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Preliminary communication

[$Cp^*FeP_6MoCp^*$]: A dinuclear complex with a P_4 and a P_2 ligand

Dedicated to: Professor Heinrich Nöth, München, on the occasion of his 70th birthday.

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Abstract

The cothermolysis of [$Cp^*Fe(\eta^5\text{-}P_5)$] (**1**) and [$Cp^*Mo(CO)_3CH_3$] (**2**) gives [$Cp^*(OC)Mo(\mu\text{-}\eta^{2:2}\text{-}P_2)_2FeCp^*$] (**3**), which on reaction with P_4 yields [$Cp^*MoP_6FeCp^*$] (**4**). Its X-ray crystal structure determination reveals, for the 'P_6' ligand, a $\mu\text{-}\eta^{4:2}\text{-}P_4$ as well as a $\mu\text{-}\eta^{2:2}\text{-}P_2$ co-ordination type. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Iron; Molybdenum; Phosphorus; 'P6' ligand; Cluster

1. Introduction

In 1985, the triple-decker sandwich complex [$Cp^*Mo(\mu\text{-}\eta^{6:6}\text{-}P_6)MoCp^*$] with hexaphosphabenzene, cyclo-P_6, as middle deck [1], was synthesized and structurally characterized. This was the starting point for a novel chapter about complexes with P_n ligands [2]. In the meantime, the sandwich compound [$Cp^*Fe(\eta^5\text{-}P_5)$] (**1**) [3] turned out to be a versatile educt. Besides the terminal co-ordination of up to four 16 VE ML_n fragments to the P lone pairs of the cyclo-P_5 ligand of **1** ([4]a), its reaction with the 12 VE fragment {$Cr(CO)_3$} gives a 30 VE triple-decker in a stacking reaction ([4]b). Other complexes show envelope conformation ([4]c), opening ([4]c) or degradation ([4]d) of the cyclo-P_5 ligand.

2. Results and discussion

The cothermolysis of **1** and **2** gives the dinuclear complex **3** with two P_2 ligands in moderate yield (c.f. the complexes: [{$Cp^*(OC)Mo$}$_2(\mu\text{-}\eta^{2:2}\text{-}P_2)_2$] ([1,5]a), [{$Cp^{*\prime}Rh$}$_2(\mu\text{-}\eta^{2:2}\text{-}P_2)_2$] ([5]b), $Cp^{*\prime} = C_5Me_4Et$, and [{Cp^*Fe}$_2(\mu\text{-}\eta^{2:2}\text{-}P_2)_2$] ([5]c)). On reaction with white phosphorus, P_4, a P_2 unit can be transferred to **3** with formation of the heterobimetallic cluster **4** containing a 'P_6' ligand (Scheme 1). **3** forms a dark-brown microcrystalline powder, **4** are red-brown needles. Both complexes are sparingly soluble in pentane, slightly soluble in toluene and readily soluble in dichloromethane[2].

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[1] X-ray crystal structure determination.

[2] Complex **3**: 198.2 mg (0.57 mmol) **1** [3] and 185.0 mg (0.56 mmol) **2** [11], dissolved in 50 ml xylene, were heated to reflux for ca. 4 h with stirring (IR: only the (CO) band of **3** at 1954 cm^{-1}). After evaporation of the solvent under oil-pump vacuum, the residue was dissolved in 20 ml dichloromethane and ca. 1 g silica gel was added. The mixture was concentrated (oil-pump vacuum) until it was free-flowing. Column chromatography (column: 3 × 6 cm, neutral Al_2O_3 (3% H_2O), petroleum ether) with petroleum ether/diethyl ether (100:1) afforded 76.4 mg (23%) dark-brown **3**.
Complex **4**: 116.7 mg (0.20 mmol) **3** and 100.0 mg (0.81 mmol) P_4, each dissolved in ca. 20 ml xylene, are heated for 90 min to 180°C (oil-bath temperature) in a pressure Schlenk tube. For its isolation c.f. the synthesis of complex **3**: 10 ml dichloromethane, silica gel as column material (column: 10 × 1 cm). 44.5 mg (36.5%) 4 were eluted with petroleum ether/diethyl ether (100:1). The red-brown microcrystalline needles of **4** can be recrystallized from dichloromethane/pentane (4:1) at −30°C.

