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Preliminary communication

USE OF COORDINATED PHOSPHAALKYNE LIGANDS IN TRANSITION METAL CLUSTER INTERLINKAGE. SYNTHESIS OF DIMOLYBDENUM-TRIRUTHENIUM AND DIMOLYBDENUM-TRIOSMIUM COMPLEXES $[Mo_2M_3(\eta^5\text{-}C_5H_5)_2(CO)_{15}(^tBuCP)]$, (M = Ru, Os) AND CRYSTAL AND MOLECULAR STRUCTURE OF DI-η^5-CYCLOPENTADIENYLTETRA-CARBONYL-μ-(3,3-DIMETHYL-1-PHOSPHABUTYNE)-*triangulo*-TRI-OSMIUM(0), $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}^tBuCP)Os_3(CO)_{11}]$

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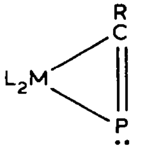
Summary

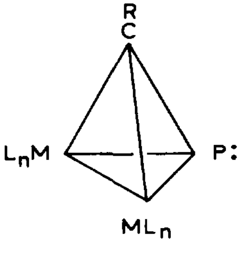
The phosphaalkyne ligand in $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(^tBuCP)]$ can be used in transition metal cluster interlinkage.

Previously [1—4] we described syntheses of novel mono- and di-nuclear phosphaalkyne complexes (Ia and Ib) in which the phosphaalkyne RC≡P is coordinated to the metal via its π-system (Ia, M = Pt, L = PPh_3 [1], L_2 = diphos [4]; L_2 = triphos [3]. Ib, L_nM = $Co(CO)_3$ [2], $Mo(\eta^5\text{-}C_5H_5)(CO)_2$ [2]; R = ^{t}Bu).

The lone pair of electrons on phosphorus in Ia and Ib is potentially available for utilisation in further bonding to transition metals and coordination of Ib to the $W(CO)_5$ fragment has been achieved [2,4].



(Ia)



(Ib)

We now report the first examples of the use of coordinated RCP ligands in transition metal cluster interlinkage which promises to have application for linking a variety of metal polyhedra. Thus treatment of Ib (ML_n = Mo(η^5-C_5H_5)-$(CO)_2$) (δ(^{31}P) −252 ppm (rel. TMP)) with [$Os_3(CO)_{11}(CH_3CN)$] in THF at room temperature leads to quantitative formation of the deep red dimolybdenum-triosmium complex [$Mo_2(\eta^5$-$C_5H_5)_2(CO)_4(^tBuCP)Os_3(CO)_{11}$] (II), ($\delta$(^{31}P) −287.4 ppm; ^{1}H($CDCl_3$): 5.2 (s, C_5H_5, (10H), 1.3 (s, ^{t}Bu, (9H)) whose IR spectrum showed the presence of only terminal carbonyl bonds (ν(CO)(THF): 2100 m, 2050ms, 2030ms, 2010s, 1975ms, 1955m, 1920m, 1910sh cm^{-1}).

