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Dialkyl complexes of nickel(II) containing chelating diphosphines. The crystal structure of $[Ni(CH_2SiMe_2Ph)_2({}^iPr_2PCH_2CH_2P^iPr_2)]$

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Abstract

The reactions of the dialkyls $[NiR_2(tmed)]$ ($R = CH_2C_6H_4$-*o*-Me or CH_2SiMe_2Ph; tmed = *N,N,N′,N′*-tetramethylethylenediamine) with the chelating phosphines $R'_2PCH_2CH_2PR'_2$ (R′ = Me, dmpe; Et, depe; ^{i}Pr, dipe) form the corresponding derivatives $[NiR_2(P–P)]$. Structures for the new compounds are proposed on the basis of IR and NMR (^{1}H, ^{13}C and ^{31}P) studies and that of $[Ni(CH_2SiMe_2Ph)_2(dipe)]$ (**2c**) has been confirmed by an X-ray crystal structure investigation which shows the complex to be monoclinic, space group $C2/c$, with cell dimensions $a = 16.947(7)$, $b = 19.011(7)$, $c = 11.082(3)$ Å, $\beta = 100.93(2)°$, $V = 2299.1$ Å^3 and $Z = 4$.

1. Introduction

Alkyl complexes of nickel constitute a widely investigated area of organonickel chemistry [1]. A number of compounds of this type, including dialkyl species $[NiR_2L_2]$ stabilized by N- or P-donors is presently known [1,2]. Dialkyl complexes of the transition metals having the two alkyl groups in mutually *cis* positions have received a great deal of attention, particularly concerning the mechanistic aspects of their thermal decomposition [3]. Reductive elimination is a common decomposition route [4] but in some cases distal H-activation processes (*e.g.* γ- or δ-elimination) in the organic fragment gives rise to metallacycle formation [5].

Earlier work has dealt with the formation of the PMe_3-containing dialkyl species $[NiR_2(PMe_3)_2]$ ($R = CH_2SiMe_3$, CH_2CMe_2Ph, or $CH_2C_6H_4$-*o*-Me) of which only the trimethylsilylmethyl derivative [2a,b] is sufficiently stable, under ordinary conditions, for full characterization. The phenyl(dimethyl)propyl neophyl compound undergoes a very facile δ-H abstraction to yield a metallacyclic product [6] while the *o*-xylyl complex undergoes spontaneous reductive elimination under the conditions in which it forms [2d].

Since the use of chelating N- and P-donors results generally in a remarkable enhancement of the thermal stability of these dialkyl complexes [1,2], we have extended our previous studies to investigate the formation of dialkyl compounds of nickel derived from the *o*-methylbenzyl, $CH_2C_6H_4$-*o*-Me (*o*-xylyl) and dimethyl(phenyl)silylmethyl, CH_2SiMe_2Ph, alkyl groups and containing the chelating diphosphines $Me_2PCH_2CH_2PMe_2$, dmpe, $Et_2PCH_2CH_2PEt_2$, depe, and $^iPr_2PCH_2CH_2P^iPr_2$, dipe. The crystal structure of one of these derivatives, *cis*-$Ni(CH_2SiMe_2Ph)_2(dipe)$ (**2c**), has been determined and is also reported. Tables 1 and 2 contain spectroscopic data for the new compounds while Tables 3–5 collect relevant structural data for **2c**.

2. Results and discussion

The addition of 2 equivalents of $Mg(CH_2C_6H_4$-*o*-$Me)Cl$ to $[NiCl_2(py)_4]$ in the presence of an excess of

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TABLE 1. $^{31}P\{^1H\}$ and ^1H NMR data for compounds **1** and **2** [a]

