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STEPWISE REDUCTION OF THE THIOCARBONYL LIGAND: HYDRIDE TRANSFER TO CS: THIOFORMYL, THIOFORMALDEHYDE, METHYLTHIOLATO, SECONDARY CARBENE, FORMYL AND IMINOFORMYL COMPLEXES OF OSMIUM

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Summary

The complexes $OsHX(CS)L(PPh_3)_2$ (X = Cl, Br; L = CO and X = Cl; L = CN-*p*-tolyl), which contain mutually *cis* hydrido and thiocarbonyl ligands, undergo transfer of the hydrido ligand to CS when treated with CO to give blue complexes containing the thioformyl ligand [Os—CHS]. $OsCl(CHS)(CO)_2(PPh_3)_2$ reacts with borohydride to give the first metal complex of the thioformaldehyde monomer, viz. $Os(\eta^2\text{-}CH_2S)(CO)_2(PPh_3)_2$, which reacts rapidly with HCl to give $OsCl(SCH_3)(CO)_2(PPh_3)_2$ and then, by a slower reaction, $OsCl_2(CO)_2(PPh_3)_2$ and CH_3SH. The ligands produced in this stepwise reduction have possible relevance as models for postulated intermediates in the Fischer—Tropsch synthesis. Synthetic routes to formyl [Os—CHO], iminoformyl [Os—CHNMe] and secondary carbene complexes [Os—CHSMe, Os—$CHNMe_2$, Os—CHOMe] are also demonstrated.

Introduction

Because of synthetic limitations, slow spasmodic growth has accompanied transition metal thiocarbonyl chemistry since the first complex, *trans*-$RhCl(CS)(PPh_3)_2$, was discovered in 1966 [1]. This area of chemistry is still small and encompasses fewer than two hundred thiocarbonyl compounds in approximately one hundred publications. An increasing number of reports have dealt with CS ligand reactions and well-characterised reaction types include: (i) nucleophilic attack at the CS carbon atom [2—11]; (ii) electrophilic attack at the CS sulphur atom (including the formation of end-to-end bridging CS dinuclear complexes) [12,13]; (iii) intramolecular isomerisation reactions involving bridging CS ligands [9,13,14]; and (iv) an intramolecular condensation reaction between CS and a thiocarboxamido ligand [15]. These studies point to the considerable versatility of the CS ligand as a reactive centre. Until recently [11,16] however, reactions of the ligand-transfer type had not been reported for the thiocarbonyl

ligand primarily because complexes containing suitable ligand combinations such as hydrido, alkyl or aryl ligands *cis* to CS were rare or not known. Here our earlier communications [16,17] concerning transfer of the hydrido ligand to CS and the further reactions of the resulting thioformyl complexes are reported in detail.

Results and discussion

In Tables 1 and 2 the IR and NMR spectra of osmium hydrido-thiocarbonyl complexes are given, while in Tables 3 and 4 the spectra of osmium thioformyl and derived complexes are reported. Table 5 lists the IR and NMR data for related adducts of $Os(CO)_2(PPh_3)_2$.

Treatment of $OsCl_2(CS)(PPh_3)_3$ [18] with sodium hydroxide in 2-methoxyethanol gives $OsH_2(CS)(PPh_3)_3$, which contains meridional phosphine and *cis*-hydrido ligands, as indicated by the ^1H NMR spectrum (Table 2). If ethanol is used as the solvent then $OsHCl(CS)(PPh_3)_3$ can be observed as an intermediate complex. Reaction of $OsH_2(CS)(PPh_3)_3$ with HCl or HBr in dichloromethane/ethanol at ambient temperatures results in the rapid cleavage of one hydrido ligand and formation of $OsHX(CS)(PPh_3)_3$. If $OsHCl(CS)(PPh_3)_3$ is heated under reflux in benzene/ethanol with excess HCl then slow cleavage of the second hydride ensues to afford $OsCl_2(CS)(PPh_3)_3$ (eq. 1).

$$OsCl_2(CS)(PPh_3)_3 \underset{HCl}{\overset{OH^-/EtOH}{\rightleftharpoons}} OsHCl(CS)(PPh_3)_3 \underset{HCl}{\overset{OH^-,\ ROH}{\rightleftharpoons}} OsH_2(CS)(PPh_3)_3$$

(R = $CH_2CH_2OCH_3$)

The ^1H NMR spectra of $OsHX(CS)(PPh_3)_3$ (Table 2) show that the hydrido ligand is *cis* to two mutually *trans* phosphine ligands and *trans* to the third phosphine ligand. Consequently, the hydrido and thiocarbonyl ligands are mutually *cis*.

TABLE 1

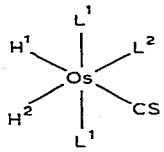
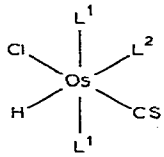
IR [a] (cm^{-1}) DATA FOR OSMIUM HYDRIDO—THIOCARBONYL COMPLEXES (L = PPh_3, R = *p*-tolyl)

Compound	ν(CS) [b]	ν(OsH)	δ(OsH)	ν(CO) [b]	ν(CN) [b]
$OsH_2(CS)L_3$	1233	2070s, 1895s	800w, 775w		
$OsHCl(CS)L_3$	1280	2100wm	820w		
$OsHBr(CS)L_3$	1273	2110wm	810w		
$OsHCl(CS)(CNR)L_2$ [c]	1275	1950w	[e]		2145
$OsHCl(CS)(CNR)L_2$ [d]	1282	1957wm	[e]		2145
$OsHCl(CO)(CS)L_2$	1295	1960m	825w, 785w	2050	
$OsHBr(CO)(CS)L_2$	1300	1958ms	820w, 787w	2050	

[a] Nujol mulls. [b] Very strong. [c] [CS *trans* to Cl + CS *trans* to CNR]. [d] CS *trans* to Cl. [e] Band obscured by arene δ(CH) at 818 cm^{-1}.

TABLE 2

^{1}H NMR [a] (τ, ppm) DATA FOR OSMIUM HYDRIDO—THIOCARBONYL COMPLEXES

Compound (L = PPh_3, R = *p*-tolyl)	Hydride chemical shift	Coupling constants (Hz)
	20.43, dtb [b], H^1	$^2J(H^1—P^1)$ 26.2 $^2J(H^1—P^2)$ 23.3 $^2J(H^1—H^2)$ 5.5
	17.32, dtb [b], H^2	$^2J(H^2—P^1)$ 28.0 $^2J(H^2—P^2)$ 60.5
	15.50, dt	$^2J(H—P^1)$ 24.5 $^2J(H—P^2)$ 93.0
$OsHBr(CS)L_3$ [c]	16.04, dt	$^2J(H—P^1)$ 24.0 $^2J(H—P^2)$ 89.0
$OsHCl(CS)(CNR)L_2$ (H *trans* to Cl)	23.78, t	$^2J(H—P)$ 13.2
$OsHCl(CS)(CNR)L_2$ (H *trans* to CNR)	12.75, t	$^2J(H—P)$ 19.0

[a] $CDCl_3$ solution. [b] dtb = double triplet of doublets. [c] Meridional phosphines and H *trans* to phosphine as for $OsHCl(CS)L_3$.

