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PLATINUM GROUP METALS IN THE FORMATION OF METAL–CARBON MULTIPLE BONDS

WARREN R. ROPER

Department of Chemistry, University of Auckland, Auckland (New Zealand)

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The platinum group metals have been central to the development of organometallic chemistry. Platinum provided the first alkene complex (Zeise, 1827), the first metal carbonyl complex (Schutzenberger, 1868), the first metal-tertiary phosphine complex (Hofmann, 1857) and even (albeit unrecognized at the time) the first transition metal carbene complex (Chugaev, 1915). It is surprising, therefore, that the remarkable development of metal–carbon multiple bond chemistry (M=C and M≡C, especially those situations without heteroatoms on the carbene or carbyne carbon) which occurred throughout the nineteen-seventies was focussed almost entirely on the elements of Groups V, VI and VII [1,2]. However, since 1980 stable ruthenium and osmium compounds with terminal carbyne ligands and ruthenium, osmium and iridium compounds with terminal methylene ligands have been discovered. Also, a substantial number of dihalocarbene complexes of these elements and a novel example of metal–carbon double bonds built into a six-membered unsaturated carbon ring (a metallabenzene) have been prepared and studied. It is these developments which will be summarised in this article. Following the well established precedents set in Volumes 100 and 200, which have been much admired by readers, I shall include some personal comments and adopt a chronological approach for describing developments where this seems to be appropriate. The opportunity will also be taken to present some recent, previously unpublished, results.

Along with other organometallic chemists I had been fascinated by the Fischer and Maasböl paper in Angewandte Chemie (1964) [3] reporting the first recognized carbene complex. Fortunately, two opportunities for me to hear Professor Fischer speak about this work presented themselves, first at the Organometallic meeting in Madison, Wisconsin, in 1965 and secondly at the 12th ICCC in Sydney, Australia, in 1969. I became interested in developing this kind of chemistry for Group VIII elements.

Stable methylene complexes of ruthenium, osmium and iridium

Our first step towards a terminal methylene complex, $L_nM{=}CH_2$, was made in 1971 when David Christian, while studying isocyanide complexes of ruthenium [4], discovered a migratory-insertion reaction between adjacent hydride and isocyanide

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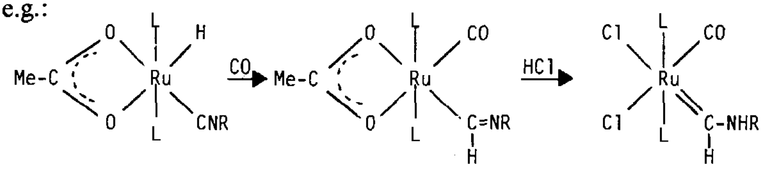
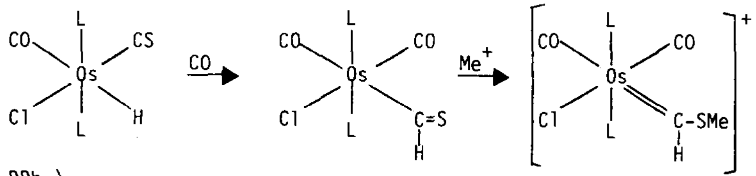
ligands to produce an iminoformyl ligand [5]. Protonation or alkylation at nitrogen converted this ligand to a "secondary" carbene ligand of the type $L_nM{=}CHNR_2$ [6], e.g.:



(L = PPh_3)

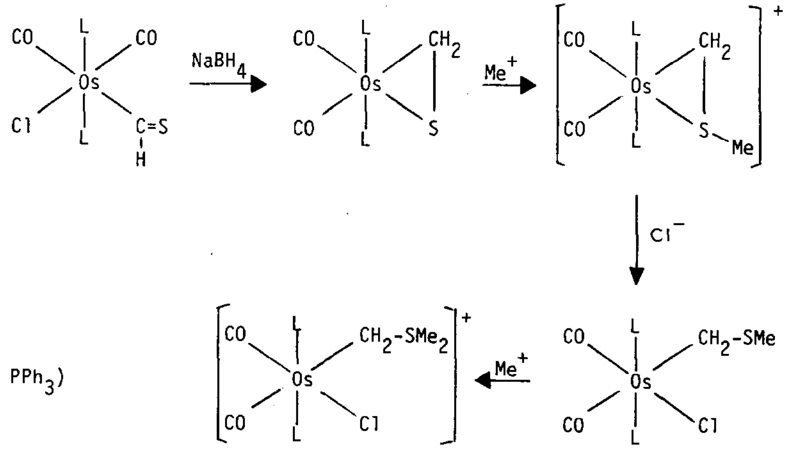
The ^1H NMR spectrum showed a characteristic low-field chemical shift for the carbene H atom and a subsequent X-ray crystallographic study [7] of a molecule chosen for providing an internal comparison of Ru–C distances to carbonyl, isocyanide and secondary carbene ligands $[RuI_2(CO)(CN\text{-}p\text{-tolyl})(CHNMe\text{-}p\text{-tolyl})(PPh_3)]$ revealed substantial multiple bonding between the carbene carbon and both metal and nitrogen substituents. Some years later Terry Collins prepared compounds with adjacent hydride and thiocarbonyl ligands and was able to promote a similar migration reaction leading to a thioformyl ligand [8]. Again, methylation at sulphur led to the sulphur substituted "secondary" carbenes, $L_nM{=}CHSMe$:



(L = PPh_3)

The most interesting feature of these thiocarbene complexes was the hydrolysis reaction which afforded the first neutral formyl complex, $Os(CHO)Cl(CO)_2(PPh_3)_2$, but, in addition, reaction with amines led to amino-carbene complexes, $L_nOs{=}CHNR_2$ [9].

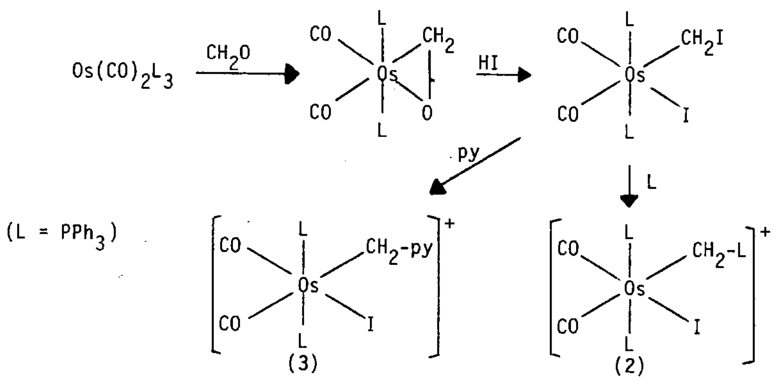
The thioformyl complex described above led us to the first thioformaldehyde complex [10] and an examination of the chemistry of this new molecule took us much closer to a methylene complex:



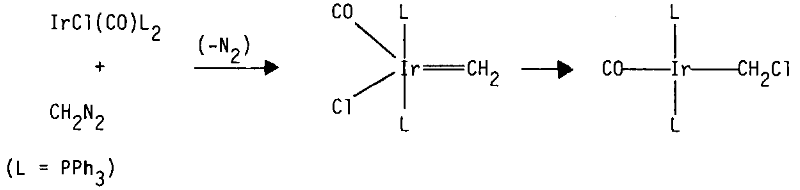
(L = PPh_3)

(1)

Molecule **1** can be regarded as a dimethylsulphide solvate of the methylene species $[OsCl(=CH_2)(CO)_2(PPh_3)_2]^+$ and suggests that a methylene ligand in such a coordination environment is likely to be very electrophilic. Related phosphine- and pyridine-coordinated methylenes (Complexes **2** and **3**) became available from the iodomethyl ligand which in turn resulted from the stable formaldehyde complex, $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$ made by Christine Headford [11,12]:

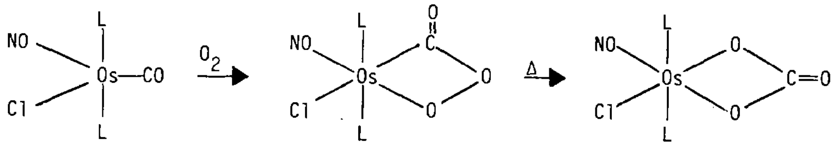


Clearly, an isolable methylene complex, unprotected by coordinated bases, was going to require a more electron-rich metal centre, preferably osmium(0) rather than osmium(II). An alternative approach, therefore, was to add a carbene precursor (for methylene this would be diazomethane) to a suitable, coordinatively unsaturated, complex. An early attempt along these lines by Mango and Dvoretzky [13], but using iridium(I) rather than osmium(0), had failed to produce an isolable methylene complex apparently because a chloride migration to the methylene ligand intercepted:



The answer to this problem lay in using $OsCl(NO)(PPh_3)_3$ where the metal centre is sufficiently electron-rich to bind strongly to the CH_2 ligand, where 5-coordination rather than 4-coordination is normal thus avoiding a migration reaction to the CH_2 ligand, and where also a measure of steric protection is afforded by the triphenylphosphine ligands thus preventing other possible reaction pathways such as a coupling reaction leading to an ethylene complex [14]. To understand how we developed the synthesis of $OsCl(NO)(PPh_3)_3$ we must look both forward and backwards in time.

