Journal of Organometallic Chemistry, 269 (1984) C15—C18
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

INSERTION OF ISOCYANIDES INTO THE 2-ONE-1-PROPYL—PALLADIUM(II) BOND: A CONVENIENT SYNTHETIC ROUTE TO C^1-PALLADATED 1-AMINO-3-ONE-1-BUTENE COMPOUNDS

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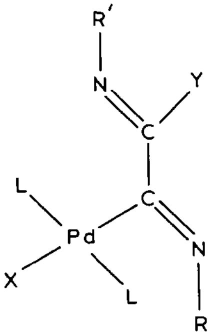
(Received March 30th, 1984)

Summary

Migratory insertion of isocyanides CNR (R = p-C_6H_4OMe, Me) into the palladium—carbon σ bond of *trans*-$[PdCl(CH_2COMe)(PPh_3)_2]$ (I) yields the 1-amino-3-one-1-butenyl complexes *trans*-$[PdCl\{C(NHR)=CHCOMe\}(PPh_3)_2]$ (IIa, R = p-C_6H_4OMe; IIb, R = Me), which have been characterized by IR, ^{1}H and ^{31}P NMR spectra. The reaction of IIa with nickel acetate gives a diamagnetic bis-chelate complex of the type $[Ni(O—N)_2]$, in which the deprotonated 1-amino-3-one-1-butenyl moiety acts as a bidentate O,N ligand.

In recent papers we showed that migratory insertion of isocyanides into the Pd—C σ bond provides a useful synthetic method for the preparation of α-diimino bidentate ligands containing a carbon—palladated imino function [1, 2]:



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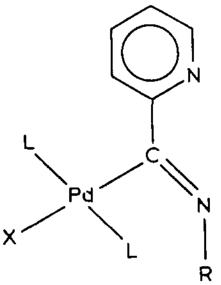
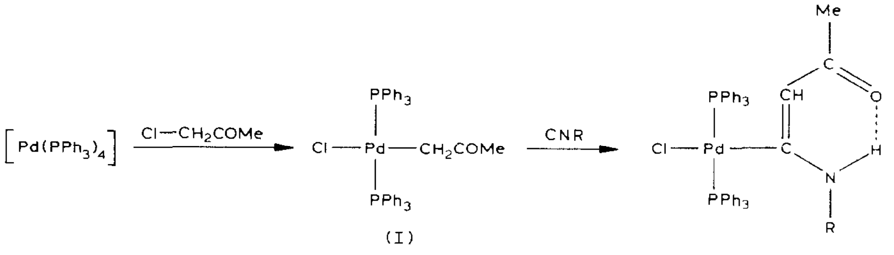


(X = halogen ; Y = H, Me, Ph ; L = tertiary phosphine)

0022-328X/84/$03.00

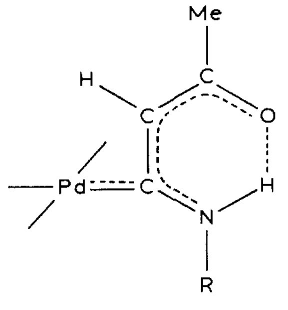
We now report that the same type of insertion can be conveniently used for the preparation of a new series of palladium(II) complexes with σ-bonded organic moieties of the β-ketoenamine type:



(1)

(IIa R = p-C_6H_4OMe ,
IIb R = Me)

Oxidative addition of chloroacetone to [$Pd(PPh_3)_4$] yields the 2-one-1-propyl complex I (ν(C=O) 1674; ν(Pd—Cl) 252 cm^{-1}) with a *trans* arrangement of PPh_3 ligands (δ(^{31}P) as a singlet at 27.3 ppm down-field from external 85% H_3PO_4; δ(CH_2) as a triplet at 2.45 ppm, with ^3J(P—H) of 7.5 Hz, in C_6D_6 solution). This compound reacts smoothly with aryl or alkyl isocyanides in benzene to give the 1-amino-3-one-1-butenyl derivatives II. In terms of valence bond theory the formulation of II in eq. 1 is a limiting structure of a hydrogen-bonded mesomeric system of type **A**. The β-ketoenamine group, however, may also assume an open configuration of type **B**. In both cases, the metal center could be involved in the delocalized π electron systems through *d* electrons of appropriate symmetry.



