Inorganica Chimica Acta, *71* (1983) 239–249

Formation of Osmium Nitrile Complexes and Phosphinimine Complexes from N-Aroylphosphinimines

GARY V. GOEDEN and BARRY L. HAYMORE*

Department of Chemistry, Indiana University, Bloomington, Ind. 47405, U.S.A.

Received September 3, 1982

Osmium(III) nitrile complexes of the type $OsCl_3(NCAr)(PPh_3)_2$ *(Ar = phenyl, p-tolyl) are formed by the action of aromatic nitriles or N-aroylphosphinimines on* $OsCl_4(PPh_3)_2$ *in refluxing p-xylene. Osmium(II) nitrile and phosphinimine complexes,* $OsCl_2(NCAr)_2(PPh_3)_2$ *and* $OsCl_2(Ar\overset{O}{\overset{\|}{C}}NPPh_3)(PPh_3)_2$*, are similarly formed by the action of the respective nitriles or phosphinimines on* $OsO_2Cl_2(PPh_3)_2$*. Depending on reaction conditions, triphenylphosphine converts* $OsO_2Cl_2(PPh_3)_2$ *to* $OsCl_4(PPh_3)_2$ *or to* $OsCl_2(PPh_3)_3$ *which are useful starting materials for syntheses of a variety of osmium carbonyl, nitrile and hydride complexes.*

Introduction

One of the few reports of a 19 electron nitrene (imide) complex is that of a paramagnetic complex, '$OsCl_3(NPh)(PPh_3)_2$' [1], ($Ph = C_6H_5$) which was prepared by the action of N-benzoylphosphinimine on '$OsOCl_3(PPh_3)_2$' [2] in refluxing *p*-xylene. Our interest in this complex centered around the structural comparison of it with the stable, 18-electron rhenium analogue, $ReCl_3(NPh)(PPh_3)_2$ [3, 4]. Owing to persistent twinning in the osmium complex, we prepared the *p*-tolyl (To) analogue which not only formed good quality single crystals, but was also found to be isomorphous with $OsCl_3(NNTo)(PPh_3)_2$ and $RuCl_3(NNTo)(PPh_3)_2$ [6]. Owing to this isomorphism and the reluctance of the osmium starting material to react with tetraphenylphosphinimine, we decided to further investigate the reported preparation of the osmium Os complexes. In our hands, the reaction of '$OsOCl_3(PPh_3)_2$' with $Ph\overset{O}{\overset{\|}{C}}NPPh_3$ produced at least two major products (one pink and one yellow) and several minor products; furthermore, the product ratios of the major products were highly dependent on the mode of preparation of the osmium starting compound. We discovered that the correct formulation of the pink paramagnetic product is $OsCl_3(NCPh)(PPh_3)_2$ which differs from the original formulation [1] by one carbon atom. We also found that the osmium starting material was a mixture of compounds, $OsCl_4(PPh_3)_2$ and a new osmium oxo complex. While this work was in progress, the work of Salmon and Walton [7] appeared which also showed '$OsOCl_3(PPh_3)_2$' to be a mixture of $OsCl_4(PPh_3)_2$ and $OsO_2Cl_2(PPh_3)_2$.

Experimental

All reactions were carried out in an inert (N_2) atmosphere using freshly distilled solvents. Infrared spectra were recorded in Nujol or Fluorolube S-30 mulls using a Perkin-Elmer 283 double-beam spectrometer and were calibrated using polystyrene or Teflon film. The NMR spectra were recorded in CH_2Cl_2 (unless otherwise noted) at ambient temperature using Varian Associates XL-100 (^{31}P) and HR-220 (^{1}H) spectrometers; internal tetramethylsilane and external 85% H_3PO_4 were used as references. Microanalyses were performed by Midwest Microlab, Ltd., Indianapolis, Indiana. The N-aryl and N-aroylphosphinimines were prepared by the interaction of triphenylphosphine and the respective aryl and aroylazides in diethyl ether. These azides were in turn prepared from the reaction of NaN_3 with the aryldiazonium salt in water or the aroylchloride in acetone. $[NH_4]_2[OsCl_6]$ [18], $[NBu_4]_2[OsBr_6]$ [18], $OsH_2(CO)(PPh_3)_3$ [19], $OsH_2(CO)_2(PPh_3)_2$ [19] and $OsH_4(PPh_3)_3$ [19] were synthesized by their respective literature methods.

Our preparation method for '$OsOCl_3(PPh_3)_2$' is included here because we had difficulty reproducing the synthesis. Yellow, brown or red products of variable composition were obtained using slight modifications. Elemental analysis of our ochre product showed that it has a bulk analysis similar

---

*Author to whom correspondence should be addressed of Corporate Research Laboratories, Monsanto Company, 800 N. Lindbergh Blvd., St. Louis, Missouri 63167.

0020-1693/83/0000-0000/$03.00

to that previously reported. Infrared spectra of our ochre product showed it to be a mixture of about equal proportions of $OsO_2Cl_2(PPh_3)_2$ and $OsCl_4(PPh_3)_2$ [2].

Mixture of $OsO_2Cl_2(PPh_3)_2$ and $OsCl_4(PPh_3)_2$

Osmium tetroxide (1.0 g) was dissolved in a solution of absolute ethanol (30 ml) and concentrated aqueous HCl (5 ml). To the above vigorously stirred solution was slowly added a warm solution of triphenylphosphine (5 g) in absolute ethanol (20 ml). The light brown mixture was refluxed for 15 min., cooled, and filtered. The product was successively washed with water, ethanol, and diethyl ether to give 2.65 g of an ochre colored powder.

Dichlorodioxobis(triphenylphosphine)osmium(VI)

To a vigorously stirred solution of osmium tetroxide (1.0 g, 3.9 mmol) in t-butanol (50 ml) and concentrated hydrochloric acid (7 ml) was slowly added a warm saturated solution of triphenylphosphine (5.0 g, 19 mmol) in 30 ml t-butanol. The mixture was stirred for 5 min. to precipitate the product which was filtered off and consecutively washed with water, ethanol and diethyl ether. The powdery product was extracted with dichloromethane (3 × 50 ml) to remove the $OsCl_4(PPh_3)_2$ impurity and yield 2.1 g (65%) of the light brown complex.

trans-*Tetrachlorobis(triphenylphosphine)osmium(IV)*

(a) To a mixture of $OsO_2Cl_2(PPh_3)_2$ (0.25 g, 0.31 mmol) and triphenylphosphine (0.50 g, 1.9 mmol) in t-butanol (30 ml) was added 5 ml of 6 *M* aqueous hydrochloric acid. The mixture was refluxed for seven hours, gradually precipitating the orange-brown product. The cooled mixture was filtered, and the product washed with ethanol and diethyl ether, and dried to yield 0.25 g (95%) of the complex, which could be recrystallized from dichloromethane.

(b) To a solution of $OsCl_2(PPh_3)_3$ (0.25 g, 0.24 mmol) in 10 ml chloroform was added N-chlorosuccinimide (0.25 g, 1.8 mmol) and the green solution immediately turned brown. The solution was gently refluxed for 5 min., filtered and reduced in volume to 2 ml to precipitate brown crystals of the product. Diethyl ether (10 ml) was added to complete precipitation, after which the product was filtered off and recrystallized from CH_2Cl_2/Et_2O to afford 0.19 g (93%) of the compound.