One phosphine ligand in $OsHX(CS)(PPh_3)_3$ [X = Cl, Br] is labile and is readily displaced by neutral ligands such as carbon monoxide and *p*-tolylisocyanide. When *mer*-$OsHCl(CS)(PPh_3)_3$ is treated with *p*-tolylisocyanide, yellow $OsHCl(CS)(CNR)(PPh_3)_2$ (R = *p*-tolyl) is formed which exhibits an hydride ^{1}H NMR triplet resonance at the very high field value of τ 23.78 ppm. This value can be compared with the corresponding value for $OsHCl(CO)(CNR)(PPh_3)_2$, τ 14.76 ppm (H *trans* to CNR) [19] or for $OsHCl(CO)_2(PPh_3)_2$, τ 13.70 ppm (H *trans* to CO) [20]. The high field value of τ 23.78 ppm suggests that $OsHCl(CS)(CNR)(PPh_3)_2$ has geometry I (Fig. 1) since hydride resonances at similar high field values were found for the complexes $RuHX(CO)(CNR)(PPh_3)_2$ with H *trans* to X [21]. Isomer I isomerises on heating in benzene to produce a further colourless isomer which displays a hydride triplet resonance at τ 12.75 ppm. That this isomer has geometry II and not geometry III is suggested by the facile trans-

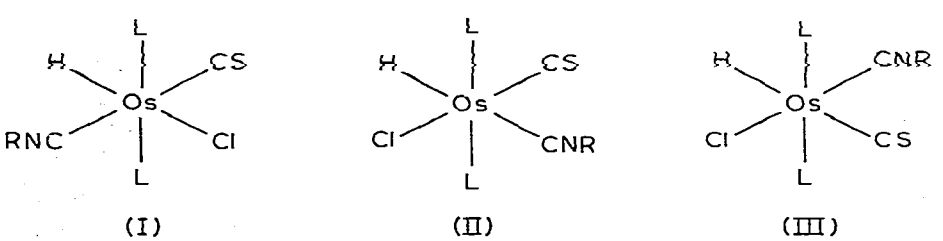


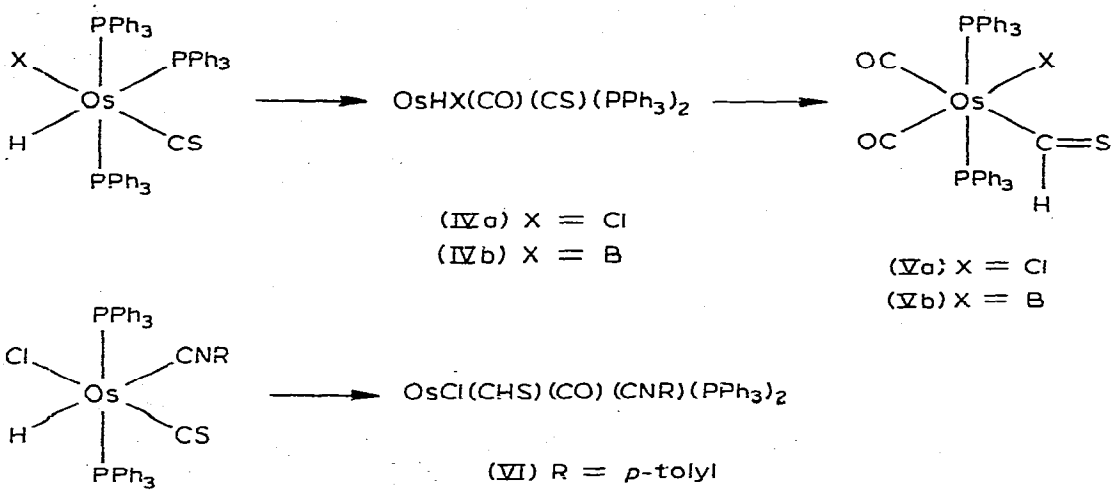
Fig. 1. Possible geometrical conformations of $OsHCl(CS)(CNR)L_2$ (L = PPh_3, R = *p*-tolyl).

fer of the hydrido ligand to the thiocarbonyl ligand which occurs when this compound is treated with carbon monoxide (implying *cis* H and CS).

Hydride transfer from metal to ligand has been achieved in this laboratory for coordinated isocyanide [22] and the nitrosyl ligand [23]. Similar reactions are probably also involved in the reduction of some carbenetungsten complexes with hydrogen to afford alkanes, although the intermediate alkyl complexes could not be isolated [24].

When benzene solutions of the colourless compounds II and $OsHX(CS)(PPh_3)_3$ are stirred under CO (40 psi) an intense blue colouration develops and addition of n-hexane affords blue crystals of the monodentate thioformyl containing complexes Va, Vb and VI in quantitative yields (Scheme 1).

SCHEME 1



The intermediate complexes IVa and IVb can be isolated if only one equivalent of CO is treated with $OsHX(CS)(PPh_3)_3$, but in the presence of excess CO at room temperature the thioformyl complexes are the only observed products. That the transfer reaction is reversible is demonstrated by the regeneration of IVa when Va is heated in dichloromethane for 9 h. Considerable decomposition accompanies this reaction. Two medium intense bands in the IR spectrum (Table 3) of each thioformyl complex occur near 1000 and 1200 cm^{-1} which can be attributed to the monodentate thioformyl ligand. A further weak band near 2830 cm^{-1} is assigned to the thioformyl ν(CH) vibration. The thioformyl proton appears in the ^1H NMR spectra in the very low field range of τ −6.93 to −7.73 ppm and weak coupling with the ^{31}P nuclei (t, ^3J(H—P) 3 Hz) is observed (Table 4).

Surprisingly, the intermediate compounds IVa and IVb do not exhibit an hydride resonance in deuterobenzene or deuterochloroform in the ^1H NMR spectra at 40°C. Yet carbonylation of the ^1H NMR samples leads to formation of the thioformyl complexes and ν(OsH) and δ(OsH) bands can be observed in the IR spectra. This is in contrast to II which both exhibits an hydride resonance and forms a thioformyl complex. One apparent explanation for this differing behaviour is that an equilibrium, which is fast on the NMR time scale, exists

TABLE 3

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

Compound [b] (L = PPh_3, R = *p*-tolyl)	ν(CO) [b]	ν(CN)	Other bands
$OsCl(CHS)(CO)_2L_2$	2050, 1970		2867w ν(CH); 1190ms, 1010m (CHS)
$OsBr(CHS)(CO)_2L_2$	2040, 2021, 1978, 1953 [e]		2865w ν(CH); 1190ms, 1011m (CHS)
$OsCl(CHS)(CO)(CNR)L_2$	1972	2130vs	2840w ν(CH); 1184m, 1000m (CHS)
$Os(\eta^2\text{-}CH_2S)(CO)_2L_2$	1985, 1915		558m ν(CS)
$OsCl(SMe)(CO)_2L_2$	2038, 1950		
$[OsCl(\eta^2\text{-}CH_2SMe)(CO)_2L_2]\text{-}CF_3SO_3$	2035, 1954		558m ν(CS) [d]
$OsCl(\eta^1\text{-}CH_2SMe)(CO)_2L_2$	2025, 2005 1952, 1934 [e]		565m ν(CS)
$[OsCl(\eta^1\text{-}CH_2SMe_2)(CO)_2L_2]\text{-}CF_3SO_3$	2035, 1957		570w ν(CS)
$[OsCl(CHSMe)(CO)_2L_2]^+$ [c]	2050, 1996		965wm [f] (carbene) [d,g]
$[OsBr(CHSMe)(CO)_2L_2]\text{-}CF_3SO_3$	2055, 1995		965wm [f] (carbene) [d]
$[OsCl(CHSMe)(CO)(CNR)L_2]\text{-}CF_3SO_3$	2003	2155vs	954m [f] (carbene) [d]
$[OsCl(CHNHMe)(CO)_2L_2]\text{-}ClO_4$	2060, 1982	1610s [h]	3245w, 2975w ν(NH); 810w (carbene) [i]
$OsCl(CHNMe)(CO)_2L_2$	2030, 1953	1589s	2747wm ν(CH); 970w (iminoformyl)
$OsCl(CHO)(CO)_2L_2$	2020, 1960 [i]		2660w, 2540w ν(CH); 1610s ν(C=O)
$OsBr(CHO)(CO)_2L_2$	2040, 1970 [i]		2695w, 2555w, ν(CH); 1609ms (νC=O)
$OsCl(CHO)(CO)(CNR)L_2$	1965, 1950 [e]	2120vs	2685w, 2564w, 2515wm ν(CH); 1602s, 1596s, 1572wm ν(C=O)
$[OsCl(CHOMe)(CO)(CNR)L_2]\text{-}CF_3SO_3$	2005	2155vs	1240s (carbene) [d]

[a] Nujol mulls. [b] Very strong. [c] Isolated as $CF_3SO_3^-$ and ClO_4^- salts. [d] CF_3SO_3 bands at 1270vs, 1225m, 1150s, 1030vs, 640vs. [e] Solid state splitting gives multiple bands. [f] Broad band. [g] ClO_4 bands ca. 1095vs, 620s. [h] δ(NH) obscured by this band. [i] ν(CO) bands due to $OsX(CHO)(CO)_2L_2$ and $OsHX(CO)_2L_2$.

between V and the five-coordinate intermediates $OsX(CHS)(CO)(PPh_3)_2$. These intermediates react with CO to give the thioformyl products.

