Lithiation and Intermolecular Exchange of Tertiary Methylphosphines in *trans*-$[NiR_2L_2]$, where R = 2,6-Dimethoxyphenyl

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2,6-Dimethoxyphenylnickel(II) complexes, *trans*-$[NiR_2L_2]$ [R = $C_6H_3(OMe)_2$-2,6; L = PMe_3, PMe_2Ph, and $PMePh_2$] and *trans*-$[NiR(Cl)L_2]$ (L = PMe_3, PMe_2Ph, and PPh_3) have been prepared from $[NiCl_2L_2]$ and LiR. Reactions of n-butyl-lithium with *trans*-$[NiR_2L_2]$ (L = PMe_3 and PMe_2Ph) in diethyl ether resulted in the facile lithiation at the methyl carbon in the L ligands, giving *trans*-$[NiR_2\{PMe_2(CH_2SiMe_3)\}_2]$ and *trans*-$[NiR_2\{PMePh(CH_2SiMe_3)\}_2]$, respectively, after treatment with $SiMe_3Cl$. The complexes *trans*-$[NiR(C_6H_2Me_3\text{-}2,4,6)(PMe_3)\{PMe_2(CH_2SiMe_3)\}]$ and *trans*-$[Ni(C_6H_2Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)\{PMe_2(CH_2SiMe_3)\}_2]$ were obtained from the corresponding PMe_3 complexes by analogous reactions in the presence of *NNN'N'*-tetramethylethylenediamine. Intermolecular tertiary phosphine exchanges have been observed between *trans*-$[NiR_2L_2]$ complexes [L = PMe_3, PMe_2Ph, $PMe_2(CH_2SiMe_3)$, and $PMePh(CH_2SiMe_3)$], as well as between *trans*-$[NiR(Cl)L_2]$ complexes, on heating their benzene solutions or on treatment with carbon monoxide. The possible mechanisms are discussed briefly.

ALTHOUGH σ-bonded organonickel(II) complexes are, in general, highly reactive and often difficult to isolate, certain complexes of types *trans*-$[NiR_2L_2]$ and *trans*-$[NiR(X)L_2]$ are relatively stable and isolable when the R groups are *ortho*-substituted aromatic groups.[1] In continuation of our own studies in this area,[2] we have investigated the preparation and properties of 2,6-dimethoxyphenylnickel(II) complexes including their reactions with n-butyl-lithium and their thermal properties. Parts of the present results have been reported in a short communication.[3]

RESULTS AND DISCUSSION

Preparation of trans-$[NiR_2L_2]$ *and trans*-$[NiR(Cl)L_2]$ *Complexes*.—Reactions of $[NiCl_2L_2]$ (L = PMe_3 or PMe_2Ph) with an excess of 2,6-dimethoxyphenyl-lithium (LiR, hereafter) in diethyl ether afforded *trans*-$[NiR_2(PMe_3)_2]$ (1a) and *trans*-$[NiR_2(PMe_2Ph)_2]$ (1b) in good yields, but $[NiCl_2(PMePh_2)_2]$ gave a mixture of *trans*-$[NiR_2(PMePh_2)_2]$ (1c) and the reductive elimination product R_2. With 1 mol equivalent of LiR, the monosubstituted complexes *trans*-$[NiR(Cl)L_2]$ [L = PMe_3 (2a) or PMe_2Ph (2b)] could be obtained. The analogous complex with L = PPh_3 (2d) was the sole arylnickel(II) complex isolated from the reaction of $[NiCl_2(PPh_3)_2]$ and an excess of LiR.

The ^1H n.m.r. spectra of these complexes comprised the expected resonances for the R and L ligands with the correct ratio of intensities. The PMe proton resonance of tertiary methylphosphine ligands was a 1 : 2 : 1 triplet due to virtual coupling, J_P *ca.* 7—8 Hz. The spectral data of the new complexes are summarized in Table 1, together with those prepared in the following reactions.

Lithiation of Co-ordinated Tertiary Methylphosphine Ligands.—Since methoxyphenyl derivatives are well known to be lithiated by n-butyl-lithium *ortho* to the

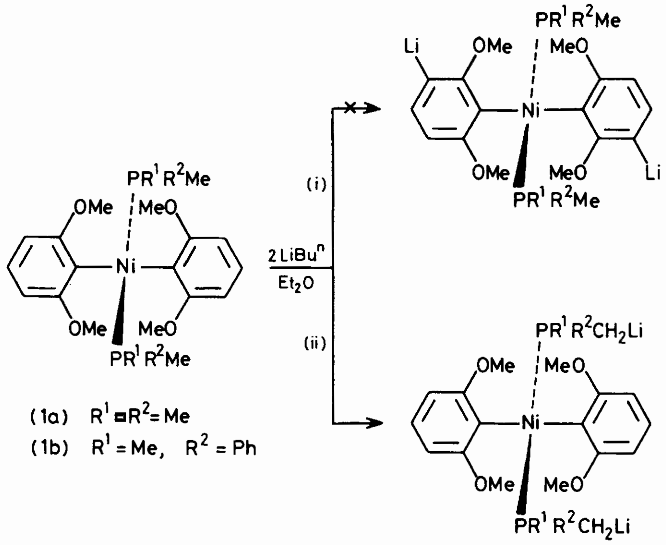
TABLE 1

Hydrogen-1 n.m.r. spectral data for organonickel(II) complexes [a]

