Cyclic Carbene–Palladium(II) Complexes Derived from the Reactions of Isocyanide–Palladium(II) Complexes with Nitrilimines and Nitrilylides

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(Received July 16, 1980)

cis-[PdCl$_2$(PPh$_2$R^1)(CN–C$_6$H$_4$–CH$_3$-*p*)] (R^1=Ph or Et) reacts with nitrilimines or nitrilylides, derived from the reactions of either *N*-phenylarenecarbohydrazonoyl chlorides or *N*-(*p*-nitrobenzyl)arenecarboximidoyl chlorides with triethylamine, to afford novel cyclic carbene–palladium(II) complexes, *viz.* 1,2,4-triazol-5(4*H*)-ylidene- or 2-imidazolin-5-ylidenepalladium(II) ones, respectively. Halogen exchange reactions of the carbene complexes with lithium bromide or sodium iodide give the corresponding dibromo- or diiodocarbene complexes, respectively. *trans*-[PdI$_2$(PPh$_2$–C$_6$H$_4$–CH$_3$-*p*)(CN–C$_6$H$_4$–NO$_2$-*p*)] also reacts with the nitrilimine or the nitrilylide to produce cyclic carbene–palladium(II) complexes. All the complexes prepared in this study are characterized by elemental analysis, IR and ^{1}H-NMR.

It has been reported that coordinated isocyanide molecules undergo nucleophilic attack by alcohols and amines to yield alkoxyamino- and diamino-carbene complexes, respectively.[1–3] Recently, these carbene complexes have received considerable interest due to their important role in the catalytic formations of formimidates,[4] formamidines,[4] and heterocyclic compounds.[5] It is well known in organic chemistry that 1,3-dipolar compounds such as nitrilimines, nitrilylides, and azides react with dipolarophiles to produce various heterocycles.[6] However, hardly any work has been reported concerning the reactions between metal complexes and the 1,3-dipolar compounds except for diazo compounds.[7–9] It has been reported that tetrakis(*t*-butyl isocyanide)nickel(0) reacts with dicyanodiazomethane to afford bis(*t*-butyl isocyanide)(*N*-*t*-butyldicyanoketenimine)nickel(0),[8] and that (*t*-butyl isocyanide)nickel(0) and -palladium(0) complexes react with diazofluorene to give *N*,*N'*-coordinate complexes.[9]

It is interesting to investigate the reactions of the 1,3-dipolar compounds with isocyanide ligands coordinated to transition metals, as an extension of the 1,3-dipolar cycloaddition reaction. It has been reported from our laboratory that both the nitrilimines[10] and the nitrilylides[11] react with *cis*-dichloro(tertiary phosphine)(*p*-tolyl isocyanide)palladium(II) complexes to afford novel cyclic carbene–palladium(II) complexes. This paper deals both with the details of the reactions mentioned above and with the reactions of the nitrilimine and the nitrilylide with a palladium(II) complex containing *p*-nitrophenyl isocyanide, which increases the electrophilicity of the carbon atom linked to palladium.

Experimental

General. All the experiments were carried out in an atmosphere of dry nitrogen. IR and ^{1}H-NMR spectra, conductivities and melting points were measured according to the previous paper.[12] *N*-Phenylbenzohydrazonoyl chloride **1**,[13] *N*-(*p*-nitrobenzyl)benzimidoyl chloride **2**,[14] diphenyl-*p*-tolylphosphine,[15] and *p*-nitrophenyl isocyanide[16] were prepared according to the published methods. *N*-Phenyl-*p*-toluohydrazonoyl chloride **3** and *N*-(*p*-nitrobenzyl)-*p*-toluimidoyl chloride **4** were synthesized in the analogous way to **1** and **2**, starting from the reactions of *p*-toluoyl chloride with phenylhydrazine and *p*-nitrobenzylamine, respectively. *cis*-Dichloro(triphenylphosphine)(*p*-tolyl isocyanide)palladium(II) **5**[3] and new complexes, *cis*-dichloro(ethyldiphenylphosphine)(*p*-tolyl isocyanide)palladium(II) **6**[3] and di-μ-iodo-diiodobis(diphenyl-*p*-tolylphosphine)dipalladium(II)[17] were synthesized according to the reported procedure with slight modification.

