

Preliminary communication

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

D.S. BOHLE and W.R. ROPER*

Department of Chemistry, University of Auckland, Auckland (New Zealand)

(Received June 4th, 1984)

Summary

Addition of I_2 to $Os(PHPh)Cl(CO)_2(PPh_3)_2$ gives $[OsCl(PHPh)(CO)_2(PPh_3)_2]^+$ and deprotonation of this cation affords $Os(PIPh)Cl(CO)_2(PPh_3)_2$. The iodo-phenylphosphido 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.

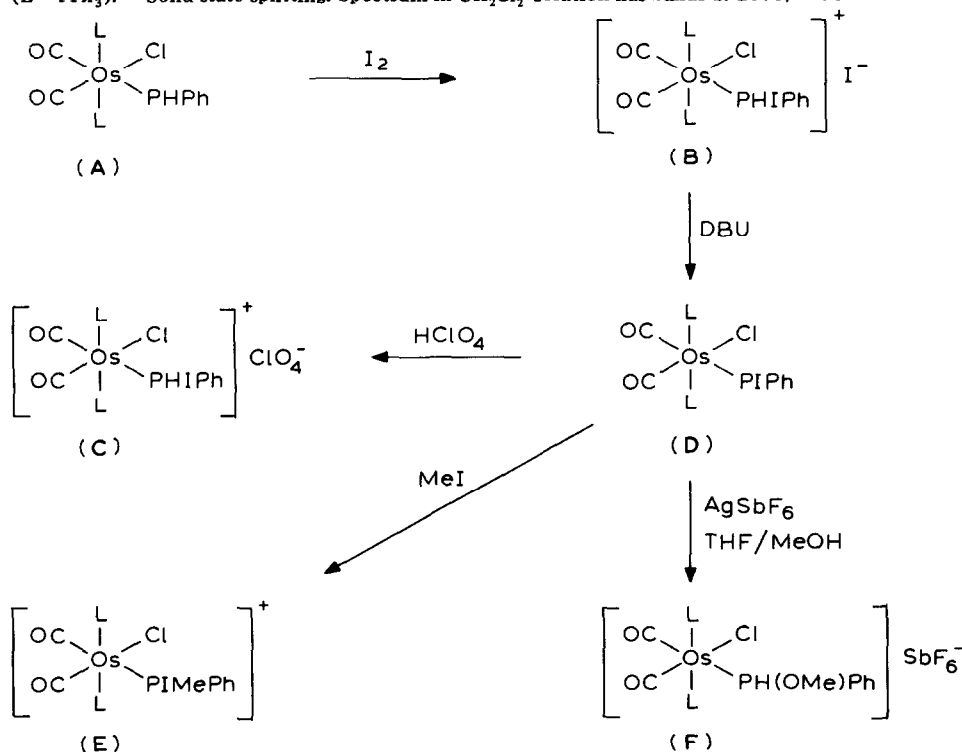
Addition of iodine to the PHPh ligand in $Os(PHPh)Cl(CO)_2(PPh_3)_2$, (A), [5] results in a cationic complex of the unusual [6] PHIPh ligand, $[OsCl(PHPh)(CO)_2(PPh_3)_2]I$ (B) (see Scheme 1 and Table 1). Deprotonation of B with the non-nucleophilic base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), results 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 ¹H NMR ^b DATA FOR OSMIUM COMPLEXES

Compound ^c	IR			¹ H NMR
	$\nu(\text{CO})$	$\delta(\text{PH})$	Other bands	Chemical shifts and coupling constants
Os(PHPh)Cl(CO) ₂ L ₂ (A)	2018, 1952	905w	2264m, $\nu(\text{PH})$	3.70, dt, PH ¹ J(PH), 196; ³ J(PH) 14 Hz
[OsCl(PHIPh)(CO) ₂ L ₂]I (B)	2060, 1991	921w, 896m	—	5.81, dt, PH ¹ J(PH), 398; ³ J(PH) 7 Hz
Os(PIPh)Cl(CO) ₂ L ₂ (D)	2024, 1969	—	394w, $\nu(\text{PI})$	—
[OsCl(PiMePh)(CO) ₂ L ₂]ClO ₄ (E)	2055, 1997	—	378w, $\nu(\text{PI})$	2.71, d, CH ₃ ² J(PH) 8 Hz
[OsCl{PH(OMe)Ph}(CO) ₂ L ₂]SbF ₆ (F)	2084, 2065 2013, 1998 ^d	903m	1020m, $\nu(\text{POMe})$	7.61, dm, PH ¹ J(PH) 402 Hz 2.90, d, CH ₃ ³ J(PH) 12 Hz

^a cm⁻¹ measured as Nujol mulls. All bands strong unless otherwise noted. ^b δ in ppm from TMS measured in CDCl₃ except for A which was measured in C₆D₆. ^c All compounds have satisfactory C and H analyses (L = PPh₃). ^d Solid state splitting. Spectrum in CH₂Cl₂ solution has bands at 2065, 1998 cm⁻¹.

