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THE PREPARATION, CHARACTERISATION AND SOME REACTIONS OF $Os_3(CO)_9(\mu_2\text{-H})(\mu_3\text{-SR})$ (R = Me or Et) *

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Summary

The complex $Os_3(CO)_9(\mu_2\text{-H})_2(\mu_3\text{-S})$ reacts with KOH/MeOH to produce the anionic complex $[Os_3(CO)_9(\mu_2\text{-H})(\mu_3\text{-S})]^-$, which reacts in turn with RO^+ (R = Me, Et) to form $HOs_3(CO)_9SR$. This complex is especially reactive towards ligands L (L = C_2H_4, CO, PR_3 and MeCN) to generate complexes of the type $Os_3(CO)_9(\mu_2\text{-H})(\mu_2\text{-SR})(L)$. At 125°C the complex $Os_3(CO)_9(\mu_2\text{-H})(\mu_2\text{-SR})(C_2H_4)$ (in the presence of C_2H_4) ejects RH and CO to form $Os_3(CO)_8(\mu_2\text{-H})(\mu_3\text{-S})(CH{=}CH_2)$. The structures of the new complexes are described and the probable reaction pathways discussed.

Introduction

A major problem encountered in studies of the osmium carbonyl clusters $Os_3(CO)_{12}$, $H_4Os_4(CO)_{12}$, $Os_5(CO)_{16}$ and $Os_6(CO)_{18}$, etc. is the severity of the conditions required to bring about chemical reaction [1]. The main difficulty lies in the reluctance of these systems to undergo ligand exchange by a CO dissociative step, as is revealed by ^{13}CO exchange studies. Compounds such as $Co_4(CO)_{12}$ undergo CO exchange under moderate conditions in a fairly short time. In contrast, exchange with $Os_3(CO)_{12}$ requires several days at 80°C and under the same conditions exchange with $Os_6(CO)_{18}$ is negligible [2]. There is evidence to suggest that both exchange and substitution reactions occur via an associative Os—Os bond-break mechanism. Reaction of $Os_3(CO)_{12}$ with ligands such as ethylene is, therefore, understandably slow under moderate conditions. Under more vigorous conditions reaction is known to lead to the stable $Os_3(CO)_9(\mu_2\text{-H})_2)(C_2H_2)$derivatives. Consequently, milder reaction pathways were sought. In two earlier publications [3,4] we reported methods by which activity

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* Dedicated to the memory of Professor Paolo Chini.

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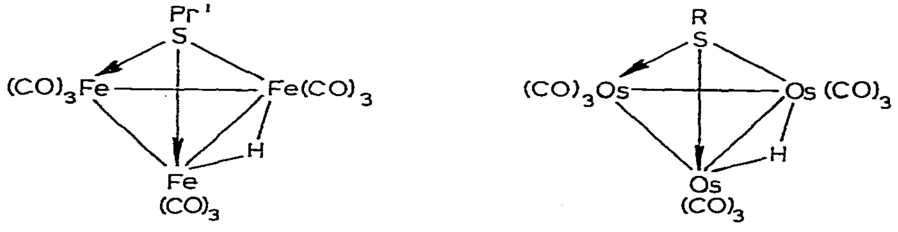
of osmium clusters may be induced. In the first, we described work on the cluster nitrosyl $Os_3(CO)_9(NO)_2$ which, because the NO ligand may function as a one- or three-electron donor, is remarkably reactive. In the second, studies of $Os_3(CO)_{11}(MeCN)$, prepared by the reaction of $Os_3(CO)_{12}$ with Me_3NO in MeCN, were described; here, the cluster was "activated" by the presence of the labile MeCN ligand. We now report work carried out on the cluster $Os_3(CO)_9$-$(\mu_2\text{-}H)(\mu_3\text{-}SR)$, which, because of the multi-donor properties of the SR group (potentially a one-, three- or five-electron donor) is also highly chemically reactive. Some aspects of this work have been previously reported [1,5,6].

