Reactivity of $[NiR(R')L_2]$ Compounds and the Crystal Structure of $[Ni(C_2Cl_3)(C_6H_2Me_3\text{-}2,4,6)(PMe_2Ph)_2]$†

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A series of compounds of the type *trans*-$[NiR(R')L_2]$ ($L = PMe_2Ph$, $R = C_2Cl_3$, R' = Ph, C_6H_4OMe-4, C_6H_4Me-2, or -4, $C_6H_2Me_3$-2,4,6; $R = C_6H_4Cl$-2, $R' = C_6H_4Me$-2 or $C_6H_2Me_3$-2,4,6; $R = C_6H_2Me_3$-2,4,6, $R' = C_6H_4Me$-2 or Ph; $L = PEt_3$, $R = C_2Cl_3$, $R' = C_6H_4Me$-2, Ph, C_6H_4OMe-4, C_6H_4Cl-4, or C_6H_4Me-4; $R = C_6H_4Cl$-2, R' = Ph, C_6H_4Me-2 or -4; $R = C_6H_4Me$-2, R' = Ph, or C_6H_4Me-4; $R = C_6H_2Me_3$-2,4,6, $R' = C_6H_4Me$-2) and *cis*-$[Ni(C_6H_2Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)(bipy)]$ (bipy = 2,2′-bipyridine) have been prepared. The proton n.m.r. signals of the *ortho* methyls of the mesityl ligand in the most hindered compound of the series $[Ni(C_2Cl_3)(C_6H_2Me_3\text{-}2,4,6)(PMe_2Ph)_2]$ appear overlapped despite the asymmetry of C_2Cl_3. The crystal structure of this compound [triclinic, space group $P\bar{1}$, $a = 12.570(3)$, $b = 12.703(3)$, $c = 9.352(2)$ Å, $\alpha = 91.70(2)$, $\beta = 90.02(2)$, $\gamma = 102.65(2)°$, $Z = 2$] indicates that this may be due to the phosphine aromatic rings. Ligand-exchange reactions of PMe_2Ph by PEt_3 in benzene, $[NiR(R')(PMe_2Ph)_2] \rightleftharpoons [NiR(R')(PMe_2Ph)(PEt_3)] \rightleftharpoons [NiR(R')(PEt_3)_2]$, are complete in 0.5 h at room temperature, no intermediates being observed. The reverse process requires reflux for 10 h and in this case the intermediates $[NiR(R')(PMe_2Ph)(PEt_3)]$ can be obtained. If the groups R and R′ contain *ortho* substituents the reaction does not take place. In refluxing benzene under nitrogen the stability of the organometallics containing PMe_2Ph is greater than those with PEt_3. Decomposition takes place *via* reductive elimination to give R–R′ or *via* homolytic cleavage to give R–H and R′–H, the most favoured pathway depending on the size and electronegativity of the groups R and R′. The reductive-elimination process involves a previous step in which a phosphine group is lost. The addition of CO to solutions of $[NiR(R')L_2]$ (when R and R′ possess *ortho* substituents) results in decomposition of the organometallics giving RCOR′. The compound $[Ni(C_6H_2Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)(bipy)]$ is also decomposed but gives R–R′. When one of the ligands (R) contains an *ortho* substituent, the corresponding two isomers (*syn* and *anti*) of the acyl derivative $[NiR(COR')L_2]$ can be detected. The compounds *cis*-$[NiR(R')(bipy)]$ show a favourable associative decomposition pathway when R and R′ are strong donor ligands.

The preparation and reactivity of organometallic complexes of nickel(II) of the type $[NiX(R)L_2]$,[1] $[NiR_2L_2]$,[1a,b,d,2] and $[NiR(R')L_2]$[1c,2a,3] has widely been studied since the work by Chatt and Shaw[1a] in 1960. The compounds are relatively stable when the ligand R is either an aromatic ring with *ortho* substituents or when it provides a similar steric hindrance, and the stability increases with the electronegativity of the organic R group. The preparative methods for these compounds depend on the size of all the ligands bonded to the metal atom, since the reactions involved are usually associative. The reactivity of these compounds has been well studied but some aspects still require clarification.

The preparation and reactivity of a number of complexes $[NiR(R')L_2]$ is described in this paper (R and R′ are aryl ligands or one of them is trichlorovinyl; L or L_2 = PEt_3, PMe_2Ph, or 2,2′-bipyridine). The chemical behaviour of these complexes has been found to be closely connected with the steric crowding around the metal atom. The relative stability of the complexes in refluxing benzene, the substitution reactions of the neutral ligand, and the reactivity with CO have been examined.

Experimental

General Remarks.—The reactions were carried out under nitrogen. The solvents used were dried and purified by distillation over sodium, and stored under nitrogen.

Infrared spectra were recorded on a Beckman I.R.-20A spectrophotometer. Proton and ^{31}P n.m.r. spectra were recorded on a Varian-XL 200 spectrometer; chemical shifts were referred to $SiMe_4$ (^1H) and H_3PO_4 (^{31}P). Mass spectra were measured on a Hewlett-Packard 5930 A mass spectrometer. G.l.c. analyses were performed on a Hewlett-Packard 5710 A instrument equipped with a column (2 m) packed with 5% SE-30 on Chromosorb Q and connected to a Hewlett-Packard 3390-A integrator.

Elemental analyses were carried out at the Institut de Química Bio-Orgànica de Barcelona (Consejo Superior de Investigaciones Cientificas).

The complexes $[NiX_2L_2]$ were prepared by published methods: $L = PEt_3$,[4] PMe_2Ph,[5] and PPh_3.[6]

Preparations.—*Complexes trans*-$[NiCl(R)L_2]$. *Method* (*a*). The organonickel complexes $[NiCl(C_2Cl_3)L_2]$ (C_2Cl_3 =

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† Bis(dimethylphenylphosphine)mesityl(trichlorovinyl)nickel(II).

Supplementary data available (No. SUP 56283, 5 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Preparation of complexes $[NiR(R')L_2]$; r.t. = room temperature

$[NiR(R')L_2]$	R′ in LiR′	Method	Solvent for $[NiCl(R)L_2]$	Addition temperature (°C)	Reaction time (min)	Reaction temperature (°C)
$[Ni(C_2Cl_3)Ph(PMe_2Ph)_2]$	Ph	(*a*)	Ether–benzene	−10	30	−10
$[Ni(C_2Cl_3)Ph(PEt_3)_2]$	Ph	(*b*)	Benzene	−20	120	−10
$[Ni(C_2Cl_3)(C_6H_4Me\text{-}2)(PMe_2Ph)_2]$	$C_6H_4Me\text{-}2$	(*a*)	Benzene	0	60	r.t.
					15	Reflux
$[Ni(C_2Cl_3)(C_6H_4Me\text{-}2)(PEt_3)_2]$	$C_6H_4Me\text{-}2$	(*a*)	Ether	r.t.	60	r.t.
$[Ni(C_2Cl_3)(C_6H_4Me\text{-}4)(PMe_2Ph)_2]$	$C_6H_4Me\text{-}4$	(*a*)	Ether–benzene	−10	30	−10
$[Ni(C_2Cl_3)(C_6H_4Me\text{-}4)(PEt_3)_2]$	$C_6H_4Me\text{-}4$	(*b*)	Benzene	−20	120	−10
$[Ni(C_2Cl_3)(C_6H_4OMe\text{-}4)(PMe_2Ph)_2]$	$C_6H_4OMe\text{-}4$	(*a*)	Ether–benzene	−10	30	−10
$[Ni(C_2Cl_3)(C_6H_4OMe\text{-}4)(PEt_3)_2]$	$C_6H_4OMe\text{-}4$	(*b*)	Benzene	−20	120	−10
$[Ni(C_2Cl_3)(C_6H_2Me_3\text{-}2,4,6)(PMe_2Ph)_2]$	$C_6H_2Me_3\text{-}2,4,6$	(*a*)	Benzene	0	60	r.t.
					15	Reflux
$[Ni(C_2Cl_3)(C_6H_4Cl\text{-}4)(PEt_3)_2]$	$C_6H_4Cl\text{-}4$	(*b*)	Benzene	−20	120	−10
$[Ni(C_6H_4Cl\text{-}2)(C_6H_4Me\text{-}2)(PMe_2Ph)_2]$	$C_6H_4Me\text{-}2$	(*a*)	Benzene	−10	30	0
$[Ni(C_6H_4Cl\text{-}2)(C_6H_4Me\text{-}2)(PEt_3)_2]$	$C_6H_4Me\text{-}2$	(*a*)	Benzene	0	30	r.t.
$[Ni(C_6H_4Cl\text{-}2)(C_6H_2Me_3\text{-}2,4,6)(PMe_2Ph)_2]$	$C_6H_2Me_3\text{-}2,4,6$	(*a*)	Benzene	0	60	r.t.
$[Ni(C_6H_4Cl\text{-}2)Ph(PEt_3)_2]$	Ph	(*a*)	Benzene	0	30	r.t.
$[Ni(C_6H_4Cl\text{-}2)(C_6H_4Me\text{-}4)(PEt_3)_2]$	$C_6H_4Me\text{-}4$	(*a*)	Benzene	0	30	r.t.
$[Ni(C_6H_4Me\text{-}2)Ph(PEt_3)_2]$	Ph	(*a*)	Ether	−10	10	−10
$[Ni(C_6H_4Me\text{-}2)(C_6H_4Me\text{-}4)(PEt_3)_2]$	$C_6H_4Me\text{-}4$	(*a*)	Ether	−10	10	−10
$[Ni(C_6H_2Me_3\text{-}2,4,6)Ph(PMe_2Ph)_2]$	Ph	(*a*)	Ether	−10	60	0
$[Ni(C_6H_2Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)\text{-}(PMe_2Ph)_2]$	$C_6H_4Me\text{-}2$	(*a*)	Ether	−10	60	0
$[Ni(C_6H_2Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)(PEt_3)_2]$	$C_6H_4Me\text{-}2$	(*a*)	Ether	r.t.	10	r.t.
					60	Reflux
$[Ni(C_6H_2Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)(bipy)]$	$C_6H_4Me\text{-}2$	(*a*)	Ether	5	30	r.t.

