Coordinative Stabilization of a Phosphido-phosphinidene Ligand

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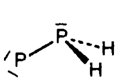
The phosphido-phosphinidene coordination mode **C** of a P_2 ligand has been realized in the trinuclear complex $[(TaL)_3(P_4)(P_2)]$ **2** (L = 1,3-$Bu^t{}_2C_5H_3$); structural proof was obtained by X-ray structure determination of the $[(TaL)_3(P_4\{Fe(CO)_4\})(P_2)]$ derivative **3**.

The novel coordination mode of a P_2-unit[1] as phosphido-phosphinidene ligand **B** may be visualized by formally replacing the two hydrogen atoms of the phosphino-phosphinidene P_2H_2 isomer **A**[2] by two transition metal complex fragments.

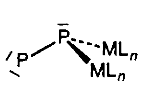
We have now prepared the complexes **2** and **3**† in 35 and 32% yields, respectively, by a procedure described in Scheme 1. Both contain trinuclear cluster cores with the phosphinidene P atom of the phosphido-phosphinidene ligand[3] of **B** being further terminally coordinated to a third transition metal fragment as shown in **C**. The P_2 ligand thus acts as a four-electron donor, a coordination mode slightly different to that found independently by Nixon's group in the triruthe-niumnonacarbonyl complex $[Ru_3(CO)_9(P_5C_5Bu^t{}_5)]$.[4] Complex **2** is obtained as a brown-green microcrystalline powder or as small square crystals, which did, however, not diffract.

Compound **3** forms yellow-green crystals which are sparingly soluble in light petroleum, moderately soluble in benzene and toluene and readily soluble in dichloromethane. Both compounds are slightly susceptible to moisture or air.

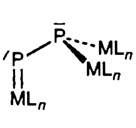
Remarkable features of the ^{31}P NMR data are the pronounced low field shift, characteristic for a bent phosphinidene phosphorus atom[3] [δ 698.8 for **2** and 701.9 for P(1) of **3**] and the extreme high field shift of the phosphorus atom at the apex of the pyramidal P_4 unit [δ −455.0 for **2** and −466.0 for P(3) of **3**]; shift values, which are close to that of white phosphorus, P_4, itself (δ −522).‡



A



B



C

Fig. 1 represents the molecular structure of **3** as established by an X-ray structure analysis.§ The Ta_3P_6-framework consists of an almost isosceles Ta_3-triangle [Ta(1)–Ta(2) = 2.936(2), Ta(1)···Ta(3) = 3.156(2) and Ta(2)···Ta(3) = 3.125(2) Å], which is capped by a P_2 phosphido-phosphinidene ligand on one side and a pyramidal P_4 unit on the other. Thus, the cluster core of **3** can be described as a severely distorted Ta_3P_5 cubane where the P(2) atom of the phosphido-

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† In the complexation reaction two further isomers are formed in an approximate 1:1 ratio and a total yield of about 10%, one with a single $\{Fe(CO)_4\}$ group attached to the P_2 unit and the other one with two $\{Fe(CO)_4\}$ groups. Separation by means of column chromatography has not yet been successful.

‡ ^{31}P NMR data (C_6D_6, chemical shifts in ppm) **2**: δ 698.8 (d, $J_{P,P}$ 465 Hz, 1P), 250.5 (d, $J_{P,P}$ 359 Hz, 2P), 156.8 (dd, $J_{P,P}$ 344, $^2J_{P,P}$ 14 Hz, 1P), −32.9 (dd, $J_{P,P}$ 465, $^2J_{P,P}$ 14 Hz, 1P), −455.0 (dt, $J_{P,P}$ 359 and 344 Hz, 1P).

3: δ 701.9 [d, $J_{P,P}$ 475 Hz, P(1)], 292.2 [d, $J_{P,P}$ 364 Hz, P(6)], 234.7 [d, $J_{P,P}$ 354 Hz, P(5)], 143.9 [d, $J_{P,P}$ 341 Hz, P(4)], −25.8 [d, $J_{P,P}$ 475 Hz, P(2)], −466.0 [ddd, $J_{P,P}$ 364, 354 and 341 Hz, P(3)].

