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COORDINATION CHEMISTRY OF THE MANGANESE AND RHENIUM FRAGMENTS $(C_5H_5)M(CO)_2$

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CONTENTS

A. INTRODUCTION

An extraordinarily rich chemistry is currently developing around the fragment $(C_5H_5)Mn(CO)_2$. Adducts of general formula $CpMn(CO)_2L$ (Cp = C_5H_5) have been detected, isolated and unequivocally characterized for a large array of exotic and unstable ligands L. The focus of interest in these complexes is generally on the ligand L, with the $CpMn(CO)_2$ moiety (mn or **1**) functioning as a pedestal, almost a vice or clamp, for the capture and display of L. The exceptional stabilizing capacity of **1** has been recognized to the point where it now should be considered by anyone attempting such capture and display. This characteristic has already been exploited in well-designed research directed towards intermediates in metal-catalyzed nitrogen fixation and CO hydrogenation. It is the purpose of this review to survey the wide range of applications of this stabilization, to attempt some preliminary account of its origin, and to point out allied topics which might profit from further study.

In the following, explicit reference will generally be made only to $(C_5H_5)Mn(CO)_3$. However, the greater general availability and lower cost of $(C_5H_4Me)Mn(CO)_3$, an automotive antiknock additive, has lead to its use in many of the studies reported here.

B. FORMATION AND PROPERTIES OF $CpMn(CO)_2$

In discussing the properties of $CpMn(CO)_2$, it is essential to specify the environment in which it is found, since **1** will generally interact strongly with its surroundings. We discuss first synthetic applications of **1** in the liquid phase, followed by a survey of matrix isolation work directed towards the "isolated" unit $CpMn(CO)_2$.

The majority of syntheses producing $CpMn(CO)_2L$ species have been carried out using light as an energy source [1]. $CpMn(CO)_3$ is quite inert to thermal substitution and substitution of CO promoted by amine oxides has been demonstrated only recently [2]. In view of the electronic spectrum and yellow color of $CpMn(CO)_3$, irradiation through Pyrex glass is satisfactory [3]. Photolysis proceeds best under a purge of some inert gas which inhibits recombination with photodissociated CO. Coordinating solvents are generally superior to hydrocarbons since the actual species $CpMn(CO)_2$ has a very brief lifetime at 25°C; such solvents provide temporary stabilization. Tetrahydrofuran (THF) is the solvent most commonly employed.

As described by Strohmeier and Müller, two procedures are available for the synthesis of $CpMn(CO)_2L$. In the first (the indirect method) [4] red $CpMn(CO)_2(THF)$ is formed in a preliminary photolysis of $CpMn(CO)_3$, preferably at reduced temperature and under a purge of an inert gas. Nitrogen is an acceptable purge gas since it is not a significantly competitive ligand in THF solvent. The UV light is then extinguished and the reaction is completed by a thermal reaction in which ligand is added at an appropriate temperature (dark reaction). For photostable ligands (or cases where a photolysis fragment of a precursor molecule is the desired ligand), $CpMn(CO)_3$ and ligand are irradiated together. In this second procedure (the direct method) [5], gross decomposition to carbonyl-free material is a common occurrence, leading to low yields ($< 10\%$). In our experience, this situation is sometimes alleviated by working in THF and at low temperatures. There are reported examples where the indirect method provides order-of-magnitude increases in yield over direct irradiation in the presence of ligand [6].

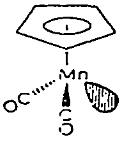
Reference will also be made in this review to complexes derived from the

TABLE 1
Carbonyl stretching frequencies [8,9]

	ν(CO) (cm^{-1})	
	A_1	B_1
$CpMn(CO)_2$ in argon	1972	1903
$CpMn(CO)_2$ in methane	1961	1893
$CpMn(CO)_2$ in Nujol	1955	1886
$CpMn(CO)_2(THF)$	1930	1845
$CpCo(CO)_2$	2030	1970

third transition series homolog, $CpRe(CO)_3$. Much of what has been said above concerning $CpMn(CO)_3$ applies to the rhenium analog. However, $CpRe(CO)_2(THF)$ is far more stable (e.g. isolable and sublimable) than the manganese analog [7], making the direct method in noncoordinating solvents an attractive alternative to photolysis in THF. In addition, $CpRe(CO)_3$ is colorless, making quartz glass apparatus preferable for photolysis reactions [3].

The fragment $CpMn(CO)_2$ is coordinatively unsaturated. The 16 valence electrons of **1** make it an acceptor for ligands whose total electron count equals two; this includes all conventional Lewis bases, as well as pairs of one-electron ligands (H, R, Cl, etc.). Although **1** is quite unstable, it has been detected after photolysis of the tricarbonyl parent both in a Nujol glass [8] and also in more conventional matrix isolation media [9]. The vibrational data in Table 1 indicate that coordination of THF, a "pure" σ donor ligand, to the fragment **1** causes the expected increase in back bonding to CO. It is noteworthy that back bonding in unsaturated (i.e. electron deficient) $CpMn(CO)_2$ exceeds that in saturated $CpCo(CO)_2$; the dominant factor here is clearly not the valence electron count, but rather the metal nuclear charge. A second and less obvious factor, that of basic geometry, differentiates $CpCo(CO)_2$ from $CpMn(CO)_2$. While the ring midpoint lies in the $Co(CO)_2$ plane in $CpCo(CO)_2$, a Walsh diagram analysis of $CpMn(CO)_2$ indicates enhanced stabilization of the HOMO with increasing pyramidality at Mn [10]. Experimental support for a pyramidal geometry in $CpMn(CO)_2$ is sparse. Although IR data allow calculation of the angle subtended at Mn by the carbonyl ligands [8], this parameter cannot be uniquely linked to pyramidality. The best structural evidence currently available derives from stereochemical studies on the related 16-electron intermediate CpMnNO(C(O)Ph), which appears to be chiral [11]. Pyramidal $CpMn(CO)_2$ has a lone pair HOMO directed as in **2**, which may account for the dependence of ν(CO) on the matrix material (Table 1). Moreover, it is clear



2

that pyramidal "unsaturated" $CpMn(CO)_2$ is actually a Lewis base! This is significant with regard to the proposed mechanism for conversion of $CpRe(CO)_3$ to $Cp_2Re_2(CO)_5$ [12]. Photolysis of $CpRe(CO)_3$ in hexane produces $CpRe(CO)_2$, which was suggested to function as a metal-centered Lewis base in condensing with $CpRe(CO)_3$.

C. STABILITY AND REACTIVITY OF $CpMn(CO)_2L$

Results obtained to date indicate that the $CpMn(CO)_2$ portion of $CpMn(CO)_2L$ complexes is quite inert to attacking nucleophilic reagents. In this respect, the cyclopentadienyl and carbonyl ligands function in an insulating fashion towards nucleophiles as do the ammine ligands in $Co(III)(NH_3)_5X$ towards Cr(II). Consequently, the majority of reactions observed with $CpMn(CO)_2L$ involve either substitution or modification of the appended unique ligand L.

While the mechanism of substitution of THF in $CpMn(CO)_2(THF)$ has not been unequivocally established, the question has been settled for $CpMn(CO)_2(SR_2)$ [13]. Substitution of R_2S by phosphine or phosphite proceeds by an S_N1 mechanism in methylcyclohexane; the rate is independent of the identity of the phosphorus ligand, it exhibits a positive $\Delta S^{\neq}$, and is not accelerated by changing to a polar solvent (nitromethane). The mechanism is analogous to that of olefin substitution in $CpMn(CO)_2(olefin)$ [14]. While these results probably relate mechanistically to substitution on $CpMn(CO)_2(THF)$, the typical duration of substitution reactions with this complex (0.5–1 h at 25°C or below) is indicative of THF being an exceptionally good leaving group.

The integrity of the $CpMn(CO)_2$ unit in its adducts with two-electron donor ligands has been breached only when the unique ligand L is a strong π-acceptor. The case of vinylidene ($:C=CH_2$) is discussed below.

Oxidative addition has been only rarely observed for $CpMn(CO)_3$. Bromine causes major disruption of the complex to give CO, polybrominated C_5 fragments and (presumably) $MnBr_2$ [15]. Protonation at Mn has been extensively investigated for the more basic (oxidizable) species $CpMn(PR_3)_{3-n}(CO)_n$ [16]. The rarity of oxidized products cannot be due to crowding caused by the increased coordination number, since $CpMn(CO)_2(H)(SiPh_3)$ and $CpMn(CO)_2(PPh_3)SnCl_3^+$ are known [17,18].

Halogen oxidative addition to $CpMn(PR_3)_{3-n}(CO)_n$ has been shown to proceed by one-electron transfer in selected instances [19].

Implicit in the above discussion of the substitutionally inert nature of $CpMn(CO)_2L$ species is the assumption that only even-electron species are present. A non-chain mechanism invoking only diamagnetic intermediates suffices to account for observations to date. However, a study of substitution reactions purposely conducted in the presence of a manganese-centered radical may reveal a synthetic technique of wide applicability, since it is now evident that many 17-electron complexes are labile [20]. Several 17-electron cations, $CpMnL_{3-n}(CO)_n^+$, have been produced from electron-rich precursors using NO^+ and ArN_2^+ [21,22]. While the lability of these remains to be tested, the reaction sequence in Scheme I may catalyze ordinarily sluggish substitution reactions.

Scheme I

Initiate: $NO^+ + CpMn(CO)_2L \rightarrow NO + CpMn(CO)_2L^+$

(1) $CpMn(CO)_2L^+ + L' \rightarrow\rightarrow CpMn(CO)_2L'^+ + L$

(2) $CpMn(CO)_2L'^+ + CpMn(CO)_2L \rightarrow CpMn(CO)_2L' + CpMn(CO)_2L^+$

Net reaction: $CpMn(CO)_2L + L' \rightarrow CpMn(CO)_2L' + L$

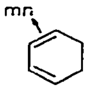
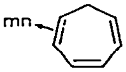
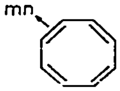
Finally, it might be productive to examine the possible generality of the observed stability of $CpMn(CO)_2L$ species along the isoelectronic series from $CpMo(CO)_2L^-$ to $CpFe(CO)_2L^+$. The latter are rather well-studied, and may indicate a trend toward diminished stability relative to Mn: $CpFe(CO)_2(CCHPh)^+$ is only marginally stable [23]. The anionic molybdenum (or chromium) complexes remain unexplored, but should be accessible by reduction (eqn. (1)) or by the more obvious photolytic route (eqn. (2)). Indeed, the photochemistry of metal carbonyl anions is a topic whose potential has yet to be tapped.

$$CpMo(CO)_2LCl + Na \rightarrow CpMo(CO)_2L^- \qquad (1)$$

$$CpMo(CO)_3^- + L \xrightarrow[h\nu]{} CpMo(CO)_2L^- + CO \qquad (2)$$

The substantial kinetic stability of the $CpMn(CO)_2L$ unit is most clearly demonstrated by surveying the many complexes of potentially bidentate ligands which in fact adopt monodentate modes when bound to **1**. These are listed in Table 2. With bidentate phosphines, ring closure is of course ultimately observed, but here, as well as with 1,3-cyclic dienes, ligand bridging is also observed, yielding **3** and **4** [25]. When the monodentate norbornadiene complex is heated to 100°C in the pure state, reaction (3) takes place; the η^2-1,3-cyclohexadiene complex reacts similarly [25]. Olefin loss, not CO dissociation, is the more facile thermal process. Thus, the

TABLE 2
$CpMn(CO)_2L$ complexes with "dangling" donor ligands

Compound	Ref.
$mn \leftarrow PPh_2(CH_2)_nPPh_2$	24
	25
	25
	26
	27
	27

3

4

= 1, 3 cyclohexadiene,
1, 5 cyclooctadiene,
norbornadiene

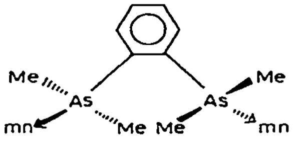
photochemical synthetic procedure often leads to metastable species which may be detected due to slow CO dissociation; subsequent ring closure is then slower than alternative reaction paths.

$$2\ CpMn(CO)_2C_7H_8 \xrightarrow[\Delta]{} [CpMn(CO)_2]_2C_7H_8 + C_7H_8 \qquad (3)$$

Addition of preformed $CpMn(CO)_2(THF)$ to a large excess of monomeric cyclopentadiene at room temperature, followed by chromatography on alumina, gives $CpMn(CO)_2C_5H_6$ and $[CpMn(CO)_2]_2C_5H_6$; the latter compound becomes the main product when less C_5H_6 is employed and the order of addition is reversed [26]. The bridged dimer has the metal atoms positioned *trans* on the C_5H_6 unit, which is itself planar [28]. The rhenium analog of the η^2-C_5H_6 complex is available by an alternative synthesis (eqn. (4)) [29]. The free double bond in $CpMn(CO)_2C_5H_6$ may be catalytically hydrogenated using Raney nickel [26], but has not been induced to assume a η^4-form ($CpMnCO(\eta^4$-$C_5H_6)$).

$$Cp_2ReH + CO \rightarrow CpRe(CO)_2C_5H_6 \qquad (4)$$

The bidentate ligand *o*-bis(dimethylarsino)benzene(diars) normally functions as a chelate to one metal. In spite of the constrained *ortho* stereochemistry of the ligand, $[CpMn(CO)_2]_2$(diars) has been prepared [25]. The crystal structure [30] of this complex shows two $CpMn(CO)_2$ units bridged by the arsine, but on opposite sides of the phenyl plane. The molecule has a crystallographic two-fold axis in the solid state (5).



