

TABLE I
Analytical and spectroscopic data for the monoalkyl complexes $[\text{NiR}(\text{X})\text{L}_2]$

	Compound			Colour	Analysis (%) ^a			<i>M</i> ^b	Selected i.r. data ^c	¹ H N.m.r. ^d		
	R	L	X		C	H	Others			Me-P	Me-C or Me-Si	CH ₃
(1)	CH ₃ SiMe ₃	PMe ₃	Cl	Yellow-orange	35.8 (36.0)	8.9 (8.7)	P 18.3 (18.6)	328 (333)		8.79 (br s)	9.57 (s)	10.51 (br t) ^e
(2)			Br	Red	31.8 (31.8)	7.3 (7.7)				8.68 (br s)	9.53 (a)	10.28 (br t) ^e
(3)			I	Dark red	28.1 (28.2)	7.0 (6.8)				8.75 (t) ^f	9.63 (s)	10.08 (br t) ^e
(4)			NCS	Yellow-green	37.4 (37.1)	7.9 (8.1)	N 4.2 (3.9)		$\nu(\text{NCS})$ 2 065vs	8.91 (br s)	9.65 (s)	10.63 (br s)
(5)			NCO	Yellow-orange					$\nu(\text{NCO})$ 2 200vs	8.76 (br s)	9.56 (s)	10.47 (br t) ^e
(6)		PMe ₂ Ph	Cl	Orange	52.1 (52.5)	7.9 (7.2)	P 13.0 (13.5)	440 (457)		8.44 (br s)	9.62 (s)	10.43 (br s)
(7)			Br	Red-orange	47.3 (47.8)	6.5 (6.6)		477 (501)		8.36 (br s)	9.54 (s)	10.33 (br s)
(8)			I	Dark red						8.29 (t) ^f	9.56 (s)	10.05 (br t) ^e
(9)			NCS	Brown	52.3 (52.5)	7.0 (6.9)	N 3.1 (2.9)	498 (480)	$\nu(\text{NCS})$ 2 070vs	8.60 (br s)	9.70 (s)	10.59 (br s)
(10)			NCO	Brown	54.3 (54.3)	7.3 (7.1)	N 2.9 (3.0)	458 (464)	$\nu(\text{NCO})$ 2 200vs	8.47 (br s)	9.53 (s)	10.49 (br s)
(11)	CH ₃ CMe ₂ Ph	PMe ₃	Cl	Red-brown	50.3 (50.6)	8.1 (8.2)		392 (379)		8.63 (br s)	8.09 (s)	8.74 (br s)
(12)			Br	Red				403 (424)		8.73 (br t)	8.15 (s)	8.91 (br t) ^g
(13)			I	Dark red	41.0 (40.8)	6.7 (6.6)		458 (471)		8.92 (t) ^f	8.39 (s)	<i>h</i>
(14)			NCS	Light brown	50.7 (50.8)	7.7 (7.9)	N 3.3 (3.5)	387 (402)	$\nu(\text{NCS})$ 2 070vs	9.00 (br s)	8.45 (s)	9.29 (br s)
(15)			NCO	Red-brown	54.9 (55.0)	9.3 (9.5)	N 4.5 (4.3)	458 (464)	$\nu(\text{NCO})$ 2 200vs	8.94 (br s)	8.28 (s)	9.21 (br s)
(16)		PMe ₂ Ph	Cl	Red-brown	61.6 (62.0)	7.4 (7.0)		403 (424)		8.50 (br s)	8.32 (s)	<i>h</i>
(17)			Br	Red-brown	57.0 (57.0)	6.6 (6.4)		477 (499)		8.56 (br s)	8.36 (s)	<i>h</i>
(18)			NCS	Red-brown	61.9 (61.6)	6.8 (6.7)	N 2.5 (2.7)	486 (510)	$\nu(\text{NCS})$ 2 070vs	8.72 (br s)	8.49 (s)	9.26 (br s)
(19)			NCO	Red-brown					$\nu(\text{NCO})$ 2 200vs	8.86 (br s)	8.59 (s)	<i>h</i>
(20)	[Ni(CH ₃ CMe ₂ Ph)(η -C ₅ H ₅)(PMe ₃)]			Yellow-green	65.1 (64.9)	8.2 (8.1)	P 9.1 (9.3)			9.06 (d) ⁱ	8.31 (s)	8.70 (d) ⁱ

^a Calculated values are given in parentheses. ^b Cryoscopically in benzene. ^c Nujol mulls. ^d Chemical shift (τ) in benzene. Data at low and high temperatures (in C₆D₆CD₂) are not shown. ^e *J*(P-H) 14.5 Hz. ^f *J*(apparent) 3 Hz. ^g *J*(P-H) 11 Hz. ^h Obscured by P-CH₃ signal. ⁱ *J*(P-H) ca. 10 Hz, 4.84 (s) (η -C₅H₅).

excess of the Grignard reagent reduces the yield by formation of an insoluble material which we have not further investigated. Dialkyl derivatives have not been detected even in the presence of excess of phosphine.

The monoalkyl complexes are unstable to oxygen both in solution and in the solid state, although as crystalline materials they can be handled in air for short periods of time without apparent decomposition. Molecular-weight determinations in benzene for some of the complexes indicate they are monomeric, and on the basis of the similarities in their physical and spectroscopic properties the remaining compounds have also been assumed to be monomeric.

Metathesis reactions of the chloro-complexes with KX

(see Scheme 1) in dry acetone or tetrahydrofuran (thf) at room temperature give the remaining complexes in Table I in almost quantitative yields. Treatment of the neophyl ($\beta\beta$ -dimethylphenethyl) complex (11) with Tl[C₅H₅] in thf affords the yellow-green cyclopentadienyl derivative (20).

Variable-temperature ¹H n.m.r. studies for [NiR(X)L₂] complexes show a square-planar structure with *trans* phosphines in solution. Owing to rapid ligand exchange, the spectrum of complex (1) exhibits at 35 °C a broad singlet at τ 8.79 and a broad triplet centred at τ 10.51 for the methyl-phosphine and the methylene protons respectively; the methyl protons of the alkyl group appear at τ 9.57, the intensities of these signals being in

TABLE 2
Analytical and spectroscopic data for the acyl complexes [Ni(COR)XL₂]

