

The reactions of alkyltrimethylphosphinenickel complexes with isocyanides and alkynes

Manfred Bochmann*, Ian Hawkins and Martin P. Sloan

School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ (Great Britain)

(Received March 16th, 1987)

Abstract

t-Butylisocyanide reacts with $\text{NiRCl}(\text{PMe}_3)_2$ ($\text{R} = \text{CH}_3$, Ia; $\text{R} = \text{CH}_2\text{SiMe}_3$, Ib) to give, successively, the products of mono- and di-insertion into the nickel–carbon bonds; with more than two equivalents of isocyanide, trimethylphosphine ligands are displaced. In contrast to related palladium reactions, cyclohexyl isocyanide gives mono-insertion products only, while benzyl isocyanide is polymerised. The reactions of diphenylacetylene with Ia and Ib in methanol give (*Z*)-vinylnickel complexes, $\text{trans-Ni}\{\text{C}(\text{Ph})\text{C}(\text{Ph})\text{R}\}\text{Cl}(\text{PMe}_3)_2$, while from reaction in diethyl ether a precursor complex $[\text{NiMeCl}(\text{PMe}_3)_2 \cdot (\text{PhC}\equiv\text{CPh})_{0.5}]$ can be isolated. On heating the (*Z*)-vinyl complexes come into thermodynamic equilibrium with their (*E*)-isomers. The vinyl complexes are stereochemically rigid and resistant to further insertion.

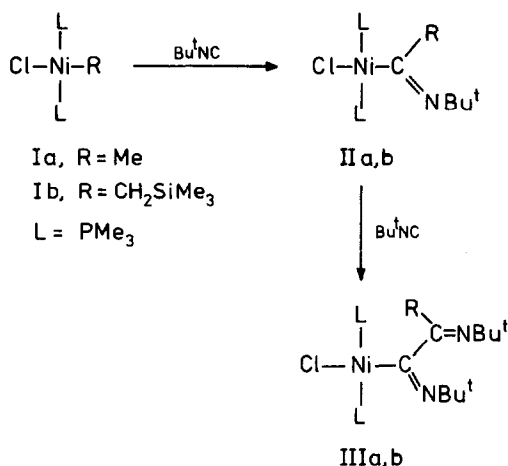
Introduction

In the preceding paper [1] we describe the reactions of carbon monoxide with cationic alkylphosphinenickel complexes. As part of our interest in the reactivity of transition metal–carbon single bonds towards unsaturated organic molecules we have extended our studies to isocyanides and alkynes, and describe here the reactions of these compounds with alkylbis(trimethylphosphine)nickel chlorides.

Results and discussion

(a) Reactions with isocyanides

While the single and multiple insertions of isocyanides RNC ($\text{R} =$ mainly *t*-butyl, cyclohexyl, aryl) into palladium- and platinum–carbon bonds have been well investigated [2], knowledge of similar reactions involving alkylnickel complexes is restricted to the reactions of $\text{CpNiR}(\text{PPh}_3)_2$ with cyclohexyl isocyanide [3] and the oxidative addition of iodomethane and benzyl chloride to $\text{Ni}(\text{CNBu}^t)_4$ [4].

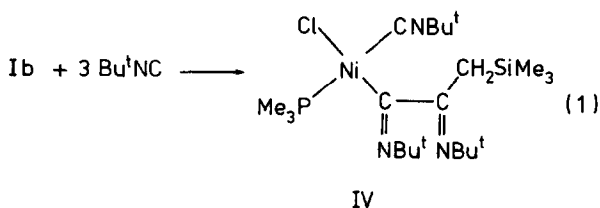


Scheme 1

The reaction of one or two equivalents of *t*-butyl isocyanide with hexane solutions of *trans*-NiRCl(PMe₃)₂ (Ia, R = Me; Ib, R = CH₂SiMe₃) at room temperature proceeds stepwise, to give the mono- and di-insertion products II and III, respectively (Scheme 1).

The compounds IIa and IIIb are isolated as yellow to orange microcrystalline solids, and IIb and IIIa as orange-red crystals. The formation of these products is usually accompanied by the precipitation of very small quantities of an insoluble yellow solid, presumably an iminoacyl isocyanide complex ($\nu(\text{C}\equiv\text{N})$ 2180, $\nu(\text{C}=\text{N})$ 1580 cm⁻¹), which could not be characterised.