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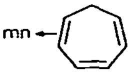
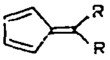
Coordination of cyclooctatetraene normally proceeds rapidly to at least tetrahapto binding. The only known dihapto cyclooctatetraene complex is $CpMn(CO)_2(\eta^2$-$C_8H_8)$, made from mn(THF) [27]. In the solid state, the olefinic ligand presents the convex face of a tub conformation to the metal, with only one double bond coordinated. The C = C axis is horizontal, and there is no ^1H NMR evidence for metal migration to other double bonds of the ring. Upon heating, the $CpMn(CO)_2$ unit resists CO loss, and $[CpMn(CO)_2]_2(C_8H_8)$, not $CpMn(CO)(\eta^4$-$C_8H_8)$, is formed. The reagent mn(THF) reacts with cycloheptatriene to produce the equally unusual dihapto complex **6** [27].



6

While substitution of more than one CO in $CpMn(CO)_3$ is unusual, exhaustive photolysis has been shown to yield CpMnL where L = benzene [25] or cycloheptatriene [31].

Fulvenes, 7, possess excessive π-electron density in comparison to the two



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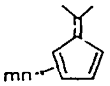
electrons required by $CpMn(CO)_2$. Direct method photolysis of $CpMn(CO)_3$ and a fulvene in THF produces both monomeric (**8**) and dimeric (**9**)



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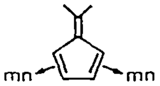
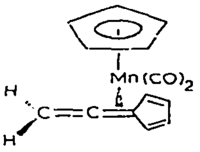


9

complexes, with coordination being to the ring carbons in each instance [32]. At −20°C, **1** binds the more complex fulvaleneallene at the first exocyclic double bond [33]. Although the product was drawn with the allene axis vertical, the weight of evidence on olefin binding to $CpMn(CO)_2$ makes conformation **10** preferable. The exocyclic protons are observed to be

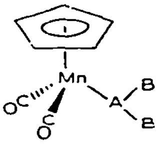


10

inequivalent. The ring protons appear as an AA′XX′ pattern, however, which requires the occurrence of facile rotation about the metal–ligand bond(s) in **10**.

D. STRUCTURE (CONFORMATION) AND BONDING

Compounds $CpMn(CO)_2L$ in which L is planar could adopt one of two high-symmetry conformations, either vertical (**11**) or horizontal (**12**). In each



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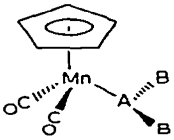


12

case, the descriptive title indicates the alignment of the ligand plane with respect to the metal-to-C_5H_5 ring line. The actual structures (Figs. 1–8 and structures **21–28**) are remarkably faithful to one or the other of these extremes, with no intermediate cases observed. The vertical conformation is adopted by **17–19** and **21–24**, while the remainder are horizontally aligned. This distinction is particularly significant in that the vertical alignment may

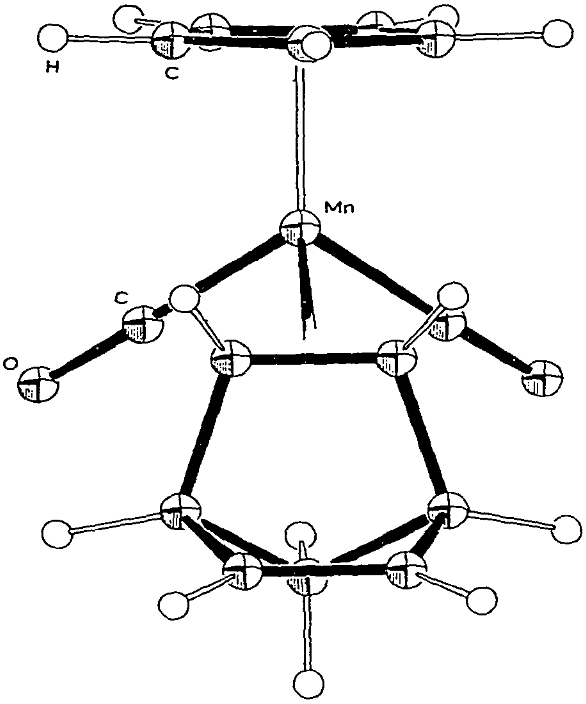


Fig. 1. $CpMn(CO)_2(C_7H_8)$ [34], **13**. One double bond of norbornadiene is not coordinated.

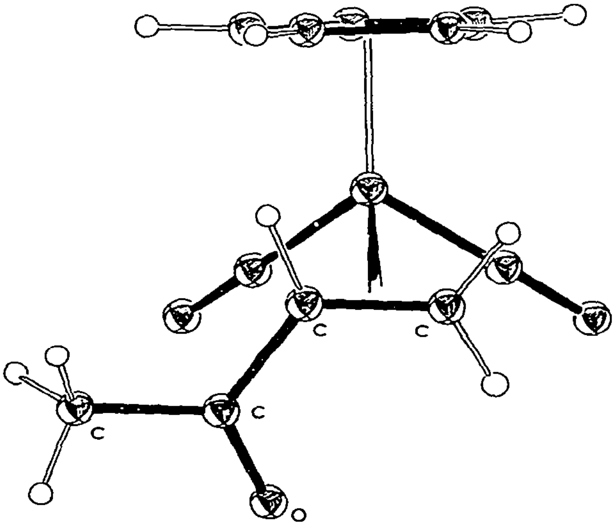


Fig. 2. $CpMn(CO)_2(H_3CC(O)CH{=}CH_2)$ [35], **14**. The oxygen of methyl vinyl ketone does not interact with the metal.

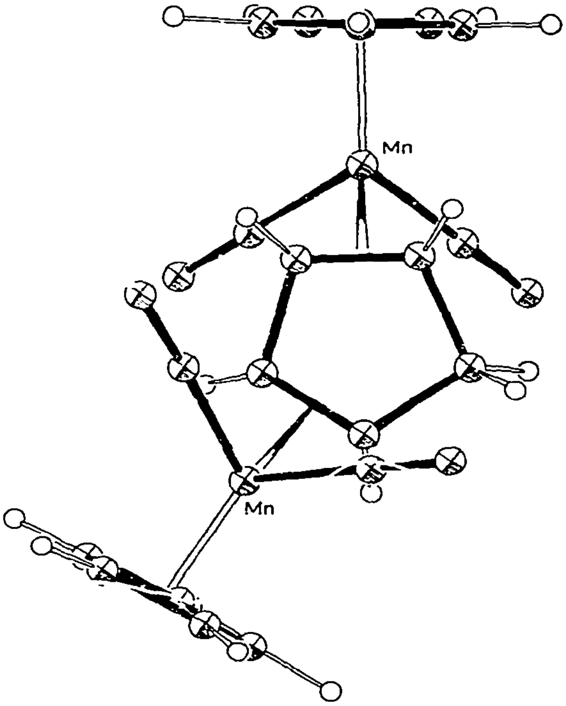


Fig. 3. $[CpMn(CO)_2]_2(C_5H_6)$ [36], **15**. The metal fragments coordinate to opposite sides of the cyclopentadiene ring.

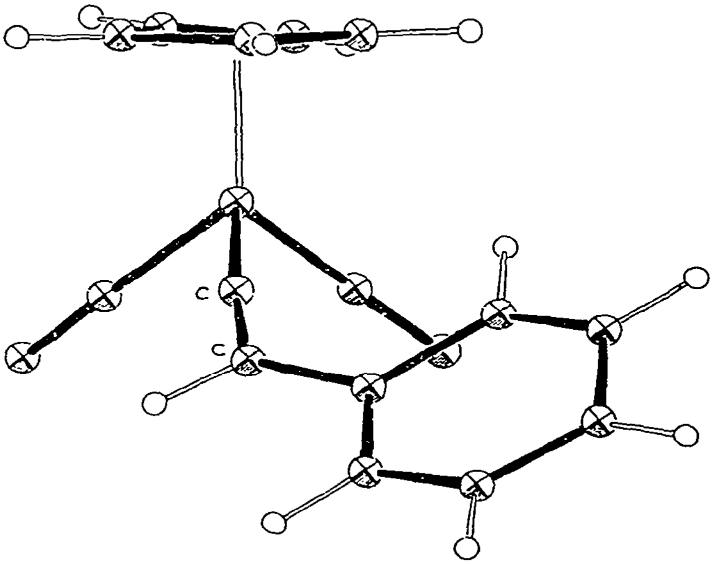


Fig. 4. $CpMn(CO)_2[C=CH(C_6H_5)]$ [37], **16**.

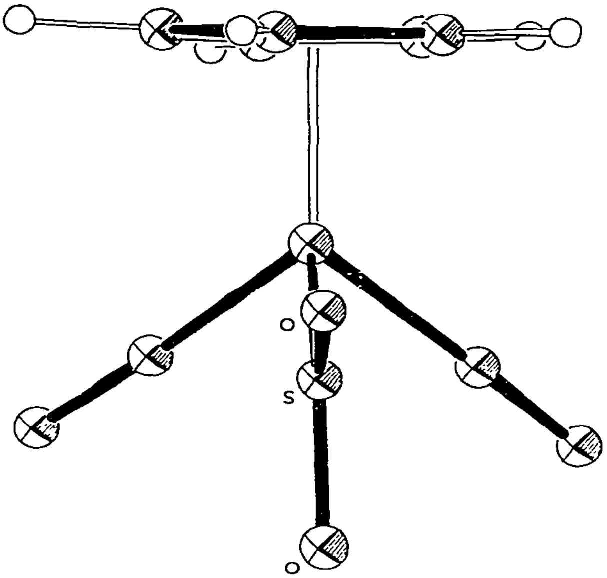


Fig. 5. $CpMn(CO)_2(\eta^1\text{-}SO_2)$ [38], **17**. Only the sulfur bonds to the metal.

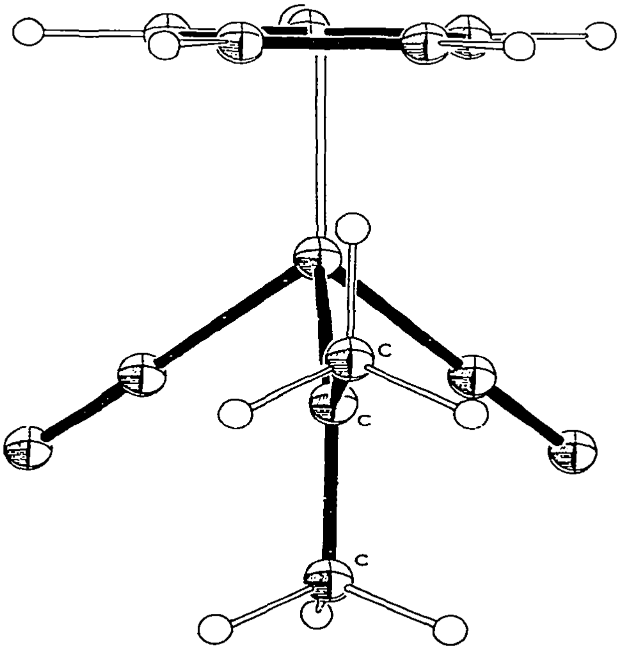


Fig. 6. $CpMn(CO)_2[C(CH_3)_2]$ [40], **18**.

