The Possibility of Free Rotation of *m*-Tolyl and Substituted Pyridine Groups about their Bonds to Square-planar Organonickel(II) Species

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For the purpose of this study 21 new organonickel(II) complexes of types *trans*-[NiRR'(PR''_3)$_2$] and *trans*-[NiR(PR''_3)$_2$L][ClO_4], where R = C_6Cl_5, mesityl, or $Cl_2C{=}CCl$ and PR''_3 = PMe_2Ph, PMe_3, or $PMePh_2$, have been prepared. Hydrogen-1 n.m.r. spectral investigations revealed that the *m*-tolyl group (R') and 3-substituted pyridine ligands (L) bonded to *trans*-[NiR(PMe_2Ph)$_2$] units are oriented perpendicularly to the nickel co-ordination plane, while those bonded to *trans*-[NiR(PMe_3)$_2$] units rotate freely about the bond to the nickel at room temperature.

In organonickel(II) chemistry, complexes of types *trans*-[NiR(X)(PR'_3)$_2$] and *trans*-[NiR_2(PR'_3)$_2$] (X = anionic ligand, *e.g.* halide; R' = alkyl or aryl group) have been shown to have considerable stability when R is an *ortho*-substituted aryl group.[1-3] This so called '*ortho* effect'[2] was accounted for originally by Chatt and Shaw[1] through a combination of steric and electronic factors, and later by Braterman and Cross[4] through a steric protection effect toward any concerted decomposition paths. In these accounts, an *ortho*-unsubstituted aryl group bonded to a nickel atom has been assumed to rotate freely around the bond. In our recent work,[5] however, we found that not only the *o*-tolyl group but also the *m*-tolyl group bonded to *trans*-[Ni(C_6Cl_5)(PMe_2Ph)$_2$] are oriented perpendicularly to the nickel co-ordination plane. In the present work, we aimed to investigate the behaviour of related ligands with respect to the presence or absence of free rotation about their bonds to *trans*-[NiR(PR'_3)$_2$] species.

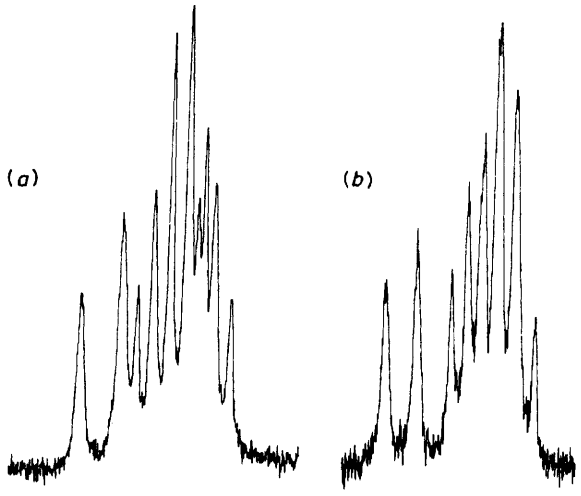
RESULTS AND DISCUSSION

We have designed a number of organonickel(II) complexes of types *trans*-[NiR(R')(PR''_3)$_2$] and *trans*-[NiR(PR''_3)$_2$L][ClO_4], the stereochemistries of which were determined by ^{1}H n.m.r. spectroscopy. Complexes that were successfully prepared together with their ^{1}H n.m.r. spectral data are summarized in Table 1.

PMe_2Ph *Complexes.*—Much of the stereochemical information for the complexes containing PMe_2Ph depends on the pattern of resonances observed for the methyl protons in the phosphine ligands, as described by Moss and Shaw[6] for *o*-tolylnickel(II) complexes.

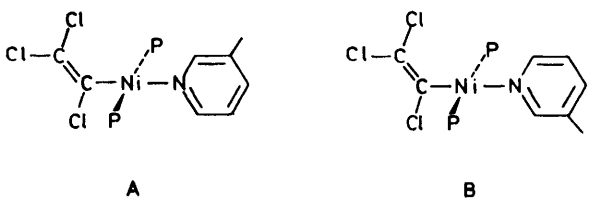
In accord with the previous observation[5] for *trans*-[Ni(C_6Cl_5)(C_6H_4Me-*m*)(PMe_2Ph)$_2$], the phosphine methyl resonance of *trans*-[Ni($C_6H_2Me_3$-2,4,6)(C_6H_4Me-*m*)(PMe_2Ph)$_2$] also consists of two overlapping 1 : 2 : 1 triplets both in dichloromethane and in benzene solutions. These results indicate that the *m*-tolyl group bonded to these *trans*-[NiR(PMe_2Ph)$_2$] moieties is oriented perpendicularly to the nickel co-ordination plane, which causes the two methyl groups on the same phosphine ligand to have different magnetic environments because there is no plane of symmetry through the two *trans* phosphorus atoms. Consistent with this result is the magnetic non-equivalence of the two *ortho*-methyl groups in the mesityl group (benzene solution spectrum).

