Journal of Organometallic Chemistry, 265 (1984) 87–94
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

STUDIES ON NUCLEOPHILIC ADDITIONS AT BRIDGING VINYL LIGANDS IN TRIOSMIUM CLUSTERS

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(Received November 18th, 1983)

Summary

The bridging vinyl clusters $[HOs_3(CH{=}CHR)(CO)_{10}]$ (R = H, Ph, or n-Bu) react with PMe_2Ph to give the zwitterionic adducts $[HOs_3(CHCHRPMe_2Ph)(CO)_{10}]$ which contain μ_2-alkylidene ligands. The adducts are not formed so readily when R = Ph or n-Bu but most readily when polar solvents are used. All three CH=CHR complexes add cyanide ion irreversibly to give the anionic clusters which were isolated as $[N(PPh_3)_2][HOs_3(CHCHRCN)(CO)_{10}]$. There is infrared evidence for the addition of various other anions. Acid reverses the addition of methoxide but HCl reacts with the cyanide adduct $[HOs_3(CHCH_2CN)(CO)_{10}]^-$ to give $[HOs_3Cl(CO)_{10}]$ and EtCN. No evidence for nucleophilic addition at $[HOs_3(PhC{=}CHPh)(CO)_{10}]$ was obtained.

Introduction

Nucleophilic addition at η-alkenes normally occurs only in cationic complexes or where the metal is in a fairly high oxidation state. With clusters, however, addition at unsaturated hydrocarbons occurs even with neutral compounds [1–4]. The first example to be reported was the addition of PMe_2Ph to $[Os_3H(\mu\text{-}CH{=}CH_2)(CO)_{10}]$ to give the zwitterionic μ-alkylidene complex $[Os_3H(\mu\text{-}CHCH_2PMe_2Ph)(CO)_{10}]$, the structure of which has been established spectroscopically and by X-ray diffraction [3]. In this paper we report addition reactions of PMe_2Ph and other nucleophiles at μ-CH=CHR (R = H, n-Bu, or Ph) complexes, extending earlier work on PMe_2Ph addition at the $CH{=}CH_2$ complex.

Results and discussion

Dimethylphenylphosphine additions. PMe_2Ph reacts readily with $[Os_3H(\mu\text{-}CH{=}CH_2)(CO)_{10}]$ (**1a**) in cyclohexane solution to give a precipitate of the adduct **2a**. The adduct is maintained on redissolving the crystals in chloroform and can be characterised by its ^1H NMR and infrared spectra in that solution. $\nu(CO)$ frequen-

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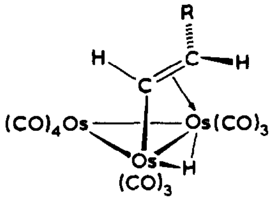
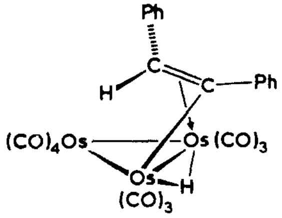


Ia: R = H
Ib: R = Ph
Ic: R = ^{n}Bu



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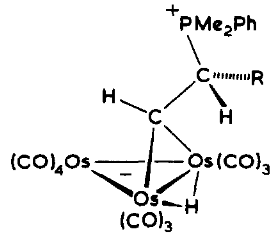
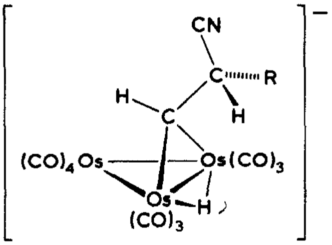


