Preliminary communication

BASIC METALS

XXIII*. SYNTHESIS AND REACTIVITY OF LEWIS-BASE OSMIUM(0) COMPLEXES

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(Received March 31st, 1980)

Summary

The complexes $C_6H_6OsL_2$ (L = PPh_3, $P(OMe)_3$) and C_6H_6OsLL' (L = PMe_3, L' = C_2H_4 and C_3H_6) have been prepared by reduction of $[C_6H_6OsIL_2]^+$ and $[C_6H_6OsILL']^+$ with $NaC_{10}H_8$ in THF. These novel osmium(0) complexes are strong Lewis bases and react with NH_4PF_6 or MeI to form stable cations containing Os—H and Os—CH_3 bonds; the reactions of the latter complexes are briefly discussed.

Our recent finding that half-sandwich type complexes of the general composition $C_5H_5ML_2$ (M = Co [2,3], Rh [2,4]) and $C_6H_6RuL_2$ [5], where L is PR_3 or $P(OR)_3$, are strong Lewis bases, and thus useful starting materials for the synthesis of hydridometal and alkylmetal cationic species, prompted us to explore the chemistry of the corresponding formerly unknown benzeneosmium compounds. We were also interested in learning whether analogous osmium(0) complexes C_6H_6OsLL' containing both a phosphine (L) and an olefin (L') are accessible.

Treatment of $[C_6H_6OsI_2]_2$ (I) with triphenylphosphine (C_6H_6, 80°C, 2 h) gives by iodide-bridge cleavage the mononuclear complex $[C_6H_6OsI_2(PPh_3)]$ (II), which upon treatment with $AgPF_6$ (CH_3NO_2, 25°C) and subsequent addition of PPh_3 (60°C, 7 h) gives the salt $[C_6H_6OsI(PPh_3)_2]PF_6$ (III). The analogous bis(trimethylphosphite) complex (IV) is obtained directly from I and $P(OMe)_3$ in the presence of NH_4PF_6 (CH_3OH, 60°C, 2 h). Synthesis of the osmium(0) compounds $[C_6H_6Os(PPh_3)_2]$ (V) and $[C_6H_6Os(P(OMe)_3)_2]$ (VI) is achieved by low-temperature reduction of III and IV with sodium dihydronaphthylide in tetrahydrofuran. The complexes V and VI are extremely sensitive to air and decom-

*For Part XXII see ref. 1.

TABLE 1

^{1}H NMR SPECTRA OF COMPLEXES [C$_6$H$_6$OsL$_2$] AND [C$_6$H$_6$OsLL′] IN C$_6$D$_6$ (δ in ppm, J in Hz; s, singlet; d, doublet; t, triplet; m, multiplet; vt, virtual triplet)

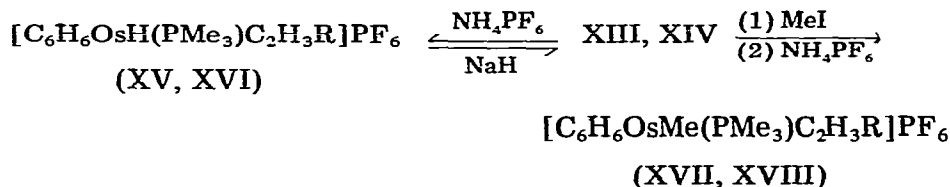| Complex	δ(C$_6$H$_6$)	J(PH)	δ(L)	J(PH)	δ(L′)
V	4.59 t	0.6	7.0 m		
VI	5.07 s		3.52 vt	a	
XIII	4.72 d	0.6	1.05 d	8.7	1.67 m
XIV	4.73 d	0.7	0.99 d	8.6	3.18 m [C$_2$H$_3$Me]
					1.60 m [C$_2$H$_3$$\overline{\text{Me}}$]

a J' = 12.4 Hz.

pose slowly even when stored under N$_2$. The ^{1}H NMR data are shown in Table 1.

