S. M. Gorun for helpful comments.

Registry No. **1**, 98839-70-4; **2**, 96556-04-6; **3**, 110827-36-6; Fe(Me_3TACN)Cl_3, 110827-37-7; [$Fe_2O(OAc)_2(TACN)_2$]I_2, 110827-38-8; [$Fe_2(OH)(OAc)_2(HBpz_3)_2$]($ClO_4$), 90886-31-0; [$Fe_2O(OAc)_2(Me_3TACN)_2$]$^+$, 110827-39-9; [$Fe_2(OH)(O_2CCH_3)_2(Me_3TACN)_2$]$^{2+}$, 110851-24-6.

Supplementary Material Available: Tables reporting thermal parameters for all atoms and fixed hydrogen atom positional parameters and χ_{obsd}, χ_{calcd}, μ_{obsd}, and μ_{calcd} for 1 and 2 (6 pages); listing of observed and calculated structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

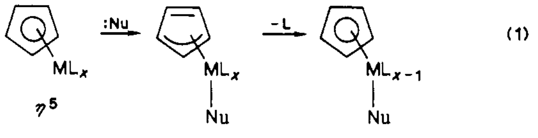
Syntheses of η^5-Heterocyclic Manganese Tricarbonyls. Effect of the Heteroatom and Heterocycle Ring Substituents on CO Substitution Reactions

David L. Kershner and Fred Basolo*

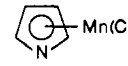
Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received April 7, 1987

Abstract: The syntheses and characterizations of some new η^5-heterocyclic manganese tricarbonyl complexes are described. Kinetic studies are reported for CO substitution reactions of these nitrogen family η^5-dimethylheterocyclic manganese tricarbonyl complexes. The results show that only the *N*-heterocycle compounds undergo CO substitution by phosphorus nucleophiles. These results are attributed to the greater electronegativity of N than that of C, P, or As. Both tricarbonyl(η^5-3,4-dimethylpyrrolyl)manganese(I) and tricarbonyl(η^5-2,5-dimethylpyrrolyl)manganese(I) substitute CO by an associative pathway in which the reaction rates are first order in concentration of metal complex and first order in concentration of entering nucleophile. The former compound also substitutes CO by a pathway that is independent of the concentration of incoming nucleophile. The second-order pathway is believed to involve a ring-slippage ($\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$) mechanism, whereas the first-order pathway appears to involve a ligand-dissociation mechanism.

The kinetics and mechanisms of carbon monoxide substitution reactions of η^5-cyclopentadienyl[1] and of η^5-indenyl[2] metal carbonyl complexes have received much attention. The reactions take place by an associative process, which is presumed to involve the intermediate formation of an η^3 bound π-cyclic group upon attack at the metal center by an incoming nucleophile (eq 1). This $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ ring slippage maintains an 18-electron count of the metal center and thereby avoids the energetically unfavorable 20-electron transition state that would result if a pair of electrons on the metal were not localized on a ligand.[1d,3]



In recent papers we have reported[4] and reviewed[5] the syntheses and CO substitution reactivity of η^5-heterocyclic metal carbonyl complexes. These compounds have been studied much less than have their η^5-carbocyclic analogues,[6] and several of the compounds investigated here had to be prepared and characterized for the first time. Most of the work in this area has involved the synthesis of tricarbonyl(η^5-pyrrolyl)manganese(I)[7] (I) and of its P analogue tricarbonyl(η^5-phospholyl)manganese(I).[8] Reactivity studies on these compounds have largely been limited to aromatic substitution reactions on the η^5-heterocyclic ring. Our earlier studies of CO substitution reactions of these compounds dealt with the N analogues of tricarbonyl(η^5-cyclopentadienyl)manganese(I) and of tricarbonyl(η^5-indenyl)manganese(I).



I

These η^5-heterocycle metal carbonyls were found[4b] to undergo associative CO substitution reactions at a much faster rate than their η^5-carbocyclic counterparts. For example, I was found to readily substitute CO at elevated temperatures with phosphorus nucleophiles, in contrast to the reported[9] inertness of the C analogue tricarbonyl(η^5-cyclopentadienyl)manganese(I). It was suggested[4b] that this enhanced reactivity may be due to the greater efficiency of the more electronegative N in removing electron density from the metal center. Such electron delocalization to the cyclic ligand is required by the proposed $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$

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(1) (a) Kowaleski, R. M.; Trogler, W. C.; Basolo, F. *Gazz. Chim. Ital.* **1986**, *116*, 105–107. Kowaleski, R. M.; Basolo, F.; Trogler, W. C.; Ernst, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 6046–6048. (b) Palmer, G. T.; Basolo, F.; Kool, L. B.; Rausch, M. D. *J. Am. Chem. Soc.* **1986**, *108*, 4417–4422. (c) Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908–5912. (d) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657–1163.

(2) (a) Liang-Nian, J.; Rerek, M. E.; Basolo, F. *Organometallics* **1984**, *3*, 740–745. (b) Rerek, M. E.; Liang-Nian, J.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1983**, 1208–1209.

(3) Basolo, F. *Inorg. Chim. Acta* **1985**, *100*, 33–39, and references therein.

(4) (a) Kershner, D. L.; Rheingold, A.; Basolo, F., *Organometallics* **1987**, *6*, 197–198. (b) Liang-Nian, J.; Kershner, D.; Rerek, M. E.; Basolo, F. *J. Organomet. Chem.* **1985**, *296*, 83–94.

(5) Kershner, D. L.; Basolo, F. *Coord. Chem. Rev.* **1987**, *79*, 279–292.

(6) For an extensive review of π-heterocyclic metal complexes see: Novi, M.; Giuseppe, G.; Dell'Erba, C. *J. Heterocycl. Chem.* **1975**, *12*, 1055–1081.

(7) (a) Kursanov, D. N.; Setkina, V. N.; Pyshnograeva, N. I. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1984**, *33*, 807–812. (b) King, R. B.; Efraty, A. *J. Organomet. Chem.* **1969**, *20*, 264–268. (c) Joshi, K. K.; Pauson, P. L.; Qazi, A. R.; Stubbs, W. H. *J. Organomet. Chem.* **1964**, *1*, 471–475.

(8) (a) Mathey, F.; Mitschler, A.; Weiss, r. *J. Am. Chem. Soc.* **1978**, *100*, 5748–5755. (b) Mathey, F. *Tetrahedron. Lett.* **1976**, *46*, 4155–4158. (c) Breque, A.; Mathey, F. *J. Organomet. Chem.* **1978**, *144*, C9–C11. (d) Mathey, F. *J. Organomet. Chem.* **1975**, *93*, 377–388.

(9) Angelici, R. S.; Lowen, W. *Inorg. Chem.* **1967**, *6*, 682–686.

