

Preliminary communication

POLYNUCLEAR METAL COMPLEXES INCORPORATING HYDRIDO-PHOSPHIDO LIGANDS

E.A.V. EBSWORTH*, A.P. McINTOSH and M. SCHRÖDER*

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ (Great Britain)

(Received June 9th, 1986)

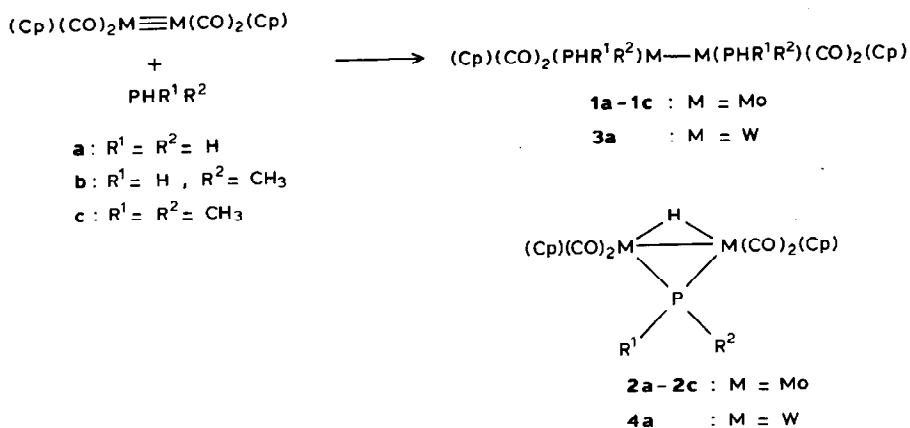
Summary

Addition of phosphines to the coordinatively unsaturated species $(\text{Cp})_2\text{M}_2(\text{CO})_4$ ($\text{M} = \text{Mo}, \text{W}$) and $\text{H}_2\text{Os}_3(\text{CO})_{10}$ yield a series of products incorporating terminal phosphine along with bridging and capping phosphido ligands formed via insertion into P–H bonds. The complexes were characterised by ^1H and ^{31}P NMR spectroscopy and mass spectrometry.

We reported recently the addition of phosphine, PH_3 , to coordinatively unsaturated monometallic centres to yield a series of PH_2 -containing hydrido complexes [1]. Extension of this work to the addition of phosphine to coordinatively unsaturated bi- and tri-nuclear metal species represents a potential route to phosphido ligands which are structurally stabilised by bridging between two or more metal centres [2,3], and should lead to a range of new μ -hydrido- μ -phosphido clusters [4]. We describe herein the addition of phosphine and alkylphosphines to $(\text{Cp})_2\text{M}_2(\text{CO})_4$ ($\text{M} = \text{Mo}, \text{W}$) and $\text{H}_2\text{Os}_3(\text{CO})_{10}$.

Reaction of $(\text{Cp})_2\text{Mo}_2(\text{CO})_4$ with PHR^1R^2 (**a**: $\text{R}^1 = \text{R}^2 = \text{H}$; **b**: $\text{R}^1 = \text{CH}_3$, $\text{R}^2 = \text{H}$; **c**: $\text{R}^1 = \text{R}^2 = \text{CH}_3$) in CD_2Cl_2 up to 223 K yields the adducts $(\text{Cp})_2\text{Mo}_2(\text{CO})_4(\text{PHR}^1\text{R}^2)_2$ (**1a–1c**) [5]; **1a** is stable only up to 233 K whereas **1b** and **1c** are stable up to 293 K [6]. Heating these adducts in CD_2Cl_2 for **a** or in toluene for **b** and **c** gives $(\text{Cp})_2\text{Mo}_2(\text{CO})_4(\mu_2\text{-H})(\mu_2\text{-PR}^1\text{R}^2)$ (**2a–2c**) via elimination of one equivalent of PHR^1R^2 from **1a–1c**. **2a** is formed at 273 K, whereas **2b** and **2c** are formed at 353 and 373 K, respectively [7]. The synthesis of **2c** by reaction of $\text{P}(\text{CH}_3)_2\text{Cl}$ with $\text{Na}(\text{Cp})\text{Mo}(\text{CO})_3$ has been reported previously [8]. $(\text{Cp})_2\text{W}_2(\text{CO})_4$ reacts similarly with PH_3 to yield at 223 K $(\text{Cp})_2\text{W}_2(\text{CO})_4(\text{PH}_3)_2$ (**3a**) [9], which on warming to room temperature rearranges to the hydridophosphido species $(\text{Cp})_2\text{W}_2(\text{CO})_4(\mu_2\text{-H})(\mu_2\text{-PH}_2)$ (**4a**) [10] (Scheme 1).

