

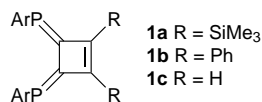
Preparation and X-ray analysis of novel carbonyltungsten(0) complexes of diphosphinidenecyclobutenes

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A sterically protected diphosphinidenecyclobutene **5** bearing a bulky 2,4,6-triisopropylphenyl group is prepared and allowed to react with $W(CO)_5(thf)$ to give a doubly tungsten-coordinated complex **8**, with chelate- and π -type coordination; the structure of the complex is confirmed by X-ray analysis.

Sterically protected phosphorus-containing multiple bonded compounds with bulky substituents are currently of interest. We have been interested in cumulated and conjugated systems^{1,2} involving phosphorus atom(s) in low coordination states, as well as diphosphenes³ and phosphathenes.⁴ Recently, Appel *et al.*,⁵ Märkl *et al.*⁶ and ourselves⁷⁻⁹ have reported the preparation and isolation of diphosphinidenecyclobutenes (**1a-c**, Scheme 1) utilizing 2,4,6-tri-*tert*-butylphenyl as a protecting group (Ar), as well as their *E/Z* isomerization about the P=C bonds.^{7,10} We have also reported on their transition metal complexes, where metals are Cr, Mo, W,^{8,11,12} Pt and Pd.¹³ We now report a new type of tungsten carbonyl complex ligated with diphosphinidenecyclobutenes carrying the 2,4,6-triisopropylphenyl group¹⁴ (Tip) as well as the Ar group.



Scheme 1 Ar = $C_6H_2Bu_3-2,4,6$

According to a slightly modified procedure employed for the preparation of **1b**, (2-phenylethynyl)(2,4,6-triisopropylphenyl)phosphinidene halides **3** were prepared by the reaction of 2-phenylethynylphosphinidene dichloride **2**¹⁵ with 2,4,6-triisopropylphenylmagnesium bromide in thf at $-78^\circ C$. Then **3** was allowed to react with Bu^tLi at $-78^\circ C$ or with Zn powder at room temp. to give diphosphane **4** as a diastereomeric mixture (d.l.: *meso* = ca. 1:1) and the mixture was refluxed in thf to give (*E,Z*)-1,2-diphenyl-3,4-bis(2,4,6-triisopropylphenyl)cyclobutene diphosphinidene **5**.[†] It should be noted that only a trace amount of (*E,E*)-**5** was observed by ^{31}P NMR spectroscopy.

In the 1H NMR spectrum of **5** in $[^2H_8]toluene$, there appeared six types of isopropyl peaks at 295 K. At higher temperatures, only two sets due to the *ortho*-isopropyl groups became coalesced, but the other two sets due to the other *ortho*-isopropyl groups remained magnetically non-equivalent. The remainder of the isopropyl groups assigned to the *para*-isopropyl groups remained unchanged even at 375 K. The fact suggests that one of the Tip groups, probably (*E*)-Tip, taking the steric congestion into account, starts to rotate at 323 K, while (*Z*)-Tip appears not to rotate even at 375 K.

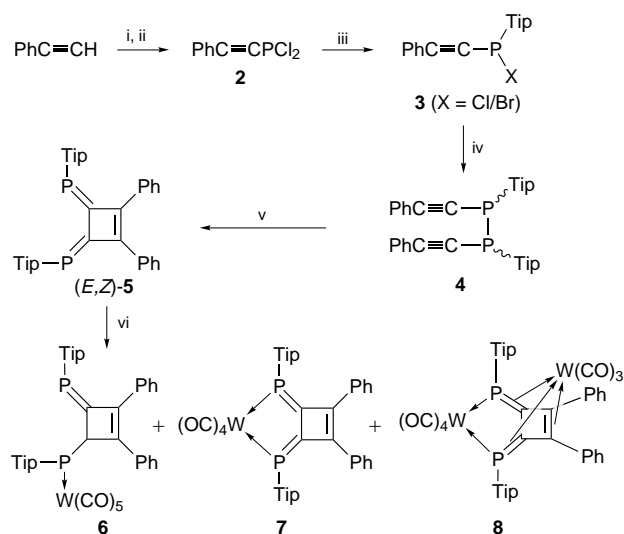
We are now able to obtain a novel class of tungsten complex by the reaction of the diphosphinidenecyclobutene **5** with $W(CO)_5(thf)$ ¹⁶ in refluxing thf.[‡] The reaction gave **8** together with **6** and **7** (Scheme 2).[†] The ^{31}P NMR chemical shift of **8** appeared at δ_P 57, indicating that the phosphorus atom is strongly shielded compared with the value in the free ligand of either δ_P 164 for (*E,E*)-**5** or δ_P 169 and 183 for (*E,Z*)-**5**.