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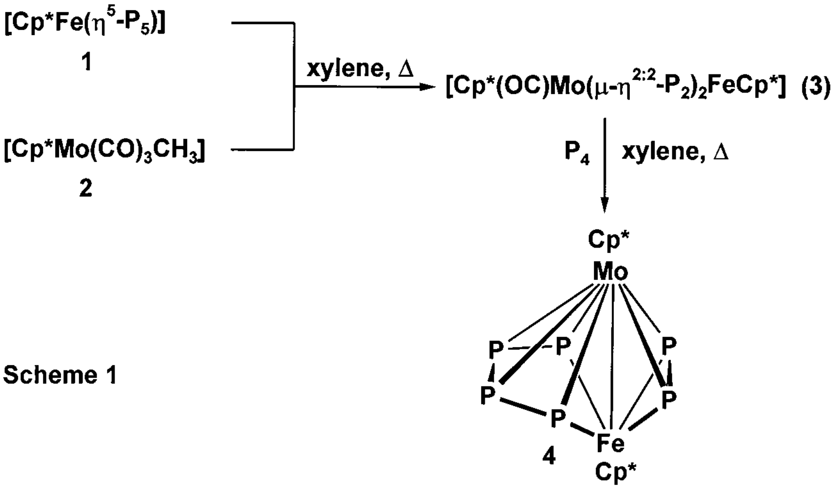

Scheme 1. The formation of the heterobimetallic cluster (**4**), containing a 'P_6' ligand, from the dinuclear complex **3**.

*2.1. NMR data of the complexes **3** and **4***

Assignment of the Cp* singlets in the ^{1}H-NMR spectrum to the complexes **3** and **4** (see Table 1) was made by comparing it with spectra of the compounds [Cp*(OC)Mo(P$_2$)$_2$FeCp*′] (**3′**) and [Cp*Mo(P$_4$)(P$_2$)FeCp*′] (**4′**), Cp*′ = C_5Me_4Et [6]. Temperature-dependent (210 → 363 K) ^{1}H- and ^{31}P-NMR studies gave no indication for a dynamic behaviour of the (P$_2$)$_2$ ligands in complex **3**. In compound **4**, the connectivities of the phosphorus atoms have been determined by a ^{31}P, ^{31}P COSY-45 NMR spectrum. Its simulation and iteration were carried out with PERCH-NMR software.

The cross peaks in the ^{31}P, ^{31}P COSY-45 NMR spectrum give evidence for a ^1J(PP) coupling between the atoms P3,4 and P5,6, respectively (simulation affords − 320 Hz). The coupling constant ^1J(PP) of − 405 Hz indicates a multiple bond character in the P4–P5 interaction (c.f. the discussion of the X-ray structure). ^1J(PP) of − 200 Hz for P1–P2 lies at the lower end of the expected range. For P1–P6 and P2–P3, a coupling constant of 55 Hz was found. This result does not favour a direct coupling between these atoms (see also Section 2.2). A coupling constant of − 33.5 Hz was detected for P1,5 and P2,4; a value which points to a coupling across the Mo atom. Obviously, such a type of coupling (Mo/Fe) may be the reason for the small coupling constant (4.4 Hz) between the atoms P1,3 and P2,6, respectively.

*2.2. Molecular structure of [Cp*Mo(μ-η$^{4:2}$-P$_4$)(μ-η$^{2:2}$-P$_2$)FeCp*] (**4**)*

Selected bond lengths (Å) and angles (°) are compiled in Table 2. Fig. 1 shows the molecular structure of compound **4**.

For complex **4** an X-ray structural study[3] reveals a butterfly skeleton (Fig. 1) for the atoms Mo1, P1, P2 and Fe1, where an additional Mo1–Fe1 bond affords a dimetalla-diphosphatetrahedrane substructure. The bond distance P1–P2 (2.08 Å) lies in the range of a P_2 4 e$^-$ donor ligand [2]. The dihedral angle at the P1–P2 axis of the 'butterfly' (P1, P2, Mo1/P1, P2, Fe1) is 101.5°; for 1,3-diphospha bicyclo[1.1.0]butane, 107.3° have been calculated (Ref. [7] and references therein). The distance of 2.765 Å between the atoms Fe1 and Mo1 has bonding character. Interestingly, the main axis of the complex has a zig-zag shape (Fig. 1) and the angles Cp$^*_{\text{(centr.)}}$–Fe1–Mo1 (170.4°) and Cp$^*_{\text{(centr.)}}$–Mo1–Fe1 (161.5°) show a different deviation from linearity. P3 to P6 form a trapezoid with alternating bond lengths: P3–P4 = 2.18, P4–P5 = 2.09 and P5–P6 = 2.18 Å; a result that formally points to a deprotonated (metalated) 6e$^-$-donor tetraphosphabutene ligand (•P–P=P–P•; c.f. the isolobal molecules H_3C–CH=CH–$CH_3(C_4H_8)$ ↔ H_2P–P=P–$PH_2(P_4H_4)$). This ligand can formally be regarded as P_4^{4-} ion ($^{2-}|\overline{\text{P}} - \text{P} = \text{P} - \overline{\text{P}}|^{2-}$).