Results and discussion

Treatment of $Os_3(CO)_9(\mu_2\text{-}H)_2(\mu_3\text{-}S)$ with KOH/MeOH produced the anionic complex $[Os_3(CO)_9(\mu_2\text{-}H)(\mu_3\text{-}S)]^-$, which was separated as the bis(triphenylphosphine)iminium (PPN^+) salt (1). Treatment of the salt 1, with $[R_3O][PF_6]$ (R = Me or Et) in dry dichloromethane brought about an immediate colour change from yellow to orange and, after separation on silica, a small amount of the complex $Os_3(CO)_{10}(\mu_2\text{-}H)(\mu_2\text{-}SR)$ (2a, R = Me; 2b, R = Et) was obtained as a yellow solid. In a separate experiment, carbon monoxide was passed through the reaction solution, and better yields of 2 were obtained. These observations were taken to indicate that the reaction proceeded via the formation of the coordinatively unsaturated intermediate $HOs_3(CO)_9(\mu_2\text{-}SR)$ (3) The reaction was therefore carried out in the presence of other potential ligands, and the results are summarised in Scheme 1.

Reaction of salt 1 with $[R_3O]^+[PF_6]^-$ (R = Me or Et) was carried out in the presence of ethylene. The clusters $Os_3(CO)_9(\mu_2\text{-}H)(\mu_2\text{-}SR)(C_2H_4)$ (4a, R = Me; 4b, R = Et) were the major products. They are air-stable, yellow crystalline materials, which can be readily purified by thin layer chromatography, but on heating at 80°C in cyclohexane they eject ethylene to generate the cluster $Os_3(CO)_9(\mu_2\text{-}H)(\mu_3\text{-}SR)$ (2) in virtually quantitative yields.

The cluster 2b (R = Et) was just sufficiently stable to permit isolation and characterisation by the usual spectroscopic methods. The analogous methyl complex 2a (R = Me) was less stable, and was characterised solely on the basis of its IR spectrum. These clusters are clearly members of the family of compounds represented by $Fe_3(CO)_9(\mu_2\text{-}H)(\mu_3\text{-}SPr\text{-}i)$ with a triply capping (SR) ligand and edge-bridging hydride (Fig. 1) [7].



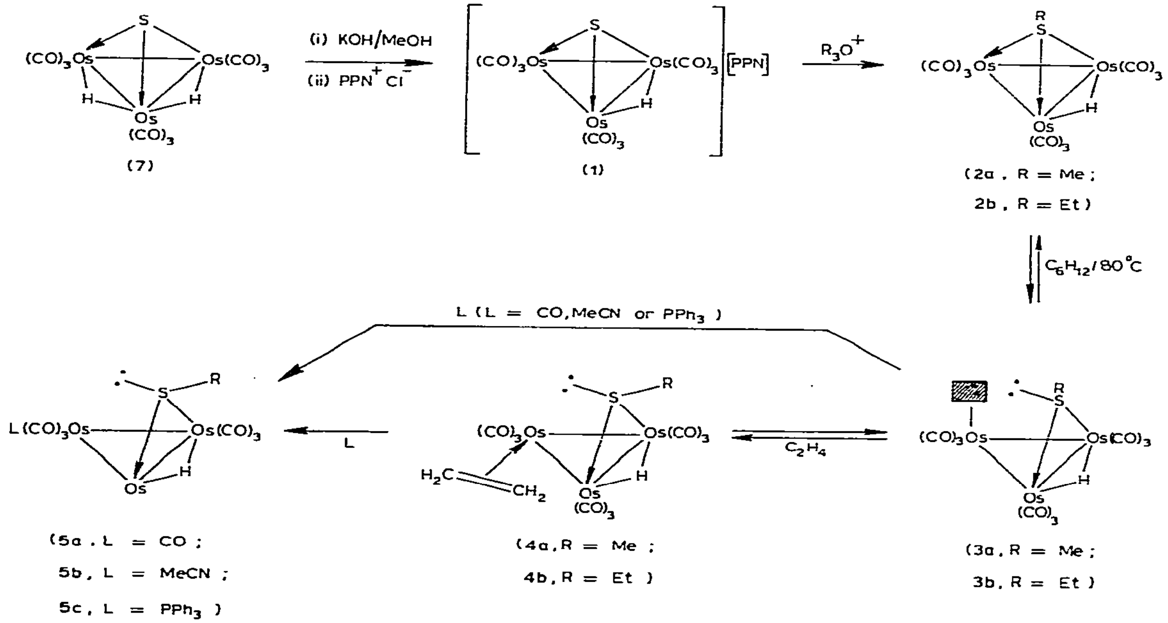
(a) (b)

