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Coordination chemistry of some low-coordinate organophosphorus compounds*

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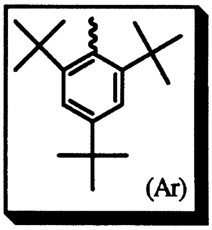
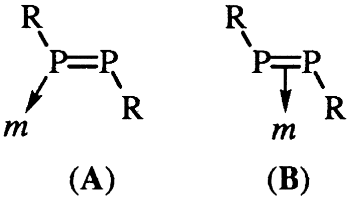
Abstract: The structures of transition metal complexes with low coordinate organophosphorus compounds are described, involving diphosphenes, phosphaethenes, phosphaallenes, phosphabutatrienes, and so on of coordination number 2.

Multiple bonds containing heavier main group elements are unstable, because the multiple-bond energies are not large. However, by utilizing a very bulky substituent as a protecting group, such as the 2,4,6-tri-*t*-butylphenyl group (abbreviated Ar) [1], we have been successful in stabilizing several low-coordinated organophosphorus compounds as stable chemical species. We have isolated highly reactive but kinetically stabilized organophosphorus compounds, such as diphosphenes (R–P=P–R), phosphaethenes ($R{-}P{=}CR_2$), phosphaallenes ($R{-}P{=}C{=}CR_2$), diphosphaallenes (R–P=C=P–R), phosphabutatrienes ($R{-}P{=}C{=}C{=}CR_2$), diphosphabutatrienes (R–P=C=C=P–R), phosphaalkynes (R–C≡P) and so on. They are interesting new-type molecules because of their unusual structures and properties (Scheme 1) [2–6].

Since such phosphorus compounds are in low coordination states of coordination number 2 or 1, they tend to be fully coordinated in the states of coordination number 3, 4 or 5. For examples, end-on (**A**) and side-on (**B**) coordinations are among those of typical complex formation patterns for diphosphenes, as illustrated in Scheme 2 [7–10]. Side-on coordination is interpreted as a π-interaction between the metal and ligand orbitals, while end-on bonding is formally attributable to a σ-interaction between them. Furthermore, upon end-on coordination, not much structural change is caused in the ligand, while upon side-on coordination, the structure of the ligand alters considerably.



Scheme 1



Scheme 2 The coordination modes.

DIPHOSPHENES

The sterically protected diphosphene **1** is prepared as a stable compound by the dechlorination reaction of the corresponding phosphonous dichloride $ArPCl_2$ with magnesium metal [1]. There is an alternative method to prepare diphosphenes especially for unsymmetrical ones such as **2**, starting from the primary phosphine $ArPH_2$ and mesitylphosphonous dichloride ($MesPCl_2$), in the presence of an organic base, such as triethylamine or DBU (diazabicyclo[5.4.0]undec-7-ene) [11].

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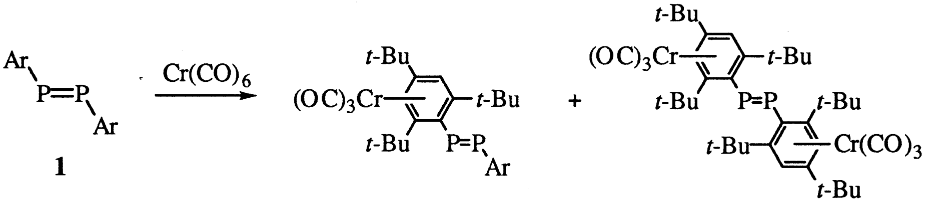
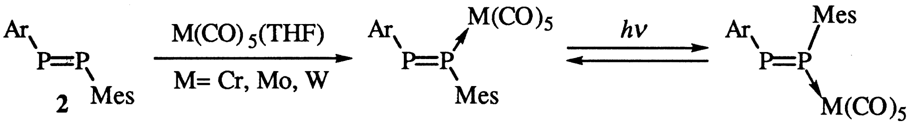
The reaction of **1** with hexacarbonylchromium(0) in refluxing dioxane leads to arene-coordinated products of η^6-type coordination, but no coordination on the P=P bond has been observed, as shown in eqn 1 (Scheme 3) [12,13].



