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NUCLEOPHILIC ADDITION TO TRANSITION METAL COMPLEXES

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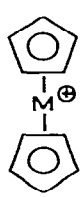
Summary

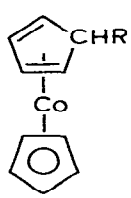
The author's studies of nucleophilic addition, chiefly to cationic complexes of the hydrocarbon metal and hydrocarbon metal carbonyl types are reviewed and related to other work in the area. Effects studied include stereospecificity, regioselectivity, competition with substitution, and rearrangements.

The ferrocenium (Ia) [1] and cobaltocenium ions (Ib) [1,2] were the first cationic transition metal complexes to become known. The former paramagnetic compound has not been found to undergo nucleophilic addition, but the latter was shown [3,4] to add organolithium compounds and Grignard reagents stereospecifically to give cyclopentadienylcyclopentadienecobalt complexes (II). Originally Wilkinson and his coworkers [3] proposed initial attack at the metal and believed they had spectral evidence to support the "*endo*" configura-



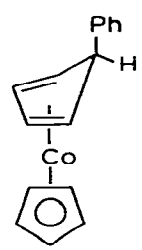
(I)

a) M = Fe
b) M = Co



(II)

a) R = Me
b) R = Ph



(III)

tion postulated to result from such attack. Churchill and Mason's demonstration [5] that the phenyl derivative (IIb) has the 5-*exo* structure (III) disproved these ideas and fitted a process involving direct attack from the less hindered side of the ring. The generality of this conclusion was accepted [6] and revised;

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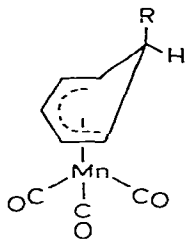
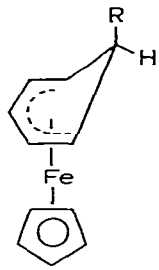
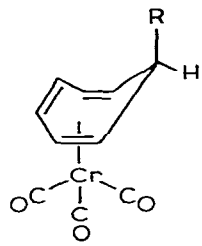
"*exo*-" structures were therefore written also for the cyclohexadienyl complexes IV and V obtained from the benzenetricarbonylmanganese and benzenecyclopentadienyliron cations [7].



(IV)

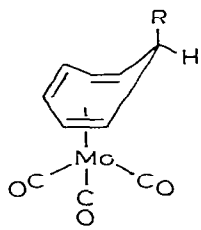


(V)



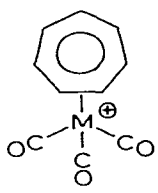
(VI)

a) R = H ; b) R = OMe, c) R = Ph



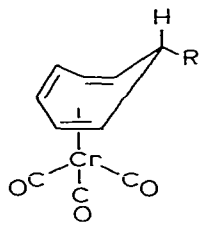
(VII)

a) R = H



(VIII)

a) M = Cr
b) M = Mo



(IX)

It has become accepted that this is the preferred direction for a wide range of kinetically controlled additions of nucleophiles to transition metal complexes, but we shall find that *endo* addition may become significant in certain cases and become the thermodynamically preferred mode where addition is reversible.

Following the preparation [8] of cycloheptatrienetricarbonyl-chromium (VIa) and -molybdenum (VIIa), our own involvement was stimulated by Dauben and Honnen's conversion [9] of the latter to the tropylium complex (VIIIb). Earlier interest in tropylium-related seven-membered ring compounds [10] induced us to seek a closer comparison of tropylium and later of tropone complexes with metal-free tropylium salts and tropones.

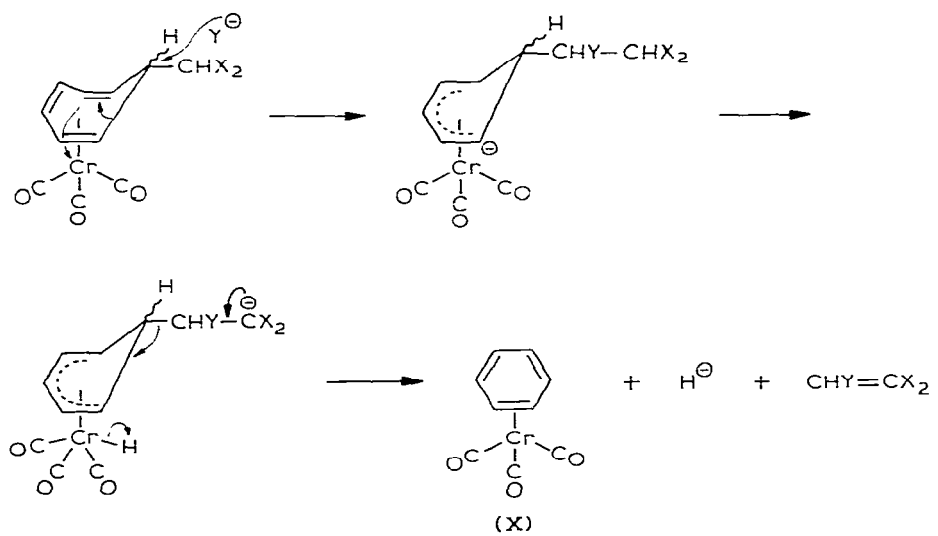
As the tropylium chromium complex (VIIIa) was found to be as accessible and similar in behaviour to the molybdenum analogue (VIIIb) most of our studies were carried out in the chromium series. Both complexes readily add hydride from sodium borohydride reverting to the parent complexes (VIa, VIIa). Other nucleophiles e.g. OMe^-, SH^-, $CH(CO_2Et)_2$ added smoothly to give pure single products, but, uncertain of the correctness of the earlier assignments [3,7] or their transferability to the cycloheptatrienechromium series, we deferred stereochemical designations [11]. These were subsequently made on the basis of Baikie and Mills' X-ray crystallographic study [12] of the phenyl derivative obtained using phenylmagnesium bromide. As in the cobalt case (III) this had added on the *exo*-face and spectral comparison with an extended series of complexes (VI) obtained using a variety of nucleophiles showed [13] that all