(c) One gram of $(NH_4)_2OsCl_6$ (2.3 mmol) and triphenylphosphine (4.0 g, 15 mmol) were added to a solution of 75 ml H_2O in 250 ml t-butanol. The mixture was refluxed for 10 h, precipitating the brown tetrachloride. The cooled mixture was then filtered, and the product was washed with methanol and ether to yield 1.68 g (86%) of the complex.

(d) A mixture of $OsH_4(PPh_3)_3$ (1.35 g, 1.37 mmol) and N-chlorosuccinimide (1.4 g, 10.8 mmol) in chloroform (30 ml) was refluxed for 10 min., rapidly turning brown in color. The mixture was cooled and ethanol was added to precipitate the brown product, which was filtered off and recrystallized from CH_2Cl_2/Et_2O to afford 0.95 g (81%) of sparkling brown crystals of the complex.

Dichlorotris(triphenylphosphine)osmium(II)

(a) This is a modification of the literature method [8]. $(NH_4)_2OsCl_6$ (6.0 g, 13.7 mmol) and triphenylphosphine (25.2 g, 96.1 mmol) were added to an aqueous t-butanol (1.5 l BuOH, 0.45 l H_2O) solution, and the mixture was refluxed for 90 hours. Reaction time may vary due to the quality and solubility of the hexachloroosmate. The mixture proceeded through various color changes and the green color of the product started to appear after 48 hours. After the allotted reaction time, the mixture was brought to room temperature and filtered. The precipitate was washed with water, methanol, and diethyl ether, and dried under vacuum to yield 13.2 g (92%) of the olive green complex. *Dibromotris(triphenylphosphine)osmium(II)* was similarly synthesized in 77% yield from $(N^nBu_4)_2OsBr_6$ (24 hours reaction time).

(b) $OsCl_4(PPh_3)_2$ (0.20 g, 0.23 mmol) and triphenylphosphine (0.43 g, 1.6 mmol) were added to an aqueous t-butanol (25 ml BuOH, 5 ml H_2O) solution. The initial deep brown mixture was refluxed for 48 h to precipitate the green product. The mixture was then cooled, filtered and the precipitate was washed with ethanol and diethyl ether to afford 0.21 g (86%) of the compound.

(c) $OsO_2Cl_2(PPh_3)_2$ (0.30 g, 0.37 mmol) and triphenylphosphine (0.68 g, 2.6 mmol) were added to t-butanol (30 ml) and water (5 ml), and the initially light brown suspension was refluxed for 5 h, precipitating the insoluble green product. The cooled mixture was filtered, and the product was washed with ethanol and diethyl ether to yield 0.33 g (85%) of the complex.

Carbonyldichlorotris(triphenylphosphine)osmium(II)

(a) To a mixture of $OsO_2Cl_2(PPh_3)_2$ (0.50 g, 0.61 mmol) and triphenylphosphine (1.5 g, 5.7 mmol) in 30 ml 2-methoxyethanol, was added 5 ml concentrated aqueous HCl and 3 ml aqueous formaldehyde (37%) solution. The mixture was refluxed for seven hours to precipitate the pale yellow product. The cooled solution was then filtered, and the product was washed with ethanol and diethyl ether to afford 0.41 g (62%) of the microcystalline, pale yellow complex.

(b) This is a modification of a published procedure [20]. Anhydrous HCl gas was bubbled through a benzene (100 ml) solution of $OsHCl(CO)(PPh_3)_3$

(0.5 g) and triphenylphosphine (0.5 g) for approximately five minutes. The flask was then stoppered and the contents stirred at ambient temperature for 11 hours to precipitate the pale yellow product. The solution was reduced in volume, filtered, and the product was washed with ethanol and diethyl ether to give 0.49 g (95%) of the complex.

(c) To a suspension of $OsCl_2(PPh_3)_3$ (0.15 g) in 2-methoxyethanol (10 ml) was added triphenylphosphine (0.45 g), 1 ml concentrated aqueous HCl, and 1 ml aqueous formaldehyde (37% solution). The mixture was refluxed for 4 h to precipitate 0.10 g (66%) of the pale yellow complex, which was filtered off, and washed with ethanol and ether.

cis-*Dicarbonyldichlorobis(triphenylphosphine)osmium(II)*

(a) A 10 ml toluene solution of *trans*-$OsCl_2(CO)_2(PPh_3)_2$ (0.25 g) was refluxed for 1 hour. The solution was reduced in volume by half and 20 ml ethanol was added to precipitate the *cis* isomer. The white product was filtered off and 0.24 g (96%) of the complex was collected.

(b) A solution of 0.50 g $OsCl_2(PPh_3)_3$ in 15 ml benzene was placed in a Fisher-Porter pressure bottle, and the vessel was charged with a 5 atm pressure of carbon monoxide. The bottle was heated to 80 °C with an oil bath, and the solution was stirred for 1 hour, during which time the green color gradually disappeared. The pressure was released, the solution was cooled, and 75 ml of ethanol was added to precipitate the product, which was filtered off, and washed with ethanol and ether to yield 0.30 g (75%) of white crystals of the complex. Recrystallization was carried out using benzene/ethanol.

(c) $OsO_2Cl_2(PPh_3)_2$ (0.30 g, 0.37 mmol) and triphenylphosphine (0.50 g, 1.9 mmol) were added to 25 ml toluene. A slow flow of carbon monoxide gas was bubbled through the solution as it was gently refluxed for 30 min. During this time the light brown suspension reacted to give a clear, nearly colorless, solution. The solution was filtered while hot; 100 ml ethanol was added; then the solution was reduced in volume to 10 ml to precipitate white crystals of the product. The precipitate was filtered off, and washed with ethanol and ether, and dried to give 0.26 g (84%) of the complex.

(d) This is a modification of a published procedure [20]. To a Fisher-Porter pressure bottle was added 0.25 g $OsCl_2(CO)(PPh_3)_3$ in 15 ml dichloromethane. The bottle was pressurized with 2 atm of carbon monoxide, and the reaction solution was stirred at room temperature for 1 h. The solution was then filtered, reduced in volume to 2 ml, and 25 ml ethanol was added to precipitate the product, which was filtered off and washed with ethanol and ether to give 0.17 g (88%) of white crystals of the complex.

(e) Anhydrous HCl gas was slowly bubbled for 3 h through a refluxing solution of $OsHCl(CO)_2(PPh_3)_2$ (0.10 g) in 10 ml benzene. The solution was filtered while hot and ethanol was added to precipitate the product which was filtered off and washed with ethanol to give 0.09 g (82%) of the compound. The same complex was analogously prepared in 86% yield from $OsH_2(CO)_2(PPh_3)_2$.

