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Preparation of Group-6 Metal(0) Carbonyl Complexes of Chelate Type Containing Diphosphinidenecyclobutene as a Bidentate Ligand

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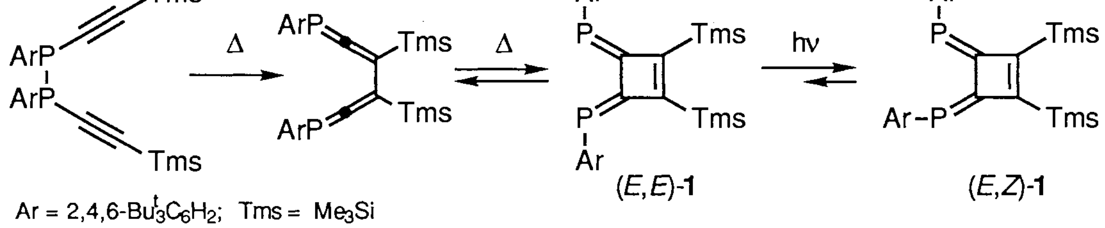
(*E*,*E*)-3,4-Bis(2,4,6-tri-*t*-butylphenylphosphinidene)-1,2-bis(trimethylsilyl)cyclobutene was allowed to react with the group-6 metal(0) carbonyls to give stable tetracarbonyl complexes of chelate type, where the metal is chromium, molybdenum, and tungsten.

Bidentate diphosphane ligands 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.1) In contrast, bidentate ligands containing phosphorus-carbon double bond are rarely used because of their instability at the low coordinated phosphorus atom. However, our recent strategy of steric protection using bulky substituents has permitted us to isolate such unusual compounds as stable species.2) By introducing an extremely bulky 2,4,6-tri-*t*-butylphenyl group (hereafter abbreviated to the Ar group) into a molecule, we have been successful in preparation of 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 have been prepared by Appel *et al.*6,7)

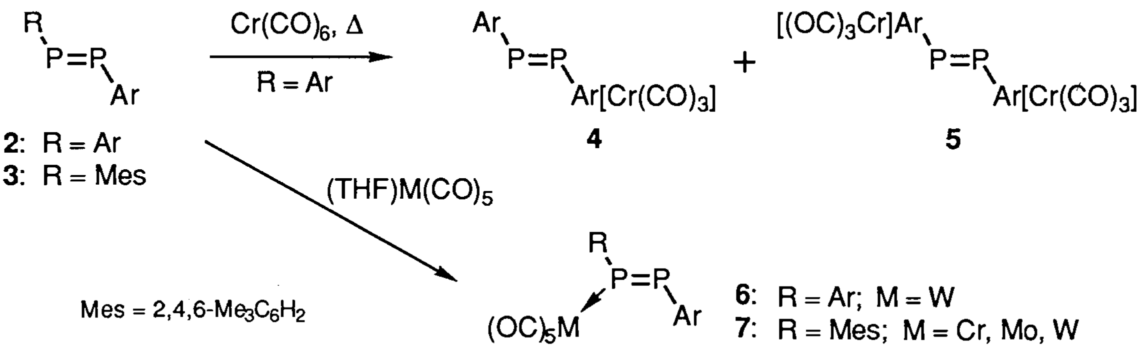
Recently, we have prepared (*E*,*E*)- and (*E*,*Z*)-3,4-bis(2,4,6-tri-*t*-butylphenylphosphinidene)cyclobutenes **1** *via* sigmatropic rearrangement from a diethynyldiphosphane and/or a 1,6-diphospha-1,2,4,5-hexatetraene.8) The diphosphinidenecyclobutenes (*E*,*E*)- and (*E*,*Z*)-**1** are regarded as conformationally rigid bidentate phosphorus ligands like dppe or BINAP, since they should be planar molecules of dimethylenecyclobutene framework. Consequently, the coordination site as well as the metal selectivities of such ligands is of interest. We report here the preparation and characterization of the group-6 metal(0) complexes of (*E*,*E*)-**1** and some attempts to prepare metal(0) complexes of (*E*,*Z*)-**1**.9)

