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NUCLEOPHILIC ADDITION TO ORGANOTRANSITION METAL CATIONS CONTAINING UNSATURATED HYDROCARBON LIGANDS

A SURVEY AND INTERPRETATION

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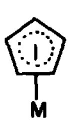
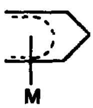
Abstract—Three simple rules are proposed that enable the prediction of the most favourable position of nucleophilic attack on 18 electron organotransition metal cations containing unsaturated hydrocarbon ligands.

Unsaturated hydrocarbons, e.g. ethylene, butadiene and benzene, do not normally undergo nucleophilic addition or substitution reactions. However, when these molecules act as ligands to metal cations they are attacked by a wide range of nucleophiles such as H^-, R^-, CN^-, MeO^- and R_3N.[1] The greater reactivity of the coordinated unsaturated hydrocarbon can be attributed broadly to metal-ligand bonding effects which result in a net withdrawal of electron density from the unsaturated hydrocarbon ligand to the positively charged metal centre. Coordination to the metal ion is therefore akin to the introduction of electron withdrawing substituents onto the hydrocarbon chain. The transfer of electron density associated with metal-ligand bonding is influenced by the number of C atoms coordinated to the metal, i.e. the ligand *hapto* number (η)[2], and the parity of the ligand *hapto* number, i.e. whether an *even* or *odd* number of ligand C atoms are attached to the metal. Furthermore, for the purpose of this review it is necessary to distinguish between ligands which are cyclically conjugated and those which are not. The former are described as *closed* and the latter as *open*. Thus η^5-cyclopentadienyl (1) is an *odd closed* ligand and η^5-pentadienyl and η^5-cyclohexadienyl (2 and 3) are *odd open* ligands. Some *even* ligands are illustrated in 4 to 6.



(1)



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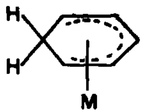

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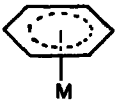
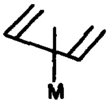


closed-η^6
(4)

closed-η^4
(5)



open-η^4
(6)

In organometallic cations with carbon monoxide coordinated to the metal nucleophilic attack can occur either at the organic ligand or the carbon monoxide. Therefore, the discussion will be limited initially to complexes which do not have ancillary carbon monoxide ligands.

1. *Nucleophilic attack on cations which do not contain carbon monoxide as a ligand*

X-Ray crystallographic and spectroscopic studies have shown that nucleophilic attack invariably occurs onto the *exo*-face of the ligand, i.e. on the side of the ligand away from the metal. The following examples are typical.[3,4]

(7)

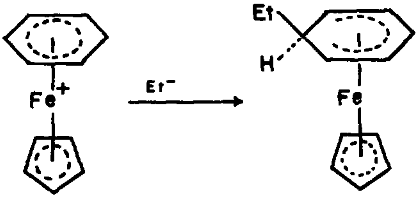
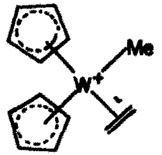
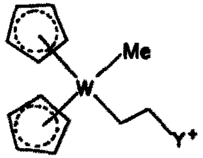
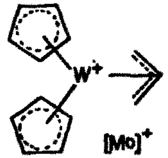
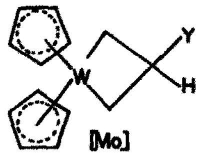
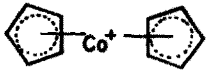
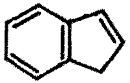
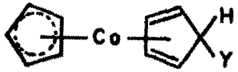
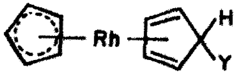
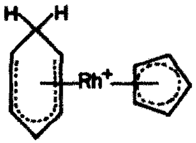
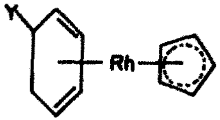
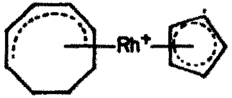
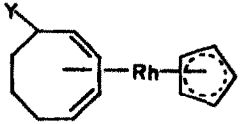
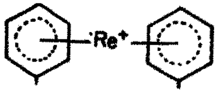
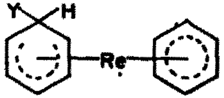
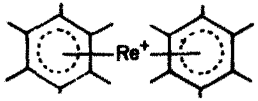
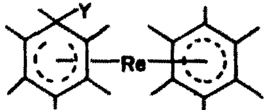


Table 1 lists examples of organotransition metal cations which undergo nucleophilic addition, and classifies them according to the *hapto* numbers of the unsaturated hydrocarbon ligands.

We find that it is possible to put forward some simple rules which if used sequentially enable a prediction of

Table 1. Nucleophilic attack on organotransition metal cations which do not contain carbon monoxide as a ligand

hapto numbers	CATION	NO.	NUCLEOPHILE Y	PRODUCT	RULES APPLIED	REF.
5/2		9	PMe_2Ph		1	7
5/3		10 11	H^-, Me^-		1, 2, 3	8
		12	$C_5H_5^-$, Ph^-, H^-, R^- 		—	9, 10, 11
5/5		7	$C_5H_5^-$, Ph^-, H^-, R^-		—	3, 9, 11
		13	H^-, OMe^-, D^-		2, 3	13, 14
		14	H^-, CN^-		2, 3	14, 15
		15	H^-		—	16
6/6		16	H^-		—	17

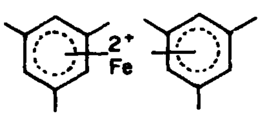
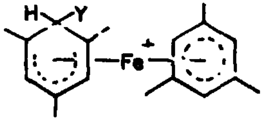
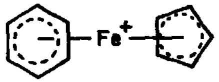
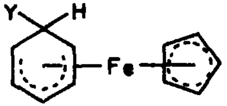
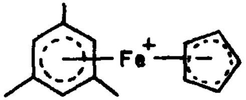
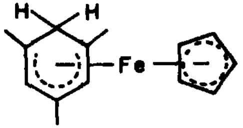
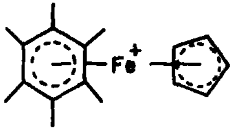
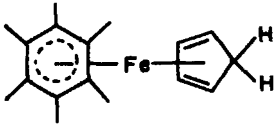
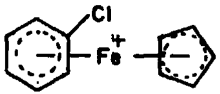
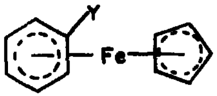
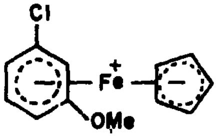
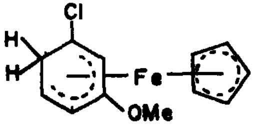
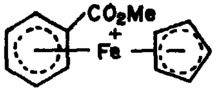
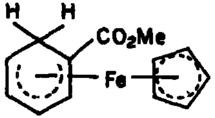
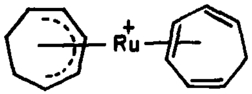
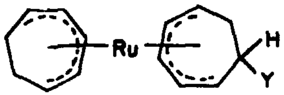
		17	CN^-, $^-CH_2NO_2$, tBu^-		—	18
6/5		18	Et^-, H^-, $PhCH_2^-$, Ph^-, $C_5H_5^-$		1	4, 19, 20
		18	H^-		1	21
		19	H^-		1	22
		20	MeO^-, PhO^-, BuS^-, PhS^-, NH_2^-, NHR^-		1	23
6/5		21	H^-		1	24
		22	H^-		1	25
		23	H^-, Me^-, CN^-, OMe^-, Me^-, $^-NH_2^-$, $^-CH(CO_2Et)_2^-$		1, 3	26

Table 1. (*Contd*)

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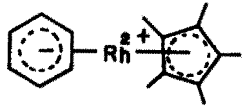
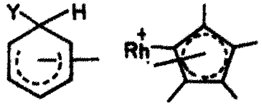
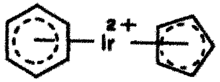
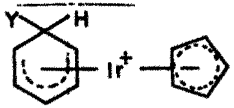
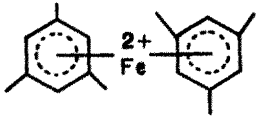
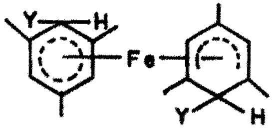
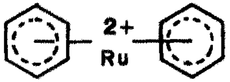
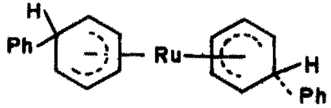
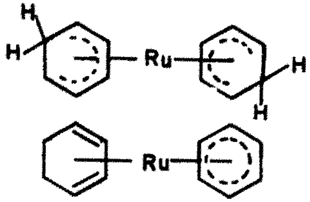
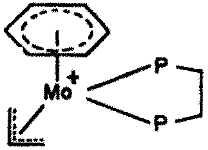
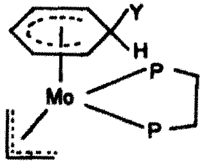
		24	H⁻, Me⁻		1	27
		25	H⁻, Me⁻		1	27
6/6 + 6/5		26	Bu⁻, Ph⁻		1	28
			Ph⁻		1	29
		27	H⁻			19
6/3		28	H⁻, CN⁻, Bu⁻		1	30