(f) To a 0.25 g sample of $OsHCl(CO)(PPh_3)_3$ was added 50 ml of an HCl saturated benzene solution. The mixture was added to a Fisher-Porter pressure vessel and placed under 3 atm carbon monoxide. The contents were heated to 80 °C with stirring for 2 h. The pressure was then released, and the reaction solution was reduced in volume to 5 ml. Ethanol (30 ml) was added to precipitate 0.17 g (83%) of the complex, which was isolated by filtration and then washed with diethyl ether.

trans-*Dicarbonyldichlorobis(triphenylphosphine)osmium(II)*

To a Fisher-Porter pressure vessel was added a solution of $OsCl_2(PPh_3)_3$ (0.50 g) in 10 ml dichloromethane, and the vessel was pressurized with 2 atm carbon monoxide. The solution was stirred at ambient temperature for one hour, gradually lightening in color. The pale yellow solution was filtered, and ethanol was added to it to precipitate pale yellow microcrystals of the product, which was recrystallized from CH_2Cl_2/EtOH to afford 0.28 g (69%) of the complex.

cis-*Dichlorobis(p-tolunitrile)bis(triphenylphosphine)osmium(II)*

(a) To a mixture of $OsO_2Cl_2(PPh_3)_2$ (0.25 g, 0.31 mmol) and triphenylphosphine (0.25 g, 0.95 mmol) in *p*-xylene (10 ml) was added 2.5 ml *p*-tolunitrile, and the solution was refluxed for 1 h. The solution was then cooled somewhat, filtered, and hexane was slowly added to precipitate bright yellow microcrystals, which were filtered off and recrystallized from benzene/hexane to yield 0.13 g (42%) of the complex.

(b) *trans*-$OsCl_2(NCTo)_2(PPh_3)_2$ (0.10 g) and *p*-tolunitrile were refluxed together in 10 ml *p*-xylene for one hour. Hexane was added to the cooled solution to precipitate the *cis* isomer; 0.07 g (70%) of the yellow complex was collected. cis-*Dibromobis(p-tolunitrile)bis(triphenylphosphine)osmium(II)* was analogously prepared in 75% yield.

trans-*Dichlorobis(p-tolunitrile)bis(triphenylphosphine)osmium(II)*

To a solution of $OsCl_2(PPh_3)_3$ (0.30 g) in 30 ml benzene was added 2 ml *p*-tolunitrile and the solution was refluxed for 1 h. The solution was filtered while hot, and hexane slowly added to precipitate the yellow product which was recrystallized from

CH_2Cl_2/Et_2O to give 0.21 g (71%) of sparkling yellow crystals of the complex. trans-*Dibromobis(p-tolunitrile)bis(triphenylphosphine)osmium(II)* was similarly prepared in 64% yield.

Carbonyldichloro(p-tolunitrile)bis(triphenylphosphine)osmium(II)

(a) *p*-Tolunitrile (2 ml) and $OsCl_2(CO)(PPh_3)_3$ (0.15 g) were refluxed together in 10 ml toluene for 1 h. The clear, nearly colorless solution was filtered while hot, and ethanol (30 ml) was added to the cooled solution to precipitate the white product; it was filtered off, washed with ethanol and diethyl ether and dried to yield 0.12 g (92%) of the complex. Recrystallization from CH_2Cl_2/CH_3OH led to the formation of a dichloromethane solvate.

(b) $OsHCl(CO)(NCTo)(PPh_3)_2$ (0.20 g) was added to 15 ml benzene and the solution was refluxed for 10 min. while anhydrous HCl gas was continuously bubbled through it. The clear solution was filtered while hot, reduced in volume to 3 ml and ethanol was added precipitating the white microcrystalline product. The mixture was filtered to give 0.16 g (77%) of the product.

Carbonylchlorohydridotris(triphenylphosphine)-osmium(II)

(a) To a mixture of $OsO_2Cl_2(PPh_3)_2$ (0.50 g, 0.61 mmol) and triphenylphosphine (1.5 g, 5.7 mmol) in 2-methoxyethanol (30 ml) was added 2 ml aqueous formaldehyde (37%) solution. The mixture was refluxed for 30 min., rapidly lightening in color, and was then cooled and filtered. The off-white product was washed with ethanol and ether to yield 0.55 g (86%) of the complex.

(b) To a mixture of $OsCl_2(PPh_3)_3$ (1.0 g, 0.96 mmol) and triphenylphosphine (1.5 g, 5.7 mmol) in 2-methoxyethanol (60 ml) was added 2 ml aqueous formaldehyde (37%) solution. The mixture was refluxed for 5 min., causing the precipitation of the white product. The cooled mixture was filtered, and the microcrystalline product was washed with ethanol and ether to afford 0.97 g (97%) of the complex.

(c) $OsCl_2(CO)(PPh_3)_3$ (0.10 g) and triphenylphosphine (0.10 g) were added to ethanol (3 ml) and benzene (7 ml). The mixture was refluxed for 2 h affording a clear pale yellow solution, which was filtered while hot and reduced in volume to 2 ml. Ethanol (20 ml) was added to precipitate the off-white product, which was filtered off, and washed with ethanol and ether to give 0.08 g (83%).

Dicarbonylchlorohydridobis(triphenylphosphine)-osmium(II)

This is a modification of a literature procedure [21]. To a Fisher-Porter pressure vessel was added a solution of 0.50 g $OsHCl(CO)(PPh_3)_3$ in 100 ml benzene, and the vessel was pressurized with 3 atm carbon monoxide. The contents were stirred at 25 °C for 1 hour forming a clear colorless solution. The vessel was vented, and the solution was filtered and reduced in volume to 5 ml. Ethanol (40 ml) was added to precipitate white crystals of the product, which were filtered off and washed with ether to yield 0.36 g (93%) of the compound after recrystallization from benzene/ethanol.

Carbonylchlorohydrido(p-tolunitrile)bis(triphenylphosphine)osmium(II)

$OsHCl(CO)(PPh_3)_3$ (0.50 g) and *p*-tolunitrile (3 ml) were refluxed together in 20 ml benzene for 3 h, during which time the white product precipitated from the reaction solution as fine white crystals. The cooled solution was filtered, and the product was washed with ethanol and ether to afford 0.29 g (67%) of the complex, which crystallized as a benzene solvate.

Trichloro(benzonitrile)bis(triphenylphosphine)-osmium(III)

(a) The mixture, '$OsOCl_3(PPh_3)_2$', (0.85 g) and benzoyltriphenylphosphinimine (0.85 g) in 40 ml *p*-xylene were refluxed for 1 hour. The solution was filtered while hot and cooled to cause precipitation of the pink product which was filtered off, and washed with ethanol to yield 0.55 g (~60%) of the complex. A yellow crystalline solid (0.09 g) was also obtained from the supernatant solution. The pink complex was similarly prepared in 45% yield from a 1:1 (molar basis) mixture of independently prepared $OsCl_4(PPh_3)_2$ and $OsO_2Cl_2(PPh_3)_2$; it was also prepared in ~65% yield from '$OsOCl_3(PPh_3)_2$' and benzonitrile.

(b) $OsCl_4(PPh_3)_2$ (0.25 g, 0.29 mmol), benzonitrile (2 ml) and triphenylphosphine (0.25 g, 0.95 mmol) were refluxed in *p*-xylene (10 ml) for 20 min. The mixture was cooled, and ethanol (30 ml) was added to complete precipitation of the product, which was filtered off and recrystallized from CH_2Cl_2/CH_3OH to yield 0.26 g (96%) of sparkling pink plates of a 1:1 CH_2Cl_2 solvate. *Trichloro(p-tolunitrile)bis(triphenylphosphine)osmium(III)* was similarly prepared in 81% yield.

(c) A solution of $OsCl_4(PPh_3)_2$ (0.25 g, 0.29 mmol) and benzoyltriphenylphosphinimine (0.25 g, 0.65 mmol) in 10 ml *p*-xylene was refluxed for 1 h. The solution was filtered while hot, then cooled to precipitate bright pink crystals of the complex. The mixture was filtered to yield 0.15 g (56%).

