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Preliminary communication

SYNTHESIS OF AN OSMIUM(II) COMPLEX WITH THE PIPh LIGAND AND A POSSIBLE TERMINAL PHENYLPHOSPHINIDENE COMPLEX INTERMEDIATE FROM IODIDE ABSTRACTION

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Summary

Addition of I_2 to $Os(PHPh)Cl(CO)_2(PPh_3)_2$ gives $[OsCl(PHIPh)(CO)_2(PPh_3)_2]^+$ and deprotonation of this cation affords $Os(PIPh)Cl(CO)_2(PPh_3)_2$. The iodophenylphosphido complex reacts with $AgSbF_6$ in THF/MeOH to give $[OsCl\{PH(OMe)Ph\}(CO)_2(PPh_3)_2]SbF_6$ suggesting the intermediacy of a phenylphosphinidene complex $[Os(=PPh)Cl(CO)_2(PPh_3)_2]^+$.

Although terminal dihalophosphido complexes, $L_nM—PX_2$, were among the first-known examples of phosphido complexes [1], a terminal monohalophosphido complex, $L_nM—PXR$, has not been reported. Complexes of the latter type are of particular interest since they are, through halide loss, potential precursors of terminal phosphinidene complexes, $[L_nM=PR]^+$. Terminal phosphinidene complexes have been implicated as intermediates but despite several recent synthetic attempts [2—4] a stable example has not yet been isolated. We describe herein,
(1) the synthesis of an osmium(II) complex with the pyramidal PIPh ligand;
(2) the nucleophilic reactivity of this molecule towards H^+ and Me^+;
(3) the reaction with Ag^+ which leads to a product indicative of a cationic phosphinidene complex intermediate.

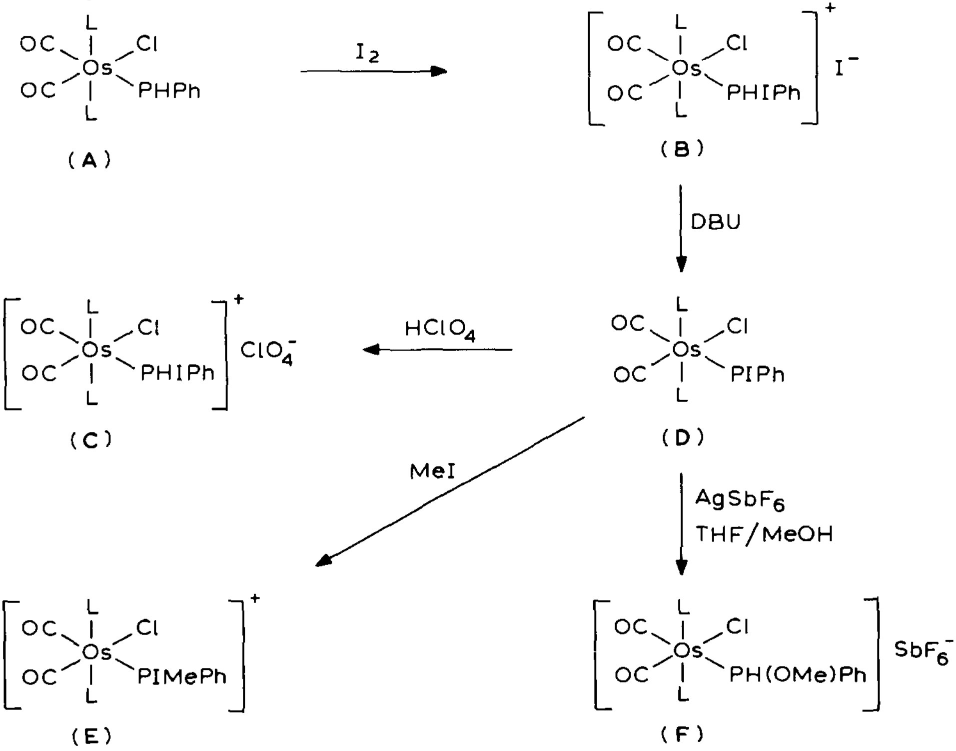
Addition of iodine to the PHPh ligand in $Os(PHPh)Cl(CO)_2(PPh_3)_2$, (A), [5] results in a cationic complex of the unusual [6] PHIPh ligand, $[OsCl(PHIPh)(CO)_2(PPh_3)_2]I$ (B) (see Scheme 1 and Table 1). Deprotonation of B with the non-nucleophilic base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), results in $Os(PIPh)Cl(CO)_2(PPh_3)_2$ (D), with the novel PIPh ligand. The PHPh ligand in A has been shown by X-ray crystallography to be pyramidal and the PIPh ligand in D is assumed to have similar geometry [5]. The deprotonation of B is re-

