Journal of Organometallic Chemistry, 303 (1986) 283–299
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PREPARATION AND REACTIONS OF PALLADIUM(II) COMPLEXES WITH C^2-BONDED HETEROAROMATIC LIGANDS *trans*-[PdCl(R_N)(PPh_3)$_2$] (R_N = 2-PYRIDYL, 2-PIRAZYL, 2-PYRIMIDYL GROUP). A NEW REACTION PATHWAY IN THE INSERTION OF ISOCYANIDES INTO THE Pd–C BOND OF *trans*-[PdXR(L)$_2$] COMPOUNDS

ROBERTA BERTANI, ADRIANO BERTON,
Centro Chimica Tecnologia Composti Metallorganici Elementi Transizione, C.N.R. Padova (Italy)

FRANCESCA DI BIANCA and BRUNO CROCIANI*
Istituto di Chimica Generale, University of Palermo (Italy)

(Received October 2nd, 1985)

Summary

The complexes *trans*-[PdCl(R_N)(PPh_3)$_2$] (I) [R_N = 2-pyridyl (2-py), 2-pyrazyl (2-pyz), 2-pyrimidyl (2-pym) group] have been prepared in high yield by deprotonation with NEt_3 of the corresponding cationic compounds *trans*-[PdCl(R_NH)(PPh_3)$_2$]$^+$ (R_NH = *N*-protonated C^2-heteroaromatic ligand) in the presence of an excess of PPh_3. In chlorinated solvents, complexes I undergo a slow reversible dimerization into the binuclear derivatives [PdCl(μ-R_N)(PPh_3)]$_2$ (II) (μ-R_N = C^2,N^1-bridging ligand). From the ^{31}P NMR spectra in 1,2-dichloroethane the following dissociation constants were obtained: 1.9 mol l^{-1} (R_N = 2-py), 5.1×10^{-2} (2-pym), 6.6×10^{-3} (2-pyz). The dimerization becomes fast and quantitative if the PPh_3, involved in the equilibrium is removed by oxidation or by reaction with [PdCl(η^3-2-MeC_3H_4)]$_2$. Only the 2-pyridyl complex Ia reacts (slowly) with CO yielding the migratory insertion product *trans*-[PdCl{C(2-py)=O}(PPh_3)$_2$], together with the dimer IIa. All the complexes I undergo migratory insertion of t-butylisocyanide with formation of *trans*-[PdCl{C(R_N) = $NCMe_3$}(PPh_3)$_2$] at rates which depend on the heterocyclic group (R_N = 2-py > 2-pyz ≫ 2-pym). The reaction of the 2-pyrazyl complex Ib with $CNCMe_3$ has been studied in detail by conductivity measurements and by IR and ^{31}P NMR spectroscopy. The data suggest a complex mechanism in which insertion occurs through rearrangement of a four-coordinate intermediate [PdCl(2-pyz)($CNCMe_3$)(PPh_3)], and through interaction of a cationic intermediate *trans*-[Pd(2-pyz)($CNCMe_3$)(PPh_3)$_2$]$^+$ (Vb) with Cl^- and with the free isocyanide of the initial equilibria. The occurrence of the latter reactions is confirmed by independent experiments in which the cationic complex Vb (isolated as perchlorate salt) is treated with an equimolar amount of [$AsPh_4$]Cl or $CNCMe_3$. The

0022-328X/86/$03.50

isocyanide-promoted insertion step represents a new mechanistic pathway for isocyanide insertion into the Pd–C bond of *trans*-[PdXR(L)$_2$] complexes.

Introduction

The complexes of d^8 metal ions of the triad nickel, palladium, and platinum with C^2-bonded nitrogen heteroaromatic ligands are generally prepared by oxidative addition of 2-haloheteroaromatics to tetrakis(triphenylphosphine)metal(0) derivatives [1,2]. With palladium, however, the reaction yields either mononuclear or binuclear products (or a mixture of the two), depending on the position of the equilibrium in eq. 1:

$$[Pd(PPh_3)_4] \xrightarrow[-2\ PPh_3]{+2\text{-}XR_N} \underset{(I)}{trans\text{-}[PdX(R_N)(PPh_3)_2]} \rightleftarrows \tfrac{1}{2}\underset{(II)}{[PdX(\mu\text{-}R_N)(PPh_3)]_2} + PPh_3 \quad (1)$$

(X = Cl, Br;

R_N = 2-pyridyl (2-py),2-pyrazyl (2-pyz),2-pyrimidyl (2-pym);

μ-R_N = C^2,N^1-bridging heterocycle)

This equilibrium is markedly influenced by the ligating ability of the N^1 nitrogen atom of R_N, as shown by the product distribution in the reactions with 2-chloropyridine, 2-chloropyrazine, and 2,6-dichloropyridine: [PdCl(μ-2-py)(PPh_3)]$_2$ [1b], a mixture of *trans*-[PdCl(2-pyz)(PPh_3)$_2$] and [PdCl(μ-2-pyz)(PPh_3)]$_2$ (molar ratio I/II of 1/4) [2c], and *trans*-[PdCl{C_5H_3(6-Cl)N-C^2}(PPh_3)$_2$] [1b,2b], respectively.

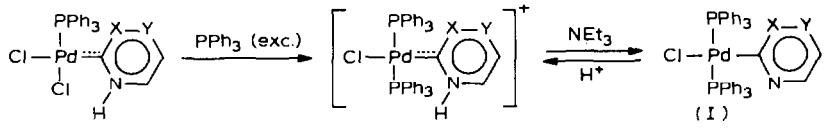
Whereas the binuclear compounds II are formed quantitatively when the mixtures I/II are treated with H_2O_2 (the oxidation of the free PPh_3 shifts the equilibrium of eq. 1 completely to the right), attempts to isolate the analytically pure complexes I by adding an excess of PPh_3 to the corresponding derivatives II give unsatisfactory results [2c]. On the other hand, the formation of mononuclear complexes with terminal R_N groups is strongly favoured when the PPh_3 ligands of I are replaced by the more basic phosphines $PMePh_2$, PMe_2Ph, and PEt_3 [1b,2a,2c,3], or by the chelating 1,2-bis(diphenylphosphino)ethane [2a].

As is shown below, the complexes of the type *trans*-[PdCl(R_N)(PPh_3)$_2$] (R_N = 2-py,2-pyz,2-pym) can be readily prepared by deprotonation of the parent N^1-protonated species, and can be isolated as pure samples from the reaction medium, because the dimerization equilibrium is slow in the presence of an excess of PPh_3. These substrates are of interest for comparative studies of reactions, such as dimerization or migratory insertion of carbon monoxide and isocyanides into the Pd–C^2 σ-bond, which are promoted by the lability of the mutually *trans*-PPh_3 ligands.

