Monatshefte für Chemie 114, 1045—1051 (1983)

Monatshefte für Chemie
Chemical Monthly

Organometallic Complexes as Ligands. Synthesis of *trans*-$[\mathrm{PdClC(=N}R\mathrm{)\{C_5H_3N(6\text{-}Cl)—}C^2\mathrm{\}(P}Ph_3\mathrm{)_2]}$ $(R = p\text{—}\mathrm{O}Me\mathrm{C_6H_4, CH_3}, c\text{-}\mathrm{C_6H_{11}}, Bu^t)$ and New Information on the Isocyanide Insertion into the Pd—C σ bond

Antonio Mantovani

Istituto di Chimica Industriale, Università di Padova, I-35100 Padova, Italy

(Received 20 December 1982. Revised 21 March 1983. Accepted 22 March 1983)

The pyridyl complex *trans*-$[\mathrm{PdCl\{C_5H_3N(6\text{-}Cl)—}C^2\mathrm{\}(P}Ph_3\mathrm{)_2]}$ easily undergoes insertion of isocyanides into the palladium—carbon bond via an ionic intermediate to give the title compounds. Details on the insertion pathway were obtained through IR, ^{31}P-NMR and conductivity measurements. The presence of the NCCN moiety in the resulting imino(2-pyridyl)methyl palladium(II) complexes is supported by formation of an 1:1 adduct with $CuCl_2$.

(Keywords: Organometallic chemistry; Insertion; Isocyanide)

Organometall-Komplexe als Liganden.
Synthese von trans-$[\mathrm{PdClC(=N}R\mathrm{)\{C_5H_3N(6\text{-}Cl)—}C^2\mathrm{\}(P}Ph_3\mathrm{)_2]}$
$(R = p\text{-}\mathrm{OMeC_6H_4, CH_3}, c\text{-}\mathrm{C_6H_{11}}, Bu^t)$
und neue Befunde zur Isocyanid-Insertion in die Pd—C-σ-*Bindung*

Der Pyridyl-Komplex *trans*-$[\mathrm{PdCl\{C_5H_3N(6\text{-}Cl)—}C^2\mathrm{\}(P}Ph_3\mathrm{)_2]}$ geht leicht — über eine ionische Zwischenverbindung — eine Isocyanid-Insertionsreaktion in die Pd—C-Bindung ein und ergibt dabei die Titelverbindungen. Details über den Ablauf dieser Insertion wurden durch IR, ^{31}P-NMR und Leitfähigkeitsmessungen erhalten. Die Gegenwart von NCCN in den resultierenden Imino(2-pyridyl)methyl-palladium(II)-Komplexen wird durch die Bildung eines 1:1-Addukts mit $CuCl_2$ unterstützt.

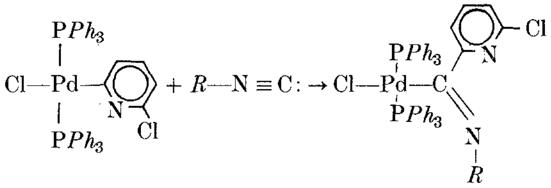
0026-9247/83/0114/1045/$ 01.40

Introduction

Earlier work[1] has been devoted to the preparation of *ad hoc* functionalized organometallic complexes, i.e. 1,4-diazabutadienes carbon-bonded to transition metals, $M\text{-}\overline{\text{C}(=\text{N}R)\text{C}}(R')(=\text{N}R'')$. Several papers have also appeared concerning the coordination properties of these ligands[1, 2]. The range of complexes of this type has now been extended to include the title ligands in which one nitrogen atom belongs to a pyridyl ring. We report herein their synthesis, characterization and new details on the isocyanide insertion.

Results and Discussion

Reaction of the pyridyl complex, *trans*-[PdCl{C_5H_3N(6-Cl)—C^2} $(PPh_3)_2$], **1**, with the appropriate isocyanide (molar ratio 1/1) affords the insertion products **2** in almost quantitative yield.