Trichloro(acetonitrile)bis(triphenylphosphine)-osmium(III)

To a solution of 0.30 g $OsCl_3(NCPh)(PPh_3)_2$ in 40 ml benzene was added 2 ml acetonitrile, and the solution was refluxed for 1 h. The pink solution was cooled and pentane was slowly added to precipitate the product, which was filtered off to afford 0.12 g (88%) of the pink complex. The filtrate was evaporated to near dryness and the resulting oil was extracted with pentane. The pentane was removed under vacuum and, the small amount of remaining liquid was shown to be nearly pure benzonitrile by mass spectroscopy.

Dichloro(N-toluoyltriphenylphosphinimine)bis(triphenylphosphine)osmium(II)

(a) A mixture of $OsO_2Cl_2(PPh_3)_2$ (0.30 g, 0.37 mmol), toluoyltriphenylphosphinimine (0.30 g, 0.76 mmol) and triphenylphosphine (0.75 g, 2.9 mmol) in *p*-xylene (15 ml) was refluxed for 3 h, forming a dark yellow-brown solution. Ethanol was slowly added to precipitate the yellow product, which was filtered off and recrystallized from CH_2Cl_2/CH_3OH to yield 0.18 g (41%) of yellow microcrystals of the complex. *Dichloro (N-benzoyltriphenylphosphinimine) bis (triphenylphosphine)osmium(II)* was analogously prepared in 42% yield.

(b) To a solution of $OsCl_2(PPh_3)_3$ (0.15 g, 0.14 mmol) and triphenylphosphine (0.55 g, 2.1 mmol) in 10 ml toluene was added toluoyltriphenylphosphinimine (0.11 g, 0.28 mmol), and the solution was refluxed for 3 h. It was then cooled and ethanol was added to precipitate the yellow product, which was filtered off, and washed with ethanol and ether to yield 0.07 g (42%) of the compound.

Carbonyltrichlorobis(triphenylphosphine)osmium(III)

(a) Four grams of $(NH_4)_2OsCl_6$ (9.1 mmol) and triphenylphosphine (18.0 g, 69 mmol) were added to a t-butanol (1.0 l)–water (0.4 l) mixture, which was brought to reflux. Then sodium hydroxide (0.4 g) was added. Carbon monoxide was slowly bubbled through the refluxing solution for 24 h, precipitating the purple product. The mixture was filtered while warm, and the deep purple microcrystalline product was washed with methanol and dried to yield 7.0 g (91%) of the complex.

(b) To a sample of $OsHCl(CO)(PPh_3)_3$ (0.25 g, 0.24 mmol) in 10 ml chloroform and 1 ml concentrated aqueous HCl, was added N-chlorosuccinimide (0.25 g, 1.8 mmol), and the solution was refluxed for two hours. The brown solution was then filtered and absolute ethanol (30 ml) was added to precipitate the product, which was filtered off, and recrystallized from CH_2Cl_2/CH_3OH to yield 0.11 g (54%) of sparkling purple-brown crystals. The same product was also prepared from $OsH_2(CO)(PPh_3)_2$:

(c) $OsHCl(CO)(PPh_3)_3$ (0.25 g) was dissolved in 10 ml chloroform and chlorine gas was slowly bubbled through the solution for fifteen minutes. The brown solution was then filtered and ethanol was added to precipitate 0.15 g (74%) of the complex.

Tribromocarbonylbis(triphenylphosphine)osmium(III)

To a mixture of $OsH_2(CO)(PPh_3)_3$ (1.0 g, 0.99 mmol) and N-bromosuccinimide (1.0 g, 5.6 mmol) in 35 ml tetrahydrofuran was added 1 ml concentrated aqueous HBr, and the mixutre was refluxed for ten minutes. The purple solution was reduced in volume to 5 ml, and ethanol was added to precipitate the product which was filtered off, washed with methanol and diethyl ether to afford 0.86 g (88%) of deep purple crystals of the complex.

Bis(triphenylphosphonium)hexabromoosmate(IV)

$(N^nBu_4)_2(OsBr_6)$ (16.3 g, 14.1 mmol), triphenylphosphine (20.3 g, 78 mmol), and 2 ml concentrated aqueous HBr were dissolved in a minimum amount of methanol (200 ml), and were refluxed for 30 min. to precipitate burgundy-red crystals of the product. The mixture was filtered, and the product was washed with methanol/ether to yield 17.83 g (93%) of the compound.

Tribromotris(triphenylphosphine)osmium(III)

(a) To a solution of $OsBr_2(PPh_3)_3$ (0.50 g, 0.44 mmol) in 25 ml CH_2Cl_2 was added 35 mg Br_2 (0.22 mmol) and the brown-green solution became purple. The solution was stirred at room temperature for one hour and then filtered. The volume of the solution was reduced to 5 ml and methanol was added to precipitate purple crystals of the product. The mixture was filtered, and the product was washed with ether to give 0.43 g (80%).

(b) Two grams of $(HPPh_3)_2OsBr_6$ (1.67 mmol), triphenylphosphine (2.00 g, 7.6 mmol) and several drops concentrated aqueous HBr were refluxed in 100 ml methanol for 24 hours. The purple crystalline solid was obtained by filtration of the warm reaction solution and washed with ether. Yield was 1.48 g (73%).

Thermolysis of N-toluoyltriphenylphosphinimine

Four grams of N-toluoyltriphenylphosphinimine was dissolved in 100 ml of *p*-xylene (0.1 *M* solution). The solution was rapidly heated to reflux and kept at that temperature during the course of the experiment. Aliquots (0.5 ml) of the reaction solution were successively removed and analyzed by ^{31}P NMR at regular time intervals for 72 hours to monitor the course of the thermolysis. The phosphinimine decomposed cleanly at 148 °C to yield triphenylphosphine oxide as the sole phosphorus containing product. The other product was identified as tolunitrile. The half-life of this reaction under these conditions was approximately 20 hours.

Results and Discussion

Our several attempts to produce '$OsOCl_3(PPh_3)_2$' from OsO_4, PPh_3 and HCl gave brown products which yielded distinctly different chlorine analyses.

TABLE I. Analytical and Spectroscopic Data for Osmium Complexes.

