*Journal of Organometallic Chemistry*, 377 (1989) 157–169
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20169

# Multiple insertion reactions of $\text{CNBu}^t$ into nickel–alkyl bonds

**Ernesto Carmona *, José M. Marín, Pilar Palma, and Manuel L. Poveda**

*Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Sevilla,*
*Universidad de Sevilla-C.S.I.C., 41071-Sevilla (Spain)*

(Received May 23rd, 1989)

## Abstract

Reaction of the *trans* square-planar complexes of nickel *trans*-$[\text{Ni(R)Cl(PMe}_3)_2]$ with an excess of $\text{CNBu}^t$ ($\geq 4$ equiv.) gives the chelated polyimino compounds $[\overline{\text{Ni(C(=NBu}^t\text{)C(=NBu}^t\text{)C(R)=N}}\text{Bu}^t\text{)Cl(CNBu}^t)]$ ($\text{R} = \text{CH}_3$, I; $\text{R} = \text{CH}_2\text{SiMe}_3$, II; $\text{R} = \text{CH}_2\text{C}_6\text{H}_4$-*o*-Me, III). Analogous complexes are formed for $\text{R} = \text{CH}_2\text{CMe}_3$ and $\text{CH}_2\text{CMe}_2\text{Ph}$ but could not be separated from other insertion products. The formation of the metallacyclic compounds I–III proceeds step-wise, as demonstrated by a study of the reaction of *trans*-$[\text{Ni(CH}_3\text{)Cl(PMe}_3)_2]$ with various proportions of $\text{CNBu}^t$ (from 1 to 4 equiv.) which revealed the formation of non-cyclic mono-, bis-, and tris-insertion products. The crystal structure of the *o*-methylbenzyl derivative III has been determined by X-ray crystallography. Complex III is triclinic, space group $P\bar{1}$, with cell dimensions $a$ 11.094(3), $b$ 11.660(3), $c$ 25.020(5) Å, $\alpha$ 77.65(3), $\beta$ 94.65(3), $\gamma$ 90.04(2)°, $V$ 3150.1 $\text{Å}^3$ and $Z = 4$. There are two independent molecules per asymmetric unit, each exhibiting distorted square-planar geometry round the nickel atoms. The *o*-methylbenzyl group gives rise to considerable steric interactions, and there is a restriction of rotation around the $\text{CH}_2$–C(6) bond in this complex.

## Introduction

The isocyanide ligand is isoelectronic with carbon monoxide and can undergo insertion into transition metal–carbon bonds yielding iminoacyl linkages, M–C(NR′)R. As inserting molecules, isocyanides are more versatile than CO, since in addition to $\eta^1$- and $\eta^2$-iminoacyl structures [1], a variety of polyimino-type products can be obtained [2–6].

We recently reported that the reactions of alkyl complexes of nickel(II), *trans*-$[\text{Ni(R)Cl(PMe}_3)_2]$, with 1 equiv. of $\text{CNBu}^t$ afford both $\eta^1$- and $\eta^2$-iminoacyl complexes [7]. In the presence of an excess of the isocyanide, products derived from successive insertions into the Ni–C bond of the alkyls are formed. These are the

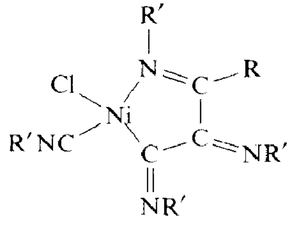
0022-328X/89/$03.50

subject of this contribution, and include bis- and tris-insertion products, the latter being formulated as [$\overline{\text{Ni(C(=NBu}^t\text{)C(=NBu}^t\text{)C(R)=N}}$Bu$^t$)Cl(CNBu$^t$)] and containing a five-membered $NiC_3N$ metallacyclic unit. The crystal structure of one such compound (R = $CH_2C_6H_4$-*o*-Me, III) is reported.

## Results and discussion

*Reaction of trans-[Ni(R)Cl(PMe$_3$)$_2$] with an excess of CNBu$^t$ ($\geq$ 4 equiv.); crystal and molecular structure of III*

The formation of polyimino-nickel complexes of type **A**, by insertion of isocyanides, CNR′, into Ni–R bonds was first reported by Otsuka et al. for the reaction of methyl iodide or alkyl chloroformates with isocyanide complexes of $Ni^0$ [2]. Analogous complexes of palladium have also been reported [3,6], and related iron species, containing metallacyclic units derived from isocyanide insertion into Fe–C bonds, are also known [4,5]. Two examples of the latter, a cyclic carbene species [4] and a 1-aza-3-ferracyclobutane ring species [5] have been structurally characterized, but to our knowledge there have been no structural investigations on polyimino chelate structures of type **A**, despite some interesting NMR features displayed by these compounds [2] that suggest restricted rotation of the alkyl group, R, due to either steric hindrance or non-planarity of the $NiC_3N$ metallacyclic unit or both.

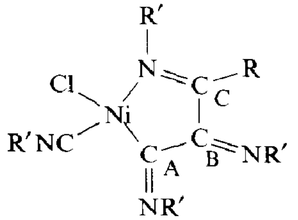

(A)

During previous studies of the formation of mono-insertion products, [Ni($\eta^1$-C(NBu$^t$)R)Cl(PMe$_3$)$_2$] [7], it became evident that the use of two or more equivalents of CNBu$^t$ in some instances led to tris-insertion products of structure **A**. With the aim of structurally characterizing one of these derivatives, the reaction of the alkyls *trans*-[Ni(R)Cl(PMe$_3$)$_2$] (R = Me, $CH_2SiMe_3$, $CH_2C_6H_4$-*o*-Me, $CH_2CMe_3$, $CH_2CMe_2Ph$) with an excess of CNBu$^t$ (4 equiv.) has been investigated.