1 **2**

(**2a**: $R = CH_3$, **2b**: $R = c\text{-}C_6H_{11}$, **2c**: $R = Bu^t$, **2d**: $R = p\text{-}OMeC_6H_4$).

A period of a few hours to about one day is required by the reaction to go to completion, depending on steric and electronic properties of R (see Exp.). The characterization of the resulting complexes is based upon analytical and spectroscopic data (Table 1).

The $^{31}P\text{-}\{^1H\}$NMR spectra of all compounds show only one resonance thus pointing to a *trans*-structure in solution. The presence of a very sharp single signal in the ^1H-NMR spectrum of **2a** (C*Me*), **2c** (CMe_3) and **2d** (O*Me*) suggests that only one configuration is assumed by the NCCN moiety in $CDCl_3$ rather than a time averaged one. Only one configuration was also assumed by the Pd(II) 1,4-diazabutadienes[1, 2]. The nujol infared spectra of all compounds **2** show a ν (C=N) band at ca. 1 600 cm^{-1} due to the alkyl(or aryl)imino group and two main absorptions in the 1 550–1 590 cm^{-1} region due to ν (C=C) and ν (C=N) of the pyridyl ring. The rather low values of the ν (Pd—Cl) band (270–280 cm^{-1}) are in accord with a structure in which the chlorine atom

Table 1. *Selected spectroscopic data*

	IR^a, cm^{-1}			NMR^d, ppm	
Compound	ν(*M*—Cl)	ν(C=N)	ν(C=C) or ν(C=N)^b	^{31}P-{^{1}H}	^{1}H
2a	270 m	1 608 s	1 573 s, 1 551 m	22.6 S	3.62 S (N*Me*)
2b	280 m	1 593 s	1 571 s, 1 552 m	22.2 S	4.6 br (C H)^e
2c	274 m	1 604 s	1 570 s, 1 550 m	17.6 S	1.49 S (CMe_3)
2d	273 m	1 605 s	^{c}	32.5 S	3.83 S (O*Me*)
4	278 m		1 564 m, 1 550 m	23.1 S^f	

[a] In nujol mull.

[b] Pyridine ring absorptions in the 1 500-1 600 cm^{-1} region.

[c] Complicated pattern.

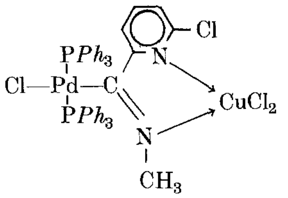
[d] In $CDCl_3$ solutions with *TMS* as internal standard (^{1}H) or 85% H_3PO_4 external standard (^{31}P).

[e] α-proton of the cyclohexyl group.

[f] ^1J(PT—P) = 3 149 Hz.

is *trans* to the σ-carbon bonded group, which is known to have a strong *trans* influence.

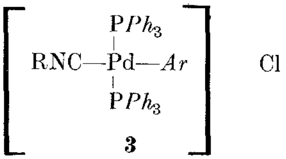
The nature of the final insertion products **2** is also confirmed through reactions involving the NCCN iminopyridyl moiety. Reaction of **2a** with $CuCl_2$ afforded an 1 : 1 adduct, the analytical data of which (see Exp.) fit very well with the formulation:



Two principal IR features were observed upon coordination of **2a**: the shift of the ν(C=N) of the imino band to lower frequency (Δν = 28 cm^{-1}) accompanied by reduction in intensity, and the shift of ν(Pd—Cl) to higher frequency (Δν more than 30 cm^{-1}). This behaviour was always encountered with the previous studied C-palladated 1,4-diazabutadienes[1, 2].

