Journal of Organometallic Chemistry, *461* (1993) 81–84

JOM 23730

X-Ray analysis of 1-phospha-1,2,3-butatriene as a ligand of carbonyltungsten complex

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(Received February 12, 1993; in revised form April 7, 1993)

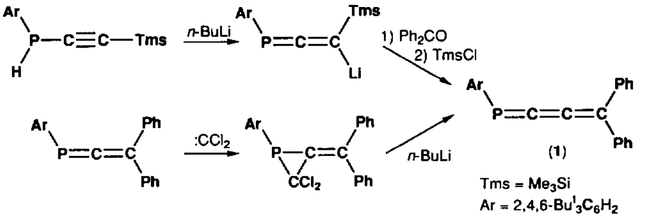
Abstract

X-Ray analysis was carried out of 4,4-diphenyl-1-(2,4,6-tri-t-butylphenyl)-1-phospha-1,2,3-butatriene as a ligand of pentacarbonyltungsten complex. The heterocumulene system was found to be planar with a rod framework coordinating to the tungsten metal at the phosphorus atom in a σ-type coordination.

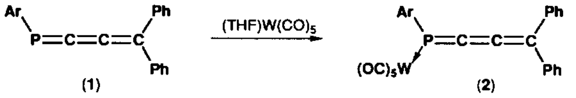
1. Introduction

Sterically protected phosphorus-containing multiple bonded compounds are currently of interest. We have been interested in the phosphacumulene system, such as 1-phosphaallenes [1] and 1,3-diphosphaallenes [2], as well as diphosphenes [3] and phosphaethenes [4]. Märkl *et al.* [5,6] and our group [7,8] have recently reported the preparation and isolation of 1-phospha-1,2,3-butatriene and 1,4-diphospha-1,2,3-butatriene, as further examples of an extended cumulene system.

We have reported the X-ray structure analysis of 3,3-diphenyl-1-(2,4,6-tri-t-butylphenyl)-1-phosphaallene [9] and its tungstenpentacarbonyl complex [10]. On the other hand, Märkl *et al.* reported the X-ray analysis of 4,4-diphenyl-1-(2,4,6-tri-t-butylphenyl)-1-phospha-1,2,3-butatriene (**1**) [5a] and we now wish to report the X-ray crystallographic analysis of **2** possessing **1** as a ligand in its pentacarbonyltungsten complex.



Scheme 1.



Scheme 2.

2. Results and discussion

Among the various kinds of possible coordination modes [11–13] as shown in Fig. 1, the 1-phospha-1,2,3-butatriene **1** was found to exhibit σ-type coordination

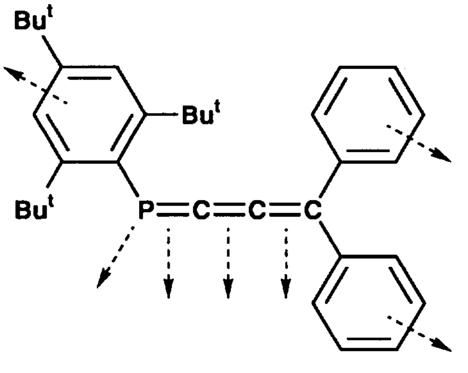


Fig. 1. Possible coordination modes of 1-phospha-1,2,3-butatriene (**1**) as a ligand to a transition metal.

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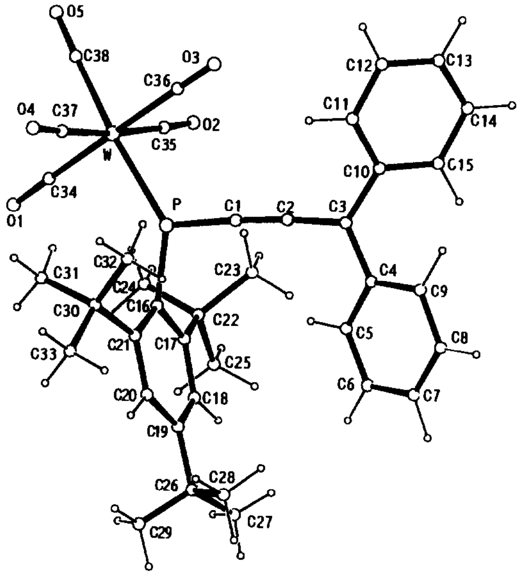

Fig. 2. Molecular structure of the [1-phospha-1,2,3-butatriene]-pentacarbonyltungsten complex (**2**) showing the atomic labelling scheme.

to the tungsten metal at the low-coordinate phosphorus atom.