When the above alkyls are stirred with an excess of CNBu$^t$ in diethyl ether as solvent variable amounts of an insoluble yellow powder precipitate out of the solution. This material exhibits very broad IR bands and possibly consists of metal-free polymeric isocyanide species, although other alternative explanations have been suggested [8]. In addition, red solutions are obtained from which pure products can be isolated by crystallization for R = Me (I), $CH_2SiMe_3$ (II), and $CH_2C_6H_4$-*o*-Me (III). Compounds I–III are red, and very soluble in common organic solvents, and can be formulated as "Ni(R)Cl(CNBu$^t$)$_4$" on the basis of analytical data. $^{31}$P NMR studies show the reaction occurs with complete loss of $PMe_3$, since only the characteristic high-field NMR resonance at ca. −63 ppm due to free $PMe_3$ is observed after the reaction mixture has been stirred for about 1 h. The IR spectra of I–III show a strong absorption centred at ca. 2170 cm$^{-1}$, attributed to a terminal isocyanide ligand, together with several medium intensity bands in the range 1670–1600 $cm^{-1}$. The position of the latter bands indicate that the remaining $CNBu^t$ groups have been involved in an insertion process that generates $C{=}NBu^t$ groups.

The $^1H$ NMR spectra of compounds I–III show resonances corresponding to the alkyl and the isocyanide groups. In II and III, the methylene protons are diastereotopic, and give rise to AB quartets. As previously pointed out, this may be due to restricted rotation of the alkyl group or to substantial deviation from planarity, or to both effects. No useful information about the structural detail of the molecules of I–III can however be obtained from these data, but the $^{13}C$ NMR spectra are much more informative and are fully in accord with the formulation of these compounds depicted in eq 1. Thus, in addition to signals corresponding to the methyl and quaternary carbons of the t-butyl groups (Table 2), three low-field singlets centred at ca. 190, 180 and 155 ppm are observed. The two signals at 190 and 180 ppm can be assigned to the carbon atoms $C^A$ and $C^B$, respectively (see eq. 1), on the basis of previous work on iminoacyl complexes of nickel [7], and also in the light of data discussed below for the bis- and tris-insertion $PMe_3$-containing products, while the signal at 155 ppm is due to the third metallacyclic carbon atom, $C^C$. No signal assignable to the nickel-bound carbon of the coordinated isocyanide ligand, $NiCNBu^t$, was observed possibly owing to unfavourable relaxation properties. Compound I (R = Me) was previously prepared by the reaction of $[Ni(CNBu^t)_4]$ with methyl chloroformate [2].

*trans*-$[Ni(R)Cl(PMe_3)_2] + 4CNBu^t \longrightarrow$



(I: R = Me,
II: $R = CH_2SiMe_3$,
III: $R = CH_2C_6H_4$-*o*-Me) (1)

Because of the intrinsic interest of the structural parameters of the metallacyclic $NiC_3N$ unit, and also to examine the possibility of restricted rotation of the alkyl group R due to steric hindrance, an X-ray crystal structure determination of the *o*-xylyl derivative III was undertaken. An ORTEP illustration of $[Ni(C({=}NBu^t)C({=}NBu^t)C(R){=}NBu^t)Cl(CNBu^t)]$, showing the atom numbering scheme is presented in Fig. 1. Tables 3 and 4 * show relevant crystal data and selected interatomic bond distances and angles. Details of the structure determination are given in the Experimental Section. The formally $Ni^{II}$ ion is in a distorted square-planar environment, with the terminal isocyanide and chloride ligands occupying mutually *cis* positions and a carbon and a nitrogen atom of the polyimino group in the remaining coordination sites. The nickel centre and the four atoms directly bonded to it are essentially in a planar distribution, although there is a small distortion toward square-pyramidal coordination manifested by the positioning of

---

* In Tables 1 and 2 are listed the analytical and NMR spectral data for compounds I–V and in Table 5, the atomic coordinates for compound III.

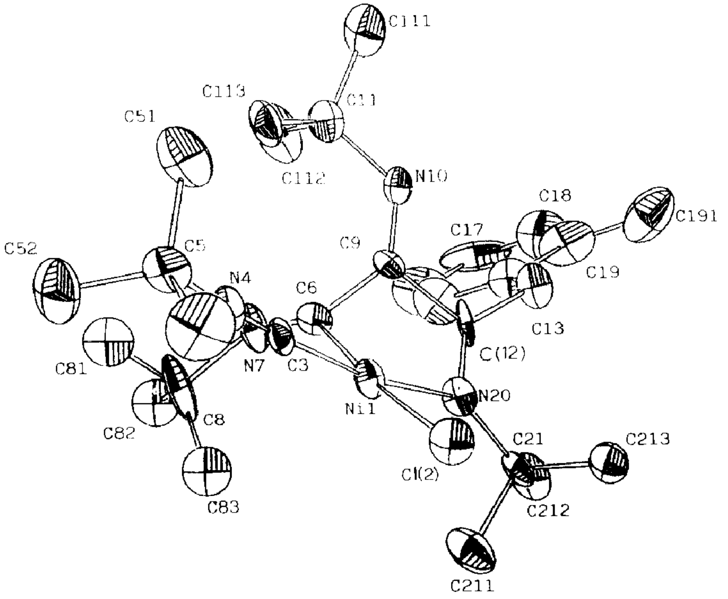


Fig. 1. ORTEP diagram of complex III. The hydrogen atoms are omitted for clarity.

the Ni$^{II}$ ion slightly above the coordination plane (+0.11 Å), probably to relieve some steric strain. The carbon atoms of the metallacyclic unit that are not directly bonded to nickel, C(9) and C(12), show considerable deviation from planarity, these deviations being of opposite sign to that of the nickel centre already alluded to and amounting −1.25 and −0.98 Å, respectively. On the other hand the atoms N(10) and C(13), directly bonded to C(9) and C(12), respectively, are also on the same side of the mean-square plane (i.e. opposite to the nickel centre). It is therefore evident that the coordination plane is not a plane of symmetry. A close inspection of the structure of III reveals considerable restriction to rotation of the *o*-xylyl group because of strong steric interactions with the Bu$^t$ groups bonded to N(10) and N(20). These steric interactions are minimized through an angle of 80.4° between the Ph ring and the C(9)C(12)N(20) plane. The Ni–C(6) bond length of 1.91(1) Å appears normal, and comparable to the Ni–C distance found in the dialkyl [Ni(CH$_2$SiMe$_3$)$_2$(py)$_2$] [9]. Similarly, the Ni–N(20) separation of 1.962(9) Å is in the range found for other complexes of Ni$^{II}$ containing N-donor ligands.

