© 1997 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 70, 2881—2893 (1997) 2881

Accounts

Coordination Chemistry of Some Low Coordinate Organophosphorus Compounds of Coordination Number 2

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(Received June 10, 1997)

The structures of transition metal complexes with low coordinate organophosphorus compounds are described; these compounds involve diphosphenes, phosphaethenes, phosphaallenes, phosphabutatrienes, and so on of coordination number 2. They are discussed in terms of X-ray crystallographic analysis and ^{31}P NMR analysis.

Phosphorus ligands are widely used not only in coordination chemistry itself but also in synthetic organic chemistry. In fact, there are several well-known transition-metal complexes with phosphorus-containing chiral ligands which catalyze organic reactions to give products with high enantioselectivity. During the catalytic process, the coordination mode and the environment around the metal are very important to control the reactions. Therefore, coordination chemistry nowadays deals with not only static but also dynamic aspects of coordination. This review article describes coordination chemistry of some low coordinate organophosphorus compounds mostly in the static aspects of structure and coordination mode, since these ligands themselves are classified in a rather new type of compounds and few dynamic studies have been carried out.

1. Low Coordinate Organophosphorus Compounds. Since a bulky substituent such as the 2,4,6-tri-*t*-butylphenyl group (abbreviated to Ar in this article) was found to be effective to stabilize low coordinate organophosphorus compounds in 1981,[1] sterically protected phosphorus compounds in low coordination states of coordination number 2 have been of current interest; they include diphosphenes (R–P=P–R), phosphaethenes ($R-P=CR_2$), 1-phosphaallenes ($R-P=C=CR_2$), 1,3-diphosphaallenes (R–P=C=P–R), 1-phosphabutatrienes ($R-P=C=C=CR_2$), and 1,4-diphosphabutatrienes (R–P=C=C=P–R). They are interesting new-type molecules because of their unusual structures and properties.[2—6]

These compounds are supposed to be unstable unless reasonably protected, since the multiple bonding involving heavier main-group elements is not strong; i.e., bonding electrons in 3s, 3p, or 3d orbital do not form a strong bond because of the long bond length and unfavorable hybridization of the sp^2 configuration. Furthermore, these compounds, even though sufficiently protected, are reactive toward either nucleophiles or electrophiles. Among the various kinds of reactivities, they serve as a ligand of transition-metal complexes. This article focuses on the formation of those transition metal complexes along with the X-ray structure and ^{31}P NMR studies.

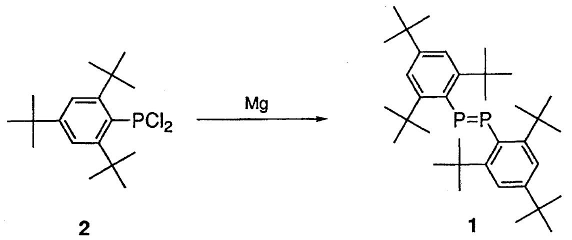
2. Transition Metal Complexes. Since such phosphorus compounds are in low coordination states of coordination number 2, they tend to be fully coordinated in the states of coordination number 3, 4, or 5. But there are several kinds of coordination modes of low coordinate organophosphorus compounds to the transition metals, depending on the nature of the ligand, the nature of the transition metals, and also on the reaction conditions. For examples, end-on (**A**) and side-on (**B**) coordinations for diphosphenes (R–P=P–R) are among the typical complex formations, as illustrated in Scheme 1.[7—9] 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. Here described is complex formation of such low coordinate organophosphorus ligands of coordination number 2 mainly with the group-6 metal carbonyls of end-on coordination type.

Scheme 1.

Structures of Transition Metal Complexes

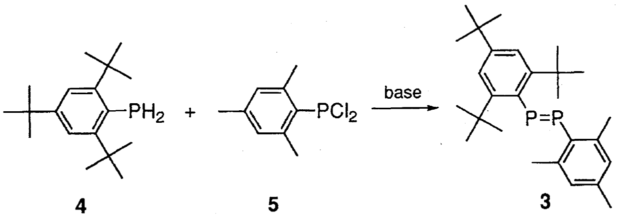
As is described above, the coordination mode depends on the nature of ligand and the metal. The following complexes are some selected examples which have been fundamentally characterized by X-ray analysis as well as ^{31}P NMR.

1. Diphosphenes. A sterically protected diphosphene **1** is prepared as a stable compound by dechlorination reaction of the corresponding phosphonous dichloride **2** with magnesium metal, as shown in Eq. 1.[1)]



(1)

There is an alternative method to prepare diphosphenes especially for unsymmetrical ones such as **3**. Starting from the corresponding primary phosphine **4** and phosphonous dichloride **5**, the unsymmetrical diphosphene **3** is available in the presence of a base such as triethylamine or DBU (diazabicyclo[5.4.0]undec-7-ene), as shown in Eq. 2.[10)]



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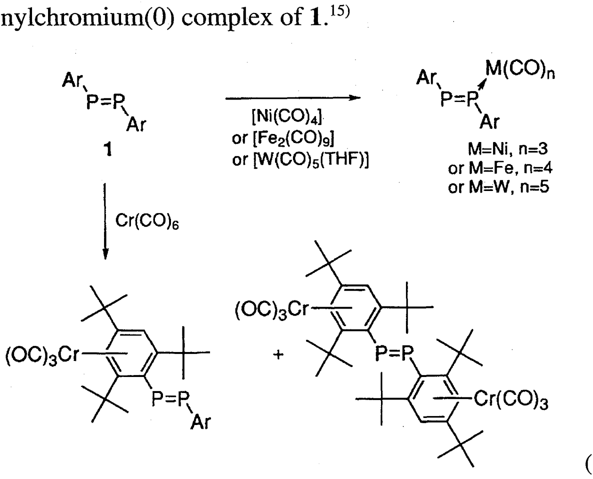
The reaction of **1** with transition metal carbonyls of nickel,[11)] iron,[12)] and tungsten[13)] leads to the terminal *P*-coordination (i.e., end-on coordination) and the X-ray structure of the iron complex is shown in Fig. 1.[12)] On the other hand, the reaction of **1** with hexacarbonylchromium(0) in refluxing dioxane leads to arene-coordinated products of η^6-type coordination, but not on the P=P bond, as shown in Eq. 3.[14)] Figure 2 shows the X-ray structure of the bis-arene tricarbonylchromium(0) complex of **1**.[15)]



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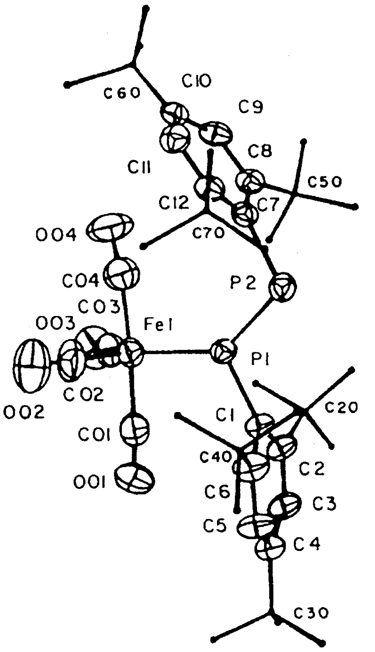


Fig. 1. X-Ray structure of [Fe{(*E*)-ArP=PAr}(CO)$_4$].[12)]

