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Preliminary communication

THE SYNTHESIS AND CHARACTERISATION OF NEW TRIOSMIUM AND TRIRUTHENIUM MAIN-GROUP METAL CLUSTERS $M_3(H)(CO)_{11}(M'R_3)$ AND $Os_3(H)(CO)_{10}(CH_3CN)(M'R_3)$ (M = Os, Ru; M' = Ge, Sn; R, aryl, alkyl)

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Summary

Displacement of the (CH_3CN) ligand from the compounds $M_3(CO)_{12-n}$-$(MeCN)_n$ (n = 1 or 2) by organo-germanes and -stannanes provides a general method for the preparation of triosmium- and triruthenium-Main-Group metal clusters of the type $M_3(H)(CO)_{11}(M'R_3)$ and $Os_3(H)(CO)_{10}(CH_3CN)(M'R_3)$ (M = Ru, Os; M = Ge, Sn).

Relatively few carbonyl clusters containing germyl or stannyl ligands have been described [1], and to our knowledge, except for $[(Me_2M')M(CO)_3]_3$ (M = Os and Ru, M' = Ge and Sn) [2,3] and $[Os_3SnH_2(CO)_{10}\{CH(SiMe_3)_2\}_2]$ [4], none contain the triosmium cluster unit. We report here the preparation of a series of compounds of general formula $M_3H(CO)_{11}(M'R_3)$ and $Os_3H(CO)_{10}(CH_3CN)(M'R_3)$ (M = Os, Ru; M' = Ge, Sn; R = aryl, alkyl) through the reaction of the activated clusters $M_3(CO)_{12-n}(CH_3CN)_n$ (n = 1 or 2) with the appropriate germane or stannane.

In a typical experiment, the cluster $Os_3(CO)_{11}(MeCN)$ [5] was treated with one equivalent of Ph_2MeGeH in dry toluene at room temperature under nitrogen, to give the new cluster $Os_3(H)(CO)_{11}(Ph_2MeGe)$. This was readily purified by thin-layer chromatography (silica gel) using a 1/1 mixture of CH_2Cl_2/hexane as eluant. The complexes were obtained as air-stable, yellow or yellow-orange crystals, and have been fully characterised on the basis of their analytical data, IR and ^1H NMR spectroscopy, as shown in Table 1.

The infrared spectra exhibit bands in the terminal carbonyl region, and are similar to those of other well established $[M_3(CO)_{11}HX]$ compounds [5].

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SCHEME 1

$$\mathrm{Ph_2RGeH + Os_3(CO)_{11}(CH_3CN)} \xrightarrow[\text{r.t., 12 h}]{\text{toluene}} \mathrm{Os_3(H)(CO)_{11}(GeRPh_2)}$$

$$\mathrm{(R = Ph, Me)} \qquad \qquad (70\text{—}80\%)$$

$$\mathrm{R_3SnH + Os_3(CO)_{11}(CH_3CN)} \xrightarrow[\text{r.t., 12 h}]{\text{toluene}} \mathrm{Os_3H(CO)_{11}(SnR_3)}$$

$$\mathrm{(R = Ph, n\text{-}Bu)} \qquad \qquad (60\text{—}70\%)$$

$$\mathrm{Ph_3M'H + Os_3(CO)_{10}(CH_3CN)_2} \xrightarrow[\text{r.t., 5 h}]{\text{toluene}}$$

$$\underset{(70\text{—}75\%)}{\mathrm{Os_3(H)(CO)_{10}(CH_3CN)(M'Ph_3)}} + \underset{(5\%)}{\mathrm{Os_3H(CO)_{11}(M'Ph_3)}}$$

$$\mathrm{(M = Ge, Sn)}$$

$$\mathrm{Ph_3M'H + Ru_3(CO)_{11}(CH_3CN)} \xrightarrow[-40^\circ\text{C, 2 h}]{\mathrm{CH_2Cl_2}} \mathrm{Ru_3H(CO)_{11}(M'Ph_3)}$$

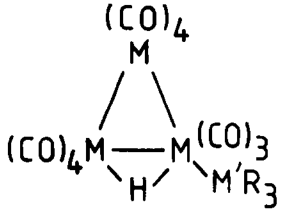
$$\mathrm{(M = Ge, Sn)} \qquad \qquad (60\%)$$