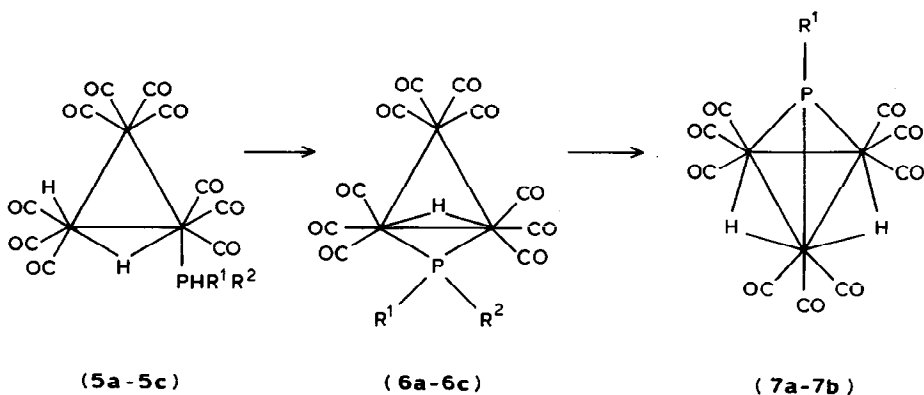
$\text{H}_2\text{Os}_3(\text{CO})_{10}$ reacts with PHR^1R^2 at room temperature to give $(\text{H})(\mu_2\text{-H})\text{Os}_3(\text{CO})_{10}(\text{PHR}^1\text{R}^2)$ (**5a–5c**) [11], incorporating terminally bound phosphine and hydride ligands and a bridging hydride [12]. Warming solutions of **5a–5c** leads to



SCHEME 1.

the formation of the corresponding bridging phosphidohydrido species, $(\mu_2\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_2\text{-PR}^1\text{R}^2)$ (**6a-6c**) [13], presumably by coupling involving elimination of H_2 . **6a** is formed at 323 K, **6b** at 343 K, and **6c** at 353 K. **6a** has been reported [14] previously as the product from decomposition of $\text{Os}_3(\text{CO})_{10}(\text{PH}_3)_2$. **6a** and **6b** react further on heating to give the 3-phosphido-capped hydrido clusters $(\mu_2\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-PR}^1)$ (**7a-7b**) [15] by loss of CO (Scheme 2). **5a** reacts at 313 K directly to give significant amounts of **7a** and small amounts of **6a**. **5b** is converted more readily into **7b** if the complex is refluxed in *p*-xylene under N_2 to drive off the excess of CO.

To our knowledge **7a** is one of the first examples of a $(\mu_3\text{-PH})$ complex, although related $\mu_3\text{-PPh}$ and $\mu_2\text{-PR}_2$ species have been reported [3]. The reactions of this new range of $(\mu_2\text{-PH}_2)$ and $(\mu_3\text{-PH})$ compounds are being investigated.



SCHEME 2.

This work was supported by the Science and Engineering Research Council. Generous loans of platinum metals from Johnson-Matthey PLC and the carrying out of the conversion of OsO_4 to $\text{Os}_3(\text{CO})_{12}$ at the University Chemical Laboratories, Cambridge, are gratefully acknowledged.

