TILDEN LECTURE*

η^5-Cyclopentadienyl and η^6-Arene as Protecting Ligands towards Platinum Metal Complexes

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1 Introduction

One of the most interesting aspects of inorganic chemical research over the last 20 years has been the development of transition metal complexes as catalysts for useful organic reactions. These complexes, being soluble in the reaction medium, are termed *homogeneous* catalysts to distinguish them from the more traditional, insoluble, *heterogeneous* catalysts (platinum on carbon, rhodium on alumina, *etc.*).

Homogeneous catalysts have several advantages over heterogeneous ones: they have defined stoicheiometries and can be reproducibly synthesized, they can be 'tuned' to optimize selectivity and can give high rates. It is therefore important that a homogeneous catalyst remains homogeneous throughout the reaction and that any intermediates are not so unstable as to decompose irreversibly to metal.

Homogeneous catalytic reactions can be described in terms of a cyclic series of stoicheiometric reactions involving a variety of species, at least some of which contain metal–carbon bonds. Platinum metals and their complexes are extremely good catalysts for hydrogen-transfer reactions. This implies that in such a catalytic cycle some of the intermediates will be metal hydrides.

Such hydride and organometallic intermediates are highly reactive and hence very labile. The common side-reaction of decomposition to the metal can occur easily under reducing conditions and therefore metal complex catalysts normally bear some stabilizing ligands. Their primary function is to bind the metal strongly so that it can undergo the changes in oxidation state, ligation, stereochemistry, and co-ordination number that take place during the catalytic cycle without precipitating the metal.

A secondary but vital role that such ligands play is to influence the course of the reaction by their steric interactions with the incoming reactants. They may well exert electronic effects too, for example by stabilizing particular oxidation states and by stabilizing or labilizing other ligands.

The ligands most commonly used for this purpose have been tertiary phosphines, especially triphenylphosphine, as for example in the hydrogenation

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catalysts [$RhCl(PPh_3)_3$], [$RuHCl(PPh_3)_3$],[1] the hydroformylation catalyst [$RhH(CO)_2(PPh_3)_2$],[2] or the ethylene dimerization catalyst [$Ni(\eta^3\text{-}C_3H_5)Br(PPh_3)$] + [$Al_2Et_3Cl_3$].[3]

Although phosphines (and related σ-donor ligands such as tertiary arsines and phosphites) are very versatile and have many advantages, the development of other types of protecting groups is of considerable interest since they may be expected to extend the range of reactivity and selectivity even further.

Clearly many variations on the R_3P type of ligand are possible; for example R_2S, RCN, RNC, R_2Se, pyrazolylborate, R_3N, *etc.* However, these are all good σ-donors too and this review concentrates on organic π-ligands that are good π-acceptors [for example η^5-cyclopentadienyl (Cp) or η^6-arene (ArH)] and seeks to define the difference in chemical behaviour at the metal when one of these replaces an equivalent number of σ-donor ligands.*

The most important oxidation states for catalytic behaviour among the platinum metals seem to be those having d^6 or d^8 electron configuration. These are Ru^{II}, Os^{II}, Rh^{III}, Ir^{III}, and Pt^{IV} and Ru^0, Os^0, Rh^I, Ir^I, Pd^{II}, and Pt^{II} respectively. The known complexes are summarized in Table 1.

Table 1 *Survey of known* $\eta^5\text{-}C_5R_5$ *and* $\eta^6\text{-}C_6R_6$ *complexes*

d^8	Ru^0	Os^0	Rh^I	Ir^I	Pd^{II}	Pt^{II}
$\eta^6\text{-}C_6R_6$	√*	√*	√*	√*	—†	—†
$\eta^5\text{-}C_5R_5$	—	—	√	√	√†	√†
d^6	Ru^{II}	Os^{II}	Rh^{III}	Ir^{III}	[Pd^{IV}]	Pt^{IV}
$\eta^6\text{-}C_6R_6$	√	√	√	√	—	—
$\eta^5\text{-}C_5R_5$	√	√	√	√	—	√

*Some of the C_6R_6 complexes are η^4-bonded (bent-benzenes).
†Some dinuclear Pd^I and Pt^I complexes are also known; see below.

The reader may wonder why η^4-complexes of cyclic ligands, cyclobutadienes (or η^n-complexes of cyclic 'open' as compared to 'closed' polyenes or complexes of acyclic ligands) are not included. The answer is that these do not, in general, show the stability towards chemical reaction that the $\eta^5\text{-}C_5R_5$ or $\eta^6\text{-}C_6R_6$ show. For example, the complexes [$M_2Cl_4(\eta^n\text{-}C_nR_n)_2$] are isostructural for M = Ru, $n = 6$; M = Rh, $n = 5$; and M = Pd, $n = 4$. Nucleophilic attack at the ring is very difficult for the rhodium complex, is possible under forcing conditions for the benzene–ruthenium complex, but is very easy for the cyclobutadiene–palladium complex. Thus (1) with alkoxide gives the ethoxytetraphenylcyclobutenyl complex (2) while triphenylphosphine removes the cyclobutadiene

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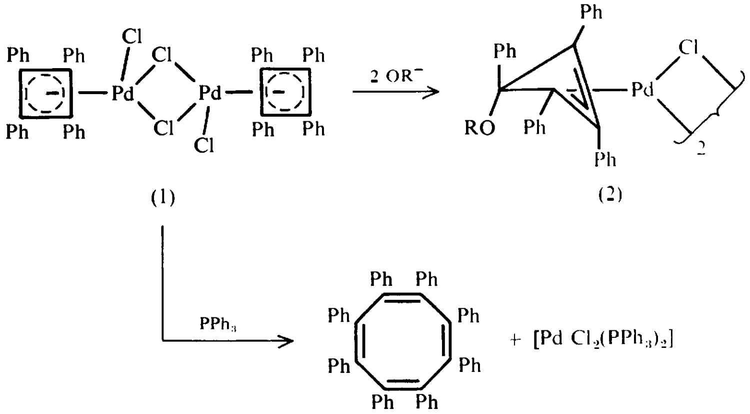
*η^6-Arene and η^5-cyclopentadienyl are formally equivalent to terdentate ligands and it may be helpful to point out that '$M(PPh_3)_2Cl$' is formally equivalent to 'M(Cp)', [and '$M(PPh_3)_3$' to '$M(C_6H_6)$'] and, for example, the repeating unit in hydrogenation catalysed by [$Rh(PPh_3)_3Cl$] is '$Rh(PPh_3)_2Cl$'.

[1] B. R. James, *Adv. Organomet. Chem.*, 1979, **17**, 319.

[2] R. L. Pruett, *Adv. Organomet. Chem.*, 1979, **17**, 1.

[3] B. Bogdanovic, *Adv. Organomet. Chem.*, 1979, **17**, 105.



(1)

(2)

altogether.[4,5] It is not clear to what extent this reactivity to nucleophiles exists in cyclobutadiene complexes of other metals since relatively few have been prepared. C_4Ph_4 has been shown[5] to be a good stabilizing ligand towards Co^I [and hence should be to Rh^I or Ir^I]; however, the unsubstituted cyclobutadiene in $[Rh(C_4H_4)(C_5H_5)]$ readily undergoes Friedel–Crafts acylation $[(MeCO)_2O\text{–}SnCl_4]$ to give $[Rh(C_4H_3COMe)(C_5H_5)]$.[6]

The position has been summarized by Davies *et al.* and a theoretical explanation offered for the results.[7] They suggest that (i) Y^- attacks preferentially at even co-ordinated polyenes, (ii) C_4R_4 is less readily attacked than other even polyenes but more readily than odd ones, and (iii) attack occurs at open polyenes in preference to closed ones. Thus one might anticipate the reactivity of L–M towards nucleophiles to be L = open polyene > C_6R_6 > C_4R_4 > C_5R_5. Therefore a cyclopentadienyl would be expected to be the least reactive and best stabilizing π-bonded ligand.

Evidence concerning the effect of substitution of the π-bonded ring on the stability and reactivity of the ligand is patchy and only qualitative. In comparing C_nH_n with C_nR_n it is clear that larger R increases the hindrance to attack at the metal and hence stabilizes the M–C_nR_n bond. However, the effect of varying R on the tendency for nucleophiles to add to C_nR_n is not obvious (see Section 3Bii*e*) but in a polyalkylated ligand, nucleophiles generally add at the unsubstituted point, *e.g.* pentamethylbenzene in (3) is attacked at the C–H to give the cyclohexadienyl complex (4).[8]

The situation can be much more complex. Thus, while the tetraphenyl complex (1) undergoes nucleophilic addition to give (2), the tetra-alkylcyclobutadiene (5) undergoes deprotonation with similar nucleophiles (alkoxide).[9] The key point, however, is that both ligands are reactive towards nucleophiles.

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[4] P. M. Maitlis, *Adv. Organomet. Chem.*, 1966, **4**, 95.

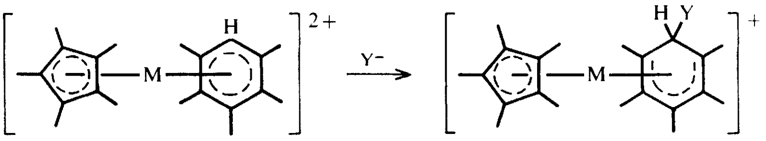
[5] A. Efraty, *Chem. Rev.*, 1977, **77**, 691.

[6] S. A. Gardner and M. D. Rausch, *J. Organomet. Chem.*, 1973, **56**, 365.

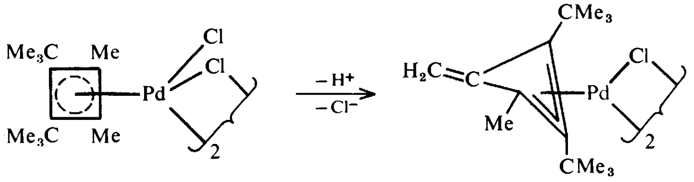
[7] S. G. Davies, M. L. H. Green, and D. M. P. Mingos, *Tetrahedron*, 1978, **34**, 3047.

[8] C. White and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1971, 3322.

[9] P. J. Ridgwell, S. N. Wetherell, E. A. Kelley, P. M. Bailey, and P. M. Maitlis, unpublished results.



(3) (4, M = Rh or Ir; Y = H or Me)



(5) (6)

2 Effect of Ring Substitution on Ring–Metal Bond Lengths

Too few data are as yet available to allow a comprehensive account of this problem to be given; in particular, only in recent years have routine *X*-ray structure studies of sufficient accuracy been carried out.

The most interesting results concern the Rh–C_5H_5 and Rh–C_5Me_5 complexes and are summarized in Table 2. From this it is clear that the metal to ring-carbon bond lengths for C_5H_5— and C_5Me_5— to rhodium [in the formal (+I) oxidation state] and C_5H_5 to rhodium [in the formal (+III) oxidation state] are all in the range 2.17—2.31 Å,* and that most are a little over 2.20 Å. This is equivalent to a perpendicular distance from Rh to the C_5R_5 plane of around 1.9 Å.

The C_5Me_5 carbon to rhodium bonds in complexes in which the metal has the formal oxidation state of (+III) are substantially shorter and lie in the range 2.11—2.21 Å, with a perpendicular distance of *ca.* 1.8 Å. If this were merely a reflection of the expected smaller radius of Rh^{III} by comparison to Rh^{I} then it should apply equally to the C_5H_5 complexes, but this does not seem to be the case.

The magnitude of the effect roughly parallels the electronegativity of the substituents on the other side of the C_5Me_5 ring, thus r(Rh–C) increases in the order $NO_3 \sim Cl < Br < I$. This means that in C_5Me_5–Rh complexes the ring–metal bonding can accommodate itself, in terms of electron-donor or acceptor properties, to a wide variety of ligand types and, in particular, that polar or hard ligands actually stabilize the C_5Me_5–Rh bonding. Thus, for example, one of the shortest mean Rh–C_5Me_5 bonds (2.115 Å) is in the tri-μ-hydroxo complex $[(RhC_5Me_5)_2(OH)_3]BPh_4$.[10]

Although data are scarcer, the same effects appear to occur in C_5Me_5–Ir complexes.† Thus, the perpendicular distances C_5Me_5–Ir in $[(IrC_5Me_5)_2X_4]$ are

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*In fact the bonding is in many cases rather distorted and reflects the asymmetry of ligand arrangements on the other side of the metal.

†Rh^{III} and Ir^{III} have effectively the same radius; for example, in $[(MC_5Me_5)_2X_4]$, the distances from metal to terminal halide are: 2.387 (Rh–Cl), 2.387 (Ir–Cl); 2.528 (Rh–Br), 2.519 (Ir–Br); and 2.706 (Rh–I), 2.694 (Ir–I).[11]

[10] M. R. Churchill, personal communication.

Table 2 *Mean values and ranges of distances from rhodium to carbon atoms and the distances from rhodium to the plane of the ring of cyclopentadienyl and pentamethylcyclopentadienyl complexes of rhodium* (I) *and of rhodium* (III)

$Rh^{I}–C_5H_5$ complexes	Rh–C(Cp) (*mean*)/Å	Rh–C(Cp) (*range*)/Å	Rh–Cp[a] Å	*Ref.*
$[Rh(C_5H_5)(C_{16}H_8Ph_2)]$	2.232	2.222—2.240(8)[b]	1.882	*c*
$[Rh(C_5H_5)(C_4Ph_4)]$	2.217	2.200—2.229(8)	1.868	*d*
$[Rh(C_5H_5)(C_2H_4)(C_2F_4)]$	2.223	2.171—2.252(6)	1.898	*e*
$[Rh(C_5H_5)(C_2H_4)(SO_2)]$	2.210	2.201—2.223(7)	1.882	*f*
		2.171—2.252		
$Rh^{I}–C_5Me_5$ complexes				
$[Rh(C_5Me_5)(PhCHCHCOCHCHPh)]$	2.222	2.196—2.237(6)	1.867	*g*
$[Rh(C_5Me_5)(C_4Ph_2HCPhC_5Ph_2H_2)]$	2.232	2.171—2.245(8)	1.848	*h*
$[Rh(C_5Me_5)(Ph_3P)(C_2H_4)]$	2.256	2.230—2.288(7)	1.911	*i*
		2.171—2.288		
$Rh^{III}–C_5H_5$ complexes				
$[Rh(C_5H_5)\{C_4(C_6F_5)_4\}(PPh_3)]$	2.261	2.238—2.286(12)	1.908	*j*
$[Rh_2(C_5H_5)_2(\mu\text{-}CPh_2)_2(\mu\text{-}CO)]$	2.290	2.266—2.312(11)	1.942	*k*
$[Rh(C_5H_5)(CO)(C_2F_5)(I)]$	2.25	2.23—2.26(3)	1.875	*l*
		2.23—2.31		

Rh^{III}–C_5Me_5 complexes				
$[Rh_2(C_5Me_5)_2Cl_4]$	2.128	2.116—2.140(4)	1.756	*m*
$[Rh_2(C_5Me_5)_2Br_4]$	2.146	2.117—2.167(7)	1.769	*n*
$[Rh_2(C_5Me_5)_2I_4]\cdot 2PhMe$	2.168	2.164—2.177(4)	1.779	*o*
$[Rh_2(C_5Me_5)_2(H)Cl_3]$	2.151	2.109—2.178(6)	1.777	*p*
$[(RhC_5Me_5)(O_2C_6H_4)]\cdot 2C_6H_4(OH)_2$	2.154	2.130—2.183(16)	1.763	*q*
$[(RhC_5Me_5)(NO_3)_2]$	2.127	2.121—2.137(4)	1.745	*r*
$[(RhC_5Me_5)(NO_3)_2(PPh_3)]$	2.182	2.161—2.207(4)	1.815	*r*
$[(RhC_5Me_5)_2(acac)_2][BF_4]_2$	2.158	2.140—2.171(6)	1.781	*s*
$[(RhC_5Me_5)(PhNHMe)][PF_6]_2$	2.175	2.166—2.192(18)	1.791	*t*
		2.109—2.207		

[a] Perpendicular distance, Rh to best plane of the C_5 carbons; [b] Estimated standard deviations in brackets; [c] M. D. Rausch, S. A. Gardner, E. F. Tokas, I. Bernal, G. M. Reisner, and A. Clearfield, *J. Chem. Soc., Chem. Commun.*, 1978, 187; [d] G. G. Cash, J. F. Helling, M. Mathew, and G. J. Palenik, *J. Organomet. Chem.*, 1973, **50**, 277; [e] L. J. Guggenberger and R. Cramer, *J. Am. Chem. Soc.*, 1972, **94**, 3779; [f] R. R. Ryan, P. G. Eller, and G. J. Kubas, *Inorg. Chem.*, 1976, **15**, 797; [g] J. A. Ibers, *J. Organomet. Chem.*, 1974, **73**, 389; [h] P. M. Bailey, K. I. Maruya, and P. M. Maitlis, unpublished results; [i] W. Porzio and M. Zocchi, *J. Am. Chem. Soc.*, 1978, **100**, 2048; [j] R. G. Gastinger, M. D. Rausch, A. Sullican, and A. Palenik, *J. Organomet. Chem.*, 1976, **117**, 355; [k] H. Ueda, Y. Kai, N. Yasuoka, and N. Kasai, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2250; [l] M. R. Churchill, *Inorg. Chem.*, 1965, **4**, 1734; [m] M. R. Churchill, S. A. Julis, and F. J. Rotella, *Inorg. Chem.*, 1977, **16**, 1137; [n] M. R. Churchill and S. A. Julis, *Inorg. Chem.*, 1979, **18**, 2918; [o] M. R. Churchill and S. A. Julis, *Inorg. Chem.*, 1979, **18**, 2918; [p] M. R. Churchill and S. W. Y. Ni, *J. Am. Chem. Soc.*, 1973, **95**, 2150; [q] P. Espinet, P. M. Bailey, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1979, 1542; [r] M. Hursthouse, K. M. Malik, M. Mingos, and S. Willoughby, *J. Organomet. Chem.*, 1980, **192**, 235; [s] W. Rigby, H.-B. Lee, P. M. Bailey, J. A. McCleverty, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1979, 387; [t] P. Espinet, P. M. Bailey, R. F. Downey, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1980, 1048.

1.801 (X = I), 1.771 (X = Br), and 1.756 Å (X = Cl),[11] close to those of the corresponding rhodium complexes.

It is interesting how little effect other ring substituents have in C_5R_5 complexes of Rh^I. Thus the C_5Cl_5 and the C_5Ph_4Cl ring–metal distances in $[Rh^I(\eta^5\text{-}C_5Cl_5)(1,5\text{-}C_8H_{12})]$ and $[Rh^I(\eta^5\text{-}C_5Ph_4Cl)(C_2H_4)_2]$ lie in the very normal ranges of 2.211—2.281(4) and 2.183—2.305(4) Å and have mean values of 2.260 and 2.262 Å respectively.[12]

Haaland[13] has summarized the effect of alkylation on the structures of the 3*d* metallocenes $[M(C_5R_5)_2]$ (M = Mn, Fe, and Co). There is no detectable change of M–C bond distance in these compounds when R = H and Me are compared. However, C_5Me_5 is a much stronger field ligand than C_5H_5, and $[Mn(C_5Me_5)_2]$ is in a low-spin ($^2E'_2$) whereas $[Mn(C_5H_5)_2]$ is in a high-spin state ($^6A'_1$). The shorter Mn–C bond in the former arises from the smaller size of low-spin Mn^{II}.