The strong nucleophilicity of the complexes V and VI is demonstrated by their smooth reactions with NH$_4$PF$_6$ and methyliodide (THF, 25°C) which produce the cations [C$_6$H$_6$OsHL$_2$]$^+$ and [C$_6$H$_6$OsMeL$_2$]$^+$ (Scheme 1). The ^{1}H NMR spectra of the osmium hydrides show a high-field triplet at δ −11.0 (J(PH) 34 Hz) for VII and −13.3 (J(PH) 35.5 Hz) for VIII, the difference reflecting the different electron densities at the metal atom.
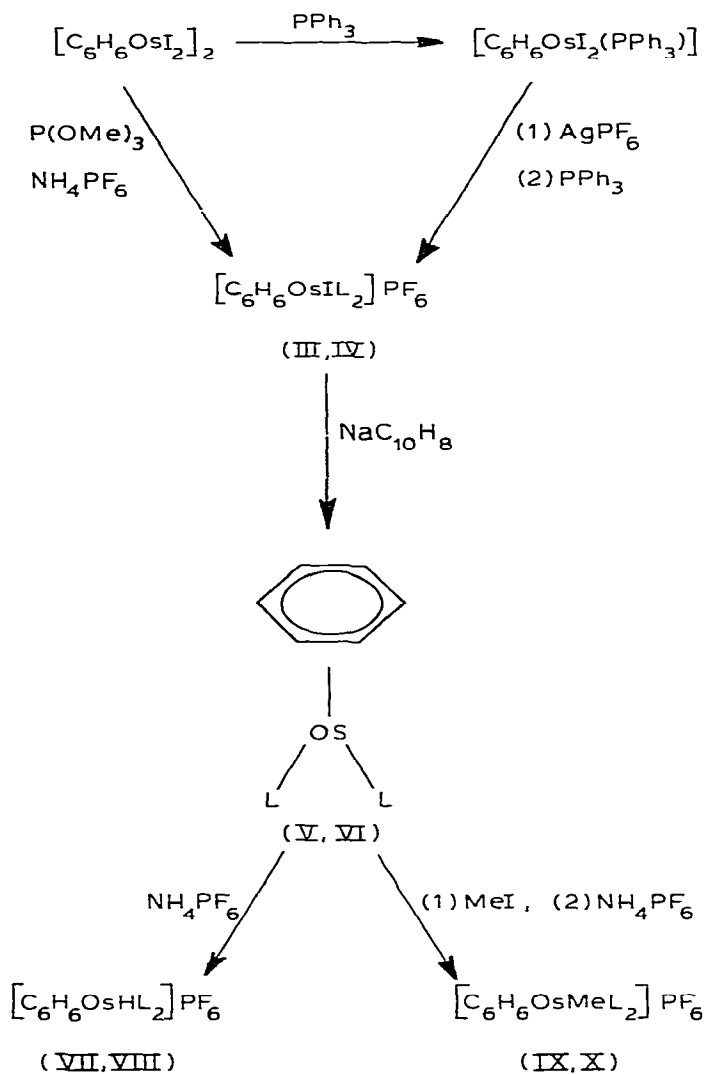
The preparation of the cationic olefin complexes [C$_6$H$_6$OsI(PMe$_3$)C$_2$H$_3$R]PF$_6$ (XI: R = H, XII: R = Me) was by the route used for the synthesis of III. Reduction of XI and XII with NaC$_{10}$H$_8$ (THF, −78°C) yields the osmium(0) compounds [C$_6$H$_6$Os(PMe$_3$)C$_2$H$_3$R] (XIII, XIV) which are somewhat more stable towards oxidation than the bis(phosphine) and bis(phosphite) analogues V and VI (for ^{1}H NMR data see Table 1).

$$I \xrightarrow{\text{PMe}_3} [C_6H_6OsI_2(PMe_3)] \xrightarrow[\text{(2) } C_2H_3R]{\text{(1) AgPF}_6} [C_6H_6OsI(PMe_3)C_2H_3R]PF_6$$

(XI, XII)

$$\xrightarrow{\text{NaC}_{10}\text{H}_8} [C_6H_6Os(PMe_3)C_2H_3R]$$

(XIII, XIV)

Treatment of XIII and XIV with NH$_4$PF$_6$ and methyl iodide (THF, 25°C) gives a quantitative yield of the cationic hydrido(olefin) and methyl(olefin) complexes [C$_6$H$_6$OsH(PMe$_3$)C$_2$H$_3$R]$^+$ and [C$_6$H$_6$OsMe(PMe$_3$)C$_2$H$_3$R]$^+$, a result which confirms the Lewis base character of the metal atom in the neutral compounds [C$_6$H$_6$Os(PMe$_3$)C$_2$H$_3$R]. The reactions of XV and XVI with NaH (THF, 25°C) provides a convenient route to the complexes XIII and XIV in a pure state.

$$[C_6H_6OsH(PMe_3)C_2H_3R]PF_6 \underset{\text{NaH}}{\overset{\text{NH}_4\text{PF}_6}{\rightleftharpoons}} \text{XIII, XIV} \xrightarrow[\text{(2) NH}_4\text{PF}_6]{\text{(1) MeI}}$$

