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Reactions of Imidoyl-palladium(II) Complexes with Electrophiles

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Synopsis. Imidoyl-palladium(II) complexes, derived from the reactions between imidoyl chlorides and tetrakis(triphenylphosphine)palladium(0), react with perchloric acid or triethyloxonium tetrafluoroborate to give new aminocarbene-palladium(II) complexes.

Tanaka and Alper[1] prepared several (*N*-arylimidoyl)chlorobis(triphenylphosphine)palladium(II) complexes with an oxidative addition of the corresponding imidoyl chlorides to tetrakis(triphenylphosphine)palladium(0). It has been reported that *N*-alkylbenzimidoyl chloride reacts with tetrakis(triphenylphosphine)platinum(0) and gives a few products, which are very difficult to be isolated.[2] This note deals with the preparation of chloro[*N*-(*p*-nitrobenzyl)-*p*-methylbenzimidoyl]bis(triphenylphosphine)palladium(II) (**1a**) and the corresponding *N*-(*p*-nitrophenyl)-*p*-methylbenzimidoyl complex (**1b**) and with the reactions of these imidoyl-palladium(II) complexes toward a few electrophiles. Crociani *et al.*[3] obtained a neutral and a cationic carbene complexes from reactions of chloro(*N*-phenylbenzimidoyl)bis(triphenylphosphine)palladium(II) with HCl and $HClO_4$, respectively.

Experimental

General Procedures. Tetrakis(triphenylphosphine)palladium(0)[4] and chloro[*N*-(*p*-tolyl)benzimidoyl]bis(triphenylphosphine)palladium(II) (**1c**)[1] were prepared according to the published methods. Imidoyl chlorides[5,6] and triethyloxonium tetrafluoroborate[7] were also synthesized according to the reported procedures. IR and ^{1}H-NMR spectra, conductivities and melting points were measured according to the previous paper.[8]

*Preparations of the Imidoyl-palladium(II) Complexes, **1a** and **1b**.* Slight excess imidoyl chloride (0.48 mmol) in benzene solution (10 ml) was added to a benzene solution (20 ml) of $[Pd(pph_3)_4]$ (0.43 mmol), and the reaction mixture was stirred for 1 d at room temperature and concentrated. Addition of hexane to the concentrated reaction mixture gave yellow precipitates. Recrystallization from benzene and hexane yielded the imidoyl-palladium(II) complexes, **1a** and **1b**.

*Reaction of **1a**, **1b**, or **1c** with Perchloric Acid.* To a benzene solution (35 ml) of the imidoyl complex (0.22 mmol) was added perchloric acid (0.24 mmol) in 10 ml of diethyl ether. Off white precipitates formed immediately, which was filtered after stirring for 3 h at room temperature. Recrystallization from dichloromethane and hexane gave the aminocarbene-palladium(II) complex, **2a**, **2b**, or **2c**.

*Reaction of **1a** or **1c** with Triethyloxonium Tetrafluoroborate.* The mixture of **1a** or **1c** (0.29 mmol) and triethyloxonium tetrafluoroborate (0.32 mmol) in dichloromethane (25 ml) was stirred for 1 d at room temperature. Addition of diethyl ether to the concentrated reaction mixture gave the aminocarbene-palladium(II) complex, **3a** or **3c**.

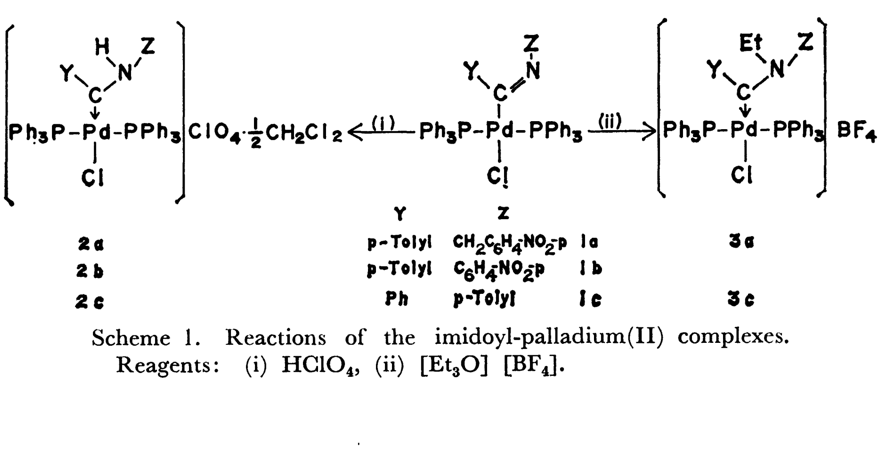
Results and Discussion

N-(*p*-Nitrobenzyl)-*p*-methylbenzimidoyl chloride reacted with equimolar amount of tetrakis(triphenylphosphine)palladium(0) in benzene at room temperature to afford *trans*-chloro[*N*-(*p*-nitrobenzyl)-*p*-methylbenzimidoyl]bis(triphenylphosphine)palladium(II) (**1a**) in good yield, similar to the case of *N*-(*p*-nitrophenyl)-*p*-methylbenzimidoyl chloride and other *N*-arylimidoyl chlorides.[1] Although Tanaka and Alper[1] used two equivalents of the imidoyl chloride, a slightly excess amount of the imidoyl chloride was enough to obtain the imidoyl-palladium(II) complexes in good yield.

Reactions of **1a**, **1b**, and **1c** with perchloric acid gave stable off white crystals **2a**, **2b**, and **2c**, respectively, which contained a half mole of dichloromethane as solvent of crystallization. Complex **1a** and **1c** also reacted with triethyloxonium tetrafluoroborate in dichloromethane to produce **3a** and **3c**, respectively. Elemental analyses, IR and ^{1}H-NMR spectra together with some properties of the complexes prepared in this study are summarized in Tables 1 and 2.

