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η^5-HETEROCYCLIC METAL CARBONYLS

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CONTENTS

A. Introduction 279
B. Background 280
C. Nitrogen group heterocyclic metal complexes 281
  (i) Nitrogen 284
  (ii) Phosphorus 284
  (iii) Arsenic 285
  (iv) Antimony 285
D. Oxygen group heterocyclic metal complexes 285
  (i) Sulfur 286
  (ii) Selenium and tellurium 286
E. Boron heterocyclic metal complexes 286
F. Reactivity of η^5-heterocyclic metal carbonyls at the metal center 286
  (i) Boron 287
  (ii) Oxygen group 287
  (iii) Nitrogen group 287
G. Summary 290
Acknowledgments 291
References 291

A. INTRODUCTION

η^5-Carbocyclic metal carbonyls are very well known, e.g. η^5-cyclopentadienyl. In spite of this the analogous η^5-heterocyclic systems, in which one or more carbon atoms are replaced by a heteroatom, have been rarely studied. Such systems are in need of further investigation, in particular in order to determine the reactivity of the metal carbonyl moiety when attached to an η^5-heterocyclic ligand compared with its reactivity when attached to a carbocycle. It is important to learn more about factors that affect CO substitution lability, because this is a necessary step in homogeneous catalysis by such compounds. Therefore, the focus of this paper is on ligand substitution reactions.

There are other reasons why further investigations of η^5-heterocyclic metal complexes are needed. One is to learn more about reactions of the

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η^5-heterocyclic rings in these compounds [1] and another is to examine any possible biological importance of such compounds. This is prompted by the fact that there is considerable information [2] on the biological role of heterocyclic compounds. Neither the ring reactivity nor the possible biological activity of η^5-heterocyclic metal complexes will be addressed here. Furthermore, since a comprehensive review [3] of π-heterocyclic metal complexes was written about a decade ago, we feel it necessary to deal mainly with work done subsequent to the review. Therefore, our attention is directed towards more recent compounds, and more specifically towards η^5-heterocyclic metal carbonyls.

B. BACKGROUND

The general properties of heterocyclic metal complexes are known. Perhaps the most important feature is the preferential formation of heteroatom metal σ bonds, instead of heterocycle–metal π bonds. This preference for σ bonding is attributed [3] to the lower ionization energies of unbonded electron pairs on the heteroatoms relative to the electrons in the π system. In other words, these unbonded electron pairs are more accessible for bonding at Lewis bases than would be the π-electrons of the heterocyclic rings. This means there is a delicate balance between σ versus π bonding, but as times π bonding does occur.

Another general consideration with regard to π-heterocyclic metal complexes is their stability relative to corresponding carbocyclic compounds. An important contribution to the bonding of cyclopentadienyl metal complexes is said [4] to be the ionic interaction between the ligand $C_5H_5^-$ and the positive metal center. Replacing $C_5H_5^-$ with a neutral arene or with a more electron withdrawing heterocyclic ligand reduces this favorable interaction. For the purpose of reference in this review, the electronegativities of some atoms are given in Table 1. In general, the more electronegative atoms such as N [5] and S [6] (O-heterocycles are not reported to form π metal complexes) form π-heterocyclic metal complexes which tend to be air unstable, whereas those of the less electronegative B [7] are air and water stable. That greater electron releasing tendency of the π-rings results in

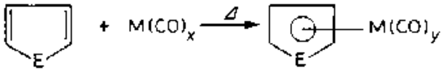
TABLE 1

Electronegativities [34]

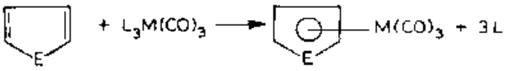
Group III	Group IV	Group V				Group VI			
B	C	N	P	As	Sb	O	S	Se	Te
1.9	2.5	3.0	2.1	2.0	1.9	3.5	2.5	2.4	2.1

more stable complexes is supported by the fact that electron releasing alkyl groups on the ring ligand enhance complex stability. It is likewise true that alkyl substituted arene metal carbonyls are generally more stable than the corresponding unsubstituted arene compounds [8].