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[3] Crystal-structure data of complex **4**: $C_{20}H_{30}FeMoP_6$, Mw = 608.1, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 11.1119(12)$, $b = 14.5231(12)$, $c = 15.6239(14)$ Å, Mo–K$_\alpha$ radiation, $\lambda = 0.71073$ Å, $T = 298$ K, $V = 2521.4(4)$ Å^3, $Z = 4$, $D_c = 1.602$ mg mm^{-3}, crystal dimensions: 0.30 × 0.22 × 0.13 mm^3, diffractometer: Stoe IPDS, range for data collection: $1.91 < \theta < 24.08°$, measured reflections 29304, independent reflections 3973 ($R_{\text{int}} = 0.0268$), R indices [$I > 2\sigma(I)$]: $R_1 = 0.0223$, $wR_2 = 0.0615$, R indices (all data): $R_1 = 0.0234$, $wR_2 = 0.0682$. Refinement method: full-matrix least-squares on F^2, structure solution: direct methods, Siemens SHELXTL. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 100917. Copies of the data can be obtained on application to the Director, CCDC 12 Union Road, Cambridge CB2 1EZ, UK (Telefax: + 44 1223 336033; e-mail: deposit@chemcrys.cam.ac.uk).

Table 1
^{1}H- and ^{31}P-NMR data[a] of the complexes **3** and **4** (in C_6D_6, 298 K, δ in ppm, J in Hz)

[Cp*(OC)Mo(P_2)$_2$FeCp*] (**3**)	[Cp*Mo(P_4)(P_2)FeCp*] (**4**)
δ ^{1}H	
1.70 s (15H, Mo)	1.15 s (15H, Fe)
1.77 s (15H, Fe)	1.30 s (15H, Mo)
δ ^{31}P	
AX spin system	AA′MM′XX′ spin system
31.3(d), −118.0(d)	302.6 (m, 2P, P4/5 = AA′)[b]
^{1}J(AX) = −460	81.0 (m, 2P, P3/6 = MM′)[b]
IR[c] (in xylene): $\tilde{\nu}$(CO) = 1954 cm^{-1} (s)	−147.5 (m, 2P, P1/2 = XX′)[b]
	NMR-software[d] and Ref. [6]

[a] FT-NMR spectrometer AC 200 and AMX 400 (Bruker). ^{1}H-NMR (200.13 or 400.14 MHz, TMS extern), ^{31}P (81.01 or 161.97 MHz, 85% H_3PO_4 as extern standard.

[b] For the assignment of numbers c.f. Fig. 1.

[c] IR: Perkin Elmer 16 PC, FT-IR spectrometer.

[d] R. Laatikainen and M. Niemitz, PERCH-NMR Software, University of Kuopio, Finland, 1995.

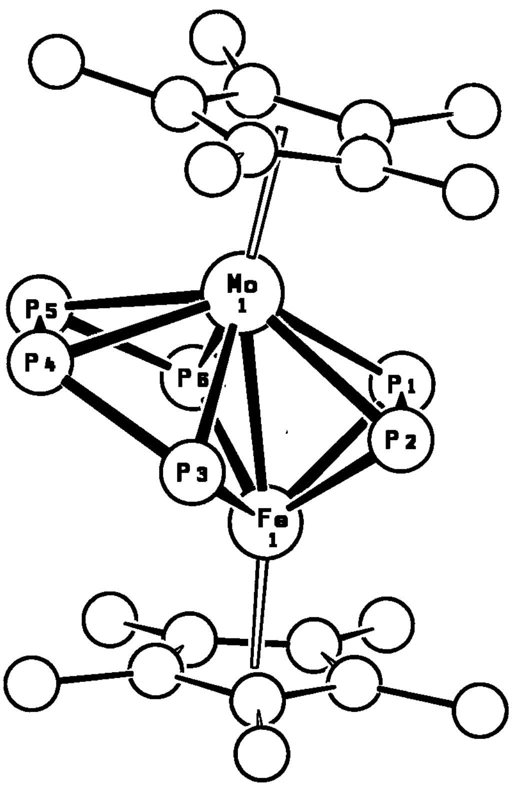

Fig. 1. Molecular structure for [Cp*Mo(μ-$\eta^{4:2}$-P_4)(μ-$\eta^{2:2}$-P_2)FeCp*] (**4**) with the atom numbering scheme.