The moderate reactivity of **1** towards isocyanide insertion proved valuable for deeper investigations on the Pd—C bond. Prior to our work, reactions of *trans*-square planar complexes [$PdI(CH_3)(PR_3)_2$]

with isocyanides were reported and a pathway for the monoinsertion reaction proposed[3]. The rapid migration of the methyl group to the coordinated isocyanide, however, allowed neither isolation nor identification of the postulated intermediate. Extensive data have been obtained which definitely support an ionic intermediate **3**:



$$\left[\begin{array}{c} \mathrm{P}Ph_3 \\ | \\ \mathrm{RNC{-}Pd{-}}Ar \\ | \\ \mathrm{P}Ph_3 \end{array}\right] \mathrm{Cl}$$

3

[Ar = 2-pyridyl(6-Cl)]

This compound is analogous to those isolated during the isocyanide insertion into the Pt—C σ- bond of *trans*-$[\mathrm{PtI}(R)(\mathrm{P}Ph_3)_2]$ ($R = \mathrm{CH_3}$ or Ph)[4].

The reaction of **1** with *tert*-butyl isocyanide was followed by conductivity measurements and IR spectroscopy in 1,2-dichloroethane. Immediately after the addition of the isocyanide the solution reached the highest value of conductivity, 20 $\mathrm{ohm^{-1}\,cm^2\,mol^{-1}}$ indicative of a high ratio of ionic species in solution[5]. The IR spectrum scanned at the same time exhibited an intense $\nu(\mathrm{C{\equiv}N})$ band arising from the coordinated isocyanide at 2 200 $\mathrm{cm^{-1}}$ and a weak $\nu(\mathrm{C{=}N})$ band due to the insertion compound at 1 602 $\mathrm{cm^{-1}}$. A steady increase of the latter absorption accompanied by an increase of electric resistance was then observed.

Further insight into the isocyanide insertion pathway and on the structure of the ionic intermediate(s) was gained on repeating the reaction in $\mathrm{CDCl_3}$ and recording the $^{31}\mathrm{P}$-$\{^1\mathrm{H}\}$NMR signals. The spectrum at ca. 15 minutes after the mixing up of the reactants at 30 °C exhibited three phosphorus peaks of comparable intensity at 21.6, 19.4 and 17.7 ppm (see Fig. 1). The first and the last were assigned to the starting complex and to the final insertion compound, respectively, by comparison with authentic samples*. Subsequent $^{31}\mathrm{P}$ spectra showed a

---

* Because of the acquisition time required before the scanning of a $^{31}\mathrm{P}$ spectrum(more or less five minutes, depending on solubility, spin relaxation, etc.) the information gathered through the $^{31}\mathrm{P}$-FT technique may need some working out when studying reactions lasting a short time. For instance, the first spectrum recorded for the reaction above showed an intense peak due to the starting Pd complex, whilst the IR spectrum of a $\mathrm{CHCl_3}$ solution registred at the same time showed only a weak absorption of the free isocyanide at 2 140 $\mathrm{cm^{-1}}$, suggesting that only a minute amount of **1** was still present. So, the $^{31}\mathrm{P}$ peak assigned to the starting material mediated between an initial situation (high concentration of **1**) and a final one (low concentration of **1**).

dramatic decrease of the peak due to the complex **1**, whereas a smooth decrease and increase were observed for the peaks of the intermediate and the final complexes, respectively. Eventually, after ca. 3 h at 30 °C, only the resonance of the insertion complex **2c** was detected (Fig. 1 b). The presence of only one resonance for the intermediate species, and the lack of any signal of free P*Ph*$_3$, rules out the possibility of release of appreciable amounts of P*Ph*$_3$ upon isocyanide coordination and suggests the *trans*-structure **3** for the intermediate ionic species.

