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Preliminary communication

X-Ray structure analyses of diphosphinidenecyclobutene and its chelate type tetracarbonylmolybdenum(0) complex

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Abstract

The structure of [(*E,E*)-3,4-bis(2,4,6-tri-t-butylphenylphosphinidene)-1,2-bis(trimethylsilyl)cyclobutene]tetracarbonylmolybdenum(0) has been analyzed by X-ray crystallography. The structure of the free ligand, diphosphinidenecyclobutene, has also been analyzed and compared with that of the metal carbonyl complex.

Bidentate diphosphane ligands with sp^3-type hybridized phosphorus atoms such as 1,2-bis(diphenylphosphino)ethane (dppe) have been widely used in organometallic chemistry as well as in organic synthesis [1]. In contrast, bidentate phosphaalkene ligands containing sp^2-type hybridized phosphorus atoms are rarely used because of their instability at a low-coordinated phosphorus atom. However, our recent strategy of steric protection using bulky substituents has permitted us to isolate those unusual compounds as stable species [2]. By introducing an extremely bulky 2,4,6-tri-t-butylphenyl group (Ar group) into a molecule, we have been successful in preparing various types of compounds carrying phosphorus atoms in low coordination states such as diphosphenes [3], phosphaalkenes [4], and phosphacumulenes [5]. Some sterically protected 1,4-diphospha-1,3-butadienes had been prepared by Appel *et al.* [6–8] and more recently a 2,2-biphosphinine had been synthesized by Mathey *et al.* [9] as a phosphorus analogue of bipyridine.

Recently, Märkl *et al.* [10] and we [11] have independently reported the preparations of 3,4-bis(2,4,6-tri-t-butylphenylphosphinidene)-1,2-bis(trimethylsilyl)-cyclobutenes (**4** and **5**) *via* sigmatropic rearrangement from 1,6-diphospha-1,2,4,5-hexatetraene (**3**) and/or diethynyldiphosphane (**2**), which was prepared from trimethylsilylethynylphosphane (**1**). The diphosphinidenecyclobutenes **4** and **5** might

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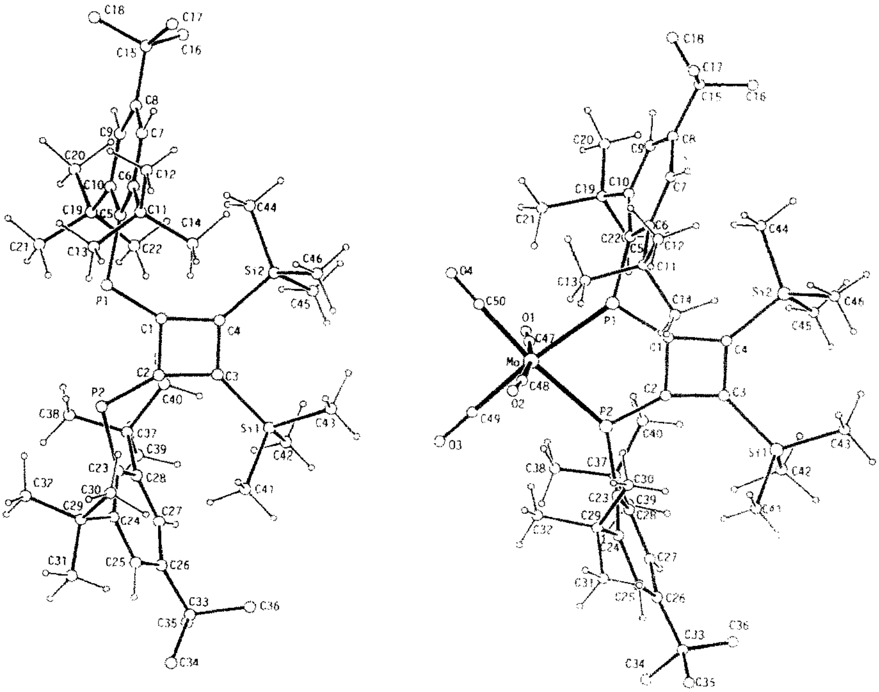


Fig. 1. X-Ray structures of **4** (left) and **6** (right) showing the atom labelling schemes.

be regarded as conformationally rigid bidentate phosphorus ligands analogous to dppe, since they are expected to be planar molecules of dimethylenecyclobutene framework. Thus, the structures of the coordination site of the metal complexes [12] as well as the free ligands are of interest. We report here the crystal structures of both (*E*,*E*)-diphosphinidenecyclobutene **4** and its molybdenum(0) complex **6** [13].