Compound	$^{31}P\{^1H\}$ NMR	^1H NMR					
		R			P–P		
		CH_2	CH_3	Aromatics	$P-CH_2-CH_2-P$	$P-CH_n$	$P-C-CH_3$
1a	29.7	2.25	2.47	7.04–7.29 m	0.58 pd $J_{HP}(app) = 15.2$	0.52 d $^2J_{HP} = 8.5$	–
1b	54.8	2.24 m	2.49	6.90–7.30 m	[b]	[b]	[b]
1c	67.9	2.25 pq $J_{HP}(app) = 3.7$	2.34	7.04–7.47 m	0.93 pd [c] $J_{HP}(app) = 10$	1.71 dh $^3J_{HH} = {}^2J_{HP} = 7$	0.85 dd $^3J_{HP} = 11$; $^3J_{HH} = 7$ 1.07 dd $^3J_{HP} = 15$; $^3J_{HH} = 7.5$
2a [d]	33.7	−0.02 dpd [c] $J_{HP}(app) = 15.6$, 5.5	0.25	7.15–7.96 m	1.39 m [e]	0.12 d $^2J_{HP} = 8$	–
2b	54.3	0.41 dpd [c] $J_{HP}(app) = 14.9$, 5.6	0.64	7.22–7.94 m	0.77 dpd [f]	1.23 dq $^3J_{HH} = {}^2J_{HP} = 7$	0.73 dt $^3J_{HP} = 14$ $^3J_{HH} = 7$
2c	72.8	0.47 m	0.64	7.10–7.90 m	[g]	1.75 dh $^3J_{HH} = {}^2J_{HP} = 7$	0.77 dd $^3J_{HP} = 15$; $^3J_{HH} = 7$ 0.97 dd $^3J_{HP} = 15$; $^3J_{HH} = 7$

[a] In C_6D_6. J in Hz. Singlets unless otherwise indicated, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, p = pseudo. [b] All the resonances due to the phosphine protons overlap, forming complex multiplets between 0.75 and 1.28 ppm. [c] $A_2XX'A'_2$ spin system. [d] ^1H NMR in CD_2Cl_2. [e] Separation between central lines 14 Hz. [f] Separation of lines 13 and 7 Hz. [g] Obscured by $P-CHMe_2$ resonances.

tmed (tmed = $Me_2NCH_2CH_2NMe_2$) has been shown to produce the dialkyl $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)_2(tmed)]$ [2d], as indicated in eqn. (1).

$$[NiCl_2(py)_4] + 2Mg(CH_2C_6H_4\text{-}o\text{-}Me)Cl \xrightarrow[-py,\ -MgCl_2]{tmed} [Ni(CH_2C_6H_4\text{-}o\text{-}Me)_2(tmed)] \quad (1)$$

Treatment of the tmed complex with PMe_3 induces reductive elimination to give $[Ni(PMe_3)_4]$ and $C_{16}H_{18}$ even with a deficiency of PMe_3 (*i.e.* less than 2 molar equivalents). A smooth substitution reaction occurs, however, in the presence of the chelating phosphines dmpe, depe and dipe, yielding the dialkyl derivatives **1a–1c** (eqn. (2)).

TABLE 2. $^{13}C\{^1H\}$ NMR data for complexes **1** and **2** [a]

Compound	R			P–P		
	CH_2	CH_3	Aromatics	$P-CH_2-CH_2-P$	$P-CH_n$	$P-C-CH_3$
1a	28.0 d ($^2J_{CP} = 51$)	22.2	121.4, 125.0, 128.2, 129.4 (4 CH) 134.6, 154.6 (2 C)	28.1 pt ($J_{CP}(app) = 23$)	[b]	–
1b	26.9 dd ($^2J_{CP} = 63, 14$)	22.2	121.2, 124.9, 128.2, 129.2 (4CH) 134.5, 154.6 (2 C)	23.1 pt ($J_{CP}(app) = 21$)	16.9 pd ($J_{CP}(app) = 19$)	8.9
1c	20.9 dd ($^2J_{CP} = 65, 15$)	21.7	121.5, 124.5, 128.6, 130.3 (4 CH) 135.5, 153.3 (2 C)	19.8 pt ($J_{CP}(app) = 20$)	24.1 pt ($J_{CP}(app) = 8$)	18.3 19.8
2a	−0.3 dd ($^2J_{CP} = 64, 17$)	3.5	127.1, 127.4, 134.2 (2, 1, 2 CH) 146.8 (C)	26.4 dd ($^1J_{CP} = 25$) ($^2J_{CP} = 20$)	11.7 d ($^1J_{CP} = 21$)	–
2b	−1.3 dd ($^2J_{CP} = 64, 17$)	3.8	127.2, 127.5, 134.0 (2, 1, 2 CH) 147.0 (C)	21.6 pt ($J_{CP}(app) = 21$)	16.8 d ($^1J_{CP} = 20$)	8.2
2c	−4.5 dd ($^2J_{CP} = 65, 18$)	4.0	127.2, 127.4, 134.0 (2, 1, 2 CH) 147.0 (C)	20.1 pt ($J_{CP}(app) = 20$)	24.4 d ($^1J_{CP} = 17$)	18.1 19.9 d ($^2J_{CP} = 5$)