References

- 1 E.A.V. Ebsworth and R. Mayo, *Angew. Chem. Int. Ed. Engl.*, 24 (1985) 68.
- 2 S.K. Kang, T.A. Albright, T.C. Wright and R.A. Jones, *Organometallics*, 4 (1985) 666 and ref. therein.
- 3 F. Iwasaki, M.J. Mays, P.R. Raithby, P.L. Taylor and P.J. Wheatley, *J. Organomet. Chem.*, 213 (1981) 185; K. Natarajan, L. Zsolnai and G. Huttner, *ibid.*, 220 (1981) 365.
- 4 V.D. Patel, A.A. Cherkas, D. Nucciarone, N.J. Taylor and A.J. Carty, *Organometallics*, 4 (1985) 1792.
- 5 M.D. Curtis and R.J. Klinger, *J. Organomet. Chem.*, 161 (1978) 23.
- 6 ^{31}P NMR (CD_2Cl_2 , 200 MHz, 223K): **1a**: $\delta(\text{P})$ -82 ppm (q), $^1J(\text{PH})$ 342 Hz; **1b**: $\delta(\text{P})$ -34 ppm (t,q), $^1J(\text{PH})$ 340 Hz; (**1c**): $\delta(\text{P})$ 5 ppm (d,m), $^1J(\text{PH})$ 337 Hz.
- 7 **2a**: ^{31}P NMR (CD_2Cl_2 , 200 MHz, 303K): $\delta(\text{P})$ 34 ppm (t,d), $^1J(\text{PH})$ 355, $^2J(\text{PH})$ 40 Hz. ^1H NMR (CD_2Cl_2 , 80 MHz, 303K): $\delta(\text{H})$ -12.8 (d, hydride), 4.82 ppm (d, PH_2). Mass spectrum: parent ion peak for **2a** m/e = 466.
2b: ^{31}P NMR (toluene- d_8 , 200 MHz, 303 K) $\delta(\text{P})$ 100 ppm (d, m), $^1J(\text{PH})$ 340, $^2J(\text{PH})_{(\text{hydride})}$ 38 Hz. ^1H NMR (toluene- d_8 , 360 MHz, 303 K) $\delta(\text{H})$ -12.5 (d, hydride), 5.59 (d, q, PMeH), 1.57 ppm (d, d, CH_3), $^2J(\text{PH})_{(\text{methyl})}$ 10.9 Hz. Mass spectrum: parent ion peak for **2b** m/e = 482.
2c: ^{31}P NMR (toluene- d_8 , 200 MHz, 303 K): $\delta(\text{P})$ 147 ppm (d, septet), $^2J(\text{PH})_{(\text{hydride})}$ 37, $^2J(\text{PH})_{(\text{methyl})}$ 9.5 Hz. ^1H NMR (toluene- d_8 , 360 MHz, 303 K) $\delta(\text{H})$ -12.1 (d, hydride), 1.5 ppm (d, CH_3), $J(\text{PH})$ 9.9 Hz. Mass spectrum: parent ion peak for **2c** m/e = 496.
- 8 R.G. Haytner, *Inorg. Chem.*, 2 (1963) 1031; R.J. Doedens and L.F. Dahl, *J. Am. Chem. Soc.*, 87 (1965) 2576.
- 9 **3a**: ^{31}P NMR (CD_2Cl_2 , 200 MHz, 223 K): $\delta(\text{P})$ -118 ppm (q), $^1J(\text{PH})$ 352 Hz.
- 10 **4a**: ^{31}P NMR (CD_2Cl_2 , 200 MHz, 303 K) $\delta(\text{P})$ -40 ppm (t,d), $^1J(\text{PH})$ 375, $^2J(\text{PH})$ 28, $^1J(\text{PW})$ 200 Hz. ^1H NMR (CD_2Cl_2 , 80 MHz, 303K): $\delta(\text{H})$ -15.5 (d, hydride), 4.94 ppm (d, PH_2). Mass spectrum: parent ion peak for **4a** m/e = 645.
- 11 **5a**: ^{31}P NMR (toluene- d_8 , 200 MHz, 213 K): $\delta(\text{P})$ -184 ppm (q, d), $^1J(\text{PH})$ 384, $^2J(\text{PH})$ 14 Hz. ^1H NMR (toluene- d_8) 360 MHz, 213 K): $\delta(\text{H})$ -20.8 (d, d, bridging hydride), -10 ppm (d, terminal hydride), $^2J_{\text{HH}}$ = 3.9 Hz.
