# REACTIONS OF METHOXYENYLPALLADIUM COMPLEXES WITH ISOCYANIDES

G. CARTURAN

*Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione del C.N.R., Calle Larga S. Marta 2137, Venezia (Italy)*

R. ZANELLA, M. GRAZIANI and U. BELLUCO

*Facoltà di Chimica Industriale, The University, Venezia (Italy)*

(Received July 10th, 1974)

## Summary

The reactions of $[Pd(C_{10}H_{12}OCH_3)LCl]$, (L = $PPh_3$, $C_6H_{11}NC$ or $CH_3NC$) with RNC (R = $C_6H_{11}$, $CH_3$) proceed in mild conditions in benzene to give a 1/1 adduct. The products of the reactions, formulated on the basis of spectroscopic properties, may be looked upon as models for the intermediate that was proposed for the transanular carbonylation of 1,5-cyclooctadiene. The reactions of isocyanides with methoxyenyl dimers of palladium are also reported.

## Introduction

Insertion reactions of carbon monoxide or isocyanides across the metal—carbon σ-bond in alkoxyenyl complexes of palladium and platinum lead to different products, depending on the metal, the diolefin, and the ancillary ligands [1]. Thus, dicyclopentadienyl derivatives of Pd$^{II}$ and Pt$^{II}$ give acyl carbonyl products (eqn. 1) [2,3]. Analogous products are obtained from insertion reactions of isocyanides, although the reaction intermediates observed suggest different mechanisms of formation [4].



$$(1)$$

The dependence of the course of insertion on the nature of the diolefin is borne out in the case of the cyclooctadienyl—Pt$^{II}$ complex which reacts with carbon monoxide to give a carbomethoxyl species (eqn. 2) [5].

$$(2)$$
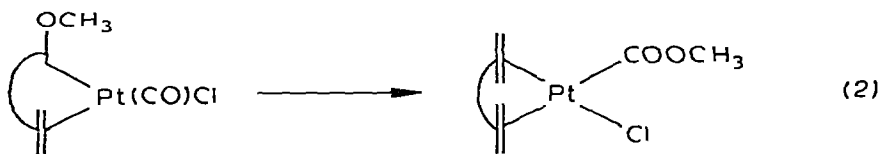
Carbon monoxide insertions are involved in the carbonylation of diolefins catalyzed by Pd[II] complexes, in which formation of a ketone of the type A [6]
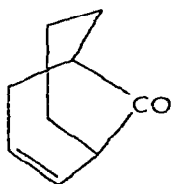


(A)

has been observed along with esters (in the case of 1,5-cyclooctadiene). No intermediate in which the organic moiety has undergone transannular carbonylation has yet been detected in the carbonylation of alkoxyenyl metal complexes. With a view to investigating the mechanism of this unusual reaction we have therefore carried out a series of reactions of isocyanides with the alkoxydienyl Pd[II] complexes I, II and III. We also hoped to be able to trap some model



(I)          (II)          (III)
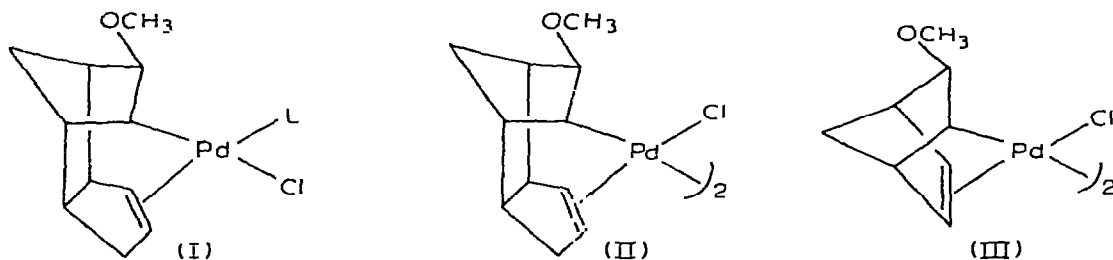
$(L = PPh_3, C_6H_{11}NC \text{ and } CH_3NC)$

intermediates having relevance to the palladium-catalyzed transannular carbonylations by taking advantage of the generally greater stability of isocyanide— over carbon monoxide—metal complexes.