As mentioned above, the reactions of the complexes *trans*-[Ni(R)Cl(PMe$_3$)$_2$] (R = CH$_2$CMe$_3$, CH$_2$CMe$_2$Ph) with an excess of CNBu$^t$ were also examined, but we were unable to isolate pure products. NMR studies however, show that compounds analogous to I–III are formed, mixed with other species resulting from subsequent insertion of CNBu$^t$ into the Ni–C bond of the initial product.

### *Sequential insertion of CNBu$^t$ into the Ni–C bond of trans-[Ni(CH$_3$)Cl(PMe$_3$)$_2$]*

In independent and parallel work, Bochmann and co-workers have reported [8] the isolation of the bis-insertion product, [Ni(C(=NBu$^t$)C(=NBu$^t$)CH$_3$)Cl(PMe$_3$)$_2$], (IV), according to the reaction sequence of Scheme 1. The poly-insertion cyclic product I, was not however observed. In order to gain further information on the reaction leading to the metallacyclic products I–III, we made a detailed study of the reaction of the methyl complex *trans*-[Ni(CH$_3$)Cl(PMe$_3$)$_2$] with various molar

*(Continued on p. 163)*

Table 1

Analytical, IR, $^{31}P\{^1H\}$ and, $^1H$ NMR data for compounds I–V

| | Analytical data [a] | | | IR ($\nu$(CN)) [b] | $^{31}P\{^1H\}$ [c] | $^1H$ NMR [c] | | |
|---|---|---|---|---|---|---|---|---|
| | C | H | N | | | $PMe_3$ | $Me_3CNC$ | Others |
| *I* [d] | 57.4 | 8.9 | | 2180, 1675 | – | – | 0.83, 1.45 | 1.93 (C–Me) |
| | (57.1) | (8.8) | | 1642, 1620 | | | 1.56, 1.65 | |
| II | 56.5 | 9.2 | | 2180, 1670 | – | – | 0.81, 1.55 | 0.18 ($SiMe_3$) |
| | (56.1) | (9.2) | | 1650, 1625 | | | 1.59, 1.62 | 2.0, 2.85 ($CH_2$)<br>$J_{AB}$ 11.4 |
| III | 63.2 | 8.6 | 11.2 | 2160, 1650 | – | – | 0.81, 1.40 | 2.0 (Me), 6.8–7.2 (Ar) |
| | (63.3) | (8.5) | (10.5) | 1630, 1600 | | | 1.55, 1.66 | 3.60, 4.52 ($CH_2$)<br>$J_{AB}$ 15.5 |
| IV | 48.0 | 9.2 | 6.7 | 1630, 1562 | −15.8 | 1.06 (pt) | 1.32, 1.75 | 2.04 (C–Me) |
| | (47.8) | (9.1) | (6.6) | | | (3.7) | | |
| V | – | – | – | 1660, 1630 | −15.1 ($P_A$) | 1.17 (m) | 1.21, 1.40 | 1.79 (C–Me) |
| | | | | 1560 | −15.3 ($P_B$)<br>$J_{AB}$ 195 | | 1.63 | |

[a] Calculated values in parentheses. [b] Nujol mull, $cm^{-1}$. [c] In $C_6D_6$. *J* in Hz. Singlets unless otherwise indicated, pt = pseudotriplet, m = multiplet. [d] Data for the known complex I are given for comparative purposes.

Table 2

$^{13}C\{^1H\}$ NMR data for compounds I–V [a]

| | $\mathit{Me}_3$CNC | $Me_3$CNC | $Me_3$CNC | $PMe_3$ | Others |
|---|---|---|---|---|---|
| I | 29.0, 30.2 | 54.9 56.5 | 156.7, 179.7 | – | 17.9 (C-*Me*) |
| | 30.3, 31.2 | 60.9 | 189.0 | | |
| II | 29.0, 30.2 | 54.6, 56.8 | 156.8, 182.0 | – | 0.3 ($SiMe_3$), 25.1 ($CH_2Si$) |
| | 30.8, 31.2 | 59.8 | 188.2 | | |
| III | 29.0, 30.2 | 54.6, 56.5 | 155.1, 181.1 | – | 19.6 (Me), 34.9 ($CH_2$) |
| | 30.6, 30.9 | 56.8, 61.3 | 188.4 | | 125.9, 126.2, 127.8, 129.7 (CH, Ar) |
| | | | | | 135.2, 135.5 (C, Ar) |
| IV | 30.4, 31.2 | 55.3, 56.5 | 171.4 | 13.7 | 18.2 (C–*Me*) |
| | | | 196.9 (t, 25.2) | (pt, 12.6) | |
| V | 29.9, 30.6 | 55.3, 56.5 | 168.7, 168.7 | 13.7 (m) | 22.9 (C–*Me*) |
| | 31.2 | | 197.4 (t, 26.5) | | |

[a] In $C_6D_6$. $J$ in Hz. Singlets unless otherwise indicated, pt = pseudotriplet, m = multiplet.