Results and discussion

Preparation and characterization of complexes I

The complexes I have been prepared in high yield by the reaction in eq. 2:



(2)

(Ia : X = Y = CH (2-py);
Ib : X = CH, Y = N (2-pyz);
Ic : X = N, Y = CH (2-pym))

When a CH_2Cl_2 suspension of the N^1-protonated compound *cis*-[$PdCl_2(R_N)(PPh_3)$] [2a,2c] is treated with an excess of PPh_3, the soluble cationic intermediate *trans*-

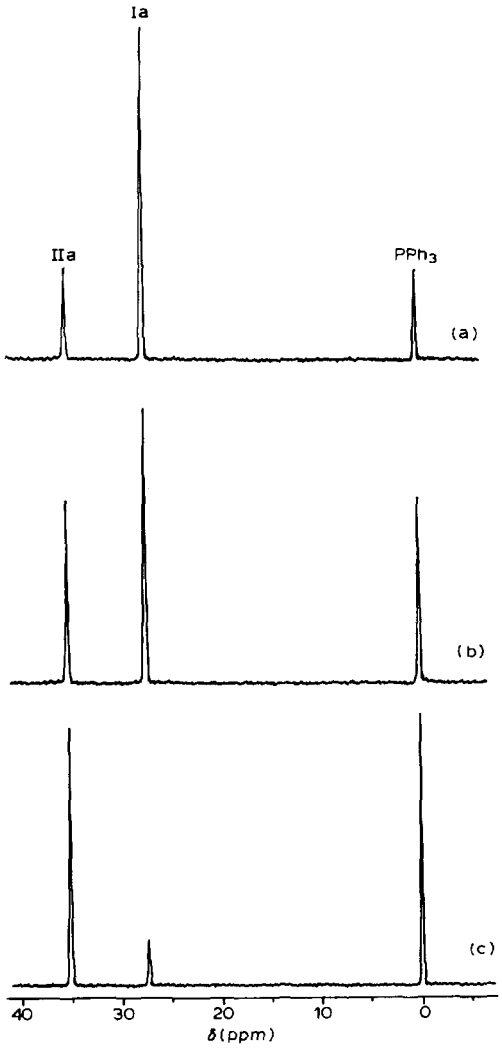


Fig. 1. ^{31}P NMR spectra at 30°C of *trans*-[PdCl(2-py)$(PPh_3)_2$] (Ia) in 1,2-dichloroethane (Ia initial concentration 0.1 *M*) at various times, showing the progress of the dimerization reaction: (a) 2 h after dissolution; (b) after 6 h; (c) after 36 h (equilibrium mixture). Chemical shifts are relative to PPh_3.

(Continued on p. 288)

TABLE 1

ANALYTICAL AND PHYSICAL DATA. CHARACTERISTIC IR ABSORPTIONS, ^1H AND ^{31}P NMR RESONANCES

Compound	Analyses (Found (calcd.) (%))				IR (cm^{-1}) [a]			^1H NMR [b]		^{31}P NMR [b]
	C	H	N	Cl	ν(C=N)	ν(Pd–Cl)	Other bands	H^6	CMe_3	
trans-[PdCl(2-py)(PPh_3)$_2$] (Ia)	65.9 (66.14)	4.6 (4.60)	1.9 (1.88)	4.8 (4.76)		289m		mk [c]		22.3s
trans-[PdCl(2-pyz)(PPh_3)$_2$] (Ib)	63.9 (64.44)	4.5 (4.46)	3.7 (3.76)	4.9 (4.75)		296m		mk [c]		22.7s
trans-[PdCl(2-pym)(PPh_3)$_2$] (Ic)	64.0 (64.44)	4.5 (4.46)	3.6 (3.76)	4.9 (4.75)		295m		mk [c]		21.1s
trans-[PdCl{C(2-py)=O}-(PPh_3)$_2$] (IIIa)	64.9 (65.30)	4.3 (4.44)	1.8 (1.81)	4.7 (4.59)	1648s [d] (1653s)	315m		8.59m		18.9s
trans-[PdCl{C(2-py)=$NCMe_3$}-(PPh_3)$_2$] (IVa)	66.2 (66.75)	5.1 (5.24)	3.3 (3.38)	4.4 (4.28)	1599s (1606s)	278m		8.21m	1.44s	18.3s

trans-[PdCl{C(2-pyz)=NCMe$_3$}-(PPh$_3$)$_2$] (IVb)	65.0 (65.22)	5.0 (5.11)	5.0 (5.07)	4.4 (4.28)	1601s (1604s)	278m		8.11dd J(H^3–H^6) 1.5 J(H^5–H^6) 2.6	1.46s	18.1s
trans-[PdCl{C(2-pym)=NCMe$_3$}-(PPh$_3$)$_2$] (IVc)					1612s (1611s)	227m		822d [e] J(H^5–H^6) 4.9	1.51s	17.5s
trans-[Pd(2-pyz)(CNCMe$_3$)-(PPh$_3$)$_2$]ClO$_4$ [f] ([Vb]ClO$_4$)	60.2 (60.55)	4.8 (4.74)	4.6 (4.71)	4.1 (3.97)			2214s [ν(C≡N)] 1090vs [ν(Cl–O)] 623s [δ(Cl–O)]	7.58dd J(H^3–H^6) 1.6 J(H^5–H^6) 2.6	0.70s	22.8s
trans-[Pd{C(2-pyz)=NCMe$_3$}-(CNCMe$_3$)(PPh$_3$)$_2$]ClO$_4$ [f] ([VIb]ClO$_4$)	61.0 (61.54)	5.2 (5.27)	5.6 (5.74)	3.8 (3.63)	1603s (1605s)		2204s [ν(C≡N)] 1098vs [ν(Cl–O)] 624s [δ(Cl–O)]	8.20dd J(H^3–H^6) 1.5 J(H^5–H^6) 2.5	0.63s 1.34s	19.4s

[a] In Nujol mulls; values in parentheses refer to CH_2Cl_2 solution. [b] NMR spectra recorded in CD_2Cl_2 solution at 30°C; ^{1}H chemical shifts (δ) in ppm from TMS; ^{31}P chemical shifts (δ) in ppm from external 85% H_3PO_4 (down-field shifts taken as positive); coupling constants in Hz; s = singlet; d = doublet; dd = doublet of doublet; m = multiplet; H^6 refers to the heterocyclic proton at position 6. [c] Masked by the intense phenyl proton resonances of PPh_3. [d] ν(C=O) band. [e] Signal of the equivalent H^4 and H^6 protons of the 2-pyrimidyl group; the H^5 proton resonates as a triplet at 6.62 ppm. [f] Molar conductivities of 96.2 and 99.0 ohm^{-1} cm^2 mol^{-1} are measured for 10^{-3} *M* MeOH solution of [Vb]ClO$_4$ and [VIb]ClO$_4$, respectively, at 25°C.

