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COORDINATION CHEMISTRY OF HALOCARBONS

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CONTENTS

A. INTRODUCTION

Halocarbons constitute one of the most important classes of organic compounds and are useful not only as intermediates in synthesis [1] but also as solvents [2]. Few synthetic procedures of any complexity in organic or organometallic chemistry fail to involve halocarbons at some stage. Yet halocarbons have been proved to form true coordination complexes, con-

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taining the M–X–R group, only in very recent years. In sharp contrast, complexes of the halide ions X^-, especially where X = Cl, Br or I, constitute one of the largest classes of coordination compounds [3]. One factor is simply that the anions X^- are much more basic than the halocarbons RX.

Those molecules which tend to form the most stable transition metal complexes generally fall into one of two categories: good σ-bases, which easily protonate, or good π-acids, which often form stable oxides. Examples include the σ-basic tertiary amines which form R_3NH^+, and the π-acidic carbon monoxide, which forms CO_2. Although some ligands such as trialkylphosphines exhibit both tendencies, very few molecules which form stable transition metal complexes do not fall into either category. One such class of ligands is the halocarbons, RX (R = alkyl, aryl; X = F, Cl, Br, I). Halocarbons are very weak bases, and only for the iodoarenes are the oxides known, and even then they are relatively unstable.

We will see in this review that halocarbons are activated by coordination towards attack at the α-carbon by nucleophiles. This means that unless care is taken to exclude nucleophiles, the complexes will decompose. This situation is difficult to arrange, since the common ligands in coordination chemistry are also good nucleophiles. Another common decomposition pathway that is often difficult to prevent is oxidative addition to the metal to give an alkyl metal halide, R–M–X [4(a),4(b)].

We shall see that the electronic structure of halocarbons dictates that the M–X–R angle in the complex must be close to 90°. This in turn implies that the effective steric bulk of the ligand will be much greater than would be the case if the angle were 180°. As Tolman has shown [5] for the ligands R_3P, increased bulk in a ligand leads to decreased stability of the complex.

In this review, we discuss the physical properties of halocarbons relevant to their ability to form coordination complexes, and the preparation and characterization of halocarbon complexes. The sections are organized by class of metal: *s*-block, *d*-block and then *p*-block. In view of the lack of true coordination complexes with a full covalent bond between the halocarbon and the metal for all but the *d*-block metals, we will also look at some examples of secondary bonding. In a secondary bond, the $M \cdots L$ bond distance lies between the sum of the van der Waals radii and of the covalent radii [6]. The resulting interaction is probably largely coulombic and very weak. Nevertheless, there seems to be a smooth gradation of $M \cdots XR$ bond lengths for halocarbon complexes, and so a sharp distinction is not possible. The literature up to March 1989 is covered.

B. PROPERTIES OF HALOCARBONS

Tables 1 and 2 list some of the physical properties of halocarbons and the halogen atoms relevant to halocarbon coordination. Each of the halogens is

TABLE 1

Some physical properties of halogen atoms

	X			
	F	Cl	Br	I
Pauling electronegativity(χ) [7]	3.98	3.16	2.96	2.66
$\Delta\chi$(C–X) [7]	1.43	0.61	0.41	0.11
Covalent radius (Å) [8]	0.64	0.99	1.14	1.33
Ionic radius of X^- (Å) [9]	1.33	1.81	1.96	2.20
van der Waals radius (Å) [10]	1.47	1.75	1.85	1.96
Ionization energy (eV) [11]	−17.42	−12.97	−11.81	−10.45
Electron affinity (eV) [12]	+3.448	+3.613	+3.363	+3.063

more electronegative than an sp^3 carbon (electronegativity, 2.5) [7]. The weak bond strength and high polarizability for the C–X bond [15], where X = Cl, Br and I, together with the fact that X^- is a good leaving group makes the α-carbon very sensitive to nucleophilic attack. The trend in the dipole moments of the halomethanes [13] shows a maximum for MeCl; the lower value for CH_3F is undoubtedly due to the much shorter C–F distance. The polarity of the chloroalkanes contributes to their great utility as solvents. The decrease in ionization energy [16] on going from fluorine to iodine shows that MeI is the strongest donor. The same trend holds for the haloarenes.

None of the halocarbons shows any great tendency to accept a proton. Gas-phase studies [18] show that the proton affinity of chloromethane is 155 kcal mol^{-1}, which can be compared with that of NH_3 at 202.3 kcal mol^{-1} and that of ethylene at 154 kcal mol^{-1}.

TABLE 2

Some physical properties of halocarbons

	RX			
	MeF	MeCl	MeBr	MeI
Dipole moment (D) [13]	1.85	1.87	1.81	1.62
C–X bond distance (Å) [14]	1.831	1.767	1.937	2.135
C–X bond dissociation energy (kcal mol^{-1}) [15]	108	83.5	70	56
Ionization energy (eV) [16]	13.04	11.3	10.65	9.85
Bond polarizability ($\times 10^{24}$ cm^2) [17]	0.96	3.67	5.04	8.09
Ionization energy of C_6H_5X (E_n^1, eV) [16]	13.85	11.7	11.25	10.55

The iodocarbons should be the best candidates as ligands, being the best donors. However, the greater ease of C–I bond cleavage implies that iodocarbons are also the most likely to react by other pathways such as oxidative addition. Applying hard–soft acid–base ideas [19], iodocarbons should bind best to soft Lewis acids, such as low-valent late transition metals, while fluorocarbons should coordinate to high-valent or earlier transition metals. At the same time, it is difficult to avoid oxidative addition in the former case and fluoride abstraction by the metal in the latter case. Haloarenes have a greater C–X bond strength which helps prevent these reactions. The chelate effect can be used to increase the binding tendency of otherwise reluctant ligands, so it is no surprise to see that chelating haloarenes are the largest class of halocarbon ligands found to date.

C. SYNTHESIS AND STRUCTURE OF HALOCARBON COMPLEXES

(i) Group 1 and 2 halocarbon complexes

Metals of the *s*-block only form weak complexes with halocarbons involving secondary bonding, rather than true coordination complexes. Although weak, these interactions may be important in a biological context, especially for the C–F bond. Glusker and coworkers have considered intramolecular interactions of the C–F bond [20], including hydrogen bonding, dipolar interactions and secondary bonding with metal cations. Their crystallographic studies of ammonium rubidium hydrogen fluorocitrate [21] and sodium fluoropyruvate [22] revealed relatively close CF $\cdots$ M contacts of 3.095 Å and 2.979 Å to Rb^+ and 2.470 Å to Na^+. In addition, literature data on rubidium fluoroorotate [23], sodium fluoroacetate [24], dipotassium tetrafluorophthalate [25], potassium hydrogen difluoromaleate [26] and potassium hydrogen difluorofumarate [26] show that one or more fluorine atoms closely approach the alkali metal cation (2.47–2.56 Å for Na^+, 2.87–3.21 Å for K^+ and 2.88–3.22 Å for Rb^+), in some cases more closely than does oxygen. The fluorine atom is part of a chelate ring in each of the structures except $K_2[C_6F_4(CO_2)_2]$ [25], in which the fluorocarbon is a monodentate group. These interactions are believed to be important in the biochemistry of fluoro-organic species. Glusker et al. have proposed a mechanism for aconitase inhibition by fluorocitrate [20] which involves secondary bonding of the C–F bond to the metal.

In several cases, secondary interactions involving a C–Cl bond have been seen. The crystal structure of calcium chloroacetate [27] shows a CCl $\cdots$ Ca distance of 3.206(1) Å, significantly longer than the sum of the ionic radii (ca. 2.7 Å). Some examples of potassium–chlorocarbon interactions include those seen in potassium hydrogen chloromaleate [28], potassium hydrogen bis(trichloroacetate) [29], potassium hydrogen bis(dichloroacetate) [30] and potassium tris(chloroacetato)stannate(II) [31]. These complexes display K $\cdots$ Cl distances of 3.24–3.46 Å.