Fig. 1. Molecular structure of (a) $HFe_3(CO)_9(\mu_3\text{-}SPr\text{-}i)$ and (b) $HOs_3(CO)_9(\mu_3\text{-}SR)$ (R = Me or Et).

The ^{1}H NMR spectrum of **2b** exhibits a methyl resonance at τ 6.8, which may be compared with the value of τ 7.4 observed for the decacarbonyl cluster $Os_3(CO)_{10}(\mu_2\text{-}H)(\mu_2\text{-}SEt)$ (**5a**) and can be taken to reflect the increased electron donation from the S ligand (5-electron donor in **2b**; 3-electron donor in **5a**).

The crystal structures of $Os_3(CO)_9(\mu_2\text{-}H)_2(\mu_3\text{-}S)$ (**7**) (X-ray and neutron diffraction) and $[Os_3(CO)_9(\mu_2\text{-}H)(\mu_3\text{-}S)][PPN]$ (**1**) (X-ray) have been established and reported previously [5]; their structural formulae are shown in Scheme 1.

Scheme 1. Formation of $HOs_3(CO)_9SR$ and some of its reactions with ligands L (L = C_2H_4, MeCN or PPh_3).



The molecular structure of the ethylene complex (**4a**) was determined by single crystal X-ray diffraction and is shown in Fig. 2. The ethylene molecule occupies an equatorial site and is clearly bound in the conventional Chatt—Dewar—Duncanson bonding mode. A full description of this molecular structure has been given elsewhere [8].

The ^{1}H NMR spectrum of this complex exhibits peaks at τ 7.51s, τ 7.55s and τ 26.85s. Because of the close proximity of the two low field resonances

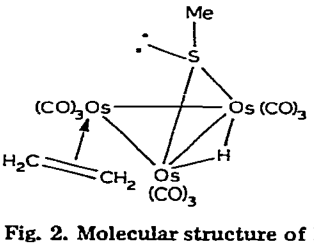


Fig. 2. Molecular structure of $HOs_3(CO)_9(\mu_2\text{-}SMe)(C_2H_4)$.

accurate integration was not possible, and the two peaks have not been assigned with precision. Irrespective of the precise assignment the ethylene resonance is a singlet, and this implies that the ethylene is rotating rapidly about the metal—olefin axis on the NMR time scale since in the ground state structure at least two proton resonances are to be expected. In keeping with the views reported earlier [6], no coupling of the ethylenic protons with the hydrido ligand was observed, such coupling not being expected for the arrangement of ligands shown.

The electronic and steric factors which influence the most favoured site for ligand occupancy within the cluster are not easy to separate. Bulky ligands and the better π-acids appear more likely to occupy an equatorial site, whereas smaller ligands and those which are poorer π-acids show a tendency to occupy the axial positions. Thus, equatorial occupancy by ethylene is in line with current views.

Preparation of clusters of the type $Os_3(CO)_9(\mu_2\text{-}H)(\mu_2\text{-}SMe)(L)$

Treatment of either **2a** or **4a** with MeCN leads to the formation of a mixture of two isomers of the compound $Os_3(CO)_9(\mu_2\text{-H})(\mu_2\text{-SMe})(MeCN)$ (in a ratio of ca. 70% (**5b**) to 30% (**5b′**)). In the ^{1}H NMR spectrum each isomer exhibited three resonances for **5b**: τ 7.46 (3), 7.50 (3), and 26.50 (1); for **5b′**: τ 7.46 (3), 7.50, and 26.27 (1). The IR spectra of the two isomers are similar (Table 2). A number of possible isomeric forms for a complex of type $Os_3(CO)_9(\mu_2\text{-H})$-$(\mu_2\text{-SMe})$ (L) are possible (see Fig. 3). They may differ in: (1) the location of the L ligand, equatorial or axial on the same Os atom; (2) the location of the L ligand, occupying sites on different Os atoms; (3) the location of the H ligand relative to the L ligand; or (4) stereochemical differences about the SMe ligand.