In the case of Ia, reaction with three or more equivalents Bu^tNC did not give isolable products, although unstable compounds were observed which, according to their IR spectra, contained terminally coordinated isocyanide ligands. However, Ib reacts with three equivalents of Bu^tNC to give orange crystals of IV (eq. 1).



Attempts to produce tri-insertion products (e.g. structure A, Fig. 1) were unsuccessful, and gave yellow powders with three or more $\nu(\text{C}=\text{N})$ frequencies in the 1550–1700 cm⁻¹ region of their IR spectra; the compounds did not give satisfactory elemental analyses.

In contrast to Bu^tNC, cyclohexyl isocyanide failed to give di-insertion products with Ia, and the iminoacyl complex V was isolated in good yield (eq. 2). The sterically more hindered alkyl complex Ib did not react with cyclohexyl isocyanide, and was recovered from the reaction mixture.

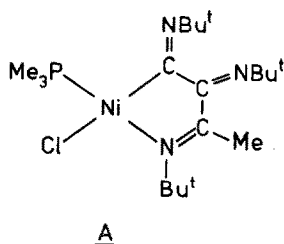
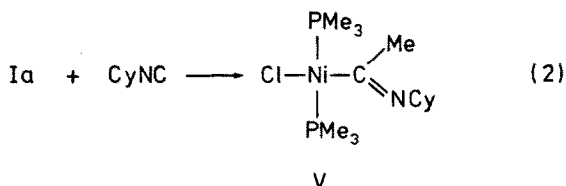


Fig. 1. Structure A.



Benzyl isocyanide is polymerised under these conditions and does not give tractable products.

The spectroscopic data for the new compounds are listed in Tables 1 and 2. It has been argued [5] that a C=N stretching frequency of an iminoacyl ligand between 1550–1620 cm^{-1} is indicative of η^1 bonding, while higher frequencies (1650–1720 cm^{-1}) are typical of η^2 coordination. While the $\nu(\text{C}=\text{N})$ values for most of the compounds described here fall within the η^1 -limits, that for IIb is an exception (1720 cm^{-1}). Since there is no reason to suppose that IIb alone is an example of a five-coordinated nickel(II) complex with an η^2 -bonded iminoacyl ligand, while all analogous complexes exhibit the familiar square-planar geometry, a more likely explanation of the observed high-frequency shift of ca. 100 cm^{-1} appears to be that in this very crowded molecule the steric repulsion between the trimethylsilylmethyl and the N-*t*-butyl substituents result in an increase in the $\text{N}=\text{C}-\text{CH}_2$ and $\text{C}=\text{N}-\text{Bu}^t$ angles, bringing them closer to the values observed for η^2 -iminoacyl [5]. A widening of these angle would imply a change of the orbital hybridisation of C and N from

Table 1

Infrared and ^1H NMR data of nickel iminoacyl complexes

IR ^a		^1H NMR ^b		
Complex	$\nu(\text{C}=\text{N})$	$\delta(\text{R})$	$\delta(\text{R}')$	$\delta(\text{PMe}_3)$ ^c
IIa	1589	2.16 (s, CH_3)	1.69 (s, Bu^t)	1.07
IIb	1720	0.18 (s, SiMe_3) 2.03 (s, CH_2Si)	1.61 (s, Bu^t)	1.03
IIIa	1629, 1562	2.05 (s,m CH_3)	1.70 (s, Bu^t) 1.30 (s, Bu^t)	1.06
IIIb	1613, 1568	0.13 (s, SiMe_3) 1.98 (s, CH_2Si)	1.75 (s, Bu^t) 1.38 (s, Bu^t)	1.12
V	1597	2.16 (s, CH_3)	1.2–2.0, (br, Cy)	1.15

^a Nujol mull, KBr plates, $[\text{cm}^{-1}]$. ^b In C_6D_6 , 60 MHz . ^c Virtual triplet, $J(\text{P}-\text{P})$ 4 Hz in all cases.