(ii) Transition metal halocarbon complexes

As early as 1966, Wilkinson and coworkers recognized that halocarbon complexation should be possible when they proposed the formulation $[RhClI(Me)(IMe)L_2]$ ($L = PPh_3$) [32] for the product of the reaction of Wilkinson's catalyst with MeI. A subsequent crystallographic study [33] showed that the true structure is $[Rh(Me)I_2(PPh_3)_2]$, and so the halocarbon is not in fact coordinated in this particular case.

From 1978 to the present, Beck and Schloter at Munich have studied a series of transition metal Lewis acids [34] such as $\{CpM(CO)_3\}^+$. On the basis of IR data, they suggested that complexation between the transition metal fragment and the solvent dichloromethane was taking place. Although no crystallographic data were obtained, it seems likely that true coordinate binding was indeed involved.

In 1982, Crabtree and Quirk synthesized a 1,2-diiodobenzene complex which was stable enough for a crystallographic study by Faller and coworkers [35]. This demonstrated that true coordination of a halocarbon is indeed possible. This ligand was successful because it is chelating and because an iodocarbon seems to be the strongest donor among the halocarbons. The choice of a cationic iridium(III) acceptor led to a suppression of oxidative addition and to an improvement in the acceptor ability of the metal. The corresponding iodomethane complex [36] showed that the ligand has a greatly enhanced sensitivity towards nucleophilic attack at carbon.

Gladysz and coworkers established the generality of the phenomenon by synthesizing a variety of halocarbon complexes of rhenium [37(a)–37(c)] and were the first to observe the M–X–R and R–M–X tautomers for a single metal center.

We will now turn to a detailed description of the halocarbon complexes of the *d*-block metals.

(iii) Groups 4 and 5

So far, few derivatives of this type have been observed. Luo and Crabtree showed that 8-fluoroquinoline displaces trifluoromethanesulfonate from titanium(IV) to give $[Cp_2Ti(8\text{-fluoroquinoline})(OTf)]OTf$. The ^{19}F NMR shows a negligible shift relative to free 8-fluoroquinoline ($\Delta\delta < 2$ ppm), implying nitrogen-only coordination of the quinoline [38].

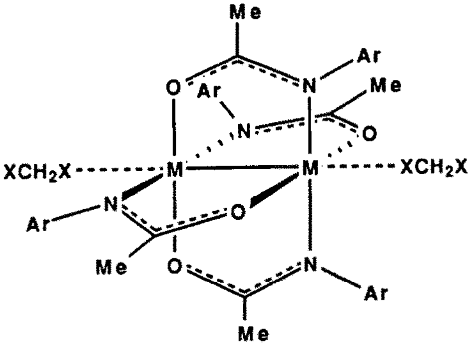


Fig. 1.

(iv) Group 6

Cotton and coworkers showed that the dimeric amido complexes $M_2(\mu_2,\eta^2\text{-ArNCOMe})_4$ (M = Cr, Mo; Ar = 2,6-xylyl) form weak axial M · · · X secondary bonds to two dihalomethane molecules (X = Cl, Br) in the solid state structures (Fig. 1) [39(a),39(b)] with distances (Cr · · · Cl = 3.58(1), 3.354(3) Å; Cr · · · Br = 3.544(5), 3.335 Å; Mo · · · Cl = 3.59(1), 3.417(6) Å; Mo · · · Br = 3.544(4), 3.390(3) Å) near the sum of the van der Waals radii. Axial ligation of donor molecules in these $[M(II)]_2$ dimers generally leads to a lengthening of the metal–metal triple bond; in these cases the effect was too small to be seen.

Beck and Schloter have described the reaction of hydrides $[Cp(CO)_3MH]$ (M = Cr, Mo, W) with triphenylmethyl cation in dichloromethane to form $[Cp(CO)_3M(F\text{–}BF_3)]$ and its PF_6^- analog [34]. Coordination of the dichloromethane solvent at low temperatures is indicated by changes in the IR frequencies of the CH_2Cl_2 group. In particular, the C–Cl frequencies at 708 and 741 cm^{-1} are perturbed. In the tungsten complex these are now

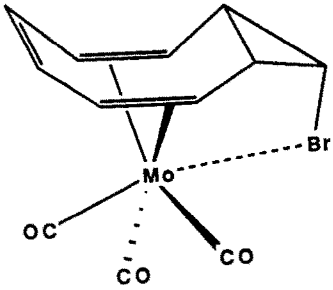


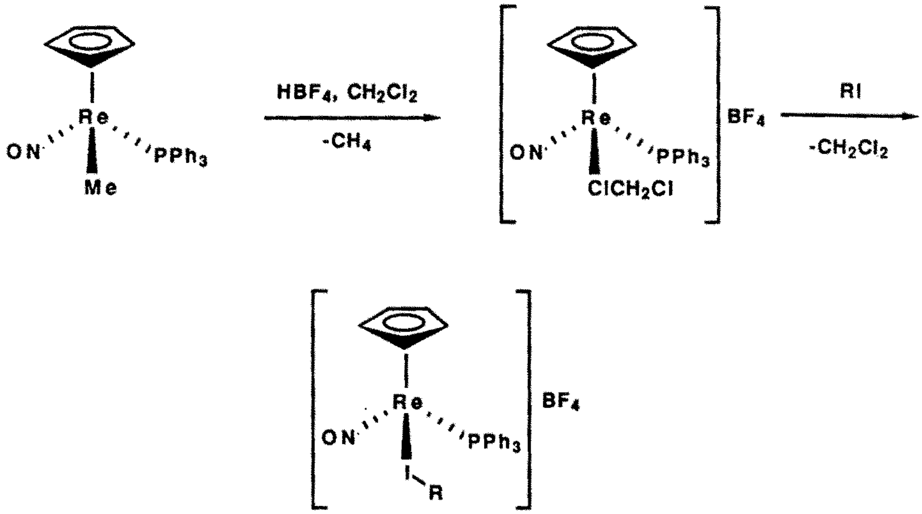
Fig. 2.

observed at 616 and 760 cm^{-1}. The complexes were unstable at room temperature, however, so no crystallographic confirmation of halocarbon binding could be obtained.

Liotta et al. reported a series of molybdenum(0) complexes of *endo*-9-halobicyclo[6.1.0]nona-2,4,6-triene ligands (halo = chloro, bromo, 9,9-dibromo) [40]. The short Mo $\cdots$ Br distance (2.734(2) Å) (Fig. 2) in the structure of one of these, $Mo(CO)_3(C_9H_9Br)$, shows that a coordinate bond is present.