2a: R = H
2b: R = Ph
2c: R = ^{n}Bu



3a: R = H
3b: R = Ph
3c: R = ^{n}Bu

cies are lower for **2a** than for **1a** because of the accumulation of negative charge at the metal atoms in the zwitterionic adduct. The addition of PMe_2Ph to cyclohexane solutions of compounds **1b** and **1c** does not lead to adduct formation. Instead slow substitution reactions take place leading to $[Os_3(CO)_{10}(PMe_2Ph)_2]$ with alkene displacement. Interestingly this complex was obtained as two separable isomers which we believe to be the 1,2-isomer (previously formed directly from PMe_2Ph and triosmium dodecacarbonyl) [5] and a new 1,1-isomer as a minor product (see Experimental Section for spectroscopic details). The equilibrium for PMe_2Ph adduct formation is unfavourable in cyclohexane or dichloromethane and relatively slow alkene displacement then occurs. Alkene displacement is faster for **1c** than for **1b** and much faster for both of these than for **1a**. However, the adduct **2b** may be obtained as yellow crystals from polar solvents such as acetone. Redissolving crystals of **2b** in chloroform showed only the ^1H NMR spectrum of PMe_2Ph and **1b**, while only partial dissociation occured on redissolving in acetone. NMR spectra of **2b** and **2c** were therefore recorded in CD_3COCD_3 in the presence of a small excess of PMe_2Ph; no **1b** or **1c** were observed under these conditions. Thus the equilibria leading to adduct formation are suppressed by substituents at the carbon at which PMe_2Ph adds but are favoured by polar solvents. The ^1H NMR spectra of compounds **2b** and **2c**, unlike that of **2a**, show diastereotopic $P\mathit{Me}_2Ph$ groups since the phosphonium centre is attached to an asymmetric carbon atom.

No evidence for PMe_2Ph adduct formation was found at all for $[HOs_3(CPh{=}CHPh)(CO)_{10}]$ (**1d**), even in polar solvents. Only the substitution products $[Os_3(CO)_{10}(PMe_2Ph)_2]$ (again as isomers) were obtained. Although the carbon atom to be attacked is substituted in the same way as that of the CH=CHPh complex (**1b**), there is a good reason why the adduct is not formed. Complexes of

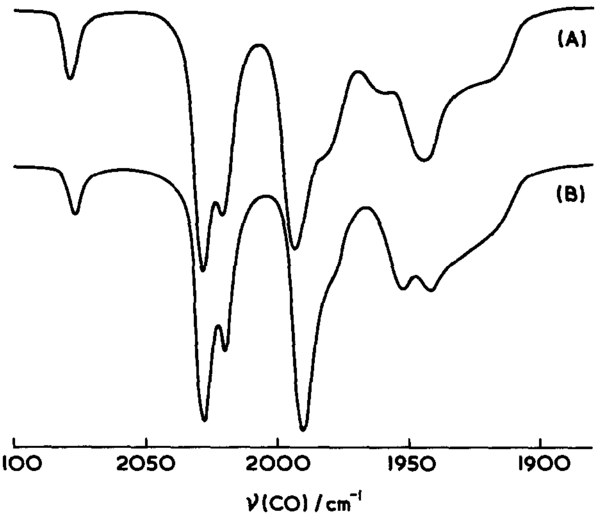


Fig. 1. Infrared spectra of ethanolic solutions of (A) $[Os_3H(CHCH_2PMe_2Ph)(CO)_{10}]$ and (B) $[Os_3H(CHCH_2CN)(CO)_{10}]^-$.

type $[HOs_3(\mu\text{-vinyl})(CO)_{10}]$ adopt one of two configurations; the CPh=CHPh complex has a different one to that of the $CH=CH_2$ and CH=CHEt complexes (see structural formulae shown) [6–8]. The CH=CHR complexes (R = H, Ph, n-Bu, Et) are almost certainly isostructural and different structurally from the CPh=CHPh complex. Nucleophilic addition of PMe_2Ph at complex **1d** would give an adduct in which the $CHPhPMe_2Ph$ group would clash with an axial CO ligand of the $Os(CO)_4$ group.