Hydride transfer to form a thioformyl ligand represents a logical first step in the complete reduction of carbon monosulphide to methyl thiol. The reduction of carbon monoxide by hydrogen to hydrocarbon products, of which methanol is one constituent, is commonly referred to as the Fischer—Tropsch synthesis [25]. This process is heterogeneously catalysed and if there is a valid analogy between transition metal complexes and the intermediate species which exist in reactions at metal surfaces then a major contribution of organometallic chemistry to surface reactions is to provide well-characterised models for plausible intermediates [26]. The mechanism of the Fischer—Tropsch reaction has been a subject of considerable speculation [25,27]. The formyl ligand [28] is an attractive possibility for the product of the first reduction step. Formaldehyde

TABLE 4

^{1}H NMR [a] (τ, ppm) DATA FOR OSMIUM THIOFORMYL AND DERIVED COMPLEXES

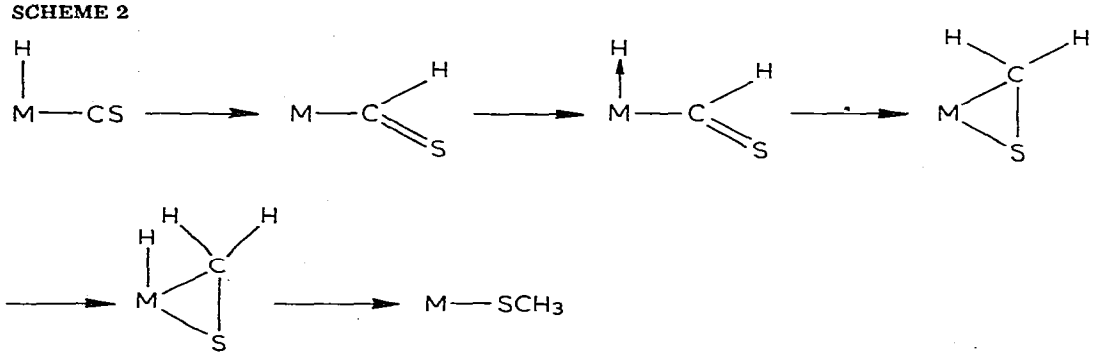
Compound (L = PPh_3, R = *p*-tolyl)	Chemical shift and coupling constants (Hz)
$OsCl(CHS)(CO)_2L_2$	—6.93, t, 1H, —CHS, ^3J(H—P) 2.2 —7.73, t, 1H, —CHS, ^3J(H—P) 2.5 (in C_6D_6)
$OsBr(CHS)(CO)_2L_2$	(a) —7.19, t, —CHS, ^3J(H—P) 2.3 (b) in C_6D_6: —7.86, t, 1H, —CHS, ^3J(H—P) 2.5
$OsCl(CHS)(CO)(CNR)L_2$	7.68, s, 3H, C_6H_4—CH_3 3.35, q, 4H, —C_6H_4— —7.50, t, 1H, CHS, ^3J(H—P) 2.3
$Os(\eta^2\text{-}CH_2S)(CO)_2L_2$	9.1, t, 2H, CH_2S, ^3J(H—P) 4.6
$OsCl(SMe)(CO)_2L_2$	8.67, s, 3H, S—CH_3
$[Os(\eta^2\text{-}CH_2SMe)(CO)_2L_2]CF_3SO_3$	8.26—8.14, m, [c] —CH_2SMe, 5H 8.18, s, S—CH_3
$OsCl(\eta^1\text{-}CH_2SMe)(CO)_2L_2$	8.47, s, 3H, S—CH_3 8.18, t, 2H, —CH_2SMe, ^3J(H—P) 9
$[OsCl(\eta^1\text{-}CH_2SMe_2)(CO)_2L_2]CF_3SO_3$	7.95, s, 6H, —$CH_2S(CH_3)_2$ 7.58, t, 2H, —CH_2SMe_2, ^3J(H—P) 7
$[OsCl(CHSMe)(CO)_2L_2]CF_3SO_3$	7.60, m, 3H, s—CH_3 —4.70, m, 1H, —CHSMe
$[OsCl(CHSMe)(CO)_2L_2]ClO_4$	7.63, m, 3H, S—CH_3 —4.70, m, 1H, —CHSMe
$[OsBr(CHSMe)(CO)_2L_2]CF_3SO_3$	7.65, m, 3H, S—CH_3 —4.68, m, 1H, —CHSMe
$[OsCl(CHSMe)(CO)(CNR)L_2]CF_3SO_3$	7.67, m, 6H, S—CH_3 + C_6H_4—CH_3 3.05, q, 4H, —C_6H_4— —4.91, m, 1H, —CHSMe
$[OsCl(CHNHMe)(CO)_2L_2]ClO_4$	7.57, m, 3H, N—CH_3 —0.13, m, 1H, —CHNHMe —0.48, s(br), 1H, N—H [b]
$OsCl(CHNMe)(CO)_2L_2$	6.15, m, 3H, N—CH_3 —0.73, m, 1H, —CHNMe
$OsBr(CHO)(CO)_2L_2$	—4.4, s(br), transient signal
$OsCl(CHO)(CO)(CNR)L_2$	6.55, s, 3H, C_6H_4—CH_3 3.35, q, 4H, —C_6H_4— —4.45, m, 1H, —CHO
$[OsCl(CHOMe)(CO)(CNR)L_2]CF_3SO_3$	7.67, s, 3H, C_6H_4—CH_3 6.03, m, 1H, O—CH_3 5.38, m, 2H, O—CH_3 3.28, m, 4H, —C_6H_4— —2.03, s(br), 0.3H, —CHOMe —3.05, s(br), 0.5H, —CHOMe

[a] $CDCl_3$ solution. [b] Exchanges with D_2O. [c] Triplet pattern obscured by S—Me signal.

complexes, for which no well-characterised examples exist, would provide a worthy clue to the nature of the second step, and methoxy complexes, for which numerous organometallic examples exist, suggest a logical third step for that part of the reaction sequence that leads to methanol. Several mononuclear transition metal complexes promote the stoichiometric reduction of carbon

monoxide, but produce different products [29—31]. Stepwise hydride migration to the carbonyl ligand to produce a formyl or formaldehyde complex has never been observed although $(\eta^5\text{-}C_5Me_5)_2ZrH(OCH_3)$ is formed when $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$ is treated with hydrogen [29]. A similar result was found when the preparation of $IrH_3(CS)(PPh_3)_2$ from $IrH(CS)(PPh_3)_3$ and hydrogen was attempted, the product being $IrH_2(SCH_3)(PPh_3)_3$ [11]. The complete reduction of an osmium thiocarbonyl complex to an hydridothiolato containing complex by one single stepwise reaction has not been achieved but, in addition to the thioformyl complexes described above, we have isolated a stable osmium complex of the thioformaldehyde ligand, which was postulated as a further intermediate in the reduction of the CS ligand to the methylthiolato ligand [11] (Scheme 2).

SCHEME 2



Two approaches to the problem of synthesising an osmium complex of the unstable thioformaldehyde monomer have been investigated; (i) inducing the transfer of both hydrides of $OsH_2(CS)(PPh_3)_3$ through reaction with CO and (ii) reaction of the thioformyl complex $OsCl(CHS)(CO)_2(PPh_3)_2$ with $NaBH_4$.

Because of the inertness of $OsH_2(CS)(PPh_3)_3$, vigorous conditions are necessary (CO at 4 atm, 140°C for 1 h) to induce any reaction to occur and two colourless products which vary in relative yields are obtained. One product is an exceptionally insoluble complex which can be shown by qualitative elemental analysis to contain sulphur and which exhibits two ν(CO) bands in the IR spectrum at 1930 and 1990 cm^{-1}. It is thought that this complex probably contains thioformaldehyde as a bridging ligand, but the product has not been further characterised. The second product is $Os(\eta^2\text{-}CH_2S)(CO)_2(PPh_3)_2$.

