Journal of Organometallic Chemistry, 296 (1985) 83–94
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SYNTHESES AND CARBON MONOXIDE SUBSTITUTION REACTIONS OF η^5-*N*-HETEROCYCLE MANGANESE TRICARBONYLS *

LIANG-NIAN JI, DAVID L. KERSHNER, MARK E. REREK, and FRED BASOLO *
Department of Chemistry, Northwestern University, Evanston, Illinois 60201 (U.S.A.)

(Received March 29th, 1985)

Summary

A new method of synthesis of η^5-pyrrolyltricarbonylmanganese(I) is reported, along with the first syntheses of η^5-indolyltricarbonylmanganese(I) and of η^5-1-pyrindinyltricarbonylmanganese(I). Kinetic studies on CO substitution reactions of these η^5-*N*-heterocyclic manganese carbonyls show that the reactions take place by a second-order process, first-order in metal complex and first-order in nucleophile. The most significant observation is that the *N*-heterocyclic compounds react faster than do their carbocyclic counterparts. This anticipated result is consistent with the greater electron-withdrawing ability of the N systems in the transition state for reaction, because N is more electronegative than is C.

Introduction

Twenty years ago we reported [1] that the rates of CO substitution of $(\eta^5$-$C_5H_5)Rh(CO)_2$ by a variety of nucleophiles are dependent on the concentration of both the rhodium complex and the incoming nucleophile. The associative (S_N2) mechanism of the reaction of this 18-electron compound was explained by transfer of an electron pair from rhodium to the cyclopentadienyl ligand, thus creating an empty metal orbital for nucleophilic attack. This was suggested, for it was known [2] that the pseudoisoelectronic $Fe(CO)_5$ reacts very slowly and by a dissociation (S_N1) process. Although our suggestion predated by a decade the Tolman [3] 16-18-electron rule, we recognized that an associative formation of a 20-electron species, $(\eta^5$-$C_5H_5)Rh(CO)_2L$, was unfavored and some process which maintained an 18-electron count at rhodium was preferred.

Cramer and Seiwell [4] were the first to suggest that this process of localizing a pair of electrons on the cyclopentadienyl ligand to permit an associative reaction be

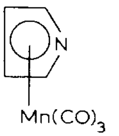
---

* Dedicated to Professor Lamberto Malatesta in recognition of his important contributions to organometallic chemistry.

viewed as ring slippage of the type $\eta^5 \rightarrow \eta^3$. Recently, Casey and co-workers [5] have also observed $\eta^5 \rightarrow \eta^1$ slippage of the cyclopentadienyl ligand in different metal complexes when allowed to react with trimethylphosphine. Mawby and co-workers [6] observed an even more efficient $\eta^5 \rightarrow \eta^3$ ring slippage in the indenyl ligand relative to cyclopentadienyl. For the (η^5-carbocycle)Rh(CO)$_2$ compounds, the indenyl compound reacts 10^8 times faster than does the cyclopentadienyl compound, and this rate enhancement has been termed the indenyl ligand effect [7].

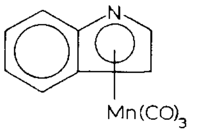
Other ligands are also known to allow electron delocalization from metal to ligand and to permit an associative pathway for substitution, while maintaining an 18-electron count on the central metal [8]. For example, the 18-electron iron tricarbonyl compounds of 1,4-dimethyltetraazabutadiene and of 1,4-diazabutadiene both undergo CO replacement by an associative mechanism [9]. The tetraaza (4 nitrogen atoms in the metallocycle ring) compound reacts 10^5 times faster than does the diaza (2 nitrogen atoms in the metallocycle ring) compound. This large rate enhancement was attributed to N being more electronegative than C, which means the tetraaza ring system has a greater tendency to attract electrons from the metal into the ring than does the corresponding diazadicarba ring system. Since these associative substitution reactions are believed to involve electron delocalization from metal to ligand, it follows that this would be more effective in the tetraaza system and provide a greater driving force for its reaction over that of the diazairon tricarbonyl.

In order to further test the importance of the presence of N in place of C in ligands which allow associative substitution reactions of 18-electron organometallic compounds, we decided to investigate the effect of a N in place of C in (η^5-C_5H_5)Mn(CO)$_3$ and in (η^5-C_9H_7)Mn(CO)$_3$ on rates of CO substitution. Fortunately, Pauson and co-workers [10] and King and Efraty [11] have reported the synthesis and some CO substitution reactions of the pyrrolyl compound (η^5-C_4H_4N)Mn(CO)$_3$. Much less is known [12] of *N*-heterocyclic compounds akin to the indenyl compound (η^5-C_9H_7)Mn(CO)$_3$. We report here a new synthesis of the pyrrolyl compound I, and what we believe are the first reported syntheses of II and III.