Complex	Solvent	Chemical shifts [b]
(1a)	$CDCl_3$	6.89 (tqt, 2 H, *p*-H, $[8]_H$, $[1.5]_P$), 6.29 (d, 4 H, *m*-H, $[8]_H$), 3.96 (s, 12 H, OMe), 0.75 (t, 18 H, PMe, [7.5])
(1c)	CH_2Cl_2	7.6—7.3 and 7.2—6.9 (m, 20 H, Ph), 6.55 (br t, 2 H, *p*-H, $[8]_H$), 5.76 (d, 4 H, *m*-H, $[8]_H$), 3.38 (s, 12 H, OMe), 1.22 (t, 6 H, PMe, $[7]_P$)
(2a)	CH_2Cl_2	6.86 (br t, 1 H, *p*-H, $[8]_H$), 6.23 (d, 2 H, *m*-H, $[8]_H$), 3.83 (s, 6 H, OMe), 0.95 (t, 18 H, PMe, $[8]_P$)
(2d)	CH_2Cl_2	7.66 (m) and 7.30 (m) (30 H, Ph), 3.24 (s, 6 H, OMe)
(3a)	$CDCl_3$	6.91 (br t, 2 H, *p*-H, $[7.5]_H$), 6.29 (d, 4 H, *m*-H, $[7.5]_H$), 3.86 (s, 12 H, OMe), 0.79 (t, 12 H, PMe, $[7.5]_P$), 0.67 (t, 4 H, PCH_2Si, $[10]_P$), −0.07 (s, 18 H, SiMe)
(3b) *meso*	$CDCl_3$	7.2—6.7 (m, 12 H, Ph and *p*-H), 6.14 (d, 2 H, *m*-H, $[8]_H$), 6.03 (d, 2 H, *m*-H, $[8]_H$), 3.69 (s, 6 H, OMe), 3.47 (s, 6 H, OMe), 1.04 (t, 6 H, PMe, [7]), 0.96 (t, 4 H, PCH_2Si, $[11]_P$), −0.30 (s, 18 H, SiMe)
rac	$CDCl_3$	7.2—6.7 (m, 12 H, Ph and *p*-H), 6.08 (d, 4 H, *m*-H, $[8]_H$), 3.58 (s, 12 H, OMe), 1.04 (t, 6 H, PMe, $[7]_P$), 0.96 (t, 4 H, PCH_2Si, $[11]_P$), −0.30 (s, 18 H, SiMe)
(4)	$CDCl_3$	6.93 (br t, 1 H, *p*-H, $[8]_H$), 6.54 (s, 2 H, *m*-H), 6.27 (d, 2 H, *m*-H, $[8]_H$), 3.74 (s, 6 H, OMe), 2.65 (s, 6 H, *o*-Me), 2.16 (s, 3 H, *p*-Me), 0.75 (t, 18 H, PMe, $[7]_P$)
(5)	$CDCl_3$	6.93 (br t, 1 H, *p*-H, $[8]_H$), 6.55 (s, 2 H, *m*-H), 6.27 (d, 2 H, *m*-H, $[8]_H$), 3.74 (s, 6 H, OMe), 2.67 (s, 6 H, *o*-Me), 2.16 (s, 3 H, *p*-Me), 0.79 (d, 2 H, PCH_2Si, $[9]_P$), 0.75 (d, 6 H, PMe_2, $[7]_P$), 0.73 (d, 9 H, PMe_3, $[7]_P$), −0.11 (s, 9 H, SiMe)
(7)	CH_2Cl_2	7.47 (br d, 1 H, *o*-H, $[6]_H$), 6.9—6.7 (m, 3 H Ph), 6.56 (s, 2 H, *m*-H), 2.68 (s), 2.65 (s), and 2.62 (s) (9 H, *o*-Me), 2.14 (s, 3 H, *p*-Me), 0.81 (t) and 0.74 (t) (16 H, PMe and PCH_2Si, $[6.5]_P$), −0.09 (s, 18 H, SiMe)
(8)	CH_2Cl_2	7.49 (br d, 1 H, *o*-H, $[6]_H$), 6.9—6.7 (m, 3 H, Ph), 6.58 (s, 2 H, *m*-H), 2.66 (s, 3 H, *o*-Me), 2.61 (s, 6 H, *o*-Me), 2.13 (s, 3 H, *p*-Me), 1.34—1.04 (m, 3 H, CMe), 0.99—0.62 (m, 17 H, PMe and PCH_2)
(10a)	$CDCl_3$	7.38 (t, 2 H, *p*-H, $[1.5]_P$), 4.20 (s, 12 H, OMe), 0.92 (t, 18 H, PMe, $[7.5]_P$)

[a] Data for (1b),[15] (2b),[17] (6),[2] and (10b)[15] have been reported previously. s = Singlet, d = doublet, t = triplet, m = multiplet, tqt = triplet plus quartet plus triplet of AB_2X_2 pattern, br = broad. [b] δ In p.p.m., J_H or J_P (in Hz) given in square brackets.

methoxy-group,[4] we attempted the reaction for complexes (1a)—(1c) in order to obtain the 3-lithiated intermediates [path (i), Scheme].



SCHEME

Treatment of (1a) with an excess of n-butyl-lithium in dry diethyl ether at 0 °C under nitrogen gave a light yellow precipitate in a few minutes. This was first treated with D_2O. The ^1H n.m.r. spectrum of deuteriated (1a) was essentially identical with that of (1a), but showed a decrease in the intensity of the PMe_3 proton resonances by *ca.* two protons. When the lithiated intermediate was treated with $SiMe_3Cl$, an air-stable orange-yellow crystalline complex *trans*-$[NiR_2\{PMe_2(CH_2SiMe_3)\}_2]$ (3a) was obtained. The formation of (3a) is confirmed by the magnetic equivalence of the four methoxy-protons and the observation of a virtually coupled PCH_2Si proton resonance in addition to those of PMe. These observations suggest that a proton was abstracted by n-butyl-lithium from the PMe_3 ligands rather than from the R groups [path (ii), Scheme]. Complex (3a) was treated with carbon monoxide (1 atm *) in the presence of MeI and decomposed, in less than 2 h at room temperature, to give R_2CO and the $[PMe_3(CH_2SiMe_3)]^+$ salt.