In 1980, Tony Wright was beginning a detailed examination of the chemistry of osmium carbyne complexes of the type $Os(\equiv CR)Cl(CO)(PPh_3)_2$ which had been prepared and described in the Ph.D. thesis submitted by James Wright in May 1980. The formal similarity of these compounds to the nitrosyl complexes $Os(NO)Cl(CO)(PPh_3)_2$ which we had prepared in 1968 [15] was obvious and Tony Wright was not too surprised to find that $Os(\equiv CR)Cl(CO)(PPh_3)_2$, just like the nitrosyl analogue, underwent a reaction with oxygen to give a crystalline 1/1 adduct. In 1968 we had described the corresponding nitrosyl product as a chelate carbonate complex [16], $Os(OC[O]O)Cl(NO)(PPh_3)_2$. In fact, as we later discovered, this is the ultimate product but there is an intermediate isomer and the IR spectrum (in the region 1700–1000 cm^{-1}) of this intermediate and of the carbyne complex-O_2 adduct were identical (except for the $\nu(Os{\equiv}C)$ band present in the latter). Wright decided to reexamine the nitrosyl complex-O_2 adduct and quickly decided that it was a peroxy-carbonyl complex (**5**):



(4) (5) (6)

(L = PPh_3)

The yellow crystalline compound **5** had IR absorptions at 1710, 1030, 760 and 662 cm^{-1} and when heated under reflux in heptane as a suspension isomerised to **6**. Complex **6** had IR absorptions at 1700, 1165, 968 and 792 cm^{-1} which compared closely with absorptions for another chelate carbonate complex, $Pt(OC[O]O)(PPh_3)_2$ at 1685, 1185, 980 and 815 cm^{-1}. The structure of **6** was fully confirmed by an X-ray crystallographic study carried out by George Clark and the structure is given in Fig. 1, [17]. Unfortunately, although **5** formed good crystals they rapidly decomposed in the X-ray beam and it was not possible to confirm crystallographically the structure of **5**. Significantly, the ^{13}C NMR spectrum of **5** revealed the carbonyl carbon at δ 169.35 ppm, as a triplet, coupling to the two equivalent trans-phosphine ligands, $^2J(C{-}P)$ 6.7 Hz, whereas **6** shows no phosphorus coupling. Simon Hoskins and Tony Wright while discussing the structure of **5** had the idea that heating **5** in the presence of excess triphenylphosphine might promote CO_2 and triphenylphosphine oxide loss

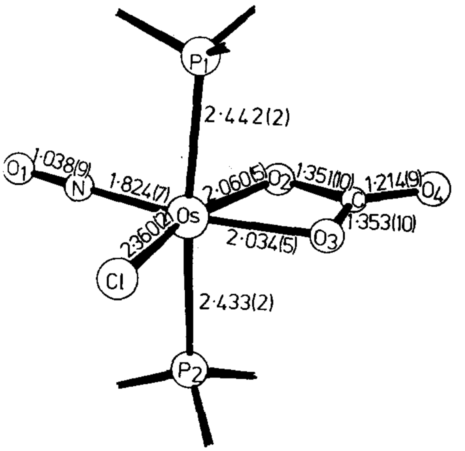
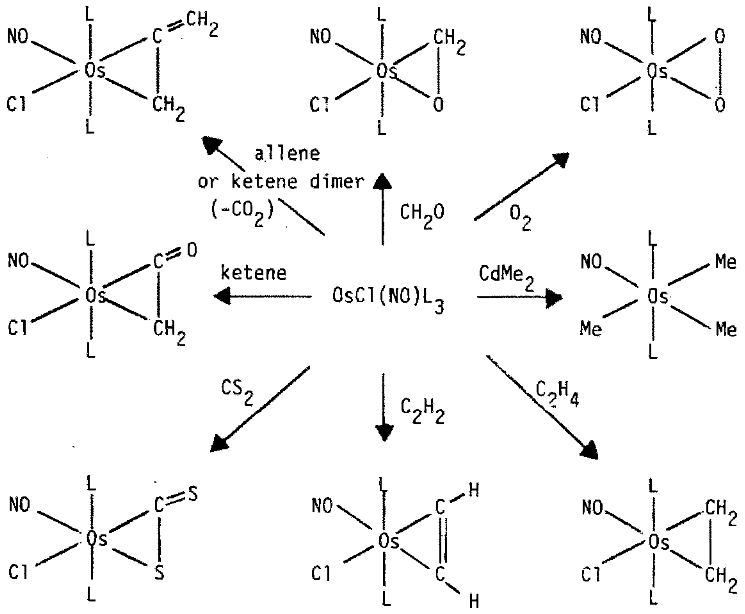
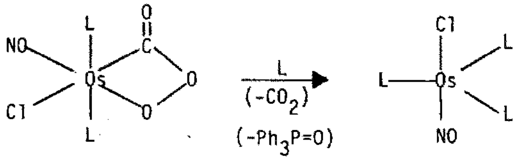


Fig. 1. Molecular structure of $Os(OC[O]O)Cl(NO)(PPh_3)_2$ (phenyl groups omitted).



SCHEME 1. Reactions of $OsCl(NO)L_3$ ($L = PPh_3$).

and give $OsCl(NO)(PPh_3)_3$ (7). This idea worked beautifully to yield 7 as air-stable green crystals in high yield [18]:

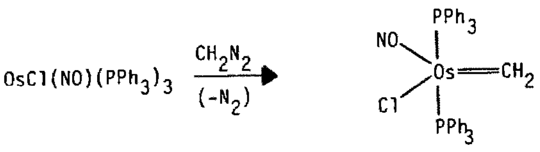


(5) (7)

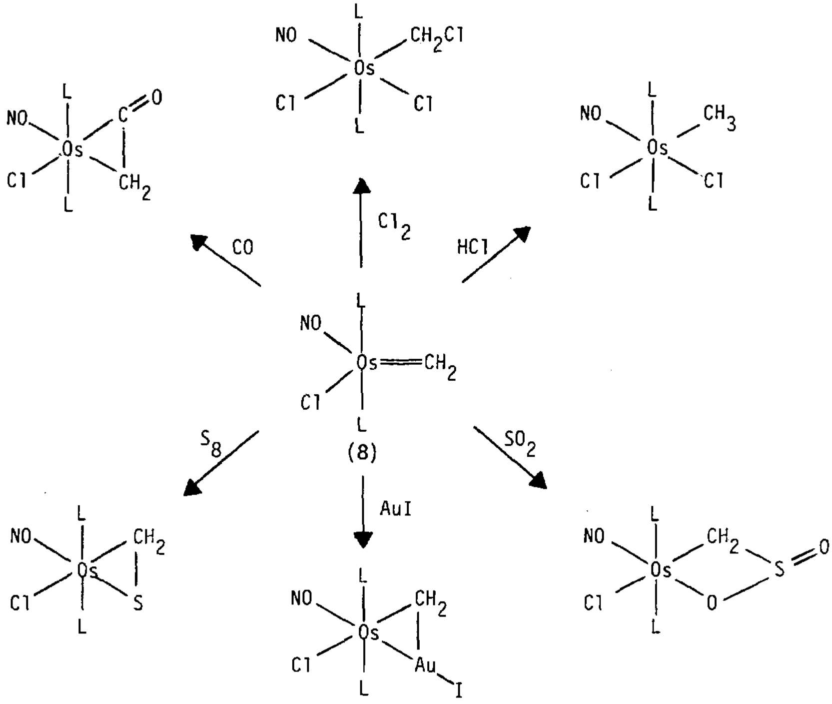
($L = PPh_3$)

Complex 7 joins a number of other tris(triphenylphosphine)-substituted five coordinate complexes of osmium(0) which we have studied since 1968. These include $[Os(CO)(NO)(PPh_3)_3]^+$ [19], $Os(CO)_2(PPh_3)_3$ [20], $Os(CS)(CO)(PPh_3)_3$ [21], and $Os(CNR)(CO)(PPh_3)_3$ [22]. The steric pressures associated with three bulky triphenylphosphine ligands lead to ligand dissociation in solution and the resulting coordinatively unsaturated species readily undergo oxidative addition reactions. A selection of these reactions for $OsCl(NO)(PPh_3)_3$ is given in Scheme 1 [23].

For the reasons briefly outlined above 7 appeared to provide an ideal coordination environment for the methylene ligand (introduced via diazomethane) and indeed this reaction leads in high yield to a mononuclear methylene complex (**8**) of quite remarkable thermal stability [18]:



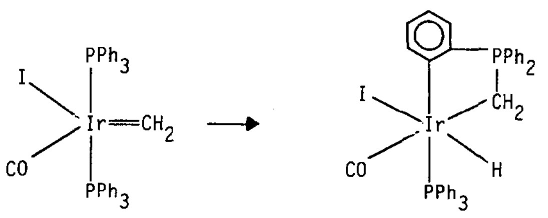
(8)



SCHEME 2. Reactions of $Os(=CH_2)Cl(NO)L_2$ ($L = PPh_3$).

