Synthesis of New Silyl-substituted Triosmium Clusters. The Reactivity of the Anion $[Os_3(CO)_{11}\{Si(OEt)_3\}]^-$ towards Group 1B and 2B Metals

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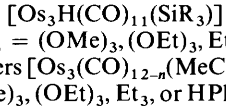
Silyl-substituted triosmium clusters of general formula $[Os_3H(CO)_{11}(SiR_3)]$ (**1**) or $[Os_3H(CO)_{10}(MeCN)(SiR_3)]$ (**2**) [$R_3 = (OMe)_3, (OEt)_3, Et_3$, or HPh_2] can be synthesized from the reaction of the silane derivatives $SiHR_3$ with the activated clusters $[Os_3(CO)_{11}(MeCN)]$ and $[Os_3(CO)_{10}(MeCN)_2]$, respectively. The complex $[Os_3H(CO)_{11}\{Si(OEt)_3\}]$ is easily deprotonated by triethylamine affording the highly reactive anion $[Os_3(CO)_{11}\{Si(OEt)_3\}]^-$ which has been isolated as the salt $[NHEt_3][Os_3(CO)_{11}\{Si(OEt)\}_3]$ (**3b**). A study of the reactivity of (**3b**) towards Group 1B and 2B metal ions has been undertaken and the reaction products characterized on the basis of their spectroscopic properties.

Very few transition-metal clusters containing silicon–metal bonds have been reported so far despite the large number of mononuclear carbonyl complexes having ligands with silicon donor atoms bonded to the metal centre.[1] The known silyl-substituted clusters have been synthesized from: (*i*) the mononuclear starting materials $[OsH_2(CO)_4]$[2] and $Na[Co(CO)_4]$;[3] (*ii*) $[M_3(CO)_{12}]$ (M = Ru or Os);[4] (*iii*) the unsaturated cluster $[Os_3H_2(CO)_{10}]$;[5] (*iv*) $[Ru_3H(CO)_{11}]^-$;[6] and (*v*) $[Co_2(CO)_8]$[7] and the appropriate silane or disilane derivatives.

Here we report the preparation of some cluster compounds of general formula $[Os_3H(CO)_{11}(SiR_3)]$ and $[Os_3H(CO)_{10}(MeCN)(SiR_3)]$ [$R_3 = (OMe)_3, (OEt)_3, Et_3$, or HPh_2] from the functionalized clusters $[Os_3(CO)_{12-n}(MeCN)_n]$ (n = 1 or 2) and $SiHR_3$ [$R_3 = (OMe)_3, (OEt)_3, Et_3$, or HPh_2] and the reactivity of the anionic cluster $[NHEt_3][Os_3(CO)_{11}\{Si(OEt)_3\}]$ towards Group 1B and 2B metal derivatives.

Results and Discussion

The compound $[Os_3(CO)_{11}(MeCN)]$ reacts in a few minutes with an excess of $SiHR_3$ in CH_2Cl_2 at room temperature, under nitrogen to afford the silyl derivatives $[Os_3H(CO)_{11}(SiR_3)]$ [$R_3 = (OMe)_3$, (**1a**); $(OEt)_3$, (**1b**); Et_3, (**1c**); or HPh_2, (**1d**)]. The products were purified by thin-layer chromatography (silica) eluting with a CH_2Cl_2–hexane mixture. The new clusters are air-stable yellow microcrystals which have been fully characterized on the basis of their analytical data, i.r. and ^1H n.m.r. spectroscopy (see Table). In particular the i.r. spectra of these new clusters exhibit in the carbonyl region the same band pattern found for the recently reported $[M_3H(CO)_{11}(M'R_3)]$ (M = Ru or Os, M′ = Ge or Sn).[8] The presence in the ^1H n.m.r. spectrum in $CDCl_3$ solution of a high-field resonance with δ between −18.32 and −18.76 is indicative of a bridging hydride consistent with the following structure with