Figure 2 is an ORTEP drawing [14] of the molecular structure for the complex **2** showing a σ-type coordination at the phosphorus atom. Table 1 lists selected bond lengths and angles for the complex **2** with those for the free ligand **1** as reported by Märkl *et al.* [5a]. Table 2 shows fractional coordinates for complex **2**.

The atoms, W, P, C(16), C(1), C(2), C(3), C(4), and (C10) are coplanar within 0.11(1) Å. This plane makes angles of 80.2(3)°, 22.6(3)°, and 38.5(3)° with the aromatic rings of 2,4,6-tri-t-butylphenyl [C(16)–C(21)] and the two phenyls on C(3) [C(4)–C(9) and C(10)–C(15)], respectively, with the dihedral angles of ∠C(1)–P–C(16)–C(17) = −75.7(6)°, ∠C(2)–C(3)–C(4)–C(5) = 23(1)°, and ∠C(2)–C(3)–C(10)–C(11) = 32(1)°. The overall conformation of the ligand phosphabutatriene **1** in **2** is quite similar to that of the free **1**, since the root mean square deviation of the corresponding atomic positions between **1** and **2** is 0.26 Å, the two phenyl rings on C(3) except *ipso*-carbons C(4) and C(10) being omitted from the calculation because of the statistical distribution of these phenyl rings in **1**. There is no appreciable change in the corresponding bond lengths of –P=C=C=C< frame for **1** and **2**, when e.s.d.'s are taken into consideration, while the bond angles of this moiety change significantly on coordination of $W(CO)_5$ as is shown in Table 1, reflecting the steric repulsion between the carbonyl groups and the ligand. The bond length of P–W [2.506(1) Å] in **2** is shorter than the 2.531(2) Å in the 1-phosphaallene-tungsten complex [10]. This shortening appears to be caused not only by the steric repulsion between the $W(CO)_5$ part and the Ph_2C part within the complex **2** being smaller than that within the 3,3-diphenyl-1-phosphaallene complex, but also by the different electronic effects between the P=C=C and P=C=C=C systems. The Ar-ring is deformed into a boat form with C(16) serving as a bow, which is commonly observed for compounds containing

TABLE 1. Some important bond lengths (Å) and angles (°) for **2** and **1** [a]

	2	1 [b]		2	1 [b]
P–W	2.506(1)		P–W–C34	92.2(2)	
W–C34	2.040(7)		P–W–C35	88.8(2)	
W–C35	2.038(8)		P–W–C36	86.2(2)	
W–C36	2.038(7)		P–W–C37	95.2(2)	
W–C37	2.043(8)		P–W–C38	175.2(2)	
W–C38	1.998(7)		C34–W–C35	92.1(2)	
P–C16	1.849(6)	1.868(5)	C34–W–C36	178.5(2)	
P–C1	1.664(6)	1.647(8)	C34–W–C37	91.0(3)	
C1–C2	1.222(9)	1.253(10)	C34–W–C38	90.2(3)	
C2–C3	1.363(9)	1.348(10)	C35–W–C36	87.9(3)	
C3–C4	1.468(10)	1.487(10)	C35–W–C37	174.8(3)	
C3–C10	1.470(11)	1.487(5)	C35–W–C38	87.0(3)	
			C36–W–C37	89.1(3)	
			C36–W–C38	91.2(3)	
			C37–W–C38	88.8(3)	
			C1–P–C16	100.7(3)	98.4(3)
			P–C1–C2	175.7(6)	178.4(5)
			C1–C2–C3	175.0(7)	178.3(6)
			C2–C3–C4	117.2(6)	118.8(5)
			C2–C3–C10	118.7(6)	121.9(6)
			C4–C3–C10	124.1(6)	

[a] Standard deviations of the least significant figures are given in parentheses. [b] Data for **1** are taken from Ref. 5a.