The phosphine methyl resonance of cationic complexes, *trans*-[Ni(C_6Cl_5)(PMe_2Ph)$_2$L][ClO_4] where L = 3-picoline



p-CH_3 region of ^{1}H n.m.r. spectra of *trans*-[Ni($Cl_2C{=}CCl$)(PMe_2Ph)(NC_5H_4Me-3)][ClO_4] in (*a*) $CDCl_3$ and (*b*) CH_2Cl_2

(NC_5H_4Me-3), methyl nicotinate ($NC_5H_4CO_2$Me-3), or 3,4-lutidine ($NC_5H_3Me_2$-3,4), consists of two distinct 1 : 2 : 1 triplets, indicating that these pyridine ligands are also oriented perpendicularly to the nickel co-ordination plane. Analogous results have been reported for *trans*-[Ni($C_6H_2Me_3$-2,4,6)(PMe_2Ph)$_2$L][ClO_4] complexes where L = 3-picoline and 3,4-lutidine.[7]



A B

The spectrum of *trans*-[Ni($Cl_2C{=}CCl$)(PMe_2Ph)$_2$(NC_5H_4Me-3)][ClO_4] in the region 1.5—2.0 p.p.m. gave a complex pattern (see Figure) but it could be analysed as consisting of four overlapping 1 : 2 : 1 triplets due to the

phosphine methyl protons and of two peaks due to the picoline methyl protons. This result is consistent with the presence of two isomers, A and B (see above), in *ca.* 1 : 1 mole ratio due to the lack of free rotation of both the Cl_2C=CCl group and 3-picoline ligand, and due to the difference in the mutual orientation of both ligands with respect to the co-ordination plane.

The magnetic non-equivalence of the two methyl groups of the 3,5-lutidine ligand in *trans*-[Ni(Cl_2C=CCl)(PMe_2Ph)$_2$($NC_5H_3Me_2$-3,5)][ClO_4] suggests the perpendicular orientation of both the Cl_2C=CCl group and the 3,5-lutidine ligand.

In the case of five-membered ring ligands, 2-methylimidazole bonded to the *trans*-[Ni(C_6Cl_5)(PMe_2Ph)$_2$]

TABLE 1

Hydrogen-1 n.m.r. spectral data for new organonickel(II) complexes, *trans*-[NiR(R′)(PR''_3)$_2$] and *trans*-[NiR(PR''_3)$_2$L][ClO_4] [a]