TABLE 1

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

Compound[c]	IR			^{1}H NMR
	ν(CO)	δ(PH)	Other bands	Chemical shifts and coupling constants
$\mathrm{Os(PHPh)Cl(CO)_2L_2}$ (A)	2018, 1952	905w	2264m,ν(PH)	3.70,dt,P*H* ^1J(PH),196; ^3J(PH) 14 Hz
$\mathrm{[OsCl(PHIPh)(CO)_2L_2]I}$ (B)	2060, 1991	921w, 896m	—	5.81,dt,P*H* ^1J(PH),398; ^3J(PH) 7 Hz
$\mathrm{Os(PIPh)Cl(CO)_2L_2}$ (D)	2024, 1969	—	394w,ν(PI)	—
$\mathrm{[OsCl(PIMePh)(CO)_2L_2]ClO_4}$ (E)	2055, 1997	—	378w,ν(PI)	2.71,d,C*H*$_3$ ^2J(PH) 8 Hz
$\mathrm{[OsCl\{PH(OMe)Ph\}(CO)_2L_2]SbF_6}$ (F)	2084, 2065 2013, 1998[d]	903m	1020m,ν(POMe)	7.61,dm,P*H* ^1J(PH) 402 Hz 2.90,d,C*H*$_3$ ^3J(PH) 12 Hz

[a] cm^{-1} measured as Nujol mulls. All bands strong unless otherwise noted. [b] δ in ppm from TMS measured in CDCl$_3$ except for A which was measured in C$_6$D$_6$. [c] All compounds have satisfactory C and H analyses (L = PPh$_3$). [d] Solid state splitting. Spectrum in CH$_2$Cl$_2$ solution has bands at 2065, 1998 cm^{-1}.



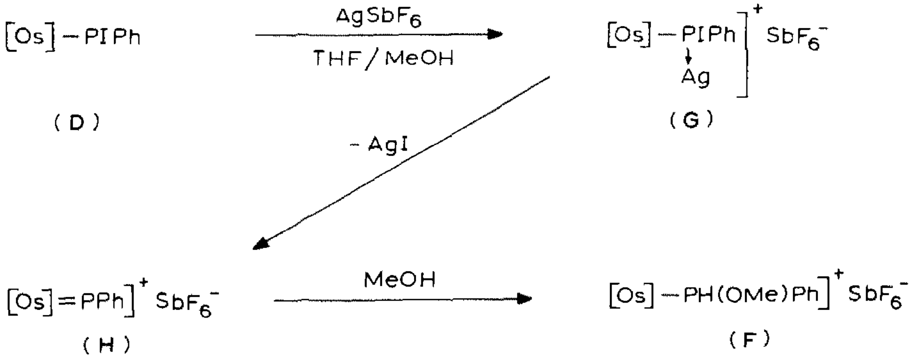
SCHEME 1. Synthesis and reactions of $\mathrm{Os(PIPh)Cl(CO)_2L_2}$ (L = PPh$_3$).

versible as addition of perchloric acid to D leads to C, the perchlorate analogue of B. Thus two high-yield steps convert the PHPh ligand in A to the PIPh ligand in D. Iodine adds similarly to other pyramidal phosphido ligands [7,8].

The nucleophilicity of the phosphido ligand in D is shown also by methylation with MeI to produce $[\mathrm{OsCl(PIMePh)(CO)_2(PPh_3)_2}]^+$, (E), which is readily crystallised as a perchlorate salt. The P—I bond in D is relatively unreactive towards alcohols, e.g., D can be purified by recrystallisation from $\mathrm{C_6H_6/MeOH}$.

With silver salts at ambient temperatures D reacts rapidly to produce an unidentified mixture of products. At low temperatures the reaction between $\mathrm{Ag^+}$ and D is less vigorous and THF suspensions of D at −78°C do not react with MeOH solutions of $\mathrm{AgSbF_6}$ (1/1). However, on warming a sequence of distinct changes occurs beginning with dissolution of the orange complex D to give a uniform yellow solution followed by production of a yellow flocculent AgI precipitate from a colourless solution as the temperature warms to 25°C. The product from the reaction, $[\mathrm{OsCl\{PH(OMe)Ph\}(CO)_2(PPh_3)_2}]\mathrm{SbF_6}$ (F), is produced in 85% yield. EtOH solutions of $\mathrm{AgSbF_6}$ react with D in an analogous manner to give $[\mathrm{OsCl\{PH(OEt)Ph\}(CO)_2(PPh_3)_2}]\mathrm{SbF_6}$.

Complexes of PH(OMe)Ph have been produced previously by insertion of a terminal phenylphosphinidene ligand into MeOH [2]. To account for the formation of F in the above reaction we suggest the mechanism shown in Scheme 2. Initial coordination of $\mathrm{Ag^+}$ by the terminal phosphido ligand in D would lead to a soluble cationic complex G with a bridging PIPh ligand. G would have additional solvent molecules coordinated to $\mathrm{Ag^+}$ not shown in Scheme 2. Elimination of AgI from G would give a cationic terminal phenylphosphinidene complex, H, which in turn inserts into the O—H bond of MeOH to give F. Attempts to isolate H have failed to give a tractable species. A neutral rather than a cationic phenylphosphinidene complex is more likely to be isolable.



SCHEME 2. Suggested mechanism for formation of $[\mathrm{OsCl\{PH(OMe)Ph\}(CO)_2(PPh_3)_2}]^+$ ($[\mathrm{Os}] \equiv \mathrm{OsCl(CO)_2(PPh_3)_2}$).

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