Results and discussion

*Reactions of [Pd($C_{10}H_{12}OCH_3$)LCl] (I) (L = PPh_3, C_6H_{11}NC, CH_3NC) with RNC (R = C_6H_{11}, CH_3)*

We studied reaction 3, which proceeds under mild conditions in $CH_2Cl_2$. Compound IV (monomeric in benzene, non-conducting in $CH_2Cl_2$) was characterized and formulated on the basis of elemental analysis, IR, NMR, and mass spectra. Proton absorption data are presented in Table 1. In some cases the complexity of the spectrum prevented assignment of all the signals. The NMR spectrum shows no signal attributable to either free or coordinated olefinic protons, as shown by integration and comparison with the signals from the phenylic protons. Based on this evidence we rule out structures V and VI, both of which

$$\left[Pd(C_{10}H_{12}\cdot OCH_3)LCl\right] \xrightarrow{(+2RNC)}$$ (IV)

(3)

(IV)
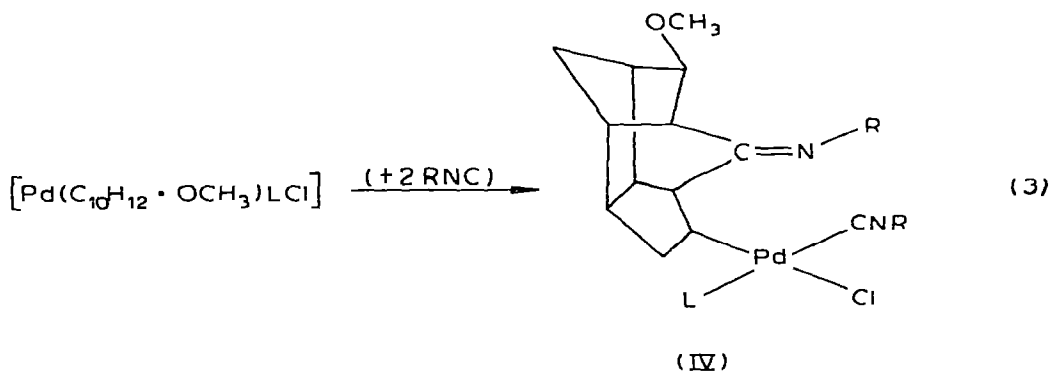
are in agreement with molecular weight and IR spectrum. The imino group protons have been assigned, in particular, for compound IVc (Table 1) on the basis of the different intensities of the terminal iso-cyanide protons (6H, $\tau$ 6.58 ppm) from those of imino protons (3H, $\tau$ 6.66 ppm). We recall that the cyclohexyl $\alpha$-proton in systems which have an amino nitrogen coordinated to palladium, has been found to absorb at $\tau$ 6.5 ppm [8], a value very close to our observed signal.

(V)

(VI)
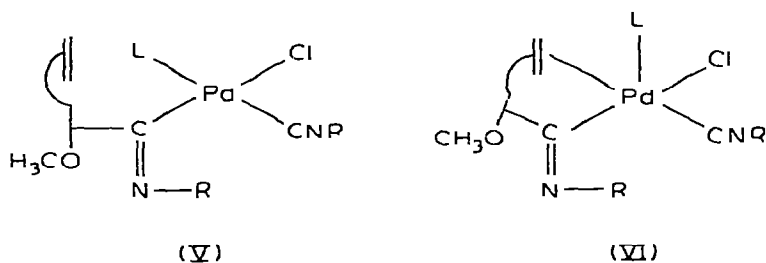
Protons bound to the $\alpha$-carbon in an imino group in platinum complexes were found to absorb at lower fields than in their palladium analogues and this appears to be a rather general trend. In fact, in $Pd^{II}$ and $Pt^{II}$ tetracyanocyclopropane complexes, the methylene protons of the organic ligand are shifted downfield upon coordination by ca. 0.5 ppm for palladium and ca. 1 ppm for platinum [9]. To the extent that a relationship between chemical shift and electron density exists, this suggests a higher electron acceptor ability from ligands for platinum(II) than for palladium(II).

