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THE TRIS(TRIPHENYLPHOSPHINE)OSMIUM ZEROVALENT COMPLEXES $Os(CO)_2(PPh_3)_3$, $Os(CO)(CNR)(PPh_3)_3$, $Os(CO)(CS)(PPh_3)_3$, $Os(CS)(CNR)(PPh_3)_3$ AND DERIVED COMPOUNDS

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Summary

Detailed procedures for the syntheses of $Os(CO)_2(PPh_3)_3$, $Os(CO)(CNR)(PPh_3)_3$ (R = *p*-tolyl), $Os(CO)(CS)(PPh_3)_3$ and $Os(CS)(CNR)(PPh_3)_3$, together with the derived complexes $Os(CO)_2(CS)(PPh_3)_2$, $Os(CO)(CS)(CNR)(PPh_3)_2$, $Os(\eta^2\text{-}C_2H_4)(CO)(CNR)(PPh_3)_2$, $Os(\eta^2\text{-}C_2H_4)(CO)(CS)(PPh_3)_2$, $Os(\eta^2\text{-}CS_2)(CO)_2(PPh_3)_2$, $Os(\eta^2\text{-}CS_2)(CO)(CS)(PPh_3)_2$, $Os(\eta^2\text{-}CS_2)(CO)(CNR)(PPh_3)_2$, $Os(\eta^2\text{-}PhC_2Ph)(CO)_2(PPh_3)_2$ and $OsH(C_2Ph)(CO)_2(PPh_3)_2$ are described.

Introduction

The tris(triphenylphosphine)-substituted mononuclear zerovalent complexes of osmium have an extremely interesting chemistry because through dissociation of a triphenylphosphine ligand (assisted by steric pressures) they present a coordinatively unsaturated, electron-rich, metal centre. Among the small molecules which have been shown to coordinate to $Os(CO)_2(PPh_3)_2$ (derived from $Os(CO)_2(PPh_3)_3$ by PPh_3 dissociation) can be listed C_2H_4 [1], PhC_2Ph [1], CS_2 [2], CSeS (as both C,S- and C,Se-bound isomers) [3], O_2 [1], S_2 and Se_2 [4]. The ethylene adduct with acids yields ethyl-osmium(II) complexes which undergo migration reactions [5]. Also, from $Os(CO)_2(PPh_3)_3$ the first *dihapto*-formaldehyde complex, $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$, was obtained [6] and from this compound in turn complexes with formyl, halomethyl and hydroxymethyl ligands [7]. Recently, $Os(CO)(CS)(PPh_3)_3$, through reaction with acetylenes, has been the source of the first metallabenzene [8] and also of metallacyclobutadiene complexes. Previously we have described the preparation of these zerovalent complexes without experimental detail [1]. We have now improved the preparation of $Os(CO)_2(PPh_3)_3$ in that it is no longer necessary to use silver salts to make the precursor hydride complexes and in this paper we describe, in detail, procedures for the preparation of $Os(CO)_2(PPh_3)_3$, $Os(CO)(CNR)(PPh_3)_3$,

$Os(CO)(CS)(PPh_3)_3$, $Os(CS)(CNR)(PPh_3)_3$, and several derivatives including the ethylene adducts $Os(\eta^2\text{-}C_2H_4)(CO)(CNR)(PPh_3)_2$, $Os(\eta^2\text{-}C_2H_4)(CO)(CS)(PPh_3)_2$ and the *dihapto*-CS_2 adducts $Os(\eta^2\text{-}CS_2)(CO)_2(PPh_3)_2$ and $Os(\eta^2\text{-}CS_2)(CO)(CNR)(PPh_3)_2$.

Results and discussion

$Os(CO)_2(PPh_3)_3$ and $Os(CO)(CS)(PPh_3)_3$

The original synthetic pathway [1] leading to $Os(CO)_2(PPh_3)_3$ followed the sequence:

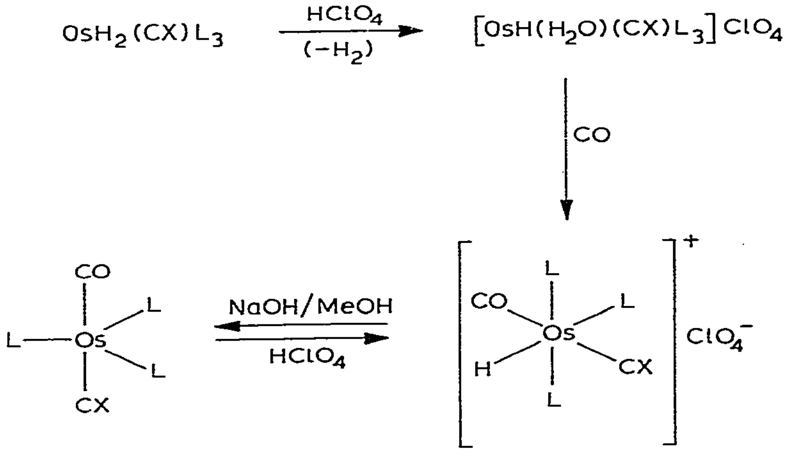
$$OsHCl(CO)(PPh_3)_3 \xrightarrow[MeCN]{AgClO_4} [OsH(CO)(MeCN)_2(PPh_3)_2]ClO_4$$

$$\xrightarrow{CO} [OsH(CO)_2(MeCN)(PPh_3)_2]ClO_4 \xrightarrow{PPh_3} [OsH(CO)_2(PPh_3)_3]ClO_4$$

