Alkyl and Acyl Derivatives of Nickel(II) containing Tertiary Phosphine Ligands

By **Ernesto Carmona,* Francisco González,*** and **Manuel L. Poveda,** Departamento de Quimica Inorgánica, Facultad de Quimica, Universidad de Sevilla, Sevilla, Spain
Jerry L. Atwood* and **Robin D. Rogers,** Department of Chemistry, University of Alabama, Alabama 35486, U.S.A.

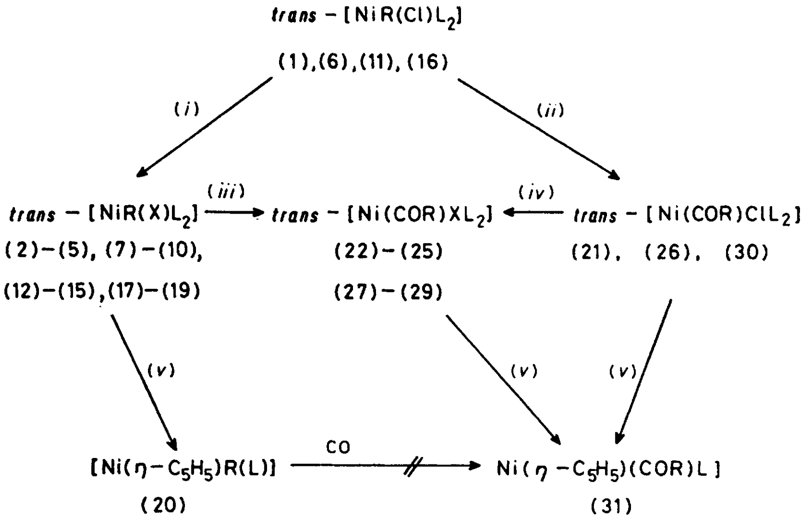
The interaction of complexes [$NiCl_2L_2$] (L = PMe_3 or PMe_2Ph) with Grignard reagents derived from Me_2PhCCH_2Cl and Me_3SiCH_2Cl yields thermally stable monoalkyl derivatives of the type [NiR(Cl)L_2], which, when L = PMe_3, afford upon carbonylation at room temperature and pressure the corresponding acyls [Ni(COR)Cl(PMe_3)$_2$]. Metathesis reactions with KX give [NiR(X)(PMe_3)$_2$] and [Ni(COR)X(PMe_3)$_2$] (X = Br, I, NCS, or NCO), while with Tl[C_5H_5], [Ni(CH_2CMe_2Ph)(η-C_5H_5)(PMe_3)] and [Ni($COCH_2CMe_2Ph$)(η-C_5H_5)(PMe_3)] can be isolated. The synthesis of [Ni($COCH_2CMe_2Ph$)Cl(PMe_2Ph)$_2$] is also reported. The acyls, [Ni(COR)X(PMe_3)$_2$], readily carbonylate solutions of the alkyl complexes, [NiR′(X)(PMe_3)$_2$], providing under certain conditions [NiR(X)(PMe_3)$_2$] and [Ni(COR′)X(PMe_3)$_2$] in almost quantitative yields. Structures for the new compounds are proposed on the basis of i.r. and ^1H n.m.r. spectroscopic studies. Those of [Ni(CH_2SiMe_3)Cl(PMe_3)$_2$] and [Ni($COCH_2SiMe_3$)Cl(PMe_3)$_2$] have been confirmed by single-crystal *X*-ray determinations. Thus [Ni(CH_2SiMe_3)Cl(PMe_3)$_2$] crystallizes in the monoclinic space group *Pc* with *a* = 15.419(3), *b* = 6.406(2), *c* = 18.711(3) Å, β = 92.02(3)°, *Z* = 4, and *R* 0.031 based on 1 906 independent observed reflections. The phosphine ligands are *trans* [P–Ni–P 164(2)°] in a square-planar arrangement. The complex [Ni($COCH_2SiMe_3$)Cl(PMe_3)$_2$] belongs to the orthorhombic space group *Pbca* with *a* = 12.668(3), *b* = 21.312(4), *c* = 28.925(4) Å, *Z* = 16, and *R* 0.049 for 1 394 independent observed reflections. The oxygen atom is not co-ordinated to the nickel atom [Ni···O 3.121(4) Å].