TABLE 1

MICROANALYTICAL DATA FOR NEW COMPOUNDS [a]

Compound	Empirical formula	Analysis (Found(calcd.)(%))		
		C	H	N
$[Os_3(CO)_9HS][PPN]$	$C_{45}H_{31}NO_9Os_3P_2S$	39.21	2.72	1.01
		(39.31)	(2.25)	(1.02)
$Os_3(CO)_9H(C_2H_4)(SMe)$	$C_{12}H_8O_9Os_3S$	16.37	1.12	
		(16.04)	(0.90)	
$Os_3(CO)_9H(PPh_3)(SMe)$	$C_{28}H_{19}O_9Os_3PS$	30.33	1.94	
		(29.68)	(1.69)	
$Os_3(CO)_9H(MeCN)(SMe)$	$C_{12}H_7NO_9Os_3S$			
(isomer I)		16.07	0.98	1.39
(isomer II)		16.30	0.88	1.46
		(15.80)	(0.77)	(1.54)
$Os_3(CO)_8H(CH{=}CH_2)S$	$C_{10}H_4O_8Os_3S$	14.54	0.65	
		(14.10)	(0.47)	

[a] Microanalytical Laboratory, Chemical Laboratory, Cambridge.

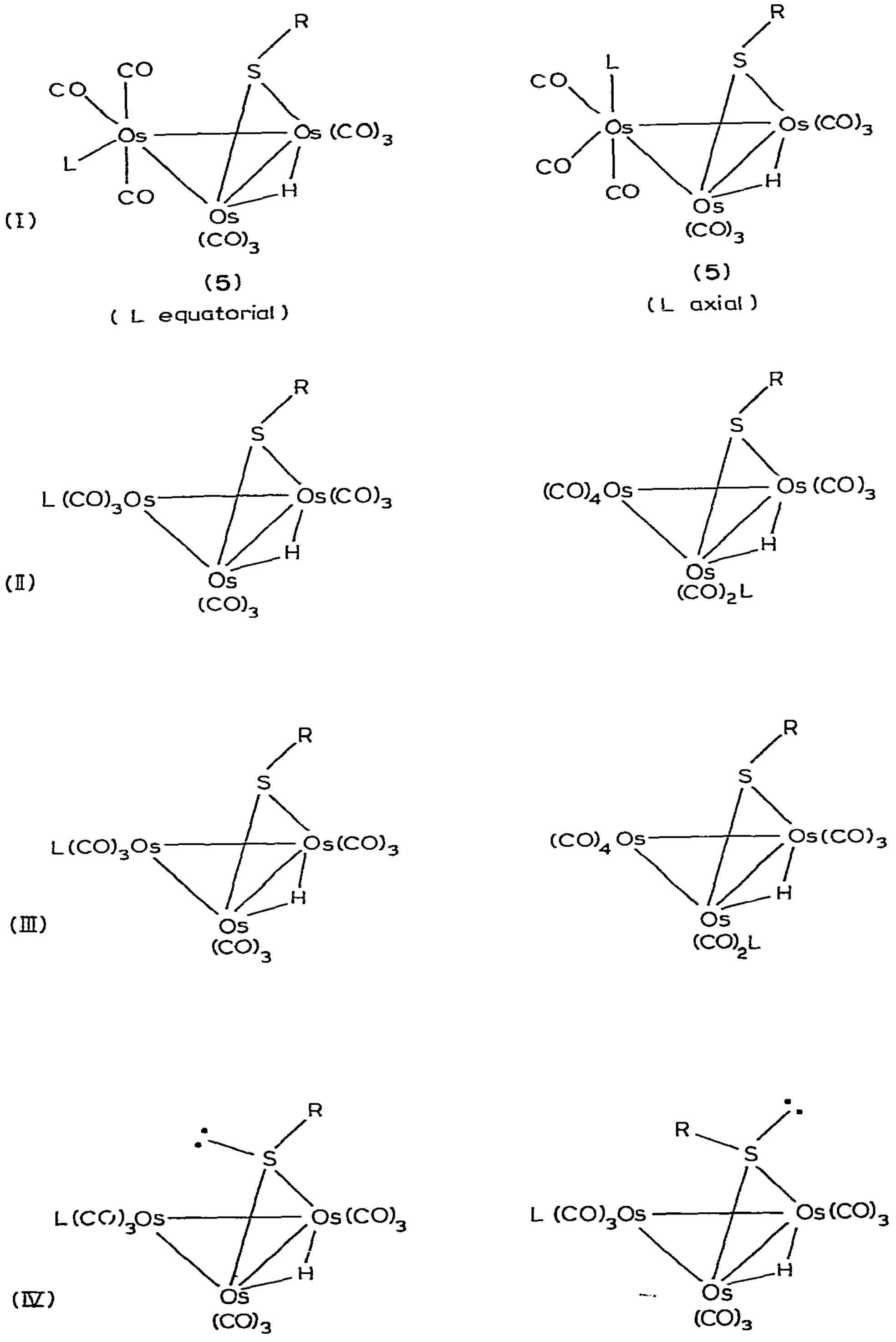


Fig. 3. Some possible isomeric forms of the complexes $Os_3(CO)_9(\mu_2\text{-}H)(\mu_2\text{-}SR)L$.

TABLE 2

SPECTROSCOPIC DATA FOR NEW COMPOUNDS

	IR cm^{-1}, C_6H_{12}	^{1}H NMR (τ, $CDCl_3$)
[$Os_3(CO)_9HS$] [PPN]	2062w, 2033s, 1995s, 1964s, 1954(sh), 1906w [a]	2.43(30 H, m), 31.16(1 H, s) [b]
