Synthesis and Properties of Dialkyl Complexes of Nickel(II). The Crystal Structure of Bis(pyridine)bis(trimethylsilylmethyl)nickel(II)

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Dichlorotetrakis(pyridine)nickel(II), $[NiCl_2(py)_4]$ (py = pyridine), reacts with trimethylsilylmethylmagnesium chloride, $Mg(CH_2SiMe_3)Cl$, in the presence of excess of pyridine, to yield the unstable dialkyl derivative $[Ni(CH_2SiMe_3)_2(py)_2]$, for which an *X*-ray crystal-structure determination shows a *cis* pyridine configuration with an N–Ni–N angle of 87.5°. Interaction of this complex with unidentate (L) or bidentate ligands (L–L) gives $[NiR_2L_2]$ or $[NiR_2(L{-}L)]$ (L = PMe_3 or PMe_2Ph; L–L = $Ph_2PCH_2CH_2PPh_2$, 2,2′-bipyridyl, 1,10-phenanthroline, or *NNN′N′*-tetramethylethylenediamine), while $PMePh_2$ and PPh_3 cause reductive elimination to $[NiL_4]$. Some neophyl analogues, $[Ni(CH_2CMe_2Ph)_2(L{-}L)]$ are also described. Structures for the new compounds are proposed on the basis of i.r., ^1H, and ^{31}P n.m.r. spectroscopic studies. Complexes $[Ni(CH_2SiMe_3)_2(PR_3)_2]$ (PR_3 = PMe_3 or PMe_2Ph) exist in solution as mixtures of *cis* and *trans* isomers, but single-crystal *X*-ray studies (to be reported separately) of $[Ni(CH_2SiMe_3)_2(PMe_3)_2]$ show *trans* phosphines with a P–Ni–P angle of 147°.

BINARY alkylnickel compounds are thermally unstable, although the Ni–C bonds can be stabilized by co-ordination of appropriate ligands. Thus, a large number of complexes of the type $[NiR(X)L_2]$ and $[NiR_2L_2]$, where L represents a nitrogen- or phosphorus-containing ligand, are known.[1] Most of these derivatives have been made by treating the appropriate substituted nickel dihalide with Grignard or organolithium reagents,[1-3] although interaction of $[Ni(acac)_2]$ (acac = acetylacetonate) with aluminium alkyls (or alkoxyalkyls), in the presence of stabilizing ligands, has also been used widely.[4]

In a previous publication [3] we have reported that the reactions of $[NiX_2L_2]$ compounds (X = halogen; L = PMe_3 or PMe_2Ph) with Grignard reagents derived from $SiMe_3(CH_2Cl)$ and CH_2ClCMe_2Ph yield thermally stable monoalkyl complexes of the type $[NiR(X)L_2]$. However the dialkyl derivatives $[NiR_2L_2]$ were not detected even when excess of the Grignard reagent and phosphine ligand were present. Subsequently we have found a general route to complexes of this type, *via* the unstable dialkyl $[Ni(CH_2SiMe_3)_2(py)_2]$ (py = pyridine), which reacts with a variety of donor ligands to give the corresponding $[Ni(CH_2SiMe_3)_2L_2]$ complexes. These and other reactions summarized in the Scheme are reported in this paper. Analytical and spectroscopic data for new compounds are given in Table 1.

RESULTS AND DISCUSSION

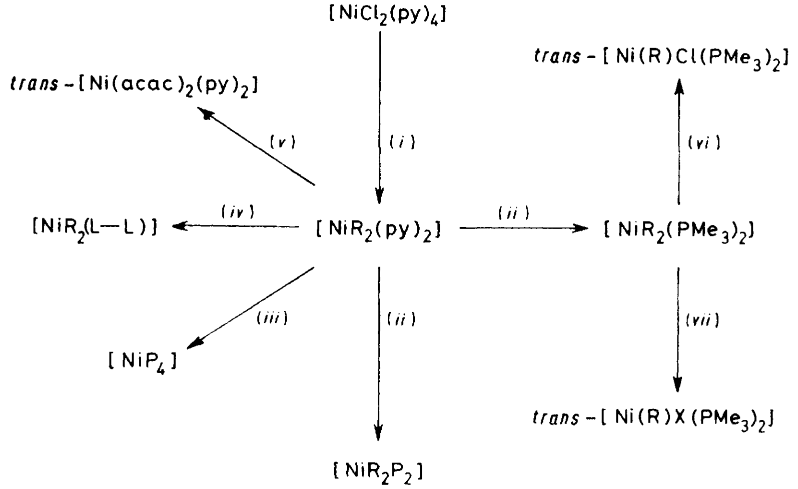
Trimethylsilylmethyl Derivatives.—(a) *With N-containing ligands.* The dichloride, $[NiCl_2(py)_4]$, reacts with two molar equivalents of $Mg(CH_2SiMe_3)Cl$, in the presence of excess of pyridine, to give the yellow-brown