Table 2. Analytical data and melting points (calculated values in parentheses)

Complex	Analysis (%)			M.p. (°C)
	C	H	Cl	
$[Ni(C_2Cl_3)Ph(PEt_3)_2]$	47.8 (47.8)	7.2 (7.0)	21.1 (21.15)	142 (decomp.)
$[Ni(C_2Cl_3)(C_6H_4OMe\text{-}4)(PEt_3)_2]$	47.3 (47.35)	7.0 (7.0)	20.0 (19.95)	130—132 (decomp.)
$[Ni(C_2Cl_3)(C_6H_4Cl\text{-}4)(PEt_3)_2]$	43.8 (44.75)	6.4 (6.4)	26.7 (26.4)	105—110 (decomp.)
$[Ni(C_6H_4Me\text{-}2)Ph(PEt_3)_2]$	64.8 (64.85)	9.2 (9.15)		124—127 (decomp.)
$[Ni(C_6H_4Me\text{-}2)(C_6H_4Me\text{-}4)(PEt_3)_2]$	64.4 (65.45)	9.3 (9.3)		80—85
$[Ni(C_6H_4Cl\text{-}2)(C_6H_4Me\text{-}4)(PEt_3)_2]$	60.3 (60.35)	8.3 (8.3)	7.0 (7.1)	92—94
$[Ni(C_6H_4Cl\text{-}2)Ph(PEt_3)_2]$	59.7 (59.6)	8.2 (8.15)	7.5 (7.35)	135 (decomp.)
$[Ni(C_6H_4Cl\text{-}2)(C_6H_4Me\text{-}2)(PEt_3)_2]$	61.0 (60.35)	8.6 (8.3)	7.4 (7.1)	140—142 (decomp.)
$[Ni(C_6H_2Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)(PEt_3)_2]$	65.5 (66.55)	9.6 (9.6)		131—133
$[Ni(C_2Cl_3)Ph(PMe_2Ph)_2]$	50.5 (53.15)	4.9 (5.0)	20.2 (19.6)	86—90 (decomp.)
$[Ni(C_2Cl_3)(C_6H_4Me\text{-}4)(PMe_2Ph)_2]$	53.9 (53.95)	5.2 (5.25)	19.0 (19.1)	95
$[Ni(C_2Cl_3)(C_6H_4Me\text{-}2)(PMe_2Ph)_2]$	54.2 (53.95)	5.3 (5.25)	18.8 (19.1)	115—117
$[Ni(C_2Cl_3)(C_6H_4OMe\text{-}4)(PMe_2Ph)_2]$	52.5 (52.45)	5.1 (5.1)	18.5 (18.6)	84
$[Ni(C_6H_4Cl\text{-}2)(C_6H_4Me\text{-}2)(PMe_2Ph)_2]$	65.3 (64.8)	6.2 (6.2)	6.8 (6.6)	100
$[Ni(C_6H_2Me_3\text{-}2,4,6)Ph(PMe_2Ph)_2]$	70.5 (70.1)	7.2 (7.2)		105—110
$[Ni(C_6H_2Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)(PMe_2Ph)_2]$	70.4 (70.5)	7.4 (7.4)		135—140 (decomp.)
$[Ni(C_6H_4Cl\text{-}2)(C_6H_2Me_3\text{-}2,4,6)(PMe_2Ph)_2]$	66.6 (65.8)	6.6 (6.6)	6.1 (6.25)	125—130 (decomp.)
$[Ni(C_2Cl_3)(C_6H_2Me_3\text{-}2,4,6)(PMe_2Ph)_2]$	55.9 (55.45)	5.6 (5.7)	18.0 (18.2)	135
$[Ni(C_6H_4Cl\text{-}2)_2(PMe_2Ph)_2]$	58.5 (60.25)	5.3 (5.4)	12.7 (12.7)	132—134
$[NiCl(C_6H_2Me_3\text{-}2,4,6)(dppe)]$	68.5 (68.75)	5.6 (5.75)	5.7 (5.8)	204—210 (decomp.)
$[NiCl(C_6H_2Me_3\text{-}2,4,6)(bipy)]$[a]	59.7 (61.75)	5.1 (5.75)	8.9 (9.6)	198—202 (decomp.)
$[Ni(C_6H_2Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)(bipy)]$[b]	73.1 (73.45)	6.1 (6.15)		183—185 (decomp.)
$[Ni(C_2Cl_3)(COC_6H_4OMe\text{-}4)(PEt_3)_2]$	49.5 (48.5)	6.4 (6.8)	18.2 (18.95)	110—112
$[Ni(C_2Cl_3)(COPh)(PEt_3)_2]$	47.5 (47.55)	6.7 (6.65)	19.8 (20.05)	98—100

[a] N 7.4 (7.6)%. [b] N 6.5 (6.6)%.

trichlorovinyl, L = PMe_2Ph or PEt_3) were prepared by oxidative-addition reactions as described by Wada and co-workers.[7]

Method (*b*). The complexes $[NiCl(R)L_2]$ [R = C_6H_4Cl-2, L = PMe_2Ph or PEt_3;[1e] R = C_6H_4Me-2, L = PEt_3;[1a] R = mesityl, L = PMe_2Ph,[1b] PEt_3,[1a] PPh_3, or ½dppe ($Ph_2PCH_2CH_2PPh_2$)] were prepared by adding the appropriate Grignard reagent to the nickel complexes $[NiCl_2L_2]$ as described previously.

$[NiCl(C_6H_4Cl\text{-}2)(PMe_2Ph)_2]$. A diethyl ether solution of 2-chlorophenylmagnesium bromide obtained from C_6H_4Br-1-Cl-2 (1.9 g, 10 mmol) and magnesium (0.48 g, 20 mmol) was added at 5 °C to a benzene solution (10 cm^3) of $[NiCl_2(PMe_2Ph)_2]$ (2.8 g, 7 mmol). The mixture was hydrolysed with dilute (2%) hydrochloric acid. The organic layer was separated, dried, and evaporated under high vacuum to eliminate C_6H_5Cl and C_6H_4Br-1-Cl-2. The oil obtained was identified as $[NiCl(C_6H_4Cl\text{-}2)(PMe_2Ph)_2]$ by n.m.r. spectroscopy.

Method (*c*). The complex [NiCl($C_6H_2Me_3$-2,4,6)(bipy)] was prepared by adding 2,2′-bipyridine (bipy) (0.17 g, 1.1 mmol) to a benzene solution (10 cm^3) of [NiCl($C_6H_2Me_3$-2,4,6)($PPh_3)_2$] (0.74 g, 1 mmol) at room temperature. The solution was stirred for 2 h and the red precipitate filtered off, washed with 2% HCl, and dried under reduced pressure. The organonickel complex was recrystallized from benzene–ether. Yield 40%.