(v) Group 7

Gladysz and coworkers have demonstrated that protonation of the rhenium alkyl complex $[Cp(NO)(PPh_3)ReCH_3]$ at low temperature results in loss of methane. The resulting Lewis acidic fragment can coordinate dichloromethane at low temperatures to form $[Cp(NO)(PPh_3)Re(ClCH_2Cl)]^+$ [37(a)–37(c)]. The best evidence comes from ^{13}C NMR studies; notably, the coordinated solvent appears downfield of the free solvent ($\Delta\delta = +24.3$) and displays coupling to phosphorus ($^3J_{C,P} = 3.8$ Hz). Displacement of CH_2Cl_2 with a variety of halocarbons yields the corresponding complexes $[Cp(NO)(PPh_3)Re(XR)]^+$ (X = I, R = Me, Et, *n*-Pr, *n*-Bu, CH_2SiMe_3, $(CH_2)_3Cl$, CH_2Cl, Ph, *p*-$CH_3OC_6H_4$; X = Br, Cl, R = Et; eqn. (1)):



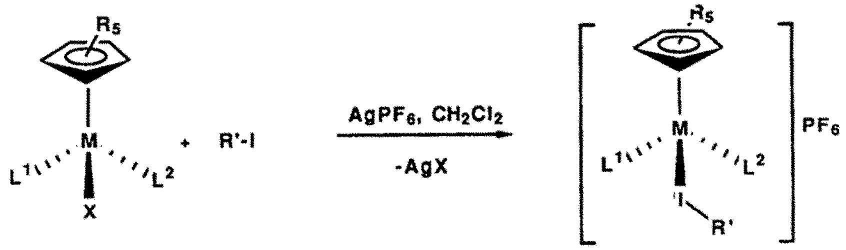
(1)

The X-ray crystal structure of the ICH_2SiMe_3 complex [37(c)] shows an Re–I distance of 2.678 Å, well within the sum of the covalent radii and even shorter than the 2.72 Å observed in the analogous $[(\eta^5\text{-}C_5H_4Me)(NO)(PPh_3)ReI]$.

(vi) Group 8

Cruz-Garritz and coworkers found that one of the thiophenoxide ligands in $Ru(SC_6F_5)_3(PMePh_2)_2$ is chelated [41], with an $Ru \cdots F$ distance of 2.489(6) Å, characteristic of secondary bonding, and an Ru–F–C angle of 117.3° (Fig. 3). Since the molecule is paramagnetic, no NMR studies could be performed to determine whether the halocarbon interaction persists in solution.

Kulawiec and Crabtree prepared a series of cationic cyclopentadienyliron and cyclopentadienylruthenium complexes of haloalkanes and haloarenes of the formula $[(C_5R_5)M(L^1)(L^2)(IR)]PF_6$ (R = H, Me; M = Fe, Ru; L = CO, PPh_3, dppe; R = Me, primary and secondary alkyl, *p*-tolyl) (see eqn. (2)) and $[Cp(CO)Ru(Ph_2PC_6H_4\text{-}o\text{-}X)]PF_6$ (X = Cl, Br), by silver(I)-mediated halide abstraction in the presence of the iodocarbon [42(a),42(b)]:



(2)

One of these, $[Cp(dppe)Ru(IMe)]^+$, can also be prepared by direct methylation of the iodide precursor [Cp(dppe)RuI] with methyl trifluoromethanesulfonate. Faller carried out a structural study of $[Cp(CO)(PPh_3)Ru(IC_6H_4\text{-}p\text{-}Me)]PF_6$, the first reported for a non-chelating haloarene. The Ru–I distance of 2.6213(1) Å is normal. Haloarenes have two *p*-type lone pairs on the halogen. The one which is conjugated with the ring is presumably the less basic of the two. Nevertheless, this is the lone pair that coordinates to

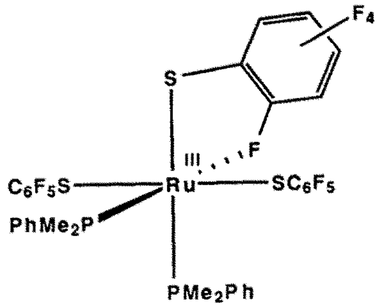


Fig. 3.

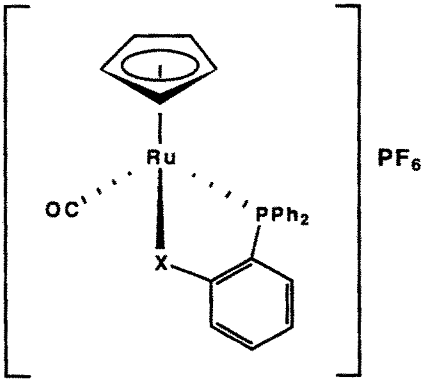


Fig. 4.

the metal, no doubt for steric reasons. The Ru–I–C angle of 102° is similar to those usually observed in chelating haloarene complexes and indicates a high degree of *p*-character of the donor orbital.

Chelating haloaryl phosphine ligands have also been studied as ligands for the $[CpRu(CO)]^+$ fragment (Fig. 4) [42(b)]. The ^{31}P NMR chelation shifts can distinguish between chelation, cyclometallation and a non-chelating structure for this ligand.

Simpson and coworkers have more recently reported [43] on the analogous complex, $[Cp(CN^tBu)(PPh_3)Ru(IMe)]^+$, formed either by displacement with iodomethane of H_2 from the dihydrogen complex or by direct methylation of the ruthenium iodide. The Ru–I bond is normal (2.670(2) Å).

(vii) Group 9: cobalt

One of the earliest reports of an M · · · XR secondary bonding distance in a transition metal complex dates from 1971. The bis(1-methyl-3-*ortho*-chlorophenyltriazine-1-oxide) cobalt(II) complex (Fig. 5) [44] shows Co · · · Cl distances of 2.943 and 3.016 Å. Zacharias and Chakravorty later prepared a series of analogous cobalt(II) and nickel(II) bis complexes of the phenyltriazene ligands $RN(O){=}N{-}N{-}C_6H_4$-*o*-X (R = alkyl; X = halogen, OMe, SMe) [45]. They proposed that these ligands are chelated to the ions in an η^3-{O, N, X} mode. The evidence for secondary halocarbon binding included magnetic and spectroscopic similarity to the cobalt complex depicted above (Fig. 5). For example, the nickel(II) halocarbon complexes are diamagnetic in the solid state, suggesting a square-planar, non-halogen-coordinated geometry, but in benzene solution there is equilibrium between the diamagnetic square-planar and paramagnetic octahedral forms. Either the solvent itself or the halocarbon might coordinate, however. None of the

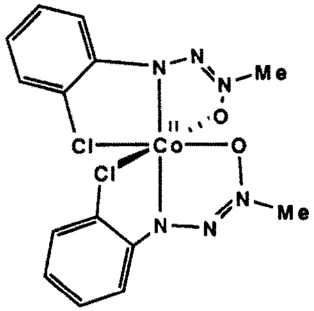


Fig. 5.

other members of this series was characterized by crystallography. A similar cobalt(II) complex, $Co(MeIm)_2(O\text{-}C_6H_2\text{-}1,3,5\text{-}Cl_3)_2$, was prepared and studied by X-ray crystallography [46]; one of the chloroaryloxide ligands chelates to the cobalt center via an *ortho* chlorine atom at a secondary bonding distance of 3.100(4) Å, resulting in a distorted square-pyramidal geometry. The other chloroaryloxide ligand chelated even more weakly, with a Co · · · Cl distance of 3.367(5) Å. The electronic spectrum of this complex in acetone is nearly identical with that obtained in the solid state, suggesting that the five-coordinate structure is maintained in solution.

A secondary-bonded fluorocarbon complex of cobalt has recently been reported. Thompson et al. prepared the cobalt(II) complexes [HB(3,5-Me_2pz)CoSR] (3,5-Me_2pz = 3,5-dimethylpyrazolato, R = C_6H_4-*p*-NO_2, C_6F_5) [47] in a bioinorganic context. In the pentafluorothiophenoxy case, an *ortho* fluoro atom closely approaches the metal center (Co · · · F = 2.64(2) Å) (Fig. 6); the authors believed that this represented a ligand-induced non-bonding contact rather than an attractive interaction, but a secondary bond seems likely.