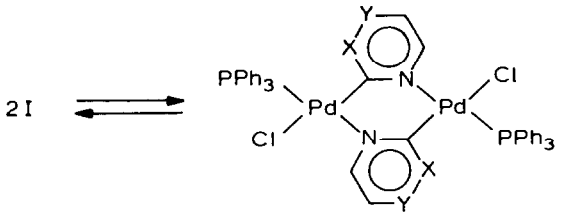
$[PdCl(R_NH)(PPh_3)_2]^+$ is formed, and this is readily deprotonated by NEt_3 to yield the products I. These complexes are stable as solids, whereas in solution they undergo a slow dimerization (see further), the rate of which is markedly lower if free PPh_3 is added to the system. For this reason analytically pure samples of I are obtained only by reprecipitation in the presence of an excess of PPh_3. The characterization is based on elemental analysis, IR spectra in the solid, and on ^1H and ^{31}P NMR spectra in CD_2Cl_2 recorded immediately after dissolution (Table 1).

The appearance of only one singlet in the ^{31}P NMR spectra suggests a *trans*-PPh_3–Pd–PPh_3 geometry for each compound. In the IR spectra a ν(Pd–Cl) band is observed in the range 296–289 cm^{-1}, which is indicative of a rather high *trans* influence for the C^2-bonded heteroaromatic ligands (cf. the ν(Pd–Cl) value of 290 cm^{-1} for *trans*-$[PdClPh(PPh_3)_2]$ [4]).

Complexes I react quantitatively with $HClO_4$ to regenerate the parent N^1-protonated cations *trans*-$[PdCl(R_NH)(PPh_3)_2]^+$ as perchlorate salts.

Dimerization reactions

In chlorinated solvents, the compounds I dimerize slowly until an equilibrium with the binuclear derivatives II and free PPh_3 according to eq. 3 is reached:



(3)

(II)

The course of the reaction can be monitored by ^{31}P NMR spectroscopy, as is shown in Fig. 1 for the dimerization of Ia in 1,2-dichloroethane at 30°C.

At equilibrium no further change in intensity of ^{31}P resonances is observed and the molar ratio I/II can be estimated from integration of the spectra. A very similar I/II equilibrium ratio is obtained in the reverse reaction of II with two equivalents of PPh_3 under the same experimental conditions. From these values and the initial concentration of I or II it is possible to calculate the dimerization constants $K = [II][PPh_3]^2/[I]^2$:

Compounds	$K(\pm 10\%, \text{mol}\,l^{-1})$
Ia/IIa	1.9
Ib/IIb	6.6×10^{-3}
Ic/IIc	5.1×10^{-2}

The constants depend markedly on the heterocyclic ligand and decrease in the order 2-py > 2-pym > 2-pyz, which parallels the order of decreasing base strength of the corresponding heterocycles: pyridine (pK_a 5.25), pyrimidine (1.31), and pyrazine (0.65) [5]. Given comparable steric requirements the formation of dimers II is therefore favoured by increasing electron-donating ability of the N^1 nitrogen atom.

The equilibrium 3 is shifted completely to the right when the free PPh_3 is oxidized

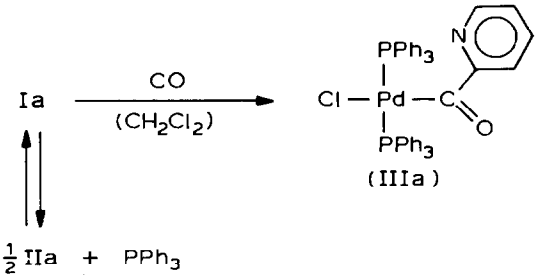
to the corresponding oxide by H_2O_2 [2c] or when it is involved in coordination to another metal center, as in reaction 4:

$$I + \tfrac{1}{2}\left[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)\right]_2 \rightarrow \tfrac{1}{2}II + \left[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_3)\right] \quad (4)$$

The ^{31}P NMR spectra of the reaction mixture in CH_2Cl_2 indicate almost immediate and quantitative formation of both products independently of the nature of the heteroaromatic ligand of I.

Migratory insertion reactions

(a) With carbon monoxide. Of the monomeric compounds I, only the 2-pyridyl derivative Ia reacts with CO (slowly, both at 1 and 40 atm) to yield the insertion product IIIa:



(5)

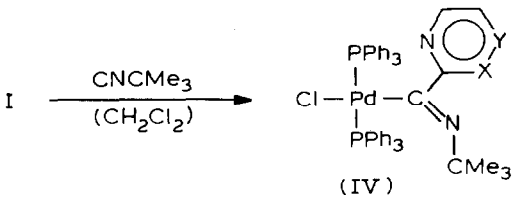
The reaction is always accompanied by dimerization of Ia to IIa even at the higher CO pressures. When no further uptake of carbon monoxide is observed (after ca. 24 h), the products consist of a mixture of IIa and IIIa together with a small amount of unreacted monomer Ia, in a molar ratio Ia/IIa/IIIa of ca. 1/4/9. Since the binuclear complex IIa does not react with carbon monoxide and the rate of CO insertion on Ia is markedly lowered by free PPh_3, the course of reaction 5 may be controlled either by thermodynamic factors, such as the establishment of a carbonylation equilibrium between Ia and IIIa, or by kinetic factors, such as a progressively reduced insertion rate caused by the increasing amount of PPh_3 liberated in the parallel dimerization reaction.