ORGANOMETALLIC compounds of nickel(II) containing σ metal-to-carbon bonds and tertiary phosphine ligands have been known for many years, but interest in these complexes has recently increased because of their value as promoters in organic synthesis.[1] The corresponding acyl derivatives are rare, the only known examples being square-planar complexes [2] of the type [Ni($COCH_3$)X(PMe_3)$_2$], some triethylphosphine derivatives,[3] and the recently reported five-co-ordinated cationic species [4] [Ni(COR)L]$^+$ [R = CH_3, C_2H_5, or $CH_2C_6H_5$; L = tris(tertiary phosphines and arsines)].

In this paper we report the synthesis and characterization of alkyl and acyl derivatives of nickel(II) of composition NiR(Cl)L_2 and Ni(COR)ClL$_2$ (R = CH_2CMe_2Ph or CH_2SiMe_3; L = PMe_3 or PMe_2Ph), and of some cyclopentadienyl and other substitution products. The reactions leading to these complexes are summarized in Scheme 1. Analytical and spectroscopic data for new compounds are given in Tables 1 and 2.

RESULTS AND DISCUSSION

Alkyl Complexes.—The dichlorides [$NiCl_2L_2$] (L = PMe_3 or PMe_2Ph) react with 1 mol equivalent of Mg(CH_2CMe_2Ph)Cl or Mg(CH_2SiMe_3)Cl in diethyl ether at low temperature to give the yellow-orange to dark red complexes [NiR(Cl)L_2] in *ca.* 60% yield. Addition of an



SCHEME 1 R = CH_2CMe_2Ph or CH_2SiMe_3; L = PMe_3 or PMe_2Ph, unless otherwise stated. (*i*) KX or NaX (X = Br, I, NCS, or NCO) in thf or Me_2CO, 25 °C, 8 h; (*ii*) L = PMe_3, R = CH_2SiMe_3 or CH_2CMe_2Ph; L = PMe_2Ph, R = CH_2CMe_2Ph; CO in light petroleum–diethyl ether, 5 min; (*iii*) L = PMe_3, conditions as in (*ii*); (*iv*) L = PMe_3, conditions as in (*i*); (*v*) L = PMe_3, R = CH_2CMe_2Ph; Tl[C_5H_5] in thf or Me_2CO, room temperature, 2 h

TABLE 1

Analytical and spectroscopic data for the monoalkyl complexes $[NiR(X)L_2]$

	Compound				Analysis (%) [a]					^1H N.m.r. [d]		
	R	L	X	Colour	C	H	Others	M [b]	Selected i.r. data [c]	Me–P	Me–C or Me–Si	CH_2
(1)	CH_2SiMe_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)		ν(NCS) 2 065vs	8.91 (br s)	9.65 (s)	10.63 (br s)
(5)			NCO	Yellow-orange					ν(NCO) 2 200vs	8.76 (br s)	9.56 (s)	10.47 (br t) [e]
(6)		PMe_2Ph	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)	ν(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)	ν(NCO) 2 200vs	8.47 (br s)	9.53 (s)	10.49 (br s)
(11)	CH_2CMe_2Ph	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)	[h]
(14)			NCS	Light brown	50.7 (50.8)	7.7 (7.9)	N 3.3 (3.5)	387 (402)	ν(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)		ν(NCO) 2 200vs	8.94 (br s)	8.28 (s)	9.21 (br s)
(16)		PMe_2Ph	Cl	Red-brown	61.6 (62.0)	7.4 (7.0)				8.50 (br s)	8.32 (s)	[h]
(17)			Br	Red-brown	57.0 (57.0)	6.6 (6.4)				8.56 (br s)	8.36 (s)	[h]
(18)			NCS	Red-brown	61.9 (61.6)	6.8 (6.7)	N 2.5 (2.7)		ν(NCS) 2 070vs	8.72 (br s)	8.49 (s)	9.26 (br s)
(19)			NCO	Red-brown				486 (510)	ν(NCO) 2 200vs	8.86 (br s)	8.59 (s)	[h]
(20)	$[Ni(CH_2CMe_2Ph)(\eta\text{-}C_5H_5)(PMe_3)]$			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 $C_6D_5CD_3$) 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–CH_3 signal. [i] J(P–H) *ca.* 10 Hz, 4.84 (s) (η-C_5H_5).

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 1 in almost quantitative yields. Treatment of the neophyl (ββ-dimethylphenethyl) complex (11) with $Tl[C_5H_5]$ in thf affords the yellow-green cyclopentadienyl derivative (20).