The IR spectrum of IV shows $\nu$(C=N) absorptions in the range 1642-1633 cm$^{-1}$ (Table 2). These $\nu$(C=N) values are generally higher, albeit to a small extent than those for isocyanides inserted across the palladium—carbon $\sigma$-bond, which fall in the range 1630-1515 cm$^{-1}$ in phosphine derivatives [8]*. In the products of the reactions of $\pi$-allyl palladium complexes with isocyanides, $\nu$(C=N) is about 1575 cm$^{-1}$ [10]; higher values (1660-1652 cm$^{-1}$) were found for other $Pd^{II}$ imino derivatives [11]. The mass spectrum of IVb was compared with that of the platinum(II) analog VII, and the comparison suggests the presence

* A possible coordination of nitrogen atom to platinum has been recently excluded in the case of trans-iodobis(triethylphosphine)-(1-chlorophenylimino)methylplatinum(II) on the basis of X-ray analysis [7].

TABLE 1

SELECTED NMR DATA[a]

| | | |
|---|---|---|
| Ic | $[Pd(C_{10}H_{12}OCH_3)(CNCH_3)Cl]$ | 3.18(CH=CH, bs): 6.43 (1H, bs): 6.56(CH$_3$NC, s): 6.73(OCH$_3$, s): 7.02(3H, bs): 7.45-7.70(3H, m): 8.36-8.80(3H, m) |
| IVa | $[Pd(C_{10}H_{12}OCH_3CH_3NC)(CH_3NC)(PPh_3)Cl]$ | 2.30-2.61(15H, bs): 6.14(1H, m): 6.42(CH$_1$–NC, bs): 6.57(1H, m): 6.74(OCH$_3$, s): 6.87 (C=NCH$_3$, bs): 7.02(1H, bs): 7.21(3H, bs): 7.34(1H, m): 7.73(1H, m): 8.00(1H, s): 8.05(1H, s): 8.31(2H, m) |
| IVb | $[Pd(C_{10}H_{12}OCH_3C_6H_{11}NC)(C_6H_{11}NC)(PPh_3)Cl]$ | 2.30-2.60(16H, bs): 6.15-6.50(2H, m): 6.70(OCH$_1$, s): 7.00(1H, bs): 7.25 (3H, bs): 7.74(1H, m), 8.20-8.80(27H, m) |
| IVc | $[Pd(C_{10}H_{12}OCH_3CH_3NC)(CH_3NC)_2Cl]$ | 6.28(1H, m): 6.40(1H, m): 6.58(OH,CH$_1$–NC, bs): 6.66 (C=NCH$_3$, bs): 6.74(OCH$_1$, s): 7.00 (1H, bs): 7.19(3H, bs): 7.32(1H, bs): 7.66(1H, m): 7.97(1H, m): 8.03(1H, m): 8.30(2H, m) |
| IVd | $[Pd(C_{10}H_{12}OCH_3C_6H_{11}NC)(C_6H_{11}NC)_2Cl]$ | 6.14-6.28(2H, m): 6.69(OCH$_3$, s): 7.00(1H, bs): 7.23(3H, bs): 7.68(1H, m): 8.20-8.60(38H, m) |
| X | $[Pd(C_7H_8OCH_3)(C_6H_{11}NC)Cl]_2$ | 5.92(1H, bs): 6.22(2H, m): 6.64(OCH$_1$, s): 7.42(1H, bs): 7.70(1H, bs): 8.24-8.70(14H, m) |
| XI | $[Pd(C_7H_8OCH_3)(C_6H_{11}NC)_2Cl]$ | 5.90(1H, bs): 6.24(2H, m): 6.68(OCH$_3$, s): 7.58(1H, bs): 7.90(1H, bs): 8.13-8.75(25H, m) |
| XII | $[Pd(C_7H_8OCH_3C_6H_{11}NC)(C_6H_{11}NC)_2Cl]$ | 6.26(2H, m): 6.72(OCH$_1$, s): 8.18-8.60(30H, m) |

[a] τ values. In CDCl$_3$ with TMS as internal standard.