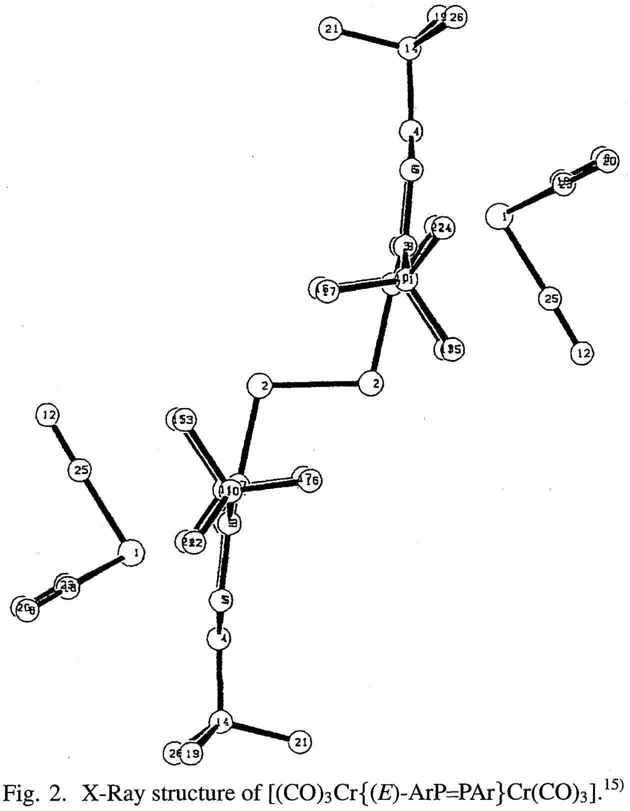
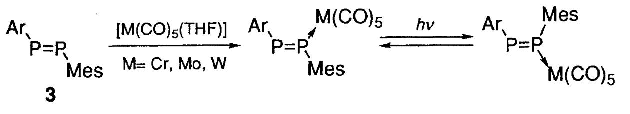


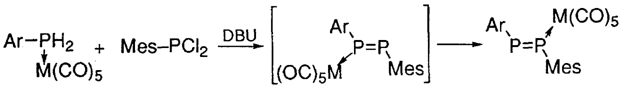
Fig. 2. X-Ray structure of [(CO)$_3$Cr{(*E*)-ArP=PAr}Cr(CO)$_3$].[15)]

Standard methods for the preparation of the transition metal complexes by ligand exchange reaction using [Cr(CO)$_5$(THF)] fail in the case of **1**, probably due to steric demand, but if one of the tri-*t*-butylphenyl groups (Ar) in **1** is replaced by the sterically less bulky mesityl group (Mes), for example, coordination occurs at the less hindered phosphorus atom in **3** to give an end-on complex.[16)] More interestingly, the *E*/*Z* photoisomerization of the diphosphene ligand takes place on the metal complexes, as shown in Eq. 4.[16] The X-ray analysis (Fig. 3) shows that the bond length of P–P is not elongated so much upon coordination to the metal, even on taking up a *cis*-configuration.[16]



(4)

It should be noted that attempts to prepare the bulkier complexes starting with phosphine transition-metal complexes and phosphonous dichloride by dehydrochlorination with DBU fail, but result in the formation of the less bulkier complexes, probably via migration of the metal moiety from one to the other,[17] as shown in Eq. 5. Some examples are shown in Table 1, where two types of tungsten complexes of unsymmetrical diphosphenes are possible and the structures are able to be assigned by the accompanied satellite signals showing $^{1}J_{PW}$.



(5)

Doubly end-on coordinated iron and the group-6 metal complexes are known for diphosphenes with less bulky substituents such as phenyl, mesityl, bis(trimethylsilyl)methyl, or bis(trimethylsilylmethyl)amino. For example, mesitylphosphonous dichloride reacts with $Na_2[Mo_2(CO)_{10}]$ to give diphosphene-metal carbonyl complexes in the *cis*- form,[18] as shown in Fig. 4, while bis(trimethylsilyl)methylphosphonous dichloride with $Na_2[Fe(CO)_4]$ gives the complex with the *trans*-diphosphene ligand[19] (see Table 1).

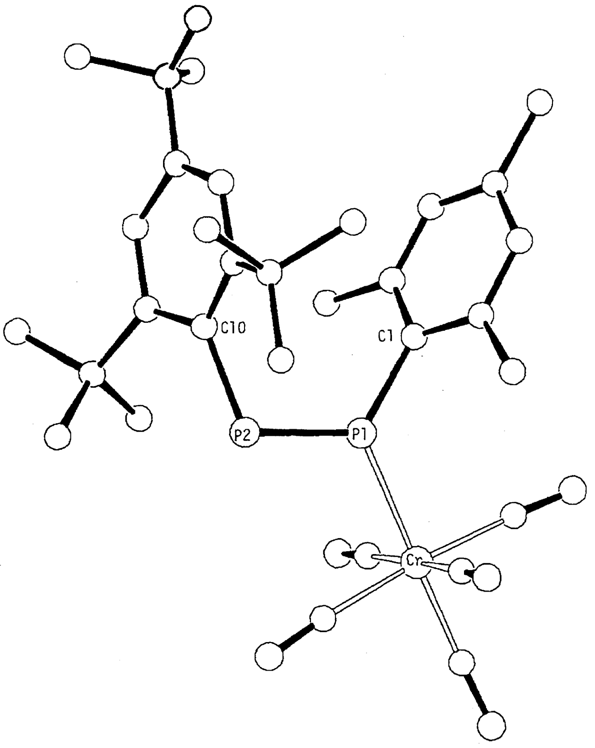


Fig. 3. X-Ray structure of $[Cr\{(Z)\text{-}ArP{=}PMes\}(CO)_5]$.[16]

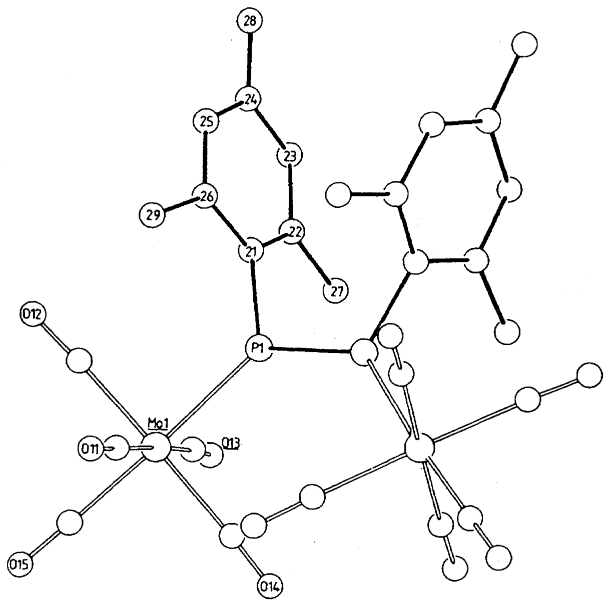
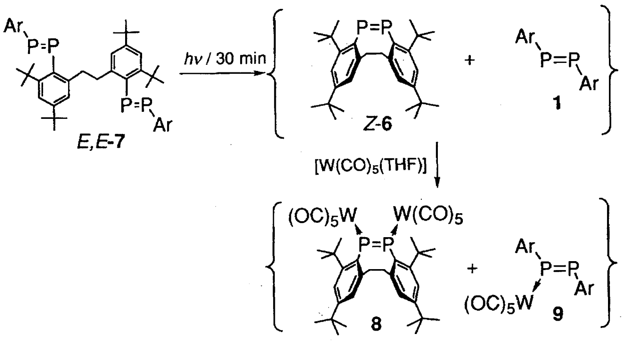


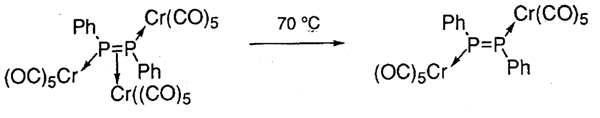
Fig. 4. X-Ray structure of $[(CO)_5Mo\{(Z)\text{-}MesP{=}PMes\}Mo(CO)_5]$.[18]

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*-**6** of the *o*-cyclophane type [(*Z*)-Arra(P=P)] was obtained together with **1** from a bisdiphosphene *E*,*E*-**7**, and attempts to stabilize *Z*-**6** by complex formation with tungsten carbonyl gave doubly end-on coordinated complex **8** (Eq. 6) together with **9**. The structure of **8** was confirmed by X-ray analysis, as shown in Fig. 5.[20]



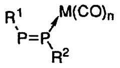
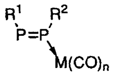
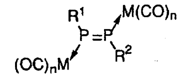
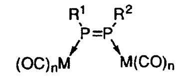
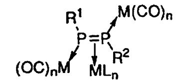
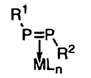
(6)

Complexes with both end-on and side-on coordinations are known for diphenyldiphosphene, which is prepared from $[Cr(CO)_5(PhPCl_2)]$ and $Na_2[Cr_2(CO)_{10}]$[21] (Figs. 6 and 7). Moreover, the triply-coordinated diphosphene loses one metal carbonyl group upon heating, as shown in Eq. 7.