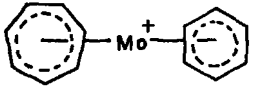
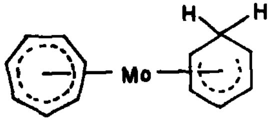
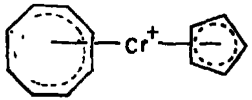
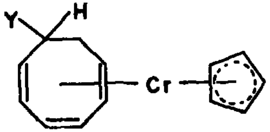
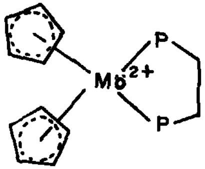
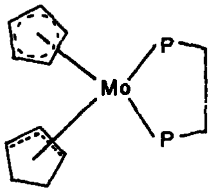
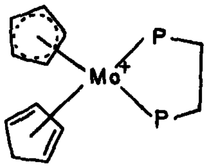
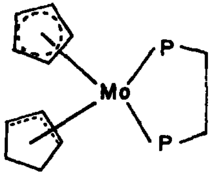
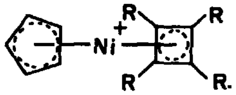
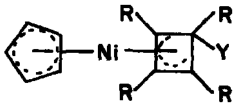
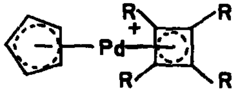
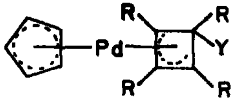
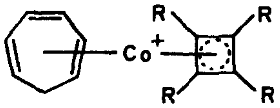
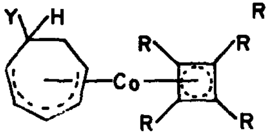
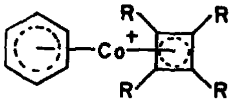
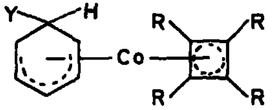
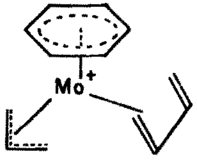
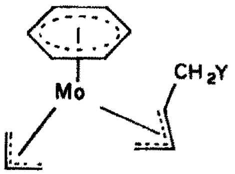
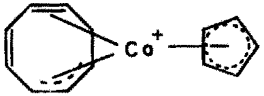
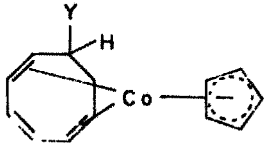
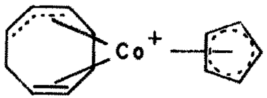
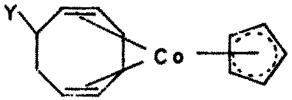
6/7			H^-		1	31
5/7		30	H^-, Me^-		1, 2, 3	32
5/5 + 5/4		31	H^-		1, 3	33, 34
		32	H^-		1, 3	34
		33	OH^-, OEt^-		1	35
		34	OH^-, OEt^-		1	35
4/6		35	H^-, Bu^-	 R = Ph	1, 2, 3	36
	 R = Ph	36	Ph^-, H^-, OH^-, OMe^-, OAc^-		1	36

Table 1. (*Contd*)

hapto numbers	CATION	NO.	NUCLEOPHILE Y	PRODUCT	RULES APPLIED	REF.
6/3/4		37	H^-, CN^-, OMe^-, SMe^-		1, 2, 3	37
2/3/5		38	CN^-		1	38
		39	CN^-, acac$^-$, H^-			39

= 1,2 bis(diphenylphosphino)ethane

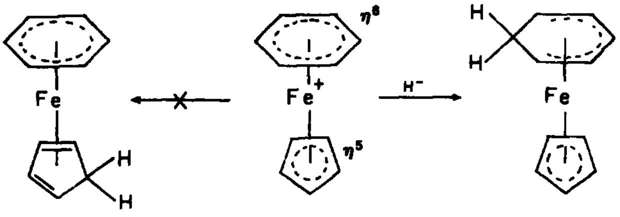
the most favourable position of attack of a nucleophile on unsaturated hydrocarbon ligands in 18-electron organotransition metal cations for reactions that are kinetically rather than thermodynamically controlled.[5]

Rule 1.† Nucleophilic attack occurs preferentially at *even* coordinated polyenes which have no unpaired electrons in the homo's.‡

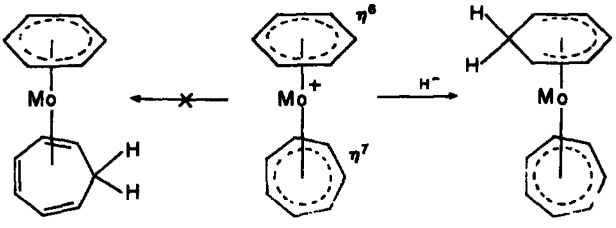
Rule 2. Nucleophilic addition to *open* coordinated polyenes is preferred to addition to *closed* polyenes.

Rule 3.† For *even open* polyenes nucleophilic attack at the terminal carbon atom is always preferred, for *odd open* polyenyls attack at the terminal carbon atom occurs only if ML_n^+ is a strong electron withdrawing group.

The following examples illustrate applications of the rules.[4,31]



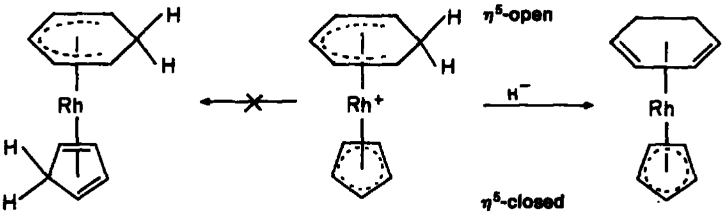
(8)



(40) (29)

The regioselectivity of the above reactions follows from the application of Rule 1. In the latter example the zerovalent compound Mo(η-C_6H_6)(η-C_7H_8) (40) is not formed even though it is isoelectronic with the well known Mo(η-C_6H_6)$_2$[40] complex and would have been the intuitively predicted product if one had regarded the cycloheptatrienyl ligand as approximating to the free aromatic tropylium cation.

Rule 2 is illustrated by the reactions of compound 13 given below.[12,13]



(13)

The large number of additional examples given in Table 1 indicate the wide scope of the rules described above. Our literature search has only uncovered three apparent exceptions to the rules, i.e. the reactions of 19[22] and 27[19] with hydride and 39[39] with hydride, cyanide and acetylacetonate (see page 3054 and Table 1).

It seems reasonable to postulate that the products of hydride attack on 19 and 27 are thermodynamically rather than kinetically controlled. *Exo*-attack on the hexamethyl benzene ring of 19 would give a sterically unfavourable product with a Me group in close proximity to the metal. It is significant that for the unsubstituted complex (8) and the trisubstituted complex (18) nucleophilic attack does occur at the benzene ring in accordance with Rule 1.[4,21]

Compound 27 gives only the expected product (41) with Ph^-[29] but a mixture of products (42 and 43) with hydride ion.[19] It follows from our rules that the initial product must be 42 which subsequently rearranges to the thermodynamically more stable product (43). Such a rearrangement is more favourable for the labile hydride ion than the phenyl ion. The above explanation could be verified by variable temperature studies.

A similar explanation can be used to explain the reactions of 39 with nucleophiles, since it is known that hydride migrations occur very easily in such systems.[41,15]

Cation 37[37] (see page 3054) demonstrates the need to apply the rules sequentially. Rule 1 (*even* before *odd*) eliminates the possibility of attack on the allyl ligand. Rule 2 (*open* before *closed*) suggests nucleophilic attack on the butadiene and attack at the terminal position of this ligand follows from Rule 3.

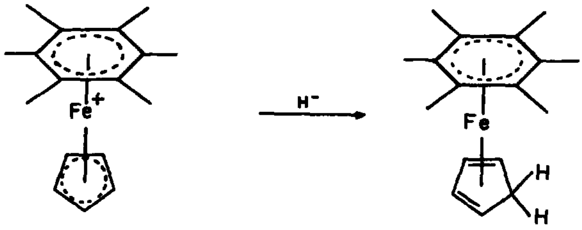
The rules provide a ready explanation for the different modes of attack on the dications (26[28] and 31)[33] which result in substitution into both rings for 26 and the same ring twice for 31.

It follows from Rules 1 and 2 that the predicted

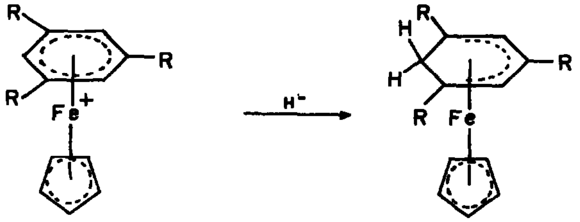
---

†These rules have been briefly described[6] in previous papers in terms of the retention of formal valency state of the metal

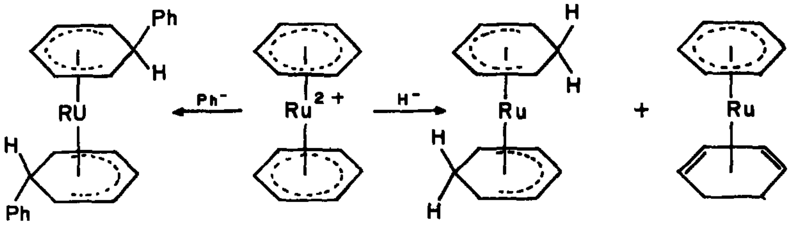
‡Although cyclo-butadiene is an *even* polyene it has unpaired electrons in its *homo* and therefore according to Rule 1 nucleophilic addition to other *even* polyenes is preferred. It is however, attacked in preference to *odd* polyenyl ligands.