Reaction of (1b) with n-butyl-lithium followed by treatment with $SiMe_3Cl$ gave an analogous complex *trans*-$[NiR_2\{PMePh(CH_2SiMe_3)\}_2]$ (3b), but as a mixture of the *meso*- and *rac* isomers with respect to the two asymmetric phosphine ligands. These can be readily distinguished in the ^1H n.m.r. spectra, since the four methoxy-groups of the *rac* isomer are magnetically identical, but those on the same phenyl group of the *meso*-isomer are non-equivalent. The relative *meso* : *rac* ratio was 62 : 38 for the initial product and varied in the recrystallized fractions, the *rac* isomer being more soluble. Complex (1c) in diethyl ether decomposed on addition of n-butyl-lithium, and no further work was performed with it.

On treating (3a) further with n-butyl-lithium followed by D_2O, *trans*-$[NiR_2\{PMe_2(CHDSiMe_3)\}_2]$ was obtained, as is evident from the observation of a weak and broad ^1H n.m.r. signal for the PCH_2Si protons. A similar higher reactivity of PCH_2Si than PMe protons is known for $[PMe_3(CH_2SiMe_3)]^+$ derivatives.[5-7]

We have extended the reaction to some other diarylnickel(II) complexes. The complex *trans*-$[NiR(C_6H_2Me_3\text{-}2,4,6)(PMe_3)_2]$ (4) reacted with n-butyl-lithium very slowly. The diethyl ether solution yielded a precipitate only *ca.* 2 h after mixing at room temperature. When this was treated with D_2O after 16 h of reaction, the ^1H n.m.r. spectrum of the product showed a decrease in intensity of the PMe_3 protons only by one proton. Thus, under these conditions the lithiated intermediate must be monolithiated. When (4) was treated with n-butyl-lithium in the presence of *NNN'N'*-tetramethylethylenediamine for 22 h at room temperature and then with $SiMe_3Cl$, a monosilylated complex *trans*-$[NiR(C_6H_2Me_3\text{-}2,4,6)(PMe_3)\{PMe_2(CH_2SiMe_3)\}]$ (5) was obtained. The ^1H n.m.r. spectrum of (5) exhibited three doublets in the PMe proton region, which are assignable to PMe_3, PMe_2, and PCH_2Si protons based on the relative intensities (Table 1). This indicates that the virtual coupling is resolved in the mixed tertiary phosphine ligand complex. The OMe protons were magnetically identical.

The complex *trans*-$[Ni(C_6H_2Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)(PMe_3)_2]$ (6) reacted with n-butyl-lithium also very slowly. So, the same reaction was carried out in the presence of *NNN'N'*-tetramethylethylenediamine, followed by addition of D_2O. The ^1H n.m.r. spectrum of the product showed a decrease in intensity of the PMe_3 protons by two protons, suggesting a double lithiation. In fact, the silylation product was well characterized as *trans*-$[Ni(C_6H_2Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)\{PMe_2(CH_2SiMe_3)\}_2]$ (7). When the lithiated intermediate of (6) was treated with MeI, *trans*-$[Ni(C_6H_2Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)(PMe_3)(PMe_2Et)]$ (8) was obtained, probably due to the lower reactivity of the second PMe_2CH_2Li group.

No report of unambiguous proton abstraction from a co-ordinated tertiary methylphosphine has yet appeared,[8] although proton abstractions from free tertiary phosphines [9] and co-ordinated diphosphines [10] have been discussed. The present results clearly indicate that proton abstraction by n-butyl-lithium from tertiary-methylphosphine co-ordinated to a transition metal has occurred even when there are other available sites for lithiation. The high reactivity of (1a) and (1b) is probably due to the presence of four methoxy-groups, which increase the reactivity of n-butyl-lithium by co-ordination, and/or which stabilize the lithiated intermediate by forming bicyclic rings with *COO*-chelated lithium ion, both above and below the nickel(II) co-ordination plane. The difficult double lithiation of (4) is tentatively attributed to the steric interference by the bulky aryl groups.

Thermal Properties and Intermolecular Tertiary Phos-

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

phine Exchanges.—The trimethylphosphine complex (1a) is stable in benzene, and no apparent change was observed in the ^{1}H n.m.r. spectrum after heating in a sealed glass tube at 100 °C for 6 h. The dimethylphenylphosphine complex (1b) gave a dark turbid solution under the same conditions, the spectrum of which showed the presence of (1b) and R_2 in a ratio of 83 : 17. The methyldiphenylphosphine complex (1c) decomposed almost completely at 65 °C in less than 3 h, but is stable at 40 °C at least for 5 h.

