Journal of Organometallic Chemistry, 236 (1982) C37—C40
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

INSERTION OF ISOCYANIDES INTO THE PALLADIUM—(2-PYRIDYL) BOND

ANTONIO MANTOVANI
Cattedre di Chimica, Facoltà di Ingegneria, University of Padova (Italy)
and BRUNO CROCIANI*
Istituto di Chimica Generale, Via Archirafi 26, University of Palermo (Italy)

(Received June 7th, 1982)

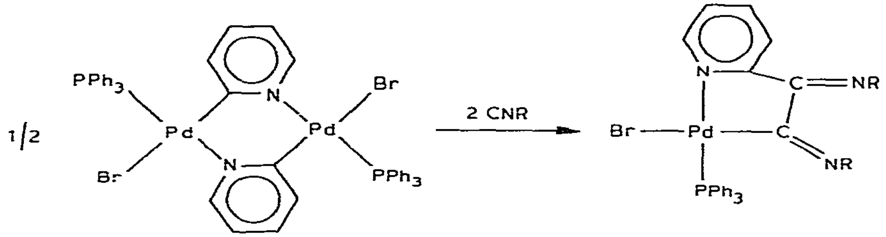
Summary

The reaction of the pyridyl-bridged binuclear complex $[\mathrm{PdBr}(\mu\text{-}2\text{-}\mathrm{C_5H_4N})(\mathrm{PPh_3})]_2$ with isocyanides CNR (R = p-$\mathrm{C_6H_4OMe}$, Me, $\mathrm{C_6H_{11}}$) yields the complex $[\overline{\mathrm{PdBr}\{\mathrm{C(=NR)C(=NR)(2\text{-}C_5H_4N}}\mathrm{)\}(PPh_3)}]$ containing a C,N-chelated 1,2-bis(imino)-2-(2-pyridyl)ethyl group, which results from successive insertions of two isocyanide molecules into the palladium—2-pyridyl bond. The mononuclear compound *trans*-$[\mathrm{PdBr(2\text{-}C_5H_4N)(PMePh_2)_2}]$ readily reacts with various CNR ligands (R = p-$\mathrm{C_6H_4OMe}$, Me, $\mathrm{C_6H_{11}}$, $\mathrm{CMe_3}$) to give the imino(2-pyridyl)methylpalladium(II) derivatives, *trans*-$[\mathrm{PdBr\{C(=NR)(2\text{-}C_5H_4N)\}(PMePh_2)_2}]$.

Complexes of palladium(II) with C-bonded 1,2-bis(imino)alkyl groups can generally be prepared by successive insertion reactions of two isocyanide molecules into Pd—Me [1,2], Pd—Ph [2a] or Pd—H [3] bonds. Due to our interest in the chemistry of this new class of ligands, we have studied the insertion of isocyanides into the Pd—C bond of 2-pyridylpalladium(II) derivatives of the type $[\mathrm{PdBr}(\mu\text{-}2\text{-}\mathrm{C_5H_4N})(\mathrm{PPh_3})]_2$ [4] and *trans*-$[\mathrm{PdBr(2\text{-}C_5H_4N)(PMePh_2)_2}]$, as a possible synthetic route to imino(2-pyridyl)methylpalladium(II) complexes (i.e., the imino-carbon palladated analogues of 2-iminomethylpyridines) (eq. 1 and 2).

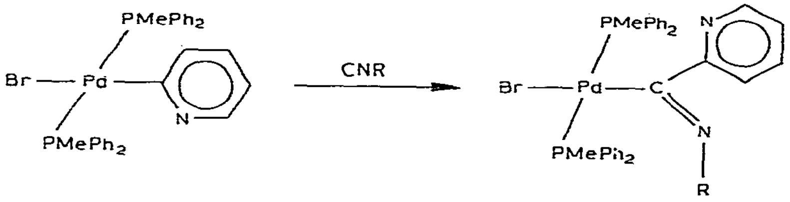
Reaction 1 can be conveniently carried out either in dichloromethane at room temperature (2—3 days) or in 1,2-dichloroethane at 60°C (7—8 h) with a molar ratio Pd/CNR = 1/2. If a Pd/CNR ratio of 1/1 is used, a mixture of I and unreacted starting product is obtained. This fact and the observed IR spectral changes during the course of the reaction suggest a stepwise mechanism