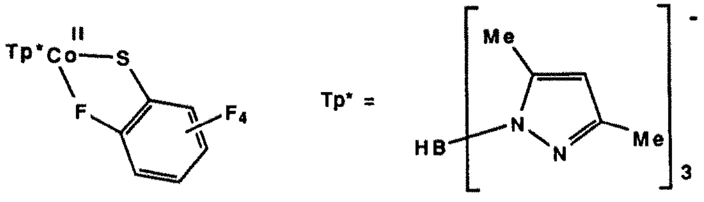
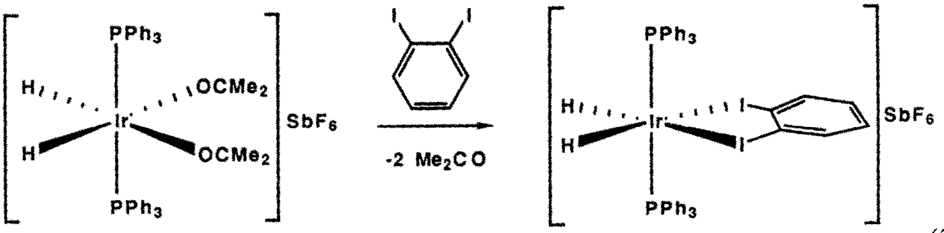


Fig. 6.

(viii) Group 9: rhodium and iridium

o-Diiodobenzene reacts with the solvento complex $[IrH_2(Me_2CO)_2(PPh_3)_2]SbF_6$ by displacement of acetone to yield the chelated complex

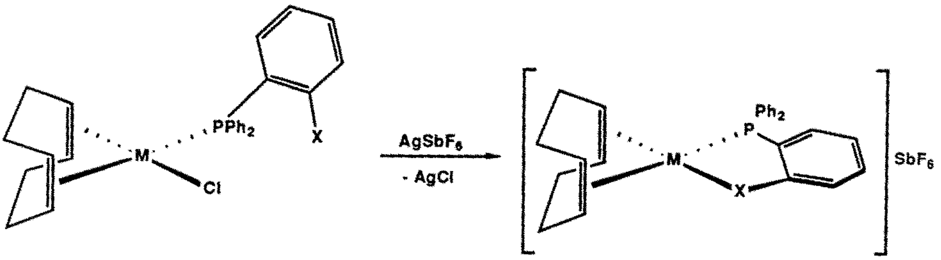
$[IrH_2(o\text{-}I_2C_6H_4)(PPh_3)_2]SbF_6$ (eqn. (3)) [35]:



(3)

The Ir–I distances (2.726(7) Å, 2.745(1) Å) are within the sum of the covalent radii. Other chelating *o*-dihalobenzenes, such as *o*-$BrIC_6H_4$, coordinate similarly, as do monodentate haloalkanes and haloarenes RI (R = Me, Et, iPr, Ph). These latter ligands, however, do not displace coordinated acetone; the complexes are prepared by hydrogenation of $[(cod)Ir(PPh_3)_2]$-SbF_6 in the presence of excess halocarbon in a non-coordinating solvent. A similar complex, $[IrH_2\{o\text{-}XC_6H_4CH{=}CH_2\}(PPh_3)_2]SbF_6$, containing a chelating *o*-halostyrene ligand [48], was shown to be an intermediate in the hydrogenation of the styrene by the iridium(III) hydride to yield $[(\eta^6\text{-}o\{X\text{-}(CH_3CH_2)C_6H_4\}Ir(PPh_3)_2]SbF_6$ (X = Cl, I). All these halocarbon complexes were also characterized by ^1H NMR; in each case, the spectra were fully consistent with the solid state structures.

The same group demonstrated halocarbon coordination in d^8 complexes. The neutral complexes $[(cod)MCl(\eta^1\text{-}Ph_2PC_6H_4\text{-}o\text{-}X)]$ (M = Rh, X = Br; M = Ir, X = Cl; M = Ir, X = Br) react with silver(I) to yield the chelated *o*-halophenyldiphenylphosphine complexes $[(cod)M(\eta^2\text{-}Ph_2PC_6H_4\text{-}o\text{-}X)]SbF_6$ (M = Rh, X = Br; M = Ir, X = Cl; M = Ir, X = Br; eqn. (4)) [49(a),49(b)]:



(4)

The X-ray crystal structures of the iridium(I) bromocarbon and chlorocarbon complexes were reported (Ir–Br = 2.473(4) Å; Ir–Cl = 2.381(4) Å). The chelate ring can be opened by displacement of halogen by MeCN. The relative instability of iridium(V) probably discourages oxidative addition in

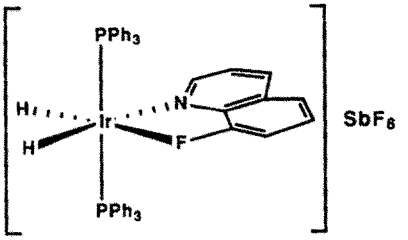


Fig. 7.

the iridium(III) complex mentioned above; however, the stability of the iridium(I) halocarbon complex, even at 110 °C, is surprising. Important factors probably include the electron-withdrawing cyclooctadiene ligand, the net positive charge, and the stability of the five-membered chelate ring. This research also demonstrated that the chelate shift in the ^{31}P NMR [50] is a useful criterion for halocarbon binding, thus allowing solution-state characterization.

Crabtree and coworkers also reported the synthesis of a chelated fluorocarbon complex [51], similar to the *o*-diiodobenzene case mentioned above, using the method described for the preparation of the bis(iodomethane) complex. The X-ray crystal structure of $[IrH_2(8\text{-fluoroquinoline})(PPh_3)_2]SbF_6$ (Fig. 7) shows an Ir ··· F secondary bond distance of 2.514(8) Å, longer than the sum of the covalent radii and similar to those previously observed for Ru(III) ··· F [41] and Co(II) ··· F [47] cases. The iridium complex, however, provides the first spectroscopic evidence that such an interaction is maintained in solution: the ^{19}F resonance displays a large downfield shift ($\Delta\delta = 46$ ppm relative to free 8-fluoroquinoline), and the hydride *trans* to fluorine shows coupling to the coordinated ^{19}F nucleus ($^2J_{H,F} = 95$ Hz). These binding criteria may be useful in demonstrating solution interaction in other cases.

Cotton and coworkers have reported a series of mononuclear iridium and rhodium complexes with chelating *o*-bromophenylphosphine ligands; these are proposed models for orthometallation processes in homogeneous catalysis. The crystal structure of the iridium(III) complex *mer*-$IrCl_3(PPh_3)(\eta^2\text{-}Ph_2PC_6F_5\text{-}o\text{-}Br)$ [52] has a chelating ligand, with an Ir–Br distance of 2.479(2) Å, which compares well with the cationic Ir(I)–Br distance of 2.473(4) Å in $[(cod)Ir(Ph_2PC_6H_4\text{-}o\text{-}Br)]SbF_6$ [49(a),49(b)]. A similar chloroarene-ligated rhodium(I) complex, $RhCl(\eta^1\text{-}\{P\}\text{-}Ph_2PC_6H_4\text{-}o\text{-}Cl)(\eta^2\text{-}\{P,Cl\}\text{-}Ph_2PC_6H_4\text{-}o\text{-}Cl)$ (Fig. 8), was prepared and characterized by NMR [53]. The two potentially chelating ligands are in equilibrium with one another between the chelated and non-chelated forms, as demonstrated by variable-temperature ^{31}P NMR. The interaction of $RhCl_3 \cdot 3H_2O$ with the ligand

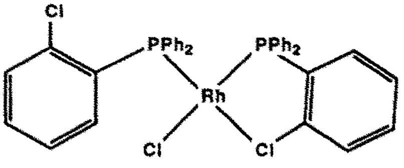


Fig. 8.