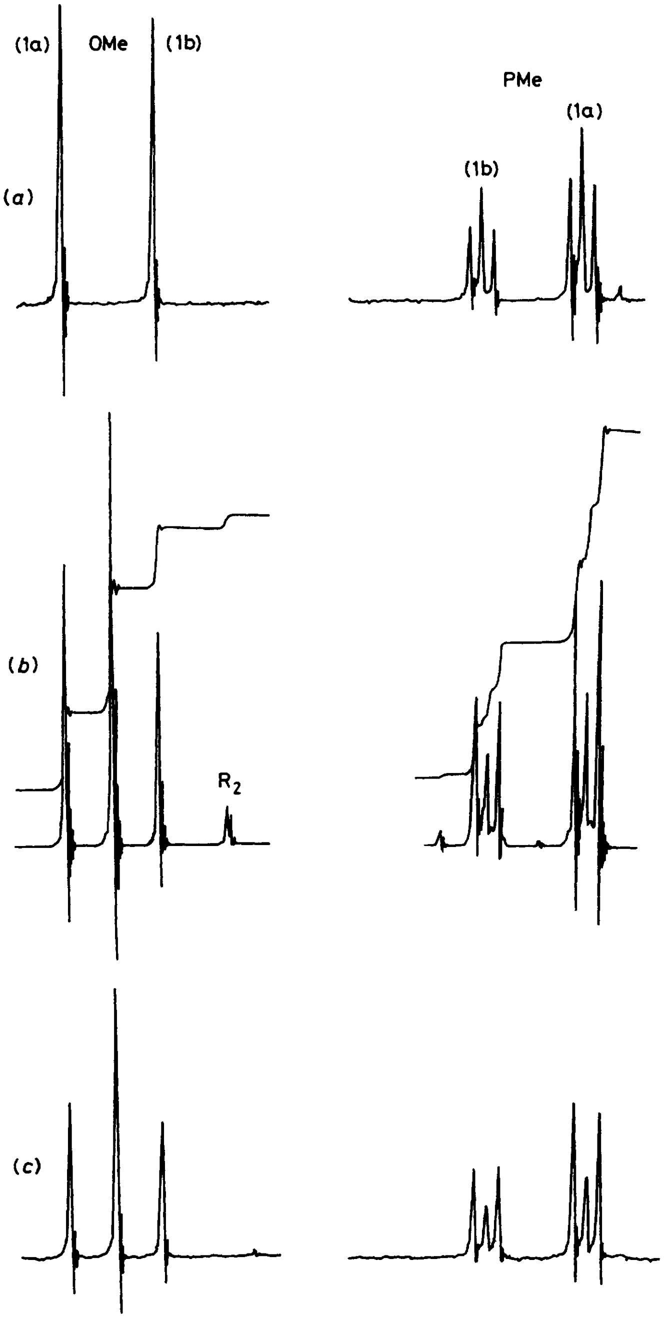
When an 84 : 16 mixture of the *meso*- and *rac* isomers of (3b) was heated in benzene (0.1 mol dm^{-3}) at 65 °C, the isomer ratio varied with time, yielding a 52 : 48 mixture in 3 h. The decomposition product R_2 was formed in *ca.* 4% yield. We had some difficulties in carrying out a precise kinetic study for this isomerization [equation (i)] by ^{1}H n.m.r. spectroscopy due to the proximity of the OMe proton resonances and to the formation of paramagnetic decomposition products on prolonged heating, but a value of $k_f = (1.0 \pm 0.1) \times 10^{-4}\ \text{s}^{-1}$ was obtained at 65 °C over 1—2.5 half-lives assuming $k_f = k_r$.

$$\text{(3b) } (\textit{meso}) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \text{(3b) } (\textit{rac}) \qquad \text{(i)}$$

$$\textit{trans}\text{-}[\mathrm{NiR_2L_2}] + \textit{trans}\text{-}[\mathrm{NiR_2L'_2}] \rightleftharpoons 2\ \textit{trans}\text{-}[\mathrm{NiR_2L(L')}] \qquad \text{(ii)}$$

This result suggests that there is an intermolecular exchange of the co-ordinated tertiary phosphine, as shown in the general equation (ii). In order to confirm this, two complexes (1a) and (1b) were heated together in benzene (0.05 + 0.05 mol dm^{-3}) for 4 h at 100 °C. The ^{1}H n.m.r. spectrum (see Figure) of the filtrate of the resultant turbid solution showed a new OMe proton resonance (δ 3.64 p.p.m.) between those due to (1a) and (1b), and another due to R_2. The intensity ratio for these resonances was 26 : 46 : 20 : 8 in order of increasing magnetic field. The spectrum in the region of the PMe protons also varied on heating; each central resonance of the initial 1 : 2 : 1 triplets decreased in intensity and, at the same time, the intensity of each terminal resonance increased. The new OMe proton resonance at δ 3.64 p.p.m. may be attributed to the mixed-ligand complex *trans*-[NiR$_2$(PMe$_3$)(PMe$_2$Ph)] (9), and its PMe proton resonances must be two doublets.

The above reaction is catalyzed by carbon monoxide. Thus, when carbon monoxide (5 cm^3) was bubbled into a 50 : 50 solution of (1a) and (1b) at room temperature we obtained a ^{1}H n.m.r. spectrum (see Figure) analogous to that obtained from the thermal reaction. The ratio of (1a) : (9) : (1b) reached *ca.* 25 : 50 : 25 in less than 3 min after bubbling CO. The PMe proton resonances also varied from two 1 : 2 : 1 triplets to two *ca.* 3 : 2 : 3 triplets. The ^{31}P-{^{1}H} n.m.r. spectrum showed two resonances [δ −2.30 (1a) and −10.78, upfield from H$_3$PO$_4$] before treatment with carbon monoxide and four resonances (δ −2.39, −4.63, −9.19, and −10.72) with almost identical intensities after the treatment. We have obtained no spectroscopic evidence for the formation of other species such as aroylnickel(II) complexes, although (1a) and (1b) decompose under carbon monoxide in the presence of MeI, giving R_2CO and the phosphonium salt. Other bases such as pyridines, trimethyl phosphite, or *N*-methylimidazole showed no such catalytic effect as carbon monoxide. We experienced difficulties in the isolation of (9) in a pure form, although a 26 : 65 : 9 mixture of (1a), (9), and (1b) could be obtained after repeated



OMe and PMe regions of the ^{1}H n.m.r. spectra of *trans*-[Ni{C$_6$H$_3$(OMe)$_2$-2,6}$_2$(PMe$_3$)$_2$] (1a) (0.05 mol dm^{-3}) + *trans*-[Ni{C$_6$H$_3$(OMe)$_2$-2,6}$_2$(PMe$_2$Ph)$_2$] (1b) (0.05 mol dm^{-3}) in benzene: (*a*) at room temperature, (*b*) after heating at 100 °C for 4 h, and (*c*) after CO bubbling at room temperature fractional recrystallizations from acetone–methanol at low temperatures.

Mixed solutions of (1a) and (3a), of (1b) and (3a), as well as of (1a) and (1b) reacted slowly in an analogous manner at 81 °C, and the amounts of the mixed-ligand complexes formed in 3 h were *ca.* 10, 32, and 13.5%, respectively. A small amount of R_2 was detected (0.5—2.0%) in each case. Mixed solutions containing (1c) gave turbid decomposition mixtures at 65 °C, and did not react at 40 °C.