The reaction of the diphosphene **2** with hexacarbonylchromium(0) in refluxing 1,4-dioxane gave π-(arene)-tricarbonylchromium(0) complexes **4** and **5**,10) whereas the reactions of **2** and **3** with (THF)M(CO)$_5$ (where M = Cr, Mo, W; THF = tetrahydrofuran) afforded the *P*-coordinated complexes **6** and **7**, respectively.11)



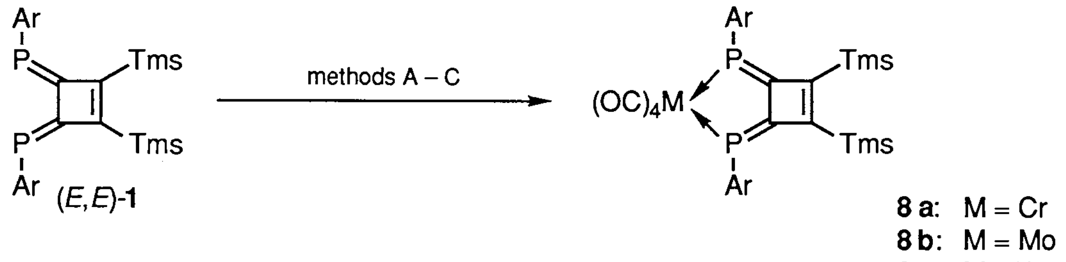
(*E*,*E*)-**1** (*E*,*Z*)-**1**

Ar = 2,4,6-$Bu^t_3C_6H_2$; Tms = Me_3Si



The reaction of (*E*,*E*)-**1** with hexacarbonylchromium(0) in refluxing dioxane (method A) afforded dark red complex **8a** of not the arene-complexation type. Thus, a solution of (*E*,*E*)-**1** (50.9 mg, 0.068 mmol) and Cr(CO)$_6$ (77.4 mg, 0.35 mmol) in dioxane (4.5 ml) was refluxed in the dark for 24 h. Removal of the solvent under reduced pressure followed by flash column chromatography (SiO$_2$ / pentane) afforded 39.6 mg (64%) of **8a**. Interestingly, the reaction of (*E*,*E*)-**1** with excess (THF)Cr(CO)$_5$ (5 mol equiv.) in THF at room temperature for 3 h (method B) afforded also the complex **8a** in 73% yield. **8a**: dark red crystals; mp > 145 °C (decomp); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.49 (4H, s, arom.), 1.68 (36H, s, *o*-Bu^t), 1.33 (18H, s, *p*-Bu^t), and −0.34 (18H, s, SiMe$_3$); ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$) δ 198.4; ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$) δ 228.0 (d, $^{2}J_{PC}$ = 8.1 Hz, CO), 220.6 (t, $^{2}J_{PC}$ = 17.4 Hz, CO), 181.4 (dd, $^{2}J_{PC}$ = 23.3 Hz and $^{3}J_{PC}$ = 19.2 Hz, P=C–$\underline{\mathrm{C}}$), 172.5 (dd, $^{1}J_{PC}$ = 49.0 Hz and $^{2}J_{PC}$ = 31.2 Hz, P=$\underline{\mathrm{C}}$–C), 156.9 (s, *o*-arom.), 151.9 (s, *p*-arom.), 130.0 (d, $^{1}J_{PC}$ = 8.6 Hz, *ipso*-arom.), 122.8 (d, $^{3}J_{PC}$ = 2.9 Hz, *m*-arom.), 39.0 (s, *o*-$\underline{\mathrm{C}}$Me$_3$), 35.2 (s, *p*-$\underline{\mathrm{C}}$Me$_3$), 34.2 (s, *o*-C$\underline{\mathrm{Me_3}}$), 31.1 (s, *p*-C$\underline{\mathrm{Me_3}}$), and −0.01 (s, SiMe$_3$); UV (hexane) 247 (log ε 4.85), 288 (4.47), and 448 nm (4.23); IR (KBr) 2013, 1928, 1915, and 1886 cm^{-1}; FAB-MS *m*/*z* 911 (M$^+$+1), 826 (M$^+$–3CO), and 798 (M$^+$– 4CO).