	Compound			Colour	Analysis (%) ^a			<i>M</i> ^b	Selected i.r. data ^c	¹ H N.m.r. ^d		
	R	L	X		C	H	Others			Me-P	Me-C or Me-Si	CH ₃
(21)	CH ₃ SiMe ₃	PMe ₃	Cl	Red	36.4 (36.5)	7.8 (8.0)	P 16.7 (17.1)	362 (361)	$\nu(\text{CO})$ 1 650vs	8.81 (br s)	9.81 (s)	7.21 (s)
(22)			Br	Red-brown	32.6 (32.5)	7.3 (7.2)		395 (406)	$\nu(\text{CO})$ 1 640vs	8.69 (br s)	9.78 (s)	7.13 (s)
(23)			I	Red-brown				423 (453)	$\nu(\text{CO})$ 1 645vs	8.61 (br s)	9.95 (s)	7.08 (s)
(24)			NCS	Yellow					$\nu(\text{CO})$ 1 620vs $\nu(\text{NCS})$ 2 070vs	8.91 (br s)	9.79 (s)	7.43 (s)
(25)			NCO	Yellow					$\nu(\text{CO})$ 1 620vs $\nu(\text{NCO})$ 2 200vs	8.73 (br s)	9.69 (s)	7.41 (s)
(26)	CH ₃ CMe ₂ Ph	PMe ₃	Cl	Yellow	50.1 (50.1)	7.4 (7.6)		423 (407)	$\nu(\text{CO})$ 1 635vs ^e	8.67 (br s) ^f	8.40 (s)	6.40 (s)
(27)			Br	Yellow-orange	45.4 (45.2)	6.9 (6.9)		413 (452)	$\nu(\text{CO})$ 1 630vs ^e	8.99 (br s)	8.60 (s)	6.59 (s)
(28)			I	Red	39.5 (40.9)	6.4 (6.2)		492 (499)	$\nu(\text{CO})$ 1 640vs ^e	7.78 (br s)	8.49 (s)	6.43 (s)
(29)			NCO	Yellow-orange	53.7 (54.1)	8.9 (8.7)	N 3.8 (3.9)	419 (414)	$\nu(\text{CO})$ 1 635vs $\nu(\text{NCO})$ 2 190vs	8.88 (br s) ^f	8.61 (s)	6.78 (s)
(30)		PMe ₂ Ph	Cl	Red	60.3 (61.0)	6.4 (6.6)		414 (361)	$\nu(\text{CO})$ 1 690vs	8.59 (br s)	8.81 (s)	6.62 (s)
(31)	[Ni(COCH ₂ CMe ₂ Ph)(η -C ₅ H ₅)(PMe ₃)]			Red	63.0 (63.2)	7.4 (7.5)	P 8.7 (8.6)	352 (361)	$\nu(\text{CO})$ 1 630vs ^e	9.09 (d) ^g	8.41 (s)	6.56 (s)

^a Calculated values are given in parentheses. ^b Cryoscopically in benzene. ^c Nujol mulls. ^d Chemical shifts (τ) in C₆H₆. Data at low and high temperatures (in C₆D₆CD₂ or CD₃COCD₃) are not shown. ^e KBr disc. ^f In CH₂Cl₂. ^g *J*(P-H) ca. 10 Hz, 4.69 (s) (η -C₅H₅).

the expected ratio of 18 : 2 : 9. On cooling at 10 °C, the methyl-phosphine resonance becomes a pseudo-triplet which is characteristic of $H_nPP'H'_n$ spin systems with strong coupling between the phosphorus nuclei. Under these conditions the methylene protons appear as a sharp triplet [$J(P-H)$ 14.5 Hz]. The spectra of similar compounds prepared in this work display essentially the same features, although the temperature at which the P-Me resonance becomes a virtually coupled triplet increases with ligand size, and when $X = I$ the triplet is observed even at 35 °C. Relevant 1H n.m.r. data for other alkyl complexes are included in Table 1 and require no further comment.

The i.r. spectra of $[NiR(X)L_2]$ compounds show absorptions characteristic of the alkyl and phosphine ligands. For the thiocyanate derivatives there is in addition a sharp band at *ca.* 2 070 cm^{-1} which can be assigned to $\nu(C-N)$. The position of this band suggests co-ordination through nitrogen⁵ and this assumption is also supported by the similarity between the visible spectra of the cyanate and thiocyanate complexes, which show a single *d-d* transition at *ca.* 24 100 cm^{-1} . The cyanate complexes have an i.r. absorption at 2 200 cm^{-1} attributed to $\nu(C-N)$ of the terminal NCO ligand.

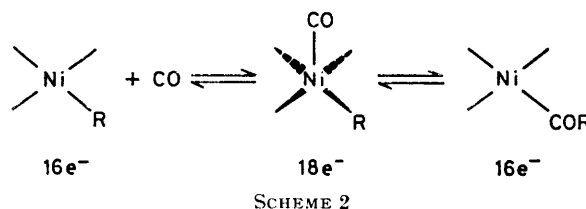
Acyl Complexes.—On bubbling CO through solutions of $[NiR(X)(PMe_3)_2]$ compounds, carbon monoxide absorption takes place in smooth reactions which lead to the corresponding acyls, $[Ni(COR)X(PMe_3)_2]$, in almost quantitative yield. The reactions cannot be reversed by heating: prolonged reflux in benzene does not yield the parent alkyl. Complexes (22)—(25) and (27)—(29) can also be prepared in good yields by metathesis reactions in acetone or thf. The acyls are more stable towards oxygen and moisture than the corresponding alkyls, no noticeable decomposition being observed after short exposures to the atmosphere (2—3 min). Molecular weight determinations, cryoscopically in benzene, indicate the compounds to be monomeric (Table 2).

Interaction of CO with a solution of the dimethyl-phenylphosphine derivative (6) gives only decomposition products, while when $R = CH_2CMe_2Ph$, (16), the corresponding acyl $[Ni(COCH_2CMe_2Ph)Cl(PMe_2Ph)_2]$, (30), can be isolated. This complex is rather unstable, decomposing slowly in solution even when kept under an inert atmosphere. To our knowledge it is the first acyl of nickel stabilized by a non-chelating phosphine other than PMe_3 or PEt_3 . On the other hand, reaction of the chloro-complex (26) with $Tl[C_5H_5]$ in dry acetone affords red crystals of (31). This compound is the first acyl-cyclopentadienyl derivative of nickel(II) to be reported.

Proton n.m.r. studies for these complexes suggest *trans*-square-planar geometries, the main difference with the spectra of the alkyl derivatives being the low-field shift of the methylene protons expected upon carbonylation. Also, co-ordination of an acyl group causes a decrease in the temperature of appearance of the P-Me pseudo-triplet. Pertinent 1H n.m.r. and i.r. data for these derivatives are included in Table 2. All the com-

plexes show a very strong i.r. absorption at 1 630—1 690 cm^{-1} due to $\nu(C-O)$ of the acyl ligand.

Previous work has shown that the insertion of carbon monoxide into Ni-C bonds occurs *via* an intermediate five-co-ordinate species containing a co-ordinated CO molecule, the proposed mechanism being as in Scheme 2.



Thus, to account for the formation of the 18-electron complex $[Ni(COCH_3)L][BPh_4]$ [$L = \text{tris}(2\text{-diphenylphosphinoethyl})\text{amine}$] from the reaction of the parent alkyl with CO, rupture of the Ni-N bond and attack of CO to give an intermediate alkyl-carbonyl species has been suggested.⁴ The reaction of $[Ni(CH_2CMe_2Ph)(\eta-C_5H_5)(PMe_3)]$, (20), with CO could similarly take place with dissociation of phosphine to give a reactive 16-electron species. Proton n.m.r. studies of solutions of complexes (20) and (31) provide no evidence of such a process, addition of free phosphine yielding separate resonances for the free and co-ordinated ligands. It is not therefore surprising that we have not been able to isolate complex (31) by action of CO on the alkyl derivative (20). The acyl can only be prepared by metathesis of (26)—(29) with $Tl[C_5H_5]$ (see below).