The above reactivity data and the previous observation that no CO insertion occurs with *trans*-[PdBr(2-py)$(PEt_3)_2$] [1b] can be rationalized on the basis of the carbonylation mechanism of *trans*-[MXR$(PR'_3)_2$] (M = Ni, Pd, Pt) proposed by Heck and coworkers [6,7], with a large predominance of the dissociative pathway involving a reactive four-coordinate transient intermediate:

In this context, the lower reactivity of the 2-pyridyl complex Ia compared to the phenyl derivative *trans*-[PdBrPh$(PPh_3)_2$] [6a], and the lack of reaction with the 2-pyrazyl and 2-pyrimidyl compounds Ib and Ic, respectively, can be primarily ascribed to a decreasing nucleophilic character of the C^2-carbon atom of the migrating ligand with the increasing number of nitrogen atoms in the heteroaromatic ring. On the other hand, the lack of insertion into the binuclear complex IIa is

essentially due to the inability of CO to cleave the Pd–N bond of the C^2,N^1-bridging 2-pyridyl ligand so as to generate the reactive four-coordinate species [PdCl(2-py)(CO)(PPh_3)].

(b) With t-butylisocyanide. When the complexes I are treated with $CNCMe_3$ (1/1 molar ratio), a migratory insertion occurs according to eq. 6, at different rate depending on the C^2-bonded heterocycle:



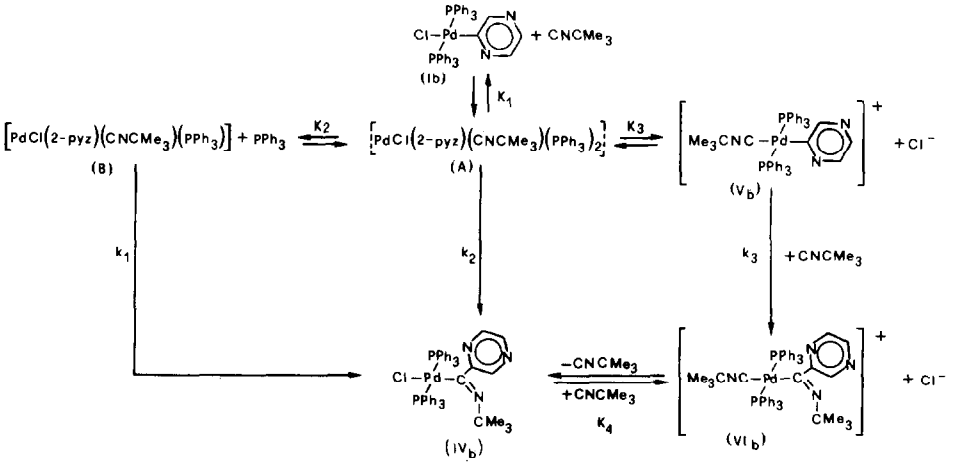
(6)

(IV)

(IVa: X = Y = CH;
IVb: X = CH, Y = N;
IVc: X = N, Y = CH)

For the 2-pyridyl complex Ia the reaction is complete in ca. 3 h at ambient temperature, whereas for the 2-pyrazyl derivative Ib it takes ca. 24 h to reach ca. 90% completion under the same experimental conditions. The reaction with the 2-pyrimidyl complex Ic is very slow, and even after 24 h at 30°C gives a mixture of products, identified by spectroscopic techniques as the insertion product IVc, the unreacted starting material Ic, and the dimer IIc, in a molar ratio IVc/Ic/IIc of ca. 3/2/1. As in the case of carbon monoxide insertion, the observed reactivity trend can be related to the different electronic properties of the heteroaromatic ligands, and in particular to reduction of the nucleophilic character of the C^2-carbon atom in the order: 2-py > 2-pyz > 2-pym.

The course of reaction 6 can be monitored by conductivity and IR measurements, and for substrates Ib and Ic also by ^{31}P NMR spectroscopy. For the 2-pyrazyl system, the evidence suggests the complex mechanism reported in Scheme 1.



SCHEME 1

The interaction of Ib with an equimolar amount of isocyanide is assumed to occur through a low-concentration five-coordinate transient species (or transition state) (**A**), from which there is fast and reversible dissociation of either PPh_3 (equilibrium K_2) or Cl^- (equilibrium K_3), or which rearranges slowly to the inserted product IVb, depending on the particular geometry it may assume, as in the case of configurationally non-rigid five-coordinate species $[PtXR(CO)(L)_2]$, proposed as intermediates in the carbonylation of $[PtXR(L)_2]$ [7]. The equilibria are shifted in favour of the cationic intermediate Vb, as indicated by the high electrical conductivity of the CH_2Cl_2 solution (at the beginning of the reaction) and its exponential decrease with time to a lower limiting value as the non-conducting product IVb is formed together with a small amount of VIb. The initial IR spectrum of the same reaction mixture shows a medium-weak $\nu(C{\equiv}N)$ band of unreacted isocyanide at 2141 cm^{-1}, and a strong $\nu(C{\equiv}N)$ absorption of coordinated isocyanide at 2210 cm^{-1} essentially due to the species Vb. The band at 2141 cm^{-1} disappears in ca. 50 min, whereas that at 2210 cm^{-1} decreases more slowly with time and moves progressively to lower wavenumbers until the weak absorption at 2202 cm^{-1} of the residual product VIb is observed after ca. 24 h. These spectral changes are accompanied by an increase of the $\nu(C{=}N)$ band of the imino group in both IVb and VIb at 1604 cm^{-1}. The cationic complex Vb was also prepared and characterized as its perchlorate salt by a different route (see Experimental and Table 1), and exhibits a $\nu(C{\equiv}N)$ band in CH_2Cl_2 solution at 2210 cm^{-1}.

The intermediate Vb reacts with Cl^- (equilibrium K_3 and step k_2) to yield the neutral product IVb, and also with the free isocyanide of equilibria K_1 and K_4 to yield the cationic product VIb (step k_3). The occurrence of these reactions was confirmed by independent experiments in which a CH_2Cl_2 solution of the complex $[Vb]ClO_4$ was treated with an equimolar amount of either $[AsPh_4]Cl$ or $CNCMe_3$. The reaction with $[AsPh_4]Cl$ affords IVb as the main product, essentially through the same mechanism as that of Scheme 1 (in the initial stage of the reaction displacement of isocyanide by Cl^- through equilibria K_3 and K_1 is, in fact, observed). The reaction of $[Vb]ClO_4$ with $CNCMe_3$ gives VIb, which can be isolated and characterized as the perchlorate salt (see Experimental and Table 1).

The establishment of equilibrium K_4 between the insertion products IVb and VIb can easily be confirmed by IR and ^{31}P NMR spectra of a CH_2Cl_2 solution of IVb upon addition of increasing amounts of $CNCMe_3$. On the other hand, the ^{31}P NMR spectrum of an equimolar mixture $[VIb]ClO_4/[AsPh_4]Cl$ in CH_2Cl_2 shows the presence of both the cation VIb and the neutral complex IVb in ca. 7/1 ratio.