The structure of **8** was confirmed by the X-ray analysis§ to reveal a novel coordination type. Fig. 1 depicts an ORTEP drawing of the molecular structure for the bis-tungsten complex **8**. There are observed two WCO moieties, one is tetracarbonyl with chelate type coordination, the other is tricarbonyl with π -coordination. The two phosphorus atoms coordinate doubly on both $W(CO)_4$ and $W(CO)_3$ adopting sp^3 type configuration. The exocyclic P=C bonds are bent strongly from the ring plane [interplanar angle between the plane P(1)P(2)C(3)C(4) and the plane C(1)-C(4) 32.3°] to adopt a good interaction with the 6π system to coordinate on $W(CO)_3$, thus exhibiting a sharp contrast to the regular group 6 metal tetracarbonyl or palladium complexes of diphosphinidenecyclobutenes, where the system is planar with all sp^2 type configuration as exemplified in W,¹¹ Mo,¹² and Pd complexes.¹³

The P=C bond lengths of **8** [av. 1.763(10) Å] are elongated upon coordination compared to those of (*E,E*)-**1a** [1.677(6) Å]¹² and (*E,E*)-**1b** [1.690(8) Å].⁵ The bond length C(1)-C(2) of **8** [1.47(1) Å] is fairly elongated compared to the values of 1.400(9) Å and 1.380(9) Å for (*E,E*)-**1a** and (*E,E*)-**1b**, respectively. Thus, the interaction between the $W(CO)_3$ group and the ligand is apparently strong, since little change in bond lengths has been observed upon coordination with the chelate.^{8,11-13}

Furthermore, in the case of compound (*E,E*)-**1c**, carrying the two Ar groups and no substituents on the cyclobutene ring, a doubly coordinated complex **9** was formed under similar conditions using $W(CO)_4(MeCN)_2$ (Scheme 3).¹⁶ Complex **9** seems to have been formed *via* **10** as an intermediate, since **10** reacted with $W(CO)_4(MeCN)_2$ to give **9**.[¶] It appeared to require less hindered environment than **1a** or **1b** to obtain double coordination products such as **8** or **9**.

Although Rau and Behrens reported on the formation and the structural analysis of (η^6 -dimethylenecyclobutene)tricar-



Scheme 2 Tip = $C_6H_2Pr^i-2,4,6$. Reagents and conditions: i, NEt_3 ; ii, PCl_3 ; iii, (Tip)MgBr; iv, Bu^tLi or Zn; v, reflux in thf; vi, $W(CO)_5(thf)$, reflux in thf.

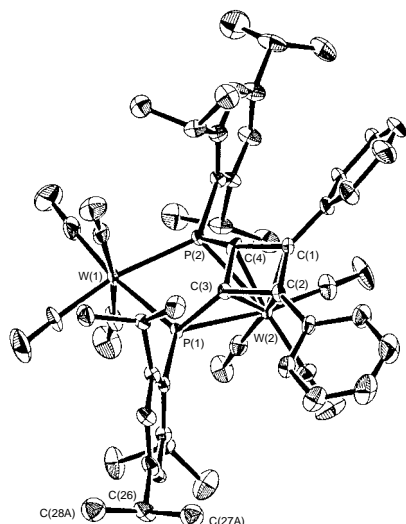
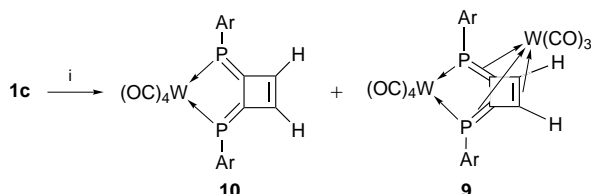