TABLE 1

Analytical and spectroscopic data for dialkyl complexes

			Analysis (%) [a]				^1H N.m.r.[c]		
	Compound	Colour	C	H	Others	*M* [b]	Si–Me	Ni–CH_2	Others
(1)	$[Ni(CH_2SiMe_3)_2(py)_2]$	Yellow-brown	53.8 (55.2)	8.3 (8.2)	N 6.2 (8.2)	*d*	9.75 (s) [e]	10.82 (s)	
(2)	$[Ni(CH_2SiMe_3)_2(tmen)]$	Yellow-brown	47.9 (48.1)	10.9 (10.9)	N 8.0 (8.0)	339 (349)	9.20 (s)	11.30 (s)	7.90 (s) (N–Me) 8.49 (s) (N–CH_2)
(3)	$[Ni(CH_2SiMe_3)_2(phen)]$	Dark blue	58.1 (58.1)	7.3 (7.3)	N 6.8 (6.8)		9.38 (s)	9.29 (s)	
(4)	$[Ni(CH_2SiMe_3)_2(bipy)]$	Dark green					9.30 (s)	9.42 (s)	
(5)	$[Ni(CH_2SiMe_3)_2(PMe_3)_2]$	Red	43.7 (43.6)	10.7 (10.4)		382 (385)	9.42 (s) *cis*, 9.45 (s) *trans*	9.69 (m) *cis*, 10.80 (t) *trans*	8.85 (d) *cis* (P–Me), 8.71 (t) *trans* (P–Me)
(6)	$[Ni(CH_2SiMe_3)_2(PMe_2Ph)_2]$	Red	56.9 (56.6)	8.6 (8.6)			9.53 (s) 9.63 (s)	9.78 (m) 10.83 (t)	8.60 (br,s) (P–Me) 8.91 (d) (P–Me)
(7)	$[Ni(CH_2SiMe_3)_2(dppe)]$	Yellow-orange	63.4 (64.7)	7.0 (7.3)	P 6.8 (6.8)	588 (631)	9.62 (s)	9.04 (m)	8.00 (m) (P–CH_2)
(8)	$[Ni(CH_2CMe_2Ph)_2(tmen)]$	Red-brown	70.8 (70.8)	7.7 (9.5)	N 4.8 (6.3)	*d*	*d*		
(9)	$[Ni(CH_2CMe_2Ph)_2(phen)]$	Dark blue	76.0 (76.0)	6.9 (6.7)	N 5.7 (5.6)	*d*	*d*		
(10)	$[Ni(CH_2CMe_2Ph)_2(bipy)]$	Dark green	74.6 (74.9)	6.9 (7.1)	N 5.5 (5.8)	*d*	*d*		

[a] Calculated values are given in parentheses. [b] Cryoscopically in benzene. [c] Chemical shifts (τ) in C_6H_6 solution referenced to the solvent resonance. [d] Instability and insolubility prevents this determination. [e] In NC_5H_5.



SCHEME R = CH_2SiMe_3 throughout. (*i*) MgRCl, excess of py, diethyl ether; (*ii*) phosphine in toluene (P = PMe_2Ph, P_2 = dppe); (*iii*) $PMePh_2$ or PPh_3 in light petroleum; (*iv*) toluene, L–L = tmen, bipy, or phen; (*v*) toluene, excess of Hacac; (*vi*) CH_2Cl_2 or $[NiCl_2(PMe_3)_2]$ in benzene; (*vii*) neat MeI or EtBr (X = I or Br respectively)

crystalline complex $[NiR_2(py)_2]$, (1), in *ca.* 70—80% yield. This compound is very unstable to air, decomposing immediately, both in solution and in the solid state. As a crystalline solid it can be kept indefinitely at room temperature under a nitrogen atmosphere, but it decomposes rapidly when kept *in vacuo*, or in solution in the absence of free pyridine, with deposition of finely divided metal.

The instability of this compound in solution prevented molecular-weight determination, although solubility and other data suggest it is a monomer. Infrared studies confirm the presence of the pyridine and alkyl ligands, and the ^1H n.m.r. spectrum (recorded in C_5H_5N or C_5D_5N) shows two singlets at τ 9.75 and 10.82 (intensity ratio 9 : 2) attributed to the Si*Me*$_3$ and the M–*CH*$_2$ protons respectively. Since these data do not provide unambiguous information regarding the geometry of this complex, and since it constitutes a rather uncommon example in the organometallic chemistry of nickel in the sense that most of the compounds of this type known have stabilizing chelating ligands containing pyridine-like rings, it was of interest to investigate its structure. The results of an *X*-ray analysis showed a *cis* disposition of the alkyl groups, an unusual geometry for $[NiR_2L_2]$ complexes where L is a non-chelating ligand.