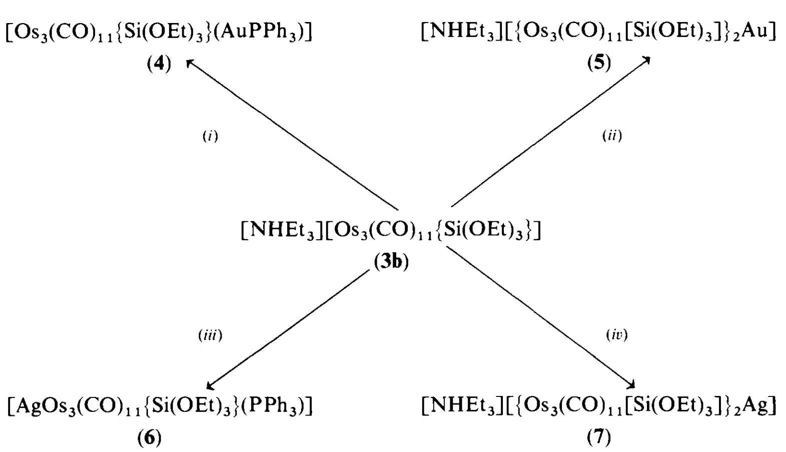


the silane group in equatorial position, terminally bound to an osmium atom, as has been found for example in the structurally characterized $[Os_3H(\mu\text{-}H)_2(CO)_{10}(SiHPh_2)]$[5] and $[Os_3(\mu\text{-}H)_3(CO)_9(SiMeCl_2)_3]$.[4]

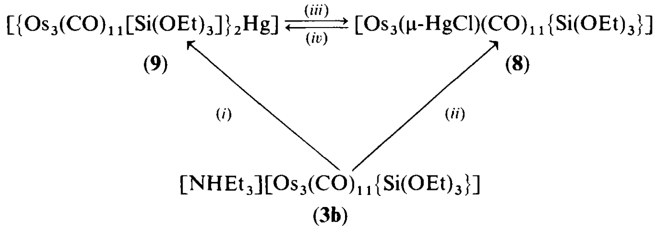
The reaction of the bis(acetonitrile) derivative $[Os_3(CO)_{10}(MeCN)_2]$, carried out with an excess of $SiHR_3$, in CH_2Cl_2, at room temperature, under nitrogen, affords $[Os_3H(CO)_{10}(MeCN)(SiR_3)]$ [$R_3 = (OMe)_3$, (**2a**); $(OEt)_3$, (**2b**); Et_3, (**2c**); or HPh_2, (**2d**)] in high yields (70—90%). Interestingly, only one MeCN ligand could be substituted although all the reactions were carried out with an excess of silane. The yellow microcrystalline products (**2**) were characterized by i.r. and ^1H n.m.r. spectroscopy (see Table) after separation by t.l.c. (silica, eluant CH_2Cl_2–hexane). The singlet resonance in the ^1H n.m.r. high-field region at δ between −16.09 and −16.56 is consistent with the presence of a bridging hydride. The reaction mechanism involved is an oxidative addition–elimination which is a general synthetic route for the formation of transition metal–silicon bonds.[1]

The cluster $[Os_3H(CO)_{11}\{Si(OEt)_3\}]$ (**1b**) can easily be deprotonated by triethylamine in heptane solution to yield quantitatively the anionic complex $[NHEt_3][Os_3(CO)_{11}\{Si(OEt)_3\}]$ (**3b**).

