Journal of Organometallic Chemistry, 162 (1978) 99—107

REDUCTIVE ELIMINATION OF BENZONITRILE FROM CYANOPHENYL COMPLEXES OF NICKEL(II)

III *. REACTIONS OF [CYANO(PHENYL)BIS(TRIETHYLPHOSPHINE)NICKEL(II)] WITH TRIETHYLPHOSPHITE. GENERAL REACTION MECHANISM

G. FAVERO, A. MORVILLO and A. TURCO

Centro di studio sulla Stabilità e Reattività dei Composti di Coordinazione, C.N.R., Istituto di Chimica Analitica, Università di Padova (Italy)

(Received May 15th, 1978)

Summary

The kinetics of the elimination of C_6H_5CN in the reaction of $Ni(CN)(C_6H_5)[P(C_2H_5)_3]_2$ with $P(OC_2H_5)_3$ have been studied in toluene at 15°C. The results and the rate law show that the elimination mainly takes place by intramolecular decomposition of the 4-coordinate $Ni(CN)(C_6H_5)[P(OC_2H_5)_3]_2$ formed in initial substitution steps. A minor contribution to the formation of C_6H_5CN comes from the 5-coordiante species $Ni(CN)(C_6H_5)[P(C_2H_5)_3][P(OC_2H_5)_3]_2$. The intimate mechanism of these reactions, involving splitting or formation of C—CN bonds in cyanophenyl complexes, is discussed in terms of the peculiar bonding properties of the CN group.

Introduction

Previous mechanistic work [1,2] on the reactions of $Ni(CN)(C_6H_5)(PR_3)_2$ complexes (R = ethyl, cyclohexyl) with phosphorus donors (tertiary phosphines, triethylphosphite) leading to reductive elimination of C_6H_5CN, has shown that this process involves 5-coordinate intermediates of the type $Ni(CN)(C_6H_5)(P)_3$ (P = coordinated phosphorus atoms). No mechanistic evidence has so far been found in favour of the unimolecular decomposition of the 4-coordinate substrate

$$Ni(CN)(C_6H_5)(PR_3)_2 \rightleftharpoons Ni(PR_3)_2 + C_6H_5CN$$

---

* For part II see ref. 2. Presented in part at the Euchem Conference on "Oxidative-Addition and Reductive-Elimination Processes", Bressanone, September 5—10, 1977.

However, this is an expected elimination path, since the reverse reaction, oxidative addition to dicoordinate $Ni(PR_3)_2$ complexes, is well established [3]. Furthermore, some $Ni(CN)(C_6H_5)(PR_3)_2$ complexes seem to be intrinsically unstable towards elimination (vide infra). In summary, the reductive elimination process appears to involve initially the familiar bimolecular process in which a reactive intermediate of increased coordination number is formed from the 4-coordinate substrate:

$$M(X)(Y)L_2 + L' \rightleftharpoons [M(X)(Y)L_2L']$$

The subsequent steps involve two complexed processes, according to the simplified scheme:

$$[M(X)(Y)L_2L'] \left\{ \begin{array}{l} \rightarrow M(X)(Y)LL' + L \text{ (substitution)} \\ \\ \rightarrow ML_2L' + XY \text{ (reductive elimination)} \end{array} \right.$$

In continuation of our study of the elimination of C_6H_5CN from $Ni(CN)(C_6H_5)L_2$ complexes, we describe below the results of a kinetic investigation of the reaction.

$$Ni(CN)(C_6H_5)(PEt_3)_2 + 4\ P(OEt)_3 \rightarrow Ni[P(OEt)_3]_4 + C_6H_5CN + 2\ PEt_3$$

The solvent was toluene and the temperature 15°C. The object was to extend our knowledge of the paths by which such reactions can proceed and of the relative importance of these paths.

Experimental

Reagents. The complex $Ni(CN)(C_6H_5)(PEt_3)_2$ was prepared by published methods [7] and had satisfactory elemental analysis and IR spectra. The phosphite $P(OEt)_3$ was purified by treatment with NaOH followed by filtration and distillation. The other reagents (PEt_3, C_6H_5CN, $C_6H_5CH_3$) were prepared and/or purified and dried by standard methods.

All preparations and reactions were carried out in the complete absence of oxygen, usually under argon.