Fig. 1 The molecular structure of bis-tungsten complex **8** showing the atomic labelling scheme; only atoms with dominant occupancy factors are displayed. Important bond lengths (Å) and angles (°): W(1)–P(1) 2.493(3), W(1)–P(2) 2.490(3), W(2)–P(1) 2.679(3), W(2)–P(2) 2.664(3), W(2)–C(1) 2.35(1), W(2)–C(2) 2.321(10), W(2)–C(3) 2.24(1), W(2)–C(4) 2.18(1), P(1)–C(3) 1.788(10), P(2)–C(4) 1.737(9), C(1)–C(2) 1.47(1), C(1)–C(4) 1.49(1), C(2)–C(3) 1.47(1), C(3)–C(4) 1.47(1); P(1)–W(1)–P(2) 73.22(9), P(1)–W(2)–P(2) 67.60(8), C(2)–C(1)–C(4) 90.0(8), C(1)–C(2)–C(3) 90.2(8), C(2)–C(3)–C(4) 90.4(8), C(1)–C(4)–C(3) 89.2(8).



Scheme 3 Ar = C₆H₂Bu^t-2,4,6. Reagents and conditions: i, W(CO)₄(MeCN)₂, thf, in the dark.

bonylchromium(0)¹⁷ and (η⁶-diisopropylidene-cyclobutene)tricarbonylchromium(0),¹⁸ this is the first example in the diphosphinidene-cyclobutene–tungsten carbonyl system, where the ligand is doubly coordinated to tungsten.

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Footnotes and References

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† Selected spectroscopic data (NMR spectra were recorded on either a Bruker AC200P, a JEOL α-500, or a Bruker AM600 spectrometer): (*E,Z*)-**5**: ¹H NMR (600 MHz, at 295 K, CDCl₃): δ 0.92 (6 H, d, *J* 6.8 Hz, *o*-CHMe), 1.00 (6 H, d, *J* 6.8 Hz, *o*-CHMe), 1.20 (6 H, d, *J* 6.9 Hz, *p*-CHMe₂), 1.25 (6 H, d, *J* 6.9 Hz, *p*'-CHMe₂), 1.32 (6 H, d, *J* 6.8 Hz, *o*'-CHMe), 1.39 (6 H, d, *J* 6.8 Hz, *o*'-CHMe), 2.75 (1 H, spt, *J* 6.9 Hz, *p*-CHMe₂), 2.75 (1 H, spt, *J* 6.9 Hz, *p*'-CHMe₂), 3.21 (2 H, m, *o*-CHMe₂), 3.72 (2 H, m, *o*'-CHMe₂); ³¹P{¹H} NMR (81 MHz, CDCl₃): δ 168.6, 182.8 (AB, *J* 17.8 Hz). **8**: dark violet crystals, mp 183 °C (decomp.); ¹H NMR (600 MHz, CDCl₃): δ 1.18 (6 H, d, *J* 6.6 Hz, *o*-CHMe), 1.31 (6 H, d, *J* 6.9 Hz, *p*-CHMe), 1.31 (12 H, d, *J* 6.9 Hz, *o*-*p*-CHMe), 1.41 (6 H, d, *J* 6.7 Hz, *o*-CHMe), 1.43 (6 H, d, *J* 6.6 Hz, *o*-CHMe), 2.94 (2 H, spt, *J* 6.9 Hz, *p*-CHMe₂), 4.35 (2 H, br s, *o*-CHMe₂), 4.46 (2 H, spt, *J* 6.7 Hz, *o*-CHMe₂); ³¹P{¹H} NMR (81 MHz, CDCl₃): δ 56.7 (satellite d, ¹J_{PW} 226 Hz); IR (KBr): ν/cm⁻¹ 2033, 1994, 1979, 1923, 1913, 1878, UV–VIS (CH₂Cl₂): λ_{max}(log ε) 254 (sh, 4.87), 272 (sh, 4.75), 321 (4.37), 456 (4.04), 603 nm (sh, 3.51); MS (FAB): *m/z* 1234 (M⁺), 1206 (M⁺ – CO). **9**: red needles, mp 180–181 °C (decomp.); ¹H NMR (500 MHz, CDCl₃): δ 1.19 (18 H, s, *p*-Bu^t), 1.65 (18 H, s, *o*-Bu^t), 1.75 (18 H, s, *o*-Bu^t), 4.66 (2 H, m, P=C–CH); ³¹P{¹H} NMR (81 MHz, CDCl₃): δ 64.6 (satellite d, ¹J_{PW} 227.6 Hz); IR (KBr): ν/cm⁻¹ 2033, 1994, 1942, 1900, 1865, 604 cm⁻¹; UV–VIS (*n*-hexane): λ_{max}(log ε) 218 (4.88), 236 (4.71),