The high thermal stability of the acyls reported seems to suggest that the equilibrium $[NiR(X)L_2] + CO \rightleftharpoons [Ni(COR)XL_2]$ lies well to the right. However, under appropriate conditions, the equilibrium can be reversed. Thus the reaction of $[Ni(COCH_2SiMe_3)Cl(PMe_3)_2]$ with $[Ni(CH_2CHMe_2Ph)Br(PMe_3)_2]$ gives $[Ni(COCH_2CMe_2Ph)Br(PMe_3)_2]$ and $[Ni(CH_2SiMe_3)Cl(PMe_3)_2]$ in almost quantitative yield (see Experimental section for details). For other systems or under different conditions, an equilibrium is established among the four possible species, as can be inferred from 1H n.m.r. studies of the reaction mixtures. For example, the 1H n.m.r. spectrum of a benzene solution of complexes (11) and (21) shows the presence of compounds (1), (11), (21), and (26) in the ratio *ca.* 6 : 1 : 1 : 6. As expected, the cyclopentadienyl derivatives (20) and (31) do not participate in exchange processes of this type.

Since the above reactions can in some cases take place in almost quantitative yield and under very mild conditions, it does not seem unreasonable to suppose that CO exchange between $[Ni(COR')XL_2]$ and $[NiR(X)L_2]$ might proceed *via* a CO bridged binuclear intermediate formed by interaction of the 18-electron five-co-ordinate intermediate $[NiR'(CO)XL_2]$ and the alkyl complex $[NiR(X)L_2]$. Further studies on these aspects and on the potential applications of these derivatives as carbonylating or decarbonylating agents are in progress.

The result of the X-ray analyses of $[Ni(CH_2SiMe_3)Cl-$

(PMe_3)₂], (1), and $[\text{Ni}(\text{COCH}_2\text{SiMe}_3)\text{Cl}(\text{PMe}_3)_2]$, (21), are given in Figures 1 and 2. Both compounds exhibit a distorted square-planar arrangement with the predicted *trans*-phosphine configuration. The Ni-P bond lengths average 2.206(7) Å in (1) and 2.201(3) Å in (21), and the Ni-Cl lengths are 2.256(10) and 2.300(10) Å in (1) and (21) respectively. Both types of bonds are similar to those found in $[\text{Ni}(\text{COCH}_3)\text{Cl}(\text{PMe}_3)_2]$ ⁶ [Ni-P 2.200(2) and Ni-Cl 2.265(3) Å]. The Ni-C bond lengths in the two determinations [1.95(2) Å in (1) and 1.84 Å in (21)] compare well with literature values.^{6,7} It is important to note that the oxygen of complex (21) is not coordinated to the nickel atom [Ni...O 3.121(4) Å]. Therefore, the Ni-C(*sp*²) distance, although shorter than

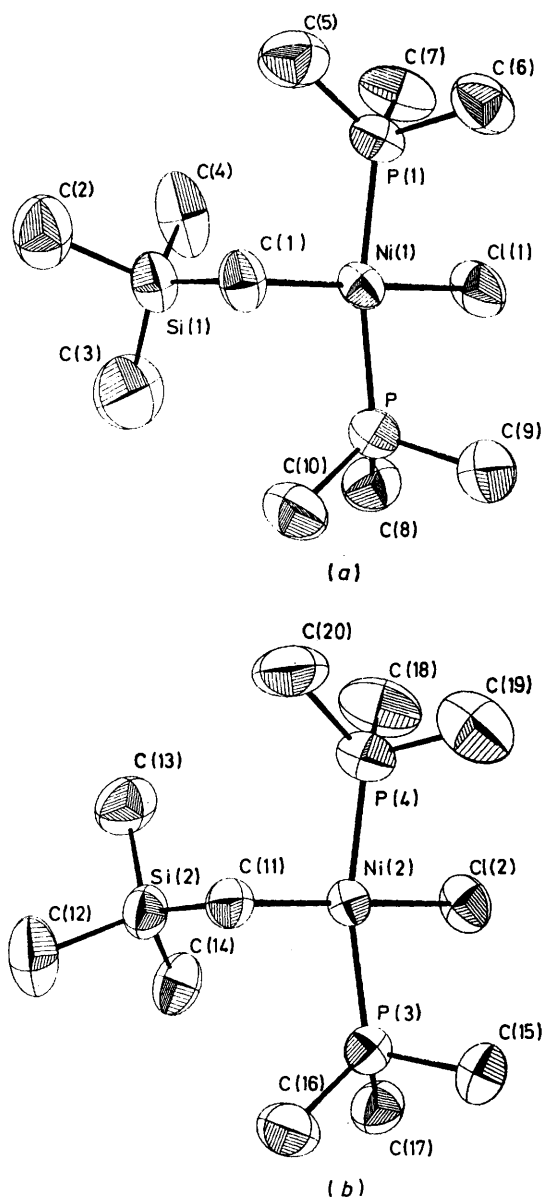


FIGURE 1 Molecular structure and atom-numbering scheme for $[\text{Ni}(\text{CH}_2\text{SiMe}_3)\text{Cl}(\text{PMe}_3)_2]$, (1). The two crystallographically independent molecules are designated *a* and *b*

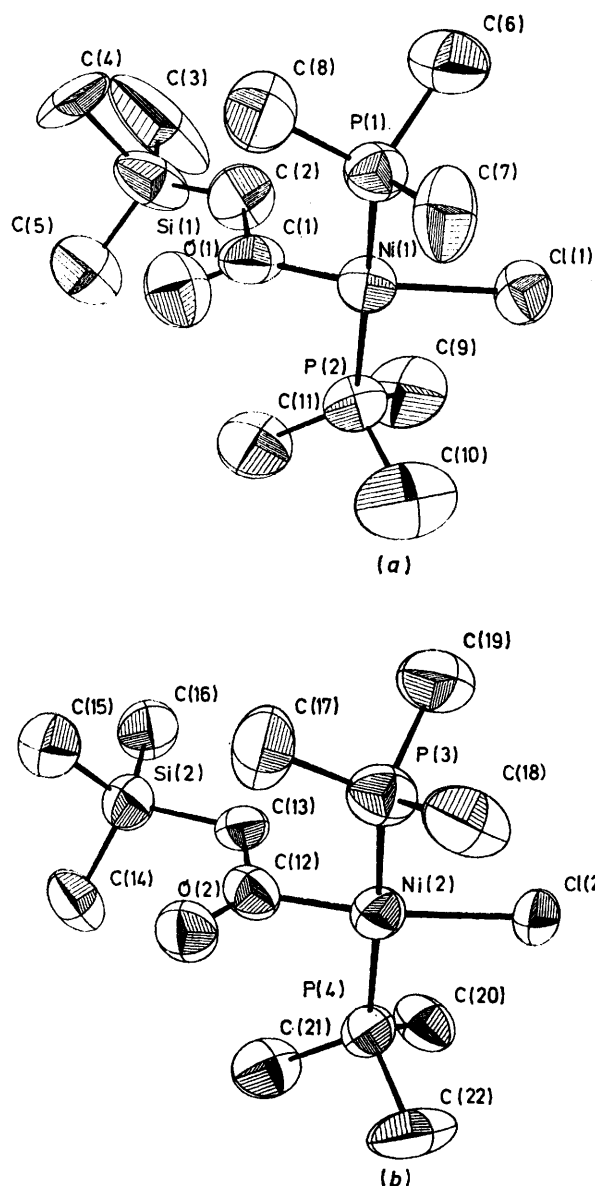


FIGURE 2 Molecular structure for $[\text{Ni}(\text{COCH}_2\text{SiMe}_3)\text{Cl}(\text{PMe}_3)_2]$, (21)

the Ni-C(*sp*³), does not show the marked contraction associated with the η^2 -acyl mode of co-ordination.⁸

The crystal structures of (1) and (21) both have two molecules in the asymmetric unit. The independent molecules do not differ in any important structural parameter, as may be seen from Tables 3 and 4 and Figures 1(a) and (b), 2(a) and (b). The unit-cell packing, typical for molecular compounds of this type, is illustrated in Figures 3 and 4 for (1) and (21), respectively.