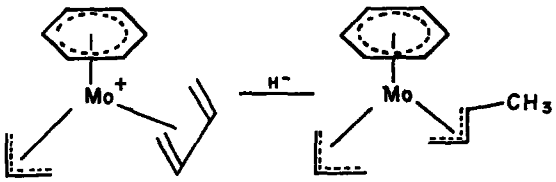
(19)



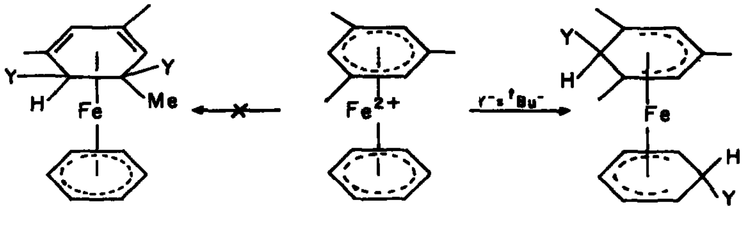
(8) R=H
(18) R=Me



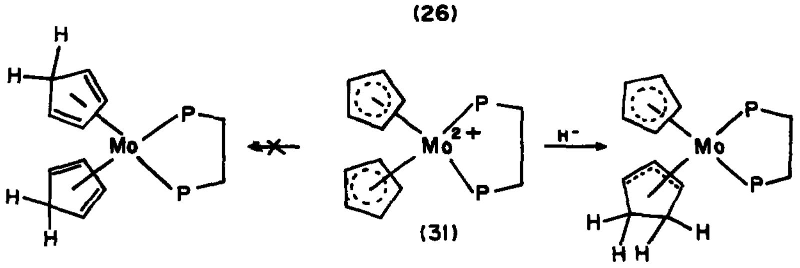
(41) (27) (42) (43)



(37)

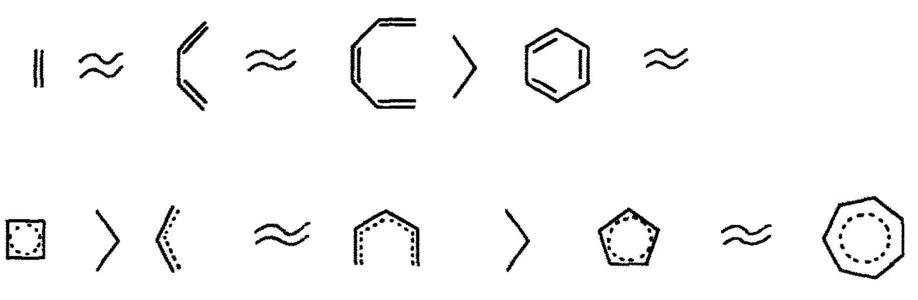


(26)

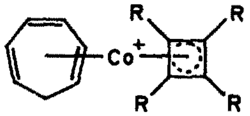


(31)

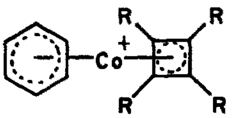
reactivity of coordinated unsaturated hydrocarbons is as shown below



This series is supported by the examples in Table 1 and by the observation that the cycloheptatriene ligand in **35** is more susceptible to nucleophilic attack than the benzene ring in **36**.[36]



(35)



(36)

2. *Theoretical basis of the rules*

In the Introduction it was noted that the greater reactivity of the coordinated polyenes could be attributed to the net withdrawal of electron density from the ligand to the positively charged metal centre. This charge transfer process may be put on a more quantitative basis using the first order perturbation theory arguments.[42]

The π-systems of the linear polyenes C_nH_{n+2} are *alternant*[43] and therefore for the neutral ligand the π electron density is equally distributed over all the C atoms. Coordination of these neutral ligands to a positively charged ML_x fragment which has 18-n valence electrons will generate the 18 electron $[C_nH_{n+2}ML_x]^+$ complexes which concern us in this paper. Previous studies[44,45] have shown that the conical ML_x^+ fragments have orbitals of the correct symmetry and energies to enter into strong bonding interactions with the polyene π-orbitals of the free polyene ligand in such a way that they will reflect the forward and back donation components implicit in the Chatt–Dewar–Duncanson bonding model.[46,47] For a positively charged metal-olefin complex the dominant charge transfer process will arise from donation of electron density from the ligand orbitals to the metal. Back donation effects will be relatively less important because of the initial positive charge on the ML_n^+ fragment. The high carbonyl stretching frequencies observed for metal CO cations (i.e. $\sim 2100\,\mathrm{cm}^{-1}$)[48] supports this assertion. Electron donation from the highest occupied molecular orbital (*homo*) of the ligand to an orbital of appropriate symmetry on the metal will be particularly influential in determining the distribution of electron density on the coordinated polyene. The relevant interaction diagrams for *even* and *odd* polyenes are illustrated in Fig. 1. If overlap is neglected the bonding molecular orbital ψ_b resulting from this interaction will have the normalised form:[49]

$$\psi_b = \sin\theta\psi_P{}^0 + \cos\theta\psi_M{}^0 \quad (1)$$

where $\psi_P{}^0$ and $\psi_M{}^0$ are the wavefunctions of the polyene *homo* and the metal acceptor orbital respectively. The mixing coefficient will be set by the relative energies of the metal and polyene orbitals and the extent of interaction between them. Figure 1 illustrates three possible situations for *odd* and *even* polyenes; $\theta \simeq 90°$ where the metal acceptor orbital lies at much higher energies than the ligand *homo* and consequently little charge transfer occurs, $\theta \sim 45°$ where the metal and ligand orbitals are well matched and finally $\theta \sim 0°$ when the metal acceptor orbital lies at much lower energies than the polyene *homo* and extensive ligand to metal charge transfer results.

The fact that the *homo* of the *even* polyene is doubly occupied whereas the *homo* of the *odd* polyene is singly occupied leads to an important general difference between these two types of ligand. In the former case all the electron density in the bonding molecular orbital originates from the polyene *homo*, but in the latter electron density is contributed by both the polyene and the metal. From eqn (1) above it is clear that electron density associated with the metal in ψ_b is equal to $2\cos^2\theta$. The resultant positive charge on the *even* polyene ligand is therefore $+2\cos^2\theta$. For an *odd* polyene metal complex, however, the charge is $2\cos^2\theta - 1$, because the metal acceptor orbital is occupied by an electron before it interacts with the polyene *homo*. Therefore, if the mixing coefficients for the *odd* and *even* polyene ligands are comparable then a coordinated *even* polyene will have a unit extra of positive charge compared to an *odd* polyene. For the situations covered by Fig. 1 this means that the charge on an *even* polyene will vary from 0 to +2.0 and that for an *odd* polyene from −1.0 to +1.0.

Figure 2 illustrates the relative energies and nodal characteristics of the homo's of the polyenes[50] C_nH_{n+2} with n = 2–6. The alternant properties of the polyenes suggest that within the Hückel approximation the *homo*'s of the *odd* polyenes are of equal energies and non-bonding. The *homo*'s of the *even* polyenes are bonding and consequently more stable than the corresponding orbitals of the *odd* polyenes. This difference could lead to somewhat larger values of the mixing coefficient for *even* polyenes (i.e. electron donation from a more stable orbital to the metal will be smaller), however this difference is unlikely to be sufficiently large to undermine the fundamental difference between *odd* and *even* polyenes noted above.

When considering the relative case of nucleophilic attack on the coordinated polyene it is the charge on a particular C atom rather than total charge on the polyene which is important. An estimate of the charge on a particular C atom can be made if the explicit forms of the polyene *homo*'s are substituted into eqn (1). Within the Hückel approximation the π molecular orbitals of the

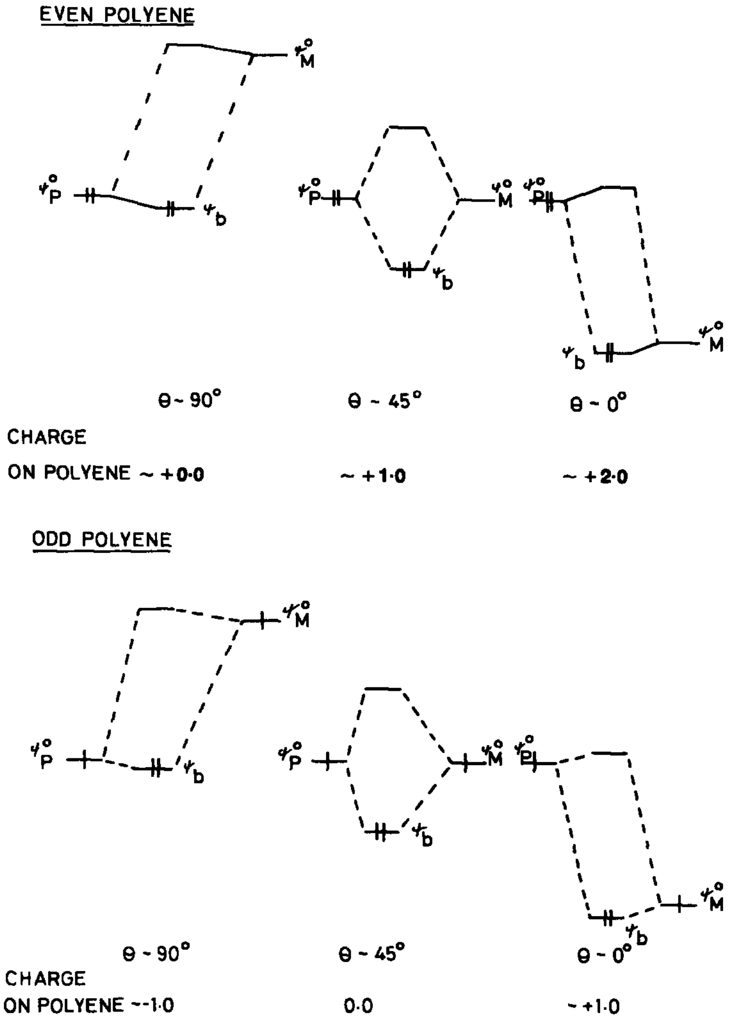


Fig. 1. Interaction diagrams for polyene homo ($\psi_p{}^0$) and metal acceptor orbital ($\psi_m{}^0$).