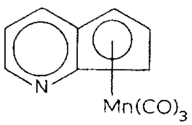
(I)

η^5-pyrrolyltricarbonyl-manganese(I)



(II)

η^5-indolyltricarbonyl-manganese(I)



(III)

η^5-1-pyrindinyltricarbonyl-manganese(I)

Also reported and discussed are the kinetics and mechanisms of CO substitution reactions of compounds I and III. The bottom line is that the *N*-heterocyclic metal carbonyls react faster than do the corresponding carbocyclic compounds, and the effect is larger if N is in the 5-membered ring than if in the 6-membered ring.

Experimental

Compounds and solvents. All manipulations involving the manganese carbonyl compounds were carried out under an atmosphere of N_2. Hexane, pentane, tetrahydrofuran, decalin, cyclohexane, and toluene were distilled over Na under a N_2 atmosphere prior to use. The hexane was stored over H_2SO_4 and washed with $NaHCO_3$ before distillation. Methylene chloride was distilled over P_4O_{10} under a N_2 atmosphere prior to use. The phosphines $P(n\text{-}Bu)_3$ [13], $P(Cy)_3$, PPh_3 and $P(OEt)_3$ were obtained from Strem Chemicals. Both $P(n\text{-}Bu)_3$ and $P(OEt)_3$ were distilled over Na under a N_2 atmosphere prior to use. PPh_3 was recrystallized from ethanol prior to use. Pyrrole (Aldrich) was distilled under N_2 and indole (Aldrich) was recrystallized from hexane prior to use. Alumina (Alocoa Chemicals) refers to 80–200 mesh activated alumina. The compounds 1,5-pyrindine [14], $Mn(CO)_5Br$ [15] and $[Mn(CH_3CN)_3(CO)_3]$ [16] were all prepared according to published procedures.

η^5-Pyrrolyltricarbonylmanganese(I), (η^5-C_4H_4N)$Mn(CO)_3$ (I). Potassium (0.35 g; 9.0 mmol) was powdered in 15 ml of refluxing toluene and pyrrole (0.65 ml; 9.2 mmol) in 15 ml of THF was added dropwise with stirring to the cooled mixture. The mixture was refluxed until no more H_2 evolved. The mixture was cooled to room temperature, a slurry of $[Mn(CH_3CN)_3(CO)_3]PF_6$ (3.0 g; 7.37 mmol) in 15 ml of THF was syringed into the reaction vessel, the syringe was washed with several 2 ml portions of THF, and the washings added to the reaction vessel. The resultant orange mixture was stirred at room temperature for 2 d. The solvent was removed in vacuum, 20 ml of hexane added, and the mixture was suction filtered through a medium frit. The volume of the resultant red solution was reduced under vacuum and the concentrated solution chromatographed on an alumina column (2.5 × 30 cm) developed with hexane. Addition of 1/4 (v/v) CH_2Cl_2/hexane eluted $Mn_2(CO)_{10}$ as a yellow band. A second more slowly moving yellow-orange band eluted the product. Removal of the solvent under vacuum yielded 0.87 g (4.2 mmol; 57% yield) of I as a yellow solid. The IR spectra of the compound agreed with the literature values for I [10,11]. No further purification of the product was undertaken. ν(CO) (decalin) 2037, 1965, 1955 cm^{-1}.

η^5-Indolyltricarbonylmanganese(I), (η^5-C_8H_6N)$Mn(CO)_3$ (II). A procedure similar to that for I was followed. A solution of indole (0.62 g; 5.3 mmol) in 15 ml of THF was added dropwise with stirring to a cold mixture of powdered potassium (0.20 g; 5.1 mmol) in 10 ml of toluene. The mixture was refluxed until all the K dissolved, the solution was cooled to room temperature and a slurry of $[Mn(CH_3CN)(CO)_3]PF_6$ (1.9 g; 4.7 mmol) in 15 ml of THF was syringed into the flask. The syringe was washed with several 2 ml portions of THF, and the washings were added to the reaction vessel. The orange-colored mixture was stirred for 2 d at room temperature. The solvent was removed in vacuum, 20 ml of CH_2Cl_2 was added to the flask, and the mixture was suction filtered through a medium frit. The dark red filtrate was reduced in volume to 4 ml and chromatographed on an alumina column (2.5 × 40 cm) developed with pentane. Elution with 1/5 (v/v) CH_2Cl_2/pentane produced three well separated bands. The first band was identified as $Mn_2(CO)_{10}$ by its IR spectrum. A mass spectrum, $m/e = 403$ for the parent ion, and ν(CO) stretches identified the second band as $Mn_2(CH_3CN)(CO)_9$ [17]. The third yellow band yielded 0.60 g (2.4 mmol; 50% yield) of the product as an oily-red residue containing a large amount of unreacted indole. Attempts to purify the product by crystallization were unsuccessful, and the compound decomposed under prolonged exposure to vacuum. A decalin solution of the compound decomposed to $Mn_2(CO)_{10}$ and a brown residue after several months in a refrigerator. The carbonyl stretches obtained agreed with those reported for η^5-2-methylindolyltricarbonyl-

manganese(I) [12]. ν(CO) (decalin) = 2038, 1964, 1954 cm^{-1}; mass spectrum, *m/e* (relative intensity) M^+ 255(9.2), $(M-\mathrm{CO})^+$ 227(8.3), $(M-2\mathrm{CO})^+$ 199(27.6), $(M-3\mathrm{CO})^+$ 171(100). The mass spectrum contained other peaks which were attributed to impurities.