Gentle heating of the thioformyl complex $OsCl(CHS)(CO)_2(PPh_3)_2$ in dichloromethane with an ethanolic solution of $NaBH_4$ produces a gradual colour change which eventually leads to a faintly yellow solution. Removal of dichloromethane affords colourless crystals of the thioformaldehyde adduct $Os(\eta^2\text{-}CH_2S)(CO)_2(PPh_3)_2$ in high yield which are contaminated by small quantities of an unidentified product (ν(CO) bands at 2025 and 1942 cm^{-1}). The pure thioformaldehyde adduct can be obtained by recrystallisation from dichloromethane/benzene, but the yield is considerably reduced by this purification procedure. Purification prior to methylation (see below) did not prove necessary since the impurity did not interfere with this reaction and could be easily separated from the methylated product. The interesting observation can be made from Table 5 that the ν(CO) bands of the adducts of $Os(CO)_2(PPh_3)_2$ represented increase with the unsaturated addend according to the series $C_2H_4 < CH_2S < S_2 < S_2Me^+$.

TABLE 5

IR [a] (cm^{-1}) AND ^1H NMR [b] (τ, ppm) DATA FOR RELATED ADDUCTS OF $Os(CO)_2(PPh_3)_2$

Compound (L = PPh_3)	ν(CO)	Chemical shift and coupling constants (Hz)	Ref.
$Os(\eta^2\text{-}C_2H_4)(CO)_2L_2$	1955, 1895	9.55, t, 4H, ^3J(H—P) 7	20
$Os(\eta^2\text{-}CH_2S)(CO)_2L_2$	1985, 1915	9.1, t, 2H, ^3J(H—P) 4.6	
$Os(\eta^2\text{-}S_2)(CO)_2L_2$	1998, 1944		34
$[Os(\eta^2\text{-}S_2Me)(CO)_2L_2]^+$	2045, 1980	8.0, s, 3H, S—CH_3	34

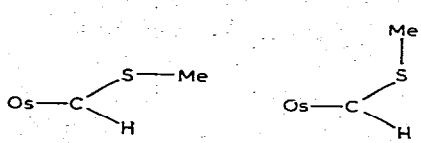
[a] Nujol mulls. [b] $CDCl_3$ solution.

The degree of electron transfer from metal to ligand thus increases in the same order and the ν(CO) values indicate that CH_2S is a better electron acceptor than C_2H_4. As numerous ethylene adducts of low valent metal centres are known many thioformaldehyde adducts ought to be stable.

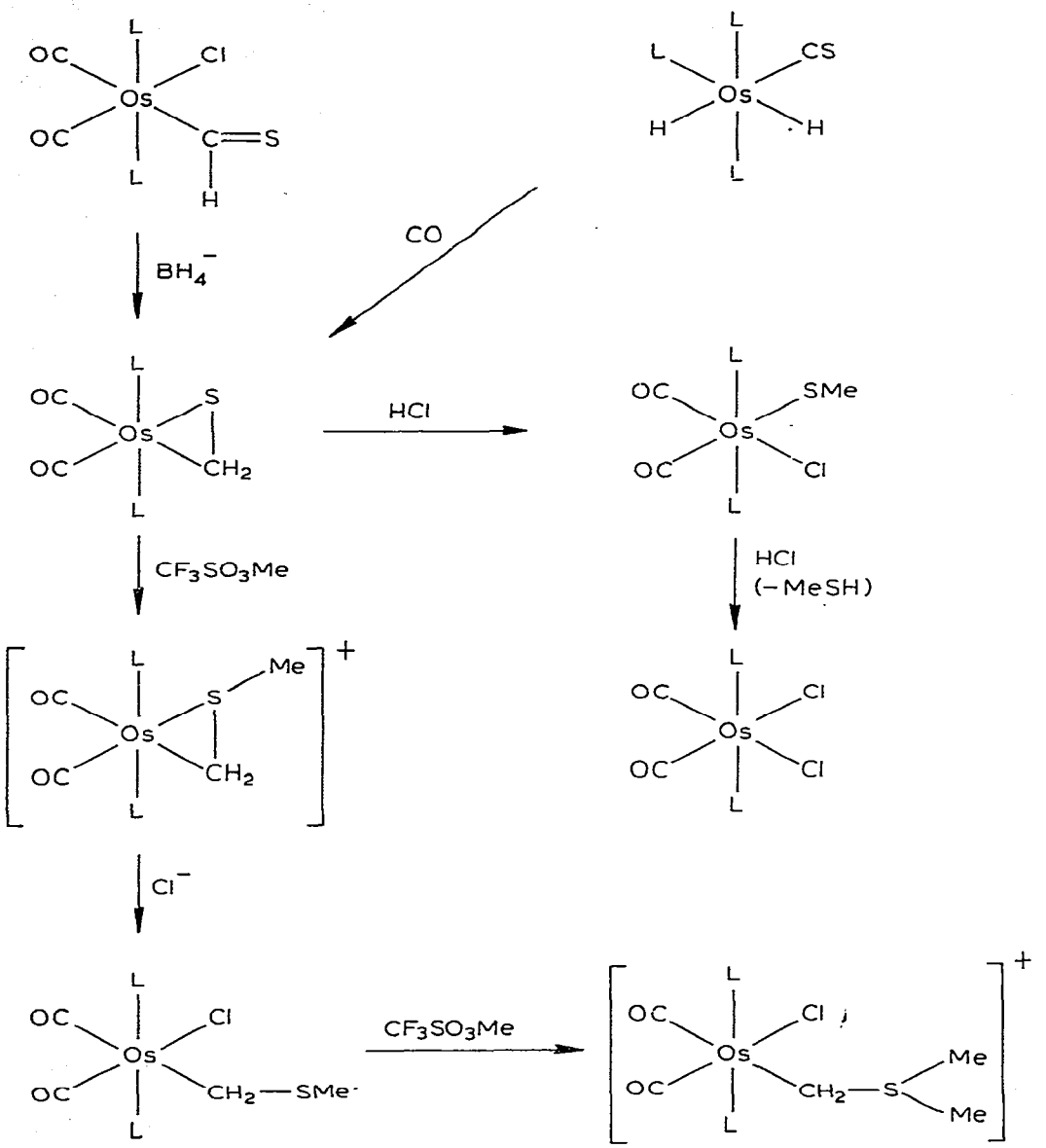
Treatment of $Os(\eta^2\text{-}CH_2S)(CO)_2(PPh_3)_2$ with HCl in dichloromethane/ethanol rapidly yields the methylthiolato-containing complex $OsCl(SMe)(CO)_2(PPh_3)_2$ (probably via initial protonation at the metal) (Scheme 3). If this compound is heated gently in the same reaction medium, methyl thiol elimination ensues to afford $OsCl_2(CO)_2(PPh_3)_2$. Thus suitable examples are now available of thioformyl, thioformaldehyde and methylthiolato complexes which are the sulphur equivalents of intermediates postulated by some authors to occur in that part of the Fischer—Tropsch synthesis [25a,27a] which leads to methanol and which probably form in stepwise fashion in the hydrogenation of CS in $IrH(CS)(PPh_3)_3$ [11].

In contrast, alkylation with methyl triflate occurs at the sulphur atom to yield $[Os(\eta^2\text{-}CH_2SMe)(CO)_2(PPh_3)_2]^+$. Chloride ion brings about ring-opening, forming $OsCl(\eta^1\text{-}CH_2SMe)(CO)_2(PPh_3)_2$ and further methylation with methyl triflate affords $[OsCl(\eta^1\text{-}CH_2SMe_2)(CO)_2(PPh_3)_2]^+$. The thioformaldehyde complex and methylated derivatives exhibit a weak band in the IR spectrum near 560 cm^{-1} which is in the lower part of the range found for the ν(CS) vibration in aliphatic sulphides.