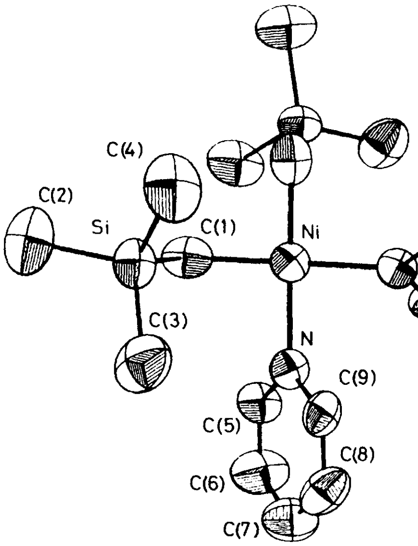


FIGURE 1 Structure and atom-numbering scheme for $[Ni(CH_2SiMe_3)_2(py)_2]$, (1). The molecule resides on a crystallographic two-fold axis

The molecular structure and atom-numbering scheme for $[Ni(CH_2SiMe_3)_2(py)_2]$, (1), are shown in Figure 1. This is the first square-planar bis(pyridine) complex of Ni^{II} to be characterized by *X*-ray crystallographic techniques. The compound exhibits the *cis* pyridine configuration with N–Ni–N 87.5(5)° (Table 2). The square-planar arrangement is further emphasized by angles C–Ni–C 87.6(7)° and C–Ni–N 178.9(5)°. The Ni–C bond length, 1.89(1) Å, is intermediate compared to the 1.84 Å value in $[Ni(COCH_2SiMe_3)Cl(PMe_3)_2]$ (ref. 3) and 1.95 Å in $[Ni(CH_2SiMe_3)Cl(PMe_3)_2]$.[3] The Ni–N length, 1.957(8) Å, falls between the 1.85 Å found in

TABLE 2

Interatomic distances (Å) and angles (°) for $[Ni(CH_2SiMe_3)_2(py)_2]$

(*a*) Distances			
Ni–N	1.957(8)	N–C(5)	1.40(1)
Ni–C(1)	1.89(1)	C(5)–C(6)	1.33(1)
C(1)–Si	1.86(1)	C(6)–C(7)	1.34(2)
Si–C(2)	1.87(1)	C(7)–C(8)	1.42(2)
Si–C(3)	1.86(1)	C(8)–C(9)	1.38(2)
Si–C(4)	1.90(1)	C(9)–N	1.32(1)
(*b*) Angles *			
N–Ni–C(1)	92.5(4)	C(1)–Ni–N′	178.9(5)
N–Ni–N′	87.5(5)	C(1)–Ni–C(1)′	87.6(7)
N–Ni–C(1)′	178.9(5)	Ni–N–C(5)	121.0(6)
Ni–C(1)–Si	116.2(5)	Ni–N–C(9)	123.4(6)
C(1)–Si–C(2)	113.1(5)	C(5)–N–C(9)	115.4(8)
C(1)–Si–C(3)	112.7(6)	N–C(5)–C(6)	121.4(9)
C(1)–Si–C(4)	111.6(6)	C(5)–C(6)–C(7)	124(1)
C(2)–Si–C(3)	107.7(7)	C(6)–C(7)–C(8)	116(1)
C(2)–Si–C(4)	105.1(6)	C(7)–C(8)–C(9)	118(1)
C(3)–Si–C(4)	106.1(7)	C(8)–C(9)–N	125(1)

* Primed atoms are related to those in Table 3 by (*Y*, *X*, − *Z*).

complexes in which the Ni atom is bound in a square-planar fashion to a polycyclic ligand,[5] and the *ca.* 2.08 Å in bis(pyridine) octahedral nickel(II) complexes.[6-8] A stereoscopic view of the unit-cell contents is shown in Figure 2.

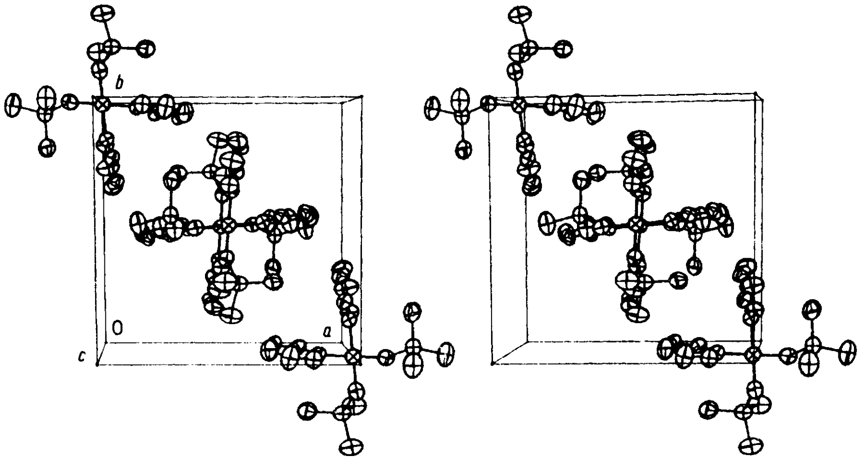


FIGURE 2 Stereoscopic view of the unit-cell packing for (1)