Although the reactivity of silyl derivatives of mono- and di-nuclear transition-metal complexes has been the subject of several papers,[1] the reactivity of silyl-substituted cluster compounds is in comparison a rather neglected field.[9] Our interest was also in finding a possible parallel to the reactivity of $[Os_3H(CO)_{11}]^-$ towards Group 1B and 2B metal derivatives.[10–13] The candidate chosen for this investigation was the anionic $[Os_3(CO)_{11}\{Si(OEt)_3\}]^-$ (**3b**). Its reaction with $[AuCl(PPh_3)]$ carried out in CH_2Cl_2 either at room temperature or at reflux temperature in the presence of $TlPF_6$ leads to the formation of $[Os_3(CO)_{11}\{Si(OEt)_3\}(AuPPh_3)]$ (**4**) (see Scheme 1) in high yield (80%). The product was purified by t.l.c. (silica gel) eluting with a n-hexane–CH_2Cl_2 mixture. The orange mixed-metal cluster (**4**) has been identified on the basis of i.r., ^1H n.m.r. (see Table), and mass spectrometry [m/z 1 506 (^{192}Os)]. It has been previously observed that because of the isolobal nature of the $[Au(PR_3)]^+$ moiety and hydride ligands the gold phosphine group replaces an hydride in the structurally characterized clusters $[AuOs_3H(CO)_{10}(PPh_3)]$[10] and $[Au_2Os_3(CO)_{10}(PEt_3)_2]$.[11] On this basis, we assume that also in our case the $Au(PPh_3)$ unit bridges an Os–Os bond replacing the bridging hydride in $[Os_3H(CO)_{11}\{Si(OEt)_3\}]$. Since it has been reported that thermolysis of $[AuOs_3H(CO)_{10}(PPh_3)]$ in CH_2Cl_2 solutions in the presence of a two-fold excess of $[N(PPh_3)_2]Cl$ yields the mixed-metal cluster anion $[\{Os_3H(CO)_{10}\}_2Au]^-$,[14] the same treatment has been applied to cluster (**4**). However in this case the reaction did not afford the expected $[N(PPh_3)_2][\{Os_3(CO)_{11}[Si(OEt)_3]\}_2Au]$ but only



Scheme 1. (*i*) [AuCl(PPh$_3$)], CH$_2$Cl$_2$, room temperature (r.t.) or reflux, in the presence of TlPF$_6$; (*ii*) [Au(CO)Cl], CH$_2$Cl$_2$, r.t., in the presence of TlPF$_6$; (*iii*) [AgCl(PPh$_3$)], CH$_2$Cl$_2$, r.t.; (*iv*) AgBF$_4$, tetrahydrofuran (thf), reflux



Scheme 2. (*i*) 0.5 Equivalent HgCl$_2$, or 0.5 equivalent Hg(O$_2$CCF$_3$)$_2$, CH$_2$Cl$_2$; (*ii*) 1 equivalent HgCl$_2$, CH$_2$Cl$_2$; (*iii*) 0.5 equivalent HgCl$_2$, CH$_2$Cl$_2$; (*iv*) on standing in CH$_2$Cl$_2$

the precursor [N(PPh$_3$)$_2$][Os$_3$(CO)$_{11}${Si(OEt)$_3$}]. In order to synthesize the dimeric gold-containing cluster [{Os$_3$(CO)$_{11}$-[Si(OEt)$_3$]}$_2$Au]$^-$ in which two cluster units are linked together by sharing a common edge-bridging gold atom, a different synthetic route was followed by treating the precursor (**3b**) with [Au(CO)Cl]. The reaction proceeds smoothly in CH$_2$Cl$_2$ in the presence of TlPF$_6$ yielding the dark brown anion [{Os$_3$(CO)$_{11}$[Si(OEt)$_3$]}$_2$Au]$^-$ (**5**) characterized on the basis of i.r., ^{1}H n.m.r. (see Table), and mass spectroscopy (*m*/*z* 2 292). This method has been successfully used in the synthesis of [Au{Pt$_3$(μ-CO)$_3$(PPh$_3$)$_3$}$_2$]PF$_6$[15] from [Pt$_3$(μ-CO)$_3$(PPh$_3$)$_4$] and [Au(L)Cl] (L = CO or Me$_2$S) in the presence of an excess of TlPF$_6$. The reaction of (**3b**) with [AgCl(PPh$_3$)], carried out in CH$_2$Cl$_2$ under nitrogen at room temperature, afforded the mixed-metal cluster [AgOs$_3$(CO)$_{11}${Si(OEt)$_3$}(PPh$_3$)] (**6**) identified by its spectroscopic data (see Table; and *m*/*z* 1 418). Compound (**3b**) reacts with AgPF$_6$ or AgBF$_4$ in a 1:2 molar ratio in refluxing thf under nitrogen generating the anionic cluster [NHEt$_3$][{Os$_3$(CO)$_{11}$[Si(OEt)$_3$]}$_2$Ag] (**7**). This compound is presumably isostructural with the previously reported [N(PPh$_3$)$_2$][{Os$_3$H(CO)$_{10}$}$_2$Ag][12] but in this case its instability prevented any attempt at crystallization.