$$\xrightarrow[MeOH]{OH^-} Os(CO)_2(PPh_3)_3$$

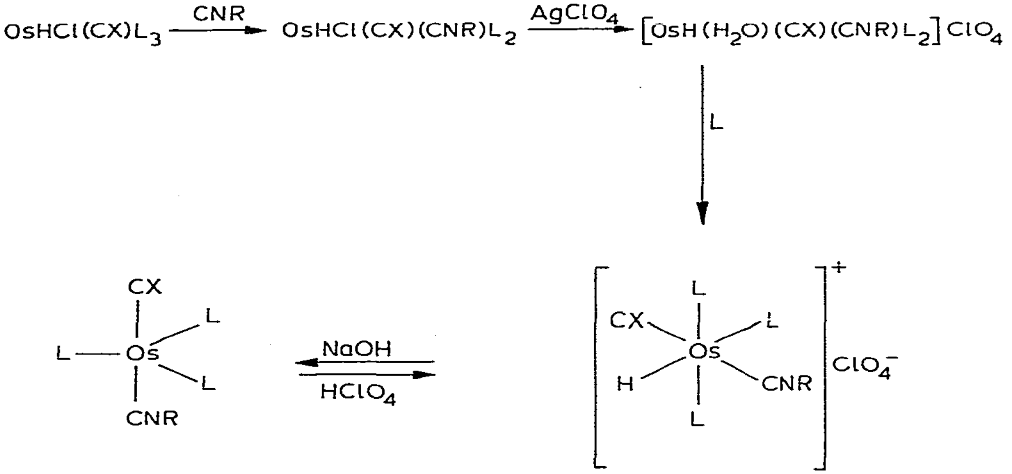
Two features make this route less than ideal. First, the use of silver perchlorate to remove chloride from $OsHCl(CO)(PPh_3)_3$ can lead to the inclusion of trace quantities of silver impurities in the product complex. These initially inconspicuous impurities promote darkening and decomposition of the subsequent intermediates and lead ultimately to considerably diminished yields of the zerovalent complex. Secondly, the substitution of acetonitrile by triphenylphosphine in the cation $[OsH(CO)_2(MeCN)(PPh_3)_2]^+$ is a prerequisite to reductive deprotonation and because the osmium cation is inert, very forcing conditions are required (heating under reflux in 2-methoxyethanol for 20 hours with a large excess of triphenylphosphine). This leads to impure $[OsH(CO)_2(PPh_3)_3]^+$ which proceeds to $Os(CO)_2(PPh_3)_3$ in the last step in only 70% yield. These problems, together with the further yield and time limitations imposed by the large number of steps involved prompted an investigation of alternative routes.

SCHEME 1
SYNTHESIS OF $Os(CO)_2L_3$ AND $Os(CO)(CS)L_3$
($L = PPh_3$, $X = O$ or S)



The solution is to be found in Scheme 1. The complex $OsH_2(CO)(PPh_3)_3$ which results from the action of NaOH on $OsHCl(CO)(PPh_3)_3$ in boiling 2-methoxyethanol reacts with perchloric acid (70% aqueous) or tetrafluoroboric acid (40% aqueous) in dichloromethane-methanol solution evolving hydrogen and forming $[OsH(H_2O)(CO)(PPh_3)_3]^+$. A crystal structure determination [9] of the related ruthenium salt $[RuH(H_2O)(CO)_2(PPh_3)_2]BF_4 \cdot EtOH$ confirms the presence of coordinated water in these cations. The BF_4^- anion is involved in a network of hydrogen bonds with the coordinated water molecule and the solvating ethanol. $[OsH(H_2O)(CO)(PPh_3)_3]^+$ is readily carbonylated to $[OsH(CO)_2(PPh_3)_3]^+$ and this cation, produced in the above way, reacts with NaOH in boiling methanol under nitrogen to afford $Os(CO)_2(PPh_3)_3$ cleanly and in high yield (90—95%). Furthermore, the zerovalent complex can be prepared by this new procedure directly from $OsH_2(CO)(PPh_3)_3$ without isolation of the intermediate complexes $[OsH(H_2O)(CO)(PPh_3)_3]^+$ and $[OsH(CO)_2(PPh_3)_3]^+$ and this sequence consequently involves much less handling than the earlier route. The overall yield, based on $OsHCl(CO)(PPh_3)_3$ lies in the range 82—88%. The geometries of the hydrido-containing complexes shown in Schemes 1 and 2, can be deduced from the splitting patterns of the hydride resonances in the ^1H NMR spectra, which arise from coupling with ^{31}P nuclei (see Table 2).