Table 3

Summary of crystal data for compound III

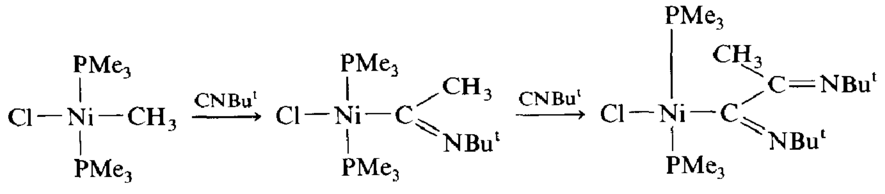
| | |
|---|---|
| Empirical formula | $C_{28}ClH_{45}N_4Ni$ |
| Color | Red |
| Space group | $P\bar{1}$ |
| Cell dimens | |
| $a$, Å | 11.094(3) |
| $b$, Å | 11.660(3) |
| $c$, Å | 25.020(5) |
| $\alpha$, deg | 77.65(3) |
| $\beta$, deg | 94.65(3) |
| $\gamma$, deg | 90.04(2) |
| $Z$ | 4 |
| $V$, Å$^3$ | 3150.1 |
| $D$ calcd, g cm$^{-3}$ | 1.12 |
| wavelength, Å | 0.71069 |
| temp., °C | 20 |
| mol. wt. | 531.2 |
| linear abs. coeff., cm$^{-3}$ | 7.21 |
| $2\theta$ range, deg | 50 |
| unique data | 9230 |
| data with $I \geq 3\sigma(I)$ | 4089 |
| $R(F)$ | 0.061 |
| $R_w(F)$ | 0.071 |

proportions of $\mathrm{CNBu^t}$ (from 1 to 4 equiv.). We recently reported [7], as have others [8], that the addition of 1 equiv. of $\mathrm{CNBu^t}$ to a solution of the above alkyl affords the $\eta^1$-iminoacyl $[\mathrm{Ni(\eta^1\text{-}C(NBu^t)CH_3)Cl(PMe_3)_2}]$, as shown in eq. 2. In the

$$trans\text{-}\left[\mathrm{Ni(CH_3)Cl(PMe_3)_2}\right] + \mathrm{CNBu^t} \longrightarrow trans\text{-}\left[\mathrm{Ni(\eta^1\text{-}C(NBu^t)CH_3)Cl(PMe_3)_2}\right] \qquad (2)$$

presence of another equivalent of $\mathrm{CNBu^t}$, the bis-insertion product IV (Scheme 1) is obtained. Compound IV is a red species that can be isolated by fractional crystallization of the product mixture. Its most notable spectroscopic feature is the appearance of the nickel-bound carbon resonance as a triplet at 197 ppm ($^2J$(PC) 25 Hz) in the $^{13}C$ NMR spectrum. This is in accord with the proposed *trans* distribution of the $\mathrm{PMe_3}$ ligands, which is firmly established by the presence of a virtually-coupled triplet in the $^1H$ NMR spectrum of IV. The other imino carbon atom in IV gives rise to a singlet at somewhat higher field (171 ppm).

Complex IV, the initial product of the reaction mixture, is always accompanied by variable amounts of the tris-insertion product, V, formed in a process competi-



(IV)

Scheme 1

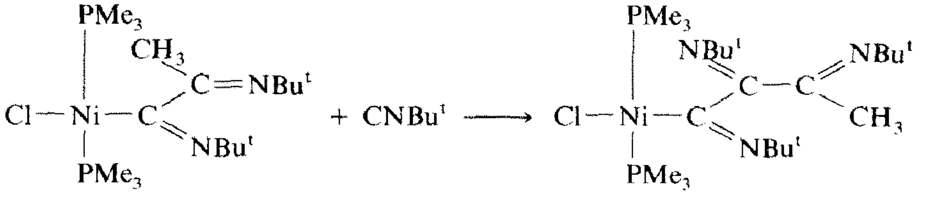
Table 4

Bond distances and angles for compound III [a]

| | A | B | | A | B |
|---|---|---|---|---|---|
| *Bond distances (Å)* | | | | | |
| Ni(1)–O(12) | 2.260(4) | 2.243(4) | C(9)–C(12) | 1.50(2) | 1.52(2) |
| Ni(1)–C(3) | 1.82(1) | 1.81(1) | N(10)–C(11) | 1.49(1) | 1.49(1) |
| Ni(1)–C(6) | 1.92(1) | 1.91(1) | C(11)–C(111) | 1.53(2) | 1.55(2) |
| Ni(1)–N(20) | 1.962(9) | 1.955(9) | C(11)–C(112) | 1.53(2) | 1.52(2) |
| C(3)–N(4) | 1.16(1) | 1.14(1) | C(11)–C(113) | 1.53(2) | 1.50(2) |
| N(4)–C(5) | 1.470(9) | 1.472(9) | C(12)–C(13) | 1.51(2) | 1.51(2) |
| C(5)–C(51) | 1.50(2) | 1.38(3) | C(12)–N(20) | 1.29(2) | 1.28(1) |
| C(5)–C(52) | 1.51(2) | 1.49(4) | C(13)–C(14) | 1.52(1) | 1.53(1) |
| C(5)–C(53) | 1.50(2) | 1.57(4) | C(14)–C(15) | 1.37(2) | 1.36(2) |
| C(6)–N(7) | 1.26(1) | 1.23(1) | C(14)–C(19) | 1.42(1) | 1.42(1) |
| C(6)–C(9) | 1.47(1) | 1.49(1) | C(15)–C(16) | 1.41(2) | 1.42(2) |
| N(7)–C(8) | 1.52(2) | 1.47(1) | C(16)–C(17) | 1.38(3) | 1.35(2) |
| C(8)–C(81) | 1.49(3) | 1.47(2) | C(17)–C(18) | 1.36(3) | 1.35(2) |
| C(8)–C(82) | 1.55(3) | 1.51(2) | C(18)–C(19) | 1.38(2) | 1.39(1) |
| C(8)–C(83) | 1.48(3) | 1.51(3) | C(19)–C(191) | 1.49(2) | 1.50(1) |
| C(9)–N(10) | 1.26(1) | 1.29(1) | | | |
| *Bond angles (°)* | | | | | |
| C(12)–Ni(1)–C(3) | 86.8(4) | 88.2(5) | N(10)–C(9)–C(12) | 119(1) | 120(1) |
| C(12)–Ni(1)–C(6) | 173.1(4) | 172.7(4) | C(9)–N(10)–C(11) | 124(1) | 122(1) |
| C(12)–Ni(1)–N(20) | 98.8(3) | 99.4(3) | N(10)–C(11)–C(av.) | 111(2) | 109(3) |
| C(3)–Ni(1)–C(6) | 92.6(6) | 92.1(6) | C–C(11)–C(av.) | 108(2) | 110(1) |
| C(3)–Ni(1)–N(20) | 169.1(6) | 167.1(6) | C(9)–C(12)–C(13) | 115(1) | 117(1) |
| C(6)–Ni(1)–N(20) | 80.6(5) | 79.1(5) | C(9)–C(12)–N(20) | 113(1) | 111(1) |
| Ni(1)–C(3)–N(4) | 173(1) | 177(1) | C(13)–C(12)–N(20) | 132(1) | 132(1) |
| C(3)–N(4)–C(5) | 173(1) | 174(1) | C(12)–C(13)–C(14) | 113(1) | 113(1) |
| N(4)–C(5)–C (av.) | 107(1) | 109(2) | C(13)–C(14)–C(15) | 125(1) | 124(1) |
| C–C(5)–C (av.) | 112(2) | 110(4) | C(13)–C(14)–C(19) | 115(1) | 115(1) |
| Ni(1)–C(6)–N(7) | 139(1) | 139(1) | C(15)–C(14)–C(19) | 120(1) | 121(1) |
| Ni(1)–C(6)–C(9) | 95(1) | 96(1) | C(14)–C(15)–C(16) | 122(2) | 121(1) |
| N(7)–C(6)–C(9) | 124(1) | 123(1) | C(15)–C(16)–C(17) | 117(2) | 117(2) |
| C(6)–N(7)–C(8) | 127(1) | 129(1) | C(16)–C(17)–C(18) | 119(2) | 123(2) |
| N(7)–C(8)–C (av.) | 107(3) | 109(2) | C(17)–C(18)–C(19) | 125(2) | 122(2) |
| C–C(8)–C (av.) | 112(3) | 109(2) | C(14)–C(19)–C(18) | 116(2) | 116(1) |
| C(6)–C(9)–N(10) | 134(1) | 135(1) | C(18)–C(19)–C(191) | 120(2) | 121(1) |
| C(6)–C(9)–C(12) | 107(1) | 105(1) | C(14)–C(19)–C(191) | 125(2) | 123(1) |

