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OCTAHEDRAL CARBYNEOSMIUM(II) COMPLEXES

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Summary

The zerovalent carbyneosmium complex, $OsCl(CC_6H_4NMe_2)(CO)(PPh_3)_2$, reacts with molecular oxygen giving a 1/1 adduct which is formulated as a divalent, octahedral complex retaining the unchanged carbyne ligand, and with a *dihapto*-peroxycarbonyl ligand, $\overline{\mathrm{Os(O_2C}}\mathrm{O)Cl(CC_6H_4NMe_2)(PPh_3)_2}$. Reaction with HCl liberates CO_2 and forms $[OsCl_2(CC_6H_4NMe_2)(H_2O)(PPh_3)_2]^+$ from which have been derived, and structurally characterised by X-ray crystallography, the two octahedral complexes, $OsCl_2(NCS)(CC_6H_4NMe_2)(PPh_3)_2$ and $[OsCl_2(CC_6H_4NMe_2)(CNR)(PPh_3)_2]^+$. The Os—carbyne distances in these two species are, respectively, 1.75(1) and 1.78(1) Å.

The dichlorocarbene complex, $OsCl_2(CCl_2)(CO)(PPh_3)_2$, reacts with lithium reagents forming $OsCl(CR)(CO)(PPh_3)_2$ [1]. The five coordinate geometry found for these molecules together with the low ν(CO) values (e.g. 1864 cm^{-1} for $OsCl(C\text{-}p\text{-tolyl})(CO)(PPh_3)_2$) suggest that an appropriate way of regarding these molecules is as zerovalent complexes, i.e. these molecules are related to $OsCl(NO)(CO)(PPh_3)_2$ [2] and $Os(CO)_3(PPh_3)_2$ [3]. This suggests that upon oxidation, a series of molecules of general formula $OsX_3(CR)(PPh_3)_2$ (X = anionic ligand) should exist (cf. $OsX_3(NO)(PPh_3)_2$) and these in turn would be related to the octahedral carbyne complexes of Group VI elements, e.g. $WX(CR)L_4$, studied extensively by Fischer and coworkers [4]. Unfortunately, many potential oxidants, e.g. chlorine, add to the osmium—carbon triple bond thereby destroying the carbyne ligand. We have now discovered an unusual reaction of the zerovalent carbyne complexes with molecular oxygen, the exact course of which is dependent on the carbyne substituent but which at least for the *p*-dimethylaminophenylcarbyne, oxidises the metal centre without interfering with the carbyne ligand.

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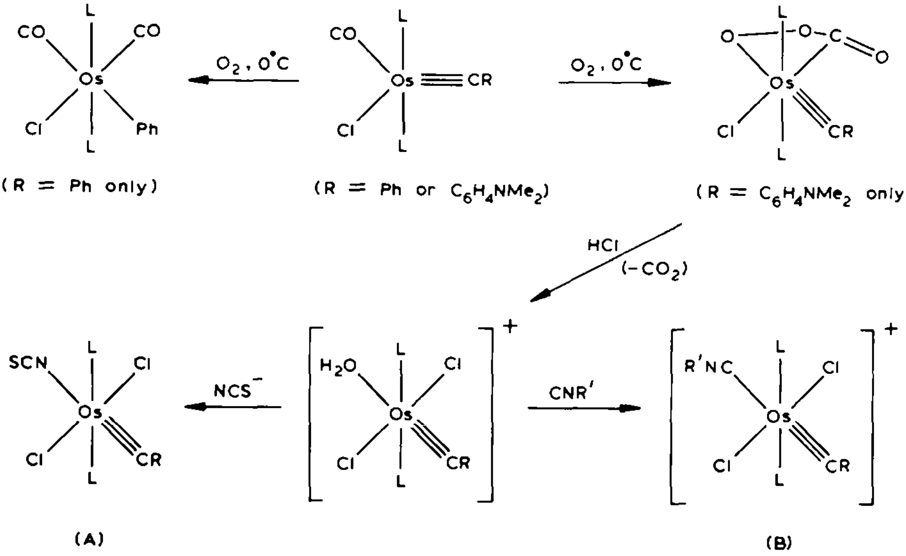
When the phenyl-carbyne complex, $OsCl(CPh)(CO)(PPh_3)_2$, is exposed to oxygen at or below 0° C, a reaction ensues from which the only isolatable product, in high yield, is $OsClPh(CO)_2(PPh_3)_2$. In contrast (see Scheme 1), the *p*-dimethylaminophenylcarbyne complex, $OsCl(CC_6H_4NMe_2)(CO)(PPh_3)_2$, when similarly exposed to oxygen rapidly forms a yellow crystalline 1/1 adduct. The IR spectrum (Table 1) indicates that a terminal CO ligand is no longer present and the new IR bands correspond closely with those found for the related oxygen adduct of $OsCl(NO)(CO)(PPh_3)_2$. Evidence will be reported elsewhere [5] indicating that this compound is $\overline{Os(O_2CO})Cl(NO)(PPh_3)_2$, and accordingly the oxidised carbyne complex is formulated as $\overline{Os(O_2CO})Cl(CC_6H_4NMe_2)(PPh_3)_2$. The further reaction of this compound with aqueous HCl, liberating CO_2, is consistent with this formulation. The resulting presumed aquo-cation $[OsCl_2\text{-}(CC_6H_4NMe_2)(H_2O)(PPh_3)_2]^+$ crystallises only with difficulty and has not given