Kinetics. The reactions were followed spectrophotometrically in toluene at 15°C by measuring the changes in optical absorbance at 340 nm of the reacting solutions. At this wavelength the absorption of $Ni(CN)(C_6H_5)(PEt_3)_2$ is fairly strong ($\epsilon \sim 3000$) and that of the reactants is very small. The usual semilog plots of absorbance (A) vs. time were used to obtain the values of the pseudo first-order rate constants k_{obsd}. The reactions were strongly retarded by PEt_3 but were totally unaffected by an excess of C_6H_5CN or by five mol % of radical scavengers (duroquinone or galvinoxyl).

Some of the kinetic studies were performed under pseudo first-order conditions. A large excess of phosphite was always present in the solutions, but it soon became evident that to ensure simple unidirectional kinetics and to obtain linear plots of $\log(A_t - A_\infty)$ vs. time it was also necessary to use a sufficient excess of phosphine. Concentrations of the reagents were as follows. [Ni(CN)-

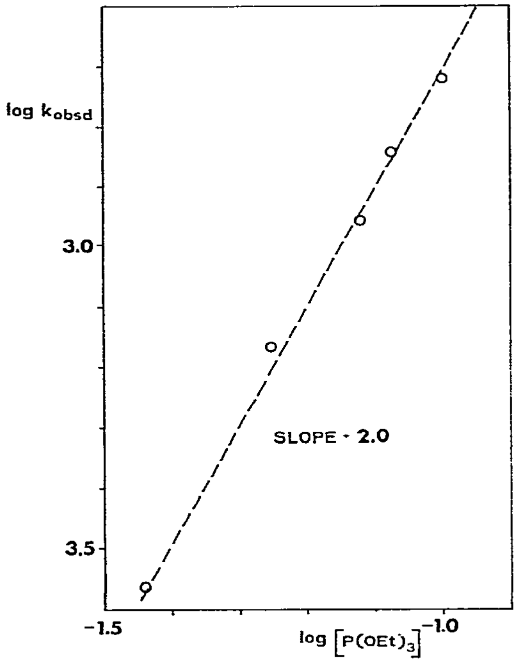


Fig. 1. Plot of log k_{obsd} vs. log[$P(OEt)_3$] to show the second order dependence on [$P(OEt)_3$]; [Complex] 3.4×10^{-4} *M*, [PEt_3] 8.5×10^{-3} *M*.

(C_6H_5)($(PEt_3)_2$], 3.4×10^{-4} *M*; [$P(OEt)_3$], in the range $3.6 \times 10^{-2} - 10^{-1}$ *M*; ([PEt_3], constant, 8.5×10^{-3} *M*). [PEt_3], in the range $5 \times 10^{-3} - 5.8 \times 10^{-2}$ *M*; ([$P(OEt)_3$], constant, 9.8×10^{-2} *M*). In Fig. 1 the double logarithmic plot of k_{obsd} against $P(OEt)_3$ shows that the reaction is of second order with respect to $P(OEt)_3$. The analogous plot of Fig. 2 gives a value of —1.53 (least-squares estimate) for the PEt_3 dependence.

Having established the reaction order with respect to $P(OEt)_3$ and PEt_3 under pseudo first-order conditions, the rate dependence on PEt_3 was investigated at low concentrations of phosphine. In these instances no phosphine was added to the solutions and the (initial) concentrations of the reagents were: [Complex], 3.4×10^{-4} *M*; [$P(OEt)_3$], in the range $5.6 \times 10^{-3} - 3.6 \times 10^{-2}$ *M*. In a single run the velocities V_t were determined by plotting the absorbance of the solution (concentration of the complex) vs. times corresponding to various complex concentrations. To investigate the dependence of the rate on PEt_3 apparent rate constants were calculated from the values of V_t. A double logarithmic plot of

$$k' = V_t/[\text{Complex}]_t[P(OEt)_3]_t^2$$

k' against [PEt_3] gave the order with respect to PEt_3 (Fig. 3). The concentrations of PEt_3 at various times were derived from those of the reactant complex assuming that the stoichiometry of the reaction was as in eq. 1.

$$Ni(CN)(C_6H_5)(PEt_3)_2 + 4\ P(OEt)_3 \rightarrow Ni[P(OEt)_3]_4 + C_6H_5CN + 2\ PEt_3 \qquad (1)$$

