8 (3) \\ C(2A)-Mn(A)-C(25A) = 86.6 (3) = C(24B)-Mn(B)-O(1B) = 35.22 (23) \\ C(24A)-Mn(A)-C(25A) = 86.6 (3) = C(24B)-Mn(B)-O(1B) = 35.22 (23) \\ C(24A)-Mn(A)-C(25A) = 86.6 (3) = C(24B)-Mn(B)-O(1B) = 35.22 (23) \\ C(24A)-Mn(A)-O(1A) = 15.2 (3) = C(24B)-Mn(B)-O(1B) = 95.1 (3) \\ Mn(A)-C(24A)-O(2A) = 177.0 (6) = Mn(B)-O(1B) = 0(1B) = 176.0 (7) \\ Mn(A)-C(25A)-O(3A) = 175.6 (7) = Mn(B)-O(1B) = 0(25B) - 0(3B) = 172.2 (7) \\ Mn(A)-O(1A)-C(4A) = 75.5 (3) = Mn(B)-O(1B) = C(4B) = 77.0 (4) \\ Mn(A)-O(1A)-C(4A) = 75.5 (3) = Mn(B)-O(1B) = C(4B) = 77.0 (4) \\ Mn(A)-O(1A)-C(4A) = 75.5 (3) = Mn(B)-O(1B) = C(4B) = 77.0 (4) \\ Mn(A)-O(1A)-C(4A) = 75.5 (3) = Mn(B)-O(1B) = C(4B) = 77.0 (4) \\ Mn(A)-O(1A)-C(4A) = 75.5 (3) = Mn(B)-O(1B) = C(4B) = 77.0 (4) \\ Mn(A)-O(1A)-C(4A) = 75.5 (3) = Mn(B)-O(1B) = C(4B) = 77.0 (4) \\ Mn(A)-O(1A)-C(4A) = 75.5 (3) = Mn(B)-O(1B) = C(4B) = 77.0 (4) \\ Mn(A)-O(1A)-C(4A) = 75.5 (3) = Mn(B)-O(1B) = C(4B) = 77.0 (4) \\ Mn(A)-O(1A)-C(4A) = 75.5 (3) = Mn(B)-O(1B) = C(4B) = 77.0 (4) \\ Mn(A)-O(1A)-C(4A) = 725 + 215 = 213 = 0 = 207 + 0 = 201 = 0 \\ Mn(A)-O(1A)-C(4A) = 725 + 215 = 213 = 0 = 207 + 0 = 201 = 0 \\ Mn(A)-O(1A)-C(4A) = 725 + 215 = 213 = 0 = 207 + 0 = 201 = 0 \\ Mn(A)-O(1A)-C(4A) = 725 + 215 = 213 = 0 = 207 + 0 = 201 = 0 \\ Mn(A)-O(1A)-C(4A) = 725 + 215 = 0 = 207 + 0 = 201 = 0 \\ Mn(A)-O(1A)-C(4A) = 725 + 215 = 0 = 207 + 0 = 201 = 0 \\ Mn(A)-O(1A)-C(4A) = 725 + 215 = 0 = 207 + 0 = 201 = 0 \\ Mn(A)-O(A)-C(A) = 203 + 0 = 200 + 0 = 200 + 0 = 200 + 0 \\ Mn(A)-C(A)-C(A) = 0 = 200 + 0 = 200 + 0 = 200 + 0 = 200 + 0 = 200 + 0 \\ Mn(A)-C(A)-C(A) = 0 = 200 + 0 = 200 + 0 = 200 + 0 = 200 + 0 = 200 + 0 = 200 + 0 = 200 + 0 = 200 + 0 = 200 + 0 = 200 + 0 = 200 +$	C(2A)-Mn(A)	-C(24A)	143.7 (3)	C(2B)-Mn(B)-C(2)	(4B) 89.2 (3)