Variable-temperature ^1H n.m.r. studies for $[NiR(X)L_2]$ 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 $[Ni(COR)XL_2]$

	Compound				Analysis (%) [a]					^1H N.m.r. [d]		
	R	L	X	Colour	C	H	Others	M [b]	Selected i.r. data [c]	Me–P	Me–C or Me–Si	CH_2
(21)	CH_2SiMe_3	PMe_3	Cl	Red	36.4 (36.5)	7.8 (8.0)	P 16.7 (17.1)	362 (361)	ν(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)	ν(CO) 1 640vs	8.69 (br s)	9.78 (s)	7.13 (s)
(23)			I	Red-brown				423 (453)	ν(CO) 1 645vs	8.61 (br s)	9.95 (s)	7.08 (s)
(24)			NCS	Yellow					ν(CO) 1 620vs ν(NCS) 2 070vs	8.91 (br s)	9.79 (s)	7.43 (s)
(25)			NCO	Yellow					ν(CO) 1 620vs ν(NCO) 2 200vs	8.73 (br s)	9.69 (s)	7.41 (s)
(26)	CH_2CMe_2Ph	PMe_3	Cl	Yellow	50.1 (50.1)	7.4 (7.6)		423 (407)	ν(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)	ν(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)	ν(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)	ν(CO) 1 635vs ν(NCO) 2 190vs	8.88 (br s) [f]	8.61 (s)	6.78 (s)
(30)		PMe_2Ph	Cl	Red	60.3 (61.0)	6.4 (6.6)			ν(CO) 1 690vs	8.59 (br s)	8.81 (s)	6.62 (s)
(31)	$[Ni(COCH_2CMe_2Ph)(\eta\text{-}C_5H_5)(PMe_3)]$			Red	63.0 (63.2)	7.4 (7.5)	P 8.7 (8.6)	352 (361)	ν(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 C_6H_6. Data at low and high temperatures (in $C_6D_5CD_3$ or CD_3COCD_3) are not shown. [e] KBr disc. [f] In CH_2Cl_2. [g] J(P–H) *ca.* 10 Hz, 4.69 (s) (η–C_5H_5).

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.

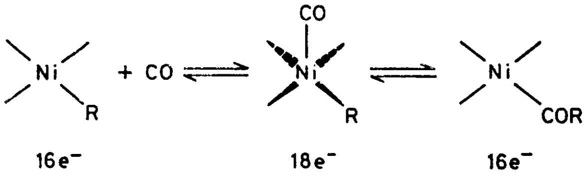
The i.r. spectra of $[NiR(X)L_2]$ compounds show absorptions characteristic of the alkyl and phosphine ligands. For the thiocyanate derivatives there is in addition a sharp band at *ca.* 2 070 cm^{-1} which can be assigned to ν(C–N). The position of this band suggests co-ordination through nitrogen [5] 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 ν(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 dimethylphenylphosphine 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 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 complexes show a very strong i.r. absorption at 1 630—1 690 cm^{-1} due to ν(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.



SCHEME 2

Thus, to account for the formation of the 18-electron complex $[Ni(COCH_3)L][BPh_4]$ [L = tris(2-diphenylphosphinoethyl)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 $[Ni(CH_2CMe_2Ph)(\eta\text{-}C_5H_5)(PMe_3)]$, (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 $[Ni(COCH_2SiMe_3)Cl(PMe_3)_2]$, (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 $[Ni(COCH_3)Cl(PMe_3)_2]$ [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 co-ordinated to the nickel atom [Ni $\cdots$ O 3.121(4) Å]. Therefore, the Ni–C(sp^2) distance, although shorter than the Ni–C(sp^3), does not show the marked contraction associated with the η^2-acyl mode of co-ordination.[8]