(1)

Scheme 3

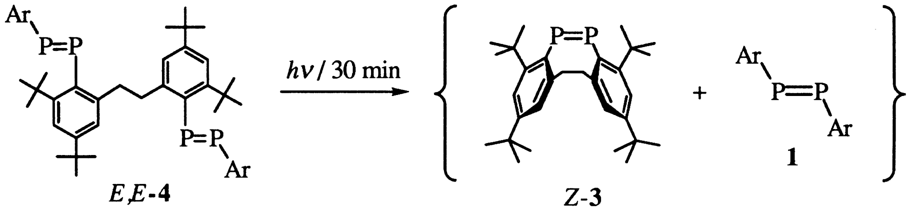
Standard methods for the preparation of transition metal complexes, i.e. by a ligand exchange reaction using Cr(CO)$_5$(THF), failed for **1**, probably due to the steric demand, but **2** gave an end-on complex [14]. More interestingly, the *E/Z* photoisomerization of the diphosphene ligand takes place on the metal complexes as shown in eqn 2 (Scheme 4). X-Ray analysis of [*Z*-**2**][Cr(CO)$_5$] (Fig. 1) shows that the bond length of P–P is not appreciably elongated upon coordination to the metal, even in the *cis*-configuration [14]. The reaction of **1** with transition metal carbonyls of tungsten [15] leads to the terminal *P*-coordination (i.e. end-on coordination).



(2)

Scheme 4

On the other hand, photolysis of diphosphenes often causes reactions of the olefin-metathesis mode. Utilizing 1,2-bis(2-bromo-3,5-di-*t*-butylphenyl)ethane (abbreviated to ArraBr$_2$) as a protecting group, an internal *cis*-diphosphene *Z*-**3** of the *o*-cyclophane type [(*Z*)-Arra(P=P)] was obtained together with **1** from a bisdiphosphene *E,E*-**4**, as shown in eqn 3 (Scheme 5). Attempts to stabilize *Z*-**3** by complex formation with W(CO)$_5$(THF) gave a doubly end-on coordinated complex together with [**1**][W(CO)$_5$]. The structure of [Z-**3**][W(CO)$_5$]$_2$ was confirmed by X-ray analysis as shown in Fig. 2 [16].



(3)

Scheme 5

PHOSPHAALKENES

Bickelhaupt *et al.* reported 1-mesityl-2,2-diphenyl-1-phosphaethene (**5**) as the first example of a phosphaethene with a localized P=C bond [17,18]. Various kinds of phosphaalkenes with the Ar group as a protecting group, such as compound **6**, are prepared from the corresponding silylphosphide and ketones or aldehydes by the method of the phospha-Peterson reaction [19,20]. These phosphaalkenes coordinate to group-6 metal carbonyls to give the corresponding stable end-on complexes [21]. However, Bickelhaupt has pointed out that in the case of the bis(triphenylphosphine)platinum(0) complex of **5**, i.e. (Ph$_3$P)$_2$Pt[MesP=CPh$_2$], the phosphaethene coordinates on the platinum metal in the side-on coordination

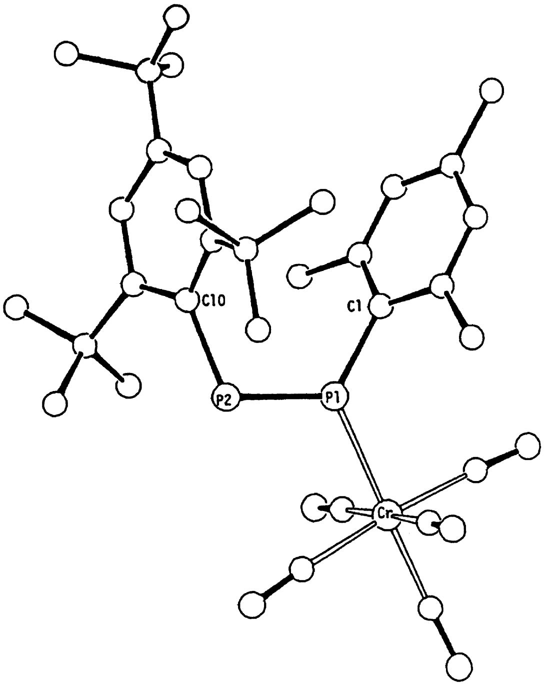


Fig. 1 Molecular structure of [*Z*-**2**][Cr(CO)$_5$].