The ease with which complex (1) loses pyridine in solution has been successfully used for the preparation, in high yields, of other dialkyl derivatives of nickel. When crystals of (1) are dissolved in neat *NNN'N'*-tetramethylethylenediamine (tmen), [$Ni(CH_2SiMe_3)_2$(tmen)], (2), is formed in quantitative yield. This compound can also be prepared, although with poorer yields, by interaction of anhydrous $NiCl_2$ with MgRX in the presence of excess of the free base. Similarly, when a solution of (1) in toluene is allowed to react at −30 °C with phen or bipy (phen = 1,10-phenanthroline, bipy = 2,2'-bipyridyl), dark solutions are obtained from which dark blue or green crystals of [$Ni(CH_2SiMe_3)_2$(phen)], (3), and [$Ni(CH_2SiMe_3)_2$(bipy)], (4), respectively, can be collected after work-up. Compounds (2)—(4) are monomeric in benzene solution, and their ^1H n.m.r. spectra (see Table 1) are in good agreement with the proposed structures. Complex (4) has been synthesized recently by a tedious and long procedure which involves the use of aluminium alkyls.[4b]

(b) *With phosphine ligands.* We have recently reported [3] that complexes of the type [$NiR_2(PR'_3)_2$] cannot be obtained by reaction of [$NiCl_2(PR'_3)_2$] or [Ni(R)Cl($PR'_3)_2$] with Grignard reagents. Despite our initial failure, we have now succeeded in isolating the dialkyl derivatives by the smooth displacement of the pyridine ligands in complex (1) with an excess of the phosphine. Thus, when a solution of (1) in light petroleum was treated with a slight excess of PMe_3 or PMe_2Ph, [$Ni(CH_2SiMe_3)_2(PMe_3)_2$], (5), and [$Ni(CH_2SiMe_3)_2(PMe_2Ph)_2$], (6), were formed in almost quantitative yields. Both compounds were isolated as red air-sensitive crystals, which are very soluble in light petroleum, benzene, and non-hydrocarbon solvents and exist as monomers in solution.

The i.r. spectra of (5) and (6) show absorptions characteristic of the alkyl and phosphine ligands. Proton n.m.r. spectroscopic studies for these complexes suggest the presence in solution of *cis* and *trans* isomers. Thus, the ^1H n.m.r. spectrum of the PMe_3 derivative (5), shows, in the methyl–phosphine region, a virtually coupled triplet centred at 8.71 p.p.m., characteristic of bis phosphine complexes with strong coupling between the phosphorus nuclei, and a doublet at 8.85 p.p.m., which indicates the presence of the *cis* isomer, for which a smaller coupling constant between the ^{31}P nuclei is generally expected. The intensity ratio for these signals is *ca.* 1 : 4. In addition, there are two singlets at 9.45 and 9.42 p.p.m. (Si–Me_3, intensity ratio 1 : 4), and a triplet and a four-line pattern at 10.80 and 9.69 p.p.m., ascribed to the methylene protons of the alkyl ligands. Although some of the resonances have close chemical shifts and overlap partially, the characteristic features of the spectra of the *cis* and *trans* isomers can be clearly distinguished. These spectra are deceptively simple and could in principle be interpreted considering separately the P–*Me* and the Ni–CH_2 regions. However this would clearly be incorrect, since if one ignores the Si–Me_3 protons the full description of the spin system for [$Ni(CH_2SiMe_3)_2(PMe_3)_2$] would be [9] $[AR_2X_9]_2$. Nevertheless our 60 MHz ^1H n.m.r. spectrum does not show the characteristic pattern of lines found for this system in similar complexes,[10] *e.g.* *cis*-[$PtMe_2(PMe_3)_2$], and a full analysis has not been attempted.

An *X*-ray crystal-structure determination [11] carried out on complex (5) shows *trans* phosphines, although the P–Ni–P angle is only 147°. Since the ^1H n.m.r. spectra of crystals of different crops invariably show the above features, there being no observable changes in the temperature range −30 to 60 °C, nor when the spectra are run in different solvents or in the presence of free PMe_3, we believe that an equilibrium between the *cis* and the *trans* isomers exists and that isomerization is slow on the n.m.r. time scale, even in the presence of free base. The existence in solution of both isomers is also confirmed by ^{31}P n.m.r. spectroscopic studies. The $^{31}P\{^1H\}$ n.m.r. spectrum of a solution of (5) shows two singlets at −16.6 and −13.9 p.p.m.* with intensity ratio of 4 : 1, due respectively to the phosphorus nuclei resonances in the *cis* and *trans* isomers. We note that for $[NiMe_2(PMe_3)_2]$ only the *trans* isomer was found to exist in solution.[2b] Both electronic and steric effects must be responsible for the different behaviour shown by complex (5), while packing effects must play an important role in determining the solid-state structure.

Proton n.m.r. data for other phosphine derivatives prepared in this work are included in Table 1. For $[Ni(CH_2SiMe_3)_2(PMe_2Ph)_2]$, (6), and possibly due to the presence of small amounts of free phosphine, the quality of the spectra is not very good, although pertinent data seem to suggest the presence of the *cis* and *trans* isomers. However, the evidence is not as conclusive as for (5) and we merely point out the position of the bands without any further assignment. The spectrum of $[Ni(CH_2SiMe_3)_2(dppe)]$, (7) [dppe = 1,2-bis(diphenylphosphino)ethane], is complex showing a singlet at 9.62 p.p.m. (Si-Me_3) and bands centred at 8.00 and 9.04 p.p.m. due to the methylene protons of the phosphine and alkyl ligands. The P-CH_2 resonance is similar to that found [2a] for $[NiMe_2(dppe)]$, consisting of a sharp doublet within a very broad doublet, while the Ni-CH_2 signal is a four-line pattern resembling closely that of the methylene protons in *cis*-$[Ni(CH_2SiMe_3)_2(PMe_3)_2]$.