(7)

Table 1. Selected Diphosphenes and Diphosphene–Transition Metal Complexes

Compound				δ_P/ppm	$^1J_\mathrm{PP}$	l(P=P)	Ref.
R^1	R^2	M(CO)$_n$	ML$_n$	($^1J_\mathrm{PW}$/Hz)	Hz	Å	
							
Ar	Ar	—	—	492.4	—	2.034(2)	[1]
Ar	Ar	W(CO)$_5$	—	486.3; 375.4(247.2)	561.5	—	[13]
Ar	Ar	Fe(CO)$_4$	—	423.6; 396.4	578.0	2.050(1)	[11]
Ar	Ar	Ni(CO)$_3$	—	449.0; 422.0	540.3	2.050(1)	[12]
Ar	Mes	—	—	540.4; 467.6	573.7	—	[10]
Ar	Mes	Cr(CO)$_5$	—	500.9; 412.3	517.6	—	[16,17]
Ar	Mes	Mo(CO)$_5$	—	486.3; 395.0	518.8	—	[16,17]
Ar	Mes	W(CO)$_5$	—	461.9; 352.8(238.0)	528.8	—	[16,17]
Tms$_2$CH	Tms$_2$CH	—	—	517	—	—	[63]
Tms$_2$CH	Tms$_2$CH	Cr(CO)$_5$	—	477.0; 446.5	510	2.027(3)	[64]
Tms$_2$CH	Tms$_2$CH	Mo(CO)$_5$	—	465.4; 433.0	515	2.006(3)	[18]
Ar	NCh$_2$	—	—	270.2; 448.8	543.5	—	[65]
Ar	NCh$_2$	W(CO)$_5$	—	395.3(272.7); 451.6	559.9	—	[65]
NCh$_2$	Ar	W(CO)$_5$	—	149.9; 296.0(258.4)	641.5	—	[65]
Ar	OAr	—	—	409.8; 534.1	572.2	—	[66]
Ar	OAr	W(CO)$_5$	—	343.2; 444.6(289.5)	564.3	—	[66]
OAr	Ar	W(CO)$_5$	—	311.3(243.5); 491.2	510.8	—	[66]
Arcr	Ar	—	—	503.2; 475.6	590.8	2.042(5)	[15]
Arcr	Arcr	—	—	499.7	—	2.045(2)	[15]
							
Ar	Ar	—	—	368	—	—	[67,68]
Ar	Ar	W(CO)$_5$	—	395.1; 306.6(249.9)	567.4	—	[13]
Ar	Mes	Cr(CO)$_5$	—	393.9; 384.9	603.0	2.039(3)	[16]
Ar	Mes	Mo(CO)$_5$	—	398.4; 359.0	585.9	—	[16]
Ar	Mes	W(CO)$_5$	—	393.1; 322.4(231.9)	576.8	—	[16]
							
Tms$_2$CH	Tms$_2$CH	Fe(CO)$_4$	—	384.6	—	2.039(1)	[19]
Tms$_2$N	Tms$_2$N	Fe(CO)$_4$	—	403.9	—	2.053(1)	[50]
Ph	Ph	Mo(CO)$_5$	—	369	—	2.021(2)	[18,21]
							
Mes	Mes	Mo(CO)$_5$	—	367.7	—	2.026	[18]
Arra		W(CO)$_5$		332(145,116)[a]	—	2.041(4)	[20]
							
Ph	Ph	Cr(CO)$_5$	Cr(CO)$_5$	97	—	2.125(6)	[18,21]
Ph	Ph	W(CO)$_5$	Pd(dppe)	17.0	344	2.186(6)	[22]
							
H	H	—	Mo(Cp)$_2$	203	—	2.146(3)	[69]
C$_6$F$_5$	C$_6$F$_5$	—	Pt(PPh$_3$)$_2$	−22	—	2.156(7)	[22,70]
Tms	Tms	—	Ni(PEt$_3$)$_2$	−62	—	2.149(2)	[71]
Ph	Ph	—	Pd(dppe)	34.3	348	2.121(4)	[22]

Ar=2,4,6-Bu$^t_3$C$_6$H$_2$; Mes=2,4,6-Me$_3$C$_6$H$_2$; Arcr=[(OC)$_3$Cr][2,4,6-Bu$^t_3$C$_6$H$_2$]; Arra=2,2′-[3,5-Bu$^t_2$C$_6$H$_2$CH$_2$]$_2$; Tms=Me$_3$Si; Ch=cyclohexyl; dppe=Ph$_2$PCH$_2$CH$_2$PPh$_2$. a) The coupling constants observed for $^1J_\mathrm{PW}$ are much smaller than the usual value (ca. 250 Hz), and the chemical shift δ_P appears slightly in a high field, probably due to some fluctional character of the bis(pentacarbonyl)tungsten complex in solution as observed for a platinum complex.[27b]

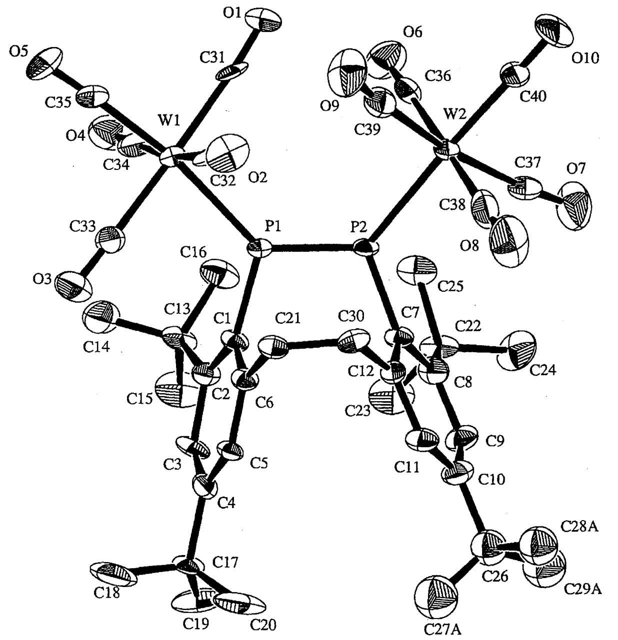


Fig. 5. X-Ray structure of $[(CO)_5W\{(Z)\text{-}Arra(P{=}P)\}W(CO)_5]$ (**8**).[20]

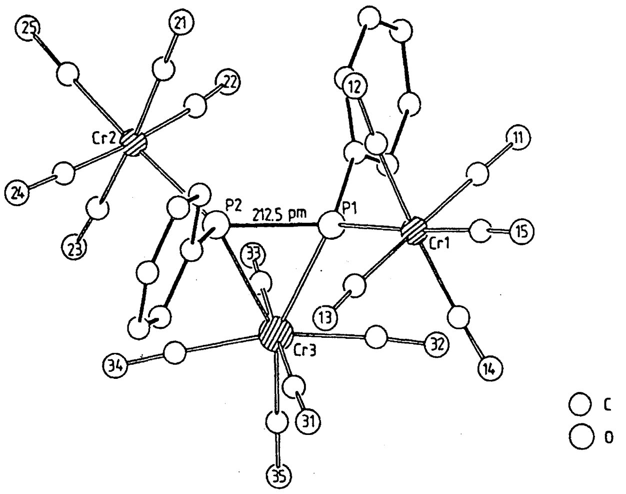


Fig. 6. X-Ray structure of $[Cr_3(CO)_{15}\{\mu_3\text{-}(E)\text{-}PhP{=}PPh\}]$.[21]