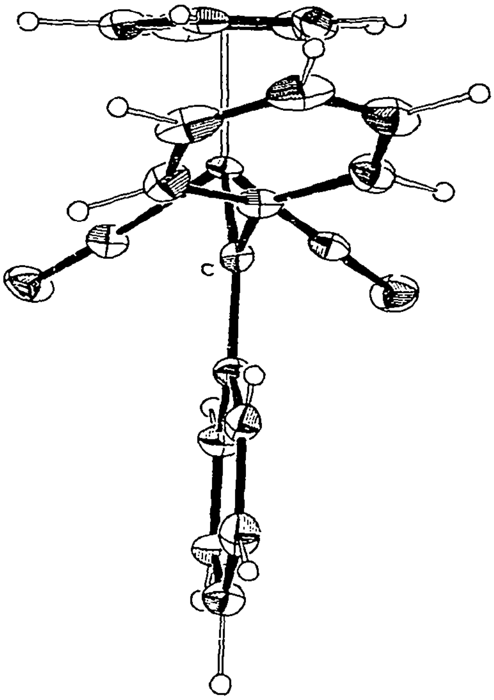


Fig. 7. $CpMn(CO)_2[C(C_6H_5)_2]$ [41], **19**.

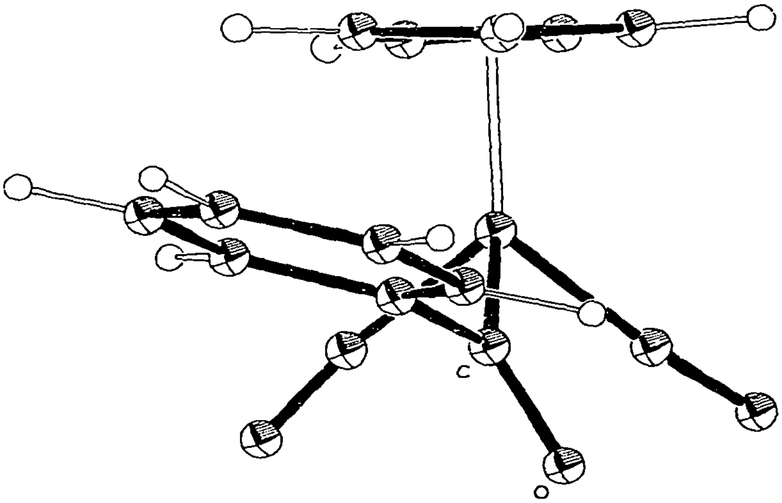
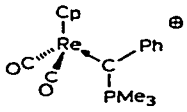
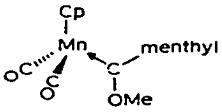


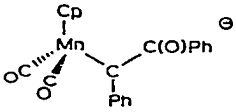
Fig. 8. $CpMn(CO)_2[\eta^1\text{-}C(O)C_6H_5]^{-1}$ [39], **20**.



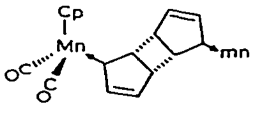
21 [42]



22 [43]



23 [44]



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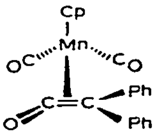
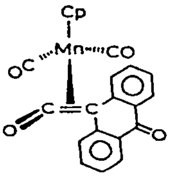
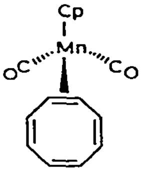


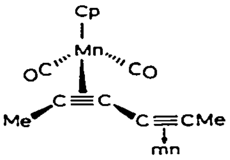
25 [46]



26 [47]

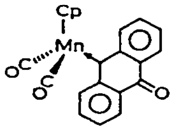


27 [27]



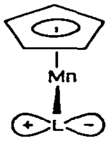
28 [48]

result in appreciable repulsion between the upper ligand group in **11** and the C_5H_5 ring. This is the origin of the phenyl group rotation in **19**, as well as the displacement of the benzoyl group away from vertical in **20**. The phenyl ring in **21** is twisted as it is in **19**. The apparent instability [47] of the carbene complex **29** may be due to repulsions of this type.



29

The superficially contradictory occurrence of both vertical and horizontal conformers for different L is in fact an expression of a single determining factor. Each observed conformation orients an empty ligand π orbital so as



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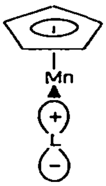


31

to make it antisymmetric with respect to the mirror plane of pyramidal $CpMn(CO)_2$ (i.e. **30** not **31**). These structures thus constitute an experimental determination of the antisymmetric character of the π-HOMO of the $CpMn(CO)_2$ fragment. For a theoretical discussion of this point, see ref. 10. With such abundant experimental support for this principle, one can predict the following conformations with some degree of confidence

$CpMn(CO)_2$ mirror plane contains ligand (**11**)	Ligand axis ⊥ to $CpMn(CO)_2$ mirror plane (**12**)
$[C(O)H]^{-1}$ (formyl)	η^2-OCR_2
η^1-CS_2 and CO_2 (carbon-bound)	η^2-CS_2 and CO_2
$[C(H)=CH_2]^{-1}$ (σ-vinyl)	η^2-allene
η_1-$C=C=CR_2$	$(\eta^3$-allyl$)^+$

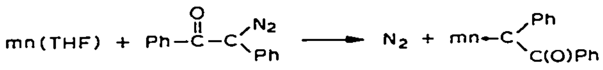
A number of these predicted structures will be compared to spectral data in the appropriate sections below.

E. REACTIONS WITH DIAZOALKANES [49]

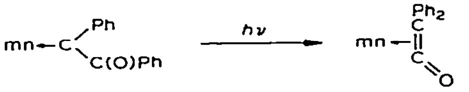
One consequence of the kinetic stability of the $CpMn(CO)_2$ fragment is the repression of ligand rearrangements which require the metal to accept more than two electrons. For example, in the free state α-keto carbenes [33] such as that derived from diazoalkane **32** undergo a rapid rearrangement (the Wolff rearrangement) to the corresponding ketene, **34**

$$\underset{\mathbf{32}}{R\text{-}C(N_2)C(O)R} \xrightarrow[-N_2]{} \underset{\mathbf{33}}{R\ddot{C}\text{-}C(O)\text{-}R} \rightarrow \underset{\mathbf{34}}{R_2C=C=O} \qquad (5)$$

However, reaction of **1** with **35** produces the phenyl benzoyl carbene complex **23** [50]. The crystal structure [44] of this complex shows a very short bond between manganese and the carbene carbon; the keto oxygen does not interact with the metal. Photolysis is required to effect rearrangement (in only 5% yield) to the isomeric diphenylketene complex (**25**). The most plausible explanation for the successful "interception" of the carbene in **23** is



1 35 23



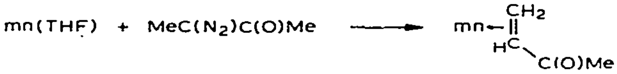
25

(6)

that a free carbene (**33**) is never present. Rather, it may be that the intact diazo compound binds to $CpMn(CO)_2$ and subsequently extrudes N_2. As a result, both the rate of nitrogen elimination from the free diazoketone and the rearrangement characteristics of the free carbene are irrelevant for the metal-mediated chemistry. In fact [51], in 45 min at 25°C, the diazoalkane **36** gives the simple adduct, accompanied by the hydrogenated dimer (hydrogen source not established) of the carbene: $[CH(CO_2Me)_2]_2$. Coordination

$$\mathrm{mn(THF)} + \underset{\mathbf{36}}{N_2C(CO_2Me)_2} \longrightarrow \mathrm{mn} \leftarrow N_2C(CO_2Me)_2$$

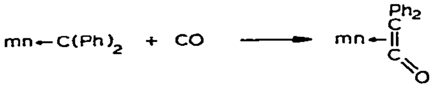
through the lone pair of the terminal nitrogen was suggested. On the other hand, free carbenes derived from diazoketones with hydrogen α to the carbene center generally undergo rearrangement to α,β-unsaturated ketones [52]: the Wolff rearrangement occurs only with higher activation energy or in the absence of such α-hydrogens. Using 3-diazo-2-butanone, (**37**), the product complex [50] indeed contains a conjugated eneone ligand (**14**, Fig. 2)



37 14

bound through the olefin. A 1,2-hydrogen migration has obviously taken place. On the basis of the available data, it is impossible to distinguish whether this is the product of the free carbene or a metal-promoted migration mechanism. If **14** arises in this reaction from a 1,2 hydrogen migration of a coordinated carbene, it stands in marked contrast to the stability of **23** (eqn. (6)).

In contrast to the above, diphenyldiazomethane behaves in expected fashion to produce $CpMn(CO)_2(CPh_2)$; see Fig. 7 [50]. At 100°C, this compound produces some tetraphenylethylene. It is unaffected by dihydrogen, presumably because the obligatory oxidative addition is precluded. Under forcing conditions (50°C, 650 bar CO), the complex "inserts" CO [33]; a carbon labeling study of this reaction should prove interesting. The diphenylketene ligand in **25** is horizontal, as predicted above. In an attempt



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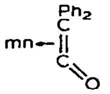
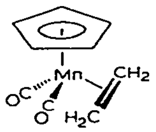
to probe whether carbene and ketene complexes are viable intermediates in the Fischer-Tropsch reaction, an attempt was made to hydrogenate **25**. Here again, forcing conditions (50°C, 750 bar H_2) result in the production of free oxocarbons (eqn. (7)) [53].



$$+\ H_2 \longrightarrow Ph_2HCC(O)H + Ph_2HCCH_2OH + \cdots \qquad (7)$$

25

In the face of the complex reactivity displayed by the functionalized diazoalkanes discussed above, an examination of the reaction of the parent diazomethane might have been expected to provide some clarification. This expectation is not borne out. Reaction of preformed mn(THF) with H_2CN_2, initially below −35°C in THF yields a mixture of **38** and **39**, which were



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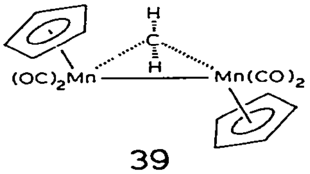


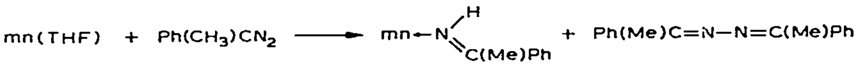
39

separated by chromatography [54]. The *trans* orientation of Cp rings in **39**, deduced from IR data, was confirmed crystallographically [55]. Since ethylene is not a decomposition product of H_2CN_2 in the absence of metals, the formation of the ethylene complex implies the operation of some form of metal-mediated dimerization reaction. It is tempting to speculate that the methylene bridged complex arises from condensation of $CpMn(CO)_2CH_2$ (never observed) with $CpMn(CO)_2THF$. Inverse addition (i.e. adding $CpMn(CO)_2THF$ to H_2CN_2 rather than the reverse, as was carried out in ref. 54) and maintenance of low temperature, might allow detection of a monomeric CH_2 complex. The dimer **39** is distinguished by having stereochemically rigid CO groups.

In a curious twist, some diazoalkane reactions result in disposal of the hydrocarbon moiety with retention of N_2 in the metal coordination sphere [56]

$$\mathrm{mn(THF)} + CF_3(H)CN_2 \rightarrow \underset{\mathbf{40}}{[CpMn(CO)_2]_2N_2} + F_2CCHF \qquad (8)$$

The observed 1,2 fluorine migration is not responsible for "misdirecting" this reaction, since diazoethane also gives **40** and ethylene [56]. A crystal structure proves N_2 in **40** to be a 4-electron donor via the lone pair on each nitrogen atom. Phenylmethyldiazomethane (**41**) does not follow this path, yielding instead the acetophenone imine complex **42** [57].

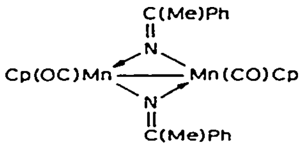


$$\mathrm{mn(THF)} + \underset{41}{Ph(CH_3)CN_2} \longrightarrow \underset{42}{\mathrm{mn}\leftarrow N\begin{matrix}\diagup H\\ \diagdown C(Me)Ph\end{matrix}} + \underset{43}{Ph(Me)C{=}N{-}N{=}C(Me)Ph} \qquad (9)$$

41 42 43

The unobserved carbene complex $CpMn(CO)_2CMePh$ has been made (ref.

57, eqn. (30)). Another isolated product, the azine **43**, is an established product of thermal decomposition of **41**. The source of the imine hydrogen was not established, but for the theme of this review, it is significant that hydrogen abstraction is preferred over decarbonylation of **1**, followed by dimerization forming the hypothetical species **44** [58]. A product similar to **42** results from reaction with 3-diazocamphor [50].