SCHEME 2
SYNTHESIS OF $Os(CO)(CNR)L_3$ AND $Os(CS)(CNR)L_3$
($L = PPh_3$, $X = O$ or S, $R = p$-tolyl)



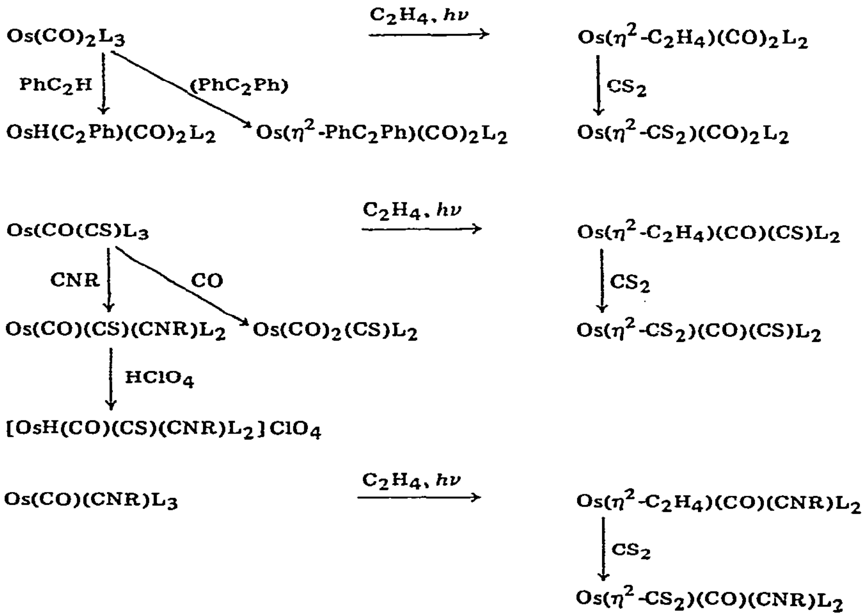
An exactly similar procedure starting with $OsH_2(CS)(PPh_3)_3$ [10] leads to $Os(CO)(CS)(PPh_3)_3$. Treatment of $[OsH(CO)(CS)(PPh_3)_3]^+$ (generated in situ) in degassed methanol solution with NaOH affords $Os(CO)(CS)(PPh_3)_3$ as a tan-coloured crystalline solid. This deprotonation reaction is much faster (reaction complete in 10 minutes in methanol under reflux) than the corresponding reaction of $[OsH(CO)_2(PPh_3)_3]^+$ to give $Os(CO)_2(PPh_3)_3$ (reaction complete in approximately 40 minutes in methanol under reflux).

$Os(CO)_2(PPh_3)_3$ reacts with ethylene to give $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$ a reaction we have already described [5].

$Os(CO)(CS)(PPh_3)_3$ also reacts with ethylene in degassed benzene when exposed to the light from a quartz-halogen lamp to afford $Os(\eta^2\text{-}C_2H_4)(CO)(CS)(PPh_3)_2$, but the reaction is reversible and, in the presence of the displaced phosphine, does not proceed to completion. Instead, mixtures of $Os(\eta^2\text{-}C_2H_4)(CO)(CS)(PPh_3)_2$ and $Os(CO)(CS)(PPh_3)_3$ are obtained, even after many hours reaction time. A pure sample of the ethylene adduct can be obtained by repeated reaction of these mixtures with ethylene (3 cycles). This process effects gradual removal of the displaced phosphine and the equilibrium $Os(CO)(CS)(PPh_3)_3 + C_2H_4 \rightleftharpoons Os(\eta^2\text{-}C_2H_4)(CO)(CS)(PPh_3)_2 + PPh_3$ is shifted in favour of the ethylene adduct. Benzene washing of the solid mixtures effectively removes the zerovalent contaminant and also affords pure $Os(\eta^2\text{-}C_2H_4)(CO)(CS)(PPh_3)_2$. Ethylene loss occurs readily in solution as evidenced by the ^1H NMR signal for free ethylene which is observed in $CDCl_3$ solutions of this adduct as a sharp singlet at τ 4.6. An unambiguous assignment for the coordinated ethylene signal has not been possible. The analogous dicarbonyl ethylene adduct contains a substantially less labile ethylene ligand [5].

$Os(CO)_2(PPh_3)_3$ also reacts with PhC_2H giving an osmium(II) hydride, $OsH(C_2Ph)(CO)_2(PPh_3)_2$ and with PhC_2Ph under the influence of light to give $Os(\eta^2\text{-}PhC_2Ph)(CO)_2(PPh_3)_2$ (see Scheme 3, and Tables 1 and 2, for IR and NMR data).

SCHEME 3
REACTIONS OF $Os(CO)_2L_3$, $Os(CO)(CS)L_3$ AND $Os(CO)(CNR)L_3$
($L = PPh_3$, R = *p*-tolyl)



Addition of carbon monoxide or *p*-tolylisocyanide to a carefully degassed benzene solution of $Os(CO)(CS)(PPh_3)_3$ affords $Os(CO)_2(CS)(PPh_3)_2$ and $Os(CO)(CS)(CNR)(PPh_3)_2$, respectively. This synthesis of $Os(CO)_2(CS)(PPh_3)_2$ is superior to the methyl thiol elimination from $OsH(\eta^1\text{-}CS_2Me)(CO)_2(PPh_3)_2$ described previously [11].