Anion additions. Addition of potassium cyanide to the vinyl complexes **1a**–**1c** in ethanol gave an immediate reaction as indicated by the shift of ν(CO) absorptions to lower frequencies. The anionic products may be isolated by addition of $[N(PPh_3)_2]Cl$. The spectra around 2000 cm^{-1} are very similar to those of the corresponding PMe_2Ph adducts (see Fig. 1). Thus the build-up of negative charge at the metal atoms is only very slightly greater, if at all, in the anion than in the zwitterionic PMe_2Ph adduct. The ^1H NMR data (Table 2) are quite consistent with these complexes having structures directly related to that established for $[HOs_3(CHCH_2PMe_2Ph)(CO)_{10}]$, that is structure **3** illustrated. The spectrum of $[HOs_3(CHCH_2CN)(CO)_{10}]^-$ is particularly simple and clear in this respect. The additions to give the cyano compounds **3** are irreversible and the adducts fairly easy to isolate. However, with most other anions the formation of adducts was only inferred from changes in the ν(CO) spectra of solutions; the products could not be isolated. $[N(PPh_3)_2][HOs_3(CHCH_2OMe)(CO)_{10}]$ was isolated in an impure state and was only characterised by its ^1H NMR and infrared spectra (see Table 1). Additions of various anions to ethanolic solutions of $[HOs_3(CH=CH_2)(CO)_{10}]$ gave infrared spectra consistent with their addition. We cannot be entirely certain that $[HOs_3(CHCH_2OEt)(CO)_{10}]^-$ is not formed in these cases, but the minor differences in the spectra (Table 1) suggest that the different anions, $[SC_6H_4Me\text{-}p]^-$, OH^-, NEt_2^-, are adding. In the case of Et_2NH addition we assume that the excess of base leads to $[Et_2NH_2][HOs_3(CHCH_2NEt_2)(CO)_{10}]$. Slow reactions often follow these

TABLE 1

INFRARED DATA FOR ADDUCTS OF $[Os_3H(CH{=}CHR)(CO)_{10}]$ (R = H, n-Bu, or Ph) WITH NUCLEOPHILES

Compound	Solvent	$\nu(CO)$ (cm^{-1})						
$[Os_3H(CHCH_2PMe_2Ph)(CO)_{10}]$	C_6H_{12} + acetone	2081m	2028vs	2021s	1995vs	1981s	1965m	1944s
$[Os_3H(CHCHPhPMe_2Ph)(CO)_{10}]$	acetone + PMe_2Ph	2080m	2031vs	2023vs	1992vs	1983sh	1962sh	1948s
$[Os_3H(CHCH\text{-}n\text{-}BuPMe_2Ph)(CO)_{10}]$	acetone + PMe_2Ph	2081m	2026vs		1993vs		1963m	1946s
$[N(PPh_3)_2][Os_3H(CHCH_2CN)(CO)_{10}]$	EtOH	2078w	2029vs	2021s	1991vs	1982sh	1953m	1942m
$[Os_3H(CHCH_2SC_6H_4Me\text{-}p)(CO)_{10}]^-$	EtOH	2075w	2024vs	2017s	1986vs	1975sh	1949m	1938sh
$[Os_3H(CHCH_2OH)(CO)_{10}]^-$	EtOH	2075w	2024vs	2017s	1994s	1985vs	1975sh	1947m
$[N(PPh_3)_2][Os_3H(CHCH_2OMe)(CO)_{10}]$	Et_2O	2074w	2023vs	2016s	1983vs		1964sh	1946sh
$[Os_3H(CHCH_2NEt_2)(CO)_{10}]^-$	$PhNMe_2$	2079w	2029vs	2022s	1994s	1982s		1943m
$[N(PPh_3)_2][Os_3H(CHCHPhCN)(CO)_{10}]$	CH_2Cl_2	2077w	2028vs	2022sh		1986vs		1948m
$[N(PPh_3)_2][Os_3H(CHCH\text{-}n\text{-}BuCN)(CO)_{10}]$	EtOH	2079m	2029vs	2020s	1990vs	1980sh	1952s	1942s

TABLE 2

^{1}H NMR DATA FOR ADDUCTS OF μ-VINYL COMPOUNDS WITH PMe_2Ph, CN^-, or OMe^- [a]