Preparation of trans-*Diiodo(diphenyl-*p*-tolylphosphine)(*p*-nitrophenyl Isocyanide)palladium(II)* **7**. *p*-Nitrophenyl isocyanide (0.78 mmol) was added to di-μ-iodo-diiodobis(diphenyl-*p*-tolylphosphine)dipalladium(II) (0.39 mmol) in dichloromethane (20 ml) and the mixture was stirred for 20 h at room temperature. After the reaction mixture had been evaporated to dryness, the residue was recrystallized twice from dichloromethane and diethyl ether to give reddish orange crystals **7**.

Yields and some properties of the new compounds, **3**, **4**, **6**, and **7** are summarized in Table 1.

*Reactions of **5** or **6** with **1** or **3**.* A benzene solution (10 ml) of triethylamine (6.5 mmol) was added to a benzene suspension (10 ml) containing **5** (0.67 mmol) and **1** (0.81 mmol). After stirring for 24 h at room temperature, the reaction mixture was filtered and the filter cake was washed with water. Recrystallization from dichloromethane and pentane gave white crystals **8a**. Yield 23%, mp 293—295 °C(dec). Complex **8b** or **8d** was also prepared in this manner from the reactions between **5** and **3**, or **6** and **3**, respectively. **8b**; yield 28%, mp 295 °C(dec): **8d**; yield 25%, mp 273 °C(dec).

*Halogen-exchange Reactions of **8a** and **8b** with Lithium Bromide or Sodium Iodide.* A methanol suspension containing **8a**(or **8b**) and five equivalents of lithium bromide was heated under reflux for 8 h. The resulting white solid was separated and washed with methanol to yield **9a**(or **9b**). **9a**; yield 65%, mp>300 °C: **9b**; yield 60%, mp>300 °C. The reaction between **8a** and sodium iodide was carried out in acetone in the same way as described above, and **10a** was produced: yield 70%, mp 275—280 °C(dec).

*Reaction of **5** with **4**.* To a benzene suspension (10 ml) containing **5** (1.14 mmol) and **4** (1.42 mmol) was added triethylamine (14.2 mmol) in 5 ml of benzene, and the reaction mixture was stirred for 4 d at ambient temperature. Addition of diethyl ether and pentane yielded an orange-yellow powder, which was washed with water and purified by passing through a silica gel column (200 mesh, 12ϕ × 150 mm). The eluent was initially benzene/hexane (1/1) and finally acetone. Yellow eluate thus obtained was evaporated to dryness, and the residue was recrystallized from dichloromethane and diethyl ether to produce **11b**: yield 33%, mp 203—204 °C(dec).

*Reactions of **6** with **2** or **4**.* This reaction was carried out in the same way as described for **11b** except for omitting the chromatography technique, and **11c** or **11d** was obtained

Table 1. Yields and properties of the new compounds

Compound	Yield %	Color	Mp °C	Found(Calcd) (%) C	H	N	^{1}H-NMR(δ/ppm)[a)] CH_3	Others
3	44[b)]	Cream	136—137	68.63 (68.71	5.37 5.44	10.94 11.45)	2.34 s	—
4	83[c)]	Greenish yellow	89	62.40 (62.68	4.54 4.59	9.70 9.72)	2.37 s	4.93 s(CH_2)
6	60[d)]	Pale yellow	200—201 (dec)	51.54 (51.94	4.24 4.36	2.67 2.75)	2.40 s	1.38 dt($PCH_2\underline{CH_3}$)[e)] 2.86 dq($P\underline{CH_2}CH_3$)[f)]
7	76[g)]	Reddish orange	176—182 (dec)	39.61 (39.80	2.70 2.70	3.42 3.57)	2.22 s	—

a) In $CDCl_3$ except for **6** (CD_2Cl_2). b) Based on *p*-toluoyl phenylhydrazine. c) Based on *N*-[(*p*-nitrophenyl)-methyl]benzamide. d) Based on *cis*-[$PdCl_2(CN-C_6H_4-CH_3$-*p*$)_2$]. e) $^3J_{PH}=20$ Hz. f) $^2J_{PH}=12$ Hz, $^3J_{HH}=8$ Hz. g) Based on [{$PdI_2(PPh_2-C_6H_4-CH_3$-*p*)}$_2$].

