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Preliminary communication

THE INTERACTION OF AN OSMIUM—CARBON TRIPLE BOND WITH COPPER(I), SILVER(I) AND GOLD(I) TO GIVE MIXED DIMETALLOCYCLOPROPENE SPECIES AND THE STRUCTURE OF $\overline{\mathrm{Os(AgCl)\ (C}}\mathrm{R)\ Cl(CO)\ (PPh_3)_2}$

G.R. CLARK, C.M. COCHRANE, W.R. ROPER* and L.J. WRIGHT
Department of Chemistry, University of Auckland, Auckland (New Zealand)

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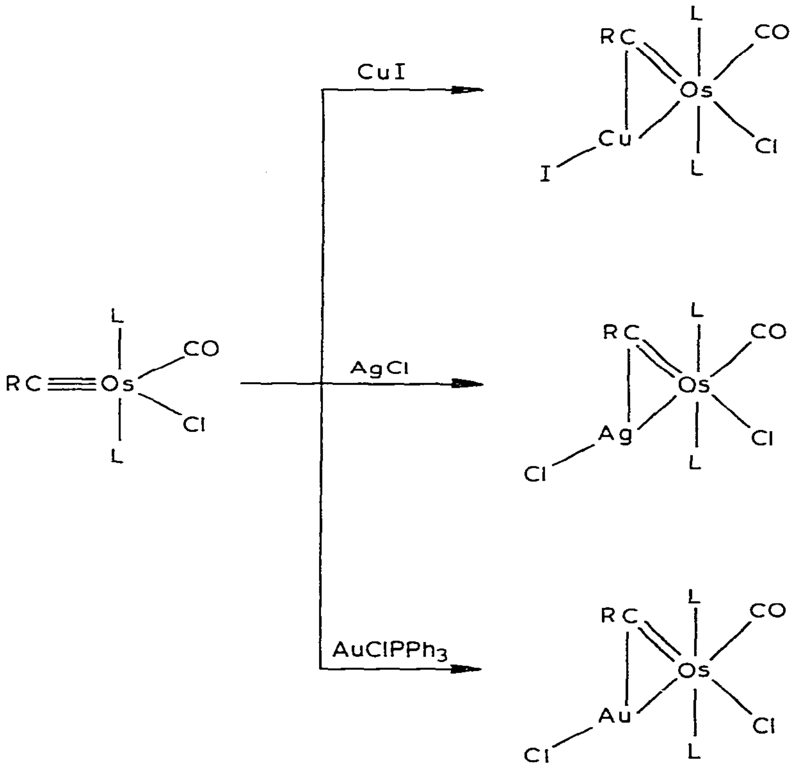
Summary

The osmium carbyne complex, $\mathrm{Os(CR)Cl(CO)(PPh_3)_2}$, (R = *p*-tolyl) reacts with Group I halides to form the mixed dimetallocyclopropene species, $\overline{\mathrm{Os(CuI)(C}}\mathrm{R)Cl(CO)(PPh_3)_2}$, $\overline{\mathrm{Os(AgCl)(C}}\mathrm{R)Cl(CO)(PPh_3)_2}$, $\overline{\mathrm{Os(AuCl)(C}}\mathrm{R)Cl(CO)(PPh_3)_2}$ and $\mathrm{[\overline{Os[Ag(OClO_3)](C}R)(CO)(MeCN)(PPh_3)_2]ClO_4}$. X-ray crystal structure determination of $\overline{\mathrm{Os(AgCl)(C}}\mathrm{R)Cl(CO)(PPh_3)_2}$ confirms the presence of a three-membered ring and the structure can be viewed as the "acetylene-like" interaction of an osmium—carbon triple bond with AgCl. In acid solution AgCl is precipitated and an alkylidene complex results from proton addition to the carbyne ligand.

An early indication that the metal—carbon triple bonds of transition metal terminal carbyne complexes will interact with suitable electrophiles was provided by the X-ray crystal structure determination of [lithium-*N,N'*-dimethylpiperazine] $\mathrm{[Ta(CCMe_3)(CH_2CMe_3)_3]}$ which revealed the *N,N'*-dimethylpiperazine-chelated Li cation associating with the Ta≡C bond [1]. We have recently described the osmium terminal carbyne complex $\mathrm{Os(CR)Cl(CO)(PPh_3)_2}$ (R = *p*-tolyl), and shown that this compound reacts with the electrophiles H^+ and Cl_2 to form carbene complexes and also shows "acetylene-like" behaviour in reacting with chalcogens forming *dihapto*-chalcoacyl derivatives [2]. In pursuing the acetylene analogy, we now describe the reactions between $\mathrm{Os(CR)Cl(CO)(PPh_3)_2}$ and Group I halides to form 1/1 complexes in which there is a direct interaction between the Os≡C bond and the Group I metal. An alternative description of these compounds is as mixed dimetallocyclopropene species and related compounds have been described from reaction between the tungsten carbyne complex $\mathrm{W(\eta^5\text{-}C_5H_5)(CR)(CO)_2}$ and various platinum(0) complexes [3].