TABLE 2

IR SPECTRA AND ANALYTICAL DATA FOR THE REACTION PRODUCTS OF ISOCYANIDES WITH METHOXYENYLPALLADIUM(II) COMPLEXES

| | Compound | m.p. (°C)[a] | Analysis found (calcd.) (%) | | | | Infrared frequencies ($\pm 3$ cm$^{-1}$) | | | M.W. in $C_6H_6$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | C | H | N | Cl | $\nu(C\equiv N)$ | $\nu(C=N)$ | $\nu(Pd-Cl)$ | |
| Ic | $[Pd(C_{10}H_{12}OCH_3)(CH_3NC)Cl]$ | 74 | 46.03 (45.10) | 5.30 (5.24) | 4.08 (4.04) | 10.66 (10.24) | 2226 vs | | 256 m | |
| IVa | $[Pd(C_{10}H_{12}OCH_3CH_3NC)(CH_3NC)(PPh_3)Cl]$ | 101 | 58.60 (61.02) | 5.25 (5.58) | 4.12 (4.31) | 5.50 (5.46) | 2225 vs | 1633 s | 260 m | 630 (649) |
| IVb | $[Pd(C_{10}H_{12}OCH_3C_6H_{11}NC)(C_6H_{11}NC)(PPh_3)Cl]$ | 103 | 65.79 (65.73) | 6.77 (6.67) | 4.11 (3.56) | 4.30 (4.51) | 2197 vs | 1637 s | 258 m | |
| IVc | $[Pd(C_{10}H_{12}OCH_3CH_3NC)(CH_3NC)_2Cl]$ | 180 | 47.58 (47.72) | 5.70 (5.56) | 9.94 (9.82) | 8.40 (8.28) | 2225 vs | 1642 s | 260 m | 440 (428) |
| IVd | $[Pd(C_{10}H_{12}OCH_3C_6H_{11}NC)(C_6H_{11}NC)_2Cl]$ | 205 | 60.78 (60.75) | 7.76 (7.65) | 6.16 (6.64) | 5.30 (5.60) | 2196 vs | 1646 s | 258 m | |
| X | $[Pd(C_7H_6OCH_3)(C_6H_{11}NC)Cl]_2$ | 122 | 48.09 (48.14) | 5.79 (5.92) | 3.69 (3.74) | 9.74 (9.47) | 2198 vs | | 300 m 268 m | 760 (748) |
| XI | $[Pd(C_7H_8OCH_3)(C_6H_{11}NC)_2Cl]$ | 90 | 54.73 (54.66) | 6.85 (6.88) | 5.83 (5.79) | 7.27 (7.33) | 2198 vs | | 275 s | |
| XII | $[Pd(C_7H_6OCH_3C_6H_{11}NC)(C_6H_{11}NC)Cl]$ | 83 | 58.69 (58.78) | 7.56 (7.48) | 7.05 (7.09) | 5.88 (5.98) | 2198 vs | 1638 s | 260 m | |

[a] All compounds melting with decomposition.
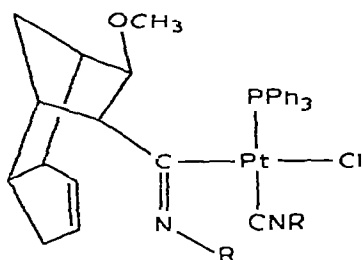
( VII )

of the organic moiety as depicted in IV. In fact, the mass spectrum of VII shows very strong peaks both at 272 [$(C_{10}H_{12}OCH_3)(C_6H_{11}NC)$] and at 163 $(272 - C_6H_{11}NC)$, whereas for IVb the peak at 163 is very weak (the 272 peak is maintained), in line with a less easy rupture of the $C_6H_{11}NC$ grouping from the organic moiety in the latter case.
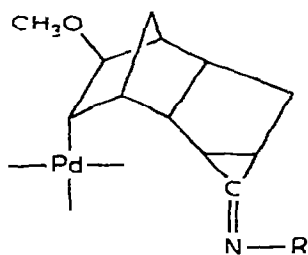


( B )

An alternative, B, also in accord with the mass spectrum, may be ruled out by the IR spectrum, as $\nu(C=N)$ for cyclopropane derivatives is generally higher than 1700 cm$^{-1}$ [12].