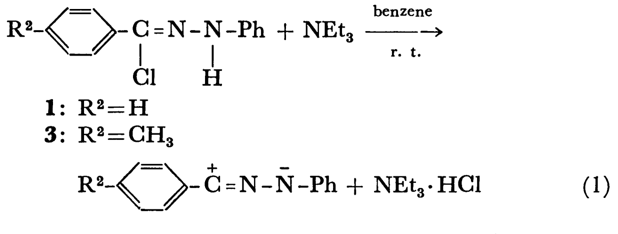
from the reactions between **6** and **2**, or **6** and **4**, respectively. **11c**; yield 35%, mp 187—189 °C(dec): **11d**; yield 33%, mp 189—191 °C(dec).

*Halogen-exchange Reactions of **11c** and **11d** with Lithium Bromide.* These reactions were carried out in acetone in the analogous way as described for **9a**, and yellow crystals, **12c** and **12d** were produced. **12c**; yield 43%, mp 185—190 °C(dec): **12d**; yield 45%, mp 195—198 °C(dec).

*Reaction of **7** with **3** or **4**.* Triethylamine (5.38 mmol) in 10 ml of benzene was added to a benzene solution (10 ml) of **7** (0.45 mmol) and **3**(or **4**) (0.54 mmol), and the reaction mixture was stirred for 3 d at room temperature. After the solvent had been removed under a reduced pressure, the residue was washed with water and recrystallized twice from benzene and hexane to give yellow brown powders **13**(or **14**). **13**; yield 13%, mp 270—275 °C (dec): **14**; yield 7%, mp 208—218 °C(dec).

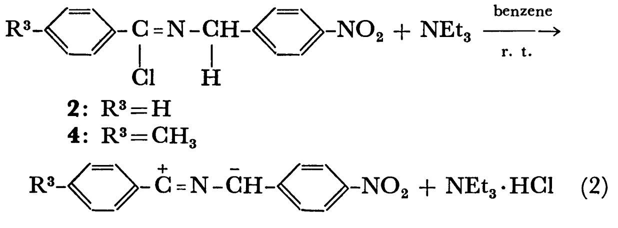
Results and Discussion

The 1,3-dipolar compounds, *N*-phenylarylnitrilimines and nitrilylides can be generated under an inert atmosphere by the reactions of triethylamine with the corresponding *N*-phenylarenecarbohydrazonoyl chlorides (Eq. 1) and *N*-(*p*-nitrobenzyl)arenecarboximidoyl chlorides (Eq. 2), respectively.[6)]



1: $R^2=H$
3: $R^2=CH_3$

(1)