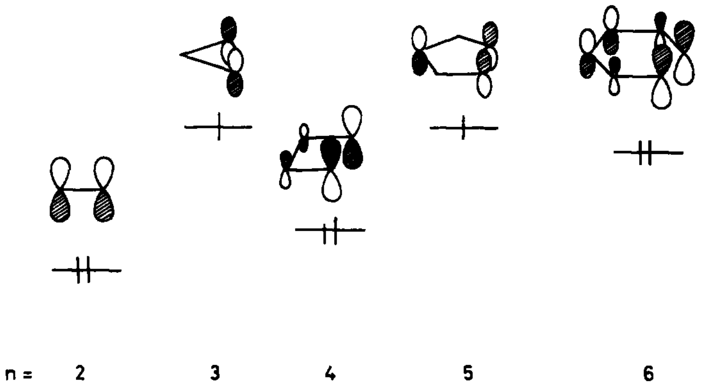


Fig. 2. Energies and nodal characteristics of polyene homo's.

polyene are given by

$$\psi_P{}^0 = \sum_{\mu=1}^{n} c_{p\mu}\phi_\mu \text{ where } c_{p\mu} = \sqrt{\frac{2}{n+1}}\sin\frac{(\pi p\mu)}{n+1}.$$ [50]

For the polyene *homo*'s $p = n/2$ if n is *even* and $(n+1)/2$ if n is *odd*. The charge on C atom μ of the polyene is therefore $2\cos^2\theta c_{p\mu}^2$ if n is *even* and $(2\cos^2\theta - 1)c_{p\mu}^2$ if n is *odd*.

The charges calculated for the terminal C atom (i.e. $\mu = 1$, or n) of a series of polyenes are shown in Fig. 3 for two values of θ corresponding to $ML_n{}^+$ being a strong electron withdrawing group ($\theta = 30°$) and a weak electron withdrawing group ($\theta = 60°$).

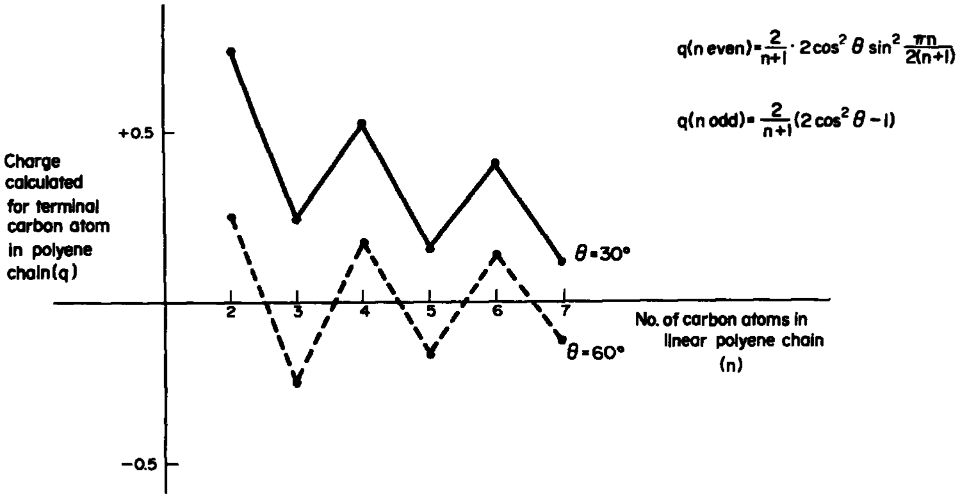
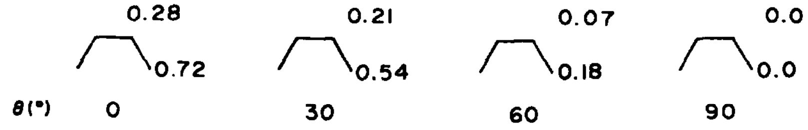


Fig. 3. Charges calculated for the terminal carbon atom in coordinated polyenes.

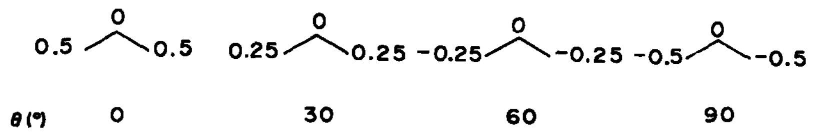
From Fig. 3 it is clear that as long as θ does not vary greatly with *n* then the charge on the terminal C atom is dominated by the parity of the polyene, i.e. the terminal C atom of an *even* polyene is more positively charged. The calculated positive charges diminish with increasing chain length for a series of polyenes with the same parity reflecting the smaller atomic coefficients at the terminal positions in the *homo*'s.

The rates of nucleophilic addition reactions of 18 electron cationic polyene complexes are likely to be charge rather than orbitally controlled especially if the nucleophile is small and highly charged and therefore the regioselectivity of such reactions is probably dominated by the positive charges on particular C atoms.[51] In such cases the perturbation theory argument given above leads directly to Rule 1, i.e. nucleophilic attack occurs preferentially at *even* coordinated polyenes.

From the perturbation theory expressions given above it can be shown that an *even* polyene will bear a positive charge whenever $\theta < 90°$ and that the charge on the terminal atoms is always larger than that on the internal C atoms. The calculated charges for the coordinated butadiene ligand at different θ values given below serve to illustrate this point..



In contrast, the terminal C atom in an *odd* polyene only bears the largest positive charge when $\theta < 45°$. For example for the coordinated allyl ligand



It follows that nucleophilic attack on an *odd* polyene will only be preferred when the metal ion is a strong electron withdrawing group. These conclusions lead naturally to Rule 3 above.

Although the arguments described above have not explicitly considered cyclic polyenes, clearly similar effects will apply except that the positive charge will be more evenly distributed amongst the C atoms making nucleophilic attack less favourable than at the corresponding *open* polyene. (Rule 2).

Although the perturbation theory arguments described above account for the rules for nucleophilic attack which have been proposed above it would also be useful to have the conclusions confirmed by more sophisticated m.o. calculations. In this respect, we note the recent important work in this field by Clack.[52,53]

3. *Effects of substituents on the polyene ring*

Further evidence supporting the view that the nucleophile attacks the C atoms with the least electron density is provided by examples on page 3058 which have electron withdrawing and releasing groups on the polyene.

For compounds 44 and 45 nucleophilic addition occurs preferentially onto the ring with the electron withdrawing carboxylate group and in the β-positions.[54]

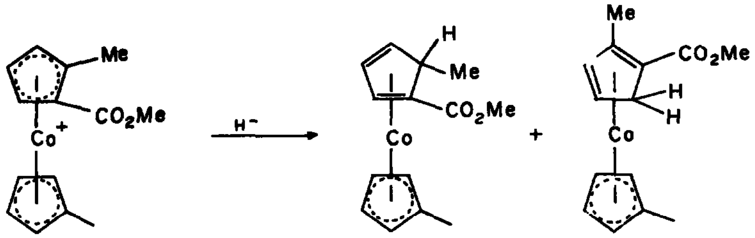
For compound 46 when X is an electron withdrawing group (e.g. $-CO_2Me$) nucleophilic attack occurs at the 2-position but when X is an electron releasing substituent (e.g. $-OMe$) attack occurs at the 3-position.[53]

Similarly compound 47 is attacked preferentially in the *meta*-position when X is strongly electron releasing ($X=NMe_2$).[55]

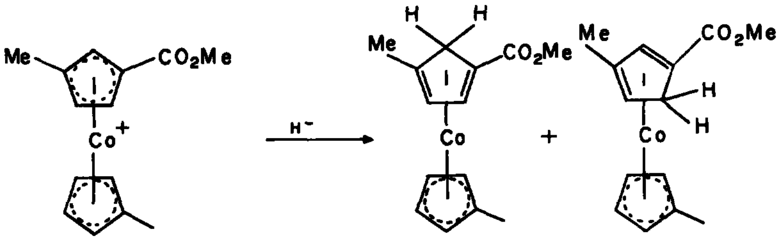
Finally in compounds 48 and 49 the OMe substituent deactivates the 5-position and attack occurs preferentially at position-1.[56]

4. *Nucleophilic attack on cations containing one or more carbon monoxide ligands*

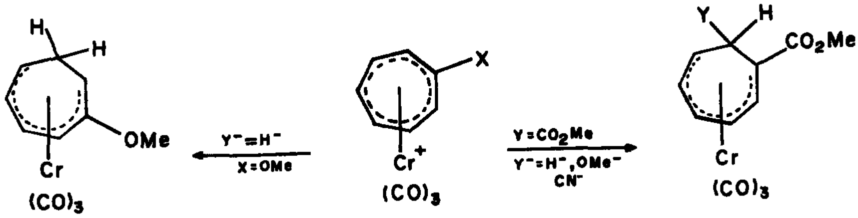
In Table 2 organometallic cations containing only one



(44)



(45)