Compound	H^a	H^b	H^c	PMe/OMe
$[Os_3H^a(CH^bCH_2{}^cPMe_2Ph)(CO)_{10}]$	−16.31(dd)	5.77(ddt)	3.38(dd)	2.37(d)
	$[J_{ab}$ 3.1; J_{bc} 7.7; J_{aP} 1.5; J_{bP} 17.2; J_{cP} 12.3; J_{MeP} 13.8]			
$[Os_3H^a(CH^bCH^cPhPMe_2Ph)(CO)_{10}]$ [b]	−16.41(dd)	6.36(ddd)	4.04(dd)	2.37(d), 2.26(d)
	$[J_{ab}$ 2.9; J_{bc} 12.5; J_{aP} 1.8; J_{bP} 15.9; J_{cP} 10.2; J_{MeP} 13.7]			
$[Os_3H^a(CH^bCH^cBuPMe_2Ph)(CO)_{10}]$ [b]	−16.41(dd)	6.28(ddd)	2.82(m)	2.37(d), 2.27(d)
	$[J_{ab}$ 3.1; J_{bc} 8.5; J_{aP} 1.9; J_{bP} 14.0; J_{MeP} 12.9, 13.1]			
$[PPN][Os_3H^a(CH^bCH_2{}^cCN)(CO)_{10}]$	−16.46(d)	6.26(dt)	2.95(d)	
	$[J_{ab}$ 3.3; J_{bc} 8.4]			
$[PPN][Os_3H^a(CH^bCH_2{}^cOMe)(CO)_{10}]$	−16.57(d)	6.47(dt)	3.71(d)	3.25(s)
	$[J_{ab}$ 3.3; J_{bc} 8.4]			
$[PPN][Os_3H^a(CH^bCH^cPhCN)(CO)_{10}]$	−16.46(d)	6.82(dd)	3.50(d)	
	$[J_{ab}$ 3.2; J_{bc} 12.2]			
$[PPN][Os_3H^a(CH^bCH^cBuCN)(CO)_{10}]$ [c]	−16.48(d)	6.32(dd)	2.27(ddd)	
	$[J_{ab}$ 3.1; J_{bc} 11.8]			

[a] δ-values given, with J values in Hz. Solvent $CDCl_3$. [b] In CD_3COCD_3 containing some PMe_2Ph. [c] n-Bu signals at δ 1.70 (m) and 0.83(t).

additions. For example, compound **1a** reacts with Et_2NH/NaOMe in refluxing methanol to give $[HOs_3(OMe)(CO)_{10}]$ (22%), $[HOs_3(OH)(CO)_{10}]$ (15%), as well as $[HOs_3(CHCH{=}NEt_2)(CO)_{10}]$ (5%). The last compound was previously reported to be formed by reactions of NEt_3 with $[Os_3(CO)_{10}(MeCN)_2]$ [9] but we do not yet understand how this compound is formed by loss of hydride from $[HOs_3(CHCH_2NEt_2)(CO)_{10}]^-$ which is presumably formed initially.

Tertiary amines do not add. Initially we thought that they did, since a solution of $[HOs_3(CH{=}CH_2)(CO)_{10}]$ in triethylamine gave a ν(CO) spectrum consistent with an adduct formation. However, if primary and secondary amine impurities and water are removed, the spectrum of the vinyl compound in NEt_3 is like that in other inert solvents. Addition of small amounts of Et_2NH to an NEt_3 solution of the complex then leads to what we presume is $[Et_3NH][HOs_3(CHCH_2NEt_2)(CO)_{10}]$. Use of $PhNMe_2$ as solvent gave a similar effect (Table 1).

No nucleophilic additions to $[HOs_3(CPh{=}CHPh)(CO)_{10}]$ could be substantiated. Treatment of the compound with Me_3NO leads to decarbonylation to give $[H_2Os_3(\mu_3\text{-}PhC_2Ph)(CO)_9]$, in which case attack has occurred at CO [8]. The alkene PhCH=CHPh is displaced in many reactions of the vinyl compound; compound **1d** in moist acetone readily gives $[HOs_3(OH)(CO)_{10}]$ while in CD_3OD the cluster $[DOs_3(OCD_3)(CO)_{10}]$ is obtained.

Protonation reactions. An excess of CF_3CO_2H reacts with $[HOs_3(CH{=}CH_2)(CO)_{10}]$ in either $CDCl_3$ or CD_2Cl_2 to give ethene and $[HOs_3(CF_3CO_2)(CO)_{10}]$ (^{1}H NMR identification). An intermediate was observed by ^{1}H NMR (singlets at δ 3.6 and −14.3) but this could not be characterised further.