$Os_3(CO)_9H(C_2H_4)(SMe)$	2093w, 2064s, 2043m, 2011s, 2001m, 1995(sh), 1991m, 1980w, 1965w	7.51(3 or 4 H, s), 7.55(4 or 3 H, s), 26.85(1 H, s)
$Os_3(CO)_9H(C_2H_4)(SEt)$	2093w, 2062s, 2041m, 2010s, 2000m, 1994(sh), 1990m, 1980w, 1967w	7.52(4 H, s), 7.54(2 H, q), 8.71(3 H, t) 26.95(1 H, s); *J*(HH) 8.0 Hz
$Os_3(CO)_9H(PPh_3)(SMe)$	2082m, 2056(sh), 2051s, 2026m, 2021(sh), 2001s, 1982s, 1962w, 1952m, 1942m	2.62(15 H, m), 6.80(1 H, s), 26.83(1 H, s)
$Os_3(CO)_9H(PPh_3)(SEt)$	2081m, 2055(sh), 2052s, 2026m, 2020(sh), 2000s, 1980s, 1961w, 1951ms	2.61(15 H, m), 7.51(2 H, q), 8.64(3 H, t), 27.0(1 H, s); *J*(HH) 8.0 Hz
$Os_3(CO)_9H(MeCN)(SMe)$(I)	2076vw, 2048s, 2030s, 1986m, 1977s, 1969w, 1955w	7.46(3 H, s), 7.50(3 H, s), 26.50(1 H, s)
$Os_3(CO)_9H(MeCN)(SMe)$(II)	2082w, 2049s, 2028s, 1997s, 1977s, 1964w, 1955w	7.46(3 H, s), 7.51(3 H, s), 26.27(1 H, s)

[a] Recorded in CH_2Cl_2. [b] Recorded in CD_2Cl_2.

