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Complexes of Osmium with Metal-Nitrogen Multiple Bonds

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New arylimido-complexes of osmium $[OsCl_2(NC_6H_4X)(PPh_3)_2]$ *(X = H, Cl, or OMe) were prepared from* $[OsCl_3O(PPh_3)_2]$ *and* $Ph_3P{=}NCOC_6H_4X$. *The preparations of* $[Os(N_3)_2(PMe_2Ph)_4]$ *and* $[OsCl_2(N_3)(PR_2Ph)_3]$ *(R = Me, Et, Pr^n, or Bu^n) were also achieved. Attempts to obtain nitrido-complexes by decomposition of these azides were not successful.*

Introduction

Although rhenium forms a large number of nitrido-[1] and organoimido-complexes[2] containing tertiary phosphines, no such osmium complexes are known. Osmium nitrido-complexes are otherwise well known, *e.g.*, $[OsNO_3]^-$ and $[OsCl_5N]^{2-}$ which have been known for more than a century.[3] The latter[4] can be reduced by stannous chloride to $[OsCl_5(NH_3)]^{2-}$.[5] Related ions are $[OsNX_4(H_2O)]^{2-}$ (X = Br, CN, or $\frac{1}{2}C_2O_4{}^{2-}$)[6] and $[OsN(OH)_2X(H_2O)]^-$ (X = F or $\frac{1}{2}$-$C_2O_4{}^{2-}$).[6]

Several polynuclear osmium nitrido-complexes are also known. Among these are $[Os_2Cl_5N]$,[7] $[Os_2NX_2(NH_3)_8]^{3+}$, (X = Cl or Br)[8] and a possibly trinuclear species most recently formulated as $[Os_3(N)_3(OH)_9(NH_3)_4]$.[8]

There are only two osmium organoimido-complexes in the literature. each prepared from OsO_4 and the appropriate amine; $[OsO_3NC(CH_3)_3]$[9] and $[OsO_3NC(CH_3)_2CH_2CH_2CH(CH_3)_2]$.[9] There thus seems no reasons why tertiary phosphine-containing nitrido- and organoimido-complexes of osmium should not exist. However, the synthesis of such complexes from hydrazines has not been achieved. Thus $[OsCl_3O(PPh_3)_2]$[10] and hydrazine yield an ammine, $[OsCl_3(NH_3)(PPh_3)_2]$, and not a nitrido-complex.[11] The osmium(V) oxo-complex reacts with aniline to give an intensely coloured purple product which is soluble in petroleum ether, but which does not seem to be the expected arylimido-complex.[12] Thus alternative methods of synthesis were sought. A successful synthesis of complexes of the type $[OsCl_3(NC_6H_4X)(PPh_3)_2]$ has been evolved, but no useful preparation of tertiary phosphine nitrido-complexes.

Results and Discussion

Arylimido-complexes of Osmium. Phosphine imines react with $[ReCl_3O(PPh_3)_2]$ to give arylimido-complexes and phosphine oxides;[13] we have applied this reaction to $[OsCl_3O(PPh_3)_2]$. Of the five phosphine imines investigated, $Ph_3P{=}NPh$ gave no isolable complexes with $[OsCl_3O(PPh_3)_2]$ whereas $Ph_3P{=}NCO \cdot C_6H_4NO_2$ apparently oxidised the osmium complex and no characterisable products were isolated. However, pink, crystalline, air-stable products were obtained from $Ph_3P{=}NCO \cdot C_6H_4X$ (X = H, p-CH_3O, or p-Cl) in xylene at reflux. The magnetic moments are consistent with osmium(V) (2.1-2.3 B.M.) but the infrared spectra in Nujol mulls show no bands assignable to $\nu(C{=}O)$ or to $\nu(Os{\equiv}N)$. The analyses and molecular weights are consistent with the formulations $[OsCl_3(NC_6H_4X)(PPh_3)_2]$.

The far-infrared spectra (Nujol mulls) of these three new complexes show a strong band assignable to ν(Os-Cl) at 310-320 cm^{-1} and a less intense band at 15 cm^{-1} lower frequency. These could be the two bands to be expected of a *meridional* arrangement of chloride ligands, but inferences of structure on such evidence are unreliable.