R	R′ or L	Solvent (θ_c/°C)	Chemical shifts [b] [coupling constant] [c]
(*a*) PR''_3 = PMe_2Ph			
$C_6H_2Me_3$-2,4,6	C_6H_4Me-*m*	CH_2Cl_2 (23)	*0.95t*[7] *and 1.03t*[7] (*P*–*Me*), 1.97s (*m*-Me), 2.18br,s (*p*-Me), 2.44s (*o*-Me), 6.4—7.3m (Ar-H), 6.53s (*m*-H)
		C_6H_6 (23)	*0.81t*[7] *and 0.89t*[7] (*P*–*Me*), 2.17s (*m*-Me), 2.41br,s (*p*-Me), *2.59s and 2.61s* (o-*Me*)
C_6Cl_5	NC_5H_4Me-3	CH_2Cl_2 (23)	*1.26t*[8] *and 1.48t*[8] (*P*–*Me*), 1.92s (3-Me), 6.8—7.6m (Ar-H), 8.16d[5] (6-H)
C_6Cl_5	NC_5H_4COOMe-3	CH_2Cl_2 (23)	*1.26t*[8] *and 1.51t*[8] (*P*–*Me*), 3.88s (O–Me), 6.9—7.3m (Ar-H), 7.47dd[7] [6] (3-H), 8.1d [d] [(7)] (4-H), 8.13s (2-H), 8.68d[6] (6-H)
C_6Cl_5	$NC_5H_3Me_2$-3,4	CH_2Cl_2 (23)	*1.25t*[8] *and 1.49t*[8] (*P*–*Me*), 1.83s (3-Me), 2.19s (4-Me), 6.9—7.4m (Ar-H), 7.99d[5] (6-H)
Cl_2C=CCl	NC_5H_4Me-3	CH_2Cl_2 (23)	*1.54t, 1.58t,* [d] *and 1.66t*[8] (*P*–*Me*), *1.78s and 1.86s* (*3-Me*), 6.9—7.5m (Ar-H), 7.90d[6] (6-H)
		$CDCl_3$ (23)	*1.56t, 1.62t,* [d] *and 1.70t*[8] (*P*–*Me*), *1.78s and 1.88s* (*3-Me*), 6.9—7.5m (Ar-H), 8.10br,s (6-H)
Cl_2C=CCl	$NC_5H_3Me_2$-3,5	CH_2Cl_2 (23)	1.56t[8] and 1.62t[8] (P–Me), *1.86s* (*3-Me*), *1.93s* (*5-Me*), 7.0—7.5m (Ar-H)
C_6Cl_5	$N_2C_3H_3$Me-2	CH_2Cl_2 (23)	*1.15t*[8] *and 1.48t*[8] (*P*–*Me*), 1.67s (2-Me), 6.8—7.5m (Ar-H)
C_6Cl_5	$N_2C_3H_3$Me-1	CH_2Cl_2 (23)	1.36t[8] (P–Me), 3.46s (N–Me), 6.64s (5-H), 6.81s (4-H), 7.04s (2-H), 7.1—7.4m (Ar-H)
		CH_2Cl_2 (−83)	*1.17br,s and 1.50br,s* (*P*–*Me*), 3.31s (N–Me), 6.67s (5-H), 6.89 (4-H), 7.0—7.5m (2-H and Ar-H)
C_6Cl_5	$N_2C_3H_3$Et-1	CH_2Cl_2 (23)	1.33t[8] (P–Me), 1.19t and 3.75q[7] (N–Et), 6.65s (5-H), 6.82s (4-H), 6.99s (2-H), 7.1—7.5m (Ar-H)
(*b*) PR''_3 = PMe_3			
$C_6H_2Me_3$-2,4,6	Br	CH_2Cl_2 (23)	1.04t[7] (P–Me), 2.12br,s (*p*-Me), 2.70s (*o*-Me), 6.52s (*m*-H)
Cl_2C=CCl	Cl	CH_2Cl_2 (23)	1.28t[8] (P–Me)
$C_6H_2Me_3$-2,4,6	C_6H_4Me-*o*	CH_2Cl_2 (23)	0.75t[7] (P–Me), 2.15br,s (*p*-Me), *2.60s and 2.61s* (*o*-*Me*), 2.66s (*o*-Me), 6.54s (*m*-H), 6.7—6.9m (Ar-H), 7.42d[6] (*o*-H)
Cl_2C=CCl	C_6H_4Me-*o*	CH_2Cl_2 (23)	1.01t[8] (P–Me), *2.58s and 2.65s* (*o*-*Me*),[e] 6.7—6.9m (*m*-H and *p*-H), 7.14br,s (*o*-H)
$C_6H_2Me_3$-2,4,6	NC_5H_4Me-2	CH_2Cl_2 (23)	0.83t[8] (P–Me), 2.18br,s (*p*-Me), *2.77s and 2.92s* (o-Me), 3.21s (2-Me), 6.65s (*m*-H), 7.4—8.0m (Ar-H) 8.91d[5] (6-H)
$C_6H_2Me_3$-2,4,6	C_6H_4Me-*m*	CH_2Cl_2 (23)	0.74t[7] (P–Me), 2.13br,s (*p*-Me), 2.20s (*m*-Me), 2.57s (*o*-Me), 6.50s (*m*-H), 6.52d [d] [(8)] (*p*-H), 6.77t[7.5] (*m*-H), 7.21d [d] [(8)], and 7.26s (*o*-H)
		CH_2Cl_2 (−83)	0.73br,s (P–Me), 2.17br,s (*p*-Me), 2.24s (*m*-Me), 2.57s (*o*-Me)
		C_6H_6 (23)	0.60t[7] (P–Me), 2.37s (*p*-Me and *m*-Me), 2.74s (*o*-Me)
		Cl_2C=CCl_2 (23)	0.74t[7] (P–Me), 2.12br,s (*p*-Me), 2.19s (*m*-Me), 2.57s (*o*-Me)
$C_6H_2Me_3$-2,4,6	NC_5H_4Me-3	CH_2Cl_2 (23)	0.82t[7] (P–Me), 2.16br,s (*p*-Me), 2.46s (3-Me), 2.81s (*o*-Me), 6.60s (*m*-H), 7.4—7.8m (4-H and 5-H), 8.57s (2-H), 8.60d [d] [(7)] (6-H)
		CH_2Cl_2 (−83)	0.82t[7] (P–Me), 2.19br,s (*p*-Me), 2.50s (3-Me), *2.79s and 2.82s* (*o*-*Me*)
$C_6H_2Me_3$-2,4,6	NC_5H_4COOMe-3	CH_2Cl_2 (23)	0.85t[7] (P–Me), 2.17br,s (*p*-Me), 2.83s (*o*-Me), 4.03s (O–Me), 6.65s (*m*-H), 7.90dd[8] [7] (5-H), 8.50d[8] (4-H), 9.21d [d] [(7)] (6-H), 9.25s (2-H)
Cl_2C=CCl	NC_5H_4Me-3	CH_2Cl_2 (23)	1.14t[8] (P–Me), 2.46s (3-Me), 7.5—7.9m (4-H and 5-H), 8.58br (2-H and 6-H)
Cl_2C=CCl	NC_5H_4Me-4	CH_2Cl_2 (23)	1.13t[8] (P–Me), 2.44s (4-Me), 7.44d[6] (3-H and 5-H), 8.51d[6] (2-H and 6-H)
Cl_2C=CCl	$NC_5H_3Me_2$-3,5	CH_2Cl_2 (23)	1.14t[8] (P–Me), 2.40s (3-Me and 5-Me), 7.53s (4-H), 8.36s (2-H and 6-H)
$C_6H_2Me_3$-2,4,6	$N_2C_3H_3$Me-2	CH_2Cl_2 (23)	0.82t[7] (P–Me), 2.18br,s (*p*-Me), *2.81s and 2.84s* [d] (o-*Me*), 2.83s (2-Me), 6.64s (*m*-H), 6.97t[2] (4-H), 7.21t[2] (5-H)
(*c*) PR''_3 = $PMePh_2$			
$C_6H_2Me_3$-2,4,6	Br	CH_2Cl_2 (23)	1.11t[7] (P–Me), 2.05br,s (*p*-Me), 2.49s (*o*-Me), 6.33s (*m*-H), 7.2—7.4m and 7.6—7.8m (Ar-H)
Cl_2C=CCl	Cl	CH_2Cl_2 (23)	1.89t[8] (P–Me), 7.2—7.5m and 7.6—8.0m (Ar-H)
Cl_2C=CCl	$NC_5H_3Me_2$-3,5	CH_2Cl_2 (23)	1.78t [d] [8] (P–Me), *1.68s and 1.78s* [d] (*3-Me and 5-Me*), 6.9—8.0m (Ar-H)
$C_6H_2Me_3$-2,4,6	$N_2C_3H_3$Me-1	CH_2Cl_2 (23)	1.05t[8] (P–Me), 2.17br,s (*p*-Me), 2.64s (*o*-Me), 3.23s (N–Me), 6.5—6.7m and 7.2—7.5m (Ar-H)