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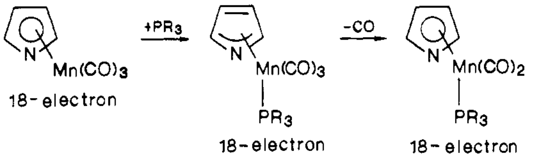
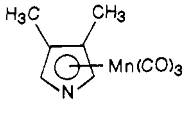
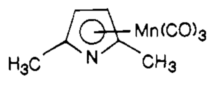
ring-slippage mechanism, in order to maintain an 18-electron count at the metal (eq 2). However, whether or not N is contained in the η^3-allyl active intermediate or transition state, as shown in eq 2, is not known. In an attempt to better understand the role of the heteroatom in the transition state, we have investigated the CO substitution reactivity of the η^5-3,4-dimethylpyrrolyl and η^5-2,5-dimethylpyrrolyl complexes of manganese tricarbonyl, II and III, respectively. Also investigated was the CO substitution reactivity of P and As analogues of III, in order to test the importance of the electronegativity of the heteroatom in promoting CO substitution reactions in these systems.



(2)



II



III

The results of this study show that only the manganese compounds containing the more electronegative N in the η^5-cyclic ligand undergo CO substitution reactions. The results suggest that the associative CO substitution reactions proceed through an η^3-2-azaallyl active intermediate or transition state. The role of the heteroatom in promoting reactivity at the metal center could be important in their syntheses and in designing more efficient homogeneous catalysts where substitution lability at the metal center is necessary.

Experimental Section

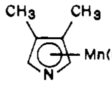
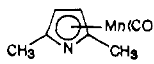
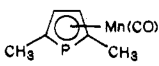
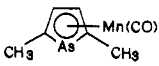
Compounds and Solvents. All manipulations involving manganese carbonyl compounds were carried out under a N_2 atmosphere with standard Schlenk techniques. Hexane, pentane, decalin, cyclohexane, xylene, and dichloromethane were purified and dried by published procedures.[10] Solvents were distilled under a N_2 atmosphere prior to use. The phosphorus nucleophiles were obtained from Strem Chemicals. The phosphines $P(n\text{-}Bu)_3$[11] and PMe_3 and the phosphites $P(OEt)_3$ and $P(OPh)_3$ were distilled over Na under a N_2 atmosphere prior to use. PPh_3 was recrystallized from hexane prior to use. Alumina (Alcoa Chemicals) refers to 80–200-mesh alumina deactivated by 8–10 h of exposure to air.

The compound (2,5-dimethylphenyl)phosphole[12] and the metal carbonyl complexes II[4a] and V[13] (Table I) were prepared according to published procedures. The compound 2,5-dimethylpyrrole (Aldrich) was distilled over BaO under a N_2 atmosphere prior to use. $Mn_2(CO)_{10}$ (Strem Chemicals) were used without further purification.

The carbonyl stretching frequencies of the various metal carbonyl complexes are shown in Table I. Table II contains the ^1H and ^{13}C NMR spectral data of these compounds.

Syntheses of Compounds. Tricarbonyl(η^5-2,5-dimethylpyrrolyl)manganese(I) (III). The synthesis of this complex, which was carried out under a N_2 atmosphere, is analogous to those previously described[4a,13] for II and V. A solution of $Mn_2(CO)_{10}$ (1.97 g, 5.05 mmol) and 2,5-dimethylpyrrole (1.18 g, 5.05 mmol) in 50 mL of xylene was refluxed for 16 h, at which time no further change in the ν_{CO} region of the IR was observed. The xylene was removed under vacuum, hexane was added to the residue, and the mixture was suction filtered through a sintered-glass frit. The resultant orange solution was concentrated under reduced pressure and subsequently chromatographed on an alumina column (2.5 × 35 cm) developed with pentane. Addition of pentane to the column eluted unreacted $Mn_2(CO)_{10}$. Addition of 1:8 (v/v) CH_2Cl_2/pentane to the column eluted the product as a yellow band. The purified product was obtained as a yellow oil at room temperature (0.90 g, 3.6 mmol, 70%) after several recrystallizations from pentane at −70 °C. MS (m/e, relative intensity): M^+ 233 (16.5), $(M - CO)^+$ 205 (7.9), $(M - 2CO)^+$ 177 (30.1), $(M - 3\ CO)^+$ 149 (100.0). IR and NMR: Tables I and II.

Table I. Carbonyl Stretching Frequencies of the η^5-Heterocyclic Manganese Tricarbonyls in Decalin

complex	ν_{CO}, cm^{-1}
 I	2037, 1965, 1955
 II	2035, 1962, 1944
$(\eta^5\text{-}C_4(CH_3)_2H_2N)Mn(CO)_2P(n\text{-}Bu)_3$	1933, 1865
$(\eta^5\text{-}C_4(CH_3)_2H_2N)Mn(CO)_2P(OEt)_3$	1953, 1888
$(\eta^5\text{-}C_4(CH_3)_2H_2N)Mn(CO)_2PPh_3$[c]	1947, 1885
 III	2035, 1958, 1950
$(\eta^5\text{-}C_4(CH_3)_2H_2N)Mn(CO)_2P(Bu)_3$	1937, 1873
$(\eta^5\text{-}C_4(CH_3)_2H_2N)Mn(CO)_2P(OEt)_3$	1966, 1896 (1)[b]
	1954, 1890 (1.5)
$(\eta^5\text{-}C_4(CH_3)_2H_2N)Mn(CO)_2PPh_3$[c]	1942, 1873
$(\eta^5\text{-}C_4(CH_3)_2H_2N)Mn(CO)_2P(OPh)_3$	1926, 1852
$(\eta^5\text{-}C_4(CH_3)_2H_2N)Mn(CO)_2PMe_3$[c]	1943, 1881
 IV	2023, 1954, 1951
$(\eta^5\text{-}C_4(CH_3)_2H_2N)Mn(CO)_2PPh_3$[c]	1948, 1892
 V	2024, 1952, 1946
$(\eta^5\text{-}C_4(CH_3)_2H_2As)Mn(CO)_2PPh_3$[b]	1944, 1888

[a] Reference 3b. For $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ values of ν_{CO} are 2023 and 2039 cm^{-1}. [b] Relative amounts of each isomer formed (see the Experimental Section). [c] In pentane.

Tricarbonyl(η^5-2,5-dimethylphospholyl)manganese(I) (IV). The synthesis of IV, carried out under a N_2 atmosphere, is analogous to that described for III. A solution of $Mn_2(CO)_{10}$ (0.85 g, 2.18 mmol) and (2,5-dimethylphenyl)phosphole (0.41 g, 2.18 mmol) in 35 mL of xylene was refluxed for 2 h, at which time no further IR ν_{CO} changes were observed. Following the procedure described for III, the product was obtained as a yellow oil (0.41 g, 1.8 mmol, 80%). ^{31}P NMR ($CDCl_3$): δ 18.44. MS (m/e, relative intensity): M^+ 250 (6.4), $(M - 2\ CO)^+$ 19.4 (10.9), $(M - 3\ CO)^+$ 166 (40.2). IR and NMR: Tables I and II.