It should be noted that only slight differentiation in either ^{31}P NMR chemical shifts or P–P bond lengths is observed upon coordination in the end-on mode of type **A**. On the other hand, coordination in the side-on mode of type **B** elongates the P–P bond length indicating loss of the double bond character to some extent (cf. Figs. 6 and 7). The palladium complex $[PdCl_2(dppe)]$ reacts with Ph(Li)P–P(Li)Ph to give the end-on coordinated diphenyldiphosphene, $[Pd\{(E)\text{–}PhP{=}PPh\}(dppe)]$[22] and the structure was confirmed by X-ray analysis (Table 1). The ^{31}P NMR data of the Pt analog suggest a very small P 3s character for the Pt–P bonds in side-on complexes. This indicates that the bonding nature of P–P is essentially a diphosphene bound to the metal rather than a diphosphido(2−) ligand bound to the metal, even in side-on coordination (Fig. 8).[22]

^{31}P NMR chemical shift of ligated ligands generally appears at a higher field than that of the free ligand, suggesting electron back donation from the metal is rather large if the chemical shifts can be discussed in terms of only electron density. Furthermore the shifts of these complexes of the group-6 metal carbonyls are correlated to each other and the structures of the tungsten complexes are apparent from the satellite coupling constant $^1J_{PW}$.

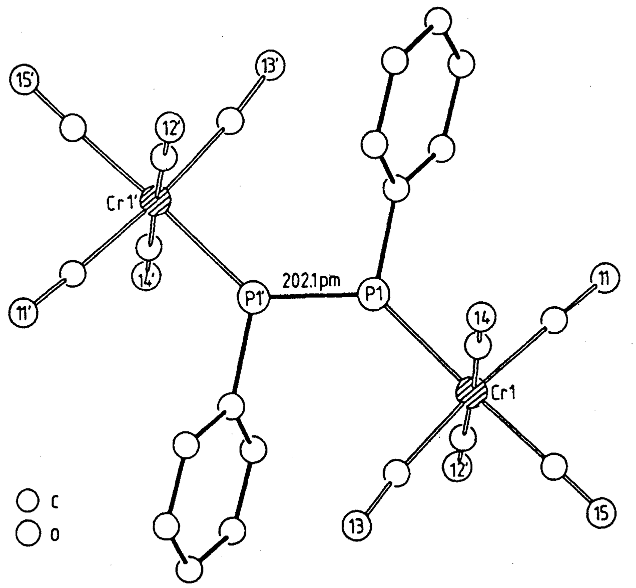


Fig. 7. X-Ray structure of $[(CO)_5Cr\{(E)\text{-}PhP{=}PPh\}Cr(CO)_5]$.[21]

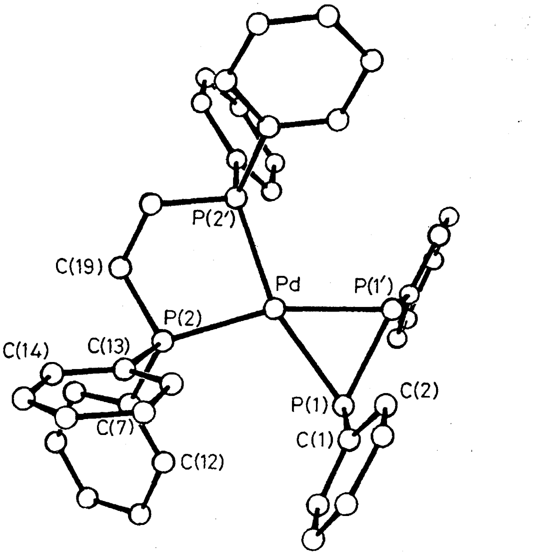
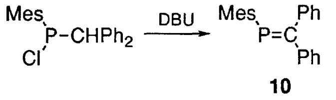


Fig. 8. X-Ray structure of $[Pd\{(E)\text{-}PhP{=}PPh\}(dppe)]$.[22]

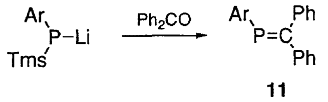
Table 1 shows some selected diphosphene-transition metal complexes of the end-on and side-on type and lists ^{31}P NMR chemical shifts δ_P and coupling constants $^1J_{PP}$ together with the P–P bond lengths if determined by X-ray analysis. In the case of tungsten complexes, $^1J_{PW}$ values observed as satellite peaks are also listed. Coordination of diphosphene to the metal in side-on fashion causes a strongly high field shift in the ^{31}P NMR, in contrast to that of end-on coördination.

2. Phosphaalkenes. A sterically protected phosphaalkene, 1-mesityl-2,2-diphenyl-1-phosphaethene (**10**), protected with the mesityl group, was prepared earlier than diphosphene **1**. Bickelhaupt et al. reported **10** as the first example of the phosphaethene with the localized P=C bond (Eq. 8).[23,24]



(8)

2.1. Phosphaethenes. Various kinds of phosphaalkenes with the Ar group as a protecting group such as compound **11** are prepared from the corresponding silylphosphide and the ketones or aldehydes (Eq. 9) by the method of the phospha-Peterson reaction.[25,26] These phosphaalkenes coordinate to the transition metal such as group-6 metal carbonyls to give the corresponding stable end-on complexes. Figure 9 depicts X-ray structure of a pentacarbonylchromium(0) complex with the phosphaalkene ligand **10**.[27a] However, Bickelhaupt has pointed out that in the case of bis(triphenylphosphine)-platinum(0) complex of **10**, i.e. [Pt(MesP=CPh$_2$)(PPh$_3$)$_2$], the phosphaethene coordinates on the platinum metal in the side-on coordination mode, according to the variable temperature NMR studies in the solution, whereas it coordinates on the metal in the end-on coordination mode in the solid state, as clarified by the X-ray analysis.[27b]



(9)

2.2. Bis(2-phosphaethenyl)benzenes. Geoffroy reported that 1,2-bis(2-phosphaethenyl)benzene derivative (**12**) forms a chelate complex **13**, while 1,3-bis(2-phosphaethenyl)benzene derivative **14** coordinates to palladium metal to afford palladated complex **15**. The X-ray analysis of **15** (Fig. 10) confirmed the structure showing that the compound results from a C–H bond activation at the 2-position to form a Pd–C bond (Eq. 10).[28,29]

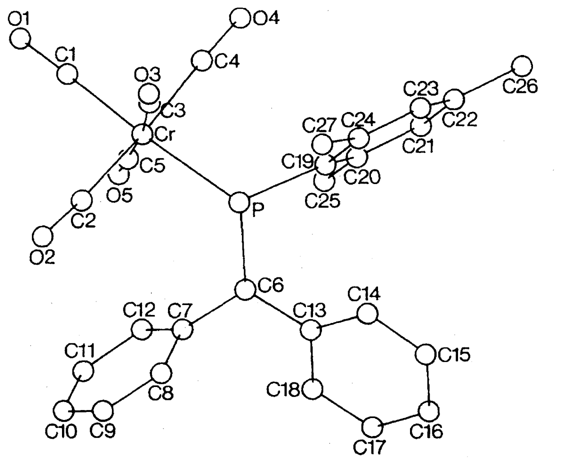


Fig. 9. X-Ray structure of [Cr(CO)$_5$(MesP=CPh$_2$)].[27a]