2: $R^3=H$
4: $R^3=CH_3$

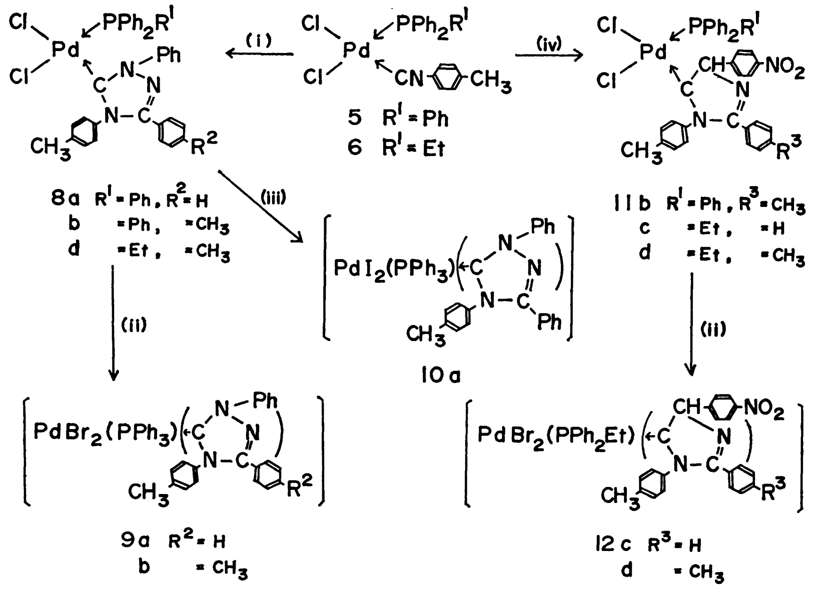
(2)

Reactions of (*p*-tolyl isocyanide)palladium(II) complexes (**5** and **6**) with the nitrilimines and the nitrilylides in benzene at room temperature gave the white complexes **8a—d**[18)] and the yellow complexes **11b—d**,[18)] respectively (Scheme 1). These complexes are very stable in both air and water, and remain unchanged after more than a half year under an inert atmosphere. Elemental analysis, ^{1}H-NMR and IR spectra together with some properties of the new complexes prepared in this work are summarized in Tables 2 and 3.

The IR spectra of **8a—d** lacked the ν(C≡N) frequency observed in the starting complexes (**5**, 2200 cm^{-1}; **6**, 2190 cm^{-1} in KBr disk), and a new band appeared at 1610 cm^{-1}. This band was assigned to a ν(C=N) frequency of the 1,2,4-triazol-5(4*H*)-ylidene group, which was formed by the cycloaddition reaction of the coordinated isocyanide with nitrilimines. The presence of two ν(Pd–Cl) frequencies in **8a—d** (Table 3) is consistent with the *cis* isomer, indicating that during the addition reaction the initial configuration is retained.

As for the ^{1}H-NMR spectrum of **8d** in CD_2Cl_2, the methyl proton resonance of the phosphine moiety appeared at δ 1.01 as a double triplet due to coupling with the ^{31}P nucleus ($^3J_{PH}=21.3$ Hz, $^3J_{HH}=8.2$ Hz). On the other hand, methylene proton signal of the phosphine ligand could not be distiguished clearly owing to overlapping with the two methyl resonances at δ 2.40 and 2.56, which were derived from the isocyanide group and the nitrilimine. A lower field doublet at δ 8.88 (2H, $^3J_{HH}=$*ca.* 8 Hz) was ascribed to the *o*-protons of the *p*-tolyl group derived from the isocyanide. Possible explanations for such a low field shift can be given by an electron transfer from the *p*-tolyl group to the electron-deficient carbene carbon and/or by a close interaction of the *p*-tolyl group with the central palladium metal. Similar signals were also observed in other triazolinylidene complexes **8a** and **8b** at δ 8.60 and 8.58 ($^3J_{HH}=$*ca.* 8 Hz), respectively. As for the ^{13}C-NMR spectrum of **8b**, the carbene signal of the 1,2,4-triazol-5(4*H*)-ylidene moiety was so weak and unresolved that it could not be detected clearly.

Metathetical reactions of **8a** and **8b** with lithium bromide or sodium iodide were performed in refluxing methanol or acetone to produce corresponding dibromo derivatives **9a**, **9b**, or diiodo one **10a**. In contrast to

