

Isocyanide Insertion into the Palladium–Carbon Bond of [PdMe(L–L)Cl] Complexes and the Reactivity of the Products toward Norbornadiene; X-Ray Crystal Structure of [Pd{C(=NC₆H₃Me₂-2,6)Me}(bpy)Cl] [L–L = bpy or phen]

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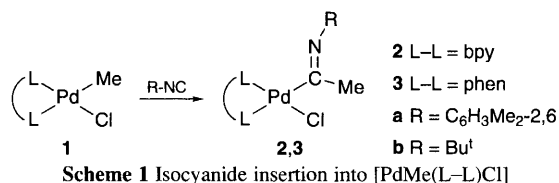
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The first examples of isocyanide insertion into methyl–palladium–chloride complexes containing 2,2'-bipyridine (bpy) and phenanthroline (phen), the X-ray crystal structure of [Pd{C(=NC₆H₃Me₂-2,6)Me}(bpy)Cl] and the novel insertion of norbornadiene into the Pd–C(=NR)Me bond are presented; the insertion mechanism of isocyanides involves displacement of the chloride and a subsequent, slower migration of the methyl group to the pre-coordinated isocyanide.

The alternating insertion of carbon monoxide and alkenes into palladium–carbon bonds leads to the formation of polyketones.^{1–5} For palladium complexes containing bidentate nitrogen ligands the stepwise insertion reactions have been observed and the intermediates isolated.^{6,7} For some systems the detailed kinetics, at low temperatures, have been unravelled.⁸ It has been reported that isocyanides, which are isoelectronic with CO, also insert into palladium–carbon bonds of complexes containing phosphine ligands.^{9–12} We are interested whether this reaction would also occur with complexes containing bidentate nitrogen ligands, since sometimes insertion reactions of these complexes are faster than those of phosphine complexes.¹³ Moreover, the direct synthesis of the polyimine analogue of polyketone would be of great interest.

Here we describe the insertion of 2,6-dimethylphenyl isocyanide and *tert*-butyl isocyanide into the palladium–carbon bond of [PdMe(bpy)Cl] and [PdMe(phen)Cl] to provide the yellow products [Pd{C(=NR)Me}(bipy)Cl] **2** and [Pd{C(=NR)Me}(phen)Cl] **3** (see Scheme 1).

This insertion reaction proved to be quantitative when 1.0 equiv. isocyanide was used in dichloromethane, while substitution of the bidentate nitrogen ligand was observed when more than 1 equiv. of the isocyanide was added. Insertions of 2,6-Me₂C₆H₃NC have been carried out at 294 K, while insertions of Bu^tNC were done at 273 K, with slow warming of the reaction mixture because otherwise uncharacterized side products were formed. The products have been characterized by ¹H and ¹³C NMR and IR spectroscopy and elemental analysis. The C=N stretch frequencies of the products **2** and **3** can be



distinguished in the IR spectrum at *ca.* 1630 cm^{–1} (see Table 1) and in the ¹³C NMR spectrum the carbon of the C=N fragments can be observed at *ca.* δ 184 (see Table 1), which are both normal values.^{9,14}

Crystals of **2a** suitable for X-ray diffraction were obtained from slow diffusion of hexanes into a solution of the complex in dichloromethane. The molecular structure is presented in Fig. 1† and shows the expected insertion product. This structure displays a square-planar surrounding of the palladium atom and a perpendicular C=N–R plane with regard to the palladium plane.

The insertion process not only depends on the nature of the isocyanide but also on the bidentate nitrogen ligand. The type of ligand that may be used is limited to strongly coordinating