Addition of 1 equivalent of HgCl$_2$ to a CH$_2$Cl$_2$ solution containing compound (**3b**) afforded in a few minutes [Os$_3$(μ-HgCl)(CO)$_{11}${Si(OEt)$_3$}] (**8**) (see Scheme 2) characterized on the basis of i.r. and n.m.r. spectroscopy (see Table). No good mass spectrum could be obtained. This compound is stable only in the solid state whereas in chlorinated solvents such as CH$_2$Cl$_2$ or CHCl$_3$ on standing at room temperature under nitrogen for a few hours it is converted into the dimeric cluster [{Os$_3$(CO)$_{11}$[Si(OEt)$_3$]}$_2$Hg] (**9**).

These symmetrization reactions are well known and have been found to occur for example in the case of the dinuclear complex [Mn$_2$(μ-HgX)(μ-PPh$_2$)(CO)$_8$] (X = Ph or Cl)[16] which in CH$_2$Cl$_2$ is stable only at temperatures below −30 °C, readily interconverting into [Hg{Mn$_2$(μ-PPh$_2$)(CO)$_8$}$_2$] at temperatures between −30 and −20 °C. In order to confirm the dimeric nature of compound (**9**) the reaction has been repeated with a 2:1 molar ratio of cluster to HgCl$_2$. As expected, the formation of (**9**) is observed which upon addition of HgCl$_2$ affords the monomeric compound (**8**). By treating the anionic cluster (**3b**) with a different mercury(II) salt such as Hg(O$_2$CCF$_3$)$_2$ again formation of compound (**9**) is observed.

Experimental

All reactions were carried out under nitrogen at room temperature unless otherwise stated. Subsequent work-up was carried out without no precaution to exclude air. The solvents were dried over the appropriate drying agents and distilled before use. Infrared spectra were recorded on a Perkin-Elmer PE 983 spectrometer, fast atom bombardment mass spectra on a Kratos MS 50 or MS 890, and ^{1}H n.m.r. spectra on a Bruker WM250 spectrometer using CDCl$_3$ or CD$_2$Cl$_2$ as the internal reference. The neutral products were separated in air by t.l.c. on 20 × 20 cm glass plates coated with a 0.25-mm layer of Merck Kieselgel 60 F$_{254}$ using the appropriate eluant. The compounds [Os$_3$(CO)$_{11}$(MeCN)], [Os$_3$(CO)$_{10}$(MeCN)$_2$],[17] and [Au(CO)Cl][18] were prepared by literature methods.

Synthesis of the Clusters [Os$_3$H(CO)$_{11}$(SiR$_3$)] (**1**).—[Os$_3$H(CO)$_{11}${Si(OMe)$_3$}] (**1a**). An excess of SiH(OMe)$_3$ was added to a CH$_2$Cl$_2$ solution (20 cm^3) of [Os$_3$(CO)$_{11}$(MeCN)] (0.100 g, 0.11 mmol). The colour of the solution immediately changed from dark yellow to light yellow and the reaction mixture was stirred for an additional 15 min. Evaporation of the solvent followed by t.l.c. eluting with n-hexane–CH$_2$Cl$_2$–ethyl acetate (1:1:1) gave [Os$_3$H(CO)$_{11}${Si(OMe)$_3$}] (**1a**) (0.090 g, 83%).