[a] In C_6D_6. J in Hz. Singlets unless otherwise indicated. [b] Complex multiplet.

$$[Ni(CH_2C_6H_4\text{-}o\text{-}Me)_2(tmed)] + P\text{–}P \xrightarrow[-tmed]{} [Ni(CH_2C_6H_4\text{-}o\text{-}Me)_2(P\text{–}P)]$$

$$P\text{–}P = \text{dmpe}, \mathbf{1a}; \text{depe}, \mathbf{1b}; \text{dipe}, \mathbf{1c} \quad (2)$$

Compounds **1** can be isolated as orange, crystalline materials in 65–70% yield. They are soluble in most common organic solvents and although stable when kept under dinitrogen, they decompose rapidly in the presence of air.

NMR data for compounds **1** are in accord with the proposed formulations. The ^1H NMR spectra show a singlet at δ 2.3–2.5 owing to the methyl protons of the *o*-xylyl group. This is in the region found for analogous complexes of this ligand [2d] and both the chemical shift of this signal and its relative intensity indicate that metallation of this moiety, as observed for related systems [7], does not occur in the present case. Somewhat unexpectedly, the Ni–CH_2 resonance of **1a** appears as a singlet at δ 2.25, apparently showing no coupling to phosphorus. The remaining derivatives **1b** and **1c** exhibit complex proton multiplets for these metal-bound methylene groups, consistent with an $A_2XX'A'_2$ spin system. It seems likely that the lack of multiplicity observed for the Ni–CH_2 signal of **1a** is due to a mathematical cancellation of some of the coupling constants characteristic of this spin system [8].

$^{13}C\{^1H\}$ NMR data for **1** are collected in Table 2 and need no further comment. It is worth mentioning, however, that the six carbon atoms of the aromatic ring give separate resonances, once again in agreement with the structure proposed for these complexes.

The analogous reaction of $[Ni(CH_2SiMe_2Ph)_2(tmed)]$, generated *in situ* by treatment of $[NiCl_2(py)_4]$ with $Mg(CH_2SiMe_2Ph)Cl$ in the presence of tmed, with the above diphosphines gives the corresponding derivatives **2a**–**2c**, as depicted in eqn. (3).

$$[Ni(CH_2SiMe_2Ph)_2(tmed)] + P\text{–}P \xrightarrow[-tmed]{} [Ni(CH_2SiMe_2Ph)_2(P\text{–}P)]$$

$$P\text{–}P = \text{dmpe}, \mathbf{2a}; \text{depe } \mathbf{2b}; \text{dipe}, \mathbf{2c} \quad (3)$$

Compounds **2** are new representatives of a known series of dialkyl complexes of composition $[Ni(CH_2SiMe_2Ph)_2L_2]$, investigated by Black and Young [2c]. They are yellow-to-orange crystalline materials and display similar properties to those of **1**. Complexes **2** can be stored for long periods under dinitrogen or under vacuum without decomposition, although they alter rapidly in the presence of air, with the exception of **2c** which can be handled in the atmosphere for 1–2 min without noticeable decomposition.

As with complexes **1**, NMR data (Tables 1 and 2) clearly support the proposed formulation. The Ni-bonded methylene group gives a $^{13}C\{^1H\}$ resonance in the region δ 0 to −4.5 ppm that appears as a doublet of doublets with a *trans* $^{13}C–^{31}P$ coupling of *ca.* 64 Hz and a *cis* coupling of *ca.* 17 Hz. For comparative purposes, in the cyclometallated complex $[\overline{Ni(CH_2\text{-}CMe_2\text{-}o\text{-}C}_6H_4)(dmpe)]$ [6b] the corresponding couplings are 66 and 18 Hz, respectively.