Equation 1 was also used to obtain the correct values of [$P(OEt)_3$] when the

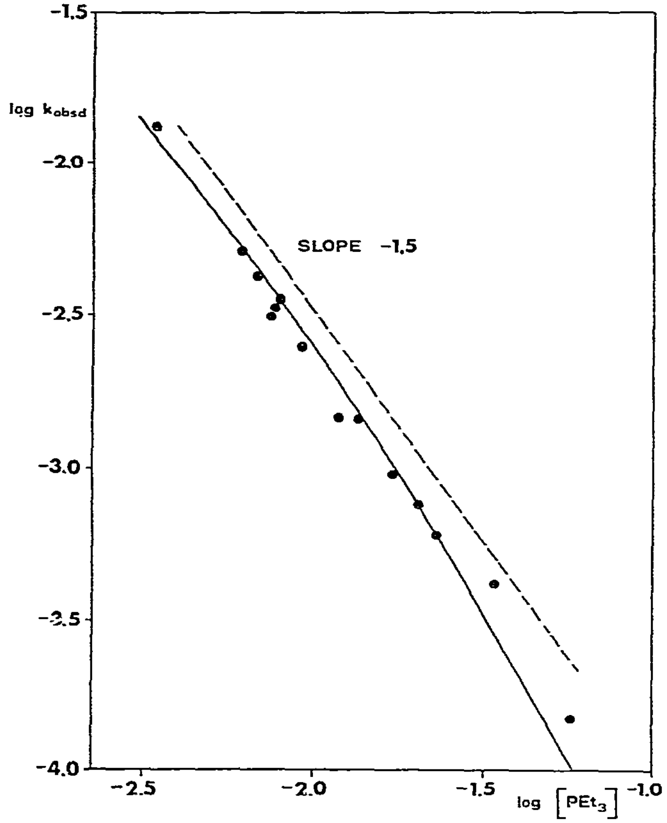


Fig. 2. Plot of log k_{obsd} vs. log[PEt$_3$]. [Complex] 3.4×10^{-4} *M*, [P(OEt)$_3$] 9.8×10^{-2} *M*. Slope determined from experimental points, —1.53. The full line represents equation 3.

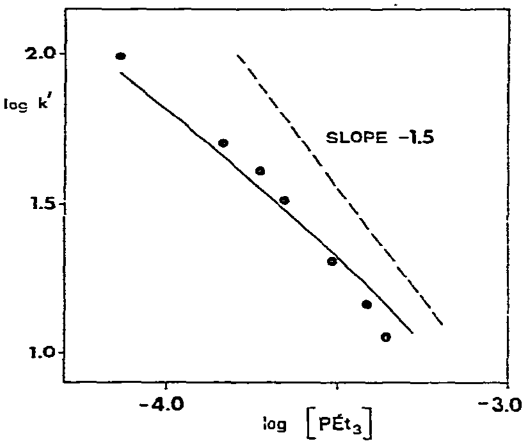


Fig. 3. The variation of log k' ($k' = V_t/[\text{Complex}]_t[\text{P(OEt)}_3]_t{}^2$) with log[PEt$_3$] to show the empirical [PEt$_3$] dependence at low phosphine concentration; [Complex] 3.4×10^{-4} — 5×10^{-5} *M*. The full line is calculated from equation 3.

amount of phosphite added to the solution was too low to ensure pseudo first-order conditions. The ^{31}P NMR spectra at ambient temperature of reacted solutions of $Ni(CN)(C_6H_5)(PEt_3)_2$ (2×10^{-2} *M*) and $P(OEt)_3$ (2×10^{-1} *M*) in toluene/C_6D_6 (5/1) confirmed that nearly all (>90%) of the phosphorus atoms bound to nickel(0) were in the phosphite form, and thus that the PEt_3 was practically entirely uncoordinated.

Results

In Fig. 1 and Fig. 2 the logarithms of the observed rate constants are plotted against the concentration of the appropriate reagent ($P(PEt)_3$ and PEt_3 respectively). The analogous plot in Fig. 3 shows the dependence of the rate on PEt_3 at low concentrations of phosphine.