C(2A) - Mn(A) - C(1A) = 82.55 (22) C(2B) - Mn(B) - C(1B) = 84.3 (3) C(3A) - Mn(A) - C(2A) = 106.7 (3) C(3B) - Mn(B) - C(2AB) = 102.7 (3) C(3A) - Mn(A) - C(25A) = 99.8 (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) - C(25A) = 129.9 (3) C(4B) - Mn(B) - C(25B) = 86.8 (3) C(4A) - Mn(A) - C(25A) = 129.9 (3) C(4B) - Mn(B) - C(25B) = 86.8 (3) C(24A) - Mn(A) - C(25A) = 86.6 (3) C(24B) - Mn(B) - C(25B) = 84.8 (3) C(24A) - Mn(A) - C(1A) = 15.6 (3) C(24B) - Mn(B) - O(1B) = 35.22 (23) C(24A) - Mn(A) - O(1A) = 12.2 (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) = 169.7 (3) C(25A) - Mn(A) - O(1A) = 175.6 (7) Mn(B) - C(24B) - O(2B) = 176.0 (7) Mn(A) - C(25A) - O(3A) = 175.6 (7) Mn(B) - C(24B) - O(2B) = 176.0 (7) Mn(A) - O(1A) - C(4A) = 75.5 (3) Mn(B) - O(1B) - C(4B) = 77.0 (4)	C(2A)-Mn(A)	-C(25A)	90.8 (3)	C(2B)-Mn(B)-C(2)	5B) 139.8 (3)
(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) - C(25A) 99.8 (3) 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(24A) - Mn(A) - C(25A) 129.9 (3) C(4B) - Mn(B) - C(25B) 86.8 (3) C(24A) - Mn(A) - C(25A) 129.9 (3) C(24B) - Mn(B) - O(1B) 35.22 (23) C(24A) - Mn(A) - O(1A) 35.6 (3) C(24B) - Mn(B) - O(1B) 95.1 (3) C(25A) - Mn(A) - O(1A) 165.6 (3) C(24B) - Mn(B) - O(1B) 95.1 (3) Mn(A) - C(25A) - O(2A) 177.0 (6) Mn(B) - C(25B) - O(3B) 172.2 (7) Mn(A) - O(1A) - O(1A) 155.6 (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)	C(2A)-Mn(A)	-0(1A)	82.55 (22)	C(2B)-Mn(B)-O(1)	.B) 84.3 (3) B) 97.5 (9)
C(3A)-Mn(A)-C(25A) 99.8 (3) C(3B)-Mn(B)-C(25B) 104.0 (3) C(3A)-Mn(A)-C(24A) 84.6 (3) C(4B)-Mn(B)-C(24B) 134.7 (3) C(4A)-Mn(A)-C(24A) 129.9 (3) C(4B)-Mn(B)-C(25B) 86.8 (3) C(24A)-Mn(A)-C(1A) 35.69 (21) C(4B)-Mn(B)-C(1B) 35.22 (23) C(24A)-Mn(A)-C(1A) 165.6 (3) C(24B)-Mn(B)-C(1B) 169.7 (3) C(25A)-Mn(A)-O(1A) 165.6 (3) C(24B)-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(24A)-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)-C(1B)-C(4B) 77.0 (4)	C(3A) - Mn(A) C(3A) - Mn(A)	-C(24A)	1067(3)	C(3B) - Mn(B) - C(4)	24B) 102.7 (3)
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Figure 3. Variable-temperature ¹³C NMR spectra of 3b.

