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Preliminary communication

AN UNUSUAL VINYLIDENE COMPLEX FROM HYDRIDE ADDITION TO THE AROMATIC RING OF THE TOLYL—CARBYNE LIGAND IN A CATIONIC OSMIUM CARBYNE COMPLEX

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Summary

The cationic osmium carbyne complex $[Os(CR)(CO)_2(PPh_3)_2]^+$ (R = *p*-tolyl) reacts with $Li(Et_3BH)$ with hydride addition to the *para*-position of the aromatic ring of the carbyne ligand giving an unusual vinylidene complex. This formulation of the product, which was suggested by the ^1H NMR data, was confirmed by an X-ray crystal structure determination.

A characteristic reaction exhibited by cationic carbyne complexes of Group VI and VII transition metals is with nucleophiles to form carbene complexes through addition of the nucleophile to the carbyne carbon atom [1,2] e.g.:

$$[(\eta^5\text{-}C_5H_5)(CO)_2Re{\equiv}CPh]^+ \xrightarrow{AlHEt_2} (\eta^5\text{-}C_5H_5)(CO)_2Re{=}CHPh$$

In the expectation of observing similar reactions for an osmium coordinated carbyne we have converted the neutral compound $Os(CR)Cl(CO)(PPh_3)_2$ (R = *p*-tolyl) [3], to the cations $[Os(CR)(CO)_2(PPh_3)_2]^+$ (Ia) and $[Os(CR)(CO)(CNR)(PPh_3)_2]^+$ (Ib) through reaction with $AgClO_4$ in the presence of either CO or CNR respectively (see Scheme 1). $[Os(CR)(CO)_2(PPh_3)_2]ClO_4$ forms orange crystals (see Table 1 for IR and ^1H NMR data). A strong band in the IR spectrum at 1375 cm^{-1} is tentatively assigned to $\nu(Os{\equiv}C)$. This is 16 cm^{-1} higher than a similar band in the neutral complex $Os(CR)Cl(CO)(PPh_3)_2$. The two carbonyl carbon atoms are observed in the ^{13}C NMR ($CDCl_3$ solution) as a triplet at 182.8 ppm downfield from TMS (^2J(CP) 9.5 Hz) and the carbyne carbon atom appears as a triplet at 331.0 ppm (^2J(CP) 11 Hz).

The chemical reactivity of the carbyne moiety in $[Os(CR)(CO)_2(PPh_3)_2]ClO_4$ is quite different from that in the neutral parent complex. Whereas

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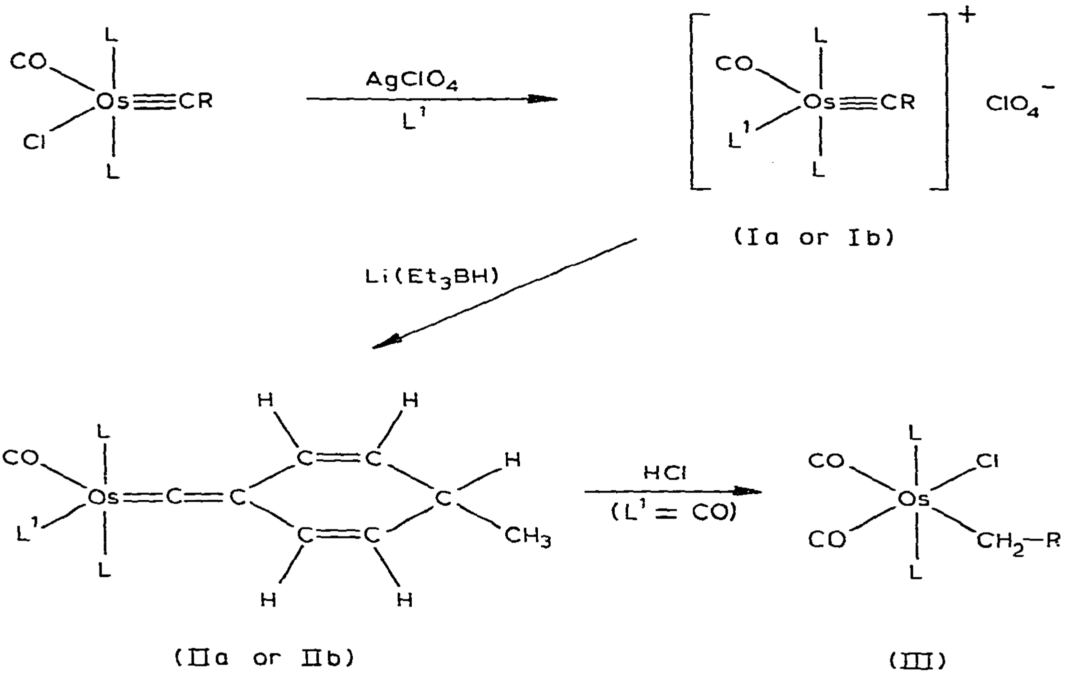


SCHEME 1. Reactions of cationic carbyne complexes (L = PPh_3, L^1 = CO (Ia and IIa) or CNR (Ib and IIb), R = *p*-tolyl).