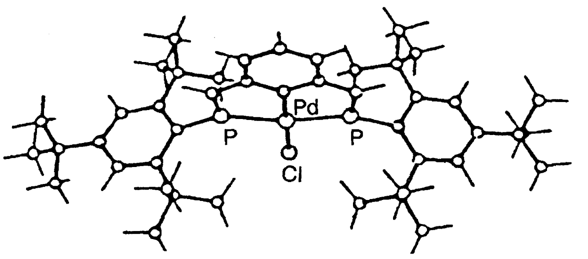
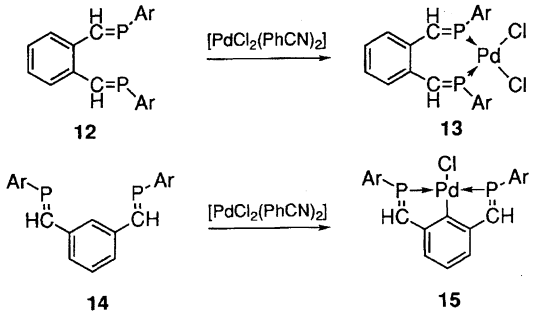
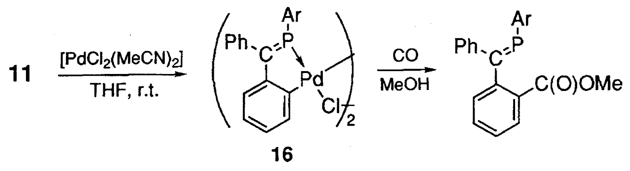


Fig. 10. X-Ray structure of palladate complex **15**.[28]



(10)

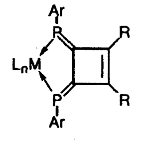
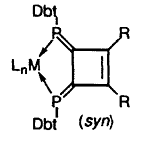
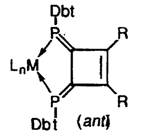
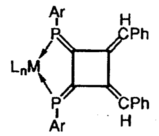
On the other hand, phosphaalkene **11** reacts with [PdCl$_2$(MeCN)$_2$] to give *o*-palladate complex **16** (Eq. 11). The structure was analyzed by X-ray crystallography indicating that the complex forms a dimeric structure.[30] The *o*-palladate complexes of the compound type **16** react with carbon monoxide under high pressure to give the corresponding esters in the presence of alcohols (Eq. 11).



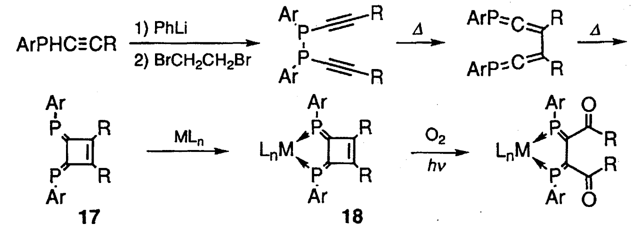
(11)

2.3. Diphosphinidenecyclobutenes. Märkl[31] and we[32] reported the synthesis and structure of diphosphinidenecyclobutene **17** (where R=Tms), as shown in Eq. 12. The shape of the cyclobutene derivatives indicates that the two phosphorus atoms behaves as a bidentate ligand depending on the configuration. 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.[33] The phosphinidenecyclobutene takes a rigid configuration, but also acts as a bidentate ligand to the transition metals to give **18**.[34] Figure 11 shows one of the examples of ligated diphosphinidenecyclobutene with tetracarbonylmolybdenum(0).[35] Table 2 shows the ^{31}P NMR chemical shifts of some transition metal complexes of diphosphinidenecyclobutenes. As shown in Eq. 13, a coupling reaction of trimethylsilylacetylene with *p*-bromonitrobenezene of the Sonogashira reaction[36] proceeds in THF–Et$_2$NH in the presence of 1.1×10^{-2} molar amount of copper(I) iodide catalyzed by 1.5×10^{-2} molar amount of palladium complexes of a diphosphinidenecyclobutene **19**

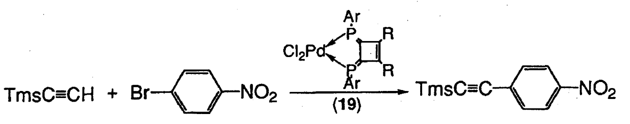
Table 2. ^{31}P NMR of Metal Complexes of Diphosphinidenecyclobutenes and Diphospha[4]-radialenes

Compound			δ_P	$^1J_{PW}$/Hz or $^1J_{PPt}$/Hz	Ref.
	R	L_nM	ppm		
	Tms	—	162.5	—	[52,53]
	Tms	$Cr(CO)_4$	198.4	—	[35]
	Tms	$Mo(CO)_4$	181.0	—	[35]
	Tms	$W(CO)_4$	161.3	257.5	[35]
	Tms	$PdCl_2$	163.1	—	[37]
	Ph	—	169.7	—	[72]
	Ph	$Cr(CO)_4$	188.9	—	[40]
	Ph	$Mo(CO)_4$	172.8	—	[40]
	Ph	$W(CO)_4$	152.5	257	[40]
	Ph	$PdCl_2$	153.1	—	[37]
	t-Bu	—	142.6	—	[73]
	t-Bu	$PdCl_2$	155.8	—	[37]
	H	—	169.8	—	[74]
	H	$PdCl_2$	162.2	—	[37]
	H	$PtCl_2$	136.9	4480	[39]
	Ph	—	168.8	—	[41]
	Ph	$Cr(CO)_4$	187.5	—	[41]
	Ph	$Mo(CO)_4$	168.0	—	[41]
	Ph	$W(CO)_4$	145.1	254	[41]
	Ph	—	168.1	—	[41]
	Ph	$Cr(CO)_4$	189.5	—	[41]
	Ph	$Mo(CO)_4$	169.4	—	[41]
	Ph	$W(CO)_4$	146.5	254	[41]
		—	190.7	—	[38]
		$W(CO)_4$	166.1	267.8	[75]
		$PtCl_2$	168.3	—	[39]

(where R=H, Tms, Ph, or Tms) to give the corresponding phenylacetylene in a good yield.[37] An X-ray analysis of one of the dichloropalladium(II) complexes with a diphosphinidenecyclobutene **17** (where R=*t*-Bu) was carried out, as shown in Fig. 12.[37] Similar results were obtained in the case of the 1,2-diphosphinidene-3,4-bis(diphenylmethylene)cyclobutane (diphospha[4]radialene).[38,39] The NMR data are also listed in Table 2.



(12)



(13)

As one of the interesting reactions of diphosphinidenecyclobutenes, diphosphinidenecyclobutenes **18** react with oxygen upon irradiation of light to give 2,3-diacyl-1,4-diphospha-1,3-butadiene ligating on the group 6 metal tetracarbonyls, as shown in Eq. 12.[40]

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 (hereafter abbreviated to Dbt) group is useful to stabilize the diphosphinidenecyclobutene system, where conformational isomerism due to the restricted rotation around the two P–Dbt bonds at the edges of the system was observed. The compound **20** consists of two rotamers, *syn*-**20** and *anti*-**20**, the ^{31}P NMR of which appeared as two singlets, δ_P at 169.1 and 168.4 in a ratio of 1 : 2. After ad-

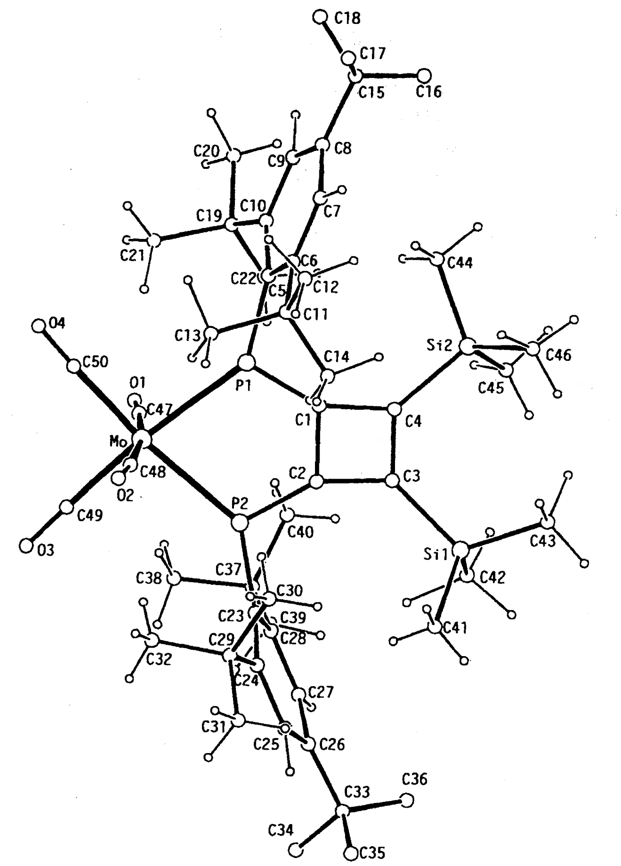


Fig. 11. X-Ray structure of [$Mo(CO)_4\{(ArP)_2C_4(Tms)_2\}$].[35]