Equilibria of the same type have been observed for the products of the reaction of the 6-chloro-2-pyridyl complex $[PdCl\{C_5H_3(6\text{-}Cl)N\text{-}C^2\}(dppe)]$, with an excess of $CNCMe_3$ [8].

The intermediate **B** could not be isolated, but its presence in the reaction mixture was strongly supported by the formation of Ph_3PS (characterized by a strong $\delta(^{31}P)$ singlet at 43.0 ppm) when an excess of sulfur was added to the reacting system $Ib/CNCMe_3$ in CH_2Cl_2, and by the changes in electrical conductivity and ^{31}P NMR spectra when reaction 6 was carried out in the presence of an equimolar amount of PPh_3. Under the same experimental conditions as those used for the system $Ib/CNCMe_3$, the conductivity of a CH_2Cl_2 solution of $Ib/CNCMe_3/PPh_3$ (molar ratio 1/1/1) is much higher, and decreases more slowly with time. This behaviour can be interpreted on the basis of the proposed mechanism by a shift of

the initial equilibria towards the cationic species Vb, and by a reduced contribution of the insertion step k_1 to the overall reaction rate.

The $\nu(C{\equiv}N)$ band of **B** is not observed in the IR spectrum of the reaction mixture Ib/$CNCMe_3$, as is probably masked by the strong $\nu(C{\equiv}N)$ absorption of Vb at 2210 cm^{-1}. Complexes of type **B** are likely to be generated in CH_2Cl_2 solution by the equilibrium reaction 7:

$$II + 2CNCMe_3 \rightleftarrows 2[PdCl(R_N)(CNCMe_3)(PPh_3)] \quad (7)$$

(R_N = 2-pyz, 2-pym)

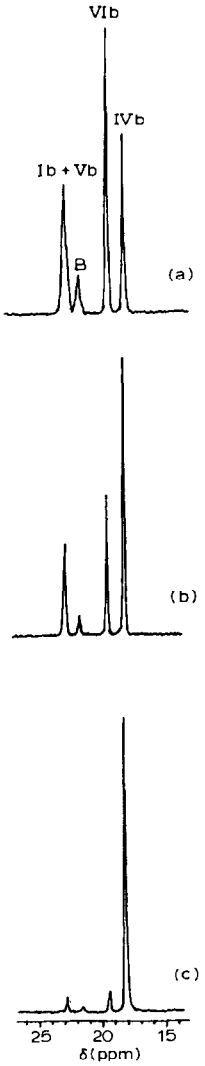


Fig. 2. ^{31}P NMR spectra at 30°C of the system *trans*-[PdCl(2-pyz)$(PPh_3)_2$] (Ib)/$CNCMe_3$ (molar ratio 1/1) in CH_2Cl_2 (Ib initial concentration 0.1 *M*) at various times: (a) 1 h after mixing of the reactants; (b) after 3 h; (c) after 24 h.

The initial IR spectra in the C≡N stretching frequency region show the presence of both free (2141 cm^{-1}) and coordinated isocyanide (2204 and 2209 cm^{-1} for R_N = 2-pyz and 2-pym, respectively). However, attempts to precipitate the product by addition of Et_2O result in precipitation of the least soluble compound, II.

In Fig. 2 and 3 are shown the ^{31}P NMR spectra at various times for the systems Ib/$CNCMe_3$ (molar ratio 1/1) and Ib/$CNCMe_3$/PPh_3 (molar ratio 1/1/1) in CH_2Cl_2 at 30°C. The resonances from Ib and Vb cannot be distinguished, as they occur at very close chemical shifts (Table 1). In contrast, the signals of the products IVb and VIb appear as two separate singlets at 18.1 and 19.4 ppm, respectively, indicating that equilibrium K_4 is slow on the NMR time scale. In Fig. 2, the

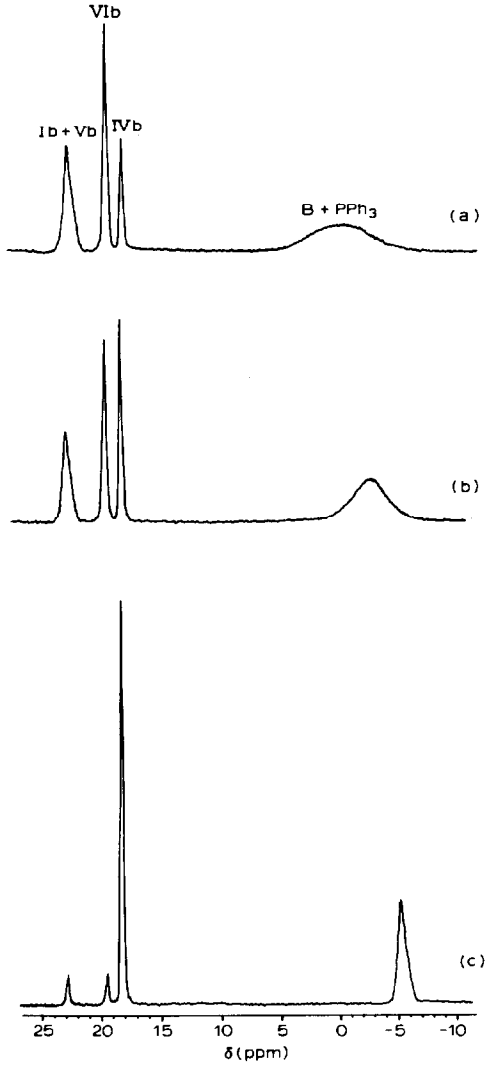


Fig. 3. ^{31}P NMR spectra at 30°C of the system *trans*-[PdCl(2-pyz)$(PPh_3)_2$](Ib)/$CNCMe_3$/PPh_3 (molar ratio 1/1/1) in CH_2Cl_2 (Ib initial concentration 0.1 *M*) at various times: (a) 1 h after mixing of the reactants; (b) after 3 h; (c) after 27 h.

additional weak and rather broad resonance at 21.6 ppm is tentatively assigned to the four-coordinate species **B**. This is further suppported by the presence of the same signal in the ^{31}P NMR spectra of the CH_2Cl_2 solutions obtained from the reaction Ib/$CNCMe_3$ (1/1) in the presence of an excess of sulfur, or from the equilibrium 7 for the system IIb/$CNCMe_3$ (1/2 molar ratio).