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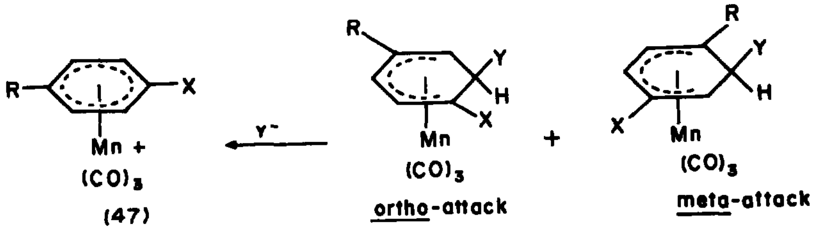
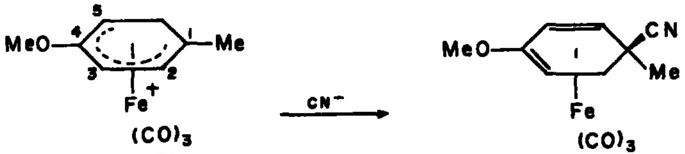


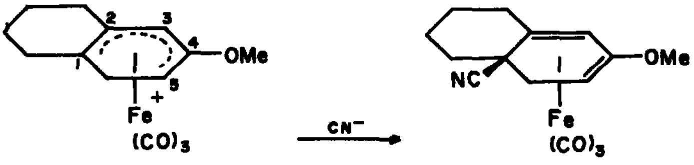
(47)

Ratio of *ortho*:*meta* attack

	R = Me X = Cl	R = Me X = Cl	R = Me X = Cl	R = H X = OMe	R = Me X = NMe$_2$
Y$^-$	H$^-$	Me$^-$	Ph$^-$	H$^-$	H$^-$
Ratio	69:31	74:26	61:39	37:63	3:97



(48)



(49)

Table 2. Nucleophilic attack on organotransition metal cations containing one unsaturated hydrocarbon ligand and at least one carbon monoxide ligand

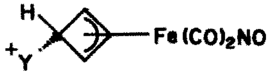
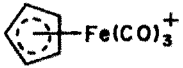
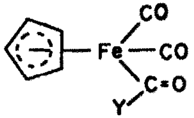
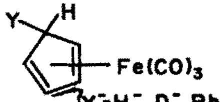
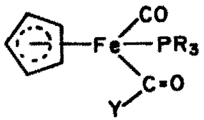
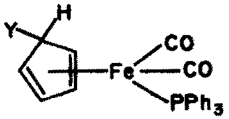
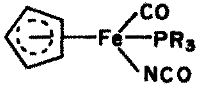
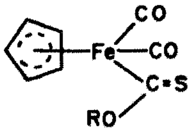
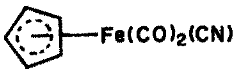
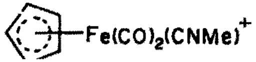
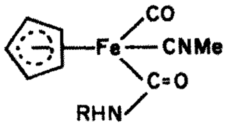
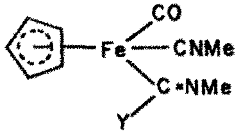
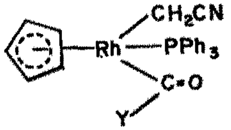
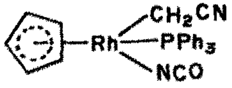
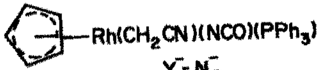
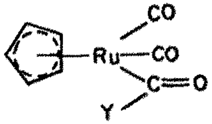
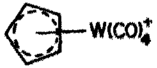
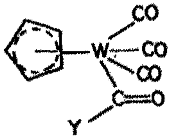
CATION	NO.	PRODUCTS DERIVED FROM ATTACK ON CO		PRODUCTS DERIVED FROM ATTACK ON HYDROCARBON		REF.
	51				Y=PPh$_3$	58
	52		YH=NH$_3$,N$_2$H$_4$,		Y$^-$=H$^-$,D$^-$,PhCH$_2^-$	59–63
 R=Ph,Et	53		YH=NH$_3$,MeOH		Y$^-$=H$^-$	64–66
			YH=N$_2$H$_4$ Y$^-$=N$_3^-$			
	54		Y$^-$=N$_3^-$			
			Y$^-$=OR$^-$			67
			Y$^-$=NCS$^-$,NCO$^-$			
	55		YH=NH$_2$R			68

Table 2. (*Contd*)

CATION	NO.	PRODUCTS DERIVED FROM ATTACK ON CO	PRODUCTS DERIVED FROM ATTACK ON HYDROCARBON	REF.
	56	 YH=NH$_2$R		68
	57	 Y$^-$=OMe$^-$		
		 Y$^-$ = N$_3^-$		69
	58	 Y$^-$=N$_3^-$		69
	59	 Y$^-$=N$_3^-$		69
	60	 YH=Me$_2$NNH$_2$ Y$^-$=OMe$^-$		70
	61	 YH= HNMe$_2$		71

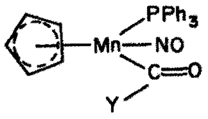
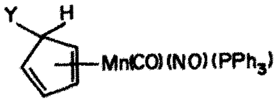
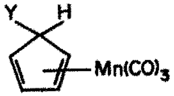
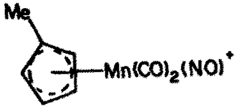
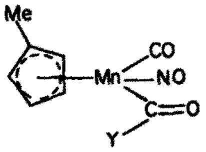
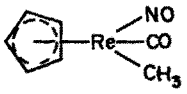
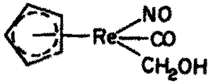
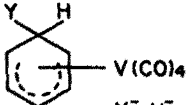
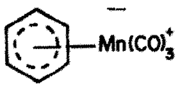
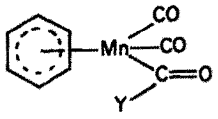
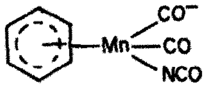
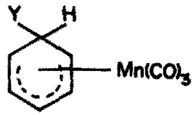
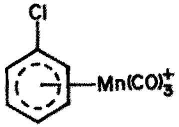
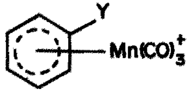
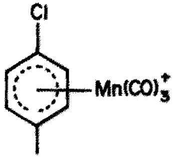
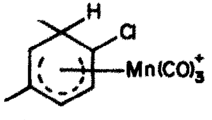
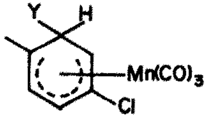
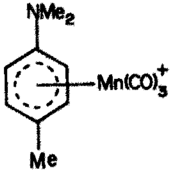
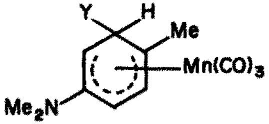
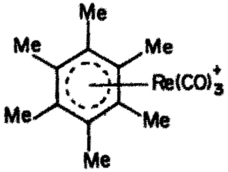
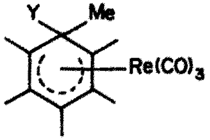
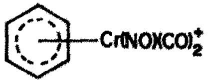
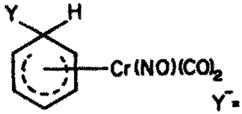
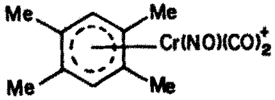
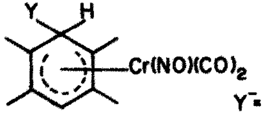
	62	 $Y^- = Me^-, Ph^-, H^-$		72, 73
	63		 $Y^- = Me^-$ or Ph^-	72
	64	 $YH = RNH_2$		74
	65	 $Y^- = BH_4^-/THF$  $Y^- = BH_4^-/H_2O$		75
	66		 $Y^- = H^-$	76
	67	 $Y^- = OMe^-$, $YH = RNH_2$  $YH = N_2H_4$	 $Y^- = CN^-, CH(CO_2Et)_2^-, NCS^-, N_3^-, OMe^-, PPh_2^-, H^-, Me^-$, and Ph^-	77–89

Table 2. (Contd)

CATION	NO.	PRODUCTS DERIVED FROM ATTACK ON CO	PRODUCTS DERIVED FROM ATTACK ON HYDROCARBON	REF.
	68		 $Y^- = H^-, OMe^-, OPh^-, SPh^-$ and N_3^-	90
	69		 $Y^- = Me^-, Ph^-$ and H^- 	55
	70		 $Y^- = H^-$	55
	71		 $Y^- = H^-$	91, 92
	72		 $Y^- = H^-$	93
	73		 $Y^- = H^-$ or Me^-	94