[a] Those data from which stereochemical information was obtained are shown in italics. s = Singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, br = broad; Ar = aryl. [b] δ in p.p.m. [c] J_P or J_H; those values in parentheses are not accurate because of the overlapping with the other resonance. [d] Overlapped with the other resonance. [e] Integration ratio = 4 : 5.

moiety is co-ordinated perpendicularly to the nickel co-ordination plane, but both *N*-methylimidazole and *N*-ethylimidazole ligands seem to be rotating freely at room temperature. At low temperature (*e.g.* −83 °C) the rotation of the *N*-methylimidazole ligand is restricted.

These results suggest that the lack of free rotation of the *m*-tolyl group, 3-substituted pyridine ligands, and 2-methylimidazole ligand is due to their non-bonded steric interaction with two PMe_2Ph ligands. Thus, the previous observation of the 1 : 2 : 1 triplet resonance of the phosphine methyl protons in *trans*-[$Ni(C_6Cl_5)(R)(PMe_2Ph)_2$], where R = 2-furyl and 2-thienyl,[5] is now understood as being due to the free rotation of the furyl and thienyl groups.

PMe_3 *Complexes.*—Hydrogen-1 n.m.r. spectra of these complexes gave a normal 1 : 2 : 1 triplet pattern for the PMe_3 protons, owing to the two phosphine ligands being mutually *trans*. The criteria used for PMe_2Ph complexes cannot be used for these complexes.

The stereochemistry of mesityl derivatives would be determined by the mesityl *o*-methyl resonances; the magnetic non-equivalence of these methyl groups has been observed for *trans*-[$Ni(C_6H_2Me_3$-2,4,6)$(PMe_2Ph)_2L$]-[ClO_4] where L = 2-picoline, 3-picoline, or 3,4-lutidine.[7]

The two *ortho*-methyl groups in *trans*-[$Ni(C_6H_2Me_3$-2,4,6)$(C_6H_4Me$-*o*$)(PMe_3)_2$] are magnetically non-equivalent due to the restricted rotation of the *o*-tolyl group, although the resonances were only separated by 0.01 p.p.m. The spectrum of *trans*-[$Ni(Cl_2C{=}CCl)(C_6H_4Me$-*o*$)(PMe_3)_2$] showed two peaks attributable to the *ortho*-methyl proton resonance, consistent with the presence of two isomers in solution. An analogous observation has been reported for *trans*-[$Ni(Cl_2C{=}CCl)(C_6H_4Me$-*o*$)(PEt_3)_2$] by Miller *et al.*[8] The mesityl *ortho*-methyl resonance of *trans*-[$Ni(C_6H_4Me_3$-2,4,6$)(PMe_3)_2(NC_5H_4Me$-2$)][ClO_4$] appeared as two distinct peaks, confirming the perpendicular orientation of the 2-picoline ligand.