There are two general methods for the syntheses of the η^5-heterocyclic metal carbonyls of the oxygen family, where the ring heteroatom is S, Se or Te. The first [9] is the direct reaction of the heterocyclic ligand with the appropriate metal carbonyl at elevated temperatures

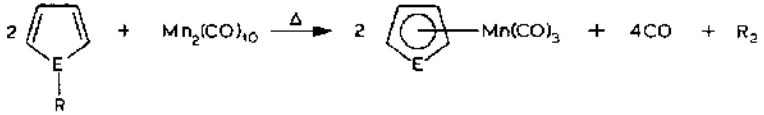


where E = S, Se or Te. The second method is the reaction of the heterocyclic ligand with an $L_3M(CO)_3$ complex



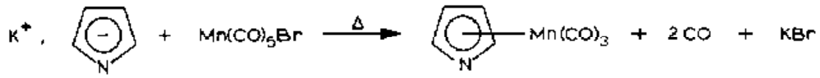
where E = S, Se or Te. The three weakly coordinating L groups (often CH_3CN) can be replaced by the 6-electron donating heterocyclic ligand.

Almost all of the η^5-heterocycles of the N family are coordinated to the $Mn(CO)_3$ moiety. Such complexes are synthesized by three routes. The first involves direct reaction between the heterocycle and $Mn_2(CO)_{10}$,



where R = H for E = N and R = C_6H_5 for E = P, As or Sb. Two other methods have been used for the *N*-heterocyclic complexes. One involves a reaction which proceeds under mild conditions between the active metal complex $[Mn(CO)_3(CH_3CN)_3]^+$ and the pyrrolyl anion.

An alternative route is a metathesis reaction at elevated temperatures.



C. NITROGEN GROUP HETEROCYCLIC METAL COMPLEXES

The nitrogen family η^5-heterocyclic metal carbonyls are the most studied of the η^5-heterocycles. These complexes are known to undergo chemical transformations at both the metal center and the ring ligand, and reactions

TABLE 2

Recent examples of η^5-heterocyclic metal carbonyls

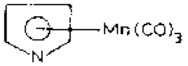
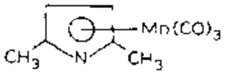
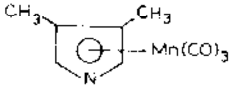
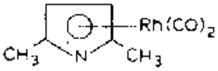
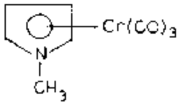
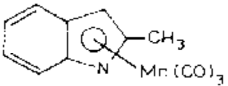
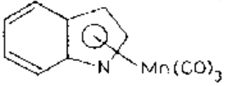
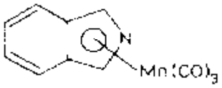
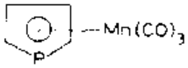
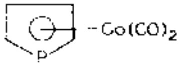
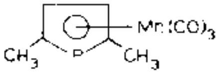
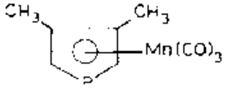
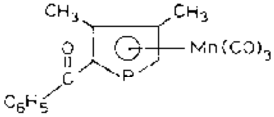
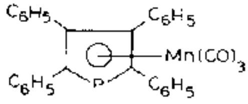
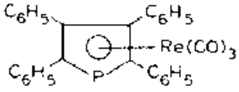
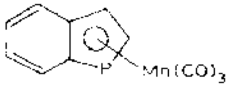
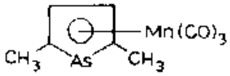
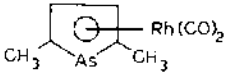
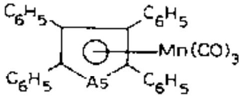
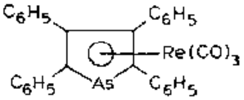
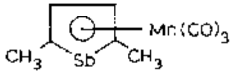
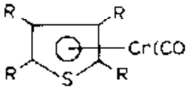
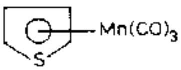
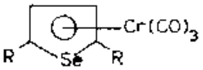
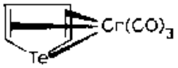
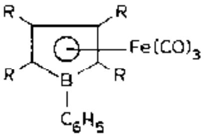
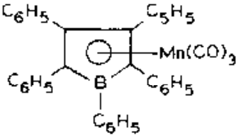
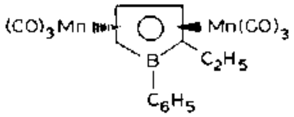
Complex	Number	Ref.
	**I**	5a, 10
	**II**	9d
	**III**	9d
	**IV**	35 (see text)
	**V**	11
	**VI**	15, 16
	**VII**	31
	**VIII**	31
	**IX**	5a
	**X**	9b
	**XI**	17
	**XII**	31
	**XIII**	9b
	**XIV**	9b
	**XV**	20
	**XVI**	20
	**XVII**	18