$Ph_2PC_6F_4$-*o*-Br yields the bis-chelated complex (Fig. 9) [54] as both the *cis*- and *trans*-Br,Cl isomers, one of which is depicted. Interestingly, the crystal structure shows that the phosphine oxide ligand has oxidatively added the C–Br bond, while the phosphine ligand chelates via bromine (Rh–Br = 2.677 Å), presumably because of the stability of five-membered chelate rings. These complexes demonstrate that a net positive charge is not required for halocarbon coordination, although it may influence bond distances; the cationic iridium(I) bromocarbon complex $[(cod)Ir(Ph_2PC_6H_4\text{-}o\text{-}Br)]^+$ [49(a),49(b)] has a significantly shorter M–Br bond than does the neutral rhodium(III) bromocarbon complex depicted above ($\Delta R(M{-}X) = 0.204$ Å).

The dimeric rhodium(II) complex, $Rh_2(O_2CMe)_4(PPh_3)_2$, is known to give the cyclometallation product $Rh_2(O_2CMe)_2(\eta^2\text{-}\{P,C\}\text{-}Ph_2PC_6H_4)_2\text{-}(MeCO_2H)_2$ upon thermolysis in acetic acid [55]. In an attempt to understand the mechanism of this process using *o*-halophenylphosphine ligands, the same workers thermolyzed the complex $Rh_2(O_2CMe)_4(\eta^1\text{-}\{P\}\text{-}Ph_2PC_6F_4\text{-}o\text{-}Br)_2$ in acetic acid to yield four products, three of which were characterized by X-ray crystallography (Fig. 10). Complexes **A** and **B** both contain two C-metallated ligands which span the Rh–Rh bond, with one and two coordinated bromine atoms respectively (Rh–Br = 2.983(1) and 2.764(2) Å). Complex **C** has one C-metallated ligand and one chelated ligand (Rh–Br = 2.62(2) Å), while the fourth product, **D**, was characterized by NMR and has a structure similar to that seen in **A**, except that a μ_2,η^2-acetate ligand has replaced the η^2-{P,C} ligand. Using the analogous chloroarene

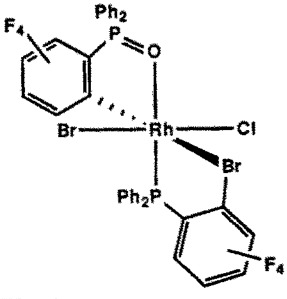


Fig. 9.

(ix) Group 10

Dahl and coworkers studied the interaction between platinum halides and triphenylmethyl chloride [58]. They reported the disordered crystal structure of one of the products, $[Ph_3C][PtCl_5(CH_2Cl_2)]$, in which they suggest that the solvent occupies the sixth coordination site, but failed to mention the $Pt \cdots Cl$ distance.

Platinum and palladium solvento complexes of the type $[M(PR_3)_2(solv)_2]^{2+}$, containing a wide range of weakly coordinating donor solvents (e.g. H_2O, tetrahydrofuran, ROH, Me_2CO, Me_2SO), have been reported. Crabtree and colleagues prepared a similar cationic palladium(II) complex, $[Pd(\eta^2\text{-}\{P,Br\}\text{-}Ph_2PC_6H_4\text{-}o\text{-}Br)_2](SbF_6)_2$ (Fig. 11) with chelating bromoarene ligands, by chloride abstraction with Ag^+ from the neutral precursor $[PdCl_2(\eta^1\text{-}\{P\}\text{-}Ph_2PC_6H_4\text{-}o\text{-}Br)_2]$ [59]. Evidence for the coordination of the bromine atoms arises from the ^{31}P chelation shift of $\Delta\delta = +36.4$ ppm, indicative of formation of a five-membered chelate ring, with no C–Br oxidative addition to give the rare palladium(IV).

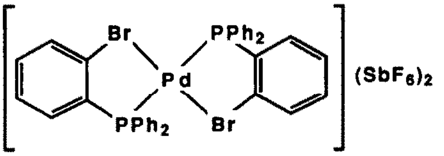


Fig. 11.

(x) Group 11

The structures of several copper(II) complexes, $CuL_2(O\text{-}C_6H_2\text{-}1,3,5\text{-}Cl_3)_2$ ($L_2 = (C_5H_5N)_2$ [60], (imidazole)$_2$ [61], *trans*-$Me_2NCH_2CH_2NMe_2$ [62] (*cis*)), with chelating *o*-chloroaryloxide ligands were subsequently reported (Fig. 12) and all exhibit short $Cu \cdots Cl$ distances (2.85–3.07 Å). Wulfsberg and coworkers showed that the ^{35}Cl nuclear quadrupolar resonance (NQR) spectrum can be diagnostic of chlorocarbon secondary bonding; those chlorine atoms which interact with the copper(II) center show NQR frequencies at 0.8–2.2 MHz lower than those for chlorine atoms which do not interact [63(a),63(b)]. The ^{35}Cl NQR technique has also been applied in the study of mercury(II) chlorocarbon complexes [64(a),64(b)]. On the basis of the NQR spectra, some classes of these complexes, e.g. $RHg\text{-}CCl_3$ and $RHg\text{-}C_6Cl_5$, show intermolecular and intramolecular $RCl \cdots Hg$ interactions. For most of these cases, however, supporting crystallographic evidence is lacking.

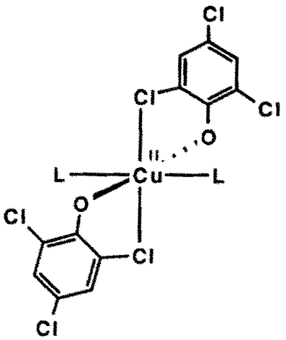


Fig. 12.

The EPR spectra of several copper(II) bis(β-diketonate) chelates in frozen $CHCl_3$–toluene show splittings which the authors ascribe to Cl ··· Cu secondary bonding [65].

The structure of the simple bromomethylsulfonate salt of silver(I) shows six-coordinate octahedral silver [66], with four oxygen atoms and two *trans* bromine atoms at 2.9709(5) Å. Interestingly, each bromine atom bridges two silver ions. The Ag–Br distance is similar to the $Ag^+ \cdots Br^-$ ionic bond distance of 2.95 Å seen in Ag_2BrNO_3.

Uson et al. prepared a mixed Ag_2Pt_2 cluster [67] in which Pt–Ag bonds were bridged by Pt–C_6F_5 groups displaying short F ··· Ag distances of 2.60(1) and 2.69(1) Å (Fig. 13). In a similar trinuclear cluster, $[Bu_4N][\{(C_6F_5)_2Pt(\mu\text{-}C_6F_5)\}_2Ag(OEt_2)]$ (Fig. 14) [68], the bridging pentafluorophenyl groups also chelate to the silver ion via one *ortho* fluorine atom per ring (Ag ··· F = 2.653(10), 2.670(10) Å).

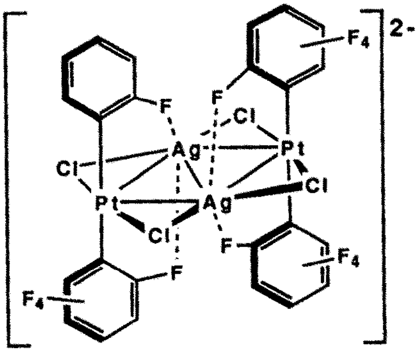


Fig. 13.

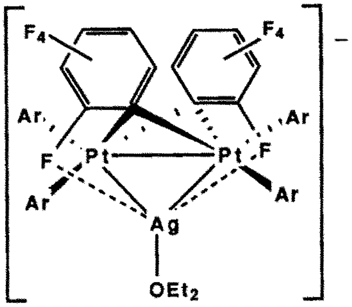


Fig. 14.