These results throw some light on the mechanism of carbonylation of olefins catalyzed by palladium(II) complexes. In fact, in a most general way, competition is likely to occur between two reaction modes. Initial insertion of CO across the palladium—carbon bond, leading to an acyl intermediate, may be followed by reaction 4, which involves formation of transannular carbonylation products [6] via insertion of the olefinic bond across the palladium—acyl bond.
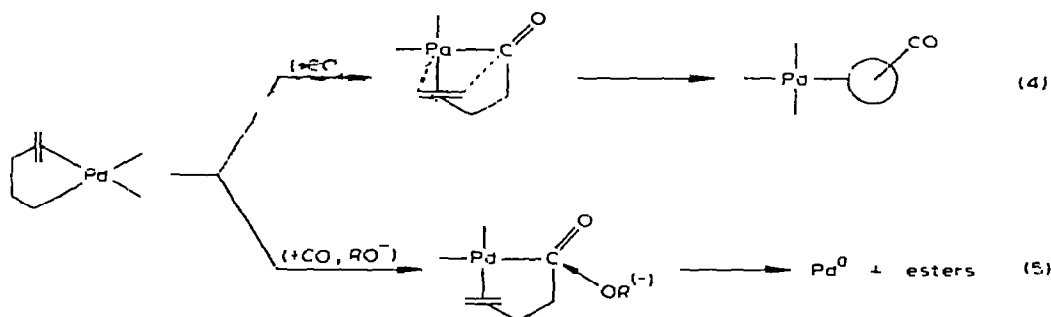


Alternatively, nucleophilic attack at the acyl carbon may occur, leading to carbonylation products, according to reaction 5 [13]. The path which is actually operative depends on the basicity of the medium [14].

(VIII)         (IX)         (6)
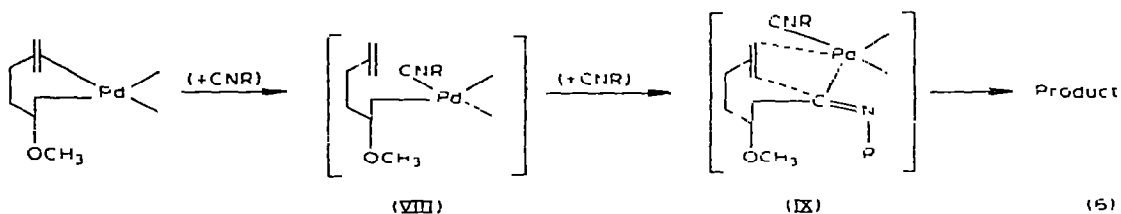
We think that reaction 3 may be written more fully as reaction 6, on the basis of the isolation of products VIII and IX from the analogous reaction with platinum [4]. For palladium complexes, even with complex/RNC molar ratios less than 1, a mixture of reactants and products is always obtained. At any rate, it cannot be ruled out that the first step of reaction is the insertion of isocyanide followed by displacement of the olefinic grouping, by analogy with observations on both platinum [2] and palladium [3] in carbonylation reactions.

In principle, these complexes may be looked upon as models for the intermediate that has been proposed for carbonylation of 1,5-cyclooctadiene catalyzed by palladium phosphine complexes [6]. This reaction gives the final carbonylated product via $\beta$-extraction (eqn. 7).
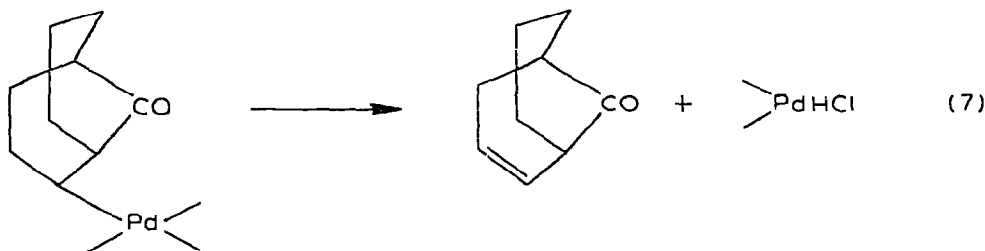