[Os$_3$H(CO)$_{11}${Si(OEt)$_3$}] (**1b**). The method used for the preparation of (**1a**) was followed for this compound, with an excess of SiH(OEt)$_3$ and [Os$_3$(CO)$_{11}$(MeCN)] (0.100 g, 0.11 mmol). Following evaporation of the solvent, the residue was

Table. I.r. and ^{1}H n.m.r. data

	Compound	$\nu(CO)^a$/cm^{-1}	^{1}H N.m.r. (δ)^b
(**1a**)	$[Os_3H(CO)_{11}\{Si(OMe)_3\}]$	2 134w, 2 086s, 2 053vs, 2 029m, 2 015m, 2 004s, 1 997w (sh), 1 988w	3.61 (s, Me), 3.58 (s, Me),^{c} -18.32 (s, OsHOs), -18.36 (s, OsHOs)^c
(**1b**)	$[Os_3H(CO)_{11}\{Si(OEt)_3\}]$	2 134w, 2 085s, 2 053vs, 2 028m, 2 014m, 2 003s, 1 987m (sh), 1 952w	3.88 [q, $Si(OC\mathit{H}_2CH_3)_3$, J 7.00], 1.27 [t, $Si(OCH_2C\mathit{H}_3)_3$, J 7.0], -18.32 (s, OsHOs)
(**1c**)	$[Os_3H(CO)_{11}(SiEt_3)]$	2 132w, 2 080s, 2 052vs, 2 042ms, 2 026m, 2 014ms, 2 002, 1 993ms,	1.50 (m, Et), -18.76 (s, OsHOs)
(**1d**)	$[Os_3H(CO)_{11}(SiHPh_2)]$	1 969w, 2 134w, 2 080m, 2 053vs, 2 047s (sh), 2 030m, 2 017m, 2 002s, 1 988w (sh), 1 976w	7.47 (m, Ph), 6.02 (s, SiH), -18.52 (s, OsHOs)
(**2a**)	$[Os_3H(CO)_{10}(MeCN)\{Si(OMe)_3\}]$	2 104m, 2 066vs, 2 040vs, 2 019vs, 2 001vs, 1 988s^d	3.62 [s, $Si(OMe)_3$], 2.60 (s, MeCN), -16.56 (s, OsHOs)
(**2b**)	$[Os_3H(CO)_{10}(MeCN)\{Si(OEt)_3\}]$	2 103mw, 2 065s, 2 039s, 2 018s, 1 999s, 1 986m^d	3.90 [q, $Si(OC\mathit{H}_2CH_3)_3$, J 7.0], 2.58 (s, MeCN), 1.28 [t, $Si(OCH_2C\mathit{H}_3)_3$, J 7.0], -16.38 (s, OsHOs)
(**2c**)	$[Os_3H(CO)_{10}(MeCN)(SiEt_3)]$	2 098m, 2 060vs, 2 031s, 2 015s, 1 995s, 1 980m, 1 951w (sh)^d	2.59 (s, MeCN), 1.06 (m, Et), -16.44 (s, OsHOs)
(**2d**)	$[Os_3H(CO)_{10}(MeCN)(SiHPh_2)]$	2 102m, 2 064s, 2 038s, 2 018s, 2 001s, 1 986ms^d	7.46 (m, Ph), 6.12 (d, SiH, J 0.6 Hz), 2.34 (s, MeCN), -16.09 (s, OsHOs)