Acidification of solutions of the adducts leads to two different types of reaction. Thus $[HOs_3(CHCH_2OMe)(CO)_{10}]^-$ reacts initially with CF_3CO_2H to give $[HOs_3(CH{=}CH_2)(CO)_{10}]$ and MeOH and with an excess of the acid the reaction described above proceeds. $[HOs_3(CHCH_2OMe)(CO)_{10}]^-$ is behaving as an activated ether and the nucleophilic addition of OMe^- is reversed. On the other hand an excess of HCl reacts with a chloroform solution of $[HOs_3(CHCH_2CN)(CO)_{10}]^-$ to give $[HOs_3Cl(CO)_{10}]$ and EtCN, identified by their NMR spectra. In this case acidolysis of the Os–C bonds has occurred as in the reactions of $[HOs_3(CHCH_2PMe_2Ph)(CO)_{10}]$ with HCl in refluxing methanol which gives $[EtPMe_2Ph]Cl$ [2]. Additions of CF_3CO_2H or CH_3CO_2H to $[HOs_3(CHCH_2CN)(CO)_{10}]^-$ give the corresponding compounds $[HOs_3(RCO_2)(CO)_{10}]$.

Attempting to establish whether protonation occurred initially at the metal in these acidifications, we added stoichiometric amounts of CF_3CO_2H to $CDCl_3$ solutions of $[HOs_3(CHCH_2PMe_2Ph)(CO)_{10}]$ and $[HOs_3(CHCH_2CN)(CO)_{10}]^-$ at different temperatures. Several new hydride NMR signals were observed indicating a mixture of hydrides, the composition of which varied with time. We do not have any evidence to identify these intermediates, but clearly the acidolysis occurs through several stages.

Experimental

The complexes $[Os_3H(\mu\text{-}CH{=}CHR)(CO)_{10}]$ (R = H [10], Ph [10], and n-Bu [11]) and $[Os_3H(\mu\text{-}CPh{=}CHPh)(CO)_{10}]$ [10] were prepared by published procedures.

Reactions of vinyl compounds with PMe_2Ph

(a) $[HOs_3(CH{=}CH_2)(CO)_{10}]$. The addition has been described [1–3].

(b) $[HOs_3(CH{=}CHPh)(CO)_{10}]$. PMe_2Ph (0.050 cm^3) was added to a solution of the CH=CHPh complex (0.040 g) in a mixture of dichloromethane (5 cm^3) and nitromethane (5 cm^3). The colour changed immediately from orange to yellow and the solvent was removed under vacuum to give a yellow oil. Crystallisation from acetone containing an excess of PMe_2Ph gave orange crystals of $[HOs_3(CHCHPhPMe_2Ph)(CO)_{10}]$ (0.030 g, 66%). (Found: C, 28.8; H, 1.9. $C_{28}H_{19}O_{10}Os_3P$ calcd.: C, 27.0; H, 1.8%).

A similar addition of PMe_2Ph (0.010 cm^3) to the CH=CHPh compound (0.040 g) in cyclohexane (20 cm^3) under nitrogen gave no initial reaction (the spectrum was unchanged around 2000 cm^{-1}). Further PMe_2Ph (0.040 g) was added. After 5 days the solution was evaporated to give an orange oil which was separated by TLC (silica, eluant = petroleum ether/dichloromethane mixture, 9/1 by volume) to give starting material (0.002 g), $[1,1\text{-}Os_3(CO)_{10}(PMe_2Ph)_2]$ (0.014 g, 31%), and $[1,2\text{-}Os_3(CO)_{10}(PMe_2Ph)_2]$. The 1,2-isomer has been formed by reaction of $[Os_3(CO)_{12}]$ with PMe_2Ph [5], while the 1,1-isomer can be alternatively formed by reaction of PMe_2Ph with $[Os_3(CO)_{10}(diene)]$ (diene = butadiene or cyclohexadiene); $\nu(CO)$ (1,1-isomer) 2091m, 2040s, 2012sh, 2005vs, 1987sh, 1980w, 1957m, 1913sh, 1908w cm^{-1} (cyclohexane solution) [12].

(c) $[HOs_3(CH{=}CH\text{-}n\text{-}Bu)(CO)_{10}]$. Addition of PMe_2Ph (0.030 cm^3) to the CH=CH-n-Bu complex (0.050 g) in acetone (30 cm^3) gave the adduct at −70°C (infrared evidence). After warming to room temperature, TLC separation after 5 h gave starting complex (0.005 g) and $[1,2\text{-}Os_3(CO)_{10}(PMe_2Ph)_2]$ (0.002 g) as the only isolable products.

(d) $[HOs_3(CPh{=}CHPh)(CO)_{10}]$. PMe_2Ph (0.010 cm^3) was added to the CPh=CHPh compound (0.023 g) in ethanol (10 cm^3). After 24 h at room temperature, TLC separation gave two isomers of $[Os_3(CO)_{10}(PMe_2Ph)_2]$, 1,1-isomer (0.001 g) and the 1,2-isomer (0.016 g).