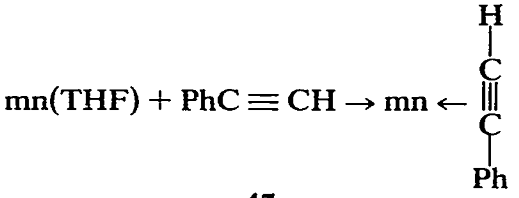


44

In view of the conformational arguments presented above, it is noteworthy that $[CpMn(CO)_2]_2[\mu_2:\eta^2\text{-}N_2]$ has a center of symmetry in the solid state. It follows that the π-donor orbitals on both $CpMn(CO)_2$ units are competing for the same π^* acceptor orbital on N_2. This suggests that back-bonding to N_2 is not significant in this complex.

F. REACTION WITH ALKYNES

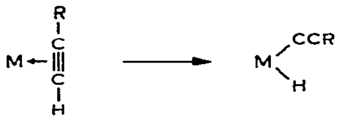
The early literature reports the instability of $CpMn(CO)_2(PhC_2H)$ from reaction (10) [59]. We have synthesized mn(HC$\equiv$CH) and found it to be similarly unstable [60].



$$\text{mn(THF)} + \text{PhC}\equiv\text{CH} \rightarrow \text{mn} \leftarrow \overset{\text{H}}{\underset{\text{Ph}}{\text{C}\equiv\text{C}}} \qquad (10)$$

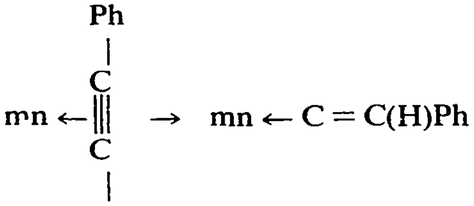
45

Terminal acetylenes generally display reactivity not found with internal alkynes, a distinction which may be associated with oxidative addition of the terminal C–H bond (eqn. (11)). In the case of mn(RC$\equiv$CH), it may be that



(11)

a particular instability results from coordination of a potential four-electron donor ligand to a metal which requires only two electrons. The electron pair in the uncoordinated orthogonal alkyne π orbital is metal–ligand antibonding, thus promoting any ligand rearrangement which moves this electron pair more remote from the metal. A careful re-examination [61] of reaction (10) confirms that a π-alkyne complex is the primary product. Chromatography on alumina isomerizes this to the monomeric phenylvinylidene complex **16** (Fig. 4) in which the vinylidene carbon is only 1.68 Å from manganese [62].



$$\text{mn}\leftarrow\begin{array}{c}\text{Ph}\\ | \\ \text{C}\\ ||| \\ \text{C}\\ | \\ \text{H}\end{array}\longrightarrow \text{mn}\leftarrow \text{C}=\text{C(H)Ph}$$

16

The CO stretching frequencies in this compound are very high, indicating the potent back bonding capacity of the vinylidene ligand. This unusual ligand markedly labilizes the metal center, since PPh_3 reacts with **16** to give $CpMn(PPh_3)CO(CCHPh)$ in 5 h at 25°C. It is also found that **16** reacts with mn(THF) to produce dimeric $[CpMn(CO)_2]_2(\mu_2\text{-}CCHPh)$ (cf. formation of $[CpMn(CO)_2]_2(\mu_2\text{-}CH_2)$, **39**). $CpRe(CO)_2(CCHPh)$ and mn(THF) react to give $Cp_2ReMn(CO)_4(CCHPh)$ in low yield, accompanied by both homonuclear vinylidene dimers [63]. Isomerization and "dimerization" of $CpMn(CO)_2(HC \equiv CH)$ also occurs on chromatography or in the presence of OH^- to give $[CpMn(CO)_2]_2(\mu_2 : \eta^1\text{-}CCH_2)$, **46** shown in Fig. 9 [60]. The corresponding rhenium chemistry has been reported [64]. While the mechanism of the acetylene-to-vinylidene rearrangement is unknown, the observed

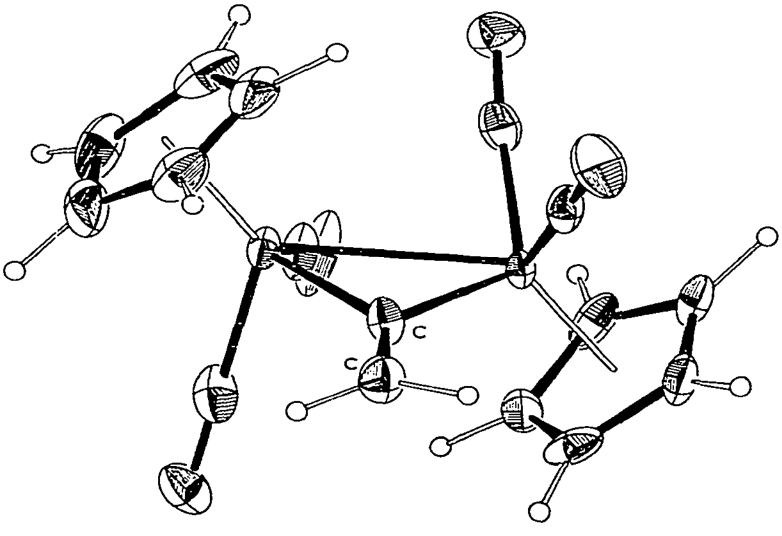
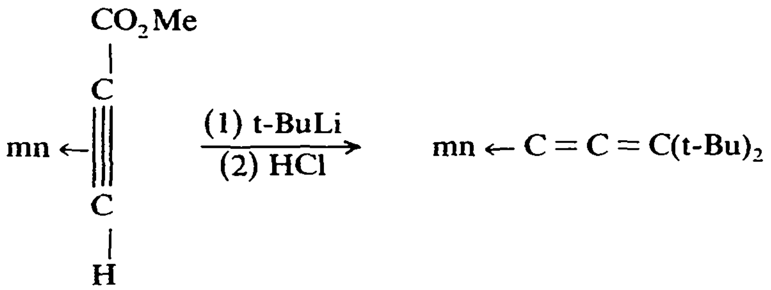


Fig. 9. $[CpMn(CO)_2]_2(C=CH_2)$, **46**.

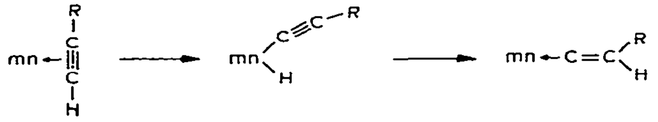
base catalysis would appear to eliminate oxidative addition (eqn. (11)). The vinylidene-bridged dimers are stereochemically rigid to 100°C, and are distinguished by containing ligands with uncoordinated carbon–carbon π-bonds.

Preformed $CpMn(CO)_2THF$ reacts with methyl propiolate ($-50 \rightarrow 25°C$) to yield the terminal acetylene complex **47** [65]. This compound was obtained in high yield (71%) after chromatography on silica gel. Reaction of **47** with 3 moles of t-BuLi gives, after protolysis, the allenylidene complex **48**.



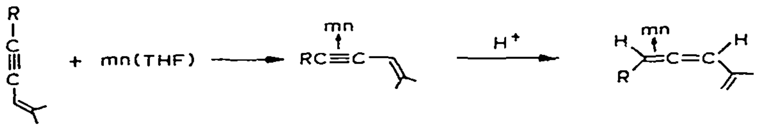
47 **48**

Presumably the three-carbon skeleton of the alkyne is retained in this reaction. In addition to the obvious alkylation of the carbomethoxy group, the reaction occurs with alteration of the bonding mode of the ligand towards Mn. As in the phenylacetylene work cited above, this rearrangement may be initiated by deprotonation of the alkyne hydrogen. The lack of a spontaneous (uncatalyzed) isomerization of this sort (eqn. (12)), is explicable in that this mechanism, as an intramolecular process, violates microscopic reversibility. Compound **48** is predicted to have a vertical orientation of the allenylidene ligand plane. The t-Bu groups appear equivalent by ^1H NMR down to $-90°C$, indicating a low rotational barrier.



(12)

Related acetylene-to-allene isomerizations have been effected, again by acid or base catalysis [66]. These include the formal [1,5] hydrogen shift in eqn. (13) and the [1,3] shift in eqn. (14) (E is an ester, aldehyde or ketone



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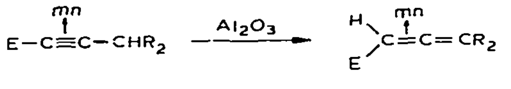
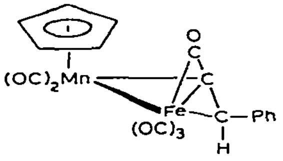


(14)

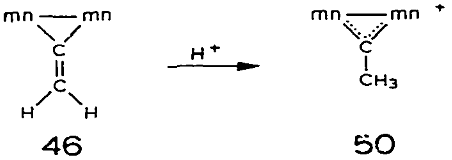


49

group). Both are high yield reactions which are claimed to represent attractive synthetic organic methodology.

The pendant π-electron density in CpMn(CO)$_2$(η^1-CCHPh) has been condensed with an Fe(CO)$_4$ unit from Fe$_2$(CO)$_9$ to produce **49** [67]. In this reaction, the α-carbon of the vinylidene group forms bonds to both iron and a carbonyl carbon.

The pendant electron density in [CpMn(CO)$_2$]$_2$(μ_2:η^1-CCH$_2$) protonates at the β-carbon to produce a cationic carbyne-bridged complex (**46**) [68].



(15)

Since all other carbyne complexes have been synthesized by abstraction of groups (H or OR) from the α-carbon, eqn. (15) represents a new synthetic route to carbynes. Cation **50** is sufficiently acidic to establish a proton

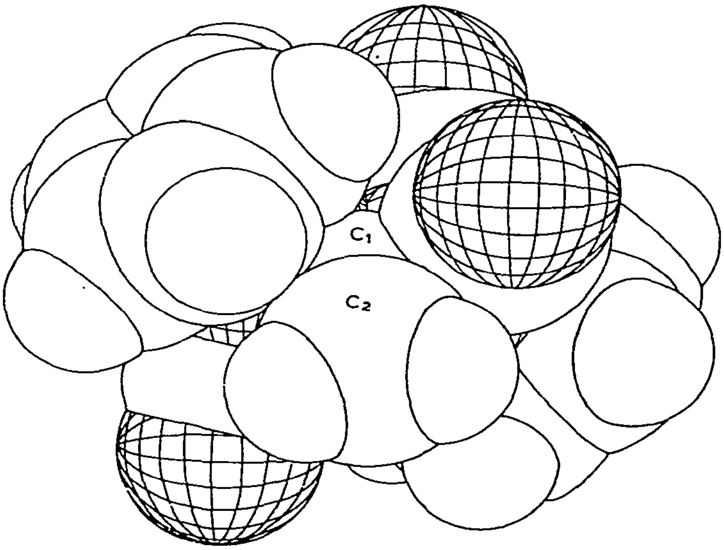


Fig. 10. Space-filling model of [CpMn(CO)$_2$]$_2$(C = CH$_2$), **46**, oriented as in Fig. 9. Hydrogen atoms have been positioned assuming C–H = 1.08 Å.

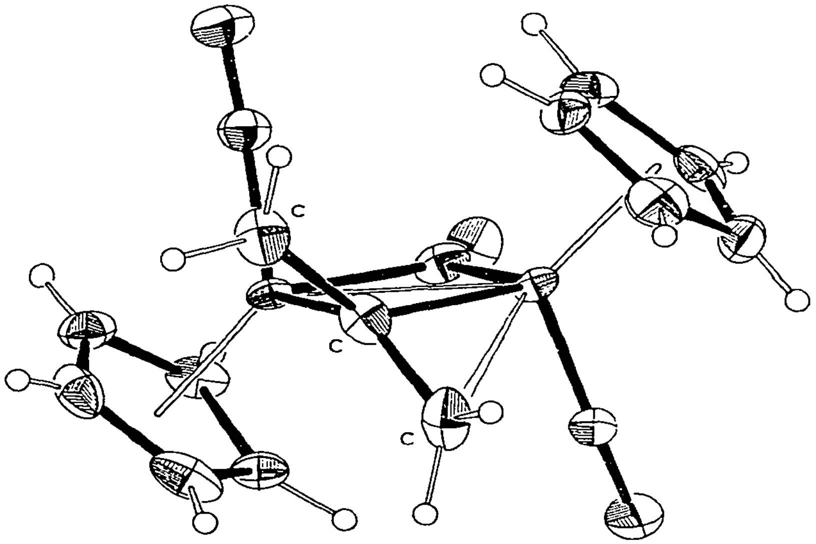


Fig. 11. $(CpMnCO)_2(\mu_2\text{-}CO)(\mu_2{:}\eta^3\text{-}C_3H_4)$, **51**.

transfer equilibrium to the β-carbon of $[CpMn(CO)_2]_2(\mu_2{:}\eta^1\text{-}CCHMe)$. Attempts to alkylate **46** with $(CH_3)_3O^+$ or $C(C_6H_5)_3^+$ fail, apparently due to the steric inaccessibility of C(2) to electrophiles larger than H^+. This is apparent from the space-filling model shown in Fig. 10 [69]. It is also clear from Fig. 10 that C(1), directly bound to both metals, is severely crowded. Since $[CpMn(CO)_2]_2CH_2$ is nearly isostructural with the vinylidene dimer **46**, substituted complexes of the sort $[CpMn(CO)_2]CR_2$ may be sterically prohibited; none is currently known.

