Intermolecular Exchanges of Tertiary Phosphine Ligands (L) between *trans*-[$NiRXL_2$] (R = $CCl{=}CCl_2$, C_6Cl_5, or $C_6H_2Me_3$-2,4,6) and of Halide Ligands (X) between *trans*-[$MRXL_2$] (M = Ni, Pd, or Pt)

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The intermolecular exchanges of tertiary phosphine ligands (L, L′) occur between *trans*-[$NiRXL_2$] and *trans*-[$NiRXL'_2$] (R = $CCl{=}CCl_2$, C_6Cl_5, or $C_6H_2Me_3$-2,4,6; X = halide, pseudohalide, or C≡CR′) in benzene to give a mixture containing *trans*-[NiRXLL′], as detected from the ^1H and/or ^{31}P-{^1H} n.m.r. spectra. The reactivity appears to depend largely on the nature of the ligands R and X, but the equilibrium constants are in the narrow range 4—9. The intermolecular exchanges of halide ligands between *trans*-[$NiRXL_2$] and *trans*-[$NiR'X'L_2$] (X, X′ = Cl, I, N_3, or NCS) are usually fast at room temperature. The relative affinities of [$NiRL_2$] moieties towards these halide ligands are almost independent of the nature of the ligands R and L (K = 0.3—3.0). The Pd and Pt moieties *trans*-[$M(C_6Cl_5)(PMe_2Ph)_2$] were comparable in the relative affinities towards X (Cl and I) ligands, although they are in favour of the M–I bond formation relative to the Ni moieties.

Although square-planar organometallic complexes are commonly known among nickel triad metals, there are far fewer reports for nickel, compared to palladium or platinum, probably due to the difficulty of preparation. Organonickel(II) complexes of the type *trans*-[$NiRXL_2$] (L = tertiary phosphine, X = halide), however, have been shown to have considerable stability when R is $CCl{=}CCl_2$, C_6Cl_5, or $C_6H_2Me_3$-2,4,6, and they are suitable for a variety of investigations.[1-11] In the present work, we have investigated the ^1H and/or ^{31}P-{^1H} n.m.r. spectra of mixtures of these complexes in order to reveal some possible intermolecular reactions. Some palladium(II) and platinum(II) complexes of the type *trans*-[$M(C_6Cl_5)X(PMe_2Ph)_2$] are also investigated for comparison.

Results and Discussion

Intermolecular Exchanges of Tertiary Phosphine Ligands between trans-[$NiRXL_2$] *Complexes.*—The intermolecular exchange of tertiary phosphine ligands by the reaction shown in equation (i) has been reported for the complexes with R = $C_6H_3(OMe)_2$-2,6.[12] The generality of the reaction has now been investigated for the present complexes (R = $CCl{=}CCl_2$, C_6Cl_5, or $C_6H_2Me_3$-2,4,6; L = PMe_3; L′ = PMe_2Ph, $PMePh_2$, or PPh_3).

$$trans\text{-}[NiRXL_2] + trans\text{-}[NiRXL'_2] \overset{K}{\rightleftharpoons} 2\ trans\text{-}[NiRXLL'] \quad (i)$$

The formation of the mixed-phosphine complexes can be detected from the ^1H and/or ^{31}P-{^1H} n.m.r. spectra.[12-14] The PMe proton resonances of symmetrical complexes are a 1 : 2 : 1 triplet {or two 1 : 2 : 1 triplets for *trans*-[$Ni(CCl{=}CCl_2)X(PMe_2Ph)_2$]} due to the virtually coupled system, while those of the mixed-phosphine complexes must be a doublet of doublets due to the ^2J_P and ^4J_P couplings, or a doublet when ^4J_P is close to zero. These resonances were observed for the present systems, but they are often highly overlapped with the original triplets, although the reactions can be monitored qualitatively with these spectra. Thus the equilibrium constants were estimated from resonance intensities of the other nuclei, and the results are summarized in Table 1. The ^{31}P-{^1H} resonances of these mixed-phosphine complexes are AB quartets, well separated from the original singlets.