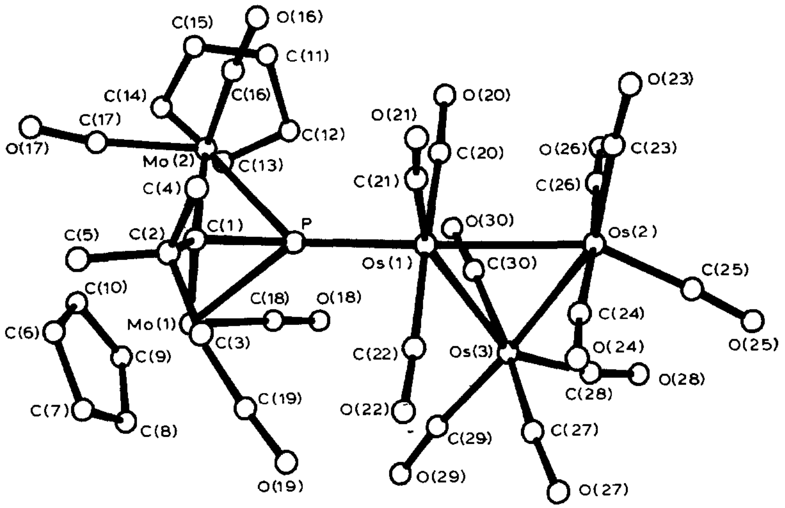


Fig. 1. The molecular structure of [$Mo_2(\eta^5$-$C_5H_5)_2(CO)_4(\mu$-$^tBuCP)Os_3(CO)_{11}$]. Selected dimensions are: Os(1)—Os(2),2.860(1), Os(1)—Os(3) 2.892(1), Os(2)—Os(3) 2.860(1), Os(1)—P 2.360(3), Mo(1)—P 2.514(3), Mo(2)—P 2.397(3), Mo(1)—C(1) 2.36(2), Mo(2)—C(1) 2.33(1), P—C(1) 1.86(1), C(1)—C(2) 1.37(2) Å; P—C(1)—C(2) 132(1)°.

The analogous deep red ruthenium complex (III) (δ(^{31}P) −234.9 ppm; ^{1}H-($CDCl_3$) 5.2 (d, C_5H_5, (10H), 1.35 s ^{t}Bu (9 H)) was obtained by direct reaction of [$Mo_2(\eta^5$-$C_5H_5)_2(CO)_4(^tBuCP)$] with [$Ru_3(CO)_{12}$] in THF in the presence of Me_3NO and exhibits a similar IR spectrum (ν(CO) hexane: 2180w, 2140s, 2120m, 2104s, 2084m, 2060w, 2036w, 2000w cm^{-1}). The ready formation of II and III from Ib is interesting in view of the complete lack of donor ability of the phosphorus atoms in the structurally related [$Co_2(CO)_6P_2$] complex [5]*.

Confirmation of the proposed structures was established by a single crystal X-ray diffraction study of the osmium complex II recrystallised from dichloromethane/heptane.

Crystal data: $C_{30}H_{19}Mo_2O_{15}Os_3P$, monoclinic, $P2_1/c$, a 16.319(1), b 12.268(2), c 18.264(2) Å, β 90.84(1)°, Z = 4. The structure was solved by heavy atom methods and refined to R = 0.055 by least-squares using 3644 reflections with $I > \sigma(I)$ measured on a CAD4 diffractometer with Mo-K_α radiation.

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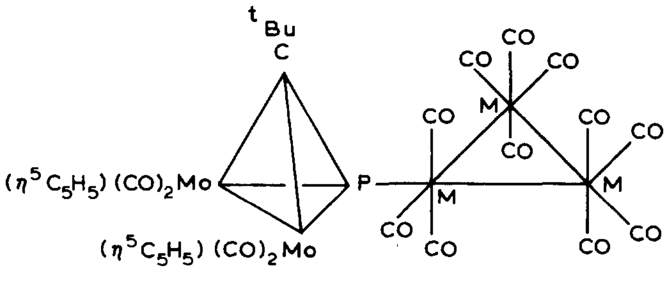
*Very recently complexes of the type [$Co_2(CO)_6P_2(MLn)_2$] (MLn = $Cr(CO)_5$, $W(CO)_5$ have been obtained by an indirect route (H. Lange, L. Zsolnai, and G. Huttner, Angew. Chem., 95 (1983) 1017).



(II, M = Os ; III, M = Ru)

An interesting feature of the structure of II is the very long C—P bond length of the coordinated phosphaalkyne (1.86(1) Å) which is typical for a single C—P bond and contrasts with the shorter C—P distances found in other phosphaalkyne complexes e.g. 1.672(17) Å in $[Pt(PPh_3)_2(^tBuCP)]$ [1], 1.695(6) Å in $[Co_2(CO)_6(^tBuCP)W(CO)_5]$ [2]; 1.719(3) Å in $[Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2(^tBuCP)$ [6] and 1.733(12) Å in $[Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2(^tBuCP)W(CO)_5]$ [4]. Typical P≡C and P=C bond lengths in uncoordinated phosphaalkynes and phosphaalkenes are 1.544 and 1.67 Å, respectively [7,8].

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