When methyl triflate is added to a benzene solution containing a thioformyl complex, a rapid colour change from blue to bright yellow occurs and addition of n-hexane affords the resulting methylthiolatocarbene cations $[OsX(CHSMe)(CO)_2(PPh_3)_2]^+$ and $[OsCl(CHSMe)(CO)(CNR)(PPh_3)_2]^+$ in quantitative yields. On methylation the thioformyl proton resonance in the NMR is shifted ca. 2 ppm upfield (Table 4), but the carbene proton no longer exhibits a simple triplet coupling pattern with the ^{31}P nuclei. Instead, one multiplet resonance for each complex near τ — 5 ppm is observed and the *S*-methyl signal is also a single structured resonance near τ 8.6 ppm. It is unlikely that this structuring is due to geometrical isomers of the carbene ligand, i.e.: since a larger separation of signals



SCHEME 3

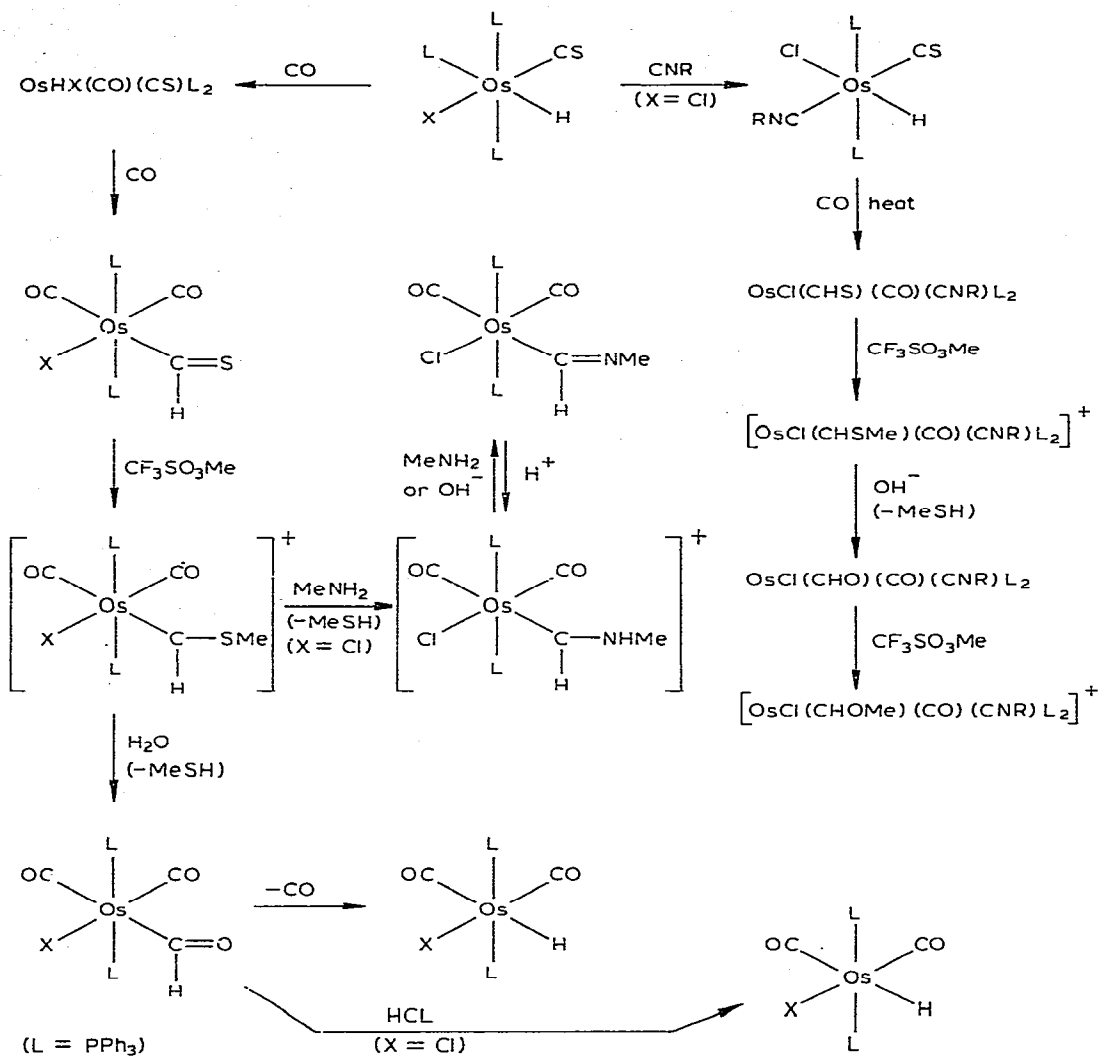


(L = PPh_3)

is observed for such isomerism [32] as in $[OsCl(CHOMe)(CO)(CNR)(PPh_3)_2]^+$ (see below). Coupling within the carbene ligand and long range coupling with the ^{31}P nuclei is the probable source of this structuring.

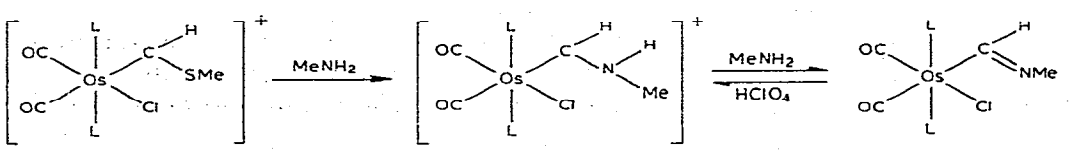
These secondary carbene complexes have proved to be very useful synthetic intermediates and, in keeping with the generally recognised electrophilic character of the carbene carbon atom [33], are reactive towards nucleophiles (see Scheme 4).

SCHEME 4



Treatment of $[OsCl(CHSMe)(CO)_2(PPh_3)_2]^+$ with excess methylamine affords the iminoformyl complex $OsCl(CHNMe)(CO)_2(PPh_3)_2$. The reaction proceeds through the intermediate carbene containing cation $[OsCl(CHNMe)(CO)_2(PPh_3)_2]^+$, which can be isolated in poor yield when one equivalent of amine is used (Scheme 5). The iminoformyl complex is protonated by $HClO_4$ to return the intermediate

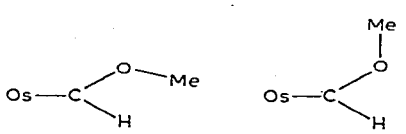
SCHEME 5



carbene cation. The ^1H NMR spectra (Table 4) suggest that only one isomer of the iminoformyl and aminocarbene complexes is present.

The thiolatocarbene complexes are so reactive with nucleophiles that a reaction occurs between the solids and moist air which results in the evolution of methyl thiol. When $[OsX(CHSMe)(CO)_2(PPh_3)_2]CF_3SO_3$ are recrystallised from dichloromethane/ethanol/water (below room temperature) white crystals of the formyl-containing complexes $OsX(CHO)(CO)_2(PPh_3)_2$ are deposited. The hydrolysis reaction is suppressed by acid and recrystallisation of $[OsCl(CHSMe)(CO)_2(PPh_3)_2]CF_3SO_3$ from dichloromethane/ethanol containing perchloric acid gives $[OsCl(CHSMe)(CO)_2(PPh_3)_2]ClO_4$. The formyl complexes are contaminated by $OsHX(CO)_2(PPh_3)_2$ and if these mixtures are recrystallised from any of the solvents dichloromethane, chloroform or benzene with ethanol then CO displacement is rapid and formation of $OsHX(CO)_2(PPh_3)_2$ is quantitative. Solid samples appear to be indefinitely stable in the absence of light. Similar behaviour was observed for $[Fe(CHO)(CO)_4]^-$, but the formation of $[FeH(CO)_4]^-$ in solution was much slower [28a]. The solution instability of $OsX(CHO)(CO)_2(PPh_3)_2$ has prevented further characterisation of these compounds. A transient signal was observed at τ —4.4 ppm in the ^1H NMR spectrum of $OsBr(CHO)(CO)_2(PPh_3)_2$ when the solid was dissolved in $CDCl_3$ and the region between τ —5 to —3 ppm scanned immediately (cf. $[Fe(CHO)(CO)_4]^-$ τ —4.95 ppm [28a]. It has been suggested that $OsCl(CHO)(CO)_2(PPh_3)_2$ may be involved in the fast reaction of $Os(CO)_3(PPh_3)_2$ which gives $OsCl_2(CO)_2(PPh_3)_2$ [16]. However, when $OsCl(CHO)(CO)_2(PPh_3)_2$ is added to a dichloromethane/ethanol solution containing HCl, $OsHCl(CO)_2(PPh_3)_2$ is obtained and there is no evidence to suggest the formation of any $OsCl_2(CO)_2(PPh_3)_2$.