(**3b**)	$[NHEt_3][Os_3(CO)_{11}\{Si(OEt)_3\}]$	2 093w, 2 036s, 2 001vs, 1 980w, 1 955w^d	3.79 [q, $Si(OC\mathit{H}_2CH_3)_3$, J 7.0], 3.17 [q, $NH(C\mathit{H}_2CH_3)_3$, J 7.3], 1.35 [t, $Si(OCH_2C\mathit{H}_3)_3$, J 7.0], 1.23 [t, $NH(CH_2C\mathit{H}_3)_3$, J 7.3]
(**4**)	$[Os_3(CO)_{11}\{Si(OEt)_3\}(AuPPh_3)]$	2 109m, 2 061s, 2 043ms, 2 029vs, 2 012ms, 1 989w, 1 974m, 1 950m	7.50 (m, Ph), 3.84 [q, $Si(OC\mathit{H}_2CH_3)_3$, J 7.0], 1.17 [t, $Si(OCH_2C\mathit{H}_3)_3$, J 7.0]^e
(**5**)	$[NHEt_3][\{Os_3(CO)_{11}[Si(OEt)_3]\}_2Au]$	2 096w, 2 057s, 2 027vs, 2 002s, 1 970m^d	3.85 [q, $Si(OC\mathit{H}_2CH_3)_3$, J 7.0], 3.17 [q, $NH(C\mathit{H}_2CH_3)_3$, J 7.1], 1.35 [t, $NH(CH_2C\mathit{H}_3)_3$, J 7.1], 1.23 [t, $Si(OCH_2C\mathit{H}_3)_3$, J 7.0]^e
(**6**)	$[AgOs_3(CO)_{11}\{Si(OEt)_3\}(PPh_3)]$	2 107mw, 2 055s, 2 025vs, 2 008m (sh), 1 988m, 1 964m	7.36 (m, Ph), 3.84 [q, $Si(OC\mathit{H}_2CH_3)_3$, J 6.9], 1.16 [t, $Si(OCH_2C\mathit{H}_3)_3$, J 6.9]^e
(**7**)	$[NHEt_3][\{Os_3(CO)_{11}[Si(OEt)_3]\}_2Ag]$	2 105mw, 2 052m, 2 022vs, 2 001m (sh), 1 980w, 1 968m, 1 943w^d	3.99 [q, $Si(OC\mathit{H}_2CH_3)_3$, J 7.0], 3.23 [q, $NH(C\mathit{H}_2CH_3)_3$, J 7.3], 1.40 [t, $NH(CH_2C\mathit{H}_3)_3$, J 7.3], 1.31 [t, $Si(OCH_2C\mathit{H}_3)_3$, J 7.0]
(**8**)	$[Os_3(\mu\text{-}HgCl)(CO)_{11}\{Si(OEt)_3\}]$	2 130m, 2 080s, 2 058s (sh), 2 049vs, 2 027ms, 2 010ms, 1 981m, 1 937w^d	4.04 [q, $Si(OC\mathit{H}_2CH_3)_3$, J 7.0], 1.32 [t, $Si(OCH_2C\mathit{H}_3)_3$, J 7.0]
(**9**)	$[\{Os_3(CO)_{11}[Si(OEt)_3]\}_2Hg]$	2 112m, 2 071s, 2 055s, 2 045vs, 2 025m, 2 012m, 1 991m, 1 970w	3.91 [q, $Si(OC\mathit{H}_2CH_3)_3$, J 7.0], 1.22 [t, $Si(OCH_2C\mathit{H}_3)_3$, J 7.0]