A similar intermolecular tertiary phosphine exchange between *trans*-[NiR(Cl)L_2] complexes, (2a) and (2b), took place rapidly at 65 °C, attaining equilibrium ($K = 4.0 \pm 0.2$) in less than 0.5 h, and slowly at room temperature. The reaction between (2a) and (2d) gave an equilibrium solution in *ca.* 3 h at 65 °C ($K =$ *ca.* 10). The large K value probably originates from the steric interaction between the large triphenylphosphine ligands and the *cis* ligands in (2d).

The precise mechanisms of these intermolecular tertiary phosphine exchanges are not known at present. The reactions between *trans*-[NiR_2L_2] complexes can proceed *via* a dissociation of the tertiary phosphine ligand as the initial step, or a partial decomposition which produces a catalytic amount of free tertiary phosphine. Thermal dissociations of tertiary phosphine from d^8 square-planar organometallic complexes to give three-co-ordinate intermediates have been discussed for Pd^{II},[11] Pt^{II},[12] and Au^{I}.[13] On the other hand, the reaction under carbon monoxide may be well explained in terms of the reversible substitution of tertiary phosphine ligands by carbon monoxide, as proposed by Garrou and Heck [14] as the initial steps in the carbonylation of *trans*-[MR(X)L_2] complexes (M = Ni, Pd, or Pt).

In order to obtain some information to distinguish the two possible mechanisms for the thermal intermolecular tertiary phosphine exchanges, a solution of *trans*-[NiR'_2L_2] complexes {R' = $C_6H[(OMe)_2\text{-}2,6]Br_2\text{-}3,5$; L = PMe_3 (10a) or PMe_2Ph (10b)} were studied in an analogous manner. These complexes were obtained by the reactions of (1a) or (1b) with an excess of *N*-bromosuccinimide.[15] When a solution of (10a) and (10b) was heated at 81 °C for 5 h we obtained a non-equilibrated mixture containing (10a), *trans*-[$NiR'_2(PMe_3)(PMe_2Ph)$] (11), (10b), and several decomposition products (not characterized) in a 37 : 18 : 36 : 9 ratio, compared with that obtained from a solution of (1a) and (1b), giving (1a), (9), (1b), and R_2 in a 39 : 24 : 35 : 2 ratio. On the other hand, both (10a) and (10b) are very stable in solutions containing MeI under carbon monoxide, and the mixture gave only 7% of (11) in 3 h under carbon monoxide. These pronounced differences in the reactivities between *trans*-[NiR_2L_2] and *trans*-[NiR'_2L_2] complexes under carbon monoxide may be understood in terms of steric rather than electronic effects. That is, the methoxy methyl groups in (1a) and (1b) can move away from the nickel atom due to possible free rotation about the C–OMe bond, and they do not prevent the attack of small molecules like carbon monoxide on the nickel atom. In complexes (10a) and (10b) the presence of ***meta***-bromine atoms would force the adjacent methoxy methyl group away toward the phosphine ligand and closer to the nickel atom. The nickel atom must be more confined by the four methoxy-groups. If the nickel atom in (10a) and (10b) is still well protected at higher temperatures from the attack of the free tertiary phosphine, the observed thermal intermolecular tertiary phosphine exchange at 81 °C must proceed *via* an initial dissociation of the tertiary phosphine to give a three-co-ordinate intermediate.

The mechanisms of the reactions between *trans*-[NiR(Cl)L_2] complexes need not be the same as above, and there is a possibility of a mechanism comprising an initial formation of a dimeric species [{NiR(Cl)L_2}$_2$] with intermolecular bridging *via* the chloride ligand, from which free tertiary phosphine can be eliminated reversibly. Organonickel(II) complexes of the general type *trans*-[NiR(X)L_2] (R = C_6Cl_5, $C_6H_2Me_3$-2,4,6, or $CCl{=}CCl_2$; X = halide) exchange the X ligand very fast in non-polar solvents, probably through such an intermediate.[16]

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were obtained on a JEOL model JNM-PS-100 spectrometer operating at 100 MHz, using $SiMe_4$ as internal standard. Phosphorus-31 n.m.r. spectra were recorded on a JEOL model JNM-FX-90Q spectrometer operating in the Fourier-transform mode at 90 MHz, using H_3PO_4 as external standard. Infrared spectra were obtained on a Hitachi 215 spectrophotometer. Analytical data for new complexes are given in Table 2.

Preparations.—*trans*-[Ni{$C_6H_3(OMe)_2$-2,6}$_2L_2$], *where* L = PMe_3 (1a), PMe_2Ph (1b), *or* $PMePh_2$ (1c). The preparation

TABLE 2

Analytical and physical data for the complexes

Complex	M.p. (θ/°C)	Analysis (%) [a] C	Analysis (%) [a] H
(1a)	183 (decomp.)	54.4 (54.5)	7.7 (7.5)
(1c)	138 (decomp.)	68.9 (68.8)	6.1 (6.1)
(2a)	178—179	43.7 (43.9)	7.3 (7.1)
(2d)	195 (decomp.)	69.9 (69.9)	5.3 (5.2)
(3a)	87—88	53.3 (53.4)	8.4 (8.3)
(3b)	120—121 [b] 102—104 [c]	60.6 60.6 (60.6)	7.6 7.6 (7.5)
(4)	175—177	59.1 (59.1)	8.3 (8.2)
(5)	98—100	58.0 (57.9)	8.4 (8.6)
(7)	66—68	59.6 (59.5)	9.3 (9.3)
(8)	149—151	63.5 (63.6)	8.8 (8.7)
(10a)	194 (decomp.) [d]	33.0 (33.0)	4.2 (4.0)

[a] Calculated values are given in parentheses. [b] 92 : 8 mixture of *meso*- and *rac* isomers. [c] 37 : 63 mixture of *meso*- and *rac* isomers. [d] **CAUTION**: This complex decomposed explosively at this temperature.

of (1b) from $[NiCl_2(PMe_2Ph)_2]$ and $Li[C_6H_3(OMe)_2$-2,6] has been reported previously.[15] It was also applied to the preparation of (1a) using $[NiCl_2(PMe_3)_2]$ (5.64 g, 20 mmol); yield 80%.