The synthetic procedure in eqn. (15) also suggests a close relationship between acetylide, vinylidene and carbyne complexes

$$[M{-}C{\equiv}CR]^n \overset{\pm H^+}{\rightleftharpoons} [M{-}C{=}CHR]^{n+1} \overset{\pm H^+}{\rightleftharpoons} [M{\equiv}C{-}CH_2R]^{n+2}$$

Dimer **46** when treated sequentially with $LiEt_3BH$, then CH_3I or n-butyl iodide, yields $[CpMnCO]_2(\mu_2\text{-}CO)(\mu_2{:}\eta^3\text{-}C_3H_4)$, **51**, Fig. 11 [68]. This complex contains a carbonyl bridge, which is uncommon in manganese chemistry. More significantly the vinylidene ligand has been elaborated to a C_3 fragment, allene, with formation of a new C = C double bond. Since one carbonyl has been consumed, and the alkyl halide is clearly not the source of the new carbon, this transformation appears to represent a reduction of CO to the hydrocarbon oxidation level.

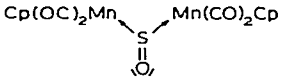
G.REACTIONS WITH POTENTIAL OXIDANTS

Heavily oxygenated Lewis bases or those in high formal oxidation states might react to oxidize Mn(I). The isolation of complexes of such oxidizing ligands with the ligand intact (a "pre-redox state") supports the theme of this review. One of the earliest examples of this is the rapid replacement of THF by SO_2 to give $CpMn(CO)_2SO_2$ [38].

The mild conditions for substitution on $CpMn(CO)_2THF$ allow monovalent manganese to survive an oxidant such as thionyl fluoride (eqn. (16)) [70]. The complex of $SO(NEt_2)_2$ is obtained analogously, and is notable for being hydrolyzed in air to $CpMn(CO)_2SO_2$; ligand reactivity follows by default in the presence of a stable metal center.

$$CpMn(CO)_2THF + SOF_2 \rightarrow CpMn(CO)_2SOF_2 \qquad (16)$$

Reaction of mn(THF) with S_8 does occur with rupture of S–S bonds, to give $[CpMn(CO)_2]_2(\mu_2\text{-}S)$ [70]. The oxidation product of this extremely air sensitive substance is $[CpMn(CO)_2]_2SO$. Although this material exhibits a band assigned as $\nu(S=O)$, it is not possible to distinguish between structures **52** and **53**.



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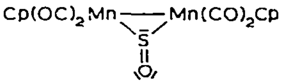
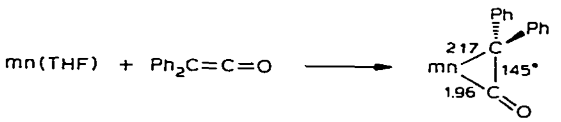


53

The typical reaction of a ketene with a metal carbonyl involves deoxygenation of the ketene [71]; it has not been established whether CO_2 or metal oxide is produced. On the other hand, reaction of mn(THF) with diphenylketene yields the adduct **25**, in which the C = C multiple bond



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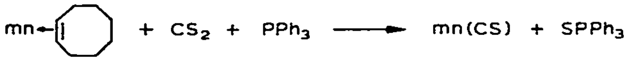
serves the donor function [72]. The compound is thermally stable to nearly 90°C. Rotation of the ketene about a line from Mn to the C = C midpoint is evident by the ^{13}C NMR equivalence of the metal-bound CO ligands; exchange with free ketene is slow on the NMR timescale, however.

H. MODIFICATION OF COORDINATED LIGANDS

The general kinetic inertness of the $CpMn(CO)_2$ unit permits modification and reconstruction of the appended ligand L with external reagents. A selection of examples follows.

(i) CS_2 and CSe_2

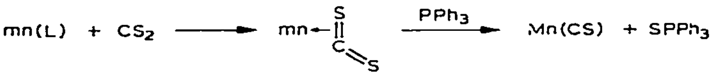
Work on the construction of CS and CSe ligands has been carried out on the $CpMn(CO)_2$ fragment (eqns. (17) and (18)) [73–75]. Early work employed cyclooctene as the leaving group (it also has a limited capacity to remove sulfur from coordinated CS_2), but THF has been employed more recently. Efficient heteroatom abstraction is possible with PPh_3, and successive applications of the C_8H_{14}/PPh_3 procedure have led to the synthesis of $CpMn(CS)_3$ [73]. The reaction proceeds through $CpMn(CO)_2(\eta^2\text{-}CS_2)$, **54**.



(17)

$$M(THF) + CSe_2 + PPh_3 \longrightarrow M(CSe) + SePPh_3 \qquad (18)$$

$$M = mn,\ re$$



54

(19)

A recent re-examination [76] of the CS_2 complex indicates that, in the absence of phosphine, it undergoes loss of CS_2, followed by condensation via the unbound sulfur of a second molecule of **54**. Dimeric **55** is said to show a (time-average) symmetry relating the two $CpMn(CO)_2$ units; the asymmetric CS_2 bridge is apparently not stereochemically rigid. Both the desulfurization (eqn. (19)) and coordination of unbound sulfur (eqn. (20)) are examples of ligand modification reactions.

55

(20)

A large fraction of the mechanistic data on the syntheses and reactivities of CS complexes has been established on the $CpMn(CO)_2$ unit. The formation of $CpMn(CO)_2CS$ by eqn. (21) proceeds by an S_N1 mechanism at a rate equal to that of substitution of cyclooctene by typical Lewis bases. Curiously (in view of the high π acidity of CS), $CpMn(CO)_2CS$ undergoes no exchange with $C^{18}O$ in 1 week at 40°C and apparently undergoes no thermal reaction with phosphorus bases [77]. Photochemical substitution with PR_3 converts $CpMn(CO)_2CS$ to $CpMnCO(CS)PR_3$ and $CpMnCS(PR_3)_2$. A kinetic study of olefin replacement in $CpMnCO(CS)(C_8H_{14})$ by PPh_3 again shows olefin loss to be the rate determining step [78].

$$mn(C_8H_{14}) + CS_2 + PPh_3 \rightarrow mn(CS) + C_8H_{14} + SPPh_3 \qquad (21)$$

(ii) SR_2 ligands

Treatment of $CpMn(CO)_2SR_2$ with the alkylating agent Me_3O^+ yields the S-alkylated product $CpMn(CO)_2(SR_2Me)^+$. These isolable complexes of the sulfonium cation ligand, $SR'R_2^+$, in some cases melt without decomposition. Neutral ligands "displace" the entire sulfonium ligand (although probably not in the simple manner portrayed in the original report) [79], while OCH_3^- and CN^- merely dealkylate it, regenerating $CpMn(CO)_2SR_2$.

(iii) Intra-ligand single bonds

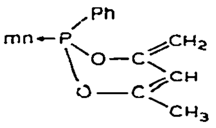
The complex $CpMn(CO)_2(PPhCl_2)$ represents a case where the primary reactive site lies on the (phosphorus) ligand. It has been prepared in two ways [80] (eqn. (22)). The complex is noteworthy in that the reactive P–Cl bond has not oxidatively added to manganese. Pseudohalogens effect the peripheral reaction shown in eqn. (23). The reaction with azide is particularly illustrative of the inertness of the $CpMn(CO)_2$ fragment (towards substitution or electron transfer), since many metal carbonyls react with N_3^- to produce coordinated NCO^- with liberation of N_2. Indeed, $CpMn(CO)_2$-$PPh(N_3)_2$ reacts with CO (1 bar) producing $CpMn(CO)_2PPh(NCO)_2$. Triphenylphosphine also reacts at the ligand azide group.

$$\begin{matrix} CpMn(CO)_2THF & & CpMn(CO)_2(PPhCl_2) & & HCl \\ & \rightarrow & \mathbf{56} & \leftarrow & + \\ +\ PPhCl_2 & & & & mn[PPh(NEt_2)_2] \end{matrix} \qquad (22)$$

$$CpMn(CO)_2PPhCl_2 + X^- \rightarrow CpMn(CO)_2PPhX_2 + 2Cl^- \qquad (23)$$

where $X = CN, NCO, SCN, N_3$

With acetylacetone in the presence of NEt_3, **56** reacts with esterification of both P–Cl bonds [81]. That portion of the ligand in **57** which is derived from acetylacetone is planar, although its carbon skeleton was found to be disordered in the X-ray study.



57

Secondary phosphines RP(H)X, where X is an electronegative group (NR_2, Cl) have no substantial lifetime, but undergo reductive elimination of HX to produce oligomers of the phosphinidene monomer, RP. Such secondary phosphines may be stabilized [82] if the lone pair is protected by coordination in a nonlabile complex (eqn. (24)). Compound **58** may be

$$\mathrm{mn(PPhH_2) + C_6H_{11}NCl_2 \rightarrow mn[PPh(H)Cl]} \qquad (24)$$

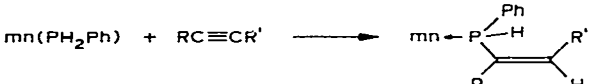
58

trapped by carrying out the reaction in the presence of cyclohexylamine, producing $\mathrm{mn[PPhH(NHC_6H_{11})]}$. Analogous results are obtained using a monochloroamine

$$\mathrm{mn(PPhH_2) + (n\text{-}C_4H_9)_2NCl \rightarrow mn[PPh(H)N(C_4H_9)_2]} \qquad (25)$$

59

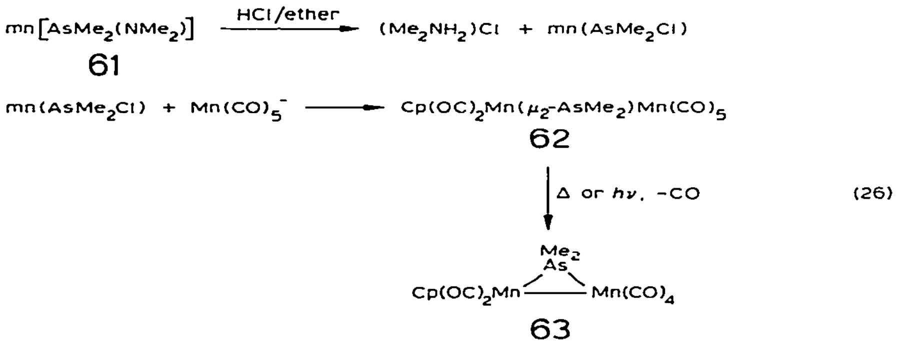
Stereospecific *trans* addition of one P–H bond in **60** [83] across alkynes



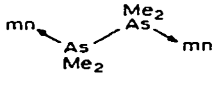
60

has been reported [84]. This reaction is exceptionally slow (10 days in refluxing THF) which may signal a radical mechanism inhibited by especially clean reaction conditions.

Deamination of **61** (available by the conventional procedure) produces the chloroarsine complex, which reacts with a host of metal carbonyl anions by displacement of Cl^- (e.g. eqn. (26)) [85]. Compound **62** contains no Mn–Mn bond. Decarbonylation of **62** produces the crowded, metal–metal bonded species **63** [86].

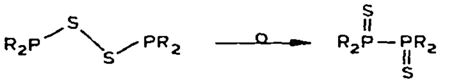


Reaction of $\mathrm{mn(AsMe_2H)}$ with molecular oxygen results in gross decomposition, but some of the following coupled product is spectroscopically detectable [87]:



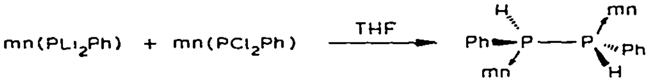
Reaction of mn(THF) with the secondary phosphine(V) sulfide $\mathrm{Me_2HP{=}S}$ effects rearrangement to a complex of the unstable P(III) sulfhydryl isomer:

mn[$PMe_2(SH)$] [88]. Deprotonation of this group, followed by coupling with mn(PMe_2Cl), yields mn($PMe_2-S-PMe_2$)mn. Autooxidation of the sulfhydryl group yields mn($PMe_2-S-S-PMe_2$)mn. The crystal structures of both dimers were reported [89]. This represents a case of ligand stabilization upon coordination, since the following intramolecular redox reaction is spontaneous:



Lithiation of the P–H bond of mn(PPh_2H) with butyl lithium gives a material (mn(PPh_2Li)?) which yields mn(PPh_2Me) on treatment with methyl iodide [90]. Using butyl lithium, mn($PPhH_2$) [83] may be monolithiated to mn(PPhHLi) (in pentane) or dilithiated in THF. The products are stable as solids, but rapidly decompose in solution. Excess butyl lithium reacts with mn(PH_3) to yield a product which may be subsequently alkylated to produce mn(PR_3). The lithio intermediate was proposed to be mn(PLi_3) [91].