Figure 1 depicts ORTEP drawings of **4** and **6** [14]. Selected bond lengths and angles, dihedral angles, and intramolecular short contacts for **4** and **6** are listed in Tables 1 and 2, respectively. The cyclobutene ring in **4** is approximately planar within 0.04(1) Å, with P1, P2, Si1, Si2, C5, and C23 deviating by −0.11(1), 0.42(1), −0.30(1), 0.27(1), 0.20(1), and 0.78(2) Å, respectively. The folding angle of the cyclobutene ring at C1–C3 axis is 8.0°. The phenyl ring [C5–C10] makes an angle of 85.2° with the cyclobutene ring, while the phenyl ring [C23–C28] makes an angle of 115.8° with this plane. This distorted conformation of **4** forms a contrast to (*E*,*Z*)-3,4-bis(2,4,6-tri-t-butylphenylphosphinidene)-1,2-bis(trimethylsilyl)cyclobutene (**5**) [10,11] where a pseudo mirror plane goes through the cyclobutene ring. The (*E*,*Z*)-derivative (**5**), which does not react with metal carbonyls, has its molecular surface almost completely covered by hydrogen atoms. The CPK modeling of **4** shows that the P1–C1–C2–P2 side of the molecule has a concavity, into which metal carbonyls are able to enter to react. The coordination of two phosphorus atoms of **4** to a molybdenum atom makes complex **6** take a more regular form than **4** itself, although the conformation of **4** is similar to that of the ligand moiety in **6**. The complex **6**, except for two trimethylsilyl groups, has an

Table 1

Selected bond lengths (Å) and angles (°), dihedral angles (°), and intramolecular short contacts (Å) for **4** [a]

Bond lengths					
C1–C2	1.498(8)	C1–C4	1.493(8)	P1–C5	1.841(6)
C2–C3	1.492(8)	P1–C1	1.678(6)	P2–C23	1.852(6)
C3–C4	1.400(9)	P2–C2	1.676(5)		
Bond angles					
C2–C1–C4	88.0(4)	P1–C1–C2	121.8(4)	C1–P1–C5	110.7(3)
C1–C2–C3	88.0(4)	P1–C1–C4	150.2(5)	C2–P2–C23	108.0(3)
C2–C3–C4	91.8(5)	P2–C2–C1	122.5(4)		
C3–C4–C1	91.7(5)	P2–C2–C3	147.7(4)		
Dihedral angles					
C4–C1–C2–C3	5.4(5)	P1–C1–C2–P2	15.5(8)	Si1–C3–C4–Si2	15(1)
C1–C2–C3–C4	−5.7(5)	P1–C1–C4–Si2	−8(1)	C1–P1–C5–C6	−96.3(5)
C2–C3–C4–C1	5.8(5)	P2–C2–C3–Si1	−29(1)	C2–P2–C23–C24	103.2(5)
C3–C4–C1–C2	−5.7(5)				
Intramolecular short contacts					
P1···C13	3.15(1)	P2···C32	3.208(8)	C5···C44	3.46(1)
P1···C21	3.074(8)	P2···C38	3.234(8)	C40···C42	3.68(1)
P2···C30	3.370(8)	C1···C22	3.47(1)	C43···C46	3.57(1)

[a] Numbers in parentheses are estimated standard deviations.

Table 2

Selected bond lengths (Å) and angles (°), dihedral angles (°), and intramolecular short contacts (Å) for **6** [a]

Bond lengths					
C1–C2	1.483(6)	P1–C1	1.680(4)	P1–Mo	2.539(1)
C2–C3	1.466(6)	P2–C2	1.686(4)	P2–Mo	2.526(1)
C3–C4	1.382(6)	P1–C5	1.836(4)		
C1–C4	1.469(6)	P2–C23	1.825(4)		
Bond angles					
C2–C1–C4	87.9(3)	P1–C1–C4	151.2(3)	P1–Mo–P2	78.10(4)
C1–C2–C3	88.0(3)	P2–C2–C1	119.9(3)	Mo–P1–C1	109.9(1)
C2–C3–C4	92.0(4)	P2–C2–C3	151.9(3)	Mo–P2–C2	110.7(1)
C3–C4–C1	91.8(3)	C1–P1–C5	109.7(2)		
P1–C1–C2	120.7(3)	C2–P2–C23	108.7(2)		
Dihedral angles					
C4–C1–C2–C3	3.3(3)	P1–C1–C2–P2	10.1(5)	C1–P1–C5–C6	−77.5(4)
C1–C2–C3–C4	−3.5(3)	P1–C1–C4–Si2	−19(1)	C2–P2–C23–C24	95.2(4)
C2–C3–C4–C1	3.6(3)	P2–C2–C3–Si1	−9(1)		
C3–C4–C1–C2	−3.5(3)	Si1–C3–C4–Si2	11.8(8)		
Intramolecular short contacts					
P1···C13	3.286(8)	C1···C14	3.248(8)	C21···C50	3.434(9)
P1···C14	3.293(7)	C2···C40	3.348(6)	C31···C48	3.447(8)
P1···C22	3.276(6)	C10···C44	3.419(8)	C43···C46	3.52(1)
P2···C30	3.244(6)	C13···C48	3.36(1)		
P2···C40	3.220(6)	C21···C47	3.487(8)		