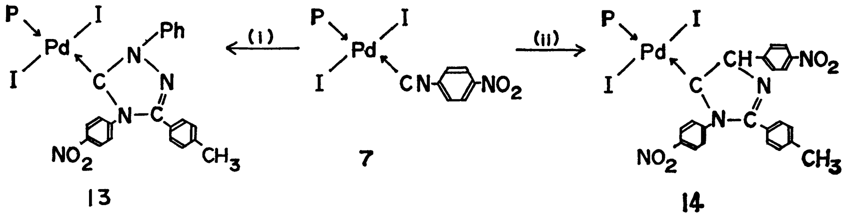


Scheme 1. Reactions of **5** and **6** with nitrilimines or nitrilylides. (i) $p\text{-R}^2\text{-C}_6\text{H}_4\text{-}\overset{+}{\text{C}}\text{=N-}\overset{-}{\text{N}}\text{-Ph}$ ($\text{R}^2=\text{H}$ or CH_3) (ii) $\text{LiBr}\cdot\text{H}_2\text{O}$ (iii) NaI. (iv) $p\text{-R}^3\text{-C}_6\text{H}_4\text{-}\overset{+}{\text{C}}\text{=N-}\overset{-}{\text{C}}\text{H-C}_6\text{H}_4\text{-NO}_2\text{-}p$ ($\text{R}^3=\text{H}$ or CH_3).

Table 2. Elemental analyses and ^{1}H-NMR spectra of the new complexes

Complex	Found(Calcd) (%)			^{1}H-NMR(δ value from TMS)$^{a)}$			
	C	H	N	CH_3		P-$\underline{\text{CH}_2}$-	PCH$_2\underline{\text{CH}_3}$
8a	61.84	4.38	5.43	2.48 $s^{b)}$		—	
	(62.38	4.29	5.60)				
8b	62.48	4.42	5.28	2.46 $s^{b)}$	2.32 $s^{c)}$	—	
	(62.80	4.48	5.28)				
8d	59.83	4.75	5.63	2.56 $s^{b)}$	2.40 $s^{c)}$	*ca.* 2.5$^{d)}$	1.01 dt$^{d)}$
	(60.31	4.78	5.86)				
9a	55.80	3.95	4.85	—$^{e)}$		—$^{e)}$	
	(55.77	3.84	5.00)				
9b	56.24	4.05	4.91	—$^{e)}$		—$^{e)}$	
	(56.26	4.01	4.92)				
10a	49.83	3.36	4.19	—$^{e)}$		—$^{e)}$	
	(50.16	3.45	4.50)				
11b	59.81	4.15	5.00	2.56 br $s^{f)}$,	2.36 br $s^{b)}$	—	
	(60.87	4.24	5.19)				
11c	58.34	4.65	5.87	2.30 br $s^{b)}$		3.16 q	1.34 t
	(57.89	4.32	5.63)				
11d	58.45	4.70	5.64	2.42 br $s^{f)}$,	2.33 br $s^{b)}$	3.18 q	1.34 t
	(58.40	4.50	5.52)				
12c	51.71	4.08	5.01	2.33 br $s^{b)}$		2.5 br	0.9 br
	(51.73	3.86	5.03)				
12d	51.82	4.19	4.88	2.28 br $s^{f)}$,	2.33 br $s^{b)}$	2.5 br	0.9 br
	(52.29	4.03	4.94)				
13	50.98	4.18	5.18	2.42 br $s^{d)}$		—	
	(51.59	3.67	5.23)				
14	50.98	3.64	4.83	2.42 br s,	2.56 br $s^{d)}$	—	
	(50.63	3.53	5.02)				

a) In CDCl_3 for **8a**, **8b**, **13**, and **14**, or in CD_2Cl_2 for **8d**, **11b**—**11d**, **12c**, and **12d**. Aromatic protons are omitted. b) Derived from isocyanide. c) Derived from nitrilimine. d) See the text. e) Not recorded. f) Derived from nitrilylide.



Scheme 2. Reactions of **7** with a nitrilimine and a nitrilylide.
(i) $p\text{-}CH_3\text{-}C_6H_4\text{-}\overset{+}{C}\text{=}N\text{-}\overset{-}{N}\text{-}Ph$. (ii) $p\text{-}CH_3\text{-}C_6H_4\text{-}\overset{+}{C}\text{=}N\text{-}\overset{-}{C}H\text{-}C_6H_4\text{-}NO_2\text{-}p$.