0022-328X/82/0000—0000/$02.75



(1)

Ia : R = p-C_6H_4OMe ; Ib : R = Me ;
Ic : R = C_6H_{11}



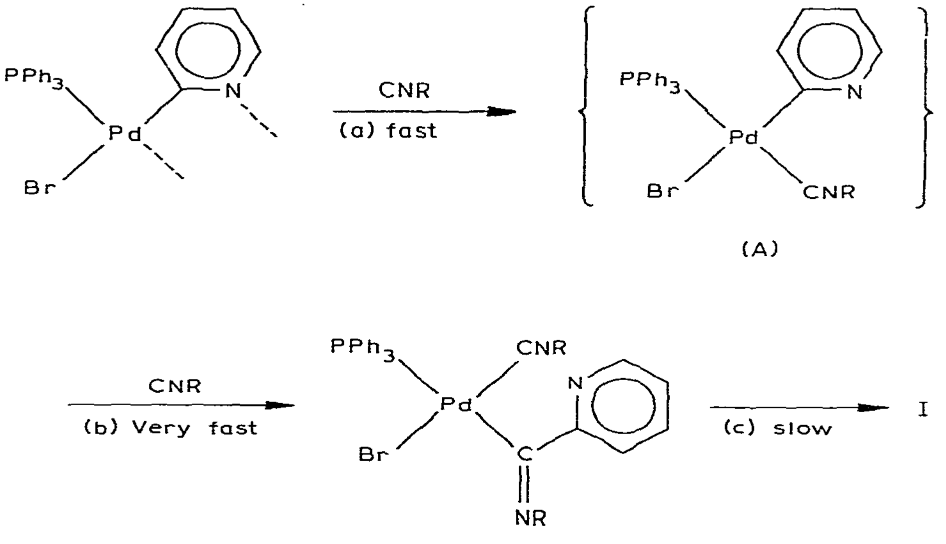
(2)

IIa : R = p-C_6H_4OMe ; IIb : R = Me ;
IIc : R = C_6H_{11} ; IId : R = CMe_3

of the type shown in eq. 3, in which the first step (a), involving a fast cleavage of the 2-pyridyl bridge, is followed by an even faster reaction (b) with a second isocyanide molecule to give the intermediate B, which then rearranges slowly to the final product I. The postulated transient A is not observed in the IR spectra of the reaction mixtures, which a few minutes after mixing of the reactants are characterized by a ν(C=N) band in the range 1600—1630 cm^{-1} (1615 cm^{-1} for R = C_6H_{11}, in CH_2Cl_2) and by a sharp ν(C≡N) absorption at ca. 2200 cm^{-1} (2202 cm^{-1} for R = C_6H_{11}), attributable to the intermediate B. However, highly reactive palladium(II) species containing isocyanides ligands *cis* to a Pd—Me bond have been previously isolated and characterized [5].

In the course of step (c), the ν(C≡N) band of the coordinated isocyanide progressively disappears with concomitant formation of a second ν(C=N) band in the range 1620—1650 cm^{-1} (1635 cm^{-1} for R = C_6H_{11}). The complexes I are monomeric species which exhibit two ν(C=N) and one ν(Pd—Br) vibrations in their IR spectra (at 1647, 1633 and 165 cm^{-1} respectively, for Ib). On the basis of *trans*- influence considerations, the low frequency position of ν(Pd—Br) (180—165 cm^{-1}) suggests a solid state configuration with the bromide ligand *trans* to the Pd—C σ bond. On the other hand, the ^1H and ^{31}P NMR spectra in $CDCl_3$ at ambient temperature indicate that only one isomer is present in solution, characterized by two non-equivalent R groups (δ(OMe) 3.68, 3.83 ppm for Ia, δ(Me) 2.95, 3.45 ppm for Ib), and by a marked low-field chemical shift of the pyridyl ring proton in position 6 ($\delta(H^6)$ in the range 9.7—9.5 ppm), due to N-coordination of the pyridyl moiety.