*Reaction of [Pd(C_7H_8OCH_3)Cl]_2 with C_6H_{11}NC*

In order to investigate the effect of the diolefin on this type of reaction, we effected reaction 8. The first step, III → X, is not a bridge-splitting reaction as observed when the entering ligand is an amine [15] but instead, prior formation of dimer (X) takes place, by analogy with the reaction with carbon monoxide [5]. By the use of an excess of isocyanide, bridge-splitting occurs as the second step, X → XI. The insertion of CNR in compound XI proceeds only under more stringent conditions (benzene at reflux).

The strong tendency of norbornadiene to give palladium—carbon bonded compounds has been traced back to the peculiar homoallylic structure of this diolefin [16]. The nortricyclene configuration has been established by a study of the stereochemistry of carbonylation of norbornadiene in methanol catalyzed by Pd^II (which gives 3-*endo*-carbethoxy-5-*exo*-methoxynortricyclene [17]) and by an X-ray structure determination on the analogue of XI with pyridine coordinated [18]. It should be noted that the same type of compound (XII) may also be obtained by the above sequence of reactions, even when bridge-splitting precedes the rearrangement of the norbornadiene moiety. Therefore, these possible reaction paths are markedly affected by the nature of the neutral reacting ligand and a systematic study of related electronic and steric factors is currently in progress.
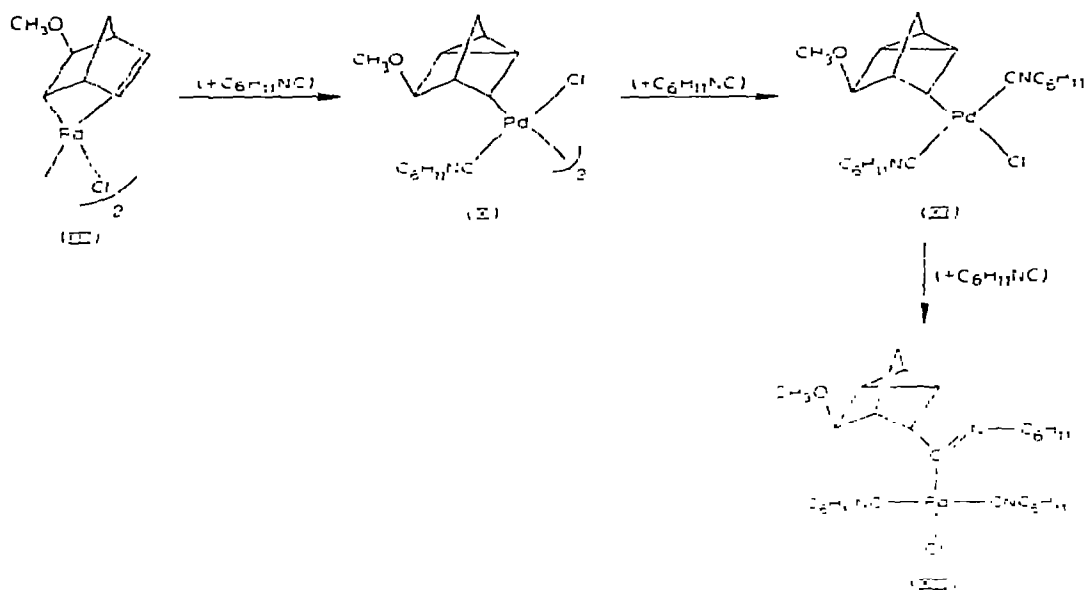
## Experimental

*Instruments.* Molecular weight determinations were carried out in benzene solution with a Vapor Pressure Osmometer, Model HP 302 B. Proton NMR spectra were obtained on a Bruker 90 MHz spectrometer, using $CDCl_3$ as solvent and TMS as internal standard. Infrared spectra ($4000$-$250$ $cm^{-1}$) were recorded on a Perkin—Elmer Model 457 spectrophotometer. An LKB 9000 instrument was used to carry out mass spectral determinations.