Compound **64** provides a route (eqn. (27)) to a complex of 1,2-diphenylphosphane (**65**) [92]. Experimental details which might identify the hydrogen source are lacking. The resultant diphosphane complex is stable under N_2 to nearly 235°C, while [Ph(H)P]$_2$ itself disproportionates [93] to $PhPH_2$ and H(PPh)$_n$H at 25°C. A crystallographic study has identified the isomer obtained as being centrosymmetric (*meso*), with a Mn–P bond length of 2.216 Å.



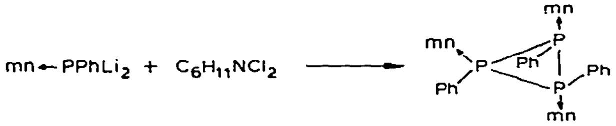
(27)

64

65

Reaction of $PhAsH_2$ with CpMn(CO)$_2$(THF) yields [94] the arsenic analog of **65** which is stable to nearly 140°C; the parent 1,2-diphenyldiarsane is unknown. Added base catalyzes the epimerization of the complex by deprotonation at arsenic. Acid catalysis of this same reaction has also been observed, and a mechanism initiated by protonation at manganese was suggested.

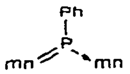
"Delithiation" of CpMn(CO)$_2$($PPhLi_2$) with $C_6H_{11}NCl_2$ effects coupling to [CpMn(CO)$_2$]$_3P_3Ph_3$, **66** [95]. This contains a stereochemically rigid



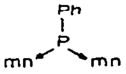
66

triangular P_3 ring which maintains one $CpMn(CO)_2$ unit distinct from the remaining two. The free cyclophosphane $(PPh)_3$ is a transient species, having been detected only in reaction mixtures; even at 0°C, it rearranges to larger rings [96].

When **66** is heated to 110°C under vacuum, it is transformed to $[CpMn(CO)_2]_2PPh$ [97]. The unusual aspect of this compound is the presence of trigonal planar phosphorus. The authors assert that the MnPMn system is a 3-center 4π-electron unit (**67**) based on the 2.18 Å manganese–

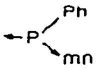


67



68

phosphorus distance (cf. 2.22 A in **66**). Since planarity is also consistent with a purely σ-bonded structure (**68**) and since the Mn–P shortening is small, alternative interpretation is possible. It is particularly significant that the Mn_2PC_x plane (C_x is the phenyl ring carbon bonded to P) bisects the $Mn(CO)_2$ angle; that is, the "ligand" $P(Ph)Mn(CO)_2Cp$ assumes a vertical conformation (**11**) with respect to the second $CpMn(CO)_2$ unit. The unit $P(Ph)Mn(CO)_2Cp$, **69**, is thus a hetero analog of a carbene ligand and the



69

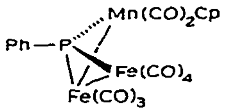
observed conformation may be attributed to strong back bonding from mn to the empty $p\pi$ orbital on phosphorus in **69**. Arsenic and antimony analogs of mn_2PPh are available by diverse routes (eqn. (28)) [98,99].

$$mn(THF) + AsCl_3 \rightarrow mn_2AsCl$$

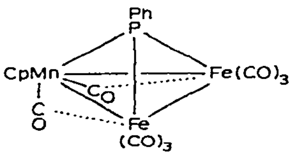
$$mn(SbI_2Ph) + K + [18]\text{-crown-6} \rightarrow mn_2SbPh \qquad (28)$$

One product of the dehalogenation of $CpMn(CO)_2(PPhCl_2)$ with $Fe_2(CO)_9$ is **70** [100]. This product, $CpMnFe_2(CO)_9(PPh)$, has been portrayed as being composed of a 3-center 4π-electron system $(CpMn(CO)_2(PPh)Fe(CO)_4)$ donating to an $Fe(CO)_3$ unit; the phosphorus atom is nearly coplanar (357°) with the other atoms of the proposed 4π-electron unit.

Compound **70** may be thermally decarbonylated [101]. The open cluster of **70** is closed in this decarbonylation by formation of an iron–manganese



70

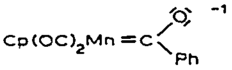


71

bond. The product, $CpMnFe_2(CO)_8(PPh)$, **71**, has approximate mirror symmetry. It exhibits two semibridging carbonyl groups ($Mn-C = 1.76$ Å; $Fe\cdots C = 2.3-2.4$ Å). The phosphorus is no longer trigonal planar. It is noteworthy that this is the first example of incorporation of a $CpMn(CO)_2$ unit into a metal cluster. The Mn–P bond length in **71** is 2.227 Å.

(iv) Formation of carbene and carbyne ligands

Organolithium reagents and alkoxides add to the carbonyl carbon of $CpMnNO(PPh_3)CO^+$ to produce acyl [102] and ester [103] complexes, respectively. The reactions proceed with retention of configuration at manganese [102], consistent with a ligand-centered reaction. The crystal structure of $[NMe_4][CpMn(CO)_2C(O)Ph]$, **20** (Fig. 8), derived from phenyl lithium and $CpMn(CO)_3$, has been discussed above. The particular vertical ligand conformation observed (oxygen away from the Cp ring) appears to be dictated by a crystal packing which layers all negative oxygen atoms of CO and C(O)Ph in the direction of a positive layer formed by NMe_4^+ cations. The fact that the ligand plane is vertical argues for the presence of back bonding as displayed in the "oxycarbene" resonance structure **72**.



$$\mathrm{Cp(OC)_2Mn{=}C{<}^{\ddot{O}^{-1}}_{Ph}}$$

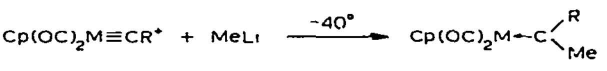
72

One of the earliest publications [104] from Fischer's laboratory dealing with carbene complexes included the preparation of $CpMn(CO)_2$-$[C(OCH_3)Ph]$ by alkylation of **72**. This oily material is distillable at 100°C. Alkoxycarbenes of manganese and rhenium lead to carbyne cations by the now standard α-abstraction procedure (eqn. (29)) [105,106].

$$CpM(CO)_2[C(OCH_3)R] + BCl_3 \rightarrow CpM(CO)_2(CR)^+ + \ldots \qquad (29)$$

$M = Mn, Re$

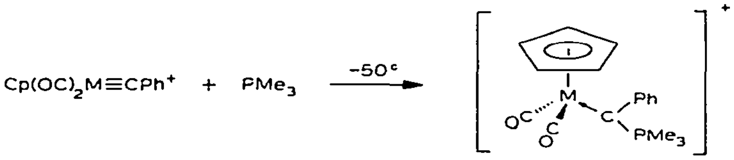
The carbyne carbon is the most electrophilic site in these cations, and a variety of nucleophiles (e.g. CN^-, SCN^- [107], OR^- [106], OCN^- [108]) add to produce new carbenoids. Reaction 30 provides a route to carbene



$$\mathrm{Cp(OC)_2M{\equiv}CR^{+} + MeLi \xrightarrow{-40^{\circ}} Cp(OC)_2M{\leftarrow}C{<}^{R}_{Me}} \qquad (30)$$

ligands free of hetero atoms [40]. Lithium cyclopentadienide reacts similarly [108]. The dimethylcarbene complex (Fig. 6) has the vertical orientation of the ligand plane, but shows NMR-equivalent methyl groups due to a low barrier to rotation about the $Mn \leftarrow C$ bond. It is remarkable that the lithium alkyls do not deprotonate $CpMn(CO)_2CCH_3^+$ to the known complex $CpMn(CO)_2(CCH_2)$.

The carbyne cations add PMe_3 to produce an ylide (or heteroatom-substituted carbene) complex, in which the ligand plane is vertically aligned (**21**) [109]. These are still electrophilic, reacting with MeLi to produce zwitterionic **73** [110] or with additional PMe_3 in an equilibrium step producing **74** [111]. Formal insertion of an aminoalkyne into the manganese carbene bond occurs slowly at 70°C (eqn. (31)) [112]. A mechanistic study of this unusual transformation would be interesting in view of the bifunctional nature of this particular substituted alkyne.



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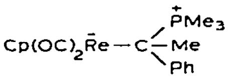
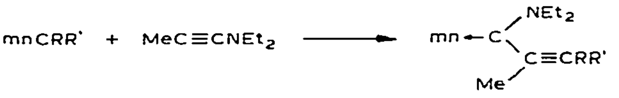


73

$Cp(OC)_2Re-CPh(PMe_3)_2^+$

74



(31)

(R, R') = (Me, OMe), (Ph, OMe) or (Ph, Ph)

(v) Nitrogenous ligands

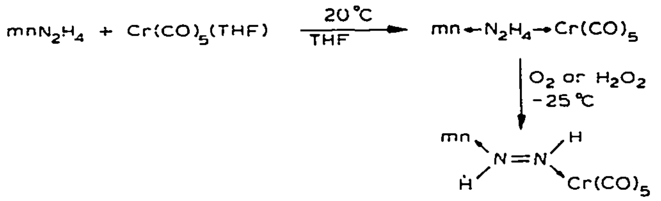
Sellmann, in an exceptionally rational synthetic sequence, has been able to capitalize on the generally inert (i.e. oxidative as well as substitutional) character of the $CpMn(CO)_2$ fragment in order to construct a complex of dinitrogen [113,114].

$$CpMn(CO)_2THF + N_2H_4 \rightarrow CpMn(CO)_2N_2H_4 \qquad (32)$$

$$CpMn(CO)_2N_2H_4 + 2H_2O_2/Cu^{2+} \xrightarrow{-40°C} \underset{\mathbf{75}}{CpMn(CO)_2N_2} + 4H_2O \qquad (33)$$

Complex **75** is air and thermally stable, as would be required if it is to survive the oxidative reaction conditions. During the course of eqn. (33) a transient blue color is observed. The species responsible for this color has been purified chromatographically and identified as *trans*-$[CpMn(CO)_2]_2(HNNH)$ [115]. This dimer decomposes at 50°C in benzene to give $CpMn(CO)_2N_2$ and $CpMn(CO)_2NH_3$; other products are not mentioned. Free diazene (HN_2H) decomposes by disproportionation to N_2 and N_2H_4.

Rational construction of an unsymmetrical complex containing a bridging diazene has been demonstrated [116]. The asymmetry leads to an AX proton



(34)

NMR pattern for the diazene protons, from which a 23.5 Hz H–H coupling constant was derived. These protons have a very low-field chemical shift (δ = ca. 15), and exchange rapidly with CH_3OD. The complex is stable to nearly 100°C (cf. free N_2H_2!) but undergoes base-induced decomposition to $Cp(OC)_2Mn{-}N_2H_4{-}Cr(CO)_5$ and (presumably) $Cp(OC)_2Mn{-}N_2{-}Cr(CO)_5$.

Some measure of the lability of THF in $CpMn(CO)_2THF$ is evident from the equilibration studies of eqn. (35) [117,118].

$$CpMn(CO)_2THF + N_2 \rightleftharpoons CpMn(CO)_2N_2 + THF \qquad (35)$$

At 100 bar, nitrogen substitutes for THF (in THF solvent) with a half life of 2.5 h. At lower imposed nitrogen pressure, the IR band of $CpMn(CO)_2N_2$ declines in intensity. Intensity changes are reversible with pressure at or below 0°C. In related work, Sellmann reported that pure $CpMn(CO)_2N_2$ dissolved in THF at 25°C is transformed into $CpMn(CO)_2THF$; evaporation of solvent from a THF solution of $CpMn(CO)_2THF$ in a flow of N_2 produces some $CpMn(CO)_2N_2$.