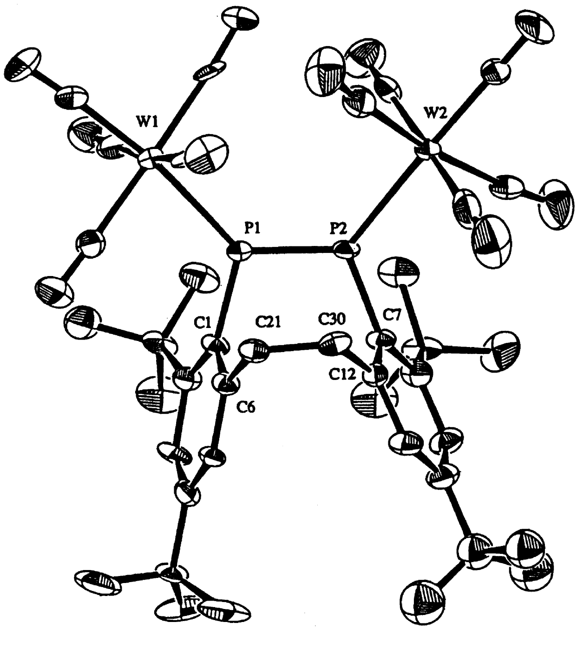
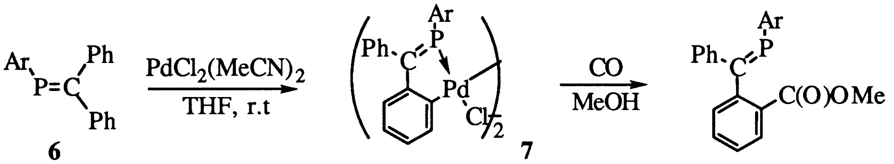


Fig. 2 Molecular structure of [*Z*-**3**][W(CO)$_5$]$_2$.

mode, according to the variable temperature NMR studies in solution, whereas it coordinates on the metal in the end-on coordination mode in the solid state, as clarified by the X-ray analysis [22].

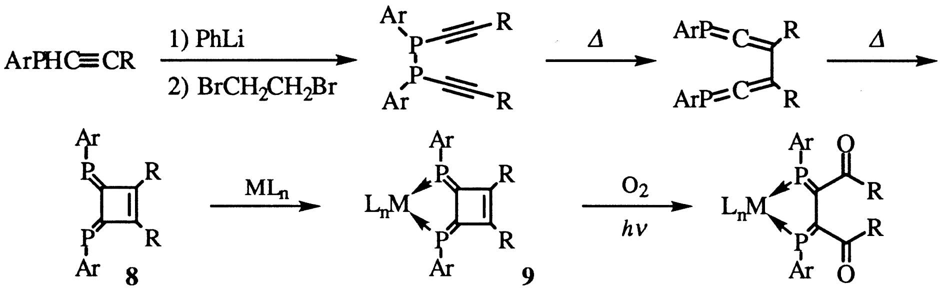
Phosphaalkene **6** reacts with PdCl$_2$(MeCN)$_2$ to give the *o*-palladate complex **7**. The structure was analyzed by X-ray crystallography indicating that the complex forms a dimeric structure and that the compound results from a C–H bond activation at the 2-position to form a Pd–C bond [23–26]. The *o*-palladate complexes of the compound type **7** react with carbon monoxide under high pressure to give the corresponding esters in the presence of alcohols (eqn 4, Scheme 6).



(4)

Scheme 6

Märkl [27] and ourselves [28] have reported the synthesis and structure of diphosphinidenecyclobutene **8** (where R = Tms = trimethylsilyl) as shown in eqn 5 (Scheme 7). The shape of the cyclobutene derivatives indicates that the two phosphorus atoms could behave as a bidentate ligand. Recently, bidentate diphosphane ligands with sp^3-type hybridized phosphorus atoms such as 1,2-bis(diphenylphosphino)ethane (dppe) or 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) have been widely used in organic synthesis as well as in coordination chemistry [29].