On stirring a benzene solution of $\mathrm{Os(CR)Cl(CO)(PPh_3)_2}$ and $\mathrm{AuCl(PPh_3)}$ at room temperature for several hours a pink solid crystallises from solution. This material analyses for the 1/1 adduct, $\mathrm{Os(CR)Cl(CO)(PPh_3)_2 \cdot AuCl}$. One ν(CO) is displayed in the IR spectrum at 1915 $\mathrm{cm^{-1}}$ while absorptions at 328 and 268 $\mathrm{cm^{-1}}$ are observed in the far-IR. (see Scheme 1 and Table I). The former is assigned to ν(Au—Cl) and the latter to ν(Os—Cl). The compound is too insoluble to obtain a satisfactory ^{1}H NMR but the *p*-tolyl group is evidenced by a characteristic sharp band at 810 $\mathrm{cm^{-1}}$ in the IR spectrum. If $\mathrm{Os(CR)Cl(CO)(PPh_3)_2}$ is stirred with a suspension of CuI under identical reaction conditions, a creamy-green solid analysing correctly for $\mathrm{Os(CR)Cl(CO)(PPh_3)_2 \cdot CuI}$ is obtained. The IR spectral features of this derivative are practically identical to those observed for the AuCl adduct except that only one bond is observed in the far IR at 255 $\mathrm{cm^{-1}}$ and is assigned to ν(Os—Cl). A benzene solution of $\mathrm{Os(CR)Cl(CO)(PPh_3)_2}$ also reacts with AgCl, although complete reaction requires 24 h and the yield of violet $\mathrm{Os(CR)Cl(CO)(PPh_3)_2 \cdot AgCl}$ is only 70%. The IR spectrum of this adduct very closely resembles the spectra of the AuCl and CuI adducts. Clearly these are all analogous compounds. It was considered likely that the Os≡C bond interacts with the MX fragments in essentially the same way that an acetylene or olefin would be expected to interact. To confirm this an X-ray crystal structure determination of $\mathrm{Os(CR)Cl(CO)(PPh_3)_2 \cdot AgCl}$ was undertaken. Violet crystals of $\overline{\mathrm{Os(AgCl)(C}}\mathrm{R)Cl(CO)(PPh_3)_2}$ are monoclinic; *a* 13.021(2), *b* 23.714(2), *c* 12.999(2) Å, β 90.56(1)°; space group



SCHEME 1: Reaction of $\mathrm{Os(CR)Cl(CO)L_2}$ with Group I halides (L = $\mathrm{PPh_3}$; R = *p*-tolyl).

TABLE 1

IR DATA[a] FOR OSMIUM COMPLEXES[b]

Compound	ν(CO)	ν(Os—Cl)	ν(M—Cl)
$Os(CuI)(CR)Cl(CO)(PPh_3)_2$	1912	255	
$Os(AgCl)(CR)Cl(CO)(PPh_3)_2$	1911	266	305
$Os(AuCl)(CR)Cl(CO)(PPh_3)_2$	1915	268	328
$[Os[Ag(OClO_3)](CR)(CO)(MeCN)(PPh_3)_2]ClO_4$	1939		
$OsCl(OClO_3)(CHR)(CO)(PPh_3)_2$	1940		

[a] In cm^{-1} measured as nujol mulls. [b] All compounds have satisfactory carbon and hydrogen analyses.

$P2_1/n$; $Z = 4$. Intensity data were collected on a Nonius CAD-4 diffractometer and the structure was solved by conventional heavy-atom methods. Full-matrix least-squares refinement has given $R = 0.036$ for 3898 reflections. The molecular geometry and pertinent bond lengths and angles are depicted in Fig. 1.

The results support the type of interaction anticipated and thus the complexes are probably most accurately described as dimetallocyclopropene derivatives. The Os≡C bond length has increased from the 1.77(2) Å observed in the parent carbyne complex to 1.839(5) Å. It is interesting to compare this interaction between silver(I) and Os≡C with the interaction between platinum(0) and W≡C in $W(\eta^5\text{-}C_5H_5)[(CR)Pt(PMe_2Ph)_2](CO)_2$ [3]. In this latter complex the W≡C bond increases from 1.82 in the parent carbyne to 1.96 Å. Using the acetylene analogy the bonding in both of these molecules can be explained in terms of the normal σ-donor, π-acceptor model. The large π-back-bonding component expected from the electron-rich platinum centre results in considerable weakening of the W≡C bond and the bond length increases 0.14 Å on coordination of $Pt(PMe_2Ph)_2$. For the more electrophilic silver atom,