Compound^a (Color)	Elemental analyses found (calculated)	ν(CO), (ν(CN))^b	ν(OsCl)^b (Other)	NMR resonances^e	
				$^{31}P^f$	$^1H^c$
$OsO_2Cl_2(PPh_3)_2$ (light brown)	C: 52.62(52.88) H: 3.60(3.70) Cl: 9.01(8.67)		316	Too insoluble	
$OsCl_4(PPh_3)_2$ (dark brown)	C: 50.74(50.48) H: 3.93(3.53) Cl: 16.21(16.56)		330	Paramagnetic	
$OsCl_2(PPh_3)_3$ (olive green)	C: 62.00(61.89) H: 4.25(4.33) Cl: 6.90(6.77)		291	−4.11(br)	
$OsBr_2(PPh_3)_3$ (olive green)	C: 56.71(57.05) H: 3.77(3.99)			−5.24(br)	
$OsCl_2(CO)(PPh_3)_3$ (pale yellow)	C: 61.41(61.39) H: 4.49(4.22) Cl: 6.44(6.58)	1962	310, 265	Too insoluble	
cis-$OsCl_2(CO)_2(PPh_3)_2$ (white)	C: 54.01(54.22) H: 3.70(3.59) Cl: 8.89(8.42)	1955, 2028	314, 290	−10.22	
trans-$OsCl_2(CO)_2(PPh_3)_2$ (pale yellow)	C: 54.10(54.22) H: 3.81(3.59) Cl: 8.80(8.42)	1971	318	−5.56	
cis-$OsCl_2(NCTo)_2(PPh_3)_2$ (yellow)	C: 60.81(61.23) H: 4.47(4.35) N: 2.95(2.75)	(2197, 2215)	300, 286	−8.29	
cis-$OsBr_2(NCTo)_2(PPh_3)_2$ (yellow)	C: 56.01(56.32) H: 3.81(4.00) N: 2.32(2.53)	(2200, 2215)		−12.31	
trans-$OsCl_2(NCTo)_2(PPh_3)_2$ (yellow)	C: 60.90(61.23) H: 4.22(4.35) N: 2.88(2.75)	(2222)	279	−5.91	
trans-$OsBr_2(NCTo)_2(PPh_3)_2$ (yellow)	C: 56.25(56.32) H: 4.28(4.00) N: 2.55(2.53)	(2225)		−7.72	
$OsCl_2(CO)(NCTo)(PPh_3)_2 \cdot CH_2Cl_2$ (white)	C: 54.21(54.38) H: 3.99(3.87) N: 1.29(1.38)	1941(2263)	310, 281	−7.43	
$OsHCl(CO)(PPh_3)_3$ (white)	C: 63.69(63.43) H: 4.59(4.45) Cl: 3.43(3.40)	1903	279 (ν(OsH) = 2103)	7.15(d), −9.66(t) $^2J_{PP}$ = 11.0 Hz	−7.06 (d of t) $^2J_{P_cH}$ = 25 Hz $^2J_{P_tH}$ = 88 Hz
$OsHCl(CO)_2(PPh_3)_2$ (white)	C: 56.74(56.54) H: 3.98(3.87) Cl: 4.69(4.39)	1971, 2042	298 (ν(OsH) = 1919)	8.33	−3.63(t) $^2J_{PH}$ = 20 Hz
$OsHCl(CO)(NCTo)(PPh_3)_2 \cdot C_6H_6$ (white)	C: 62.70(62.86) H: 4.67(4.55) N: 1.39(1.44)	1898^d	284 (ν(OsH) = 2071)	14.84	−1.89(t) $^2J_{PH}$ = 35 Hz
$OsCl_3(NCTo)(PPh_3)_2 \cdot CH_2Cl_2$ (pink)	C: 52.81(52.88) H: 3.97(3.84) N: 1.21(1.37)	(2254)	326, 315, 304	Paramagnetic	
$OsCl_3(NCPh)(PPh_3)_2 \cdot CH_2Cl_2$ (pink)	C: 52.69(52.36) H: 3.89(3.70) N: 1.28(1.39)	d	323, 309	Paramagnetic	

(continued on facing page)

TABLE I *(continued)*

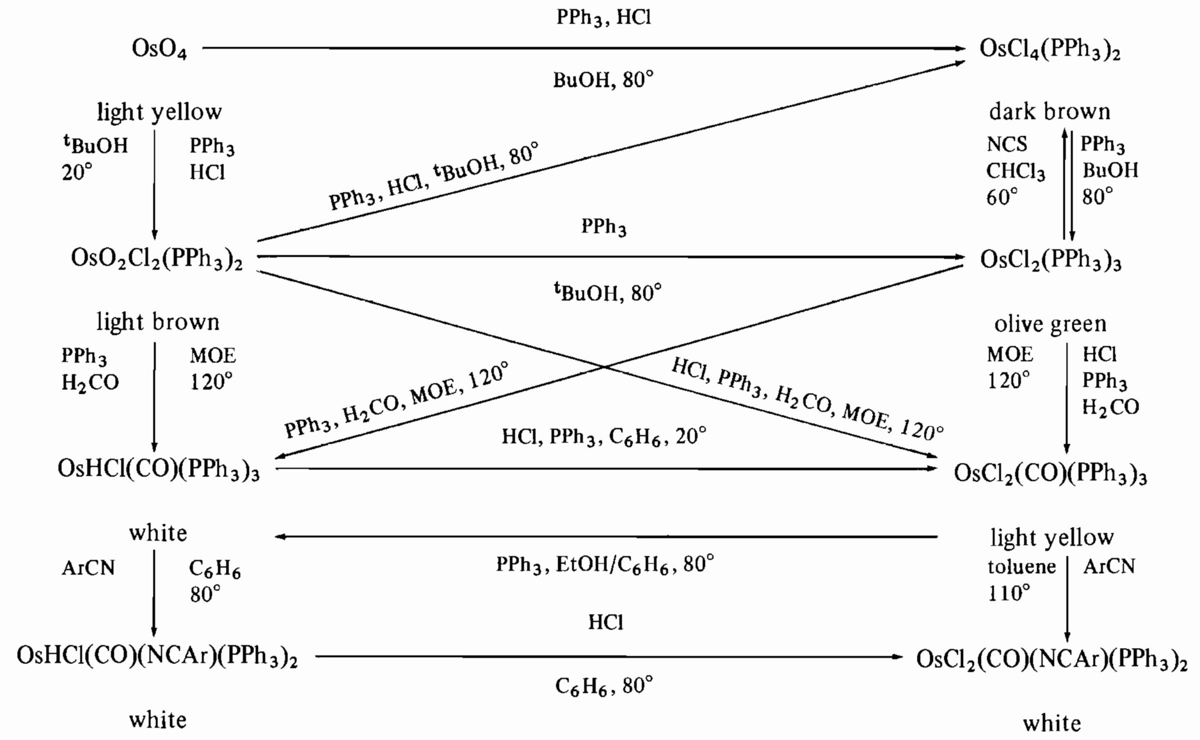
Compound[a] (Color)	Elemental analyses found (calculated)	ν(CO), (ν(CN))[b]	ν(OsCl)[b] (Other)	NMR resonances[e]	
				^{31}P[f]	^{1}H[c]
$OsCl_3(NCMe)(PPh_3)_2$ (pink)	C: 53.11(52.94) H: 4.00(3.86) N: 1.69(1.62)	d	318, 301	Paramagnetic	
$OsCl_2(ToC(O)NPPh_3)(PPh_3)_2$ (yellow)	C: 62.40(63.05) H: 4.09(4.44) N: 1.01(1.19)	1505	318, 306 (ν(PN) = 1110)	Too insoluble	
$OsCl_2(PhC(O)NPPh_3)(PPh_3)_2$ (yellow)	C: 62.29(62.78) H: 4.53(4.32) N: 1.30(1.20)	1509	327, 310 (ν(PN) = 1110)	Too insoluble	
$OsCl_3(CO)(PPh_3)_2$ (purple)	C: 52.49(52.34) H: 3.59(3.56) Cl: 12.12(12.52)	1971	327, 290	Paramagnetic	
$OsBr_3(CO)(PPh_3)_2$ (purple)	C: 45.04(45.23) H: 3.29(3.08)	2018		Paramagnetic	
$(HPPh_3)_2OsBr_6$ (burgundy red)	C: 35.89(36.14) H: 2.71(2.70)		(ν(PH) = 2385)		
$OsBr_3(PPh_3)_3$ (purple)	C: 53.05(53.30) H: 3.56(3.73)			Paramagnetic	

[a]Abbreviations: To = p-$CH_3C_6H_4$-, Ph = C_6H_5-, Me = CH_3-. [b]Units in wave numbers (cm^{-1}). [c]$CDCl_3$ solution; proton NMR measured only for hydrides. [d]ν(CN) absent. [e]Units in ppm (δ) reference to internal Me_4Si(^{1}H) or external 85% H_3PO_4(^{31}P). [f]CH_2Cl_2 solution.