TABLE 2 (continued)

Complex	Number	Ref.
	**XVIII**	31
	**XIX**	35 (see text)
	**XX**	20
	**XXI**	20
	**XXII**	21
 [a]	**XXIII**	23, 40
	**XXIV**	22
 [a]	**XXV**	25
	**XXVI**	26
	**XXVII**	7
	**XXVIII**	7
	**XXIX**	27

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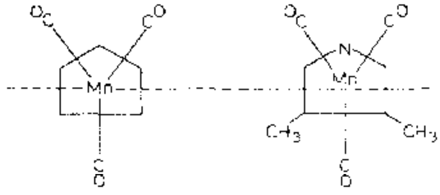
[a] R = H, alkyl, or aryl group.

at both are sensitive to the electronegativity of the heteroatom. It follows that attachment of a π-ring to a strong electron sink such as $Mn(CO)_3^+$ increases reactivity towards nucleophilic substitution reactions on the ring ligand. In fact, it is believed that the phospholyl [9b] and arsolyl [9c] complexes become aromatic only after being complexed to the $Mn(CO)_3^+$ moiety.



$(\eta^5\text{-}C_5H_5)Mn(CO)_3$ III

Fig. 1. Slippage of $Mn(CO)_3$ moiety towards the N ring atom in **III** compared with a ring centroid structure of the corresponding η^5-cyclopentadienyl compound.

(i) Nitrogen

The reactions of $(\eta^5\text{-}C_4H_4N)Mn(CO)_3$ (complex **I** in Table 2), which is isoelectronic with $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, were recently reviewed [10]. The pyrrolyl complexes are known [5] to be more reactive to CO substitution and less air stable than are corresponding cyclopentadienyl complexes. Another difference is the distortion of the $M(CO)_3$ moieties away from the center of the pyrrole rings, with slippage towards the N atom. Complexes **III** [9d] and **V** [11] (Table 2; henceforth always refer to Table 2 for compounds) both exhibit this behavior (Fig. 1). This type of allyl–ene interaction was also suggested [12] in an early nuclear quadrupole resonance study of **I**. By contrast $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ has the metal carbonyl fragment symmetrically situated with respect to the cyclopentadienyl ring center [13]. Another feature of the pyrrolyl compounds is that the CO molecules of the $M(CO)_3$ fragment are oriented so as to place a CO group *trans* to N. It was suggested [14] this conformation minimizes the electronic repulsions between the discrete orbitals on the ring ligand and those on the $M(CO)_3$ moiety.