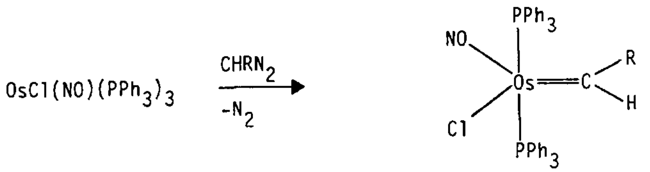
Complex **8** has good air-stability as a solid and a melting-point over 200°C. X-ray crystal structure determination revealed a trigonal bipyramidal geometry and an osmium–carbon distance of 1.92(1) Å appropriate for a double bond. The carbene ligand orientation is perpendicular to the equatorial plane thus maximising π-overlap with the carbene carbon $2p$-orbital. From a chemical point of view, what is interesting about this molecule is that the electrophilicity which had been associated with CH_2 fragments bound to osmium(II) was now absent. Complex **8** does not coordinate triphenylphosphine or pyridine to the carbene carbon atom. This neutral, d^8, methylene complex behaves as though it has a rather non-polar Os=C bond and many of the reaction presented in Scheme 2 suggest a "metalla-alkene" nature for this linkage. The Os=C bond in **8** functions as a ligand towards gold(I), adds HCl and Cl_2, with S_8 forms a thioformaldehyde complex (elemental Se and Te similarly form selenoformaldehyde and telluroformaldehyde complexes) and with SO_2 provides an example of a complexed sulfene molecule (CH_2SO_2) [24]. The reaction with CO to form complexed ketene probably involves the nitrosyl ligand in changing from 3*e*-donor to 1*e*-donor in order to allow coordination of CO before C–C bond formation occurs.

The methyleneosmium complex is not unique. Ruthenium forms $Ru(=CH_2)Cl(NO)(PPh_3)_2$ [23] and iridium yields $Ir(=CH_2)I(CO)(PPh_3)_2$ [25]. This iridium methylene is less stable than the ruthenium and osmium examples and solutions at room temperature rearrange to an *ortho*-metallated ylide-phosphorus complex (**9**) [25]:



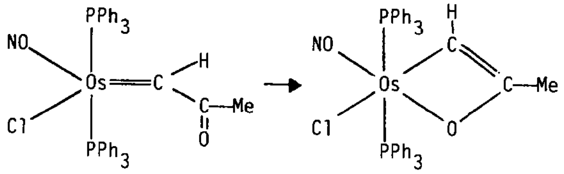
(9)

Mark Gallop extended this carbene-complex forming reaction with $OsCl(NO)(PPh_3)_3$ by using $CHRN_2$ (R = Me, Ph, C[O]OEt, and C[O]Me) as carbene precursors. For the first three diazoalkanes the carbene complex was isolated:



(R = Me, Ph, CO_2Et)

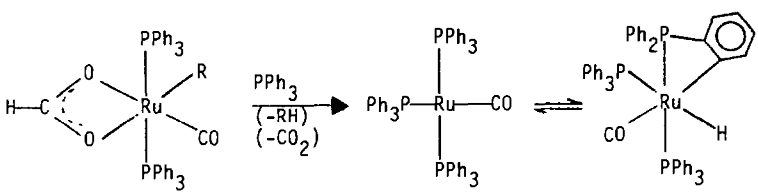
However, in the case of R = C[O]Me the observed product was not the carbene complex **10**, but instead the metallacycle **11** [26]:



(10) (11)

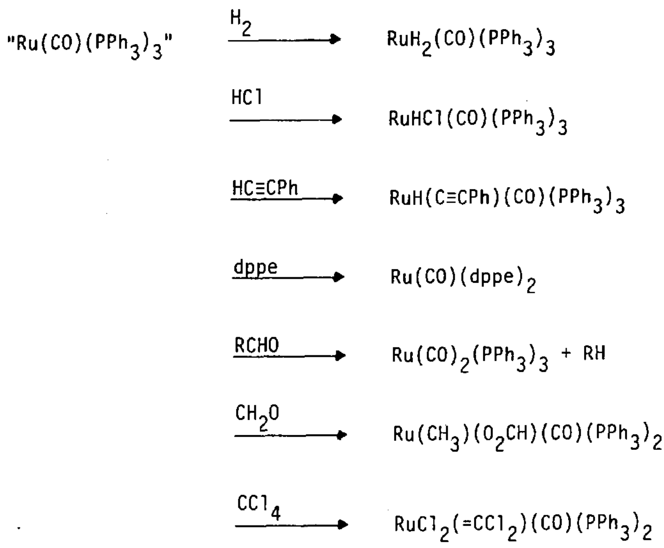
Dihalocarbene complexes of ruthenium, osmium and iridium

We first detected a dihalocarbene complex while studying another tris(triphenylphosphine) zerovalent complex, $Ru(CO)(PPh_3)_3$ [27]. The lengthy synthesis we had developed for this molecule involved, as a reduction step from ruthenium(II), the elimination of hydrocarbon (RH) from adjacent R and H ligands. The R group (R = *o*-tolyl was most effective) was introduced using a mercury transfer reagent (HgR_2) and the hydride ligand by the thermal decarboxylation of a formate ligand [28]:



(12) (13)

The solid product, $\overline{Ru(C_6H_4P}Ph_2)H(CO)(PPh_3)_2$ (**13**) was obviously an *ortho*-metallated hydride complex of ruthenium(II) (from IR data) but in solution this must



SCHEME 3. Reactions of $\overline{Ru(C_6H_4PPh_2)}H(CO)(PPh_3)_2$.

exist to some extent as the zerovalent complex **12** (cf. the isoelectronic $RhCl(PPh_3)_3$) as evidenced by various oxidative addition reactions. Some of these are given in Scheme 3. The last reagent listed, CCl_4, gives as one of several products, an orange crystalline complex (in very low yield) which we identified as $RuCl_2(=CCl_2)(CO)(PPh_3)_2$. The dichlorocarbene ligand was revealed by a medium intensity IR band at 860 cm^{-1}, and more tellingly, by a rapid reaction with primary amines to give quantitatively the corresponding isocyanide complexes.

$$RuCl_2(=CCl_2)(CO)(PPh_3)_2 + 3RNH_2 \rightarrow RuCl_2(CNR)(CO)(PPh_3)_2 + 2(RNH_3)Cl$$

At this time the literature had only one report of a dichlorocarbene complex, the porphyriniron derivative $Fe(=CCl_2)(H_2O)TPP$ [29] (TPP = mesotetraphenylporphyrin). We were particularly attracted by the synthetic possibilities offered by an electrophilic carbene centre with two excellent leaving groups as substituents. Foremost in our minds was the possibility that the CCl_2 ligand would be a good precursor for thiocarbonyl and selenocarbonyl ligands (which we had been studying for some years) and perhaps even for the then unknown tellurocarbonyl ligand. We therefore concentrated on finding a satisfactory synthetic route to complexes of CCl_2 and other dihalocarbene ligands ($=CF_2$, $=CBr_2$, $=CFCl$, etc.). Although the mechanism by which $Ru(CO)(PPh_3)_3$ and CCl_4 react together is unknown it seemed likely that a L_nRuCCl_3 complex intermediate was involved and accordingly efforts were made to prepare such an intermediate by alternative methods. Whereas many CF_3 complexes of transition metals are known [30,31] few CCl_3 complexes have been reported. However, $Hg(CCl_3)_2$ is easily made [32] and proves to be an excellent reagent for transferring CCl_3 groups to Group VIII metals and the immediate rearrangement of these species leads to isolable dichlorocarbene complexes [33], e.g.,

$$OsHCl(CO)(PPh_3)_3 + Hg(CCl_3)_2 \rightarrow OsCl_2(=CCl_2)(CO)(PPh_3)_2 + PPh_3 + CHCl_3 + Hg$$

In related reactions, $RuCl_2(=CCl_2)(CO)(PPh_3)_2$ [34], $OsCl_2(=CCl_2)(CS)(PPh_3)_2$ [23], and $IrCl_3(=CCl_2)(PPh_3)_2$ [35] were prepared. The structure of purple, $IrCl_3(=CCl_2)(PPh_3)_2$ is depicted in Fig. 2. The measured C–Cl bond distances are no shorter than regular C–Cl bonds and π-donation to the carbene p-orbital must be exclusively from the metal. This is reflected in the short Ir–C distance of 1.872(7) Å. As expected the CCl_2 ligands in all of the complexes given above underwent substitution reactions with many nucleophilic reagents and a selection of typical examples is shown in Scheme 4. One of the most interesting reactions is that producing the previously unknown tellurocarbonyl ligand. Scheme 5 details the synthesis and some reactions of osmium tellurocarbonyl complexes. James Wright first isolated $OsCl_2(CTe)(CO)(PPh_3)_2$ (**14**) as orange crystals from the reaction between $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ and NaTeH [33]. The structure of **14** is depicted in Fig. 3 [36]. The Os–C distances reveal that the CTe ligand is more tightly bound to osmium than the CO ligand and the Os–Cl distances show a pronounced *trans*-influence for the CTe ligand. In accord with this observation the chloride *trans* to CTe is rapidly removed as AgCl through reaction with $AgSbF_6$ in MeCN. The resulting cation **15** is reduced to the green zerovalent tellurocarbonyl complex $Os(CTe)(CO)_2(PPh_3)_2$ (**16**) through reaction with methoxide in the presence of CO. This reduction, successfully developed by Tony Hill, probably involves methoxide attack at CO to give an intermediate methoxycarbonyl complex which is subject to a second methoxide addition releasing $(MeO)_2CO$ and forming **16**. A cobalt complex of $(MeO)_2CO$ has been described [37]. The structure of **16** is shown in Fig. 4 [38]. There is no significant difference between the Os–C distances to tellurocarbonyl and carbonyl ligands in this molecule. One way of viewing the structure of **16** would be to regard the metal-tellurocarbonyl ligand interaction as a carbide bridge between osmium and tellurium. Bharat Makan found that the tellurium atom in this neutral complex was rapidly methylated by iodomethane to the tellurocarbyne species, $[Os(\equiv CTeMe)(CO)_2(PPh_3)_2]^+$ (**17**), the structure of which is shown in Fig. 5 [39].