(XV, XVI)
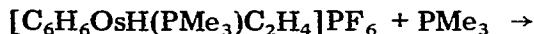
$$[C_6H_6OsMe(PMe_3)C_2H_3R]PF_6$$

(XVII, XVIII)

The reactions of the hydrido(olefin) complexes XV and XVI with NaI (acetone, 50°C, 10 min) lead to insertion of the olefin into the hydride—osmium bond to form the compounds [C$_6$H$_6$Os(C$_2$H$_4$R)(PMe$_3$)I]. These in turn react with AgPF$_6$ (acetone, 25°C) to yield the hydrido(olefin) complexes [C$_6$H$_6$OsH(PMe$_3$)C$_2$H$_3$R]PF$_6$.

$$[C_6H_6OsI_2]_2 \xrightarrow{PPh_3} [C_6H_6OsI_2(PPh_3)]$$

P(OMe)$_3$

NH$_4$PF$_6$

(1) AgPF$_6$

(2) PPh$_3$

$$[C_6H_6OsIL_2]PF_6$$

(III, IV)

NaC$_{10}$H$_8$

OS

L   L

(V, VI)

NH$_4$PF$_6$

(1) MeI , (2) NH$_4$PF$_6$

$$[C_6H_6OsHL_2]PF_6$$

(VII, VIII)

$$[C_6H_6OsMeL_2]PF_6$$

(IX, X)

SCHEME 1. III, V, VII, IX: L = PPh$_3$; IV, VI, VII, X: L = P(OMe)$_3$.

Treatment of the methyl(olefin) complexes [C$_6$H$_6$OsMe(PMe$_3$)C$_2$H$_3$R]PF$_6$ (XVII: R = H; XVIII: R = Me) with NaI does not lead to insertion but to displacement of the olefin to give [C$_6$H$_6$OsMe(PMe$_3$)I]. The difference in reactivity between the hydrido(olefin) and the methyl(olefin) cations is also found in the reactions of XV and XVII with trimethylphosphine. Whereas XV reacts with PMe$_3$ (acetone, 25°C, 12 h) to give a mixture of [C$_6$H$_6$OsEt(PMe$_3$)$_2$]PF$_6$ (XIX) and [C$_6$H$_6$OsH(PMe$_3$)C$_2$H$_4$PMe$_3$]PF$_6$ (XX), the reaction of XVII with PMe$_3$ (acetone, 25°C, 5 min) produces only [C$_6$H$_6$OsMe(PMe$_3$)C$_2$H$_4$PMe$_3$]PF$_6$ (XXI). The reaction of the methyl(propene) complex XVIII with trimethylphosphine (acetone, 50°C, 8 h) gives [C$_6$H$_6$OsMe(PMe$_3$)$_2$]PF$_6$ as the sole product.
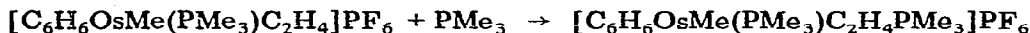
$$[C_6H_6OsH(PMe_3)C_2H_4]PF_6 + PMe_3 \rightarrow$$

(XV)

$$[C_6H_6OsEt(PMe_3)_2]PF_6 + [C_6H_6OsH(PMe_3)C_2H_4PMe_3]PF_6$$

$$(XIX) \qquad\qquad (XX)$$

$$[C_6H_6OsMe(PMe_3)C_2H_4]PF_6 + PMe_3 \rightarrow [C_6H_6OsMe(PMe_3)C_2H_4PMe_3]PF_6$$

$$(XVII) \qquad\qquad (XXI)$$

In conclusion, there is no single case of a migration of the methyl group to the olefin in the reactions of cationic methyl(olefin) complexes $[C_6H_6RuMe(PMe_3)-C_2H_4]^+$ [6] and $[C_6H_6OsMe(PMe_3)C_2H_3R]^+$ with neutral or anionic nucleophiles Nu. The interaction of the analogous hydrido(olefin) complexes with the same nucleophiles Nu lead either to insertion or, in the case of XV and Nu = PMe₃, to addition of Nu to the olefin. The differences in behaviour towards PMe₃ between $[C_6H_6RuH(C_2H_4)PMe_3]^+$ (which only gives $[C_6H_6RuEt(PMe_3)_2]^+$ [6]) and $[C_6H_6OsH(C_2H_4)PMe_3]^+$ (which gives both XIX and XX) may be explained by the fact that the ethylene(hydrido)ruthenium cation is in equilibrium with the ethylruthenium complex, whereas the corresponding ethylene(hydrido)osmium cation is the only species detectable by ¹H NMR spectroscopy and deuteration experiments in solution.

Acknowledgements

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