When the procedure was applied to $[NiCl_2(PMePh_2)_2]$ (5.30 g, 10 mmol), orange crystals of (1c) were obtained after recrystallization from acetone without heating above 40 °C; yield 1.79 g (24%). On concentration of the filtrates under reduced pressure, a mixture of (1c) and $[C_6H_3(OMe)_2$-2,6$]_2$ was obtained. Separation of (1c) from this mixture was unsuccessful, but $[C_6H_3(OMe)_2$-2,6$]_2$ could be obtained after repeated recrystallizations from acetone (10 cm^3)–ethanol (20 cm^3) as white crystals; yield 0.22 g, m.p. 173—174 °C (Found: C, 69.8; H, 6.7. $C_{16}H_{18}O_4$ requires C, 70.6; H, 6.6%). ^1H N.m.r. ($CDCl_3$): δ 7.29 (AB_2 quartet, overlapped with $CDCl_3$ resonance, *p*-H), 6.65 (AB_2 doublet, 4 H, *m*-H, J_H 8 Hz), and 3.71 p.p.m. (s, 12 H, OMe). Compound (1c) decomposed in $CDCl_3$.

trans-$[Ni\{C_6H_3(OMe)_2$-2,6$\}(Cl)L_2]$, *where* L = PMe_3 (2a), PMe_2Ph (2b), *or* PPh_3 (2d). The preparation of (2b) from $[NiCl_2(PMe_2Ph)_2]$ and $Li[C_6H_3(OMe)_2$-2,6] has been reported previously.[17] It was also applied to the preparation of (2a) using $[NiCl_2(PMe_3)_2]$ (10 mmol).

To a suspension of $Li[C_6H_3(OMe)_2$-2,6], prepared from resorcinol dimethyl ether (6.2 g, 45 mmol) and a 15% n-hexane solution of n-butyl-lithium (29 cm^3, 45 mmol) in dry diethyl ether (100 cm^3), was added $[NiCl_2(PPh_3)_2]$ (9.81 g, 15 mmol) in small portions at 0 °C under nitrogen. The mixture was stirred for 24 h at room temperature to give a dark solution with a yellow precipitate. It was cooled to 0 °C and methanol (100 cm^3) was added. The precipitate was filtered off in air and recrystallized once from dichloromethane (50 cm^3)–n-hexane (300 cm^3), then from acetonitrile to give (2d) as orange-brown crystals; yield 2.20 g (19%). On concentration of the filtrate, a mixture of $[C_6H_3(OMe)_2$-2,6$]_2$ and PPh_3 was obtained, but no further work was performed.

Reactions of trans-$[Ni\{C_6H_3(OMe)_2$-2,6$\}_2(PMe_3)_2]$ (1a).—(*a*) *With n-butyl-lithium followed by treatment with* $SiMe_3Cl$. To a solution of (1a) (2.425 g, 5 mmol) in dry diethyl ether (100 cm^3) was added a 15% n-hexane solution of n-butyl-lithium (15 mmol) at 0 °C under nitrogen to give a light yellow precipitate in a few minutes. The suspension was stirred for 4 h at room temperature, then neat $SiMe_3Cl$ (2.5 cm^3, 20 mmol) was added at 0 °C. The mixture was stirred for 4 h at room temperature. The solvents were then removed under reduced pressure and the residue was extracted in air with n-hexane–water containing ammonium chloride. The n-hexane layer was separated, the solvent was removed under reduced pressure, and the residual yellow solid was recrystallized from methanol to give orange needle crystals of *trans*-$[Ni\{C_6H_3(OMe)_2$-2,6$\}_2\{PMe_2(CH_2SiMe_3)\}_2]$ (3a); yield 45—55%.

(*b*) *With n-butyl-lithium followed by treatment with* D_2O. To the suspension of lithiated intermediate, prepared as above from (1a) (1 mmol) and a 15% n-hexane solution of n-butyl-lithium (3 mmol) in dry diethyl ether (20 cm^3), was added D_2O (1 cm^3) at 0 °C, and the mixture was stirred for 0.5 h. Diethyl ether (30 cm^3) was added, and the mixture was washed repeatedly with water. The solvents were removed under reduced pressure, and the residual yellow solid was recrystallized from methanol to give *trans*-$[Ni\{C_6H_3(OMe)_2$-2,6$\}_2\{PMe_2(CH_2D)\}_2]$; yield 0.32 g (65%), m.p. 183 °C (decomp.). ^1H N.m.r. ($CDCl_3$): δ 6.91 (t + q + t of AB_2X_2 pattern, 2 H, *p*-H, J_H 7.5, J_P 1.5), 6.31 (d, 4 H, *m*-H, J_H 7.5), 3.98 (s, 12 H, OMe), and 0.77 p.p.m. (t, 16 H, PMe and PCH_2, J_P 7.5 Hz).