belonged to this *exo* series (VI). These comparisons were convincing because in many cases the corresponding *endo*-complexes (IX) could be prepared [14] and consistent differences were observed. The *endo*-isomers are the major and sometimes exclusive products when 7-substituted cycloheptatrienes are treated with chromium carbonyl derivatives [$Cr(CO)_6$, $Cr(CO)_3L_3$ where L = MeCN, NH_3, pyridine etc] — apparently preserving the preferred pseudo-equatorial substituent position during the reaction.

The 7-substituted cycloheptatrienes required for this are readily accessible by adding nucleophiles to the uncomplexed tropylium ion or by substituting methoxide in 7-methoxycycloheptatriene with other nucleophiles. The close similarity in behaviour of the chromium complexes and the metal free systems extends to this latter reaction. Thus 7-*exo*-methoxy complex VIb reacts very smoothly [13] with phenylmagnesium bromide to yield exclusively 7-*exo*-phenyl complex (VIc). The preservation of the *exo* configuration implies that an S_N1 type process is involved, so that in principle we are again adding to the cation VIIIa; the method derives a practical advantage from the solubility of the neutral complex VIb; the salts of the cation VIIIa normally have to be used in suspension and dissolve only as they react.

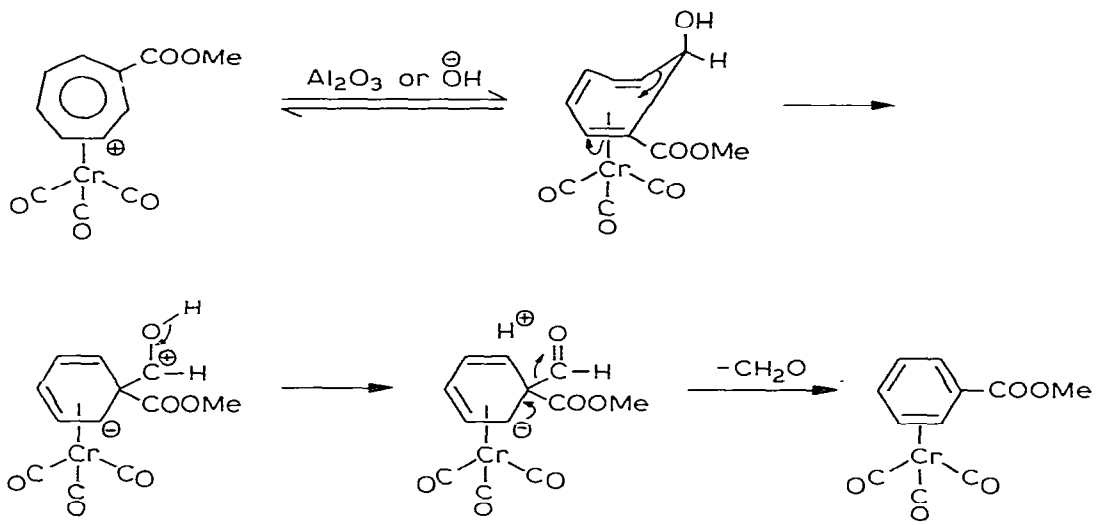
Certain (weakly nucleophilic) bases fail to add to the cation VIIIa but, especially in aqueous medium, cause its reductive coupling to a mixture of the mono- and bis-chromium tricarbonyl complexes of ditropyl [15]. The portion of chromium(0) split off is thought to be responsible for the reducing action. A more interesting side reaction was observed with both cyclopentadienide and diethyl malonate ions when these were used in excess [16]. The initial product is the expected complex (VI; R = C_5H_5 or $CH(COOR')_2$) but the presence of acidic hydrogens on the α-carbon allows these or the *endo* isomers (IX) to undergo a base-catalysed ring contraction yielding benzenetricarbonylchromium (X). A possible mechanism suggested [14] for this change is as shown (Scheme 1).