The second order dependence on the concentration of phosphite is best understood as arising from a rapid pre-equilibrium:

$$Ni(CN)(C_6H_5)(PEt_3)_2 + P(OEt)_3 \rightleftharpoons Ni(CN)(C_6H_5)(PEt_3)[P(OEt)_3] + PEt_3$$

followed by a rate determining step involving the reaction with a new molecule of phosphite:

$$Ni(CN)(C_6H_5)(PEt_3)[P(OEt)_3] + P(OEt)_3 \rightarrow \text{products}$$

The inverse dependence of the rate on the concentration of PEt_3 is in agreement with this scheme, but there may be an ambiguity in the interpretation of the fractional order. Figure 2 shows that, under pseudo first-order conditions (large excess of phosphine) the observed order of the reaction with respect to PEt_3 is −1.53. On the other hand, as the rate data in Fig. 3 show, the reaction order determined at low concentrations of phosphine ranges from −1 to −1.5. These changes show that there is no real basis for a genuine fractional order, and favour a multistep process with single steps of integral order. The values of the slope ranging from −1 to −1.5 suggest the need for terms which are proportional to $[PEt_3]^{-1}$ and $[PEt_3]^{-2}$.

The course of all the rate runs, summarized in the kinetics data of Fig. 1, 2, 3, is in agreement with the empirical rate expression (eq. 2) *. This rate law and

$$V = \frac{a[P(OEt)_3]^2[\text{Complex}](a'[PEt_3] + b')}{b[PEt_3]^2 + c[PEt_3] + d[P(OEt)_3] + e[P(OEt)_3][PEt_3]} \qquad (2)$$

the available facts are consistent with the mechanism given in Scheme 1 (F = PEt_3, P = $P(OEt)_3$).

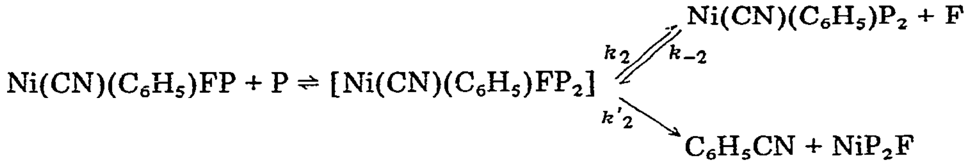
The inclusion in the rate law of the factor $(a'[PEt_3] + b')$ and of the term $e[P(OEt)_3][PEt_3]$ is related to the contribution of the reaction path k'_2, which involves a labile intermediate of composition $Ni(CN)(C_6H_5)FP_2$. The contribution of the k'_2 path to the rate is very small; it would become important only at high phosphine concentrations. The k_2 path is clearly predominant over the

---

* The values of the coefficients (determined by a least-squares program) of the rate data of Fig. 2 are: $a'/a = 2.5 \times 10^{-6}$ (12); $b'/b = 1.28$ (10); $b/a = 16230$ (11); $c/a = 320$(6); $d/a = 4.47 \times 10^{-8}$ (45); $e/a < 10^{-20}$ (in parenthesis are percentage standard deviations).

SCHEME 1

$$\mathrm{Ni(CN)(C_6H_5)F_2 + P \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ni(CN)(C_6H_5)FP + F}$$



$$\mathrm{Ni(CN)(C_6H_5)FP + P \rightleftharpoons [Ni(CN)(C_6H_5)FP_2]} \begin{array}{l} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Ni(CN)(C_6H_5)P_2 + F} \\ \xrightarrow{k'_2} \mathrm{C_6H_5CN + NiP_2F} \end{array}$$

$$\mathrm{Ni(CN)(C_6H_5)P_2 \xrightarrow{k_3} C_6H_5CN + NiP_2}$$

entire range of concentrations studied. Thus the k'_2 path can be omitted and, correspondingly, eq. 2 simplifies to eq. 3, with $a = k_1k_2k_3$, $b = k_{-1}k_{-2}$, $c = k_{-1}$,

$$V = \frac{a[\mathrm{P(OEt)_3}]^2[\mathrm{Complex}]}{b[\mathrm{PEt_3}]^2 + c[\mathrm{PEt_3}] + d[\mathrm{P(OEt)_3}]} \tag{3}$$

$d = k_2$ [*]. This simplified form of the rate equation gives as good least-squares fits as before (eq. 2) up to a phosphine concentration of about 2.5×10^{-2} M as shown by the values of the percentage standard deviations.

Further confirmation of the validity of the rate law was obtained by comparing rates of reaction observed at low concentrations of phosphine (Fig. 3) with rates calculated by the use of eq. 3. In Fig. 3 log k' and log $k_{(\mathrm{calcd})}$ are plotted against log[$\mathrm{PEt_3}$]; the data refer to concentrations of phosphine which had not been used to obtain the rate equation. The agreement is very good; the average difference between calculated and observed rates is about 15% and there are no systematic trends in the deviations.

