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Iminophosphorane Complexes of Palladium(II)

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Iminophosphorane complexes of palladium [$(C_6H_5)_3P$=N–C_6H_4–X-*p*]$PdCl_2(CH_3CN)$ (X=NO_2, **1A**; $COOC_2H_5$, **2A**; Cl, **3A**; H, **4A**; CH_3, **5A**) have been prepared by ligand-substitution reaction between $(C_6H_5CN)_2PdCl_2$ and the parent iminophosphoranes, followed by recrystallization from acetonitrile–ethyl acetate. Other iminophosphoranes (X=OCH_3, and $(C_6H_5)_2(CH_3)P$=N–$Si(CH_3)_3$), however, gave only dimeric complexes with the [(Iminophosphorane)$PdCl_2$]$_2$ composition. Complexes **1A**—**5A** and {[$(C_6H_5)_3P$=N–C_6H_4–X-*p*]$PdCl_2$}$_2$ (X=NO_2, **1B**; $COOC_2H_5$, **2B**; Cl, **3B**; H, **4B**; CH_3, **5B**) are also discussed. The ligand-exchange reaction of **2B** and **5B** with α,α′-bipyridine, $(C_6H_5)_3P$, and $(CH_3O)_3P$ took place, liberating the parent iminophosphorane.

Iminophosphoranes represented as two resonance hybrides, $R_3\overset{+}{P}$–$\overset{-}{N}$R′↔R_3P=NR′, are isoelectronic with phosphorus ylides. Numerous transition metal complexes of phosphorus,[1–10] nitrogen,[11–13] and sulfur[14–16] ylides have recently been prepared. Information on iminophosphorane complexes has, however, been limited to those of V(0),[19] Co(II),[17,18] Cu(II),[17] Mo(0),[20] and W(0),[20] there is no known palladium complex. In this paper, the quantitative preparation of palladium(II) complexes with aryliminotriphenylphosphoranes and *N*-trimethylsilyliminodiphenylmethylphosphorane will be described, and the IR spectra of these complexes will be discussed.

Experimental

All the preparations of the iminophosphorane complexes were carried out under an atmosphere of nitrogen or argon. The IR spectra were recorded on a JASCO Model DS-403G spectrometer calibrated with polystyrene. The proton NMR spectra were recorded on a JEOL C60-HL instrument, with TMS as the internal reference. The analyses were carried out by the Microanalytical Center of Kyoto University, Japan.

Starting Materials. The dichlorobis(benzonitrile)palladium(II) was prepared according to the method of Kharasch *et al.*[21] The *p*-substituted phenyliminotriphenylphosphoranes were obtained by the interaction of dibromotriphenylphosphine with *p*-substituted anilines in the presence of triethylamine.[22] The *N*-trimethylsilyliminodiphenylmethylphosphorane was prepared by a method reported previously.[23]

Preparation of [$(C_6H_5)_3P$=N–C_6H_4–X-p]$PdCl_2(CH_3CN)$ *(X=NO_2, 1A; $COOC_2H_5$, 2A; Cl, 3A; H, 4A; CH_3, 5A).* The preparation of the phenyliminotriphenylphosphorane complex (**4A**) will be described as a representative example. A benzene suspension (10 ml) of dichlorobis(benzonitrile)palladium(II) (0.1046 g, 2.730 mmol) and phenyliminotriphenylphosphorane (0.0964 g, 2.730 mmol) was stirred overnight under an inert atmosphere. Dark brown precipitates (**4B**) were thus obtained quantitatively (0.1437 g). When **4B** was recrystallized from the mixed solvent of acetonitrile–ethyl acetate (1:2) at 0 °C for few days, a black violet microcrystalline complex (**4A**) was obtained. The time required for the recrystallization increased upon substitution of an electron-releasing group on the phenyl ring; it was overnight for *p*-NO_2(**1A**) and *p*-$COOC_2H_5$(**2A**), a few days for *p*-Cl(**3A**) and *p*-H(**4A**), and three months for *p*-CH_3(**5A**). The analytical data and melting points of the complexes are shown in Table 1. The dark brown precipitates, which must be dinuclear complexes **1B-4B**, could not be isolated in an analytical pure form except for **5B**. Consequently, a definitive determination was achieved by means of the monomeric complexes, **1A-5A**, which were obtained by a cleavage of dichlorobridging in the crude **1B-5B** by means of a large volume of acetonitrile.