Other types of η^5-N-heterocyclic metal carbonyls are known, such as $(\eta^5$-2-methylindolyl$)Mn(CO)_3$ [15] **VI** and the much less stable $(\eta^5$-indolyl$)Mn(CO)_3$ [5a] **VII**. An X-ray structure of **VI** [16] showed no slippage of the metal carbonyl moiety towards the N atom, unlike the pyrrolyl analogues. There is also an example of an $(\eta^5$-1-pyrindinyl$)Mn(CO)_3$ [5a] complex **IX**, in which the N atom is in the six-membered ring.

(ii) Phosphorus

The η^5-P-heterocyclic metal carbonyls are more air stable and less reactive towards CO substitution than are the N counterparts. Bonding of $Mn(CO)_3^+$ to the phospholyl ring is likewise different than it is to the pyrrolyl ring. An X-ray structure of **XIV** [9b] showed the metal carbonyl moiety is located at the center of the heterocyclic ring (no slippage towards P) and a CO group is almost eclipsed by the P (Fig. 2).

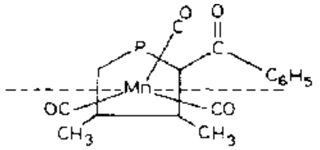


Fig. 2. Bonding of $Mn(CO)_3$ moiety towards the 2-benzoyl-3,4-dimethylphospholyl ligand.

The compound $(\eta^5-C_4H_4P)Co(CO)_2$ **XI** was prepared [17] but not further studied. Compound **XVII** [18], corresponding to N compound **VII**, is less reactive towards electrophilic substitution reactions on the five-membered ring than its phospholyl counterparts. The decreased reactivity was attributed to the electron-withdrawing ability of the fused benzene ring.

(iii) Arsenic

There are several examples of η^5-arsolyl metal tricarbonyl complexes, but because no unsubstituted arsole compounds are known, all arsolyl metal complexes bear substituents on the arsolyl ring. An X-ray structure of **XX** [19] shows the $Mn(CO)_3$ moiety is equidistant from all four heterocyclic ring C atoms, as was found with the phospholyl complex **XIV**. These complexes were obtained in higher yield [20], and they are much more air stable than are their pyrrolyl analogues.

(iv) Antimony

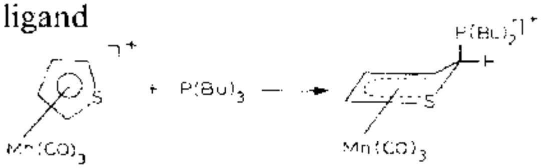
We were able to find a report [21] of only one Sb heterocyclic metal carbonyl. No reactivity studies were reported, but ^{13}C NMR experiments are said to indicate the complexed heterocycle is aromatic.

D. OXYGEN GROUP HETEROCYCLIC METAL COMPLEXES

The oxygen family π-heterocyclic metal carbonyls have not been studied as much as have the analogous compounds of the nitrogen family. We could find no report of a π-O-heterocyclic metal complex, perhaps because oxygen is too electronegative (Table 1) to permit electron delocalization and π interaction with the metal. Most of this work has dealt with the syntheses of these complexes. Such heterocyclic complexes are similar to the well known $(\eta^6-C_6H_6)M(CO)_3$ systems. However, little is known [3,22] about the reactivity of the heterocyclic complexes. In general, the π-heterocyclic metal carbonyls are less thermodynamically stable [23] than are the analogous π-arene compounds.

(i) Sulfur

The π-thiophene metal complexes are the most studied of the oxygen family heterocyclic complexes, but little work has been done [22] on their reactivity. There is a report [24] on the lithiation of **XXIII** (R = H) at −50 °C. Also, the cationic complex **XXIV** is known [23] to undergo nucleophilic attack at the thiophene ring to form a tetrahapto coordinated ligand



This reaction is analogous to that observed [1] with $[(\eta^6\text{-benzene})Mn(CO)_3]^+$.