The analogous rhenium chemistry was reported recently [7]. Photolysis of $CpRe(CO)_3$ in THF yields $CpRe(CO)_2THF$, which is isolable as a solid and sublimable at 25°C. Accompanying this enhanced stability (relative to manganese) is a reduced propensity for substitution of THF; most reactions must be carried out at or above 0°C (eqns. (36) and (37)). The monodentate

$$CpRe(CO)_2THF + N_2 \xrightarrow[100\ \text{bar}]{\text{toluene}} CpRe(CO)_2N_2 + THF \qquad (36)$$

$$CpRe(CO)_2THF + N_2H_4 \xrightarrow[0^\circ C]{THF} CpRe(CO)_2N_2H_4 \qquad (37)$$

$$CpRe(CO)_2THF + NH_3 \rightarrow \text{no reaction} \qquad (38)$$

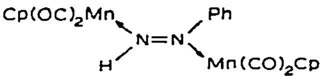
hydrazine complex is unstable in acetone at 20°C or on chromatography (silica at −20°C), yielding $CpRe(CO)_2N_2$, $CpRe(CO)_3NH_3$ and decomposition products. Equation (38) fails as a thermal reaction, but gives $CpRe(CO)_2NH_3$ under irradiation in hexane. Oxidation of ligated hydrazine has been effected, and precise attention to detail has allowed detection and

$$CpRe(CO)_2N_2H_4 + 2H_2O_2/Cu^{2+} \xrightarrow[-20°C]{THF} CpRe(CO)_2N_2 + 4H_2O$$

separation of $[CpRe(CO)_2]_2(HNNH)$, whose protons are exchangeable with CD_3OD at 0°C.

The complex $CpMn(CO)_2N_2$ is currently the premier model for study of the reactivity of coordinated dinitrogen. In the opinion of the author, the progress made with this complex is due to the resistance of the $CpMn(CO)_2$ unit to attack by redox and substitutional reagents; the N_2 unit becomes the primary reactive site by default, and nitrogenous products are detectable or isolable due to the substantial strength of the Mn–N link.

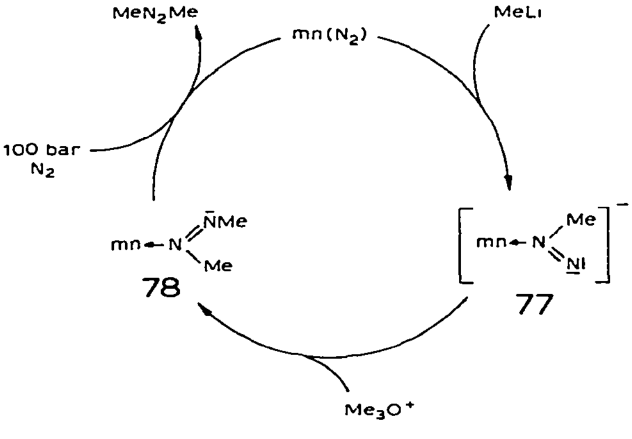
Organolithium compounds typically attack metal carbonyls at the carbonyl carbon, producing acyl complexes of reduced overall charge. However, phenyllithium reacts with $CpMn(CO)_2N_2$ at −30°C to produce $CpMn(CO)_2(N_2Ph)^-$. It is suggested [119] that both Mn and the phenyl group are bound to the same nitrogen atom. This anion may be protonated at the remaining nitrogen to yield an unstable monomeric complex of the very unstable ligand phenyldiazene, PhNNH. Chromatography (at −60°C!) separates this from the "carbene product" $CpMn(CO)_2[C(OH)Ph]$. The $^1\eta$-phenyldiazene complex may also be extracted from the reaction mixture by conversion to the more stable deep blue dimer **76** by reaction with



76

mn(THF) at −30°C. The two Cp rings of the dimer show resolvable ^1H NMR signals. Both mn(PhNNH) and **76** are also formed by Cu(II) oxidation of $mn(PhHNNH_2)$. Thermal decomposition (above −15°C) of the

Scheme II



monomeric phenyldiazene complex proceeds thus

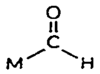
$$CpMn(CO)_2(PhN_2H) \rightarrow CpMn(CO)_2N_2 + C_6H_6$$

so completing a laborious route for conversion of PhLi to benzene. Dimeric **76** decomposes thermally to benzene and $[CpMn(CO)_2]_2N_2$.

Although NN scission fails in this case, derivatization of N_2 to an organonitrogen species (MeN_2Me) has been effected (see Scheme II) [120]. The structure suggested for **77** resembles that of the phenyl analog, and the methyl groups in **78** are distinguishable by ^{1}H NMR, which indicates to the authors that the azomethane ligand cannot be "side on" bonded. Below −30°C protic acids react with **77** to regenerate $CpMn(CO)_2N_2$ along with CH_4.

(vi) Hydrogen transfer to coordinated CO

The process of catalyzed conversion of synthesis gas ($CO + H_2$) to liquid fuels and petrochemicals could be envisioned as passing through metal-bound aldehyde and alcohol oxidation levels prior to hydrocarbon production. The reactivity of metal formyl complexes (**79**) is therefore of central importance



79

to any catalytic scheme which incorporates such an intermediate. There was, until recently, a notable absence of such complexes. The first example [121], available via

$$Fe(CO)_4^{2-} + HC(O)OC(O)CH_3 \rightarrow Fe(CHO)(CO)_4^- + O_2CCH_3^- \tag{39}$$

decomposes by disassembly of the formyl group

$$Fe(CHO)(CO)_4^- \rightarrow HFe(CO)_4^- + CO \tag{40}$$

via a mechanism which probably involves a preequilibrium dissociation of a terminal carbonyl ligand; the 16-electron species $Fe(CHO)(CO)_3^-$ is implicated. It might therefore be possible to study the inherent reactivity of the formyl M(CHO) group towards other reagents if the preequilibrium dissociation were inhibited as it is in the fragment $CpMn(CO)_2$.

$$\begin{array}{ll} L_nMCHO \rightleftharpoons & L_{n-1}MCHO + L \\ & \quad\downarrow \\ & L_{n-1}M(H)CO \end{array} \tag{41}$$

The major current synthetic path to the formyl ligand employs hydride transfer from a trialkylborohydride anion to a coordinated carbonyl [122,123]

$$MCO + R_3BH^- \rightarrow M(CHO)^- + R_3B \qquad (42)$$

By the nature of the reaction, it requires minimal back bonding to the carbonyl moiety, as found in cationic carbonyls. Current work centers around hydride transfer to $CpM(CO)_2NO^+$ (M = Mn and Re), since $(MeC_5H_4)Mn(CO)_3$ does not react with $LiEt_3BH$ in one week at 25°C [124]. In the former case, the presumed primary product CpMnCO(CHO)NO undergoes rapid secondary reactions. CpReCO(CHO)NO is isolable [125,126], however, (eqn. (43)) and is among the first neutral metal formyl complexes. Dilute solutions of **80** may be formed so as to limit its decom-

$$CpRe(CO)_2NO^+ + MR_3BH \rightarrow \underset{\mathbf{80}}{CpReCO(CHO)NO} + M^+ + R_3B \qquad (43)$$

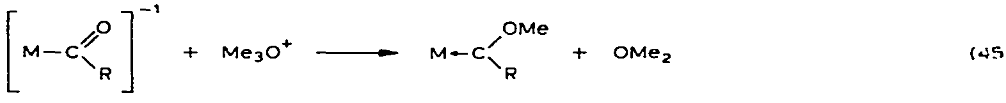
M,R = (K,i-PrO); (Li,Et)

position to a 10 h half-life, yielding the expected decarbonylation product CpReCO(H)NO [125]. The analogous, but more stable $CpReNO(PPh_3)CHO$ has been made similarly [125]. Both complexes show characteristic low field resonances for the formyl proton (δ 14–17) and the formyl (carbenoid?) carbon (δ 250–270).

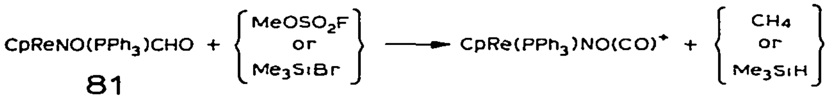
As in the case of nitrogenous ligands bound to $CpM(CO)_2$ (M = Mn and Re), it is possible to carry out reactions on a bound formyl ligand with no net loss of Cp and CO ligands. For example, reduction of formyl to methyl (eqn. (44)) has been effected [125,126]. This reaction does not occur with the

$$CpReCO(CHO)NO + BH_3{\cdot}THF \rightarrow CpReCO(CH_3)NO \qquad (44)$$

more relevant reductant, H_2 [126]. The crystal structure [127] of $CpReNO(PPh_3)CHO$, **81**, reveals a somewhat off-vertical alignment of the formyl plane, due in part to the nonequivalence of the NO and PPh_3 ligands [128]. The Re–CHO distance, 2.055(10) Å, is described as being short, suggesting significant carbene character. The $Re–CH_3$ bond length in $CpRe(CO)_2(CH_3)Br$ is 2.32 Å [129]. In contrast to the tendency of acyl and aroyl metal complexes to alkylate at oxygen (eqn. (45)), compound **81** reacts



(45)



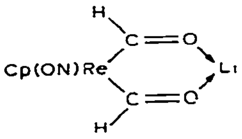
81

$$\underset{\mathbf{81}}{CpReNO(PPh_3)CHO} + \left\{\begin{matrix} MeOSO_2F \\ \text{or} \\ Me_3SiBr \end{matrix}\right\} \longrightarrow CpRe(PPh_3)NO(CO)^+ + \left\{\begin{matrix} CH_4 \\ \text{or} \\ Me_3SiH \end{matrix}\right\} \qquad (46)$$

with excess electrophile at 25°C (eqn. (46)) by hydride transfer. The mobility and reactivity of the formyl hydrogen is one of the major discoveries of this research area, and represents what is probably the major difference in the chemistry of the formyl group relative to its acyl and aroyl homologs. Complex **81** is reduced by BH_3/THF and also by Cp_2ZrHCl to yield $CpReNO(PPh_3)CH_3$. Thus, simple electrophiles (including strong acids) attack the formyl hydrogen, while hydridic electrophiles (B or Zr(IV)) succeed in hydrogen transfer. The formyl **80** reacts with $LiEt_3BH$ to add

$$\underset{\mathbf{80}}{\mathrm{CpReCO(CHO)NO}} + \mathrm{LiBEt_3H} \rightarrow \mathrm{Li[CpRe(CHO)_2NO]} + \mathrm{BEt_3}$$

additional hydride to the remaining carbonyl ligand rather than to the formyl group. The resulting bis formyl complex, the first of its kind, almost certainly exists as a diketonate chelate (**82**). It also exhibits low field formyl



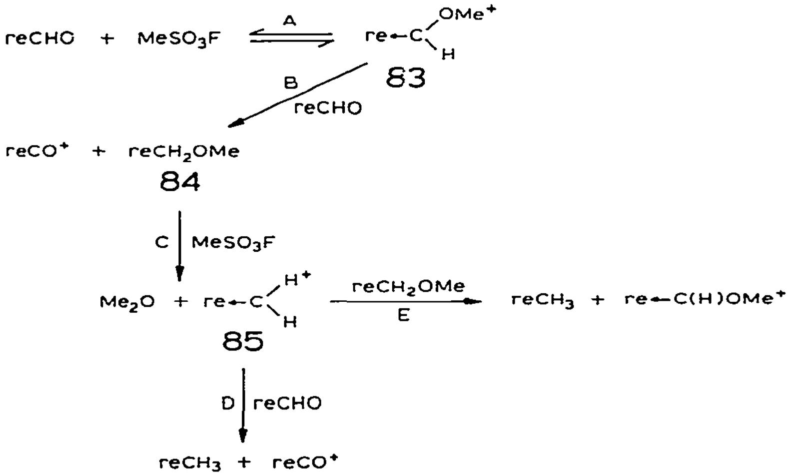
82

carbon and proton resonances [125,126], and reacts with acid to yield H_2 and **80** rather than the hoped-for protonated complex [125].

In the range 38–50°C, **81** decomposes by a first-order process to give 16% yield of $CpReCO(NO)CH_3$ as well as other uncharacterized products; some reductive hydrogen transfer is thus possible.

The rapid room temperature transfer of hydride to electrophiles (eqn. (46)) has been carefully reinvestigated at low temperature by NMR [130]. In this

Scheme III



way, it was possible to establish the reaction sequence of intermolecular hydride transfers shown in Scheme III (re = $CpReNO(PPh_3)^+$).