Organolithium reagents. Method (*i*). Metallic lithium (0.2 g, 30 mmol) was cut into chips which were allowed to fall into a flask containing diethyl ether (10 cm^3). Several drops of a solution of aryl bromide (10 mmol) in ether (20 cm^3) were then added. The rest of the solution was added and the mixture stirred for 30 min, at room temperature for R′ = C_6H_4Me-2 or -4, or C_6H_4OMe-4, at reflux for R′ = mesityl or Ph.

Method (*ii*). A n-hexane solution (3 cm^3) of 1.6 mol dm^{-3} n-butyl-lithium was added to diethyl ether (10 cm^3) at room temperature and stirred for 10 min. After cooling to 0 °C, the aryl bromide R′Br (R′ = C_6H_4Cl-4, Ph, or C_6H_4OMe-4) (4 mmol) was added and the resulting solution stirred at this temperature for 1 h. The reaction was monitored by gas chromatography of the hydrolysed solutions.

Disubstituted organometallic complexes [NiR(R′)L_2]. The complexes [NiR(R′)L_2] were prepared by reaction of the organolithium reagent LiR′ (4 mmol) with [NiCl(R)L_2] (1 mmol) under the conditions given in Table 1.

Method (*a*). A filtered solution of LiR′, prepared by reaction of metallic lithium with aryl bromide, was added to a solution of [NiCl(R)L_2] in diethyl ether.

Method (*b*). A solution of [NiCl(R)L_2] was added to an ether solution of the organolithium reagent LiR′ prepared by metal–halogen exchange between n-butyl-lithium and the corresponding aryl bromide. The solutions obtained were hydrolysed with 2% hydrochloric acid, washed, and the organic layer dried with Na_2SO_4. The solvent was removed under reduced pressure. The light yellow complexes [NiR(R′)L_2] were precipitated with methanol and recrystallized from benzene–methanol. Violet [Ni($C_6H_2Me_3$-2,4,6)(C_6H_4Me-2)(bipy)] was recovered directly from the reaction solution and recrystallized from benzene–ether. The yields were 50—60%. Analytical data for the new complexes are given in Table 2.

Substitution Reactions.—The organometallic complex (0.2 g) was dissolved in benzene (25 cm^3). To the deoxygenated solution, free ligand was added (in 1:6 Ni:L molar ratio, unless otherwise stated), and the resulting mixture was refluxed under nitrogen for 10 h. The cold solution was washed with five 20-cm^3 portions of 2% HCl, water, and dried over Na_2SO_4. Then it was concentrated to 1/20 of its initial volume and treated with methanol (5 cm^3). A yellow precipitate of the starting complex or the substituted derivative may be obtained. When mixtures of [NiCl(C_2Cl_3)($PMe_2Ph)_2$] and [NiCl(C_2Cl_3)(PMe_2Ph)(PEt_3)] were obtained, the first precipitate consisted of [NiX(R)L_2] and in order to precipitate the mixed-ligand complex the solvent was removed *in vacuo* and the residue treated with 2% HCl, filtered, and recrystallized from a small amount of cold methanol. The progress of the reaction was monitored by n.m.r. spectroscopy at room temperature using samples comprising 1—2 cm^3 of the benzene solution mixed with the same amount of C_6D_6, under nitrogen.

For the preparation of [Ni(C_2Cl_3)Ph(PEt_3)(PMe_2Ph)] and [NiCl(C_2Cl_3)(PEt_3)(PMe_2Ph)], the bis(triethylphosphine) precursor must be used as a starting material together with a Ni:PMe_2Ph molar ratio of 1:3. Yields were about 20 and 50% respectively.

Thermolysis.—The thermal decompositions were carried out at 80 °C in Schlenk flasks fitted with a condenser, under a N_2 atmosphere, using freshly recrystallized [NiR(R′)L_2] (150—200 mg) in either benzene or heptane solution (20 cm^3). As the reaction progressed the clear yellow solutions turned progressively brown and finally a black precipitate appeared. After 15 h under reflux the solution was cooled and washed with 1% HCl. The organic layer was concentrated to 2 cm^3 and methanol (10 cm^3) added. The remaining organometallic compound was filtered off and the solution analysed for arenes by gas chromatography. Nickel dimethylglyoximate was precipitated from the aqueous layer.

Alternatively, the cooled reacted solution was filtered to remove any metallic nickel, and the solvent separated by vacuum transfer. The traps containing the solvent and small amounts of decomposition products were analysed by gas chromatography.

The different compounds derived from R and R′ were identified by their mass spectra.

Reaction of [NiR(R′)L_2] *with* CO.—Carbon monoxide was introduced into a vessel containing [NiR(R′)L_2] (0.2 mmol) in acetone (5—10 cm^3) at 0 °C under nitrogen. After 1—2 h the colour of the solution was discharged, except for the mesityl derivatives and the compound with bipy (8 h). Then the solutions were concentrated under reduced pressure, treated with benzene, washed with 2% HCl and water, and dried with Na_2SO_4. The resulting solutions were analysed by gas chromatography and mass spectrometry to characterize the ketones RCOR′.

The process can be followed by n.m.r. spectroscopy by carrying out the reaction in a n.m.r. tube provided with two needles (one for N_2 and the other for CO).

When the starting complex was [Ni(C_2Cl_3)Ph($PEt_3)_2$] or [Ni(C_2Cl_3)(C_6H_4OMe-4)($PEt_3)_2$], pale yellow crystals started to precipitate after 45 min under CO. The temperature was then lowered to −30 °C and the vessel purged with nitrogen. The precipitate was collected after 1 h and recrystallized from benzene–methanol. Yield 30%.

Crystallography for [Ni(C_2Cl_3)($C_6H_2Me_3$-2,4,6)(PMe_2-Ph$)_2$].— *Crystal data*. $C_{27}H_{33}Cl_3NiP_2$, M = 584.58, triclinic, space group $P\bar{1}$, a = 12.570(3), b = 12.703(3), c = 9.352(2) Å, α = 91.70(2), β = 90.02(2), γ = 102.65(2)°, U = 1 456(1) Å^3, Z = 2, D_c = 1.33 g cm^{-3}, $F(000)$ = 608, Mo-K_α radiation, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 10.59 cm^{-1}. Room temperature.

A prismatic crystal (0.1 × 0.1 × 0.2 mm) was mounted on a Philips PW-1100 four-circle diffractometer. The unit cell was measured by centring of 25 reflections ($4 \leqslant \theta \leqslant 12°$) and refined by least squares. Graphite-monochromated Mo-K_α radiation was used. Intensities were measured with the ω-scan technique (scan width 0.8°, scan speed 0.03° s^{-1}, scan range $2 \leqslant \theta \leqslant 30°$). 5 552 Independent reflections were collected, of which 5 486 were considered observed [$I > 2.5\sigma(I)$]. Lorentz polarization, but not absorption, corrections were made.

Structure determination. The Ni, P, and Cl atoms were located from a Patterson synthesis and the remaining non-hydrogen atoms from a Fourier synthesis. The structure was refined isotropically and anisotropically by least squares using the SHELX 76 [8] computer program. The function minimized was $w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F_o) + 0.0113\,|F_o|^2]^{-1}$ in the last cycles.

Anomalous dispersion corrections were made using values of f' and f'' from ref. 9. Thirty hydrogen atoms (of 33) were located from a difference synthesis, and refined with an overall isotropic thermal parameter. The final R factor was 0.048 (R' = 0.062).

Results and Discussion

Preparation of [NiR(R′)L_2].—The complexes *trans*-[NiX(R)L_2] (some of which have been previously described) are obtained on treating $[NiCl_2L_2]$ (L = PEt_3, PMe_2Ph, or PPh_3) with a slight excess of the corresponding Grignard reagent MgRBr (R = C_6H_4Me-2, $C_6H_2Me_3$-2,4,6, and C_6H_4Cl-2) prepared in ether.