η^5-1-Pyrindinyltricarbonylmanganese(I), (η^5-C_8H_6N)Mn(CO)$_3$ (III). The preparation of this compound is similar to that used by King and Efraty [18] for the η^5-indenyltricarbonylmanganese(I) analogue. A solution of 1,5-pyrindine (3.83 g; 32.7 mmol) in 10 ml THF was added dropwise to a suspension of powdered potassium (1.25 g; 32.0 mmol) cooled to room temperature in 50 ml of toluene. The resultant green mixture was refluxed for 2 h, at which time all the potassium had dissolved. The solution was cooled to room temperature, a solution of Mn(CO)$_5$Br (4.12 g; 15.0 mmol) in 50 ml of THF was added dropwise with stirring, and the resultant orange solution was stirred overnight at room temperature.

The solvent was removed in vacuum, 20 ml of CH_2Cl_2 was added to the reaction flask, and the mixture was suction filtered through a medium frit. The solvent was removed in vacuum, pentane was added to the flask, and the residue was chromatographed on an alumina column (2.5 × 32 cm) developed with pentane. Elution with 1/7 (v/v) CH_2Cl_2/pentane produced a yellow band, $Mn_2(CO)_{10}$, and a slower moving orange-yellow band which yielded 2.14 g (8.34 mmol; 56% yield) of the product as a dark red oil. Attempts to purify the compound by crystallization and sublimation were unsuccessful.

The IR carbonyl stretches of the product agree closely with those reported for η^5-indenyltricarbonylmanganese(I) [18]. ν(CO) (decalin) 2045, 1955, 1945 cm^{-1}; mass spectrum, *m/e* (relative intensity) M^+ 255(18.8), $(M-\mathrm{CO})^+$ 227(9.8), $(M-2\mathrm{CO})^+$ 199(27.0), $(M-3\mathrm{CO})^+$ 171(83.0). The mass spectrum contained additional peaks attributed to impurities.

η^5-1-Pyrindinyldicarbonyltriphenylphosphinemanganese(I), (η^5-C_8H_6N)Mn(PPh$_3$)(CO)$_2$ (IV). Following the method used by King and Efraty [18] for η^5-indenyldicarbonyltriphenylphosphinemanganese(I), a solution of unpurified (III) (0.07 g; 0.3 mmol) in 15 ml of cyclohexane was added via a syringe to a solution of PPh$_3$ (0.15 g; 0.57 mmol) in 5 ml of cyclohexane. The stirred solution was exposed to a 550 W low pressure Hg lamp for 2.5 h at which time no further change in the IR occurred. The solvent was removed in vacuum, hexane was added to the residue, and the dark red oil chromatographed on an alumina column (2.5 × 20 cm) developed with hexane. Addition of 1/6 (v/v) CH_2Cl_2/hexane eluted an orange band. Recrystallization of the eluent from hexane yielded 0.058 g (0.123 mmol; 41% yield) of the product as orange crystals. ν(CO) (CH_2Cl_2) 1938, 1875 cm^{-1}; mass spectrum, *m/e* (relative intensity) M^+ 489(1.9), $(M-2\mathrm{CO})^+$ 433(100), $(M-(2\mathrm{CO}+\mathrm{PPh}_3))^+$ 171(16.9).

Instrumentation. Infrared spectra were recorded on either a Perkin–Elmer 283 or a Nicolet 7199 FT-IR spectrometer using 0.1 mm KBr cells. Kinetic measurements were done 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 an HP5985A spectrometer using 70 eV ionization.

Kinetic measurements. Decalin reaction mixtures of 3.0 ml were placed in the constant temperature bath. The solutions were approximately 5×10^{-3} *M* in metal complex, and the reactions were carried out under pseudo-first order conditions with at least a ten-fold excess of added nucleophile. The IR cells were flushed with N_2 and sealed with rubber septa prior to use. Aliquots were removed periodically over 3–4 half lives to measure the absorbance changes in the carbonyl stretching region. The rates of reaction for the first substitution were monitored by measuring the decrease of the highest carbonyl absorption. The rates of reaction for the second substitution were determined by measuring the increase in the carbonyl absorption of the disubstituted product. Plots of $-\ln A$ vs. time for the first substitution and $-\ln A_\infty - A$ vs. time for the second substitution were linear over 3–4 half lives (linear correlation coefficient > 0.995). The slope of these lines yielded k_{obs}.

Since all reaction products gave similar carbonyl stretching frequencies to those of the triphenylphosphine derivatives, no attempt was made to isolate the other substituted products.