Dicarbonyl(triphenylphosphine)(η^5-2,5-dimethylpyrrolyl)manganese(I). A solution of I (0.26 g, 1.1 mmol) and PPh_3 (0.38 g, 1.5 mmol) in 40 mL of cyclohexane and under a N_2 atmosphere was irradiated with a 550-W high-pressure Hg lamp. After 8 h of irradiation, no further changes in the ν_{CO} region of the IR were observed. The resultant cloudy red mixture was filtered through a sintered-glass frit, the filtrate was concentrated under vacuum, and the oily residue was syringed onto an alumina column (2.5 × 30 cm) developed with pentane. Addition of pentane to the column eluted $Mn_2(CO)_{10}$, and addition of 1:5 (v/v) CH_2Cl_2 pentane eluted the product. The solvent was removed under vacuum, pentane was added to the residue, and the concentrated solution was placed in a freezer (−35 °C). After several days the product was obtained as yellow crystals (0.10 g, 0.21 mmol, 20%). MS (m/e, relative intensity): M^+ 467 (3.2), $(M - PPh)^+$ 205 (12.3), $(M - PPh_3 - 2\ CO)^+$ 149 (60.9). IR and NMR: Tables I and II. Anal. Calcd for $C_{26}H_{23}MnNO_2P$: C, 66.81; H, 4.93; N, 3.00. Found: C, 66.74; H, 5.11; N, 2.88.

Dicarbonyl(triethyl phosphite)(η^5-2,5-dimethylpyrrolyl)manganese(I). The synthesis of this complex is similar to a literature method[14] and utilizes several equivalents of Me_3NO as a reactant. A solution of III (0.35 g, 1.5 mmol) and $P(OEt)_3$ (0.33 g, 1.93 mmol) in 25 mL of toluene was warmed to 65 °C, and Me_3NO (0.6 g, 8 mmol) was added under a

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(10) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972.

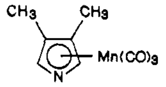
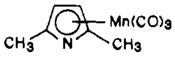
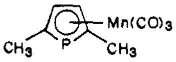
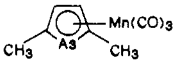
(11) Abbreviations: $P(n\text{-}Bu)_3$ = tri-n-butylphosphine, $P(OEt)_3$ = triethyl phosphite, PMe_3 = trimethylphosphine, $P(OPh)_3$ = triphenyl phosphite, CH_2Cl = dichloromethane, Me_3NO = trimethylamine N-oxide.

(12) Märkl, G.; Potthast, R. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 86.

(13) Thiollet, G.; Poiblanc, R.; Voight, D.; Mathey, F. *Inorg. Chim. Acta* **1978**, *30*, L294.

(14) Pyshnograeva, N. I.; Batsanov, A. S.; Struchkov, Yu. T.; Ginzburg, A. G.; Setkina, V. N. *J. Organomet. Chem.* **1985**, *297*, 69–76.

Table II. ^1H NMR and ^{13}C NMR Data of η^5-Heterocyclic Manganese Tricarbonyls in $CDCl_3$

complex	^1H NMR, δ: Me, H_{ring}, PR_3	^{13}C NMR, δ: Me, C_β, C_α, CO
 II[b]	1.98, 5.91	9.8, 105.0, 105.6, 223.9
$(\eta^5-C_4(CH_3)_2H_2N)Mn(CO)_2PPh_3$	1.6, 5.13, 7.23	
 III	2.16, 4.96	16.9, 85.9, 123.9, 224.9
$(\eta^5-C_4(CH_3)_2H_2N)Mn(CO)_2PPh_3$	1.60, 4.27, 7.15	
$(\eta^5-C_4(CH_3)_2H_2N)Mn(CO)_2PMe_3$	2.0, 4.4, 1.26 (9.51)[b]	
$(\eta^5-C_4(CH_3)_2H_2N)Mn(CO)_2P(OEt)_3$	1.80, 4.25, 0.95, 3.65	
 IV	1.8, 5.2, (9.75), (3.75)[a]	16.3, 92.8, 127.8, 223.5 (19.9), (5.29), (150.1)[b]
 V[c]	1.91, 5.40	18.3, 93.5, 128.4, 224.2
$(\eta^5-C_4(CH_3)_2H_2As)Mn(CO)_2PPh_3$	1.80, 5.35, 7.4	

[a] Reference 4a. [b] Phosphorus coupling in Hz. [c] Reference 13.

purge of N_2 to the solution in portions over a 3-h period, at which time no further changes in the ν_{CO} region of the IR occurred. The solvent was removed under reduced pressure, pentane was added to the residue, and the mixture was suction filtered through a sintered-glass frit. The resultant orange solution was concentrated under vacuum and chromatographed on an alumina column (2.5 × 25 cm) developed with pentane. Addition of pentane to the column eluted $Mn_2(CO)_{10}$, and addition of 1:4 (v/v) CH_2Cl_2/pentane eluted the product. The product solution was evaporated to dryness, pentane was added to the residue, and the concentrated solution was placed in a freezer (−35 °C). After several days the product was obtained as yellow crystals (0.075 g, 0.20 mmol, 14%). MS (*m/e*, relative intensity): M^+ 371 (13.9), $(M - 2\,CO)^+$ 315 (81.4), $(M - (2\,CO - P(OEt)_3))^+$ 149 (31.5). IR and NMR: Tables I and II.

The reaction of I with $P(OEt)_3$ in the presence of a 550-W high-pressure Hg lamp yielded the product in approximately 50% yield.

Dicarbonyl(trimethylphosphine)(η^5-2,5-dimethylpyrrolyl)manganese(I). This complex was synthesized with Me_3NO in a manner similar to that described above for the triethyl phosphite derivative of III. The reaction of III (0.18 g, 0.79 mmol), PMe_3 (~0.090 g, 1 mmol), and Me_3NO (0.3 g, 4 mmol) at 25 °C and under a N_2 atmosphere yielded the product (0.085 g, 0.30 mmol, 38%) as yellow, needlelike crystals. MS (*m/e*, relative intensity): M^+ 281 (8.9), $(M - 2\,CO)^+$ 225 (55), $(M - (2\,CO - PMe_3))^+$ 149 (100). IR and NMR: Tables I and II.

Dicarbonyl(triphenylphosphine)(η^5-3,4-dimethylpyrrolyl)manganese(I). This complex was synthesized with use of UV irradiation under a N_2 atmosphere in a manner similar to that described for the triphenylphosphine derivative of III. A solution of II (0.17 g, 0.73 mmol) and PPh_3 (0.25 g, 0.95 mmol) of yielded the product (0.080 g, 0.17 mmol, 13%) as yellow needles after recrystallization in pentane. MS (*m/e*, relative intensity): M^+ 467 (2.5), $(M - 2\,CO)^+$ 411 (55.6), $(M - (2\,CO - PPh_3))^+$ 149 (14.0). IR and NMR: Tables I and II. Anal. Calcd for $C_{26}H_{23}MnNO_2P$: C, 66.81; H, 4.93; N, 3.00. Found: C, 66.57; H, 5.22; N, 2.82.