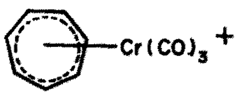
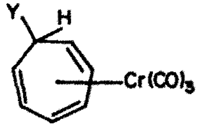
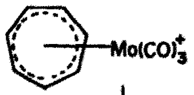
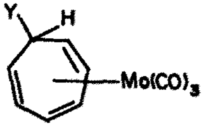
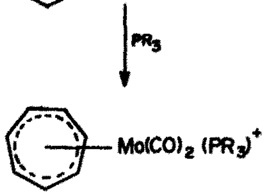
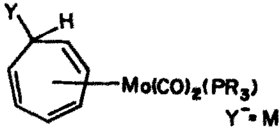
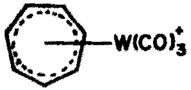
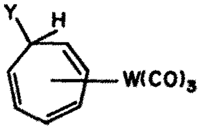
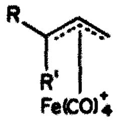
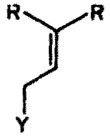
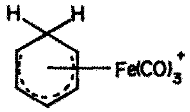
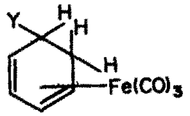
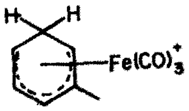
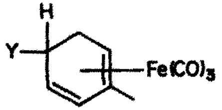
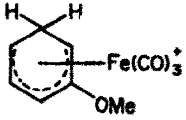
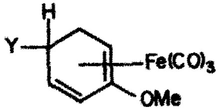
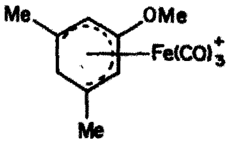
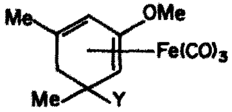
	74	 Y^-=PPhEt$_2$, PBu$_3$, CH$_2$CO$_2$Et$^-$, Me$^-$, Ph$^-$, PhC$_2^-$, ^{t}BuC$_6$H$_4$, Me$_2$NH, S^{2-}, SH$^-$, OMe$^-$, $^-$CH(CO$_2$Et)$_2^-$ CN$^-$, indole, acac.	95–104
	75	 Y^-=OMe$^-$, acac$^-$, tBu$^-$	104, 105
 R_3=(OPh)$_3$, Ph$_3$, Ph$_2$Me	76	 Y^-= Me$^-$, H$^-$	106, 107
	77	 Y^-= OMe$^-$, acac$^-$	104
	(78)R=MeR′=H (79)R′=H (80)R=R′=Me	 Y=PPh$_3$, C$_5$H$_5$N, Et$_2$NH Y$_2$Cd=R$_2'$Cd Y=C$_4$H$_5$N, (CH$_3$COCHCO$_2$Me)$^-$	108, 109
	(81)R=R′=H (82)R=Me, R′H —(83)R=R′=Me (84)R=R′=Ph	 Y^-=H$^-$, YH=MeNH$_2$, PhNH$_2$ Y=R$_3$N, YH=H$_2$O, Y^-=tBuO$^-$ YH=RNH$_2$, HO YHC$_6$H$_4$Me	110–118

Table 2. (*Contd*)

CATION	NO.	PRODUCTS DERIVED FROM ATTACK ON CO	PRODUCTS DERIVED FROM ATTACK ON HYDROCARBON	REF.
	(85)		 Y^-=OMe^-, CN^-, $acac^-$, Me^-, OAc^-, H^- R_2Zn, R_2Cd, $PhSnMe_3$, C_4H_9N, $P(OMe)_3$, PPh_3, H_2O, $PhNH_2$ indole, morpholine, C_4H_4X, X=NH, O, S, dimedone, S^{2-}, Cp_2Fe, $C_6H_{10}O$, HSO_3^-, H_2PO_3, S_2O_4	119–120
	(86)		 Y =$(C_3H_7)_2Cd$, $(C_3H_5)_2Zn$	123
	(87)		 Y^-=(R_3B^-)–C≡C–R, CN^-, acac, dimedone, enamines	126, 129, 133
	88		 Y^-=H^-, OH^-, morpholine	126

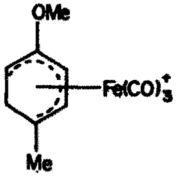
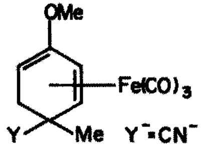
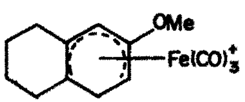
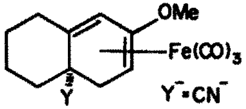
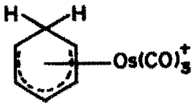
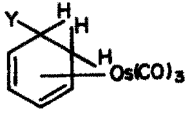
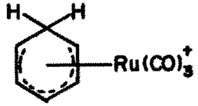
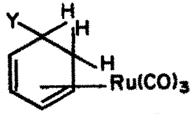
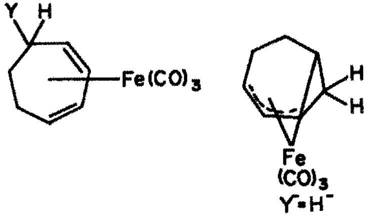
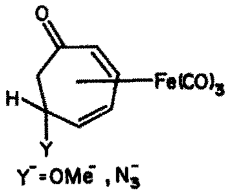
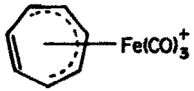
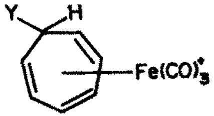
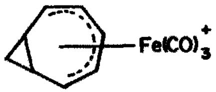
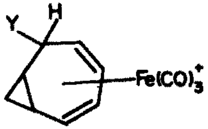
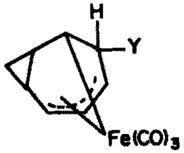
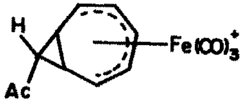
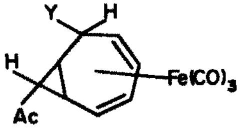
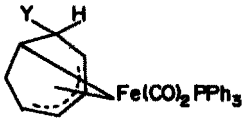
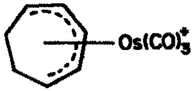
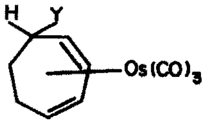
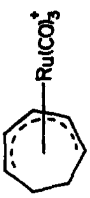
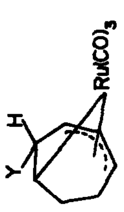
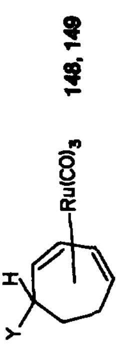
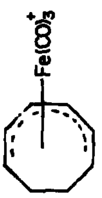
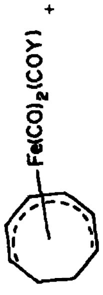
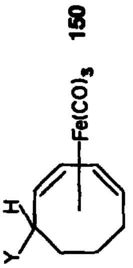
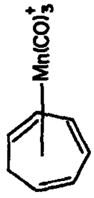
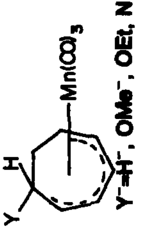
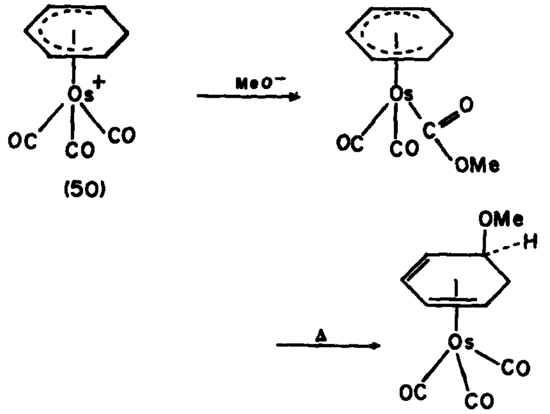
	89	 $Y^- = CN^-$	56
	90	 $Y^- = CN^-$	56
	91	 $Y^- = H^-, OMe^-, acac^-$, dimedone	57, 129
	92	 $YH = C_4H_5N, C_4H_4O$	127
	93	 $Y^- = H^-, CN^-, OEt^-, CH(CO_2Et)_2^-$ $acac^-, PPh_3$	121, 129 134–139
	94		140

Table 2. (*Contd*)

CATION	NO.	PRODUCTS DERIVED FROM ATTACK ON CO	PRODUCTS DERIVED FROM ATTACK ON HYDROCARBON	REF.
	95		 $Y^- = C_3H_5^-$	141
	96		 	142–145
	97		$Y^- = OMe^-$ 	146, 147
	98		 $Y^- = H^-, CN^-$	135
	99		 Y^-=acac$^-$, (dimedone)$^-$	129

	100	 $Y^-=H^-, D^-, CN^-$  $Y^-=H^-, D^-, OMe^-$	148, 149
	101	 $Y^-=OMe^-$ + 	150
	102	 $Y^-=H^-, OMe^-, OEt, NMe_2^-, CN^-, Me^-, Ph^-$	151–154

unsaturated hydrocarbon ligand and at least one carbon monoxide ligand are listed. The compounds in Table 2 may undergo nucleophilic attack either on the hydrocarbon ligand or on the C atom of a carbon monoxide ligand. As shown in the Table products from both types of reaction are observed. We note however that for those nucleophiles where attack is likely to be irreversible (e.g. alkyl) (i.e. the product will be kinetically controlled) it is generally the hydrocarbon which is attacked. When the nucleophile is such that the product of addition to the unsaturated hydrocarbon is labile then the isolated product is that derived from attack on carbon monoxide. In the case of methoxide attack on compound 50 attack occurs initially at the carbonyl and subsequent rearrangement leads to the observed *exo*-product.[57]



In Table 3 organometallic cations containing 2 or more unsaturated hydrocarbon ligands and at least one carbon monoxide ligand are listed. The cations are again classified according to the *hapto*-numbers of the hydrocarbon ligands.