The isocyanide-containing thiolatocarbene complex $[OsCl(CHSMe)(CO)(CNR)(PPh_3)_2]CF_3SO_3$ is more resistant to hydrolysis than the dicarbonyl analogues and reacts only very slowly with water to produce the formyl complex $OsCl(CHO)(CO)(CNR)(PPh_3)_2$. In dichloromethane/ethanol/water solution containing NaOH hydrolysis proceeds rapidly and $OsCl(CHO)(CO)(CNR)(PPh_3)_2$ can be isolated in a pure form. In contrast, if base is added in the hydrolyses of $[OsX(CHSMe)(CO)_2(PPh_3)_2]^+$ then the only products observed are $OsHX(CO)_2(PPh_3)_2$. Recrystallisation of $OsCl(CHO)(CO)(CNR)(PPh_3)_2$ occurs without apparent decomposition. That only one geometrical isomer is formed is indicated by the presence of only one broad singlet formyl proton resonance in the NMR spectrum at τ —4.45 ppm. As found for the thioformyl complexes, $OsCl(CHO)(CO)(CNR)(PPh_3)_2$ is alkylated by methyl triflate. The resulting methoxycarbene-containing product $[OsCl(CHOMe)(CO)(CNR)(PPh_3)_2]CF_3SO_3$ is the sole example of a stable formyl ligand reaction derivative. Two separate signals are observed in the ^1H NMR spectrum for the —CHOMe and O—CH_3 resonances (τ —3.05 ppm, 0.5H, τ —2.03 ppm, 0.3H—CHOMe; τ 5.38 ppm, 2H, τ 6.03 ppm, 1H, O—CH_3) indicating the presence of geometrical isomers for the carbene ligand, i.e.:



The same structuring is observed for each of these resonances as was noted for

the carbene and iminoformyl complexes discussed above, indicating coupling within the carbene ligand and with the ^{31}P nuclei.

Experimental

Solvents were degassed either by the freeze-thaw method using nitrogen (<6 vpm oxygen) or by passing a stream of nitrogen through the boiling solvent for 10 minutes prior to use. Reactions involving heating under reflux were performed in a nitrogen atmosphere. Characterisation of new compounds was achieved by means of elemental analysis, IR and ^1H NMR spectroscopy. Analytical data were obtained from the Microanalytical Laboratory, University of Otago and these services of Prof. A.D. Campbell are gratefully acknowledged. IR spectra (4000—400 cm^{-1}) were measured on a Shimadzu IR 27g spectrometer or a Perkin—Elmer 397 spectrometer as Nujol mulls or dichloromethane solutions between KBr plates. ^1H NMR spectra were recorded on a Varian Associates T60 spectrometer using tetramethylsilane (τ 10 ppm) as internal calibrant. Melting points (uncorrected) were measured on a Reichert hot-stage microscope. Osmium tetroxide was obtained commercially from Johnson—Matthey Chemicals Limited. $(NH_4)_2[OsCl_6]$ [35] and $OsCl_2(PPh_3)_3$ [36] were prepared by the literature methods.

$OsH_2(CS)(PPh_3)_3$. $OsCl_2(CS)(PPh_3)_3$ (2.0 g), triphenylphosphine (0.1 g) and sodium hydroxide (0.5 g) were heated under reflux in 2-methoxyethanol (20 ml) for 20 min. The resulting suspension was cooled on ice. Filtration gave vivid white crystals which were redissolved in dichloromethane and filtered through a celite pad. Ethanol was added and on removal of the dichloromethane vivid white crystals deposited (1.72 g, 91.8%). M.p. 174—176°C. Anal. Found: C, 64.58; H, 5.00; P, 8.95. $C_{55}H_{47}OsP_3S$ calcd.: C, 64.56; H, 4.67; P, 9.08%.

$OsHCl(CS)(PPh_3)_3$. $OsH_2(CS)(PPh_3)_3$ (1.0 g) was dissolved in dichloromethane (25 ml), and ethanol (10 ml) and concentrated hydrochloric acid (0.5 ml) were added. Vigorous hydrogen evolution ensued and when this had ceased the dichloromethane was removed to afford vivid white crystals which formed vivid white crystals of the hemidichloromethane solvate when recrystallised from dichloromethane/ethanol (1.06 g, 98.6%). ^1H NMR ($CDCl_3$) shows τ 4.73 ppm (s, 1H, CH_2Cl_2). M.p. 171—174°C. Anal. Found: C, 60.52; H, 4.61; P, 8.17%. $C_{55}H_{46}ClOsP_3S(CH_2Cl_2)_{0.5}$ calcd.: C, 60.59; H, 4.30; P, 8.45%.

$OsHBr(CS)(PPh_3)_3$. $OsH_2(CS)(PPh_3)_3$ (1.0 g) was dissolved in dichloromethane (25 ml), and ethanol and concentrated hydrobromic acid (ca. 49%, 0.5 ml) were added. Vigorous hydrogen evolution ensued and when this had ceased the dichloromethane was removed to afford white crystals which formed crystals of the solvated complex $OsHBr(CS)(PPh_3)_3 \cdot (CH_2Cl_2)_{0.33}$ on recrystallisation from dichloromethane/ethanol (1.07 g, 96.9%). ^1H NMR ($CDCl_3$) shows τ 4.78 ppm (s, 0.66 H, CH_2Cl_2). M.p. 176—180°C. Anal. Found: C, 58.71; H, 4.24; P, 8.20%. $C_{55}H_{46}BrOsP_3S \cdot (CH_2Cl_2)_{0.33}$ calcd.: C, 58.79; H, 4.16; P, 8.22%.

$OsHCl(CS)(CNR)(PPh_3)_2$. (a) Isomer I. $OsHCl(CS)(PPh_3)_3 \cdot (CH_2Cl_2)_{0.5}$ (1.0 g) was dissolved in benzene (50 ml) and *p*-tolyl isocyanide (0.11 g, 1.03 eq.) was added. The solution volume was lowered to 15 ml and hexane was added to afford a yellow solid which was collected and washed with hexane. Recrystallisation from dichloromethane/ethanol gave a yellow crystalline solid which was

contaminated by the isomer with hydride *trans* to isocyanide and which contained 0.25 mol of dichloromethane of solvation (0.67 g, 78.9%). ^{1}H NMR ($CDCl_3$) shows τ 4.75 ppm (s, 0.5H, CH_2Cl_2). M.p. 133—135°C, Anal. Found: C, 58.58; H, 4.46; N, 1.51; P, 6.69. $C_{45}H_{38}ClNOsP_2S \cdot (CH_2Cl_2)_{0.25}$ calcd.: C, 58.21; H, 4.16; N, 1.50; P, 6.63%.

(b) Isomer II. (i) OsHCl(CS)(CNR)(PPh_3)$_2$ (H *trans* Cl) (0.5 g) in benzene solution (30 ml) was heated under reflux for 2 h. Ethanol (30 ml) was added and upon evaporation of the solvent mixture white crystals deposited (0.46 g, 94.2%). M.p. 239—241°C. Anal. Found: C, 58.99; H, 4.19; N, 161. $C_{45}H_{38}ClNOsP_2S$ calcd.: C, 59.23; H, 4.09; N, 1.54%.

(ii) $[OsH(CS)(CNR)(PPh_3)_3]ClO_4$ (0.3 g) and lithium chloride (0.1 g) were heated in ethanol solution under reflux for 2 h. The white crystalline solid was collected and washed with ethanol and hexane (0.215 g, 97.3%). M.p. 239—241°C.

OsHCl(CO)(CS)(PPh_3)$_2$. OsHCl(CS)(PPh_3)$_3 \cdot (CH_2Cl_2)_{0.5}$ (0.3 g) was dissolved in benzene (50 ml) in a closed flask and carbon monoxide (6.5 ml at 1 atm and 20°C, ca. 1 eq.) was introduced through a rubber septum. The solution was shaken for 15 min. The volume of the solution was reduced to 10 ml and hexane was added to afford cream crystals which were washed with hexane. Recrystallisation from dichloromethane/hexane gave cream cubes (0.2 g, 89.1%). M.p. 188—190°C. Anal. Found: C, 54.93; H, 3.82; P, 7.60. $C_{38}H_{31}ClOOsP_2S$ calcd.: C, 55.43; H, 3.80; P, 7.52%.