Furthermore, our attempts to use this product in subsequent reactions were frustrated by our inability to obtain reproducible yields. A careful reevaluation of our reaction conditions showed that the chlorine content of our product increased and the color of our product deepened with increasing refluxing time; in addition, the relative intensity of the Os–O stretching band (842 cm^{-1}) in the infrared spectra of the products decreased with increasing refluxing time. We soon determined that reproducible elemental analyses (C, H, Cl) could be obtained if the reaction mixture was stirred at room temperature for several minutes and then filtered. However, the chlorine content of this light brown product was low for '$OsOCl_3(PPh_3)_2$' but corresponded reasonably well to a formula of '$OsOCl_2(PPh_3)_2$'. Recent work has shown that the ESCA and infrared spectra of a product similarly obtained are consistent with the formulation, $OsO_2Cl_2(PPh_3)_2$ [7]. Attempted recrystallization of '$OsOCl_3(PPh_3)_2$' from CH_2Cl_2 gave moderate yields (~50%) of a dark brown crystalline product which analyzed for $OsCl_4(PPh_3)_2$. This identification was confirmed by comparing it to an authentic sample which was prepared by several independent methods. The osmium(III) complex, $OsCl_3(CO)(PPh_3)_2$, can be similarly prepared by the chlorination of $OsH_2(CO)(PPh_3)_3$ or the phosphine reduction of $(NH_4)_2OsCl_6$ in the presence of carbon monoxide and base. The reaction sequence shown in Fig. 1 amply illustrates the reactions of OsO_4 with triphenylphosphine in the presence and absence of HCl. Osmium tetroxide is quickly reduced by

$$\underset{\substack{\text{burgundy red}\\ R = H,\ C_2H_5}}{(R_4N)_2OsCl_6} \xrightarrow[{}^t\text{BuOH, } 80\ ^\circ\text{C}]{\text{HCl, } PPh_3} \underset{\text{dark brown}}{OsCl_4(PPh_3)_2} \xleftarrow[CHCl_3,\ 60\ ^\circ\text{C}]{\text{NCS}} \underset{\text{white}}{OsH_4(PPh_3)_3}$$

$$\underset{\text{burgundy red}}{(NH_4)_2OsCl_6} \xrightarrow[{}^t\text{BuOH, } 80\ ^\circ\text{C}]{\text{CO, } PPh_3} \underset{\text{purple}}{OsCl_3(CO)(PPh_3)_2} \xleftarrow[CHCl_3,\ 60\ ^\circ\text{C}]{\text{NCS}} \underset{\text{white}}{OsH_2(CO)(PPh_3)_3}$$



MOE = 2-methoxyethanol
NCS = N-chlorosuccinimide

Fig. 1. Reaction scheme for osmium complexes.

PPh_3 and HCl to Os(VI), $OsO_2Cl_2(PPh_3)_2$, under mild conditions. Under more vigorous conditions, a further reduction to Os(IV), $OsCl_4(PPh_3)_2$, takes place. If no acid is present, the reduction of either Os(VI) or Os(IV) continues to Os(II), $OsCl_2(PPh_3)_3$. Tert-butanol is the solvent of choice because it is not reducing in nature and will not act as a carbonyl source. The reduction of $OsCl_6^{2-}$ using PPh_3 to $OsCl_2(PPh_3)_3$ in t-butanol proceeds through $OsCl_4(PPh_3)_2$ which can be observed as an intermediate; when HCl is present, the reduction stops at $OsCl_4(PPh_3)_2$ which can be isolated in good yield in a pure state. During the reduction of $OsO_2Cl_2(PPh_3)_2$ using PPh_3 to $OsCl_2(PPh_3)_3$, $OsCl_4PPh_3)_2$ is *not* directly observed as an intermediate; this reaction proceeds faster than the phosphine reduction of $OsCl_4(PPh_3)_2$. It appears that reactions of $OsO_2Cl_2(PPh_3)_2$ in the presence of PPh_3 go through $OsCl_4(PPh_3)_2$ if HCl is present or $OsCl_2(PPh_3)_3$ if HCl is absent. In some reactions of $OsO_2Cl_2(PPh_3)_2$ or OsO_4, the t-butanol could be replaced by isopropanol or ethanol. However, in the presence of refluxing ethanol as solvent, $OsO_2Cl_2(PPh_3)_2$ was slowly (12 hours) converted to $OsCl_2(CO)(PPh_3)_3$ if HCl was present and $OsHCl(CO)(PPh_3)_3$ if it was absent. When the higher boiling 2-methoxyethanol was used as the solvent, reaction times were reduced (~5 hours); similarly, the addition of formaldehyde which is a better carbonyl source than primary alcohols reduced reaction times even further during the deliberate syntheses of carbonyl complexes. $OsHCl(CO)(PPh_3)_3$ was readily converted to $OsCl_2(CO)(PPh_3)_3$ by the action of HCl or to $OsHCl(CO)_2(PPh_3)_2$ by carbon monoxide. The stable *cis* dicarbonyl, $OsCl_2(CO)_2(PPh_3)_2$, was produced from $OsHCl(CO)_2(PPh)_2$ and HCl, from $OsCl_2(CO)(PPh_3)_3$ and CO and from $OsHCl(CO)(PPh_3)_3$ in the presence of HCl and CO (See Fig. 2). The mixed carbonyl–nitrile complex, $OsCl_2(CO)(NCTo)(PPh_3)_2$, was similarly formed *via* $OsHCl(CO)(NCTo)(PPh_3)_2$ from $OsHCl(CO)(PPh_3)_3$ or formed directly from $OsCl_2(CO)(PPh_3)_3$ and tolunitrile.