Table 3. IR spectra[a)] and molar conductivities of the new complexes

Complex	$\nu(NO_2)$ cm^{-1}	$\nu(Pd\text{-}Cl)$ cm^{-1}	Λ_M[b)] $\Omega^{-1}\,cm^2\,mol^{-1}$
6	—	336 s, 284 vs	—
8a	—	322 s, 279 vs	—
8b	—	317 s, 277 vs	—
8d	—	318 s, 274 vs	—
11b	1505, 1330 vs	272 br s	19.9[c)]
11c	1510, 1330 vs	269 br s	11.5[c)], 0.63[d)]
11d	1510, 1330 vs	261 br s	10.5[c)]

a) Values in KBr disk. b) Molar conductivity in 10^{-3} mol dm^{-3} solution at 25 °C. c) In acetone. d) In dichloromethane. $\Lambda_M = 91.3\ \Omega^{-1}\,cm^2\,mol^{-1}$ in 0.24×10^{-3} mol dm^{-3} methanol solution.

the moderate solubility of **8a**—**d** in dichloromethane, these dibromo or diiodo complexes have very low solubility in this solvent, and so ^{1}H-NMR spectra could not be obtained.

On the basis of these results and the elemental analyses, **8a**—**d**, **9a**—**b**, and **10a** are assigned to new cyclic carbene–palladium(II) complexes, which are formed by the 1,3-dipolar cycloaddition reactions of nitrilimines onto the C≡N triple bond of the coordinated isocyanide ligand.

Complexes **11b**—**d** were also ascribed to novel cyclic carbene–palladium(II) complexes containing a 2-imidazolin-5-ylidene group, which was formed by the reaction of nitrilylides with the ligating isocyanide in the analogous way as described for **8a**—**d** (Scheme 1). In the IR spectra of **11b**—**d**, both the ν(C=N) band at 1590 cm^{-1}, associated with the 2-imidazolin-5-ylidene group, and the $\nu(NO_2)$ band of the nitrilylide moiety were observed (Table 3). The far-IR spectra of **11b**—**d** showed only one broad band due to ν(Pd–Cl) frequency ranging from 261 to 272 cm^{-1}, in contrast to two bands in **8a**—**d**. It is known that ν(Pd–Cl) frequencies in *trans*-[$PdCl_2L_2$] fall in the range of 357—5 cm^{-1} [19)] and is almost insensitive of the ligand L. This suggests that **11b**—**d** have a *cis* configuration rather than a *trans* one, and broadening of the band probably comes from the partial overlapping of two bands.

As for the ^{1}H-NMR spectra of **11c** and **11d**, the ethyl resonances of the phosphine moiety were observed at rather low field in comparison with those of **8d**. This suggests that a relatively stronger electron transfer from the phosphine ligand to the carbene moiety is present in **11b**—**d**. Complex **11b**, which has a weaker σ-donor ability ligand, triphenylphosphine, instead of ethyldiphenylphosphine, always contains some amounts of triethylamine, unless a column chromatography purification is performed. This triethylamine probably interacts with the electron-deficient carbene carbon and forms a weak ylidic bond. This fact also supports the deshielded ethyl resonance of the phosphine ligand. The methine proton resonance of the 2-imidazolin-5-ylidene moiety could not be distinguished because of its overlapping with phenyl signals.

Molar conductivity of **11b**—**d** (Table 3) exhibited rather high values in acetone and methanol attributable to the dissociation equilibria as shown in Eq. 3. However, **11c** behaved as a nonelectrolyte in dichloromethane showing a very low molar conductivity value. These facts indicate that the solvent which has coordinating ability, displaces the chloro ligand linked to palladium to afford ionic species.