380 (3.94), 456 (3.66), 505 (sh, 3.54), 598 nm (3.30); MS (FAB): *m/z* 1166 (M⁺), 1138 (M⁺ – CO), 968 (M⁺ – 7CO – 2). **10**: orange powder, mp 198–199.5 °C (decomp.); ¹H NMR (200 MHz, CDCl₃): δ 1.34 (18 H, s, *p*-Bu^t), 1.63 (36 H, s, *o*-Bu^t), 6.45 (2 H, dd, ³J_{PH} = ⁴J_{PH} 3.6 Hz, P=C–CH); ³¹P{¹H} NMR (81 MHz, CDCl₃): δ 154.1 (satellite d, ¹J_{PW} 250.1 Hz); UV–VIS (*n*-hexane): λ_{max}(log ε) 242 (4.79), 319 (4.12), 413 (4.09), 482 nm (3.45); MS (FAB): *m/z* 898 (M⁺), 870 (M⁺ – CO).

‡ Preparative procedure: **8**: under argon, a solution of phenylethynylphosphonous dichloride **2** (356 mg, 1.8 mmol)¹⁵ in thf (10 ml) was cooled at –78 °C and was allowed to react with triisopropylphenylmagnesium bromide (1.8 mmol) and the mixture was warmed to room temp. to give phenylethynylphosphinous chloride **3** (X = Cl, δ_P 40) together with the bromide **3** (X = Br, δ_P 22) (chloride : bromide = 1 : 0.8). The mixture of the halides **3** (X = Cl, Br) was allowed to react with Zn (261 mg, 4.0 mmol) in thf (7 ml) at room temp. for 3 h to give the corresponding diphosphane **4** as a diastereomeric mixture (δ_P –66, –65); D,L : *meso* = ca. 1 : 1. It was then refluxed in thf for 24 h to give (*E,Z*)-**5**. The ligand (*E,Z*)-**5** was allowed to react with W(CO)₅(thf) (1.7 mmol) in refluxing thf for 9 h. **8** (62 mg, 0.051 mmol)† was isolated in 6% yield based on **2**, together with **6** [δ_P 114 (satellite d, ¹J_{PW} 265 Hz) and 186, AB, ⁴J_{PP} 8 Hz] and **7** [δ_P 139, ¹J_{PW} 251 Hz].

§ Crystal data for **8**: recrystallised from ethanol–benzene. C₅₃H₅₆O₇P₂W₂, *M* = 1234.67, monoclinic, space group P2₁/n, *a* = 10.241(3), *b* = 25.462(4), *c* = 20.219(3) Å, β = 92.61(2)°, *U* = 5266(1) Å³, *Z* = 4, *T* = 223 K, *D_c* = 1.557 g cm⁻³; 9529 reflections with 2θ ≤ 50.0° were recorded on a four-circle diffractometer using graphite-monochromated Mo-Kα radiation. Of these, 6693 with *I* > 3σ(*I*) were judged as observed. The structure was solved using SIR92.¹⁹ The non-hydrogen atoms, except for C(27) and C(28), were refined anisotropically. Atoms C(27) and C(28) were disordered and refined isotropically (occupancy factor for the dominant: 0.55). Hydrogen atoms except for those on C(26)–C(28) were included, but their positions were not refined. *R* = 0.054, *R_w* = 0.064, CCDC 182/653.

¶ Preparative procedure: **9** (*E,E*)-**1c** (86 mg, 0.14 mmol) was allowed to react with 0.43 mmol of W(CO)₄(MeCN)₂ in refluxing thf (30 ml) for 1.5 h to give **9** in 54% yield.† **10**: a mixture of diphosphinidene-cyclobutene (*E,E*)-**1c** (31 mg, 0.051 mmol) and W(CO)₄(MeCN)₂ (40 mg, 0.11 mmol) was dissolved in thf (20 ml) and the solution was stirred at room temp. for 21 h to give **10** (20 mg, 43% yield).†

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