Reaction of trans-$[Ni\{C_6H_3(OMe)_2$-2,6$\}_2(PMe_2Ph)_2]$ (1b) *with n-Butyl-lithium followed by Treatment with* $SiMe_3Cl$.—A solution of (1b) (2.44 g, 4 mmol) in dry diethyl ether (200 cm^3) was treated as above with a 15% n-hexane solution of n-butyl-lithium (15 mmol) at 0 °C under nitrogen to give a light yellow precipitate in a few minutes. The suspension was stirred for 2 h at 0 °C, and then $SiMe_3Cl$ (17 mmol) was added. The mixture was stirred for 15 h at room temperature, and then washed in air with water containing ammonium chloride, and then repeatedly with water. The solvents were removed under reduced pressure, and the residual yellow solid was washed with methanol (40 cm^3) to give *trans*-$[Ni\{C_6H_3(OMe)_2$-2,6$\}_2\{PMePh(CH_2SiMe_3)\}_2]$ (3b); yield 2.26 g (77%). This product was found to be a 62 : 38 mixture of *meso*- and *rac* isomers from the ^1H n.m.r. spectrum, which also showed the absence of any other impurity such as (1b) or *trans*-$[Ni\{C_6H_3(OMe)_2$-2,6$\}_2(PMe_2Ph)\{PMePh(CH_2SiMe_3)\}]$, although on cooling the methanol wash gave a mixture of such complexes. Fractional recrystallization of the mixture of *meso*- and *rac* isomers from acetone (40 cm^3)–methanol (40 cm^3) gave three fractions (1.11 g, m.p. 117—118 °C; 0.43 g, m.p. 102—104 °C; and 0.01 g, m.p. 107—109 °C) of yellow-orange crystals. From the ^1H n.m.r. spectra the first fraction was found to be a 80 : 20 mixture of *meso*- and *rac* isomers of (3b), the second was 37 : 63 mixture, and the third was almost pure *rac* isomer. The first fraction was again recrystallized from acetone (20 cm^3)–methanol (10 cm^3) to give a 92 : 8 mixture (m.p. 120—121 °C), and then a 84 : 16 mixture (m.p. 116—117 °C). The former mixture was used for the elemental analysis, as was the 37 : 63 mixture.

Reactions of trans-$[Ni\{C_6H_3(OMe)_2$-2,6$\}_2\{PMe_2(CH_2SiMe_3)\}_2]$ (3a).—(*a*) *With n-butyl-lithium followed by treatment with* D_2O. A solution of (3a) (0.63 g, 1 mmol) in dry diethyl ether (20 cm^3) was treated as above with a 15% n-hexane solution of n-butyl-lithium (5 mmol). The mixture was stirred at 0 °C for 2 h, then D_2O (1 cm^3) was added, and the mixture was stirred for 1 h at 0 °C. Working up as above and recrystallization from methanol gave orange-yellow crystals of *trans*-$[Ni\{C_6H_3(OMe)_2$-2,6$\}_2\{PMe_2(CHDSiMe_3)\}_2]$; yield 0.254 g (40%), m.p. 88 °C. ^1H N.m.r. ($CDCl_3$): δ 6.92 (t + q + t, 2 H, *p*-H, J_H 7.8, J_P 1.5), 6.30 (d, 4 H, *m*-H, J_H 7.8), 3.88 (s, 12 H, OMe), 0.78 (t, 12 H, PMe, J_P 7.5 Hz), 0.66 (br, 2 H, PCHDSi), and −0.06 p.p.m. (s, 18 H, SiMe).

(*b*) *With* MeI *under carbon monoxide*. A solution of (3a) (0.315 g, 0.5 mmol) in MeI (5 cm^3) was placed under carbon monoxide, and it was stirred vigorously for 2 h at room temperature. Methyl iodide was removed under reduced pressure, and the residue was extracted with dichloromethane–6% aqueous HCl solution (10 cm^3). Evaporation of the CH_2Cl_2 layer yielded $[C_6H_3(OMe)_2$-2,6$]_2CO$ after recrystallization from ethanol; 0.116 g (77%), m.p. 205—206 °C (Found: C, 67.6; H, 6.0. $C_{17}H_{18}O_5$ requires C, 67.5; H, 6.0%). I.r. (Nujol): 1 680s cm^{-1} (ν_{CO}). ^1H N.m.r. (CH_2Cl_2): δ 7.31 (AB_2, q, 2 H, *p*-H, J_H 8.2), 6.59 (AB_2, d, 4 H, *m*-H, J_H 8.2 Hz), and 3.67 p.p.m. (s, 12 H, OMe). To the aqueous HCl layer was added saturated ammonium hexafluorophosphate until precipitation was complete, giving $[PMe_3(CH_2SiMe_3)]PF_6$; yield 0.88 g (28.5%). ^1H N.m.r. (CD_3CN): δ 1.75 (d, 9 H, PMe, J_P 14), 1.50 (d, 2 H, PCH_2Si, J_P 19 Hz), and 0.22 p.p.m. (s, 9 H, SiMe), similar to that reported for $[PMe_3(CH_2SiMe_3)]Cl$.[5]

trans-$[Ni\{C_6H_3(OMe)_2-2,6\}(C_6H_2Me_3-2,4,6)(PMe_3)_2]$ (4).—To a suspension of $Li[C_6H_3(OMe)_2-2,6]$, prepared from resorcinol dimethyl ether (0.8 cm^3) and a 15% n-hexane solution of n-butyl-lithium (5 mmol) in dry diethyl ether (10 cm^3), was added *trans*-$[Ni(C_6H_2Me_3-2,4,6)Br(PMe_3)_2]$ (1.64 g, 4 mmol) [2] in small portions at 0 °C under nitrogen. The mixture was stirred at room temperature for 4 h. Diethyl ether (50 cm^3) was added, the solution was washed repeatedly with water, and then the solvents were removed under reduced pressure. The residue was washed with methanol and was recrystallized from n-hexane to give orange-yellow crystals of (4); yield 1.55 g (83%).

Reactions of trans-$[Ni\{C_6H_3(OMe)_2-2,6\}(C_6H_2Me_3-2,4,6)(PMe_3)_2]$ (4).—(*a*) *With n-butyl-lithium followed by treatment with* D_2O. To a solution of (4) (0.467 g, 1 mmol) in dry diethyl ether (20 cm^3) was added a 15% n-hexane solution of n-butyl-lithium (5 mmol) under nitrogen. The mixture was stirred at room temperature for 16 h to give a white precipitate. To this suspension was added D_2O (1.0 cm^3) dropwise at 0 °C, and the mixture was stirred vigorously for 1 h. It was diluted by adding diethyl ether (30 cm^3), and was washed repeatedly with water. The solvents were removed under reduced pressure, and the residue was recrystallized from n-hexane to give *trans*-$[Ni\{C_6H_3(OMe)_2-2,6\}(C_6H_2Me_3-2,4,6)(PMe_3)\{PMe_2(CH_2D)\}]$; yield 0.274 g (58%), m.p. 174—175 °C. ^1H N.m.r. ($CDCl_3$): δ 6.90 (br t, 1 H, *p*-H, J_H 8), 6.52 (s, 2 H, *m*-H), 6.26 (d, 2 H, *m*-H, J_H 8), 3.74 (s, 6 H, OMe), 2.65 (s, 6 H, *o*-Me), 2.15 (s, 3 H, *p*-H), and 0.74 p.p.m. (t, 17 H, PMe and PCH_2D, J_P 7 Hz).

