Electrophilic Addition of an Osmium-bound Chloromethylene Ligand to the Benzene Ring of a Triphenylphosphine Ligand. Synthesis of Metallacyclic and Metallabicyclic Complexes. *X*-Ray Structures of $[\overline{\mathrm{OsCl(CO)_2}(o\text{-}\mathrm{PPh_2C_6H_4C}}\mathrm{HCl)(PPh_3)}]$ and $[\overline{\overline{\mathrm{OsCl(CO)_2}(o\text{-}\mathrm{PPh_2C_6H_4C}}\mathrm{HC_6H_4P}}\mathrm{Ph_2}\text{-}o)]$

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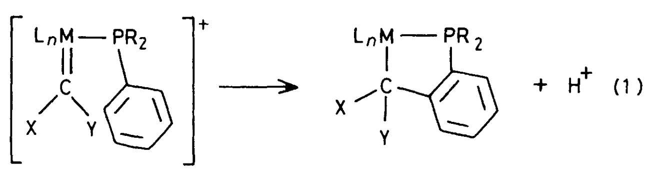
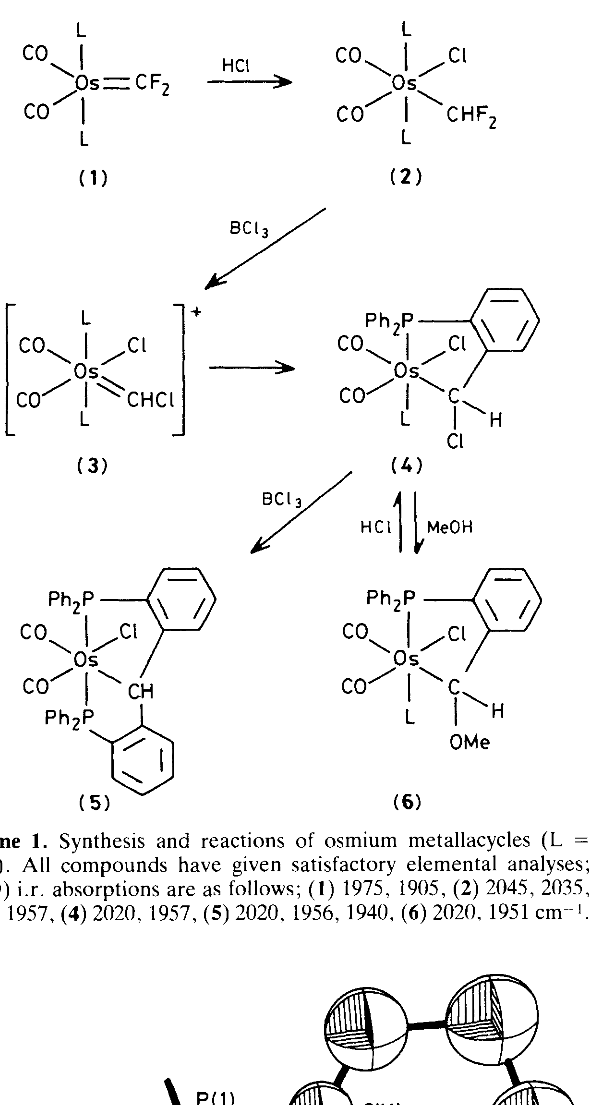
$Os(CHF_2)Cl(CO)_2(PPh_3)_2$ reacts with BCl_3 to give the title metallacycle, (**4**), which is the product of addition of a CHCl-ligand to the benzene ring of ligated triphenylphosphine and further reaction with BCl_3 generates the title metallabicyclic complex, (**5**).

The most electrophilic carbene ligands, *i.e.*, those in cationic complexes and without π-donor heteroatom-substituents, frequently react with unactivated alkenes to form cyclopropanes.[1] When the carbene complex also involves an aromatic phosphine ligand there is the possibility of an intramolecular reaction in which the electrophilic carbene ligand substitutes a benzene ring of the phosphine ligand.