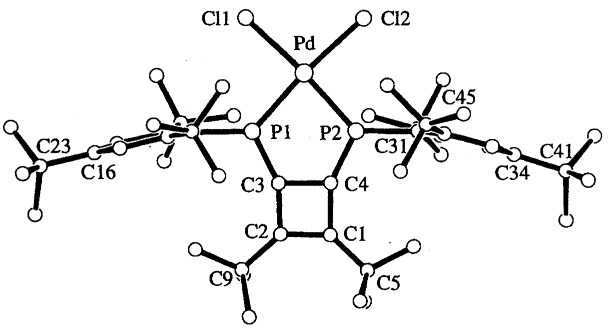


Fig. 12. X-Ray structure of [$PdCl_2\{(ArP)_2C_4Bu^t_2\}$].[37]

dition of [$M(CO)_5(THF)$] to this mixture, where M equals Cr (**A**), Mo (**B**), and W (**C**), the ^{31}P NMR of the reaction products appeared as two singlets again in a ratio of about 1 : 2, respectively, due to *syn*-**21** and *anti*-**21** with complete retention of conformation (Eq. 14). The compounds **21A**—**C** were purified by column chromatography to give dark purple complexes and the structure of *syn*-**21C** was unambiguously determined by X-ray analysis (Fig. 13).[41] On the other hand, *anti*-**21C** was analyzed by HPLC using a chiral HPLC column and a baseline separation was attained; each separated enantiomer showed the symmetrical CD spectrum. These results indicate that asymmetric environment can be created in the diphosphinidenecyclobutene–transition metal complex system.

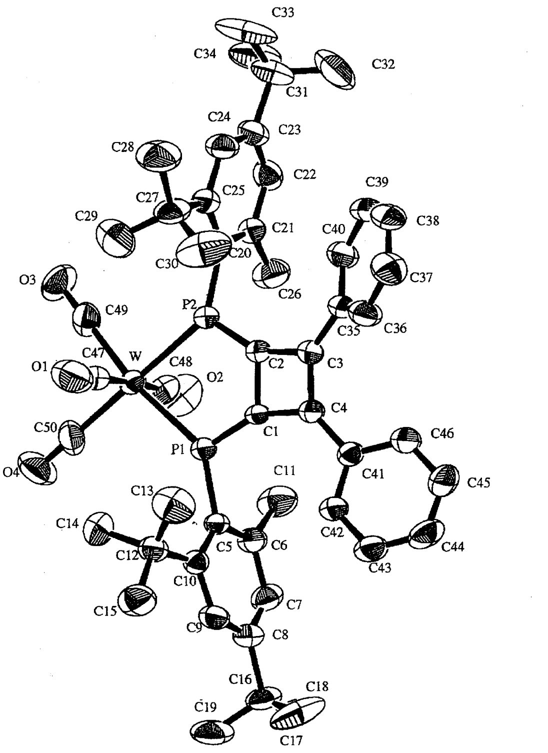
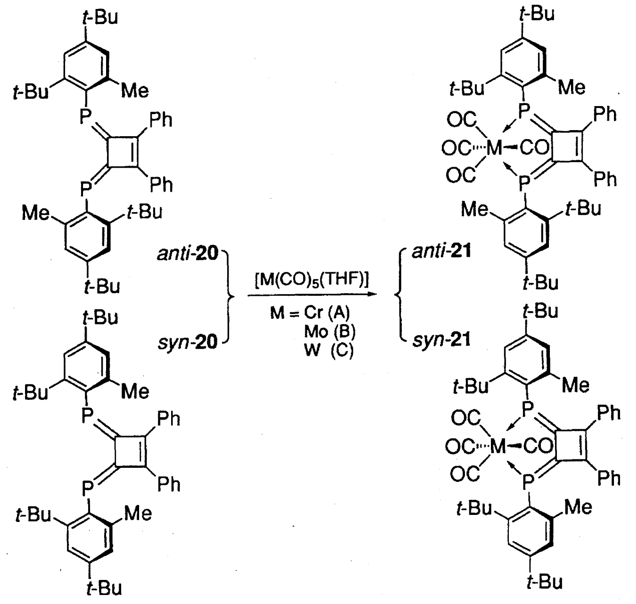


Fig. 13. X-Ray structure of [$W(CO)_4\{(DbtP)_2C_4Ph_2\}$] (*syn*-**21C**).[41]



(14)

3. Phosphacumulenes. Phosphacumulenes such as phosphaallenes, diphosphaallenes, and phosphabutatrienes and diphosphabutatrienes also behave as ligands to the transition metal complexes. The following are some examples for the transition metal complexes of phosphacumulenes.

3.1. Phosphaallene. 1-Phosphaallene **22** can be prepared by either the Peterson reaction or the phospha-Peterson reaction, as shown in Eq. 15. The phosphaallene[42,43] behaves as a ligand to the transition metal complex to give an end-on complex like phosphaalkenes. Figure 14 shows the X-

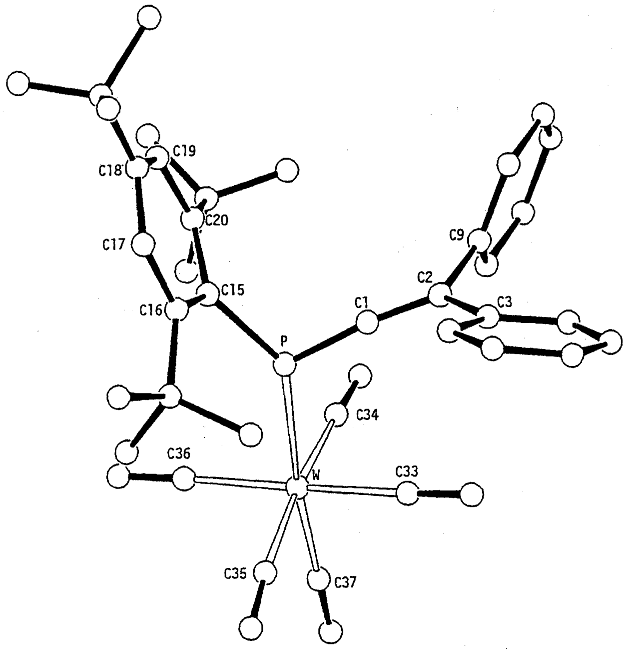
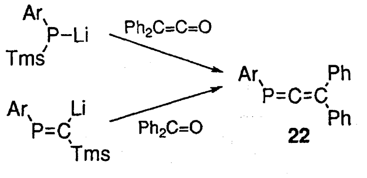


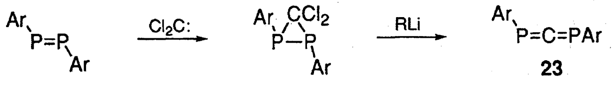
Fig. 14. X-Ray structure of $[W(CO)_5(ArP=C=CPh_2)]$.[44]

ray structure of the pentacarbonyltungsten complex of **22**.[44] The tricarbonylnickel complex is very similar in shape to the tungsten complex.[45]