[a] **A** and **B**: the two independent molecules of III found in the crystal structure.

tive with that leading to IV. Addition of 1 equiv. of CNBu$^t$ to solutions of IV gives a mixture in which the tris-insertion compound V predominates (eq. 3). We have



(IV) (V) (3)

Table 5

Atomic coordinates and $U_{\mathrm{iso}} = (U_{11}U_{22}U_{33})^{1/3}$ for compound III

Molecule **A**: atoms Ni(1) until C(213); molecule **B**: atoms Ni(2) until last. The serial numbers of atoms in molecule **B** are obtained by adding 20 to the corresponding atoms in molecule **A** (except for Ni).

| ATOM | $x$ | $y$ | $z$ | $U_{\mathrm{iso}}$ |
|---|---|---|---|---|
| Ni(1) | 0.2089(2) | 0.0417(2) | 0.1907(1) | 0.0430 |
| Cl(2) | 0.3224(4) | −0.0683(4) | 0.2639(2) | 0.0614 |
| C(3) | 0.1069(11) | 0.0713(13) | 0.2399(5) | 0.0396 |
| N(4) | 0.0526(10) | 0.0872(11) | 0.2753(4) | 0.0501 |
| C(5) | −0.0025(14) | 0.1053(13) | 0.3244(5) | 0.0490 |
| C(51) | −0.1363(17) | 0.0882(18) | 0.3149(7) | 0.0851 |
| C(52) | 0.0521(19) | 0.0152(17) | 0.3729(7) | 0.0797 |
| C(53) | 0.0233(16) | 0.2289(16) | 0.3288(7) | 0.0730 |
| C(6) | 0.1242(11) | 0.1498(10) | 0.1310(5) | 0.0383 |
| N(7) | 0.0296(10) | 0.1542(12) | 0.0993(5) | 0.0551 |
| C(8) | −0.0753(15) | 0.0700(21) | 0.1061(7) | 0.0699 |
| C(81) | −0.1573(24) | 0.1161(24) | 0.1411(11) | 0.1086(89) |
| C(82) | −0.1340(23) | 0.0752(23) | 0.0473(10) | 0.1027(85) |
| C(83) | −0.0320(25) | −0.0517(26) | 0.1287(12) | 0.1095(91) |
| C(9) | 0.2280(10) | 0.2270(11) | 0.1191(5) | 0.0342 |
| N(10) | 0.2428(9) | 0.3354(10) | 0.1141(4) | 0.0420 |
| C(11) | 0.1457(13) | 0.4202(13) | 0.1185(6) | 0.0610 |
| C(111) | 0.2035(16) | 0.5373(17) | 0.1232(7) | 0.0788 |
| C(112) | 0.0741(14) | 0.3816(15) | 0.1687(7) | 0.0673 |
| C(113) | 0.0619(18) | 0.4427(18) | 0.0653(8) | 0.0963 |
| C(12) | 0.3308(11) | 0.1519(15) | 0.1104(5) | 0.0277 |
| C(13) | 0.4293(14) | 0.2184(15) | 0.0791(5) | 0.0603 |
| C(14) | 0.3918(15) | 0.2630(14) | 0.0184(5) | 0.0455 |
| C(15) | 0.2813(18) | 0.2453(17) | −0.0069(6) | 0.0765 |
| C(16) | 0.2507(23) | 0.2903(21) | −0.0631(8) | 0.1052 |
| C(17) | 0.3341(28) | 0.3596(17) | −0.0920(8) | 0.0779 |
| C(18) | 0.4440(22) | 0.3754(21) | −0.0665(8) | 0.1211 |
| C(19) | 0.4792(17) | 0.3304(15) | −0.0120(7) | 0.0705 |
| C(191) | 0.6013(19) | 0.3566(20) | 0.0111(9) | 0.1171 |
| N(20) | 0.3214(9) | 0.0423(10) | 0.1340(4) | 0.0372 |
| C(21) | 0.3994(13) | −0.0512(12) | 0.1245(5) | 0.0395 |
| C(211) | 0.3325(16) | −0.1640(16) | 0.1435(7) | 0.0745 |
| C(212) | 0.5220(14) | −0.0563(14) | 0.1572(7) | 0.0620 |
| C(213) | 0.4151(15) | −0.0401(16) | 0.0629(6) | 0.0648 |
| Ni(2) | 0.7186(2) | 0.4337(2) | 0.2905(1) | 0.0417 |
| Cl(22) | 0.7824(4) | 0.3879(4) | 0.2148(2) | 0.0647 |
| C(23) | 0.8509(13) | 0.5240(12) | 0.2934(6) | 0.0427 |
| N(24) | 0.9367(10) | 0.5775(11) | 0.2950(5) | 0.0451 |
| C(25) | 1.0515(14) | 0.6410(15) | 0.2930(8) | 0.0352 |
| C(251) | 1.0591(29) | 0.7075(33) | 0.3324(17) | 0.0532 |
| C(252) | 1.0579(39) | 0.7116(39) | 0.2364(16) | 0.0935 |
| C(253) | 1.1578(38) | 0.5478(38) | 0.3030(18) | 0.1410(149) |
| C(26) | 0.6754(11) | 0.4551(10) | 0.3602(5) | 0.0309 |
| N(27) | 0.6266(10) | 0.5302(9) | 0.3797(4) | 0.0404 |
| C(28) | 0.5876(15) | 0.6503(13) | 0.3529(6) | 0.0558 |
| C(281) | 0.4800(20) | 0.6814(18) | 0.3780(9) | 0.0956 |
| C(282) | 0.6904(23) | 0.7305(16) | 0.3624(10) | 0.1085 |
| C(283) | 0.5622(21) | 0.6644(21) | 0.2915(10) | 0.1334(87) |
| C(29) | 0.6876(11) | 0.3289(10) | 0.3888(5) | 0.0250 |
| N(30) | 0.7513(10) | 0.2706(9) | 0.4314(4) | 0.0471 |
| C(31) | 0.8298(13) | 0.3304(12) | 0.4680(5) | 0.0410 |