Ar–P [15]. The bow [C(16)] and the stern [C(19)] of this boat-shaped benzene ring are bent up by 7.2° and 3.0°, respectively, from below [C(17)–C(18)–C(20)–C(21)].

3. Experimental details

3.1. *Preparation of* $[W(CO)_5][ArP{=}C{=}C{=}CPh_2]$ *(2)*

The ligand 4,4-diphenyl-1-(2,4,6-tri-t-butylphenyl)-1-phospha-1,2,3-butatriene (**1**) was prepared as reported [7]. The reaction of **1** (406.8 mg, 0.87 mmol) with 3.4 equiv of (tetrahydrofuran)W(CO)$_5$ was carried out at room temperature in THF (20 ml) to give the complex (**2**) as a red solid (638.6 mg) in 93% yield after chromatographic purification (silica gel/pentane). Mp 136–137°C, ^{31}P NMR (81 MHz, CDCl$_3$) δ_P 91.6, ^1J(PW) = 290 Hz; ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.36 (9H, s, p-^{t}Bu), 1.71 (18H, s, o-^{t}Bu), 7.1–7.3 (5H, m, Ph), 7.3–7.4 (3H, m, Ph), 7.46 (2H, d, J(PH) = 3.2 Hz,

TABLE 2. Fractional coordinates ($\times 10^4$) (with esds) [a] and isotropic displacement coefficients (nm$^2 \times 10^{-1}$) for complex **2**

	x	y	z	U_{eq} [b]
W	3884.9(1)	1451.4(1)	609.1(2)	43.8(1)
P	4712(1)	1981(1)	2365(1)	38.7(5)
O1	4552(3)	−188(3)	1086(5)	80(2)
O2	5051(3)	1913(3)	−1037(5)	87(2)
O3	3248(3)	3107(3)	195(5)	87(2)
O4	2575(3)	1043(4)	2012(5)	90(3)
O5	2923(3)	897(4)	−1748(5)	89(2)
C1	4801(3)	2912(4)	2488(5)	49(2)
C2	4917(4)	3588(3)	2594(6)	53(2)
C3	5108(4)	4327(4)	2742(6)	56(2)
C4	5683(4)	4514(4)	3738(7)	63(3)
C5	6179(5)	3989(6)	4209(8)	92(4)
C6	6688(6)	4149(6)	522(1)	122(5)
C7	6706(7)	4834(6)	575(1)	115(5)
C8	6231(6)	5377(5)	5263(9)	102(4)
C9	5697(4)	5238(4)	4263(7)	79(3)
C10	4738(5)	4883(5)	1900(8)	66(3)
C11	4022(5)	4779(4)	1396(8)	81(3)
C12	3657(6)	5278(7)	55(1)	108(5)
C13	4018(6)	5880(6)	23(1)	114(5)
C14	4733(7)	6006(6)	68(1)	118(5)
C15	5102(5)	5511(5)	1539(9)	90(4)
C16	5365(3)	1668(4)	3669(6)	39(2)
C17	6134(3)	1702(3)	3610(5)	42(2)
C18	6603(3)	1725(4)	4686(5)	51(2)
C19	6382(4)	1691(4)	5799(6)	54(2)
C20	5641(4)	1586(4)	5807(6)	58(2)
C21	5125(4)	1561(3)	4782(6)	47(2)
C22	6479(3)	1643(4)	2456(6)	49(2)
C23	6370(5)	2374(5)	1675(7)	73(3)
C24	6154(4)	975(5)	1716(7)	71(3)
C25	7305(5)	1520(6)	2728(8)	91(4)
C26	6918(4)	1746(5)	6954(6)	71(3)
C27	7664(5)	1989(8)	6790(8)	115(5)
C28	6648(7)	2372(9)	771(1)	147(7)
C29	6923(8)	1064(9)	764(1)	181(7)
C30	4314(4)	1374(4)	4911(6)	56(2)
C31	4067(4)	676(4)	4170(6)	64(3)
C32	3796(4)	2029(5)	4537(8)	80(3)
C33	4247(5)	1166(7)	6225(7)	93(4)
C34	4315(4)	397(4)	898(6)	54(2)
C35	4643(4)	1738(4)	−437(6)	59(2)
C36	3473(4)	2514(4)	358(6)	61(3)
C37	3053(4)	1193(4)	1532(7)	62(3)
C38	3261(4)	1092(5)	−875(6)	64(3)