SCHEME 1



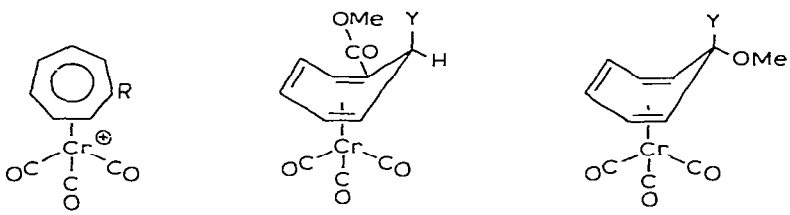
To explain the even more facile contraction [17] of carbomethoxytropyliumtricarbonylchromium Sneeden [18] has modified this mechanism as shown in Scheme 2. But although the isolation [19] of cyclohexadienyltricarbonylchro-

SCHEME 2



mium anions from nucleophilic addition to the benzene complex may lend some credence to this scheme it remains highly speculative and lacks explanation of the driving force for the first step.

In a later study [20] we briefly examined directive effects of substituents in tropyliumtricarbonylchromium salts on the addition of a nucleophile. The ester XIa added nucleophiles preferentially to the 2-position giving 1,7-disubstituted cycloheptatriene complexes (XII) as major products.



(XI a, R = COOMe, XI b, R = OMe) (XII) (XIII)

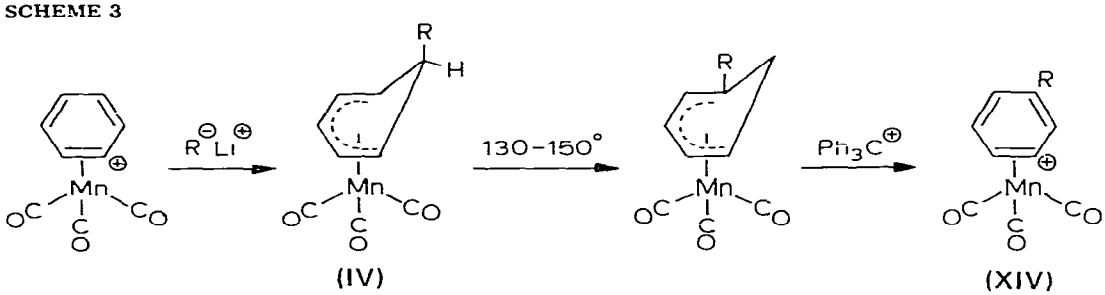
The methoxytropylium complex (XIb) on the other hand reacted chiefly in the substituted (1-) position giving the 7,7-disubstituted products [20]. With some nucleophiles this resulted in partial loss of the initial methoxy substituent, but it provided a high yield of the 7,7-dimethoxy complex (XII; Y = OMe) and allowed facile conversion of the salt (XIb) to troponetricarbonylchromium [21].

The substituted tropylium complexes (XI) above were available from the 7-*endo*-substituted complexes (IX) by hydride abstraction using salts of the tri-

phenylcarbenium cation. This is highly stereospecific for *exo*-hydrogen abstraction and fails to react with the *exo*-substituted complexes (VI; R ≠ H) unless the substituent itself is abstractable. Indeed the exclusive hydride abstraction [21] from the 7-*endo*methoxycycloheptatriene complex (IX; R = OMe) is further illustration of the high stereospecificity since uncomplexed methoxycycloheptatriene (like the *exo* complex VIb) reacts only by methoxide abstraction. Other reagents, notably *N*-bromosuccinimide [22] can abstract *endo*-hydride from certain other, e.g. cobalt [22] and iron [23] complexes, but destroy many others including these chromium compounds. However a two step method is available to convert the 7-*exo*-substituted compounds (VI) into the substituted tropylium complexes (XI). This depends on the ability of these complexes VI to rearrange by 1,5-*endo*-hydrogen migration [24] giving 3-substituted cycloheptatriene complexes from which the 7-*exo*-hydrogen can then be abstracted.

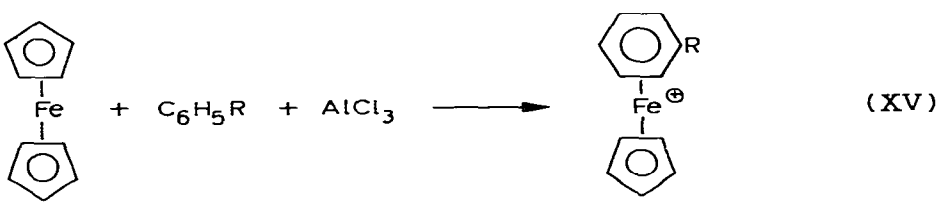
This method can be extended to the cyclopentadienecobalt complexes discussed above [25]. Thus the *exo*-phenyl complex (III) does not lose its 5-*endo*-hydrogen to any of a range of potential abstracting agents tried; but on heating it readily rearranges by migration of this hydrogen and the product (probably a mixture of 1- and 2-phenylcyclopentadienecyclopentadienylcobalt) readily affords phenylcobaltocenium salts on treatment with trityl salts or other oxidants [25]. To these seven and five-membered ring examples may be added the six-membered ring manganese complexes IV. Thus the *exo*-methyl compound (IV; R = Me) has been shown [26] to rearrange at 135°C to a mixture of 1- and 2-methyl-isomers and the *exo*-phenyl compound (IV; R = Ph) at 150°C gives largely the 1-phenyl isomer. Each of these products contains readily abstractable 6-*exo*-hydrogens and again the overall sequence (Scheme 3) represents substitution of the initial cation by the nucleophile R^-:

SCHEME 3



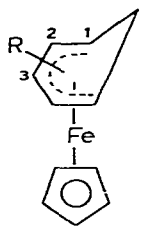
(IV) (XIV)