When complex (5) is dissolved in CH_2Cl_2 a rapid reaction takes place with formation of a small amount of a unidentified colourless solid and a solution from which $[Ni(CH_2SiMe_3)Cl(PMe_3)_2]$ can be isolated in high yields. The dichloro-derivative $[NiCl_2(PMe_3)_2]$ has not been detected, in contrast to the behaviour of $[NiEt_2(bipy)]$ which reacts with CH_2Cl_2 *via* the carbene moiety $:CH_2$ to give $[NiCl_2(bipy)]$ and organic products formed by insertion of $:CH_2$ into the nickel–ethyl bonds.[12] The reactions of (5) with MeI, EtBr, and $[NiCl_2(PMe_3)_2]$ are similar (see Scheme) giving mainly the monoalkyls $[Ni(CH_2SiMe_3)X(PMe_3)_2]$. The iodine derivative reacts further with excess of MeI yielding $[PMe_4]I$ and insoluble, nickel-containing materials as the final products.

While the reactions of $[Ni(CH_2SiMe_3)_2(py)_2]$ with PMe_3, PMe_2Ph, and dppe give the corresponding dialkylphosphine derivatives, as described above, interaction with $PMePh_2$ and PPh_3 affords $[NiL_4]$ in quantitative yields, possibly by reductive elimination of the alkyl groups of unstable $[NiR_2L_2]$. Reaction of complex (1) with Hacac also causes removal of the alkyl ligands with formation of *trans*-$[Ni(acac)_2(py)_2]$. Finally, action of SMe_2, $C_6H_5C{\equiv}CH$, C_6H_6, $C_6H_5CH_3$, *NN*-dimethylpiperazine, or $P(OMe)_3$ on solutions of $[Ni(CH_2SiMe_3)_2(py)_2]$ afforded only decomposition products.

Neophyl Derivatives.—Attempts to prepare the bis(neophyl)(ββ-dimethylphenethyl) derivatives, $[Ni(CH_2CMe_2Ph)_2L_2]$, were generally unsuccessful due to thermal instability of the complexes. In fact we only succeeded in isolating the tmen, (8), phen, (9), and bipy, (10), derivatives, although for the first compound no satisfactory analytical data have been obtained.

The reaction of $[NiCl_2(py)_4]$ with $Mg(CH_2CMe_2Ph)Cl$ in the presence of excess of tmen yields, under certain conditions, a crystalline, slightly sticky solid, which decomposes rapidly on attempted recrystallisation, even in the presence of a large excess of tmen. The interaction of this complex, which we tentatively formulate as $[Ni(CH_2CMe_2Ph)_2(tmen)]$, (8), with phen or bipy yields dark blue or dark green crystals of $[Ni(CH_2CMe_2Ph)_2(L{-}L)]$ [L-L = phen, (9) or bipy, (10)]. Infrared spectroscopic studies showed absorptions characteristic of the neophyl and nitrogen-containing ligands, but insolubility and thermal instability of the complexes made characterization difficult.

EXPERIMENTAL

Microanalyses were by Butterworth Microanalytical Consultancy Ltd., Middlesex. Molecular weights were measured cryoscopically in benzene under nitrogen. Infrared spectra were recorded using Nujol mulls on a Perkin-Elmer 577 spectrometer. Hydrogen-1 n.m.r. spectra were obtained at 60 MHz on a Perkin-Elmer R-12B instrument. Phosphorus-31 Fourier-transform n.m.r. spectra were recorded on a Varian XL-100-12 instrument.

All the preparations and manipulations were carried out under oxygen-free nitrogen following conventional Schlenk-tube techniques. Solvents were dried and degassed before use. The light petroleum used had b.p. 40—60 °C. The ligands PMe_3 and PMe_2Ph were prepared according to literature methods.[13]

$[Ni(CH_2SiMe_3)_2(py)_2]$, (1).—A stirred suspension of $[NiCl_2(py)_4]$ (0.44 g, *ca.* 1.0 mmol) in diethyl ether (30 cm^3) at −60 °C was treated with pyridine (0.4 cm^3) and $Mg(CH_2SiMe_3)Cl$ (1.5 cm^3 of a *ca.* 1.45 mol dm^{-3} diethyl ether solution). The resulting mixture was stirred at room temperature for 3—4 h. The solvent was then removed under reduced pressure and the residue extracted with light petroleum (30 cm^3), with some added pyridine (0.3 cm^3). The solution was centrifuged and the product crystallised as red-brown needles by removing part of the solvent and cooling at −30 °C (yield 70—80%). Purification can be achieved by recrystallisation from light petroleum, in the presence of pyridine, at −30 °C.