Discussion

The elimination of $\mathrm{C_6H_5CN}$ is a multistage process consisting of the following steps. One phosphine ligand in the starting complex is replaced by one phosphite in a reversible process. The mixed complex thus formed reacts further with phosphite giving a 5-coordinate intermediate, which can undergo two types of breakdown (Scheme 1). It can either give benzonitrile and a 3-coordinate nickel(0) complex by reductive elimination (k_2' path) or alternatively, it can undergo further substitution of phosphine by phosphite (k_2 path) yielding a 4-coordinate phosphitonickel(II) complex. This complex gives, by reductive elimination, benzonitrile and a 2-coordinate nickel(0) compound (k_3 step).

In conclusion at least two possible routes exist for the reaction, and they are summarized in Scheme 2 (P = phosphorus atom of a phosphine or of a phosphite ligand)

---

[*] The least-squares fit gives the following values for the reaction coefficients: $b/a = 25130$ (12); $c/a = 140$ (14); $d/a = 0.24$ (20) (in parentheses are percentage standard deviations).

SCHEME 2

$$\begin{tikzcd}
\mathrm{Ni(CN)(C_6H_5)P_2} \arrow[r, rightleftharpoons] \arrow[d, shift left, "+\mathrm{P}"] & \mathrm{NiP_2 + C_6H_5CN} \arrow[d, shift left, "+\mathrm{P}"] \\
\mathrm{Ni(CN)(C_6H_5)P_3} \arrow[r, rightleftharpoons] \arrow[u, shift left, "-\mathrm{P}"] & \mathrm{NiP_3 + C_6H_5CN} \arrow[u, shift left, "-\mathrm{P}"] \arrow[d, shift left, "+\mathrm{P}"] \\
& \mathrm{NiP_4} \arrow[u, shift left, "-\mathrm{P}"]
\end{tikzcd}$$

The first route (a 4-coordinate path) leaves a 2-coordinate nickel(0) atom; the second route (a 5-coordinate path) yields a 3-coordinate nickel(0) complex. But since the solutions contain excess ligands, 2-, 3- and 4-coordinate nickel(0) complexes will all be present in the ratios determined by the appropriate stability constants. Moreover, these systems are generally reversible [5] (even though some steps can be very slow). These considerations justify an overall picture of the type shown in Scheme 2.

The reaction profiles for the two different elimination paths are schematically represented in Fig. 4.

The available information [6] suggests that in the majority of cases a 4-coordinate route will require a higher activation energy. This approach emphasizes the role of an external reagent P (the "promoter") in assisting the elimination of