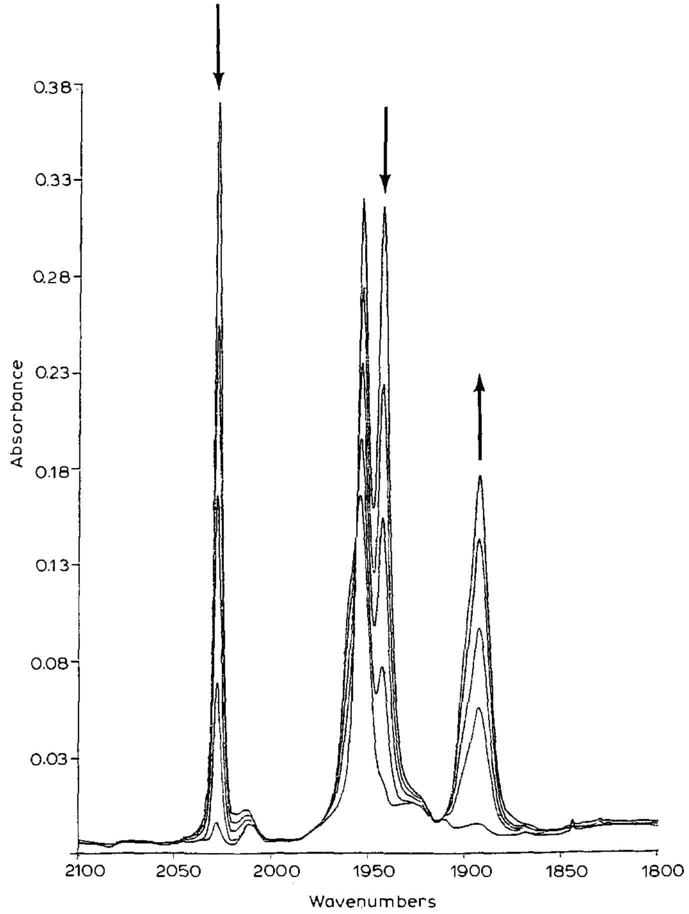


Fig. 1. Absorbance vs. time for the reaction

$$(\eta^5\text{-}C_8H_6N)Mn(CO)_3 + P(OEt)_3 \rightarrow (\eta^5\text{-}C_8H_6N)Mn(CO)_2P(OEt)_3 + CO$$
(III)

in decalin at 130°C.

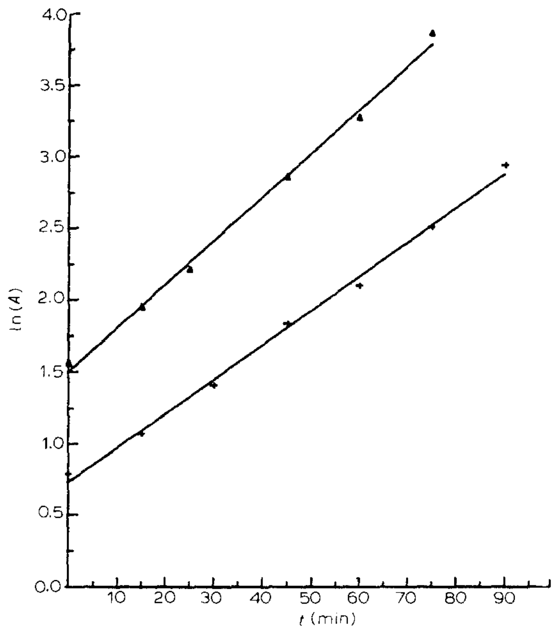


Fig. 2. Plot of −ln A vs. time for the reaction

$(\eta^5\text{-}C_8H_6N)Mn(CO)_3 + L \rightarrow (\eta^5\text{-}C_8H_6N)Mn(CO)_2L + CO$
(III)

in decalin at 130°C. ▲ = P(n-Bu)$_3$; + = P(OEt)$_3$.

Results

The reaction of III with P(n-Bu)$_3$ or P(OEt)$_3$ yields a mono-substituted product. The IR spectral changes in the carbonyl region versus time for the reaction of III with P(OEt)$_3$ in decalin at 130°C are shown in Fig. 1. Plots of −ln A vs. time for the reactions of III with P(n-Bu)$_3$ and with P(OEt)$_3$ at 130°C are shown in Fig. 2.

Compound I reacts with P(OEt)$_3$ or P(Ph)$_3$ to form a mono-substituted product.