Addition of PPh_3 (spectrum (a) of Fig. 3) brings about the disappearance of the signal at 21.6 ppm and some broadening of the signal of Ib and Vb at 22.8 ppm, while the PPh_3 resonance appears as a very broad band at ca. −1.5 ppm. With time the singlet at 22.8 ppm decreases in intensity and sharpens, while the PPh_3 band moves to higher field. After 27 h (spectrum (c)) the latter signal appears as a broad singlet at −5.2 ppm (cf. $\delta(^{31}P)$ of PPh_3 at −5.4 ppm in CD_2Cl_2). Since the complexes Ib, [Vb]ClO_4, IVb, and [VIb]ClO_4 do not undergo fast exchange with added PPh_3 in CD_2Cl_2, the ^{31}P NMR spectra of Fig. 3 can be interpreted in terms of a fast K_2 equilibrium, which causes coalescence of **B** and PPh_3 resonances into a broad band whose chemical shift moves towards that of PPh_3 as the concentration of **B** decreases with time, and of much slower K_1 and K_3 equilibria, which only cause some broadening of the signal at 22.8 ppm.

The ^{31}P NMR spectra show also that the reactions are not 100% complete even after 24 h, and that product VIb is initially formed faster than IVb. With time, the concentration of VIb decreases and that of IVb increases, as the isocyanide liberated in the equilibrium K_4 reacts further with Ib and/or Vb.

The four-coordinate intermediate **B** undergoes the insertion step k_1 probably through a spontaneous (or solvent-assisted) process when the 2-pyz and $CNCMe_3$ ligands are *cis* to each other, as in the case of the complex *trans*-[PdIMe($CNCMe_3$)$_2$] [9]. A halide-promoted process through a five-coordinate transition state (corresponding to step k_2) was proposed for reaction of isocyanides with square-planar complexes [MXR(L)$_2$] (M = Pd, Pt) [9,10]. The "isocyanide-promoted" insertion step k_3 represents a new pathway in the insertion of isocyanides into the Pd–C σ-bond of *trans*-[PdXR(L)$_2$] compounds, which was not observed in the previous studies [9,11], probably because of the high reaction rates or the occurrence of multiple insertion processes. Studies aimed at elucidating the mechanism of step k_3 are in progress.

Formation of cationic products of type VI is observed also in the slow reactions of the 2-pyrimidyl complex Ic with $CNCMe_3$, and of the 2-pyridyl derivative *trans*-[PdCl(2-py)(PEt_3)$_2$] with methylisocyanide [12]. In the former case, the insertion processes leading to IVc and VIc (characterized by ^{31}P singlets at 17.5 and 18.7 ppm, respectively) are accompanied by dimerization of the starting substrate to the binuclear compound IIc (^{31}P singlet at 28.4 ppm in CH_2Cl_2). For the latter case, the change of ^{31}P NMR spectra with time is reported in Fig. 4.

As can be seen, four distinct resonances are detected, corresponding to the starting compound *trans*-[PdCl(2-py)(PEt_3)$_2$] (Id) (singlet at 12.7 ppm), to the cationic intermediate *trans*-[Pd(2-py)(CNMe)(PEt_3)$_2$]$^+$ (Vd) (15.9 ppm), to the neutral product *trans*-[PdCl{C(2-py)=NMe}(PEt_3)$_2$] (IVd) (14.3 ppm), and to the cationic product *trans*-[Pd{C(2-py)=NMe}(CNMe)(PEt_3)$_2$]$^+$ (·VId) (17.2 ppm). No signal attributable to a four-coordinate species of the type [PdCl(2-py)(CNMe)(PEt_3)] is observed. In line with previous observations on the carbonylation of [MXR(L)$_2$] substrates [7], this suggests that the dissociation equilibrium K_2 of Scheme 1 becomes negligible with more basic phosphines, such as PEt_3. Thus, the

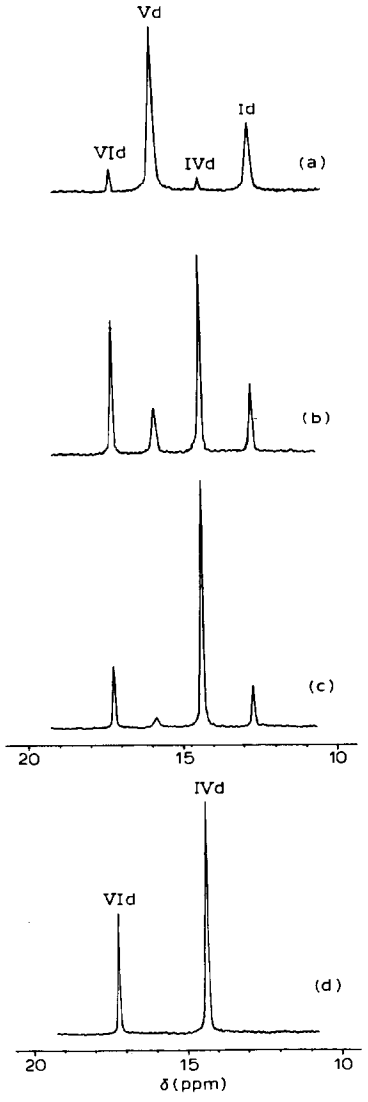


Fig. 4. ^{31}P NMR spectra of the reaction mixture *trans*-[PdCl(2-py)$(PEt_3)_2$](Id)/CNMe (molar ratio 1/1) in CH_2Cl_2 (Id initial concentration 0.05 *M*) at various times: (a) 20 min after mixing of the reactants; (b) after 150 min; (c) after 300 min (the reaction was carried out at 40°C, but the spectra were recorded at 30°C); (d) ^{31}P NMR spectrum at 30°C of the reaction mixture *trans*-[PdCl{C(2-py)=NMe}$(PEt_3)_2$] (IVd)/CNMe (molar ratio of ca. 1/1) in CD_2Cl_2, showing the formation of the cationic complex *trans*-[Pd{C(2-py)=NMe}(CNMe)$(PEt_3)_2]^+$ (VId), according to equilibrium K_4 of Scheme 1.

insertion of CNMe into the Pd–C bond of *trans*-[PdCl(2-py)$(PEt_3)_2$] proceeds essentially through equilibria K_1 and K_3 and steps k_2 and k_3.

In support of our assignments, the spectrum (d) of Fig. 4 shows the equilibrium mixture IVd/VId obtained in the reaction of *trans*-[PdCl{C(2-py)=NMe}$(PEt_3)_2$] with CNMe in a molar ratio of ca. 1/1.