EXPERIMENTAL

Microanalyses were by Butterworth Microanalytical Consultancy Ltd., Middlesex. Molecular weights were measured cryoscopically in benzene under nitrogen. Spectroscopic instruments (Perkin-Elmer): i.r., model 577; ¹H n.m.r., R 12B.

TABLE 3

Interatomic distance (Å) and angles (°) for
[Ni(CH₂SiMe₃)Cl(PMe₃)₂], (1)

Ni(1)—Cl(1)	2.264(3)	Ni(2)—Cl(2)	2.249(3)
Ni(1)—P(1)	2.213(3)	Ni(2)—P(3)	2.212(3)
Ni(1)—P(2)	2.201(3)	Ni(2)—P(4)	2.198(3)
Ni(1)—C(1)	1.96(1)	Ni(2)—C(11)	1.94(1)
P(1)—C(5)	1.78(1)	P(3)—C(15)	1.83(1)
P(1)—C(6)	1.85(1)	P(3)—C(16)	1.82(1)
P(1)—C(7)	1.84(1)	P(3)—C(17)	1.83(1)
P(2)—C(8)	1.84(1)	P(4)—C(18)	1.81(2)
P(2)—C(9)	1.81(1)	P(4)—C(19)	1.82(2)
P(2)—C(10)	1.81(1)	P(4)—C(20)	1.82(2)
Si(1)—C(1)	1.85(1)	Si(2)—C(11)	1.85(1)
Si(1)—C(2)	1.88(1)	Si(2)—C(12)	1.86(1)
Si(1)—C(3)	1.84(2)	Si(2)—C(13)	1.88(1)
Si(1)—C(4)	1.88(1)	Si(2)—C(14)	1.87(1)
Cl(1)—Ni(1)—P(1)	87.9(1)	Cl(2)—Ni(2)—P(3)	87.8(1)
Cl(1)—Ni(1)—P(2)	87.6(1)	Cl(2)—Ni(2)—P(4)	87.3(1)
Cl(1)—Ni(1)—C(1)	173.5(4)	Cl(2)—Ni(2)—C(11)	172.4(3)
P(1)—Ni(1)—P(2)	166.0(1)	P(3)—Ni(2)—P(4)	162.0(1)
P(1)—Ni(1)—C(1)	91.9(4)	P(3)—Ni(2)—C(11)	93.1(3)
P(2)—Ni(1)—C(1)	94.1(4)	P(4)—Ni(2)—C(11)	94.1(3)
Ni(1)—P(1)—C(5)	122.4(5)	Ni(2)—P(3)—C(15)	107.2(4)
Ni(1)—P(1)—C(6)	108.1(4)	Ni(2)—P(3)—C(16)	122.1(4)
Ni(1)—P(1)—C(7)	116.9(4)	Ni(2)—P(3)—C(17)	117.6(4)
C(5)—P(1)—C(6)	101.2(6)	C(15)—P(3)—C(16)	102.3(6)
C(5)—P(1)—C(7)	102.4(7)	C(15)—P(3)—C(17)	104.1(5)
C(6)—P(1)—C(7)	103.2(6)	C(16)—P(3)—C(17)	101.2(6)
Ni(1)—P(2)—C(8)	115.0(4)	Ni(2)—P(4)—C(18)	102.7(7)
Ni(1)—P(2)—C(9)	112.0(4)	Ni(2)—P(4)—C(19)	107.9(5)
Ni(1)—P(2)—C(10)	122.1(5)	Ni(2)—P(4)—C(20)	124.9(5)
C(8)—P(2)—C(9)	101.4(6)	C(18)—P(4)—C(19)	102.7(7)
C(8)—P(2)—C(10)	102.0(6)	C(18)—P(4)—C(20)	102.0(8)
C(9)—P(2)—C(10)	101.6(6)	C(19)—P(4)—C(20)	98.5(7)
Ni(1)—C(1)—Si(1)	112.6(6)	Ni(2)—C(11)—Si(2)	111.5(6)
C(1)—Si(1)—C(2)	108.9(6)	C(11)—Si(2)—C(12)	109.9(6)
C(1)—Si(1)—C(3)	112.9(7)	C(11)—Si(2)—C(13)	111.4(5)
C(1)—Si(1)—C(4)	113.7(6)	C(11)—Si(2)—C(14)	114.2(5)
C(2)—Si(1)—C(3)	107.3(8)	C(12)—Si(2)—C(13)	108.2(7)
C(2)—Si(1)—C(4)	104.5(7)	C(12)—Si(2)—C(14)	105.6(7)
C(3)—Si(1)—C(4)	109.0(8)	C(13)—Si(2)—C(14)	107.2(7)

All preparations and other operations were carried out under oxygen-free nitrogen following conventional Schlenk techniques. Solvents were dried and degassed before use. The light petroleum used had b.p. 40–60 °C. The ligands PMe₃ and PMe₂Ph were prepared according to literature methods.⁹

[Ni(CH₂SiMe₃)Cl(PMe₃)₂], (1).—To a stirred suspension of [NiCl₂(PMe₃)₂] (0.30 g, ca. 1.0 mmol) in diethyl ether (25 cm³) at –60 °C was added Mg(CH₂SiMe₃)Cl (0.6 cm³ of a ca. 1.45 mol dm^{–3} diethyl ether solution). The resulting mixture

TABLE 4

Interatomic distances (Å) and angles (°) for
[Ni(COCH₂SiMe₃)Cl(PMe₃)₂], (21)