In contrast, the *ortho*-methyl resonance of *trans*-[$Ni(C_6H_2Me_3$-2,4,6$)(C_6H_4Me$-*m*$)(PMe_3)_2$] was a sharp singlet in several solvents and at low temperatures down to −83 °C. Although no decisive conclusion can be drawn from these results alone, the following collective results seem to suggest that the *m*-tolyl group in the complex is rotating freely about its bond to the nickel, at least at room temperature. The mesityl *ortho*-methyl resonance of *trans*-[$Ni(C_6H_2Me_3$-2,4,6$)(PMe_3)_2L][ClO_4$] where L = 3-picoline and methyl nicotinate was also a singlet. The methyl resonance of the 3-picoline ligand in *trans*-[$Ni(Cl_2C{=}CCl)(PMe_3)_2(NC_5H_4Me-3)][ClO_4$] was a sharp singlet, and so the presence of only one isomer is expected for these complexes, probably due to the free rotation of the pyridine ligands under these conditions. The 2,6-ring protons, as well as the 3,5-ring protons of the 4-picoline ligand in *trans*-[$Ni(Cl_2C{=}CCl)(PMe_3)_2(NC_5H_4Me-4)][ClO_4$] were magnetically equivalent, probably due to the free rotation of the ligand about the bond to the nickel. The two methyl groups of the 3,5-lutidine ligand in *trans*-[$Ni(Cl_2C{=}CCl)(PMe_3)_2(NC_5H_3Me_2$-3,5$)][ClO_4$] were also magnetically equivalent. However, at −83 °C, the rotation of the 3-picoline ligand in *trans*-[$Ni(C_6H_2Me_3$-2,4,6$)(PMe_3)_2(NC_5H_4Me$-3$)][ClO_4$] must be restricted.

The features of the ^1H n.m.r. spectra of a wide series of PMe_3 complexes can be accounted for best by assuming the presence of free rotation of the *m*-tolyl group, as well as of *ortho*-unsubstituted pyridine ligands, at room temperature. The different behaviours of the *m*-tolyl group and *ortho*-unsubstituted pyridine ligands between PMe_2Ph and PMe_3 complexes may be due to steric factors; the Tolman cone angles of these phosphine ligands are 122 and 118°, respectively.[9]

The 2-methylimidazole ligand bonded to the *trans*-[$Ni(C_6H_2Me_3$-2,4,6$)(PMe_3)_2$] moiety is oriented perpendicularly to the nickel co-ordination plane, as is evident from the magnetic non-equivalence of the mesityl *ortho*-methyl groups.

$PMePh_2$ *Complexes.*—We experienced difficulties in preparing $PMePh_2$ complexes, in general, and have succeeded in isolating only two complexes at present. The ^1H n.m.r. spectrum of *trans*-[$Ni(Cl_2C{=}CCl)(PMePh_2)_2(NC_5H_3Me_2$-3,5$)][ClO_4$] showed two peaks for the methyl resonance of the 3,5-lutidine ligand, which indicates the perpendicular orientation of both the $Cl_2C{=}CCl$ group and the 3,5-lutidine ligand in the complex. On the other hand, the *N*-methylimidazole ligand in *trans*-[$Ni(C_6H_2Me_3$-2,4,6$)(PMePh_2)_2(N_2C_3H_3Me$-1$)][ClO_4$] seems to rotate freely about its bond to the nickel, since only one peak was observed for the mesityl *ortho*-methyl protons.

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were determined on a JEOL model JNM-PS-100 spectrometer operating at 100 MHz, using tetramethylsilane as internal standard. Analytical and physical data for new organonickel(II) complexes are summarized in Table 2. The starting complexes, *trans*-[$Ni(C_6Cl_5)(PMe_2Ph)_2Cl$],[10] *trans*-[$Ni(C_6H_2Me_3$-2,4,6$)(PMe_2Ph)_2Br$],[7] and *trans*-[$Ni(Cl_2C{=}CCl)(PMe_2Ph)_2Cl$] [11] were prepared as described previously.

trans-[$Ni(C_6H_2Me_3$-2,4,6$)(PMe_3)_2Br$].—The Grignard reagent, 2,4,6-$Me_3C_6H_2MgBr$, was prepared from magnesium turnings (0.5 g, 20 mmol) and 2-bromomesitylene (4.6 g, 23 mmol) in dry diethyl ether (15 cm^3) containing two or three drops of methyl iodide as the initiator. The mixture was stirred overnight at room temperature under a nitrogen atmosphere. The reagent thus prepared was added dropwise to a slurry of [$Ni(PMe_3)_2Cl_2$] (4.23 g, 15 mmol) in diethyl ether (30 cm^3) at 0 °C under a nitrogen atmosphere. The mixture was stirred at room temperature for 2 h. Benzene (50 cm^3) was added, the solution was cooled to 0 °C, and cold water containing ammonium bromide was added to hydrolyse the excess of Grignard reagent. The organic layer was washed repeatedly with water at room temperature to remove traces of inorganic impurities, and was filtered using cylindrical filtering paper. The solvents were removed under reduced pressure, and the residual yellow solid was recrystallized from acetone or acetone–ethanol to give brown crystals of *trans*-[$Ni(C_6H_2Me_3$-2,4,6$)(PMe_3)_2Br$] in a yield of 4.1 g (66%).