Dicarbonyl(triphenylphosphine)(η^5-2,5-dimethylphospholyl)manganese(I). The reaction of IV with PPh_3 either in the presence of UV irradiation or with excess Me_3NO produced the product in extremely low yields (<5%). The IR of the ν_{CO} region showed product bands similar to those of the other monosubstituted η^5-heterocycle metal carbonyls. No ^1H NMR or elemental analyses could be obtained.

Dicarbonyl(triphenylphosphine)(η^5-2,5-dimethylarsolyl)manganese(I). This complex was synthesized by using UV irradiation as described above for the triphenylphosphine derivative of II. The irradiation of a cyclohexane solution of V (0.30 g, 1.0 mmol) and PPh_3 (0.29 g, 1.2 mmol) for 12 h under a N_2 atmosphere, followed by chromatography on alumina and then recrystallization from pentane, yielded the orange-yellow, crystalline product (0.23 g, 0.44 mmol, 44%). Because of its low volatility, the complex required heating and chemical ionization in order to measure the mass spectrum. Only the parent peak (M^+, 528) could be assigned, owing to the rapid fragmentation of the compound. IR and NMR: Tables I and II. Anal. Calcd for $C_{26}H_{23}AsMnO_2P$: C, 59.1; H, 4.36; As 14.2. Found: C, 59.3; H, 4.23; As, 13.99.

Instrumentation. Infrared spectra were recorded on either a Perkin-Elmer 283 or a Nicolet 7199 FT-IR spectrometer with 0.1-mm CaF_2 cells. Nuclear magnetic resonance spectra were obtained on either a Varian 400 FT-NMR or a Varian 390 spectrometer. Kinetic experiments were performed in a Polyscience Model 90 constant-temperature bath, with temperature regulated to +0.2 °C. The mass spectra were obtained by Dr. D. Hung of Northwestern University Analytical Services Laboratory on a HP5985A spectrometer using 70-eV ionization. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Kinetic Measurements. Decalin reaction mixtures of 2.0 mL and approximately 2×10^{-3} M in metal complex was placed in the constant-temperature bath. Aliquots were removed periodically over 2–3 half-lives to measure the absorbance changes in the carbonyl stretching region. The IR cells were flushed with N_2 and sealed with rubber septa prior to use. The rates of reaction for the first substitution were monitored by measuring the decrease in the highest carbonyl absorption. Plots of $-\ln A$ vs time were linear over 2–3 half-lives (linear correlation coefficient >0.995). The slope of these lines, which were obtained from at least six absorbance/time pairs, yielded k_{obsd}. In all cases, at least a 40-fold excess of incoming nucleophile was used so as to maintain pseudo-first-order reaction conditions.

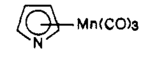
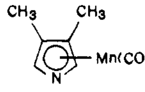
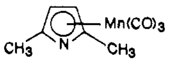
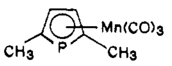
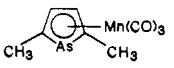
Since all of the reaction products gave similar carbonyl stretching frequencies, only the triphenylphosphine derivatives were fully characterized.

Results

Reactions of N-group heterocycles with $Mn_2(CO)_{10}$ in refluxing xylene afforded η^5-heterocyclic manganese tricarbonyl complexes. The new compounds III and IV were isolated as oils, so no elemental analyses were obtained. Both compounds were characterized by their IR spectra (Table I), their ^1H and ^{13}C NMR spectra (Table II), and their mass spectra. Monosubstituted derivatives of these tricarbonyl complexes were prepared and isolated either by UV irradiation of a cyclohexane solution, which contains the metal tricarbonyl complex and the entering ligand, or by addition of excess of Me_3NO to a toluene solution of the metal tricarbonyl and the entering ligand. The resultant IR carbonyl stretching frequencies (Table I) of monosubstituted compounds prepared by these methods are identical with the IR carbonyl stretching frequencies of the derivatives obtained in the kinetic studies by thermal CO substitution.

Compound II reacts with $P(OEt)_3$ in decalin at elevated temperatures to produce a monosubstituted product. The IR ν_{CO} spectral changes for this reaction in Decalin at 150 °C are shown

Table III. Rate Constants and Activation Parameters for Associative-Substitution Reactions of (η^5-pyrrolyl)Mn(CO)$_3$ Complexes in Decalin

complex	L	T, °C	k, M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/deg·mol
 I^a	P(n-Bu)$_3$	130	3.88 × 10^{-4}	15.1 (±1.6)	-37.4 (±3.9)
	P(OEt)$_3$	130	0.43 × 10^{-4}	22.7 (±0.1)	-22.6 (±2.4)
 II	P(n-Bu)$_3$	130	1.36 × 10^{-4}	14.72 (±0.89)	-40.3 (±2.2)
		140	2.09 × 10^{-4}		
		150	3.41 × 10^{-4}		
	P(OEt)$_3$	130	1.32 × 10^{-5}	26.4 (±1.9)	-15.8 (±4.6)
		140	3.16 × 10^{-5}		
		150	6.57 × 10^{-5}		
 III	P(n-Bu)$_3$	130	1.18 × 10^{-6}	15.7 (±1.2)	-48.2 (±1.5)
		140	2.05 × 10^{-6}		
		150	3.13 × 10^{-6}		
	P(OEt)$_3$	130	2.14 × 10^{-6}	26.45 (±0.80)	-19.4 (±1.0)
		140	4.99 × 10^{-6}		
		150	10.7 × 10^{-6}		
 IV	P(n-Bu)$_3$	140	b		
 V	P(n-Bu)$_3$	140	b		

^{a}Reference 4b. ^{b}No reaction.

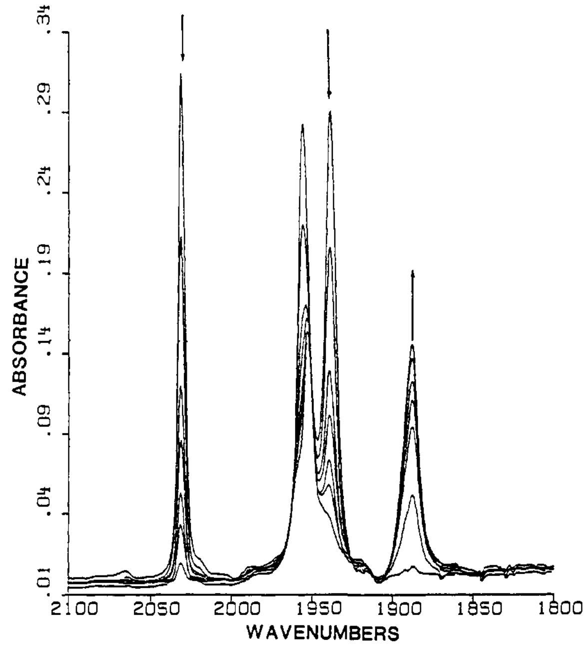


Figure 1. Absorbance changes vs time for the reaction of compound II. (η^5-C$_4$(CH$_3$)$_2$H$_2$N)Mn(CO)$_3$ + P(OEt)$_3$ → (η^5-C$_4$(CH$_3$)$_2$H$_2$N)Mn(CO)$_2$P(OEt)$_3$ + CO in Decalin at 150 °C.