Once the nature of the osmium starting materials had been established, the course of the reactions with aroylphosphinimines became less confusing. When pure starting materials were used, only one principle product was isolated from each reaction in reasonable yield. In refluxing *p*-xylene, the aroylphosphinimines as well as aromatic nitriles produced the same pink product from

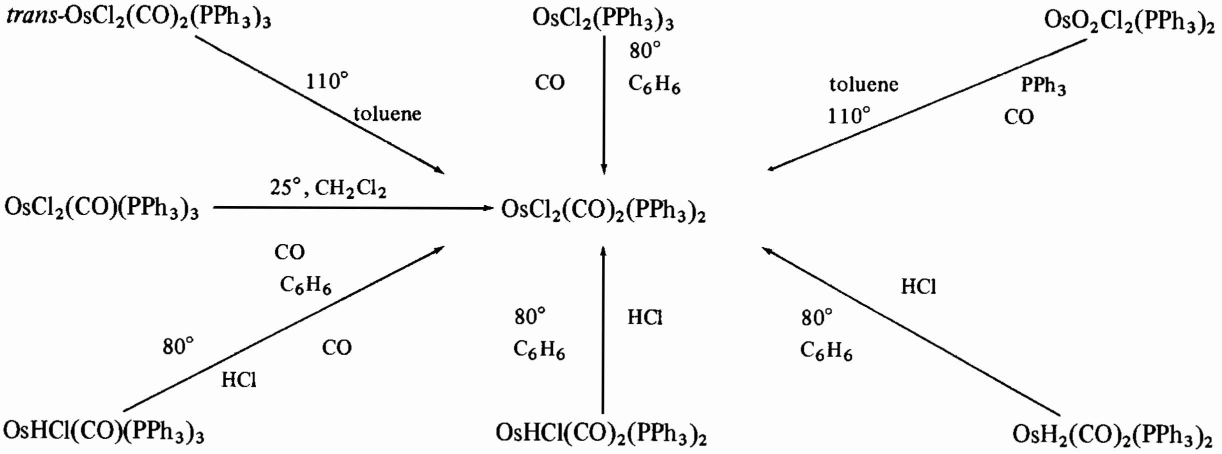
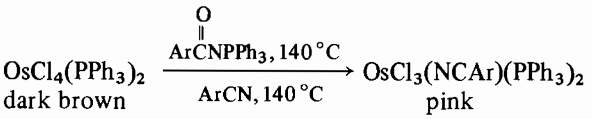
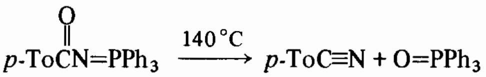


Fig. 2. Syntheses of *cis*-$OsCl_2(CO)_2(PPh_3)_2$.



$$\underset{\text{dark brown}}{OsCl_4(PPh_3)_2} \xrightarrow[\text{ArCN, 140 °C}]{\text{Ar}\overset{\overset{\displaystyle O}{\|}}{C}\text{NPPh}_3\text{, 140 °C}} \underset{\text{pink}}{OsCl_3(NCAr)(PPh_3)_2}$$

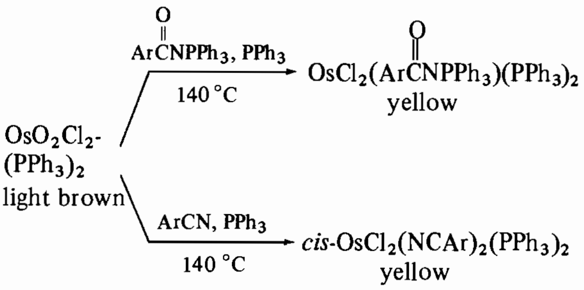
$OsCl_4(PPh_3)_2$ in excellent yield. The addition of free PPh_3 to these reactions seemed to improve yields only slightly. The pink products were completely characterized: (1) The elemental analyses of the CH_2Cl_2 solvates were quite good. (2) The pink products could be readily prepared directly from aromatic nitriles. (3) The C—N stretching vibration was clearly located in the infrared spectrum at 2254 cm^{-1} when Ar = *p*-tolyl; ν(CN) in free *p*-tolunitrile is 2228 cm^{-1}. It is interesting that no bands in this region of the infrared spectra were detectable in the analogous acetonitrile or benzonitrile complexes. Other infrared bands due to coordinated C_6H_5CN (1596, 1445 cm^{-1}), *p*-$CH_3C_6H_4CN$ (1604, 1505 cm^{-1}) and CH_3CN (1440, 1363 cm^{-1}) were, however, observed in the spectra of the respective pink products. (4) Under the preparative conditions in refluxing *p*-xylene, toluoylphosphinimine was shown to decompose to *p*-tolunitrile and triphenylphosphine oxide in the absence of any metal. Although free nitriles are produced this way in refluxing *p*-xylene, this rate of nitrile production seems to be slower than the formation of $OsCl_3(NCAr)(PPh_3)_2$ under similar conditions. We thus speculate that there is an osmium assisted decomposition of aroylphosphinimines. Beyond those described in the Experimental Section, detailed kinetic or mechanistic studies were not carried out. (5) Free acetonitrile quantitatively displaced benzonitrile from $OsCl_3(NCPh)(PPh_3)_2$ which was prepared from benzoylphosphinimine.



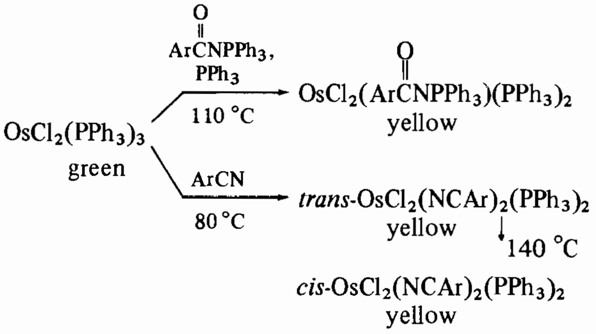
$$p\text{-To}\overset{\overset{\displaystyle O}{\|}}{C}N{=}PPh_3 \xrightarrow{140\,°C} p\text{-To}C{\equiv}N + O{=}PPh_3$$

$$\underset{\text{pink}}{OsCl_3(NCPh)(PPh_3)_2} + CH_3CN \xrightarrow{80\,°C} \underset{\text{pink}}{OsCl_3(NCCH_3)(PPh_3)_2} + PhCN$$

The reactions of nitriles and phosphinimines with $OsO_2Cl_2(PPh_3)_2$ in refluxing *p*-xylene followed different courses to give two different yellow products. The addition of free PPh_3 to these reaction mixtures greatly improved yields, and

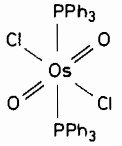


$OPPh_3$ was isolated as a by-product in each case. Indeed, $OsO_2Cl_2(PPh_3)_2$ is transformed into $OsCl_2(PPh_3)_3$ in the presence of PPh_3, and $OsCl_2(PPh_3)_3$ undergoes similar reactions to produce the same two yellow products. One can view both yellow products

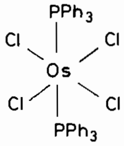


as simple ligand additions and/or substitutions to the coordinatively unsaturated $OsCl_2(PPh_3)_3$. When $OsCl_2(PPh_3)_3$ reacts with natural ligands (L) such as nitriles or carbon monoxide, the kinetic product is the *trans* isomer of $OsCl_2L_2(PPh_3)_2$ which on heating gives the more stable *cis* isomer. $RuCl_2(PPh_3)_3$ is known to behave in a similar manner towards both nitriles and CO [9, 10].

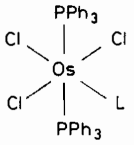
Based on available spectroscopic data, the most likely stereochemistries of the reported compounds are given below (*1–8*).