Strauss and coworkers showed that saturated dichloroalkanes can ligate to silver(I) in the solid state structures of some salts of weakly coordinating anions. The Ag^+ salt of pentafluorotellurate(−1) ("teflate"), crystallized from 1,2-dichloroethane, exists as a teflate-bridged dimer of the formula $[\{(ClCH_2CH_2Cl)Ag\}_2(\mu\text{-}OTeF_5)_2]$ (Fig. 15) [69], with a bidentate dichloroethane molecule bound to each square-planar silver ion. The short Cl ··· Ag distances (2.626–2.914 Å) are slightly longer than the distances observed in covalent Ag–Cl bonds (e.g. 2.512 Å in (dppe)AgCl). The dimers are weakly bridged to one another in a chain by ligand chlorine atoms (Ag ··· Cl = 3.000 Å). Secondary interactions also occur between the silver ions and fluorine atoms of the anion (Ag ··· F = 2.82, 2.95 Å). More recently, this group also reported the structure of a fascinating example of dichloromethane coordination. Interaction of silver(I) teflate with palladium dichloride in dichloromethane yields the trinuclear complex $[\{(CH_2Cl)_2Ag(\mu\text{-}OTeF_5)_2\}_2Pd]$ (Fig. 16) [70]. Each silver(I) has two bidentate CH_2Cl_2 ligands (Cl ··· Ag = 2.775(2)–2.882(2) Å) and is bridged to the central square-planar palladium(II) by two teflate anions. Shifts in the solid state IR C–Cl stretching frequencies, similar to those observed by Beck and Schloter [34],

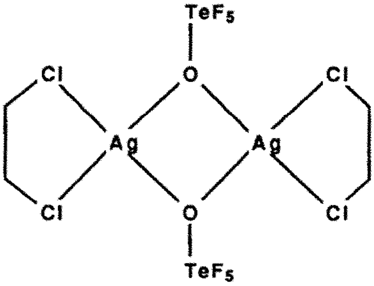


Fig. 15.

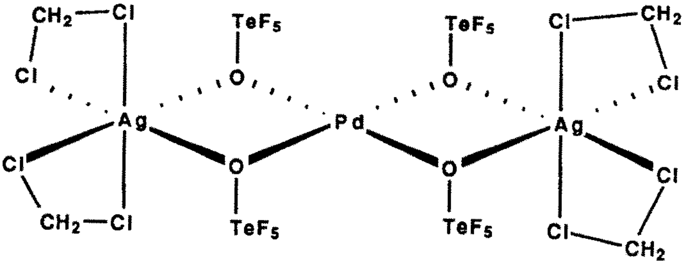


Fig. 16.

are diagnostic of coordination. The M–Cl–C angles in these structures are dependent on the nature of the ligand; the dichloromethane complex displays angles of 92.1(2)–94.5(3)°, while the average corresponding angles in the dichloroethane complex are 103.0(8)°. Although solution spectroscopic techniques were not employed, the high solubility of these complexes in chlorinated solvents argues strongly in favor of halocarbon coordination in solution.

(xi) Choice of metal, counter-ion and solvent

The overwhelming majority of true coordination compounds of halocarbons have an octahedral d^6 configuration. This is especially favorable because the undesirable oxidative addition would lead to a less-favorable seven-coordinate d^4 situation. Almost all these compounds are also cationic. A new positive charge greatly increases the electrophilicity of a metal. This suggests that RX-to-metal direct donation dominates the bonding, because a cationic charge is expected to minimize the contribution of back donation [71]. (Czech et al. have performed a molecular orbital study [71] of the bonding in the complexes $[Cp(NO)(PH_3)Re(XR)]^+$ ($XR = ClCH_2Cl$, IMe) and found negligible backbonding.) The metal must have a small ligand *cis* to the halocarbon, because the M–X–R angle is close to 90°, and so the alkyl group approaches at least one *cis* ligand quite closely. The d^0 metals tend to form such strong bonds to halides that they tend to abstract halide ion from RX rather than simply coordinate to it.

We particularly looked for a d^8 halocarbon complex because this should be the least stable with respect to oxidative addition. A chelating bromoarylphosphine was shown to bind to a cationic iridium(I) species [49(a),49(b)] and to a dicationic palladium(II) species [59], but as discussed in the next section, oxidative addition was easily induced in the iridium case by neutralizing the positive charge. This also illustrates the protective effect of the positive charge, which presumably inhibits metal-to-halocarbon electron transfer in the first step of oxidative addition.

Since halocarbon complexes can react with weak nucleophiles, either to displace the halocarbon or to undergo nucleophilic attack at a haloalkane, special care must be taken in the choice of solvent and counter-ion. This is a problem common to electrophilic complexes in general. Although solutions must be developed for individual cases, halocarbon solvents and BF_4^- and PF_6^- anions have proved to be most useful to date.

(xii) Halocarbon complexes of the f*-block metals*

San Filipo and coworkers showed that the lanthanide shift reagents $Yb(fod)_3$ and $Eu(fod)_3$ (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato) induce chemical shift displacements in the ^1H NMR spectra of primary and secondary fluoroalkanes [72], indicating some degree of secondary bonding. The absence of this effect with chloroalkanes, bromoalkanes or iodoalkanes is consistent with the hard–soft acid–base theory; these softer Lewis bases would not be expected to interact strongly with the hard lanthanide complexes.

(xiii) Halocarbon complexes of the p*-block elements*

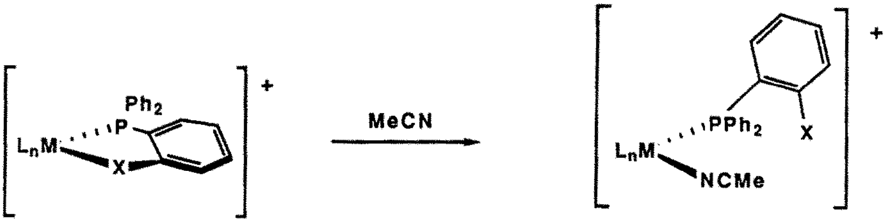
In 1953, Brown and coworkers presented evidence for compound formation between halocarbons and main group Lewis acids [73(a),73(b)] Vapor pressure measurements of MeCl–$GaCl_3$ mixtures, for example, clearly show the formation of a 1 : 1 adduct. Similar results were obtained for other halogens (bromine and iodine) and metals (aluminum). None of these complexes were isolated or further characterized. These studies are relevant to Friedel–Crafts alkylation because $R[AlX_4]$ is sometimes considered to be the active species, but in fact the adduct $[RX–AlX_3]$ may be involved instead [74].

The ^{19}F NMR spectra of a series of 2,6-dibromo-4-fluorothiophenoxide complexes of several main group metal fragments (PhHg, Ph_3Sn, Ph_3Pb) have been measured [75]. A comparison of the spectra with those obtained from purely organic analogs (e.g. $MeSC_6H_2$-2,6-Br_2-4-F) led these authors to propose that weak metal–bromoarene secondary bonding may be present.