TABLE 1

IR DATA (cm^{-1}) FOR OSMIUM COMPLEXES [a]

Compound	ν(CO)	ν(CS)	ν(CN)	Other bands
$[OsH(H_2O)(CO)(PPh_3)_3]^+$	1930			
$[OsH(CO)_2(PPh_3)_3]^+$	1985			
$[OsH(H_2O)(CS)(PPh_3)_3]^+$		1295		3400w ν(OH)
$[OsH(CO)(CS)(PPh_3)_3]^+$	2045	1310		
$OsHCl(CO)(CNR)(PPh_3)_2$	1920, 1910		2125	273 ν(Os—Cl)
$[OsH(H_2O)(CO)(CNR)(PPh_3)_2]^+$	1935		2150	
$[OsH(CO)(CNR)(PPh_3)_3]^+$	1980		2150	
$[OsH(H_2O)(CS)(CNR)(PPh_3)_2]^+$		1297	2159	3200w ν(OH)
$[OsH(CS)(CNR)(PPh_3)_3]^+$		1286	2165	
$[OsH(CO)(CS)(CNR)(PPh_3)_2]^+$	2055	1319	2165	
$Os(CO)_2(PPh_3)_3$	1895			
$Os(CO)(CS)(PPh_3)_3$	1890	1230		
$Os(CO)(CNR)(PPh_3)_3$	1895		2060	
$Os(CS)(CNR)(PPh_3)_3$		1222	1950, 1820(br)	
$Os(CO)_2(CS)(PPh_3)_2$	1955, 1890	1230		
$Os(CO)(CS)(CNR)(PPh_3)_2$	1890, 1865	1232, 1222	2060, 2036	
$Os(\eta^2\text{-}C_2H_4)(CO)(CS)(PPh_3)_2$	1945	1237		
$Os(\eta^2\text{-}C_2H_4)(CO)(CNR)(PPh_3)_2$	1880		2060, 2045	
$Os(\eta^2\text{-}CS_2)(CO)_2(PPh_3)_2$	2000, 1940			1115 ν(C=S)
$Os(\eta^2\text{-}CS_2)(CO)(CS)(PPh_3)_2$	2020, 1995	1280		1112 ν(C=S)
$Os(\eta^2\text{-}CS_2)(CO)(CNR)(PPh_3)_2$	1905		2120	1070 ν(C=S)
$Os(\eta^2\text{-}PhC_2Ph)(CO)_2(PPh_3)_2$	1980, 1900			1705m ν(C≡C)
$OsH(C_2Ph)(CO)_2(PPh_3)_2$	2030, 1980			2115, 2110w ν(C≡C)

[a] Measured as Nujol mulls. All bands strong or very strong unless noted otherwise.

Perchloric acid reacts instantaneously with $Os(CO)(CS)(CNR)(PPh_3)_2$ in dichloromethane-ethanol solution to afford $[OsH(CO)(CS)(CNR)(PPh_3)_2]ClO_4$. Since the ^{1}H NMR spectrum indicates a *trans*-arrangement of phosphine ligands there are three possible geometries for this cation. If this is the kinetic product then the actual geometry must be dependent on the site of protonation of $Os(CO)(CS)(CNR)(PPh_3)_2$ and a structure determination of this cation would be particularly interesting.

$Os(CO)(CNR)(PPh_3)_3$ and $Os(CS)(CNR)(PPh_3)_3$

The isocyanide-containing zerovalent complexes $Os(CO)(CNR)(PPh_3)_3$ and $Os(CS)(CNR)(PPh_3)_3$ result from the straightforward sequence illustrated in Scheme 2. The reductive deprotonation of $[OsH(CO)(CNR)(PPh_3)_3]^+$ and $[OsH(CS)(CNR)(PPh_3)_3]^+$ is much slower (approximately 8 hours in ethanol under reflux) than for the analogous carbonyl compounds. This may reflect the greater net donor properties of *p*-tolylisocyanide when compared with carbonyl.

TABLE 2

^{1}H NMR DATA ($CDCl_3$) FOR OSMIUM(II) HYDRIDE COMPLEXES

Compound	Hydride chemical shift (τ) and coupling constants (Hz)
$[OsH(H_2O)(CO)(PPh_3)_3]^+$	17.07, dt, $^2J(HP_{trans}) = 94.0$, $^2J(HP_{cis}) = 25.5$
$[OsH(CO)_2(PPh_3)_3]^+$	19.41, dt, $^2J(HP_{trans}) = 42.5$, $^2J(HP_{cis}) = 23.2$
$[OsH(H_2O)(CS)(PPh_3)_3]^+$	15.18, dt, $^2J(HP_{trans}) = 82.6$, $^2J(HP_{cis}) = 25.0$
$[OsH(CO)(CS)(PPh_3)_3]^+$	17.90, dt, $^2J(HP_{trans}) = 38.0$, $^2J(HP_{cis}) = 22.0$
$OsHCl(CO)(CNR)(PPh_3)_2$	14.76, t, $^2J(HP) = 20.0$
$[OsH(H_2O)(CO)(CNR)(PPh_3)_2]^+$	13.97, t, $^2J(HP) = 18.0$
$[OsH(CO)(CNR)(PPh_3)_3]^+$	19.40, dt, $^2J(HP_{trans}) = 50.0$, $^2J(HP_{cis}) = 24.0$
$[OsH(H_2O)(CS)(CNR)(PPh_3)_2]^+$	11.98, t, $^2J(HP) = 18.0$
$[OsH(CS)(CNR)(PPh_3)_3]^+$	17.65, dt, $^2J(HP_{trans}) = 50.0$, $^2J(HP_{cis}) = 24.5$
$[OsH(CO)(CS)(CNR)(PPh_3)_2]^+$	16.57, t, $^2J(HP) = 13.5$

$Os(CO)(CNR)(PPh_3)_3$ forms an ethylene adduct under the influence of light and the ethylene may in turn be replaced by CS_2 forming $Os(\eta^2\text{-}CS_2)(CO)(CNR)(PPh_3)_2$ (see Scheme 3).