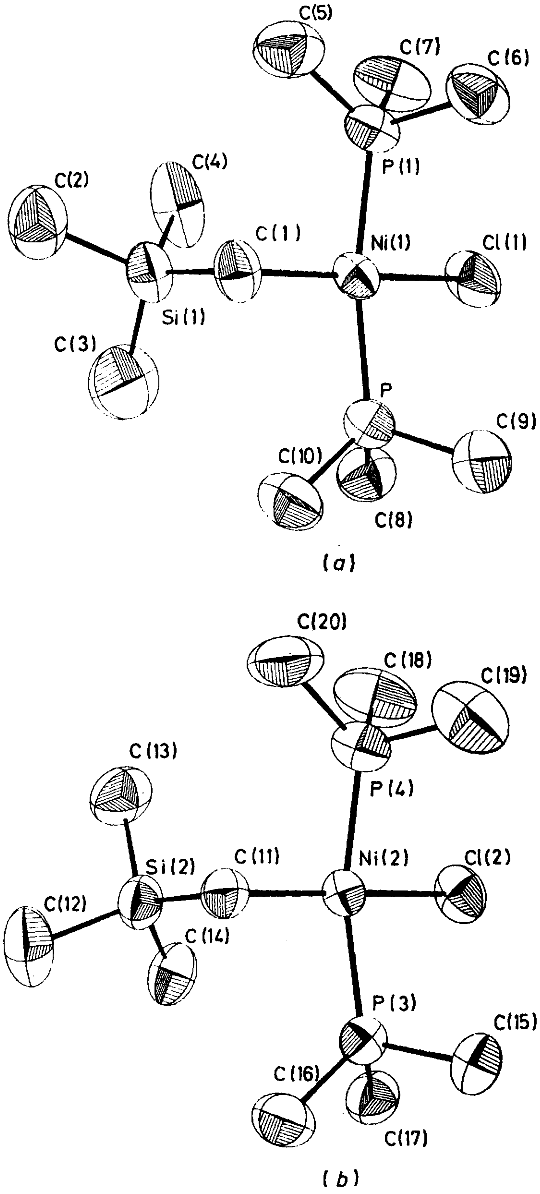


FIGURE 1 Molecular structure and atom-numbering scheme for $[Ni(CH_2SiMe_3)Cl(PMe_3)_2]$, (1). The two crystallographically independent molecules are designated *a* and *b*

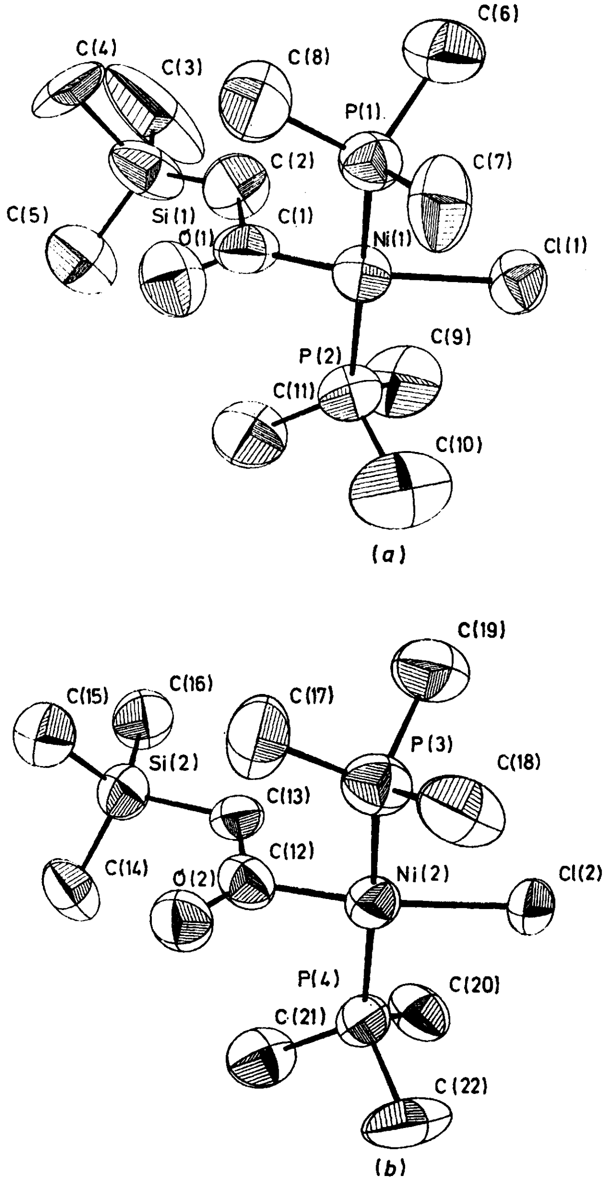


FIGURE 2 Molecular structure for $[Ni(COCH_2SiMe_3)Cl(PMe_3)_2]$, (21)

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

TABLE 3

Interatomic distance (Å) and angles (°) for $[\mathrm{Ni(CH_2SiMe_3)Cl(PMe_3)_2}]$, (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)	117.4(5)
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)