Preparation of {[$(C_6H_5)_3P$=N–C_6H_4–OCH_3-p]$PdCl_2$}$_2$ *(6B).* A benzene suspension (10 ml) of dichlorobis(benzonitrile)palladium(II) (0.2763 g, 7.204 mmol) and anisyliminotriphenylphosphorane (0.2763 g, 7.204 mmol) was stirred under an inert atmosphere overnight. Dark brown precipitates (**6B**) were thus obtained quantitatively (0.4010 g); they were recrystallized from an acetonitrile–ethyl acetate (1:2) mixed solvent. The resulting crystals were dichlorodi-μ-chlorobis(*p*-anisyliminotriphenylphosphorane)dichloropalladium(II) with one molecule of acetonitrile as the solvent of crystallization; mp 143—145 °C. Found: C, 52.83; H, 4.04; N, 3.37%. Calcd for $C_{52}H_{37}Cl_4N_3O_2P_2Pd_2$: C, 53.73; H, 4.08; N, 3.61%. PMR ($CDCl_3$): τ 8.70 (s, CH_3), τ 6.30 (s, OCH_2), τ 2.16—2.76 (m, C_6H_5 and C_6H_4). IR (KBr disk): 1238 cm^{-1} [ν(P=N)], (free 1334 cm^{-1}; Δν 96 cm^{-1}); 302, 310, 332, and 348 cm^{-1} [ν(Pd–Cl)].

Preparation of {[$(C_6H_5)_2(CH_3)P$=N–$Si(CH_3)_3$]$PdCl_2$}$_2$ *(7B).* To a benzene (8 ml) solution of dichlorobis(benzonitrile)palladium(II) (0.2421 g, 6.325 mmol), *N*-trimethylsilylimino-

Table 1. Analytical data and melting points of aryliminophosphorane complexexes of palladium [$(C_6H_5)_3P$=N–C_6H_4–X-*p*]$PdCl_2(CH_3CN)$

Complex	X	Mp(°C)	Analyses (%)		
			C	H	N
			Found(Calcd)	Found(Calcd)	Found(Calcd)
1A[a)]	NO_2	209—211	50.38(50.63)	3.80(3.60)	6.66(6.81)
2A	$COOC_2H_5$	165—166	53.57(54.10)	4.39(4.23)	4.17(4.35)
3A	Cl	182—185	51.66(51.51)	3.84(3.66)	4.54(4.62)
4A	H	170—171	54.25(54.61)	4.03(4.05)	4.78(4.90)
5A	CH_3	170—172	54.74(55.36)	4.26(4.31)	4.99(4.78)
5B[b)]	CH_3	229—230.5	54.94(55.12)	4.05(4.07)	2.97(2.57)

a) [$(C_6H_5)_3P$=N–C_6H_4–X-*p*]$PdCl_2(CH_3CN)$. b) {[$(C_6H_5)_3P$=N–C_6H_4–X-*p*]$PdCl_2$}$_2$

diphenylmethylphosphorane (0.1410 g, 6.285 mmol) was added under argon. The mixture was then stirred overnight. Orange precipitates were recrystallized from the dichloromethane–*n*-hexane (1: 1) mixed solvent or benzene (0.2301 g, 92%); mp 168—170 °C. Found: C, 41.39; H, 4.68; N, 2.83 %. Calcd for $C_{32}H_{44}Cl_4N_2P_2Si_2Pd_2$: C, 41.35; H, 4.77; N, 3.01%.

*Reaction of α,α′-Bipyridine and Triphenylphosphine with Dichlorodi-μ-chlorobis(*p*-ethoxycarbonyliminotriphenylphosphorane)dipalladium(II) (2B).* A benzene (11 ml) solution of 2B (0.1610 g, 1.335 mmol) and α,α′-bipyridine (0.0417 g, 2.671 mmol) was stirred for one day. Dichloro(α,α′-bipyridine)palladium(II) was precipitated (0.0825 g, 96%) and the parent iminophosphorane was quantitatively liberated in a benzene solution. They were identified by comparison with authentic samples. A similar procedure was used in the reaction of 7B with four equimolar amounts of triphenylphosphine; the reaction gave quantitatively dichlorobis(triphenylphosphine)palladium(II) and the parent iminophosphorane. In the case of two equimolar amounts of triphenylphosphine, the reaction proceeded with one half mole of dichlorobis(triphenylphosphine)palladium(II); one half mol of **7B** was recovered.

*Reaction of Trimethylphosphite with Dichlorodi-μ-chlorobis(*p*-tolyliminotriphenylphosphorane)dipalladium(II) (5B).* To a benzene (7 ml) solution of 5B (0.1627 g, 1.497 mmol), trimethylphosphite (0.0276 g, 5.990 mmol) was added under nitrogen. After the mixture had been stirred at room temperature for 3 hr, the solvent was evacuated. The white residue was recrystallized from chloroform–ether. Dichlorobis(trimethylphosphite)palladium(II) was thus obtained (0.1053 g, 81%).