TABLE 1

OBSERVED RATE CONSTANTS AS A FUNCTION OF P(n-Bu)$_3$ CONCENTRATION FOR CARBON MONOXIDE SUBSTITUTION OF Mn(η^5-C$_4$H$_4$N)(CO)$_3$ AND OF Mn(η^5-C$_8$H$_6$N)(CO)$_3$ IN DECALIN (eq. 2)

Complex	T (°C)	[P(n-Bu)$_3$]	k_{obs} (s^{-1})×10^{-4}
Mn(η^5-C$_4$H$_4$N)(CO)$_3$ (I)	142	0.0806	0.640
		0.283	2.04
		0.419	2.77
Mn(η^5-C$_8$H$_6$N)(CO)$_3$ (III)	130	0.134	3.23
		0.201	5.42
		0.469	12.0

However, the reaction of I with the stronger nucleophiles, $P(n\text{-}Bu)_3$ or $P(Cy)_3$, proceeds further to form the di-substituted complex. The initial three band pattern of I gives way to an intermediate pattern containing both mono-substituted (1945 and 1880 cm^{-1}) and di-substituted (1900 cm^{-1}) complexes. The mono-substituted product eventually reacts to form the di-substituted complex. The mono- and di-substitued complexes have IR spectra in the carbonyl region very similar to that of the known compounds $(\eta^5\text{-}C_4H_4N)Mn(PPh_3)(CO)_2$ [11] $(\eta^5\text{-}C_5H_5)Mn(PPh_3)_2CO$ [19], respectively.

Table 1 shows the dependence of k_{obs} on the concentration of $P(n\text{-}Bu)_3$ for the first substitution of I and III. Plots of k_{obs} vs. $P(n\text{-}Bu)_3$ concentration for these two reactions are shown in Fig. 3.

Table 2 contains the carbonyl stretches of the various substrates and their substituted products. Table 3 shows the results of a temperature dependence study on the substitution reactions of I and of III with $P(OEt)_3$ and with $P(n\text{-}Bu)_3$. The calculated activation parameters are also given in Table 3.

Attempts to study the kinetics of carbonyl substitution for the η^5-indolyltricarbonylmanganese(I) (II) were unsuccessful due to its thermal instability.

Discussion

Although π-bonded *N*-heterocyclic metal carbonyls have been known [10–12] for 20 years, almost no work has been reported on these compounds since the original

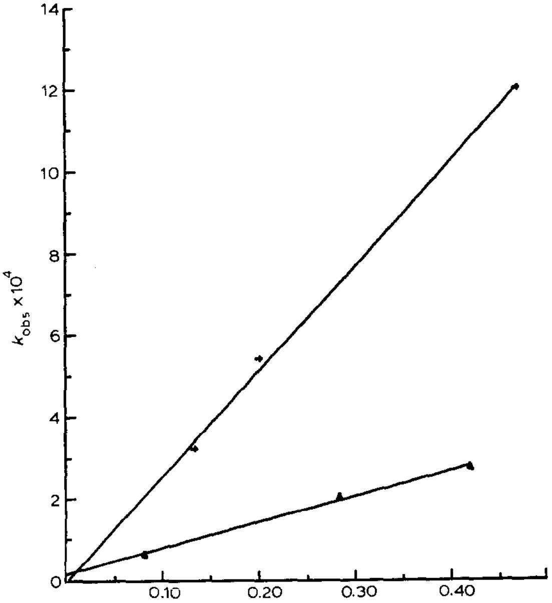


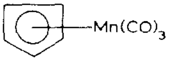
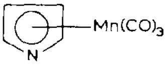
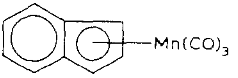
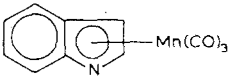
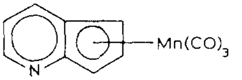
Fig. 3. Plot of k_{obs} vs. $P(n\text{-}Bu)_3$ concentration for the reaction:

$(\eta^5\text{-}L)Mn(CO)_3 + P(n\text{-}Bu)_3 \rightarrow (\eta^5\text{-}L)Mn(CO)_2P(n\text{-}Bu)_3 + CO$

in decalin. ▲ = $(\eta^5\text{-}C_4H_4N)Mn(CO)_3$ (I), 142°C; + = $(\eta^5\text{-}C_8H_6N)Mn(CO)_3$ (III), 130°C.

TABLE 2

CARBONYL STRETCHING FREQUENCIES OF THE η^5-COORDINATED MANGANESE TRICARBONYLS IN DECALIN

Complex	Ref.	ν(CO) (cm^{-1})
	[20]	2034, 1949 [a]
 (I)	this work	2037, 1965, 1955
$(\eta^5\text{-}C_4H_4N)Mn(CO)_2P(OEt)_3$	this work	1960, 1895
$(\eta^5\text{-}C_4H_4N)Mn(CO)_2P(n\text{-}Bu)_3$	this work	1945, 1880
$(\eta^5\text{-}C_4H_4N)Mn(CO)_2PPh_3$	this work	1950, 1890
$(\eta^5\text{-}C_4H_4N)Mn(CO)_2P(Cy)_3$	this work	1938, 1974
$(\eta^5\text{-}C_4H_4N)Mn(CO)(P(n\text{-}Bu)_3)_2$	this work	1900
$(\eta^5\text{-}C_4H_4N)Mn(CO)(P(Cy)_3)_2$	this work	1880
	[18]	2023, 1950, 1930 [b]
 (II)	this work	2038, 1964, 1954
 (III)	this work	2035, 1955, 1945
$(\eta^5\text{-}C_8H_6N)Mn(CO)_2P(OEt)_3$	this work	1955, 1895
$(\eta^5\text{-}C_8H_6N)Mn(CO)_2P(n\text{-}Bu)_3$	this work	1940, 1877
$(\eta^5\text{-}C_8H_6N)Mn(CO)_2PPh_3$	this work	1938, 1875 [c]