Table 2

Spectroscopic data of IV

IR (cm ⁻¹) ^a	¹ H NMR ^b	¹³ C NMR ^b
2175	0.20 (s, 9H, SiMe ₃)	0.8 C(1)
1660	0.84 (s, 9H, PMe ₃)	24.8 C(2)
1643	1.56	28.7
1620	1.60 (3s, 27H, Bu ^t)	29.9 C(9)
	1.63	30.5 C(CH ₃) ₃
		30.9
		54.2
		56.2 C(CH ₃) ₃
		59.9
		156.4 C(6)
		181.6 C(7), C(8)
		187.7

^a Nujol mull, KBr plates. ^b In C₆D₆, 100 MHz.

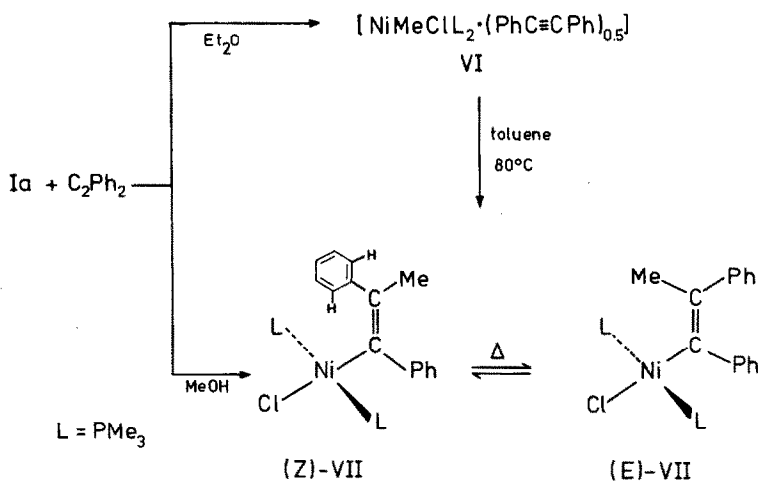
pure *sp*² towards *sp*, and an increase in the C=N stretching frequency with a concomitant strengthening of the C=N bond.

The reactions of *t*-butyl and cyclohexyl isocyanide with Ia, Ib reveal significant differences between the reactivity of nickel complexes and their palladium analogues. For example, PdMeI(PMe₃)₂ reacts with Bu^tNC to give a mono-insertion product only, analogous to IIa, while cyclohexyl isocyanide gives successively mono-, di-, and tri-insertion products, even in the presence of bulky phosphine ligands, such as PMePh₂ [2f]; the explanation advanced for the difference in reactivity of Bu^tNC and CyNC as the result of greater steric hindrance in the case of Bu^tNC may be valid for palladium, but evidently can not be extended to nickel, where Bu^tNC is the more reactive partner.

Attempts to prepare cationic nickel iminoacyl complexes, analogous to [Ni(COMe)(PMe₃)₃][BF₄] [1], were unsuccessful. Treatments of IIa with TIBF₄ and PMe₃ in THF gave a brown crystalline material, which on the basis of the NMR spectra, was formulated as the bis(phosphine) complex [Ni{C(=NBu^t)Me}-(PMe₃)₂][BF₄]. On standing or under vacuum the brown crystals ($\nu(\text{C}=\text{N})$ 1735 cm⁻¹) readily decomposed to a yellow powder ($\nu(\text{C}=\text{N})$ 1726 cm⁻¹). The IR data are consistent with η^2 -bonded iminoacyl groups in cationic complexes [6]. Neither compound gave satisfactory elemental analyses.

(b) Reactions with disubstituted alkynes

Stereochemically rigid square-planar metal alkyl bis(phosphine) complexes, e.g. *trans*-MRX(PR')₂ (M = Ni, Pd, Pt) are not generally expected to react with alkynes to give insertion products, since this reaction proceeds via the dissociative displacement of a phosphine ligand L by the alkyne prior to *cis*-insertion [7,8]. For this reason, NiMe(acac)L reacts readily with alkynes if L is a labile triphenylphosphine ligand, while the reaction is very slow if a more basic trialkylphosphine ligand is present, e.g. L = tricyclohexylphosphine [8]. In I, however, the trimethylphosphine ligands undergo rapid intermolecular exchange at room temperature [9,10], and alkyne insertions were therefore expected to be facile.