(15)

3.2. Diphosphaallene. 1,3-Diphosphaallene **23**[46] can be prepared by various methods. Recently we have developed a phosphorus version of the Doering–Moore–Skattebøl reaction for preparation of low coordinate phosphacumulenes, as shown in Eq. 16.[47] The structure of the 1,3-diphosphaallene **23** is determined by X-ray analysis by Karsch et al.[48] The compound has various kinds of reactivities toward transition metals, including the mono- and bismetallated complexes as end-on complexes. The structure of the latter end-on complex is shown in Fig. 15.[49] The 1,3-diphosphaallene reacts with $[Pt(C_2H_4)(PPh_3)_2]$ to give a side-on complex, as illustrated in Eq. 17.[50] The reaction with $[Fe_3(CO)_{12}]$ gives a rearranged product involving hydrogen migration, the structure of which is confirmed by X-ray analysis (Fig. 16).[51]



(16)

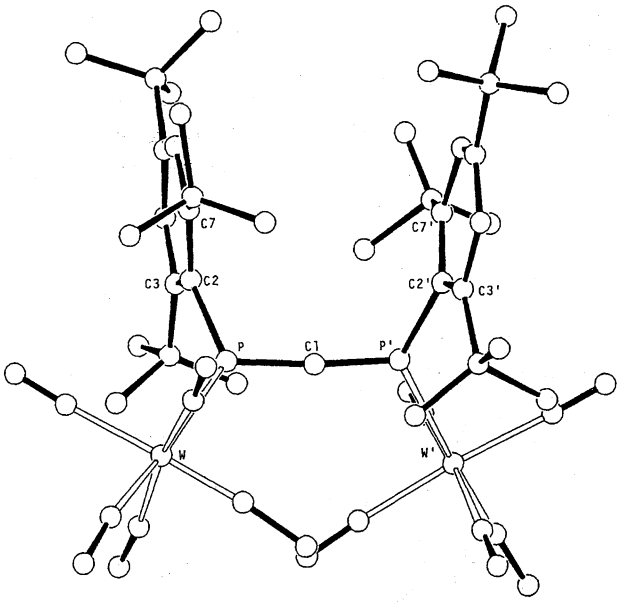


Fig. 15. X-Ray structure of $[(CO)_5W[ArP=C=PAr]W(CO)_5]$.[49]

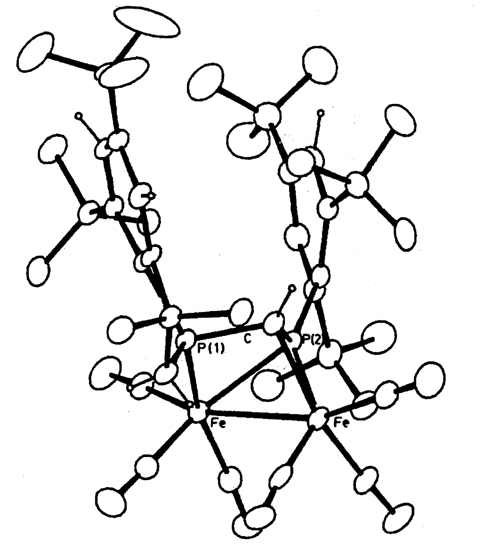
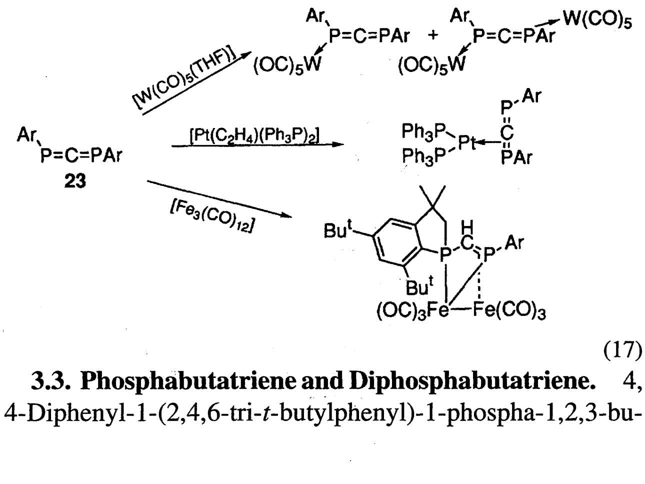


Fig. 16. X-Ray structure of $[Fe_2(CO)_6(ArP=CH–PCH_2(CMe_2)C_6H_2Bu^t_2)]$.[51]



(17)

3.3. Phosphabutatriene and Diphosphabutatriene. 4,4-Diphenyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phospha-1,2,3-butatriene **24** can be prepared by either the method reported by Märkl or that by ourselves, as shown in Eq. 18.[52,53] The 1-phosphabutatriene behaves as a ligand to give a tungsten complex and is analyzed by X-ray crystallography, as shown in Fig. 17.[54] The ^{13}C NMR signals are assignable by preparation of ^{13}C-labeled compound at the terminal carbon to indicate that the coupling constants J_{PC} do not diminish according to the number of bonds; i.e., $^2J_{PC}$ is smaller than $^3J_{PC}$ for 1-phosphabutatriene.[55] Bis(2,4,6-tri-*t*-butylphenyl)-1,4-diphosphabutatriene **25** was prepared also by Märkl or ourselves, as shown in Eq. 19,[56—58] and its bis(pentacarbonyltungsten) complex was confirmed by X-ray analysis.[58] Table 3 shows some ^{31}P NMR features of tungsten complexes among phosphaethene, 1-phosphaallene, 1-phosphabutatriene, and 1,4-diphosphabutatriene, where the negative $\Delta\delta_P$ values exhibit a shift to a high field upon coordination.

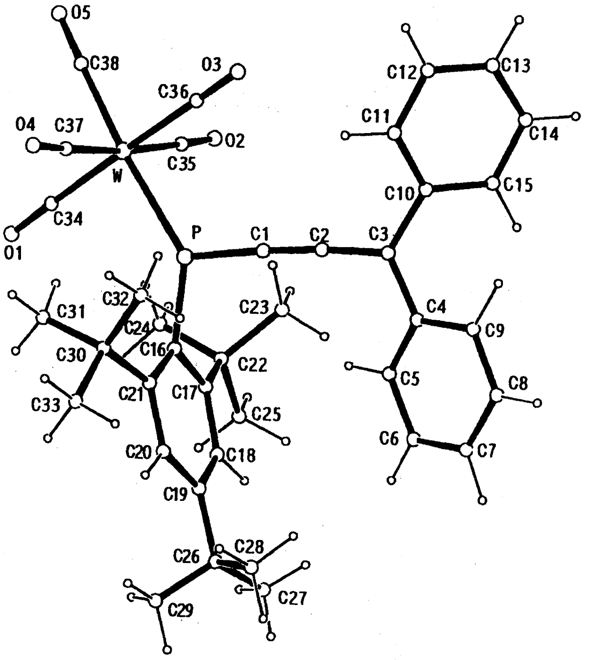
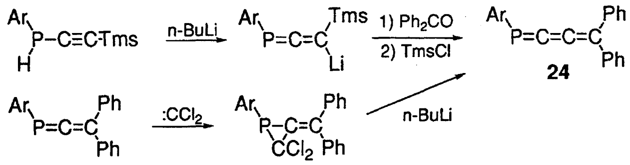
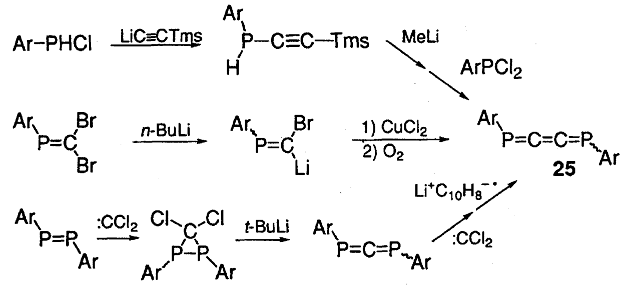