In this communication we describe (i) an attempted synthesis of a cationic CHCl-complex which immediately forms a metallacycle of the type illustrated in equation (1), (ii) an *X*-ray crystal structure determination of this product (**4**), (iii) the further conversion of (**4**) into a metallabicyclic complex through an intramolecular Friedel–Crafts reaction, and (iv) the crystal structure of this product (**5**).





Scheme 1. Synthesis and reactions of osmium metallacycles (L = PPh_3). All compounds have given satisfactory elemental analyses; ν(CO) i.r. absorptions are as follows; (**1**) 1975, 1905, (**2**) 2045, 2035, 1980, 1957, (**4**) 2020, 1957, (**5**) 2020, 1956, 1940, (**6**) 2020, 1951 cm^{-1}.

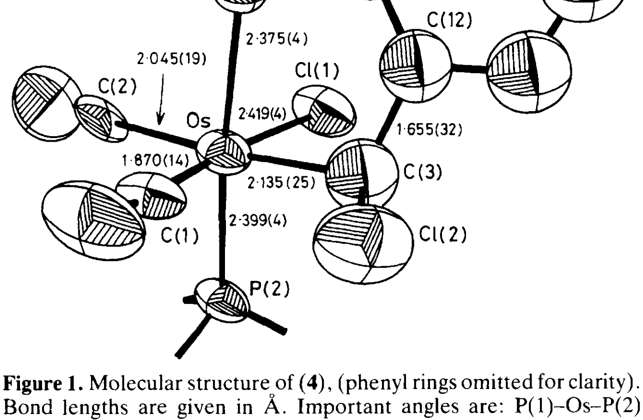


Figure 1. Molecular structure of (**4**), (phenyl rings omitted for clarity). Bond lengths are given in Å. Important angles are: P(1)–Os–P(2) 175.0(1), Os–C(3)–Cl(2) 106.1(1), Os–C(3)–C(12) 110.4(2), C(12)–C(3)–Cl(2) 99.7(2)°.

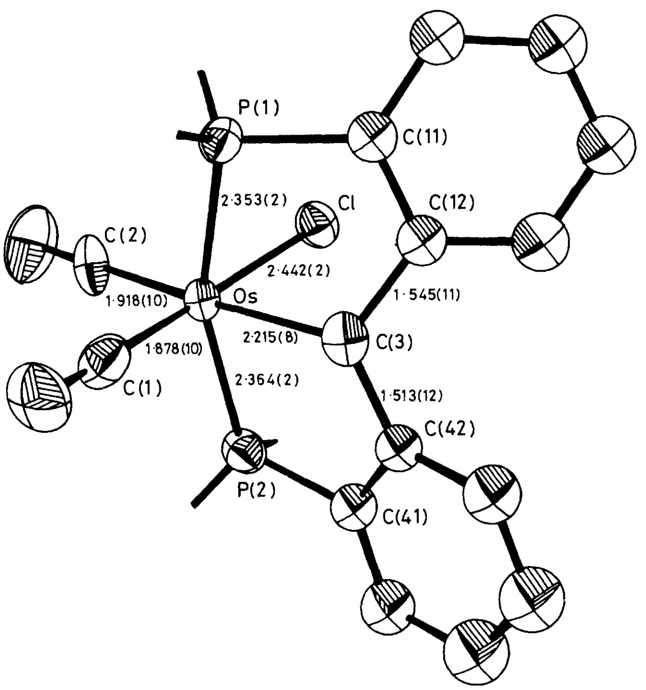


Figure 2. Molecular structure of (**5**), (phenyl rings omitted for clarity). Bond lengths are given in Å. Important angles are: P(1)–Os–P(2) 159.4(1), Os–C(3)–C(12) 114.7(6), Os–C(3)–C(42) 110.3(5), C(12)–C(3)–C(42) 117.6(7)°.