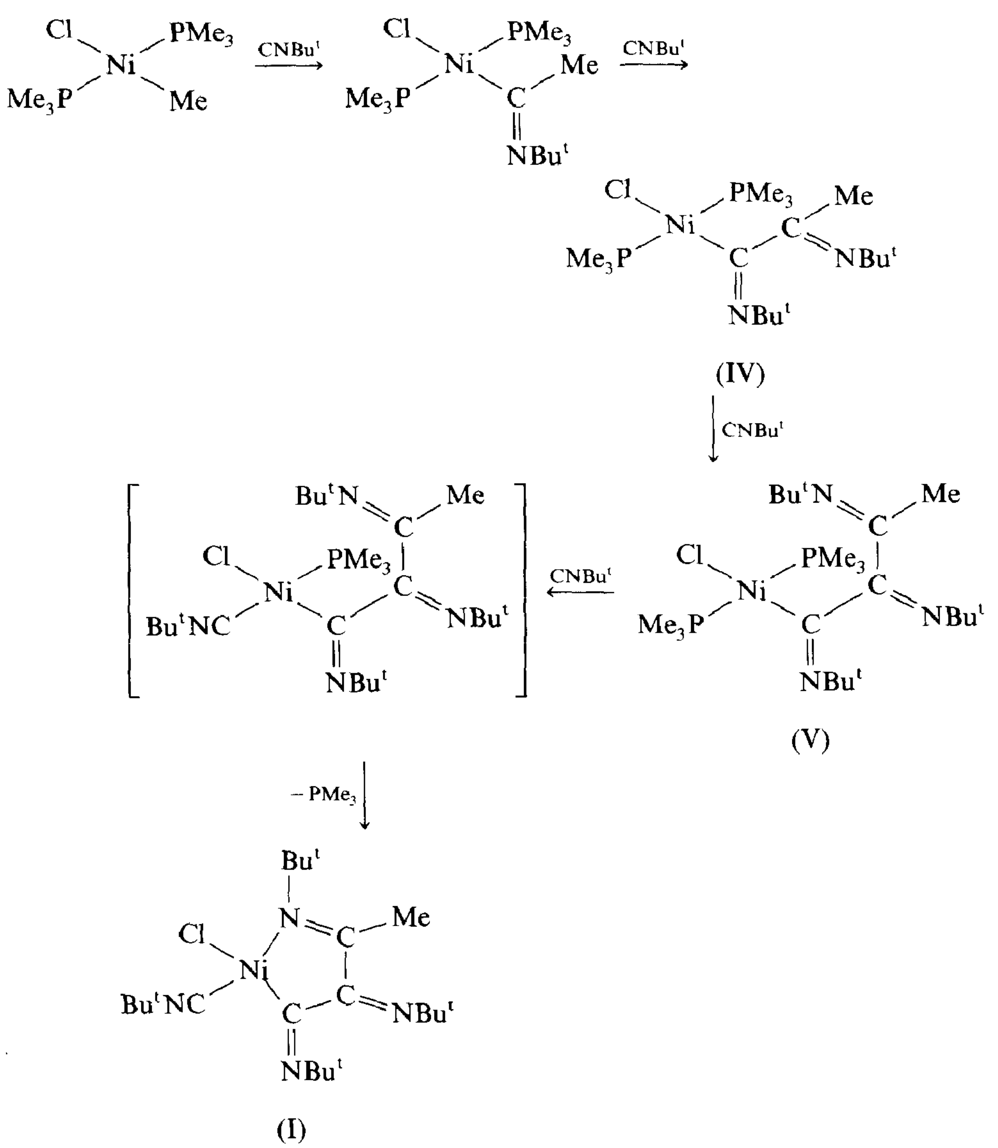
Table 5 (continued)