(5)

Scheme 7

In fact, the phosphinidenecyclobutene **8** is configurationally stable and also acts as a bidentate ligand to the transition metals to give **9** [30,31]. X-ray analysis of one of the dichloropalladium(II) complexes with a diphosphinidenecyclobutene **8** (where R = *t*-Bu) was carried out, as shown in Fig. 3 [32] for complex **10**. Similar results were obtained in the case of 1,2-diphosphinidene-3,4-bis(diphenylmethylene)cyclobutane (diphospha [4] radialene) [33,34]. As an additional interesting reaction of diphosphinidenecyclobutenes, diphosphinidenecyclobutenes **9** reacted with oxygen upon irradiation of light to give the corresponding 2,3-diacyl-1,4-diphospha-1,3-butadiene ligating on the group 6 metal tetracarbonyls as shown in eqn 5 [35].

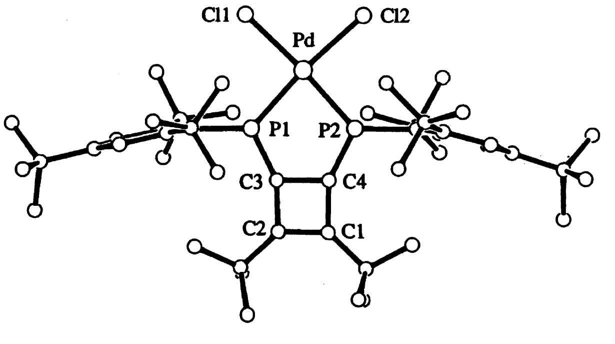
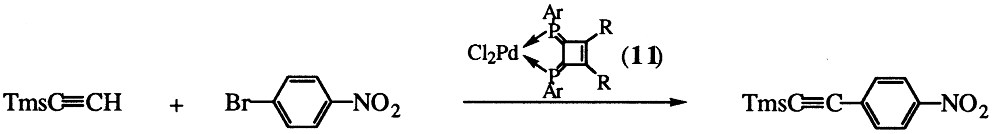


Fig. 3 Molecular structure of **10**.

As shown in eqn 6 (Scheme 8), a coupling reaction of trimethylsilylacetylene with *p*-bromonitrobenzene of the Heck or Sonogashira type proceeds in THF-Et$_2$NH in the presence of 1.1 mol% of copper(I) iodide catalyzed by 1.5 mol% of palladium complexes of a diphosphinidenecyclobutene **11** (where R = H, *t*-Bu, Ph, or Tms) to give the corresponding phenylacetylene in a good yield [32].

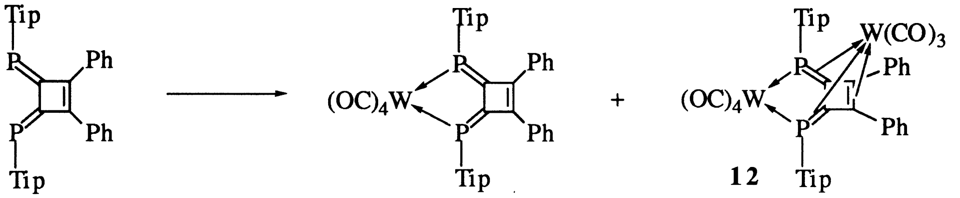
Depending on the protecting groups and the substituents on the cyclobutene ring, the chelated complex



(6)

Scheme 8

9 may react further with a tungsten carbonyl to give a doubly coordinated complex, such as **12**, where Tip = 2,4,6-triisopropylphenyl, as shown in eqn 7 (Scheme 9). The structure of **12** was confirmed by X-ray analysis (Fig. 4) [36].



(7)