(ii) Selenium and tellurium

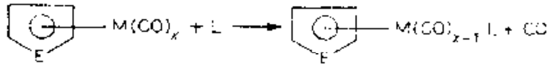
We find only two examples of Se-η^5-heterocyclic metal carbonyls [25] **XXV** and only one example of a Te complex [26]. Bonding of the Te compound was described as an η^4-butadiene and a Te-σ type interaction, **XXVI**. The Se and the Te complexes appear to be more stable than those of thiophene, but no reactivity studies were reported on these complexes.

E. BORON HETEROCYCLIC METAL COMPLEXES

A few examples are known [7] of η^5-borole metal carbonyl complexes. These complexes are interesting in that the borole ligand is a four-electron donor. An X-ray study [27] of **XXIX** showed it has a "triple-decker sandwich" structure. Furthermore, no interaction between the $Mn(CO)_3$ moieties in the three-decker compound was observed. This would imply the presence of 16-electron coordinatively unsaturated metal centers: if correct, it suggests ready CO substitution by associative reactions. Unfortunately, no reactivity studies on **XXIX**, or any other η^5-borole metal complex, have been reported.

F. REACTIVITY OF η^5-HETEROCYCLIC METAL CARBONYLS AT THE METAL CENTER

The remainder of this report deals primarily with CO substitution reactions of the (η^5-heterocyclic)metal carbonyl complexes



Such reactions are known to occur thermally, photochemically, and in the presence of $(CH_3)_3NO$.

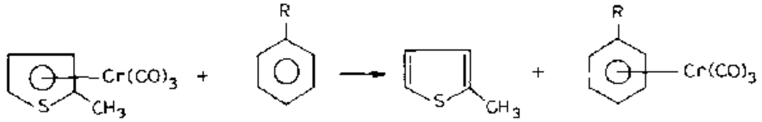
(i) Boron

No report was found of substitution studies of π-B-heterocyclic metal complexes.

(ii) Oxygen group

There are no reports of CO substitution reactions of oxygen group η^5-heterocyclic metal complexes. It is known [22] that nucleophilic attack on $[(\pi\text{-thiophene})Mn(CO)_3]^+$ occurs at the thiophene ring and not at the metal center. It was reported [3] that $(\pi\text{-thiophene})Cr(CO)_3$ complexes are photochemically unstable, decomposing to produce free thiophene ligand.

There is a report [23] that $(\pi\text{-thiophene})Cr(CO)_3$ reacts with benzene derivatives to produce $(\pi\text{-benzene})Cr(CO)_3$ complexes



It was suggested that formation of the π-benzene complexes is thermodynamically favored.

(iii) Nitrogen group

The CO substitution reactions of the $(\eta^5\text{-heterocyclic})Mn(CO)_3$ complexes have been known for some time. Early studies [28] used UV radiation to produce CO substituted products. A recent study [29] reports that CO substitution reactions proceed readily in the presence of 4–5 molar excess $(CH_3)_3NO$. Both the above methods are generally applicable to all nitrogen family heterocyclic complexes.

Recently it was observed [5a,9d,31] that for the nitrogen family heterocyclics related to cyclopentadienyl, only $(\eta^5\text{-N-heterocyclic})Mn(CO)_3$ complexes undergo CO substitution reactions at elevated temperatures with an excess of nucleophile. Kinetic studies showed these substitution reactions proceed by an associative (Sn2 or Ia) pathway. The enhanced reactivity of the N complexes over corresponding P, As [30] or Sb (as well as C) compounds is tentatively attributed to the greater electronegativity of N (Table 1), which can assist removal of electron density from the metal center during reaction. The proposed mechanism [33] involves nucleophilic attack at the metal center accompanied by a "slippage" of the ring coordination from $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$, while maintaining an 18-electron count at the metal throughout the reaction pathway