Compound **85** has been detected spectroscopically and **83** and **84** have been isolated. It has therefore been possible to directly verify the single-step reactions B, D and E. It is not possible to observe step C in isolation since reactions D and/or E are faster than C. Compound **85** exhibits inequivalent carbene proton resonances at −70°C, indicating restricted rotation about the $Re \leftarrow CH_2$ bond and a vertical alignment of the carbene plane. While reaction A was not directly observed, due to more rapid subsequent steps, it is eminently reasonable as an example of Fischer's original route to an alkoxy carbene complex. In summary, the products of electrophilic attack of $MeSO_3F$ on reCHO are $reCH_3$, $reCO^+$ and Me_2O. The metal complexes are not produced precisely in the simple 1:2 stoichiometry predicted by eqn.

$$3reCHO + 2MeSO_3F \rightarrow reCH_3 + 2reCO^+ + Me_2O + 2SO_3F^- \qquad (47)$$

(47) due to the variety of competing bimolecular reactions portrayed in Scheme III.

As indicated above, the key conclusion to be drawn from this study is the high reactivity and bimolecular transfer ability of the formyl hydrogen. The accessibility of cationic carbene complexes, $reCHX^+$, makes even the α-protons of the alkoxymethyl complex, $reCH_2OR$, function as a hydridic reductant. The observed reaction sequence has been termed "electrophile-induced disproportionation of a neutral formyl". In the opinion of this observer, it would be preferable to emphasize that any electrophilic carbon (e.g. carbene) is suitable to accept hydride from the donors reCHO and $reCH_2OMe$. In this rhenium system an attacking electrophile is required to produce the carbenes **83** and **85** (CF_3CO_2H and Me_3SiCl also are effective), but it is also consumed stoichiometrically as it abstracts oxygen (Me_2O and $(Me_3Si)_2O$ are detected); this requirement for oxygen abstraction is a feature shared by CO hydrogenation reactions effected by several transition metal systems [131–133].

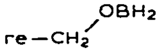
Well before the recent growth of interest in Fischer-Tropsch chemistry, it was reported that $NaBH_4$ in THF reduces $CpReNO(CO)_2^+$ to $CpReNO(CO)CH_3$ [134]. This obviously multistep reaction was carefully reexamined recently [135] and the following transformations were observed in dry THF solvent at 25°C

$$\underset{\textbf{80}}{CpRe(CO)_2NO^+} + BH_4^- \rightarrow CpReCO(NO)CH_3 \qquad (48)$$

$$CpRe(CO)NO(CHO) + BH_4^- \rightarrow CpReCO(NO)CH_3 \qquad (49)$$

$$\underset{\textbf{86}}{CpRe(CO)NO(CH_2OH)} + BH_4^- \xrightarrow{slow} CpReCO(NO)CH_3 \qquad (50)$$

Each reaction was carried out with a 1 : 1 stoichiometry. The first two reactions are notably faster than the third. Compound **86**, an attractive



$re{-}CH_2{-}OBH_2$

87

potential intermediate in the sequential reduction, was rejected as an intermediate in eqns. (48) and (49) on the basis of reaction (50) being slow. It was concluded that reaction (50) lacks an important third component, BH_3, which is produced in eqns. (48) and (49). Thus, in dry THF, a single hydride transfer in eqn. (48) produces reCHO and BH_3, and excess borane has already been shown to yield $reCH_3$ (eqn. (44)). The borate ester **87** is a plausible intermediate analogous to, but of higher reactivity than **86**. It is currently unknown whether BH_4^- adds to the CO ligand of **80** (cf. **81**) or elsewhere; nevertheless the liberated BH_3 apparently rapidly reduces this anion in eqn. (49). Finally, attack by the nucleophilic hydride on **86**, while slower than eqns. (48) and (49), does represent an example of ligand activation, since normal alcohols are not reduced to alkanes by $NaBH_4$. Note also (eqn. (48)) that one mole of BH_4^- can supply up to 3 hydrogen atoms and six reducing equivalents to $CpRe(CO)_2NO^+$ in aprotic medium.

When the above reactions are carried out in 1 : 1 THF : H_2O, remarkable differences are observed, each of which confirms the importance of BH_3 as a reagent in eqns. (48) and (49). Thus, at 0°C in only 15 min

$$CpRe(CO)_2NO^+ + BH_4^- \rightarrow CpReCO(NO)CHO \tag{51}$$

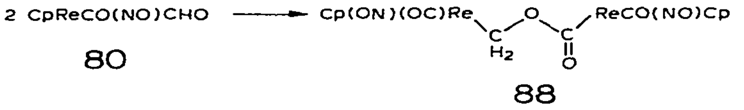
$$CpReCO(NO)CHO + BH_4^- \rightarrow CpReCO(NO)CH_2OH \tag{52}$$

Thus, in this aqueous medium BH_4^- delivers only one hydride (two reducing equivalents), apparently due to rapid hydrolysis of BH_3 by water. Equation (52) represents the first neutral hydroxymethyl complex (see also ref. 136).

The results of Sweet and Graham [135] are enlightening in a number of respects. On the one hand, in demonstrating the polyhydridic nature of BH_4^-, the reductant is shown to be bifunctional in character: the first two reducing equivalents are delivered (as H^-) from a nucleophilic reagent (BH_4^-), while the remaining ones are provided by BH_3, a reagent of opposite (electrophilic) polarity. On the other hand, it is exactly this bifunctional character which allows eqn. (48) to proceed beyond the formyl complex, since the work of Gladysz and co-workers [130] (see Scheme III) has shown that electrophilic activation of the formyl is required for further (bimolecular) reduction by CpReCO(NO)CHO and, presumably, by boron hydrides. The chemistry is clearly novel and complex.

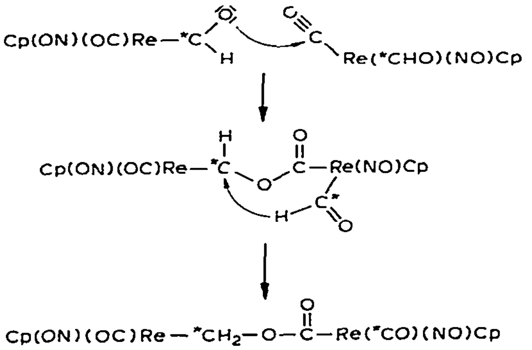
It is also noteworthy that the reaction of $NaBH_4$ with $CpMn(CO)_2NO^+$ in a two-phase benzene/water mixture gives a 60% yield of $[CpMn(CO)NO]_2$, while the reaction in a single phase (dry(?)THF) is complex to the point of being synthetically useless [137].

The decomposition of **80** at high concentrations (e.g. neat oil) does not occur by decarbonylation, but rather by a "Cannizzaro-like" bimolecular



(53)

disproportionation [136]. All spectroscopic data are consistent with the formation of **88** as an equimolar mixture of two diastereomers (both metal centers are chiral). For example, the ring proton chemical shifts of diastereomers differ by 0.002 ppm! The suggested mechanism (eqn. (54)),



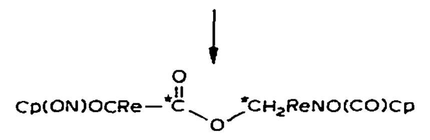
(54)

involving nucleophilic (oxygen) attack on the carbonyl ligand of a second formyl complex, has been justified by the previous observation (**82**) that the CO ligand of CpReCO(NO)CHO undergoes nucleophilic attack by $LiEt_3BH$. It would be desirable to demonstrate the role-change of the CO units required by this mechanism (see labels in eqn. (54)). It would also be desirable to rule out a hydride-transfer mechanism passing through **89** by combining authentic samples of $CpRe(CO)_2NO^+$ and **82**.

$[Cp(ON)OCRe{-}CO^+, (OHC)_2ReNOCp^-]$

89

Finally, there is another possible mechanism which does not implicate interchange of the roles of the two carbonyl units in **80**. Formyl hydride transfer to the carbon of a second formyl group, if nearly synchronous with O–C bond formation (eqn. (55)) must be evaluated. This overall process



(55)

amounts to addition of *C–H across the *C = O bond of a second mole of the formyl complex. Given the availability of $CpReCO(NO)CH_2OH$ [135,136], it may be possible to test this reaction sequence by combining $CpRe(CO)_2NO^+$ with $CpReCO(NO)CH_2O^-$. Mechanistic studies of this sort are significant to modeling of CO reduction processes since the proposed mechanism (eqn. (54)), if it is indeed operative, obviously is relevant only to polycarbonyl (or minimally formyl carbonyl) reagents; the existence of such highly ligated sites on a metal surface is not attractive. The last mechanism suggested (eqn. (55)), being a reaction of two formyl groups, does not suffer this limitation.

Metallo ester **88** offers an alternative route to the first example of a hydroxymethyl complex. Methanolysis of **88** produces $CpReNO(CO)CO_2Me$ and the desired $CpReCO(NO)CH_2OH$, **89**. A slower (4–5 days) subsequent reaction with methanol converts **89** to the corresponding methyl ether, $CpReCO(NO)CH_2OCH_3$. Acid hydrolysis of this ether, followed by workup under basic conditions allows isolation of the hydroxymethyl complex **89**. The OH proton in this complex exchanges with D_2O, and the complex undergoes an acid-catalyzed self condensation to **90**.

$$Cp(ON)OCRe{-}CH_2OCH_2ReCO(NO)Cp$$

90

This unusually facile alcohol-to-ether condensation is suggested to proceed via the cationic carbene complex **85**, a reaction known for alkoxymethyl complexes.

$$CpReCO(NO)CH_2OH + H^+ \rightleftarrows \underset{\mathbf{85}}{CpReCO(NO)CH_2^+} + H_2O$$

The same cationic complex $CpRe(CO)_2NO^+$ which provides an entry to a possible Fischer-Tropsch intermediate may be carried through one cycle of the water/gas shift reaction [126]. This shift reaction is used to enrich synthesis gas in hydrogen (or indeed to generate hydrogen whenever it is required), or to reduce CO_2. The electrophilic carbonyls in $CpRe(CO)_2NO^+$ add one equivalent of hydroxide to produce a bound carboxylate group. This reaction is reversible. Treatment of **91** with NEt_3 gives not simply

$$CpRe(CO)_2NO^+ \underset{CF_3CO_2H}{\overset{OH^-}{\rightleftharpoons}} \underset{\mathbf{91}}{CpReCO(CO_2H)NO}$$

$CpReCO(CO_2)NO^-$, but decarboxylation to $CpReCO(H)NO$ (after workup). The overall transformation is thus

$$CpRe(CO)_2NO^+ + OH^- \rightarrow CpReCO(H)NO + CO_2$$

due apparently to the weak binding of CO_2 to the fragment $CpRe(CO)NO^-$.

In summary, it has been possible to detect or isolate two unusual ligands, $-CO_2H$ and $-CH_2OH$, each of which has the potential to decompose by β-hydrogen elimination. This migration, which requires the creation of unsaturation in the fragment CpRe(NO)CO, does not occur precisely because of the stability of this fragment.

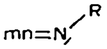
I. CONCLUSIONS

It is evident that the $CpMn(CO)_2$ moiety quite literally supports a broad range of unusual molecular fragments. Moreover, the stability of the Mn–Cp and Mn–CO bonds makes these compounds ideal subjects in which to study the reactivity of the unique ligand. This was recognized very early [138] in the production of coordinated hydrogen isocyanide (HNC) by protonation of $mn(CN)^-$.

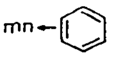
Some ligands, such as CO_2 and O_2, are significantly absent from the list of groups which have been incorporated into $CpMn(CO)_2L$. The two electron acceptor number of the $CpMn(CO)_2$ fragment is compatible with the more unusual fragments **92–96**. There is a notable scarcity of trivalent manganese

$mn{=}BX$

92



93



94

$mn \leftarrow ClCH_2Cl$

95

$mn \leftarrow OCH_2$

96

compounds of the form $CpMn(CO)_2XY$, where X and Y are 1-electron ligands such as H, alkyl, halide, vinyl, etc. Synthesis of $CpMn(CO)_2H_2$ or, better, $CpMn(CO)_2HX$ would immensely broaden the catalytic potential of this molecular class; $CpRe(CO)_2Br_2$ and $CpRe(CO)_2MeBr$ are known. In this regard, the "environmental effect" displayed by the IR data in Table 1 (compare argon and methane) may betray an incipient interaction of $CpMn(CO)_2$ with sp^3 C–H bonds. Moreover, the orbital analysis of pyramidal $CpMn(CO)_2$, which predicts a metal-based lone pair, might allow binding of Lewis acids (**97–99**).

$mn \rightarrow AlR_3$ $mn \rightarrow CR_3^+$ $mn \rightarrow BH_3$

97 **98** **99**

Finally, the incorporation of $CpMn(CO)_x$ fragments into cluster compounds remains almost untouched. Compounds ranging from doubly bonded $[CpMn(CO)_2]_2$ on through $[CpMn(CO)_2]_3$ and $Cp_4Mn_4(CO)_6$ are all potential electron-precise species which deserve attention.

ACKNOWLEDGEMENTS

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