[a] Cyclohexane. [b] KBr pellet. [c] CH_2Cl_2.

papers. The reasons why little work has been done with these compounds is that they are less stable than their carbocyclic counterparts. The first syntheses of (η^5-*N*-heterocyclic)Mn(CO)$_3$ compounds were accomplished by either the reaction of $Mn_2(CO)_{10}$ with pyrrole or of $Mn(CO)_5Br$ with the sodium salt of the *N*-heterocyclic anion. We now report a new method of synthesis, starting with $[Mn(CO)_3(CH_3CN)_3]^+$ which has the three good leaving ligands CH_3CN (eq. 1).

$$[Mn(CO)_3(CH_3CN)_3]PF_6 + K(N\text{-heterocycle}) \rightarrow (\eta^5\text{-}N\text{-heterocycle})Mn(CO)_3 + KPF_6 + 3CH_3CN \qquad (1)$$

This method of synthesis has enabled us to prepare compound II. The other new compound III was prepared by one of the earlier methods.

Kinetic data in Table 1 show that the rates of CO substitution depend on the nature and the concentration of the entering ligand (eq. 2).

$$(\eta^5\text{-ligand})Mn(CO)_3 + L \xrightarrow{k} (\eta^5\text{-ligand})Mn(CO)_2(L) + CO \qquad (2)$$

TABLE 3

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE SUBSTITUTION REACTIONS OF (η^5-C_4H_4N)Mn(CO)$_3$ (I) AND OF (η^5-C_8H_6N)Mn(CO)$_3$ (III) IN DECALIN (eq. 2)

Complex	L	T (°C)	k_1 (M^{-1} s^{-1})	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (eu)
(η^5-C_4H_4N)Mn(CO)$_3$ (I)	P(n-Bu)$_3$ [a]	130	3.88×10^{-4}	15.1 (±1.6)	−37.4 (±3.9)
		142	7.35×10^{-4}		
		151	10.1×10^{-4}		
	P(OEt)$_3$	129	0.43×10^{-4}	22.7 (±0.1)	−22.6 (±2.4)
		143	1.19×10^{-4}		
		151	2.04×10^{-4}		
	PPh$_3$ [a]	130	0.19×10^{-4}		
	P(Cy)$_3$ [a]	130	0.38×10^{-4}		
(η^5-C_8H_6N)Mn(CO)$_3$ (III)	P(n-Bu)$_3$ [b]	120	1.54×10^{-3}	14.9 (±0.9)	−34.0 (±2.3)
		130	2.70×10^{-3} [b]		
		140	4.14×10^{-3}		
	P(OEt)$_3$	110	0.429×10^{-3}	14.5 (±1.3)	−36.5 (±3.2)
		120	0.826×10^{-3}		
		130	1.14×10^{-3}		
		140	1.96×10^{-3}		

[a] For the second substitution:

$$(\eta^5\text{-}C_4H_4N)Mn(CO)_2L + L \xrightarrow{k_2} (\eta^5\text{-}C_4H_4N)Mn(CO)L_2 + CO$$

$k_2 = 9.38\times10^{-5}\ M^{-1}\ s^{-1}$ (L = P(n-Bu)$_3$);

$9.1\times10^{-5}\ M^{-1}\ s^{-1}$ (L = P(Cy)$_3$)

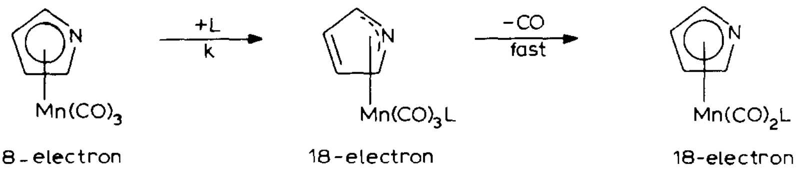
[b] For the reaction of the η^5-indenyltricarbonylmanganese(I):

$$(\eta^5\text{-}C_9H_7)Mn(CO)_3 + P(n\text{-}Bu)_3 \xrightarrow{k_1} (\eta^5\text{-}CH_7)Mn(CO)_2P(n\text{-}Bu)_3 + CO$$

$k_1 = 6.46\times10^{-5}\ M^{-1}\ s^{-1}$ at 130°C [7].

The reaction is second order, in accord with an associative (S_N2) mechanism reported [7] earlier for the analogous carbocyclic compounds. This mechanism is also supported by the low values of $\Delta H^\ddagger$ and the negative values of $\Delta S^\ddagger$ (Table 3). The plots in Fig. 3 are linear and go through the origin, which suggests the reactions are entirely second order with no evidence for a dissociative pathway with a nonzero intercept.