OsHBr(CO)(CS)(PPh_3)$_2$. OsHBr(CS)(PPh_3)$_3 \cdot (CH_2Cl_2)_{0.33}$ (0.3 g) was dissolved in benzene (50 ml) in a closed flask and carbon monoxide (6.2 ml at 1 atm and 20°C, ca. 1 eq.) was introduced through a rubber septum. The solution was shaken for 15 min. The volume of the solution was reduced to 10 ml and ethanol was added to afford pale yellow crystals which were washed with ethanol. Recrystallisation from dichloromethane/ethanol gave pale yellow crystals (0.21 g, 91.2%). M.p. 182—185°C. Anal. Found: C, 52.38; H, 3.80; P, 7.26. $C_{38}H_{31}BrOOsP_2S$ calcd.: C, 52.59; H, 3.60; P, 7.14%.

OsCl(CHS)(CO)$_2$(PPh_3)$_2$. OsHCl(CS)(PPh_3)$_3 \cdot (CH_2Cl_2)_{0.5}$ (1.0 g) was stirred in dry benzene (20 ml) under carbon monoxide (40 psi) for 1 h. Hexane was added to afford sky blue crystals which were washed with hexane. ^{1}H NMR (C_6D_6) shows presence of 0.66 mol n-hexane of solvation (τ 9.13, 8.80 ppm, 2 m, 9.3 H, C_6H_{14}) (0.82 g, 99.3%). M.p. 128—130°C. Anal. Found: C, 57.05; H, 4.48; P, 6.59. $C_{39}H_{31}ClO_2OsP_2S \cdot (C_6H_{14})_{0.66}$ calcd.: C, 56.83; H, 4.44; P, 6.81%.

OsBr(CHS)(CO)$_2$(PPh_3)$_2$. OsHBr(CS)(PPh_3)$_3 \cdot (CH_2Cl_2)_{0.33}$ (1.0 g) was treated as above to afford blue crystals of OsBr(CHS)(CO)$_2$(PPh_3)$_2 \cdot C_6H_{14}$ (0.85 g, 97.9%). ^{1}H NMR (C_6D_6) shows presence of 1 mol n-hexane of solvation (τ, 9.10, 8.77, 2 m, 14 H, C_6H_{14}). M.p. 161—162°C. Anal. Found: C, 55.13; H, 4.74; P, 6.44. $C_{39}H_{31}BrO_2OsP_2S \cdot (C_6H_{14})$ calcd.: C, 55.04; H, 4.62; P, 6.31%.

OsCl(CHS)(CO)(CNR)(PPh_3)$_2$. OsHCl(CS)(CNR)(PPh_3)$_2$ (H *trans* to Cl) (1.0 g) was stirred in dry benzene (30 ml) under carbon monoxide (40 psi) for 1.5 h. The intense blue colouration which is characteristic of the thioformyl complexes developed more slowly than in either of the above two complexes. Hexane was added to afford sky blue needles which were washed with hexane and dried at room temperature (1.0 g, 97.0%). An analytical sample was recrystallised from

dry benzene/petroleum spirit to give sky blue needles which were washed with petroleum spirit. M.p. 205—207°C. Anal. Found: C, 58.73; H, 4.38; N, 1.53. $C_{46}H_{38}ClNOOsP_2S$ calcd.: C, 58.74; H, 4.07; N, 1.49%.

Os(η^2-CH_2S)$(CO)_2(PPh_3)_2$. $OsCl(CHS)(CO)_2(PPh_3)_2 \cdot (C_6H_{14})_{0.66}$ (0.5 g) was heated under reflux in a solution of dichloromethane (30 ml) and ethanol (10 ml) containing sodium borohydride (0.1 g) for 30 min. Evaporation of the dichloromethane yielded cream crystals which were collected and washed with water and ethanol. The solid was dissolved in dichloromethane and the solution passed through a celite pad. Ethanol was added and the dichloromethane removed to afford cream crystals (0.43 g). Recrystallisation from dichloromethane/benzene afforded white crystals of the solvate $Os(\eta^2\text{-}CH_2S)(CO)_2(PPh_3)_2 \cdot (CH_2Cl_2)_{0.25}$ which were collected and washed with ethanol (0.23 g, 46.7%). ^1H NMR ($CDCl_3$) shows τ 4.73 ppm (s, 0.5 H, CH_2Cl_2). M.p. 193—195°C. Anal. Found: C, 56.49; H, 4.15; P, 7.65. $C_{39}H_{32}O_2OsP_2S \cdot (CH_2Cl_2)_{0.25}$ calcd.: C, 56.25; H, 3.91; P, 7.39%.

$OsCl(SMe)(CO)_2(PPh_3)_2$. $Os(\eta^2\text{-}CH_2S)(CO)_2(PPh_3)_2 \cdot (CH_2Cl_2)_{0.25}$ (0.15 g) was dissolved in dichloromethane (30 ml) and ethanol (10 ml) containing concentrated hydrochloric acid (0.01 ml) was added. Removal of the dichloromethane afforded yellow ochre crystals which were collected and washed with ethanol (0.145 g, 94.9%). An analytical sample was recrystallised from dichloromethane/ethanol to give yellow ochre crystals. M.p. 185—188°C. Anal. Found: C, 54.94; H, 4.00; P, 6.57%. $C_{39}H_{33}ClO_2OsP_2S$ calcd.: C, 54.89; H, 3.90; P, 7.26%.

$OsCl(\eta^1\text{-}CH_2SMe)(CO)_2(PPh_3)_2$. $[Os(\eta^2\text{-}CH_2SMe)(CO)_2(PPh_3)_2]CF_3SO_3 \cdot H_2O$ (0.3 g) and lithium chloride (0.1 g) were heated under reflux in ethanol solution (20 ml) for 15 min. The white crystals were collected and washed with ethanol (0.24 g, 90.5%). An analytical sample was recrystallised from dichloromethane/ethanol. M.p. 167—168°C. Anal. Found: C, 55.34; H, 4.39; P, 7.32. $C_{40}H_{35}ClO_2OsP_2S$ calcd.: C, 55.39; H, 4.07; P, 7.14%.

$[OsCl(\eta^1\text{-}CH_2SMe_2)(CO)_2(PPh_3)_2]CF_3SO_3$. $OsCl(\eta^1\text{-}CH_2SMe)(CO)_2(PPh_3)_2$ (0.2 g) was dissolved in dry benzene (20 ml) and methyl triflate (0.05 ml) was added. After 10 min stirring hexane (10 ml) was added and the white crystals were collected and washed with hexane (0.23 g, 96.7%). An analytical sample was recrystallised from dichloromethane/ethanol/cyclohexane to give white crystals of the solvate $[OsCl(\eta^1\text{-}CH_2SMe_2)(CO)_2(PPh_3)_2]CF_3SO_3 \cdot (C_6H_{12})_{0.66}\text{-}(H_2O)_2$. ^1H NMR ($CDCl_3$) shows τ 8.53 ppm (s, 8H, C_6H_{12}), τ 7.70 ppm (s, 4H, H_2O). M.p. 183—187°C. Anal. Found: C, 49.21; H, 4.46; P, 5.49%. $C_{42}H_{38}ClF_3O_5OsP_2S_2 \cdot (C_6H_{12})_{0.66}(H_2O)_2$ calcd.: C, 49.17; H, 4.48; P, 5.51%.

$[Os(\eta^2\text{-}CH_2SMe)(CO)_2(PPh_3)_2]CF_3SO_3$. $Os(\eta^2\text{-}CH_2S)(CO)_2(PPh_3)_2 \cdot (CH_2Cl_2)_{0.25}$ (0.3 g) was stirred in dry benzene (30 ml) and methyl triflate (0.1 ml) was added. After 20 min hexane (10 ml) was added and the white crystals were collected and washed with hexane (0.35 g, 97.9%). An analytical sample was recrystallised from dichloromethane/ethanol/cyclohexane to yield white crystals of the solvate $[Os(\eta^2\text{-}CH_2SMe)(CO)_2(PPh_3)_2]CF_3SO_3 \cdot H_2O$. ^1H NMR ($CDCl_3$) shows τ 8.40 ppm (s, 2H, H_2O), IR (cm^{-1}) shows ν(OH) 3500 w(br), δ(OH) 1625w. M.p. 235—238°C. Anal. Found: C, 49.27; H, 4.01; P, 6.44. $C_{41}H_{35}F_3O_5OsP_2S_2 \cdot H_2O$ calcd.: C, 49.29; H, 3.73; P, 6.20%.