5b: ^{31}P NMR (toluene- d_8 , 200 MHz, 213 K): $\delta(\text{P})$ -130 ppm (t, m), $^1J(\text{PH})$ 386, $^2J(\text{PH})$ 14 Hz. ^1H NMR (toluene- d_8) 360 MHz, 213 K): $\delta(\text{H})$ -21 (d, d, bridging hydride), -10 ppm (d, terminal hydride), $^2J(\text{HH})$ 3.8 Hz.
5c: ^{31}P NMR (toluene- d_8 , 200 MHz, 213 K): $\delta(\text{P})$ -86 ppm (d, m), $^1J(\text{PH})$ 390, $^2J(\text{PH})$ 13 Hz. ^1H NMR (toluene- d_8) 360 MHz, 213 K) $\delta(\text{H})$ -21 (d, d, bridging hydride), -10 ppm (d, terminal hydride), $^2J(\text{HH})$ 3.8 Hz.
- 12 J.R. Shapley, J.B. Keister, M.R. Churchill and B.C. DeBoer, *J. Amer. Chem. Soc.*, 97 (1975) 4145.
- 13 **6a**: ^{31}P NMR (CD_2Cl_2 , 200 MHz, 303 K): $\delta(\text{P})$ -276 ppm (d, d, d) $^1J(\text{PH})$ 421, 397, $^2J(\text{PH})$ 16 Hz. ^1H NMR (CDCl_3 , 360 MHz, 303 K): $\delta(\text{H})_{(\text{hydride})}$ -19.92 ppm (d, d, d), $^2J(\text{PH})$ 16 Hz, $J(\text{HH})$ 5.0 Hz. $\delta(\text{H})_{(\text{PH}_2)}$ 4.96 (d, d, d), 5.24 ppm (d, d, d) [14].
6b: ^{31}P NMR (toluene- d_8 , 200 MHz, 303 K): $\delta(\text{P})$ -70 ppm (d, d, q), $^1J(\text{PH})$ 412, $^2J(\text{PH})_{(\text{hydride})}$ 16.7, $^2J(\text{PH})_{(\text{methyl})}$ 11.7 Hz. ^1H NMR (toluene- d_8 , 80 MHz, 303 K): $\delta(\text{H})$ -19.6 (d, d, hydride), 0.95 (d, d, CH_3), 5.6 ppm (d, q, PH). Mass spectrum: parent ion peak m/e = 899.
6c: ^{31}P NMR (toluene- d_8 , 200 MHz, 303 K): $\delta(\text{P})$ -29.8 ppm (d, q, q), $^2J(\text{PH})_{(\text{hydride})}$ 17.4, $^2J(\text{PH})_{(\text{methyl-1})}$ 11.5, $^2J(\text{PH})_{(\text{methyl-2})}$ 10.4 Hz. ^1H NMR (toluene- d_8 , 80 MHz, 303 K): $\delta(\text{H})$ -18.8 (d, hydride), 1.16 (d, CH_3), 1.64 ppm (d, CH_3). Mass spectrum: parent ion peak m/e = 912.
- 14 S.B. Colbran, B.F.G. Johnson, J. Lewis and R.M. Sorrell, *J. Organomet. Chem.*, 296 (1985) C1.
- 15 **7a**: ^{31}P NMR (toluene- d_8 , 200 MHz, 303 K): $\delta(\text{P})$ 15 ppm (d, t), $^1J(\text{PH})$ 435, $^2J(\text{PH})$ 10.2 Hz. ^1H NMR (toluene- d_8) 360 MHz, 303 K) $\delta(\text{H})$ -22 (d, hydride), 3.1 ppm (d, PH), $^2J(\text{PH})$ 10.2, $^3J(\text{HH})$ 0.54 Hz.
7b: ^{31}P NMR (toluene- d_8 , 200 MHz, 303 K): $\delta(\text{P})$ 105 ppm (q, t), $^2J(\text{PH})_{(\text{methyl})}$ 13.7, $^2J(\text{PH})_{(\text{hydride})}$ 10.2 Hz. ^1H NMR (toluene- d_8 , 80 MHz, 303 K): $\delta(\text{H})$ -21.5 (d, hydride), 1.95 ppm (d, CH_3). Mass spectrum: parent ion peak m/e = 870.