As shown in the Table the Rules described above may often be used to predict the kinetically preferred products of nucleophilic attack. There are exceptions however. For example attack on cation (104) by D^- and CN^- gives the predicted products while attack by i-PrS^- does not.[157] Such exceptions may arise because the regioselectivity is not always governed by the charge distribution on the polyene. For the highly polarisable i-PrS^- ligand the regioselectivity may be orbitally controlled.[51]

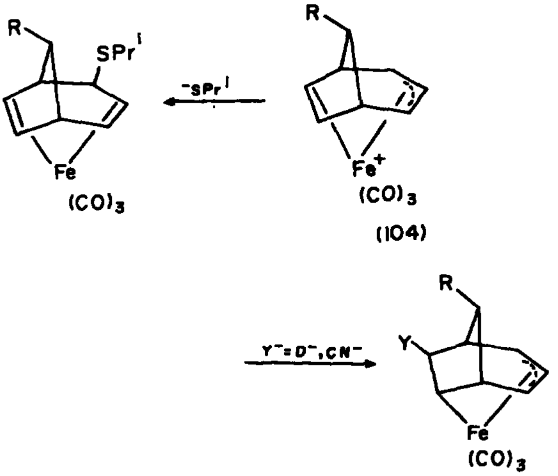
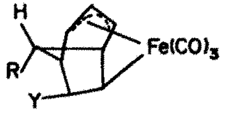
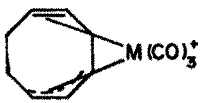
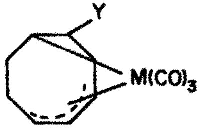
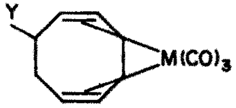
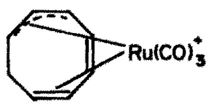
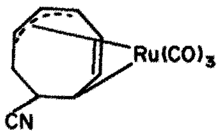
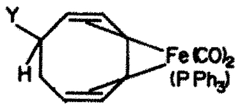
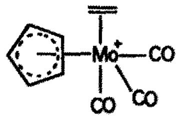
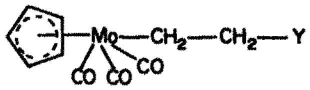
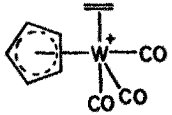
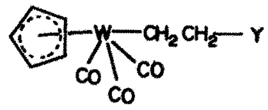


Table 3. Nucleophilic attack on organotransition metal cations containing two or more unsaturated hydrocarbon ligands and at least one carbon monoxide ligand

η	CATION	NO.	NUCLEOPHILE	PRODUCT	REF.	RULE NO.
2/3		R=H 103 R=Ac, Bz 104	$Y^-=CN^-$ $Y^-=D^-$, CN^-		155, 156	1
		M=Ru 105 M=Fe 106 M=Os 107	CN^-, H^-, acac$^-$	 (Major)  (minor)	157–161	1
		108	CN^-		162	1
		109	$Y^-=H^-$, acac$^-$	 	161	1
		110	NH_3, RNH_2, CN^-		163	1
		111	NH_3, RNH_2, CN^-		163	1

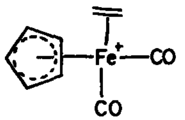
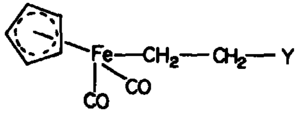
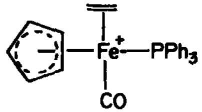
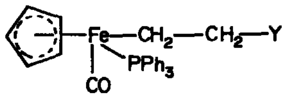
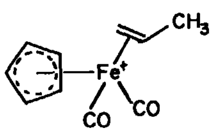
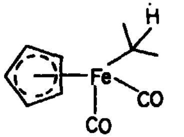
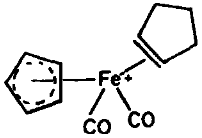
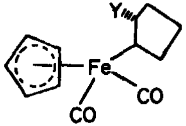
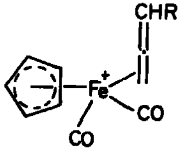
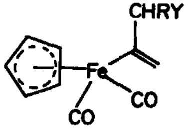
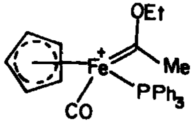
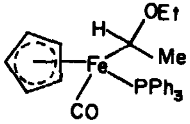
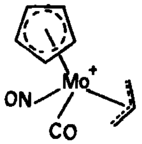
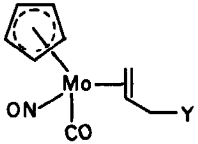
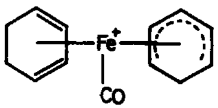
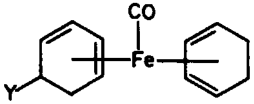
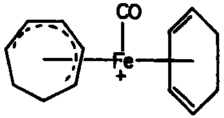
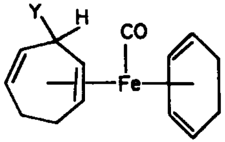
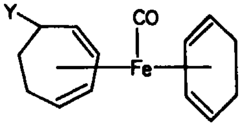
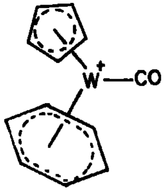
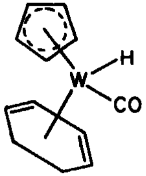
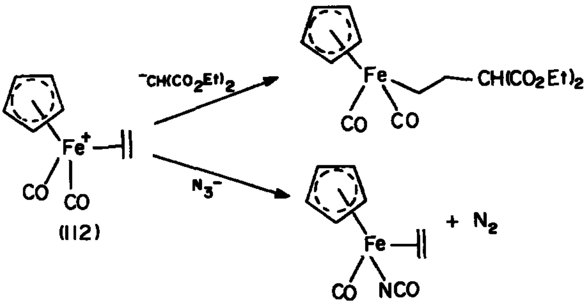
2/5		112	CN⁻, N_3^-		164, 165	1
		113	CN⁻, $Ph_3PCH_2^-$, $^-PO(OMe)_2$		166,167	1
		114	H⁻		168	1
		115	$CH(CO_2Et)_2^-$		169	1
2/5		116	H⁻, Et_2NH, PPh_3		170, 171	1
		117	H⁻		172	
3/5		118	H⁻, OMe⁻, AcO⁻, Cp⁻		173	2, 3

Table 3. (*Contd*)

η	CATION	NO.	NUCLEOPHILE	PRODUCT	REF.	RULE NO.
4/5		119	H^-, D^-		174	
		120	H^-, CN^-		175–177	
			$acac^-Me^-$			
6/5		121	H^-, H^+, H^-		178	1 then 1,2,3

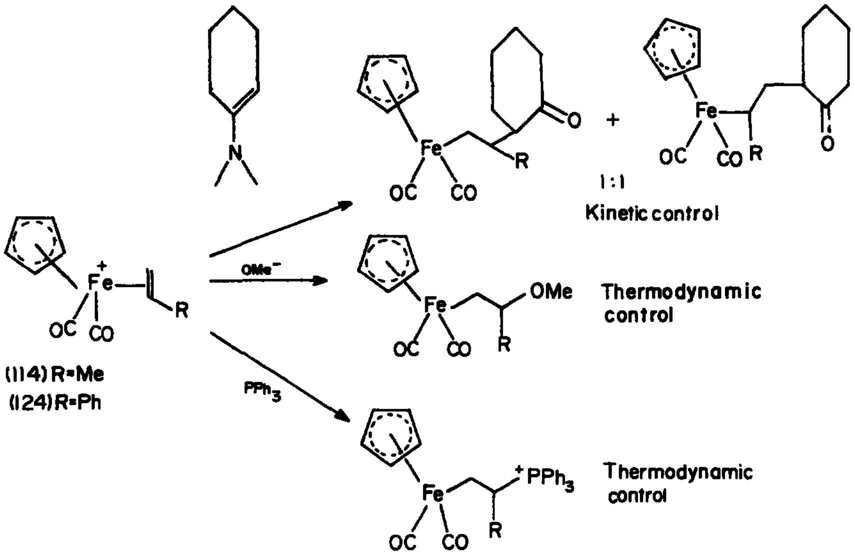
5. *Influence of the nucleophile*

The influence of the nucleophile on the product formed is emphasised by the reactions of compound **112** shown below. This difference can be interpreted in terms of reversible addition of azide to the ethylene ligand but as irreversible addition to a carbon monoxide ligand leading to formation of coordinated isocyanate and the liberation of molecular nitrogen.

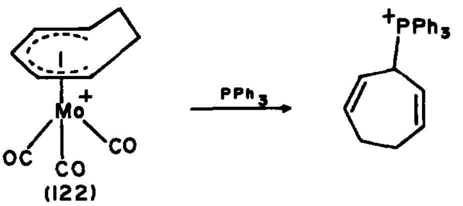


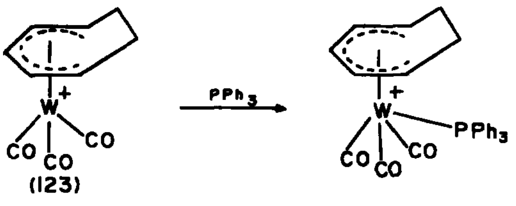
The difference in regioselectivity in the reactions of **114** and **124** with nucleophiles may also be explained in terms of kinetic vs thermodynamic control.

The many reactions of the cations [Fe(η-C$_5$H$_5$)(CO)$_2$(olefin)]$^+$ have recently been reviewed.[169]



The unexpected variety of products obtained on reaction of compounds **119** and **120** with nucleophiles is probably either the result of ready hydride rearrangements of the initially formed products or of initial attack on the metal followed by rearrangements.[174–177] It is interesting that the only other case where a pentadienyl ligand is attacked in the 3-position is the reaction of the 16-electron cation (**122**) with Ph$_3$P.[179] The initial attack is presumably onto the metal as has been reported for the cation (**123**).[179]



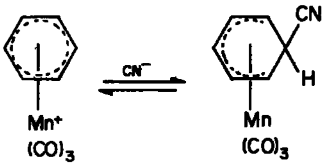


Evidence supporting the view that certain nucleophiles can give labile products from addition to unsaturated hydrocarbon ligands has been mentioned briefly above and may be further illustrated by the reversible reactions and rearrangements illustrated on page 3072.