Scheme 2

Addition of one equivalent of diphenylacetylene to a diethyl ether solution of Ia followed by crystallisation of the product from a light petroleum/diethyl ether mixture yielded red-brown crystals (VI). They contained diphenylacetylene, but no vinylnickel group arising from an alkyne insertion into the nickel–methyl bond. The ^{13}C NMR spectrum shows a peak for alkyne-C at +90.0 ppm, as for free diphenylacetylene, supporting the formulation of VI as the product of co-crystallisation of the two reactants in the stoichiometry $[\text{NiMeCl}(\text{PMe}_3)_2 \cdot (\text{PhC}\equiv\text{CPh})_{0.5}]$.

Heating a solution of VI in toluene at 80°C for 2 h led to the recovery of some Ia and isolation of the desired alkyne insertion product VII as a 46/54 mixture of (Z) and (E) isomers (Scheme 2). Pure (Z)-VIII is obtained in good yield from diphenylacetylene and Ia at room temperature if methanol is used as the solvent. The (Z) isomer is the kinetic product of the reaction, and a thermodynamic (E)/(Z) equilibrium is established on heating.

Repeat experiments showed that traces of trimethylphosphine very effectively suppress the alkyne insertion, so that VI is produced instead. This finding supports the dissociative mechanism suggested for these reactions [8].

Complex (Z)-VII forms golden-yellow air-stable crystals, though its solutions decompose rapidly in air. It is soluble in aromatic and ethereal solvents and sparingly soluble in saturated hydrocarbons, and decomposes in chlorinated solvents. Complex (E)-VII was not isolated pure.

In contrast to I, trimethylphosphine exchange in VII is very slow at room temperature, so that the $\text{C}=\text{C}-\text{CH}_3$ and PMe_3 signals appear in the ^1H NMR spectrum as well-resolved triplets ($J(\text{P}-\text{H})$ 3.4 and 3.9 Hz respectively) (Table 3).

Crucial for the assignment of the (Z) stereochemistry of the vinyl ligand is the broadened doublet at δ 9.1 ppm, integrating for two H atoms. The two *ortho*-hydrogens of the freely rotating phenyl group β to the metal centre both spend some time located above the nickel coordination plane and, although too distant for a bonding interaction, experience deshielding due to the magnetic anisotropy of the nickel atom [11]. The β -methyl group of the (E)-isomer is subject to a similar low-field shift from 2.3 to 2.7 ppm.

Table 3

Spectroscopic data of nickel vinyl complexes

Complex	^1H NMR (C_6D_6)
$[\text{NiMeCl}(\text{PMe}_3)_2 \cdot (\text{Ph}_2\text{C}_2)_{0.5}]$ (VI)	-0.7 (s, 3H, Ni-CH ₃) 0.9 (s, br, 18H, P-CH ₃) 7.0-7.8 (m, 5H, Ph)
$\text{Ni}\{\text{C}(\text{Ph})\text{C}(\text{Ph})\text{Me}\}\text{Cl}(\text{PMe}_3)_2$ ((Z)-VII)	0.8 (t, 18H, J 3.9 Hz, P-CH ₃) 2.3 (t, 3H, J 3.4 Hz, =C-CH ₃) 7.6-7.7 (m, 8H, α -Ph and β -C ₆ H ₃) 9.1 (d, br, 2H, o -H of β -Ph)
(E)-VII	0.8 (t, 18H, P-CH ₃) 2.7 (t, 3H, J 3.4 Hz, =C-CH ₃) 7.6-7.7 (m, 10H, Ph)
$\text{Ni}\{\text{C}(\text{Ph})\text{C}(\text{Ph})\text{CH}_2\text{SiMe}_3\}\text{Cl}(\text{PMe}_3)_2$ (VIII)	0.0 (s, 9H, SiMe ₃) 1.02 (t, 18H, J 3.8 Hz, P-CH ₃) 3.30 (br, 2H, CH ₂ Si) 6.86-7.06 (m, 8H, α -Ph and β -C ₆ H ₃) 7.43-7.60 (br, 2H, o -H of β -Ph)

The trimethylsilylmethyl complex Ib reacts with diphenylacetylene in methanol to give the (Z)-vinyl complex $\text{Ni}\{\text{C}(\text{Ph})=\text{C}(\text{Ph})\text{CH}_2\text{SiMe}_3\}\text{Cl}(\text{PMe}_3)_2$ (VIII), with a structure analogous to that of VII.