trans-[$Ni(C_6H_2Me_3$-2,4,6$)(PMePh_2)_2Br$].—This complex was prepared in 77% yield in a manner similar to the PMe_3 complex using [$Ni(PMePh_2)_2Cl_2$] (5.3 g, 10 mmol).

trans-[$Ni(Cl_2C{=}CCl)(PMe_3)_2Cl$].—To a suspension of [Ni-

$(PMe_3)_2Cl_2$] (5.64 g, 20 mmol) in 80 cm^3 of tetrachloroethylene–ethanol (1 : 1) was added dropwise a solution of sodium tetrahydroborate (1.6 g, 40 mmol) dissolved in ethanol (100 cm^3) at room temperature under a nitrogen atmosphere. The mixture was stirred for 0.5 h, and then the solvents were removed by heating under reduced pressure. The residue was extracted with diethyl ether–water, the ethereal layer was separated, and the solvent was removed under reduced pressure. The residue was recrystallized from n-hexane to give yellow-brown crystals of *trans*-[Ni(Cl_2C=CCl)(PMe_3)$_2$Cl] in a yield of 4.8 g (64%).

trans-[Ni(CCl_2=CCl)($PMePh_2$)$_2$Cl].—This complex was prepared in 44% yield in a manner similar to the PMe_3 complex using [Ni($PMePh_2$)$_2Cl_2$] (20 mmol).

trans-[Ni($C_6H_2Me_3$-2,4,6)(C_6H_4Me-*m*)(PMe_2Ph)$_2$].— An ethereal solution of *m*-tolyl-lithium was prepared from a 15% n-hexane solution of n-butyl-lithium (2.5 cm^3, 4.0 mmol) and *m*-bromotoluene (0.50 cm^3, 4.1 mmol). The two reagents were mixed in dry diethyl ether (10 cm^3) under a nitrogen atmosphere at 0 °C, and the solution was stirred at room temperature for 1 h. The solution was cooled to 0 °C, and a dry benzene (10 cm^3) solution of *trans*-[Ni($C_6H_2Me_3$-2,4,6)(PMe_2Ph)$_2$Br] (1.07 g, 2 mmol) was added. The mixture was stirred at 0 °C for 0.5 h. Diethyl ether (20 cm^3) was added, and the mixture was washed with cold water, repeatedly. The solvents of the organic layer were removed under reduced pressure, and the residue was recrystallized from acetone to give yellow-orange crystals of *trans*-[Ni($C_6H_2Me_3$-2,4,6)(C_6H_4Me-*m*)(PMe_2Ph)$_2$] in a yield of 0.992 g (91%).

trans-[Ni(C_6Cl_5)(PMe_2Ph)$_2$(NC_5H_4Me-3)][ClO_4].—To a solution of *trans*-[Ni(C_6Cl_5)(PMe_2Ph)$_2$Cl] (0.31 g, 0.5 mmol)

TABLE 2

Analytical and physical data for new organonickel(II) complexes *trans*-[NiR(R′)(PR''_3)$_2$] and *trans*-[NiR(PR''_3)$_2$L][ClO_4]