Ni(1)—Cl(1)	2.294(4)	Ni(2)—Cl(2)	2.307(3)
Ni(1)—P(1)	2.203(4)	Ni(2)—P(3)	2.199(4)
Ni(1)—P(2)	2.196(4)	Ni(2)—P(4)	2.206(4)
Ni(1)—C(1)	1.78(2)	Ni(2)—C(12)	1.89(1)
P(1)—C(6)	1.85(1)	P(3)—C(17)	1.77(1)
P(1)—C(7)	1.78(1)	P(3)—C(18)	1.82(1)
P(1)—C(8)	1.78(1)	P(3)—C(19)	1.78(1)
P(2)—C(9)	1.79(2)	P(4)—C(20)	1.77(2)
P(2)—C(10)	1.76(2)	P(4)—C(21)	1.81(1)
P(2)—C(11)	1.79(2)	P(4)—C(22)	1.81(1)
C(1)—O(1)	1.25(2)	C(12)—O(2)	1.20(1)
C(1)—C(2)	1.56(2)	C(12)—C(13)	1.50(2)
C(2)—Si(1)	1.73(1)	C(13)—C(14)	1.88(1)
Si(1)—C(3)	1.72(2)	Si(2)—C(14)	1.85(1)
Si(1)—C(4)	1.90(2)	Si(2)—C(15)	1.84(2)
Si(1)—C(5)	1.82(2)	Si(2)—C(16)	1.82(1)
Cl(1)—Ni(1)—P(1)	90.5(1)	Cl(2)—Ni(2)—P(3)	91.2(1)
Cl(1)—Ni(1)—P(2)	91.2(2)	Cl(2)—Ni(2)—P(4)	91.5(1)
Cl(1)—Ni(1)—C(1)	166.1(6)	Cl(2)—Ni(2)—C(12)	168.6(5)
P(1)—Ni(1)—P(2)	165.9(2)	P(3)—Ni(2)—P(4)	169.2(2)
P(1)—Ni(1)—C(1)	90.7(5)	P(3)—Ni(2)—C(12)	89.5(4)
P(2)—Ni(1)—C(1)	91.0(5)	P(4)—Ni(2)—C(12)	89.9(4)
Ni(1)—P(1)—C(6)	114.6(5)	Ni(2)—P(3)—C(17)	120.1(5)
Ni(1)—P(1)—C(7)	111.5(5)	Ni(2)—P(3)—C(18)	113.7(5)
Ni(1)—P(1)—C(8)	121.3(5)	Ni(2)—P(3)—C(19)	114.0(5)
C(6)—P(1)—C(7)	102.4(7)	C(17)—P(3)—C(18)	101.2(7)
C(6)—P(1)—C(8)	102.4(7)	C(17)—P(3)—C(19)	102.9(7)
C(7)—P(1)—C(8)	102.2(6)	C(18)—P(3)—C(19)	102.7(7)
Ni(1)—P(2)—C(9)	114.8(6)	Ni(2)—P(4)—C(20)	116.7(5)
Ni(1)—P(2)—C(10)	110.9(6)	Ni(2)—P(4)—C(21)	120.3(5)
Ni(1)—P(2)—C(11)	121.2(5)	Ni(2)—P(4)—C(22)	107.9(5)
C(9)—P(2)—C(10)	103.4(9)	C(20)—P(4)—C(21)	102.8(7)
C(9)—P(2)—C(11)	102.7(8)	C(20)—P(4)—C(22)	105.2(8)
C(10)—P(2)—C(11)	101.7(9)	C(21)—P(4)—C(22)	102.2(7)
Ni(1)—C(1)—O(1)	130(1)	Ni(2)—C(12)—O(2)	125(1)
Ni(1)—C(1)—C(2)	114(1)	Ni(2)—C(12)—C(13)	110(1)
O(1)—C(1)—C(2)	116(1)	O(2)—C(12)—C(13)	125(1)
C(1)—C(2)—Si(1)	126(1)	C(12)—C(13)—Si(2)	115.8(9)
C(2)—Si(1)—C(3)	119.1(9)	C(13)—Si(2)—C(14)	111.0(6)
C(2)—Si(1)—C(4)	107.0(9)	C(13)—Si(2)—C(15)	111.1(6)
C(2)—Si(1)—C(5)	116.0(7)	C(13)—Si(2)—C(16)	103.6(7)
C(3)—Si(1)—C(4)	96(1)	C(14)—Si(2)—C(15)	107.8(7)
C(3)—Si(1)—C(5)	111.4(8)	C(14)—Si(2)—C(16)	112.9(7)
C(4)—Si(1)—C(5)	103.4(9)	C(15)—Si(2)—C(16)	110.4(6)

was stirred at this temperature for 30 min, then at 0 °C for 2–3 h, and finally for 4 h at room temperature. The solvent was removed *in vacuo* and the product dissolved in light petroleum (30 cm³). The solution was centrifuged to separate some insoluble material and the product crystallized by removing part of the solvent and cooling at –30 °C.

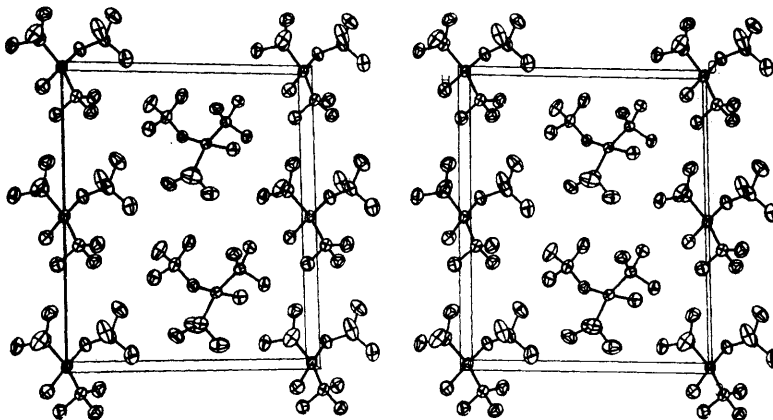


FIGURE 3 Stereoscopic view of the unit-cell packing for (1)

Recrystallization from light petroleum gave yellow-orange needles of the pure product in *ca.* 60% yield.

The complex $[\text{Ni}(\text{CH}_2\text{SiMe}_3\text{Cl}(\text{PMe}_2\text{Ph})_2)]$, (6), was prepared and purified similarly (orange crystals, yield 60%).

$[\text{Ni}(\text{CH}_2\text{CMe}_2\text{Ph})\text{Cl}(\text{PMe}_3)_2]$, (11).—A diethyl ether solution *ca.* 0.63 mol dm^{-3} in $\text{Mg}(\text{CH}_2\text{CMe}_2\text{Ph})\text{Cl}$ (6.6 cm^3) was syringed onto a diethyl ether suspension (40 cm^3) of $[\text{NiCl}_2(\text{PMe}_3)_2]$ (1.16 g , *ca.* 4.16 mmol) with stirring at -60°C . The mixture was warmed to 25°C and stirred at this temperature for 5–6 h. The volume was then reduced *in vacuo* to $10\text{--}15 \text{ cm}^3$. Addition of light petroleum (40 cm^3) and centrifugation afforded a solution which upon cooling at -30°C yielded the required product as well formed red-brown crystals in *ca.* 70% yield. This material is useful for synthetic purposes. Further purification was achieved by recrystallization from diethyl ether–light petroleum (1 : 3) at -30°C .

extracted with light petroleum (20 cm^3). Filtration and evaporation to *ca.* 4 cm^3 , followed by cooling at -80°C , afforded yellow-green crystals of the complex which was recrystallized from light petroleum at -80°C to give the pure product in *ca.* 70–80% yield.

$[\text{Ni}(\text{COCH}_2\text{SiMe}_3)\text{Cl}(\text{PMe}_3)_2]$, (21).—Carbon monoxide was bubbled (20°C , 1 atm) * through a solution of (1) (0.10 g , *ca.* 0.3 mmol) in benzene (5 cm^3) for *ca.* 5 min. The colour changed from yellow-orange to red. The solvent was removed *in vacuo* and the product crystallized from light petroleum at 5°C to afford red crystals in approximately quantitative yield.

Complexes (22)–(25) were obtained when the corresponding alkyls were treated with CO in benzene or diethyl ether or when (21) was stirred in thf or acetone with the corresponding KX as in the synthesis of (2): (22) and (23) as red-brown crystals; (24) and (25) as yellow crystals.