REACTIVITY OF HALOCARBON COMPLEXES

(i) Halocarbon substitution

Most coordinated halocarbons can easily be displaced with other donor ligands. For example, chloride or acetate readily displaces iodomethane from the iridium(III) bis(iodomethane) complex $[IrH_2(MeI)_2(PPh_3)_2]SbF_6$ to give $[IrH_2(PPh_3)_2X]_n$ ($X = Cl^-$, $MeCO_2^-$) [36]. $[Cp(NO)(PPh_3)Re(IR)]BF_4$ also undergoes substitution to give $[Cp(NO)(PPh_3)Re(L)]BF_4$ with a wide variety of ligands, such as RCN, CO, $CH_2{=}CH_2$, $Ph_3P{=}O$ and CN^- [37(d)]. The ruthenium(II) halocarbon complexes $[(C_5R_5)L_2Ru(IR')]PF_6$ ($R = H$, Me; $L_2 =$ dppe, $(CO)_2$, $(CO)(PPh_3)$; $R' =$ Me, primary and secondary alkyl, *p*-tolyl) also undergo displacement to give the corresponding acetonitrile complexes [42(a),42(b)]. Chelated *o*-halophenylphosphine ligands also react with external ligands via ring-opening halocarbon displacement (eqn. (7)) ($L_nM = \{(cod)Ir\}$, $\{(cod)Rh\}$ [49(a),49(b)], $\{Cp(CO)Ru\}$ [42(b)]):



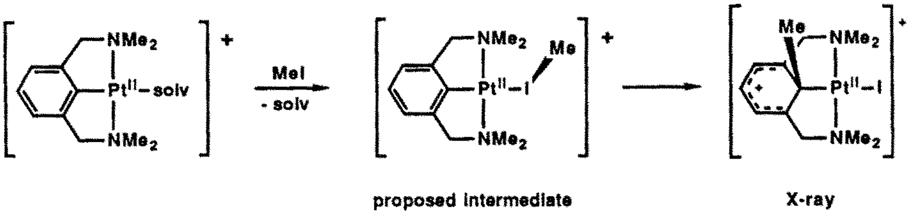
(7)

The chelating ruthenium complexes $[Cp(CO)Ru(Ph_2PC_6H_4\text{-}o\text{-}X)]PF_6$ were used to determine relative binding strengths of halocarbons; the order was found to be chelating bromoarene > chelating chloroarene > iodomethane > *p*-iodotoluene [42(b)].

(ii) Oxidative addition

An important reaction of halocarbons and transition metal species is oxidative addition [4(a),4(b)]. Both radical (stoichiometric and chain) and two-electron (S_N2 type) mechanisms have been observed, depending on the metal complex, the halocarbon and the specific reaction conditions. A concerted three-center mechanism for two-electron oxidative addition of halocarbons has been proposed but not yet substantiated [36]. In cases where electron transfer is the first step, halocarbon complexes are much more reasonable intermediates than for the S_N2 pathway, where attack of the metal takes place at carbon and not X.

van Koten and coworkers described an interesting case of oxidative addition of iodomethane to a platinum(II) solvento complex (eqn. (8)):



(8)

The resulting η^1-cyclohexenyl species was characterized crystallographically [76]. In a theoretical study of this alkyl migration, Hoffmann and coworkers [77] found that interaction of the model platinum(II) fragment $[(C_6H_5)Pt(NH_3)_2]^+$ and MeI gives a stable iodomethane complex $[(C_6H_5)(NH_3)_2Pt(IMe)]^+$. The Pt–I–C angle of 100° and Pt–I distance of 2.5811 Å are very similar to those observed in crystallographically characterized iodomethane complexes [36,43]. They found that the barrier to methyl migration is low; this suggests that concerted oxidative addition via the halocarbon complex may be a viable pathway.

The stability of iridium(III) relative to iridium(V) is one of the likely reasons why oxidative addition does not occur in $[IrH_2(IR)_2(PPh_3)_2]^+$. However, upon reduction of this dihydride with 3,3-dimethyl-1-butene, a spontaneous oxidative addition of the halocarbon takes place to give the crystallographically characterized dimer $[\{(PPh_3)_2MeIr\}_2(\mu\text{-}I)_2]^{2+}$ (Fig. 17) [36]. The proposed mechanism involves transfer of the H-ligands to the alkene to give $Me_3CCH_2CH_3$ and the 16-electron iridium(I) complex $[Ir(PPh_3)_2(IMe)_2]^+$. This is thought to undergo oxidative addition to give $[Ir(I)(Me)(PPh_3)_2]^+$ which subsequently dimerizes. In principle, a concerted mechanism of R–X addition might apply to such a reaction, although the stereochemical studies required to test this have not yet been carried out.

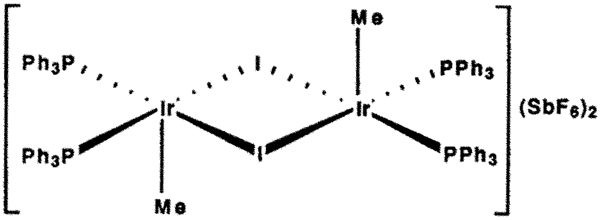
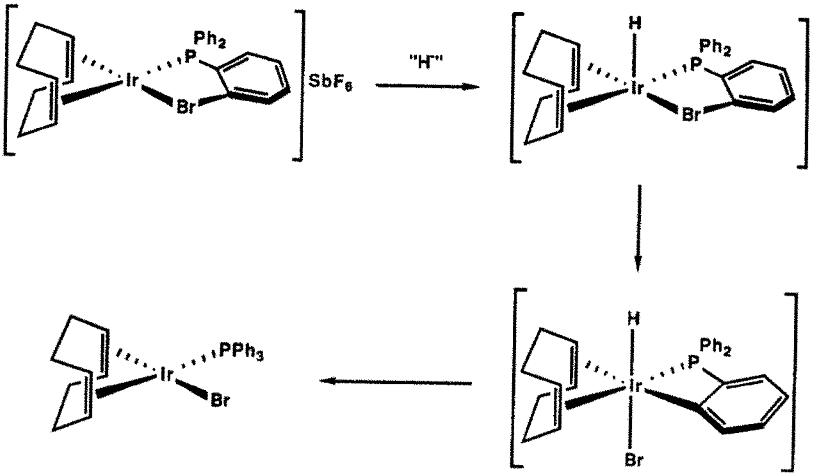


Fig. 17.

Although the coordinated C–X bond does not oxidatively add to iridium(I) in $[(cod)Ir(Ph_2PC_6H_4\text{-}o\text{-}X)]^+$, Burk et al. found that addition of hydride anion induces rapid oxidative addition [49(b)]. This is consistent with the idea that it is the positive charge on the iridium(I) species which prevents oxidative addition. Addition of H^- removes the positive charge and the intermediate $[(cod)IrH(\eta^2\text{-}\{P,Br\}\text{-}Ph_2PC_6H_4\text{-}o\text{-}Br)]$ can then undergo oxidative addition. The resulting cyclometallated iridium(III) hydride can then reductively eliminate to give $[(cod)IrBr(PPh_3)]$ as the final product (see eqn. (9)).

The synthesis and characterization of halocarbon complexes of rhenium(I) by Gladysz and coworkers provided an excellent opportunity for the study of oxidative addition via halocarbon complexation, since rhenium(III) is a readily accessible oxidation level. In fact, the dichloromethane complex

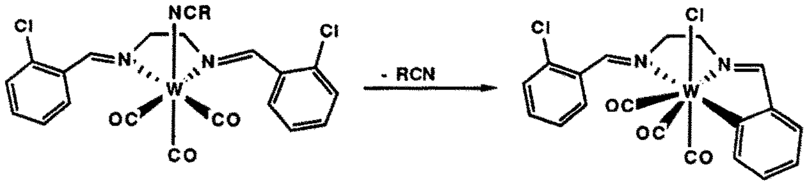


(9)

$[\eta^5\text{-}C_5H_4Me)(NO)(PPh_3)Re(ClCH_2Cl)]BF_4$ decomposes at −35 °C to give the oxidative addition product $[(\eta^5\text{-}C_5H_4Me)(NO)(PPh_3)Re(Cl)(CH_2Cl)]BF_4$ [37(b)]. The authors concluded that oxidative addition does not necessarily proceed directly via the dichloromethane complex; it may also proceed through a spectroscopically observed but as yet unidentified intermediate which is neither the 16-electron cation nor the corresponding BF_4^- complex. The products of halomethane oxidative addition, $[(C_5R_5)(NO)(PPh_3)Re(X)(CH_3)]^+$ (X = Br, I), have been prepared by X_2 oxidation of the Re–methyl complex [37(c)] but do not appear to be accessible directly from the corresponding halocarbon complexes. Nevertheless, the two tautomers exist, and information concerning their interconversion should become available in due course.