The effect seems to be confined to complexes containing hard ligands, with the metal, therefore, in an intermediate oxidation state. Further careful *X*-ray studies, for example on arene–Ru^{II} complexes, would be of considerable interest.

Another variation is the use of the indenyl (benzcyclopentadienyl) ligand. In principle this ligand can bond either η^3- or η^5- (or even η^6- to the benz-ring) and this should allow some unusual chemistry to take place. In fact, a crystal structure of an indenyl–rhodium(I) complex shows that the bonding is between η^3- and η^5-, with three short Rh–C bonds (2.176, 2.179, and 2.190 Å) and two long ones (2.312 and 2.319 Å) to the carbons of the five-membered ring.[14]

3 Cyclopentadienyl Complexes

A. Ruthenium and Osmium.—The half-sandwich complexes are of the type $[(MC_5R_5)L^1L^2X]$ where R is usually H, X is often Cl or another uninegative ligand, and L^1 and L^2 are neutral ligands, *e.g.* PR_3 and CO. The complexes $[(MCp)_2(CO)_4]$ (7) were originally made by reaction of CpNa with $[Ru(CO)_2I_2]$ or $[Os(CO)_3Cl_2]$;[15] more recent methods include:

$$C_5H_6 + [Ru_3(CO)_{12}] \rightarrow [(RuCp)_2(CO)_4]^{16}$$

(7*a*)

$$TlCp + [Ru_2(CO)_6Cl_4] \rightarrow [(RuCp)_2(CO)_4]^{17}$$

$$C_5H_6 + PPh_3 + RuCl_3 \text{ or } H_2[OsBr_6] \rightarrow [(MCp)(PPh_3)_2X]^{18}$$

(8)

$$C_5H_6 + [Os(PPh_3)_3Br_2] \rightarrow [(OsCp)(PPh_3)_2Br]^{19}$$

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[11] M. R. Churchill and S. A. Julis, *Inorg. Chem.*, 1979, **18**, 1215, 2918.

[12] V. W. Day, K. J. Reimer, and A. Shaver, *J. Chem. Soc., Chem. Commun.*, 1975, 403.

[13] A. Haaland, *Acc. Chem. Res.*, 1979, **12**, 415.

[14] P. Caddy, M. Green, E. O'Brien, L. E. Smart, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1980, 962.

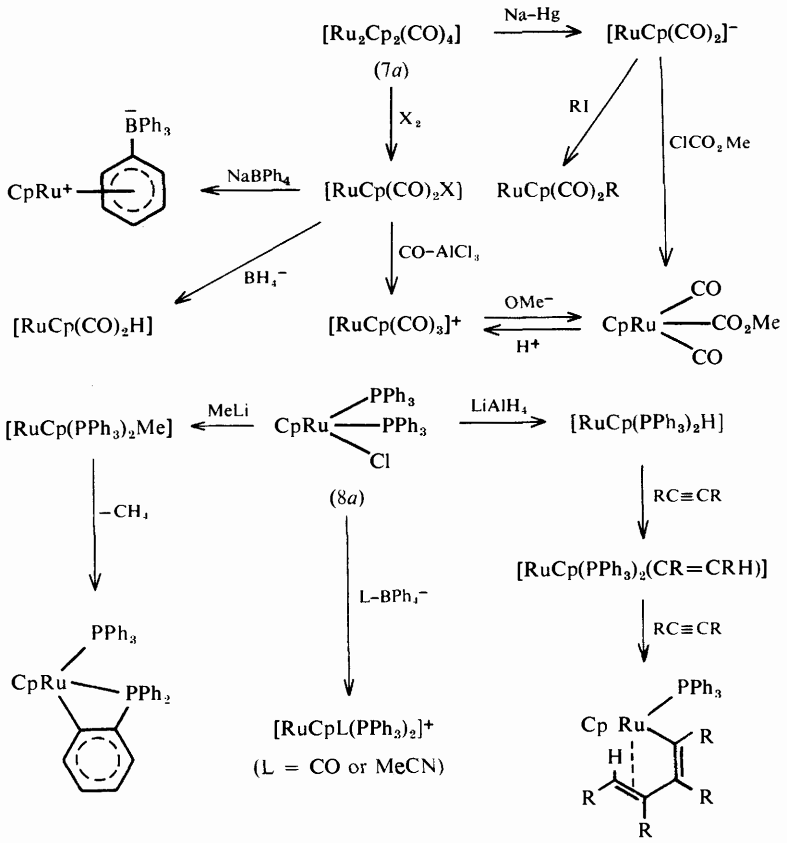
[15] E. O. Fischer and A. Vogler, *Z. Naturforsch., Teil B*, 1962, **17**, 421; E. O. Fischer and K. Bittler, *ibid.*, 1962, **17**, 274.

[16] A. P. Humphries and S. A. R. Knox, *J. Chem. Soc., Dalton Trans.*, 1975, 1710.

[17] T. Blackmore, J. D. Cotton, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1968, 2931.

[18] M. I. Bruce and N. J. Windsor, *Aust. J. Chem.*, 1977, **30**, 1601.

[19] T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1971, 2376.



Scheme 1

The carbonyls in the ruthenium complex (*7a*) are fluxional[20,21] but the osmium analogue (*7b*) appears to be static, with all the carbonyls terminal.[20] The M–M bond in (7) can be broken, for example by halogen,[22,23] to give $[(MCp)(CO)_2X]$; only one CO is easily replaced by phosphines but the alternative routes to the phosphine complexes (8) listed now make these readily available. An extensive series of reactions occur with these complexes and some[19,22–27] are depicted in

[20] R. D. Fischer and A. Vogler, *Angew. Chem.*, 1965, **77**, 724.

[21] J. G. Bullitt, F. A. Cotton, and T. J. Marks, *Inorg. Chem.*, 1972, **11**, 671.

[22] A. Davison, J. A. McCleverty, and G. Wilkinson, *J. Chem. Soc.*, 1963, 1133.

[23] R. J. Haines and A. L. Du Preez, *J. Am. Chem. Soc.*, 1971, **93**, 2820.

[24] A. E. Kruse and R. J. Angelici, *J. Organomet. Chem.*, 1970, **24**, 231.

[25] T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1974, 106.

[26] M. I. Bruce, R. C. F. Gardner, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1976, 81.

[27] R. J. Haines and A. L. du Preez. *J. Organomet. Chem.*, 1975, **84**, 357.

Scheme 1; it appears, however, that little chemistry has been tried on such systems in the absence of at least one additional stabilizing ligand (CO or PPh_3).

An interesting indication of what else may be possible is the synthesis of the Ru^{IV} tribromide complex (9), stabilized by peralkylcyclopentadienyl.[28]

$$[(RuC_5Me_4Et)(CO)_2Br] + Br_2 \rightarrow \underset{(9)}{[(RuC_5Me_4Et)(CO)Br_3]}$$

B. Rhodium and Iridium.—(i) *Preparation.* The classical route uses sodium cyclopentadienide and a suitable chloro-rhodium or -iridium precursor:[29–31]

$$[\{RhCl(1,5\text{-}C_8H_{12})\}_2] + 2NaCp \rightarrow [(RhCp)(1,5\text{-}C_8H_{12})]$$

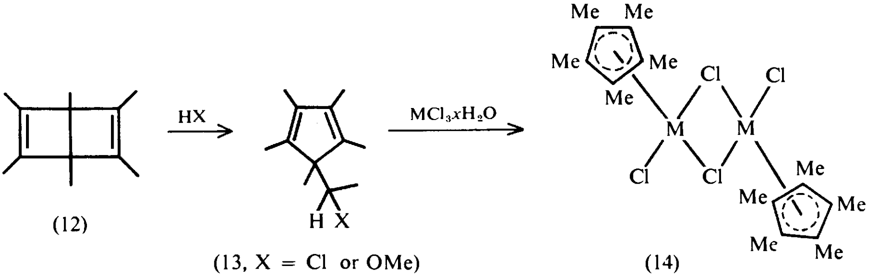
$$[\{RhCl(CO)_2\}_2] + 2NaCp \rightarrow \underset{(10)}{[(RhCp)(CO)_2]}$$

$$[IrCl(CO)_3] + 2NaCp \rightarrow \underset{(11)}{[(IrCp)(CO)_2]}$$

An alternative method for the preparation of more sensitive compounds uses cyclopentadienylthallium, *e.g.*[32]

$$[\{RhCl(\eta^3\text{-}C_3H_5)_2\}_2] + 2TlCp \rightarrow [(RhCp)(\eta^3\text{-}C_3H_5)(\eta^1\text{-}C_3H_5)]$$

The peralkylated cyclopentadienyl complexes can be prepared from the cyclopentadiene and $RhCl_3$ hydrate.[33,34] A more convenient preparation of the pentamethylcyclopentadienyl complexes (14) is from hexamethyl 'Dewar' benzene {hexamethylbicyclo[2.2.0]hexadiene, (12)}.[35,36] This latter reaction proceeds *via* an initial acid-catalysed ring contraction to (13). The M^{III} complexes (14) can be reduced to formally five-co-ordinate M^{I} complexes; for example:[35]



(12)

(13, X = Cl or OMe)

(14)

$$\underset{(14b)}{[(IrC_5Me_5)_2Cl_4]} + CO \xrightarrow{Na_2CO_3\text{-}EtOH} [(IrC_5Me_5)(CO)_2]$$

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[28] I. W. Nowell, K. Tabatabaian, and C. White, *J. Chem. Soc., Chem. Commun.*, 1979, 547.

[29] J. Chatt and L. M. Venanzi, *Nature (London)*, 1956, **177**, 852; *J. Chem. Soc.*, 1957, 4735.

[30] E. O. Fischer and K. Bittler, *Z. Naturforsch., Teil B*, 1961, **16**, 225.

[31] E. O. Fischer and K. Brenner, *Z. Naturforsch., Teil B*, 1962, **17**, 774.

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[33] B. L. Booth, R. N. Haszeldine, and M. Hill, *J. Chem. Soc. (A)*, 1969, 1299.

[34] T. Dooley, G. Fairhurst, C. D. Chalk, K. Tabatabaian, and C. White, *Transition Met. Chem.*, 1978, **3**, 299.

[35] J. W. Kang, K. Moseley, and P. M. Maitlis, *J. Am. Chem. Soc.*, 1969, **91**, 5970.

[36] B. L. Booth, R. N. Haszeldine, and M. Hill, *J. Organomet. Chem.*, 1969, **16**, 491.

Conversely, the $\mathrm{M^I}$ complexes can be oxidized to $\mathrm{M^{III}}$:

$$[(\mathrm{IrC_5Me_5})(\mathrm{CO})_2] + \mathrm{I_2} \text{ or } \mathrm{EtI} \rightarrow [(\mathrm{IrC_5Me_5})(\mathrm{CO})\mathrm{I_2}]^{37,38}$$

$$[(\mathrm{MCp})(\mathrm{diene})] + \mathrm{I_2} \rightarrow [\{(\mathrm{MCp})\mathrm{I_2}\}_n]^{39,40}$$

However, for Rh–Cp complexes, cleavage of the ring is easy:[41]

$$2[(\mathrm{RhCp})(\mathrm{CO})(\mathrm{PPh_3})] + 2\mathrm{HCl} \rightarrow [\{\mathrm{Rh}(\mathrm{CO})(\mathrm{PPh_3})\mathrm{Cl}\}_2] + 2\mathrm{CpH}$$

(ii) *Properties.* Since the aim of this review is to elaborate on the type of chemistry that is possible at the metal, using $\mathrm{C}_n\mathrm{R}_n$ as a protecting group, the reactions of the $\mathrm{C_5R_5}$–rhodium and –iridium complexes will be developed in relation to the appropriate liganding atom, beginning with H, hydride.

(*a*) *Hydride complexes.* Mononuclear hydrides of two types are known, *i.e.* $[(\mathrm{MCp})\mathrm{LL'H}]^+$ and $[(\mathrm{MCp})\mathrm{LXH}]$. The former arise by protonation of $[(\mathrm{MCp})\mathrm{LL'}]$; since these complexes are very strong bases, a serendipitous protonation sometimes occurs. The overall reaction is equivalent to an oxidative addition $\mathrm{M^I} \rightarrow \mathrm{M^{III}}$:

$$[(\mathrm{MCp})(\mathrm{CO})(\mathrm{PR_3})] + \mathrm{HCl} \rightarrow [(\mathrm{MCp})(\mathrm{CO})\mathrm{H}(\mathrm{PR_3})]\mathrm{Cl}^{41,42,43}$$

An interesting variant on this reaction occurs when one ligand is η^2-ethene[43,44] and there is a ligand-migration of the hydride onto the co-ordinated ethene to give a σ-ethyl complex:

$$\begin{tikzcd} {[(\mathrm{RhCp})(\mathrm{L})(\mathrm{C_2H_4})] + \mathrm{H}^+} \arrow[r] & {[(\mathrm{RhCp})(\mathrm{H})\mathrm{C_2H_4}(\mathrm{L})]^+} \arrow[d] \\ {[(\mathrm{RhCp})(\mathrm{C_2H_5})\mathrm{LX}]} & {[(\mathrm{RhCp})(\mathrm{C_2H_5})\mathrm{L}]^+} \arrow[l, "\mathrm{X}^-"'] \end{tikzcd}$$

$$(\mathrm{L} = \mathrm{PMe_3} \text{ or } \mathrm{C_2H_4})$$

The neutral complexes [MCpLXH] arise by cleavage of dinuclear hydrides,[45] or by oxidative addition of HX;[46] for example:

$$\underset{(16)}{[(\mathrm{IrC_5Me_5})_2(\mu\text{-}\mathrm{H_2})\mathrm{Cl_2}]} + 2\mathrm{L} \rightarrow [(\mathrm{IrC_5Me_5})\mathrm{H}(\mathrm{Cl})\mathrm{L}]$$

$$[(\mathrm{RhCp})(\mathrm{CO})_2] + \mathrm{R_3SiH} \xrightarrow{h\nu} [(\mathrm{RhCp})\mathrm{CO}(\mathrm{H})(\mathrm{SiR_3})]$$

In the absence of extra ligands, hydrides show a strong tendency to bridge metal atoms; this is especially noticeable in the $\mathrm{C_5Me_5}$ complexes. For example,

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[37] J. W. Kang and P. M. Maitlis, *J. Organomet. Chem.*, 1971, **26**, 393.

[38] R. B. King and A. Efraty, *J. Organomet. Chem.*, 1971, **27**, 409.

[39] R. J. Angelici and E. O. Fischer, *J. Am. Chem. Soc.*, 1963, **85**, 3733.

[40] H. Yamazaki, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 582.

[41] F. Faraone, C. Ferrara, and E. Rotondo, *J. Organomet. Chem.*, 1971, **33**, 221.

[42] F. Faraone, R. Pietropaolo, G. G. Troilo, and P. Piraino, *Inorg. Chim. Acta*, 1973, **7**, 729.

[43] H. Werner and R. Feser, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 157.

[44] R. Cramer, *J. Am. Chem. Soc.*, 1965, **87**, 4717; L. P. Seiwell, *Inorg. Chem.*, 1976, **15**, 2560.

[45] D. S. Gill and P. M. Maitlis, *J. Organomet. Chem.*, 1975, **87**, 359.

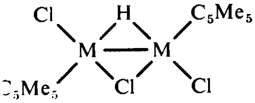
[46] A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, 1971, **10**, 1.

the complexes (15*a*, M = Rh) and (15*b*, M = Ir) are formed when the chlorides (14*a*) and (14*b*) are treated with hydrogen and base, or borohydride, or propan-2-ol and base;[47–49] under more vigorous conditions, for iridium, the complexes (16)[45] and (17)[47,50] form readily.

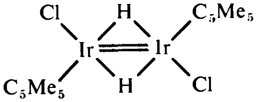
Carboxylate complexes derived from (14) activate hydrogen directly without base to give the μ-hydrido complexes (18);[47] di-μ-hydrido complexes (19) are also easily formed.[47,51]

The μ-hydrido complexes (15*a*) and (15*b*) react stoicheiometrically with dienes to give π-allylic complexes (21) initially; in some cases (Section 3Bii*e*) these can eliminate HCl to give the M^{I} diene complexes.[52]

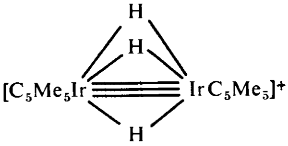
Kinetic studies[53] indicated that the rate-determining step is independent both



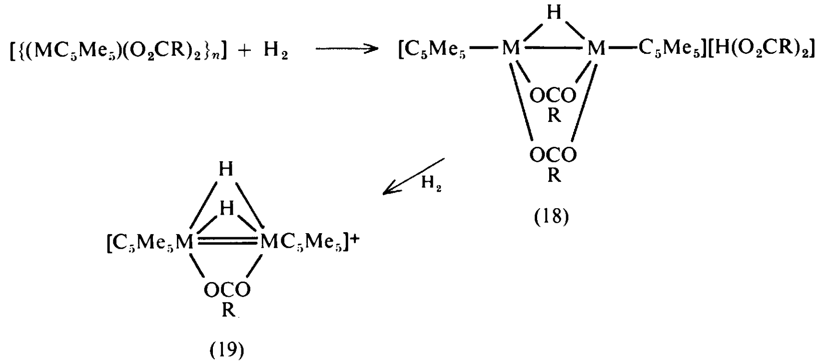
(15*a*, M = Rh)
(15*b*, M = Ir)

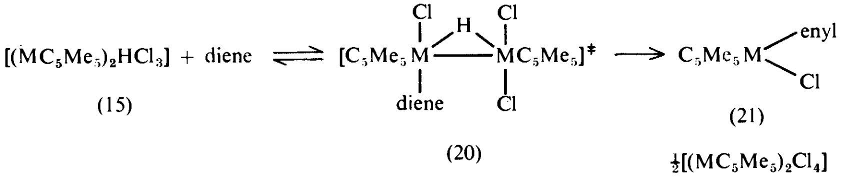


(16)



(17)





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[47] C. White, A. J. Oliver, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1973, 1901.

[48] M. R. Churchill and S. W. Y. Ni, *J. Am. Chem. Soc.*, 1973, **95**, 2150.

[49] M. R. Churchill, S. A. Julis, and F. J. Rotella, *Inorg. Chem.*, 1977, **16**, 1137.

[50] R. Bau, W. E. Carroll, R. G. Teller, and T. F. Koetzle, *J. Am. Chem. Soc.*, 1977, 99, 3872.

[51] A. Nutton, P. M. Bailey, and P. M. Maitlis, unpublished results.

[52] H. B. Lee and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1975, 2316.

[53] H. B. Lee, K. Moseley, C. White, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1975, 2322.

of the concentration and the nature of the diene and involves the opening of a M—Cl—M bridge to create a vacant site at which the diene can co-ordinate prior to further (fast) hydrogen-transfer.