The organometallics of type $[NiCl(C_2Cl_3)L_2]$ (L = PEt_3 or PMe_2Ph) have been prepared by the procedure of Wada and co-workers[7] which involves an oxidative addition of C_2Cl_4 to the nickel(0) complex, obtained '*in situ*' by treating $[NiCl_2L_2]$ with $NaBH_4$. The compounds are yellow crystalline solids except for $[NiCl(C_6H_4Cl\text{-}2)(PMe_2Ph)_2]$ which is obtained as an oil. The benzene solution of the latter shows a single ^{31}P n.m.r. signal at $\delta - 5.7$ p.p.m.

The organometallics *cis*-$[NiCl(C_6H_2Me_3\text{-}2,4,6)(L\text{-}L)]$ (L–L = bipy or dppe) have been obtained by treating $[NiCl(C_6H_2Me_3\text{-}2,4,6)(PPh_3)_2]$ with the corresponding neutral ligand.

The disubstituted compounds $[NiR(R')L_2]$ are prepared by treatment of the corresponding intermediate $[NiX(R)L_2]$ with the lithium derivatives LiR′ under appropriate conditions. According to Chatt and Shaw,[1a] and Rausch and Tibbetts,[2a] the reaction is sensitive to the size of the ligands attached to the nickel atom in the intermediate complex; this behaviour indicates that the replacement of the ligand X by an organic group R′ in $[NiX(R)L_2]$ may have an associative character. It has been observed that on treating $[NiCl(C_2Cl_3)L_2]$ with mesityl-lithium the disubstituted organometallic is obtained only when L = PMe_2Ph, but with *o*-tolyl-lithium the disubstituted products are obtained for L = PMe_2Ph and PEt_3.

On treating the complex $[NiCl(C_2Cl_3)L_2]$ with an excess of LiR′ (R′ = Ph, C_6H_4Me-4, or C_6H_4OMe-4) at temperatures above −10 °C complete decomposition occurs and substantial amounts of the coupling products $R'\text{–}C_2Cl_3$ and R′–R′ are recovered. The same behaviour has been observed on treating the intermediates $[NiX(R)L_2]$ with lithium derivatives at temperatures and concentrations higher than those used for preparation of the disubstituted organometallics $[NiR(R')L_2]$. The decomposition seems to be favoured when R is an electronegative ligand and R′ does not possess *ortho* substituents. It may be due to the formation of ionic species of the types $[NiRR'_2L]^-$ or $[NiRR'_3]^{2-}$ analogously to that described by Yamamoto and co-workers[10] for the induced isomerizations of $[PdR_2L_2]$ by LiR′.

The reaction of $[NiCl(C_2Cl_3)(PMe_2Ph)_2]$ and LiPh, in the presence of *o*-bromotoluene, in molar ratio 1:13:1, gives Ph–Ph, $2\text{-}MeC_6H_4\text{–}Ph$, $Ph\text{–}C_2Cl_3$, and unaltered *o*-bromotoluene in the ratio 5:0.3:1:0.63; accordingly, the formation of the coupling products R′–R′ does not take place by reductive elimination of the complexes $[NiR'_2L_2]$, as in the coupling reaction of RBr and LiR′ catalysed by $[NiX_2(L\text{-}L)]$.

The complex *cis*-$[Ni(C_6H_2Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)(bipy)]$ is the only species with this configuration which has been isolated on treating *cis*-$[NiCl(C_6H_2Me_3\text{-}2,4,6)(L\text{-}L)]$ (L–L = dppe or bipy) with *o*-tolyl-lithium. When the complex *cis*-$[NiCl(C_6H_2Me_3\text{-}2,4,6)(dppe)]$ is treated with organolithium reagents only the coupling products $R'\text{–}C_6H_2Me_3$-2,4,6 are obtained.

The compounds $[NiR(R')L_2]$ are pale yellow solids, except for $[Ni(C_6H_2Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)(bipy)]$ which is violet. The dry recrystallized products are air stable except for $[Ni(C_6H_4Me\text{-}2)R'(PEt_3)_2]$ and $[Ni(C_2Cl_3)R'(PMe_2Ph)_2]$ (R′ = Ph or C_6H_4Me-4) which decompose slowly. All of them decompose in chlorinated solvents. The complex $[Ni(C_6H_4Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)(bipy)]$ is scarcely soluble in the usual solvents and decomposes slowly in alcohol. The complexes which contain PMe_2Ph are in general more soluble than their PEt_3 analogues. Analytical results agree with the proposed formulations. All of the complexes show diamagnetic behaviour.

Proton and ^{31}P n.m.r. (Table 3) spectra indicate a *trans* geometry for all the compounds. Both *syn* and *anti* isomers are observed for all the compounds with non-symmetrical ligands, but we have not been able to separate them by crystallization in accord with Wada and Kumazoe.[11] It has been found that the ^{31}P signal for a series of analogous complexes where only the group R′ is varied $[Ni(C_6H_2Me_3\text{-}2,4,6)R'(PMe_2Ph)_2]$ (R′ = Ph, C_6H_4Me-2, C_6H_4Cl-2, or C_2Cl_3) or $[Ni(C_2Cl_3)R'(PEt_3)_2]$ (R′ = Cl, Ph, or C_6H_4Me-2) shifts towards lower fields on decreasing the size of R′. This could be due to the increase of the C–P–C angle.[12] The structures of $[Ni(C_2Cl_3)_2(PMe_2Ph)_2]$[13] and $[Ni(C_2Cl_3)(C_6H_2Me_3\text{-}2,4,6)(PMe_2Ph)_2]$, described below, are not, at least, contrary to this explanation. The mean C–P–C angles are 104.4 and 102.6° for the first and second complex and the corresponding chemical shifts are 0.35, −0.25 {*syn* and *anti* forms of $[Ni(C_2Cl_3)_2(PMe_2Ph)_2]$} and −4.13, which would indicate less crowding for C_2Cl_3. Rotation of the ligands R and R′ around the Ni–C bond must be hindered since the signals do not widen appreciably on warming solutions of the *syn* and *anti* isomers in $[^2H_8]$toluene.

The proton n.m.r. spectra of the compounds containing PMe_2Ph show several triplets (assignable to the methyl groups of the phosphine ligand) whose number depends on the symmetry of the organic ligands R. Only one triplet appears if there is a symmetry plane through the P–Ni–P bond; otherwise two triplets occur. The complexes without this plane of symmetry and possessing *syn* and *anti* isomers give rise to four triplets which are not overlapped in the spectrum of $[Ni(C_6H_4Cl\text{-}2)(C_6H_4Me\text{-}2)(PMe_2Ph)_2]$.

If the ligands contain *o*-methyl groups, the signals appear at fields lower than expected due to the magnetic effect of the central ion. When the group R′ is asymmetric, the mesityl signal appears split; however this is not so for $[Ni(C_2Cl_3)(C_6H_2Me_3\text{-}2,4,6)(PMe_2Ph)_2]$ due probably to the effect of the benzene rings of the phosphine, as discussed below.

Crystal Structure of $[Ni(C_2Cl_3)(C_6H_2Me_3\text{-}2,4,6)(PMe_2Ph)_2]$.—The molecular structure of $[Ni(C_2Cl_3)(C_6H_2Me_3\text{-}2,4,6)(PMe_2Ph)_2]$ is shown in the Figure together with the

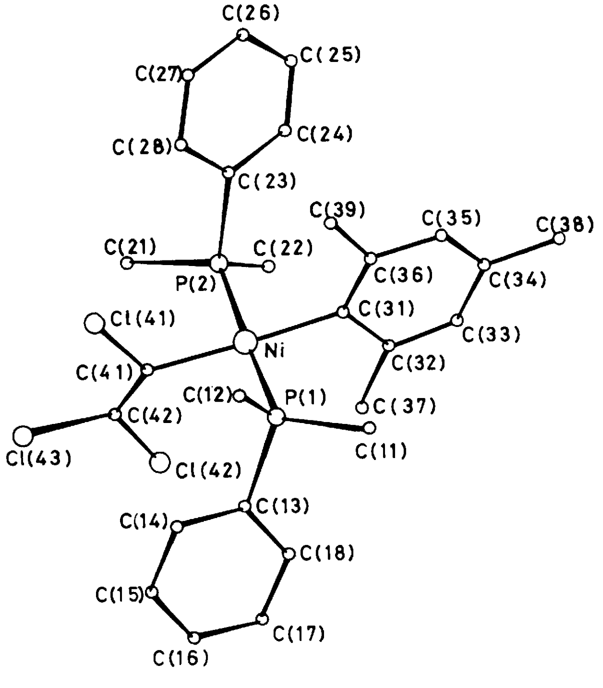


Figure. Molecular structure of $[Ni(C_2Cl_3)(C_6H_2Me_3\text{-}2,4,6)(PMe_2Ph)_2]$