Signals of the aromatic ring protons in the ^{1}H NMR spectrum of **8a** appeared in the usual region (7.49 ppm), indicating that it is not the arene complex, since the ^{1}H signals of the metal-coordinated aromatic protons for **4** and **5** appeared elsewhere in the upper field (δ 6.17 and 6.26, respectively). The ^{13}C NMR of **8a** showed two signals in the carbonyl region due to two kinds of carbonyl ligands [δ_C 228.0 (d, J_{PC} = 8.1 Hz) and 220.6 (t, J_{PC} = 17.4 Hz)]. The triplet signals at δ_C 220.6 suggested that the complex is of chelate structure, where the metal atom is equally coordinated by two phosphorus atoms. Thus, we carried out the reaction of (*E*,*E*)-**1** with 1.7 mol equiv. of (bicyclo[2.2.1]hepta-2,5-diene)tetracarbonylchromium(0) in refluxing toluene for 19 h (method C) to result in the formation of the same chromium(0) complex **8a** in 71% yield.



method A: M(CO)$_6$, Δ; method B: (THF)M (CO)$_5$; method C: (*nor*-C$_7$H$_8$)M(CO)$_4$
nor-C$_7$H$_8$ = bicyclo[2.2.1]hepta-2,5-diene

Table 1. Reactions of (E,E)-**1** with Metal(0) Carbonyls

Entry	Method[a)]	Reagent	Mol ratio[b)]	Temp / °C	Time / h	Product	Yield / %
1	A	$Cr(CO)_6$	5.1	100	24	**8a**	64
2	A	$Mo(CO)_6$	5.1	100	1	**8b**	76
3	A	$W(CO)_6$	4.8	100	24	**8c**	8
4	B	$(THF)Cr(CO)_5$	5.0	r.t.	3	**8a**	73
5	B	$(THF)Mo(CO)_5$	5.0	r.t.	3	**8b**	75
6	B	$(THF)W(CO)_5$	4.3	r.t.	3	**8c**	58
7	C	(*nor*-C_7H_8)$Cr(CO)_4$	1.7	110	19	**8a**	71
8	C	(*nor*-C_7H_8)$Mo(CO)_4$	1.5	r.t.	20	**8b**	44
9	C	(*nor*-C_7H_8)$W(CO)_4$	1.5	110	4	**8c**	43

a) Refer to the text. b) Molar ratio: metal(0) carbonyl reagent / (E,E)-**1**.

