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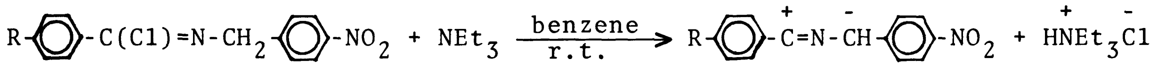
REACTIONS OF AN ISOCYANIDE-PALLADIUM(II) COMPLEX WITH NITRILYLIDES

Katsuma HIRAKI and Yoshio FUCHITA
Department of Industrial Chemistry, Faculty of Engineering,
Nagasaki University, Bunkyo-machi, Nagasaki 852

cis-$[PdCl_2(PPh_2Et)(CN-C_6H_4-CH_3-p)]$ reacted with nitrilylides, derived from *N*-[(*p*-nitrophenyl)methyl]arylcarboximidoyl chlorides and triethylamine, to afford novel cyclic carbene-palladium(II) complexes,
cis-$[PdCl_2(PPh_2Et)\{\overline{CN(C_6H_4-CH_3-p)C(C_6H_4-R-p)=N-C}H(C_6H_4-NO_2-p)\}]$.

The reactions of an isocyanide ligand coordinated to transition metals with various nucleophiles such as alcohols and amines have been widely studied.[1,2,3] We previously reported that nitrilimines undergo 1,3-dipolar cycloaddition onto the C≡N bond in coordinated isocyanide ligand and produce cyclic carbene-palladium(II) complexes.[4] As an extension of our previous work, reactions of an isocyanide-palladium(II) complex with nitrilylides,[5] yielded from *N*-[(*p*-nitrophenyl)methyl]arylcarboximidoyl chlorides and triethylamine, were investigated.



A benzene solution of triethylamine was added to a suspension of *cis*-dichloroethyldiphenylphosphine(*p*-tolyl isocyanide)palladium(II)[4] 1 and *N*-[(*p*-nitrophenyl)-methyl]benzenecarboximidoyl chloride.[5] The suspension gradually changed from yellow to orange homogeneous solution. After being stirred for three days at room temperature, the mixture was filtered off and the filtrate was concentrated by evaporating the solvent. Addition of diethyl ether to the concentrated solution precipitated yellow powder, which was washed with hot water and recrystallized from dichloromethane and diethyl ether to give yellow powder 2: yield 35%; m.p. 187-189°C(dec.). Found: C, 57.11; H, 4.38; N, 5.45%. Calcd for $C_{36}H_{32}Cl_2N_3O_2PPd$: C, 57.89; H, 4.32; N, 5.63%.

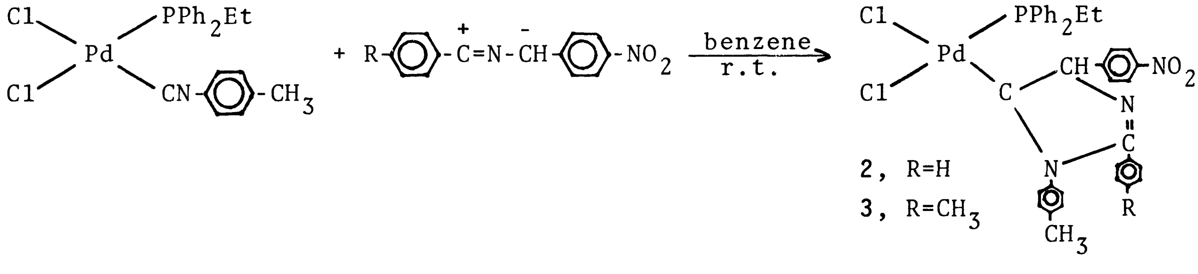
A new compound *N*-[(*p*-nitrophenyl)methyl]-*p*-toluenecarboximidoyl chloride, prepared from *p*-methyl-*N*-[(*p*-nitrophenyl)methyl]-benzamide and thionyl chloride, also reacted with 1 in the presence of triethylamine to afford yellow powder 3: yield 33%; m.p. 189-191°C(dec.). Found: C, 58.45; H, 4.70; N, 5.64%. Calcd for $C_{37}H_{34}Cl_2N_3O_2PPd$: C, 58.40; H, 4.50; N, 5.52%.

Halogen metathetical reactions of 2 and 3 with lithium bromide in refluxing acetone gave corresponding dibromo derivatives 4 and 5, respectively: 4, yield 43%; m.p. 185-190°C(dec.). Found: C, 51.71; H, 4.08; N, 5.01%. Calcd for $C_{36}H_{32}Br_2N_3O_2PPd$: C, 51.73; H, 3.86; N, 5.03%. 5, yield 45%; m.p. 195-198°C(dec.). Found: C, 51.82; H, 4.19; N, 4.88%. Calcd for $C_{37}H_{34}Br_2N_3O_2PPd$: C, 52.29; H, 4.03; N, 4.94%.

All these new complexes **2**, **3**, **4**, and **5** are stable in air and water, and are soluble in common organic solvents except for petroleum ether and diethyl ether. Molar conductivity values of **2** and **3** in acetone solution (10^{-3} M. at 25°C) are 11.5 and 10.5 ohm^{-1}cm^{2}mol^{-1}, respectively, indicating that they are non-electrolytes.

As for the IR spectra of the complexes **2**, **3**, **4**, and **5**, the ν(C≡N) band observed in the original complex **1** (2190 cm^{-1}) was absent. A medium strong band at 1590 cm^{-1} was newly observed, which was assignable to ν(C=N) band of 1,2,4-triarylimidazolin-5-ylidene group, formed by the cycloaddition reaction between isocyanide group and the nitrilylides. Furthermore, $\nu_s(NO_2)$ and $\nu_{as}(NO_2)$ bands were observed at 1330 and 1510 cm^{-1}, respectively. The ^{1}H-NMR spectrum of **2** exhibited an ethyl resonance (δ 1.34 and 3.16 for methyl and methylene protons, respectively) and a methyl one (δ=2.30), and that of **3**, derived from *N*-[(*p*-nitrophenyl]methyl]-*p*-toluenecarboximidoyl chloride, exhibited two methyl resonances (δ=2.33, 2.42) besides an ethyl one.

These results indicate that the complexes **2** and **3** contain both ethyldiphenylphosphine and the 1,2,4-triarylimidazolin-5-ylidene group. In conclusion, nitrilylides as well as nitrilimines undergo 1,3-dipolar cycloaddition reaction onto the C≡N bond in coordinated isocyanide ligand to produce novel cyclic carbene-palladium(II) complexes.



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