TABLE 4

Interatomic distances (Å) and angles (°) for $[\mathrm{Ni(COCH_2SiMe_3)Cl(PMe_3)_2}]$, (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)–Ci(2)	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)

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 $\mathrm{PMe_3}$ and $\mathrm{PMe_2Ph}$ were prepared according to literature methods.[9]

$[\mathrm{Ni(CH_2SiMe_3)Cl(PMe_3)_2}]$, (1).—To a stirred suspension of $[\mathrm{NiCl_2(PMe_3)_2}]$ (0.30 g, *ca.* 1.0 mmol) in diethyl ether (25 cm^3) at −60 °C was added $\mathrm{Mg(CH_2SiMe_3)Cl}$ (0.6 cm^3 of a *ca.* 1.45 mol dm^{-3} diethyl ether solution). The resulting mixture 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 cm^3). The solution was centrifuged to separate some insoluble material and the product crystallized by removing part of the solvent and cooling at −30 °C.

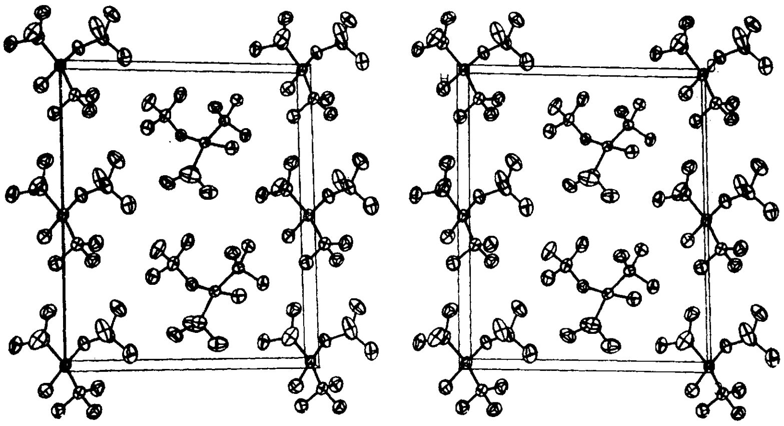


FIGURE 3 Stereoscopic view of the unit-cell packing for (1)

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

The complex [Ni(CH_2SiMe_3)Cl(PMe_2Ph)$_2$], (6), was prepared and purified similarly (orange crystals, yield 60%).

[Ni(CH_2CMe_2Ph)Cl(PMe_3)$_2$], (11).—A diethyl ether solution *ca.* 0.63 mol dm^{-3} in Mg(CH_2CMe_2Ph)Cl (6.6 cm^3) was syringed onto a diethyl ether suspension (40 cm^3) of [$NiCl_2$(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—15 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.

[Ni($COCH_2SiMe_3$)Cl(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.

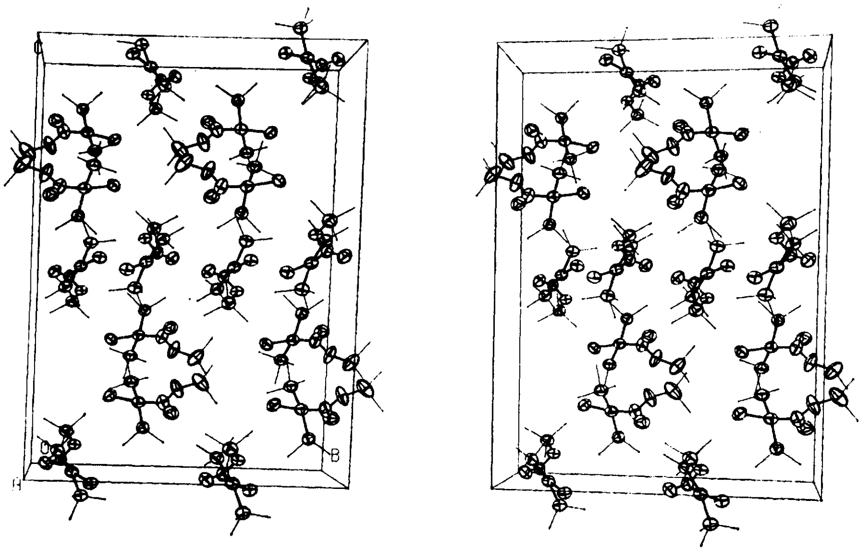


FIGURE 4 Unit-cell packing for (21)

The complex [Ni(CH_2CMe_2Ph)Cl(PMe_2Ph)$_2$], (16), was prepared and purified similarly, as red-brown crystals in *ca.* 60% yield.