Preparation of $[N(PPh_3)_2][Os_3H(CHCH_2CN)(CO)_{10}]$

A mixture of potassium cyanide (0.030 g), $[Os_3H(CH{=}CH_2)(CO)_{10}]$ (0.347 g) and $[N(PPh_3)_2]Cl$ (excess) in ethanol (170 cm^3) was heated for 5 min on a steam bath. Most of the solvent was removed under vacuum and diethyl ether (50 cm^3) was added to precipitate the excess of $[N(PPh_3)_2]Cl$, which was then filtered off. The yellow ether solution was washed with water and dried over $MgSO_4$. Evaporation to dryness gave orange crystals of the product (0.480 g, 84%) (Found: C, 41,5; H, 2,5; N, 1.9. $C_{49}H_{34}N_2O_{10}Os_3P_2$ calcd.: C, 40.8; H, 2.4; N, 1.9%). Similar treatments of $[Os_3H(CHCHPh)(CO)_{10}]$ and $[Os_3H(CHCH\text{-}n\text{-}Bu)(CO)_{10}]$ also gave the complexes $[N(PPh_3)_2][Os_3H(CHCHRCN)(CO)_{10}]$ (R = Ph or n-Bu) as yellow or orange solids which were characterised by infrared (ν(CN) 2220 cm^{-1}) and NMR spectroscopy (see Tables) but which were not obtained analytically pure.

Preparation of $[N(PPh_3)_2][Os_3H(CHCH_2OMe)(CO)_{10}]$

A solution of $[N(PPh_3)_2]Cl$ (0.17 g), sodium methoxide (0.010 g), and $[Os_3H(CH{=}CH_2)(CO)_{10}]$ (0.078 g) in methanol (20 cm^3) was allowed to stand for 30 min before evaporation to dryness under vacuum. Extraction with CH_2Cl_2 (2 cm^3) and addition of diethyl ether (30 cm^3) gave a precipitate of $[N(PPh_3)_2]Cl$ which was filtered off. Evaporation gave the product as a yellow oil (analytically impure) which was characterised by its spectra (see Tables).

Reaction of $[HOs_3(CH{=}CH_2)(CO)_{10}]$ with diethylamine and methanolic sodium methoxide

Diethylamine (1 cm^3), sodium methoxide (0.010 g) and the vinyl cluster (0.100 g) were dissolved in methanol (40 cm^3) and heated under reflux for 3 h under nitrogen. Removal of solvent and TLC separation gave $[HOs_3(OMe)(CO)_{10}]$ (0.022 g, 22%), $[HOs_3(CHCH{=}NEt_2)(CO)_{10}]$ (0.005 g, 5%), and $[HOs_3(OH)(CO)_{10}]$ (0.015 g, 15%), all characterised by comparison of their spectra with those of authentic samples.

Protonation reactions

Reaction of $[N(PPh_3)_2][HOs_3(CHCH_2CN)(CO)_{10}]$ with hydrogen chloride. HCl gas was bubbled through a solution of the complex (0.043 g) in $CDCl_3$ (0.5 cm^3) in an NMR tube. The ^{1}H NMR spectrum showed the quantitative formation of $[HOs_3Cl(CO)_{10}]$ and CH_3CH_2CN, both characterised by comparison of spectra with those of authentic samples. A similar treatment of $[N(PPh_3)_2][HOs_3(CHCH_2OMe)(CO)_{10}]$ but with trifluoroacetic acid gave $[HOs_3(CH{=}CH_2)(CO)_{10}]$ quantitatively.

Reaction of $[HOs_3(CHCH_2PMe_2Ph)(CO)_{10}]$ with hydrogen chloride. HCl gas was bubbled through a solution of the cluster (0.046 g) in chloroform. The ^{1}H NMR spectrum showed only $[HOs_3Cl(CO)_{10}]$ and $[EtPMe_2Ph]^+$ as products. The cluster was isolated after chromatography (0.034 g, 85%) as orange crystals.

Acknowledgements

We thank the SERC for a research studentship and Johnson-Matthey Ltd for a generous loan of osmium tetraoxide.

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