Table 3. Proton and ^{31}P n.m.r. data for diorganonickel(II) complexes

	PMe$_2$Ph			R and/or R′
Complex	δ(P)[a]	δ(CH$_3$)	J(P–H)[b]/Hz	δ(CH$_3$)
[Ni(C$_2$Cl$_3$)(C$_6$H$_4$Me-4)(PMe$_2$Ph)$_2$]		1.01(t)	3.6	2.15
		1.12(t)		
[Ni(C$_2$Cl$_3$)(C$_6$H$_4$Me-2)(PMe$_2$Ph)$_2$]	−3.31	0.88—1.12	*c*	2.14
				2.28
[Ni(C$_2$Cl$_3$)(C$_6$H$_4$OMe-4)(PMe$_2$Ph)$_2$]		1.02(t)	3.6	3.36
		1.12(t)		
[Ni(C$_2$Cl$_3$)(C$_6$H$_2$Me$_3$-2,4,6)(PMe$_2$Ph)$_2$][d]	−4.13	1.04(t)	3.5	2.23 (*para*)
		1.10(t)		2.29 (*ortho*)
[Ni(C$_6$H$_2$Me$_3$-2,4,6)Ph(PMe$_2$Ph)$_2$]	−2.77	1.04(t)	3.6	2.23 (*para*)
				2.60 (*ortho*)
[Ni(C$_6$H$_2$Me$_3$-2,4,6)(C$_6$H$_4$Me-2)(PMe$_2$Ph)$_2$][e]	−3.17	0.89(t)	3.2	1.75 (*o*-tolyl)
		1.17(t)		2.22 (p-mesityl)
				2.31 (*o*-mesityl)
				2.45 (*o*-mesityl)
[Ni(C$_6$H$_4$Cl-2)(C$_6$H$_2$Me$_3$-2,4,6)(PMe$_2$Ph)$_2$]	−3.96	0.97(t)	3.4	2.26 (*para*)
		0.92(t)		2.38 (*ortho*)
				2.69 (*ortho*)
[Ni(C$_6$H$_4$Cl-2)(C$_6$H$_4$Me-2)(PMe$_2$Ph)$_2$]	−1.84	0.78(t)		2.00
	−0.40	0.95(t)		
			3.6	
		0.89(t)		2.69
		0.99(t)		
[Ni(C$_6$H$_4$Cl-2)$_2$(PMe$_2$Ph)$_2$]	−0.52	0.97(t)	3.7	
	−0.84	1.01(t)		
[Ni(C$_6$H$_2$Me$_3$-2,4,6)(C$_6$H$_4$Me-2)(bipy)]				2.40 (*p*-mesityl)
				2.92 3.13 3.48 } (*o*-mesityl and -tolyl)
[Ni(C$_2$Cl$_3$)Ph(PEt$_3$)$_2$]	13.39			2.78
[Ni(C$_2$Cl$_3$)(C$_6$H$_4$Me-2)(PEt$_3$)$_2$]	10.72			2.86
	11.40			3.42
[Ni(C$_2$Cl$_3$)(C$_6$H$_4$OMe-4)(PEt$_3$)$_2$][f]				
[Ni(C$_6$H$_4$Cl-2)Ph(PEt$_3$)$_2$]				2.29
[Ni(C$_6$H$_4$Cl-2)(C$_6$H$_4$Me-4)(PEt$_3$)$_2$]				2.83
[Ni(C$_6$H$_4$Cl-2)(C$_6$H$_4$Me-2)(PEt$_3$)$_2$]	+8.44			3.03
	+8.65			2.91
[Ni(C$_6$H$_4$Me-2)Ph(PEt$_3$)$_2$]	+11.65			2.31 (*p*-tolyl)
[Ni(C$_6$H$_4$Me-2)(C$_6$H$_4$Me-4)(PEt$_3$)$_2$]				2.92 (*o*-tolyl)
[Ni(C$_6$H$_2$Me$_3$-2,4,6)(C$_6$H$_4$Me–2)(PEt$_3$)$_2$]	+6.09			2.35 (*p*-mesityl)
				2.85
				2.93
				2.95

[a] Chemical shifts in p.p.m. with respect to internal 85% H_3PO_4 (in C_6D_6). [b] Virtual coupling. [c] Broad unresolved signal. [d] δ(aromatic) 6.58 and 6.60. [e] δ(aromatic) 6.51 and 6.54. [f] δ(aromatic) 6.77(d, *meta*), 7.29(d, *ortho*); J(H–H) 7.42 Hz.

atomic numbering. The unit cell contains two molecules linked by van der Waals interactions. The distance between C(37) and Cl(42) of the next molecule is 4.59 Å (1 − *x*, 1 − *y*, 1 − *z*). Positional parameters and the more significant bond distances and angles are collected in Tables 4 and 5.

The nickel atom has an approximately square-planar co-ordination. The deviations from the mean plane defined by the inner co-ordination sphere NiC$_2$P$_2$ are: Ni, 0.015(1); P(1), −0.020(1); P(2), −0.021(1); C(31), 0.013(3), and C(41), 0.013(3) Å. The bond angles P(2)–Ni–P(1) [177.24(4)°] and C(41)–Ni–C(31) [178.4(1) Å] deviate from the expected 180°, probably due to steric effects between the C and P atoms [mean C ··· P is 2.93(3) Å]. The Ni–P bonds have an eclipsed conformation with C(11), P(1), Ni, C(31) and C(21), P(2), Ni, C(41) atoms nearly on a plane. The corresponding torsion angles are −4.8(1) and −7.2(1)°.

Slightly different Ni–P distances for the two phosphorus atoms of the molecule are observed [2.194(1) and 2.205(1) Å], but surprisingly the Ni–C distances are nearly the same [Ni–C(31) 1.936(3) and Ni–C(41) 1.933(3) Å] in spite of the large electronegativity difference between the ligands. Nevertheless, the Ni–C distances are similar to those found in other compounds of this type: two isomers of [Ni(C$_2$Cl$_3$)$_2$(PMe$_2$Ph)$_2$],[13] 1.91(1) and 1.93(3) Å; [Ni(C$_6$F$_5$)$_2$(PMePh$_2$)$_2$],[14] 1.939(3) Å; and [Ni{C$_6$H$_3$(OMe)$_2$-2,6}$_2$(PMe$_2$Ph)$_2$],[15] 1.933(5) and 1.954(5) Å.

The trichlorovinyl (C$_2$Cl$_3$) and mesityl (C$_6$H$_2$Me$_3$-2,4,6) ligands are planar, the angles between these planes and the NiC$_2$P$_2$ mean plane being 88.0(1) and 87.7(1)°, respectively. The angle between both planes is 6.3(1)°. The opening of the C(42)–C(41)–Ni and Cl(43)–C(42)–C(41) bond angles of the trichlorovinyl group is similar to that found in [Ni(C$_2$Cl$_3$)$_2$(PMe$_2$Ph)$_2$] and must be the result of steric interactions between the nickel and chlorine atoms [Ni ··· Cl(41) 3.179(1), Cl(41) ··· Cl(43) 3.129(2), Cl(43) ··· Cl(42) 2.921(2), and Cl(42) ··· Ni 3.329(1) Å] since the *o*-methyl substituents of the