The availability of such processes invites consideration of repeated substitution and hence interest in the orientation of further nucleophilic attack. Our studies of this question in the tropyliumchromium series were mentioned above. For cationic arene complexes we first studied this feature [27—29] using the readily available arene-iron complexes XV. These can be made with a variety of substituents (R) by treating ferrocene with the appropriate arene, C_6H_5R in the presence of aluminium tri-chloride or -bromide:



(XV)

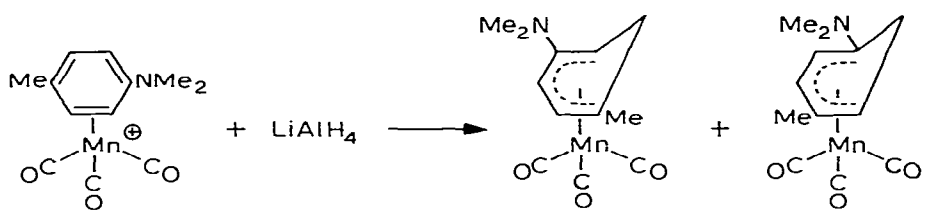
The effects of the substituents R on nucleophilic addition appear small when compared to the well-known directive effects of the same substituents in electrophilic substitution of the parent arenes. Typically R = CH_3 had no noticeable effect other than to hinder addition to the substituted position, the reaction of the toluene complex (XV; R = Me) with sodium borohydride giving [27] an apparently statistically determined (2 : 2 : 1) mixture of the 1-, 2- and 3-methylcyclohexadienyl complexes (XVI; R = Me).



(XVI)

The chlorobenzene complex (XV; R = Cl) with the same reagent gave a 4 : 1 ratio of 1- and 2-isomers with rather little attack at the *p*-position to give the 3-substituted compound [28]. The anisole complex (XV; R = OMe) gave a 1 : 5 : 3 ratio of the products of attack *o*-, *m*- and *p*- to the initial substituent [29]. The effect of a carbomethoxy group was studied by McGreer and Watts [30] who observed predominant *ortho* hydride attack and find the ratio of *o*- : *m*- : *p*-addition to be 89 : 7 : 4%.

The effects of chloro-, methoxy- and dimethylamino-substituents were also examined briefly [31] in the arenetricarbonylmanganese cations (XIV). The first two had effects similar to those noted with the iron complexes (XV). The dimethylamino group has much the strongest effects of the groups studied in these series as shown by the lithium aluminium hydride addition [31] to the *N*,*N*-dimethyl-*p*-toluidine complex:

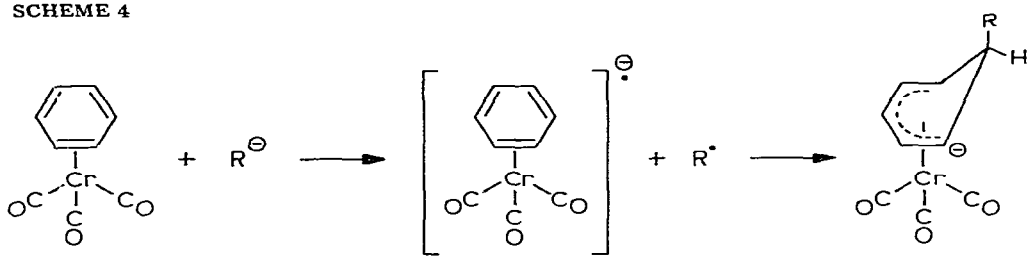


97 : 3

For other nucleophiles, e.g. methyllithium, the directive effects were similar [23,31]. The relatively weak effects noted in these additions can be rationalised on the assumption that the metal interferes with transmission of electronic effects: thus it reduces the importance of resonance relative to inductive influence compared with effects operating in electrophilic aromatic substitution. However Semmelhack and his coworkers [32] have observed much more dramatic effects in the addition of carbanions to the neutral arenetricarbonylchromiums suggesting that entirely different explanations may have to be sought. One interpretation being considered is a mechanism involving charge

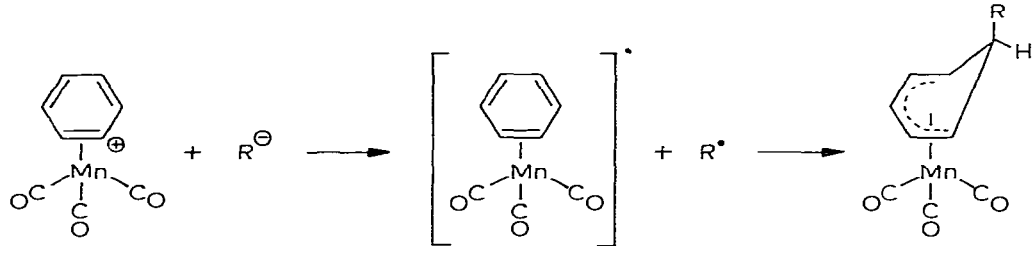
transfer as a first step rather than direct addition (Scheme 4):