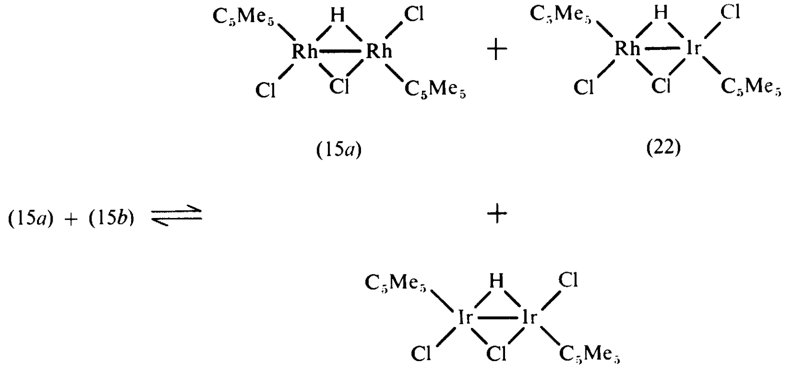
The inertness of the M—H—M bridge which the transition state (20) implies is at first surprising. However, *X*-ray studies show that the hydrides act as very strong binders and have the effect of 'glueing' the two metal atoms together. Thus Table 3 shows that the metal-metal separation decreases quite markedly as the number of bridging hydrides increases until the limit is reached in (17). This implies that a significant degree of metal-metal bonding is present in each of these bridged hydrides; indeed (17) has been described as containing a 'triply protonated iridium—iridium triple bond'.[50]

Although the bridged hydrides are not highly reactive they do undergo a number of interesting reactions. One such is the equilibration of (15*a*) and (15*b*) to give the mixed hydride (22) and (15*a*) and (15*b*) in the statistically expected ratio of 2:1:1.[47]

Table 3 *Metal-metal separations in some dinuclear* C_5Me_5–Rh *and* –Ir *complexes*

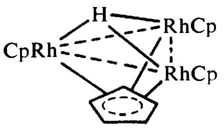
Complex	M···M/Å	*Ref.*
$[Rh_2(C_5Me_5)_2Cl_4]$ (14*a*)	3.719(1)	*a*
$[Ir_2(C_5Me_5)_2Cl_4]$ (14*b*)	3.769(1)	*a*
$[Rh_2(C_5Me_5)_2HCl_3]$ (15*a*)	2.906(1)	*b*
$[Ir_2(C_5Me_5)_2HCl_3]$ (15*b*)	2.903(1)	*c*
$[Ir_2(C_5Me_5)_2H(OCOCF_3)_2]^+$	3.02	*d*
$[Rh_2(C_5Me_5)_2H_2(OAc)]^+$ (19)	2.681(1)	*d*
$[Ir_2(C_5Me_5)_2H_3]^+$ (17)	2.455(1)	*e*

[a] M. R. Churchill and S. A. Julis, *Inorg. Chem.*, 1979, **18**, 1215, 2918; [b] M. R. Churchill and S. W. Y. Ni, *J. Am. Chem. Soc.*, 1973, **95**, 2150; [c] M. R. Churchill, S. A. Julis, and F. J. Rotella, *Inorg. Chem.*, 1977, **16**, 1137; [d] P. M. Bailey and P. M. Maitlis, unpublished results; [e] R. Bau, W. E. Carroll, R. G. Teller, and T. F. Koetzle, *J. Am. Chem. Soc.*, 1977, **99**, 3872.

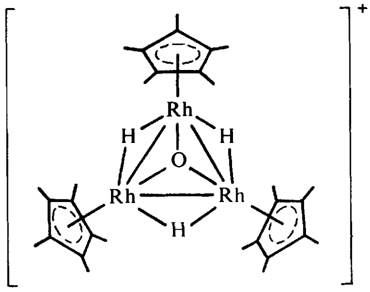


(15*a*) (22)

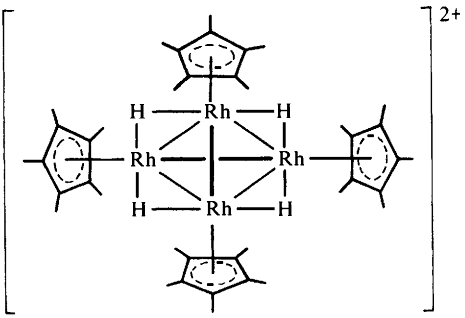
(15*b*)



(23)



(24)



(25)

In addition to the mono- and di-nuclear hydrides a number of cluster hydrides are also known. The curious but very stable complex $[Rh_3Cp_3(\mu_3\text{-}Cp)(\mu_3\text{-}H)]$ (23) was obtained as a by-product from the reaction of $RhCl_3$ and MgCpBr in ether–benzene.[54]

Similarly stable are the trinuclear and tetranuclear clusters (24)[55] and (25)[56] which were recently obtained from $[(RhC_5Me_5)_2(OH)_3]^+$ with either hydrogen in water or propan-2-ol and water. Indeed, not only are these complexes rather inert in a chemical sense, but they are also very rigid. The barrier to movement of the hydrides in (24) is at least 21 kcal mol^{-1}.[55] The hydrogens bridge Rh–Rh edges in (24) but their exact position in the distorted tetrahedron in (25) is not so clear; it was originally believed that they were bridging the longer edges[56] but recent n.m.r. results[57] have brought this interpretation into question.

One characteristic feature of the chemistry of the platinum metals is their ability to move hydrogen, both between organic substrates and between mole-

[54] E. O. Fischer, O. S. Mills, E. F. Paulus, and H. Wawersik, *Chem. Commun.*, 1967, 643.

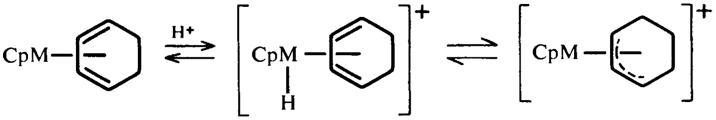
[55] A. Nutton, P. M. Bailey, N. C. Braund, R. J. Goodfellow, R. S. Thompson, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1980, 631; A. Nutton, P. M. Bailey, and P. M. Maitlis, *J. Organomet. Chem.*, in the press.

[56] P. Espinet, P. M. Bailey, P. Piraino, and P. M. Maitlis, *Inorg. Chem.*, 1979, **18**, 2706.

[57] R. J. Goodfellow, personal communication.

cular hydrogen and organic ligands. Metal hydrides are always implicated in these reactions even though they may sometimes remain undetected. The C_5Me_5–Rh and –Ir complexes are very adept at carrying out such reactions catalytically and these are discussed below. However, a group of stoicheiometric hydrogen-transfer reactions involving protonated diene complexes should be mentioned.[58–63] Typical is the reaction sequence (26) ⇌ (27) ⇌ (28);[58] labelling studies show that all the cyclohexadiene hydrogens *endo* to the metal exchange with added acid. The intermediate hydride (27) can usually be observed only for M = Ir. With cyclo-octatetraene acting as the diene the reactions are more complex, and a bicyclic cation (30) is intermediate in the formation of (31) from (29). Again, a hydride [precursor to (30)] can be observed in the n.m.r. spectrum for the iridium complexes.[60,61]

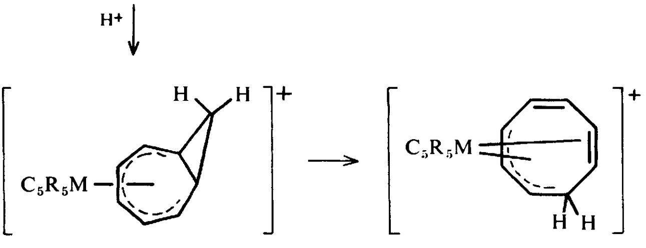
(*b*) *Carbonyl complexes.* All the mononuclear carbonyls have been made. The ν(CO) are 1987, 2051 for $[RhCp(CO)_2]$;[30] 1957, 2037 for $[IrCp(CO)_2]$;[31] 1965, 2020 for $[(RhC_5Me_5)(CO)_2]$;[37] and 1925, 2000 cm^{-1} for $[(IrC_5Me_5)(CO)_2]$.[35] As expected, the more electron-releasing C_5Me_5 ligand causes the ν(CO) to come at lower frequency.



(26) (27) (28)

$C_5R_5M(\eta^4\text{-}C_8H_8)$

(29)



(30) (31)

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[58] B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *J. Chem. Soc., Dalton Trans.*, 1972, 2084.
[59] J. Evans, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1972, 2668.
[60] J. Evans, B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *J. Chem. Soc., Dalton Trans.*, 1974, 2375.
[61] A. K. Smith and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1976, 1773.
[62] J. Evans, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1977, 510.
[63] L. A. Oro, *Inorg. Chim. Acta*, 1977, **21**, L6.

One carbonyl is easily replaced by a phosphite or phosphine,[64] and both the dicarbonyl and the monocarbonyl-monophosphine complexes readily undergo oxidative addition:

$$[(MC_5R_5)(CO)_2] + X\text{–}Y \rightarrow [(MC_5R_5)(CO)(X)(Y)]$$

M = Rh, R = H, X = C_nF_{2n+1}, Y = I[65]
M = Rh, R = H, X = Y = I[66]
M = Rh, R = H, X = H, Y = SiR_3[46]
M = Ir, R = Me, X = C_nF_{2n+1}, Y = I[38]
M = Rh, R = H, X = Y = SR[67]

Only the lower alkyl halides and those that are activated react; in this case oxidative addition is often followed by a fast alkyl migration onto carbonyl to give the acyl:

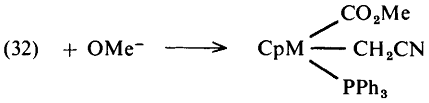
$$[(M(Cp)(CO)L] + R^1X \rightarrow [(MCp)(CO)R(L)]^+X^- \rightarrow [(MCp)(COR)(L)X]$$

M = Rh or Ir, L = PMe_2Ph or PPh_3, R^1 = Me or Et, X = I[68,69]
M = Rh, L = PPh_3, R = benzyl, X = Cl, Br, or I[70]

$[(RhC_5Me_5)(CO)_2]$ reacts with methyl iodide to give $[(RhC_5Me_5)(COMe)(CO)I]$;[37] the iridium analogue reacts to give either $[(IrC_5Me_5)(CO)_2Me]^+I^-$ [37] or a mixture of $[(IrC_5Me_5)(CO)(Me)(I)]$ and $[Ir(C_5Me_5)(CO)I_2]$,[38] depending on the conditions. No methyl migration onto CO was observed here. The ease of oxidative addition to Rh^I is greater for $[(RhCp)(PR_3)(CO)]$ than for $[(RhCp)(CO)_2]$ and both are more difficult to add to than is $[Rh(PPh_3)_3Cl]$.[41]

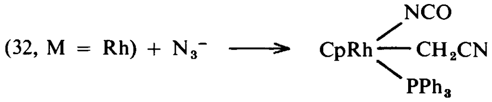
$$[(MCp)(PPh_3)(CO)] + ClCH_2CN \longrightarrow [(MCp)(PPh_3)(CO)(CH_2CN)]^+$$

(32)



$$(32) + OMe^- \longrightarrow CpM(CO_2Me)(CH_2CN)(PPh_3)$$

(33)



$$(32, M = Rh) + N_3^- \longrightarrow CpRh(NCO)(CH_2CN)(PPh_3)$$

(34)

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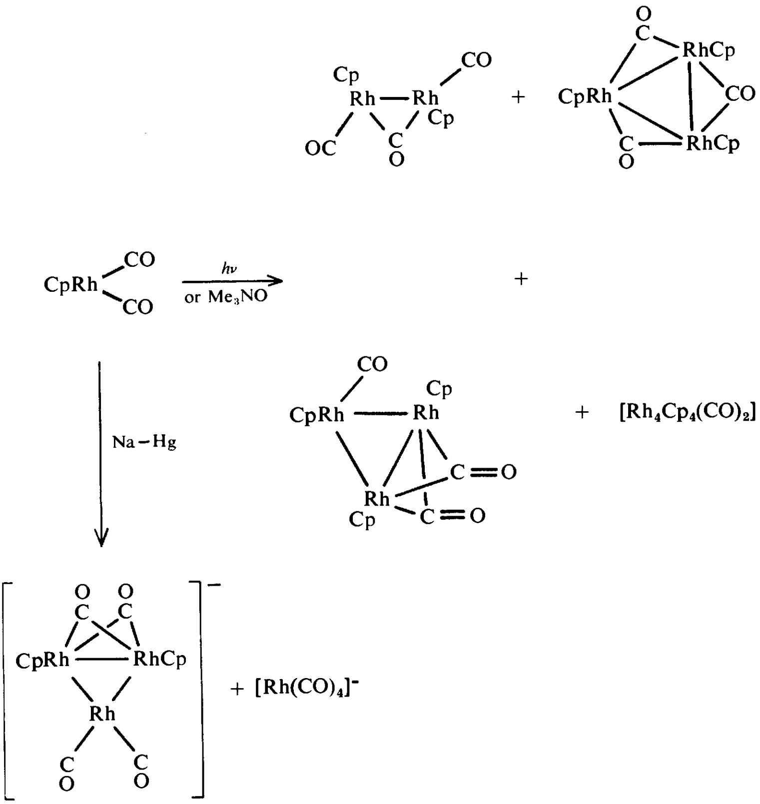
[64] H. Neukomm and H. Werner, *Helv. Chim. Acta*, 1979, **57**, 1067.
[65] J. A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, 1964, 4200.
[66] R. B. King, *Inorg. Chem.*, 1966, **5**, 82.
[67] N. G. Connelly, G. A. Johnson, B. A. Kelly, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1977, 436.
[68] A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, 1970, **9**, 243, 2653.
[69] A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.*, 1970, **9**, 2658.
[70] A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.*, 1971, **10**, 1653.



Scheme 2

Chloroacetonitrile oxidatively added to $[(MCp)(CO)(PPh_3)]$ to give (32), which reacted with methanol to give (33) and with azide to form the cyanate complex (34).[71]

$[(RhCp)(CO)_2]$ easily forms di-, tri-, and tetra-nuclear clusters (Scheme 2) on irradiation, on treatment with Me_3NO, or with sodium amalgam.[72–79] The

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[71] F. Faraone, F. Cusmano, P. Piraino, and R. Pietropaolo, *J. Organomet. Chem.*, 1972, **44**, 391.

[72] E. F. Paulus, E. O. Fischer, H. P. Fritz, and H. Schuster-Woldan, *J. Organomet. Chem.*, 1967, **10**, P3; E. F. Paulus, *Acta Crystallogr., Sect. B*, 1969, **25**, 2206.

[73] O. S. Mills and E. F. Paulus, *J. Organomet. Chem.*, 1967, **10**, 331.

[74] O. S. Mills and J. P. Nice, *J. Organomet. Chem.*, 1967, **10**, 337.

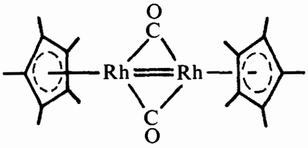
[75] J. Evans, B. F. G. Johnson, J. Lewis, and J. R. Norton, *J. Chem. Soc., Chem. Commun.*, 1975, 79.

[76] J. Evans, B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J. Chem Soc., Chem. Commun.*, 1975, 576.

[77] R. J. Lawson and J. R. Shapley, *J. Am. Chem. Soc.*, 1976, **98**, 7433.

[78] R. J. Lawson and J. R. Shapley, *Inorg. Chem.*, 1978, **17**, 772.

[79] W. D. Jones, M. A. White, and R. G. Bergman, *J. Am. Chem. Soc.*, 1978, **100**, 6770.



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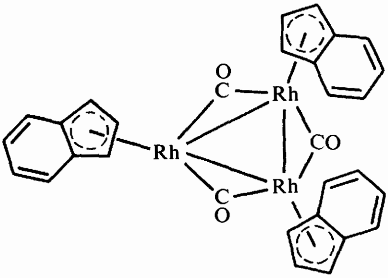

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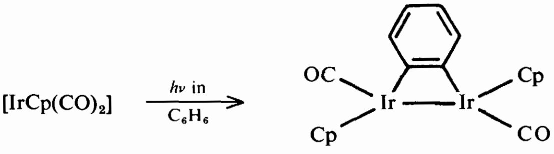

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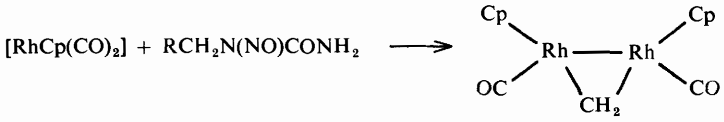
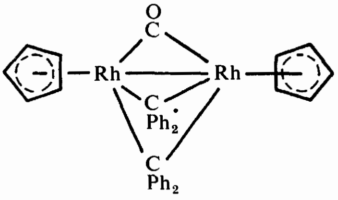


(38)



(39)

structures of all except the tetranuclear cluster have been determined[72–74,79] and mechanisms have been proposed for the fluxional processes that the neutral di-and tri-nuclear complexes undergo.[75–78]

$[(RhC_5Me_5)(CO)_2]$ forms the blue dinuclear carbonyl (35) on heating,[80] while [Rh(indenyl)$(CO)_2$] gives the trinuclear carbonyl (36).[81]

Irradiation of $[(IrCp)(CO)_2]$ in benzene gives the dinuclear *ortho*-phenylene

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[80] A. Nutton and P. M. Maitlis, *J. Organomet. Chem.*, 1979, **166**, C21.

[81] P. Caddy, M. Green, E. O'Brien, L. E. Smart, and P. Woodward, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 648.

adduct (37); this presumably proceeds *via* a co-ordinatively unsaturated and highly reactive 'IrCpCO' species.[82]

Reaction of [(RhCp)(CO)$_2$] with RCH$_2$N(NO)CONH$_2$ (R = H or Me) gives the bridged methylene complex (38);[83] the related complex (39) has also been reported.[84]

Reactions of [(MC$_5$R$_5$)(CO)$_2$] with acetylenes are discussed in Section 3Bii*g*.

(*c*) *σ-Alkyl and -aryl compounds*. The oxidative addition of alkyl halides to carbonyl complexes [(MC$_5$R$_5$)(CO)L] has already been discussed in Section 3Bii*b*.[37,38,40,65,68–71] The related complex (40) undergoes similar reactions to give (42) *via* the salt (41);[85] [(RhCp){P(OMe)$_3$}$_2$] reacts similarly.[86]

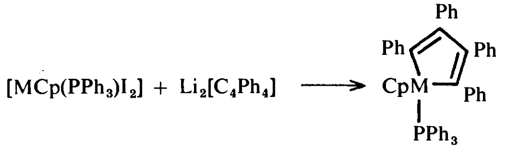
$$\begin{tikzcd}
\underset{(40)}{[(\mathrm{RhCp})(\mathrm{C_2H_4})(\mathrm{PPh_3})]} + \mathrm{RI} \arrow[r] & \underset{(41)}{[(\mathrm{RhCp})(\mathrm{C_2H_4})(\mathrm{PPh_3})\mathrm{R}]\mathrm{I}} \arrow[dl, "-\mathrm{C_2H_4}"] \\
\underset{(42)\ \mathrm{R} = \mathrm{Me\ or\ C_3F_7}}{[(\mathrm{RhCp})(\mathrm{PPh_3})\mathrm{R}(\mathrm{I})]} &
\end{tikzcd}$$

The complex [RhCp(PPh$_3$)(Br)(CF$_2$CF$_2$Br)] undergoes dehydrohalogenation with zinc to give the η^2-tetrafluoroethene complex [RhCp(PPh$_3$)(CF$_2$=CF$_2$)].[85]

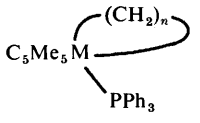
The other common way of preparing M–C σ-bonded complexes in this series is by the reaction of the dihalo-complexes with Grignard or organo-lithium reagents. In this case either the mono- (43) or the di-alkyl compound (44) may be formed.[35,40,87]

$$[(\mathrm{MC_5R_5})\mathrm{X_2L}] + \mathrm{RM'} \rightarrow \underset{(43)}{[(\mathrm{MC_5R_5})\mathrm{X(R)L}]} \xrightarrow{\mathrm{RM'}} \underset{(44)}{[(\mathrm{MC_5R_5})(\mathrm{R})_2\mathrm{L}]}$$

However, when the metal bears one perfluoroalkyl group, as in [(MCp)(PPh$_3$)(R$_f$)I] (R$_f$ = perfluoroalkyl), then the product from reaction with methyl Grignard is [(MCp)(PPh$_3$)(Me)I][87] rather than the mixed dialkyl.