6. *Applications of rule* 3

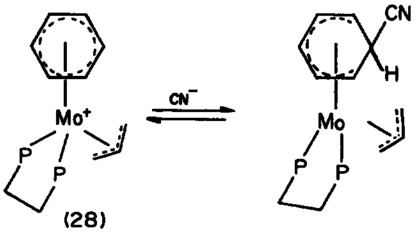
When the hydrocarbon ligand being attacked is *open* then it is necessary to apply Rule 3, since unlike the simple *closed* systems the carbon atoms are inequivalent. For the allyl ligand there are two possible positions of attack, i.e. at the terminal C atoms (C-1 or C-3) or at the centre C atom (C-2). As shown on page 3073 examples of both modes of addition have been observed.

It is possible to correlate the position of attack with the electron richness of the metal. When the metal is electron rich as in **10** and **11** the allyl ligand behaves more like () and the nucleophile attacks the carbon atom with the least electron density namely C-2. However when the metal is electron poor, by virtue of electron withdrawing ligands such as CO or NO, as in **78** and **118** the allyl ligand behaves as () and the nucleophile attacks C-1



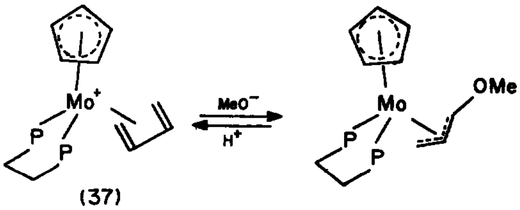
(67)

Ref. 180



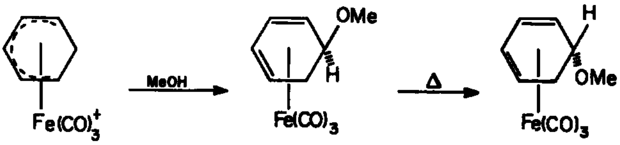
(28)

Ref. 30



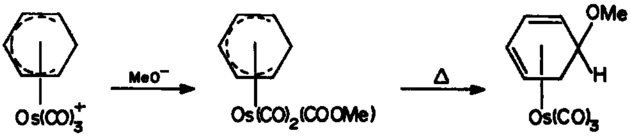
(37)

Ref. 37



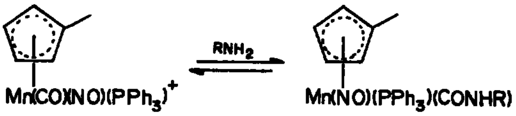
(85)

Ref. 124



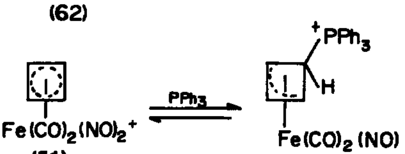
(91)

Ref. 57



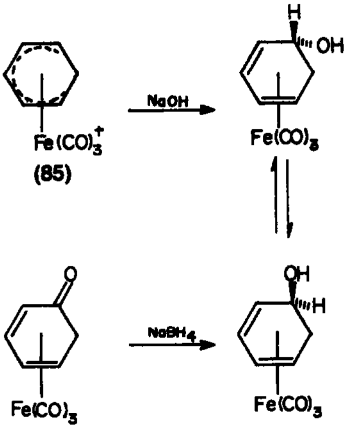
(62)

Ref. 74



(51)

Ref. 181



(85)

Ref. 109

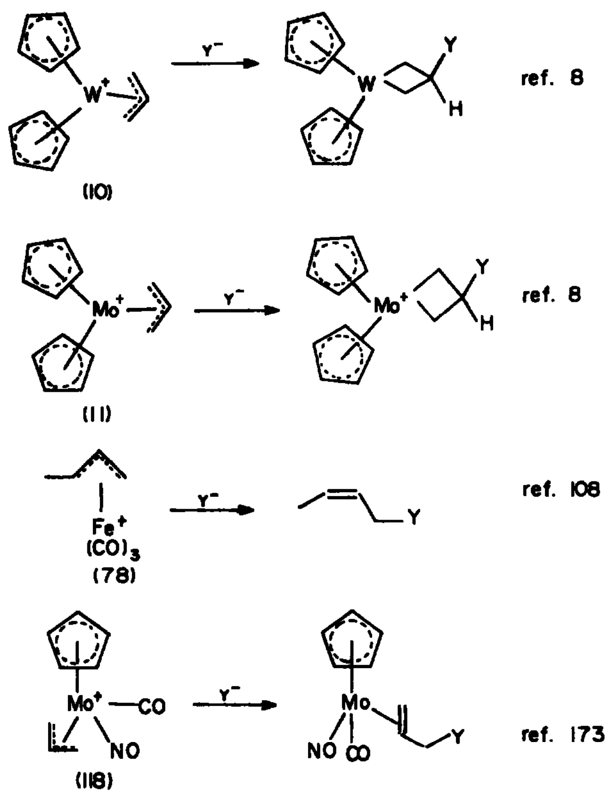
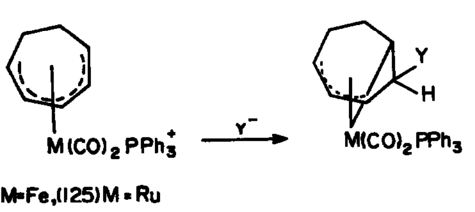


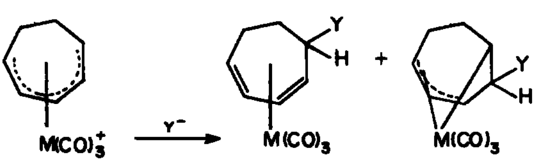
Fig. 4. Nucleophilic attack on organometallic cations containing the allyl ligand.

or C-3 since these are now the C atoms with the least electron density.

A similar situation arises for the pentadienyl ligands. Electron poor metals will be expected to lead to attack at C-1, C-3 or C-5 whereas for electron rich metals attack at C-2 or C-4 will be preferred. The examples shown below illustrate this.[134,135,148,149]



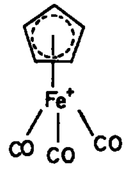
(98)M=Fe,(125)M=Ru



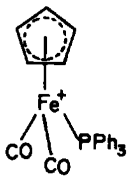
(93)M=Fe(100)M=Ru

Nucleophilic attack on the relatively electron rich compounds (98 and 125) preferentially occurs at C-2 whereas in the less electron rich compounds (93 and 100) a mixture of C-1 and C-2 products is observed.

Support for the assumption that exchange of a carbon monoxide ligand for triphenylphosphine increases the electron density on the metal is provided by CO IR frequency data. For compounds 98 $\nu_{co} = 2050$, 2007 cm^{-1},[135] 93 $\nu_{co} = 2100$, 2055 cm^{-1},[182] 52 $\nu_{co} = 2120$, 2070 cm^{-1},[183] and 53 $\nu_{co} = 2055$, 2010 cm^{-1}.[184] The shifts to lower wavenumbers can be related to an increase in the electron density at the metal.



(52)



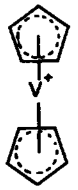
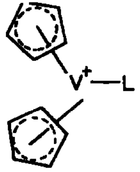
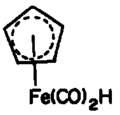
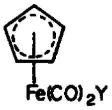
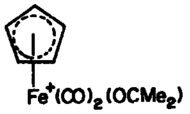
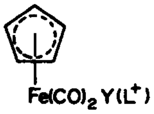
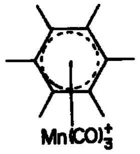
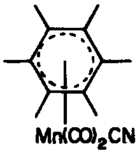
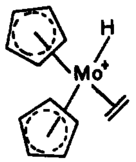
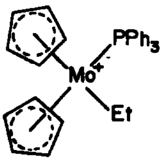
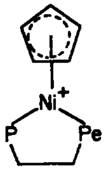
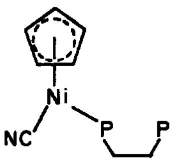
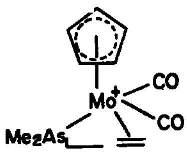
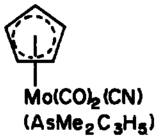
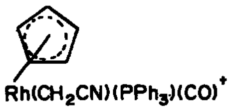
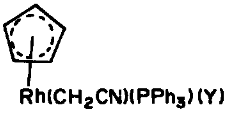
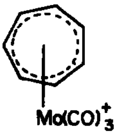
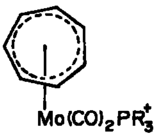
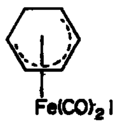
(53)

For *even open* ligands electron density will always tend to be least at the terminal C atoms and as expected attack always occurs there.

7. *Miscellaneous examples*

Table 4 lists some examples of organotransition metal cations that lead either to additon of the nucleophile to the metal or to ligand substitution. Addition to the metal occurs when the cation has 16 or fewer electrons. Ligand substitution occurs when the 18-electron cation can be readily converted to a 16-electron cation by dissociation of a 2-electron ligand. The nucleophile subsequently attacks the 16-electron intermediate cation giving the new 18 electron product.

Table 4. Nucleophilic addition to the metal and ligand substitution reactions of organotransition metal cations

CATION	NO	NUCLEOPHILE	PRODUCT	REF.
	126	L = H_2O, $(CH_3)_2CO$, C_5H_5N		185
	52	H^-		66
	127	$Y^- = Br^-$, N_3^-, SCN^-, NO_3^-		186
	128	$Y^- = NCS^-$, NO_3^- (L = PPh_3, Et_2S)		187
	29	CN^-		79
	130	PPh_3		188
	131	CN^-		189
	132	CN^-		190
	133	$Y^- = Cl^-$, SCN^-, $YSO_2^- = PhSO_2$		191
	75	PR_3		179
	85	I^-		119, 125

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