TABLE 1

IR DATA[a] AND ^{1}H NMR DATA[b] FOR OSMIUM COMPLEXES[c]

Compound	ν(CO)	ν(CN)	Chemical shifts
$[Os(CR)(CO)_2(PPh_3)_2]ClO_4$ (Ia)	2010, 1944		7.78, s, 3H, $C_6H_4CH_3$
$[Os(CR)(CO)(CNR)(PPh_3)_2]ClO_4$ (Ib)	1934	2118	7.83, s, 3H, $C_6H_4CH_3$ 7.74, s, 3H, $C_6H_4CH_3$
$Os(C_8H_8)(CO)_2(PPh_3)_2$ (IIa)	1956, 1897		9.34, d, 3H, CH_3, ^3J(HH) 7.5 Hz 5.64—5.30, m, 2H, =CH 4.86—4.55, m, 2H, =CH
$Os(C_8H_8)(CO)(CNR)(PPh_3)_2$ (IIb)	1895	2068	9.34, d, 3H, CH_3, ^3J(HH) 7.5 Hz 7.83, s, 3H, $C_6H_4CH_3$ 5.90—4.28, m, 4H, =CH
$OsCl(CH_2R)(CO)_2(PPh_3)_2$	2014, 1947		7.82, s, 3H, $C_6H_4CH_3$ 7.05, t, 2H, CH_2—R ^3J(HP) 8 Hz 3.93, dd, 4H, $C_6H_4CH_3$ ^3J(HH) 49 Hz, ^5J(HH) 8 Hz

[a] In cm^{-1}, measured as Nujol mulls. All bands listed are strong. [b] τ values measured in $CDCl_3$ solution. [c] Satisfactory elemental analyses obtained for all compounds reported.

$Os(CR)Cl(CO)(PPh_3)_2$ reacts instantly with acids HX to form $OsClX(CHR)(CO)(PPh_3)_2$, $[Os(CR)(CO)_2(PPh_3)_2]ClO_4$ can be recovered unchanged after 2 h in a strongly acidic CH_2Cl_2/EtOH/aqueous HCl solution.

When $Li(Et_3BH)$ is added to a solution of Ia or Ib in THF or CH_2Cl_2 the solution rapidly turns yellow and yellow crystals of the respective vinylidene complexes IIa or IIb are obtained upon addition of hexane. IIa displays two ν(CO) bands in the IR spectrum at 1956 and 1897 cm^{-1}, values which are close to those observed for other related dicarbonyl zerovalent complexes of osmium e.g., $Os(CS)(CO)_2(PPh_3)_2$ [4] at 1955 and 1890 cm^{-1}. IR absorptions at 1649 and 1604 cm^{-1} are probably associated with the carbon—carbon double bonds of the vinylidene ligand. The methyl protons of the ligand are observed as a doublet in the ^1H NMR at τ 9.34 (^3J(HH) 7.5 Hz). This observation first suggested the vinylidene formulation. The proton derived from $Li(Et_3BH)$ has not been identified in the ^1H NMR and broad multiplets at τ 4.54—5.64 which integrate for 4 protons are assigned to the alkene protons of the ligand.

An X-ray crystal structure determination was undertaken to confirm the vinylidene formulation. IIa crystallises in the orthorhombic system (space group $Pna2_1$) with a 17.147(2), b 9.488(2), c 23.304(4) Å, $Z = 4$. Intensity data were collected on an Enraf–Nonius CAD-4 diffractometer using Mo-K_α radiation and a total of 2782 unique reflections with $I > 3\sigma(I)$ were recorded. The structure was solved by Patterson and Fourier methods and has been refined to $R = 0.035$. The molecular geometry together with pertinent bond lengths and angles is depicted in Fig. 1. The molecule has trigonal bipyramidal geometry with the phosphine ligands mutually *trans*. Of particular interest are the bond lengths and angles associated with the vinylidene fragment. C(7) is clearly sp^3-hybridised and the bond to C(10) tilts out of the plane of the C(4)—C(9) ring. The alternation of double and single bonds implied by the valence bond structure drawn out in Scheme 1 is clearly present. The vinylidene complex IIb has similar spectral properties to IIa (see Table 1).