The desired imino(2-pyridyl)methylpalladium(II) derivatives can be easily prepared by reaction 2, involving insertion of one isocyanide molecule into the Pd—C σ-bond of the mononuclear complex *trans*-[PdBr(2-C_5H_4N)-



(A)

(B)

(3)

$(PMePh_2)_2]$*. In this case, as expected [5b], the insertion rate is markedly influenced by the nature of the entering CNR ligand: in benzene, the reaction is almost immediate for R = p-C_6H_4OMe at room temperature, whereas it takes 5—6 h for completion at 60°C when R is an alkyl group. Infrared and electrical conductivity measurements in 1,2-dichloroethane show that reaction 2 proceeds essentially through an ionic intermediate, which may be formulated as $[Pd(2\text{-}C_5H_4N)(CNR)(PMePh_2)_2]Br$, in accordance with the proposed insertion mechanism on *trans*-$[PtX(R')(L)_2]$ substrates [5b,6]. The IR spectra of the monomeric complexes II show a $\nu(C{=}N)$ band in the range 1615—1605 cm^{-1} and a $\nu(Pd{-}Br)$ band in the range 185—175 cm^{-1}. The *trans*-arrangement of the $PMePh_2$ ligands is indicated by the triplet pattern of $\delta(P{-}Me)$ signals in the ^1H NMR spectra (IIa, $\delta(P{-}Me)$ 1.90 ppm, $^2J(P{-}H)+^4J(P'{-}H) = 6.4$ Hz, in CD_2Cl_2) and by the occurrence of only one singlet in the ^{31}P NMR spectra (IIa, $\delta(P)$ 4.65 ppm down-field from external H_3PO_4). In contrast to compounds I, in II the pyridyl ring proton in position 6 resonates at higher field, 8.7—8.5 ppm, the same range in which the corresponding signal of the free ligand 2-(p-methoxyphenylimino)methylpyridine is observed ($\delta(H^6)$ 8.67 ppm).

Attempts to extend reaction 2 to the platinum(II) derivatives, *trans*-$[PtBr(2\text{-}C_5H_4N)(L)_2]$ (L = PPh_3, $PMePh_2$) (obtained from oxidative addition of 2-bromopyridine to $[Pt(L)_4]$) gave only a poor yield of insertion products, even with the more reactive p-CNC_6H_4OMe ligand, in line with the much reduced tendency of isocyanides to insert into the Pt—C σ-bonds [5b].

Preliminary results show that both compounds I and II can act as N-donor ligands towards various transition metal centers, such as cobalt(II), nickel(II), copper(II) and zinc(II). Of particular interest are the binuclear complexes

---

*This compound can be conveniently prepared by oxidative addition of 2-bromopyridine to the $[Pd_2(dba)_3]\cdot CHCl_3/2\ PMePh_2$ system (dba = dibenzylideneacetone) [7].

Pd^{II}/Cu^{II}, the catalytic activity of which in the oxidation of olefins we are currently investigating.

Financial support by C.N.R. (Progetto Finalizzato: Chimica Fine e Secondaria) is gratefully acknowledged.

References

1 Y. Yamamoto and H. Yamazaki, Inorg. Chem., 13 (1974) 438.
2 (a) B. Crociani, M. Nicolini and R.L. Richards, J. Organometal. Chem., 104 (1976) 259; (b) B. Crociani and R.L. Richards, ibid., 154 (1978) 65.
3 P.L. Sandrini, A. Mantovani and B. Crociani, J. Organometal. Chem., 185 (1980) C13.
4 K. Nakatsu, K. Kinoshita, H. Kanda, K. Isobe, Y. Nakamura and S. Kawaguchi, Chem. Lett., (1980) 913.
5 (a) S. Otsuka, A. Nakamura, T. Yoshida, M. Nurato and K. Ataka, J. Amer. Chem. Soc., 91 (1969) 7196; (b) S. Otsuka and K. Ataka, J. Chem. Soc., Dalton, (1976) 327.
6 P.M. Treichel, K.P. Wagner and R.W. Hess, Inorg. Chem., 12 (1973) 1471.
7 T. Ukai, H. Kawazura, Y. Ishii, J.J. Bonnet and J.A. Ibers, J. Organometal. Chem., 65 (1974) 253.

JOURNAL OF ORGANOMETALLIC CHEMISTRY, VOL. 236, No. 1

AUTHOR INDEX