Fig. 17. X-Ray structure of [W(CO)$_5$(ArP=C=C=CPh$_2$)].[54]

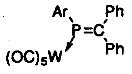
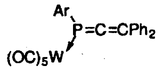
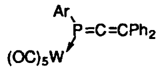
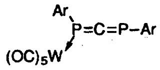
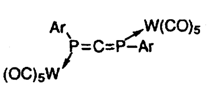
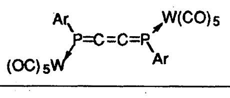


(18)



(19)

Table 3. ^{31}P NMR of Tungsten Complexes of Phosphaethene and Phosphacumulenes

Compound	δ_P	$^1J_{PW}$	δ_P (free ligand)	$\Delta\delta_P$[a]	Ref.
	ppm	Hz	ppm	ppm	
	200.3	285.7	242.4	42.1	[76]
	54.1	267.4	72.5	18.4	[44]
	54.1	267.4	72.5	18.4	[44]
	129.6 150.0	271.0 —	142.7 142.7	13.1 −7.3	[49] [60]
	144.3	285.0	142.7	−1.6	[49] [60]
	105.0	169.6[b]	180.6	75.6	[58]

a) $\Delta\delta_P = \delta_P$ (free ligand) $-\delta_P$. b) The coupling constant observed for $^1J_{PW}$ are much smaller than the usual value (ca. 270—290 Hz), and the chemical shift δ_P appears slightly in a high field, probably due to some fluctional character of the bis(pentacarbonyl)tungsten complex in solution as observed for platinum complex.[27b]

NMR Chemical Shifts Correlation

The NMR chemical shifts are governed by diamagnetic, paramagnetic, neighboring-atom, and steric effect terms.[59] The main contributor to ^{31}P shielding might be the paramagnetic term; however, the mechanism as to how the different metal atoms directly change these parameters is not clear. It is interesting to note that the ^{31}P NMR chemical shifts of the group-6 metal complexes having low coordinate phosphorus compounds as a ligand correlate with each other, as shown in Fig. 18.[60—62] and Fig. 19.[60] Good correlation factors include diphosphenes, phosphaethenes, phosphacumulenes, and phosphines. Therefore using this relationship the spectral assignment can be possible in these series of compounds.

Conclusion

Transition metal complexes with low coordinate organophosphorus compounds as a ligand are described in terms of structure and reactivity. As mentioned at the beginning of this article, however, this is not a complete survey of the studies on the transition metal complexes with low coordinate organophosphorus compounds. Studies on phosphaalkynes (RC≡P) and phosphinidenes (RP:) of coordination number 1 as a ligand are missing, which should be briefly mentioned here. The former ligand was first reported by Becker (where R = *t*-Bu)[77] and the chemistry as well as the coordination chemistry has been extensively developed by Regitz,[78] Nixon,[79] Binger,[80] Märkl (where R = Ar),[81] and ourselves.[82] The latter complexes of the terminal phosphinidene type of angular and linear modes, have been char-

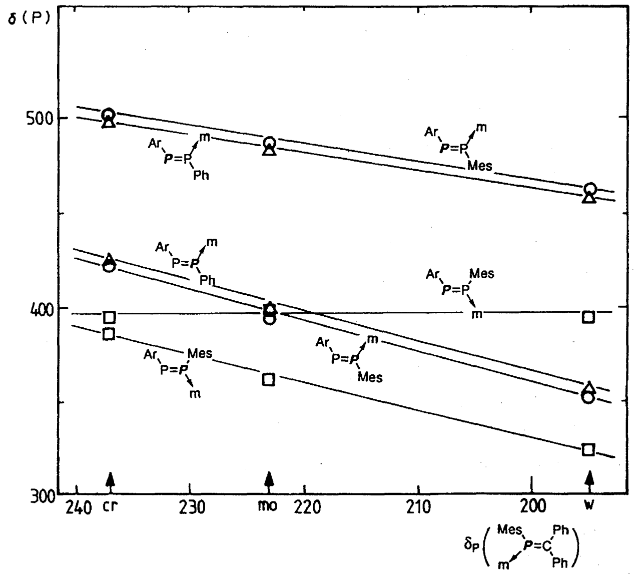


Fig. 18. Plots of δ_P values of some diphosphene transition metal complexes against δ_P [M(CO)$_5$(MesP=CPh$_2$)].[60]

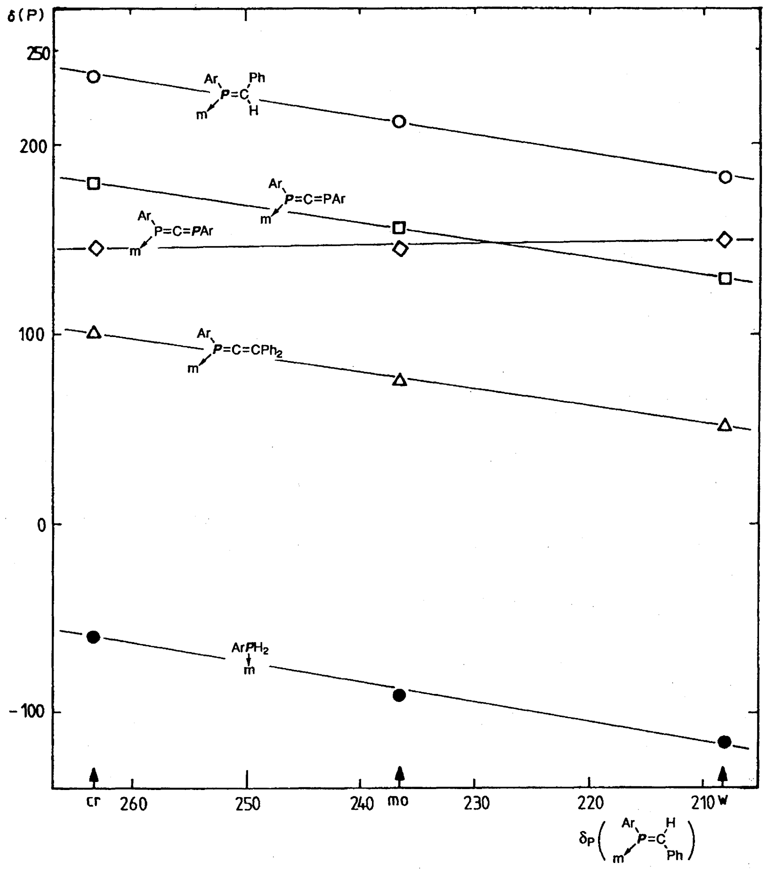


Fig. 19. Plots of δ_P values of group-6 metal complexes of phosphaethenes, phosphaallenes, and primary phosphine against δ_P [M(CO)$_5${(*E*)-ArP=CHPh}].[60]

acterized by Lappert,[83] Cowley,[84] Mathey,[85] Stephan,[86] and many others and the complexes, M (=PR), turn out to be useful in synthetic studies as well as coordination studies.

The structure of the transition metal complexes with low coordinate organophosphorus compounds depends on the ligand and transition metal. Although only a little study has been done on the application of these complexes, there will be a lot of possibilities to utilize such complexes to synthetic as well as structural studies, as suggested in this article.

The support of our work by the Ministry of Education, Science, Sports and Culture, and by the Asahi Glass Science Funds from the Asahi Glass Foundation is greatly acknowledged. The author thanks Prof. Ken Hirotsu at Osaka City University who took the X-ray analyses of most of our earlier compounds described here. He also thanks those whose names are given in the list of references for their dedicated collaboration.

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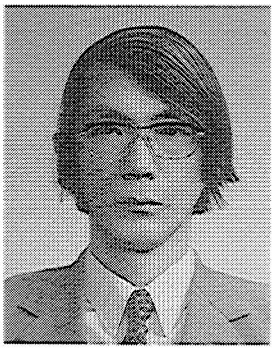

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