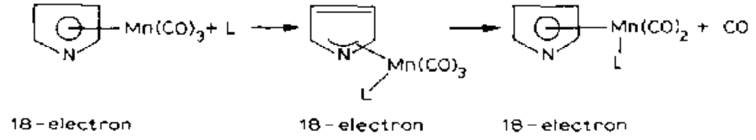
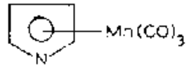
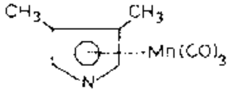
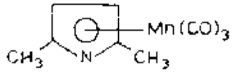
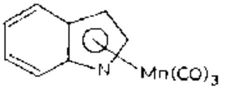
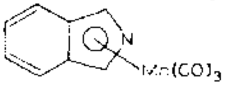


TABLE 3

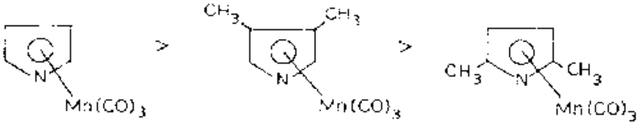
Rate constants for the CO substitution reactions of (η^5-heterocyclic)$Mn(CO)_3$ complexes with $P(n\text{-}Bu)_3$ at 130 °C in decalin [a]

Complex	k (M^{-1} s^{-1})	Ref.
	3.88×10^{-4}	5a
	1.86×10^{-4}	9d
	1.24×10^{-6}	9d
	2.70×10^{-3}	5a
	9.14×10^{-6}	31
	Very fast	31

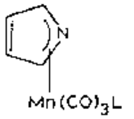
[a] For the reaction of tricarbonyl(η^5-indenyl)manganese(I): $(\eta^5\text{-}C_9H_7)Mn(CO)_3 + P(n\text{-}Bu)_3 \xrightarrow{k_1} (\eta^5\text{-}C_9H_7)Mn(CO)_2P(n\text{-}Bu)_3 + CO$ $k_1 = 6.46 \times 10^{-5}$ M^{-1} s^{-1} at 130 °C [33b].

This slippage mechanism then avoids the energetically unfavorable 20-electron transition state or active intermediate, otherwise required by an associative reaction. It should be noted [32] that the corresponding $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ does not undergo thermal CO substitution reactions.

Recent work [9d] showed that dimethyl substituted pyrrolyl complexes **II** and **III** substitute CO at a slower rate than does **I**. Referring to the above, such a result is expected on electronic grounds because methyl groups are electron donating, which is expected to make less favorable the localization of an electron pair on the ring during reaction. Furthermore, these results are consistent with steric retardation of the rates of associative reactions. But the important finding is that the position of the two methyl groups on the pyrrolyl ring has a large effect on the rate of CO substitution (Table 3). The 2,5-dimethylpyrollyl complex **II** reacts 100 times more slowly than does the 3,4-dimethylpyrrolyl complex **III**. Thus the rates of CO substitution decrease in the order

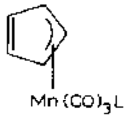


These results suggest a 2-azallyl transition state (**A**) which, in light of the inertness [32] of (η^5-C_5H_5)Mn(CO)$_3$, is expected to be more stable than is the allyl group **B**.



A

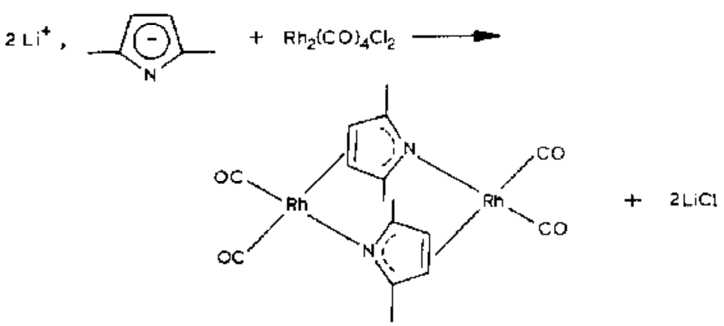
>



B

Further support for the importance of **A** was provided by an X-ray structure [9d] of **III**, which clearly showed slippage of the Mn(CO)$_3$ moiety towards the N atom. By contrast, the X-ray structure [13] of (η^5-C_5H_5)Mn(CO)$_3$ shows no slippage of Mn(CO)$_3$ which is symmetrically situated relative to the ring.