SCHEME 1. Synthesis and Reactions of Osmium Carbyne Complexes ($L = PPh_3$, R′ = *p*-tolyl)

TABLE 1

IR DATA[a] FOR OSMIUM CARBYNE COMPLEXES[b]

Compound	ν(CO)	ν(Os≡C)	Other bands
$OsCl(CPh)(CO)(PPh_3)_2$	1860	1355	
$OsCl(CC_6H_4NMe_2)(CO)(PPh_3)_2$	1855	1380	
$OsClPh(CO)_2(PPh_3)_2$	2010, 1940		298(Os—Cl)
$\overline{Os(O_2CO})Cl(CC_6H_4NMe_2)(PPh_3)_2$		1405	1680, 1058 (peroxycarbonyl)
$[OsCl_2(CC_6H_4NMe_2)(H_2O)(PPh_3)_2]ClO_4$		1420	
$OsCl_2(NCS)(CC_6H_4NMe_2)(PPh_3)_2$		1410	2105 (NCS)
$[OsCl_2(CC_6H_4NMe_2)(CN\text{-}p\text{-tolyl})(PPh_3)_2]ClO_4$		1415	2210 (CN-*p*-tolyl)

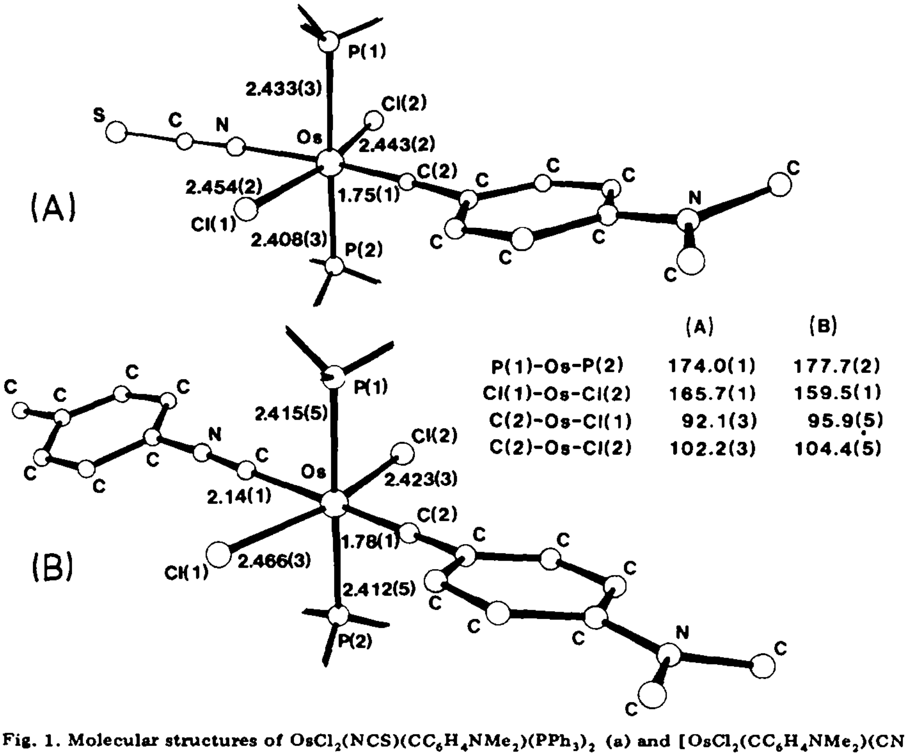
[a] In cm^{-1} measured as nujol mulls. [b] All compounds have satisfactory elemental analyses except $[OsCl_2\text{-}(CC_6H_4NMe_2)(H_2O)(PPh_3)_2]ClO_4$ (see text).