It is known that isocyanates can react with metal oxo-complexes to eliminate carbon dioxide and form an organoimido-complex[14] and phosphine imines decompose to give the nitrene $:NCOC_6H_4X$, which rearranges to the isocyanate, XC_6H_4NCO. Thus the arylimido-complexes might have been formed from isocyanate derived from the phosphine imine via nitrene. However no product could be isolated from the reaction of PhNCO with $[OsCl_3O(PPh_3)_2]$. Hence, that possible route for the formation of the arylimido-complexes could not be confirmed.

Azido-complexes of Osmium. Azido-complexes have been used as precursors in the synthesis of nitrido-complexes,[1] *e.g.*:

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[10] J. Chatt, G.J. Leigh, D.M.P. Mingos, and R.J. Paske, *J. Chem. Soc. (A)*, 2636 (1968).
[11] D. Bright and J.A. Ibers, *Inorg. Chem., 8*, 1078 (1969).
[12] J. Chatt. J.R. Dilworth, and G.J. Leigh, unpublished observations.
[13] Chatt and J.R. Dilworth, *Chem. Comm.*, 549 (1972).
[14] I.S. Kolomnikov, Yu.D. Koreshkov, T.S. Lobeeva, and M.E. Vol'pin, *Chem. Comm.*, 1432 (1970).

Table I. New Complexes of Osmium.

			Analyses [a]				
		M.p.°	C	H	N	Cl	M.W.
cis-$[Os(N_3)_2(PMe_2Ph)_4]$	white plates	167.172(d)	46.6(46.5)	5.4(5.4)	10.1(10.2)	—	—
$[OsCl_2(N_3)(PMe_2Ph)_3]$ [c]	purple prisms	109-113(d)	40.0(40.2)	4.8(4.6)	5.8(5.9)	10.4(9.9)	692(718)
$[OsCl_2(N_3)(PEt_2Ph)_3]$	purple prisms	140-143(d)	44.7(44.9)	5.8(5.7)	5.1(5.2)	—	unstable in solution
$[OsCl_2(N_3)(PPr^n{}_2Ph)_3]$	purple prisms	126-129(d)	49.7(48.8)	6.8(6.5)	4.7(4.7)	—	unstable in solution
$[OsCl_2(N_3)(PBu^n{}_2Ph)_3]$	purple prisms	98-104(d)	51.5(52.0)	7.5(7.4)	4.3(4.3)	—	unstable in solution
$[OsCl_2\{(CH_3)_2CO\}(PMe_2Ph)_3][ClO_4]$	red prisms	90-100(d)	39.2(39.0)	5.0(4.7)	—	—	—
$[OsCl_3(NPh)(PPh_3)_2]$ [b]	pink prisms	232-238(d)	55.3(55.2)	3.8(3.8)	1.5(1.6)	13.0(11.7)	943(912)
$[OsCl_3(NC_6H_4OCH_3)(PPh_3)_2]$ [d]	pink plates	196-202(d)	54.6(54.7)	4.0(3.9)	1.7(1.5)	—	1138(942)
$[OsCl_3(NC_6H_4Cl)(PPh_3)_2]$ [d]	pink needles	190-196(d)	53.5(53.5)	3.6(3.6)	1.7(1.5)	15.1(15.2)	737(946)

[a] Required values in parentheses. [b] Oxygen: found 0.2%, requires 0.0%. [c] Phosphorus: found 12.3%, requires 12.1%. [d] Too insoluble for accurate measurements of molecular weight.

$$[ReCl_3(PMe_2Ph)_3] \longrightarrow [ReCl_2(N_3)(PMe_2Ph)_3] \longrightarrow [ReCl_2N(PMe_2Ph)_3]$$

It was hoped to adapt this synthesis to osmium-nitrido complexes and also to osmium(II) dinitrogen complexes, *e.g.*:

$$[OsCl_3(PMe_2Ph)_3] \longrightarrow [OsCl_2(N_3)(PMe_2Ph)_3] \longrightarrow [OsCl_2(N_2)(PMe_2Ph)_3] + \tfrac{1}{2}N_2$$

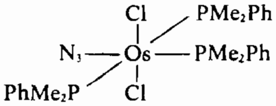
However, although some azido-complexes were obtained, degradation to pure nitrido- or dinitrogen-complexes was not achieved.