The reaction (i) occurs commonly between the present complexes in benzene when X = halide, but the apparent reactivities depend largely on the kind of R ligand. While reactions between the $CCl{=}CCl_2$ complexes [(1), (2), and (7) in Table 1] were observed at room temperature, those between analogous C_6Cl_5 complexes [(3), (4), and (5)] required heat for a prolonged period. The reaction for the $C_6H_2Me_3$-2,4,6 complex, (6), also required heat, but it was accompanied by partial decomposition before the equilibrium was attained. The equilibrium constant of this system was measured with the reaction mixture catalyzed by carbon monoxide. Because of the high reactivity of the $CCl{=}CCl_2$ complexes, isolation of the mixed-phosphine complex is difficult. But, as the C_6Cl_5 complexes are very inert, it is reasonable that some [$Ni(C_6Cl_5)Cl(PPh_3)L$] complexes have been isolated.[15]

The pseudohalides (X) appear to react faster than the halides. The qualitative reactivities observed for the $C_6H_2Me_3$-2,4,6 complexes were in the order of X = N_3 (8) > NCS > Br (6) > I. Worth noting here is that the PMe proton resonance of *trans*-[$Ni(CCl{=}CCl_2)(CN)(PMe_3)_2$] (Table 3) exceptionally was a sharp singlet, due probably to the more rapid intermolecular exchange of the PMe_3 ligands than the ^1H n.m.r. time-scale. A broad singlet resonance of PMe protons has been observed also for some *trans*-[$NiRXL_2$] complexes (R = alkyl, X = halide or pseudohalide).[16]

Interestingly, the ethynyl complexes [X = C≡CPh or $C{\equiv}CC_6H_4OMe$-*p* (9)] reacted very fast at room temperature when R = $CCl{=}CCl_2$. Here, again, the effect of the R group is pronounced, and the analogous ethynyl complexes (R = C_6Cl_5, X = C≡CH or C≡CPh) did not react at room temperature at least for 24 h, or decomposed on heating. Complexes with common 3- or 4-substituted phenyl and some vinyl groups as X were often susceptible to reductive elimination on heating.[17] Complexes (10) showed exceptional thermal stability, and exchanged the tertiary phosphines very slowly at 81 °C (11% after 21 h), or very quickly under carbon monoxide at room temperature.

The equilibrium constants (K) were in the range 4—5 for the exchange between PMe_3 and PMe_2Ph ligands, but they became slightly larger between PMe_3 and $PMePh_2$ or PPh_3. Analogous deviations of K from the statistical value have been reported for the formation of *cis*-[$PdCl_2LL'$] [13] and *trans*-[$Ni\{C_6H_3(OMe)_2\text{-}2,6\}Cl(PMe_3)(PPh_3)$].[12]

Table 1. Intermolecular exchanges of tertiary phosphine ligands [equation (i), L = PMe_3] in C_6H_6

	R	X	L′	Conditions [a]	*K* [b]	^{31}P-{^{1}H} or ^{1}H n.m.r. spectral data [c]
(1)	$CCl{=}CCl_2$	Cl	PMe_2Ph	r.t., 30 min	4.4	^{31}P: −5.36(L′), *−5.94*(L′), *−11.41*(L), −12.19(L) [343]
(2)	$CCl{=}CCl_2$	Cl	$PMePh_2$	r.t., a few hours	5.4	^{31}P: +7.92(L′), *+7.67*(L′), *−10.70*(L), −12.19(L) [334]
(3)	C_6Cl_5	Cl	PMe_2Ph	100 °C, 48 h	4.5	^{31}P: −5.94(L′), *−5.32*(L′), *−14.06*(L), −14.28(L) [317]
(4)	C_6Cl_5	Cl	$PMePh_2$	100 °C, 48 h	6.1	^{32}P: +7.81(L′), *+9.35*(L′), *−13.73*(L), −14.28(L) [315]
(5)	C_6Cl_5	Cl	PPh_3	81 °C, 48 h	8.7	^{31}P: *+20.96*(L′), +18.83(L′), *−13.51*(L), −14.28(L) [308]
(6)	$C_6H_2Me_3$-2,4,6	Br	PMe_2Ph	r.t., under CO, 1 h	4.6	^{1}H:[d] 2.69 s (L), *2.60*s, 2.55 s (L′)
(7)	$CCl{=}CCl_2$	I	PMe_2Ph	r.t., a few hours	4.0	^{31}P: −3.55(L′), *−4.33*(L′), *−10.97*(L), −11.87(L) [317]
(8)	$C_6H_2Me_3$-2,4,6	N_3	PMe_2Ph	r.t., 1 h	4.2	^{1}H:[d] 2.66 s (L), *2.55* s, 2.46 s (L′)
(9)	$CCl{=}CCl_2$	$C{\equiv}CC_6H_4OMe$-p	PMe_2Ph	r.t., 5 min	4.2	^{31}P: +0.0(L′), *−0.69*(L′), *−7.58*(L), −8.21(L) [306]
(10)	$CCl{=}CCl_2$	$C_6H_3(OMe)_2$-2,6	PMe_2Ph	r.t., under CO, 15 min	4.8	^{1}H:[e] 3.48 s and 3.45 s (L), *3.29* s and *3.26* s, 3.15 s, and 3.07 s (L′)