$[Ni(CH_2SiMe_3)_2(tmen)]$, (2).—(*a*) Complex (1) (0.39 g, *ca.* 1.0 mmol) was stirred in neat *NNN'N'*-tetramethylethylenediamine (2 cm^3) for 30 min. Evaporation under reduced pressure and crystallisation of the residue from light petroleum at −30 °C gave the complex as brown crystals in *ca.* 90% yield. This compound can be obtained directly from $[NiCl_2(py)_4]$, $Mg(CH_2SiMe_3)Cl$, and excess of tmen.

(*b*) To a suspension of anhydrous $NiCl_2$ (0.26 g, *ca.* 2.0 mmol) in diethyl ether (30 cm^3) at −60 °C, tmen (2 cm^3) and $Mg(CH_2SiMe_3)Cl$ (3.0 cm^3 of a *ca.* 1.45 mol dm^{-3} diethyl ether solution) were added. The mixture was stirred at this temperature for 30 min and then at room temperature for 4—5 h. The solvent was removed *in vacuo*, the residue extracted with light petroleum, and the complex crystallised at −30 °C (yield 30—40%).

$[Ni(CH_2SiMe_3)_2(phen)]$, (3).—To a stirred solution of (1) (0.35 g, *ca.* 0.9 mmol) in toluene (10 cm^3) at −10 °C, anhy-

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* Phosphorus-31 chemical shifts are to high frequency of external 85% H_3PO_4.

drous phen (0.16 g, *ca.* 0.9 mmol) was added. The mixture was warmed to 25 °C and the colour changed from red to dark blue. The stirring was continued for 1 h at this temperature. Removal of the solvent and crystallisation of the residue from diethyl ether–light petroleum afforded the pure complex as dark blue crystals in *ca.* 90% yield.

$[Ni(CH_2SiMe_3)_2(bipy)]$, (4).—This complex was prepared as (3) above, and crystallisation achieved from light petroleum in almost quantitative yield. The ^1H n.m.r. spectra was identical to that of a pure sample, although we had no difficulties in observing the Ni–CH_2 resonance which could not be unambiguously assigned in the original report.[4b]

$[Ni(CH_2SiMe_3)_2(PMe_3)_2]$, (5).—(*a*) Complex (1) (0.58 g, *ca.* 1.5 mmol), trimethylphosphine (0.4 cm^3, *ca.* 4.0 mmol), and light petroleum (5 cm^3) were stirred for 4—5 min at 0 °C. The colour changed from red to yellow. The solvent was removed *in vacuo* and the residue dissolved in light petroleum, centrifuged, and crystallised from a small volume of this solvent (*ca.* 1 cm^3) at -30 °C as well formed dark red crystals in *ca.* 90—95% yield.

(*b*) A diethyl ether solution (1.5 cm^3) *ca.* 1.45 mol dm^{-3} in $Mg(CH_2SiMe_3)Cl$ was syringed onto a mixture of $[NiCl_2(py)_4]$ (0.44 g, *ca.* 1.0 mmol), pyridine (0.3 cm^3), trimethylphosphine (0.3 cm^3, *ca.* 0.3 mmol), and diethyl ether (30 cm^3) with stirring at -60 °C. The suspension was warmed to 25 °C and stirred at this temperature for 1 h. Evaporation to dryness *in vacuo*, extraction with light petroleum and centrifugation, followed by partial removal of the solvent (final volume *ca.* 1 cm^3) and cooling at -30 °C, gave the desired product as dark red crystals in 80% yield.

$[Ni(CH_2SiMe_3)_2(PMe_2Ph)_2]$, (6).—This complex was prepared and purified by the methods reported above for the trimethylphosphine analogue, and collected as red crystals in *ca.* 80% yield.

$[Ni(CH_2SiMe_3)_2(dppe)]$, (7).—(*a*) Complex (1) (0.39 g, *ca.* 1.0 mmol) in toluene (10 cm^3) at -30 °C was treated with a slight excess of dppe (0.42 g, *ca.* 1.05 mmol). After stirring at room temperature for 15 min the solvent was removed *in vacuo* and the residue extracted with diethyl ether (20 cm^3). Centrifugation and cooling at -30 °C afforded the complex as yellow-orange needles in *ca.* 80—90% yield.

(*b*) Treatment of $[NiCl_2(dppe)]$ (0.53 g, *ca.* 1.0 mmol) in diethyl ether (30 cm^3) with $Mg(CH_2SiMe_3)Cl$ (1.5 cm^3 of a *ca.* 1.45 mol dm^{-3} diethyl ether solution) gave, after stirring for 2 h at 25 °C, a yellow-orange solution and a white precipitate. The mixture was centrifuged and the solution cooled at -30 °C overnight. The yellow-orange needles were collected and dried *in vacuo* (yield 80%).