| ATOM | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|
| C(311) | 0.9099(15) | 0.2276(16) | 0.5029(6) | 0.0686 |
| C(312) | 0.9108(15) | 0.4238(14) | 0.4376(6) | 0.0437 |
| C(313) | 0.7509(15) | 0.3818(16) | 0.5033(6) | 0.0648 |
| C(32) | 0.6044(12) | 0.2640(12) | 0.3547(5) | 0.0421 |
| C(33) | 0.5535(12) | 0.1497(12) | 0.3845(5) | 0.0439 |
| C(34) | 0.4520(11) | 0.1683(12) | 0.4197(5) | 0.0366 |
| C(35) | 0.4217(13) | 0.2746(13) | 0.4294(7) | 0.0529 |
| C(36) | 0.3308(16) | 0.2845(17) | 0.4649(7) | 0.0754 |
| C(37) | 0.2701(15) | 0.1861(20) | 0.4846(7) | 0.0691 |
| C(38) | 0.2986(14) | 0.0795(17) | 0.4755(6) | 0.0689 |
| C(39) | 0.3903(12) | 0.0651(13) | 0.4426(5) | 0.0463 |
| C(391) | 0.4173(16) | −0.0523(13) | 0.4306(6) | 0.0627 |
| N(40) | 0.5891(9) | 0.3200(9) | 0.3045(4) | 0.0321 |
| C(41) | 0.4950(13) | 0.2889(13) | 0.2612(6) | 0.0547 |
| C(411) | 0.5445(14) | 0.1881(16) | 0.2387(6) | 0.0579 |
| C(412) | 0.3720(12) | 0.2605(15) | 0.2848(6) | 0.0484 |
| C(413) | 0.4785(14) | 0.3977(16) | 0.2161(7) | 0.0465 |
| C(2511) | 1.1194(46) | 0.6177(49) | 0.2507(22) | 0.0955(163) |
| C(2521) | 1.1195(56) | 0.6168(58) | 0.3489(26) | 0.1290(211) |
| C(2531) | 0.9962(55) | 0.7825(54) | 0.2794(27) | 0.1286(210) |
| C(811) | −0.0379(126) | −0.0223(128) | 0.0831(60) | 0.1499(502) |
| C(821) | −0.1051(49) | 0.0117(50) | 0.1565(22) | 0.0161(142) |
| C(831) | −0.1458 | 0.1561 | 0.0516 | 0.0638(250) |

been unable to isolate analytically pure V, but mixtures of this species and of the bis-insertion complex IV (ca. 9/1 by $^{31}$P NMR spectroscopy) can be obtained, thereby allowing full spectroscopic characterization of this species. Interestingly, the $^{31}$P NMR spectrum of V consists of an AB spin system ($\delta_A$ −15.1, $\delta_B$ −15.3 ppm; $^2J_{AB}$ 195 Hz). The high value found for the phosphorus-to-phosphorus coupling constant is clearly indicative of a *trans* arrangement of these ligands, and their chemical inequivalence is probably a consequence of restricted rotation within the organic polyimino chain due to steric hindrance. A similar situation was observed in

$C_6H_{11}$) into the Pd–C bonds of [Pd(CH$_3$)I(PMe$_2$Ph)$_2$], although in this case the observation of $^1$H NMR multiplets for the phosphine methyl groups was assigned to diastereotopic methyl groups rather than to inequivalence of the phosphine ligands [2]. In the $^{13}$C NMR spectrum of V, the Ni–*C*(NBu$^t$) signals appear as a triplet ($^2J$(PC) 26.5 Hz), and the other two iminocarbon atoms give singlets at 171 and 168 ppm.

Complex V, which contains a polyimino chain formed by triple insertion of CNBu$^t$ into the Ni–C bond of the alkyl *trans*-[Ni(CH$_3$)Cl(PMe$_3$)$_2$], cannot be cyclized to afford a product having structure of type **A** but containing a PMe$_3$ rather than a CNBu$^t$ ligand. Thus V was recovered after heating of its solutions for about 30 min at 70 °C, although some decomposition was observed. By contrast, addition of CNBu$^t$ to solutions of V affords the metallacyclic compound I. Monitoring of the course of this reaction by $^{31}$P NMR spectroscopy reveals no evidence for the presence of intermediates, and this suggests that substitution of one of the PMe$_3$ ligands in V by CNBu$^t$ is followed by a fast cyclization to give compound I. Thus



Scheme 2

the first three equivalents of CNBu$^t$ readily undergo insertion into the Ni–C bond present, but for the fourth, displacement of one of the PMe$_3$ ligands is preferred. The resulting intermediate species, for which no spectroscopic evidence was observed, could undergo fast cyclization, possibly as a result of the *trans* labilizing effect exerted by the CNBu$^t$ ligand on the *trans*-PMe$_3$ group. Formation of the cyclic products I–III can thus be suggested to occur as depicted in Scheme 2 for the methyl derivative I

## Experimental

Microanalyses were by the Pascher, Microanalytical Laboratory, Bonn. Perkin–Elmer Models 577 and 684 spectrometers were used for IR spectra and a

Varian XL-200 instrumental for NMR studies. The $^{13}C$ resonance of the solvent was used as internal standard, but chemical shifts are reported with respect to $SiMe_4$. $^{31}P$ NMR shifts are relative to external 85% $H_3PO_4$. All preparations and other operations were carried out under oxygen-free nitrogen, by conventional Schlenk techniques. Solvents were dried and degassed before use. The petroleum ether used had a boiling point of 40–60 °C. The compounds $CNBu^t$ [10], $[Ni(R)Cl(PMe_3)_2]$ (R = Me [11], $CH_2SiMe_3$ [12] and $CH_2C_6H_4$-*o*-Me [13]) were prepared by published methods.

Typical preparations for the new complexes are described below.