(45)



(46, n = 4, 5, or 6)

[82] M. D. Rausch, R. G. Gastinger, S. A. Gardner, R. K. Brown, and J. S. Wood, *J. Am. Chem. Soc.*, 1977, **99**, 7870.

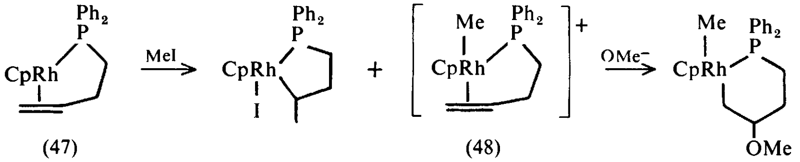
[83] W. A. Herrmann, C. Krüger, R. Goddard, and I. Bernal, *J. Organomet. Chem.*, 1977, **140**, 73.

[84] P. Hong, N. Nishii, K. Sonogashira, and N. Hagihara, *J. Chem. Soc., Chem. Commun.*, 1972, 993; H. Ueda, Y. Kai, N. Yasuoka, and N. Kasai, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2250.

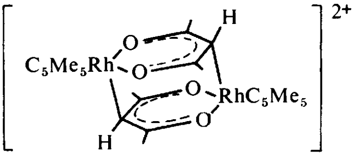
[85] A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, 1971, **10**, 1165.

[86] H. Neukomm and H. Werner, *J. Organomet. Chem.*, 1976, **108**, C26.

[87] S. A. Gardner and M. D. Rausch, *Inorg. Chem.*, 1974, **13**, 997.



(47) (48) (49)



(50)

Cyclic complexes (45)[88] or (46)[89,90] can also be made from the appropriate di-lithium or -magnesium reagent.

An unusual reaction is (47) → (48) → (49).[91] β-Diketonates can also bridge two metals by one C— and two O— bonds, as in (50);[92] the C–Rh bond [2.287(6) Å] is substantially longer than most other Rh–C(sp^3) bonds (2.04—2.08 Å).

The *ortho*-phenylene and methylene complexes (37), (38), and (39) have already been commented on in Section 3Bii*b*.

(*d*) *Complexes from mono-olefins and chelating di-olefins.* These comprise the complexes $[(MC_5R_5)(CH_2{=}CHR)_2]$, $[(MC_5R_5)(CH_2{=}CHR)L]$, and $[(MC_5R_5)$-(diene)]. The ethene Cp complex (51) is obtained by the action of CpNa on $[Rh_2(C_2H_4)_4Cl_2]$[93] while the C_5Me_5 complexes (52) are made from $[(MC_5Me_5)_2Cl_4]$ and ethene in the presence of alcohol and base.[94] Analogous reactions give the complexes of chelating dienes[29,35,36,94,95]

$$[Rh_2(C_2H_4)_4Cl_2] + 2CpNa \rightarrow \underset{(51)}{[(RhCp)(C_2H_4)_2]}$$

$$[(MC_5Me_5)_2Cl_4] + C_2H_4 + EtOH\text{–}base \rightarrow \underset{(52)}{[(MC_5Me_5)(C_2H_4)_2]}$$

^{1}H N.m.r. studies have shown that the ethenes in (51) and (52) rotate about

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[88] S. A. Gardner and M. D. Rausch, *J. Organomet. Chem.*, 1974, **78**, 415.

[89] P. Diversi, G. Ingrosso, and A. Lucherini, *J. Chem. Soc., Chem. Commun.*, 1977, 52.

[90] P. Diversi, G. Ingrosso, A. Lucherini, W. Porzio, and M. Zocchi, *J Chem. Soc., Chem. Commun.*, 1977, 811.

[91] J. L. S. Curtis and G. E. Hartwell, *J. Organomet. Chem.*, 1974, **80**, 119.

[92] W. Rigby, H.-B. Lee, P. M. Bailey, J. A. McCleverty, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1979, 387.

[93] R. B. King, *Inorg. Chem.*, 1963, **2**, 528.

[94] K. Moseley, J. W. Kang, and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1970, 2875.

[95] R. Cramer, *J. Am. Chem. Soc.*, 1964, **86**, 217.

their axes to the metal.[94,95] The rates of rotation decrease in the order $C_5H_5Rh > C_5Me_5Rh > C_5Me_5Ir$.

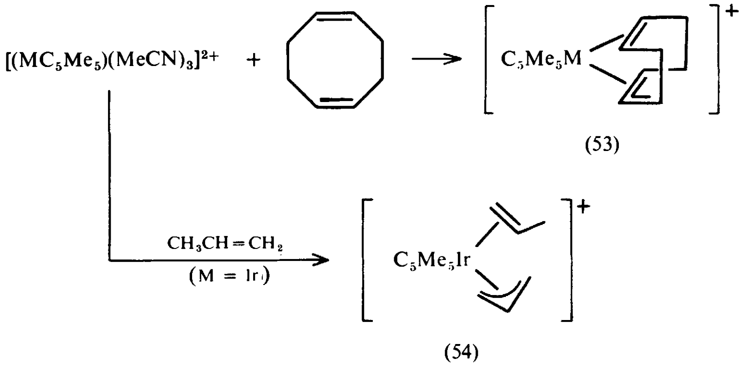
The ethenes in $[(RhC_5R_5)(C_2H_4)_2]$ are replaced slowly by other olefins, phosphines, and phosphites,[44,95,96,97] but SO_2 and PF_3 displace one and two olefins respectively in fast reactions.[97,98] While the main substitution reaction is a dissociative one involving $[(RhC_5R_5)(C_2H_4)]$ as intermediate, displacements *via* associative reactions do also occur. This is believed to be the reason why the electronegativity of the cyclopentadienyl is important since the rate of displacement of ethene by nucleophiles decreases in the order η^5-C_5H_4CN > Cp > η^5-C_5Me_5, with the more electronegative ligand strongly favouring substitution.[97]

Under suitable conditions, cyclo-octadiene in $[(RhCp)(1,5\text{-}C_8H_{12})]$ is displaced by phosphites.[64]

The ethenes in $[Rh(indenyl)(C_2H_4)_2]$ are easily displaced (at 20 °C) by carbon monoxide {to give $[Rh(indenyl)(CO)_2]$} or isocyanides {to give $[Rh(indenyl)(Bu^tNC)_2]$}.[81] This is probably due to the ease with which the indenyl group can become η^3-bonded, allowing a 16-electron transition state where nucleophilic attack can readily occur. By contrast, complex (51) does not exchange under ambient conditions, since a transition state in which Cp is η^3-bonded is of very high energy.

Ethene, in the cationic complexes $[(RhCp)(PR_3)(C_2H_4)R]^+$ that arise from oxidative addition reactions, is very easily displaced by iodide[85] or other ligands.[43]

The dicationic tris-solvent complexes $[(MC_5Me_5)L_3]^{2+}$ (L = MeCN) (Sections 3Bii*k*, 3Bii*l*) react with a variety of mono- and di-olefins. Olefin complexes are formed initially, but, except for the stable norbornadiene (nbd) complex $[(MC_5Me_5)(MeCN)(nbd)]^{2+}$, they mostly deprotonate. Thus cyclo-octa-1,5-diene gives (53) while propene gives the allylic complex (54).[99]



(53)

(54)

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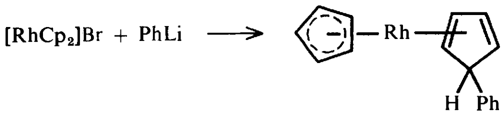
[96] R. Cramer, *J. Am. Chem. Soc.*, 1972, **94**, 5681.

[97] R. Cramer and L. P. Seiwell, *J. Organomet. Chem.*, 1975, **92**, 245.

[98] R. Cramer, *J. Am. Chem. Soc.*, 1967, **89**, 5377.

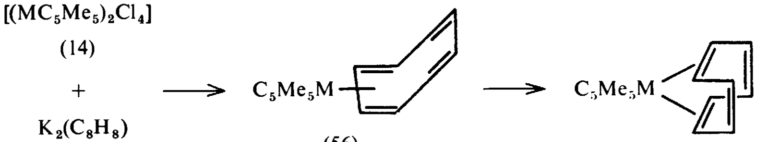
[99] C. White, S. J. Thompson, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1978, 1305.



(55)

(*e*) *Complexes from conjugated dienes, η^3-allylic, and η^5-pentadienyl ligands.* A number of cyclobutadiene complexes are known, largely derived from reactions with acetylenes; see also Section 3Bii*g*. Little is known about their reactivity except for an electrophilic substitution already mentioned.[6]

Other [(MCp)diene] complexes may be obtained by reaction of the appropriate [M_2(diene)$_2Cl_2$] with CpTl or CpNa,[58,59,60,62,63] or, for η^4-cyclopentadiene complexes, by reaction of organo-lithium compounds with rhodicenium salts. The incoming group is *exo* to the metal as in (55).[39] The ethenes in [Rh(indenyl)-(C_2H_4)$_2$] are easily displaced by isoprene, penta-1,3-diene, and other dienes to give the appropriate diene complex.[81]

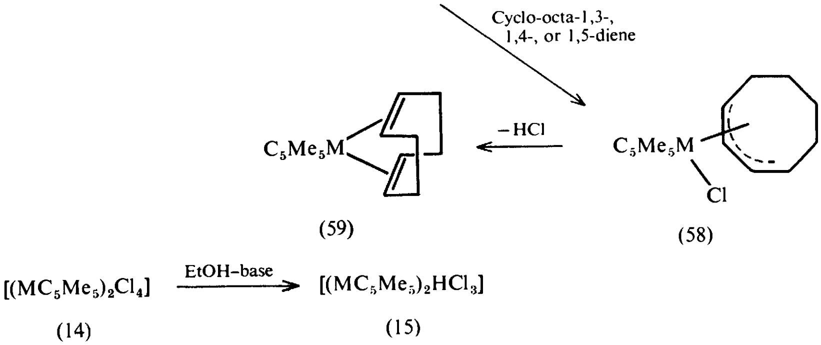


(56)

(57)

Two methods have been used to make [(MC_5Me_5)(diene)] complexes, both starting from [(MC_5Me_5)$_2Cl_4$] (14). Since cyclo-octatetraene forms the dianion $C_8H_8^{2-}$, this was allowed to react directly with (14) to give initially, at low temperature, the 1–4-η^4-isomer (56), which isomerized to the 1,2:5,6-η^4-isomer (57) on warming; the rhodium complex (56*a*) isomerized faster than the iridium complex (56*b*).[61]

The more general way to the [(MC_5Me_5)(diene)] complexes is by reaction of (14) with the diene in the presence of alcohol and base. This is a surprisingly complex reaction, proceeding *via* metal hydrides and metal–allyl intermediates which reductively eliminate to give the metal–diene product. All the various steps have been defined and analysed and a detailed mechanism has been elucidated for the reaction of the metal hydride with the diene (Section 3Bii*a*). During the overall reaction, isomerization of olefin also occurs. Complexes $[(MC_5Me_5)(\text{diene})]$ which have been made include (diene) = cyclohexa-1,3-diene,[53,100] norbornadiene,[53] dibenzylideneacetone,[101] isoprene,[52] 2,3-dimethylbutadiene,[52] and 2-methylpenta-1,3-diene.[52] Since it illustrates the complexities of the reaction well, the overall process has been illustrated in Scheme 3 for the cyclo-octadienes, all of which give the same cyclo-octenyl complex (58) at approximately the same rates. Loss of HCl (reductive elimination) from (58) involves yet another isomerization to give the 1,5-cyclo-octadiene complex (59).



Scheme 3

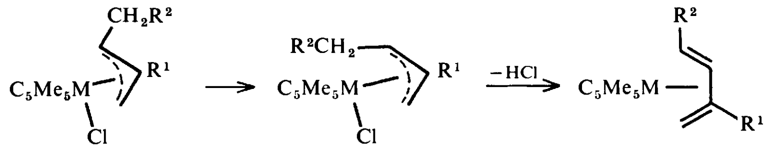
The reaction of $[MCp(C_5Me_5)]^+$ {easily formed from $[(MC_5Me_5)_2Cl_4]$ and cyclopentadiene in the presence of base} with borohydride gives the unexpected product $[M(Cp)(C_5Me_5H)]$, where attack has occurred *exo* on the C_5Me_5 ring. None of the other isomer is detectable in the rhodium complex, but the iridium complex gives 70 % $[Ir(\eta^5\text{-}Cp)(\eta^4\text{-}C_5Me_5H)]$ and 30 % $[Ir(\eta^4\text{-}C_5H_6)(\eta^5\text{-}C_5Me_5)]$.[94] *exo*-H $[Rh(Cp)(C_5Me_5H)]$ regenerates the rhodicenium cation in a facile reaction with chloroform,[94] *e.g.*

$$[Rh(Cp)(C_5Me_5H)] + CDCl_3 \rightarrow [Rh(Cp)(C_5Me_5)]Cl + CDHCl_2$$

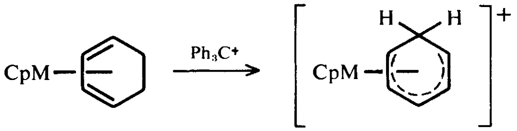
For acyclic dienes the tendency to eliminate reductively has been correlated with the structure of the intermediate allylic complex. Only when this allyl ligand has an alkyl group in the 1-*anti*-position or when it has substituents at both the 2- and at the 1-*syn*-positions (so that isomerization to the 1-*anti*-position can occur) can reductive elimination to give the diene complex [*s-cis* configuration] occur (Scheme 4).

Other allylic complexes are obtained by protonation of diene complexes (Section 3Bii*a*)[58–63] as well as by deprotonation [*e.g.* complex (53)][99] and by hydride abstraction, *e.g.* (26) → (60).[58,102] Reaction with hexafluoroacetone also gives allylic complexes, *e.g.* (61) → (62).[103]

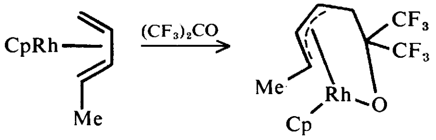
[100] K. Moseley and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1970, 2884.
[101] H.-B. Lee and P. M. Maitlis, *J. Organomet. Chem.*, 1973, **57**, C87.
[102] J. Lewis and A. W. Parkins, *J. Chem. Soc.* (*A*), 1967, 1150; 1969, 953.
[103] M. Green and B. Lewis, *J. Chem. Soc., Dalton Trans.*, 1975, 1137.



Scheme 4



(26) (60)



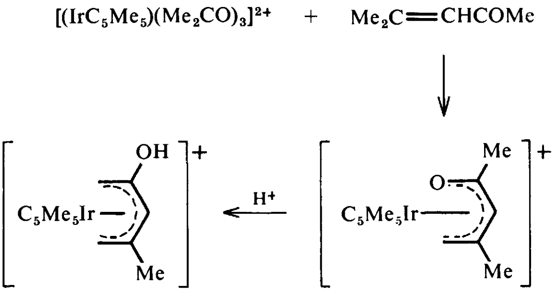
(61) (62)

Allylic complexes are also obtained from allylmercurials and cyclopentadienyl–rhodium or –iridium halo-complexes.[104]

η^3-Allylic groups are quite easily cleaved with acid:[32]

$$[(\mathrm{RhCp})(\eta^3\text{-}\mathrm{C_3H_5})\mathrm{Cl}] + \mathrm{HCl} \rightarrow [(\mathrm{RhCp})\mathrm{Cl_2}]_n + \mathrm{C_3H_6}$$

When the tris-acetone complex $[\mathrm{Ir(C_5Me_5)(Me_2CO)_3}](\mathrm{PF_6})_2$ (formed *in situ*) was treated with mesityl oxide, the unusual complex (63) was obtained; this isomerized to the pentadienyl complex (64) with acid.[105] The tris-acetone complex also promoted the aldol condensation of acetone; see also Section 4Aii*l*.



(64) (63)

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[104] A. N. Nesmeyanov and A. Z. Rubezhov, *J. Organomet. Chem.*, 1979, **164**, 259.

[105] C. White, S. J. Thompson, and P. M. Maitlis, *J. Organomet. Chem.*, 1977, **134**, 319.

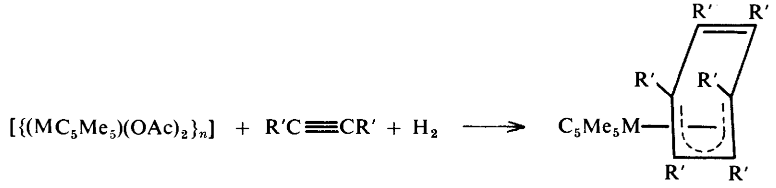
Cyclohexadienyl complexes derived from benzenes are discussed in Section 3Bii*f.*

(*f*) η^6- and *η^4-Arene-η^5-cyclopentadienyl complexes.* Two types of $[(MC_5R_5)(arene)]^{n+}$ complexes are known; those in which the arene is 'bent', η^4-bonded [where four sp^2 carbons are bonded and two are not ($n = 0$)[106]], and those where the arene is equivalently η^6-bonded ($n = 2$).* Recently it has become clear that a sub-set of the latter, where the arene bears a substituent —OH or —NRR′, can exist in η^5-forms.

The η^4-arene complexes (65)[107] and (66)[108] are formed as shown from the appropriate acetylene. The rhodium complex (66*a*) exhibits fluxionality, with the $C_6(CO_2Me)_6$ ring moving about the metal in a series of 1,2-shifts, with $\Delta G^{\ddagger} = 20.1$ kcal mol^{-1}. The iridium complex is static at accessible temperatures.[108]

The dicationic tris-solvent complexes $[(MC_5Me_5)L_3]^{2+}$ (L = Me_2CO or MeCN) react readily with a variety of arenes to give $[(MC_5Me_5)(\eta^6\text{-arene})]^{2+}$ (arene = benzene, methylbenzenes, tetramethylthiophene, *etc.*).[109,110] These complexes can also be made, but less conveniently, by reaction of the arene with $[(MC_5Me_5)(OCOCF_3)_2]$ in trifluoroacetic acid.[8] The iridium arenes are more inert than the rhodium ones (for example, towards displacement by solvent), and it is found that the stability for a given metal parallels the degree of methylation, hexamethylbenzene giving the most stable complexes.[8,109]

(65, R = CF_3)



(66, R′ = CO_2Me)

*The former are also most conveniently regarded as having the metal in the (+I) oxidation state while it is M^{III} in the latter complexes.

[106] M. R. Churchill and R. Mason, *Proc. R. Soc. London, Ser. A*, 1966, **292**, 61.

[107] R. S. Dickson and G. Wilkinson, *J. Chem. Soc.*, 1964, 2699.

[108] J. W. Kang, R. F. Childs, and P. M. Maitlis, *J. Am. Chem. Soc.*, 1970, **92**, 720.