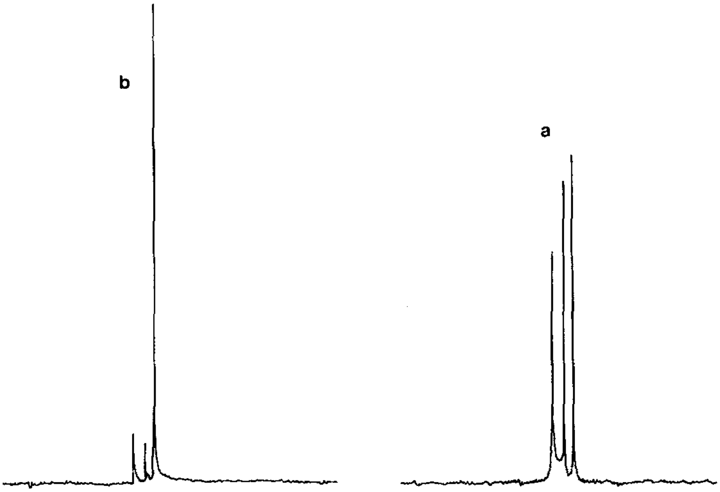


Fig. 1. ^{31}P-{^{1}H}NMR spectra (30 °C, $CDCl_3$) of an equimolecular mixture of **1** and *tert*-butylisocyanide: *a* after 15 min.; *b* after 3 h

Insertion of isocyanides was also attempted on the analogous derivative of Pt(II), *trans*-[PtCl{C_5H_3N(6-Cl)—*C*^{2}}(P*Ph*$_3$)$_2$]. Even using *p*-ClC_6H_4NC, which is known to be fairly reactive[6], no detectable amount of monoinsertion compounds was formed. The ionic intermediate characterized via IR failed to undergo insertion even after prolonged heating. Such a behaviour may be attributed to the high stability of the Pt—C bond and to the scarce nucleophilicity of the migrating carbon atom, due to the presence of both nitrogen and chlorine atoms in the aromatic ring. Indeed, closely related Pt(II) complexes containing a phenyl group, gave isocyanide insertion compounds under the same conditions[4, 7].

Experimental

The ^1H and ^{31}P-$\{^1H\}$ NMR spectra were recorded as $CDCl_3$ solutions on a Varian FT-80 spectrometer operating in the *Fourier* transform mode; TMS was used as internal standard (^1H) and 85% H_3PO_4 as external standard (^{31}P). Infared spectra were recorded on a Perkin-Elmer 597 instrument. The starting materials *trans*-$[PdCl\{C_5H_3N(6\text{-}Cl)\text{—}C^2\}(PPh_3)_2]$[8,9], *p*-$OMeC_6H_4NC$[10] and CH_3NC[10] were obtained as previously described. Bu^tNC and *c*-$C_6H_{11}NC$ were commercially available (EGA). The complex *trans*-$[PtCl\{C_5H_3N(6\text{-}Cl)\text{—}C^2\}(PPh_3)_2]$ was obtained similarly to the Pd analogue but using a higher temperature (ca. 115°), see below.

trans-$[\overline{PdClC(=NBu^t)\{C_5H_3N(6\text{-}Cl)\text{—}C^2}\}(PPh_3)_2]$, **2c**

To the starting palladium complex **1** (0.78 g, 1 mmol) dissolved in 1,2-dichloroethane (50 ml) was added *tert*-butylisocyanide (0.083 g, 1 mmol). The course of the reaction was monitored by following the increase of the $\nu(C=N)$ band of the insertion product at 1602 cm^{-1} and the disappearance of the $\nu(C\equiv N)$ band of the coordinated isocyanide at 2220 cm^{-1}. The reaction went to completion in ca. 1 day. The solution was subsequently evaporated *in vacuo* to a small volume and diethyl ether was added until crystallization just began. Precipitation of the yellow crystalline compound **2c** was completed by addition of some *n*-hexane. Recrystallization of **2c** was achieved by dissolution in CH_2Cl_2, treatment with charcoal, filtration, concentration and precipitation as above. Yield 0.55 g, 70%; M.p. 118–121 °C. Anal. Calcd. for $PdC_{46}H_{42}Cl_2N_2P_2$: C 64.08, H 4.91, Cl 8.22, N 3.25. Found: C 63.74, H 4.72, Cl 8.29, N 3.34.

Synthesis of **2a**, **2b** *and* **2c**

These complexes were all obtained by the same method as reported above. The only variance was the time required: **2a** ca. 6 h; **2b** ca. 10 h; **2d** ca. 3 h. All compounds were analyzed and found to be pure. Their melting points were: **2a** 195–198°; **2b** 163–165°; **2d** 191–194°.