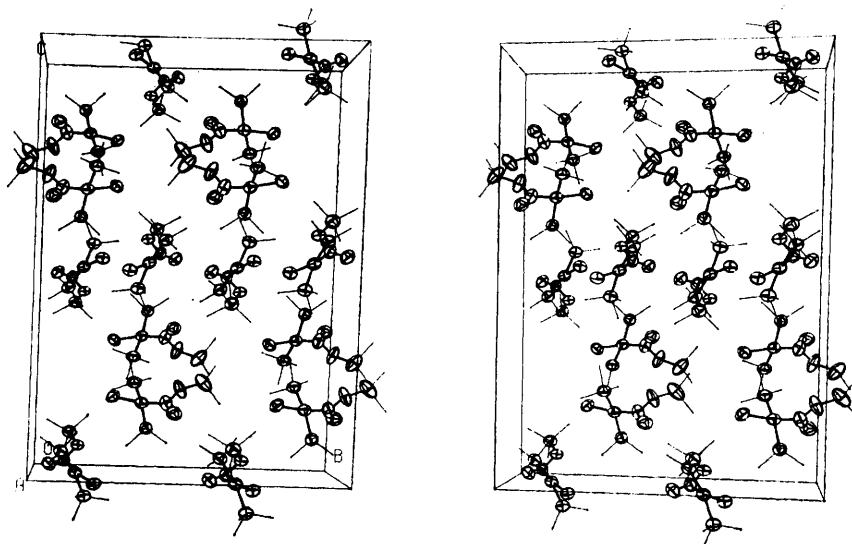


FIGURE 4 Unit-cell packing for (21)

The complex $[\text{Ni}(\text{CH}_2\text{CMe}_2\text{Ph})\text{Cl}(\text{PMe}_2\text{Ph})_2]$, (16), was prepared and purified similarly, as red-brown crystals in *ca.* 60% yield.

$[\text{Ni}(\text{CH}_2\text{SiMe}_3)\text{Br}(\text{PMe}_3)_2]$, (2).—Complex (1) (0.33 g , 1 mmol) and excess of KBr were stirred in tetrahydrofuran (thf) or acetone (30 cm^3) for 8–10 h at room temperature. The solvent was removed *in vacuo* and the product crystallized from light petroleum as well formed red crystals in almost quantitative yield. Similar reactions of (1) with the appropriate KX afforded the following complexes: (3) as dark red crystals; (4) as yellow-green crystals; (5) as yellow-orange crystals. From (6) were obtained: (7) as red-orange crystals; (8) as dark red crystals; (9) and (10) as brown crystals. From (11) were obtained: (12) as red crystals; (13) as dark red crystals; (14) as light brown crystals; (15) as red-brown crystals. From (16) were obtained: (17)–(19) as red-brown crystals.

$[\text{Ni}(\text{CH}_2\text{CMe}_2\text{Ph})(\eta\text{-C}_5\text{H}_5)(\text{PMe}_3)]$, (20).—A solution of the chloro-complex (11) (0.10 g , *ca.* 0.26 mmol) in acetone (30 cm^3) was stirred for 20 min with $\text{Tl}[\text{C}_5\text{H}_5]$ (0.08 g , *ca.* 0.3 mmol); during this time the colour changed from red to yellow. The solvent was removed *in vacuo* and the residue

* Throughout this paper: 1 atm = 101 325 Pa.

$[\text{Ni}(\text{COCH}_2\text{CMe}_2\text{Ph})\text{Cl}(\text{PMe}_3)_2]$, (26).—A solution of the chloro-complex (11) (0.38 g , *ca.* 1 mmol) in diethyl ether–light petroleum (1 : 1) (20 cm^3) was treated with CO (20°C , 1 atm) for 10–15 s after which time a yellow microcrystalline compound precipitated. The solid was filtered off and recrystallized from diethyl ether–acetone to afford yellow crystals in approximately quantitative yield. The following compounds were obtained similarly or by metathesis reactions of (26) in thf or acetone: (27) as yellow-orange crystals; (28) as red crystals; (29) as yellow-orange crystals.

$[\text{Ni}(\text{COCH}_2\text{CMe}_2\text{Ph})\text{Cl}(\text{PMe}_2\text{Ph})_2]$, (30).—Carbon monoxide was bubbled through a solution of (16) (0.20 g , *ca.* 0.38 mmol) in light petroleum (30 cm^3) for 5 min. The red precipitate which formed was shown by ^1H n.m.r. spectroscopy to contain a co-ordinated acyl group. Treatment with CO was continued for another 5 min. The solvent was removed *in vacuo* and the complex crystallized from diethyl ether–light petroleum as red crystals. Recrystallization of this material must be carried out quickly to avoid decomposition.

$[\text{Ni}(\text{COCH}_2\text{CMe}_2\text{Ph})(\eta\text{-C}_5\text{H}_5)(\text{PMe}_3)]$, (31).—A procedure similar to that followed for the synthesis of (20) affords red

TABLE 5
Final fractional co-ordinates for
[Ni(CH₂SiMe₃)Cl(PMe₃)₂], (1)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Ni(1)	0.00 0	0.592 7(2)	0.000 0
Ni(2)	0.406 4(1)	-0.096 5(2)	0.250 43(8)
Cl(1)	0.075 7(2)	0.371 8(6)	0.072 9(2)
Cl(2)	0.301 4(2)	-0.330 2(5)	0.271 2(2)
P(1)	0.083 8(2)	0.492 6(5)	-0.087 0(2)
P(2)	-0.054 2(2)	0.730 7(5)	0.096 2(2)
P(3)	0.315 9(2)	0.051 7(5)	0.171 6(2)
P(4)	0.468 8(3)	-0.196 3(6)	0.351 8(2)
Si(1)	0.827 7(2)	0.612 2(6)	-0.096 7(2)
Si(2)	0.571 0(2)	-0.054 4(5)	0.158 7(2)
C(1)	-0.074 0(7)	0.756(2)	-0.065 6(8)
C(2)	-0.215(1)	0.731(2)	-0.182 4(8)
C(3)	-0.260(2)	0.624(3)	-0.033 0(9)
C(4)	-0.151 0(9)	0.332(2)	-0.120(1)
C(5)	0.065 1(9)	0.574(2)	-0.177 1(7)
C(6)	-0.194 0(7)	0.596(2)	-0.068 0(7)
C(7)	0.102(1)	0.211(2)	-0.096 6(8)
C(8)	-0.113 3(8)	0.547(2)	0.152 4(7)
C(9)	0.029 6(8)	0.823(2)	0.158 1(7)
C(10)	-0.127 2(8)	0.952(2)	0.091 9(7)
C(11)	0.503 0(6)	0.077(2)	0.224 1(5)
C(12)	0.634 3(9)	0.143(2)	0.109 5(8)
C(13)	0.649 6(9)	-0.241(3)	-0.203 5(7)
C(14)	0.508 2(8)	-0.205(2)	0.088 7(7)
C(15)	0.223 4(7)	0.149(2)	0.220 4(6)
C(16)	0.346 3(8)	0.279(2)	0.120 0(6)
C(17)	0.266 8(8)	-0.114(2)	0.102 2(6)
C(18)	0.484(1)	-0.474(2)	0.365 8(8)
C(19)	0.398(1)	-0.124(2)	0.423 0(8)
C(20)	0.570(1)	-0.091(3)	0.389 6(7)
H(1)[C(1)]	-0.035	0.499	-0.105
H(2)[C(1)]	-0.049	0.849	-0.056
H(3)[C(2)]	-0.272	0.653	-0.205
H(4)[C(2)]	-0.165	0.737	-0.221
H(5)[C(2)]	-0.233	0.891	-0.169
H(6)[C(3)]	0.243	0.569	0.020
H(7)[C(3)]	-0.324	0.565	-0.049
H(8)[C(3)]	-0.265	0.796	-0.031
H(9)[C(4)]	-0.104	0.321	-0.162
H(10)[C(4)]	-0.213	0.278	-0.142
H(11)[C(4)]	0.130	0.234	-0.076
H(12)[C(5)]	0.049	0.735	-0.185
H(13)[C(5)]	0.006	0.480	-0.184
H(14)[C(5)]	0.110	0.525	-0.218
H(15)[C(6)]	0.220	0.520	-0.020
H(16)[C(6)]	0.191	0.761	-0.059
H(17)[C(6)]	0.234	0.561	-0.111
H(18)[C(7)]	0.124	0.115	-0.053
H(19)[C(7)]	0.155	0.229	-0.133
H(20)[C(7)]	0.048	0.137	-0.125
H(21)[C(8)]	-0.170	0.474	0.127
H(22)[C(8)]	-0.135	0.653	0.193
H(23)[C(8)]	-0.071	0.433	0.175
H(24)[C(9)]	0.065	0.948	0.135
H(25)[C(9)]	0.072	0.691	0.168
H(26)[C(9)]	0.003	0.874	0.208
H(27)[C(10)]	-0.190	0.907	0.069
H(28)[C(10)]	-0.105	1.091	0.064
H(29)[C(10)]	-0.134	0.991	0.147
H(30)[C(11)]	0.542	0.107	0.270
H(31)[C(11)]	0.477	0.233	0.199
H(32)[C(12)]	0.682	0.241	0.139
H(33)[C(12)]	0.588	0.250	0.083
H(34)[C(12)]	0.667	0.056	0.070
H(35)[C(13)]	0.696	-0.202	0.246
H(36)[C(13)]	0.684	-0.308	0.160
H(37)[C(13)]	0.604	-0.355	0.223
H(38)[C(14)]	0.472	-0.345	0.104
H(39)[C(14)]	0.563	-0.252	0.059
H(40)[C(14)]	0.465	-0.110	0.056
H(41)[C(15)]	0.188	0.013	0.237
H(42)[C(15)]	0.184	0.230	0.179
H(43)[C(15)]	0.236	0.252	0.264
H(44)[C(16)]	0.362	0.407	0.155
H(45)[C(16)]	0.290	0.319	0.086