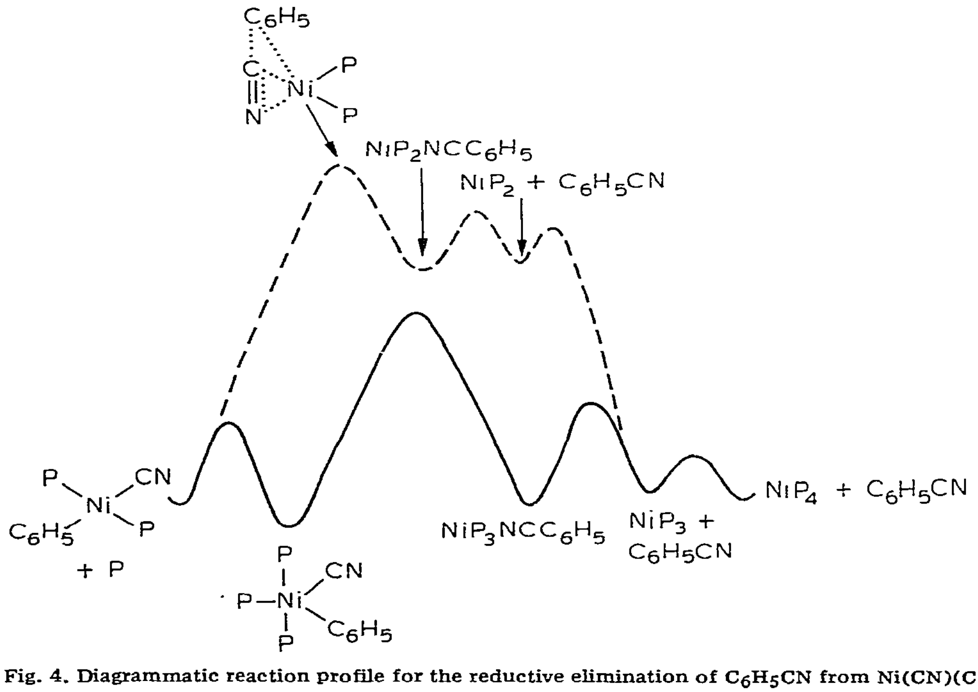


Fig. 4. Diagrammatic reaction profile for the reductive elimination of C_6H_5CN from $Ni(CN)(C_6H_5)(P)_2$ in the reaction with phosphorus donor ligands (P = phosphite or phosphine). Energies are not in scale. Activation profiles: full line, 5-coordinate path, dotted line, 4-coordinate path.

X—Y from complexes of the type $M(X)(Y)L_2$:

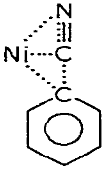
$$M(X)(Y)L_2 + nP \rightarrow ML_2P_n + X\text{—}Y$$

The present work shows that even the 4-coordinate path can become an easy decomposition route:

$$M(X)(Y)L_2 \rightarrow ML_2 + X\text{—}Y$$

The result is not completely unexpected, in view of the apparent instability of some of the $Ni(CN)(C_6H_5)L_2$ complexes. Thus, in spite of persistent attempts, we failed to obtain the complexes with L = PPh_3 (Ph = phenyl), PEt_2Ph, $Ph_2P(CH_2)_4PPh_2$, $Et_2P(CH_2)_2PEt_2$, $P(OEt)_3$ and $P(OPh)_3$ by oxidative addition of C_6H_5CN to NiL_4 or also, for the first three ligands, by chloride—cyanide exchange from $Ni(Cl)(C_6H_5)L_2$.

Before discussing briefly the intimate mechanism of the reaction we wish to point out that the reaction was totally unaffected by radical scavengers such as galvinoxyl or duroquinone. Moreover, the eliminated products were exclusively and almost quantitatively benzonitrile, nickel(0) complexes, and free phosphine. This behaviour is different from that of the halide derivatives. Under the same experimental conditions complexes of the type $Ni(Cl)(C_6H_5)(PR_3)_2$ will eliminate diphenyl and other products but not C_6H_5Cl [7]. In one case the elimination involves phenyl—cyanide coupling, in the other phenyl—phenyl coupling. It is highly improbable that this difference is due to thermodynamic factors. It is much more likely that the peculiar bonding properties of the cyanide group allow the formation of low-energy transition states which are not possible for the halide derivatives. Such bonding properties may be related to the π-bonding system of the CN group; π-interactions between benzonitrile and nickel(0) complexes are well known and can give rise to stable compounds [8]. This kind of an interaction is precluded to halo complexes. A concerted synchronous bond making—bond breaking process, with a transition state of the type:



is not conceivable for the halide derivatives. It is also true that concerted reductive eliminations are quite rare. Well established cases of concerted elimination of two one-electron carbon—carbon ligands from a metal center appears to be confined exclusively to compounds of gold(III), platinum(IV) and mercury(II) [6].

On the basis of these considerations, we believe that the same behaviour, involving making and breaking of carbon—cyanide bonds on a complexed metal atom can be expected for other nitriles, not only for those of the aryl type.

Acknowledgement

We wish to thank Dr. R. Ettorre and Dr. M. Basato for helpful discussions and Mr. F. Bergamin for technical assistance.

References

1 G. Favero and A. Turco, J. Organometal. Chem., 105 (1976) 389.
2 G. Favero, M. Gaddi, A. Morvillo and A. Turco, J. Organometal. Chem., 149 (1978) 395.
3 M. Foà and L. Cassar, J. Chem. Soc. Dalton, (1975) 2572.
4 D.H. Gerlack, A.R. Kane, G.W. Parshall, J.P. Jesson and E.L. Muetterties, J. Amer. Chem.,Soc., 93 (1971) 3543.
5 G. Favero, A. Frigo and A. Turco, Gazz. Chim. Ital., 104 (1974) 869.
6 P.J. Davidson, M.F. Lappert and R. Pierce, Chem. Rev., 76 (1976) 219.
7 G.W. Parshall, J. Amer. Chem. Soc., 96 (1974) 2630.
8 I.W. Bassi, C. Benedicenti, M. Calcaterra, R. Intrito, G. Rucci and C. Santini, J. Organometal. Chem., 144 (1978) 225.