One of the main objectives of this work was the formation of metallacyclic complexes of the type $[\overline{Ni(CH_2SiMe_2\text{-}o\text{-}C}_6H_4)(P\text{–}P)]$ by thermal δ-H elimination from the dialkyls $[Ni(CH_2SiMe_2Ph)_2(P\text{–}P)]$ (**2**). This kind of transformation has allowed the isolation of the related complex $[\overline{Ni(CH_2CMe_2\text{-}o\text{-}C}_6H_4)(PMe_3)_2]$ containing a metallated phenyldimethylpropyl ligand [6a]. Our efforts to metallate compounds

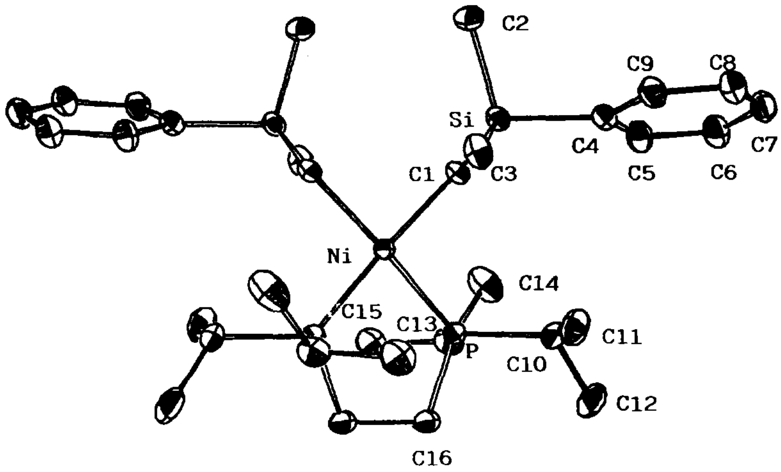

Fig. 1. ORTEP drawing of the structure of complex **2c**. Unlabelled atoms are related to the labelled ones by a 2-fold axis.

TABLE 3. Crystal and refinement data for **2c**

Formula	$C_{32}H_{54}NiP_2Si_2$
M_r	615.6
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	16.947(7)
b (Å)	19.011(7)
c (Å)	11.082(3)
β (°)	100.93(2)
V (Å^3)	2299(1)
Z	4
F(0 0 0)	1328
ρ(calc.) (g cm^{-3})	1.17
Temperature (°C)	22
μ (cm^{-1})	7.3
Crystal dimensions (mm)	0.08×0.12×0.03
Diffractometer	Enraf–Nonius CAD4
Radiation	Graphite-monochromated Mo Kα (λ = 0.71069 Å)
Scan technique	ω–2θ
Data collected	(−21, 0, 0) to (21, 24, 14)
Reflections collected	4295
Unique data	4120
Unique data (I) ≥ $2\sigma(I)$	2615
R_F (%)	4.4
$R(w)_F$ (%)	4.8
Average shift/error	0.09

TABLE 4. Bond lengths (Å) and angles (°) for **2c**

Ni–P	2.188(1)	C4–C9	1.399(6)
Ni–C1	2.014(4)	C5–C6	1.386(7)
P–C10	1:849(5)	C6–C7	1.370(7)
P–C13	1.860(5)	C7–C8	1.362(9)
P–C16	1.815(5)	C8–C9	1.389(7)
Si–C1	1.847(4)	C10–C11	1.510(8)
Si–C2	1.872(5)	C10–C12	1.529(9)
Si–C3	1.875(5)	C13–C14	1.494(8)
Si–C4	1.893(5)	C13–C15	1.523(8)
C4–C5	1.390(7)		
P–Ni–C1	92.7(1)	Si–C4–C9	120.1(3)
Ni–P–C16	111.3(2)	Si–C4–C5	123.8(3)
Ni–P–C13	114.5(2)	C5–C4–C9	116.0(4)
Ni–P–C10	122.0(2)	C4–C5–C6	121.7(5)
C13–P–C16	102.4(2)	C5–C6–C7	120.7(5)
C10–P–C16	102.2(2)	C6–C7–C8	119.2(5)
C10–P–C13	102.0(2)	C7–C8–C9	120.3(5)
C3–Si–C4	105.6(2)	C4–C9–C8	121.9(5)
C2–Si–C4	104.8(2)	P–C10–C12	114.8(4)
C2–Si–C3	104.4(2)	P–C10–C11	110.9(4)
C1–Si–C4	110.9(2)	C11–C10–C12	110.0(5)
C1–Si–C3	117.3(2)	P–C13–C15	110.9(3)
Cl–Si–C2	112.8(2)	P–C13–C14	113.1(4)
Ni–C1–Si	116.3(2)	C14–C13–C15	109.9(4)
C1–Ni–C1′	89.0(1)	P–Ni–P′	87.26(9)