Scheme 9

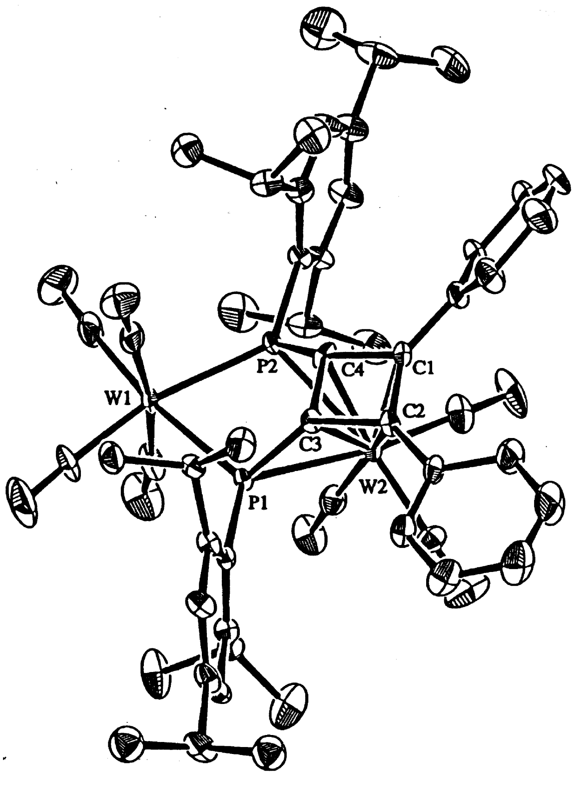
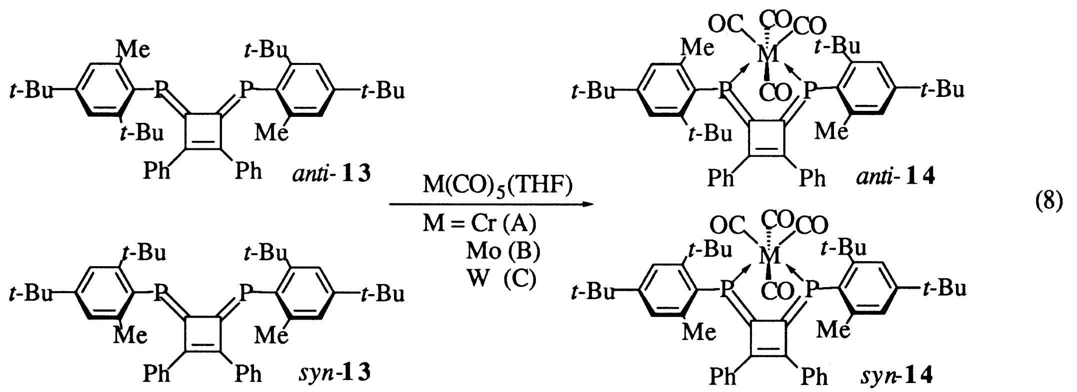


Fig. 4 Molecular structure of **12**.

On the other hand, we have developed several protecting groups other than the Ar group and found that the 2,4-di-*t*-butyl-6-methylphenyl (abbreviated to Dbt) group is also useful for the stabilization of the diphosphinidenecyclobutene system. Interestingly, the Dbt group exhibited conformational isomerism due to the restricted rotation around the two P–Dbt bonds at the edges of the system. Compound **13** consists of two rotamers, *syn*-**13** and *anti*-**13**, according to ^{31}P NMR studies. After addition of $M(CO)_5(THF)$ to this mixture, where M equals the group 6 metals such as Cr (**A**), Mo (**B**), and W (**C**), the ^{31}P NMR spectrum of the reaction products appeared as two singlets again due to *syn*-**14** and *anti*-**14** with complete retention of conformation (eqn 8, Scheme 10).



Scheme 10

The compounds **14 A–C** were purified through column chromatography to give dark purple complexes and the structure of *syn*-**14C** was unambiguously determined by X-ray analysis (Fig. 5) [37]. On the other hand, *anti*-**14C** was analyzed by HPLC using a chiral HPLC column and a baseline separation was attained, the CD spectra of the separated enantiomers were identical in magnitude but opposite in sign. These results indicate that an asymmetric environment can be created in the diphosphinidenecyclobutene–transition metal complex system.

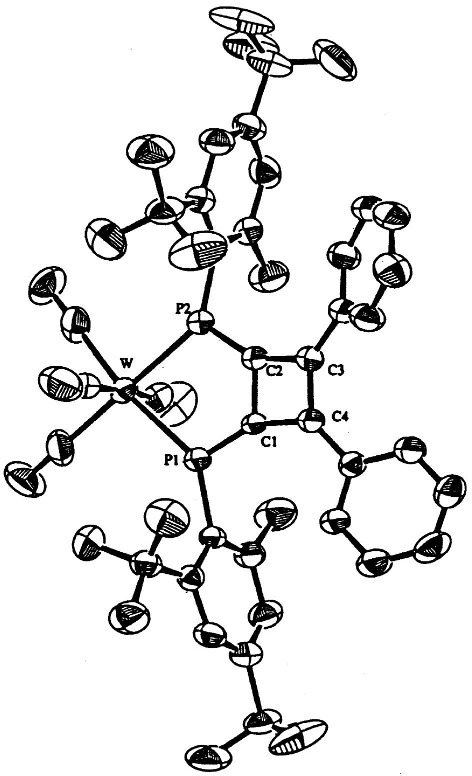


Fig. 5 Molecular structure of *syn*-**14**.