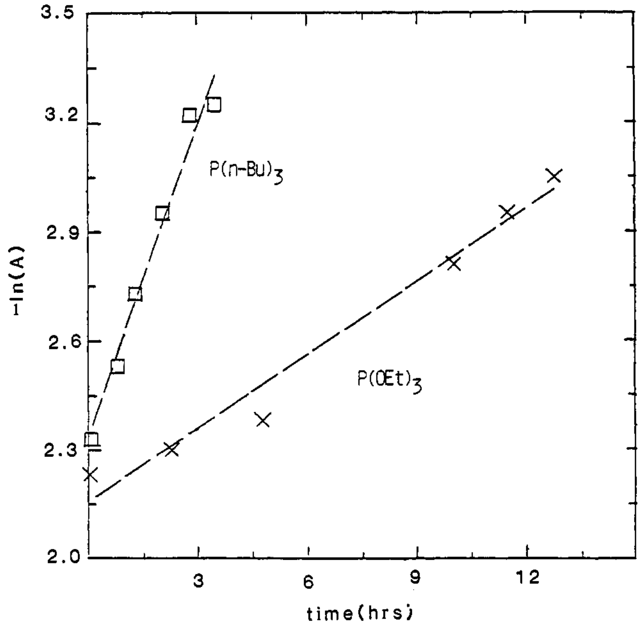


Figure 2. Plot of -ln A vs time for the reaction of compound II. (η^5-C$_4$(CH$_3$)$_2$H$_2$N)Mn(CO)$_3$ + L → (η^5-C$_4$(CH$_3$)$_2$H$_2$N)Mn(CO)$_2$L + CO in Decalin at 140 °C. L = P(Bu)$_3$ or P(OEt)$_3$.

in Figure 1. The reaction of II with the more basic P(n-Bu)$_3$ proceeds further to form a disubstituted complex. However, a 500-fold excess of P(n-Bu)$_3$ was needed in order to drive the reaction to completion. No rate data were obtained for the second substitution. Plots of -ln A vs time for the reactions of II with P(OEt)$_3$ and with P(n-Bu)$_3$ are shown in Figure 2.

The reaction of III with P(OEt)$_3$ in Decalin and at elevated temperatures produces two monosubstituted products as seen in the ν_{CO} region of the IR. The synthesis of this monosubstutited compound with Me$_3$NO or with UV irradiation at room temperature also produces two isomers in ratios similar to those formed in the high-temperature kinetic runs. The two isomers resist separation by recrystallization or by column chromatography. The relative amounts of these isomers remains unchanged even after heating a Decalin solution of the isomers at 140 °C for 2 weeks.

The reaction of III with the other phosphorus nucleophiles yields only one monosubstituted product.

Heating Decalin solutions (~140 °C) of II or of III in the absence of added nucleophile produces no perceptible IR ν_{CO} changes. Therefore, it is unlikely that the disappearance of the metal complexes in the kinetic studies is due to decomposition. Furthermore, the final kinetic IR spectra in the CO stretching region agree well with monosubstituted compounds prepared by photochemical reactions or by the use of Me$_3$NO.

The dependence of k_{obsd} on the concentration of P(OEt)$_3$ for CO substitution reactions of II and III is shown in Figure 3. Table I contains the carbonyl stretching frequencies, and Table II contains the ^{1}H and ^{13}C NMR data of the various substrates and their substituted products. The results of a temperature dependence study on substitution reactions of II and III with P(OEt)$_3$ and P(n-Bu)$_3$ are given in Tables III and IV, respectively, with

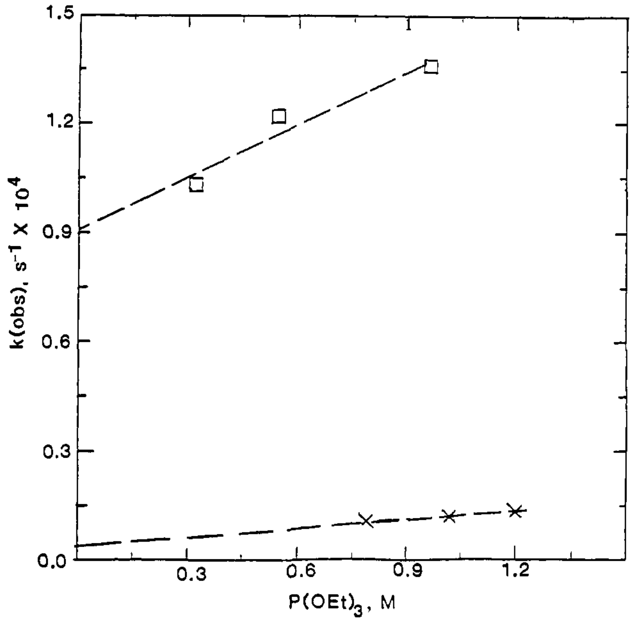


Figure 3. Plot of k_{obsd} vs $P(OEt)_3$ concentration for the reaction (η^5-L)$Mn(CO)_3$ + $P(OEt)_3$ → (η^5-L)$Mn(CO)_2P(OEt)_3$ + CO in Decalin at 150 °C. Key: □ = II; × = III.

Table IV. Rate Constants and Activation Parameters for the Dissociative-Substitution Reaction of (η^5-3,4-Dimethylpyrrolyl)$Mn(CO)_3$ in Decalin

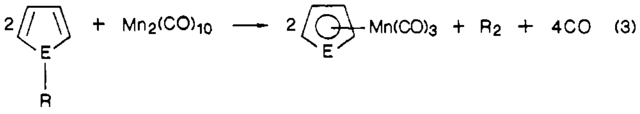
L	T, °C	k, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/deg·mol
$P(n\text{-}Bu)_3$	130	1.16×10^{-5}	37.6 (±1.1)	11.5 (±2.7)
	140	3.52×10^{-5}		
	150	1.12×10^{-4}		
$P(OEt)_3$	130	0.960×10^{-5}	35.8 (±0.6)	6.8 (±0.7)
	140	2.83×10^{-5}		
	150	8.37×10^{-5}		

calculated errors of 1 standard deviation.