[a] To attain the equilibrium; r.t. = room temperature. [b] Equilibrium constants, estimated from the following resonances. [c] Resonances due to the mixed phosphine complexes are given in italics; the ^{31}P-{^{1}H} spectral data were analysed as an AB spin system. $^2J_{PP}$ values (Hz) are given in square brackets. [d] 2,6-Me_2 protons. [e] 2,6-$(OMe)_2$ protons.

Table 2. Intermolecular exchanges of halide ligands [equation (ii)] in C_6H_6

	M	R	X	L	M′	R′	X′	L′	Conditions [a]	*K* [b]
(11)	Ni	$CCl{=}CCl_2$	Cl	PMe_3	Ni	C_6Cl_5	I	PMe_3	r.t., <5 min	0.9
(12)	Ni	$CCl{=}CCl_2$	Cl	PMe_2Ph	Ni	C_6Cl_5	I	PMe_2Ph	r.t., <5 min	0.8
(13)	Ni	$CCl{=}CCl_2$	Cl	$PMePh_2$	Ni	C_6Cl_5	I	$PMePh_2$	r.t., 24 h	0.8
(14)	Ni	$CCl{=}CCl_2$	Cl	PMe_3	Ni	$CCl{=}CCl_2$	I	$PMePh_2$	r.t., <5 min	*ca.* 3
(15)	Ni	C_6Cl_5	Cl	PMe_3	Ni	C_6Cl_5	I	PMe_2Ph	r.t., <5 min	1.6
(16)	Ni	C_6Cl_5	Cl	PMe_3	Ni	C_6Cl_5	I	$PMePh_2$	60 °C, 1 h	2.3
(17)	Ni	$C_6H_2Me_3$-2,4,6	Cl	PMe_2Ph	Ni	C_6Cl_5	I	PMe_2Ph	r.t., <5 min	1.0
(18)	Ni	$CCl{=}CCl_2$	Cl	PMe_2Ph	Ni	$C_6H_2Me_3$-2,4,6	N_3	PMe_2Ph	r.t., <5 min	1.0
(19)	Ni	C_6Cl_5	Cl	PMe_2Ph	Ni	$C_6H_2Me_3$-2,4,6	N_3	PMe_2Ph	r.t., <5 min	0.9
(20)	Ni	$CCl{=}CCl_2$	Cl	PMe_3	Ni	$C_6H_2Me_3$-2,4,6	NCS	PMe_3	r.t., <5 min	0.4 [c]
(21)	Ni	C_6Cl_5	Cl	PMe_2Ph	Ni	$C_6H_2Me_3$-2,4,6	NCS	PMe_2Ph	r.t., <5 min	0.3
(22)	Ni	C_6Cl_5	I	PMe_2Ph	Ni	$C_6H_2Me_3$-2,4,6	NCS	PMe_2Ph	r.t., <5 min	0.3
(23)	Ni	$C_6H_2Me_3$-2,4,6	Cl	PMe_2Ph	Pd	C_6Cl_5	I	PMe_2Ph	r.t., <5 min [d]	<0.01
(24)	Ni	$C_6H_2Me_3$-2,4,6	Cl	PMe_2Ph	Pt	C_6Cl_5	I	PMe_2Ph	r.t., a few hours [d]	<0.01
(25)	Pd	C_6Cl_5	Cl	PMe_2Ph	Pt	C_6Cl_5	I	PMe_2Ph	r.t., a few hours	*ca.* 1

[a] To attain the equilibrium. [b] Equilibrium constants. [c] In CH_2Cl_2. [d] Observations for the reverse reaction.