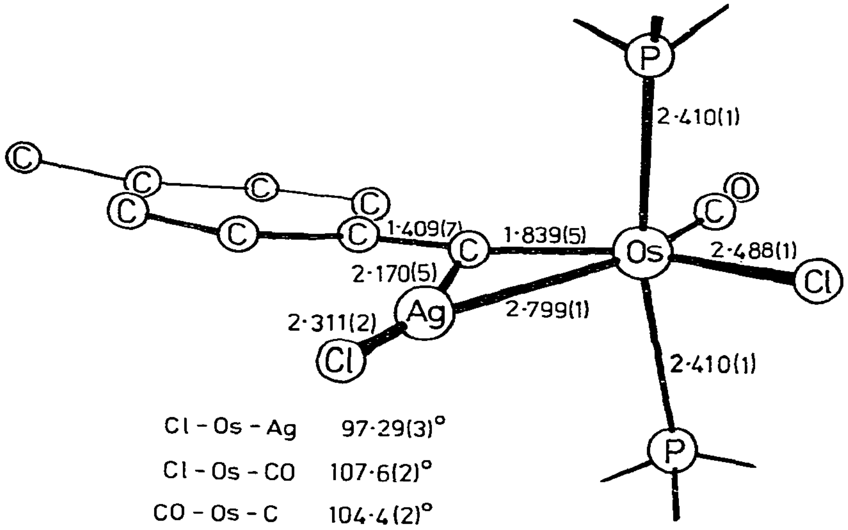
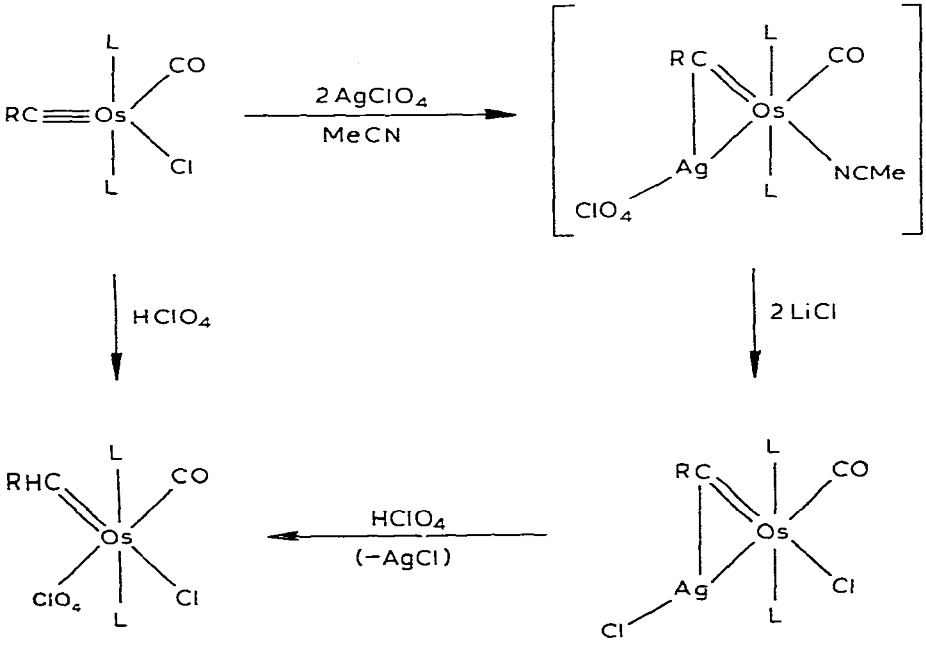


Fig. 1. The inner coordination sphere of $Os(AgCl)(CR)Cl(CO)(PPh_3)_2$ with the phenyl groups of the triphenylphosphine ligands excluded for clarity.

however, π-backbonding is far less important and consequently the Os≡C bond distance increases by only 0.07 Å on coordination of AgCl. The other M—C and M—M bond distances are also compatible with a weaker interaction between Os≡C and silver(I) than between W≡C and platinum(0). AgCl can be readily cleaved from $\overline{\mathrm{Os(AgCl)(C}}\mathrm{R)Cl(CO)(PPh_3)_2}$ by reaction with acid. Thus on stirring this complex with $HClO_4$ in a dichloromethane/ethanol mixture, white AgCl is immediately precipitated and orange $OsCl(OClO_3)(CHR)(CO)(PPh_3)_2$ is formed. This same complex is obtained through direct reaction of $Os(CR)Cl(CO)(PPh_3)_2$ with $HClO_4$.

Reaction of $Os(CR)Cl(CO)(PPh_3)_2$ with $AgClO_4$ (2 equivalents) in acetonitrile/dichloromethane solution results in the formation of a precipitate of AgCl and the pink compound isolated from solution is $[\overline{\mathrm{Os[Ag(OClO_3)](C}}\mathrm{R)(CO)(MeCN)(PPh_3)_2]ClO_4}$ (see Scheme 2). When a dichloromethane solution of this compound is treated with LiCl in ethanol the colour changes rapidly to violet and $\overline{\mathrm{Os(AgCl)(C}}\mathrm{R)Cl(CO)(PPh_3)_2}$ is formed in good yield. This provides a more convenient preparative route to this complex than the direct reaction of AgCl with $Os(CR)Cl(CO)(PPh_3)_2$.



SCHEME 2: Reactions of $Os(CR)Cl(CO)L_2$ with $AgClO_4$ ($L = PPh_3$; R = p-tolyl).

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