The P and the As compounds, IV and V, respectively (see Table I), were found to be inert toward thermal CO substitution. No detectable reaction occurred even after 7 days at 140 °C and with at least a 500-fold excess of $P(n\text{-}Bu)_3$ or $P(OEt)_3$.

Discussion

The CO substitution reactivity of η^5-carbocyclic metal carbonyl complexes is fairly well developed.[1-3] In contrast to this, little is known about CO substitution reactions of the analogous η^5-heterocyclic metal carbonyl compounds and, more specifically, about how the heteroatom affects reactivity at the metal center. One reason little is known about the effect of the heteroatom in such systems is that relatively few η^5-heterocyclic metal carbonyls have been prepared and studied.[5,6] Therefore, it was necessary to first prepare the required new compounds and investigate their CO substitution reactions. The parent compounds were prepared by the reaction of $Mn_2(CO)_{10}$ with the desired heterocycle, which probably takes place as represented in eq 3, where E = N, P, or As and R = H when E is N and R = C_6H_5 when E is P or As.



(3)

Thermal substitution of CO by a phosphine or phosphite to afford the monosubstituted derivative takes place with the (η^5-N-heterocyclic)$Mn(CO)_3$ compounds. Corresponding compounds (where E in eq 3 is C, P, or As) do not react thermally to form the monosubstituted derivatives, even after 7 days at 140 °C with a 500-fold excess of $P(n\text{-}Bu)_3$. Monosubstituted phosphine or phosphite derivatives of all compounds can be conveniently prepared either by photochemical reactions or by reactions with added Me_3NO. For the (η^5-N-heterocyclic)$Mn(CO)_3$, which react thermally, the spectral properties of monosubstituted products are identical with those of products prepared by the three different methods. As a synthetic method the thermal reaction is the least useful, because it only works for N-heterocycle systems, and even here a large excess of ligand must be added in order to enhance the rate of reaction. The presence of excess ligand in the reaction mixture then makes it difficult to isolate and purify the monosubstituted product.

That only compounds I–III, which contain N, react at the kinetic study conditions suggests the reactivity may reflect the greater electronegativity of N (3.0),[15] relative to C (2.5), P (2.1), and As (2.0). This greater reactivity of the η^5-N-heterocyclic compounds may be attributed to the greater electron-withdrawing ability of the more elecronegative N atom in the π-ring. That such electron withdrawal may be important is consistent with an $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ mechanism (eq 2), which requires delocalization of electron density into the cyclic ligand in the transition state for reaction. Likewise, the greater electron withdrawal of the η^5-N-heterocyclic ligands tends to weaken the ground-state Mn–CO bond, as can be seen from the higher energy CO stretching frequencies of the pyrrolyl compounds (Table I). The molecular orbital description[16] also agrees with a weakened Mn–CO bond. For these "piano stool" complexes, the highest occupied molecular orbitals (HOMOs) are composed of metal to carbonyl π-back-bonding interactions. Thus, when the ligand cyclopentadienyl is replaced by pyrrolyl, the energy of the HOMOs increrases, resulting in a destabilization of the Mn–CO bonds. Unfortunately, the corresponding C, P, and As ring manganese carbonyls do not undergo thermal CO substitution at the conditions used, so it has not yet been possible to further test any correlation between reactivity and electronegativity of the ring atom.

Of further interest are the differences in reactivity between pyrrolyl complexes II and III. Both of these η^5-dimethylpyrrolyl complexes undergo associative CO substitution reactions, with a linear dependence of observed rate constant on $P(OEt)_3$ concentration (Figure 3). However, compound II also exhibits a ligand-independent pathway (vide infra), as shown by the extrapolated nonzero intercept in Figure 3 at zero $P(OEt)_3$ concentration. No detectable ligand-independent pathway was observed for I or III.

Rate data for the ligand-dependent CO substitution reactions of II and III show that the rate law is first order in metal complex and first order in entering nucleophile. Table III shows that the rates for the ligand-dependent processes of II and III are slower than those of the unsubstituted complex I. The slower rates are in accord with an $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ mechanism where the methyl electron-donating substituents retard electron delocalization into the ring ligand, and the slower rates are also consistent with an associative reaction where increased substitution on the η^5-cyclic ligand leads to a more crowded transition state.[17] The low enthalpies of activation and large negative entropies of activation (Table III) are additional support of an associative reaction. These activation parameters also reflect the nucleophilic character of $P(n\text{-}Bu)_3$ and $P(OEt)_3$. The more basic[19] $P(n\text{-}Bu)_3$ forms a stronger metal–phosphorus bond in the transition state than does $P(OEt)_3$, as exhibited by the smaller $\Delta H^{\ddagger}$ values for reactions of $P(n\text{-}Bu)_3$ versus $P(OEt)_3$ for all three compounds (I–III in Table III). Conversely, the smaller $P(OEt)_3$ (109° cone angle[18]) nucleophile forms a less sterically demanding transition state than does the larger $P(n\text{-}Bu)_3$ (132° cone angle) nucleophile, as indicated by the less negative $\Delta S^{\ddagger}$ values for $P(OEt)_3$ versus $P(n\text{-}Bu)_3$ for the three compounds (Table III).

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(15) Pritchard, H. O.; Skinner, H. A. *Chem. Rev.* **1955**, *55*, 745–786.

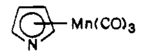
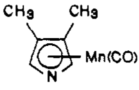
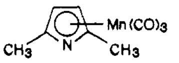
(16) Albright, T. A.; Hoffmann, R. *Chem. Ber.* **1978**, *111*, 1578–1590.

(17) Basolo, F.; Pearson, R. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1967; p 162.

(18) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348. (b) Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985–987.

(19) The pK_a values of pyrrole (23.1), 3,4-dimethylpyrrole (24.8), and 2,5-dimethylpyrrole (24.8) were measured in DMSO. Satish, A. V.; Bordwell, F. G., private communication.

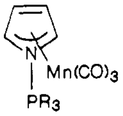
Table V. Changes in Pyrrolyl Ring Carbon Atom ^{13}C Chemical Shifts in $CDCl_3$ upon Complexation to $Mn(CO)_3$

		free pyrrolyl anion		$\Delta\delta^a$	
no.		C_α	C_β	C_α	C_β
I	 I	127.2	106.6	20.3	20.1
II	 II	126.8	113.8	20.2	8.52
III	 III	135.8	105.5	11.9	19.5

[a] $\delta[C_i^{Me_4Si}$(free pyrrolyl anion)] − $\delta[C_i^{Me_3Si}(\eta^5$-pyrrolyl)]. Data for the dimethylpyrrolyl anions were computed from the chemical shifts of the free dimethylpyrroles in $CDCl_3$ by invoking known[22] additivity relationships. ^{13}C NMR [δ(3,4-dimethylpyrrole), δ(2,5-dimethylpyrrole) (C_i)]: 118.0, 127.2 (C_α); 115.4, 107.1 (C_β); 10.1, 16.9 (C_{Me}). [b] Reference 22a.