All the solid zerovalent complexes react with air on standing to produce a surface darkening. This occurs most rapidly for the isocyanide-containing complexes where surface deterioration is apparent after several hours. The IR spectrum of solid $Os(CS)(CNR)(PPh_3)_3$ exhibits an unusual ν(CN) band which is very broad (250 cm^{-1}) with two prominent peaks at 1950s and 1820s cm^{-1}.

Experimental

General experimental conditions and instrumentation were as described previously [10].

$OsHCl(CO)(PPh_3)_3$

$(NH_4)_2[OsCl_6]$ (2.0 g), triphenylphosphine (12 g) (preferably with a small quantity of seed crystals of $OsHCl(CO)(PPh_3)_3$) in 2-(β-methoxy)ethoxyethanol (methyl digol) (57 ml) were heated under reflux for 1 h. Large white crystals of the product were deposited after 35 min. The mixture was cooled to room temperature and the crystals were filtered, washed with ethanol and hexane and dried at 60°C (4.45 g, 94%). The IR spectrum was identical to that reported in the literature [12].

$OsH_2(CO)(PPh_3)_3$

$OsHCl(CO)(PPh_3)_3$ (2.0 g), triphenylphosphine (0.2 g) and sodium hydroxide (0.5 g) were heated under reflux in 2-methoxyethanol (50 ml) for 30 min. The mixture was cooled in an ice bath and the white crystalline solid was collected and washed with ethanol, water and then ethanol again. The solid was dissolved in dichloromethane with triphenylphosphine (0.1 g) (and filtered through a celite pad if any undissolved NaCl was apparent) and ethanol was added. Removal of dichloromethane afforded white crystals (1.85 g, 95.7%). The IR spectrum was identical to that reported in the literature [13].

$[OsH(H_2O)(CO)(PPh_3)_3]BF_4$

$OsH_2(CO)(PPh_3)_3$ (1.85 g) was heated gently in a degassed solution comprised of dichloromethane (70 ml), methanol (10 ml) and tetrafluoroboric acid (ca. 40%) (1 ml) until dissolution had been effected. The slow evolution of hydrogen was evident. The dichloromethane was removed and water was added slowly until crystallisation was complete. (Diethyl ether was also found to be effective for inducing crystallisation.) Recrystallisation from dichloromethane-ethanol-water yielded large colourless hexagonal crystals of the solvate $[OsH(H_2O)(CO)(PPh_3)_3]BF_4 \cdot (CH_3CH_2OH)$ (2.05 g, 96.5%). The ^1H NMR spectrum ($CDCl_3$) shows one ethanol per complex. M.p. 132—138°C. Anal. Found: C, 59.03; H, 4.66; P, 7.90. $C_{55}H_{48}BF_4O_2OsP_3 \cdot (CH_3CH_2OH)$ calcd.: C, 59.17; H, 4.70; P, 8.03%.

$[OsH(CO)_2(PPh_3)_3]BF_4$

$OsH_2(CO)_2(PPh_3)_3$ (1.85 g) was treated as above to afford a dichloromethane-methanol solution of $[OsH(H_2O)(CO)(PPh_3)_3]BF_4$. This solution was then heated under carbon monoxide (60 psi) to 80°C for 1.5 h. This solution was then usually used as a solution of $[OsH(CO)_2(PPh_3)_3]BF_4$. The product can be isolated by adding water which affords a colourless oil. Recrystallisation of this oil from ethanol yielded large colourless hexagonal crystals (1.35 g, 65.6%). M.p. 208—212°C. Anal. Found: C, 59.88; H, 4.30; P, 8.18. $C_{56}H_{46}BF_4O_2OsP_3$ calcd.: C, 60.00; H, 4.14; P, 8.23%.

$Os(CO)_2(PPh_3)_3$

A dichloromethane-methanol solution of $[OsH(CO)_2(PPh_3)_3]BF_4$ was prepared as described above from $OsH_2(CO)(PPh_3)_3$ (1.85 g). The dichloromethane was removed and methanol was added to bring the total volume of the solution to 60 ml. The solution was then heated to boiling under nitrogen and crushed sodium hydroxide (0.6 g) and triphenylphosphine (0.2 g) were added. The solution was heated under reflux for 1 h. The yellow needles were removed by filtration and washed with ethanol and hexane (1.8 g, 94.8%). Recrystallisation from benzene-petroleum spirit gave yellow prisms. M.p. 164—166°C. Anal. Found: C, 65.16; H, 4.54; P, 8.39. $C_{56}H_{45}O_2OsP_3$ calcd.: C, 65.73; H, 4.39; P, 9.00%.

$Os(\eta^2\text{-}CS_2)(CO)_2(PPh_3)_2$

$Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$ [5] (0.5 g) was heated under reflux in degassed benzene (50 ml) containing 10 ml of a degassed solution of carbon disulphide in benzene (1% w/w, 1.1 equiv.). The solution was heated under reflux for 30 min, and the solvent volume was reduced to 10 ml. Ethanol was added and the pink needles were collected (0.475 g, 89.6%). A sample was recrystallised from benzene-ethanol. M.p. 193—197°C. Anal. Found: C, 55.58; H, 3.90; P, 7.23. $C_{39}H_{30}O_2OsP_2S_2$ calcd.: C, 55.31; H, 3.54; P, 7.02%.

$Os(PhC_2Ph)(CO)_2(PPh_3)_2$

$Os(CO)_2(PPh_3)_3$ (0.5 g) and diphenylacetylene (0.2 g) were dissolved in benzene (20 ml) under nitrogen and exposed to a 500 watt quartz-halogen lamp. After 1—2 h, the orange solution was reduced in volume and petroleum spirit added. This solution was reduced in volume and more petroleum spirit added.