[a] Numbers in parentheses are estimated standard deviations.

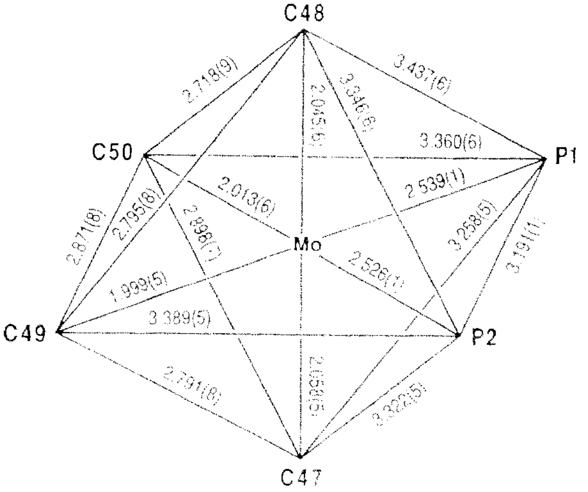


Fig. 2. Octahedral framework around the molybdenum atom of **6** (values in Å).

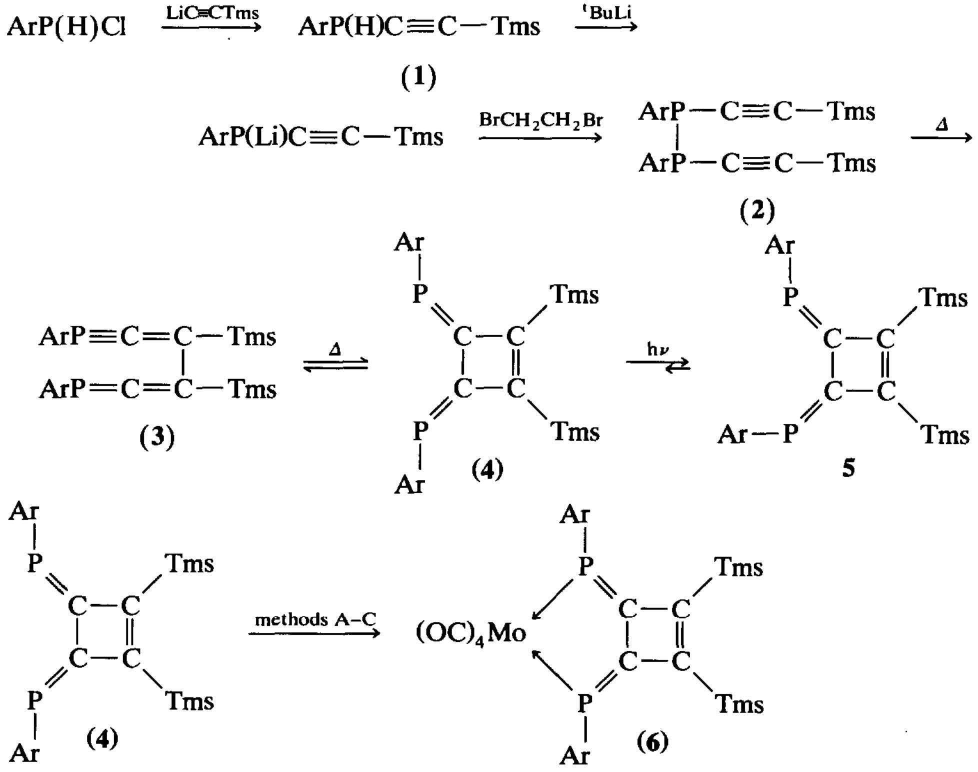
approximate two-fold axis which goes through the molybdenum atom and the midpoint of C1–C2 bond. The cyclobutene ring of **6** is almost planar within 0.02(1) Å with P1, P2, Si1, Si2, C5, C23, and Mo deviating by 0.163(8), −0.183(8), 0.087(9), −0.335(9), 0.50(1), −0.42(1), and −0.10(1) Å, respectively. The folding angle of this ring at C1–C3 is 4.9°. The phenyl rings [C5–C10] and [C23–C28] in **6** make angles of 76.3 and 102.7° with the cyclobutene ring, respectively. Figure 2 shows the octahedral framework around the molybdenum atom of compound **6**, where a mirror plane goes through Mo, C47, C48, midpoint of P1–P2, and midpoint of C49–C50.