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 ³¹P NMR spectra and its ¹H NMR resonances are probably masked by resonances of the other major isomers. For 4b and 4d, the most abundent isomer is assignable to A because of its most upfield resonance (Scheme IV). This structural assignment stems from the stereochemistry of $(\eta^5$ -dienyl)Mn(CO)₂(P(OCH₂)₃CEt) as well as the ³¹P 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 ¹H and ³¹P 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 ¹H 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 ³¹P 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 $\Delta G^* = 15.7 \pm 0.4 \text{ kcal mol}^{-1}$.

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 $(\eta^{5}$ -CH₂CHCHCOR)Mn(CO)₂L (L = CO, PPh₃; R = OCH₃, CH₃) 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 $(\eta^{5}$ -dienyl)Mn(CO)₂(P(OCH₂)₃CEt)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 ³¹P and ¹H 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 $(\eta^5$ -C₅H₇)Mn(CO)₃,⁸ which exhibits only one carbonyl resonance at 23 °C. These



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

Facile $\eta^5 \rightleftharpoons \eta^3$ 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 CHCl₃ and CH₂Cl₂, 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 - $CH_2CHCHCOOCH_3)Mn(CO)_3L$ (L = CH_3CN (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_2Cl_2 or $CHCl_3$ below 15 °C the complexes re-form 3a nearly quantitatively, whereas 6a still retains its η^3 -CH₃CN 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 CH₃CN, acetone, and THF. This trend is similar to that for the reported metal-oxaallyl complexes CpM(CO)₃(η^3 -CH₂CHRO) (R = OR, R, NR₂; M = Mo, W).¹⁴ In the latter, the trend in allyl stability is observed as follows: R = NR₂ > 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 $(\eta^5-NC_4H_4)Mn(CO)_3^{15}$ 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 BF₃·(C₂H₅)₂O, 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-boradienyl¹⁶ analogues.

Treatment of a dichloromethane solution of **3b** with 2.3 equiv of BF₃·(C₂H₅)₂O at -78 °C, followed by addition of 2.4 equiv of RNH₂, affords (η^5 -CH₂CHCHC(CH₃)NR)-Mn(CO)₃ (R = (CH₃)₂CH (7a), (CH₃)₃C (7b)) in high yields. In a blank test, BF₃·(C₂H₅)₂O 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 (C₈H₁₄N⁺). The iminic carbons of 7a and 3b, which are close to those of the free imine and ketone counterparts.

The ¹H 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=CCH₃) 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



support of the η^5 -azadienyl structure IV is provided by the

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

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Manganese-Oxapentadienyl Compounds

variable-temperature ¹³C 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 pentadienyl¹⁷ 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 (~ 2010 , ~ 1925 , ~ 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 $\eta^5 \rightleftharpoons \eta^3$ 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 Mn₁–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 η^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 compound 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. Mn₂(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-butenoate⁷ were prepared according to the procedures in the literature.

All ¹H (400-MHz), ¹³C (100-MHz), and ³¹P (40.2-MHz) NMR spectra were obtained on either a JEOL FX-100 or a Bruker AM-400 spectrometer; the ¹H and ¹³C 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): ν (CO) 2111 (vs), 2056 (vs), 2019 (vs), 1984 (vs), 1965 (vs), 1704 (s) cm⁻¹; ν (C=C) 1593 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): trans isomer (65%), § 1.61 (d, 2 H, H¹), 3.64 (s, 3 H, OCH₃), 5.60 (d, 1 H, H³), 7.42 (dt, 1 H, H²), $J_{12} = 9.5$ Hz, $J_{23} = 15.0$ Hz; cis isomer (35%), δ 2.31 (d, 2 H, H¹), 3.65 (s, 3 H, OCH₃), 5.40 (d, 1 H, H³), 6.70 (dt, 1 H, H²), $J_{12} = 9.5$ Hz, $J_{23} = 10.8$ Hz. Mass spectrum (12 eV): m/e 294 (M⁺). Anal. Calcd for C₁₀H₇MnO₇: 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 CH₂Cl₂): v(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, CDCl₃): trans isomer (70%), δ 1.98 (d, 2 H, H¹), 2.05 (s, 3 H, CH₃), 5.70 (d, 1 H, H³), 7.20 (dt, 1 H, H²), J_{12} = 8.2 Hz, J_{23} = 15.5 Hz; cis isomer (30%), δ 2.10 (s, 3 H, CH₃), 2.20 (d, 2 H, H¹), 5.40 (d, 1 H, H³), 6.50 (d, 1 H, H²), J_{12} = 9.0 Hz, J_{23} = 10.5 Hz. Anal. Calcd for C₁₀H₇MnO₆: 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 CH₂Cl₂): v(CO) 2082 (vs), 2065 (vs), 1992 (vs), 1965 (vs), 1705 (s) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 2.22 (d, 1 H, H¹). 2.49 (d, 1 H, H⁴), 2.98 (d, 1 H, H²), 3.74 (s, 3 H, OCH₃), 5.64 (ddd, 1 H, H³), $J_{12} = 13.0$ Hz, $J_{23} = 7.5$ Hz, $J_{34} = 10.3$ Hz. Mass spectrum (12 eV): m/e 266. Anal. Calcd for C₉H₇MnO₆: C, 40.60; H, 2.53. Found: C, 40.82; H, 2.74.