Neither acetylene itself, nor alkynes $\text{RC}\equiv\text{CR}$ with less electron-withdrawing substituents ($\text{R} = \text{Me}, \text{Et}, \text{SiMe}_3$), react with Ia or Ib. Dimethylacetylene dicarboxylate and $\text{HC}\equiv\text{CCOOMe}$ react with Ia at -70°C to give orange products, which rapidly decompose above -40°C with trimerisation of the alkynes, generating $\text{C}_6(\text{CO}_2\text{Me})_6$ and $\text{C}_6\text{H}_3(\text{CO}_2\text{Me})_3$, respectively.

Complex VII does not react with carbon monoxide (1 bar) at room temperature. *t*-Butylisocyanide displaces the trimethylphosphine ligands without insertion into the Ni-C bond; a pure product could not be isolated.

Experimental

Experiments were carried out under an inert gas atmosphere by standard Schlenk techniques. Solvents were distilled from sodium-benzophenone (diethyl ether, tetrahydrofuran, 40/60 petroleum ether), sodium (toluene) or magnesium methoxide (methanol) under nitrogen. Infrared spectra were recorded with a Perkin-Elmer 684 spectrometer (Nujol mulls, KBr plates), NMR data were obtained on Jeol PMX 60 (^1H) and FX-100 (^1H , ^{13}C , ^{31}P) spectrometers. Melting points were taken in capillaries sealed under N_2 , and are uncorrected. Isocyanides [12] and the alkylnickel complexes Ia [9] and Ib [10] were prepared by published procedures; cyclohexyl isocyanide and alkynes were used as supplied. The procedure used for the preparation of *trans*- $\text{Ni}\{\text{C}(\text{=N}^t\text{Bu})\text{Me}\}\text{Cl}(\text{PMe}_3)_2$ (IIa) is typical for the reactions with isocyanides.

trans- $\text{Ni}\{\text{C}(\text{N}^t\text{Bu})\text{Me}\}\text{Cl}(\text{PMe}_3)_2$ (IIa). 150 mg (1.8 mmol) *t*-butyl isocyanide was added at room temperature to a solution of 470 mg (1.8 mmol) *trans*- $\text{NiMeCl}(\text{PMe}_3)_2$ (Ia) in 20 ml light petroleum (b.p. 40 – 60°C). The mixture was stirred for 1 h, concentrated in vacuo to ca. 5 ml, and left to crystallise at -20°C .

527 mg of microcrystalline yellow IIa was obtained (1.53 mmol, 85%), m.p. 94°C.

IR (Nujol mull, KBr plates): 1620m, 1587s, 1420m, 1350m, 1285, 1280m, 1228, 1205, 1074, 943vs, 855, 753, 728s, 670m, 560, 550m, cm^{-1} . Found: C, 41.43; H, 8.63; N, 4.83; Cl, 10.08. $\text{C}_{12}\text{H}_{30}\text{ClNNiP}_2$ calc.: C, 41.84; H, 8.72; N 4.07; Cl, 10.30%.

Similarly were obtained:

trans-Ni{C(NBu')CH₂SiMe₃}Cl(PMe₃)₂ (IIb) from Ib (550 mg, 1.65 mmol) and one equivalent Bu'NC, as orange rhombic plates (550 mg, 1.3 mmol, 80%), m.p. 50°C (dec.).

IR: 1720s, 1365, 1300, 1280, 1246, 1238, 1195, 1145, 1110, 1043s, 950s, br, 850vs, 730, 675, 618, 545w cm^{-1} . Found: C, 43.47; H, 9.22; N, 2.91. $\text{C}_{15}\text{H}_{38}\text{ClNNiP}_2\text{Si}$ calc.: C, 43.24; H, 9.19; N, 3.35; Cl, 8.51%.

trans-Ni{C(NBu')C(NBu')Me}Cl(PMe₃)₂ (IIIa) from 470 mg (1.8 mmol) Ia and two equivalents of Bu'NC, as red-orange prisms (577 mg, 1.35 mmol, 75%), m.p. 75°C.