The corresponding bond distances and angles of the central π-system in **4**, **6**, **5**, and (*E*,*E*)-3,4-bis(2,4,6-tri-t-butylphenylphosphinidene)-1,2-diphenylcyclobutene (**7**) [8] are in good agreement if the standard deviations are taken into account. The angles C4–C1–P1 and C3–C2–P2 are opened to 150.2(5) and 147.7(4)° in **4**, and 151.2(3) and 151.9(3)° in **6**, respectively, and are comparable to an average value of 147.3(4)° for **7** [8], 147.4(5) [11] and 147.0(3)° [10] for **5**, reflecting the large steric repulsions among the substituents. The bond distances of P1–Mo and P2–Mo, and the bond angle of P1–Mo–P2 are 2.539(1), 2.526(1) Å and 78.10(4)°, respectively.

The intramolecular short contacts (Tables 1 and 2) induce the deformation of the bulky Ar groups, which is commonly observed for an Ar–P containing compound [15]. The phenyl group [C5–C10] in **4** has an envelope form with C5 serving as the flap. The other phenyl groups in **4** and **6** are in boat forms with C5 and C23 serving as the bow and C8 and C26 as the stern.

Experimental (see Scheme 1)

Preparation of (E,E)-3,4-Bis(2,4,6-tri-t-butylphenylphosphinidene)-1,2-bis(trimethylsilyl)cyclobutene (4). The diphosphinidenecyclobutene **4** was prepared as described previously [11]. Chloro(2,4,6-tri-t-butylphenyl)phosphine [16–18] was allowed to react with (trimethylsilylethynyl)lithium to give 2,4,6-tri-t-butylphenyl(trimethylsilylethynyl)phosphine (**1**) [19], and the phosphine **1** was lithiated with two equiv. of t-butyllithium in THF at −78°C. Then 0.5 equiv. of 1,2-dibromoethane was added at that temperature to give 1,2-bis(2,4,6-tri-t-butylphenyl)-1,2-bis(trimethylsilylethynyl)diphosphane (**2**). The diphosphane **2** was unstable towards heat and gradually isomerized, even at room temperature, to a phosphaallenyl compound, 3,4-bis(trimethylsilyl)-1,6-bis(2,4,6-tri-t-butylphenyl)-1,6-diphospha-1,2,4,5-hexatetraene (**3**). This phosphaallenyl compound **3** was further converted, but very slowly, at room temperature to the (*E,E*)-3,4-diphosphinidenecyclobutene **4**. Yellow crystals. M.p.: 160–162°C. ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = 7.39$ (4 H, s, arom.), 1.56 (36 H, s, *o*-^{t}Bu), 1.31 (18 H, s, *p*-^{t}Bu), and −0.33 (18 H, s, $SiMe_3$). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 25°C): $\delta = 162.9$. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 25°C): $\delta = 183.9$ (dd, $J(PC) = 18.3$ and 14.1 Hz; $P = C$), 176.2 (pseudo *t*, $J(PC) = 4.6$ Hz; $CSiMe_3$), 154.8 (s, *o*-arom.), 149.5 (s, *p*-arom.), 136.8 (pseudo t, $J(PC) = 29.0$ Hz, *ipso*-arom.), 121.9 (s, *m*-arom.), 38.3 (s, *o*-CMe_3), 35.0 (s, *p*-CMe_3), 33.4 (pseudo t, $J(PC) = 3.7$ Hz, *o*-CMe_3), 31.3 (s, *p*-CMe_3), and 0.4 (s, $SiMe_3$). UV (hexane): $\lambda = 255$ (log ϵ 4.37), 298 (4.39), 314 (4.41), and 368 nm (sh, 3.69). IR (KBr): 1591 and 1477 cm^{-1}. MS *m/z* (rel. intensity): 746 (M^+, 100), 689 ($M^+ - {}^t$Bu, 73), and 373 ($ArPC_2Tms$, 36). The yield of **4** based on **1** was 44% together with **3** (35% yield), after 30 min refluxing in toluene without the isolation process of **2**. Because of facile photoisomerization by sunlight between **4** and **5**, the whole procedure treating **4** was carried out in the dark [20*].