(d) Synthesis of $(\eta^5$ -CH₂CHCHCOOCH₃)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 at 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): ν (CO) 2036 (s), 1958 (s), 1933 (s), 1556 (w) cm⁻¹. ¹H NMR (400

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MHz, CDCl₃): δ 1.95 (d, 1 H, H¹), 3.52 (s, 3 H, OCH₃), 3.55 (d, 1 H, H⁴), 4.92 (d, 1 H, H²), 5.47 (ddd, 1 H, H³), J_{12} = 13.5 Hz, J_{23} = 6.0 Hz, J_{34} = 7.4 Hz. ¹³C NMR (100 MHz, CDCl₃): δ 52.45 (OCH₃), 57.01 (CH³), 60.67 (CH¹H²), 105.54 (CH⁴), 165.45 (CO-OCH₃), 217.1, 221.9, 223.5 (M–CO). Mass spectrum (12 eV): m/e 238 (M⁺). Anal. Calcd for C₈H₇MnO₅: C, 40.34; H, 2.94. Found: C, 40.72; H, 2.70.

(e) Synthesis of $(\eta^5$ -CH₂CHCHCOCH₃)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. ¹H NMR (benzene- d_6): δ 1.75 (s, 3 H, CH₃), 2.50 (d, 1 H, H¹), 3.25 (d, 1 H, H⁴), 4.43 (d, 1 H, H²), 4.64 (ddd, 1 H, H³), $J_{12} = 13.5$ Hz, $J_{23} = 5.10$ Hz, $J_{34} = 7.0$ Hz. ¹³C NMR (100 MHz, toluene- d_8 , 25 °C): δ 23.9 (CH₃), 69.9 (CH¹H²), $J_{23} = 0.000$ 76.60 (CH3), 105.8 (CH4), 170 (COCH3), 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 -CH₂CHCHCOOCH₃)Mn(CO)₂(PMe₃) (4a). PMe₃ (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 CH₂Cl₂-hexane gave orange plates (0.42 g, 1.47 mmol). IR (in CH₂Cl₂): ν (CO) 1944 (vs), 1873 (vs) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 0.74 (dd, 1 H, H¹), 1.12 (9 H, d, PCH₃), 2.98 (d, 1 H, H²), 3.33 (s, 3 H, OCH₃), 3.62 (d, 1 H, H⁴), 5.20 (m, 1 H, H³), J₁₃ = 9.2 Hz, J_{1-P} = 6.7 Hz, J₂₃ = 6.4 Hz, J₃₄ = 6.0 Hz. ³¹P NMR (40.25 MHz, CDCl₃): δ 33.2. Anal. Calcd for C₁₀H₁₆MnO₄P: C, 41.96; H, 5.59. Found: C, 42.14; H, 5.45.

(g) Synthesis of $(\eta^{5}$ -CH₂CHCHCOOCH₃)Mn(CO)₂(PPh₃) (4b). This complex was prepared similarly from the thermal reaction between PPh₃ (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 CH₂Cl₂): ν (CO) 1951 (vs), 1878 (vs) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): major isomer, δ 2.20 (d, 1 H, H²), 3.26 (d, 1 H, H¹), 3.55 (s, 3 H, OCH₃), 4.48 (d, 1 H, H⁴), 5.27 (complex m, 1 H, H³), 7.06-7.40 (complex m, 15 H, PC₆H₅), $J_{13} = 10.5$ 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, H¹), 3.40 (d, 1 H, H²), 4.60 (m, 1 H, H⁴), 5.20 (m, 1 H, H³), $J_{13} = 10.5$ Hz, J_{23} = 6.4 Hz, $J_{34} = 5.4$ Hz, $J_{P-4} = 2.2$ Hz. ³¹P NMR (40.25 MHz, CDCl₃): 75.2 (major isomer), 63.88 (minor isomer). Anal. Calcd for C₂₅H₂₂MnO₄P: C, 63.56; H, 4.66. Found: C, 63.50; H, 4.87.