This procedure was repeated until precipitation was complete (0.42 g, 89%). A sample was recrystallized slowly from benzene-petroleum spirit as mustard-coloured needles of the benzene solvent (IR 750 cm^{-1}). M.p. 179—183°C. Anal. Found: C, 67.09; H, 4.62; P. 6.49. $C_{58}H_{46}O_2OsP_2$ calcd.: C, 67.82; H, 4.52; P, 6.03%.

cis-$OsH(C_2Ph)(CO)_2(PPh_3)_2$

$Os(CO)_2(PPh_3)_3$ (0.2 g) was dissolved in benzene (20 ml) under nitrogen. To this solution was added phenylacetylene (0.2 g). After several hours when the colour had faded to pale yellow, the solution was evaporated to an oil and the oil treated with petroleum spirit to give an off-white solid. The solid was recrystallized from dichloromethane-ethanol as cream needles (0.09 g, 55%). M.p. 222—225°C. Anal. Found: C, 63.10; H, 4.53; P, 7.02. $C_{46}H_{36}O_2OsP_2$ calcd.: C, 63.29; H, 4.16; P, 7.10%.

$[OsH(H_2O)(CS)(PPh_3)_3]BF_4$

$OsH_2(CS)(PPh_3)_3$ [10] (1.0 g) was dissolved in dichloromethane (25 ml), and ethanol (10 ml) and tetrafluoroboric acid (ca. 40%, 0.5 ml) were added. After effervescence had ceased the solvent volume was reduced to 5 ml. Slow addition of water effected crystallisation of white needles which were washed with an ethanol-water mixture (1/1) and dried at room temperature (1.05 g, 95.3%). An analytical sample was recrystallised from dichloromethane-ethanol-water. M.p. 140—143°C. Anal. Found: C, 58.61; H, 4.83; P, 8.48. $C_{55}H_{48}BF_4OOsP_3S$ calcd.: C, 58.61; H, 4.29; P, 8.24%.

$[OsH(H_2O)(CS)(PPh_3)_3]ClO_4$

$OsH_2(CS)(PPh_3)_3$ [10] (1.0 g) was dissolved in dichloromethane (25 ml), and ethanol (10 ml) and perchloric acid (70%, 0.5 ml) were added. After effervescence had ceased the solvent volume was reduced to 5 ml. Air contact with the solution was kept to a minimum. Slow addition of water effected crystallisation of white crystals of the 1/1 aquo solvate which were washed with an ethanol-water mixture (1/1) and dried at room temperature (1.07 g, 94.6%). ^1H NMR ($CDCl_3$) shows τ 6.26 [s, 2 H, coordinated H_2O] and τ 8.02 [s, 2 H, solvating H_2O]. Recrystallisation as for the BF_4^- salt above. M.p. 123—125°C. Anal. Found: C, 57.16; H, 4.39; P, 8.06. $C_{55}H_{48}ClO_5OsP_3S \cdot H_2O$ calcd.: C, 57.06; H, 4.35; P, 8.03%.

$[OsH(CO)(CS)(PPh_3)_3]ClO_4$

$OsH_2(CS)(PPh_3)_3$ [10] (2.0 g) was dissolved in dichloromethane (50 ml) and methanol (50 ml) containing perchloric acid (70%, w/w; 1 ml) was added. After hydrogen evolution had ceased the solution was stirred under an atmosphere of carbon monoxide for 2 h. The dichloromethane was removed and the resulting methanolic solution was used as a solution of the title compound for further reactions. A solid sample was obtained by adding water to precipitate the cationic complex as a pale yellow oil. The oil was dissolved in dichloromethane (30 ml) and washed twice with water (40 ml). Ethanol (2 ml) was added and the solution volume lowered to 10 ml. The rapid addition of petroleum spirit afforded a white floccular solid (2.1 g, 93.4%). M.p. 117—

119°C. This material was not of analytical purity but the IR and ^1H NMR spectra and further reactions confirm the formulation.

$Os(CO)(CS)(PPh_3)_3$

$OsH_2(CS)(PPh_3)_3$ (2.0 g) was treated as above to produce a methanolic solution of $[OsH(CO)(CS)(PPh_3)_3]ClO_4$ which was made up to a total volume of 60 ml with methanol and triphenylphosphine (0.2 g) was added. A stream of nitrogen was passed through the solution for 10 min and the degassed solution was then heated under reflux and crushed sodium hydroxide (1.0 g) was added. After 20 min the solution was allowed to cool to room temperature and the tan crystals were collected and washed with methanol and hexane and allowed to dry at room temperature (2.0 g, 97.5%). M.p. 159—161°C. Anal. Found: C, 63.75; H, 4.86. $C_{56}H_{45}OOsP_3S$ calcd.: C, 64.11; H, 4.32%.

$Os(CO)_2(CS)(PPh_3)_2$

$Os(CO)(CS)(PPh_3)_3$ (0.5 g) in degassed benzene (25 ml) was heated under carbon monoxide (100 psi) to 160°C until a pale-yellow solution had formed. Ethanol was added and removal of the benzene afforded yellow-orange crystals which were collected and washed with ethanol and hexane (0.34 g, 87.5%). The compound could be recrystallised without substantial loss from dichloromethane-ethanol to give orange platelets. M.p. 195—196°C. Anal. Found: C, 57.32; H, 3.96; P, 7.84. $C_{39}H_{30}O_2OsP_2S$ calcd.: C, 57.48; H, 3.71; P, 7.60%.