The precise mechanism of these reactions is not known at present, and need not be the same for all cases. However, the pronounced reactivity in (1), (2), (7), (8), or (9) seems to suggest a mechanism comprising an initial formation of a dimeric species, $[NiRXL_2{\cdot}NiRXL'_2]$, with intermolecular bridging *via* the X ligand. Such a dimer species has recently been postulated for the *cis–trans* isomerization of $[PtX_2L_2]$ complexes in non-polar solvent,[18] and dimeric nickel(II) complexes $[\{NiRXL\}_2]$ are well known.[2,19] In order to obtain more direct information, the intermolecular exchanges of halide ligands were investigated, since the dimer species assumed here is also a possible intermediate for this reaction.

Intermolecular Exchanges of Halide Ligands between trans-$[NiRXL_2]$.—The intermolecular exchange of halide ligands [equation (ii)] was observed between the present complexes

$$\textit{trans}\text{-}[MRXL_2] + \textit{trans}\text{-}[M'R'X'L'_2] \xrightleftharpoons{K} \textit{trans}\text{-}[MRX'L_2] + \textit{trans}\text{-}[M'R'XL'_2] \quad \text{(ii)}$$

in benzene, and some representatives are summarized in Table 2.

In most cases, the reactions were too rapid at room temperature to follow, attaining equilibrium before the spectral measurements. This is so even between two C_6Cl_5 complexes [(15) of Table 2] or between a C_6Cl_5 complex and a $C_6H_2Me_3$-2,4,6 complex, (17), probably indicating that such bulky phenyl groups do not interfere with the dimerization of these complexes. Exceptions are those reactions concerning *trans*-$[Ni(C_6Cl_5)I(PMePh_2)_2]$, complexes (13) and (16), which required many hours to attain equilibrium at room temperature. The inertness may probably be attributable to the bulkiness of $PMePh_2$ ligands as well as of the C_6Cl_5 group. The reaction concerning *trans*-$[Ni(CCl{=}CCl_2)I(PMePh_2)_2]$, (14), was very fast. The spectrum of (14) further varied gradually on standing at room temperature due to the intermolecular exchange of the tertiary phosphine ligands.

The equilibrium constants of reactions between a $CCl{=}CCl_2$ complex and a C_6Cl_5 complex, (11)—(13), were close to unity. This is so even between a $C_6H_2Me_3$-2,4,6 and a C_6Cl_5 or $CCl{=}CCl_2$ complex when X, X′ are Cl, I, or N_3, complexes (17)—(19). This result is astonishing in a sense, because we expected some difference in the so-called ' hard and soft acid ' character between these nickel moieties. Some properties of carbene complexes of these moieties have recently been compared, and differed considerably.[11] Since equation (ii) contains only the M–X bond exchange, the entropy change must be negligible between both sides of the equation. Thus, the equilibrium constant represents a relationship among the four M–X bond strengths, indicating that the bond energy difference between Ni–Cl and Ni–I or Ni–N_3 bonds in $[Ni(C_6Cl_5)X(PMe_2Ph)_2]$ is identical with that in $[Ni(C_6H_2Me_3\text{-}2,4,6)X(PMe_2Ph)_2]$. The equilibrium of the reactions between complexes containing different tertiary phosphine ligands lies only slightly apart from the side containing a complex with iodide and the bulkier tertiary phosphine ligands together, complexes (14)—(16). The equilibrium of exchanges between Cl or I and NCS ligands lies slightly towards the formation of *trans*-$[Ni(C_6H_2Me_3\text{-}2,4,6)(NCS)L_2]$ (20)—(22).