(h) Synthesis of $(\eta^{5}$ -CH₂CHCHCOCH₃)Mn(CO)₂(PMe₃) (4c). This complex was similarly prepared from a boiling cyclohexane solution (30 mL) of PMe₃ (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. ¹H NMR (400 MHz, benzene-d₆): δ 1.89 (dd, 1 H, H¹), 2.01 (s, 3 H, OCH₃), 3.01 (d, 1 H, H²), 4.48 (d, 1 H, H⁴), 4.91 (m, 1 H, H³), $J_{13} = 12.0$ Hz, $J_{23} = 6.4$ Hz, $J_{34} = 6.6$ Hz. ³¹P NMR (40.25 MHz, benzene-d₆): δ 32.1. Anal. Calcd for C₁₀H₁₆MnO₃P: C, 44.44; H, 5.93. Found: C, 44.65; H, 6.14.

(i) Synthesis of $(\pi^{5}$ -CH₂CHCHCOCH₃)Mn(CO)₂(PPh₃) (4d). This complex was prepared similarly from a refluxing cyclohexane solution (30 mL) of PPh₃ (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. ¹H NMR (400 MHz, -40 °C, toluene-d₈): isomer A (82%), 2.02 (dd, 1 H, H¹), 2.05 (s, 3 H, CH₃), 3.65 (d, 1 H, H²), 4.45 (d, 1 H, H⁴), 5.05 (m, 1 H, H³), $J_{13} = 10.8$ 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, H¹), 3.58 (d, 1 H, H²), 4.88 (m, 1 H, H⁴), 5.00 (m, 1 H, H³), $J_{13} = 10.4$ 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 ¹H NMR spectroscopy because it is probably masked by resonances of other isomers. ³¹P NMR (40.25 MHz): δ 74.1 (82%), 63.0 (16.5%), 61.2 (1.5%). Anal. Calcd for C₁₀H₁₆MnO₃P: C, 44.44; H, 5.93. Found: C, 44.70; H, 6.10.

(j) Synthesis of Mn(CO)₃(PMe₃)(η^{3} -CH₂CHCHCOOCH₃) (5a). PMe₃ (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 CH₂Cl₂-hexane gave yellow platelike crystals. IR (CH₂Cl₂): ν (CO) 2014 (vs), 1933 (vs), 1914 (vs), 1713 (s) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): syn isomer (45%), δ 0.75 (d, 9 H, PCH₃), 0.81 (d, 1 H, H¹), 1.77 (d, 1 H, H⁴), 2.34 (dd, 1 H, H²), 3.62 (s, 3 H, OCH₃), 5.92 (ddd, 1 H, H³), J₁₃ = 11.9 Hz, J₂₃ = 7.7 Hz, J₃₄ = 14.7 Hz, J_{2.P} = 2.4 Hz, J_{P-CH₃} = 6.0 Hz; anti isomer (32%), δ 0.48 (d, 1 H, H²), 1.16 (9 H, d, PCH₃), 1.91 (d, 1 H, H¹), 2.44 (d, 1 H, H⁴), 3.40 (s, 3 H, OCH₃), 5.58 (m, 1 H, H³), J₁₃ = 12.0 Hz, J₂₃ = 7.4 Hz, J₃₄ = 7.0 Hz, J_{3-P} = 2.0 Hz, J_{P-CH₃} = 8.0 Hz; syn isomer (22%), δ 0.83 (9 H, d, PCH₃), 1.81 (d, 1 H, H¹), 2.13 (d, 1 H, H⁴), 2.81 (dd, 1 H, H²), 3.53 (s, 3 H, OCH₃), 4.98 (m, 1 H, H³), J₁₃ = 10.0 Hz, J₂₃ = 7.5 Hz, J₃₄ = 10.9 Hz, J_{4-P} = 3.3 Hz, J_{P-CH₃} = 8.2 Hz. Anal. Calcd for C₁₁H₁₆MnO₅P: C, 42.04; H, 5.10. Found: C, 42.14; H, 5.03.