Reaction of **2a** *with* $CuCl_2$

To 0.5 mmol of **2a** (0.379 g) dissolved in dichloromethane (20 ml) were added 0.5 mmol (0.067 g) of $CuCl_2$ dissolved in dry methanol (10 ml). The colour of the solution turned rapidly to brown. After 1 h, the solution was concentrated and precipitation completed by addition of diethyl ether. An ochre crystalline product was obtained in virtual quantitative yield; m.p. 226–228 °C. Anal. Calcd. $CuPdC_{43}H_{36}Cl_4N_2P_2$: MW 954.53; C 54.11, H 3.80, Cl 14.86, N 2.93. Found: MW 930 (in 1,2-dichloroethane); C 54.49, H 3.85, Cl 14.94, N 2.85. $\nu(C=N)$ 1580 w; $\nu(Cu\text{—}Cl)$ 330 ms and 300 m; $\nu(Pd\text{—}Cl)$ masked by the Cu—Cl stretchings.

Synthesis of trans-$[PtCl\{C_5H_3N(6\text{-}Cl)\text{—}C^2\}(PPh_3)_2]$, 4

A solution of 2,6-dichloropyridine (0.814 g, 5.5 mmol) in oxygen-free toluene (80 ml) was prepared in a 250-ml two-necked flask equipped with a nitrogen supply and a reflux condenser. To this solution, $[Pt(PPh_3)_4]$ (5 mmol) was added and the reaction mixture was kept stirring at 115 °C for 12 h. Precipitation of a white product took place during the reaction. The mixture was then concentrated to small volume (20 ml) and the precipitation completed by addition of ethyl ether. The compound was recrystallyzed from CH_2Cl_2/ethyl ether. Yield 3.9 g, 90%; m. p. 255-258°C. Anal. Calcd. for $PtC_{41}H_{33}Cl_2NP_2$: MW 867.72, C 56.75, H 3.83, N 1.61, Cl 8.17. Found: MW 885 (in 1,2-dichloroethane); C 57.02, H 3.75, N 1.68, Cl 8.25.

Reaction of trans-[PtCl{C_5H_3N(6-Cl)—*C*²} (P*Ph*$_3$)$_2$] *with* *p*-ClC_6H_4NC

The platinum complex was reacted with *p*-ClC_6H_4NC (molar ratio 1/1) in refluxing benzene. The reaction was monitored via IR and a strong band at 2200 cm^{-1} developed fast. Afterwards only a slight decrease of such band was observed. Concentration of the solution after ca. 8 h and precipitation with diethyl ether did not show any band of insertion products around 1600 cm^{-1}, suggesting that the only coordinated ionic intermediate was formed.

References

[1] *Crociani B.*, *Mantovani A.*, *Scrivanti A.*, J. Organomet. Chem. **233**, 387 (1982), and references therein.

[2] *Crociani B.*, *Nicolini M.*, *Mantovani A.*, J. Organomet. Chem. **177**, 365 (1979).

[3] *Yamamoto Y.*, *Yamazaki H.*, Inorg. Chem. **13**, 438 (1973).

[4] *Treichel P. M.*, *Hess R. W.*, J. Amer. Chem. Soc. **92**, 15 (1970).

[5] *Geary W. J.*, Coord. Chem. Rev. **7**, 81 (1971).

[6] *Otsuka S.*, *Ataka K.*, J. Chem. Soc., Dalton Transaction **1976**, 327.

[7] *Treichel P. M.*, *Wagner K. P.*, *Hess R. W.*, Inorg. Chem. **12**, 1471 (1973).

[8] *Isobe K.*, *Nanjo K.*, *Nakamura Y.*, *Kawaguchi S.*, Chem. Lett. **1979**, 1193.

[9] *Mantovani A.*, J. Organomet. Chem., in press.

[10] *Appel R.*, *Kleinstuck R.*, *Ziehn K. D.*, Angew. Chem., int. Ed. **10**, 132 (1971).