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Preliminary communication

SYSTEMATIC SYNTHESIS AND CHARACTERISATION OF PHOSPHIDO-BRIDGED TRIOSMIUM CARBONYL CLUSTERS*

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Summary

Phosphine-substituted triosmium clusters $Os_3(CO)_{11}PR^1R^2H$ (a: $R^1 = R^2 = H$; b: $R^1 = Ph$, $R^2 = H$; c: $R^1,R^2 = Ph$) have been found to yield, via a deprotonation/protonation sequence, the phosphido-bridged clusters $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}PR^1R^2)$: the intermediate anions $[(Os_3(CO)_{10}(\mu\text{-}PR^1R^2))^-]$ and $[((\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}PR^1))^-]$ in this systematic synthesis are described.

An area of research attracting much current interest is the synthesis and reactivity of transition metal clusters stabilised by bridging phosphorus ligands [1,2]. Hydrido-phosphide bridged osmium clusters have been previously made in low to moderate yields by the thermolysis of the appropriate phosphine with $Os_3(CO)_{12}$ [2]. Herein is reported a systematic high yield synthesis to these compounds via previously unobserved, intermediate, phosphido-bridged osmium cluster monoanions.

Reaction of $Os_3(CO)_{11}(MeCN)$ (1) with PR^1R^2H rapidly gives the corresponding phosphine-substituted cluster $Os_3(CO)_{11}PR^1R^2H$ (2) (a: $R^1 = R^2 = H$; b: $R^1 = Ph$, $R^2 = H$; c: R^1, $R^2 = Ph$) (~95%, Scheme 1). Deprotonation of these clusters with an appropriate base yields the corresponding phosphido-bridged anions 3 which were characterised spectroscopically but not isolated. Reaction of these monoanions with HCl(g) cleanly gives the hydrido-phosphido bridged clusters $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}PR^1R^2)$ (4) (~90%, overall yield from $Os_3(CO)_{11}(MeCN)$).

Complexes 2a and 4a can also be synthesised from the complex $Os_3(CO)_{11}P(SiMe_3)_3$ (6) (from $Os_3(CO)_{11}(MeCN)$ and $P(SiMe_3)$) [4] quan-

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*This paper is dedicated to Professor Malatesta, whose work has been so seminal in the development of organometallic chemistry.

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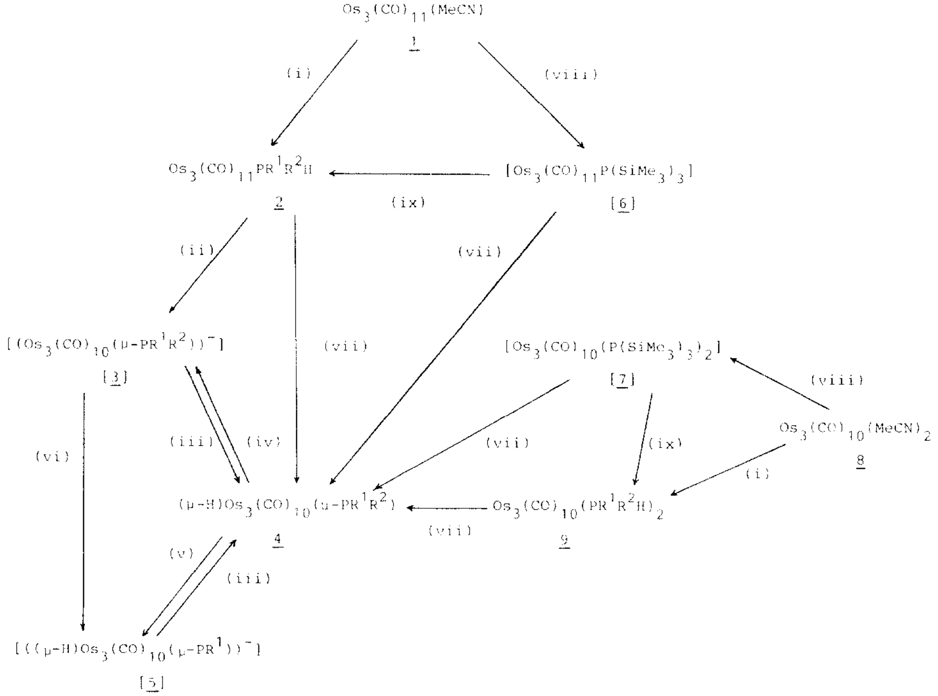

Scheme 1. Reagents and conditions: [a: $R^1 = R^2 = H$; b: $R^1 = Ph$, $R^2 = H$; c: $R^1, R^2 = Ph$] (i) 1a PH_3, toluene, 40° C; 1b,1c PR^1R^2H, CH_2Cl_2. (ii) 2a 10 equiv. PPNCl, CH_2Cl_2; 2a,2b $NH_3(g)$, THF; 2a—2c DBU, THF. (iii) 4a—4c HCl(g), THF, 0° C. (iv) 3a,3c 10 equiv. PPNCl/NEt_3, CH_2Cl_2, 0° C or DBU, THF. (v) 5b only: Et_4NCl/NEt_3, THF or DBU, THF. (vi) 3b, THF reflux, 1 min. (vii) 4b only: 1/20 equiv. PPNCl, CH_2Cl_2. (viii) $P(SiMe_3)_3$, CH_2Cl_2, 0° C. (ix) $R^1 = R^2 = H$ only, 3 equiv. MeOH, CH_2Cl_2.

titative by IR) thereby avoiding the use of PH_3. Reaction of 6 in CH_2Cl_2 with MeOH gives 2a (~95%) whereas with catalytic amounts of PPNCl 4a (~90%) is formed. The latter reaction illustrates the non-passive role of CH_2Cl_2 which is confirmed by the observation that CD_2Cl_2 gives $(\mu\text{-D})Os_3(CO)_9(\mu\text{-PD}_2)$*.