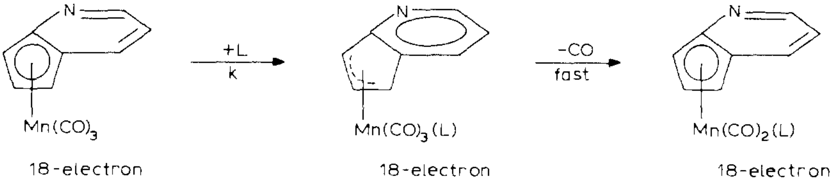
In contrast to the reported [21] thermal CO substitution inertness of (η^5-C_5H_5)Mn(CO)$_3$, its N-heterocycle analogue readily substitutes one CO with a variety of phosphines and phosphites in decalin solution at elevated temperatures (eq. 3).



(3)

This is in accord with the rule [8] that 18-electron transition metal organometallic compounds may undergo associative substitution reactions providing a pair of electrons can be localized on a ligand in the transition state for reaction. Localization of electron density on a *N*-heterocyclic ligand should exceed that of the corresponding carbocyclic ligand, because N is more electronegative than is C. This then may account for the greater substitution reactivity of the η^5-pyrrolyl metal complex over that of the corresponding η^5-cyclopentadienyl metal complex. Note that the values of ν(CO) (Table 2) are similar for corresponding *N*-heterocycle and carbocycle compounds, which suggests the presence of N in place of C does not greatly enhance electron withdrawal of the cyclic ligand in the ground states of the compounds. However, the rate enhancement of the N over the C system indicates that in the transition state where electron flow to the ligand is required, N is more effective than is C in promoting this.

Indenyl, compared with cyclopentadienyl, is known [6,7] to greatly enhance associative rates of ligand substitution of metal complexes. This is attributed to localization of a pair of electrons on the indenyl ligand which allows for the full aromaticity of the benzene ring (eq. 4 shows the corresponding N system).



(4)

Again here the rate of CO substitution is accelerated by the replacement of a C with a N in the indenyl ligand. Data in Table 3 show that the η^5-pyrindinyl compound reacts 40 times faster than does the corresponding η^5-indenyl compound. This is not a large rate enhancement compared with that for η^5-pyrrolyl relative to η^5-cyclopentadienyl. Unfortunately a quantitative comparison is not possible, because (η^5-C_5H_5)Mn(CO)$_3$ does not react even after three days at 130°C [21].

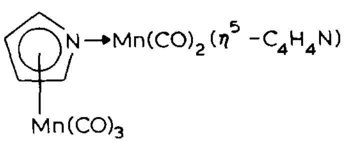
It seems reasonable that the presence of N in the η^5-ring of the ligand would have a greater electron-withdrawing effect, thus greater rate enhancement, than would a N in the fused 6-membered ring further away from the metal bonding site. We were hopeful this could be tested by preparing, for the first time, and studying the η^5-indolyl compound II. Although it was possible to prepare and characterize the desired compound, it was not possible to study its thermal substitution reactions. Even at temperatures of only 70°C, a decalin solution of II decomposes to give $Mn_2(CO)_{10}$ and other unidentified decomposition products. Since substitution reactions with the best nucleophiles require temperatures of at least 100°C, it was not possible to obtain kinetic data on this system. It is known [10–12] that *N*-heterocyclic metal carbonyls, where N is in the η^5-ring, are much less stable than are the corresponding carbocyclic metal carbonyls. We also observed that these compounds are much less stable in the solvents tetrahydrofuran, dimethylsulfoxide, and nitrobenzene than in decalin.

No attempt was made to determine how the nucleophilic strength of the entering ligand correlates with its proton basicity [22] or its size [23]. However, the results appear to be similar to what was observed [7] for the corresponding carbocyclic compounds with both basicity and size being important factors in nucleophilic reactivity. For instance, $P(n\text{-}Bu)_3$ is more reactive than is $P(Cy)_3$ which has about the same basicity but has a much larger cone angle; whereas $P(n\text{-}Bu)_3$ is more reactive because of its greater basicity than is $P(OEt)_3$ with a smaller cone angle.

The more basic ligands $P(n\text{-}Bu)_3$ and $P(Cy)_3$ react with I beyond the first step to replace a second CO (eq. 5).

$$(\eta^5\text{-}C_4H_4N)Mn(CO)_2(L) + L \xrightarrow{k_2} (\eta^5\text{-}C_4H_5N)Mn(CO)(L)_2 + CO \qquad (5)$$

Footnote (a) of Table 3 gives the values of k_2 for these reactions, both of which are also second order. As usual, the values of k_2 are about 10 times smaller than are the values of k_1. Finally it should be mentioned that one must always be aware of the fact that unlike carbocyclic ligands in these compounds, the *N*-heterocyclic ligands have a N atom capable of σ bonding to the metal, IV.



