

Preliminary communication

**Preparation and X-ray structure of the
bis(pentacarbonyltungsten) complex of 1,3-diphosphaallene
with η^1 -coordination mode**

Masaaki Yoshifuji ^{*}, Koza Toyota

Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Sendai 980 (Japan)

Takashi Niitsu, Naoki Inamoto,

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113 (Japan)

and Ken Hirotsu ^{*}

Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558 (Japan)

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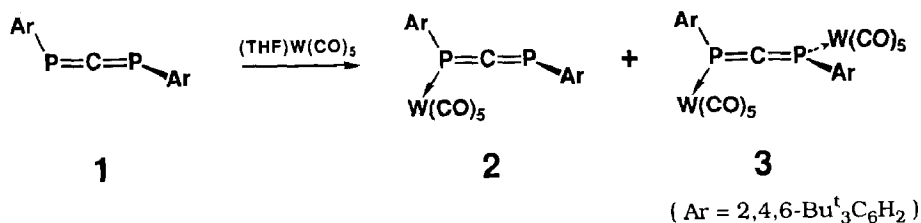
Abstract

The bis(pentacarbonyltungsten) complex of 1,3-bis(2,4,6-tri-*t*-butylphenyl)-1,3-diphosphaallene with η^1 -coordination mode has been isolated and its crystal structure determined by X-ray analysis.

Sterically protected phosphorus-containing multiple-bonded compounds are currently of much interest. Several reports have been published on phosphacumulenes, including phosphaaallenes [1–4] and 1,3-diphosphaallenes [5–7] carrying the 2,4,6-tri-*t*-butylphenyl group (abbreviated to Ar) as a kinetically protecting group. These phosphacumulenes contain low-coordinated phosphorus atom(s) (coordination number 2) and are interesting molecules because of their several coordination modes as ligand to transition metals [8,9].

We have reported several transition metal complexes of Group 6 with these phosphaaallenes [10], and demonstrated that the coordination to the Group 6 metal occurs at the phosphorus atom in η^1 -fashion by taking into account the chemical shift correlation and phosphorus–tungsten coupling constants in solution ³¹P NMR. On the other hand, diphosphaallene **1** has been known to coordinate platinum and palladium as a π -type ligand [11,12].

We now report preliminary results on the preparation and X-ray analysis of the bis(pentacarbonyltungsten) complex with 1,3-bis(2,4,6-tri-*t*-butylphenyl)-1,3-diphosphaallene.



Scheme 1.

The phosphallaene **1** was allowed to react with an excess of (tetrahydrofuran)- $\text{W}(\text{CO})_5$ to give the monocoordinated complex **2** [10] and the dicoordinated complex **3**. These complexes were purified by gel permeation column chromatography.

The structure of **3** was unambiguously established by X-ray crystallographic analysis, whereas attempts to get suitable crystals for X-ray analysis of complex **2** have failed so far. Figure 1 shows an ORTEP drawing [13] of the molecular structure of **3**, which depicts the first X-ray analysis of the η^1 -type doubly coordinated 1,3-diphosphaallene. Some selected bond distances and angles for **3** together with the data for **1** [7] are listed in Table 1. The diphosphaallene part in **3** has a similar conformation to non-coordinated **1**. The P–W bond distances are 2.522(6) Å and 2.517(5) Å. The P=C bond lengths are 1.62(2) Å and 1.63(2) Å. The W, P, C1, and C2 atoms and W', P', C1', and C2' atoms are coplanar within 0.03 Å and 0.09 Å, respectively, and these planes make an angle of 68.6(5)°. The C2–C7 atoms and

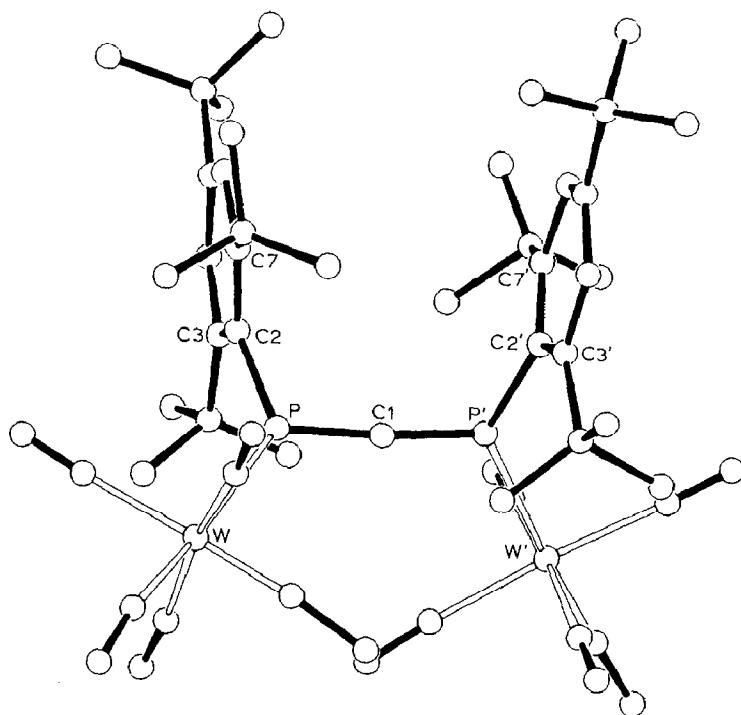
Fig. 1. Molecular structure of the tungsten complex **3**.