PR''_3	R	R′ or L	M.p. (θ_c/°C) [a]	Analyses (%) [b] C	H	N
PMe_3	$C_6H_2Me_3$-2,4,6	Br	164—166	43.6 (43.95)	7.25 (7.15)	
	Cl_2C=CCl	Cl	121—122	25.5 (25.5)	5.00 (4.80)	
$PMePh_2$	$C_6H_2Me_3$-2,4,6	Br	179—181 [c]	63.8 (63.85)	5.75 (5.65)	
	Cl_2C=CCl	Cl	143—145	53.75 (53.8)	4.35 (4.20)	
PMe_2Ph	$C_6H_2Me_3$-2,4,6	C_6H_4Me-*m*	149—150 [c]	70.3 (70.5)	7.55 (7.40)	
	C_6Cl_5	NC_5H_4Me-3	189—191	43.1 (43.3)	3.85 (3.75)	1.90 (1.80)
		NC_5H_4COOMe-3	204—206	42.05 (42.45)	3.55 (3.55)	1.80 (1.70)
		$NC_5H_3Me_2$-3,4	194—195	44.05 (44.05)	4.10 (3.95)	1.90 (1.75)
	Cl_2C=CCl	NC_5H_4Me-3	163—164	43.6 (43.8)	4.45 (4.45)	2.15 (2.15)
		$NC_5H_3Me_2$-3,5	159—160 [c]	44.55 (44.7)	4.70 (4.65)	2.15 (2.10)
	C_6Cl_5	$N_2C_3H_3$Me-2	235 [c]	40.8 (40.75)	3.70 (3.70)	3.65 (3.65)
		$N_2C_3H_3$Me-1	215—216 (209—210)	40.6 (40.75)	3.65 (3.70)	3.95 (3.65)
		$N_2C_3H_3$Et-1	177—178	41.4 (41.6)	3.85 (3.90)	3.80 (3.60)
PMe_3	$C_6H_2Me_3$-2,4,6	C_6H_4Me-*o*	173—174 [c]	62.6 (62.75)	8.90 (8.60)	
	Cl_2C=CCl	C_6H_4Me-*o*	168—169 [c] (163—165) [c]	41.9 (41.65)	5.95 (5.85)	
	$C_6H_2Me_3$-2,4,6	NC_5H_4Me-2	186—187 [c]	48.25 (48.25)	7.10 (6.95)	2.70 (2.70)
		C_6H_4Me-*m*	151—152	62.55 (62.75)	8.80 (8.60)	
		NC_5H_4Me-3	184—186 [c]	48.2 (48.25)	7.10 (6.95)	2.70 (2.70)
		NC_5H_4COOMe-3	*ca.* 135 [c]	46.25 (46.65)	6.55 (6.40)	2.45 (2.45)
	Cl_2C=CCl	NC_5H_4Me-3	152—153 [c]	31.7 (31.5)	4.75 (4.70)	2.65 (2.60)
		NC_5H_4Me-4	165—167 [c]	31.45 (31.5)	4.90 (4.70)	2.75 (2.60)
		$NC_5H_3Me_2$-3,5	153—154 [c]	32.8 (32.9)	5.10 (4.95)	2.50 (2.55)
	$C_6H_2Me_3$-2,4,6	$N_2C_3H_3$Me-2	(174—178) [c]	44.6 (44.7)	6.95 (6.70)	5.60 (5.50)
$PMePh_2$	Cl_2C=CCl	$NC_5H_3Me_2$-3,5	180 [c]	52.6 (52.8)	4.50 (4.45)	1.70 (1.75)
	$C_6H_2Me_3$-2,4,6	$N_2C_3H_3$Me-1	163 [c] (158) [c]	61.4 (61.65)	5.95 (5.70)	3.80 (3.95)

[a] In an evacuated capillary (in air). [b] Calculated values are given in parentheses. [c] With decomposition.

in acetone (15 cm^3) was added silver perchlorate (0.104 g, 0.5 mmol) dissolved in acetone (5 cm^3). Silver chloride precipitate was removed by filtration, and 3-picoline (0.05 cm^3, 0.5 mmol) was added. The solvent was removed under reduced pressure, and the residue was recrystallized from ethanol to give yellow-brown crystals of *trans*-[Ni-(C_6Cl_5)(PMe_2Ph)$_2$(NC_5H_4Me-3)][ClO_4] in a yield of 0.243 g (62%).

trans-[Ni(C_6Cl_5)(PMe_2Ph)$_2$(NC_5H_4COOMe-3)][ClO_4].— A solution of *trans*-[Ni(C_6Cl_5)(PMe_2Ph)$_2$Cl] (1 mmol) in benzene (10 cm^3) was added dropwise to a solution of silver perchlorate (1 mmol) in benzene (30 cm^3). The silver chloride precipitate was removed by filtration, and methyl nicotinate (0.137 g, 1 mmol) was added to the filtrate with stirring. The yellow precipitate produced in a few min was separated by filtration, and was recrystallized from ethanol to give yellow-brown crystals of *trans*-[Ni(C_6Cl_5)(PMe_2Ph)$_2$(NC_5H_4-COOMe-3)][ClO_4] in 45% yield.

trans-[Ni(C_6Cl_5)(PMe_2Ph)$_2$($NC_5H_3Me_2$-3,4)][ClO_4].— This complex was prepared in 90% yield in a manner similar to the methyl nicotinate complex using *trans*-[Ni(C_6Cl_5)(PMe_2-Ph)$_2$Cl] (0.5 mmol) and 3,4-lutidine (0.05 cm^3, 0.5 mmol) in benzene (20 cm^3).