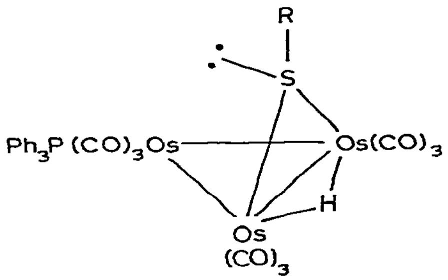
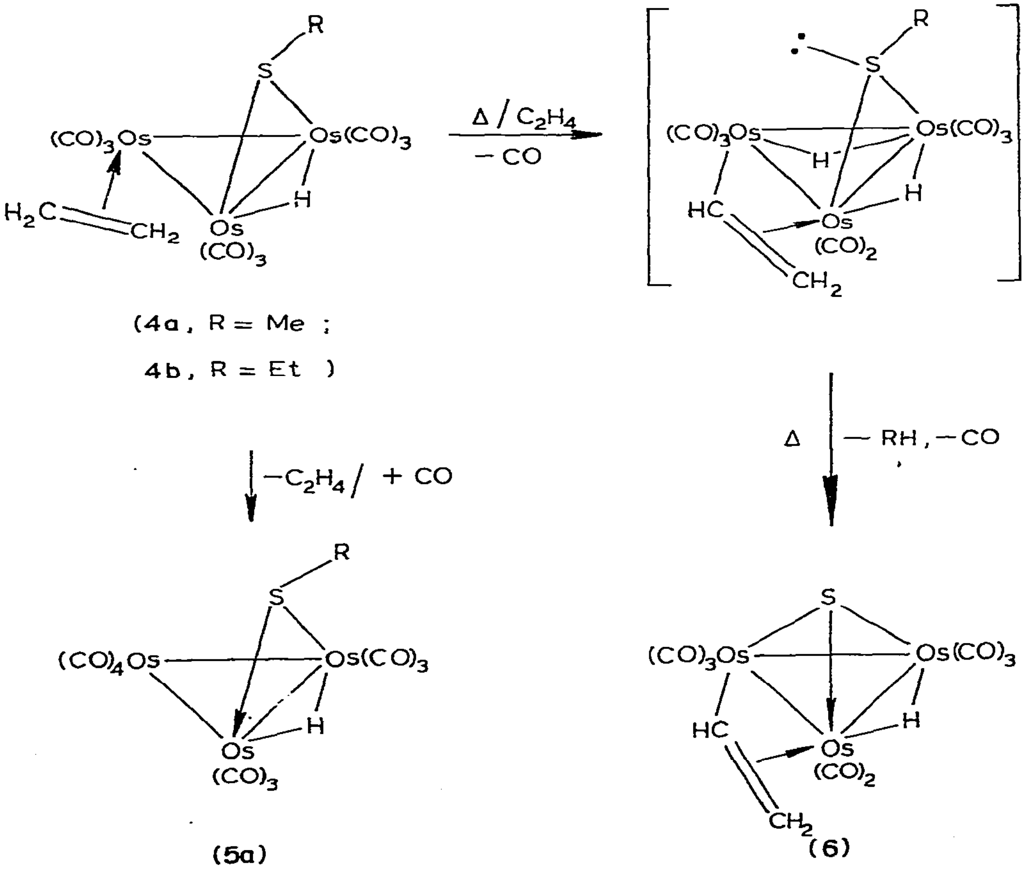


Fig. 4. Probable molecular structure of $Os_3(CO)_9(\mu_2\text{-}H)(\mu_2\text{-}SR)PPh_3$.

Clearly even within this framework other possibilities exist. We favour possibility 1, mainly because of the route by which these complexes are produced and the two isomeric forms are those shown in Fig. 3(I).

Triphenylphosphine reacted with either 2a or 4a to produce a compound of composition $Os_3(CO)_9(\mu_2\text{-}H)(\mu_2\text{-}SMe)(PPh_3)$ (5c). In this instance the ^1H NMR exhibited only one high field resonance and showed no evidence of coupling to

Scheme 2. Some reactions of $Os_3(CO)_9(\mu_2\text{-}H)(\mu_2\text{-}SR)(C_2H_4)$ (R = Me or Et).