A most important point to note is that the position of the methyl substituents on the η^5-pyrrolyl ring has a marked effect on the rate of associative CO substitution reactions. Thus, compound II reacts 10^2 times more rapidly than does compound III although two methyl groups are present on both rings (Table III). It is most unlikely that this difference is due to electronic factors because the IR ν_{CO} bands of the two complexes are approximately equal in energy, suggesting the electron density on the metals are about the same, which then makes the Mn to CO π bonding similar in both compounds. Likewise, the measured[19] pK_a's of 3,4-dimethylpyrrole and 2,5-dimethylpyrrole, the precursors to II and III (eq 3), respectively, are almost identical, suggesting comparable electronic characteristics of both rings. A more plausible explanation for the large difference can be given on steric grounds.

Evidence in support of a steric argument may be obtained from the kinetic data in Table III. Complex III is more reactive toward $P(OEt)_3$ than it is toward the more basic, but larger, $P(n\text{-}Bu)_3$.[18] The opposite is observed for II and I, both of which are more reactive toward $P(n\text{-}Bu)_3$. These results suggest that the incoming nucleophile finds the metal center in the η^5-2,5-dimethylpyrrolyl complex less accessible than in the corresponding η^5-3,4-dimethylpyrrolyl compound. This requires the incoming nucleophile to attack Mn on the side of the molecule nearest the N atom of the η^5-ring. Unfortunately, a detailed molecular orbital description[20] of these complexes has not yet been done, so further speculation would at best be tenuous. An alternative explanation for the observed reactivity differences is that the associative CO substitution reactions of III proceed through a much more crowded transition state than occurs with II (or I). A transition state consistent with these results would contain an η^3-2-azaallyl bonding mode of the metal moiety to the pyrrolyl ligand (VI). Further support for VI is found[4a] in the X-ray structure of II, which shows a "slip-distortion" of the $Mn(CO)_3$ moiety away from the ring centroid toward N. It appears that this slippage is largely steric in origin since no allylene type bonding is observed in the pyrrolyl ring of II.



VI

This steric distortion is also evident in solution as is apparent from the shielding effects (Table V) of the pyrrolyl anion carbon atoms upon complexation to the $Mn(CO)_3$ moiety. Inequivalent shielding of the C_α and C_β atoms, which is a qualitative indicator of an unsymmetrical bonding interaction to the metal center,[21] is mainly a consequence of the methyl substituents. Unsubstituted complex I exhibits equal shielding of the C ring atoms as evidenced by almost equal $\Delta\delta$ values of C_α and C_β. In contrast, the dimethylpyrrolyl complexes display an unsymmetrical interaction of the ring atoms with the metal center as shown by unequal values of $\Delta\delta$ for C_α and C_β. However, for the three compounds shielding is always largest at the unsubstituted ring atoms. This suggests the unsubstituted C ring atoms have stronger interactions with the metal carbonyl moiety, and they are necessarily closer to the metal than are the ring C atoms bearing methyl substituents. These ground-state repulsions are also expected to occur in the transition state for reaction (eq 2). Thus, the presumed η^3-2-azaallyl transition state will be more easily accessible for complexes I and II than for complex III, which shows significant steric distortions of the $Mn(CO)_3$ moiety away from the N ring atom.

An alternative explanation as to why $P(n\text{-}Bu)_3$ reacts more rapidly with compounds I and II but less rapidly with III than does $P(OEt)_3$ was suggested by one of the reviewers of this paper. The suggestion is that this could be an electronic effect on the transition state. The methyl groups in the 2,5-positions of III are expected to make the η^3-2-azaalyl of the transition state or active intermediate more electron rich than the allyl derived from I or II where the methyl groups in the 3,4-positions are not attached to the 2-azaallyl moiety. Therefore, the energy of the more electron-rich transition state may be lowered more by $P(OEt)_3$, which is a better π-acid than is $P(n\text{-}Bu)_3$.

An interesting observation is that the CO substitution reaction of III with $P(OEt)_3$ under thermal conditions, in the presence of UV irradiation or with Me_3NO as a reactant, produces two monosubstituted products. Infrared absorbance measurements show that the isomer containing the lower ν_{CO} stretches is always formed in higher yield (1.5:1) than its counterpart. Furthermore, the IR ν_{CO} region shows no change in the relative amounts of the two isomers even after a Decalin solution of the isomers was heated at 140 °C for 2 weeks. Of the phosphorus ligands used, this result is unique for $P(OEt)_3$. The large phosphite $P(OPh)_3$ as well as the phosphines studied, including the small PMe_3 ligand, all react with III to form only one monosubstituted product. No further studies concerning this result have been undertaken, and it is not understood why $P(OEt)_3$ is the only ligand studied to show this property.

We now return to the ligand-independent pathway, which only II exhibits. This result is surprising in that the 2,5-dimethylpyrrolyl analogue shows no such behavior. The rate constants and activation parameters for this pathway are contained in Table IV. The large enthalpies of activation and small, positive entropies of activation are similar for both phosphorus nucleophiles used in this study, and these are indicative of a dissociative reaction[23] in which bond breaking and very little bond making are occurring. A I_d mechanism[24] is consistent with these results, and such a dissociative process relieves steric repulsions between the methyl groups and the $Mn(CO)_3$ moiety. Another contribution to Mn–CO bond cleavage may be that it is assisted by interaction of Mn with the lone pair of electrons on N. There is a report[25] that describes the bonding in tricarbonyl(η^5-tellurophene)chromium(0) as an η^4-butadiene and a Te–σ interaction. Heterocycles of the

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(20) A theoretical paper[16] used molecular orbital theory to describe the conformational preferences of $M(CO)_3$ moieties coordinated in η^5 fashion to π-heterocycles.

(21) (a) Efraty, A.; Jubran, N.; Goldman, A. *Inorg. Chem.* **1982**, *21*, 868–873. (b) Nesmeyanov, A. N.; Fedin, E. I.; Fedorov, L. A.; Petrovskii, P. V. *J. Struct. Chem.* (*Engl. Transl.*) **1972**, *13*, 964–972.

(22) Pugmire, R. J.; Grant, D. M. *J. Am. Chem. Soc.* **1968**, *90*, 4232–4238.

(23) (a) Palmer, G. T.; Basolo, F. *J. Am. Chem. Soc.* **1985**, *107*, 3122–3129. (b) Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 557–599, and references therein.

(24) (a) Covey, W. D.; Brown, T. L. *Inorg. Chem.* **1973**, *12*, 2820–2825. (b) Langford, C. H.; Gray, H. B. *Ligand Substitution Processes*; Benjamin: New York, 1965; Chapter 1.