Reaction of $[Ni(CH_2SiMe_3)_2(py)_2]$, (1), *with* $PMePh_2$ *or* PPh_3.—A solution of (1) (0.47 g, *ca.* 1.2 mmol) in light petroleum (20 cm^3) at -30 °C was treated with the phosphine (5.0 mmol). The mixture was stirred at room temperature for a few minutes, after which time a crystalline solid separated. This was collected, washed with diethyl ether, and dried *in vacuo*. The yellow-orange and red products were identified as $[Ni(PMePh_2)_4]$ and $[Ni(PPh_3)_4]$ respectively, by comparison of their i.r. and ^1H n.m.r. spectra with those of authentic samples.

Reaction of $[Ni(CH_2SiMe_3)_2(py)_2]$, (1), *with* Hacac.—A solution of (1) (0.47 g, *ca.* 1.2 mmol) in toluene (10 cm^3) at -10 °C was stirred with an excess of acetylacetone (1 cm^3). On warming to room temperature, the mixture became colourless and a grey precipitate separated. This was collected and crystallised from methanol as blue crystals, identified (m.p. and i.r.) as *trans*-$[Ni(acac)_2(py)_2]$.

Reaction of $[Ni(CH_2SiMe_3)_2(PMe_3)_2]$, (5), *with* CH_2Cl_2.—Compound (5) (0.19 g, *ca.* 0.5 mmol) was dissolved in neat CH_2Cl_2 and stirred at room temperature for 2—3 min, when a small amount of a white microcrystalline solid was formed. The supernatant solution was filtered and the solvent evaporated under reduced pressure to give a red-brown residue which, after crystallisation from light petroleum, was shown by i.r. and ^1H n.m.r. to be pure[3] $[Ni(CH_2SiMe_3)Cl(PMe_3)_2]$.

Reaction of $[Ni(CH_2SiMe_3)_2(PMe_3)_2]$, (5), *with* MeI.—Complex (5) (0.19 g, *ca.* 0.5 mmol) was stirred (30 min) with neat methyl iodide (5 cm^3), some decomposition being evident after this time. The solvent was removed *in vacuo* and the residue extracted with light petroleum (10 cm^3). Concentration and cooling at -30 °C afforded dark red crystals of a compound identified[3] (i.r. and ^1H n.m.r.) as $[Ni(CH_2SiMe_3)I(PMe_3)_2]$. The yield of this complex was shown to be very sensitive to the reaction time, $[PMe_4]I$ being the main product after stirring at room temperature for 2 h.

Reaction of $[Ni(CH_2SiMe_3)_2(PMe_3)_2]$, (5), *with* C_2H_5Br.—A solution of (5) (0.19 g, *ca.* 0.5 mmol) in neat ethyl bromide (5 cm^3) was stirred for 2 h. The resulting clear solution was evaporated and $[Ni(CH_2SiMe_3)Br(PMe_3)_2]$ was obtained by crystallisation from light petroleum at -30 °C. The i.r. and ^1H n.m.r. spectra of this product were identical to those of a pure sample.[3]

Reaction of $[Ni(CH_2SiMe_3)_2(PMe_3)_2]$, (5), *with* $[NiCl_2(PMe_3)_2]$.—Complex (5) (0.19 g, *ca.* 0.5 mmol) and $[NiCl_2(PMe_3)_2]$ (0.28 g, *ca.* 1.0 mmol) were dissolved in benzene (5 cm^3) and the resulting dark red solution stirred for 2 h. Evaporation *in vacuo*, extraction with light petroleum (20 cm^3), and cooling at -30 °C afforded crystals of unreacted $[NiCl_2(PMe_3)_2]$. The resulting solution was concentrated to *ca.* 5 cm^3 and cooled at -30 °C. The complex $[Ni(CH_2SiMe_3)Cl(PMe_3)_2]$, identified by i.r. and ^1H n.m.r., separated as yellow-orange crystals.

$[Ni(CH_2CMe_2Ph)_2(tmen)]$, (8).—To a stirred suspension of $[NiCl_2(py)_4]$ (0.88 g, *ca.* 2.0 mmol) in diethyl ether, at -60 °C, excess of tmen (1.2 cm^3) and $Mg(CH_2CMe_2Ph)Cl$ (8.0 cm^3 of a *ca.* 0.5 mol dm^{-3} diethyl ether solution) were added. The mixture was stirred for 5—10 min at room temperature, during which time the colour changed to dark red. The solvent was quickly removed under reduced pressure, the residue extracted with cold light petroleum (20 cm^3) with some added tmen (0.5 cm^3), and the mixture centrifuged (2—3 min). The product was obtained as red-brown, slightly sticky crystals, by removal of the solvent (final volume *ca.* 5 cm^3) and cooling at -30 °C. Further purification could not be achieved since the complex decomposes in solution even in the presence of excess of tmen (yield 30—40%).

$[Ni(CH_2CMe_2Ph)_2(phen)]$, (9).—Complex (8) (0.22 g, *ca.* 0.5 mmol) and anhydrous phen (0.09 g, *ca.* 0.5 mmol) were dissolved in benzene (10 cm^3) and the resulting dark blue solution stirred for 10—15 min at room temperature. After removal of the solvent *in vacuo*, and crystallisation from diethyl ether–tetrahydrofuran (1 : 1), $[Ni(CH_2CMe_2Ph)_2(phen)]$ was collected as dark blue crystals in *ca.* 30—40% yield. This compound is indefinitely stable under nitrogen in the solid state, but decomposes slowly in solution.