[a] Numbers in parentheses are estimated standard deviations. [b] Equivalent isotropic U_{eq} is defined as one-third the trace of the orthogonalized U_{ij} tensor.

m-Ar), 7.5–7.7 (2H, m, Ph), ^{13}C NMR (150 MHz, $CDCl_3$) 31.20 (s, *p*-C*Me*$_3$), 34.72 (s, *o*-C*Me*$_3$), 35.07 (s, *p*-*C*Me$_3$), 39.03 (s, *o*-*C*Me$_3$), 122.68 (d, $^3J = 7.5$ Hz, *m*-Ar), 122.76 (d, $^1J = 58.6$ Hz, *i*-Ar), 128.27 (d, $J = 6.9$ Hz, Ph), 128.38 (d, $J = 4.5$ Hz, Ph), 128.50 (d, $J = 3.2$ Hz, Ph), 128.73 (d, $J = 8.9$ Hz, Ph), 128.93 (d, $J = 5.4$ Hz, Ph), 129.60 (d, $J = 8.3$ Hz, Ph), 131.80 (d, $^4J = 10.1$ Hz, *i*-Ph), 137.42 (d, $^4J = 15.9$ Hz, *i*-Ph′), 138.33 (d, $^3J = 16.1$ Hz, P=C=C=*C*), 152.00 (d, $^2J = 2.1$ Hz, *o*-Ar), 154.94 (d, $^2J = 26.1$ Hz, P=C=*C*=C), 155.53 (s, *p*-Ar), 175.79 (d, $^1J = 104.5$ Hz, P=*C*=C=C), 196.33 (d, $^2J = 10.8$ Hz, CO_{eq}), 199.37 (d, $^2J = 136.1$ Hz, CO_{ax}), FAB-MS *m/z* 790 (M^+), IR (KBr) ν 2071, 1990, 1953, 1934, 1590, 1459, 1396 cm^{-1}, UV-VIS (hexane) λ_{max} (log ϵ) 228 (4.86), 263 (sh, 4.51), 283 (4.35), 316 (3.97), 380 (4.04), 483 (sh, 4.34), 516 (4.69) nm. Analysis: Found: C, 57.53; H, 5.04. Calcd. for $C_{38}H_{39}O_5PW$: C, 57.73; H, 4.97%.

3.2. *X-Ray structure determination of* $[W(CO)_5]$-$[ArP{=}C{=}C{=}CPh_2]$ *(2)*

The complex **2** was recrystallized from hexane. $C_{38}H_{39}O_5PW$, $M_r = 790.47$. Monoclinic, space group $P2_1/a$, $a = 18.503(2)$, $b = 17.752(3)$, $c = 11.370(2)$ Å, $\beta = 98.79(1)°$. $U = 3691(1)$ Å^3, $Z = 4$, $D_c = 1.422$ g cm^{-3}, $\mu = 32.76$ cm^{-1}. 6488 reflections with $2\theta \leq 50.0°$ were recorded on a four-circle diffractometer using graphite-monochromated Mo-Kα radiation. Of these, 4547 with $F > 3\sigma(F)$ were judged as observed. The structure was solved using SHELX86 [16]. Full-matrix least-squares refinement with anisotropic temperature factors for nonhydrogen atoms (Table 2) and isotropic hydrogens converged to $R = 0.033$ [17]. Atomic coordinates and thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

This work was supported in part by the Grants-in-Aid for Scientific Research (Nos. 02403008 and 03214101) from the Ministry of Education, Science and Culture, Japanese Government and the Funds from the Asahi Glass Foundation. The authors thank the Research Centre for Protein Engineering, Institute for Protein Research at Osaka University for computation. We thank Tosoh Akzo Co., Ltd. for donating organolithium reagents and Shin-Etsu Chemical Co., Ltd. for organosilicon compounds.

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