$[OsCl(CHSMe)(CO)_2(PPh_3)_2]CF_3SO_3$. $OsCl(CHS)(CO)_2(PPh_3)_2 \cdot (C_6H_{14})_{0.66}$ (0.5 g) was dissolved in benzene (25 ml) and methyl triflate (0.2 ml) was added.

After stirring for 10 min hexane (10 ml) was added and the yellow crystals were collected and washed with benzene and hexane. ^{1}H NMR ($CDCl_3$) shows the presence of benzene of solvation τ 2.63 ppm (s, 4H, C_6H_6) giving the composition $[OsCl(CHSMe)(CO)_2(PPh_3)_2]CF_3SO_3 \cdot (C_6H_6)_{0.66}$ (0.58 g, 98.6%). M.p. 138—140°C. Anal. Found: C, 50.70; H, 4.12; P, 5.63. $C_{41}H_{34}ClF_3O_5OsP_2S_2 \cdot (C_6H_6)_{0.66}$ calcd.: C, 50.62; H, 3.59; P, 5.80%.

$[OsCl(CHSMe)(CO)_2(PPh_3)_2]ClO_4$. $[OsCl(CHSMe)(CO)_2(PPh_3)_2]CF_3SO_3 \cdot (C_6H_6)_{0.66}$ (0.3 g) was recrystallised from dichloromethane/ethanol (30 ml, 2/1) containing perchloric acid (70%, 0.1 ml) to afford pale yellow crystals (0.24 g, 88.4%). M.p. 260—264°C. Anal. Found: C, 50.24; H, 3.6. $C_{40}H_{34}Cl_2O_6OsP_2S$ calcd.: C, 49.74; H, 3.55%.

$[OsBr(CHSMe)(CO)_2(PPh_3)_2]CF_3SO_3$. $OsBr(CHS)(CO_2)(PPh_3)_2 \cdot C_6H_{14}$ (0.5 g) was treated with methyl triflate in dry benzene as above to yield yellow crystals. ^{1}H NMR ($CDCl_3$) shows τ 2.65 ppm (s, 6H) attributable to benzene of solvation giving the composition $[OsBr(CHSMe)(CO)_2(PPh_3)_2]CF_3SO_3 \cdot C_6H_6$. M.p. 136—139°C. Anal. Found: C, 49.65; H, 3.70; P, 5.47. $C_{41}H_{34}BrF_3O_5OsP_2S_2 \cdot (C_6H_6)$ calcd.: C, 49.60; H, 3.54; P, 5.44%.

$[OsCl(CHSMe)(CO)(CNR)(PPh_3)_2]CF_3SO_3$. $OsCl(CHS)(CO)(CNR)(PPh_3)_2$ (0.5 g) was treated with methyl triflate in dry benzene to yield yellow crystals. ^{1}H NMR ($CDCl_3$) shows τ 2.75 ppm (s, 1H) attributable to benzene of solvation giving the composition $[OsCl(CHSMe)(CO)(CNR)(PPh_3)_2]CF_3SO_3 \cdot (C_6H_6)_{0.167}$. M.p. 195—200°C. Anal. Found: C, 53.04; H, 4.17; N, 1.21. $C_{48}H_{41}ClF_3NO_4OsP_2S_2 \cdot (C_6H_6)_{0.167}$ calcd.: C, 52.66; H, 3.79; N, 1.25%.

$[OsCl(CHNHMe)(CO)_2(PPh_3)_2]ClO_4$. $[OsCl(CHSMe)(CO)_2(PPh_3)_2]CF_3SO_3 \cdot (C_6H_6)_{0.66}$ (0.3 g) was dissolved in dichloromethane (30 ml) and 1 ml of a solution of methylamine in ethanol (ca. 33%) was added. Perchloric acid (70%, 0.5 ml) was added and on reduction of the solvent volume white crystals were deposited which were collected and washed with ethanol and hexane (0.24 g, 87.7%). An analytical sample was recrystallised from dichloromethane/ethanol/cyclohexane to afford colourless crystals. M.p. 205—207°C. Anal. Found: C, 50.43; H, 4.08; N, 1.63. $C_{40}H_{35}Cl_2NO_6OsP_2$ calcd.: C, 50.64; H, 3.72; N, 1.48%.

$OsCl(CHNMe)(CO)_2(PPh_3)_2$. $[OsCl(CHNHMe)(CO)_2(PPh_3)_2]ClO_4$ (0.2 g) was dissolved in dichloromethane/ethanol (30 ml, 3/1) and a solution of sodium hydroxide (0.1 g) in ethanol (10 ml) was added. Upon reduction of the solvent volume white feathery crystals formed which were collected and washed with ethanol. Recrystallisation was achieved from dichloromethane/ethanol (0.179 g, 100%). M.p. 220—222°C. Anal. Found: C, 56.48; H, 4.55; N, 2.01. $C_{40}H_{34}ClNO_2OsP_2$ calcd.: C, 56.63; H, 4.04; N, 1.65%.

$OsCl(CHO)(CO)_2(PPh_3)_2$. $[OsCl(CHSMe)(CO)_2(PPh_3)_2]CF_3SO_3 \cdot (C_6H_6)_{0.66}$ (0.3 g) was recrystallised from dichloromethane (40 ml)/ethanol (10 ml)/water (5 ml) by removal of dichloromethane under reduced pressure without the application of heat. The white crystals were collected and washed with ethanol (0.22 g). IR indicates a mixture of $OsCl(CHO)(CO)_2(PPh_3)_2$ and $OsHCL(CO)_2(PPh_3)_2$ (ca. 9/1) but further purification was not possible.

$OsBr(CHO)(CO)_2(PPh_3)_2$. $[OsBr(CHSMe)(CO)_2(PPh_3)_2]CF_3SO_3 \cdot C_6H_6$ (0.3 g) was treated as above to afford white crystals (0.21 g). IR indicates a mixture of $OsBr(CHO)(CO)_2(PPh_3)_2$ and $OSHBr(CO)_2(PPh_3)_2$ (ca. 4 : 1) but further purification was not possible.

OsCl(CHO)(CO)(CNR)(PPh_3)$_2$. [OsCl(CHSMe)(CO)(CNR)(PPh_3)$_2$]CF_3SO_3 · $(C_6H_6)_{0.167}$ (0.3 g) was dissolved in dichloromethane (30 ml) and a solution of ethanol (20 ml) and water (5 ml) containing sodium hydroxide (0.05 g) was added. Upon reduction of the solvent volume white crystals deposited which were collected and washed with ethanol (0.13 g, 52.4%). An analytical sample was recrystallised from dichloromethane/hexane. M.p. 151—153°C (darkens above 130°C). Anal. Found: C, 59.44; H, 4.74; N, 1.36. $C_{46}H_{38}ClNO_2OsP_2$ calcd.: C, 59.77; H, 4.14; N, 1.52%.

[OsCl(CHOMe)(CO)(CNR)(PPh_3)$_2$]CF_3SO_3. OsCl(CHO)(CNR)(PPh_3)$_2$ (0.1 g was dissolved in dry benzene (10 ml) and methyl triflate (0.03 ml) was added. After stirring for 5 min hexane was added and the solvent was decanted from the oily solid which was washed twice with hexane. Recrystallisation from dichloromethane/hexane yielded pale lemon crystals which were collected and washed with hexane and dried at room temperature. The crystals contain 0.5 e dichloromethane of solvation (0.11 g, 86.7%). ^{1}H NMR ($CDCl_3$) shows τ 4.70 ppm (s, 1H, CH_2Cl_2). M.p. 108—112°C. Anal. Found: C, 51.97; H, 4.96; N, 1.2 $C_{48}H_{41}ClF_3NO_5OsP_2S \cdot CH_2Cl_2$ calcd.: C, 51.50; H, 3.74; N, 1.24%.

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