Experimental

The N^1-protonated complexes *cis*-[$PdCl_2(R_NH)(PPh_3)$] [2a,2c] and the isocyanides [13] were prepared by published methods. Isocyanides were stored in Schlenk tubes in the dark under N_2 at $-10°C$ and distilled before use. All other reagents and solvents were of analytical grade and were used without further purification. Infrared spectra were recorded with a Perkin–Elmer 983 instrument, using Nujol mulls and CsI plates in the range 4000–200 cm^{-1}. For IR spectra in solution, 0.5 mm CaF_2 cells were used. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded with a Varian FT80A spectrometer operating at 79.542 and 32.203 MHz, respectively, at 30°C. The ^{31}P NMR spectra of CH_2Cl_2 and 1,2-dichloroethane solutions were run with external lock on D_2O. Conductivity measurements were carried out with a Philips PR 9500 bridge.

All reactions were carried out at room temperature unless otherwise stated. The solvents were evaporated to small volume or to dryness at reduced pressure in a rotary evaporator.

Preparation of trans-[PdCl(R_N)(PPh_3)$_2$] (I)

A suspension of *cis*-[$PdCl_2(R_NH)(PPh_3)$] (3 mmol) in CH_2Cl_2 (80 ml) was treated with PPh_3 (1.58 g, 6 mmol) and stirred until complete dissolution (ca. 30 min). The resulting cationic complex *trans*-[$PdCl(R_NH)(PPh_3)_2]^+$ was deprotonated with NEt_3 (0.45 ml). After addition of NEt_3 the solvent was evaporated to dryness, and the solid was stirred with water (90 ml), filtered off, washed 3–4 times with water, and dried in vacuo. It was redissolved in CH_2Cl_2 (50 ml), and PPh_3 (0.79 g, 3 mmol) and charcoal were added to the mixture. After filtration, the solution was concentrated to small volume and diluted with Et_2O to give the product I as off-white or pale-yellow microcrystalline solid. The yields were 78% for Ia, 86% for Ib, to 84% for Ic.

Reactions of I with $HClO_4$, H_2O_2, and [PdCl(η^3-2-MeC_3H_4)]$_2$

(a) Methanolic $HClO_4$ 0.22 *M* (3.4 ml of a solution prepared by diluting 6 ml of 60–62% aqueous perchloric acid to 250 ml with MeOH) was added to a CH_2Cl_2 solution of I (0.5 mmol in 30 ml of solvent). The mixture was worked up as described elsewhere [2c] to yield almost quantitatively the N^1-protonated cationic complex *trans*-[$PdCl(R_NH)(PPh_3)_2$]ClO_4.

(b) A solution of compound I (1 mmol) in ca. 80 ml of CH_2Cl_2 was treated with an excess of H_2O_2 (2 ml of a 30% aqueous solution). After stirring for 2–3 h the solution was dried (Na_2SO_4), filtered, and concentrated to small volume. Addition of Et_2O gave the binuclear complex II as a yellow precipitate, which was identified by comparison of its IR and ^{31}P NMR spectra with those of an authentic sample [1b,2c].

(c) The methally complex [PdCl(η^3-2-MeC_3H_4)]$_2$ (0.02 g, 0.05 mmol) was added to a CH_2Cl_2 solution of I (0.1 mmol in 2 ml of solvent). The ^{31}P NMR spectrum of the solution recorded immediately after the addition, showed quantitative formation of the dimer II (characterized by a singlet in the range 29.9–28.4 ppm) and of [PdCl(η^3-2-MeC_3H_4)(PPh_3)] (characterized by a singlet at 23.4 ppm). Compound II can be precipitated by diluting with Et_2O.

Reaction of I with carbon monoxide

A solution of the 2-pyridyl complex Ia (1.49 g, 2 mmol) in CH_2Cl_2 (70 ml) was

saturated with CO at a pressure of 1 atm. A slow insertion took place, whose progress was monitored by IR spectroscopy from the increase with time of the ν(C=O) band of product IIIa at 1653 cm^{-1}. When no further increase of ν(C=O) was observed (after ca. 24 h) the solvent was evaporated to dryness and the residue was washed several times with Et_2O. The resulting yellow solid (1.29 g) was shown to be a mixture of compounds Ia/IIa/IIIa in ca. 1/4/9 molar ratio by ^1H and ^{31}P NMR spectral analysis. Similar results were obtained in a separate experiment with a CO pressure of 40 atm. The product IIIa was separated by fractional precipitation: in this the mixture (0.5 g) was redissolved in CH_2Cl_2 (70 ml) and treated with charcoal, and the solution was filtered then concentrated to a volume of ca. 10 ml and the complex IIIa was precipitated as a yellow-greenish microcrystalline solid by dropwise addition of Et_2O (25 ml). An analytically pure sample (0.26 g) was obtained by a further precipitation from the same solvents.

A series of reactions carried out under comparable experimental conditions (CO pressure of 1 atm, Ia initial concentration of 0.03 *M*) but with increasing amounts of added PPh_3 showed that the insertion rate decreased markedly with increasing concentration of free PPh_3.

No insertion took place with the 2-pyrazyl and 2-pyrimidyl derivatives Ib and Ic, respectively, nor with the binuclear complexes II.

Reaction of I with t-butylisocyanide

The course of the reaction of I with $CNCMe_3$ in CH_2Cl_2 was followed by conductivity measurements, and by IR and ^{31}P NMR spectroscopic techniques.

(a) The complex Ia (0.50 g, 0.67 mmol) dissolved in CH_2Cl_2 (40 ml) was allowed to react with an equimolar amount of $CNCMe_3$ (6.7 ml of a CH_2Cl_2 solution 0.1 *M*). When the insertion was complete (ca. 3 h), the deep-yellow solution was treated with charcoal, filtered, and concentrated to small volume. Addition of Et_2O gave a yellow precipitate, which was redissolved in CH_2Cl_2/C_6H_6 (2/1 v/v). Evaporation of the more volatile CH_2Cl_2 solvent and dilution with Et_2O caused precipitation of product IVa (0.35 g, 63%).

(b) The reaction of the 2-pyrazyl complex Ib (0.37 g, 0.5 mmol) with an equimolar amount of $CNCMe_3$ was carried out in the way described above for Ia, yielding the yellow product IVb (0.25 g, 60%). In this case the insertion was almost complete in ca. 24 h.