Table 4. Positional parameters with standard deviations for the non-hydrogen atoms of $[Ni(C_2Cl_3)(C_6H_2Me_3\text{-}2,4,6)(PMe_2Ph)_2]$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ni	3 009(0)	2 387(0)	2 310(0)
P(1)	3 622(1)	1 400(1)	3 866(1)
C(11)	3 194(5)	1 445(5)	5 730(5)
C(12)	3 242(4)	−52(3)	3 424(6)
C(13)	5 099(3)	1 679(3)	3 989(4)
C(14)	5 701(4)	1 198(4)	3 023(5)
C(15)	6 828(4)	1 480(4)	3 017(6)
C(16)	7 374(5)	2 280(5)	3 980(7)
C(17)	6 802(5)	2 727(5)	4 980(7)
C(18)	5 657(4)	2 438(4)	4 989(5)
P(2)	2 314(1)	3 351(1)	786(1)
C(21)	2 912(5)	3 509(5)	−1 001(5)
C(22)	2 367(5)	4 763(3)	1 311(6)
C(23)	880(3)	2 798(3)	377(4)
C(24)	55(4)	3 258(4)	923(5)
C(25)	−1 029(4)	2 807(5)	590(6)
C(26)	−1 295(5)	1 922(5)	−285(7)
C(27)	−498(6)	1 455(5)	−820(8)
C(28)	588(5)	1 879(4)	−509(7)
C(31)	2 086(3)	2 832(3)	3 759(4)
C(32)	2 471(3)	3 781(3)	4 593(4)
C(33)	1 789(4)	4 161(4)	5 556(4)
C(34)	735(4)	3 599(4)	5 796(4)
C(35)	365(4)	2 615(5)	5 052(5)
C(36)	1 020(3)	2 232(3)	4 029(4)
C(37)	3 636(4)	4 409(4)	4 447(6)
C(38)	5(6)	4 037(6)	6 841(6)
C(39)	567(4)	1 175(4)	3 281(6)
C(41)	3 913(3)	1 963(3)	824(4)
Cl(41)	3 330(1)	764(1)	−225(1)
C(42)	4 867(4)	2 448(4)	400(5)
Cl(42)	5 497(1)	3 647(1)	1 323(2)
Cl(43)	5 643(1)	2 103(2)	−1 007(2)

Table 5. Selected bond lengths (Å) and angles (°) of $[Ni(C_2Cl_3)(C_6H_2Me_3\text{-}2,4,6)(PMe_2Ph)_2]$*

Ni–P(1)	2.194(1)	P(2)–C(23)	1.822(3)
Ni–P(2)	2.205(1)	$\langle C–C_{benzene}\rangle_{2x}$	1.38(2)
Ni–C(31)	1.936(3)	$\langle C–C_{benzene}\rangle_{3x}$	1.40(1)
Ni–C(41)	1.933(3)	C(32)–C(37)	1.515(5)
P(1)–C(11)	1.827(3)	C(34)–C(38)	1.516(4)
P(1)–C(12)	1.835(3)	C(36)–C(39)	1.492(5)
P(1)–C(13)	1.816(3)	C(41)–C(42)	1.290(5)
$\langle C–C_{benzene}\rangle_{1x}$	1.39(1)	C(41)–Cl(41)	1.801(3)
P(2)–C(21)	1.831(4)	C(42)–Cl(42)	1.756(4)
P(2)–C(22)	1.833(4)	C(42)–Cl(43)	1.740(3)
P(2)–Ni–P(1)	177.24(4)	Ni–P(2)–C(22)	116.8(1)
C(31)–Ni–P(1)	90.2(1)	Ni–P(3)–C(23)	113.4(1)
C(31)–Ni–P(2)	87.7(1)	C(21)–P(2)–C(22)	100.7(2)
C(41)–Ni–P(1)	91.3(1)	C(21)–P(2)–C(23)	102.0(2)
C(41)–Ni–P(2)	90.7(1)	C(22)–P(2)–C(23)	104.1(2)
C(41)–Ni–C(31)	178.4(1)	Ni–C(41)–C(42)	129.6(3)
Ni–P(1)–C(11)	119.2(1)	Ni–C(41)–Cl(41)	116.7(2)
Ni–P(1)–C(12)	113.2(1)	C(42)–C(41)–Cl(41)	113.6(3)
Ni–P(1)–C(13)	113.5(1)	C(41)–C(42)–Cl(42)	117.3(3)
C(11)–P(1)–C(12)	101.8(2)	C(41)–C(42)–Cl(43)	129.4(3)
C(11)–P(1)–C(13)	103.6(2)	Cl(42)–C(42)–Cl(43)	113.3(2)
C(12)–P(1)–C(13)	103.7(2)	C(31)–C(32)–C(37)	120.4(3)
Ni–P(2)–C(21)	117.7(2)	C(31)–C(36)–C(39)	121.9(3)

* $\langle\quad\rangle_{nx}$ represents weighted mean value for atoms of C(*nx*) phenyl ring (see Figure).

mesityl group are at larger distances [Cl(41) ··· C(39) 4.857(4) and Cl(42) ··· C(37) 3.955(4) Å]. The C(36)–C(39) and C(37)–C(32) distances of the *ortho*-substituted methyls are also slightly different [1.492(5) and 1.515(5) Å] and in the opposite direction to what would be expected from Cl ··· Me effects. This may arise from interactions with the phenyl rings of the phosphines.

The trend toward linearity of the trichlorovinyl group and the two different C–Cl distances [C(41)–Cl(41) 1.801(3) and C(42)–Cl 1.756(4) and 1.740(3) Å] must have an electronic origin. A similar behaviour has been observed for the vinyl ligand in $[Pt(CCl{=}CH_2)_2(PMe_2Ph)_2]$.[16] The C_α–Cl distances are larger than expected, the whole ligand approaches linearity but the C(41)–C(42) double-bond distance [1.290(5) Å] remains similar to those [1.37(2) and 1.28(3) Å] in $[Ni(C_2Cl_3)_2(PMe_2Ph)_2]$ or that [1.316(7) Å] in $[Pt(CCl{=}CH_2)_2(PMe_2Ph)_2]$.

Substitution Reactions.—The exchange between free and co-ordinated phosphine is slow at room temperature since the ^{31}P n.m.r. spectra of solutions of $[Ni(C_2Cl_3)R'L_2]$ (L = PEt_3 or PMe_2Ph; R′ = *p*-substituted phenyl) and free phosphine show unbroadened signals. Only $[NiCl(C_2Cl_3)(PMe_2Ph)_2]$ shows a significant broadening of the peaks, although without an increase in conductivity. All the reactions were carried out in refluxing benzene for 10 h as a reference time. When no substitution takes place the starting product is recovered in 75% yield, and the major decomposition products are R–R′, phosphine, and phosphine oxide.

The substitution process is observed only when one of the organic ligands has an *ortho* substituent; when both groups R contain such substituents, the reaction does not take place. Thus, the process may be considered associative. The products obtained in the reference time can be explained by the equilibria (1) where steps (i) and (ii) are faster than the corresponding

$$\begin{tikzcd}
{[NiR(R')(PMe_2Ph)_2]} \arrow[r, shift left, "\text{(i), }PEt_3"] & {[NiR(R')(PMe_2Ph)(PEt_3)]} \arrow[l, shift left, "\text{(iv), }PMe_2Ph"] \arrow[d, shift left, "\text{(ii), }PEt_3"] \\
 & {[NiR(R')(PEt_3)_2]} \arrow[u, shift left, "\text{(iii), }PMe_2Ph"]
\end{tikzcd} \quad (1)$$

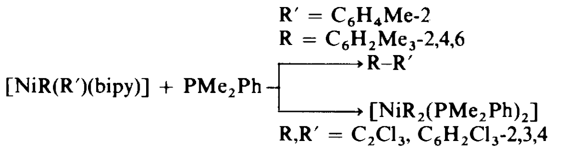
reverse reactions (iv) and (iii), and (ii), (iii) are faster than (i), (iv). This pattern is observed for R $= C_2Cl_3$ and R′ = C_6H_4OMe-4 on following the reaction in both directions by ^{31}P n.m.r. The reaction shifts to the right at room temperature in 45 min and the spectrum does not show the existence of the intermediate. However, for the reverse reaction after 3 h in refluxing benzene, the n.m.r. spectrum shows the presence of $[Ni(C_2Cl_3)(C_6H_4OMe\text{-}4)(PEt_3)_2]$ and signals for the intermediate with two different phosphines. Therefore, $[NiR(R')(PEt_3)_2]$ must be used as a starting material for preparation of the compounds with mixed phosphines. When the formation of the five-co-ordinate intermediate is sterically plausible, the reaction depends on electronic rather than steric factors according to the cone angles of the two phosphines.[17] The *trans* effect of PEt_3 is greater than that of PMe_2Ph. For the cobalt complexes $[CoR_2L_2]$ a similar behaviour is observed.[18]

A similar behaviour is observed for the substitution reaction with the free bidentate ligands dppe and bipy. The starting compounds remain unaltered except in the reaction between dppe and the PMe_2Ph complexes. In this case the substitution yields $[NiCl(C_2Cl_3)(dppe)]$ from $[NiCl(C_2Cl_3)(PPh_3)_2]$, but the disubstituted compound decomposes readily under these conditions and only the coupling products R–R′ are recovered.