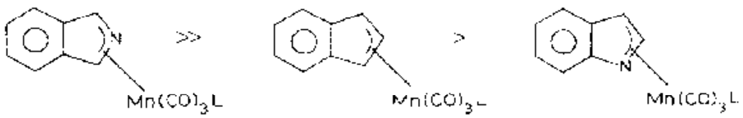
Yünlü recently attempted to prepare compounds **IV** and **XIX** by a methasis reaction of the type represented by eqn. 5, but using $Rh_2(CO)_4Cl_2$. Instead of obtaining the desired compounds, the reaction of $Rh_2(CO)_4Cl_2$ with lithium 2,5-dimethylpyrrolide afforded a most interesting dimeric product.



This is the first report [35] of a pyrrolido ligand bridging two metals via σ-bonding to nitrogen and η^2 π-bonding, whereas ligand bridging via σ-bonding to nitrogen and η^5 π-bonding is well known [3]. Compounds **IV** and **XIX** have not yet been prepared.

A considerable amount of work [33] has been done on what now is referred to as the indenyl effect on the rates of ligand substitution of (η^5-indenyl) metal complexes. For example, (η^5-indenyl)Mn(CO)$_3$ is believed to undergo CO substitution 10^8 times faster than (η^5-C_5H_5)Mn(CO)$_3$. Recently, the CO substitution reactions of **VII** have been studied [5a]. This N-analogue of (η^5-indenyl)Mn(CO)$_3$ is about 40 times more reactive towards CO substitution than is the η^5-indenyl complex. Again this was attributed to the greater electron-withdrawing ability of N relative to C.

Preliminary results [31] on CO substitution reactions of **VII** and **VIII** show that the latter is several orders of magnitude more reactive than is **VII** (Table 3). Noteworthy is the fact that **VII** is less reactive than is (η^5-indenyl)Mn(CO)$_3$, even though **VII** contains the more electronegative N (relative to C) in its ring. This suggests that factors other than electronegativity of the heteroatom are important in affecting rates of ligand substitution of η^5-heterocyclic metal carbonyls. Here again, as mentioned above with structures **A** and **B**, the driving force for reaction appears to be the greater stability of the 2-azallyl transition state.



In the case of the N-analogues of (η^5-indenyl)Mn(CO)$_3$, it appears that both electronegativity of the heteroatom and its position in the ring ligand are important factors in contributing to the rate of CO substitution.

G. SUMMARY

The lack of attention given to the η^5-heterocyclic metal carbonyls is unfortunate because the reactivity of these complexes, e.g. CO substitution, can differ markedly from that of their carbocyclic analogues. In many cases, these differcences can be attributed to the electronegativity of the heteroatom which affects the electron withdrawing ability of the π-heterocycle. As the π-heterocycle becomes more electron withdrawing, less electron density resides on the metal center, enabling associative nucleophilic substitutions to occur more readily. However, recent studies indicate that in some systems the electronegativity of the heteroatom cannot, in itself, fully explain the differences in CO substitution reactivity between the π-heterocyclic metal carbonyls and their parent π-carbocyclic complexes. Work in out laboratory may help to elucidate some of these other, more subtle, factors.

Ligand substitution reactivity of the π-heterocyclic metal carbonyls is only one of several aspects of π-heterocyclic metal chemistry yet to be fully investigated. The observed difference in reactivity between the π-heterocyclic metal complexes and their carbocyclic analogues suggests a much broader range of rates of ligand substitution can be achieved by the use of π-heterocyclic systems. More work is needed in order to better understand the potential synthetic and catalytic applications of π-heterocyclic metal carbonyls.

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