(4a, R = Me ;
4b, R = Et)

(5a)

(6)

the ^{31}P nucleus. On these grounds we propose the structure given in Fig. 4, although on the basis of the present information we cannot be certain of the precise site of the PPh_3 ligand (axial or equatorial).

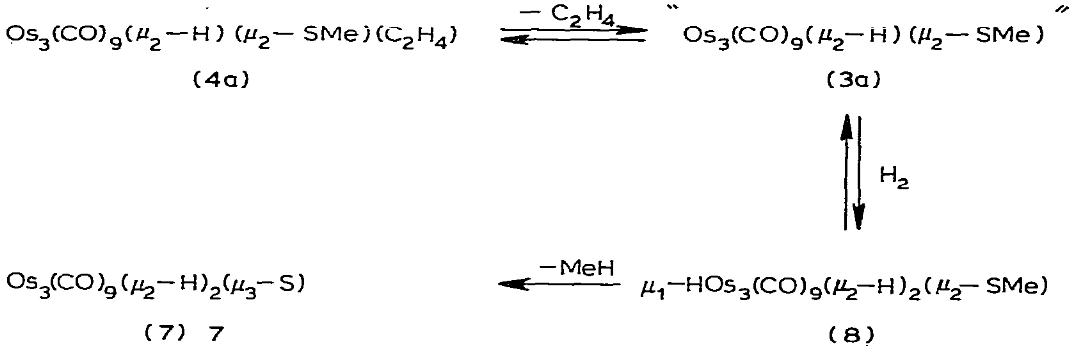
Formation of $Os_3(CO)_8(\mu_2\text{-}H)(\mu_3\text{-}S)(CH{=}CH_2)$ from (4a)

As mentioned above, complex 4a is a very convenient source of $Os_3(CO)_9(\mu_2\text{-}H)(\mu_3\text{-}S)$ (3). However, if complex 4a is heated in the presence of ethylene, which presumably decreases the possibility of ethylene dissociation, then the complex $Os_3(CO)_8(CH{=}CH_2)(\mu_2\text{-}H)_2(\mu_3\text{-}S)$ (6) is produced together with some $Os_3(CO)_{10}(\mu_2\text{-}H)(\mu_2\text{-}SMe)$ (Scheme 2). Complex 6 was fully characterised on the basis of the usual analytical spectroscopic data (Tables 1 and 2). In the course of this reaction both CO and CH_4 for complex 4a or C_2H_6 for complex 4b are eliminated (as identified by mass spectrometry) and a possible reaction sequence is given in Scheme 2.

Reaction of 4a with hydrogen

Treatment of 4a with H_2 under ambient conditions gives high yields of the complex $Os_3(CO)_9(\mu_2\text{-}H)_2(\mu_3\text{-}S)$ (7). By monitoring the efluent gases by mass spectrometry we were able to establish that only CH_4 and C_2H_4 were produced, suggesting as a possible reaction sequence that shown in Scheme 3. In keeping with this suggestion we were able to detect a reaction intermediate by monitoring the variation in the IR spectrum of the reaction solution with time. This unstable intermediate, which exhibited bands ν(CO) at 2028w, 2074m, 2050s, 1998m and 1955w cm^{-1} (pentane) in its infrared spectrum, is tentatively formulated at $(\mu_1\text{-}H)Os_3(CO)_9(\mu_2\text{-}H)_2(\mu_2\text{-}SMe)$ (8).

Scheme 3. Possible reaction sequence for reaction of H_2 with $Os_3(CO)_9(\mu_2\text{-}H)(\mu_2\text{-}SMe)(C_2H_4)$.



Conclusions

It is clear from this work that the ability of sulphur ligands (SR^-) to function as a 5- or 3-electron donor when bound to an Os_3 cluster unit brings about an increased reactivity of that cluster. We must also conclude that the SR capping group does not necessarily block one side of the Os_3 triangle towards approach of an incoming substrate. Indeed its partial dissociation occurs more readily than the conventional CO ejection for $Os_3(CO)_{12}$.