A similar behaviour has been observed in the substitution reaction of $[Ni(aryl)_2(PEt_3)_2]$ with dmpe ($Me_2PCH_2CH_2PMe_2$).[19]

The reaction between $[Ni(C_6H_2Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)(bipy)]$ and PMe_2Ph was followed by ^1H n.m.r. spectroscopy. Only the signals of the starting product and the coupling product, ($2,4,6\text{-}Me_3C_6H_2\text{–}C_6H_4Me\text{-}2$), are observed during the course of the reaction. Decomposition is complete after 10 h. In this case the presence of free phosphine seems to favour the decomposition process since if the reaction is carried out in the absence of free ligand, decomposition only reaches 18%. The same behaviour has been observed by Yamamoto *et al.*[20] in the reactions of $[NiR_2(bipy)]$ and olefins. The presence of phosphines also favours the reductive elimination of $[NiMe(C_6H_4X)(dmpe)]$.[19]

The course of the reaction depends on the pathway followed by the five-co-ordinate intermediate (Scheme).[21] The reductive elimination is the most favourable pathway when the R,R′ groups are of low electron affinity; similarly, for the direct elimination in $[NiR_2L_2]$, Hoffmann[22] has proposed that the better the σ-bonding ability of the leaving group the more readily the elimination reaction proceeds. No intramolecular exchange of phosphines takes place when an equimolar mixture of $[Ni(C_2Cl_3)(C_6H_4Me\text{-}2)(PMe_2Ph)_2]$ and $[Ni(C_2Cl_3)(C_6H_4Me\text{-}2)(PEt_3)_2]$ in benzene is refluxed for 15 h. The ^{31}P spectra of the benzene solutions washed with 1% HCl show only the signals of the starting compounds. On the other hand, an equimolar mixture of $[NiCl(C_2Cl_3)(PMe_2Ph)_2]$ and $[NiCl(C_2Cl_3)(PEt_3)_2]$ in benzene under the same conditions afforded $[NiCl(C_2Cl_3)(PMe_2Ph)(PEt_3)]$. The ^{31}P spectra of the solutions show signals for the two *trans* phosphines and one corresponding to a small amount of $[NiCl(C_2Cl_3)(PMe_2Ph)_2]$. When the benzene solution of the same mixture is left to stand at room temperature very little exchange is observed after 5 h, but if carbon monoxide is then bubbled through it for 5 min the exchange is strongly accelerated. The exchange may be initiated by free phosphine produced by partial decomposition of the complexes and follows the same substitution pattern as with free phosphine. The compounds $[NiCl(C_2Cl_3)L_2]$ ($L = PMe_2Ph$ and PEt_3) are recovered in 100 and 92% yield respectively, after 15 h in refluxing benzene under nitrogen. Therefore, the slight excess of $[NiCl(C_2Cl_3)(PMe_2Ph)_2]$ observed despite having started with equimolecular amounts of the two complexes $[NiCl(C_2Cl_3)L_2]$ may be related to the greater stability of the compound containing PMe_2Ph. Phosphine exchange is also observed with mixtures of $[NiCl(C_2Cl_3)(PMe_2Ph)_2]$ and $[Ni(C_6H_4Cl\text{-}2)(C_6H_4Me\text{-}4)(PEt_3)_2]$. These results are in good agreement with the observations of Wada *et al.*[23] on complexes of this type. In the case of the compounds $[NiX(R)L_2]$, the intermolecular exchange may in part occur *via* binuclear species, but this pathway is not possible with $[NiR(R')L_2]$ complexes.



Scheme.

Thermal Decomposition of the Complexes $[NiR(R')L_2]$ *in Solution.*—The thermal decomposition reactions of some of the complexes prepared, $[NiR(R')L_2]$, have been studied. The compounds partially decompose under the conditions used (15 h reflux, under nitrogen), see Table 6. At least, 85% of the products are coupling products R–R′. In some cases coupling products R–R, or reduction products R–H arising from homolytic cleavage of the M–C bond, are observed. The effect of some additives has also been studied. The nickel arising from the decomposition of the organometallic is recovered as a black powder except when the complex contains the organic group

Table 6. Thermal decomposition reactions

Compound	Additive	% Decomposition	Decomposition mechanism*
$[Ni(C_2Cl_3)(C_6H_4Me\text{-}2)(PEt_3)_2]$		36	100% R-R′
$[Ni(C_6H_4Cl\text{-}2)(C_6H_4Me\text{-}2)(PEt_3)_2]$		40	100% R-R′
	O_2	58	100% R-R′
$[Ni(C_6H_4Me\text{-}2)Ph(PEt_3)_2]$		46	100% R-R′
	$NiBr_2$	62	100% R-R′
	PEt_3	36	85% R-R′ 15% R-H + R′-H
$[Ni(C_6H_4Me\text{-}2)(C_6H_4Me\text{-}4)(PEt_3)_2]$		59	91% R-R′ 9% R-H + R′-H
$[Ni(C_6H_4Cl\text{-}2)(C_6H_4Me\text{-}4)(PEt_3)_2]$		24	100% R-R′
$[Ni(C_6H_2Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)(PEt_3)_2]$		82	94% R-R′ 6% R-H + R′-H
$[Ni(C_2Cl_3)(C_6H_4Me\text{-}2)(PMe_2Ph)_2]$		14	100% R-R′
$[Ni(C_6H_4Cl\text{-}2)(C_6H_2Me_3\text{-}2,4,6)(PMe_2Ph)_2]$		8	92% R-R′ 8% R-H + R′-H
$[Ni(C_6H_2Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)(PMe_2Ph)_2]$		20	97% R-R′ 3% R-H + R′-H
$[Ni(C_6H_2Me_3\text{-}2,4,6)Ph(PMe_2Ph)_2]$		28	87% R-R′ 13% R-H + R′-H
	O_2	30	94% R-R′ 6% R-H + R′-H
$[Ni(C_6H_4Cl\text{-}2)(C_6H_4Me\text{-}2)(PMe_2Ph)_2]$		40	100% R-R′
	$NiBr_2$	51	100% R-R′
	PMe_2Ph	22	100% R-R′
$[Ni(C_6H_2Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)(bipy)]$		18	100% R-R′

* Percentage by reductive elimination or homolytic cleavage.

C_2Cl_3; in this case a red solution (365—370 nm), which probably contains the complex $[NiCl_2L_2]$, is formed. The phosphine is recovered at the end of the reaction as phosphine oxide or free phosphine. The amount of phosphonium salts which can be formed is negligible since the mass balance for R and R′ amounts to about 95%. Practically no decomposition occurs (1%) for $[Ni(C_2Cl_3)(C_6H_2Me_3\text{-}2,4,6)(PMe_2Ph)_2]$ under the conditions used.

If the thermal decomposition reaction is carried out in n-heptane (same boiling point as benzene) the rate of decomposition is approximately twice that in benzene. The reaction products are similar, with a slightly higher ratio of R–H to R–R′. The decomposition rate decreases if free phosphine is added, in agreement with the accepted mechanism for reductive-elimination processes [equation (2)].[24] The homolytic cleavage

$$[NiR(R')L_2] \longrightarrow \text{`}NiR(R')L\text{'} + L \longrightarrow R\text{–}R'(+RH) \quad (2)$$

can take place directly in the four-co-ordinate complex; therefore, for complexes having a weak M–C bond an increase in the amount of R–H should be observed on adding free ligand. The nature of the three-co-ordinate intermediate is not well defined; its stabilization could be achieved by co-ordination of solvent molecules. Although reductive elimination in a three-co-ordinate species with a trigonal-planar geometry is forbidden by symmetry,[21] it seems necessary that for concerted elimination to take place the ligands should occupy adjacent positions. The process is very sensitive to the configuration of the metal atom. Organometallics with square-planar geometry $[Co(C_6Cl_5)_2L_2]$[25] (L = phosphine or amine) and with tetrahedral geometry $[Co(C_6F_5)_2(bipy)]$[26] decompose giving homolytic cleavage products R–H, but $[NiR(R')L_2]$ give coupling products R–R′.