SCHEME 4



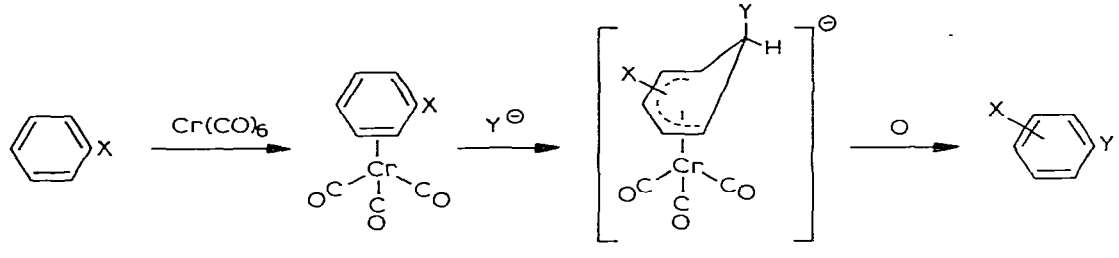
If correct the orientation is then governed by the free electron density distribution in the intermediate radical anion. This explanation appears attractive, but even if correct in this case, it does not follow that it applies to additions to cations, e.g. in the form outlined in Scheme 5:

SCHEME 5

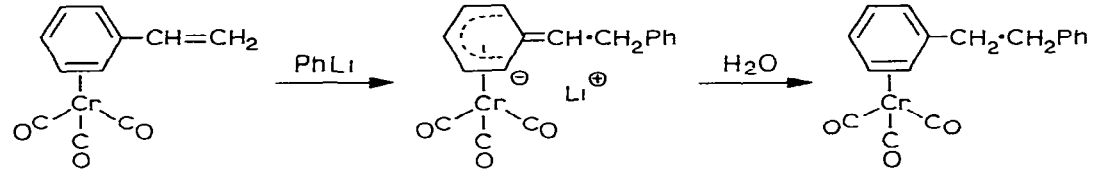


From a practical synthetic point of view the elucidation of the unusual directive effects in the chromium compounds and the orientations available to a wide range of substituents through the overall nucleophilic substitution process [32] represented by Scheme 6 promises to be most valuable:

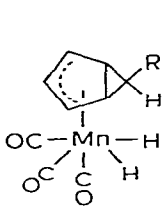
SCHEME 6



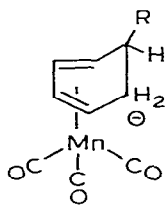
It has also been shown that the tendency to add nucleophiles can to some degree be transferred into the side-chain permitting e.g. the reaction [33]:



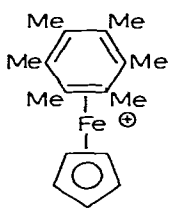
It should also be noted that in contrast to the numerous and varied additions to cationic complexes, other neutral complexes have not been found to parallel the arenetricarbonylchromiums in their ability to add carbanions. The nearest comparison is to the addition of lithium aluminium hydride to the cyclohexadienyltricarbonylmanganese complexes IV which, after hydrolysis, yield [34] dihydridomanganese complexes tentatively formulated as XVII. But this structure remains speculative and the initial hydride adduct, conceivably XVIII, from which such a product arises has neither been isolated nor yet been observed spectroscopically.



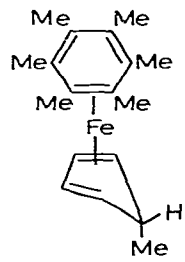
(XVII)



(XVIII)



(XIX)



(XX)

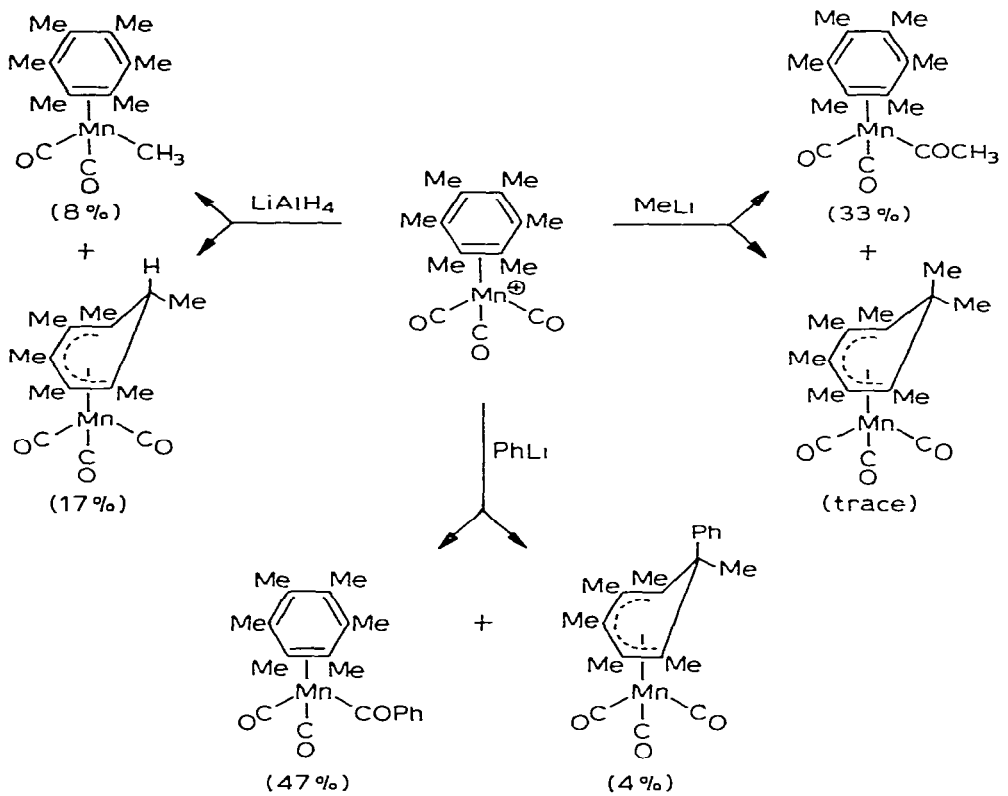
Whatever the precise mechanism of nucleophilic additions, steric effects are probably responsible for the low probability of attack at substituted positions ("ipso" attack). In the case of the areneiron complexes (XV) some addition to such positions occurred when the benzene ring was at least tetramethyl substituted. Moreover the behaviour of the hexamethylbenzene complex (XIX) revealed an interesting effect of the size of the attacking nucleophile: Whereas hydride ($NaBH_4$) yields [27] the 1,2,3,4,5,6-*endo*-hexamethylcyclohexadienyl compound of type XVI, addition of methyllithium is diverted to the cyclopentadienyl ring and yields [23] the 5-*exo*-methylcyclopentadiene complex XX.