2 have proved unsuccessful. Thus, heating benzene solutions of **2a**–**2c** at 75°C for 21 days affords only the starting dialkyls as demonstrated by ^1H and ^{31}P NMR studies of the reaction mixtures. Small amounts of other unidentified materials were also detected, but their NMR resonances were unlike those expected for the C–H activation products. The inertness of these complexes containing silylalkyl ligands towards cyclometallation is not unexpected in view of the results reported in the literature for other related complexes [2c,9]. Therefore, the enhanced thermal stability of compounds **2** that allows prolonged heating at temperatures around 80–90°C without extensive decomposition is not sufficient to induce kinetically the δ-H elimination reaction.

2.1. X-Ray structure of **2c**

The geometry proposed for compounds **1** and **2** on the basis of spectroscopic studies has been confirmed by a single-crystal X-ray structural determination on complex **2c**. Figure 1 shows an ORTEP perspective view of the molecules of **2c** while important structural data are collected in Tables 3–5. The structure consists of individual molecules of the title compound held together by van der Waals forces. The Ni atom exhibits an approximately square-planar configuration, the maximum deviation from the best least-square plane corresponding to C1 (0.31 Å). The value of 89.0(1)° found for the C1–Ni–C1′ angle is close to the ideal value of 90° and it is very similar to that of 87.6(7)° found in $[Ni(CH_2SiMe_3)_2(PMe_3)_2]$ [2b]. The Ni–C bond length of 2.014(4) Å is normal, well within the range found for other alkyl complexes of Ni^{II}, *e.g.* 1.89(1) Å in $[Ni(CH_2SiMe_3)_2(py)_2]$ [2a]; 2.08(2) Å in $[Ni(CH_2SiMe_3)_2(PMe_3)_2]$ [2b]; and 1.95(2) Å in

TABLE 5. Atomic parameters for **2c**

Atom	x	y	z	U_{eq} [a]
Ni	0.5000(0)	0.3173(0)	0.7500(0)	35(0)
P	0.5673(1)	0.2340(1)	0.6781(1)	45(0)
Si	0.6323(1)	0.4410(1)	0.8443(1)	45(0)
Cl	0.5747(2)	0.3929(2)	0.7115(3)	42(1)
C2	0.6031(3)	0.5360(3)	0.8468(5)	64(2)
C3	0.6258(3)	0.4078(3)	1.0014(4)	63(2)
C4	0.7432(3)	0.4422(2)	0.8386(4)	49(1)
C5	0.7739(3)	0.4273(3)	0.7337(4)	64(2)
C6	0.8554(3)	0.4317(3)	0.7327(5)	75(2)
C7	0.9086(3)	0.4526(3)	0.8354(6)	71(2)
C8	0.8808(3)	0.4675(3)	0.9401(5)	75(2)
C9	0.7993(3)	0.4626(3)	0.9421(5)	64(2)
C10	0.6784(3)	0.2325(3)	0.7079(5)	63(2)
C11	0.7122(3)	0.2425(3)	0.8430(6)	83(2)
C12	0.7153(4)	0.1672(3)	0.6601(7)	99(3)
C13	0.5422(3)	0.2230(3)	0.5084(4)	62(2)
C14	0.5768(4)	0.2795(4)	0.4405(5)	95(3)
C15	0.4516(4)	0.2189(3)	0.4638(5)	80(2)
C16	0.5433(3)	0.1481(2)	0.7329(5)	65(2)

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

$[Ni(CH_2SiMe_3)Cl(PMe_3)_2]$ [10]. The Ni–P distances are also normal and compare well with those found in related alkyl complexes of Ni (2.188(1) Å (av.) in **2c**; 2.158(4) Å in $[Ni(CH_2SiMe_3)_2(PMe_3)_2]$ [2b]; and 2.188(5) Å in $[Ni(CH_2SiMe_3)(PMe_3)_3]BF_4$ [11]).