$Os(CO)(CS)(CNR)(PPh_3)_2$

$Os(CO)(CS)(PPh_3)_3$ (0.5 g) in degassed benzene (10 ml) and *p*-tolylisocyanide (0.06 g, 1.07 eq.) in degassed methanol (10 ml) were mixed and heated under reflux for 1 h. Addition of degassed methanol (60 ml) gave orange crystals which were collected and washed with methanol (0.26 g, 60.3%). M.p. 150—151°C. This compound was not analysed, the formulation follows from the IR spectrum and the protonation reaction described below.

$[OsH(CO)(CS)(CNR)(PPh_3)_2]ClO_4$

$Os(CO)(CS)(CNR)(PPh_3)_2$ (0.1 g) was added to a solution of ethanol (10 ml) containing perchloric acid (ca. 70%; 0.1 ml) and dichloromethane (20 ml) was added. On removal of the dichloromethane, colourless crystals deposited which were collected and washed with ethanol and hexane (0.1 g, 90%). Recrystallisation from dichloromethane-ethanol-cyclohexane afforded white needles of the solvate $[OsH(CO)(CS)(CNR)(PPh_3)_2]ClO_4 \cdot (C_6H_{12})_{0.67}$. ^1H NMR ($CDCl_3$) shows τ 7.88 [s, 8 H, C_6H_{12}]. M.p. 151—153°C. Anal. Found: C, 56.44; H, 4.47; N, 1.27. $C_{46}H_{38}ClNO_5OsP_2S \cdot (C_6H_{12})_{0.67}$ calcd.: C, 56.62; H, 4.37; N, 1.32%.

$Os(\eta^2\text{-}C_2H_4)(CO)(CS)(PPh_3)_2$

(a) $Os(CO)(CS)(PPh_3)_3$ (1.0 g) was stirred in degassed benzene (120 ml) in a 250 ml pyrex flask under an atmosphere of ethylene. The light from a 500 watt quartz-halogen sun lamp (Thorne) was directed at the flask which was cooled by a constant air flow across the surface. After 2 h the light source was removed and the solvent volume was reduced to 10 ml under reduced pressure with a continuous ethylene stream being passed through the solution. Ethanol was added to give a brown solid and the solvent volume was further reduced in open conditions. The brown solid was collected and washed with benzene until only a yellow crystalline solid remained which was washed with ethanol and dried at room temperature (0.12 g, 15.5%). M.p. 124—128°C. Anal. Found: C, 58.33; H, 5.18; P, 7.74. $C_{40}H_{34}OOsP_2S$ calcd.: C, 58.95; H, 4.21; P, 7.60%.

(b) The above process was repeated but hexane was used instead of ethanol to isolate the brown solid which was not washed with benzene but was instead reacted with ethylene in benzene as above. A further brown solid was similarly isolated from this reaction and a further repetition of the reaction gave a yellow solid (0.38 g, 48.9%) which was characterised by comparison of the IR spectrum with that of a sample produced by method (a).

$Os(\eta^2\text{-}CS_2)(CO)(CS)(PPh_3)_2$

$Os(CO)(CS)(PPh_3)_3$ (1.0 g) was heated under reflux in degassed benzene (60 ml) containing carbon disulphide (0.15 ml) for 30 min. The solvent volume was lowered to 20 ml, ethanol was added and the remaining benzene was removed. The yellow-orange feathery crystals were collected and washed with ethanol (0.8 g, 97.3%). M.p. 155—157°C. Anal. Found: C, 54.21; H, 3.81; P, 6.81. $C_{39}H_{30}OOsP_2S_3$ calcd.: C, 54.28; H, 3.50; P, 7.18%.

$OsHCl(CO)(CNR)(PPh_3)_2$

$OsHCl(CO)(PPh_3)_3$ (3.65 g) and *p-tolylisocyanide* (0.45 g) were heated under reflux in benzene (180 ml) for 10 min. The solution was cooled and evaporated with continual addition of ethanol (100 ml). When reduced to 50 ml, hexane (50 ml) was added to ensure complete crystallisation (3.14 g, 100%). Recrystallisation was from dichloromethane-ethanol. M.p. 246—249°C. Anal. Found: C, 60.45; H, 4.56; N, 1.53. $C_{45}H_{38}ClNOOsP_2$ calcd.: C, 60.30; H, 4.27; N, 1.57%.

$[OsH(H_2O)(CO)(CNR)(PPh_3)_2]ClO_4$

$OsHCl(CO)(CNR)(PPh_3)_2$ (2.10 g) and silver perchlorate (0.495 g) in a mixture of benzene (50 ml) and ethanol (20 ml) were heated under reflux for 3 h. The solvent was removed under reduced pressure and the residue dissolved in a minimum of dichloromethane and gravity filtered to yield a pale yellow solution. Ethanol (30 ml) was added and the solution treated with activated charcoal (0.2 g) and filtered. Removal of the solvent to 15—20 ml effected crystallization which was completed by the addition of hexane. The slightly sticky solid was filtered and washed on the filter with ice-cold ethanol (10 ml) to produce a free flowing white crystalline solid which was washed with hexane and dried at 60°C (2.10—2.20 g, 94—98%). Recrystallization for analysis was from dichloromethane-ethanol. M.p. 152—157°C. Anal. Found: C, 56.09; H, 4.54; N, 1.44. $C_{45}H_{40}ClNO_6OsP_2$ calcd.: C, 55.24; H, 4.12; N, 1.43%.