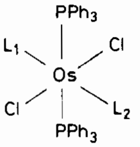
1



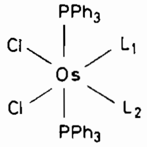
2



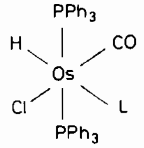
3



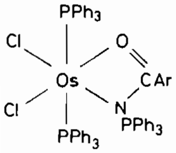
4



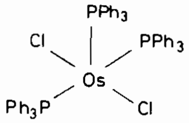
5



6



7



8

The presence of a single infrared band assignable to ν(OsCl) and ν(OsO) suggests the all-*trans* geometry (*1*) for $OsO_2Cl_2(PPh_3)_2$. The linear OsO_2^{2+} moiety is commonly observed [11]. The isomorphism of $OsCl_4(PPh_3)_2$ and $ReCl_4(PPh_3)_2$ [7] coupled with the *trans* structures of similar Os(IV) and Re(IV) complexes with different phosphine ligands [12] suggest that the phosphine ligands are *trans* (*2*) in $OsCl_4(PPh_3)_2$. Geometry (*3*) is assumed for $OsCl_3(CO)(PPh_3)_2$ and $OsCl_3(NCR)(PPh_3)_2$ owing to the similarity of the infrared spectra in the Os–Cl stretching region with those of $OsCl_3(NH_3)(PPh_3)_2$ [13] and $OsCl_3(N_2To)(PPh_3)_2$ [5] whose structures are either known or can be inferred with reasonable certainty. As noted earlier, we found the CH_2Cl_2 solvates of $OsCl_3(N_2To)(PPh_3)_2$, $OsCl_3(NCTo)(PPh_3)_2$ and $RuCl_3(N_2To)(PPh_3)_2$ to be isomorphous. The less stable *trans* isomers of $OsCl_2L_2(PPh_3)_2$ ($L_1 = L_2$ = CO, $L_1 = L_2$ = NCAr) undoubtedly have geometry *4*. The presence of one band assignable to ν(OsCl), ν(CO) or ν(CN) coupled with a single resonance (singlet) in the ^{31}P NMR spectra are consistent with this geometry. The analogous ruthenium complexes are known and are thought to have similar structures [10]. The remaining complexes of the sort $OsCl_2L_1L_2(PPh_3)_2$ ($L_1 = L_2$ = CO; $L_1 = L_2$ = NCAr; L_1 = CO, L_2 = NCAr; L_1 = CO, L_2 = PPh_3) have geometry *5* with *cis* chloro ligands and *trans* phosphine ligands. The ^1H and ^{31}P NMR spectra and the positions of ν(OsCl) in $OsHCl(CO)L(PPh_3)_2$ (L = CO, PPh_3, NCAr) suggest that these compounds have geometry *6* with *trans* phosphines and Cl *cis* to H. When L = CO, H must be *trans* to CO and when L = PPh_3, the large H–P coupling constant (NMR spectrum) to the unique phosphine shows that H is *trans* to PPh_3; the bromo analogue, $OsHBr(CO)(PPh_3)_3$, is known to have geometry *6* [14]. When L = NCAr, the high value of ν(OsH) suggests that the hydride is *trans* to a sigma donor (NCAr); when H is *trans* to a pi acceptor such as CO, ν(OsH) usually drops below ν(CO). The square pyramidal geometry (*8*) for $OsCl_2(PPh_3)_3$ has been established from ^{31}P NMR [8]; the Ru analogue is known to have this structure and similar ^{31}P NMR behavior [15, 8]. The aroylphosphinimine complex probably contains a chelating phosphinimine ligand (*7*) which is postulated to be present in other aroyl- or acylphosphinimine complexes [16]. The value of ν(CO) in  $OsCl_2(To\overset{\overset{O}{\|}}{C}NPPh_3)(PPh_3)_2$ occurs at 1505 cm^{-1} and is about 50 cm^{-1} lower than that in the free ligand (1555 cm^{-1}); this shift to lower energy is also seen in  $CoCl_2(R\overset{\overset{O}{\|}}{C}NPPh_3)_2$ [16].

There is now ample evidence to doubt the existence of both $OsOCl_3(PPh_3)_2$ and $OsCl_3(NAr)(PPh_3)_2$. In separate reactions, we showed that a 40/60 mixture of $OsO_2Cl_2(PPh_3)_2$ and $OsCl_4(PPh_3)_2$ gave the nearly same reaction products as '$OsOCl_3(PPh_3)_2$'. We have learned that $OsO_2Cl_2(PPh_3)_2$ is one of the most useful starting materials in preparing osmium–phosphine complexes. Unfortunately, we have yet to produce a nitrene complex of osmium; tetraphenylphosphinimine seems to react with $OsO_2Cl_2(PPh_3)_2$, $OsCl_4(PPh_3)_2$ and $OsCl_2(PPh_3)_3$, but only intractable brown solids are obtained. Our original intent was to compare $OsX_3(NR)(PPh_3)_2$, $RhX_3(NR)(PPh_3)_2$ and $IrX_3(NR)(PPh_3)_2$ [17] with $ReX_3(NR)(PPh_3)_2$ [4] and ascertain what effect, if any, one or two extra electrons would have on the geometry of the nitrene ligands. The comparison of the Re and Os analogues is presently impossible. However, the structures of the rhodium and iridium complexes should yield interesting chemical information about nitrene ligands.

Acknowledgement

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

References

1 B. Bell, J. Chatt, J. A. Dilworth and G. J. Leigh, *Inorg. Chim. Acta, 6*, 635 (1972).

2 J. Chatt, C. D. Falk, G. J. Leigh and R. J. Paske, *J. Chem. Soc. (A)*, 2288 (1969).

3 J. Chatt and G. A. Rowe, *J. Chem. Soc. (A)*, 4019 (1962).

4 D. Bright and J. A. Ibers, *Inorg. Chem., 7*, 1099 (1968).

5 B. L. Haymore and J. A. Ibers, *Inorg. Chem., 14*, 2784 (1975).

6 B. L. Haymore and J. A. Ibers, *Inorg. Chem., 14*, 3060 (1975).

7 D. J. Salmon and R. A. Walton, *Inorg. Chem., 17*, 2379 (1978).

8 P. A. Hoffman and K. G. Caulton, *J. Am. Chem. Soc., 97*, 4221 (1975).

9 J. D. Gilbert and G. Wilkinson, *J. Chem. Soc. (A)*, 1749 (1969).

10 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem., 28*, 945 (1966); B. R. James and L. D. Markham, *Inorg. Nucl. Chem. Letter, 7*, 373 (1971).

11 W. P. Griffith, *J. Chem. Soc.*, 245 (1964); W. P. Griffith, *J. Chem. Soc. (A)*, 211 (1969).

12 J. Chatt, G. J. Leigh, D. M. P. Mingos and R. J. Paske, *J. Chem. Soc. (A)*, 2636 (1968); L. Aslanov, R. Mason, A. G. Wheeler and P. O. Whimp, *J. Chem. Soc., Chem. Commun.*, 30 (1970).

13 D. Bright and J. A. Ibers, *Inorg. Chem., 8*, 1078 (1969).

14 P. L. Orioli and L. Vaska, *Chem. Soc. Proceed.*, 333 (1962).

15 G. J. La Placa and J. A. Ibers, *Inorg. Chem., 4*, 778 (1965).

16 W. Beck, W. Rieber and H. Kirmaier, *Z. Naturforsch., 32B*, 528 (1977).

17 M. J. McGlinchey and F. G. A. Stone, *Chem. Commun.*, 1265 (1970).

18 F. P. Dwyer and J. W. Hogarth, *Inorg. Syn., 5*, 204 (1957).

19 J. J. Levinson and S. D. Robinson, *J. Chem. Soc. (A)*, 2947 (1970).

20 J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, 3504 (1966).

21 K. R. Lainge and W. R. Roper, *J. Chem. Soc. (A)*, 1889 (1969).