Several examples have been reported in which chelating halocarbon complexes, generally containing *o*-halophenylphosphine ligands, also contain the corresponding cyclometallated ligand. These complexes include the pyrazolate-bridge rhodium(II) dimers $[Rh_2(CO)(Br)(pz)_2(\eta^2\text{-}\{P,C\}\text{-}Ph_2PC_6F_4)\text{-}(\eta^2\text{-}\{P,Br\}\text{-}Ph_2PC_6F_4Br)]$ [57] and the mononuclear $[RhClBr(\eta^2\text{-}\{P,Br\}\text{-}Ph_2PC_6F_4Br)\text{-}(\eta^2\text{-}\{O,C\}\text{-}Ph_2P(O)C_6F_4)]$ [54], both of which were described above. Although no mechanistic studies were undertaken, it is reasonable to suspect that oxidative addition may proceed through the halogen-coordinated chelate ring. In neither case does oxidative addition occur to give a mononuclear four-membered chelate ring; in the binuclear cases, the P–C chelating ligand spans an Rh–Rh bond, with the bromide ligand apparently having migrated to the phosphorus-coordinated metal, while in the mononuclear case, only the phosphine oxide ligand has undergone oxidative addition, apparently since the resulting chelate ring is five-membered.

Richmond et al. have investigated the chelation-assisted oxidative addition of haloarenes to zerovalent tungsten (for example, eqn. (10)) [78]:



(10)

In competitive reactions between two different halogens, the steric and electronic natures of the chelate arm appear to be more important than the nature of the halogen. For example, the rigidity and delocalization provided by the imine arm of the ligand (Fig. 18) induce oxidative addition of the chloroarene rather than of the iodoarene [79]. Although no intermediates have been detected, the authors suggested that oxidative addition in these and other (e.g. fluoroarene addition [80]) cases may involve formation of halocarbon complexes.

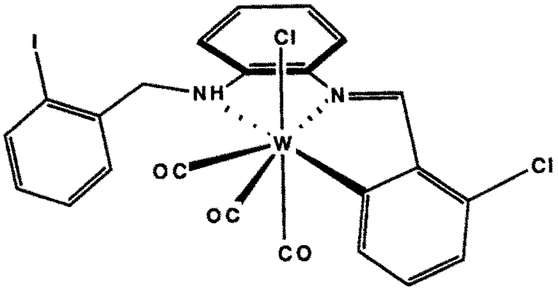


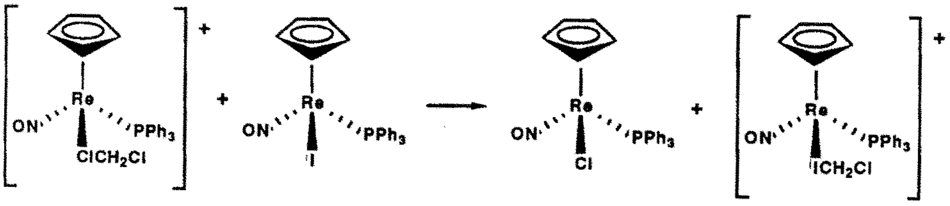
Fig. 18.

(iii) *Nucleophilic attack at halocarbon*

Halocarbons RX (X = Cl, Br and I) are widely employed as electrophiles in organic reactions [1], owing to the availability of the C–X σ^* orbital and to the ability of the halide anion to act as a leaving group. The enhancement of this function by Lewis acids is well known. In the Friedel–Crafts alkylation [74], the reagent $RX\text{–}AlX_3$ acts as a source of an electrophilic R^+ species capable of attacking an arene; the exact nature of this species is in doubt, but a halocarbon complex is a reasonable formulation. Silver(I)-promoted solvolysis of alkyl halides [81] is a second example of an organic reaction in which halocarbon complexation is likely to be an important factor.

The first isolable iodomethane complex, $[IrH_2(MeI)_2(PPh_3)_2]SbF_6$, was found to methylate tertiary amines at a rate 10^5–10^6 times faster than does free iodomethane [36].

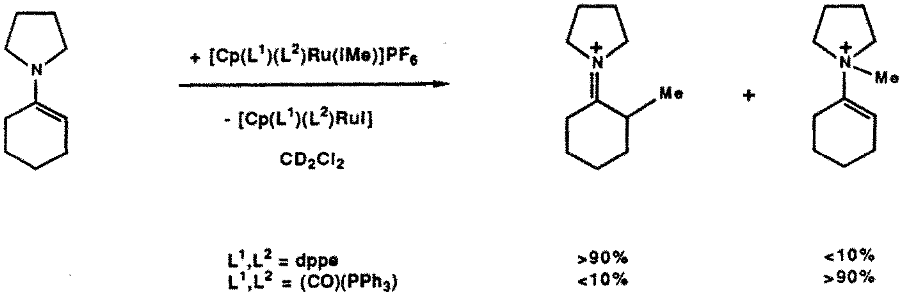
Gladysz and coworkers showed that alkylation of triphenylphosphine with $[Cp(NO)(PPh_3)Re(IEt)]^+$ to give $[Cp(NO)(PPh_3)ReI]$ and Ph_3PEt^+ is second order with $\Delta H^* = 12.9 \pm 0.6$ kcal mol^{-1} and $\Delta S^* = -12.0 \pm 0.9$ cal mol^{-1} K^{-1} [37(c)]. The rate is $(3.3 \pm 1.3) \times 10^5$ times faster than for free EtI. Reaction with bromide also results in alkylation rather than in ligand displacement, generating bromoethane and the rhenium iodide complex. The dichloromethane complex $[Cp(NO)(PPh_3)Re(ClCH_2Cl)]^+$ alkylates the corresponding rhenium iodide, as shown in eqn. (11):



(11)

All these results can be interpreted in terms of either an increased polarization of the C–X bond increasing the availability of the orbital at carbon, or an increase in the ability of the halide to act as a leaving group on coordination.

Kulawiec and Crabtree demonstrated C–C bond formation by attack of the pyrrolidine enamine of cyclohexanone on their ruthenium iodomethane complex, which yields 2-methylcyclohexanone in 80% yield (eqn. (12)) [42(a)]:



(12)

The most significant feature is the greater than 90% selectivity for carbon over undesired nitrogen alkylation, which is much better than is the case for the free halocarbon (less than 5%). Interestingly, the related iodomethane complex $[Cp(CO)(PPh_3)Ru(IMe)]PF_6$ showed the reverse selectivity and favors N-alkylation [42(b)]. This may arise either because there is less hindrance at the methyl group or because the metal center is more electrophilic in the latter case. The same ruthenium complex was also shown to alkylate a wide range of nucleophiles, including chloride, fluoride, benzoate, and *p*-toluenesulfonate anions, as well as triphenylphosphine, pyridine and triethylamine. The success of the reaction with *p*-toluenesulfonate demonstrates that the iodomethane complex is even more electrophilic than methyl *p*-toluenesulfonate.

E. CONCLUSIONS

Complexes containing intact halocarbons can indeed exist as stable well-characterized species which are often easy to prepare. Not only do these constitute a new class of coordination compound, but they are also unusually reactive. They may find use as synthetic intermediates both in organic and inorganic chemistry.

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