TABLE 5 (Continued)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
H(46)[C(16)]	0.400	0.244	0.087
H(47)[C(17)]	0.248	-0.262	0.125
H(48)[C(17)]	0.310	-0.143	0.059
H(49)[C(17)]	0.209	-0.035	0.082
H(50)[C(18)]	0.435	-0.579	0.344
H(51)[C(18)]	0.492	-0.502	0.422
H(52)[C(18)]	0.544	-0.501	0.341
H(53)[C(19)]	0.338	-0.212	0.422
H(54)[C(19)]	0.381	0.041	0.434
H(55)[C(19)]	0.441	-0.178	0.465
H(56)[C(20)]	0.615	-0.174	0.356
H(57)[C(20)]	0.590	-0.113	0.445
H(58)[C(20)]	0.569	0.071	0.376

crystals of this complex after crystallization from light petroleum at 5 °C. This product was not detected after prolonged treatment of (20) with CO.

Carbon Monoxide Exchange Reactions.—To a solution of [Ni(COCH₂SiMe₃)Cl(PMe₃)₂], (21) (62 mg, *ca.* 0.17 mmol), in light petroleum-diethyl ether (1 : 1) (6 cm³) was added [Ni(CH₂CMe₂Ph)Br(PMe₃)₂], (12) (61 mg, *ca.* 0.14 mmol), in 6 cm³ of the same solvent mixture. The solution was stirred at room temperature for a few minutes when a yellow solid precipitated. The solid was filtered off, washed with light petroleum (2 cm³), and dried *in vacuo*. It was shown (i.r. and ¹H n.m.r.) to be identical to a pure sample of [Ni(COCH₂CMe₂Ph)Br(PMe₃)₂], (27). The filtrate and washing liquids were taken to dryness, and the residue dissolved in C₆H₆. The ¹H n.m.r. spectrum was identical to that of [Ni(CH₂SiMe₃)Cl(PMe₃)₂], (1). Weak resonances due to the slight excess of (21) were also observed.

Complexes (11) and (21), and (13) and (21), were dissolved, in an equimolar ratio, in C₆H₆ (0.5 cm³). The course of the reaction was followed by ¹H n.m.r. spectroscopy, the equilibrium being attained after standing for several hours at 35 °C. In both cases the equilibrium favours the formation of the neophyl-acyl derivatives. Similar studies were carried out with other couples of complexes. However, the reaction of [Ni(COCH₂CMe₂Ph)(η -C₅H₅)(PMe₃)], (31), and [Ni(CH₂CMe₂Ph)Cl(PMe₃)₂], (11), did not give [Ni(COCH₂CMe₂Ph)Cl(PMe₃)₂], (26), even when the conditions were such as to insolubilize the latter complex, if formed.

X-Ray Data Collection, Structure Determination and Refinement for [Ni(CH₂SiMe₃)Cl(PMe₃)₂], (1).—*Crystal data.* C₁₀H₂₉ClNiP₂Si, *M* = 333.5, Monoclinic, *a* = 15.419(3), *b* = 6.406(2), *c* = 18.711(3) Å, β = 92.02(3)°, *U* = 1 847.0 Å³, *Z* = 4, *F*(000) = 712, *D*_c = 1.20 g cm⁻³, λ = 0.710 69 Å, μ (Mo-K α) = 14.0 cm⁻¹, space group *Pc*. The lattice parameters were determined from a least-squares refinement of the angular settings of 15 reflections (2 θ > 32°) accurately centred on an Enraf-Nonius CAD-4 diffractometer.

A crystal of dimensions 0.15 × 0.22 × 0.10 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 -2 θ scan technique in a manner similar to that previously described.¹⁰ All reflections in one independent quadrant of data were measured out to 2 θ ≤ 50°; 1 906 were considered observed [*I* ≥ 3 σ (*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.¹¹ No corrections were made for extinction. Atomic scattering factors for Ni,