(A)

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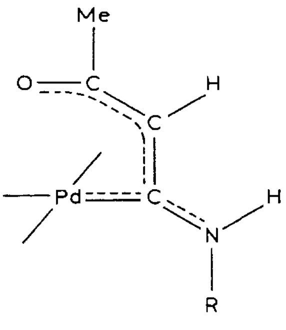


(B)

The IR spectra in the solid state suggest that the 1-amino-3-one-1-butenyl group has an arrangement of type A, characterized by a broad ν(N—H) band at ca. 3000 cm^{-1}, indicative of rather strong hydrogen bonding, and by two intense absorptions at 1565 and 1530 cm^{-1}, assigned to coupled ν(C$\overset{...}{-}$O) and ν(C$\overset{...}{-}$C) vibrations. The corresponding bands of *cis*-$MeCOCH{=}CHNH_2$, with an intramolecular hydrogen bond, were observed at 3305 , 1643 and 1502 cm^{-1}, respectively, in $CHCl_3$ solution [3]. The Pd—Cl stretch appears at 298 cm^{-1} for both IIa and IIb.

Some characteristic NMR data of II in $CDCl_3$ are reported in Table 1, along with those of 4-methylamino-3-butene-2-one for comparison [4]. The appearance of δ(NH) as a broad resonance at markedly low field is reasonably accounted for in terms of a configuration of type **A** (in the intramolecularly hydrogen bonded *cis*-MeCOCH=CHNHMe, δ(NH) is observed at 9.6 ppm). For complex IIa only signals of structure **A** are present in solution, whereas for IIb there is an additional group of signals of lower intensity which can be assigned to structure **B**, with a molar ratio **A**/**B** of ca. 10/1. The high field shift of δ(N—Me) and δ(C—Me) resonances of IIb relative to those of MeCOCH=CHNHMe is essentially due to the shielding effect of phenyl ring currents of the mutually *trans* PPh_3 ligands.

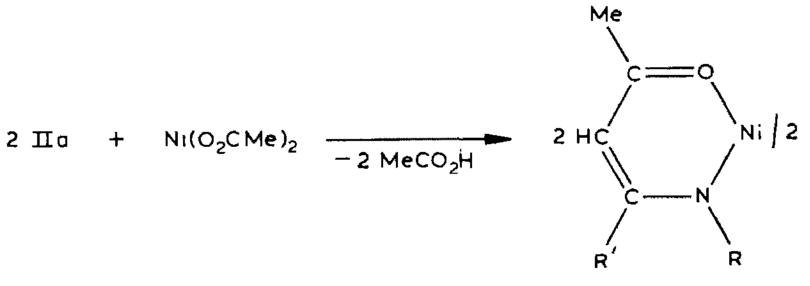
TABLE 1

CHARACTERISTIC ^1H AND ^{31}P NMR DATA

Compound	N—H	C—H	N—Me	C—Me	^{31}P
IIa [a]	11.6(br)	5.15t ^4J(P—H) 2.2		1.44s	21.8s
IIb [a]	10.0(br)	4.97t ^4J(P—H) 2.0	2.51d ^3J(H—H) 5.0	1.45s	22.3s
IIb [b]	n.o.	4.77 [c]	2.23d ^3J(H—H) 4.5	2.02s	n.o.
MeCOCH=CHNHMe [d]	9.6	4.98d	2.98d ^3J(H—H) 5.1	2.02s	
MeCOCH=CHNHMe [e]	n.o.	5.19d	2.78d ^3J(H—H) 4.2	2.10s	

[a] Structure A. [b] Structure B. [c] Weak unresolved signal. [d] *Cis* configuration with intramolecular hydrogen bond [4]. [e] *Trans* configuration [4].

Compound IIa reacts rapidly with anhydrous nickel acetate yielding the trinuclear diamagnetic complex IIIa:



(2)

(IIIa)

(R = p-C_6H_4OMe ; R' = *trans*-$PdCl(PPh_3)_2$)

The typical ν(C⋯O), ν(C⋯C), ν(Pd—Cl) vibrations and the δ(CH), δ(CMe) resonances of IIa are almost unchanged in IIIa, suggesting that the 1-amino-3-one-1-butenyl group has similar steric and electronic properties in both the hydrogen bonded form of IIa and the deprotonated chelating form of IIIa.

Further studies on the coordinating abilities of II are in progress.

Financial support by Ministero della Pubblica Istruzione (Research Fund 40%, 1982) is gratefully acknowledged.

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