(a) *Osmium(II) Azido-complexes.* *Trans*-$[OsCl_2(PMe_2Ph)_4]$ and *trans*-$[OsCl_2(Ph_2PCH_2CH_2PPh_2)_2]$ do not react with sodium azide during 28 h in acetone at reflux. However, crude $[OsCl_2(PMe_2Ph)_4]$, which apparently contains about 10% of the *cis*-isomer, reacts with an excess of sodium azide to give a mixture from which *cis*-$[Os(N_3)_2(PMe_2Ph)_4]$ can be isolated. The structure was assigned on the basis of the ^1H n.m.r. spectrum in deuteriochloroform, in which the methyl resonances are found as a doublet at $\tau = 8.50$, $|^2J_{PCH}| = 8.0$ Hz, and a triplet at $\tau = 8.60$, $|^2J_{PCH} + ^4J_{POsPCH}| = 7.4$ Hz. This diazide does not react with 1,2-bis(diphenylphosphino)ethane during 23 h in benzene at room temperature. The products of the thermal decomposition of this complex had no spectral properties characteristic of nitrido-species.

(b) *Osmium(III) Azido-complexes.* *Mer*-$[OsCl_3(PR_3)_3]$ ($PR_3 = PMe_2Ph, PEt_2Ph, PPr^n{}_2Ph$, or $PBu^n{}_2Ph$) react with an excess of sodium azide in acetone to give $[OsCl_2(N_3)(PR_3)_3]$ wich are unstable in solution and must be isolated pure from the mother liquors. They cannot be recrystallised. We were unable to prepare the corresponding bromides pure by this route.

An alternative preparation involves the prior reaction of *mer*-$[OsCl_3(PMe_2Ph)_3]$ with silver perchlorate in acetone, from which $[OsCl_2(acetone)(PMe_2Ph)_3][ClO_4]$ can be isolated. This reacts with sodium azide to form $[OsCl_2(N_3)(PMe_2Ph)_3]$ but the yield is low.

The azides are purple crystalline solids. The dimethylphenylphosphine complex is a non-conductor in nitrobenzene solution and has a solid state magnetic moment of 1.95 B.M. The other complexes were not tested. The asymmetric azide stretching frequency is in the range 2050-2065 cm^{-1}. $[OsCl_2(N_3)(PMe_2Ph)_3]$ has only one band in the far-infrared spectrum assignable to $\nu(Os\text{-}Cl)$ (315 cm^{-1}), indicating that the chloride ligands are mutually *trans*. The following structure is suggested.



When solutions of $[OsCl_2(N_3)(PR_3)_3]$ are heated, or exposed to sunlight or u.v. irradiation in a variety of solvents, $\nu_{as}(N_3)$ disappears, and new absorptions are observed in the range 1000-1150 cm^{-1}. This is the region in which $\nu(Os\equiv N)$ is to be expected. However, no pure nitrogen-containing compounds were isolated from these solutions.

Attempts to cleave the coordinated azide by chemical means also yielded unsatisfactory results. Amalgamated zinc causes decomposition. Copper bronze, which causes the decomposition of benzenesulphonyl azide *via a* copper-nitrene intermediate,[15] gives unpurifiable mixtures apparently, from their i.r. spectra, containing $Os\equiv N$. An excess of sodium borohydride forms $[OsH_4(PR_3)_3]$. Sulphuric acid, which aids the formation of $[Ru(NH_3)_5(N_2)]^{2+}$ from $[Ru(NH_3)_5(N_3)]^{2+}$, merely removes the azide ion from our complexes as hydrazoic acid.

The complex $[OsCl_2(thf)(PR_3)_3]$ (thf = tetrahydrofuran) reacts with dinitrogen, losing thf and yielding a dinitrogen complex. It reacts with our azido-com-

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(15) H. Kwart and A.A. Kahn, *J. Amer. Chem. Soc.*, *89*, 1950 (1967).

plexes to yield complexes which could not, however, be purified.