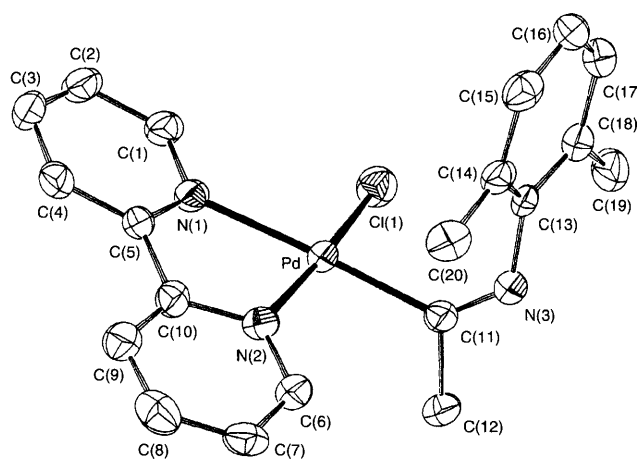


Fig. 1 Molecular structure of **2a**. The hydrogen atoms and CH₂Cl₂ are omitted for clarity. Selected bond lengths (Å): Pd–Cl(1) 2.3081(18), Pd–N(1) 2.146(5), Pd–N(2) 2.066(5), Pd–C(11) 1.976(5), N(3)–C(11) 1.258(8). Selected bond angles (°): N(1)–Pd–N(2) 78.91(19), Cl(1)–Pd–C(11) 89.55(18), N(3)–C(11)–C(12) 119.2(5).

Table 1 Selected spectral data for complexes **2–5**

Compound	L–L	R	IR ν(C=N)(KBr)/ cm ^{–1}	¹ H NMR ^a CH ₃	¹³ C NMR ^b	
					CH ₃	C=N
2a	bpy	C ₆ H ₃ Me ₂ -2,6	1623	2.29	29.1	183.7
2b	bpy	Bu ^t	1636	2.49	29.4	183.4
3a	phen	C ₆ H ₃ Me ₂ -2,6	1629	2.38	29.8	173.4
3b	phen	Bu ^t	1637	2.69	30.2	— ^c
4a	bpy	C ₆ H ₃ Me ₂ -2,6	— ^d	1.94	19.2	197.4
5a	phen	C ₆ H ₃ Me ₂ -2,6	— ^d	2.00	18.9	197.6

^a ¹H NMR in CDCl₃ at 300.13 MHz and 293 K. ^b ¹³C NMR in CDCl₃ at 75.48 MHz and 293 K. ^c Not observed. ^d ν(C=N) is obscured by aromatic frequencies.

ligands like bpy and phen, since for ligands like α -diimine and bis(arylimino)acenaphthene (Ar-BIAN)⁶ substitution of the ligand by isocyanide occurs. The bpy complex is more reactive than the phen complex.

The reaction of [PdMe(bpy)Cl] with Bu^tNC in dichloromethane can also be monitored by IR, ¹H NMR spectroscopy and conductivity measurements. After addition of the isocyanide to a solution of [PdMe(bpy)Cl] in dichloromethane at 273 K, the IR spectrum shows a very intense vibration at 2210 cm⁻¹ which is assigned to an isocyanide, σ -coordinated to palladium^{9,10,15} while in the ¹H NMR spectrum the methyl attached to the palladium atom shifts from δ 1.04 in the starting complex to δ 0.93 in the intermediate complex. Slowly warming the reaction mixture shows a decreasing intensity of the σ -coordinated isocyanide and increasing intensity of the imine C=N vibration at 1643 cm⁻¹ in the IR spectrum. In the ¹H NMR spectrum decreasing intensity of the signal at δ 0.93 and increasing intensity of the signal at δ 2.49 (see Table 1) from product **2b** can be observed.

Addition of Bu^tNC to a solution of [PdMe(bpy)Cl] in acetonitrile at 273 K led to a dramatic increase of the conductivity from 3.6 to 161.7 Ω^{-1} cm² mol⁻¹ in 3 min which indicates that during the reaction the chloride is substituted by the isocyanide to form an ionic intermediate containing a σ -coordinated isocyanide. Subsequent warming of the reaction mixture leads to a decrease in conductivity (10.7 Ω^{-1} cm² mol⁻¹) and apparently the ions recombine to the non-conducting species **2b**.

On the basis of these measurements a mechanism for the isocyanide insertion into the palladium-carbon bond of [PdMe(L-L)Cl] complexes can be postulated which is shown in Scheme 2.

Such a mechanism has been proposed before for palladium complexes containing phosphine ligands.¹⁵ The intermediate containing the σ -coordinated isocyanide can be observed, because migration of the methyl group is relatively slow.