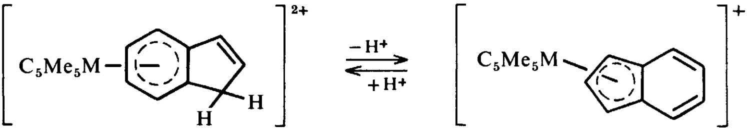
[109] C. White, S. J. Thompson, and P. M. Maitlis, *J. Chem Soc., Dalton Trans.*, 1977, 1654.

[110] M. J. H. Russell, C. White, A. Yates, and P. M. Maitlis, *J. Chem Soc., Dalton Trans.*, 1978, 857.

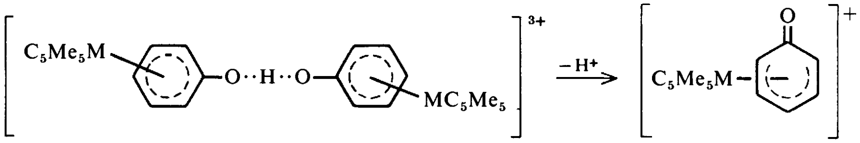
As the arenes are in a field of very high positive charge, they readily undergo nucleophilic attack; one example is the reaction (3) → (4) already discussed. Deprotonation also occurs readily even in mildly nucleophilic solvents.

Two dramatic examples of this may be cited. The indene complex (67), where the metal is η^6-bonded to the benzene ring, becomes η^5-bonded to the five-membered ring in (68) on loss of H^+; this reaction is reversed in strong acid. The iridium indole complex behaves similarly.[109]

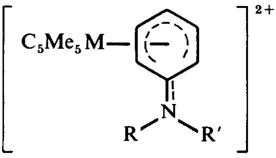
Reaction of phenol with $[(MC_5Me_5)(Me_2CO)_3]^{2+}$ gives (69), which with base gives the complex (70), where the PhO ligand is best represented by the η^5-oxocyclohexadienyl, rather than the η^6-phenate, form [ν(CO) 1635 cm^{-1}].[111]



(67) (68)



(69) (70)



(71)

Spectroscopic and *X*-ray data also suggest η^5-binding for the aniline complexes (71)[112] and a similar binding is also possible among complexes bearing partially deprotonated *meta*- and *para*-dihydroxybenzenes as ligands.[113] η^5-Binding appears to stabilize these molecules; thus the anisole complexes $[(MC_5Me_5)(PhOMe)]^{2+}$, where n.m.r. spectroscopy favours an η^6-bonding, are very labile.[112]

(*g*) ***Products from reactions with acetylenes.*** Cyclopentadienyl–rhodium and –iridium complexes, especially the carbonyls, react readily with acetylenes

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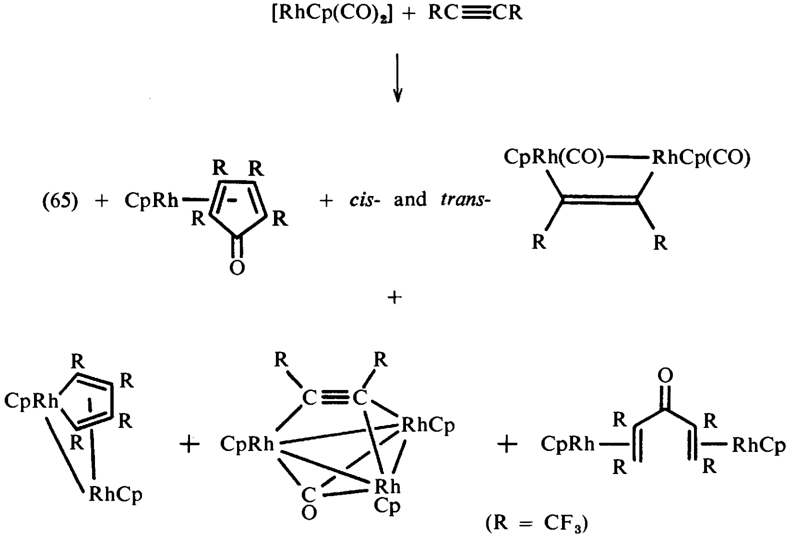
[111] C. White, S. J. Thompson, and P. M. Maitlis, *J. Organomet. Chem.*, 1977, **127**, 415.

[112] P. Espinet, P. M. Bailey, R. F. Downey, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1980, 1048.

[113] P. Espinet and P. M. Maitlis, *J. Organomet. Chem.*, 1979, **179**, 49.

(particularly those activated with electron-withdrawing substituents, CF_3, C_6F_5, or CO_2Me) to give a bewildering variety of complexes. One product, (65), from the reaction of $[RhCp(CO)_2]$ and hexafluorobut-2-yne has already been mentioned; others are collected in Scheme 5.[114–116] Other acetylenes give similar ranges of products.



Scheme 5

One of the phosphines in $[(RhCp)(PPh_3)_2]$ is displaced by $MeO_2CC{\equiv}CCO_2Me$ under nitrogen to give the monoacetylene complex, $[(RhCp(PPh_3)(MeO_2CC_2CO_2Me)]$,[117] but the Cp analogue of (66) is formed in the presence of air. Presumably the air oxidizes the second triphenylphosphine away to leave a second vacant site at which cyclotrimerization can then occur. Reactions of $[(RhCp)(Ph_3P)_2]$ with olefins are consistent with this idea.

The complex [Rh(indenyl)(isoprene)] reacts readily with hexafluorobut-2-yne to give the η^4-cyclohexa-1,3-diene complex (72, $R = CF_3$).[14]

Even amongst these strange complexes, the products (73) and (74) from the reaction of $[(RhC_5Me_5)_2Cl_4]$ with phenylacetylene in the presence of base are unusual. In both cases the acetylene has oligomerized, with the loss of two H^+, to give complexes containing in one case a tetramer and in the other a pentamer of the acetylene which have formed cyclobutadiene rings. The structures of both (73) and (74) have been confirmed by *X*-ray structure determinations.[118]

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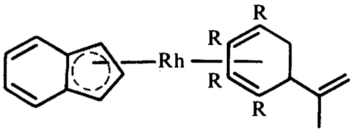
[114] R. S. Dickson and H. P. Kirsch, *Aust. J. Chem.*, 1972, **25**, 2535; 1974, **27**, 61.

[115] R. S. Dickson, S. J. Johnson, H. P. Kirsch, and D. J. Lloyd, *Acta Crystallogr., Sect. B*, 1977, **33**, 2057.

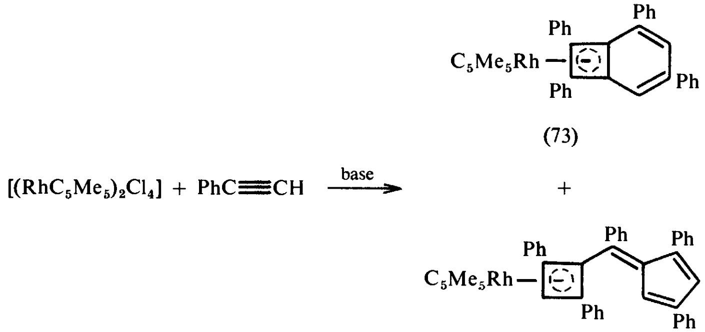
[116] R. S. Dickson and G. N. Pain, *J. Chem. Soc., Chem. Commun.*, 1979, 277.

[117] Y. Wakatsuki and H. Yamazaki, *J. Organomet. Chem.*, 1979, **64**, 393.

[118] J. Moreto, K. I. Maruya, P. M. Bailey, and P. M. Maitlis, unpublished results.



(72)



(73)

(74)

(*h*) *Catalytic reactions.* Rhodium and iridium complexes are, in general, good at catalysing hydrogen-transfer reactions and those under review are typical. Little has been reported on the activity of the Cp complexes and certainly, under hydrogen, $[(RhCp)_2Cl_4]$ rapidly decomposes to metal. However, the C_5Me_5 complexes are good and reasonably stable catalysts. Reactions which can be catalysed include olefin hydrogenation,[119] olefin[119] and diene[53,58,61,100] isomerization, and hydrosilylation;[120] these occur under mild conditions (20—50 °C/1 atm). Under more forcing conditions (20 °C/100 atm) dienes are also hydrogenated. Arenes are hydrogenated at 40—60 °C/50—100 atm,[121] but recent results show that those reactions are now not completely homogeneous and that tiny amounts of catalytically active metal are formed; the occurrence of both homogeneous and heterogeneous catalysis greatly complicates analysis of the reaction.[120]

A curious feature of the olefin hydrogenation is that the μ-hydrido complexes such as (15), (16), and (17) are all less active than the dinuclear $[(MC_5Me_5)_2Cl_4]$ complexes (14); the activity towards cyclohexene (in propan-2-ol–NEt_3) decreases in the order (14*a*) > (15*a*) and (14*b*) > (15*b*) > (16) > (17). (Furthermore the mononuclear phosphine adducts $[(MC_5Me_5)Cl_2(PR_3)]$ are also inactive.[119]) The kinetic data also agree with this in showing that the key step is a predissociation into mononuclear complexes (half-order in catalyst) that bear a vacant site at

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[119] D. S. Gill, C. White, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1978, 617.

[120] A. Millan and P. M. Maitlis, unpublished results.

[121] M. J. H. Russell, C. White, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1977, 427.

which reaction can be initiated. Thus (Section 3Bii*a* and Table 3), since the metal–metal separation decreases in the order (14*b*) > (15*b*) > (16) > (17) and (14*a*) > (15*a*), it is reasonable to suppose that in the μ-hydrides (15), (16), or (17) it may well be more difficult to form the needed reactive mononuclear species than from (14).

The suggested path by which the reaction [of (14)] occurs is:

$$m_2Cl_4 \rightleftharpoons 2mCl_2 \qquad [m = (MC_5Me_5)] \tag{a}$$

$$mCl_2 + H_2 \rightleftharpoons mHCl + HCl \tag{b}$$

$$mHCl + H_2 \rightleftharpoons mH_2 + HCl \tag{c}$$

$$mH_2 + \text{olefin} \rightleftharpoons mH_2\,(\text{olefin}) \xrightarrow{\text{fast}} m + \text{alkane} \tag{d}$$

$$m + H_2 \rightleftharpoons mH_2 \tag{e}$$

In this scheme steps (*a*)—(*c*) initiate (the reversible formation of HCl explains the need for base), while the catalytic cycle is carried by steps (*d*) and (*e*).[119,122]

It has recently been discovered that catalysts such as $[(RhC_5Me_5)_2(OH)_3]Cl$ (which are active in propan-2-ol without base) may be further activated by aerial oxidation prior to hydrogenation, or by the addition of small amounts of $[Rh_2(diene)_2Cl_2]$ or similar complexes not stabilized towards hydrogenation. The oxidation by air appears to 'burn off' some of the C_5Me_5 protecting groups, and analytical data suggest that species of the type '$Rh_5(C_5Me_5)_4(OH)_n(OAc)_mCl_p$' are formed. These catalysts are stable towards decomposition to metal under mild conditions, give faster rates of olefin hydrogenation, and allow the hydrogenation of dienes at 20 °C/1 atm.[122]

Hydrogen-transfer hydrogenation reactions are quite common but an extremely unusual one is the conversion of acetaldehyde into acetic acid and ethanol in water; other aldehydes react entirely analogously:[123]

$$2RCHO + H_2O \rightarrow RCH_2OH + RCO_2H$$

The reaction proceeds comfortably in the temperature range 20—90 °C and is catalysed by a wide variety of water-soluble and partially water-soluble catalysts such as $[(RhC_5Me_5)_2(OH)_3]^+Cl^-$, $[(RhC_5Me_5)_2Cl_4]$, and $[(RuC_6Me_6)_2(OH)_3]Cl$ (Section 4Aii*l*). Rhodium and iridium complexes give equal amounts of alcohol and acid, and intermediates that are hydride complexes can be intercepted. The reaction is again half-order in catalyst (dimer), showing the importance of the mononuclear species, and a reaction mechanism has been suggested in which two cycles are present, these being (i)

aldehyde + metal complex + water → acid + metal hydride

and (ii)

aldehyde + metal hydride + water → alcohol + starting metal complex

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[122] J. E. Hamlin, K. Hirai, V. C. Gibson, and P. M. Maitlis, unpublished results.

[123] J. Cook, J. E. Hamlin, A. Nutton, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1980, 144.

For Rh and Ir catalysts the two cycles are equally coupled; for Ru catalysts, more acid than alcohol is formed and hydrogen is evolved.[123]

The C_5R_5–Rh and –Ir complexes also undergo a variety of H–D exchange reactions, including:

$$[\{RhC_5(CH_3)_5\}_2(OH)_3]Cl + D_2O\text{–}NaOD \xrightarrow{90\,^{\circ}C} [\{RhC_5(CD_3)_5\}_2(OD)_3]Cl + H_2O$$

and

$$[(RhC_5H_5)(C_2H_4)_2] + C_6D_6 \xrightarrow{130\,^{\circ}C} [(RhC_5D_5)(C_2D_4)_2] + C_6H_6$$

Mechanisms have been proposed for both these reactions.[124,125]

The tri-μ-hydroxy complex, $[(RhC_5Me_5)_2(OH)_3]Cl$, is also active for catalysing the oxygenation of triphenylphosphine (to triphenylphosphine oxide) and of tetrahydrofuran to γ-butyrolactone $(\overline{CH_2CH_2CH_2OCO})$.[126] As is the case with phosphine-based catalysts, some oxidation of the (here C_5Me_5) ligand also occurs.

(*j*) *Complexes with other Group IV ligands.* Oxidative additions of R_3MH ($M = Si$, $R = Me$, Ph, $PhCH_2$, or Cl; $M = Ge$ or Sn, $R = Me$) to $[(RhCp)(CO)_2]$ to give $[(RhCp)(CO)(MR_3)_2]$ have been reported.[46,127] $SnCl_4$ also reacts to give $[(RhCp)(CO)Cl(SnCl_3)]$.[46]

(*k*) *Complexes with N or P ligands.* In many complexes, especially those where Cp is present, PR_3, $P(OR)_3$, or aliphatic or aromatic amines have been used as co-ligands to block vacant sites and to stabilize complexes.

Amine ligands are sometimes rather weakly bound and readily lost in solution or on drying the solid in vacuum.[35,128]

The dinuclear azide complex (75) reacts stepwise with CO to give finally the cyanate complex $[(RhC_5Me_5)_2(NCO)_4]$, which can also be made directly. Terminal azides react more readily than bridging ones. CS_2 also reacts with (75) to give $[(RhC_5Me_5)_2(SCN)_4]$.[128]

Labile hydrazine complexes $[(RhC_5Me_5)X_2(NH_2NR^1R^2)]$ have been prepared from $[(RhC_5Me_5)_2X_4]$ and $R^1R^2NNH_2$.[129]

Tris-solvent complexes $[(MC_5Me_5)(L)_3](PF_6)_2$ of varying degrees of stability have been obtained by reaction of $[(MC_5Me_5)_2Cl_4]$ with $AgPF_6$ in the appropriate solvent or in the presence of the ligand, L. Stable complexes are obtained where $L = MeCN$ or py or NH_3,[109] but one, two, or three MeCN's in the first are easily enough substituted, especially for $M = Rh$, to make it a valuable synthetic precursor.[109,112,113] Another nitrile complex (76) is obtained by the unusual route shown.[130]

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[124] J. W. Kang and P. M. Maitlis, *J. Organomet. Chem.*, 1971, **30**, 127.

[125] L. P. Seiwell, *J. Am. Chem. Soc.*, 1974, **96**, 7134.

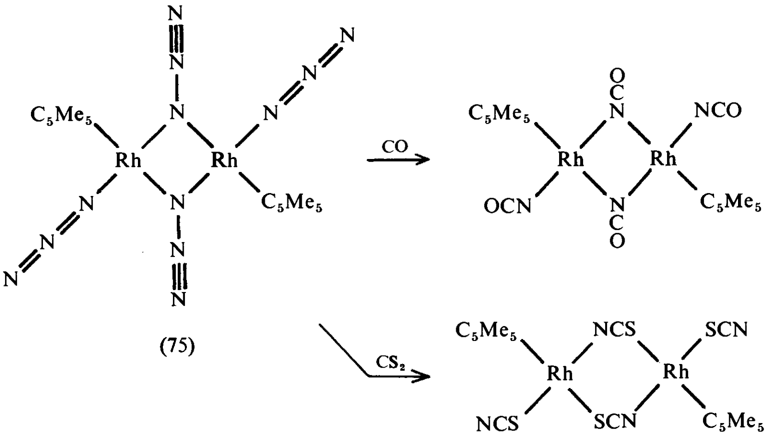
[126] K. Hirai, A. Nutton, and P. M. Maitlis, *J. Mol. Catal.*, 1980, **10**, 203.

[127] R. Hill and S. A. R. Knox, *J. Organomet. Chem.*, 1975, **84**, C31; *J. Chem. Soc., Dalton Trans.*, 1975, 2623.

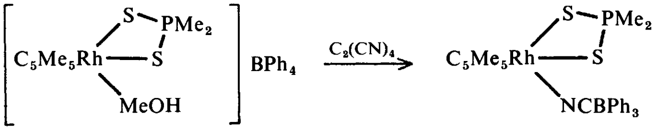
[128] W. Rigby, P. M. Bailey, J. A. McCleverty, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1979, 371.

[129] W. Rigby, J. A. McCleverty, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1979, 382.

[130] M. C. Cornock, D. R. Robertson, T. A. Stephenson, C. L. Jones, G. H. W. Milburn, and L. Sawyer, *J. Organomet. Chem.*, 1977, **135**, C50.



(75)



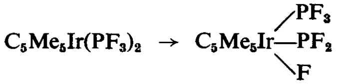
(76)

One nitrosyl complex, $[(RhCp)(NO)(PR_3)]^+PF_6^-$, has been made by the reaction of $[NO][PF_6]$ with $[(RhCp)(CO)(PR_3)]$. On reaction with halogens the NO is displaced.[42]

Phosphine and phosphite ligands bind better to Rh or Ir than the amines but, for example, the complex $[(RhCp)(PPh_3)_2]$ easily undergoes oxidation by air in the presence of olefins or acetylenes.[117] Part of the reason for such reactivity may arise from steric factors. Thus it was found that while the tris-complexes $[(MC_5Me_5)L_3]^{2+}$ could be prepared for the small ligands L = $(MeO)_3P$, $(EtO)_3P$, or Me_2PhP, only a mono-triphenylphosphine complex $[(RhC_5Me_5)(MeCN)_2(PPh_3)]^{2+}$ could be isolated, and triphenyl phosphite gave the *ortho*-metallated product $[(\overline{RhC_5Me_5)\{P(OPh)_3\}\{P(OPh)_2OC}_6H_4\}]PF_6$.[131]

It is clear that the C_5Me_5 ligand is large and that it shields even the other half of the co-ordination sphere of the metal quite effectively (Section 5).