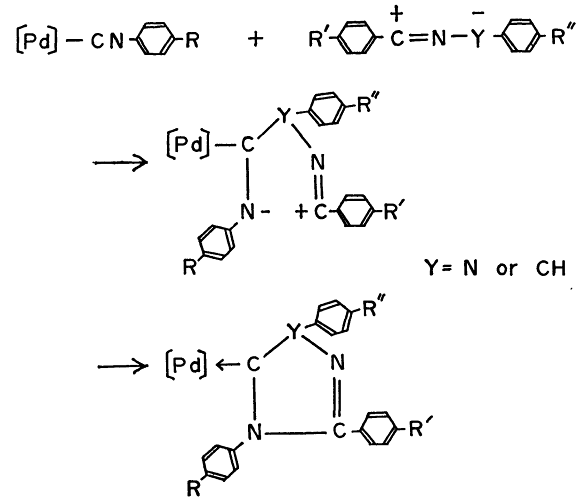
$$[PdCl_2(\text{Phosphine})(\text{Carbene})] + \text{Solv.} \rightleftharpoons [PdCl(\text{Phosphine})(\text{Carbene})(\text{Solv})]^+ + Cl^- \quad (3)$$

Complexes **11c** and **11d** reacted with lithium bromide in the analogous way as described for **9** to afford dibromo derivatives **12c** and **12d**, respectively. In the ^{1}H-NMR spectra of these two complexes, the splitting of the ethyl signals was not observed clearly owing to their fairly low solubility in CD_2Cl_2 or $CDCl_3$. It is not obvious whether *trans-cis* isomerization took place during the metathetical reaction or not.

A new (*p*-nitrophenyl isocyanide)palladium(II) complex **7** was synthesized from the reaction of di-μ-iodo-diiodobis(diphenyl-*p*-tolylphosphine)dipalladium(II) with *p*-nitrophenyl isocyanide in dichloromethane at room temperature, and reacted with the nitrilimine or the nitrilylide to produce **13** or **14**, respectively, similar to the cases of **5** and **6**. Complexes **13** and **14** contain one molecule of benzene as a solvent of crystallization (δ 7.38 in their ^{1}H-NMR).

The IR spectra of these two complexes lacked the C≡N stretching frequency at 2180 cm^{-1}, which was observed in the original complex **7**. The $\nu(NO_2)$ bands were also observed at 1490, 1320 (for **13**), and 1510, 1240 cm^{-1} (for **14**), but ν(C=N) bands were obscured owing to overlapping with the absorptions of benzene at 1590 cm^{-1}. The ^{1}H-NMR spectrum of **13** showed only one broad methyl resonance, which possibly arises from an accidental coincidence of the two methyl resonances in both the nitrilimine and the phosphine moieties. On the other hand, **14** showed two methyl resonances derived from the nitrilylide and the phosphine ligand, but the assignment of these resonances could not be performed.

A stepwise mechanism was proposed for the reactions of ligating isocyanides with the 1,3-dipolar compounds resulting in the formation of cyclic carbene–palladium(II) complexes, analogous to the mechanism for nucleophilic attack of amine on the ligating isocyanide.[2] It may involve a nucleophilic attack of the anion of the 1,3-dipolar compound upon the isocyanide carbon to result in the formation of an amide anion. Subsequently, the ring closure took place between the amide anion and a carbonium ion of the 1,3-dipolar compound to yield the cyclic carbene complex (Eq. 4).



(4)

Another 1,3-dipolar compound, *p*-tolyl azide, reacted with **7** in refluxing benzene, but gave no isolable product. In the case of the reaction with **5**, only the starting materials were recovered.

We wish to express our gratitude to Professor Keinosuke Hamada and Mr. Hirofumi Morishita of Nagasaki University for far-IR measurements, and also to Mrs. Hisako Mazume and Miss Yumi Kojima of Nagasaki University for their technical assistance.

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18) Suffix **a** or **b** represents the products which contain both PPh_3 and the cyclic carbene moiety derived from the *C*-phenyl- or *C*-*p*-tolyl-typed 1,3-dipolar component, respectively. Similarly, suffix **c** or **d** does the products which involve both PPh_2Et and the cyclic carbene moiety derived from the *C*-phenyl- or *C*-*p*-tolyl-typed 1,3-dipolar component, respectively.

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