Interestingly, the acidity of the coordinated phosphine-ligand in the clusters 2 follows the reverse order found for the free ligand (pK_a: PPh_2H ~10^{22}, $PPhH_2$ ~10^{25}, PH_3 ~10^{28}) [4]. Thus, 2a is deprotonated by excess PPNCl in CH_2Cl_2 whereas both **2b,2c** are unaffected by PPNCl. **2b** is deprotonated with $NH_3(g)$ in THF whereas for **2c** the stronger base DBU is required.

Furthermore, treatment of 2a with catalytic amounts of PPNCl in dichloromethane gives 4a directly. We believe Cl^- ion deprotonates 2a to give the terminal phosphane species $[(Os_3(CO)_{11}PH_2)^-]$ as an unobserved intermediate. The relevant reaction steps are:

$$Os_3(CO)_{11}PH_3 + Cl^- \rightarrow [(Os_3(CO)_{11}PH_2)^-] + HCl \tag{1}$$

$$[(Os_3(CO)_{11}PH_2)^-] \rightarrow [(Os_3(CO)_{10}(\mu\text{-}PH_2))^-] + CO \tag{2}$$

$$[(Os_3(CO)_{10}(\mu\text{-}PH_2))^-] + HCl \rightarrow (\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}PH_2) + Cl^- \tag{3}$$

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*ν(CO) same as **2a**, *m/e*: 893 (calc (^{2}D, ^{192}Os)893).

The driving force for this catalytic cycle derives from the loss of CO and concommitant bridging of the PH_2 unit in step 2, and the fact that under the reaction conditions both equilibria 1 and 2 lie to the right; i.e. 3a is more basic than $[(Os_3(CO)_{11}PH_2)^-]$.

Given this sequence of reaction steps it is not surprising that 4a is also formed on treatment of $Os_3(CO)_{10}(PH_3)_2$ (6a) (synthesised from $Os_3(CO)_{10}(MeCN)_2$

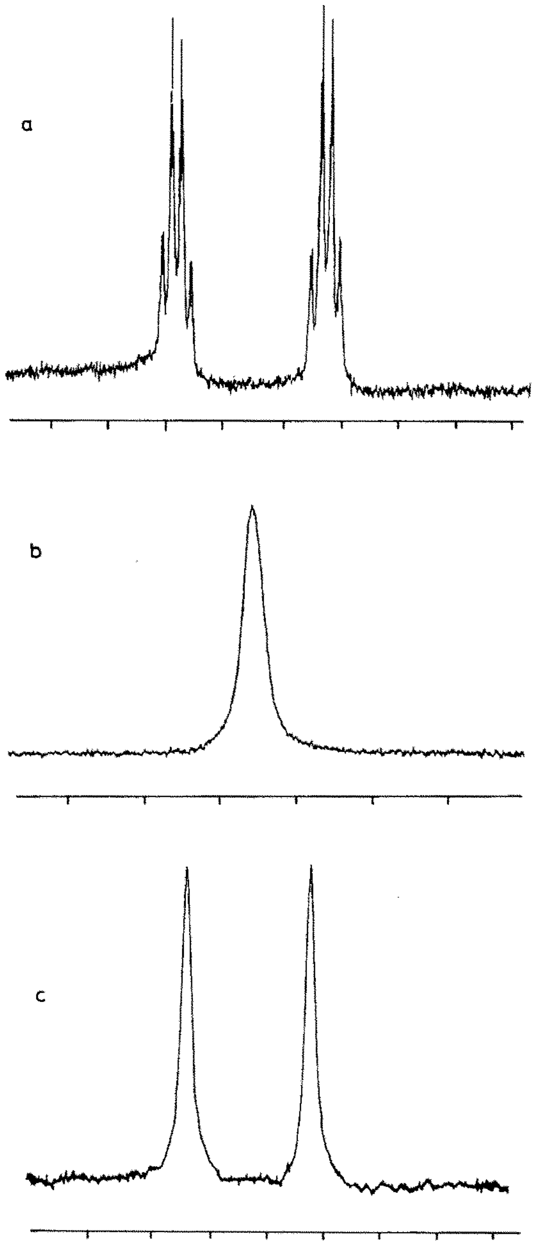

Fig. 1. ^{31}P NMR spectra at 20°C in THF of (a) $HOs_3(CO)_{10}PPhH$ (4b); (b) + DBU (5b); (c) + DBU, 60°C 1 min, (3b).