*$[\overline{Ni(C(=NBu^t)C(=NBu^t)C(CH_2C_6H_4\text{-}o\text{-}Me)=N}Bu^t)Cl(CNBu^t)]$ (III).* To a stirred, cold (−40 °C) suspension of 140 mg of $[Ni(CH_2C_6H_4$-*o*-$Me)Cl(PMe_3)_2]$ in diethyl ether (40 $cm^3$) were added 4 equiv. of $CNBu^t$ (1.6 $cm^3$ of a 1 *M* solution in $Et_2O$). The mixture was stirred for 24 h at room temperature then taken to dryness, and the residue was extracted with a petroleum ether/$Et_2O$ mixture (1/2, 40 $cm^3$). Centrifugation, partial removal of the solvent, and cooling at −30 °C afforded complex III as red crystals in 50% yield. An analytical sample was obtained by recrystallization from petroleum ether.

A similar procedure gave the compounds I and II in 50% yield.

*$[Ni(C(=NBu^t)C(=NBu^t)CH_3)Cl(PMe_3)_2]$ (IV).* Neat $CNBu^t$ (2 equiv.) was added from a syringe to a cold (−40 °C) solution of $[Ni(CH_3)Cl(PMe_3)_2]$ (258 mg, 1 mmol) in 30 $cm^3$ of diethyl ether. After 2 h stirring at room temperature the volatiles were removed under vacuum and the residue extracted with 40 $cm^3$ of petroleum ether. Centrifugation of the extract and cooling at −30 °C furnished yellow microcrystals of IV in 30% yield. Purification was achieved by recrystallization from petroleum ether.

Addition of 1 equiv. of $CNBu^t$ to complex IV gave compound V, as shown by $^{31}P$ NMR spectroscopy. Although V has been fully characterized spectroscopically (see Results and discussion) we were unable to obtain analytically pure samples of this complex, since it always crystallized with some of the bis-insertion product IV.

*X-Ray structure determination of $[\overline{Ni(C(=NBu^t)C(=NBu^t)C(CH_2C_6H_4\text{-}o\text{-}Me)=N}\text{-}Bu^t)Cl(CNBu^t)]$ (III).* An air sensitive single crystal of III (0.25 × 0.20 × 0.25 mm) was sealed in a glass capillary under $N_2$ and mounted on the goniometer head of an Enraf–Nonius CAD-4 diffractometer. Graphite-monochromated Mo-$K_\alpha$ radiation was used. The unit cell constants were obtained by the least-squares refinement of $\sin^2\theta/\lambda^2$ values for 25 accurately centred reflections; 9230 independent reflections with $2\theta \leq 50°$ were measured, using $\omega/2\theta$ scans. Three standard reflections were checked periodically, their intensity variation being within 6% throughout data collection. The data were corrected for Lorentz and polarization effects, and 4089 reflections were considered observed ($I \geq 3\sigma(I)$). The scattering factors for neutral atoms and anomalous dispersion corrections were taken from ref. 14. The structure was solved by Patterson and Fourier methods (two independent molecules per asymmetric unit, **A** and **B**, were found) and refined by full-matrix least-squares using *F*'s. 3159 reflections were used in the refinement [15a*]. The isotropic refinement converged at $R = 0.14$. Rotational disorder was detected during the course of the anisotropic refinement for the methyl carbon atoms C(81) to C(83) of molecule **A** and C(251) to C(253) of molecule **B** (extent of disorder: 20 and 40%,

---

* Reference number with asterisk indicates a note in the list of references.

respectively). Some degree of non-resolvable disorder was also found for the rest of the methyl carbon atoms. Some of the H atoms were located by Fourier-difference synthesis; the remainder were placed at calculated positions, and all H atoms were included in the refinement with fixed contributions. The structure finally converged at $R = 0.061$, $R_w = 0.071$ [15b*] (weights computed from a Chebgshev series with three parameters: 5.21, 7.14 and 3.55). All the computations were made with the Oxford CRYSTALS package [16]. Thermal parameters and a list of observed and calculated structure factors are available from the authors.

## Acknowledgment

We thank the Dirección General de Política Científica (Spain) for financial support.

## References

1 J.P. Collman, L.S. Hegedus, J.R. Norton, and R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books: Mill Valley CA 1987; L.D. Durfee, and I.A. Rothwell, Chem. Rev., 88 (1988) 1059.
2 S. Otsuka, A. Nakamura, T. Yoshida, M. Naruto, and K. Ataka, J. Am. Chem. Soc., 95 (1973) 3180.
3 Y. Yamamoto, and H. Yamazaki, Inorg. Chem., 13 (1974) 438.
4 K. Aoki, and Y. Yamamoto, Inorg. Chem., 15 (1976) 48.
5 G. Bellachiona, G. Cardaci, and P. Zanazzi, Inorg. Chem., 26 (1987) 84.
6 P.M. Maitlis, P. Espinet, and M.J.H. Russell in G. Wilkinson and F.G.A. Stone (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, 1982, Vol. 6, Chap. 38.4.
7 Submitted for publication.
8 M. Bochmann, I. Hawkins, and M.P. Sloan, J. Organomet. Chem., 332 (1987) 371.
9 E. Carmona, F. Gonzalez, M.L. Poveda, J.L. Atwood, and R.D. Rogers, J. Chem. Soc. Dalton Trans., (1981) 777.
10 G.W. Gokel, R.P. Widera, and W.P. Weber, Org. Synth., 55 (1976) 96.
11 H.F. Klein, and H.H. Karsch, Chem. Ber., 106 (1973) 1433.
12 E. Carmona, F. Gonzalez, M.L. Poveda, J.L. Atwood, and R.D. Rogers, J. Chem. Soc. Dalton Trans., (1980) 2108.
13 E. Carmona, J.M. Marín, M. Paneque, and M.L. Poveda, Organometallics, 6 (1987) 1757.
14 International Tables for X-ray Crystallography, Kynoch Press: Birminham 1974, Vol. IV, p. 72–98.
15 (a) The number of reflections used in the refinement was limited to those having $|F_0| \geq 2.65$ (range of $|F_0|$ values: 1.01–43.57), CRYSTALS package; LIST 28 facility; (b) $R$ values calculated only for reflections used in the refinement.
16 D.J. Watkin, J.R. Carruthers, and P.W. Betteridge, CRYSTAL User Guide; Chemical Crystallography Laboratory, University of Oxford: Oxford, 1986.