Extensive diversion of nucleophilic attack away from the polymethylated arene rings was again noted in the manganese series [35], in this case with both lithium aluminium hydride and with methyllithium. Carbonyl ligands as the new site of attack were now reduced to methyl by the former and converted to acetyl by the latter reagent (Scheme 7).

The amounts of these products of addition to the carbonyl group relative to those of "normal" ring addition again reveal the steric effect of the adding nucleophile.

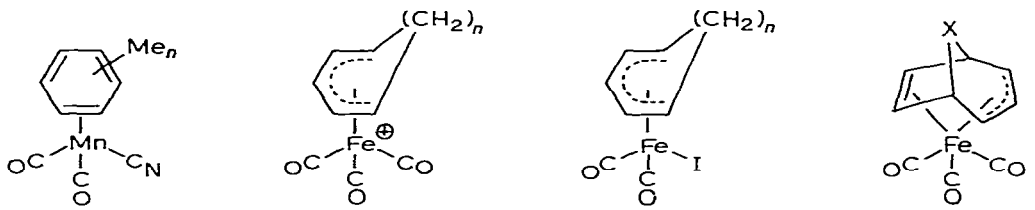
Addition to carbonyl had previously been noted with certain nucleophiles which do not give stable ring adducts in the arenetricarbonylmanganese series [36,37], particularly alkoxide ions and amines. A third mode of attack occurs [37] with cyanide which adds rapidly but reversibly to the ring at 0° C, but yields the cyanomanganese complexes (XXI) by the irreversible substitution of a carbonyl group at 20° C. Such carbonyl substitution has most commonly been observed with halide ions as attacking nucleophiles. Thus the cyclopenta-, -hexa-, -hepta- and -octadienyltricarbonyliron cations (XXII) and unconjugated analogues (XXIV) all react [38—42] with iodide yielding the iododicarbonyl complexes (XXIII; n = 0—3, and XXV). In related complexes e.g. the cyclopentadienyliron cations XXVI where L is a more labile ligand than CO, a wide

SCHEME 7



range of pseudohalogens and other nucleophiles cause similar displacement of such a ligand e.g. acetone [43] (XXVI; L = $Me_2(CO)$).

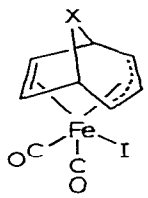
When only more strongly held ligands (XXVI; L = CO or PPh_3) are present the behaviour of the complexes further illustrates the importance of the nu-



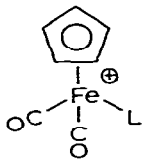
(XXI) (XXII) (XXIII) (XXIV)

cleophile in determining the site of attack: The triphenylphosphine-substituted cation (XXVI; L = PPh_3) reacts rather smoothly with sodium borohydride to yield [44] the diene complex (XXVII; R = H; L = PPh_3) and the tricarbonyl complex (XXVI; L = CO) reacts similarly with $NaBH_3CN$ under mild conditions [38]. The apparent formation of the hydride XXVIII in the earlier work [44] using $NaBH_4$ must be ascribed to the ready conversion of the initially formed cyclopentadienetricarbonyliron (XXVII; R = H, L = CO) to this hydride [35]. Indeed, the ease of this reaction would make it difficult to establish whether a

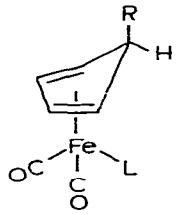
small amount of direct attack at the metal competes with the hydride addition to the ring.