So far I have considered only the CCl_2 ligand. It had been reported in 1978 that

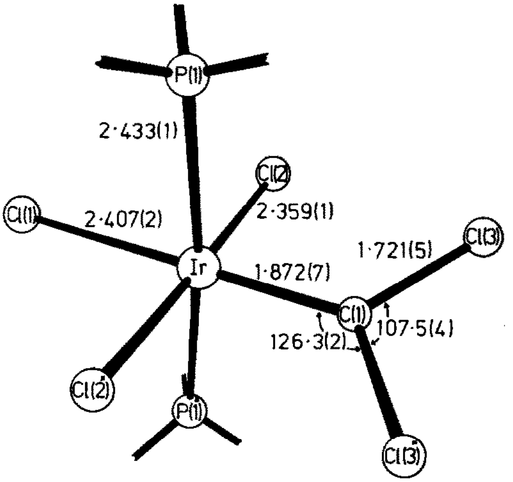
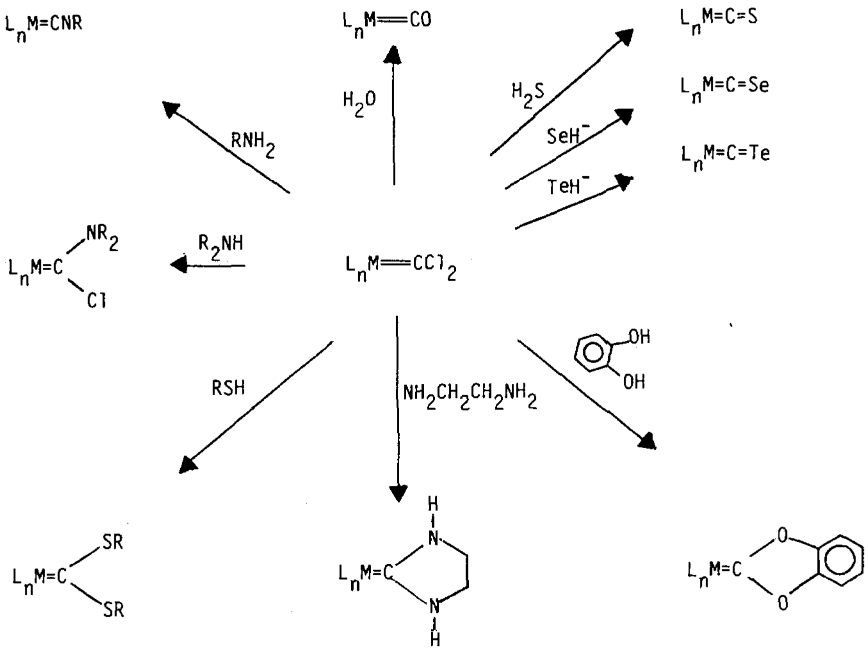


Fig. 2. Molecular structure of $IrCl_3(=CCl_2)(PPh_3)_2$ (phenyl groups omitted).



SCHEME 4. Typical reactions of CCl_2 complexes.

CF_2 complexes could be produced by fluoride abstraction from $MoCF_3$ complexes using SbF_5 and detected spectroscopically [40]. We began to look for stable CF_2 complexes of Ru and Os and Simon Hoskins opened up this area by finding that a

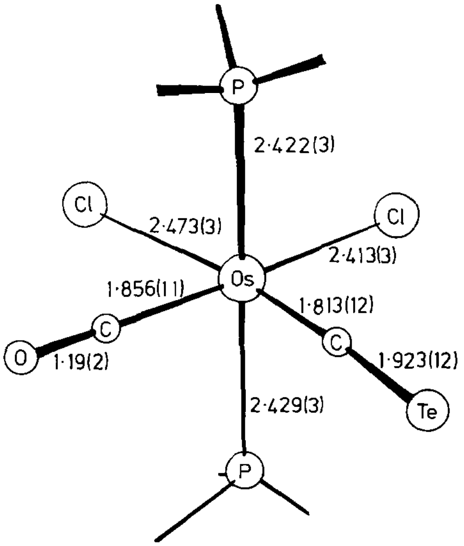
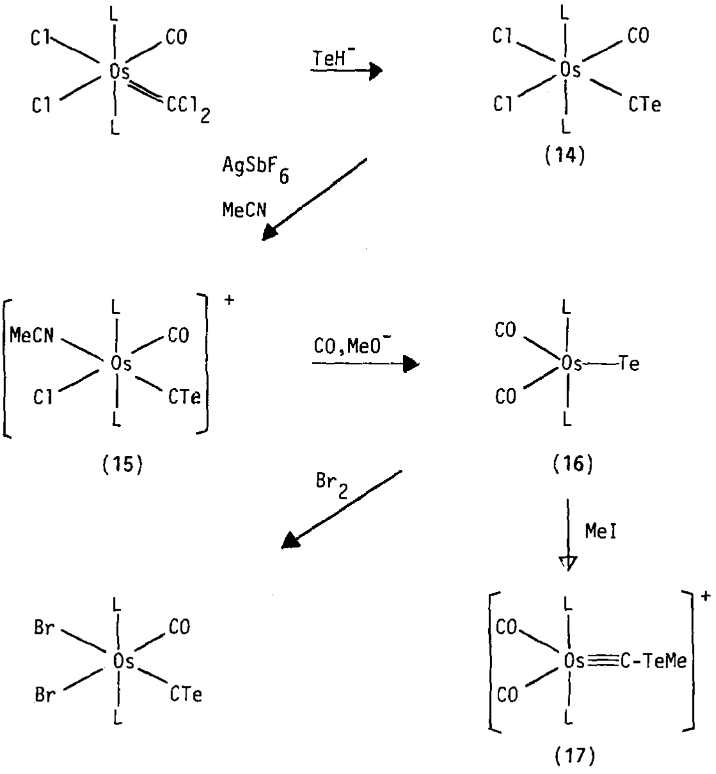


Fig. 3. Molecular structure of $OsCl_2(CTe)(CO)(PPh_3)_2$ (phenyl groups omitted).



SCHEME 5. Osmium tellurocarbonyl complexes and derivatives (L = PPh_3).

$Ru^{II}CF_3$ derivative resulted from oxidative addition of $Hg(CF_3)_2$ to $Ru(CO)_2(PPh_3)_3$ [41] (see Scheme 6). The product, $Ru(CF_3)(HgCF_3)(CO)_2(PPh_3)_2$ (**18**) proved to have an interesting structure. The C–F bond distances of the CF_3 group bound to

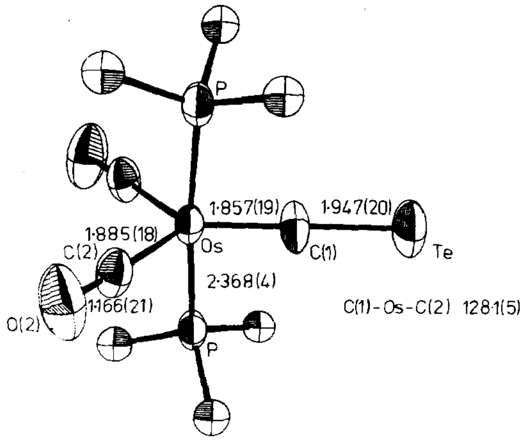


Fig. 4. Molecular structure of $Os(CTe)(CO)_2(PPh_3)_2$ (phenyl groups omitted).