$[OsH(CO)(CNR)(PPh_3)_3](ClO)_4$

$[Os(H_2O)(CO)(CNR)(PPh_3)_2]ClO_4$ (1.47 g) and triphenylphosphine (0.5 g) in benzene (30 ml) were heated under reflux for 30 min. If the product deposited as an oil, the solution was cooled and seeded to give a white crystalline mass. Hexane (30 ml) was added and the solid removed by filtration. This product was used without purification (1.80 g, 96%). Recrystallization from dichloromethane-ethanol-cyclohexane yielded prisms of a mixed solvate, $[OsH(CO)(CNR)(PPh_3)_3](ClO_4)\cdot(CH_2Cl_2)\cdot(C_6H_{12})_{0.5}$. ^1H NMR ($CDCl_3$) shows τ 8.57 (s, 6 H, C_6H_{12}) and τ 4.70 (s, 2 H, CH_2Cl_2). M.p. 155—160°C. Anal. Found: C, 59.38; H, 4.77; N, 0.92. $C_{67}H_{61}Cl_3NO_5OsP_3$ calcd.: C, 59.63; H, 4.56; N, 1.04%.

$Os(CO)(CNR)(PPh_3)_3$

$[OsH(CO)(CNR)(PPh_3)_3]ClO_4$ (1.50 g) was dissolved in ethanol (20 ml) and the solution filtered. Crushed sodium hydroxide (0.6 g) was added and the solution heated under reflux for 8 h. The orange crystals were filtered and washed with ethanol and hexane (1.17, 85%). M.p. 148—152°C. Anal. Found: C, 67.09; H, 4.93; N, 1.24. $C_{63}H_{52}NOOsP_3$ calcd.: C, 67.41; H, 4.67; N, 1.25%.

$Os(\eta^2\text{-}C_2H_4)(CO)(CNR)(PPh_3)_2$

$Os(CO)(CNR)(PPh_3)_3$ (0.5 g) was dissolved in benzene (50 ml) in a 250 ml vessel and the vessel flushed with ethylene. After ca. 1 h in direct sunlight, (or under the quartz-halogen lamp) the solution faded to pale yellow. The solvent was evaporated and the slow addition of petroleum spirit resulted in the formation of pale yellow needles of the product (0.24 g, 60%). Recrystallization was from benzene-petroleum spirit. Characterization was limited to formation of the carbon disulphide adduct.

$Os(\eta^2\text{-}CS_2)(CO)(CNR)(PPh_3)_2$

To $Os(\eta^2\text{-}C_2H_4)(CO)(CNR)(PPh_3)_2$ (0.15 g) dissolved in benzene (20 ml) was added carbon disulphide (0.04 g). The mixture was heated under reflux for 5 min after which it was cooled and reduced in volume. The addition of ethanol gave orange crystals of the product which were recrystallized from dichloromethane-ethanol (0.13 g, 80%). M.p. 154—156°C. Anal. Found: C, 58.89; H, 4.19; N, 1.22; P, 6.59. $C_{46}H_{37}NOOsP_2S_2$ calcd.: C, 59.02; H, 3.99; N, 1.50; P, 6.62%.

$[OsH(H_2O)(CS)(CNR)(PPh_3)_2]ClO_4$

$OsHCl(CS)(CNR)(PPh_3)_2$ [10] (H *trans* to CNR) (0.5 g) was dissolved in dichloromethane (40 ml). Silver perchlorate (0.114 g, 1 eq.) in ethanol (15 ml) was added and the mixture was stirred for 15 min. Removal of the dichloromethane gave white crystals which were collected and washed with ethanol and hexane (0.51 g, 93.6%). Recrystallization from dichloromethane-ethanol gave large colourless crystals. M.p. 179—180°C. Anal. Found: C, 54.73; H, 4.32; N, 1.48. $C_{45}H_{40}ClNO_5OsP_2S$ calcd.: C, 54.34; H, 4.05; N, 1.41%.

$[OsH(CS)(CNR)(PPh_3)_3]ClO_4$

$[OsH(H_2O)(CS)(CNR)(PPh_3)_2]ClO_4$ (0.5 g) and triphenylphosphine (0.16 g) were heated under reflux in toluene (30 ml) for 2 h. Hexane was added and the lemon crystals were collected and washed with hexane (0.61 g, 97.9%). Recrystallization from dichloromethane-ethanol-cyclohexane gave large lemon crystals. M.p. 180°C. Anal. Found: C, 61.27; H, 4.32; N, 1.18; P, 7.79. $C_{63}H_{53}ClNO_4OsP_3S$ calcd.: C, 61.08; H, 4.31; N, 1.13; P, 7.50%.

Os(CS)(CNR)(PPh₃)₃

$[OsH(CS)(CNR)(PPh_3)_3]ClO_4$ (0.2 g) was heated under reflux in degassed ethanol (25 ml) containing triphenylphosphine (0.05 g) and sodium hydroxide (0.1 g) was added. After 8 h the solution was allowed to cool to room temperature and the red-orange crystals were collected and washed with ethanol and dried at room temperature (0.15 g, 81.6%). M.p. 141—143°C. Characterisation was limited to the IR spectrum.

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