^{a} In n-hexane. ^{b} In $CDCl_3$; J(HH) in Hz. ^{c} Minor isomer. ^{d} In CH_2Cl_2. ^{e} In CD_2Cl_2.

chromatographed eluting with n-hexane–CH_2Cl_2 (1:1) to give yellow microcrystals of compound (**1b**) (0.087 g, 77%).

$[Os_3H(CO)_{11}(SiEt_3)]$ (**1c**). This cluster was prepared from an excess of $SiHEt_3$ and $[Os_3(CO)_{11}(MeCN)]$ (0.100 g, 0.11 mmol) by a procedure analogous to that used for (**1a**). Removal of the solvent and subsequent t.l.c. eluting with n-hexane–CH_2Cl_2 (2:1) afforded the yellow microcrystalline compound (**1c**) (0.071 g, 66%).

$[Os_3H(CO)_{11}(SiHPh_2)]$ (**1d**). A route similar to that used for the synthesis of (**1a**) was followed. Starting with an excess of SiH_2Ph_2 and $[Os_3(CO)_{11}(MeCN)]$ (0.100 g, 0.11 mmol), 0.091 g (79%) of compound (**1d**) was obtained as a yellow solid.

Synthesis of the Clusters $[Os_3H(CO)_{10}(MeCN)(SiR_3)]$ (**2**).—$[Os_3H(CO)_{10}(MeCN)\{Si(OMe)_3\}]$ (**2a**). To a solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.200 g, 0.21 mmol) in CH_2Cl_2 (20 cm^3) an equimolar amount of $SiH(OMe)_3$ was added by a syringe. The colour of the solution immediately changed from dark yellow to light yellow and the reaction mixture was stirred for 15 min. The solvent was evaporated to dryness and the residue was chromatographed eluting with n-hexane–CH_2Cl_2–ethyl acetate (1:1:1). Two yellow bands were collected which were in order of elution $[Os_3H(CO)_{11}\{Si(OMe)_3\}]$ (0.009 g) and $[Os_3H(CO)_{10}(MeCN)\{Si(OMe)_3\}]$ (**2a**) (0.174 g) [Found: C, 16.8; H, 0.95. Calc. for (**1a**), $C_{14}H_{10}O_{14}Os_3Si$: C, 16.8; H, 1.00. Found: C, 17.7; H, 1.30. Calc. for (**2a**), $C_{15}H_{13}NO_{13}Os_3Si$: C, 17.8; H, 1.30%]. The formation of compound (**1a**) was due to the presence in trace amount of $[Os_3(CO)_{11}(MeCN)]$ in the starting material.

$[Os_3H(CO)_{10}(MeCN)\{Si(OEt)_3\}]$ (**2b**). To a solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.200 g, 0.21 mmol) an excess of $SiH(OEt)_3$ was added and the solution which turned light yellow was stirred for 15 min. The solvent was evaporated to dryness and the residue was chromatographed eluting with n-hexane–CH_2Cl_2 (2:1) to give compound (**2b**) (0.199 g, 88%) as yellow microcrystals.

$[Os_3H(CO)_{10}(MeCN)(SiEt_3)]$ (**2c**). The method used for the preparation of (**2b**) was followed for this compound using an excess of $SiHEt_3$ and $[Os_3(CO)_{10}(MeCN)_2]$ (0.200 g, 0.21 mmol). The yellow solid (**2c**) was obtained in high yield (0.184 g, 85%) after t.l.c.

$[Os_3H(CO)_{10}(MeCN)(SiHPh_2)]$ (**2d**). This cluster compound was prepared from $[Os_3(CO)_{10}(MeCN)_2]$ (0.200 g, 0.21 mmol) and an excess of SiH_2Ph_2 by a procedure analogous to that used for (**2b**). It was obtained as yellow microcrystals (0.166 g, 72%) after t.l.c. eluting with n-hexane–CH_2Cl_2 (1:1).

Preparation of $[NHEt_3][Os_3(CO)_{11}\{Si(OEt)_3\}]$ (**3b**).—A few drops of NEt_3 were added to a n-heptane solution (30 cm^3) of $[Os_3H(CO)_{11}\{Si(OEt)_3\}]$ (0.040 g) and the reaction mixture stirred for 2 h when the solution became colourless and a yellow precipitate formed. The solution was evaporated to dryness and the residue washed with Et_2O quantitatively to yield $[NHEt_3][Os_3(CO)_{11}\{Si(OEt)_3\}]$ (**3b**).

Reactions of $[NHEt_3][Os_3(CO)_{11}\{Si(OEt)_3\}]$ (**3b**).—*With* $[AuCl(PPh_3)]$. One molar equivalent of $[AuCl(PPh_3)]$ (0.017 g, 0.03 mmol) and an excess of $TlPF_6$ (0.040 g) were added to a solution of compound (**3b**) (0.040 g, 0.03 mmol) in CH_2Cl_2 (20 cm^3) and the reaction mixture was stirred for 15 min. Removal of the solvent followed by t.l.c. eluting with n-hexane–CH_2Cl_2 (3:2) yielded $[Os_3(CO)_{11}\{Si(OEt)_3\}(AuPPh_3)]$ (**4**) (0.042 g, 80%). Repetition of the reaction in refluxing CH_2Cl_2 led to a larger amount of decomposition and lower yields of (**4**).