(k) Synthesis of $Mn(CO)_3(PPh_3)(\eta^3-CH_2CHCHCOOCH_3)$ (5b). This complex was prepared similarly from the reaction between PPh₃ (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 CH₂Cl₂): ν (CO) 2015 (vs), 1948 (vs), 1917 (vs), 1710 (s) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): anti isomer, δ 2.80 (d, 1 H, H²), 3.01 (d, 1 H, H⁴), 3.35 (d, 1 H, H¹), 3.51 (s, 3 H, OCH₃), 4.13 (m, 1 H, H³), 7.02-7.45 (15 H, m, PC₆H₅), $J_{13} = 13.4$ Hz, $J_{23} = 7.1$ Hz, $J_{34} = 7.1$ Hz. Anal. Calcd for C₂₆H₂₂MnO₅P: C, 62.40; H, 4.40. Found: C, 62.19; H, 4.31.

(1) Synthesis of $(\pi^3$ -CH₂CHCHCOOCH₃)Mn(CO)₃(CH₃CN) (6a). Compound 3a (0.25 g, 1.05 mmol) was dissolved in 20 mL of CH₃CN, 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 CH₃CN): ν (CO) 2022 (vs), 1929 (vs), 1712 (s) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 2.01 (s, 3 H, CH₃CN), 2.07 (d, 1 H, H¹), 2.42 (d, 1 H, H⁴), 3.58 (d, 1 H, H²), 3.75 (s, 3 H, OCH₃), 5.68 (m, 1 H, H³). Anal. Calcd for C₁₀H₁₀MnO₅N: C, 43.01; H, 3.58. Found: C, 43.12; H, 3.42.

(m) Synthesis of $(\pi^3$ -CH₂CHCHCOOCH₃)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. ¹H NMR (400 MHz, CD₃COCD₃): δ 1.64 (d, 1 H, H¹), 2.04 (s, 6 H, (CH₃)₂CO), 3.50 (s, 3 H, OCH₃), 3.58 (d, 1 H, H²), 5.09 (d, 1 H, H⁴), 5.69 (ddd, 1 H, H³), J₁₃ = 13.4 Hz, J₂₃ = 7.0 Hz, J₃₄ = 10.9 Hz. Anal. Calcd for C₁₁H₁₃MnO₆: C, 44.59; H, 4.39. Found: C, 44.80; H, 4.21.

(n) Synthesis of $(\pi^3$ -CH₂CHCHCOOCH₃)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. ¹H NMR (400 MHz, THF-d₈): δ 1.60 (t, 4 H, J = 8.0 Hz), 1.84 (d, 1 H, H¹), 3.46 (s, 3 H, OCH₃), 3.50 (d, 1 H, H²), 3.54 (t, 4 H, J = 8.0 Hz), 5.00 (d, 1 H, H⁴), 5.58 (ddd, 1 H, H³), J₁₃ = 13.3 Hz, J₂₃ = 7.6 Hz, J₃₄ = 11.8 Hz. Anal. Calcd for C₁₂H₁₅MnO₆: C, 46.45; H, 4.84. Found: C, 46.27; H, 4.92.

(o) Synthesis of $(\pi^5$ -CH₂CHCHC(CH₃)NCH(CH₃)₂)Mn-(CO)₃ (7a). Complex 3b (0.14 g, 0.63 mmol) in 15 mL of CH₂Cl₂ was treated with 0.18 mL of BF₃·Et₂O (0.23 g, 1.70 mmol) at -78 °C, and the mixture was stirred for 0.5 h. After slow addition of (CH₃)₂CHNH₂ (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 CH₂Cl₂ 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 CH₂Cl₂): ν (CO) 2005 (vs), 1924 (vs), 1912 (vs) cm⁻¹. ¹H NMR (400 MHz, benzene-d₆): δ 0.73 (d, 3 H, CHCH₃), 0.76 (d, 3 H, CHCH₃'), 0.82 (s, 3 H, NC(CH₃)), 1.84 (d, 1 H, H¹), 2.64 (m, 1 H, NCH), 2.66 (d, 1 H, H²), 3.49 (d, 1 H, H⁴), 4.69 (ddd, 1 H, H³), J₁₃ = 12.5 Hz, J₂₃ = 7.4 Hz, J₃₄ = 6.0 Hz. ¹³C