Similar results were obtained in the reactions of molybdenum and tungsten carbonyl complexes, *i.e.* chelate complexes **8b** and **8c** were obtained regardless of the types of the starting carbonyl complexes used for the reactions with (E,E)-**1**. The yields of **8b** and **8c** by methods A, B, and C under various reaction conditions are listed in Table 1. The formation of molybdenum complex **8b** seems to be the most facile among the three metal complexes. The tungsten complex showed satellite peaks due to ^{183}W in ^{31}P NMR spectrum ($^1J_{PW}$ = 257.7 Hz), while the coupling constant is within the typical values observed for σ-type tungsten complexes with lowly coordinated phosphorus compounds.[12)] **8b**: dark red crystals; mp > 180 °C (decomp); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.49 (4H, d, $^4J_{PH}$ = 1.2 Hz, arom.), 1.68 (36H, s, o-Bu^t), 1.32 (18H, s, p-Bu^t), and −0.33 (18H, s, $SiMe_3$); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ 181.0; ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 216.8 (dd, $^2J_{PC}$ = 39.9 Hz and $^2J_{PC}$ = 11.3 Hz, CO), 209.9 (t, $^2J_{PC}$ = 11.9 Hz, CO), 182.1 (dd, $^2J_{PC}$ = 22.0 Hz and $^3J_{PC}$ = 19.7 Hz, P=C–$\underline{C}$), 173.1 (dd, $^1J_{PC}$ = 49.3 Hz and $^2J_{PC}$ = 31.0 Hz, P=$\underline{C}$–C), 156.7 (s, o-arom.), 151.8 (s, p-arom.), 129.6 (dd, $^1J_{PC}$ = 5.8 Hz and $^4J_{PC}$ = 4.2 Hz, *ipso*-arom.), 122.7 (pseudo t, J_{PC} = 3.2 Hz, m-arom.), 39.0 (s, o-$\underline{C}Me_3$), 35.2 (s, p-$\underline{C}Me_3$), 34.2 (s, o-C$\underline{Me_3}$), 31.0 (s, p-C$\underline{Me_3}$), and 0.03 (s, $SiMe_3$); UV (hexane) 243 (log ε 4.69), 289 (4.26), and 430 nm (4.21); IR (KBr) 2025, 1934, 1913, and 1892 cm^{-1}; FAB-MS m/z 956 (M$^+$). **8c**: dark red crystals; mp > 205 °C (decomp); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.50 (4H, d, $^4J_{PH}$ = 1.3 Hz, arom.), 1.68 (36H, s, o-Bu^t), 1.33 (18H, s, p-Bu^t), and −0.33 (18H, s, $SiMe_3$); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ 161.3 (satellite, $^1J_{P^{183}W}$ = 257.7 Hz); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 207.0 (d, $^2J_{PC}$ = 31.0 Hz, CO), 204.1 (t, $^2J_{PC}$ = 10.6 Hz, CO), 184.3 (dd, $^2J_{PC}$ = 25.9 Hz and $^3J_{PC}$ = 22.7 Hz, P=C–$\underline{C}$), 172.1 (dd, $^1J_{PC}$ = 52.5 Hz and $^2J_{PC}$ = 33.5 Hz, P=$\underline{C}$–C), 156.9 (s, o-arom.), 152.0 (s, p-arom.), 128.6 (s, *ipso*-arom.), 122.8 (pseudo t, J_{PC} = 3.5 Hz, m-arom.), 39.1 (s, o-$\underline{C}Me_3$), 35.2 (s, p-$\underline{C}Me_3$), 34.3 (s, o-C$\underline{Me_3}$), 31.0 (s, p-C$\underline{Me_3}$), and −0.11 (s, $SiMe_3$); UV (hexane) 242 (log ε 4.33), 286 (3.93), and 428 nm (3.86); IR (KBr) 2021, 1927, 1905, and 1886 cm^{-1}; FAB-MS m/z 1042 (M$^+$), 1014(M$^+$–CO), and 460 (ArPW).

We have reported the linear relationship among the ^{31}P NMR chemical shifts of phosphaalkene-group 6 metal(0) carbonyl complexes.[12)] This correlation is also observed for the complexes **8a**-**c**, where the correlation coefficient was 0.999. It should be noted here that the slope for **8a**-**c** is gentle (0.67) compared to those for other monodentate phosphorus ligands in low coordination state (*ca.* 0.85) since two phosphorus atoms coordinate at one metal center, suggesting chelate structures for **8a**-**c**.

The complexes **8a-c** thus isolated were reluctant to photo-isomerization and no change was observed after 1-h irradiation of **8a** in C_6D_6 with a medium pressure mercury lamp, whereas the free ligand **1** causes facile *E-Z* photoisomerization.[8a)]

Compared to (*E,E*)-**1**, (*E,Z*)-**1** seems not to form metal(0) complex of any kind because of the disfavored configuration of the lone pairs of phosphorus atoms as well as large steric hindrance around the phosphorus atoms. Indeed, (*E,Z*)-**1** remained unchanged under such reaction conditions as with either 5 equiv. of $Cr(CO)_6$ in refluxing dioxane in the dark for 24 h or with 5 equiv. of $(THF)Cr(CO)_5$ in THF in the dark at room temperature for 2 h. No formation of either π-complex on arene or σ-complex at P=C was observed.

In conclusion, (*E,E*)-**1** involving the rigid diphosphinidenecyclobutene structure as a preorganized bidentate ligand formed the group-6 metal(0) carbonyl complexes of chelate type. X-Ray crystal structure analyses of both **8b** and the free ligand (*E,E*)-**1** are in progress as well as preparative work to obtain complexes with metals other than the group 6.

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