Ar = 2,4,6-$^tBu_3C_6H_2$; Tms = Me_3Si

Method A: $Mo(CO)_6$, Δ; method B:P (thf)$Mo(CO)_5$; method C: (bicyclo[2.2.1] hepta-2,5-diene)$Mo(CO)_4$

Scheme 1

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* Reference number with asterisk indicates a note in the list of references.

Preparation of [(E,E)-3,4-Bis(2,4,6-tri-t-butylphenylphosphinidene)-1,2-bis(trimethylsilyl)cyclobutene]tetracarbonylmolybdenum(0) **(6)**. The complex **6** was prepared according to the following three methods [12]. A solution of **4** (25.0 mg, 0.033 mmol) and 5.1 mol. equiv. of $Mo(CO)_6$ (44.0 mg, 0.17 mmol) in dioxane (2.5 ml) was refluxed in the dark for 1 h (method A). Removal of the solvent under reduced pressure followed by flash column chromatography (SiO_2/pentane) afforded 24.1 mg (76%) of **6**. The reaction of **4** with excess $(THF)Mo(CO)_5$ (5 mol equiv.) in THF at room temperature for 3 h (method B) also afforded the complex **6** in 75% yield. The reaction of **4** with 1.5 mol equiv. of (bicyclo[2.2.1]hepta-2,5-diene)tetracarbonylmolybdenum(0) in refluxing toluene for 20 h (method C) gave the same molybdenum(0) complex **6** in 44% yield.

Crystal data and data collection for **4**. The compound **4** was recrystallized from benzene/acetonitrile. $C_{46}H_{76}P_2Si_2$, $M = 747.23$, monoclinic, space group $P2_1/n$, $a = 9.543(1)$, $b = 33.486(3)$, $c = 15.218(2)$ Å, $\beta = 99.96(1)°$, $U = 4789.6(9)$ Å^3, $Z = 4$, $D_c = 1.037$ g cm^{-3}, radiation: Cu-K_α ($\lambda = 1.5418$ Å), $\mu = 15.00$ cm^{-1}, data collection: ω-scan, 2θ range: 2–120°, number of independent reflections: 5957, number of reflections used ($I > 2\sigma(I)$): 4075.

Crystal data and data collection for **6**. The complex **6** was recrystallized from pentane. $C_{50}H_{76}MoO_4P_2Si_2$, $M = 955.21$, monoclinic, space group $P2_1/n$, $a = 16.116(3)$, $b = 12.329(1)$, $c = 28.208(7)$ Å, $\beta = 97.89(3)°$, $U = 5552(2)$ Å^3, $Z = 4$, $D_c = 1.143$ g cm^{-3}, radiation: Mo-K_α ($\lambda = 0.7107$ Å), $\mu = 3.64$ cm^{-1}, data collection: ω-scan, 2θ range: 1–50°, number of independent reflections: 9783, number of reflections used ($I > 3\sigma(I)$): 6929. Both structures of **4** and **6** were solved using SHELX86 [21]. All hydrogen atoms, except for those of *p*-t-butyl groups, could be located on difference Fourier syntheses. Full-matrix least-squares refinements with anisotropic temperature factors for non-hydrogen atoms and isotropic hydrogens converged to $R = 0.075$ and $R_w = 0.098$ for **4** and $R = 0.058$ and $R_w = 0.059$ for **6** [22]. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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20 The synthesis and X-ray structure of (*E*,*Z*)-**5** has been reported independently by us [11] and by Märkl *et al.* [10]. It should be noted that Märkl *et al.* assigned a singlet peak (δ(P) 164.91) in ^{31}P NMR to that for (*E*,*Z*)-**5** [10]. However, as we have reported in the previous paper [11], (*E*,*Z*)-**5** was observed in AB pattern (δ(P) 197.4 and 176.6, ^3J(PP) = 14.6 Hz), although the X-ray structures for (*E*,*Z*)-**5** were both the same. It seems likely that the spectroscopic data reported by Märkl *et al.* for "(*E*,*Z*)-**5**" correspond to those of our (*E*,*E*)-**4** (δ(P) 162.9), the structure of which was confirmed by the X-ray analysis as shown in this text. This discrepancy may be due to the facile *E*−*Z* photosiomerization [11], which can take place during the recrystallization process for the X-ray analysis. All our recrystallization processes for (*E*,*Z*)-**5**, (*E*,*E*)-**4**, and **6** were performed *in the dark*.

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