The iridium bis-trifluorophosphine complex undergoes a spontaneous internal oxidative addition:[132,133]



$$C_5Me_5Ir(PF_3)_2 \rightarrow C_5Me_5Ir(PF_3)(PF_2)F$$

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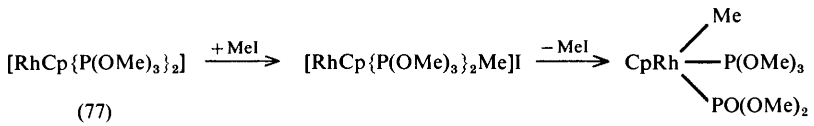
[131] S. J. Thompson, C. White, and P. M. Maitlis, *J. Organomet. Chem.*, 1977, **136**, 87.
[132] R. B. King and A. Efraty, *J. Am. Chem. Soc.*, 1971, **93**, 5260.
[133] R. B. King and A. Efraty, *J. Am. Chem. Soc.*, 1972, **94**, 3768.



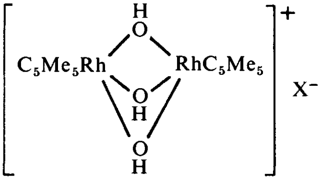
$$[RhCp\{P(OMe)_3\}_2] \xrightarrow{+MeI} [RhCp\{P(OMe)_3\}_2Me]I \xrightarrow{-MeI} CpRh(Me)\{P(OMe)_3\}\{PO(OMe)_2\}$$

(77) (78)

The rhodium analogue does not do this but undergoes normal oxidative addition with iodine and perfluoroalkyl iodides.[132,133]

The bis(trimethyl phosphite) complex (77) undergoes an unusual Arbuzov reaction with methyl iodide to give (78).[86]

(*l*) ***Complexes with O or S ligands.*** One of the most surprising features of this chemistry is the readiness with which C_5Me_5 complexes bearing oxy-ligands are formed. For example, the very stable tri-μ-hydroxo complex (79, X = Cl) is made simply by heating a solution of $[(RhC_5Me_5)_2Cl_4]$ in aqueous sodium hydroxide and crystallizes out in large orange needles.[124] The structures have been confirmed by *X*-ray analysis for $X = BPh_4$[10] and $OH{\cdot}11H_2O$,[51] and also for the iridium complex $[(IrC_5Me_5)_2(OH)_3]OAc{\cdot}14H_2O$.[51] These complexes have an extensive chemistry; for example, the polynuclear hydrides (24) and (25) are made from (79).[55,56] They also are good catalysts[122,123] (Section 3Bii*h*).



(79)

A wide range of carboxylate complexes of empirical formula $[(MC_5Me_5)(OCOR)_2]nH_2O$ can be made.[124] Their structures are not known with certainty but they may well be ionic, with tri-μ-carboxylate groups, *i.e.* $[(MC_5Me_5)_2(OCOR)_3][OCOR]$. These are also useful synthetic precursors and catalysts.[108,119] Other *O*-bonded ligands include nitrate, nitrite,[45,128] and β-diketonates.

The tris-solvent species $[(MC_5Me_5)(L)_3][PF_6]_2$ ($L = Me_2CO$) can be made *in situ* (see also Sections 3Bii*e* and 4Aii*l*).[109] This undergoes aldol condensation at the same time as it promotes a remarkable solvolysis of the PF_6 to give complex (80), which contains bridging PO_2F_2 ligands.[111,134]

The tris-acetone complexes are very labile and are convenient starting materials from which other sensitive dicationic complexes may be obtained.[109,111,112]

An unusual blue 5-co-ordinate mononuclear Rh^{III} complex (81, X = Y = O)

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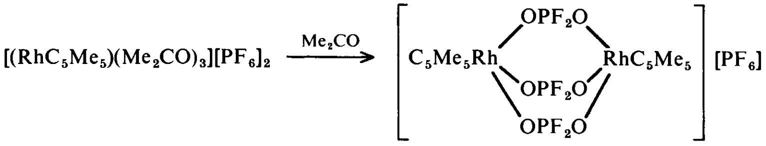
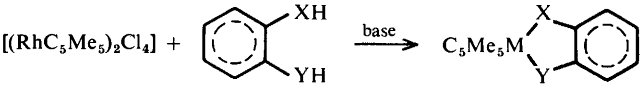
[134] S. J. Thompson, P. M. Bailey, C. White, and P M Maitlis, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 490.



(80)



(81, X = Y = O;
X = O, Y = NH)

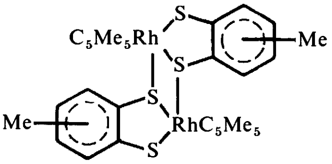
has been made which forms weak adducts with phosphines.[135] The related complexes (81, X = NH, Y = O or NH) are also known, as are the dinuclear disulphide analogues (82).[136]

E.s.r. evidence has indicated the formation of a C_5Me_5–Rh^{II} dioxygen complex by oxidation of (79, X = Cl) with H_2O_2.[126]

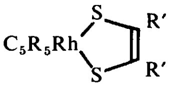
The i.r. spectra of the tris-(dimethyl sulphoxide) complexes $[(MC_5Me_5)(Me_2SO)_3][PF_6]_2$ show that the Me_2SO is *O*-bonded to Rh both in the solid and in solution, and is *O*- and *S*-bonded in the solid and only *S*-bonded in solution to Ir.[109] This shows that Ir is a softer metal centre than Rh and is in keeping with its other properties, for example, the formation of more stable olefin and arene complexes.

It may be noted that when attempts were made to prepare $[(CoC_5Me_5)(Me_2SO)_3]^{2+}$ by the action of $AgPF_6$ in Me_2SO on $[(CoC_5Me_5)_2I_4]$, the product, $[Co(Me_2SO)_6][PF_6]_2$ had lost the C_5Me_5 ligand.[137] This shows that Co^{II} is a better leaving group than Rh^{II} or Ir^{II} and that the C_5Me_5 ligand therefore stabilizes it less than Co does the heavier metals.

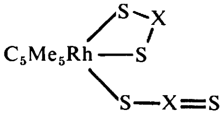
Other sulphur-containing complexes are the mononuclear dithiolenes (83, R = R′ = H,[138] R = Me, R′ = CN[136]), dithiocarbamates, dithiophosphates,



(82)



(83)



(84)

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[135] P. Espinet, P. M. Bailey, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1979, 1542.

[136] M. J. H. Russell, C. White, A. Yates, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1978, 849.

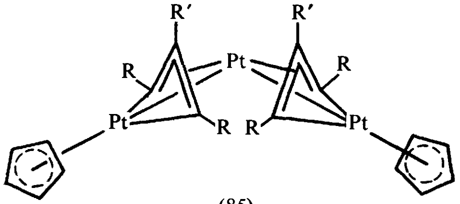
[137] G. Fairhurst and C. White, *J. Chem. Soc., Dalton Trans.*, 1979, 1524.

[138] R. B. King and C. A. Eggers, *Inorg. Chem.*, 1968, **7**, 340.

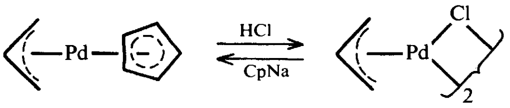
and related ligands (84, X = $CNMe_2$,[136,139] CMe,[136,139] PPh_2,[139] or PMe_2[139]). The dithiocarbamates favour bidentate binding and the n.m.r. spectra show that exchange between unidentate and bidentate ligands occurs.[136,139] The dinuclear complexes $[(RhCp)_2(SR)_2]$ are obtained by oxidative addition of RSSR to $[RhCp(CO)_2]$.[67] Other complexes with bridging RS,[136] as well as with Me_2S[136,140] and dithian[136] ligands, have been prepared, and the *S*-bonded SO_2 complex $[(RhCp)(C_2H_4)SO_2]$ has been characterized.[98,141] Tetramethyl- and dimethyl-thiophen π-bond weakly to C_5Me_5M and are displaced by MeCN and even by hexamethylbenzene.[110]

(*m*) *Complexes with halide ligands.* These have all been discussed above since many of the MC_5R_5 complexes in the (+III) oxidation state bear halides. In general, halides are easily displaced (*e.g.* by Ag^+ salts) and displace each other in the order I > Br > Cl. However, when $[(RhC_5Me_5)_2Br_4]$ was crystallized in the presence of $C_2H_4Cl_2$, very substantial exchange of Br for Cl in the complex occurred.[142]

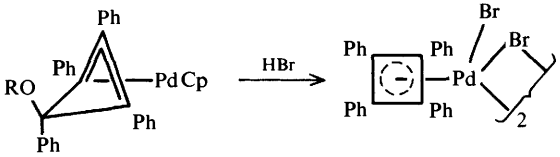
C. Palladium and Platinum.—Although quite a large number of cyclopentadienyl-palladium and -platinum complexes have been made, ranging from the simple



(85)



(86) (87)



(88) (89)

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[139] D. R. Robertson and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, 1978, 486.

[140] H. P. Fritz and K. E. Schwarzhans, *Angew. Chem.*, 1965, **77**, 724; *J. Organomet. Chem.*, 1966, **5**, 283.

[141] R. R. Ryan, P. G. Eller, and G. J. Kubas, *Inorg. Chem.*, 1976, **15**, 797.

[142] M. R. Churchill and S. A. Julis, *Inorg. Chem.*, 1978, **17**, 3011.

$[(PtCp)Me_3]$[143] to the 'quadruple-decker' (85),[144] little attention has been paid to Cp as a stabilizing ligand.

The main reason is almost certainly the ease with which it is removed. For example, $[(PdCp)(\eta^3\text{-}C_3H_5)]$ (86) reacts with HCl, $HgCl_2$, or $FeCl_3$ to give (87);[145] further, (86) loses both ligands on reaction with tertiary phosphines and gives $[Pd^0L_2]$, where L = $P(C_6H_{11})_3$, PBu^t_2Ph, *etc.*[146] The alkoxycyclobutenyl complex (88) gives the cyclobutadiene (89) with HBr even under mild conditions.[147]

However, a group of compounds containing an extra phosphine, the neutral $[(MCp)(PR_3)R']$ and the cationic $[(MCp)(PR_3)L]^+$, are now attracting attention. The synthesis is usually by reaction of μ-dihalo: complexes with [TlCp]:[148,149,150]

$$[M_2(PR_3)_2X_4] + 2[TlCp] \rightarrow \underset{(90)}{2[(MCp)(PR_3)X]} \xrightarrow{R'MgX} \underset{(91)}{[(MCp)(PR_3)R']}$$

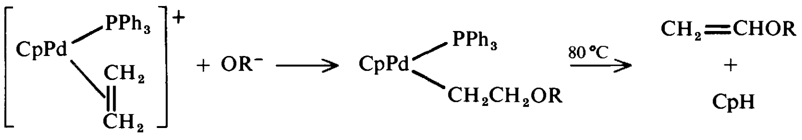
$$[M_2Cl_2(PR_3)_2R'_2] + 2[TlCp] \rightarrow (91)$$

$$(90) + L \xrightarrow{Ag^+} \underset{(92)}{[(MCp)(PR_3)L]^+} \quad (L = CO \text{ or } C_2H_4)$$

$$[PtCl_2(PR_3)L] + CpTl \xrightarrow{Ag^+} (92, M = Pt)$$

Again, the Cp ring is relatively easily cleaved; $[(PdCp)(PPh_3)R]$ regenerates $[Pd_2(PPh_3)_2R_2Cl_2]$ with HCl[149] but some useful reactions have been carried out. For example, (91, M = Pd) inserts SO_2 to give $[(PdCp)(SO_2R')(PR_3)]$,[151] and the ethene complex (93) reacts with alkoxide to give (94).[152] Studies using *cis*-CDH=CDH show that attack of alkoxide on (93) is *trans*; thermal decomposition of (94) yields vinyl ethers and cyclopentadiene.

A variety of bis(pentasubstituted cyclopentadienylpalladium) acetylene complexes (95) have been prepared as shown in Scheme 6.[153] This also shows



(93) (94)

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[143] S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1965, 1529.

[144] A. Keasey and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1978, 1830.

[145] S. P. Gubin, A. Z. Rubezhov, B. L. Winch, and A. N. Nesmeyanov, *Tetrahedron Lett.*, 1964, 2881.

[146] S. Otsuka, T. Yoshida, M. Matsumoto, and K. Nakatsu, *J. Am. Chem. Soc.*, 1976, **98**, 5850.

[147] P. M. Maitlis, A. Efraty, and M. L. Games, *J. Am. Chem. Soc.*, 1965, **87**, 719.

[148] R. J. Cross and R. Wardle, *J. Organomet. Chem.*, 1970, **23**, C4.

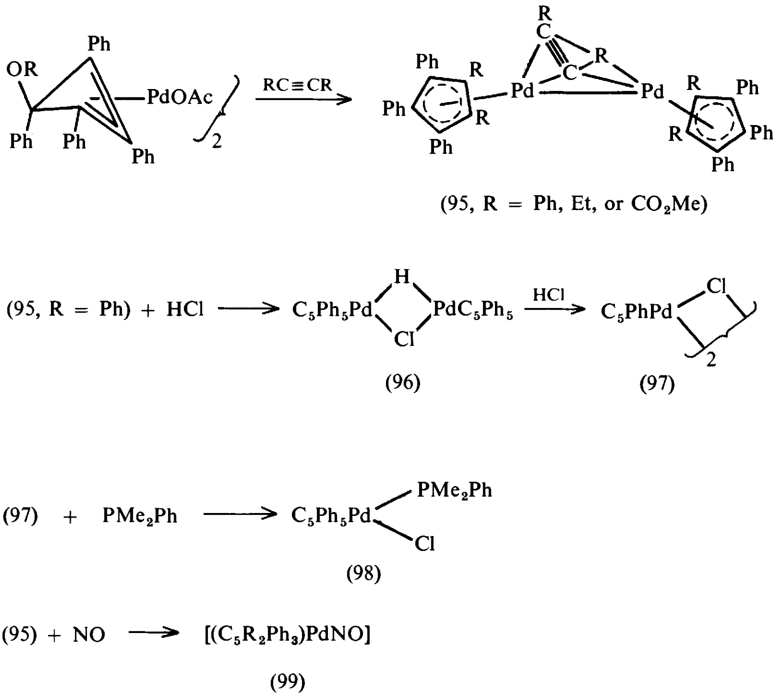
[149] K. Suzuki and K. Hawaki, *Inorg. Chim. Acta*, 1976, **20**, L15.

[150] T. Majima and H. Kurosawa, *J. Organomet. Chem.*, 1977, **134**, C45.

[151] G. K. Turner and H. Felkin, *J Organomet. Chem.*, 1976, **121**, C29.

[152] T. Majima and H. Kurosawa, *J. Chem. Soc., Chem. Commun.*, 1977, 610.

[153] T. R. Jack, C. J. May, and J. Powell, *J. Am. Chem. Soc.*, 1977, **99**, 4707.



(95, R = Ph, Et, or CO_2Me)

(96)

(97)

(98)

(99)

Scheme 6

some reactions of (95), notably that with a stoicheiometric amount of HCl to give what is believed to be the μ-hydride (96), which then reacts further to give the dinuclear μ-dichloro-complex (97) and the mononuclear phosphine derivative (98). The μ-acetylene complex (95) also reacts with NO to give the purple nitrosyl (99),[153] which is much more stable than the unsubstituted [(PdCp)NO].[154]

There has been little interest in η^5-C_5Me_5 complexes but the syntheses of the η^4-pentamethylcyclopenta*diene* complexes $[MCl_2(C_5Me_5R)]$ have been reported.[155] The platinum complex $[PtCl_2(\eta^4\text{-}C_5Me_5H)]$ was very stable but it underwent reaction with bromine to give low yields of a rather insoluble orange-red material, formulated as $[(PtC_5Me_5)_2Br_3]Br_3$.[156]

4 Arene Complexes

A. Ruthenium and Osmium.—(i) *Introduction and synthetic methods.* Bis-arene

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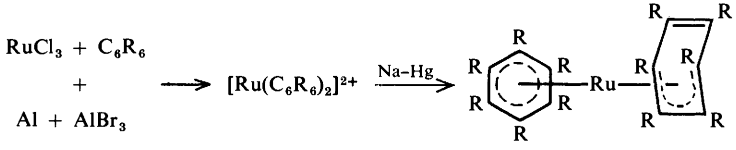
[154] E. O. Fischer and A. Vogler, *Z. Naturforsch., Teil B*, 1963, **18**, 771; E. O. Fischer and H. Schuster-Woldan, *ibid.*, 1964, **19**, 766.

[155] P. V. Balakrishnan and P. M. Maitlis, *J. Chem. Soc. (A)*, 1971, 1715; 1721.

[156] S. H. Taylor and P. M. Maitlis, *J. Organomet. Chem.*, 1977, **139**, 121.

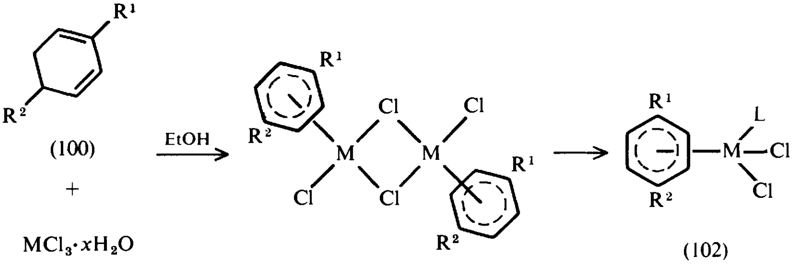
ruthenium compounds are available *via* the Fischer synthesis (Scheme 7);[157,158] zerovalent $[Ru(C_6R_6)_2]$ have one arene η^6- and one η^4-bonded[159,160] and can also be made by the reaction of Ru atoms with benzene.[161]



Scheme 7

The (η^6-benzene)-(η^4-cyclohexa-1,3-diene) complexes $[(MC_6H_6)(C_6H_8)]$ have been made by reduction of $[Ru(C_6H_6)_2]^{2+}$ [162] and by reaction of ruthenium or osmium trichloride with cyclohexa-1,3-diene in the presence of Pr^iMgBr in ether.[163] The stability of these complexes to air decreases in the order Os > Ru > Fe.[163]

A more convenient entry to these and other arene–metal complexes derives from the reaction of a cyclohexadiene with the metal trichloride in ethanol to give $[(MArH)_2Cl_4]$ (101).[164–167] These complexes were initially believed to be polymeric but are now accepted to be dinuclear, and isostructural with the $[(MC_5Me_5)_2Cl_4]$ complexes (14). A particularly useful starting material is the commercially available ψ-phellandrene (100, R^1 = Me, R^2 = Me_2CH), which gives the *p*-cymene complexes (101, R^1 = Me, R^2 = Me_2CH).[167,168] The *p*-cymene can be displaced by other arenes (for example, hexamethylbenzene)



(100)

(101*a*, M = Ru)
(101*b*, M = Os)

(102)

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[157] E. O. Fischer and R. Böttcher, *Z. Anorg. Allg. Chem.*, 1957, **291**, 305.

[158] E. O. Fischer and C. Elschenbroich, *Chem. Ber.*, 1970, **103**, 162.

[159] G. Huttner and S. Lange, *Acta Crystallogr., Sect. B*, 1972, **28**, 2049.

[160] M. Y. Darensbourg and E. L. Muetterties, *J. Am. Chem. Soc.*, 1978, **100**, 7425.

[161] P. L. Timms and R. B. King, *J. Chem. Soc., Chem. Commun.*, 1978, 898.

[162] D. Jones, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 4458.

[163] E O Fischer and J Müller, *Chem. Ber.*, 1963, **96**, 3217.

[164] G. Winkhaus and H. Singer, *J. Organomet. Chem.*, 1967, **7**, 487.