^1H NMR data **2** (C_7D_8, T = 273 K): δ 6.44 (m, 2H), 5.98 (m, 2H), 5.45 (m, 2H), 5.43 (m, 1H), 4.74 (m, 2H), 1.56 (s, 18H), 1.49 (s, 18H), 1.14 (s, 18H).

3 (C_6D_6, T = 298 K): δ 6.70 (m, 2H), 6.50 (m, 1H), 6.01 (m, 1H), 5.55 (m, 2H), 5.09 (m, 1H), 4.89 (m, 1H), 4.23 (m, 1H), 1.45 (s, 9H), 1.35 (s, 9H), 1.25 (s, 9H), 0.91 (s, 9H), 0.87 (s, 9H), 0.67 (s, 9H). ν(CO)/cm^{-1} in light petroleum: 2039vs, 1969m, 1946s, 1927s; in KBr: 2035vs, 1962m, 1940s, 1923s.

§ *Crystal data* for **3**: $C_{43}H_{63}O_4P_6FeTa_3 \cdot$ *ca.* 0.75 CH_2Cl_2. Orthorhombic, space group *Fdd*2, a = 32.883(3), b = 40.815(5), c = 17.078(2) Å, V = 22 920(4) Å^3, D_c = 1.70 g cm^{-3}, max residual electron density 1.55 e Å^{-3}. 5814 unique reflections were recorded, 3787 of which were 'observed' with $I > 2.0\,\sigma(I)$ (ω–2θ scan) using Mo-Kα radiation (λ = 0.71073 Å), graphite monochromator, on an Enraf-Nonius CAD4 diffractometer.

Solution by SHELXS 86 and refinement by SHELX 76. $R(R_w)$ = 0.076 (0.080). The high residual electron density is due to incorporated solvent (CH_2Cl_2) residing at x/a = 0.298, y/b = 0.368, z/c = 0.402 and on a twofold axis $x/a = y/b = 0$, z/c = −0.479. Both positions are populated to about 50%. Additional disorder of the solvent hampered their inclusion into structural refinement.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