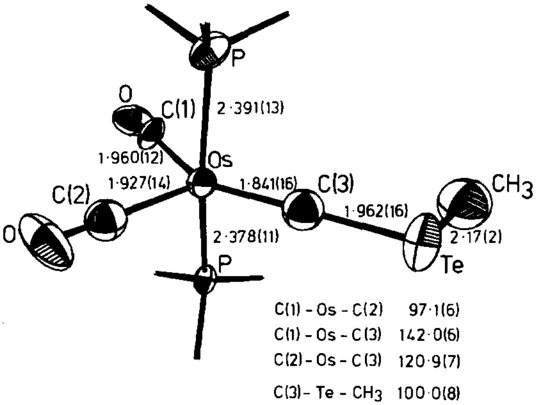
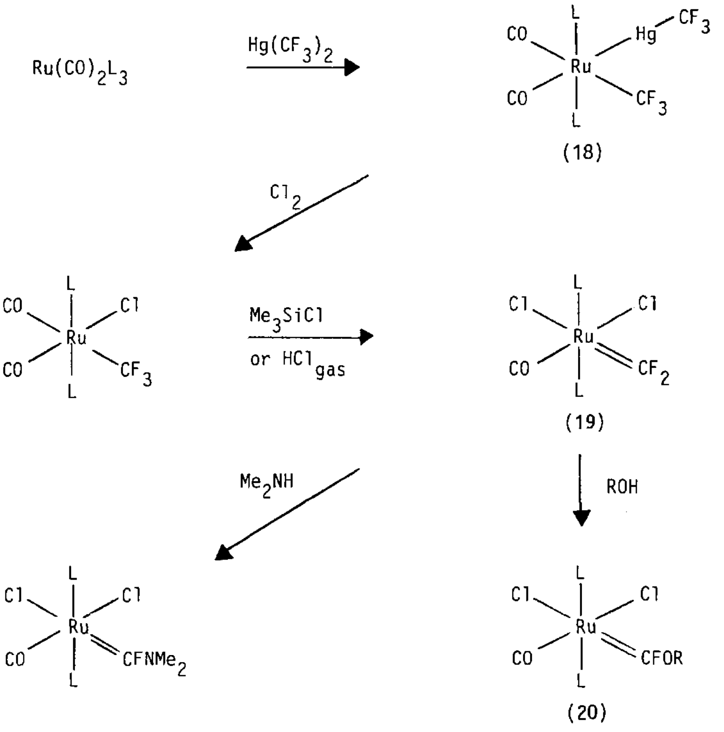


Fig. 5. Molecular structure of $[Os(\equiv CTeMe)(CO)_2(PPh_3)_2]^+$ (phenyl groups omitted).

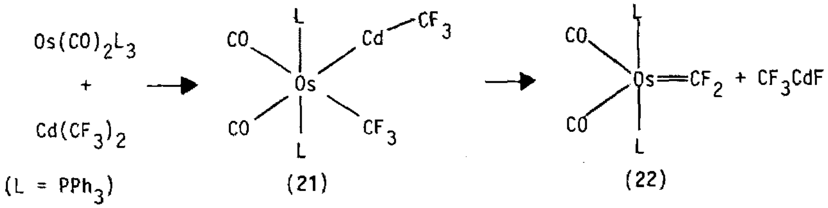


SCHEME 6. Synthesis and reactions of Ru^{II}-CF_2 complexes ($L = PPh_3$).

Ru were found to be approx. 0.1 Å longer than for the CF_3 group bound to Hg. This specific bond-weakening effect of the ruthenium(II) centre on the C–F bonds translates into an easy removal of fluoride from $Ru(CF_3)Cl(CO)_2(PPh_3)_2$ by either HCl gas or Me_3SiCl to yield the neutral CF_2 complex, $RuCl_2(=CF_2)(CO)(PPh_3)_2$ (**19**). Complex **19** is extremely moisture sensitive being hydrolysed to

$RuCl_2(CO)_2(PPh_3)_2$. Alcohols and secondary amines convert **19** to fluoroalkoxy- and fluoroamino-carbene complexes, respectively. The structure of **20** for R = CH_2CMe_3 has been determined [42].

The reaction between $Hg(CF_3)_2$ and $Os(CO)_2(PPh_3)_3$ produced $Os(CF_3)(HgCF_3)(CO)_2(PPh_3)_2$ but only in very low yield. In an effort to increase the yield Simon Hoskins decided to try the much more reactive $Cd(CF_3)_2$ [43] instead of $Hg(CF_3)_2$. This produced one of those happy surprises which the synthetic chemist can look forward to every now and again. Instead of producing $Os(CF_3)(CdCF_3)(CO)_2(PPh_3)_2$ the immediate reaction product was the zerovalent CF_2 complex, $Os(=CF_2)(CO)_2(PPh_3)_2$ (**22**).



The intermediate **21** was not detected. It is reasonable to suppose that the Os–Cd bond is weaker than the Os–Hg bond. In comparable molecules, Ni–Cd bonds have been shown to be longer than Ni–Hg bonds [44]. $Cd(CF_3)_2$ was found to produce the same result with other zerovalent complexes and in this way $Ru(=CF_2)Cl(NO)(PPh_3)_2$, $Ru(=CF_2)(CO)_2(PPh_3)_2$, $Os(=CF_2)Cl(NO)(PPh_3)_2$, and $Os(=CF_2)(CO)(CS)(PPh_3)_2$ were produced. The structures of $Ru(=CF_2)(CO)_2(PPh_3)_2$ [45], $Os(=CF_2)Cl(NO)(PPh_3)_2$ [46] and $Os(=CF_2)(CO)_2(PPh_3)_2$ [46] have been determined and the structure of $Os(=CF_2)Cl(NO)(PPh_3)_2$ is shown in Fig. 6. The carbene plane is perpendicular to the equatorial plane of the trigonal bipyramid and the Os–CF_2 distance, 1.967(6) Å makes an interesting comparison with the Os–C distance of 1.92(1) in the exactly comparable methylene complex $Os(=CH_2)Cl(NO)$-

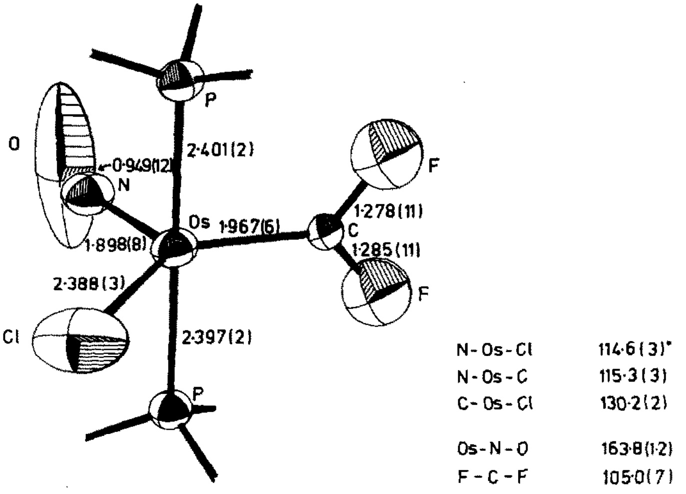
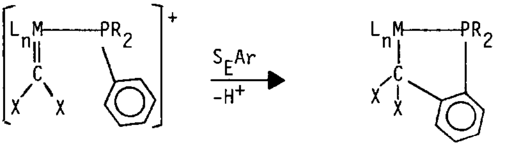


Fig. 6. Molecular structure of $Os(=CF_2)Cl(NO)(PPh_3)_2$ (phenyl groups omitted).

$(PPh_3)_2$. In all of the zerovalent CF_2 complexes the CF_2 ligand is much less reactive towards nucleophilic reagents than the CF_2 ligand in $RuCl_2(=CF_2)(CO)(PPh_3)_2$.

The $\nu(CO)$ values for dihalocarbene complexes like $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ and $Ru(=CF_2)(CO)_2(PPh_3)_2$ are very high, and comparison with matching complexes of other ligands makes it clear that dihalocarbene ligands must be regarded as strong π-acceptor ligands and ranked along with ligands like CS. The $\nu(CF)$ values for a number of CF_2 complexes are listed in Table 1. A variation of almost 200 cm^{-1} is apparent in these values and it is very interesting to find that the measured C–F distances (see Table 1) in $Os(=CF_2)Cl(NO)(PPh_3)_2$, $Os(=CF_2)(CO)_2(PPh_3)_2$ and $Ru(=CF_2)(CO)_2(PPh_3)_2$ exactly follow the bond strength order suggested by the $\nu(CF)$ values. A reasonable conclusion then is that fluorine, (but probably not chlorine or bromine) functions as a π-donor towards the carbene carbon atom in these complexes. When the metal centre is electron-rich, e.g., in $Ru(=CF_2)(CO)_2(PPh_3)_2$, fluorine π-donation will be minimal, when the metal centre is electron-poor, e.g., $[CpFe(=CF_2)(CO)_2]^+$, π-donation from fluorine will be more significant. This is exactly the "competitive π-donation" situation recognized in the structural chemistry of other heteroatom-substituted carbene complexes [48].

One further aspect of dihalocarbene complex chemistry must be mentioned. All of the compounds I have described have two *trans*-PPh_3 ligands. There are limits to the coexistence of PPh_3 and CX_2 ligands in the coordination sphere of octahedral ruthenium(II), osmium(II) and iridium(III) complexes. A particularly electrophilic carbene ligand results when the metal is insufficiently electron-rich, i.e., when there are accompanying π-acceptor ligands and especially when the complex species bears an overall positive charge. In this situation the carbene ligand can attack a benzene ring of a PPh_3 ligand in the following way:



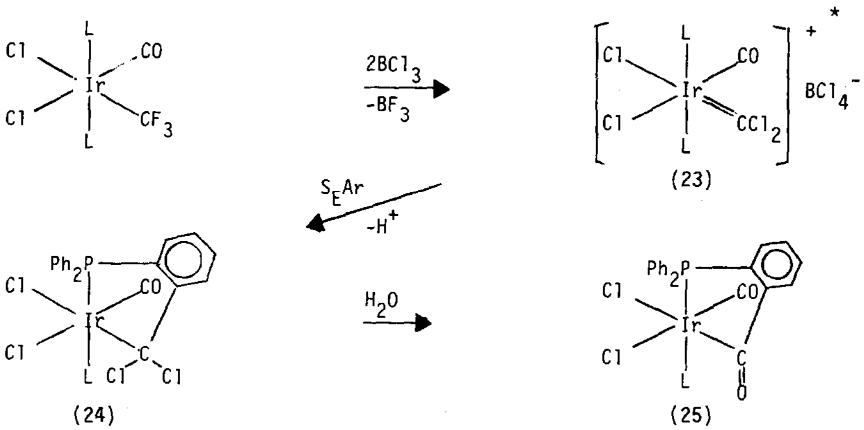
We first encountered an example of this reaction while attempting to prepare a CHCl complex [49] but I will illustrate here with CCl_2 and CBr_2 complexes studied by Tarra Greene and Linda Boyd.