[165] G. Winkhaus, H. Singer, and M. Kricke, *Z. Naturforsch., Teil B*, 1967, **21**, 1109.

[166] R. A. Zelonka and M. C. Baird, *J. Organomet. Chem.*, 1972, **35**, C43; *Can. J. Chem.*, 1972, **50**, 3063.

[167] M. A. Bennett and A. K. Smith, *J. Chem. Soc , Dalton Trans.*, 1974, 233.

[168] M. A. Bennett, T. N. Huang, T. W. Matheson, and A. K. Smith, *Inorg. Synth.*, in the press.

simply by heating the complex to 180 °C in the presence of an excess of hexamethylbenzene.[168] Cyclohexa-1,4-dienes can also be used in the synthesis; the other product was shown to be the cyclohexene.[169]

These reactions allow a very easy entry to a large range of half-sandwich complexes since the arene can be varied so widely and easily. Although they probably have not quite the stability of the Rh– or Ir–C_5Me_5 complexes, these compounds make up for this by their versatility and (not least important) their cost, since Ru is only one-seventh the price of Rh.

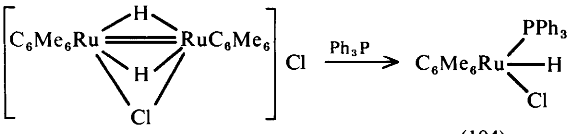
The chlorine bridges in the dinuclear complexes (101) are cleaved by a variety of ligands L = R_3P, $P(OR)_3$, Me_2SO, MeCN, *etc.* to give mononuclear complexes (102). The *X*-ray structure determination of two adducts (102, M = Ru; L = $PMePh_2$; $R^1 = R^2 =$ H, and R^1 = Me, R^2 = Me_2CH) have confirmed the assigned structures.[170]

(ii) ***Properties.*** Although the number of complexes made is not yet as great as the number of Rh- and Ir–C_5R_5 complexes known, a similar organization of this Section will be made, to allow comparison, since the complexes are usually isostructural and have many properties in common.

(*a*) *Hydride complexes.* The dimethyl sulphoxide complex $[(RuC_6H_6)Cl_2(Me_2SO)]$ is soluble in water; in the presence of triethylamine the orange aqueous solution is hydrogenated to a red-violet one, the n.m.r. spectrum of which shows the presence of a hydride, tentatively formulated as $[(RuC_6H_6)_2H_2Cl_2(Me_2SO)_2]$.[169] Reaction of $[(RuC_6Me_6)_2Cl_4]$ with aqueous basic propan-2-ol gave the di-μ-hydride (103) (also isolated as the PF_6^- salt); a related hydride, together with a tri-μ-hydride, is obtained from $[(RuC_6H_3Me_3)_2Cl_4]$.[171] The relationship to the Rh and Ir hydrides described in Section 3Bii*a* is obvious.

Complex (103) reacts with triphenylphosphine to give (104),[171] which is also obtained from $[(RuC_6Me_6)(PPh_3)Cl_2]$;[172] analogues of (104) with fewer methyl groups in the ring become progressively less stable, and the benzene complex decomposes below 20 °C.

The zerovalent $[(RuC_6H_6)LL']$ [L = PMe_3, L′ = PMe_3, PMe_2Ph, or $P(OMe)_3$] are easily protonated (even by NH_4PF_6) to $[(RuC_6H_6)L(L')H][PF_6]$.[173] A



(103)

(104)

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[169] R. Iwata and I. Ogata, *Tetrahedron*, 1973, **29**, 2753; I. Ogata, R. Iwata, and Y. Ikeda, *Tetrahedron Lett.*, 1970, 3011.

[170] M. A. Bennett, G. B. Robertson, and A. K. Smith, *J. Organomet. Chem.*, 1972, **43**, C41.

[171] M. A. Bennett, T. N. Huang, and T. W. Turney, *J. Chem. Soc., Chem. Commun.*, 1979, 312.

[172] M. A. Bennett, T. N. Huang, A. K. Smith, and T. W. Turney, *J. Chem. Soc., Chem. Commun.*, 1978, 582.

[173] H. Werner and R. Werner, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 683.

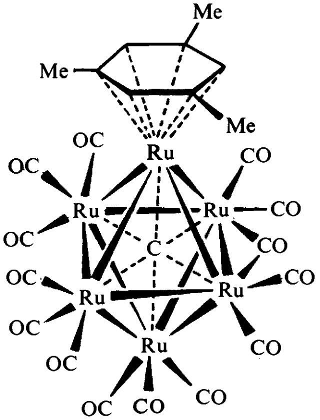
similar reaction with (105) gives the hydride (106), which is in equilibrium with the σ-ethyl complex (107).[174]

$$\begin{tikzcd}
{\begin{matrix}[(RuC_6H_6)(PMe_3)(C_2H_4)] \\ (105)\end{matrix}} \arrow[r, "CF_3CO_2H"] & {\begin{matrix}[(RuC_6H_6)(PMe_3)(C_2H_4)H]^+ \\ (106)\end{matrix}} \arrow[d, shift left] \\
{\begin{matrix}[(RuC_6H_6)(PMe_3)_2(C_2H_5)]^+ \\ (108)\end{matrix}} & {\begin{matrix}[(RuC_6H_6)(PMe_3)(C_2H_5)]^+ \\ (107)\end{matrix}} \arrow[l, "PMe_3"'] \arrow[u, shift left]
\end{tikzcd}$$

Ruthenium-hydrides are also involved as intermediates in diene isomerizations and in protonation reactions of co-ordinated dienes[175] similar to (26) ⇌ (28) (Section 3Bii*a*); see also Section 4A.

(*b*) *Carbonyl complexes.* The best known of these are the purple arene–carbide clusters $[Ru_6(ArH)C(CO)_{14}]$ (109) (ArH = C_6H_6 or 1,3,5-$C_6H_3Me_3$), obtained by heating $Ru_3(CO)_{12}$ in the arene.[176,177] The sequence shown in Scheme 8 has been developed for the synthesis of a variety of mononuclear carbonyl complexes.[174] No insertion of CO into Ru–Me is observed, as indicated by the formation of (110).

(*c*) *σ-Alkyl complexes.* Reaction of $[(RuC_6H_6)_2Cl_4]$ with dimethylmercury in the presence of a phosphine gives $[(RuC_6H_6)(PR_3)(Me)Cl]$.[166,178] An interesting development has been the synthesis of the chiral $[(RuC_6H_6)(PPh_2NHCHMePh)Me(Cl)]$ by this method and its resolution into optical enantiomers.[179] The reaction



(109)

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[174] H. Werner and R. Werner, *J. Organomet. Chem.*, 1979, **174**, C63 and C67.

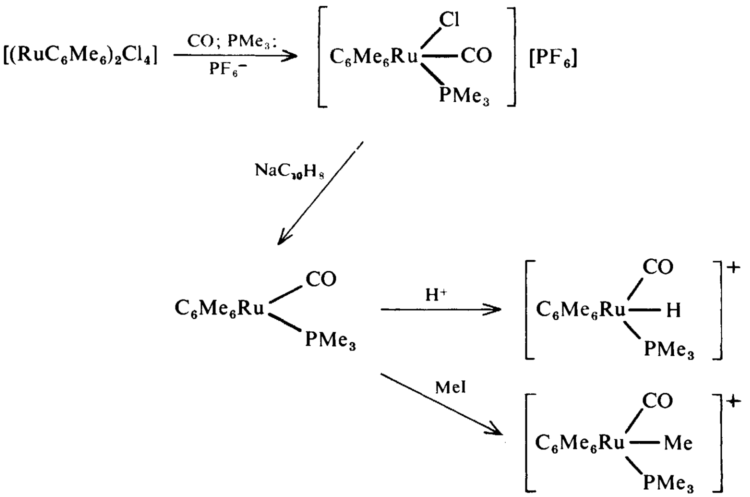
[175] M. A. Bennett and T. W. Matheson, *J. Organomet. Chem.*, 1978, **153**, C25.

[176] B. F. G. Johnson, R. D. Johnston, and J. Lewis, *J. Chem. Soc., Chem. Commun.*, 1967, 1057; *J. Chem. Soc.* (*A*), 1968, 2865.

[177] R. Mason and W. R. Robinson, *Chem. Commun.*, 1968, 468.

[178] R. A. Zelonka and M. C. Baird, *J. Organomet. Chem.*, 1972, **44**, 383.

[179] H. Brunner and R. G. Gastinger, *J. Chem. Soc., Chem. Commun.*, 1977, 488.



(110)

Scheme 8

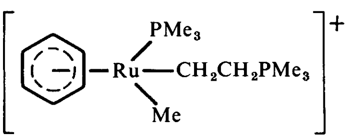
of $[(RuArH)(PMe_2Ph)Cl_2]$ with methyl-lithium gives the dimethyl compounds $[(RuArH)(PMe_2Ph)Me_2]$; here again it was noted that permethylation of the arene stabilizes the complex and that the benzene complex decomposed even at −40 °C.[167]

The zerovalent $[(RuC_6H_6)LL']$ undergo oxidative addition of methyl iodide to give $[(RuC_6H_6)LL'Me]^+$ ($L = L' = PMe_3$; $L = PMe_3$, $L' = P(OMe)_3$ or PMe_2Ph).[173] The σ-ethyl complex (108) is formed as shown above;[174] however, when $[(RuC_6H_6)(PMe_3)(C_2H_4)Me]^+$ {obtained by addition of MeI to $[(RuC_6H_6)(PMe_3)(C_2H_4)]$, and related to the hydride (106)} is treated with Me_3P the product is not a σ-propyl complex but (111), in which the phosphine has attacked the olefin.[174]

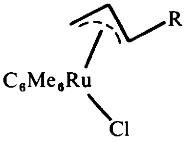
(*d*) *Complexes from mono-olefins and chelating di-olefins.* The zerovalent complexes $[(RuArH)(C_2H_4)_2]$ and $[(RuArH)(1,5\text{-}C_8H_{12})]$ are made from the appropriate $[(RuArH)_2Cl_4]$ and ethene (or cyclo-octa-1,5-diene) in the presence of Zn[175] or sodium carbonate[168,175] and ethanol, or isopropyl magnesium bromide.[180] The di-μ-hydride (103) reacts with ethene in propan-2-ol to give $[(RuC_6Me_6)(C_2H_4)_2]$ directly;[171] hydrogen transfer occurs with cyclo-octene to give cyclo-octane and $[(RuC_6Me_6)(1,5\text{-}C_8H_{12})]$, which can also be made by the reaction of (103) with C_8H_{12}.[171]

Reaction of $[(RuC_6H_6)(PMe_3)Cl_2]$ with $AgPF_6$ and ethene in acetone gives the cationic ethene complex $[(RuC_6H_6)(PMe_3)Cl(C_2H_4)]^+$, which can be reduced with sodio-naphthalene to the zerovalent $[(RuC_6H_6)(PMe_3)(C_2H_4)]$.[174] It is interesting

[180] J. Müller, C. G. Kreiter, B. Mertschenk, and S. Schmitt, *Chem. Ber.*, 1975, **108**, 273.



(111)

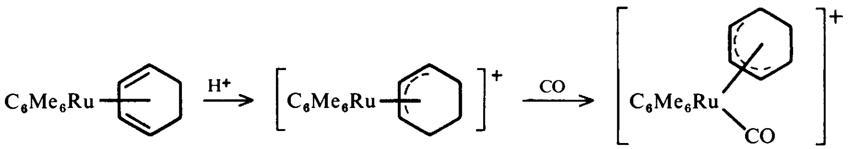


(112)

that methyl migration onto the CO in (110) could not be effected by either iodide or more phosphine; loss of C_6Me_6 occurred under these conditions.

(*e*) *Complexes from conjugated dienes, η^3-allylic, and η^5-pentadienyl ligands.* The reaction of $[(RuArH)_2Cl_4]$ with cyclohexa-1,3- or 1,4-diene in ethanol–base gives $[(RuArH)(1,3\text{-}C_6H_8)]$,[168,175] which can also be made from the diene or cyclohexene and (103) in propan-2-ol; in the latter case the other product is cyclohexane.

When acyclic mono-olefins (MeCH=CHR) are treated with (103) the products are the η^3-allyls (112),[171] which are also accessible by reaction of $[(MC_6H_6)_2Cl_4]$ with allylmercurials (both for Ru and Os),[105] or tetra-allyltin.[178] $[(RuC_6Me_6)(1,3\text{-}C_6H_8)]$ is protonated to give (113), which reacts with CO to give (114).[175] Cycloheptatriene reacts with $[(RuArH)_2Cl_4]$ in ethanol and base to give the η^5-cycloheptadienyl complex $[(RuArH)(C_7H_9)]^+$.[175] Under certain conditions the arene in (RuArH) complexes is attacked by nucleophiles to give η^5-cyclohexadienyl complexes; these are discussed in Section 5Aii*h*. η^6-Arene-η^5-cyclopentadienyl complexes were mentioned in Section 3A.



(113) (114)

(*f*) *Bis-arene and related complexes.* Since they were the first arene–ruthenium compounds to be made, some routes to $[Ru(ArH)_2]^{2+}$ have already been mentioned in Section 4Ai. A more convenient synthesis is from $[(RuArH)_2Cl_4]$ *via* the tris-acetone complex (115).[181,182] By this means, a wide variety of (ArH) have been introduced, including benzene and methylated benzenes, PhX (X = OMe, OH, NMe_2, Cl, COMe, CO_2Me, CO_2H, and CF_3), and naphthalene. The complexes (116) can also be made by treating $[(RuArH)_2Cl_4]$ directly with $AgPF_6$ or $AgBF_4$ in acetone in the presence of HPF_6 or HBF_4.[182]

The arene in (116) is much less labile in these dicationic ruthenium complexes than in the corresponding (arene)(C_5Me_5)–Rh or –Ir complexes (Section 3Bii*f*);

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[181] M. A. Bennett, T. W. Matheson, G. B. Robertson, W. L. Steffen, and T. W. Turney, *J. Chem. Soc., Chem. Commun.*, 1979, 32.

[182] M. A. Bennett and T. W. Matheson, *J. Organomet. Chem.*, 1979, **175**, 87.

$$[(RuArH)_2Cl_4] \xrightarrow{Ag^+;\ Me_2CO} \underset{(115)}{[(ArH)Ru(Me_2CO)_3]^{2+}}$$

$$(115) + Ar'H \longrightarrow \underset{(116)}{[(ArH)Ru(Ar'H)]^{2+}}$$

for example, chlorobenzene is strongly enough bound to ruthenium to be easily solvolysed to co-ordinated methoxybenzene.[182]

The tetramethylthiophen(*p*-cymene)ruthenium dication has been made.[110]

(*g*) *Catalytic reactions*. The activity of $[(RuArH)_2Cl_4]$ as a hydrogenation catalyst (of pent-1-ene at 30 °C/20 atm) in benzene in the presence of pyrrolidine was first noted in 1970.[169] That paper also reported that the activity was lower in dimethylformamide (DMF), where the predominant reaction was the isomerization of pent-1-ene to pent-2-enes which were hydrogenated more slowly. However, the highest hydrogenating activity was associated with samples containing an excess of '$RuCl_2$'.[169] A further study[183] examined the hydrogenation of olefins by $[(RuC_6H_6)_2Cl_4]$ in DMF (30 °C/1 atm). An order of reactivity: hex-1-ene > dimethyl maleate > cyclo-octene, methyl sorbate > allyl acetate > maleic acid was found; hex-1-ene was also isomerized to hex-2-ene. The rate of hydrogenation was found to be first order both in '$(RuC_6H_6)Cl_2$' and in hydrogen, and a mechanism was suggested involving a benzene–ruthenium(I) hydride.[183] However, it is not clear what the catalytically active species was and the catalyst was not recovered at the end of the reaction; since DMF is such a good co-ordinating solvent, it could well displace the benzene completely during the reaction. $[(RuC_6Me_6)(PPh_3)H(Cl)]$ and complex (103) have both been reported to be efficient catalysts for the hydrogenation of arenes and substituted arenes to cyclohexanes.[171,172] Under these more vigorous conditions (50 °C/50 atm H_2), some decomposition to catalytically active metal does occur,[184] just as for the $[(RhC_5Me_5)_2Cl_4]$ catalysts. $[(Ru(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)]$ has also been reported to catalyse the hydrogenation of benzene at high temperatures (90 °C/2—3 atm); cyclohexenes were also formed, and extensive H–D exchange occurred in $D_2 + C_6H_6$ or $H_2 + C_6D_6$ reactions.[185] Although the reaction mixtures were described as homogeneous, it is possible that here, too, very small amounts of highly catalytically active metal were formed during the reactions.

With all these reactions the question of the true homogeneity of the solutions should be raised, since small amounts of very finely divided metal can have a disproportionately large effect on reaction rates; a simple practical test has been developed to resolve the question quantitatively and unambiguously.[186]

$[(RuC_6Me_6)(PPh_3)H(Cl)]$ also catalyses the transfer of hydrogen from 1-phenylethanol to olefins, dienes, and acetylenes.[172]

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[183] A. G. Hinze, *Recl. Trav. Chim. Pays-Bas*, 1973, **92**, 542.

[184] M. A. Bennett, personal communication.

[185] J. W. Johnson and E. L. Muetterties, *J. Am. Chem. Soc.*, 1977, **99**, 7395.

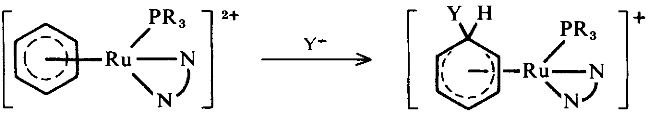
[186] J. E. Hamlin, K. Hirai, A. Millan, and P. M. Maitlis, *J. Mol. Catal.*, 1980, **7**, 543.

[Ru (*p*-cymene)$_2$Cl$_4$] and [(RuC$_6$Me$_6$)$_2$(OH)$_3$]Cl are active catalysts for the disproportionation of aldehydes to alcohols and carboxylic acids (Section 3Bii*g*) but for these ruthenium catalysts the reaction is largely an oxidation to the carboxylic acid, with hydrogen being produced.[123]

(*h*) *Nucleophilic attack at the arene.* A number of workers have reported that the arene ring is attacked by nucleophiles under suitable conditions to give η^5-cyclohexadienyl complexes. Since these latter are of only limited stability such reactions clearly put a limit on the stringency of reaction conditions that can be applied to arene–ruthenium complexes while retaining the arene as a protecting ligand.