trans-[Ni(Cl_2C=CCl)(PMe_2Ph)$_2$(NC_5H_4Me-3)][ClO_4].—To a solution of *trans*-[Ni(Cl_2C=CCl)(PMe_2Ph)$_2$Cl] (0.501 g, 1 mmol) in acetonitrile (20 cm^3) was added a solution of silver perchlorate (1 mmol) in acetonitrile (10 cm^3). The silver chloride precipitate was removed by filtration, and 3-picoline (0.10 cm^3) was added to the filtrate. The solvent was removed under reduced pressure, and the residue was recrystallized from ethanol to give yellow-orange crystals of *trans*-[Ni(Cl_2C=CCl)(PMe_2Ph)$_2$(NC_5H_4Me-3)][ClO_4] in a yield of 0.530 g (80%).

trans-[Ni(Cl_2C=CCl)(PMe_2Ph)$_2$($NC_5H_3Me_2$-3,5)][ClO_4].— This complex was prepared in 78% yield in a manner similar to that above using *trans*-[Ni(Cl_2C=CCl)(PMe_2Ph)$_2$Cl] (1 mmol) and 3,5-lutidine (0.1 cm^3, 1 mmol) in acetonitrile.

trans-[Ni(C_6Cl_5)(PMe_2Ph)$_2$L][ClO_4], *where* L = *2-Methylimidazole, N-Methylimidazole, or N-Ethylimidazole.*—These complexes were prepared in 62, 55, and 76% yields respectively in manners similar to the methyl nicotinate complex, the 3-picoline complex, and the 3-picoline complex respectively.

trans-[Ni($C_6H_2Me_3$-2,4,6)(C_6H_4Me-*m*)(PMe_3)$_2$].—This complex was prepared in 58% yield in a manner similar to *trans*-[Ni($C_6H_2Me_3$-2,4,6)(C_6H_4Me-*m*)(PMe_2Ph)$_2$] using *trans*-[Ni-($C_6H_2Me_3$-2,4,6)(PMe_3)$_2$Br] (0.820 g, 2 mmol) and *o*-tolyl-lithium (an excess) which was prepared from *o*-bromotoluene and n-butyl-lithium.

trans-[Ni(Cl_2C=CCl)(C_6H_4Me-*o*)(PMe_3)$_2$].—This complex was prepared in 56% yield in a manner similar to the above using *trans*-[Ni(Cl_2C=CCl)(PMe_3)$_2$Cl] (0.753 g, 2 mmol) and *o*-tolyl-lithium. This was recrystallized from ethanol.

trans-[Ni($C_6H_2Me_3$-2,4,6)(C_6H_4Me-*m*)(PMe_3)$_2$].— This complex was prepared in 62% yield in a manner similar to the above using *trans*-[Ni($C_6H_2Me_3$-2,4,6)(PMe_3)$_2$Br] (2 mmol) and *m*-tolyl-lithium.

trans-[Ni($C_6H_2Me_3$-2,4,6)(PMe_3)$_2$(NC_5H_4Me-2)][ClO_4].— This complex was prepared in 53% yield in a manner similar to *trans*-[Ni(Cl_2C=CCl)(PMe_2Ph)$_2$(NC_5H_4Me-3)][ClO_4] using *trans*-[Ni($C_6H_2Me_3$)-2,4,6(PMe_3)$_2$Br] (1 mmol), silver perchlorate, and 2-picoline in acetonitrile.

trans-[Ni($C_6H_2Me_3$)(PMe_3)$_2$L][ClO_4], *where* L = *3-Picoline, Methyl Nicotinate, or 2-Methylimidazole.*—These complexes were prepared in 74, 60, and 49% yields respectively in manners similar to the above using 3-picoline, methyl nicotinate, or 2-methylimidazole.

trans-[Ni(Cl_2C=CCl)(PMe_3)$_2$L][ClO_4], *where* L = *3-Picoline, 4-Picoline, or 3,5-Lutidine.*—These complexes were prepared in 80, 77, and 85% yields respectively in manners similar to the above using *trans*-[Ni(Cl_2C=CCl)(PMe_3)$_2$Cl] (1 mmol) and 3-picoline, 4-picoline, or 3,5-lutidine.

trans-[Ni(Cl_2C=CCl)($PMePh_2$)$_2$($NC_5H_3Me_2$-3,5)][ClO_4].— This complex was prepared in 60% yield in a manner similar to the above using *trans*-[Ni(Cl_2C=CCl)($PMePh_2$)$_2$Cl] (0.625 g, 1 mmol), silver perchlorate, and 3,5-lutidine (0.10 cm^3) in acetonitrile (30 cm^3). This was recrystallized from acetone–ethanol.

trans-[Ni($C_6H_2Me_3$-2,4,6)($PMePh_2$)$_2$($N_2C_3H_3$Me-1)][ClO_4]. —This complex was prepared in 58% yield in a manner similar to the above using *trans*-[Ni($C_6H_2Me_3$-2,4,6)-($PMePh_2$)$_2$Br] (0.658 g, 1 mmol), silver perchlorate, and *N*-methylimidazole in acetone–acetonitrile (4 : 1). This was recrystallized from acetone–ethanol without heating.

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