satisfactory elemental analyses. However, two derivatives, one neutral, $OsCl_2(NCS)(CC_6H_4NMe_2)(PPh_3)_2$ and one cationic, $[OsCl_2(CC_6H_4NMe_2)(CN\text{-}p\text{-tolyl})(PPh_3)_2]^+$ have been thoroughly characterised including X-ray crystal structure determinations.

$OsCl_2(NCS)(CC_6H_4NMe_2)(PPh_3)_2$ forms monoclinic orange needles; *a* 10.167(4), *b* 21.283(3), *c* 21.629(3) Å, *β* 102.77(2)°, space group $P2_1/c$, Z = 4. The structure was solved by conventional heavy-atom methods and refined by full-matrix least-squares employing anisotropic thermal parameters for all non-hydrogen atoms except the carbons of the triphenylphosphine ligands. Final *R* is 0.038 for 3015 observed reflections. The asymmetric unit contains one dichloromethane solvent molecule of crystallisation.

$[OsCl_2(CC_6H_4NMe_2)(CN\text{-}p\text{-tolyl})(PPh_3)_2]ClO_4$ forms dark orange triclinic tablets; *a* 15.518(2), *b* 17.246(2), *c* 13.254(2) Å, *α* 108.70(1), *β* 112.17(1), *γ* 92.87(1)°, space group $P\bar{1}$, Z = 2. The structure was solved as above. At the present stage of refinement (phenyl rings restrained to rigid groups, all other non-hydrogen atoms assigned anisotropic thermal parameters) *R* is 0.057 for 5101 observed reflections. The asymmetric unit contains at least one tetrachloroethane solvent molecule. The structure contains possible solvent disorder which is still under investigation.

The geometries of the two complexes are depicted in Fig. 1. The phosphines are each mutually *trans* as are the chloride ligands. The Os—P and Os—Cl distances are normal. The Os—carbyne distance of 1.75(1) for A and 1.78(1) for B compare closely with the value 1.77(2) found for OsCl(C-*p*-tolyl)(CO)-



	(A)	(B)
P(1)-Os-P(2)	174.0(1)	177.7(2)
Cl(1)-Os-Cl(2)	165.7(1)	159.5(1)
C(2)-Os-Cl(1)	92.1(3)	95.9(5)
C(2)-Os-Cl(2)	102.2(3)	104.4(5)

Fig. 1. Molecular structures of $OsCl_2(NCS)(CC_6H_4NMe_2)(PPh_3)_2$ (a) and $[OsCl_2(CC_6H_4NMe_2)(CN\text{-}p\text{-tolyl})(PPh_3)_2]ClO_4$ (b) with phenyl groups of the triphenylphosphine ligands omitted for clarity.

$(PPh_3)_2$ [1] and no oxidation state or charge dependence of this distance is apparent. The remarkable shortness of these Os—C distances is well-illustrated by comparison with the other Os—C distance in molecule B, to the *trans*-located *p*-tolylisocyanide ligand which is bound at 2.14(1) Å.

The presence of the carbyne ligand distorts the geometry in the square coordination plane by repelling the chloride ligands to give Cl(1)—Os—Cl(2) angles substantially less than 180°. For B, the Cl(2) bond is at 104.4(5)° to the carbyne ligand. A similar distortion was observed in the trigonal bipyramidal complex Os(C-*p*-tolyl)Cl(CO)$(PPh_3)_2$ where the Cl—Os—carbyne angle is 132.9° instead of the expected 120°. It can be noted that distortion of Cl atoms away from osmium—nitrogen triple bonds has also been observed [6].

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