Early n.m.r. experiments indicated that [(RuC$_6$H$_6$)$_2$Cl$_4$] that was dissolved in [^{2}H$_6$]Me$_2$SO was attacked by BH$_4^-$, CN$^-$, or even OH$^-$ at the benzene ring but no products were isolated.[166]

N.m.r. spectra also indicated that the benzene rings in [(RuC$_6$H$_6$){HB-(pyrazolyl)$_3$}]$^+$ [187] and in [(RuC$_6$H$_6$)(Cp)]$^+$ [188] were attacked by hydride. Products (118) containing η^5-cyclohexadienyl rings were isolated from the reaction of the dicationic complexes (117) with a variety of nucleophiles.[188]



(117)

(118, $\overset{\frown}{N\;\;N}$ = *o*-phen or bipy,
Y = H, CN, or OH)

(*j*) *Complexes with other Group IV ligands.* Benzene reacts with *trans*-[Ru(CO)$_4$(MCl$_3$)$_2$] to give [(RuC$_6$H$_6$)(CO)(MCl$_3$)$_2$] (M = Ge or Si).[189]

(*k*) *Complexes with N or P ligands.* In addition to the mononuclear 1:1 adducts (102) with amines,[167,192] ionic 1:2 and 1:3 adducts are known, for example [(RuArH)L$_2$Cl]$^+$ (L = NH$_3$[190,191] or py;[192] L$_2$ = *o*-phen,[188] bipy,[188] or en[193]) and [(RuArH)L$_3$)]$^{2+}$ (L = NH$_3$[194] py,[193] or NH$_2$NR$_2$[193]). The NH$_3$ complexes can also be formed directly from ammonium salts:[190,194]

$$[(\mathrm{RuC_6H_6})_2\mathrm{Cl_4}] + \mathrm{NH_4PF_6} \xrightarrow{\mathrm{H_2O}} [(\mathrm{RuC_6H_6})\mathrm{Cl}(\mathrm{NH_3})_2]^+ + [(\mathrm{RuC_6H_6})_2\mathrm{Cl_3}]^+$$

$$[(\mathrm{RuC_6H_6})_2(\mathrm{OH})_3]\mathrm{Cl} + \mathrm{NH_4PF_6} \rightarrow [(\mathrm{RuC_6H_6})(\mathrm{NH_3})_3]^{2+}$$

[187] D. J. O'Sullivan and F. J. Lalor, *J. Organomet. Chem.*, 1973, **57**, C58; R. J. Restivo, G. Ferguson, D. J. O'Sullivan, and F. J. Lalor, *Inorg. Chem.*, 1975, **14**, 3046.

[188] D. R. Robertson and T. A. Stephenson, *J. Organomet. Chem.*, 1977, **142**, C31.

[189] R. K. Pomeroy and W. A. G. Graham, *Canad. J. Chem.*, 1975, **53**, 2985; L. Y. Y. Chan and W. A. G. Graham, *Inorg. Chem.*, 1975, **14**, 1778.

[190] D. R. Robertson, T. A. Stephenson, and T. Arthur, *J. Organomet. Chem.*, 1978, **162**, 121.

[191] R. O. Gould, C. L. Jones, D. R. Robertson, and T. A. Stephenson, *Cryst. Struct. Commun.*, 1978, **7**, 27.

[192] T. Arthur and T. A. Stephenson, *J. Organomet. Chem.*, 1979, **168**, C39.

[193] R. H. Crabtree and A. J. Pearman, *J. Organomet. Chem.*, 1977. **141**, 325.

[194] D. R. Robertson and T. A. Stephenson, *J. Organomet. Chem.*, 1978, **157**, C47.

The reaction of $[(\mathrm{MArH})\mathrm{X}_2(\mathrm{py})]$ with $[(\mathrm{MArH})\mathrm{X}(\mathrm{py})_2]^+$ in the presence of HBF_4 in methanol gives the tri-μ-chloro- or -bromo-cations $[(\mathrm{MArH})_2\mathrm{X}_3]$ $[\mathrm{BF}_4]$.[192] Mixed chloro-bromo-complexes can also be made.

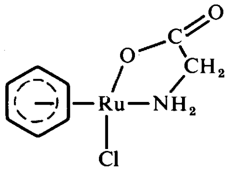
In general, amine ligands only displace benzene very slowly; for example, $[(\mathrm{RuC}_6\mathrm{H}_6)_2\mathrm{Cl}_3]^+$ reacts with pyridine to give $[(\mathrm{RuC}_6\mathrm{H}_6)\mathrm{Cl}(\mathrm{py})_2]$ and then $[\mathrm{Ru}(\mathrm{py})_4\mathrm{Cl}_2]$.[190,195]

Acetonitrile forms mono-,[166] bis-,[166] and tris-adducts.[167,181] Phosphines and phosphites also form analogous mono-,[164–167,190] bis-,[173] and tris-adducts.[181] However, excess ligand often causes loss of the arene;[167,190,193] for example, $\mathrm{PMe}_2\mathrm{Ph}$ gives the $[\mathrm{Ru}_2(\mathrm{PPhMe}_2)_6\mathrm{Cl}_3]^+$ cation.[167] Phosphines and phosphites also stabilize the zerovalent $[(\mathrm{RuArH})\mathrm{L}_2]$ complexes.[173] Mixed amine–phosphine complexes are also known.[188]

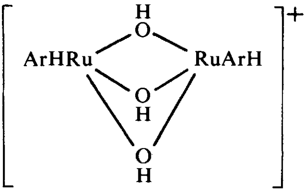
The arenes in $[(\mathrm{RuArH})\mathrm{Cl}_2(\mathrm{PR}_3)]$ can be replaced by other arenes to give $[(\mathrm{RuAr}^1\mathrm{H})\mathrm{Cl}_2(\mathrm{PR}_3)]$; *p*-cymene is the most labile.[167]

Reaction of amino-acid anions with $[(\mathrm{RuC}_6\mathrm{H}_6)_2\mathrm{Cl}_4]$ gave chiral complexes; n.m.r. studies showed that (119) epimerized slowly at the metal in solution.[196]

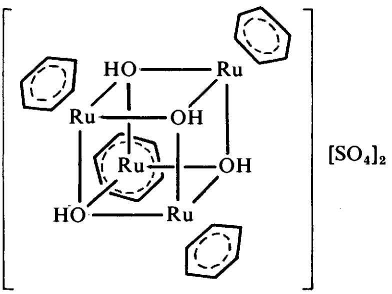
(*l*) *Complexes with O and S ligands*. Reaction of $[(\mathrm{RuArH})_2\mathrm{Cl}_4]$ with aqueous base gives the tri-μ-hydroxo complexes (120),[194,195] analogous to the rhodium complex (79). These do not react with phosphines.[194] If the reaction of $[(\mathrm{RuC}_6\mathrm{H}_6)_2\mathrm{Cl}_4]$ is



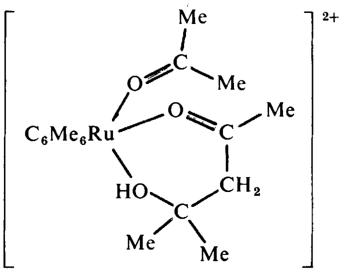
(119)



(120)



(121)



(122)

[195] D. R. Robertson and T. A. Stephenson, *J. Organomet. Chem.*, 1976, **116**, C29.
[196] D. F. Dersnah and M. C. Baird, *J. Organomet. Chem.*, 1977, **127**, C55.

carried out carefully in the presence of sodium sulphate then the product is the tetranuclear complex (121).[197]

When $[(RuC_6H_6)_2Cl_4]$ is treated with a sodium alkoxide or if (120) is dissolved in an alcohol, then the tri-μ-alkoxy complexes $[(RuC_6H_6)_2(OR)_3]^+$ (R = Me or Et), analogous to (120), are obtained.[194] This reaction may be contrasted with that of $[(RhC_5Me_5)_2(OH)_3]^+$ with alcohols to give (24), (25), or carboxylate complexes.[51]

$[(RhC_6Me_6)_2Cl_4]$ forms the tris-acetone complex $[(RuC_6Me_6)(Me_2CO)_3]^{2+}$. However, in contrast to the very labile rhodium and iridium analogues, which were only known in solution, this ruthenium complex could be isolated at low temperature and its further reactions studied in more detail. One reaction is the solvolysis of PF_6^- to co-ordinated $PO_2F_2^-$ in $[(RuC_6Me_6)_2(PO_2F_2)_3]^+$ [compare (80)] and the other is the aldol condensation to give (122), isolated as the BF_4^- salt.[181]

Dimethyl sulphoxide appears to be a very good ligand to Ru^{II},[169] and probably bonds through the S. Dithiophosphates form complexes $[(RuC_6H_6)(S_2PR_2)L]^+$ (L = py, PR'_3, *etc.*) as well as $[(RuC_6H_6)(S_2PR_2)_2]$. In the first the S_2PR_2 is bidentate, while one is bidentate and one unidentate in the bis-complexes; the complexes do not exchange in solution but are less stable than their C_5Me_5–Rh analogues and decompose fairly easily.[139] The use of stronger nucleophiles to synthesize related complexes, such as $S_2CNR_2^-$ or S_2COR^-, causes loss of the benzene ring.[198]

(*m*) *Complexes with halide ligands.* Many of the Ru^{II} arene complexes bear chloride, and this can be exchanged for bromide and iodide;[167] syntheses of the tri-μ-halo-complexes $[(RuArH)_2X_3]^+$ have been mentioned above[192] and the preparation of $Cs^+[(RuC_6H_6)Cl_3]^-$ has been described.[190]

B. Rhodium and Iridium.—Apart from the arene-cyclopentadienyl complexes already discussed in Section 3Bii*f*, only a few arene complexes are known; in general, the arene is easily removed and hence is a poor protecting ligand.

Bis(hexamethylbenzene)rhodium(II) cation has been made by the Fischer method;[199a] on reduction (Zn,HCl), the (η^6-hexamethylbenzene)(η^4-hexamethylcyclohexa-1,3-diene)rhodium(I) cation is formed[199b] [not bis(hexamethylbenzene)rhodium(I) as originally reported]. Reaction of $[Rh(diene)_2]^+$ with arenes gives $[Rh(arene)(diene)]^+$ (diene = cyclo-octa-1,5-diene or norbornadiene; ease of formation decreases in the order arene = $C_6Me_6 > C_6Me_3H_3 >$ xylene > toluene > benzene), and reaction of $[Rh(C_2H_4)_2(acac)]$ with an arene in the presence of Ph_3C^+ gives $[Rh(arene)(C_2H_4)_2]^+$.[200] A variant on the first method, which also works for Ir, consists in treating the cyclohexadiene complex with

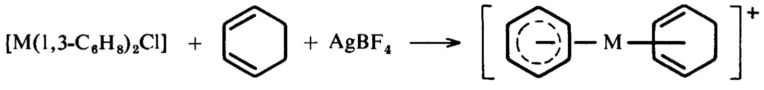
[197] R. O. Gould, C. L. Jones, D. R. Robertson, and T. A. Stephenson, *J. Chem. Soc., Chem. Commun.*, 1977, 222.

[198] D. R. Robertson and T. A. Stephenson, *J. Organomet. Chem.*, 1976, **107**, C46.

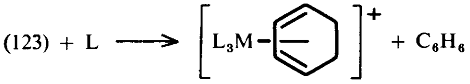
[199a] E. O. Fischer and H. H. Lindner, *J Organomet. Chem.*, 1964, **1**, 307.

[199b] M. R. Thompson, C. S. Day, V. W. Day, R. I. Mink, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1980, **102**, 2979.

[200] M. Green and T. A. Kuc, *J. Chem. Soc., Dalton Trans.*, 1972, 832



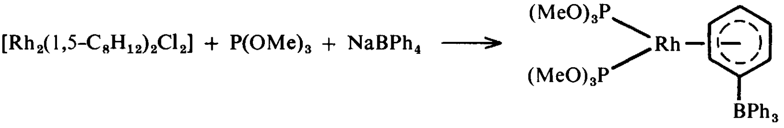
(123)



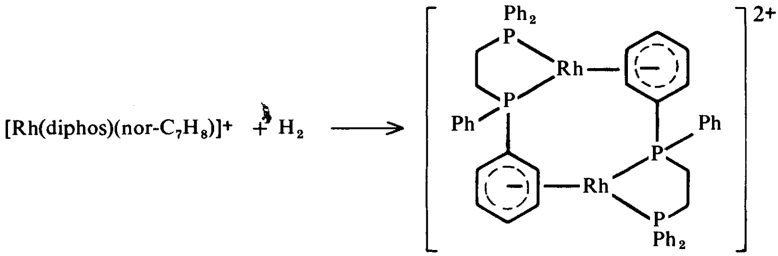
$AgBF_4$ in the presence of excess cyclohexadiene. This gives (123); the benzene is replaced by mesitylene to give $[M(C_6Me_3H_3)(1,3\text{-}C_6H_8)]^+$ but reactions with phosphines, pyridine, or acetonitrile all cause loss of the arene.[201]

Phenyl groups attached to B and to P also π-bond to Rh, as in $[Rh\{P(OMe)_3\}_2BPh_4]$ (124)[202] and $[Rh_2(diphos)_2]^{2+}$ (125)[203] (see also Refs. 23 and 27). In the latter complex the Rh · · · arene interaction is very weak and breaks up even in methanol solution. The related complexes $[Rh(diphos)(arene)]^+$ have also been made and their equilibrium constants decrease in the order (arene) = xylene ($500 M^{-1}$) > toluene (97) > benzene (1).[203]

C. Palladium and Platinum.—Apart from the dinuclear bis-benzene complexes $[Pd_2(C_6H_6)_2Al_2Cl_8]$ and $[Pd_2(C_6H_6)_2Al_4Cl_{14}]$ (only stable in the solid state)[204] and the unusual η^2-hexakis(trifluoromethyl)benzene complex $[Pt\{C_6(CF_3)_6\}(PEt_3)_2]$,[205] the only other arene complexes are (127), made by the reaction of



(124)



(125)

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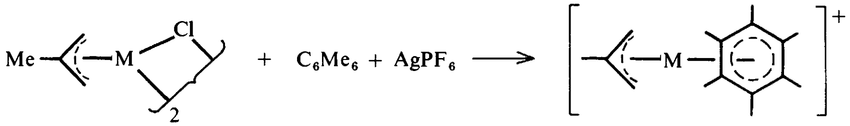
[201] P. T. Draggett, M. Green, and S. F. W. Lowrie, *J. Organomet. Chem.*, 1977, **135**, C60.
[202] M. J. Nolte, G. Gafner, and L. M. Haines, *J. Chem. Soc., Chem., Commun.*, 1969, 1406.
[203] J. Halpern, D. P. Riley, A. S. C. Chan, and J. J. Pluth, *J. Am. Chem. Soc.*, 1977, **99**, 8055.
[204] G. Allegra, G. T. Casagrande, A. Immirizi, L. Porri, and G. Vitulli, *J. Am. Chem. Soc.* 1970, **92**, 289.
[205] J. Browning, M. Green, B. R. Penfold, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1973, 31.



(126) (127)

hexamethylbenzene with the 2-methylallyl complex (126).[206] The palladium complex (127*a*) could actually be isolated as an unstable orange solid but the platinum one (127*b*) could only be confirmed by n.m.r. spectroscopy at low temperatures. The C_6Me_6 appears to be η^6-bonded, but this is not certain.

The arenes are so weakly bound that even poorly co-ordinating ligands or solvents remove them. Clearly there seems little point in looking for stabilizing ligands here.

5 Summary and Conclusions

Ligands which are π-bonded and π-acid in character can stabilize complexes of the platinum metals as well as can the more normal σ-donor ligands.

Such stabilizing ability varies with the nature of the π-ligand. It is greatest for η^5-cyclopentadienyl since this ligand is least readily attacked or displaced. Substitution of the cyclopentadienyl hydrogens (for example by alkyl groups) leads to significant further stabilization. This is partly for steric reasons, as attack at both the ring and at the metal are further inhibited, and partly for electronic reasons, since the ring is bound more tightly to the metal, especially in higher oxidation states.

However, the stabilizing ability of, for example, η^5-C_5Me_5 is not uniform to all metals but depends on what decomposition paths are available. For example, Rh^{II} is a poor leaving group from C_5Me_5 and hence $[(Rh^{III}C_5Me_5)XY]$ complexes are very stable.* Cobalt(II) however, is a good leaving group, and hence $[(Co^{III}C_5Me_5)XY]$ complexes are much less stable.

The same picture can be used to understand the stability of $[(Ru^{II}\eta^6\text{-arene})XY]$ complexes and their osmium counterparts. Although the arenes are very stable and hence are good leaving groups, Ru^{II} and Os^{II}, except in the presence of certain ligands, are unfavourable oxidation states, and hence would be poor leaving groups. To complete the argument, arene–iron(II) complexes should be very unstable towards loss of the arene.

Here too, the more heavily substituted arene complexes show the highest stability.

η^4-C_4 ligands appear to be poor at stabilizing metal complexes since they show high reactivity towards nucleophiles; the same applies to 'open' cyclic and to acyclic polyene ligands. Further, no effective π-ligands for stabilizing palladium or platinum have yet been developed. Even the η^3-allylic [to M^{II}] and the hindered and conjugated olefin ligands [to M^0] that allow the easy isolation of

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*The loss of $C_5Me_5^-$, even in very polar media, is even more difficult.

[206] D. J. Mabbott, B. E. Mann, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1977, 294.

stable complexes of these metals do not stabilize them during catalytic reactions. In fact most of the reactions catalysed by palladium involve oxidation rather than reduction.

Complexes with π-ligands have so far shown catalytic activity broadly similar to that shown by complexes of the same metals bearing conventional σ-donor ligands. They also show the same problems; for example, during catalytic oxidation reactions, especially those involving direct oxygenation, both the stabilizing ligands and the substrates are slowly oxidized.

Two properties of C_nR_n–metal complexes deserve comment. One is the high tendency they have to form dinuclear structures with either two or three bridging groups, as in $[(MC_nR_n)_2X_4]$ or $[(MC_nR_n)_2X_3]^+$. Hydrides are especially adept at acting as the bridging ligands; since they bind strongly, this effect can decrease the activity of the complexes in catalysis of hydrogen transfer.

A more useful aspect is the ability of the peralkyl π-bonded ligand to stabilize moderate oxidation states (in particular, those bearing 'hard' ligands such as hydroxide, nitrate, sulphate, *etc.*) as well as low oxidation states. This allows the development of an organometallic and catalytic chemistry in aqueous media. Since such catalysts avoid the need for an (expensive) organic solvent they could prove very useful.

More detailed comparisons of activity between catalysts bearing π-acid and those bearing σ-donor ligands are difficult since mechanisms have yet to be fully explored for the former. A key feature of the activity of the phosphine-based catalysts is the preferential labilization of certain *trans*-ligands. By their nature as terdentate ligands, spanning three *fac* sites, η^5-C_5Me_5 and η^6-C_6R_6 cannot do this. Effectively therefore the π-ligands shield a sizeable portion of the co-ordination sphere of the metal. Estimates can be made of this shielding in terms of cone angle,[207] based on *X*-ray structures and including the van der Waals radii for all the hydrogens, and these are listed in Table 4.

For comparison, cone angles of some organophosphorus compounds often used as ligands are included. It is evident that while C_nR_n are larger than most

Table 4 *Cone angles for* MC_nR_n *and related species*

π-ligands		*σ-donor ligands*[a]	
Rh^{III}–C_5Me_5	188°	$P(mesityl)_3$	212°
Rh^{I}–C_5Me_5	182°	$P(o\text{-}tolyl)_3$	194°
Rh^{III}–C_5H_5	148°	PBu^t_3	182°
Rh^{I}–C_5H_5	150°	PPh_3	145°
Ru^{0}–C_6Me_6	192°	$P(OPh)_3$	128°
Ru^{II}–C_6H_6	162°	PMe_3	118°
		$P(OEt)_3$	109°

[a] from ref. 207.

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[207] C. A. Tolman, *Chem. Rev.*, 1977, 77, 313.

single PR_3 ligands, their steric effect should not be as great as that of even two moderately sized phosphines. Further extrapolation is difficult since two (or more) *cis*-PR_3 can pack more efficiently by interleaving R groups than their cone angles suggest. This cannot happen so easily for C_nR_n ligands.