TABLE 1

$\nu(CF)$ VALUES AND STRUCTURAL PARAMETERS FOR CF_2 COMPLEXES

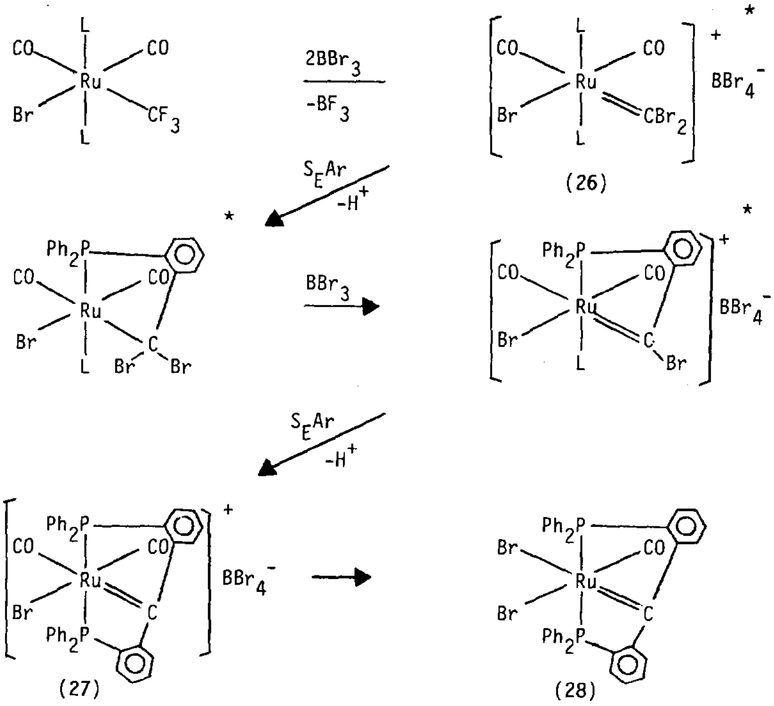
Compound [a]	$\nu(CF)$ (cm^{-1})	l(M–C) (Å)	l(C–F) (Å)
$[CpFe(=CF_2)(CO)_2]^+$	1233, 1200 [b]		
$RuCl_2(=CF_2)(CO)L_2$	1210, 1155		
$Os(=CF_2)Cl(NO)L_2$	1154, 1020	1.967(6)	1.278(11), 1.285(11)
$Ru(=CF_2)Cl(NO)L_2$	1142, 1022		
$Os(=CF_2)(CO)_2L_2$	1122, 990	1.915(15)	1.331(18), 1.407(17)
$Os(=CF_2)(CO)(CS)L_2$	1100, 990		
$Ru(=CF_2)(CO)_2L_2$	1092, 980	1.83(1)	1.36(1), 1.37(1)

[a] L = PPh_3. [b] Data from ref. 47.



SCHEME 7. Metallacycles from electrophilic substitution of CCl_2 ligand on PPh_3 ligand ($L = PPh_3$) (* not isolated).

Scheme 7 indicates that attempted synthesis of **23**, the cationic iridium(III) analogue of neutral $OsCl_2(=CCl_2)(CO)(PPh_3)_2$, leads to spontaneous metallacycle formation in **24**. **24** with two α-Cl atoms is readily hydrolysed to the metallacyclic acyl complex **25**. The structure of **25** has been confirmed by X-ray crystallography



SCHEME 8. Metallabicycles from electrophilic substitution of CBr_2 ligand on PPh_3 ligands ($L = PPh_3$) (* not isolated).

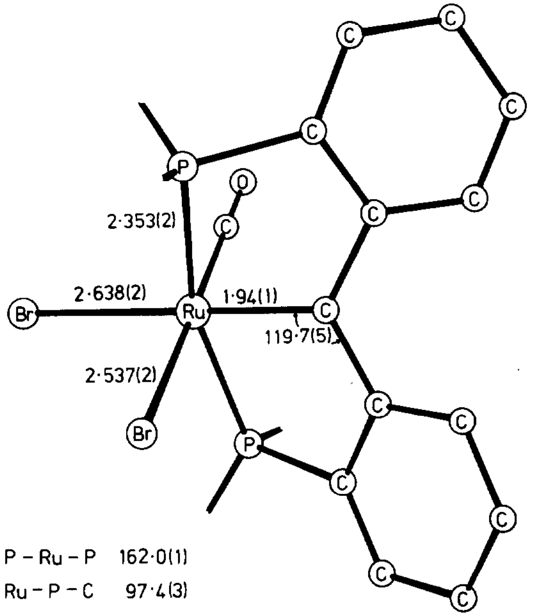


Fig. 7. Molecular structure of $RuBr_2(CO)(Ph_2PC_6H_4CC_6H_4PPh_2)$ (phenyl groups omitted).

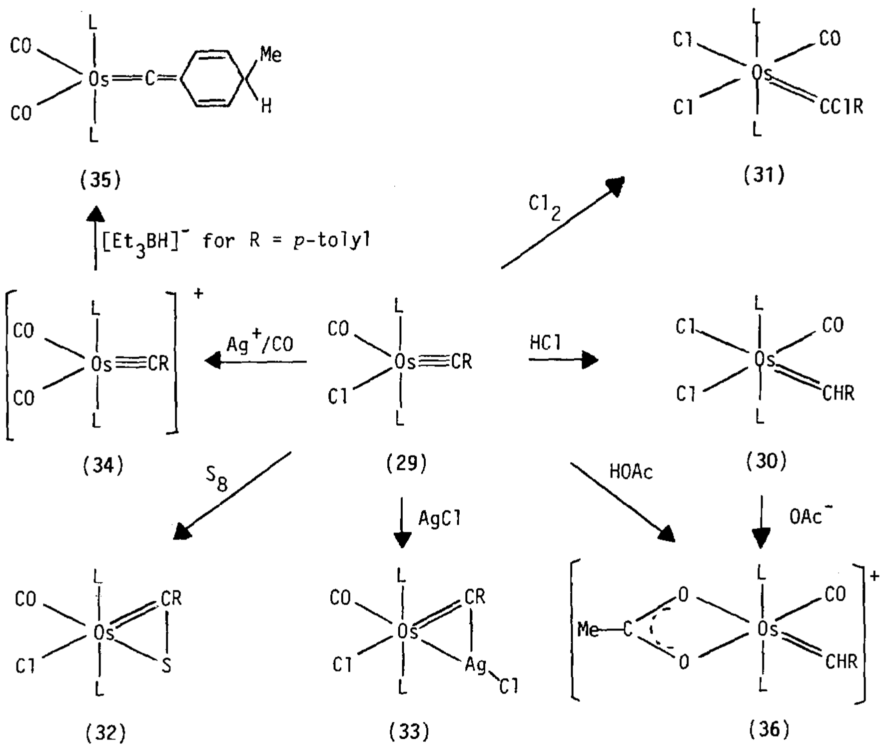
[50]. In a related study, outlined in Scheme 8, a reaction aimed at the preparation of a CBr_2 complex (**26**) leads immediately to the novel metallabicyclic complex **27** as red crystals in high yield. On standing **27** loses CO and forms the neutral, purple complex, $RuBr_2(CO)(PPh_2C_6H_4CC_6H_4PPh_2)$ (**28**). The structure of **28** is depicted in Fig. 7 [51]. Interesting as these compounds are, their formation necessarily limits the range of dihalocarbene complexes which is accessible to those compounds where the metal centre is reasonably electron-rich. There will, no doubt, be a restriction at the other end of the scale also, i.e., when the metal centre becomes too electron-rich, a dihalocarbene complex may become unstable with respect to a halocarbyne complex:

$$L_nM{=}CX_2 \longrightarrow [L_nM{\equiv}C{-}X]^+X^-$$

We have not yet demonstrated this experimentally.