TABLE 1

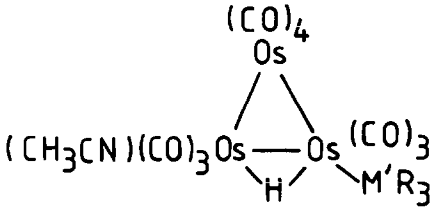
ANALYTICAL AND SPECTROSCOPIC DATA

Compound	ν(CO) (cm^{-1}) [a]	^{1}H NMR [b] (δ ppm)	Analysis (Found (Calcd.) (%))			Molecular [c] weight (mass spectral) *m/e*
			C	H	N	
$Os_3H(CO)_{11}$-$GePh_3$	2136(w), 2085(s), 2053(vs), 2032(m), 2018(m), 2002(s), 1973(w)	—18.4	29.12 (29.41)	1.36 (1.35)		1190
$Os_3H(CO)_{11}$-$(GeMePh_2)$	2136(w), 2083(s), 2053(vs), 2030(m), 2016(m), 2002(s) 1970(w)	—18.5	25.84 (25.68)	1.19 (1.24)		1128
$Os_3H(CO)_{11}$-$(SnPh_3)$	2136(w), 2084(s), 2054(vs), 2030(m), 2020(m), 2002(s) 1962(w)	—18.6	27.91 (28.30)	1.13 (1.30)		1234
$Os_3H(CO)_{11}$-$[Sn(n\text{-}Bu)_3]$	2136(w), 2083(s), 2053(vs), 2030(m), 2018(m), 2000(s), 1963(w)	—18.5	23.68 (23.60)	2.31 (2.39)		1174
$Os_3H(CO)_{10}$-$(CH_3CN)(GePh_3)$	2102(m), 2066(s), 2040(s), 2020(s), 2003(s), 1987(m)	—16.1	31.58 (30.09)	1.79 (1.58)	1.26 (1.17)	—
$Os_3H(CO)_{10}$-$(CH_3CN)(SnPh_3)$	2102(m), 2065(s), 2038(s), 2020(s), 2005(s), 1990(m)	—16.4	29.37 (28.98)	1.76 (1.53)	1.09 (1.12)	— —
$Ru_3H(CO)_{11}GePh_3$	2127(w), 2079(m), 2050(vs), 2010(sh), 2004(m)	—17.8	38.52 (38.00)	1.78 (1.74)		— —
$Ru_3H(CO)_{11}(SnPh_3)$	2127(w), 2078(m), 2050(vs), 2010(sh), 2003(m)	—18.0	35.84 (36.18)	1.86 (1.66)		—

[a] In CH_2Cl_2. [b] In $CDCl_2$, hydride resonance. [c] Based on ^{192}Os, ^{74}Ge and ^{118}Sn;



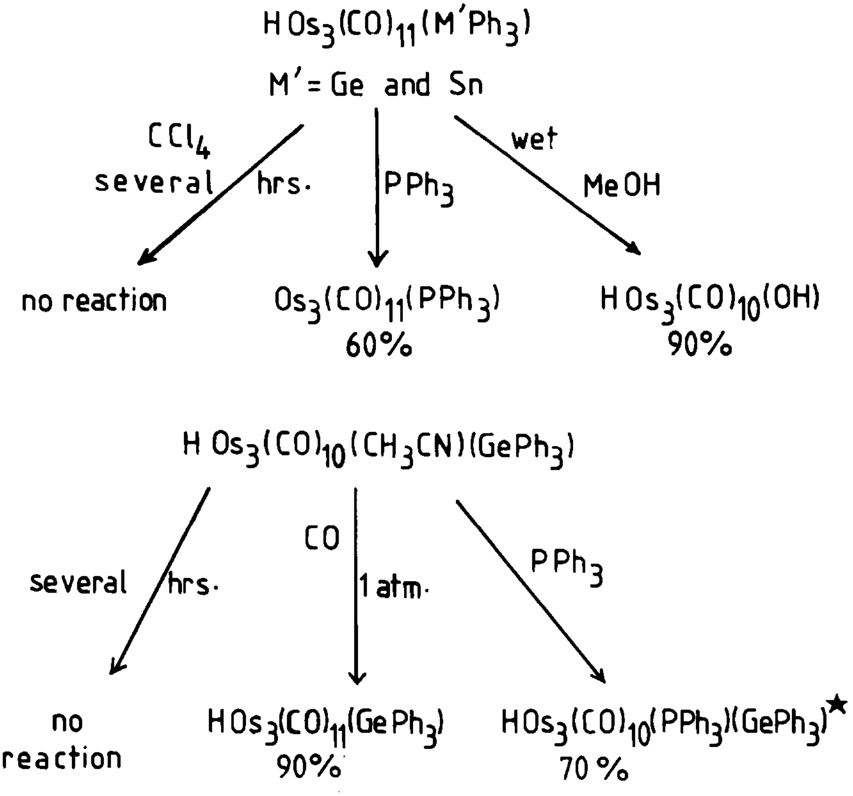
and



M = Os and Ru , M' = Ge and Sn

The ^{1}H NMR spectra in CD_2Cl_2 shows one singlet high-field resonance, with δ between −16 and −18 ppm, as expected for a bridging hydride ligand [6]. Furthermore the clusters are stable in CCl_4 at room temperature for several hours, which is also indicative of a bridging H ligand [7,8]. On the basis of these observations, we propose a structure involving one bridging H ligand and one terminally-bonded Main-Group metal ligand, as shown in Fig. 1.

Treatment of $Os_3(H)(CO)_{11}(GePh_3)$ with one equivalent of PPh_3 in toluene at room temperature for 5 days results in reductive elimination of Ph_3GeH to afford the known cluster $Os_3(CO)_{11}(PPh_3)$ (80% based upon reacted Os_3'H)-



SCHEME 2. * IR(CH_2Cl_2): 2102m, 2066s, 2040s, 2020s, 2003s, 1998m; NMR (δ, ppm): −18.7 (H, d, J(P—H) −10 Hz).

$(CO)_{11}(GePh_3)$) [5]; wet methanol gives $Os_3H(CO)_{10}(OH)$ quantitatively (Scheme 2). Similar results are observed with $Os_3H(CO)_{11}(SnPh_3)$. Treatment of $Os_3H(CO)_{10}(CH_3CN)(GePh_3)$ with one equivalent of Ph_3P in hexane at 40° C for 4 h results only in displacement of the CH_3CN ligand without reductive elimination of Ph_3GeH. Passing CO into a solution of $Os_3H(CO)_{10}(CH_3CN)(GePh_3)$ in toluene at 40° C likewise gives a quantitative yield of the complex $Os_3H(CO)_{11}(GePh_3)$ (Scheme 2).

Further studies are in progress in both series, and results of previous work with triosmium clusters bearing silane ligands will appear shortly [9].

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