TABLE 6

Final fractional co-ordinates for
[Ni(COCH₂SiMe₃)Cl(PMe₃)₂], (21)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Ni(1)	0.929 5(2)	0.651 3(1)	0.672 27(7)
Ni(2)	0.964 5(2)	0.856 2(1)	0.503 11(8)
Cl(1)	1.018 9(4)	0.743 6(2)	0.683 8(2)
Cl(2)	0.823 8(3)	0.793 3(2)	0.482 8(2)
P(1)	1.023 3(4)	0.632 5(3)	0.609 7(2)
P(2)	0.807 8(5)	0.678 9(3)	0.722 3(2)
P(3)	0.869 0(4)	0.904 2(3)	0.555 9(2)
P(4)	1.056 0(4)	0.824 5(3)	0.442 6(2)
Si(1)	0.907 5(5)	0.454 8(4)	0.723 8(3)
Si(2)	1.261 0(5)	0.883 4(3)	0.590 1(2)
O(1)	0.808(1)	0.547 9(7)	0.651 8(5)
O(2)	1.120(1)	0.944 6(7)	0.516 1(4)
C(1)	0.884(2)	0.573(1)	0.672 8(8)
C(2)	0.946(2)	0.529(1)	0.706 0(8)
C(3)	0.983(2)	0.416(2)	0.764(2)
C(4)	0.934(3)	0.399(1)	0.674(2)
C(5)	0.767(2)	0.444(1)	0.734 9(7)
C(6)	1.168(2)	0.632(1)	0.618 8(7)
C(7)	1.007(2)	0.692 8(9)	0.567 7(7)
C(8)	1.003(2)	0.563 2(9)	0.576 1(7)
C(9)	0.856(2)	0.698(1)	0.778 7(7)
C(10)	0.744(2)	0.749(1)	0.704 8(8)
C(11)	0.698(2)	0.629(1)	0.734 6(8)
C(12)	1.087(2)	0.894(1)	0.527 5(7)
C(13)	1.138(1)	0.852 3(9)	0.562 4(6)
C(14)	1.365(1)	0.898 0(9)	0.546 5(7)
C(15)	1.235(2)	0.958(1)	0.620 3(7)
C(16)	1.297(2)	0.823(1)	0.631 2(7)
C(17)	0.921(2)	0.970(1)	0.585 4(7)
C(18)	0.745(2)	0.935(1)	0.533 8(6)
C(19)	0.827(2)	0.854(1)	0.601 9(6)
C(20)	1.066(2)	0.743(1)	0.434 4(7)
C(21)	1.191(2)	0.851(1)	0.434 1(6)
C(22)	0.991(2)	0.854(1)	0.391 1(6)
H(1)[C(2)]	0.964	0.554	0.736
H(2)[C(2)]	1.024	0.523	0.693
H(3)[C(3)]	0.984	0.461	0.794
H(4)[C(3)]	1.058	0.408	0.760
H(5)[C(3)]	0.933	0.386	0.781
H(6)[C(4)]	0.855	0.413	0.653
H(7)[C(4)]	0.949	0.354	0.663
H(8)[C(4)]	0.990	0.432	0.657
H(9)[C(5)]	0.712	0.457	0.708
H(10)[C(5)]	0.759	0.488	0.761
H(11)[C(5)]	0.749	0.406	0.753
H(12)[C(6)]	1.199	0.628	0.584
H(13)[C(6)]	1.158	0.673	0.630
H(14)[C(6)]	1.178	0.589	0.640
H(15)[C(7)]	0.991	0.733	0.583
H(16)[C(7)]	1.060	0.700	0.547
H(17)[C(7)]	0.942	0.683	0.548
H(18)[C(8)]	0.923	0.557	0.561
H(19)[C(8)]	1.038	0.568	0.551
H(20)[C(8)]	1.010	0.524	0.597
H(21)[C(9)]	0.858	0.652	0.785
H(22)[C(9)]	0.814	0.726	0.799
H(23)[C(9)]	0.932	0.719	0.780
H(24)[C(10)]	0.736	0.779	0.677
H(25)[C(10)]	0.762	0.780	0.729
H(26)[C(10)]	0.667	0.739	0.709
H(27)[C(11)]	0.634	0.642	0.742
H(28)[C(11)]	0.683	0.597	0.708
H(29)[C(11)]	0.710	0.599	0.762
H(30)[C(13)]	1.086	0.836	0.590
H(31)[C(13)]	1.157	0.814	0.543
H(32)[C(14)]	1.376	0.857	0.536
H(33)[C(14)]	1.342	0.934	0.520
H(34)[C(14)]	1.434	0.920	0.556
H(35)[C(15)]	1.310	0.970	0.637
H(36)[C(15)]	1.180	0.951	0.640
H(37)[C(15)]	1.217	0.993	0.588
H(38)[C(16)]	1.252	0.803	0.659
H(39)[C(16)]	1.333	0.781	0.609
H(40)[C(16)]	1.342	0.841	0.654
H(41)[C(17)]	0.959	0.970	0.604

TABLE 6 (Continued)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
H(42)[C(17)]	0.961	1.018	0.575
H(43)[C(17)]	0.838	0.975	0.582
H(44)[C(18)]	0.679	0.947	0.555
H(45)[C(18)]	0.732	0.904	0.522
H(46)[C(18)]	0.763	0.973	0.502
H(47)[C(19)]	0.867	0.846	0.619
H(48)[C(19)]	0.762	0.868	0.623
H(49)[C(19)]	0.800	0.814	0.580
H(50)[C(20)]	1.113	0.732	0.402
H(51)[C(20)]	1.018	0.724	0.443
H(52)[C(20)]	1.116	0.715	0.460
H(53)[C(21)]	1.181	0.897	0.434
H(54)[C(21)]	1.235	0.827	0.458
H(55)[C(21)]	1.227	0.834	0.409
H(56)[C(22)]	1.013	0.842	0.369
H(57)[C(22)]	0.992	0.902	0.391
H(58)[C(22)]	0.911	0.844	0.392

Cl, P, Si, and C were taken from Cromer and Waber,¹² and the scattering for Ni corrected for the real and imaginary components of anomalous dispersion using the values of Cromer and Liberman.¹³ Scattering factors for hydrogen were from ref. 14.

The positions of the Ni atoms were 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 $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o| = 0.074$. Conversion into anisotropic thermal parameters and further refinement gave $R = 0.044$. 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 $R = 0.031$ and $R' = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w(F_o)^2]^{1/2} = 0.031$. The largest parameter shifts in the final cycle of refinements were less than one hundredth of their estimated standard deviations. A final difference Fourier showed no feature greater than $0.3 \text{ e } \text{Å}^{-3}$. The standard deviation of an observation of unit weight was 1.25. Unit weights were used at all stages; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta) / \lambda$ was noted. The final values of the positional parameters are given in Table 5. The observed and calculated structure-factor amplitudes and thermal parameters are given in Supplementary Publication No. SUP 22811 (24 pp.).*

X-Ray Data Collection, Structure Determination, and Refinement for [Ni(COCH₂SiMe₃)Cl(PMe₃)₂], (21).—Crystal data. C₁₁H₂₉ClNiOP₂Si, $M = 361.5$, Orthorhombic, $a = 12.668(3)$, $b = 21.312(4)$, $c = 28.925(4) \text{ Å}$, $U = 7809.2 \text{ Å}^3$, $Z = 16$, $F(000) = 3072$, $D_c = 1.23 \text{ g cm}^{-3}$, $\lambda = 0.71069 \text{ Å}$, $\mu(\text{Mo-K}\alpha) = 13.4 \text{ cm}^{-1}$, space group *Pbca*. The lattice parameters were determined as above based on 15 reflections with $2\theta > 28^\circ$.

A crystal of dimensions $1.20 \times 0.52 \times 0.24 \text{ mm}$ was sealed in a thin-walled capillary under a nitrogen atmosphere. The data collection procedure was the same as given above. All reflections in one independent quadrant out to $2\theta \leq 36^\circ$ were measured: 1394 were considered observed [$I \geq 3\sigma(I)$]. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

The structure was solved by the methods described above. Refinement with isotropic temperature factors gave $R = 0.096$. The employment of anisotropic thermal parameters led to $R = 0.070$, and addition of the hydrogen atoms followed by further refinement gave final values of $R =$

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

0.049 and $R' = 0.049$. The standard deviation of an observation of unit weight was 1.59. A final difference Fourier showed no feature greater than $0.3 \text{ e } \text{Å}^{-3}$. Unit weights were used, and no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was observed. The final values of the positional parameters are given in Table 6. The observed and calculated structure-factor amplitudes and thermal parameters are given in SUP 22811.

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