Nitrosyl hexafluorophosphate reacts with $[RuCl(N_3)(das)_2]$ {das = *o*-phenylenebis(dimethylarsine)} to yield $[RuCl(N_2)(das)_2][PF_6]$.[16] It reacts with our complexes in methanol to form purple solutions which show a band at about 2220 cm^{-1} in the infrared spectrum. These solutions are unstable, and rapidly turn brown, losing the strong infrared band. This may indicate that they contained an unstable dinitrogen complex, *c.f.*, $[Os(NH_3)_5(N_2)]^{3+}$.[17]

(c) *Osmium(IV) Azido-complexes.* Under a variety of conditions, *trans*-$[OsCl_4(PEt_2Ph)_2]$ and *trans*-$[OsCl_4(PEt_2Ph)_2]$ react with sodium azide to give complex mixtures which have bands attributable to $\nu(Os{\equiv}N)$ in their infrared spectra but which could not be separated.

Multiple bonds from oxygen and nitrogen to transition metals are expected to become less stable as one moves from left to right in the Periodic Table. Our results for osmium, when compared with earlier findings for rhenium,[2] are consistent with this.

Experimental Section

Carbon, hydrogen, nitrogen, chlorine, and phosphorus analyses were carried out by Mr. A.G. Olney, University of Sussex. The oxygen analysis was by Dr. A. Bernhardt, Germany. Melting points were determined in air on an Electrothermal melting-point apparatus. Infrared spectra were obtained on Pye-Unicam SP (4000-400 cm^{-1}) and Grubb-Parsons DM4 (650-200 cm^{-1}) spectrometers. ^1H n.m.r. spectra were obtained for deuteriochloroform solutions with Varian HA-100 and Jeol PS-100 spectrometers, using tetramethylsilane as an internal standard. Magnetic susceptibilities were determined using a Faraday balance. Molecular weights in solution were measured using a Perkin-Elmer-Hitachi 115 molecular-weight bridge.

Solvents were dried and distilled in dinitrogen before use. All manipulations were carried out under pure, dry dinitrogen. Compounds $Ph_3P{=}NCOC_6H_4X$ (X = H, Cl or OMe),[18] $[OsCl_2(PMe_2Ph)_4]$,[19] $[OsCl_2(PMe_2Ph)_3(thf)]$,[20] $[OsCl_3O(PPh_3)_2]$,[10] *mer*-$[OsCl_3(PR_3)_3]$ (PR_3 = PMe_2Ph, PEt_2Ph, $PPr^n{}_2Ph$ or $PBu^n{}_2Ph$),[10] and *trans*-$[OsCl_4(PR_3)_2]$ (PR_3 = PMe_2Ph or PEt_2Ph)[10] were prepared as described.

cis-*Diazidotetrakis(dimethylphenylphosphine)osmium (II).* A mixture of crude dichlorotetrakis(dimethylphenylphosphine)osmium(II) (0.32 g) and sodium azide (0.09 g) in acetone (15 ml) was stirred at room temperature for 4.5 h. After filtration, the filtrate was evaporated to dryness at 0.1 mmHg. The residue was recrystallised from 6 ml benzene-hexane(1:1) as colourless *plates* (0.047 g, 14%). The i.r. spectrum showed $\nu_{as}(N_3)$ as 2050 cm^{-1}.

Azidodichlorotris(dimethylphenylphosphine)osmium (III). Acetone (20 ml) was added to a finely powdered mixture of *mer*-$[OsCl_3(PMe_2Ph)_3]$ (0.45 g) and sodium azide (0.41 g). The resulting suspension was rapidly heated to boiling, boiled for 8 min, and filtered hot. The volume of the filtrate was reduced to 4 ml at 0.1 mmHg, and hexane (10 ml) added. The product crystallised as purple *prisms* (0.30 g, 68%). The i.r. spectrum shows $\nu_{as}(N_3)$ at 2060 cm^{-1} and longer wavelength absorptions at 366 m,sh; 352 s; 315s cm^{-1}.

Azidodichlorotris(diethylphenylphosphine)osmium (III). A mixture of finely powdered *mer*-trichlorotris(diethylphenylphosphine)osmium(III) (0.12 g) and sodium azide (0.15 g) was stirred in acetone (10 ml) for 1.3 h at 35°C to give a purple solution. After cooling to room temperature, the mixture was filtered and the solid residue extracted with benzene (2×10 ml). The combined extract was reduced to 2 ml at 0.1 mmHg, and the product crystallised as purple *prisms* by the addition of hexane (10 ml). Yield 0.07 g (58%), i.r. spectrum shows $\nu_{as}(N_3)$ at 2050 cm^{-1}.