IR: 1628s, 1560s, 1420, 1360, 1350, 1295, 1280, 1270, 1200s, 935vs, 893, 840, 830, 740, 728, 670, 650, 620, 583, 550, 438 cm^{-1} . Found: C, 47.82; H, 9.35; N, 6.39; Cl, 8.30. $\text{C}_{17}\text{H}_{39}\text{ClN}_2\text{NiP}_2$, calc.: C, 47.76; H, 9.13; N, 6.55; Cl, 8.30%.

trans-Ni[{C(NBu')}]₂CH₂SiMe₃}Cl(PMe₃)₂ (IIIb) from 290 mg (0.87 mmol) Ib and 144 mg (1.74 mmol) Bu'NC, as yellow microcrystals (208 mg, 0.42 mmol, 48%), m.p. 95°C.

IR: 1615s, 1568s, 1420, 1365s, 1300, 1295, 1282, 1273, 1240, 1198, 1150, 945vs, 913, 900, 845vs, 800, 775, 750, 728s, 670, 640, 620, 598, 488 cm^{-1} . Found: C, 47.72; H, 9.41; N, 5.90; Cl, 6.96. $\text{C}_{20}\text{H}_{47}\text{ClN}_2\text{NiP}_2\text{Si}$ calc.: C, 48.06; H, 9.48; N, 5.60; Cl, 7.09%.

Ni[{C(NBu')}]₂CH₂SiMe₃}Cl(CNBu')(PMe₃) (IV) from 110 mg (0.33 mmol) Ib and 83 mg (1.0 mmol) Bu'NC, as orange needles (60 mg, 0.12 mmol, 36%), m.p. 81°C (dec.).

IR: 2175s, 1645, 1620s, 1575m, 1360, 1293, 1245, 1230, 1200, 1140, 1035, 1010, 895, 855s, 765, 693, 660, 620, 600, 545, 520 cm^{-1} . Found: C, 51.87; H, 9.24; N, 8.67; $\text{C}_{22}\text{H}_{47}\text{ClN}_3\text{NiPSi}$ calc.: C, 52.13; H, 9.35; N, 8.29%.

trans-Ni{C(NC₆H₁₁)Me}Cl(PMe₃)₂ (V) from 180 mg (0.69 mmol) Ia and 150 mg (1.38 mmol) cyclohexyl isocyanide, as yellow plates (195 mg, 0.52 mmol, 76%), m.p. 88–89°C.

IR: 1597s, 1420, 1340, 1300, 1285, 1280, 1235, 1150, 1095s, 1058, 940vs, 915, 888, 850, 842, 795, 730s, 668, 612, 535, 507 cm^{-1} . Found: C, 45.90; H, 8.74; N, 3.77; Cl, 9.81. $\text{C}_{14}\text{H}_{32}\text{ClNNiP}_2$ calc.: C, 45.38; H, 8.71; N, 3.78; Cl, 9.57%.

[NiMeCl(PMe₃)₂ · (PhC≡CPh)_{0.5}] (VI) Diphenylacetylene (150 mg, 0.84 mmol) was added to a solution of 220 mg (0.84 mmol) Ia in 10 ml diethyl ether which contained 0.05 ml trimethylphosphine. The mixture was stirred at room temperature for 2 h, concentrated, and kept at –10°C overnight to give VI as red-brown prisms (180 mg, 0.51 mmol, 61%), m.p. 85°C (dec.).

IR: 3050w, 1600w, 1573w, 1495s, 1465s, 1420s, 1305, 1285, 1170, 1155, 1073, 1021, 940vs, 860, 855, 770s, 735s, 695, 670, 540, 520, 468 cm^{-1} . Found: C, 47.82; H, 7.24; Cl, 10.43. $\text{C}_{14}\text{H}_{26}\text{ClNiP}_2$ calc.: C, 47.97; H, 7.49; Cl, 10.11%.

trans-(Z)-Ni{C(Ph)C(Ph)Me}Cl(PMe₃)₂ ((Z)-VII) from 580 mg (2.2 mmol) Ia and 400 mg diphenylacetylene (2.2 mmol) in 20 ml methanol at room temperature. The product is obtained as orange prisms (720 mg, 1.64 mmol, 74%), m.p. 177°C.

More can be obtained from the filtrate. The insertion will also proceed in diethyl ether if the sample of Ia is free from all trimethylphosphine traces.