$[Ni(CH_2CMe_2Ph)_2(bipy)]$, (10).—This complex was prepared as (9) above, and crystallisation achieved from relatively large volumes of diethyl ether, as dark green crystals in *ca.* 30—40% yield.

X-Ray Data Collection, Structure Determination, and Refinement for $[Ni(CH_2SiMe_3)_2(NC_5H_5)_2]$.—*Crystal data.* $C_{18}H_{32}N_2NiSi_2$, $M = 391.4$, Tetragonal, $a = 13.423(9)$, $c = 12.940(9)$ Å, $U = 2.331.5$ Å^3, $Z = 4$, $D_c = 1.11$ g cm^{-3}, μ(Mo-K_α) = 9.28 cm^{-1}, space group $P4_12_12$. The lattice parameters were determined from a least-squares refinement of the angular settings of 15 reflections ($2\theta > 30°$) accurately centred on an Enraf–Nonius CAD-4 diffractometer.

A crystal of dimensions 0.26 × 0.32 × 0.80 mm was sealed in a thin-walled capillary under a nitrogen atmosphere. Data were collected on the diffractometer with graphite-crystal monochromated molybdenum radiation. The diffracted intensities were collected by the ω—2θ scan technique in a manner similar to that previously described.[14] All unique reflections in one independent octant of data were measured out to $2\theta \leqslant 50°$; 696 were considered observed $[I \geqslant 3\sigma(I)]$. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Full-matrix least-squares refinement was carried out using the SHELX computer program library.[15] No corrections were made for extinction. Atomic scattering factors for Ni, Si, N, and C were taken from Cromer and Waber,[16] and the scattering for Ni corrected for the real and imaginary components of anomalous dispersion using the values of Cromer and Liberman.[17] Scattering factors for hydrogen were from ref. 18.

TABLE 3

Final fractional co-ordinates for $[Ni(CH_2SiMe_3)_2(py)_2]$

Atom	x/a	y/b	z/c
Ni	0.488 7(1)	0.488 7(1)	0.000 0
Si	0.451 0(3)	0.718 7(3)	0.046 7(3)
N	0.351 0(7)	0.477 4(8)	−0.048 4(6)
C(1)	0.499(1)	0.622 4(9)	−0.044 4(8)
C(2)	0.483(1)	0.849(1)	0.006(1)
C(3)	0.313(1)	0.712(1)	0.066(1)
C(4)	0.507(2)	0.704(1)	0.180 7(9)
C(5)	0.327 6(9)	0.487(1)	−0.153 4(7)
C(6)	0.235(1)	0.477(1)	−0.187(1)
C(7)	0.157(1)	0.456(1)	−0.125(1)
C(8)	0.178(1)	0.443(1)	−0.019(1)
C(9)	0.276(1)	0.454 6(9)	0.012 6(9)
H(1)[C(1)]	0.456	0.631	−0.115
H(2)[C(1)]	0.575	0.640	−0.058
H(3)[C(2)]	0.555	0.845	−0.029
H(4)[C(2)]	0.470	0.922	0.037
H(5)[C(2)]	0.425	0.831	−0.049
H(6)[C(3)]	0.267	0.650	0.083
H(7)[C(3)]	0.299	0.727	−0.022
H(8)[C(3)]	0.297	0.777	0.104
H(9)[C(4)]	0.491	0.634	0.215
H(10)[(4)]	0.470	0.764	0.222
H(11)[(4)]	0.588	0.718	0.185
H(12)[(5)]	0.386	0.502	−0.209
H(13)[(6)]	0.216	0.484	−0.271
H(14)[(7)]	0.078	0.441	−0.154
H(15)[(8)]	0.119	0.427	0.039
H(16)[(9)]	0.293	0.439	0.093

The position of the Ni atom was deduced from the inspection of a Patterson map and the subsequent calculation of Fourier-difference maps allowed the location of the remaining non-hydrogen atoms. Refinement with isotropic temperature factors led to $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.115$. Conversion to anisotropic thermal parameters and further refinement gave $R = 0.073$. The hydrogen-atom positions were determined from a difference-Fourier map but their parameters were not refined. Additional cycles of refinement led to final values of $R = 0.058$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}} = 0.060$. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. A final difference Fourier showed no feature greater than 0.3 e Å^{-3}. The standard deviation of an observation of unit weight was 1.09. Unit weights were used at all stages; no systematic variation of $w(|F_o| - |F_c|)$ against $|F_o|$ or $(\sin \theta)/\lambda$ was noted. (Refinement in the space group $P4_32_12$ resulted in $R = 0.066$, and therefore $P4_12_12$ was taken as the correct choice.) The final positional parameters are given in Table 3. The observed and calculated structure-factor amplitudes and thermal parameters are given in Supplementary Publication No. SUP 22972 (8 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

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