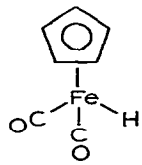
(XXV)



(XXVI)



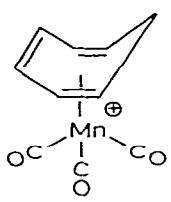
(XXVII)



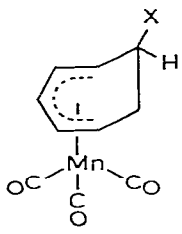
(XXVIII)

On the other hand, when pentafluorophenyllithium is the nucleophile, the phosphine complex (XXVI; L = PPh_3) again reacts by ring addition giving [45] the *exo*-adduct (XXVII; R = C_6F_5; L = PPh_3) (56%) whereas the tricarbonyl (XXVI; L = CO) is apparently attacked both at the metal and at a carbonyl group yielding $C_5H_5Fe(CO)_2C_6F_5$ (13%) and $C_5H_5Fe(CO)_2COC_6F_5$ (18%) as the only isolated products [45].

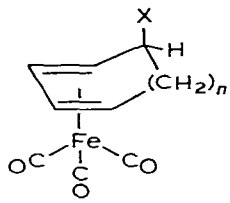
Reverting to ring additions we must note that stable anions e.g. alkoxides, add readily to the non-aromatic cations, but tend not to give stable adducts with complexes having aromatic rings as ligands. Thus as noted above, alkoxides add to a carbonyl group of the arenemanganese cations (XIV) and cyanide only adds reversibly to their aromatic rings; in contrast, the analogous non-aromatic cycloheptatrienetricarbonylmanganese cations (XXIX) give stable ring adducts (XXX a, b) with these nucleophiles [46].



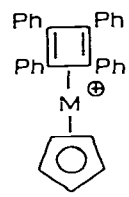
(XXIX)



(XXX)
(a) X = OR
(b) X = CN



(XXXI)

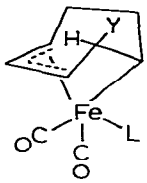


(XXXII)

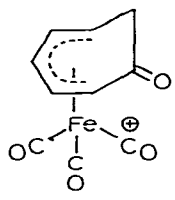
Similarly addition of these anions X to the cyclodienyliron complexes XXII yields the appropriately substituted diene complexes (XXXI) except in the case of the aromatic cyclopentadienyl complex (XXII; n = 0). The arenecyclopentadienyliron cations XV also fail to add such stable anions. In this sense therefore the tropylium rings in the chromium complexes VIIIa and XI and the cyclobutadiene rings [47] in e.g. XXXII (M = Ni or Pd) which do undergo such additions may be described as "less aromatic" than the metal complexed cyclopentadienyl and benzene rings.

While cyclohexadienyl cations of the type XXII (n = 1) apparently always add nucleophiles to one end of the unsaturated system this is not true with larger ring systems. Thus although substituted diene complexes (XXXI; n = 2) seem to be formed cleanly from the cycloheptadienyltricarbonyliron cation

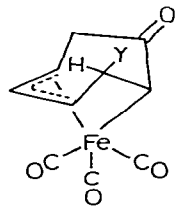
(XXII; n = 2) with many nucleophiles [40,48], Aumann [49] demonstrated that sodium borohydride adds chiefly to C-2 of this cation yielding the π-allylic complex XXXIII (L = CO, Y = H) and Johnson, Lewis et al. [50] showed that similar addition occurs both with hydride and cyanide giving e.g. XXXIII (L = PPh_3, Y = CN) when the corresponding triphenylphosphine or -amine substituted cation is used. Eisenstadt [51] found that similar addition to the protonated tropone complex XXXIV depends on the nucleophile, hydride and cyanide giving the allylic complexes XXXV (Y = H or CN) whereas methoxide and azide yield the dienones XXXVI (Y = OMe or N_3).



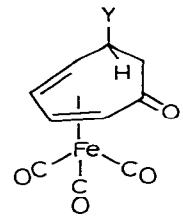
(XXXIII)



(XXXIV)

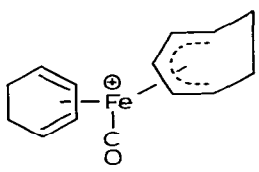


(XXXV)

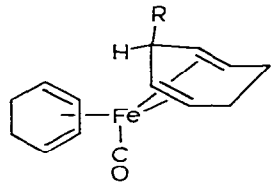


(XXXVI)

A third mode of addition to cycloheptadienyliron cations was observed, again by the Cambridge group [52], when adding sodium borohydride or cyanide to the cycloheptadienylcyclohexadienecarbonyliron cation XXXVII. *exo*-Addition to the 3-position was shown to occur giving cyclohepta-1,4-diene complexes (XXXVIII). These rearrange at 60°C to conjugated isomers XXXIX bearing the nucleophile on C-2, i.e. apparently resulting from a 1,3-*endo*-hydrogen shift. This mode of nucleophilic attack must also be involved in the addition of triphenylphosphine to the (16-electron) cycloheptadienyltricarbonylmolybdenum cation from which Salzer and Werner [53] isolated cyclohepta-1,4-dien-3-yltriphenylphosphonium tetrafluoroborate.