3. Experimental details

Microanalyses were by Pascher Microanalytical Laboratory, Remagen (Germany) and the Microanalytical Service of the University of Seville. Perkin–Elmer models 577 and 684 spectrometers were used for IR spectra and a Varian XL-200 instrument for NMR studies. Unless otherwise indicated, NMR spectra were recorded using C_6D_6 as the solvent. 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. Most assignments on ^{13}C NMR were supported by gated decoupling experiments. All preparations and other operations were carried out under oxygen-free argon or 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 ligands dmpe, depe, and dipe were prepared by the addition of an excess of the corresponding Grignard reagent to the halide $Cl_2PCH_2CH_2PCl_2$ and the dialkyls $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)_2(tmed)]$ [2d] and $[Ni(CH_2SiMe_2Ph)_2(tmed)]$ [2c] were prepared by published methods.

The complexes $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)_2(P\text{-}P)]$ were synthesized starting from the dialkyl $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)_2(tmed)]$, following the procedure described below for the dmpe derivative **1a**.

A solution of $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)_2(tmed)]$ (0.45 g, 1.16 mmol) in diethyl ether (35 ml) cooled to −10°C was treated with *ca.* 0.25 ml of dmpe (*ca.* 1.15 mmol). The original red of the solution changed to orange. The mixture was stirred at room temperature for 30 min and the solvent stripped *in vacuo* to produce a brown-yellow residue that was kept under dynamic vacuum for 2 h in order to eliminate the liberated tmed. Diethyl ether was then added until dissolution of the residue. After centrifugation, the solvent was partially evaporated *in vacuo* and the mixture cooled at −30°C. The title compound was isolated (0.3 g) as orange crystals. From the mother liquor, a further 0.04 g were obtained (0.34 g, 70%). Anal. Found: C 63.2; H, 8.1. $C_{22}H_{34}NiP_2$ calc.: C, 63.1; H, 8.1%.

The derivatives **1b** and **1c** can be obtained by the procedure described for **1a** in the form of orange crystals (66%) from Et_2O and orange needles (64%) from a 1 : 1 mixture of petroleum ether/diethyl ether, respectively.

The synthesis of the complexes $[Ni(CH_2SiMe_2Ph)_2(P\text{-}P)]$ (**2a–2c**) was carried out starting from the brown-yellow $[Ni(CH_2SiMe_2Ph)_2(tmed)]$. A typical preparation is as follows.

3.1. $[Ni(CH_2SiMe_2Ph)_2(dipe)]$ (2c)

To a solution of $[Ni(CH_2SiMe_2Ph)_2(tmed)]$ (0.3 g, 0.67 mmol) in diethyl ether (40 ml) cooled to −50°C dipe was added (0.8 ml of a solution *ca.* 1 M in THF). After stirring for 15 min at this temperature, the solution was warmed to room temperature and stirred for a further 4 h. There was no appreciable change in the colour. The mixture was then evaporated to dryness, extracted with petroleum ether (20 ml), and centrifuged. Concentration of the solution and cooling at −20°C yielded the desired product as red-orange crystals (0.23 g, 56%). Anal. Found: C, 61.7; H, 9.6. $C_{32}H_{58}NiP_2Si_2$ calc.: C, 62.0; H, 9.4%.

Following a similar procedure and using the corresponding phosphines, compounds **2a** and **2b** were obtained as pale yellow crystals (46%) and orange crystals (49%), respectively. **2a**: Anal. Found: C, 55.7; H, 8.1. $C_{24}H_{42}NiP_2Si_2$ calc.: C, 56.6; H, 8.3%. **2b**: Found: C, 59.3; H, 9.0. $C_{28}H_{50}NiP_2Si_2$ calc.: C, 59.5; H, 8.9%.

3.2. X-Ray structure determination of $[Ni(CH_2SiMe_2Ph)_2(dipe)]$ (2c)

A summary of the basic crystal data is given in Table 3. A red prismatic crystal was coated with an epoxy resin and mounted on a CAD4 diffractometer. The cell dimensions were refined by least-squares fitting the values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ni, P and Si were taken from the International Tables for X-Ray Crystallography [12]. The structure was solved by Patterson and Fourier methods. An empirical absorption correction [13] was applied at the end of the isotropic refinement. The final refinement was made with fixed isotropic temperature factors and calculated coordinates for hydrogen atoms and with anisotropic thermal motion for the non-hydrogen atoms. Most of the calculations were carried out with the X-Ray 80 system [14]. Coordinates for the H atoms, thermal parameters and a list of observed and calculated structure factors are available from the authors.

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