The addition of $NiBr_2$ or O_2 to the reacting mixtures produces the same effect for the complexes $[NiR(R')L_2]$ irrespective of the stabilizing ligand. Both reagents act as phosphine scavengers either by complexation or by oxidation. The effect is greater for the PEt_3 complexes in accord with their greater rate of decomposition. When reductive-elimination products are observed in the course of the thermal decomposition reactions, it is also observed that O_2 increases the relative amount of coupling products due probably to oxidation of the nickel intermediate.

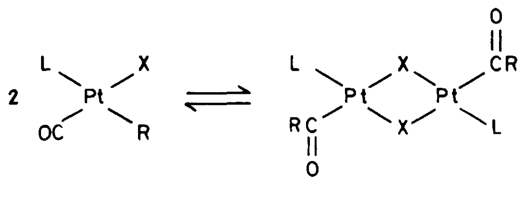
A confirmation of the intramolecular character of these processes comes from the isotopic double-labelling studies by Kochi.[24] In our case, the thermal decomposition of the complexes $[NiR(R')L_2]$ does not lead to the formation of coupling products R–R or R′–R′, indicating that the process must be intramolecular. Some Ph–Ph is formed in the thermal decomposition of $[Ni(C_6H_2Me_3\text{-}2,4,6)Ph(PMe_2Ph)_2]$, but on carrying out the same reaction in heptane, approximately the same amount is formed, indicating that the biphenyl is formed by transfer from the phosphine to the ligand R or by coupling of the phenyl liberated by homolytic cleavage.

It is apparent from Table 6 that the complexes with L = PEt_3 decompose faster than those with L = PMe_2Ph. When the decomposition rates of complexes $[NiR(R')L_2]$ (with the same R and L) are compared it is observed that the rates decrease with increase in both the electronegativity and the steric crowding of the organic ligands, with the exception of that for $[Ni(C_6H_2Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)(PEt_3)_2]$. The formation of R–H depends on the electronegativity of the organic ligands and on their size. The only organometallic with chlorinated organic ligands which gives R–H is $[Ni(C_6H_4Cl\text{-}2)(C_6H_2Me_3\text{-}2,4,6)(PMe_2Ph)_2]$. Formation of homolytic cleavage products is also observed when one of the ligands is mesityl. Therefore, it seems that the coupling process will be more hindered on increasing the size of the organic ligands, and that the unsaturated intermediate is stabilized on increasing the electronegativity of the organic groups. The *cis* arrangement of the ligands R and R′ favours the reductive-elimination process, as suggested by the products of thermal decomposition of the complexes $[Ni(C_6H_2Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)L_2]$ (L = PEt_3, PMe_2Ph, or $\frac{1}{2}$bipy).

Therefore, the relative stability of the organometallics depends basically on the dissociation of the neutral ligand, which is favoured both when the ligands are more basic and when the attack of the solvent is less hindered. The nature of the decomposition products depends on the stability of the metal–carbon σ bond in the three-co-ordinate intermediate or in the complex itself. An increase in the basicity of the ligands lowers this stability in both cases, although it is also possible that the steric crowding may hinder the coupling reaction.

Carbon Monoxide Insertion Reactions.—The formation of aroyl derivatives and organic decomposition products incorporating CO is accepted to occur *via* a process of migration of R towards CO. The reaction has been widely studied in square-planar compounds $[MX(R)L_2]$ by Garrou and Heck[27] and Anderson and Cross.[28] Direct insertions from five-co-ordinate adducts like $[PtI(Ph)(CO)(PR_3)_2]$[29] have been found to take place, also from four-co-ordinate species $[MX(R)L(CO)]$ obtained *via* ligand displacement.

A careful study of the equilibrium (3) seems to indicate that



(3)

the process occurs by migration of R. However, a direct insertion from five-co-ordinate species predominates with more basic phosphines as they are difficult to exchange with CO.

The corresponding ketones are always obtained on treating the compounds $[Ni(C_6Cl_5)R'(PMe_2Ph)_2]$[3d,30] or $[NiR_2L_2]$ (R = alkyl)[31] with an excess of CO, and in some cases (and depending on the reaction temperature) even the diketones RCOCOR can be isolated.[31]

The reactions of the compounds $[NiR(R')L_2]$ prepared in this work were carried out in benzene or acetone; the effect of the temperature is important when acyl derivatives are formed since the decomposition processes are slow at low temperature. The reaction takes place *via* a pathway analogous to that described in the literature.[27,28] The mesityl derivatives decompose more slowly than the other compounds, due probably to the steric hindrance of this ligand which inhibits the formation of the five-co-ordinate intermediate. Only the signals of the starting complex and decomposition products, assigned to $[Ni(CO)_3(PMe_2Ph)]$ and $[Ni(CO)_2(PMe_2Ph)_2]$, are observed on monitoring the reaction between $[Ni(C_2Cl_3)(C_6H_4Me\text{-}2)(PMe_2Ph)_2]$ and CO in benzene at +5 °C by ^{31}P n.m.r. spectroscopy. Signals indicating formation of acyl derivatives in detectable amounts are not observed in any case. Therefore, the presence of *ortho* substituents in the organic groups R and R′ must prevent stabilization of the acyl derivatives, and only the corresponding ketones are formed. The presence of diketones has not been detected either by gas chromatography or by mass spectrometry. Strongly electronegative groups such as C_6Cl_5, C_2Cl_3, or $C_6H_3Cl_2\text{-}2,3$ do not undergo insertion under these conditions. Accordingly, acetone solutions of $[NiCl(R)L_2]$ (L = PMe_2Ph or PEt_3; R = $C_6H_3Cl_2\text{-}2,3$ or C_2Cl_3) are unchanged when treated with CO at atmospheric pressure for 6 h at room temperature. However, the acyl derivatives of the compounds with ligands C_6Cl_5 or C_2Cl_3 are stabilized when the *trans* ligand is aromatic, and does not have *ortho* or *para* electron-withdrawing groups.

The reactions of [Ni(C_2Cl_3)(C_6H_4OMe-4)($PMe_2Ph)_2$] and [Ni(C_2Cl_3)Ph($PEt_3)_2$] with CO were followed by ^{31}P n.m.r. spectroscopy. The signals of the starting products completely disappear after 30 min and two signals of similar intensity (assignable to the two possible isomers of the acyl derivative) appear. Subsequently, these two signals also disappear and two others assignable to [Ni(CO)$_2L_2$] and [Ni(CO)$_3$L] appear at $\delta = +22.57$ and $+21.45$ for L = PEt_3 and at -4.59 and -6.74 for L = PMe_2Ph. The ratio [Ni(CO)$_2L_2$]:[Ni(CO)$_3$L] observed is 9:1 although the amount of [Ni(CO)$_3$L] increases with the handling of the samples. Signals assignable to the five-co-ordinate species were not observed. The products [Ni(C_2Cl_3)(COPh)($PEt_3)_2$] [δ(P) = 10.03 and 10.38 p.p.m.] and [Ni(C_2Cl_3)(COC$_6H_4$OMe-4)($PEt_3)_2$] [δ(OMe) = 3.24 and 3.23 p.p.m.] have been isolated as solids and characterized. The reaction probably takes place by direct insertion of CO in the initial five-co-ordinate species, since the phosphines PMe_2Ph and PEt_3 are basic enough to exclude the possibility of displacement by CO. However, the acceleration observed in the phosphine exchange in the presence of CO seems to indicate that such displacement occurs to some degree.

According to Garrou and Heck,[27] [Ni(CO)$_2L_2$] is formed due to direct insertion in the five-co-ordinate species, and [Ni(CO)$_3$L] is formed *via* the intermediate [NiX(R)L(CO)]. Thus, the decomposition products obtained indicate that a major pathway for the reaction is direct insertion in the five-co-ordinate species.

The acyl derivatives slowly decarbonylate in the solid state. If CO is bubbled through a benzene solution of [Ni($C_6H_2Me_3$-2,4,6)(C_6H_4Me-2)(bipy)] at 5 °C, the corresponding ketone is not detected and the only decomposition product obtained is 2,4,6-$Me_3C_6H_2$–C_6H_4Me-2. The decomposition reaction is extremely slow; after 6 h some starting product still remains. No other species are detected by proton n.m.r. spectroscopy; therefore, the complex is labilized in the presence of CO, undergoing reductive elimination rather than insertion. However, the complexes [NiR$_2L_2$] (R = alkyl; L = bipy or dppe)[31] give the corresponding ketones.

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