Experimental

Preparation of [$Os_3(CO)_9HS$][PPN]

$Os_3(CO)_9H_2S$ (1 g) was dissolved in methanol (15 ml) containing KOH (0.4 g). After 10 min [PPN][Cl] (2.5 g) in methanol was added. After 1 week yellow crystals had separated, and were removed by filtration to give 1.25 g of crude product. More crystals were deposited on concentrating the mother liquor and setting it aside for a few days. The product was purified by dissolving it in a minimum volume of CH_2Cl_2, filtering the solution and adding a little MeOH, which caused the precipitation of a yellow salt; this was washed with MeOH. (Yield 810 mg, 50%).

Preparation of $Os_3(CO)_9H(C_2H_4)(SR)$ (R = Me, Et)

[$Os_3(CO)_9HS$][PPN] (350 mg) in dry CH_2Cl_2 (10 ml) was slowly (15 min) added to a stirred suspension of [Me_3O][PF_6] (prewashed with dry ether) in CH_2Cl_2 while C_2H_4 was passed through. After being left under C_2H_4 for 30 min the solution was evaporated and the yellow residue extracted with ether. Yellow $Os_3(CO)_9H(C_2H_4)(SMe)$ separated as fastest moving band on TLC after elution with hexane/ether (90/10), yield 160 mg (70%). The Et analogue was prepared similarly using [Et_3O][BF_4].

Effect on heat on $Os_3(CO)_9H(C_2H_4)(SR)$

$Os_3(CO)_9H(C_2H_4)(SEt)$ (50 mg) was heated in cyclohexane (30 ml) under reflux for 5 min. The solution darkened and its IR spectrum showed that $Os_3(CO)_9H(SEt)$ was the major species present. The reaction was repeated in pentane, and $Os_3(CO)_9H(SEt)$ was formed in about 80% yield after 1 h. For the Me derivative, refluxing in pentane gave $Os_3(CO)_9H(SMe)$ in about 50% yield after 2 h.

$Os_3(CO)_9H(C_2H_4)(SMe)$ (40 mg) was heated in boiling n-octane (25 ml) under C_2H_4 for 40 min (or n-heptane for 3 h). After cooling and removal of solvent, TLC of the residue, with elution with hexane/ether (95/5), gave several bands, the main band, the first, being a mixture of $Os_3(CO)_8H(CH{=}CH_2)S$ (present in the higher ratio at the top of the band) and $Os_3(CO)_{10}H(SMe)$ (present in higher ratio at the bottom of the band. After two repetitions of the TLC, with careful splitting of the band into two portions each time, a few mg of yellow $Os_3(CO)_8(CH{=}CH_2)S$ was isolated. The same reaction with the Et analogue gave an inseparable mixture of $Os_3(CO)_{10}H(SEt)$ and the vinyl adduct.

Preparation of other adducts, $Os_3(CO)_9H(L)(SR)$

These were prepared in several ways. The adducts were prepared as for C_2H_4 by treating $[Os_3(CO)_9HS]^-$ with $[R_3O]^+$ in the presence of an excess of the ligand L. Alternatively the adducts were prepared by treating $Os_3(CO)_9(C_2H_4)$-(SR) with the ligand L in boiling cyclohexane for 30 min (L = MeCN) or refluxing pentane for 3 h (L = PPh_3). Yields of adducts were high (~ quantitative for L = MeCN and PPh_3). All adducts were isolated by TCL with elution with hexane/ether mixtures.

Reaction of $Os_3(CO)_9(H)(S)(C_2H_4)$ with H_2

H_2 was bubbled through a refluxing hexane solution (15 ml) of $Os_3(CO)_9H(C_2H_4)(SMe)$ (15 mg) and complete conversion into $Os_3(CO)_9H_2S$ occurred within 1 min. At room temperature in pentane the reaction took 60 h and the appearance of an intermediate was observed in the IR spectrum.

Addition of EtSH (few drops) to a pentane solution of $Os_3(CO)_9H(SEt)$ at room temperature caused an immediate reaction. TLC revealed considerable decomposition, but the fastest moving band was $Os_2(CO)_6(SEt)_2$.

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