Table 1

Some selected bond distances (Å) and angles (°)

Atom	1 ^a	3
P–W		2.522(6)
P'–W'		2.517(5)
P–C1	1.635(8)	1.62(2)
P'–C1	1.630(8)	1.63(2)
P–C2	1.86 ^b	1.85(2)
P'–C2'	1.88 ^b	1.86(2)
P–C1–P'	172.6(5)	171(1)
C1–P–C2	100.3(4)	110(1)
C1–P'–C2'	99.9(4)	108(1)
W–P–C1		120.3(9)
W'–P'–C1		119.1(9)
W–P–C2		129.9(5)
W'–P'–C2'		131.5(5)

^a Data taken from Ref. 7. ^b Values calculated from atomic coordinates deposited at the Cambridge Crystallographic Data Centre.

C2'–C7' atoms are also coplanar within 0.03 Å and 0.05 Å, respectively, and the former and the latter rings make angles of 88(1)° and 90(1)° with the W, P, C1, C2 and W', P', C1', C2' planes, respectively. Dihedral angles C2–P⋯P'–C2' and W–P⋯P'–W' are 71.4(8)° and 66.2(4)°, respectively. In the uncoordinated diphosphaallene **1**, the dihedral angle C2–P⋯P'–C2' is 83.0°, whereas in the complex **3** the angle is compressed by about 10°, probably because of steric congestion on coordination, while the π -system of the Ar rings and $p\pi$ of the P=C system are perpendicular. The crystal structure of **3** is quite different from that observed for bis(triethylphosphine)palladium complex [12], where the P=C bond that is η^2 -ligated to palladium is lengthened to 1.73(3) Å.

Experimental

Preparation of [W(CO)₅]₂[ArP=C=PAr] (3). The starting material, bis(2,4,6-tri-*t*-butylphenyl)-1,3-diphosphaallene (**1**) was prepared from diphosphirane, obtained from bis(2,4,6-tri-*t*-butylphenyl)diphosphene and dichlorocarbene, followed by ring opening with methylolithium, as described before [6]. The phosphaallene **1** (89.3 mg, 0.158 mmol) and hexacarbonyltungsten(0) (304.2 mg, 0.864 mmol) were dissolved in THF (3 ml) and were irradiated with a mercury lamp at 0 °C for 13 h to give the tungsten complexes of **1**. These complexes were purified by recycling preparative HPLC over gel permeation columns (Japan Analytical Industry, Co., Ltd., JAIGEL H1 + H2) using THF as eluent to give **3** in 27% yield and **2** [10] in 23% yield. **3**: m.p. 174.5–176.5 °C (decomposition), ³¹P {¹H} NMR: δ_p 144.3 accompanied by satellite peaks of an AA'X pattern with ¹J_{PW} = 285.0 Hz, ²J_{P–C–P} = 97.7 Hz, and ³J_{PW} = 17.0 Hz due to ¹⁸³W of 14.4% natural abundance.

X-Ray structure determination of 3. Compound **3** was recrystallized from pentane. C₄₇H₅₄O₁₀P₂W₂, *M* = 1208.59, monoclinic, space group *P*2₁/*a*, *a* 19.988(6), *b* 21.989(5), *c* 11.688(3) Å, β = 98.25(2), *U* 5084(2) Å³, *Z* = 4, *D*_c 1.579 g cm⁻³. 6655 reflections with $2\theta \leq 45^\circ$ were recorded on a four circle diffractometer using

graphite-monochromated Mo- K_{α} radiation. Of these 3803 [with $I > 2\sigma(I)$] were judged observed. The structure was solved using MULTAN 80 [14]. At the last stage of the refinement, hydrogen atoms (calculated) were included in the structure factor calculations only. Full matrix least-squares refinement [15] with anisotropic temperature factors for nonhydrogen atoms converged to $R = 0.075$. The large thermal motion and/or partial disorder of t-butyl and carbonyl groups are the cause of low resolution of the X-ray data, resulting in large e.s.d.'s of the atomic coordinates. Atomic coordinates and thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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