Results and Discussion

The reaction between dichlorobis(benzonitrile)palladium(II) and aryliminotriphenylphosphorane in benzene took place at room temperature overnight under an inert atmosphere to give dark brown precipitates with the composition of $\{[(C_6H_5)_3P{=}N{-}C_6H_4{-}X{-}p]PdCl_2\}_2$ (X=NO_2, **1B**; $COOC_2H_5$, **2B**; Cl, **3B**; H, **4B**; CH_3, **5B**) in a quantitative yield. When these precipitates, **1B**—**5B**, were recrystallized from an acetonitrile–ethyl acetate (1: 2) mixed solvent, the palladium-chloride bridge of **1B**—**5B** was cleaved with acetonitrile to give $[(C_6H_5)_3P{=}N{-}C_6H_4{-}X{-}p]PdCl_2(CH_3CN)$ (X=NO_2, **1A**; $COOC_2H_5$, **2A**; Cl, **3A**; H, **4A**; CH_3, **5A**). The IR absorptions of the ν(P=N) stretching frequencies of free and complexed aryliminotriphenylphosphoranes, those of the ν(Pd–Cl) region, and those of the ν(C≡N) region are summarized in Table 2.

The difference in stretching frequencies, Δν(P=N), between free and complexed aryliminotriphenylphosphoranes shows that the electron-releasing substituent strengthens the bonding of the Pd–N bond except in the case of the *p*-methyl substituent, as is shown in Fig. 1.

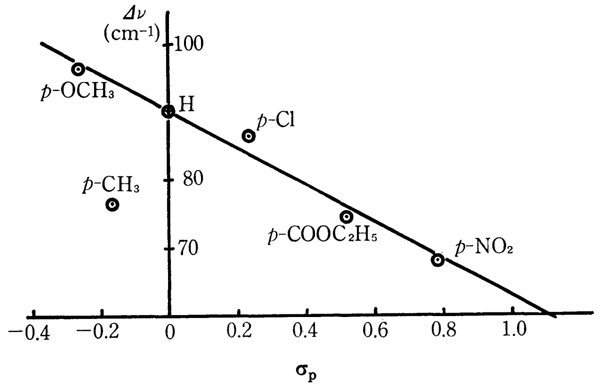
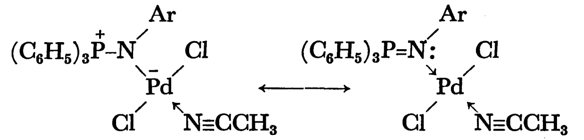


Fig. 1. A correlation between Δν(P=N) and Hammett constants (σ_p) in aryliminotriphenylphosphorane complexes.

There are four ν(Pd–Cl) absorptions in the initially formed dimeric complexes (B); they became a simple band after recrystallization from acetonitrile–ethyl acetate. This fact supports the view that readily coordinating acetonitrile cleaved the dichlorobridging to afford the monomeric complex (A). The PMR spectrum of **5A** also indicates the presence of coordinated acetonitrile at τ 8.00 as a sharp singlet.

Monomeric aryliminotriphenylphosphorane complexes containing acetonitrile as a coordinated ligand can be represented by two resonance structures, the zwitter-ionic form (**C**) and the coordinated form (**D**):



C　**D**

The *trans* configuration of acetonitrile and aryliminotriphenylphosphorane is favorable, since the ν(C≡N) band of the complex was at the higher frequencies [2311—2329 cm⁻¹; each value is closer in order to the complexed ν(P=N) and ν(Pd–Cl) bands] than is that of free acetonitrile (2255 cm⁻¹), as is shown in Table 2. Aryliminotriphenylphosphorane, which has an electron-attracting substituent, displays a weak

Table 2. Infrared spectra of parent iminophosphoranes, $(C_6H_5)_3P{=}N{-}C_6H{-}X{-}p$; bridging dimers, $\{[(C_6H_5)_3P{=}C{-}N{-}C_6H_4{-}X{-}p]PdCl_2\}_2$ (**B**); and mononuclear complexes, $[(C_6H_5)_3P{=}N{-}C_6H_4{-}X{-}p]PdCl_2(CH_3CN)$ (**A**)

Complex	X	ν (P=N) cm⁻¹		Δν(P=N) cm⁻¹	ν (Pd–Cl) cm⁻¹					ν (C≡N) cm⁻¹
		free	complexed **A** and **B**		**B**				**A**	**A**
1	NO_2	1364	1296	68	308	319	329	349	334	2311
2	$COOC_2H_5$	1356	1282	74	303	322	330	341	330	2313
3	Cl	1339	1253	86	295	310	333	361	330	2313
4	H	1338	1248	90	303	312	323	345	322	2315
5	CH_3	1325	1249	76	302	314	327	349	319	2329

trans effect on acetonitrile, which coordinates at the lone pair of the nitrogen atom. Alternatively, the monomeric complex (**A**) exhibits one distinct ν(Pd–Cl) frequency in the region of 319—334 cm^{-1}. This also suggests a *trans*-configuration structure with a higher symmetry.