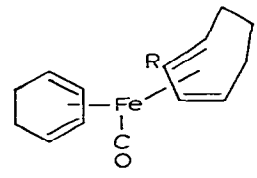


(XXXVII)



(XXXVIII)

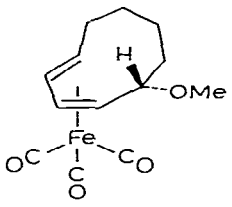
R = H, D or CN



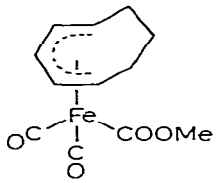
(XXXIX)

We have noted examples of nucleophilic attack at the metal or addition to a carbonyl group occurring in place of or in competition with *exo*-addition to the organic ligand. The fourth mode, *endo*-addition at this ligand, was first demonstrated conclusively by Hine, Johnson and Lewis [54] in the reaction of cyclohexadienyltricarbonyliron salt (XXII; n = 1) with methanol which yield the *exo*-methoxycyclohexadiene complex XXXI (X = OMe, n = 1) rapidly, but the *endo*-isomer predominates after 24 h reflux. Simultaneously Schiavon et al. [41] showed that *endo*-methoxycyclooctadiene complex XL is slowly formed from the cyclooctadienyl compound XXII (n = 3) which initially yields a mixture of the *exo*-isomer XXXI (X = OMe, n = 3) and the methoxycarbonyl complex XLI. But whether a direct transfer of nucleophile from the latter or any similarly metal-bound group to the ring occurs is made doubtful by the more

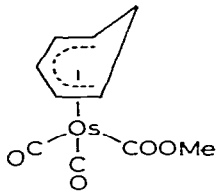
detailed study [55] of the related methoxycarbonyl(cyclohexadienyl)osmium complex (XLII). This is the first product of methoxide attack on cyclohexadienyltricarbonylosmium cations at 0° C; its thermal rearrangement yields *exo*-methoxycyclohexadienetricarbonylosmium and follows first order kinetics - i.e. its mechanism must be dissociative involving reversal of the addition to regenerate the cation. The latter, like its iron analogue yields the *endo*-methoxycyclohexadiene complex in refluxing methanol and the metal-coordinated complex XLIII has been suggested as an intermediate [55].



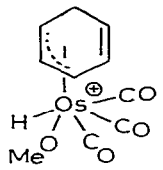
(XL)



(XLI)

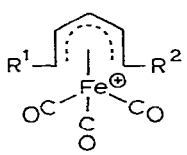


(XLII)

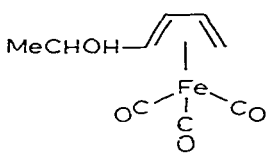


(XLIII)

High selectivity in the direction of nucleophilic addition to unsymmetrical cations was first noted by Mahler and Pettit [56] who showed that water adds apparently exclusively to the substituted end of the hexadienyltricarbonyliron cation XLIV (R^1 = Me; R^2 = H) yielding the alcohol XLV. Reeves et al. [57] confirmed and extended this result showing that for disubstituted pentadienyl complexes XLIV (R^1 and $R^2 \neq$ H) attack is preferentially at the less hindered position. More sterically demanding nucleophiles e.g. NEt_3, $AsPh_3$ (but not



(XLIV)



(XLV)

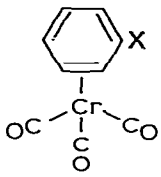
$PhNH_2$) add [58a] only to the unsubstituted end of the hexadienyl complex XLIV (R^1 = Me, R^2 = H). The available results are probably too limited to justify generalised conclusions.

A much fuller discussion including theoretical consideration of factors affecting the side of nucleophilic addition to a wide range of cationic hydrocarbon-transition metal complexes is given by Davies, Green and Mingos [58b].

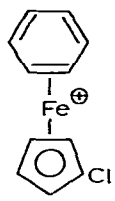
The widest range of carbon and other nucleophiles have been employed in studies of the synthetic potential of substituted and unsubstituted cyclohexadienyltricarbonyliron cations by Birch and Pearson [59] by Kane-Maguire [60] and by others [61]. Detailed consideration of this work and the equally synthetically useful studies of nucleophilic additions to alkene(cyclopentadienyl)-dicarbonyliron cations chiefly by Rosenblum and his school [62,63] is beyond the scope of this brief review.

Finally we must note that nucleophilic addition is also the key step in aromatic nucleophilic substitution. The activating effect of transition metal groupings on such substitutions was first noted by Whiting [64] in the case of chloro- and fluorobenzene tricarbonylchromium (XLIV; X = Cl or F). The synthetic potential of these substitutions has recently attracted renewed attention

[65,66]. Analogous substitutions of the chlorobenzenecyclopentadienyliron cation (XV; R = Cl) and the benzene(chlorocyclopentadienyl)iron cation (XLVII) were studied extensively by Nesmeyanov et al. [67]. Semmelhack's



(XLVI)



(XLVII)

work [68] on chlorobenzenechromium (XLVI; X = Cl) and our own [28] on the iron complex XV (R = Cl) shows that carbanions and hydride which add irreversibly to these compounds preferentially attack unsubstituted positions. This also applies to the chlorobenzenetricarbonylmanganese cation (XIV; R = Cl) which behaves quite analogously [26,69]. Substitution becomes possible when the nucleophile adds to positions bearing good leaving groups and hence occurs smoothly with these halobenzene complexes and all those nucleophiles whose addition is readily reversible.

Acknowledgement

The work described here would not have been possible without the devoted cooperation of numerous students and colleagues whose contribution is gratefully acknowledged.

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