(c) The reaction of the 2-pyrimidyl complex Ic (0.37 g, 0.5 mmol) with $CNCMe_3$ (5 ml of a CH_2Cl_2 solution 0.1 *M*) in CH_2Cl_2 (30 ml) was very slow, and the insertion was not complete even after 24 h at 30°C. Concentration of the solution and addition of Et_2O yielded a yellow precipitate (0.30 g), which was shown to be a mixture of compounds IVc/Ic/IIc in ca. 3/2/1 molar ratio by ^1H and ^{31}P NMR spectral analysis.

Preparation of trans-[Pd(2-pyz)(CNCMe$_3$)(PPh$_3$)$_2$]ClO$_4$ ([Vb]ClO$_4$)

This compound was prepared in 82% yield by deprotonation of *trans*-[Pd(2-pyzH)($CNCMe_3$)(PPh_3)$_2$](ClO_4)$_2$ (0.99 g, 1 mmol) with an excess of NEt_3 (0.3 ml), following the procedure reported for the analogous complex *trans*-[Pd(2-py)(CNC_6H_4OMe-*p*)(PPh_3)$_2$]ClO_4 [14].

Reaction of [Vb]ClO$_4$ with [AsPh$_4$]Cl

The reaction of [Vb]ClO_4 (0.18 g, 0.2 mmol) with [$AsPh_4$]Cl · H_2O (0.087 g, 0.2

mmol) in CH_2Cl_2 (3 ml) was monitored by IR and ^{31}P NMR spectroscopy, after filtration of the sparingly soluble salt $[AsPh_4]ClO_4$. Some isocyanide was initially displaced by Cl^- ions, as was indicated by a weak band at 2141 cm^{-1}. With time the $\nu(C{\equiv}N)$ band of cation Vb at 2210 cm^{-1} decreased in intensity, with concomitant increase of the $\nu(C{=}N)$ absorption of the insertion products at 1604 cm^{-1}. The ^{31}P NMR spectra showed that in the early stages of the reaction the cationic compound VIb was formed in much higher concentration than IVb. Eventually (after ca. 24 h), the neutral complex IVb was the predominant product of the reaction.

Reaction of [Vb]ClO_4 with t-butylisocyanide

A solution of the complex [Vb]ClO_4 (0.45 g, 0.5 mmol) in 10 ml of CH_2Cl_2 was treated with an equimolar amount of $CNCMe_3$ (5 ml of a CH_2Cl_2 solution 0.1 *M*). The IR spectra of the solution showed that insertion of isocyanide into the Pd-2-pyz bond took place as shown by the decrease of $\nu(C{\equiv}N)$ for free $CNCMe_3$ at 2141 cm^{-1} and the concomitant increase of $\nu(C{=}N)$ for the product at 1605 cm^{-1}. The reaction was complete in ca. 8 h. After standing overnight the solution was concentrated to small volume and diluted with Et_2O to precipitate the yellow compound [VIb]ClO_4, which was purified by reprecipitation from the same solvents (0.35 g, 72%).

Reaction of trans-[PdCl(2-py)(PEt_3)$_2$] (Id) with methylisocyanide

The complex *trans*-[PdCl(2-py)(PEt_3)$_2$] (Id) was generated in situ by deprotonation of *trans*-[PdCl(2-pyH)(PEt_3)$_2$]Cl (0.25 g, 0.51 mmol) with NEt_3 (0.1 ml) in CH_2Cl_2 (9 ml). The isocyanide CNMe (1.1 ml of a CH_2Cl_2 solution 5×10^{-1} *M*) was added and the solution was heated at 40°C. The progress of the reaction was monitored by IR and ^{31}P NMR spectroscopy. After 8 h, the product *trans*-[PdCl{C(2-py)=NMe}(PEt_3)$_2$] (IVd) was isolated as described elsewhere [12]. This compound reacted reversibly with CNMe in CH_2Cl_2 solution to yield the cationic derivative *trans*-[Pd{C(2-py)=NMe}(CNMe)(PEt_3)$_2$]$^+$ (VId), characterized in the equilibrium mixture by a ^{31}P singlet at 17.2 ppm and by a $\nu(C{\equiv}N)$ band at 2218 cm^{-1}.

Acknowledgments

Financial support from Ministero della Pubblica Istruzione (Research Fund 60%) is gratefully acknowledged.

References

1 (a) K. Isobe, Y. Nakamura and S. Kawaguchi, Bull. Chem. Soc. Jpn., 53 (1980) 139; (b) K. Isobe and S. Kawaguchi, Heterocycles, 16 (1981) 1603.
2 (a) B. Crociani, F. Di Bianca, A. Giovenco and A. Scrivanti, J. Organomet. Chem., 251 (1983) 393; (b) B. Crociani, F. Di Bianca, A. Giovenco and A. Scrivanti, J. Organomet. Chem., 269 (1984) 295; (c) B. Crociani, F. Di Bianca, A. Giovenco and A. Scrivanti, J. Organomet. Chem., 291 (1985) 259.
3 A. Mantovani and B. Crociani, J. Organomet. Chem., 236 (1982) C37.
4 D.R. Coulson, Chem. Commun., (1968) 1530.
5 Handbook of Tables for Organic Compound Identification, 3rd ed., The Chemical Rubber Co., Cleveland, Ohio, 1967 p. 436–437.
6 (a) P.E. Garrou and R.F. Heck, J. Amer. Chem. Soc., 98 (1976) 4115; (b) N. Sugita, J.V. Minkiewicz and R.F. Heck, Inorg. Chem., 17 (1978) 2809.

7 G.K. Anderson and R.J. Cross, Acc. Chem. Res., 17 (1984) 67.
8 A. Campagnaro, A. Mantovani and P. Uguagliati, Inorg. Chim. Acta, 99 (1985) L15.
9 S. Otsuka and K. Ataka, J. Chem. Soc., Dalton Trans., (1976) 327.
10 P.M. Treichel, K.P. Wagner and R.W. Hess, Inorg. Chem., 12 (1973) 1471.
11 Y. Yamamoto and H. Yamazaki, Inorg. Chem., 13 (1974) 438.
12 B. Crociani, M. Sala, A. Polo and G. Bombieri, Organometallics, submitted for publication.
13 (a) Organic Syntheses, J.D. Roberts (Ed.), Wiley, New York, 41 (1961) 14; (b) J. Casanova Jr., R.E. Schuster and N.D. Werner, J. Chem. Soc., (1963) 4280.
14 B. Crociani, F. Di Bianca, R. Bertani and C. Bisi Castellani, Inorg. Chim. Acta, 101 (1985) 161.