(*b*) *With n-butyl-lithium followed by treatment with* $SiMe_3Cl$. To a solution of (4) (1 mmol) in dry diethyl ether (20 cm^3) containing *NNN'N'*-tetramethylethylenediamine (1 cm^3) was added a 15% n-hexane solution of n-butyl-lithium (5 mmol) under nitrogen. The mixture was stirred at room temperature for 22 h, and then $SiMe_3Cl$ (5 mmol) was added. The mixture was stirred at room temperature for 23 h, and then diethyl ether (30 cm^3) was added. It was washed once with water containing ammonium chloride, and then repeatedly with water. The solvents were removed under reduced pressure, and the residue was recrystallized from methanol to give yellow crystals of *trans*-$[Ni\{C_6H_3(OMe)_2-2,6\}(C_6H_2Me_3-2,4,6)(PMe_3)\{PMe_2(CH_2SiMe_3)\}]$ (5); yield 0.377 g (70%).

Reactions of trans-$[Ni(C_6H_2Me_3-2,4,6)(C_6H_4Me-2)(PMe_3)_2]$ (6).—(*a*) *With n-butyl-lithium followed by treatment with* D_2O. To a solution of (6) [2] (0.421 g, 1 mmol) in dry diethyl ether (20 cm^3) containing *NNN'N'*-tetramethylethylenediamine (1 cm^3) was added a 15% n-hexane solution of n-butyl-lithium (5 mmol) at 0 °C under nitrogen. The mixture was stirred at room temperature for 18.5 h, and then D_2O (0.8 cm^3) was added. The mixture was stirred for 1 h at 0 °C, diluted by adding diethyl ether (30 cm^3), and washed with water as above. The solvents were removed under reduced pressure, and the residue was recrystallized from methanol to give *trans*-$[Ni(C_6H_2Me_3-2,4,6)(C_6H_4Me-2)\{PMe_2(CH_2D)\}_2]$; yield 0.195 g (46%), m.p. 171 °C (decomp.). ^1H N.m.r. (CH_2Cl_2): δ 7.40 (d, 1 H, *o*-H, J_H 6), 6.9—6.6 (m, 3 H, Ph), 6.52 (s, 2 H, *m*-H), 2.65 (s, 3 H, *o*-Me), 2.61 and 2.60 (overlapped, 6 H, *o*-Me), 2.13 (br s, 3 H, *p*-Me), and 0.76 p.p.m. (t, 10 H, PMe, J_P 10 Hz).

(*b*) *With n-butyl-lithium followed by treatment with* $SiMe_3Cl$. To a reaction mixture obtained as above from (6) (1 mmol) and a 15% n-hexane solution of n-butyl-lithium (5 mmol) in dry diethyl ether (20 cm^3) containing *NNN'N'*-tetramethylethylenediamine (1 cm^3) under nitrogen was added $SiMe_3Cl$ (7 mmol) at 0 °C. The mixture was stirred at room temperature for 4 h, and then diluted by adding diethyl ether (30 cm^3). It was washed with water as above, the solvents were removed under reduced pressure, and the residue was recrystallized from acetone (3 cm^3)–methanol (10 cm^3) to give yellow crystals of *trans*-$[Ni(C_6H_2Me_3-2,4,6)(C_6H_4Me-2)\{PMe_2(CH_2SiMe_3)\}_2]$ (7); yield 0.255 g (45%).

(*c*) *With n-butyl-lithium followed by treatment with* MeI. To a reaction mixture obtained as above from (6) (1 mmol) and a 15% n-hexane solution of n-butyl-lithium (5 mmol) in dry diethyl ether (20 cm^3) containing *NNN'N'*-tetramethylethylenediamine (1 cm^3) under nitrogen was added MeI (2 cm^3) at 0 °C. The mixture was stirred at room temperature for 4.5 h, diluted by adding diethyl ether (30 cm^3), and washed with water as above. The solvents were removed under reduced pressure, and the residue was recrystallized from acetone (5 cm^3)–methanol (10 cm^3) to give yellow crystals of *trans*-$[Ni(C_6H_2Me_3-2,4,6)(C_6H_4Me-2)(PMe_3)(PMe_2Et)]$ (8); yield 0.226 g (52%).

trans-$[Ni\{C_6H[(OMe)_2-2,6]Br_2-3,5\}_2L_2]$, *where* L = PMe_3 (10a) *or* PMe_2Ph (10b).—To a solution of (1a) (6 mmol) in acetone (120 cm^3) was added at 0 °C a solution of *N*-bromosuccinimide (5.34 g, 30 mmol) in acetone (240 cm^3). The mixture was stirred for 1 h at 0 °C to give a purple solution. Methanol (120 cm^3) was added, and the mixture was stirred for 0.5 h at 0 °C. The resultant precipitate was recrystallized from ethyl methyl ketone to give brown crystals of (10a); yield 1.58 g (33%).

Complex (10b) has been reported previously.[15]

Thermal Properties and Intermolecular Tertiary Phosphine Exchanges.—Benzene solutions (2—20 cm^3) of complexes were heated in a sealed glass tube *in vacuo* or in a glass tube under nitrogen. Refluxing baths (500 cm^3) of water (100 °C), benzene (81 °C), methanol (65 °C), or dichloromethane (40 °C) in a 500 cm^3 three-necked flask were used as thermostats. The reactions were monitored by ^1H n.m.r. spectroscopy.

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