(IV)

This type of interaction has been reported [24] but a millimolar decalin solution of $(\eta^5\text{-}C_4H_4N)Mn(CO)_3$ was allowed to stand at 130°C for 71 h with no detectable change in its IR spectrum. This shows that at the conditions of our kinetic studies such an interaction is of minor or no importance.

These results show, as was expected, that *N*-heterocyclic ligands enhance the rates of associative substitution reactions in η^5-ring systems over corresponding carbocyclic organometallic compounds. However, the rate enhancement is modest and the compounds are much less stable than are their carbocyclic counterparts. In our continuing quest for ligands that give substitution labile organometallic compounds which may improve their use as homogeneous catalysts, the use of *N*-heterocyclics does not look too promising.

Acknowledgment

I (F.B.) want to thank the Editors of the JOMC for their invitation to publish an article in this special issue honoring my long time friend Professor Lamberto Malatesta.

We thank the National Science Foundation and the donors of the Petroleum Research Foundation administered by the American Chemical Society for support of this research. L.N.J. was on leave from Zhongshan (Sun Yatsen) University and thanks the Ministry of Education of the People's Republic of China for support. D.L.K. thanks the Graduate School of Northwestern University for a Fellowship. We thank Professor Anthony Barrett for his advice with the syntheses of some N-heterocyclics.

References

1 H.G. Schuster-Woldan, and F. Basolo, J. Am. Chem. Soc., 88 (1966) 1657.
2 D.F. Keeley, and R.E. Johnson, J. Inorg. Nucl. Chem., 11 (1959) 33; F. Basolo, and A. Wojcicki, J. Am. Chem. Soc., 83 (1961) 520.

3 C.A. Tolman, Chem. Soc. Rev., 1 (1972) 337.
4 R. Cramer, and L.P. Siewell, J. Organomet. Chem., 92 (1975) 245.
5 C.P. Casey, and J.M. O'Connor, Organometallics, 4 (1985) 384 and ref. therein.
6 A.J. Hart-Davis, and R.J. Mawby, J. Chem. Soc., A, (1969), 2403; P.J. Jones and R.J. Mawby, Inorg. Chim. Acta, 6 (1972) 157.
7 M.E. Rerek, L.N. Ji, and F. Basolo, J. Chem. Soc. Chem. Commun., (1983) 1208; Organometallics, 3 (1984) 740; M.E. Rerek, and F. Basolo, J. Am. Chem. Soc., 106 (1984) 5908.
8 F. Basolo, Coord. Chem. Revs., 43 (1982) 7; Inorg. Chim. Acta, 100 (1985) 33.
9 C.Y. Chang, C.E. Johnson, T.G. Richmond, Y.T. Chen, W.C. Trogler, and F. Basolo, Inorg. Chem., 20 (1981) 3167; Q.Z. Shi, T.G. Richmond, W.C. Trogler, and F. Basolo, Organometallics, 1 (1982) 1033.
10 K.K. Joshi, and P.L. Pauson, Proc. Chem. Soc., (1962) 326; K.K. Joshi, P.L. Pauson, A.R. Qazi, and W.H. Stubbs, J. Organomet. Chem., 1 (1964) 471.
11 R.B. King, and A. Efraty, J. Organomet. Chem., 20 (1969) 264.
12 P.L. Pauson, A.R. Qazi, and B.W. Rockett, J. Organomet. Chem., 7 (1967) 325.
13 Abbreviations: $P(n\text{-}Bu)_3$ = tri-n-butylphosphine, $P(Cy)_3$ = tricyclohexylphosphine, PPh_3 = triphenylphosphine, $P(OEt)_3$ = triethylphosphite, THF = tetrahydrofuran.
14 M.M. Robinson, J. Am. Chem. Soc., 80 (1958) 6254.
15 B.R. King, (Ed.), Organometallic Synthesis, Vol. 1, 1965, p. 174.
16 R.H. Reimann, and E. Singleton, J. Chem. Soc. Dalton, (1974) 808.
17 M.L. Ziegler, H. Haas, and R.K. Shelmire, Chem. Ber., 98 (1965) 2454.
18 R.B. King, and A. Efraty, J. Organomet. Chem., 23 (1970) 527.
19 N.G. Connelly, and M.D. Kitchen, J. Chem. Soc. Dalton, (1977) 931.
20 G. Fiedler, Z. Physik, Chem., 37 (1963) 79.
21 R.J. Angelici, and W. Lowen, Inorg. Chem., 6 (1967) 682.
22 W.A. Henderson, and C.A. Streuli, J. Am. Chem. Soc., 88 (1966) 3929.
23 C.A. Tolman, Chem. Rev., 77 (1977) 313.
24 N.I. Pyshnograeva, V.N. Setkina, V.G. Andrianov, Yu.T. Struchkov, and D.N. Kursanov, J. Organomet. Chem., 157 (1978) 431.