PHOSPHACUMULENES

Phosphacumulenes, such as phosphaallenes, diphosphaallenes, phosphabutatrienes, and diphosphabutatrienes, also behave as a ligand to transition metal complexes. Some examples of transition metal complexes of phosphacumulenes are as follows. 2,2-Diphenyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaallene (**15**) can be prepared by either the Peterson reaction or the phospha-Peterson reaction. The phosphaallene [38,39] behaves as a ligand to the transition metal complex to give an end-on complex like phosphaalkenes. Figure 6 shows the X-ray structure of the pentacarbonyltungsten complex of **15** [40]. The tricarbonylnickel complex is very similar in shape to the corresponding tungsten complex [41].

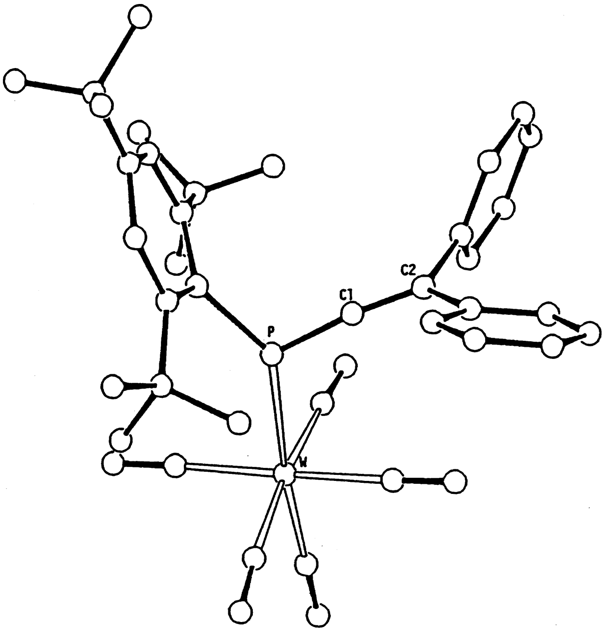
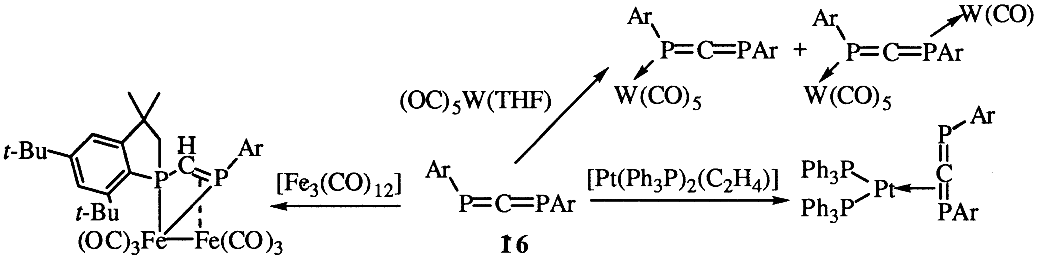


Fig. 6 Molecular structure of [**15**][W(CO)$_5$].

1,3-Diphosphaallene **16** [42] can also be prepared by various methods. Recently we have developed a phosphorus version of the Doering-Moore-Skattebøl reaction for the preparation of low coordinate phosphacumulenes [43]. The structure of the 1,3-diphosphaallene **16** was determined by X-ray analysis by Karsch *et al.* [44]. The compound has various kinds of reactivities toward transition metals, including the mono-and bismetallated complexes as end-on complexes. One of the structures of the latter end-on complexes is shown in Fig. 7 [45], while the diphosphaallene **16** reacts with [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] to give a side-on complex, as illustrated in eqn 9 (Scheme 11) [46].



(9)

Scheme 11

The reaction of **16** with [Fe$_3$(CO)$_{12}$] gives a rearranged product involving hydrogen migration, the structure of which was confirmed by the X-ray analysis [47].