The bond distances Mo1–P3/P6 = 2.44/2.44 Å; Mo1–P4/P5 = 2.59/2.59 Å, Mo1–P1/2 = 2.53/2.54 Å; Fe1–P1/2 = 2.29/2.30 Å and Fe1–P3/P6 = 2.28/2.28 Å reflect the high symmetry of the Mo(P_4)Fe(P_2) skeleton. An unsymmetric arrangement was found for the Cp*Mo1 fragment lying above the P_4 trapezoid (2.44/2.59 Å). In contrast to the 28 VE-triple-decker [Cp*Mo(μ-$\eta^{6:6}$-P_6)MoCp*] [1], the six phosphorus atoms of **4** define two planes with an interplanar angle of 144° between P1,2,3,6/P3,4,5,6. Almost equal pairs of intra-ring angles are found for: P1,2 = 106.9/107.0°, P3,6 = 129.6° and P4,5 = 109.1/109.6°. Difficulties arise upon attempted interpretation of the P···P distances of 2.50 and 2.51 Å for P2···P3 and P1···P6, respectively. In the chemistry of complexes with P_n ligands [2], to the best of our knowledge, the longest intact P–P bond of 2.46 Å has been found for [RhCl(η^2-P_4)(PPh_3)$_2$] [8]. Thus, the distances of 2.50/2.51 Å in **4** can be regarded as non-bonding and the ligands are best described as μ-$\eta^{4:2}$-P_4 as well as μ-$\eta^{2:2}$-P_2 co-ordination type.

Table 2
Selected bond lengths (Å) and angles (°) for [Cp*Mo(μ-$\eta^{4:2}$-P_4)(μ-$\eta^{2:2}$-P_2)FeCp*] (**4**)

Bond lengths (Å)			
Mo1–P1	2.5321(9)	P1–P2	2.082(2)
Mo1–P2	2.5391(9)	P2···P3	2.500(2)
Mo1–P3	2.4443(10)	P3–P4	2.179(2)
Mo1–P4	2.5878(11)	P4–P5	2.092(2)
Mo1–P5	2.5905(11)	P5–P6	2.181(2)
Mo1–P6	2.4352(9)	P1···P6	2.508(2)
Fe1–P1	2.2932(19)	P3···P6	3.539
Fe1–P2	2.2979(10)	Mo1–Fe1	2.7646(4)
Fe1–P3	2.2836(9)	Mo1–Cp$^{*}_{\text{(centr.)}}$	2.044
Fe1–P6	2.2774(9)	Fe1–Cp$^{*}_{\text{(centr.)}}$	1.754
Bond angles (°)			
P1–P2–P3	106.96(5)	P1–P6–P5	129.61(5)
P2–P1–P6	106.89(5)	P2–P3–P4	129.59(6)
P3–P4–P5	109.12(7)	Mo1–Fe1–Cp$^{*}_{\text{(centr.)}}$	170.4
P4–P5–P6	109.64(7)	Fe1–Mo1–Cp$^{*}_{\text{(centr.)}}$	161.5

The large differences in P–P bond lengths and the folding angle of 144° for the ‘P6’ ligand (c.f. the sandwich complex [Cp*Fe{Et_2B_2(CPr^i)$_2$CMe}] [9]a) do not allow a description of **4** as a 30 VE triple-decker complex. (c.f. Ref. [2]). According to the Wade/Mingos rules ([10]a), the formal electron count gives 9 SEP (skeletal electron pairs) or 54 cluster electrons. This result is consistent with a closo-structure of the 8 vertices polyhedron **4**. More meaningful are the following considerations: (a) The skeleton of **4** can also be regarded as a 6 vertices polyhedron (distorted Mo1, Fe1, P3,4,5,6 pentagonal pyramid) with additional coordination of a $P_2$4 e$^-$ donor ligand (isolobal with HC≡CH, c.f. Fig. 1). The resulting electron count of 8 SEP is in accordance with a nido structure (nido-pentagonal bipyramid). The folding angle at P3, P6 of the five-membered ring (Fe1, P3–P6) is 22.7°. (b) For polyhedra with a common edge (pentagonal pyramid Mo1, Fe1, P3,4,5,6/tetrahedrane Mo1, Fe1, P1,2; Fig. 1) the electron count ([10]b) of 54 cluster electrons is the correct number for complex **4**. Fig. 1 shows that in the heterobimetallic cluster **4** both metal atoms fulfill the 18 e^- rule.

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