N-(*p*-Nitrobenzyl)imidoyl complex **1a** is fairly unstable and turns pink within a week even under dry nitrogen atmosphere, whereas *N*-arylimidoyl complexes **1b** and **1c** are considerably stable in the same conditions. Trans configurations of **1a** and **1b** were inferred by the similarity of the structures to the complexes of Tanaka and Alper,[1] and ν(Pd–Cl) frequencies of **1a** and **1b** are reasonable (see Table 2).

On the basis of molar conductivities, elemental analyses, IR and ^{1}H-NMR spectra, complexes **2a**—**2c**, **3a**, and **3c** were assigned to new cationic aminocarbene-palladium(II) complexes, which were formed by an addition of a proton or an ethyl group to the secondary



Scheme 1. Reactions of the imidoyl-palladium(II) complexes.
Reagents: (i) $HClO_4$, (ii) $[Et_3O]$ $[BF_4]$.

TABLE 1. YIELD AND PROPERTIES OF THE PALLADIUM(II) COMPLEXES

	Yield	Mp[a]	Color	Found(Calcd), (%)			^{1}H-NMR data (δ-value from TMS)[b]		Λ_M[c]
	%	°C		C	H	N	-CH$_3$	Others	
1a	81	186—198	Off white	65.57 (66.60	4.55 4.71	2.96 3.05)	2.20 s	4.88 s (CH$_2$)	—
1b	85	165—175	Yellow	67.16 (66.31	4.59 4.56	2.88 3.09)	2.25 s	—	—
2a	70	186—198	Off white	58.78 (58.21	4.36 4.27	2.58 2.64)	2.26 s	5.15 d (CH$_2$)[d], 10.40 b (NH) 5.29 s ($\frac{1}{2}$CH$_2$Cl$_2$)	120
2b	65	215—220	Off white	58.22 (57.84	4.18 4.13	2.79 2.67)	2.36 s	5.33 ($\frac{1}{2}$CH$_2$Cl$_2$)[e]	114
2c	95	180—185	Off white	60.71 (60.44	4.24 4.42	1.27 1.40)	2.43 s[f] 2.47 s[f]	—[e]	136
3a	60	190—195	Pale yellow	60.71 (61.47	4.66 4.67	2.71 2.71)	2.26 s	1.16 t (NCH$_2$C$\underline{H}_3$)[g], 4.99 s (CH$_2$)[f] 3.48 q (NC$\underline{H}_2$CH$_3$)[g], 5.04 s (CH$_2$)[f]	128
3c	65	215—220	White	62.56 (63.96	4.66 4.85	1.48 1.43)	—[h]	—[h]	138

a) With decomposition. b) In CDCl$_3$, except for **2c** and **3a**(CD$_2$Cl$_2$). The aromatic protons are omitted. c) Molar conductivity, Ω^{-1} cm^2 mol^{-1}, in 10^{-3} M acetonitrile solution at 25 °C. d) Coupled with NH proton. $^3J=$ 6 Hz. e) NH proton is not observed. f) See the text. g) $^3J=7$ Hz. h) Not detected owing to its high insolubility.

nitrogen atom on the imidoyl ligand. The ^{1}H-NMR spectrum of **2c** showed two singlets at δ 2.43 and 2.47, assignable to two magnetically nonequivalent methyl protons in two isomers as shown in Fig. 1. Complex **3a** also exhibited nonequivalent two methylene resonances of *N*-(*p*-nitrobenzyl) group at δ 4.99 and 5.04. These isomers were caused by the restricted rotation around the C–N bond. Analogous isomerism probably exists in other aminocarbene complexes, in consideration of two ν(Pd–Cl) frequencies in their Far-IR spectra.

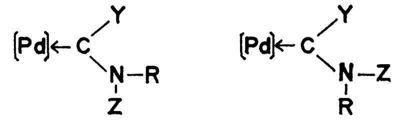


Fig. 1. Isomers for **2**(R=H) and **3**(R=Et).

The ν(Pd–Cl) frequency of the aminocarbene complexes is shifted to a higher wave number relative to that of the corresponding imidoyl complexes. These results indicate that the aminocarbene ligand has a weaker trans influence than the imidoyl one has.[9] On the other hand, the ν(C–N) frequency of the former complexes is lower than the ν(C=N) of the corresponding latter complexes. This is attributable to a decreased carbon–nitrogen bond order in the aminocarbene moiety.

Dimethyl sulfate reacted with **1c**, but gave no isolatable pure product. Other alkylating reagents such as methyl iodide and allyl iodide did not react with the imidoyl complex, and only the starting materials were recovered. This paper presents the first example of ethylation onto the nitrogen atom of an imidoyl ligand.

TABLE 2. IR SPECTRA[a] OF THE PALLADIUM(II) COMPLEXES

	ν(NH)	ν(C-N) {ν(C=N)}[b]	ν(NO$_2$)	ν(ClO$_4$) {ν(BF$_4$)}[c]	ν(Pd-Cl)
1a	—	1590[b]	1350, 1519	—	272
1b	—	1560[b]	1322, 1500	—	273
2a	3152	1561	1340, 1510	1082	301, 309
2b	3149 3206	1544	1337, 1512	1086	300, 310
2c	3202	1556	—	1104	300, 308
3a	—	1565	1340, 1515	1080[c]	301, 311
3c	—	1540	—	1080[c]	305, 312

a) Values in cm^{-1}, in KBr disk. b) ν(C=N) for **1a** and **1b**. c) ν(BF$_4$) for **3a** and **3c**.

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