Table III. Summary of Crystal and Diffraction Data

formula $MnC_8H_7O_4$ $MnPC_{26}H_{22}O_3$ color habitred chunkyellow chunkcryst dimens, mm $0.28 \times 0.60 \times 0.20 \times 0.25 \times 0.35$ 0.60 $P2_1/c$ $P2_1/c$	
color habitred chunkyellow chunkcryst dimens, mm $0.28 \times 0.60 \times 0.20 \times 0.25 \times 0.35$ 0.60space group P_{21}/c	
cryst dimens, mm $0.28 \times 0.60 \times 0.20 \times 0.25 \times 0.35$ 0.60 space group $P_{21/c}$ $P_{21/c}$	
$\begin{array}{c} 0.60\\ \text{space group} \qquad P_{21}/c \qquad P_{21}/c \end{array}$	
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 K α (λ = Cu K α (λ = 1.5405 Å	Å)
0.710 73 Å)	
2θ range, deg 2-45 2-100	
scan type $\theta/2\theta$ $\theta/2\theta$	
scan speed (variable), 4.19-114.65 1.648-8.24 deg/min	
scan param (ω) 1.28 + (K α 0.70 + 0.14 tan θ	
separation)	
no. of rflns collected 2499 (2032 > 4539 (2728 > $2\sigma(I)$) $3\sigma(I)$)	I
no. of indep rflns 1209 (1103 > 4539 (2728 > $2\sigma(I)$) $3\sigma(I)$)	I
weighting scheme $w^{-1} = \sigma^2(F) + w^{-1} = \sigma^2(F)$ 0.0006 F^2	
final R. R., % 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_9): δ 21.8, 19.4 (CH(CH₃)₂), 24.9 (NCCH₃), 45.9 (CH¹H²), 51.3 (CH(CH₃)₂), 59.3 (CH³), 105.1 (CH⁴), 171.2 (NC(CH₃)), 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 (C₈H₁₄N⁺). Anal. Calcd for C₁₁H₁₄MnNO₃: C, 50.19; H, 5.32; N, 5.32. Found: C, 50.20; H, 5.44; N, 5.42.

(p) Synthesis of $(\eta^5$ -CH₂CHCHC(CH₃)NC(CH₃)₃)Mn(CO)₃ (7b). Complex 2 (0.22 g, 1.0 mmol) in 20 mL of CH₂Cl₂ was treated with 0.18 mL of BF·Et₂O (0.23 g, 1.70 mmol) at -78 °C and the mixture was stirred for 0.5 h. After slow addition of (CH₃)₃CNH₂ (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 CH₂Cl₂): ν (CO) 2014 (vs), 1928 (vs), 1917 (vs). ¹H NMR (400 MHz, benzene- d_6): δ 0.84 (s, 9 H, (CH₃)₃C), 1.13 (s, 3 H, NCCH₃), 2.06 (d, 1 H, H¹), 2.69 (d, 1 H, H²), 3.48 (d, 1 H, H⁴), 4.73 (m, 1 H, H³), $J_{13} = 12.4$ Hz, $J_{23} = 6.4$ Hz, $J_{34} = 6.7$ Hz. ¹³C NMR (100 MHz, benzene- d_6): 23.05 (NC₃CH₃), 30.13 (-C(CH₃)₃), 47.31 (CH¹H²), 56.4 (-C(CH₃)₃), 58.1 (CH⁴), 103.4 (CH³), 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 (C₇H₁₃N⁺). Anal. Calcd for C₁₂H₁₆MnNO₃: 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 $CD_3C_6D_5$, 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 ¹H resonances of the methyl and hydroxyl groups of methanol below ambient temperature and between the ¹H 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 ΔG^* at each temperature T, by using the Eyring equation:

$$k_{c} = (k'/\hbar)Te^{-\Delta G^{*}/RT}$$

where k' = Boltzmann constant, $\hbar = \text{Planck constant divided by } \pi$, 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 K α 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 K α 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.