With $[Au(CO)Cl]$. The cluster (**3b**) (0.050 g, 0.04 mmol) was stirred with 1 molar equivalent of $[Au(CO)Cl]$ (0.011 g) in CH_2Cl_2 (20 cm^3). The solution turned dark brown immediately and the reaction was stopped after 30 min. The reaction mixture was filtered through Celite under N_2, the solvent was evaporated under vacuum, and the residue washed with Et_2O to afford dark brown $[NHEt_3][\{Os_3(CO)_{11}[Si(OEt)_3]\}_2Au]$ (**5**) (0.024 g, 46%).

With $[AgCl(PPh_3)]$. Equimolar amounts of compound (**3b**) (0.025 g, 0.02 mmol) and $[AgCl(PPh_3)]$ (0.009 g) were stirred in CH_2Cl_2 (15 cm^3) for 25 min. The colour changed from yellow to orange. Removal of the solvent and purification of the residue by t.l.c. with n-hexane–CH_2Cl_2 (3:2) gave two bands. The major product isolated was identified as $[AgOs_3(CO)_{11}\{Si(OEt)_3\}(PPh_3)]$ (**6**) (0.010 g, 32%). The second small fraction was an uncharacterized product.

With $AgBF_4$. Silver tetrafluoroborate (0.004 g, 0.02 mmol) and compound (**3b**) (0.040 g, 0.035 mmol) were refluxed in thf for 30 min. The solvent was filtered through Celite and evaporated *in vacuo* to yield the dark orange solid $[NHEt_3][\{Os_3(CO)_{11}[Si(OEt)_3]\}_2Ag]$ (**7**) (0.004 g, 10%).

With $HgCl_2$. (*i*) An acetone solution of mercury(II) chloride (0.005 g, 0.02 mmol) was added to a CH_2Cl_2 solution (20 cm^3) of compound (**3b**) (0.020 g, 0.02 mmol) and the mixture which immediately turned orange was stirred for 3 min. The solution was filtered through a short silica column (1 × 3 cm), and reduced in volume. On addition of hexane and on cooling to −20 °C orange needles of $[Os_3(\mu\text{-}HgCl)(CO)_{11}\{Si(OEt)_3\}]$ (**8**) (0.011 g, 51%) were formed.

(*ii*) An acetone solution of mercury(II) chloride (0.004 g, 0.015 mmol) was treated with (**3b**) (0.035 g, 0.03 mmol) for 5 min. The solvent was evaporated *in vacuo* and the residue chromatographed eluting with n-hexane–CH_2Cl_2 (1:1) to yield $[\{Os_3(CO)_{11}[Si(OEt)_3]\}_2Hg]$ (**9**) (0.016 g, 46%). Compound (**8**) on standing in chlorinated solution at room temperature under N_2 decomposes in a few hours to the dimeric (**9**) characterized on the basis of its i.r. spectrum.

With $Hg(O_2CCF_3)_2$. Mercury(II) trifluoroacetate (0.008 g, 0.02 mmol) and compound (**3b**) (0.045 g, 0.04 mmol) were allowed to react in CH_2Cl_2 (20 cm^3) for 5 min. Removal of the solvent followed by t.l.c. eluting with n-hexane–CH_2Cl_2 (1:1) afforded the dark yellow oily compound (**9**) (0.024 g, 53%).

Synthesis of $[\{Os_3(CO)_{11}[Si(OEt)_3]\}_2Hg]$ (**9**).—To a CH_2Cl_2 solution of compound (**8**) (0.050 g, 0.04 mmol) a solution of $HgCl_2$ (0.005 g, 0.02 mmol) in acetone was added and the mixture was stirred for 5 min. The solution was filtered through a silica pad and evaporated to dryness to yield compound (**9**) (0.031 g, 70%).

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