Several CCl_2-complexes are accessible from CCl_3-precursors.[2] Following this procedure we sought a CHCl-complex from a $CHCl_2$-precursor. BCl_3 is an effective reagent for converting α-fluoroalkyl-ligands into α-chloroalkyl-ligands[3] and since the CHF_2-ligand was readily available to us we examined the reaction of BCl_3 with this ligand. $Os(=CF_2)(CO)_2(PPh_3)_2$, (**1**),[4] adds HCl to form $Os(CHF_2)Cl(CO)_2(PPh_3)_2$, (**2**). When (**2**) is allowed to react with BCl_3 at −78 °C in CH_2Cl_2 and the solution warmed to room temperature the high-yield product is (**4**). The expected intermediate (**3**) must undergo rapid conversion into (**4**) (see Scheme 1).

The structure of (**4**) was proved by single crystal *X*-ray diffraction[†] and Figure 1 depicts the molecular geometry. The

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[†] *Crystal data* for (**4**): $C_{45}H_{35}Cl_2O_2OsP_2$, M = 930.04, monoclinic, space group $P2_1/c$, a = 17.737(6), b = 12.328(3), c = 18.907(5) Å, β = 103.01(2)°, U = 4028.3 Å^3, D_c = 1.40 g cm^{-3} for Z = 4, $F(000)$ = 1676, $\lambda(Mo\text{-}K_\alpha)$ = 0.71069 Å, $\mu(Mo\text{-}K_\alpha)$ = 32.5 cm^{-1}. 4523 Reflections [$F > 3\sigma(F)$] were collected on a CAD4 diffractometer. The crystals were of poor quality with high mosaic spread. The structure was solved by Patterson and difference Fourier techniques and refined by full-matrix least-squares (all atoms anisotropic except phenyl carbon and hydrogen atoms) to $R = R_w$ = 0.074. *Crystal data* for (**5**): $C_{39}H_{28}ClO_2OsP_2$, M = 815.59, monoclinic, space group $P2_1/c$, a = 9.835(1), b = 19.925(2), c = 17.913(3) Å, β = 105.70(1)°, U = 3379.4 Å^3, D_c = 1.60 g cm^{-3} for Z = 4, $F(000)$ = 1604, $\lambda(Mo\text{-}K_\alpha)$ = 0.71069 Å, $\mu(Mo\text{-}K_\alpha)$ = 42.21 cm^{-1}. 3590 Reflections [$F > 3\sigma(F)$] were collected on a CAD4 diffractometer. The structure was solved by Patterson and difference Fourier techniques and refined by full-matrix least-squares (all atoms except phenyl carbon and hydrogen atoms anisotropic) to R = 0.043, R_w = 0.061.

The atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

C–Cl distance is long and the α-Cl atom in (**4**) is reactive, *e.g.*, recrystallisation from MeOH converts (**4**) into (**6**), which can be reconverted into (**4**) by the action of HCl. A further intriguing manifestation of this acid chloride-like reactivity is that (**4**), in the presence of more BCl_3, reacts to generate in high yield the metallabicyclic complex (**5**). Here the ring-forming reaction occurs to a benzene ring on the other PPh_3 ligand. This reaction could be viewed as an intramolecular Friedel–Crafts reaction. The structure of (**5**)† is depicted in Figure 2. The tridentate ligand in (**5**) bears an interesting resemblance to the tridentate ligand in the iridium complex, $\mathrm{IrHCl(PBu^t{}_2CH_2CH_2CHCH_2CH_2PBu^t{}_2)}$, resulting from a reaction involving the preformed ligand $\mathrm{Bu^t{}_2P[CH_2]_5PBu^t{}_2}$.[5] The assembly of (**5**) in two high-yield steps from (**2**) is an illustration of a method of ligand synthesis which promises to make available a great variety of metallabicyclic complexes for investigation.

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