[Ni(CH_2SiMe_3)Br(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.

[Ni(CH_2CMe_2Ph)(η-C_5H_5)(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 Tl[C_5H_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

[Ni($COCH_2CMe_2Ph$)Cl(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.

[Ni($COCH_2CMe_2Ph$)Cl(PMe_2Ph)$_2$], (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 ^{1}H 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.

[Ni($COCH_2CMe_2Ph$)(η-C_5H_5)(PMe_3)], (31).—A procedure similar to that followed for the synthesis of (20) affords red

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

TABLE 5

Final fractional co-ordinates for $[Ni(CH_2SiMe_3)Cl(PMe_3)_2]$, (1)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
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
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 $[Ni(COCH_2SiMe_3)Cl(PMe_3)_2]$, (21) (62 mg, *ca.* 0.17 mmol), in light petroleum–diethyl ether (1 : 1) (6 cm^3) was added $[Ni(CH_2CMe_2Ph)Br(PMe_3)_2]$, (12) (61 mg, *ca.* 0.14 mmol), in 6 cm^3 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 cm^3), and dried *in vacuo*. It was shown (i.r. and ^{1}H n.m.r.) to be identical to a pure sample of $[Ni(COCH_2CMe_2Ph)Br(PMe_3)_2]$, (27). The filtrate and washing liquids were taken to dryness, and the residue dissolved in C_6H_6. The ^{1}H n.m.r. spectrum was identical to that of $[Ni(CH_2SiMe_3)Cl(PMe_3)_2]$, (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 C_6H_6 (0.5 cm^3). The course of the reaction was followed by ^{1}H 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 $[Ni(COCH_2CMe_2Ph)(\eta\text{-}C_5H_5)(PMe_3)]$, (31), and $[Ni(CH_2CMe_2Ph)Cl(PMe_3)_2]$, (11), did not give $[Ni(COCH_2CMe_2Ph)Cl(PMe_3)_2]$, (26), even when the conditions were such as to insolubilize the latter complex, if formed.

X-*Ray Data Collection, Structure Determination and Refinement for* $[Ni(CH_2SiMe_3)Cl(PMe_3)_2]$, (1).—*Crystal data.* $C_{10}H_{29}ClNiP_2Si$, $M = 333.5$, Monoclinic, $a = 15.419(3)$, $b = 6.406(2)$, $c = 18.711(3)$ Å, $\beta = 92.02(3)°$, $U = 1\,847.0$ Å^3, $Z = 4$, $F(000) = 712$, $D_c = 1.20$ g cm^{-3}, $\lambda = 0.710\,69$ 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 ($2\theta > 32°$) 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—2θ scan technique in a manner similar to that previously described.[10] All reflections in one independent quadrant of data were measured out to $2\theta \leqslant 50°$; 1 906 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.[11] No corrections were made for extinction. Atomic scattering factors for Ni,

TABLE 6

Final fractional co-ordinates for $[Ni(COCH_2SiMe_3)Cl(PMe_3)_2]$, (21)

Atom	x/a	y/b	z/c
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
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 $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}} = 0.031$. 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 e 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 $[Ni(COCH_2SiMe_3)Cl(PMe_3)_2]$, (21).—*Crystal data.* $C_{11}H_{29}ClNiOP_2Si$, $M = 361.5$, Orthorhombic, $a = 12.668(3)$, $b = 21.312(4)$, $c = 28.925(4)$ Å, $U = 7\,809.2$ Å^3, $Z = 16$, $F(000) = 3\,072$, $D_c = 1.23$ g cm^{-3}, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K)_\alpha = 13.4$ cm^{-1}, space group *Pbca*. The lattice parameters were determined as above based on 15 reflections with $2\theta > 28°$.

A crystal of dimensions 1.20 × 0.52 × 0.24 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 $2\theta \leqslant 36°$ were measured: 1 394 were considered observed $[I \geqslant 3\sigma(I)]$. 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 $R =$

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* 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 e 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.

We thank Miss M. Mojarro for the preparation of some of the complexes, and Refinería La Rábida for generous gifts of solvents. M. L. P. gratefully acknowledges the Ministerio de Universidades e Investigación of Spain for a research scholarship, and J. L. A. thanks the U.S. National Science Foundation for partial support.

[0/225 *Received, 7th February*, 1980]

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