(25) Öfele, K.; Dotzauer, E. *J. Organomet. Chem.* **1972**, *42*, C87–C90.

nitrogen family are also known[8a,d,21,26] to function simultaneously as π-bonders and heteroatom σ-donors, but always each bonding mode is to two different metal centers. Such an interaction in our pyrrolyl systems requires the metal center be situated relatively close to the N atom. This is difficult for III, because the $Mn(CO)_3$ moiety would experience a large steric repulsion from the methyl groups ortho to the N atom.

Acknowledgment. We thank the National Science Foundation for the support of this research. D.L.K. thanks the graduate school at Northwestern University for a fellowship. We thank A. V Satish for measuring the pK_a's of the dimethylpyrrole molecules.

Registry No. I, 32761-36-7; II, 105899-94-3; III, 94280-88-3; IV, 110825-42-8; V, 68229-11-8; (η^5-3,4-$C_4(CH_3)_2H_2N)Mn(CO)_2P(n$-Bu$)_3$, 110825-43-9; ($\eta^5$-3,4-$C_4(CH_3)_2H_2N)Mn(CO)_2P(OEt)_3$, 110825-44-0; ($\eta^5$-3,4-$C_4(CH_3)_2H_2N)Mn(CO)_2PPh_3$, 110825-45-1; ($\eta^5$-2,5-$C_4(CH_3)_2H_2N)Mn(CO)_2P(Bu)_3$, 110825-46-2; ($\eta^5$-2,5-$C_4(CH_3)_2H_2N)Mn(CO)_2P(OEt)_3$, 110825-47-3; ($\eta^5$-2,5-$C_4(CH_3)_2H_2N)Mn(CO)_2PPh_3$, 110825-48-4; ($\eta^5$-2,5-$C_4(CH_3)_2H_2N)Mn(CO)_2P(OPh)_3$, 110825-49-5; ($\eta^5$-2,5-$C_4(CH_3)_2H_2N)Mn(CO)_2PMe_3$, 110825-50-8; ($\eta^5$-2,5-$C_4(CH_3)_2H_2P)Mn(CO)_2PPh_3$, 110825-51-9; ($\eta^5$-2,5-$C_4(CH_3)_2H_2As)Mn(CO)_2PPh_3$, 110825-52-0.

Supplementary Material Available: Table of observed rate constants, k_{obsd}, for reactions of (η^5-pyrrolyl)$Mn(CO)_3$ complexes with different concentrations of $P(n$-Bu$)_3$ or $P(OEt)_3$ at different temperatures in Decalin solution (1 page). Ordering information is given on any current masthead page.

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(26) Abel, E. W.; Clark, N.; Towers, C. *J. Chem. Soc., Dalton Trans.* **1979**, 1552–1556.

Effects of Paramagnetic and Diamagnetic Transition-Metal Monosubstitutions on ^{183}W and ^{31}P NMR Spectra for Keggin and Wells–Dawson Heteropolytungstate Derivatives. Correlations and Corrections. ^{183}W NMR Two-Dimensional INADEQUATE Studies of α-$[(D_2O)ZnO_5X^{n+}W_{11}O_{34}]^{(10-n)-}$ Wherein $X^{n+} = Si^{4+}$ and P^{5+}

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Abstract: ^{31}P NMR spectra are reported for α_1 and α_2 isomers of $[(H_2O)M^{n+}O_5P_2W_{17}O_{56}]^{(10-n)-}$ complexes wherein $M^{n+} = Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}$, and Mn^{3+} and for α-$[(D_2O)M^{2+}O_5PW_{11}O_{34}]^{5-}$ complexes wherein $M^{2+} = Zn^{2+}, Ni^{2+}$, and Co^{2+}. ^{183}W NMR spectra are reported for the α_2 isomers of $[(D_2O)M^{2+}O_5P_2W_{17}O_{56}]^{8-}$ wherein $M^{2+} = Co^{2+}, Ni^{2+}$, and Zn^{2+}; for α_1-$[(D_2O)Zn^{2+}O_5P_2W_{17}O_{56}]^{8-}$; and for α-$[(D_2O)M^{2+}O_5X^{m+}W_{11}O_{34}]^{(10-m)-}$ wherein $M^{2+} = Co^{2+}, Ni^{2+}$, and Zn^{2+} and $X^{m+} = P^{5+}$ and Si^{4+}. Those spectra show that when either α_1 or α_2 isomers of the Wells–Dawson 17-tungsto derivatives are prepared and purified by standard methods, there is always a significant proportion of the other isomer present as impurity. The spectra provide the first direct proofs of the structures of these α_1 and α_2 substitution isomers. The degrees of ^{31}P NMR line broadenings caused by the paramagnetic atoms are explained in terms of the orbital degeneracy or nondegeneracy of the electronic states of the paramagnetic ions. The extents of the NMR chemical shifts for P atoms nearest the substitution sites may be explained in terms of contact shifts modified by some dipolar contribution and/or second-order effects. Effects of possible partial delocalization of unpaired electron spins are discussed. Errors in previous reports of the ^{31}P NMR spectra of some of these complexes are explained. In the ^{183}W NMR spectra, signals are not observed from those W atoms which are structurally adjacent to the paramagnetic atoms. ^{183}W NMR 2D INADEQUATE studies of $[(D_2O)ZnO_5X^{n+}W_{11}O_{34}]^{(10-n)-}$ wherein $X^{n+} = Si^{4+}$ and P^{5+} are presented. Differences and similarities relative to 2D studies of other substituted Keggin 11-tungsto derivatives are noted.

This paper reports ^{183}W NMR spectra for α_2-$[(D_2O)M^{n+}O_5P_2W_{17}O_{56}]^{(10-n)-}$ complexes wherein $M^{n+} = Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}$, and Mn^{3+}. These spectra prove[1] that the preparative procedures usually used in the past[2] yield primarily α_2 isomers (cap-substituted α Wells–Dawson structures[6]) but that, in each case, a significant proportion of the complexes in the recrystallized product is the belt-substituted α_1 isomer.[3a] See Figure 1. This conclusion is confirmed by ^{31}P NMR, which also shows that standard preparations[3b] for α_1 species (via the α_1-lacunary 17-tungstodiphosphate made in the presence of Li^+) lead to 2–11% of the product complexes present being α_2. Although

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(1) While the common assumption is that the complexes prepared according to Weakley and Malik[2] are α_2 isomers when produced in the absence of Li^+ ions,[3b] because it was shown[4] by ^{183}W NMR that it is the α_2-lacunary species that forms under such conditions, there has not heretofore been unambiguous evidence for the isomer assignment for these substituted species. Indirect evidence, based on electrochemical and ESR studies[4,5] for the V^{4+}-substituted complex, is confirmed herein.

(2) (a) Malik, S. A.; Weakley, T. J. R. *J. Chem. Soc., Chem. Commun.* **1967**, 1094. (b) Malik, S. A.; Weakley, T. J. R. *J. Chem. Soc. A* **1968**, 2647. (c) Tourné, C. M.; Tourné, G. F.; Malik, S. A.; Weakley, T. J. R. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3875.

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