When a strongly electron-releasing *p*-methoxy substituent was introduced, acetonitrile could not cleave the dichlorobridging and gave only the dimeric complexes (**B**), in contrast to the above complexes (**1**—**5**).

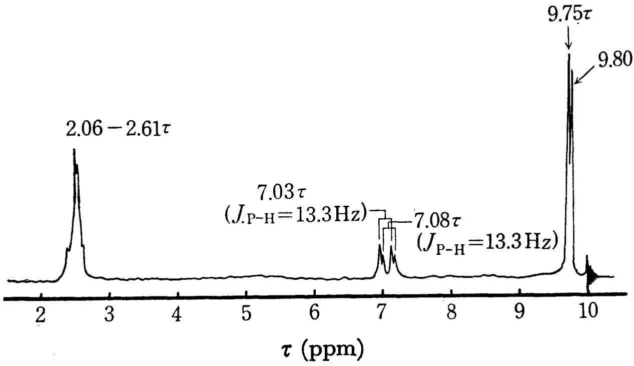
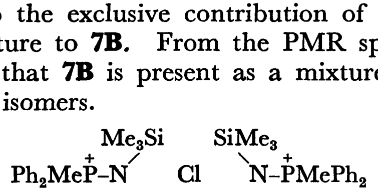
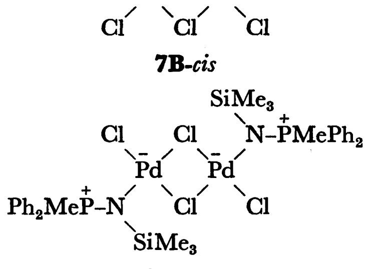


Fig. 2. Proton magnetic resonance spectrum of $\{[(C_6H_5)_2(CH_3)P{=}N{-}Si(CH_3)_3]PdCl_2\}_2$, **7B** in $CDCl_3$.
Proton ratio at τ 7.03: 7.07=2: 1, and τ 9.75: 9.08 =2: 1.

When *N*-trimethylsilyliminodiphenylmethylphosphorane was used instead of *N*-aryliminotriphenylphosphoranes as a ligand, a stable dimeric complex (**7B**) was obtained. The PMR spectrum, shown in Fig. 2, suggests the presence of two isomers. Four ν(Pd–Cl) bands were observed at 306, 328, 350, and 361 cm^{-1}, indicative of a dimeric structure. The ν(P=N) in benzene was observed at 1070 cm^{-1}, 227 cm^{-1} lower than the free ligand (at 1307 cm^{-1} in benzene). Such a large absorption difference compared with the aryliminotriphenylphosphorane complexes may be ascribed to the exclusive contribution of the zwitterionic structure to **7B**. From the PMR spectrum, we concluded that **7B** is present as a mixture of *cis* and *trans* (1: 2) isomers.



7B-*cis*



7B-*trans*

$Ph=C_6H_5$, $Me=CH_3$

Such a zwitter-ionic structure had previously been established by an X-ray analysis of the nickl-phosphorus ylide complex.[24] It is interesting that the Si–N bond in **7B** is quite stable to hydrolysis. Such a stabilization can be explained in terms of the enhanced (2p-3d)π interaction, which is induced by the transmission of the negative charge on the anionic palladium to vacant 3d orbitals on the silicon atom through rehybridized 2p orbitals on the central nitrogen atom.

Finally, the ligand substitution of aryliminotriphenylphosphorane complexes was attempted with **2B**. The coordinated *p*-ethoxycarbonylphenyliminotriphenylphosphorane was selectively liberated by α,α'-bipyridine or triphenylphosphine to give the dichloro(α,α'-bipyridine)palladium(II) or the dichlorobis(triphenylphosphine)palladium(II) complex. A similar result was obtained by the reaction of **5B** with trimethylphosphite. These results suggest that aryliminotriphenylphosphoranes are weaker ligands than α,α'-bipyridine, triphenylphosphine, and trimethylphosphite.

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