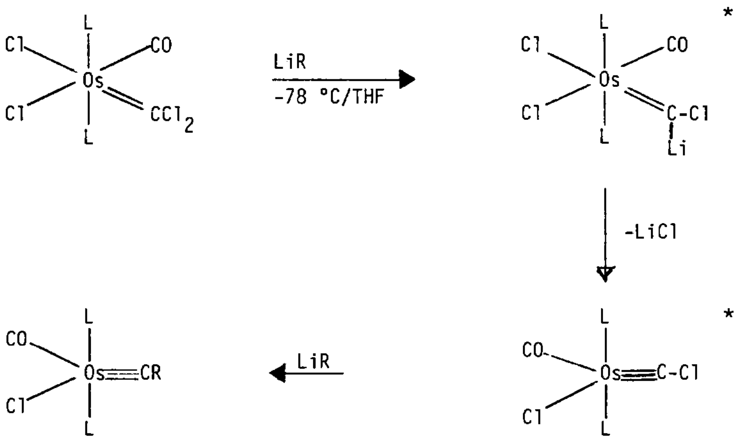
Carbyne complexes of ruthenium and osmium

In the previous section I have emphasized that a characteristic feature of the dichlorocarbene ligand is the ease with which it undergoes substitution reactions. James Wright, while making a systematic study of this feature examined the reaction between $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ and two equivalents of PhLi. A reasonable expectation, in the light of the reactions he had already carried out, was that the product would be $OsCl_2(=CPh_2)(CO)(PPh_3)_2$. However, the product was a green crystalline solid with a $\nu(CO)$ band in the IR spectrum at 1858 cm^{-1}. From what we knew of related compounds this value was far too low for $OsCl_2(=CPh_2)(CO)(PPh_3)_2$. Furthermore, there was a very puzzling, strong, IR band at 1358



SCHEME 9. Reactions of $Os(\equiv CR)Cl(CO)L_2$ ($L = PPh_3$, R = Ph, p-tolyl).

cm^{-1}. As synthetic chemists, we have always found that the true nature of unexpected reaction products is most quickly revealed by looking at the derivatives formed in simple chemical reactions. In this case addition of HCl gave a red crystalline product which was unambiguously recognized (from the characteristic low-field chemical shift in the ^1H NMR spectrum) as $OsCl_2(=CHPh)(CO)(PPh_3)_2$. We began to suspect the presence of an osmium–carbon triple bond in the green material, and attempted formation of a cation through reaction with $AgClO_4$ in MeCN, which gave a product retaining silver, again suggesting a multiple bond associating with silver(I). Elemental analysis supported the formulation $Os(\equiv CPh)Cl(CO)(PPh_3)_2$ (**29**) and George Clark and Karen Marsden were able to confirm this by single crystal X-ray crystallography. The structure revealed a very short Os–C distance of 1.78(2) Å and it was now clear that the IR band at 1358 cm^{-1} was to be associated essentially with $\nu(Os\equiv C)$ [52]. Selected reactions of **29** are presented in Scheme 9. Some puzzles remained, for while the carbyne complexes which had been studied by Fischer [1] typically underwent reactions with nucleophiles to return carbene complexes, **29** did not react with nucleophiles but with electrophiles instead. The addition reactions given in Scheme 9 (HCl forming the CHPh complex **30**; Cl_2 forming the CClPh complex **31**; and S_8 forming the *dihapto*-thioacyl **32**) are conveniently thought of as the reactions of a metallaalkyne. The same is true of the association with AgCl (**33**), AuCl and CuI [53]. To further underline the reluctance of the carbyne carbon atom to add a nucleophile even the cation [Os(≡C-p-



(29)

SCHEME 10. Formation of Os($\equiv$CR)Cl(CO)L_2 (L = PPh_3) (* not isolated).

tolyl)$(CO)_2(PPh_3)_2]^+$ (**34**) reacts with Li(Et_3BH) by remote attack on the tolyl group to give the very unusual vinylidene species **35** the structure of which was confirmed by X-ray crystallography [54].

The reaction between $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ and PhLi which forms **29** deserves further comment. We have found that $OsCl_2(=CClPh)(CO))PPh_3)_2$ (from Cl_2 addition to **29**) does not form **29** upon reaction with PhLi. The mechanism shown in Scheme 10 therefore seems the most reasonable. The overall reaction proceeds rapidly in THF even at −78°C and even with the reactants partially suspended rather than dissolved. The first step must be lithium–halogen exchange followed by LiCl elimination to effect a reduction. Rapid substitution of Cl in the chlorocarbyne complex, Os($\equiv$CCl)Cl(CO)$(PPh_3)_2$ would then yield the product.

The structure of the carbeneosmium(II) complex $OsCl_2(=CHPh)(CO)(PPh_3)_2$ (**30**) is shown in Fig. 8 and reveals several interesting features [55]. The Os–C

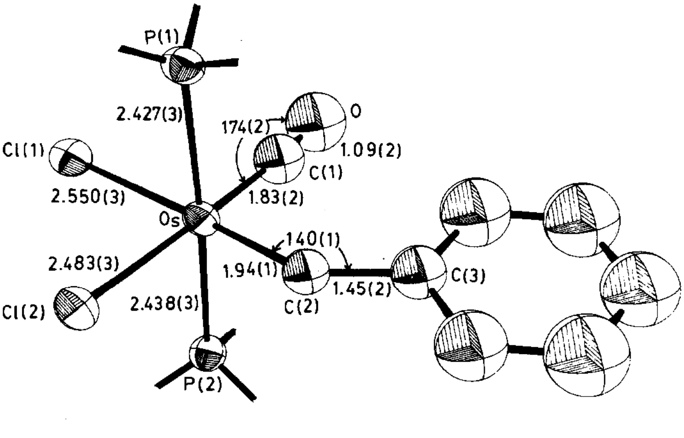
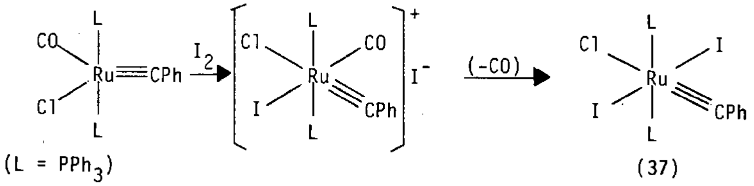


Fig. 8. Molecular structure of $OsCl_2(=CHPh)(CO)(PPh_3)_2$ (phenyl groups omitted).

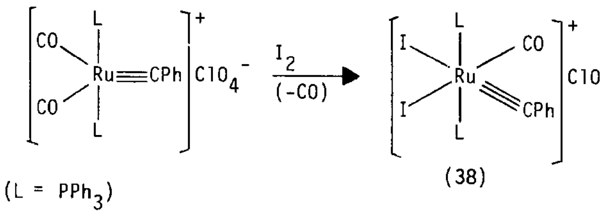
distance is not significantly different from that found in the methylene complex **8** and the phenyl substituent and the carbene plane lie in the equatorial plane of the octahedron. The Os–Cl distance *trans* to the carbene ligand is the longest Os–Cl bond we have observed. Replacement of this chloride with other neutral or anionic ligands occurs readily and **36** is an example of a stable cationic non-heteroatom carbene complex which can be compared with the base-stabilised methylene complexes mentioned at the beginning of this article, e.g., $[OsCl(CH_2SMe_2)(CO)_2(PPh_3)_2]^+$.

So far the carbyne complexes I have described have been five-coordinate species. Oxidation at the metal centre by two units should produce a set of octahedral carbyne complexes. By considering the analogy between the carbyne ligand and either the nitrosyl ligand (3*e* donor) or the nitride ligand, reasonable formulae would be $OsX_3(\equiv CR)L_2$ or $[OsX_2(\equiv CR)L_3]^+$. The difficulty is to find an oxidising agent which will not attack the Os≡C bond. There are presently two ways of doing this. Scheme 9 shows that Cl_2 adds to **29** to give the chlorocarbene complex, $OsCl_2(=CClR)(CO)(PPh_3)_2$ (**31**). Reaction with I_2 proceeds quite differently as illustrated here with reactions of the ruthenium carbyne complexes [23]:



(L = PPh$_3$)

(37)

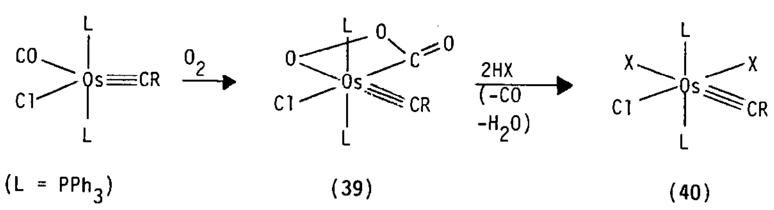


(L = PPh$_3$)

(38)

Complexes **37** and **38** retain IR activity in the 1350–1400 cm^{-1} region associated with ν(Ru≡C). **38** can be reduced by PhLi to $Ru(\equiv CPh)I(CO)(PPh_3)_2$.

The second way to oxidise the five-coordinate carbyne complexes involves the use of molecular oxygen. Here the intermediate is a chelate peroxy carbonyl complex **39**.



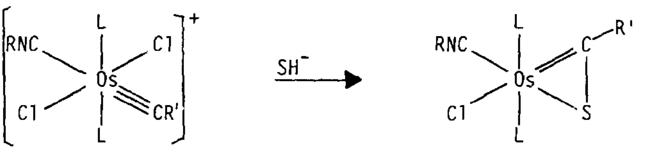
(L = PPh$_3$)

(39)

(40)

X-ray crystal structure determinations have been carried out on two derivatives of **40**, viz.: $Os(NCS)Cl_2(\equiv CC_6H_4NMe_2\text{-}4)(PPh_3)_2$ and $[OsCl_2(\equiv CC_6H_4NMe_2\text{-}4)(CN\text{-}p\text{-tolyl})(PPh_3)_2]^+$ [56]. These reveal Os–C distances of 1.75(1) and 1.78(1) Å respectively, which are not significantly different from the Os–C distance found in the parent five-coordinate complex **29**.