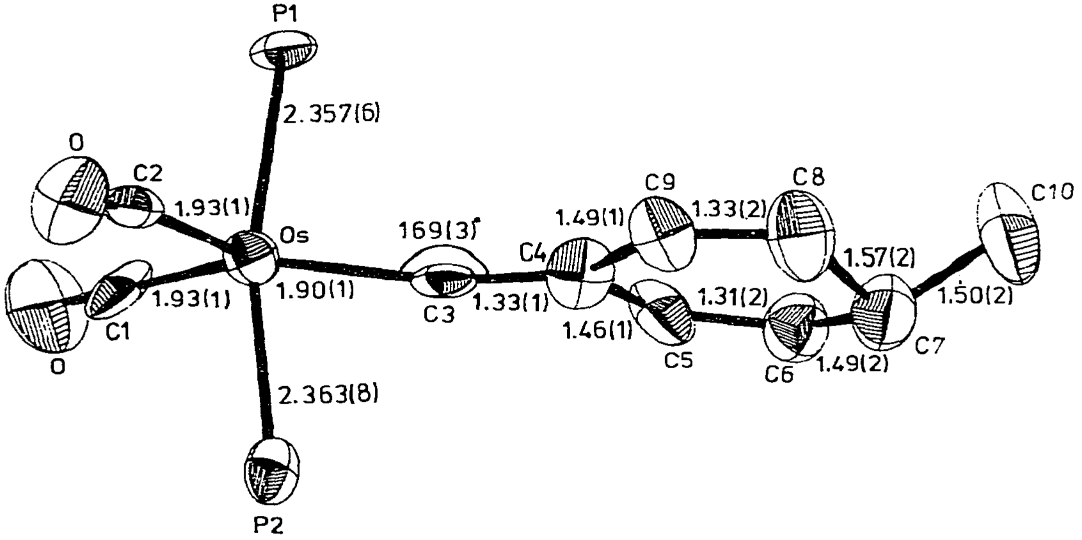
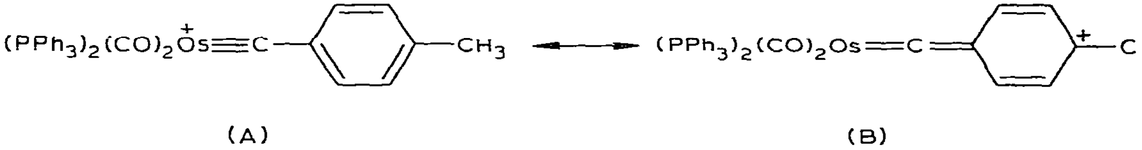


Fig. 1. The inner coordination sphere of osmium vinylidene complex IIa with the phenyl groups of the triphenylphosphine ligands excluded for clarity.

The unexpected result of hydride addition to the *para*-position of the aromatic ring in Ia and Ib rather than formation of zerovalent carbene complexes, $Os(CHR)(CO)_2(PPh_3)_2$ and $Os(CHR)(CO)(CNR)(PPh_3)_2$ suggests a significant contribution to the bonding in Ia by the resonance hybrid B:



X-ray crystal structure determination of Ia is in progress and it will be interesting to see if comparison with the structure already found for Os(CR)Cl(CO)$(PPh_3)_2$ [3] supports a contribution from hybrid B.

A solution of IIa in CH_2Cl_2/EtOH reacts with conc. aqueous HCl over several minutes at 30°C to form the substituted benzyl derivative $OsCl(CH_2R)(CO)_2(PPh_3)_2$. This may indicate that IIa is in equilibrium with the valence tautomer $Os(CHR)(CO)_2(PPh_3)_2$ which reacts directly with HCl forming the observed benzyl species but other mechanisms are possible.

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References

1 E.O. Fischer, U. Schubert, and H. Fischer, Pure and Appl. Chem., 50 (1978) 857.
2 E.O. Fischer and A. Frank, Chem. Ber., 111 (1978) 3740.
3 G.R. Clark, K. Marsden, W.R. Roper, and L.J. Wright, J. Amer. Chem. Soc., 102 (1980) in press.
4 T.J. Collins, W.R. Roper, and K.G. Town, J. Organometal. Chem., 121 (1976) C41.