*Azidodichlorotris(di-*n*-propylphenylphosphine)osmium (III).* A mixture of finely powdered *mer*-trichlorotris-(di–*n*–propylphenylphosphine)osmium(III) (0.12 g) and sodium azide (0.10 g) was stirred in acetone (10 ml) at 32°C for 10 min. The mixture was filtered, and the solvent removed from the filtrate at 0.1 mm Hg. The resultant oil formed purple *crystals* in 3.5 ml of a benzene-hexane mixture (1:2.5). Yield 0.065 g, 56%. The i.r. spectrum showed $\nu_{as}(N_3)$ at 2055 cm^{-1}.

*Azidodichlorotris(di-*n*-butylphenylphosphine)osmium (III).* A mixture of finely powdered *mer*-trichlorotris(di-*n*-butylphenylphosphine)osmium(III) (0.105 g) and sodium azide (0.047 g) was stirred in acetone (10 ml) at 32°C for 1.1 h. The purple solution was evaporated to 0.5 ml at 0.1 mmHg and hexane (0.5 ml) and methanol (1.0 ml) added. At 0°C, this solution deposited purple *crystals* (0.075 g, 72%), i.r. spectrum showing $\nu_{as}(N_3)$ at 2060 cm^{-1}.

(Acetone)dichlorotris(dimethylphenylphosphine)osmium(III). Finely powdered *mer*-trichlorotris(dimethylphenylphosphine)osmium(III) (0.40 g) and silver perchlorate (0.20 g) were stirred in acetone (15 ml) for 15 min at room temperature. Silver chloride was filtered off and the red filtrate reduced to 3 ml at 0.1 mmHg. The product separated as red *crystals* (0.26 g, 54%). The molar conductivity in nitrobenzene solution (1.24×10^{-3} molar) was found to be 20.2 ohm^{-1}. The i.r. spectrum shows $\nu(CO)$ at 1560 cm^{-1}.

This complex reacts with sodium azide in acetone to give the azidodichloro-complex, identical with the material described above, in 39% yield. We found no indication that any of these azido-complexes are explosive or pyrophoric.

Trichloro(phenylimido)bis(triphenylphosphine)osmium

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(17) J. Chatt, J.R. Dilworth, H.P. Gunz, G.J. Leigh, and J.R. Sanders, *Chem. Comm.*, 90 (1970).

(18) H. Staudinger and E. Hanser, *Helv. Chim. Acta*, *4*, 861 (1927).

(19) B. Bell, J. Chatt, and G.J. Leigh, in preparation.

(20) J. Chatt, G.J. Leigh, and R.L. Richards, *J. Chem. Soc.* (*A*), 2243 (1970).

(*V*). Trichlorooxobis(triphenylphosphine)osmium(V) (0.50 g) and triphenylphosphinebenzoylimine (0.50 g) were heated in *p*-xylene (25ml) under reflux for 1 h. On cooling the solution, the complex precipitated as a bright pink *solid* (0.33 g, 61%) which was recrystallised as pink prisms from dichloromethane-methanol. The magnetic moment in the solid state is 2.27 B.M.

Trichloro-p-*methoxyphenylimidobis*(*triphenylphosphine*)*osmium*(*V*). Trichlorooxobis(triphenylphosphine)-osmium(V) (0.50 g) and triphenylphosphine-*p*-methoxybenzoylimine (0.5 g) were heated in *p*-xylene (25 ml) under reflux for 2 h. The complex crystallised from the solution upon cooling as a reddish *solid* (0.23 g, 40%), which was recrystallised from dichloromethane-methanol as pink plates. The magnetic moment in the solid state is 2.16 B.M.

Trichloro-p-*chlorophenylimidobis*(*triphenylphosphine*)-*osmium*(*V*). Was prepared as above in 55% yield, but using triphenylphosphine-*p*-chlorobenzoylimine. The magnetic moment in the solid state is 2.13 B.M.