4,4-Diphenyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phospha-1,2,3-butatriene **17** can be prepared by the method reported by Märkl or by ourselves [48,49]. The phosphabutatriene behaves as a ligand to give a tungsten complex, which has been analyzed by X-ray crystallography, as shown in Fig. 8 [50]. Bis(2,4,6-tri-*t*-butylphenyl)-1,4-diphosphabutatriene (**18**) was prepared by Märkl as well as by ourselves [51–53]. The structure of its bis(pentacarbonyltungsten) complex was confirmed by X-ray analysis, as shown in Fig. 9 [53].

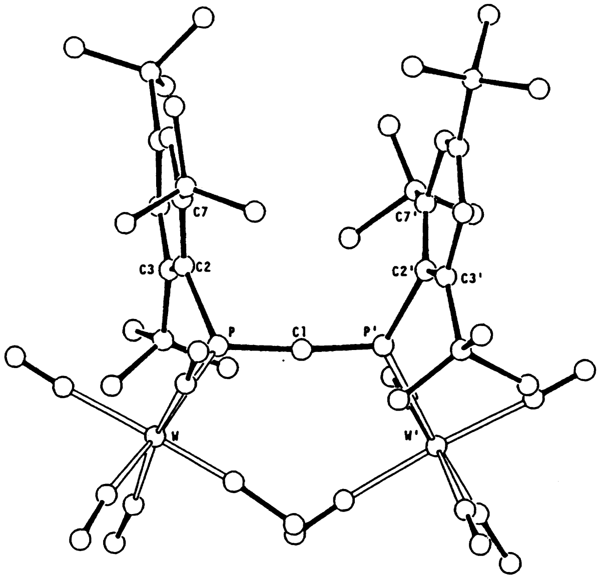


Fig. 7 Molecular structure of [**16**][W(CO)$_5$]$_2$.

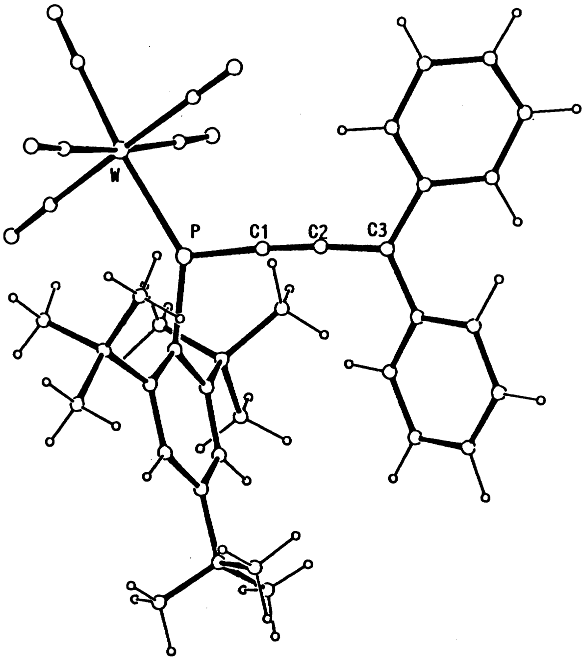


Fig. 8 Molecular structure of [**17**][W(CO)$_5$].

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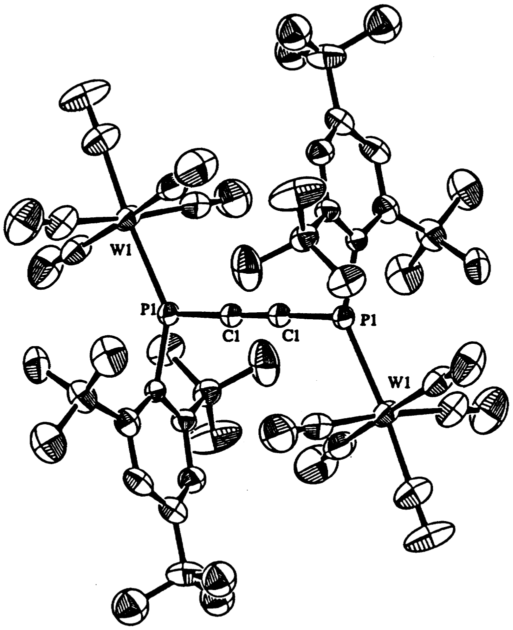

Fig. 9 Molecular structure of [**18**][W(CO)$_5$]$_2$.

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