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REACTIONS OF ISOCYANIDE-PALLADIUM(II) COMPLEXES WITH NITRILIMINES. NOVEL CYCLIC CARBENE-PALLADIUM(II) COMPLEXES

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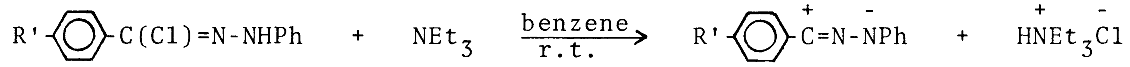
cis-$[PdCl_2(PPh_2R)(CN\text{-}C_6H_4\text{-}CH_3\text{-}p)]$ (R=Ph or Et) reacted with nitrilimines, derived from *N*-phenylarylcarbohydrazonyl chlorides and triethylamine, to afford novel cyclic carbene-palladium(II) complexes, *cis*-$[PdCl_2(PPh_2R)\{CN(C_6H_4\text{-}CH_3\text{-}p)C(C_6H_4\text{-}R'\text{-}p)\text{=}N\text{-}NPh\}]$.

It has been reported that an isocyanide ligand coordinated to transition metals reacts with amine or alcohol to give stable diamino- or alkoxyamino-carbene complexes.[1,2] Interest in these reactions led us to investigate the reactions of the isocyanide-palladium(II) complexes with nitrilimines, which were derived from *N*-phenylarylcarbohydrazonyl chlorides and triethylamine.[3]



A benzene solution of triethylamine was added to a benzene suspension of *cis*-dichloro(*p*-tolyl isocyanide)triphenylphosphinepalladium(II)[4] **1** and *N*-phenylbenzenecarbohydrazonyl chloride.[3] The suspension was stirred for 24 h at room temperature and turned brownish yellow. The resulting solid was collected, washed with water, and recrystallized from dichloromethane and *n*-pentane to give white powder **2**. *N*-Phenyl-*p*-toluenecarbohydrazonyl chloride[5] reacted similarly with **1** and triethylamine to afford **3**. Metathetical reactions of **2** and **3** with lithium bromide in refluxing methanol gave corresponding dibromo derivatives **4** and **5**, respectively. A new isocyanide-phosphine-palladium(II) complex, *cis*-$[PdCl_2(PPh_2Et)(CN\text{-}C_6H_4\text{-}CH_3\text{-}p)]$ **6**, prepared from *cis*-dichlorobis(*p*-tolyl isocyanide)palladium(II) and ethyldiphenylphosphine in chloroform, also reacted with *N*-phenyl-*p*-toluenecarbohydrazonyl chloride and triethylamine to afford **7**.

The complexes, **2**, **3**, **4**, **5**, and **7**, were stable in air and water, and were moderately soluble in dichloromethane and chloroform, and sparingly soluble in benzene.

As for IR spectra, these five complexes lacked the C≡N stretching vibration at *ca*. 2200 cm^{-1}, which was observed in the original complex, **1** or **6**. The former five complexes showed a new band near 1610 cm^{-1}, which was assignable to the C=N stretching vibration of 2,4,5-triaryl-1,2,4-triazolin-3-ylidene group, formed by the cycloaddition reaction between isocyanide group and the nitrilimine.

^{1}H-NMR spectrum of **3** exhibited two methyl resonances, indicating that **3** contained two kinds of *p*-tolyl group, derived from isocyanide group and the nitrilimine. The complex **2**, derived from *N*-phenylbenzenecarbohydrazonyl chloride, showed only one

Table 1. Some properties of the new complexes

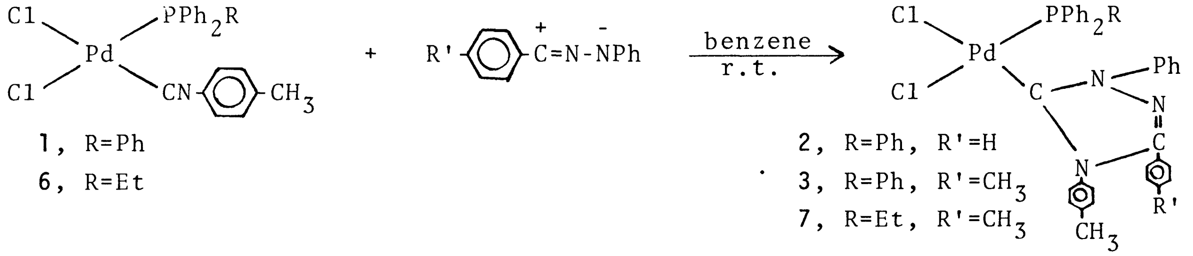
No.	Yield (%)	Color	M.P. (°C)	^{1}H-NMR$^{f)}$ (δ-value from TMS) CH$_3$ (from isocyanide)	CH$_3$ (from nitrilimine)	Ethyl CH$_3$	Ethyl CH$_2$
2	23$^{a)}$	White	293-295(dec.)	2.48			
3	28$^{a)}$	White	295(dec.)	2.46	2.32		
4	65$^{b)}$	Yellow-white	>300	2.60			
5	60$^{c)}$	White	>300	2.60	2.43		
6	50$^{d)}$	Pale-yellow	200-201(dec.)	g) 2.40		1.38	2.86
7	25$^{e)}$	White	273(dec.)	g) 2.56	2.40	1.01	*ca.* 2.5

a) from **1**. b) from **2**. c) from **3**. d) from *cis*-[PdCl$_2$(CN-C$_6$H$_4$-CH$_3$-*p*)$_2$]. e) from **6**. f) CDCl$_3$ was used as solvent unless noted elsewhere. Phenyl proton resonances are omitted. g) Solvent: CD$_2$Cl$_2$. See the text about ethyl resonance of **7**.

methyl resonance. Furthermore, **7** exhibited both two methyl resonances (Table 1) and an ethyl one [CH$_3$ at δ 1.01 ppm, *J*(P-CH$_3$)=21.3 Hz, *J*(CH$_2$-CH$_3$)=8.2 Hz; CH$_2$ overlapped with the former methyl resonances], indicating that **7** contained both ethyldiphenylphosphine and the 2,4,5-triaryl-1,2,4-triazolin-3-ylidene group.

On the basis of these results and elemental analyses, **2**, **3**, and **7** were assigned to new cyclic carbene complexes which were produced by the cycloaddition reaction between nitrilimines and coordinated isocyanide moiety of **1** or **6**.

Lower field methyl resonance of **7** was attributed to the methyl group derived from isocyanide moiety, in comparison with the shift of the methyl resonance caused by the conversion to **2** or **3** from **1** (**1**. *p*-CH$_3$ δ=2.28).



1, R=Ph
6, R=Et

2, R=Ph, R'=H
3, R=Ph, R'=CH$_3$
7, R=Et, R'=CH$_3$

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