IR: 3070, 1590, 1580, 1565, 1490, 1465, 1420, 1360, 1300, 1280, 1080, 1065, 1030, 988, 940vs, 850, 770s, 743, 730s, 700s, 678, 650, 630, 610, 575, 532, 495 cm^{-1} . Found: C, 57.51; H, 7.04; Cl, 8.07. $\text{C}_{21}\text{H}_{31}\text{ClNiP}_2$ calc.: C, 57.38; H, 7.11; Cl, 8.06%.

trans-(Z)-Ni{C(Ph)C(Ph)CH₂SiMe₃}Cl(PMe₃)₂ (VIII) was similarly obtained from 214 mg (0.64 mmol) Ib and 114 mg (0.64 mmol) diphenylacetylene in 20 ml THF after 4 h at room temperature, as yellow needles (200 mg, 0.39 mmol, 61%), m.p. 115°C.

IR: 3070, 1598, 1570, 1545, 1490, 1465, 1420, 1300, 1285, 1247, 1068, 1037, 945vs, 880, 850s, 835s, 780, 773, 748, 735, 705s, 685, 670, 655, 630, 593, 555, 543, 495 cm^{-1} . Found: C, 56.30; H, 7.59; Cl, 7.02. $\text{C}_{24}\text{H}_{39}\text{ClNiP}_2\text{Si}$ calc.: C, 56.32; H, 7.68; Cl, 6.93%.

References

- 1 M. Bochmann, I. Hawkins, M.B. Hursthouse and R.L. Short, *J. Organomet. Chem.*, 332 (1987) 361.
- 2 (a) E. Singleton and H.E. Oosthuizen, *Adv. Organomet. Chem.*, 22 (1983) 209; (b) Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Japan* 43 (1970) 2653; (c) Idem, *ibid.*, 43 (1970) 3634; (d) K.P. Wagner, P.M. Treichel and J.C. Calabrese, *J. Organomet. Chem.*, 71 (1974) 299; (e) P.M. Treichel, K.P. Wagner and R.W. Hess, *Inorg. Chem.*, 12 (1973) 1471; (f) Y. Yamamoto and H. Yamazaki, *ibid.*, 13 (1974) 438; (g) B. Crociani, M. Nicolini and R.L. Richards, *J. Organomet. Chem.*, 104 (1976) 259; (h) Y. Yamamoto and H. Yamazaki, *Inorg. Chim. Acta*, 41 (1980) 229; (i) A. Campagnaro, A. Mantovani and P. Uguagliati, *ibid.*, 99 (1985) L15; (j) R. Bertani, A. Berton, F. di Bianca and B. Crociani, *J. Organomet. Chem.*, 303 (1986) 283.
- 3 Y. Yamamoto, H. Yamazaki and N. Hagihara, *Bull. Chem. Soc. Japan*, 41 (1968) 582.
- 4 S. Otsuka, A. Nakamura and T. Yoshida, *J. Am. Chem. Soc.* 91 (1969) 7196; S. Otsuka, A. Nakamura, T. Yoshida, M. Naruto and K. Ataka, *ibid.*, 95 (1973) 3180.
- 5 R.D. Adams and C.F. Chodosh, *Inorg. Chem.*, 17 (1978) 41.
- 6 H. Werner, S. Lotz and B. Heiser, *J. Organomet. Chem.*, 209 (1981) 197; M. Bochmann and L.M. Wilson, *J. Chem. Soc. Chem. Comm.*, (1986) 1610.
- 7 (a) H. Berke and R. Hoffmann, *J. Am. Chem. Soc.*, 100 (1978) 2079; (b) E.G. Samsel and J.R. Norton, *ibid.*, 106 (1984) 5505.
- 8 J.M. Huggins and R.G. Bergman, *J. Am. Chem. Soc.*, 103 (1981) 3002.
- 9 H.F. Klein and H.H. Karsch, *Chem. Ber.*, 106 (1973) 1433.
- 10 E. Carmona, F. Gonz  les, M.L. Poveda, J.L. Atwood and R.D. Rogers, *J. Chem. Soc. Dalton*, (1980) 2108.
- 11 P.W. Jolly and G. Wilke, *The Organic Chemistry of Nickel*, Vol. 1, Academic Press, 1974, p. 200.
- 12 W.P. Weber, G.W. Gokel and I.K. Ugi, *Angew. Chem. Intern. Ed. Engl.*, 11 (1972) 530.