Interestingly, the neutral complexes **2a** and **3a** are very reactive towards norbornadiene insertion analogous to the insertion of norbornadiene into the palladium-carbon bond of the complexes [Pd{C(O)Me}(Ar-BIAN)Cl]⁶ and [Pd{C(OMe)(bpy)Cl}].⁷ The insertion of norbornadiene into the Pd-C(=NR)Me bond, which to our knowledge has never been observed before, takes place quantitatively when the complexes **2a** and **3a** are stirred in dichloromethane with 5 equiv. of norbornadiene for 30 min and for 16 h, respectively (see Scheme 3). The products **4a** and **5a** have been characterized by ¹H and ¹³C NMR spectroscopy and FAB-MS (see Table 1 for selected spectral data).

In the complexes **4a** and **5a** the nitrogen atom of the carboimine group is coordinated to the palladium centre, as is inferred from conductivity data.[‡] Both complexes are very stable compared with the analogous γ -keto-alkyl complexes which decompose within a few minutes.⁷ The strong coordina-

tion of the imine nitrogen compared with a carbonyl oxygen is the probable cause of this stability.

Attempts to insert a subsequent isocyanide into the palladium-carbon bond of complexes **4a** and **5a**, the putative next step in a copolymerization of isocyanides and alkenes, leads to substitution of the bidentate nitrogen ligand by CN-R and no insertion was observed.

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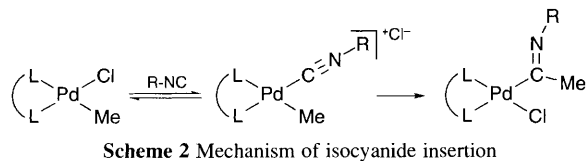
Footnotes

† Crystal data for compound **2a**, C₂₀H₂₀ClN₃Pd·CH₂Cl₂, *M*_r = 529.20, yellowish, cut crystal (0.15 × 0.38 × 0.63 mm), monoclinic, space group *P*2₁/*c* (no. 14) with *a* = 9.0647(11), *b* = 16.405(3), *c* = 16.284(2) Å, β = 117.860(9)°, *U* = 2140.9(5) Å³, *Z* = 4, *D*_x = 1.642 g cm⁻³, *F*(000) = 1064, μ (Mo-K α) = 12.5 cm⁻¹, 9910 reflections measured, 4910 independent, *R*_{int} = 0.080, (1.9° < θ < 27.5°, ω scan, *T* = 150 K, Mo-K α radiation, graphite monochromator, λ = 0.71073 Å) on an Enraf-Nonius CAD4-Turbo diffractometer on rotating anode. Data were corrected for Lp effects and for a linear decay of 1% of the reference reflections, but not for absorption. The structure was solved by automated Patterson methods (DIRDIF92). Refinement on *F*² was carried out by full-matrix least-squares techniques (SHELXL-93); no observance criterion was applied during refinement. Refinement converged at a final *wR*₂ value of 0.1452, *R*₁ = 0.0570 [for 3224 reflections with *F*_o > 4 σ (*F*_o)], *S* = 1.047, for 256 parameters. Weights were optimized in the final refinement cycles. A final difference Fourier map showed no residual density outside -1.95 and 1.22 e Å⁻³ (near Pd). Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

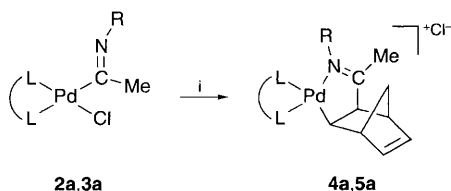
‡ Compound **4a** exhibits a high equivalent conductance of 140.2 Ω^{-1} cm² mol⁻¹ when compared with [PdMe(bipy)Cl] and **2a** (3.6 and 2.7 Ω^{-1} cm² mol⁻¹, respectively).

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Scheme 2 Mechanism of isocyanide insertion



Scheme 3 Reagents and conditions: norbornadiene insertion: R = C₆H₃Me₂-2,6; i, norbornadiene, 293 K, CH₂Cl₂