These oxidised carbyne complexes now display the same reactivity as that found for Group VI carbyne complexes, i.e., nucleophilic attack at the carbyne carbon, e.g.:



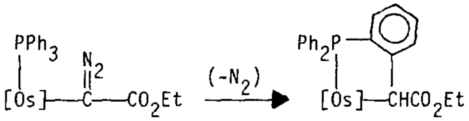
(L = PPh_3, R = *p*-tolyl, R' = C_6H_4-NMe_2-4)

It should be noted that the same type of *dihapto*-thioacyl complex is accessible by reaction between S_8 and $Os(\equiv CR)Cl(CO)(PPh_3)_2$.

While the above results have provided an interesting range of ruthenium and osmium carbyne complexes it is unlikely that the preparative method will apply equally successfully to other transition metals. Satisfactory general synthetic routes to transition metal carbyne complexes are still few in number. One interesting possibility which Mark Gallop was able to examine briefly is N_2 loss from an α-transition metal-substituted diazoalkane:

$$L_nM\text{-}C[N_2]R \xrightarrow{-N_2} L_nM{\equiv}CR$$

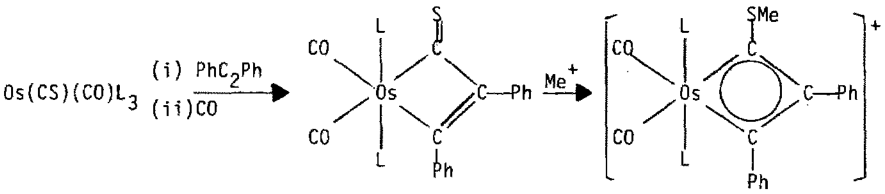
The necessary precursor was prepared by oxidative addition of $Hg(C[N_2]CO_2Et)_2$ to $OsCl(NO)(PPh_3)_3$. $Os(C[N_2]CO_2Et)(HgC[N_2]CO_2Et)Cl(NO)(PPh_3)_2$ upon reaction with I_2 lost first the $-C[N_2]CO_2Et$ function from Hg followed by the Os–Hg bond leaving $Os(C[N_2]CO_2Et)ClI(NO)(PPh_3)_2$. This molecule lost N_2 when heated but the isolated product was not the carbyne complex but instead the metallacycle in which the carbyne ligand had inserted into an *ortho*-CH bond on one PPh_3 ligand [57]:



([Os] = $OsClI(NO)(PPh_3)$)

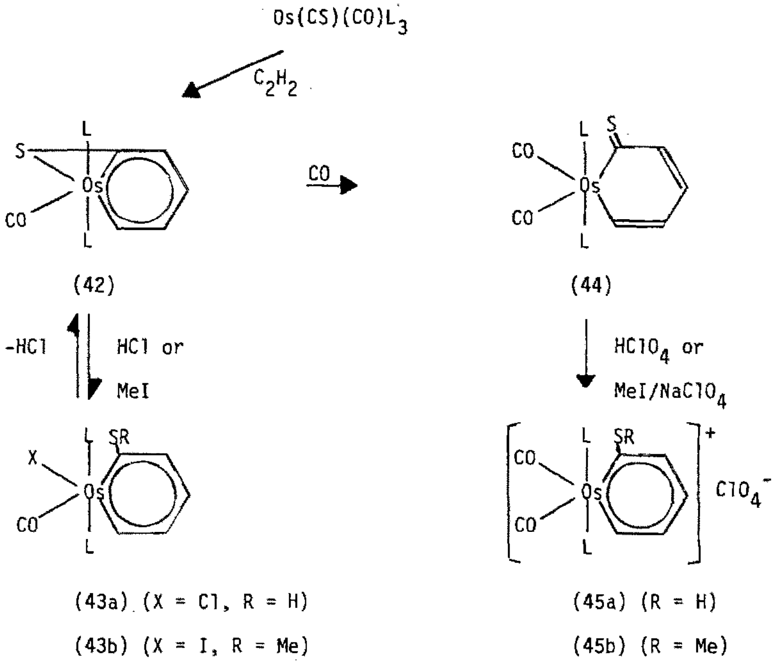
Metallabenzenes and metallacyclobutadienes

Aromaticity is an idea which has fascinated chemists since the days of Kekulé. With M=C and M≡C now well established as functional groups, interesting possibilities are opened-up for building these entities into cyclic carbon molecules where electron delocalisation might occur. Replacement of CH in C_6H_6 by N or P leads to the aromatic molecules pyridine and λ^3-phosphabenzene [58] and there seemed no reason, in principle, why an appropriate L_nM fragment could not also replace CH leading to a "metallabenzene". A cyclisation reaction between one M≡C unit and two alkynes offered a possible synthetic route. Accordingly, Greg Elliott began exploring reactions between $Os(\equiv CR)Cl(CO)(PPh_3)_2$ and various alkynes. His initial efforts met with no success and believing this to be because of the inertness of the five-coordinate 18 electron **29** we considered using a tris(triphenylphosphine) complex (providing coordinative unsaturation through dissociation of one PPh_3), which included as one of the accompanying ligands a carbyne precursor. I have already explained in an early section how methylation at tellurium of a low-valent tellurocarbonyl complex leads to a tellurocarbyne complex. This is a general reaction for electron-rich chalcocarbonyl complexes, we therefore concluded that the molecule to test with alkynes was $Os(CS)(CO)(PPh_3)_3$ [21]. The reaction with diphenylacetylene produced a four-membered metallacyclobutene which could be methylated at S to a metallacyclobutadiene [59]:

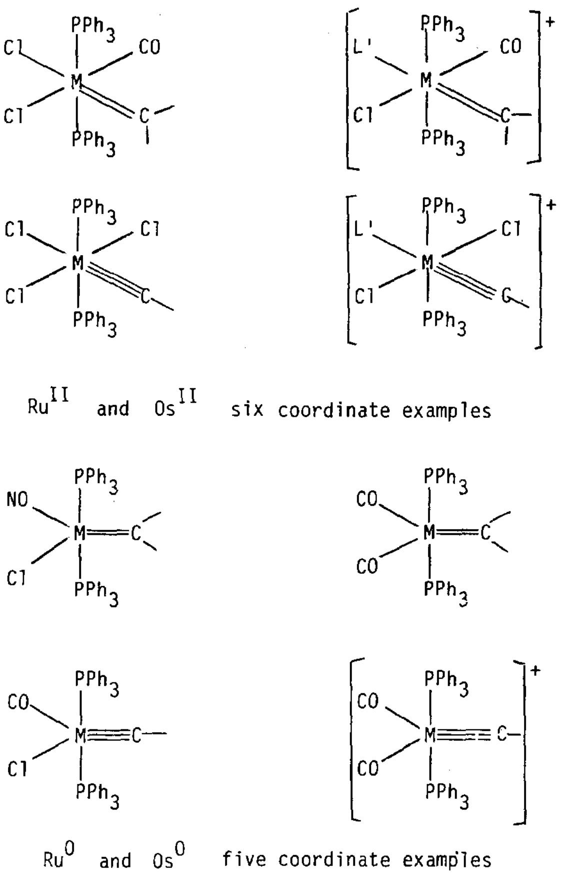


(L = PPh_3)

Of even greater interest was the reaction of $Os(CS)(CO)(PPh_3)_3$ with C_2H_2 [60]. This can be followed in Scheme 11. The first product, **42**, is a brown crystalline solid. Complex **42** is protonated at S (giving **43a**) or methylated at S (giving **43b**). Both **43a** and **43b** are blue. The protonation is reversed by bases. An X-ray crystal structure determination of **42** confirmed that the 6-membered metallacycle is perfectly planar, that the two Os–C distances are identical, and that the C–C distances around the ring show no alternation and all distances are typical for aromatic C–C bonds. Thus it is appropriate to regard **42**, **43a** and **43b** and **45b** as osmabenzenes.



SCHEME 11. Synthesis and reactions of osmabenzenes (L = PPh_3).



SCHEME 12. Ru and Os structural types involving M–C multiple bonds (L′ = CO, CNR, etc.).

Complex **44**, which is derived from **42** upon reaction with CO presumably has localised C=C double bonds but there is no structural evidence to prove this.

Conclusion

Our studies have shown that many compounds of ruthenium(II), osmium(II), iridium(III), ruthenium(0), osmium(0), and iridium(I), which involve either double or triple bonds between metal and carbon, exist, and are quite easily isolated. The stable compounds all have a pair of *trans*-PPh_3 ligands which must afford some steric protection to the multiple linkages. Scheme 12 illustrates the structural types which have been found for Ru and Os. Whether or not these same metal fragments will be equally effective in forming multiple bonds to elements other than carbon is a question awaiting an answer. There are some encouraging signs in the case of M–P multiple bonds [61,62].

Acknowledgements

I wish to thank my coworkers, especially those named in the text. My colleagues, George Clark, Cliff Rickard and Joyce Waters, gave indispensable assistance through providing crystal structure determinations.

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