SCHEME 1. Synthesis and reactions of Os(PIPh)Cl(CO)₂L₂ (L = PPh₃).

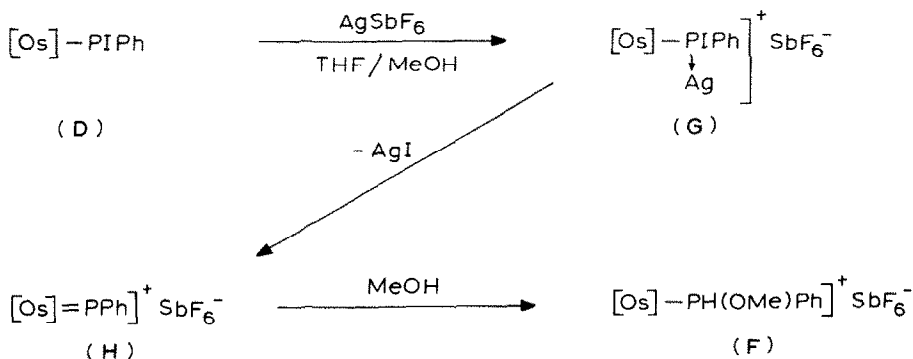
versible as addition of perchloric acid to D leads to C, the perchlorate analogue of B. Thus two high-yield steps convert the PHPh ligand in A to the PIPh ligand in D. Iodine adds similarly to other pyramidal phosphido ligands [7,8].

The nucleophilicity of the phosphido ligand in D is shown also by methyla-

tion with MeI to produce $[\text{OsCl}(\text{P}(\text{MePh})(\text{CO})_2(\text{PPh}_3)_2)]^+$, (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 $\text{C}_6\text{H}_6/\text{MeOH}$.

With silver salts at ambient temperatures D reacts rapidly to produce an unidentified mixture of products. At low temperatures the reaction between Ag^+ and D is less vigorous and THF suspensions of D at -78°C do not react with MeOH solutions of 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, $[\text{OsCl}\{\text{PH}(\text{OMe})\text{Ph}\}(\text{CO})_2(\text{PPh}_3)_2]\text{SbF}_6$ (F), is produced in 85% yield. EtOH solutions of AgSbF_6 react with D in an analogous manner to give $[\text{OsCl}\{\text{PH}(\text{OEt})\text{Ph}\}(\text{CO})_2(\text{PPh}_3)_2]\text{SbF}_6$.

Complexes of $\text{PH}(\text{OMe})\text{Ph}$ 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 Ag^+ by the terminal phosphido ligand in D would lead to a soluble cationic complex G with a bridging PIPh ligand. G would have addi-



SCHEME 2. Suggested mechanism for formation of $[\text{OsCl}\{\text{PH}(\text{OMe})\text{Ph}\}(\text{CO})_2(\text{PPh}_3)_2]^+$ ($[\text{Os}] \equiv \text{OsCl}(\text{CO})_2(\text{PPh}_3)_2$).

tional solvent molecules coordinated to 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.

We thank Johnson-Matthey for a generous loan of OsO_4 .

References

- W. Malisch and R. Alsmann, *Angew. Chem. Int. Ed. Engl.*, **15** (1976) 769.
- A. Marinetti and F. Mathey, *J. Amer. Chem. Soc.*, **104** (1982) 4484.
- K.M. Flynn, M.M. Olmstead and P.P. Power, *J. Amer. Chem. Soc.*, **105** (1983) 2085.
- G. Huttner, H.D. Müller, A. Frank and H. Lorenz, *Angew. Chem. Int. Ed. Engl.*, **14** (1975) 572.
- D.S. Bohle, T.C. Jones, C.E.F. Rickard and W.R. Roper, *J. Chem. Soc., Chem. Comm.*, (1984) 865.
- A. Marinetti and F. Mathey, *Organometallics*, **1** (1982) 1488.
- R.C. Dobbie and P.R. Mason, *J. Chem. Soc., Dalton Trans.*, (1974) 2439.
- W. Malisch, R. Maisch, J.J. Colquhoun and W. McFarlane, *J. Organomet. Chem.*, **220** (1981) C1.