*Materials.* All the solvents were reagent grade quality. Methyl isocyanide and cyclohexyl isocyanide were prepared by the methods reported in the literature [19], as were the complexes [Pd(C$_{10}$H$_{12}$OCH$_3$)Cl]$_2$ (II) [20], [Pd(C$_{10}$H$_{12}$OCH$_3$)(PPh$_3$)Cl] (Ia) [21], [Pd(C$_{10}$H$_{12}$OCH$_3$)(C$_6$H$_{11}$NC)Cl] (Ib) [4] and [Pd(C$_7$H$_8$OCH$_3$)Cl]$_2$ (III) [20]. Elemental analyses were performed by Dornis und Kolbe, Mulheim (Germany).

*[Pd(C$_{10}$H$_{12}$OCH$_3$)(CH$_3$NC)Cl] (Ic).* To a stirred CH$_2$Cl$_2$ solution of [Pd(C$_{10}$H$_{12}$OCH$_3$)Cl]$_2$ (II) (0.610 g, 1 mmol) kept at 0°C under nitrogen methyl isocyanide (0.084 g, 2 mmol) in 10 ml of the same solvent was added dropwise. After the addition the solvent was partially removed at reduced pressure and, by addition of petroleum ether, the pale yellow solid [Pd(C$_{10}$H$_{12}$OCH$_3$)-(CH$_3$NC)Cl] was obtained. It was recyrstallized from benzene/hexane.

*[Pd(C$_{10}$H$_{12}$OCH$_3$CH$_3$NC)(PPh$_3$)(CH$_3$NC)Cl] (IVa).* To a stirred CH$_2$Cl$_2$ solution of [Pd(C$_{10}$H$_{12}$OCH$_3$)(PPh$_3$)Cl] (Ia) (0.567 g, 1 mmol) kept at −10°C under nitrogen, methyl isocyanide (0.084 g, 2 mmol) in 15 ml of the same solvent was added dropwise. The solution turned yellow-orange and was maintained at 0°C for 1 h. The solvent was removed to give a colourless oil, which was washed with ethyl ether. The crude product was dried under vacuum and crystallized on cooling at − 60°C from dichloromethane/pentane solution.

*[Pd(C$_{10}$H$_{12}$OCH$_3$C$_6$H$_{11}$NC)(PPh$_3$)(C$_6$H$_{11}$NC)Cl] (IVb).* Using the same procedure, this product was obtained as an off-white solid.

*[Pd(C₇H₈OCH₃)(C₆H₁₁NC)Cl]₂(X)*. To a stirred solution of [Pd(C₇H₈-OCH₃)Cl]₂ (III) (0.265 g, 0.5 mmol) in CH₂Cl₂ kept at 0°C under nitrogen, cyclohexyl isocyanide (C₆H₁₁NC)(0.109 g, 1 mmol) in 10 ml of the same solvent was added dropwise. Partial removal of the solvent and addition of n-hexane gave the product as an off-white solid.

*[Pd(C₇H₈OCH₃)(C₆H₁₁NC)₂Cl] (XI)*. This complex was prepared either by slow addition of a CH₂Cl₂ solution of cyclohexyl isocyanide to a solution of [Pd(C₇H₈OCH₃)Cl]₂ (III) in the same solvent, using a molar ratio Pd/RNC of 1/2, or using [Pd(C₇H₈OCH₃)(C₆H₁₁NC)Cl]₂ (X) as parent compound dissolved in CH₂Cl₂ and adding the stoichiometric amount of C₆H₁₁NC. In both cases the reactions were carried out at —10°C under nitrogen and the product was collected as a yellow solid after addition of ether and cooling to —60°C.

*[Pd(C₇H₈OCH₃C₆H₁₁NC)(C₆H₁₁NC)₂Cl] (XII)*. A solution of [Pd(C₇H₈-OCH₃)(C₆H₁₁NC)₂Cl] (XI) (0.241 g, 0.5 mmol) in 20 ml of benzene was stirred and treated under nitrogen with C₆H₁₁NC (0.054 g, 0.5 mmol). The solution was refluxed for 1 h, and then treated with charcoal and filtered. Evaporation of the solvent left an oily product which was washed with ether and dried under vacuum giving a yellow-brown solid.