and PH_3(g) or $P(SiMe_3)_3$/MeOH, Scheme 1) with PPNCl. Attack by Cl^- and loss of the most labile ligand, PH_3, from the resulting monoanion is expected:

$$Os_3(CO)_{10}(PH_3)_2 + Cl^- \xrightarrow{-HCl} [(Os_3(CO)_{10}(PH_3)(PH_2))^-] \xrightarrow{-PH_3}$$

$$[(Os_3(CO)_{10}(\mu\text{-}PH_2)^-] \xrightarrow{+HCl} (\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}PH_2) \quad \text{(4a)}$$

Deprotonation of **4b** does not give **3b** but a monoanion with spectral characteristics and reactivity that suggest the phosphorus bound hydrogen atom, not the hydride, is lost. Most importantly, collapse of the doublet of multiplets in the ^{31}P NMR spectrum of **4b** to a single multiplet for the resulting monoanion is observed (Fig. 1). Hence we suggest deprotonation of **4b** gives $[(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}PPh)^-]$ (**5b**). Heating a THF solution of **5b** rapidly forms **3b**. Thus **5b** appears to be the kinetic product in the deprotonation of **4b**. We are currently determining whether deprotonation of **4a** to **3a** goes via **5a** as an intermediate. This, the extension of the above systematic syntheses to higher nuclearity Os clusters and the reactions of the molecules detailed here with small organic molecules will be reported later.

Selected spectroscopic data (new compounds)

2 (a): ν(CO) (CH_2Cl_2): 2112w, 2058ms, 2038ms, 2022vs, 1989 cm^{-1}; ^1H NMR ($CDCl_3$): 4.92 (d, J(P—H(1)) 375 Hz, 1 PH_3) ppm; ^{31}P NMR (CH_2Cl_2); —336.8 (q, J(P—H) 382 Hz, 1PH_3) ppm; m/z 918 (calcd. (^{192}Os) 918).

[3] (a): ν(CO) (THF): 2067w, 2006s, 1995vs, 1982s, 1965m, 1930ms cm^{-1}; ^{31}P NMR (CH_2Cl_2): —236.3 (d of d, J(P—H) 380 Hz, J(P—H(2)) 347 Hz, (b) ν(CO) (THF): 2067w, 2003s, 1993vs, 1966m, 1926ms cm^{-1}; ^{31}P NMR (THF): —127.7 (d of m, J(P—H) 380 Hz, 1*P*PhH) ppm. (c): ν(CO) (THF): 2059w, 2003s, 1990vs, 1970s, 1920m cm^{-1}. ^{31}P NMR (THF): —64.8 (broad m, *P*Ph_2).

4 (a): ν(CO) (C_6H_{12}): 2107w, 2066vs, 2057s, 2026vs, 2010s, 2000vs, 1986w, 1962vw cm^{-1}; ^1H NMR ($CDCl_3$): 5.24 (d of d of d, J(P—H(1)) 425 Hz, J(H(1)—H(2) 9.5 Hz, J(H(1)—H(3)) 5.0 Hz, 1 P*H*), 4.96 (d of d, J(P—H(2)) 397 Hz, J(H(1)—H(2)) 9.5 Hz, 1 P*H*), −19.92 (d of d, J(P—H(3)) 16 Hz, J(H(1)—H(3)) 5.0 Hz, 1 Os*H*) ppm; ^{31}P NMR (CH_2Cl_2): −276.25 (d of d of d, J(P—H(1)) 425 Hz, J(P—H(2)) 397 Hz, J(P—H(3)) 16 Hz, 1PH_2) ppm; m/z 890 (calcd. (^{192}Os) 890). (c) ν(CO) (C_6H_{12}): 2104w, 2057vs, 2054s, 2021vs, 2015ms, 1991s, 1978w, 1953vw cm^{-1}; ^1H NMR ($CDCl_3$): 7.89m, 7.54m, 7.24m, 6.77m (PPh_2), −18.08 (d, J(P—H) 19.7 Hz). ^{31}P NMR (THF): −124.6 (broad m, *P*Ph_2), m/z; 1042 (calcd. (^{192}Os) 1042).

[5] (b) :ν(CO) (THF): 2062mw, 2029vs, 2003s, 1978s, 1956m, 1926w, cm^{-1}; ^{31}P NMR (THF: —170.4 (m, 1 *P*Ph) ppm.

[6] ν(CO) (CH_2Cl_2): 2111w, 2055ms, 2038ms, 2020vs, 1948m cm^{-1}.

[7] ν(CO) (CH_2Cl_2): 2092w, 2020ms, 2006vs, 1970m cm^{-1}.

9 (a): ν(CO) (CH_2Cl_2): 2094w, 2036ms, 2020ms, 2007vs, 1971m cm^{-1}. ^1H NMR ($CDCl_3$): 4.81 (d, J(P—H) 373 Hz, 2 PH_3) ppm; ^{31}P NMR (CH_2Cl_2): —336.7 (q, J(P—H) 376 Hz, 2 PH_3) ppm; m/z: 924 (calcd. (^{192}Os) 924).

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