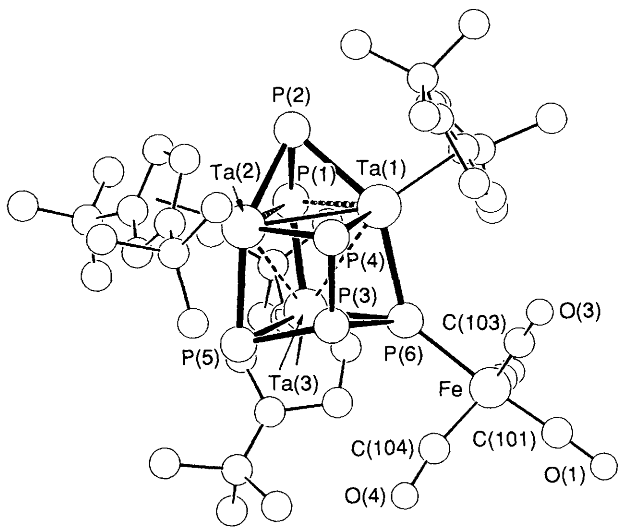


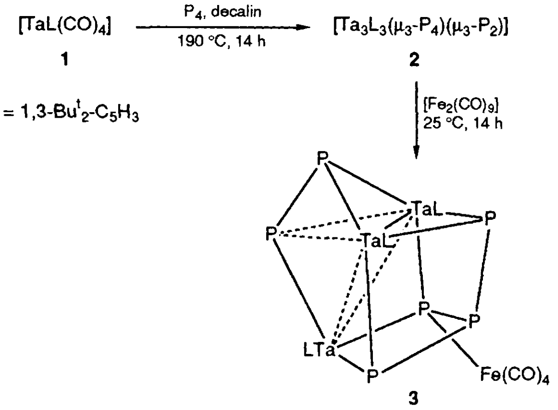
Fig. 1 Molecular structure of **3**. Selected bond lengths (Å) and angles (°). P(1)–P(2) 2.088(15), P(3)–P(4) 2.170(15), P(3)–P(5) 2.203(15), P(3)–P(6) 2.226(16), P(1)···Ta(1) 2.681(11), P(1)···Ta(2) 2.728(11), P(1)–Ta(3) 2.328(11), P(2)–Ta(1) 2.497(11), P(2)–Ta(2) 2.500(11), P(4)–Ta(1) 2.492(11), P(4)–Ta(2) 2.482(11), P(5)–Ta(2) 2.519(11), P(5)–Ta(3) 2.407(12), P(6)–Ta(1) 2.528(11), P(6)–Ta(3) 2.398(11), P(3)···Ta(1) 2.902(11), P(3)···Ta(2) 2.837(11), P(3)···Ta(3) 2.816(11), Ta(1)–Ta(2) 2.936(2), Ta(1)···Ta(3) 3.156(2), Ta(2)···Ta(3) 3.125(2); P(2)–P(1)–Ta(3) 129.3(6).

phosphinidene ligand caps the slightly folded P(1), Ta(2), P(4), Ta(1) face (sum of angles = 357.8°) only by half (see Fig. 2).

Alternatively the cluster core of **3** may be viewed as a Ta_3P_6 homocubene, with the phosphinidene P atom P(1) bridging the Ta(3)–P(2) edge of a Ta_3P_5 cubane. The pyramidal P_4 unit of **3** can be envisaged as being directly related to the P_4 tetrahedron where three of its original six edges are still intact. The individual bond lengths of the remaining edges [P(3)–P(4),(5),(6) = 2.170(15), 2.203(15), 2.226(16) Å] average at 2.20 Å, a value which is almost identical with that of 2.21 Å found for the P_4 molecule itself.

As shown by the P–P–P angles of 111.8(6) [P(4)–P(3)–P(5)], 109.5(6) [P(4)–P(3)–P(6)] and 108.8(6)° [P(5)–P(3)–P(6)] the pyramidal P_4 unit is notably obtuse with respect to the parent molecule.

The Ta–P bond lengths within the cluster core of **3** can be divided into three groups: The shortest contact is found between the phosphinidene P atom P(1) and Ta(3) [2.328(11) Å]. This accounts for some double bond character which is already suggested by the diamagnetism of this compound. All Ta–P bond distances including the three basal P atoms of the P_4 unit and the capping P(2) atom of the phosphido-phosphinidene ligand lie within the range of 2.398(11) [Ta(3)–P(6)] to 2.528(11) [Ta(1)–P(6)] Å. By far the longest Ta–P distances are those between the Ta atoms Ta(1) and Ta(2) and the phosphinidene atom P(1) of the P_2 ligand [Ta(1)···P(1) = 2.681(11), Ta(2)···P(1) = 2.728(11) Å]. These long contacts are probably implicated by the cluster geometry of **3**.



Scheme 1

In the bent phosphido-phosphinidene ligand a P(2)–P(1)–Ta(3) bond angle of 129.3(6)° is found. The P(1), P(2), Ta(1), Ta(2) subunit of **3** simulates a diphospha-dimetallatetrahedrane and the short P(1)–P(2) bond length of 2.088(15) Å lies well within the range found for other members of this class (2.019–2.154 Å).[1] Compound **2** possesses a Ta_3P_6 framework identical to that of **3**. The absence of the $\{Fe(CO)_4\}$ group attached to it leads, however, to a higher degree of symmetry. Thus, a mirror plane through the bent P_2Ta unit and the opposite edge of the pyramidal P_4 ligand bisects the molecule as clearly indicated by NMR spectroscopy.‡

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