*[Pd(C₁₀H₁₂OCH₃CH₃NC)(CH₃NC)₂Cl] (IVc)*. (a) To a 1 mmol sample of [Pd(C₁₀H₁₂OCH₃)Cl]₂ (II) in CH₂Cl₂ stirred under nitrogen, 6 mmol of CH₃NC in the same solvent was gently added at —10°C. The solution turned orange-yellow, and was allowed to stand at 0°C for 4 h. The reaction mixture was tested by IR spectroscopy until no free isocyanide was detected. Evaporation to dryness gave the crude product which was washed with ether and n-hexane to give a yellow-brown solid.

(b) The same compound was prepared under similar experimental conditions using [Pd(C₁₀H₁₂OCH₃)(CH₃NC)Cl] (Ic) as starting material with a molar ratio Pd/CH₃NC of 1/2.

The analogous cyclohexyl isocyanide derivative (IVd) was also prepared in the same way.

# References

1 For general surveys.
  (a) P.M. Maitlis, The Organic Chemistry of Palladium, Academic Press, New York, 1971.
  (b) U. Belluco, Organometallic and Coordination Chemistry of Platinum, Academic Press, London, 1974.
  (c) P.M. Treichel, Advan. Organometal. Chem., 11 (1973).
2 G. Carturan, M. Graziani and U. Belluco, J. Chem. Soc. A, (1971) 2509.
3 G. Carturan, M. Graziani, R. Ros and U. Belluco, J. Chem. Soc. Dalton Trans., (1972) 262.
4 R. Zanella, G. Carturan, M. Graziani and U. Belluco, J. Organometal. Chem., 65 (1974) 417.
5 A. Vitagliano and G. Paiaro, J. Organometal. Chem., 49 (1973) C49.
6 S. Brewis and P.R. Hughes, Chem. Commun., (1966) 6.
7 K.P. Wagner, P.M. Treichel and J.C. Calabresse, J. Organometal. Chem., 56 (1973) C33.
8 Y. Yamamoto and H. Yamazaki, Bull. Chem. Soc. Jap., 43 (1970) 2653.
9 M. Lenarda, R. Ros, M. Graziani and U. Belluco, J. Organometal. Chem., 65 (1974) 407.
10 T. Boschi and B. Crociani, Inorg. Chim. Acta, 5 (1971) 477.
11 S. Otsuka, A. Nakamura and T. Yoshida, J. Amer. Chem. Soc., 91 (1969) 7196.
12 H. Quast, E. Schmitt and R. Frank, Angew. Chem. Int. Ed. Engl. 10 (1971) 651.
13 (a) J. Tsuji, M. Morikawa and J. Kiji, J. Amer. Chem. Soc., 86 (1964) 4851.
  (b) L.F. Hines and J.K. Stille, J. Amer. Chem. Soc., 94 (1972) 458.
  (c) M. Graziani, G. Carturan and R. Ros, Chim. Ind. (Milan), 55 (1973) 775.
14 T. Hosokawa and P.M. Maitlis, J. Amer. Chem. Soc., 95 (1973) 4924.

15  M. Green and R.I. Hancock, J. Chem. Soc. A, (1967) 2054.
16  D.R. Coulson, J. Amer. Chem. Soc., 91 (1969) 200.
17  J.K. Stille and L.F. Hines, J. Amer. Chem. Soc., 92 (1970) 798.
18  E. Forsellini, G. Bombieri, B. Crociani and T. Boschi, J. Chem. Soc. D. Chem. Commun., (1970) 1203.
19  L. Malatesta and F. Bonati, Isocyanide Complexes of Metals, Wiley-Interscience, New York, 1969.
20  J. Chatt, L.M. Vallarino and L.M. Venanzi, J. Chem. Soc., (1957) 3443.
21  B. Crociani, P. Uguagliati, T. Boschi and U. Belluco, J. Chem. Soc. A, (1968) 2869.