No exchange of Cl and $C\equiv CPh$ ligands was observed between some $[NiR(Cl)L_2]$ and $[NiR'(C\equiv CPh)L_2]$ complexes. For the observed facile exchange of tertiary phosphine ligands between ethynyl complexes (9), we tentatively propose that the ethynyl ligand bridges the other molecule *via* its π electrons forming an asymmetric dimer species, from which the intermolecular exchange of the ethynyl ligand is impossible.

Comparison of Ni^{II}, Pd^{II}, *and* Pt^{II} *Complexes by Intermolecular Exchanges of Halide Ligands.*—The investigation of intermolecular exchange of halide ligands was extended to the comparison of Ni^{II}, Pd^{II}, and Pt^{II} in *trans*-$[M(C_6Cl_5)X(PMe_2Ph)_2]$. These complexes were chosen because we have previously prepared the carbene complexes of these metals, *trans*-$[M(C_6Cl_5)(PMe_2Ph)_2\{C(OR)R'\}]ClO_4$.[9]

The Cl and I ligand exchange between the nickel and the palladium or the platinum complexes resulted in the complete formation of Ni–Cl and Pd–I or Pt–I bonds, complexes (23) and (24), as confirmed by the reverse reactions. Unexpected was the result of the reaction between the palladium and the platinum complexes, which gave an equilibrium of all the four

Table 3. Analytical and spectral data for the new complexes

Complexes [a]	Method of preparation [b]	M.p. (θ_c/°C)	Analysis (%) [c] C	H	N	X [d]	^{1}H N.m.r. (p.p.m.) [e] and i.r. (cm^{-1}) [f] spectral data
$[Ni(CCl{=}CCl_2)I(PMe_3)_2]$	I(82)	140—141	20.3 (20.5)	4.2 (3.9)		49.5 (49.8)	1.13 (t, 18 H, PMe, $[8]_P$)
$[Ni(CCl{=}CCl_2)I(PMe_2Ph)_2]$	I(94)	129—130	36.5 (36.5)	3.9 (3.7)		39.3 (39.4)	1.51 (t, 6 H, PMe, $[8]_P$), 1.42 (t, 6 H, PMe, $[8]_P$)
$[Ni(CCl{=}CCl_2)I(PMePh_2)_2]$	II(30)	152—153	47.0 (46.9)	3.8 (3.7)		32.5 (32.6)	1.98 (t, 6 H, PMe, $[7.5]_P$)
$[Ni(C_6H_2Me_3\text{-}2,4,6)I(PMe_3)_2]$	II(63)	164—166	39.6 (39.4)	6.5 (6.4)		27.7 (27.8)	2.60 (s, 6 H, *o*-Me), 2.18 (s, 3 H, *p*-Me), 0.91 (t, 18 H, PMe, $[7]_P$)
$[Ni(C_6Cl_5)I(PMe_3)_2]$	II(73)	230—240 [g]	24.6 (24.6)	3.3 (3.1)		52.1 (51.8)	0.87 (t, 18 H, PMe, $[8]_P$)
$[Ni(C_6Cl_5)I(PMePh_2)_2]$	II(74)	206—207	45.9 (46.0)	3.4 (3.1)		36.6 (36.4)	2.24 (t, 6 H, PMe, $[7.5]_P$)
$[Pd(C_6Cl_5)I(PMe_2Ph)_2]$	I(55)	185 [g]	34.9 (34.8)	3.1 (2.9)		39.8 (40.1)	1.54 (t, 12 H, PMe, $[7]_P$)
$[Pt(C_6Cl_5)I(PMe_2Ph)_2]$	I(82)	191	31.2 (31.2)	2.8 (2.6)		35.9 (35.9)	1.59 (tt, 12 H, PMe, $[7_P]$, $[30]_{Pt}$)
$[Ni(CCl{=}CCl_2)(N_3)(PMe_2Ph)_2]$	III(92)	76—77	42.2 (42.6)	4.4 (4.4)	7.9 (8.3)		1.25 (t, 6 H, PMe, $[7.5]_P$), 1.19 (t, 6 H, PMe, $[7.5]_P$); 2 060vs (N_3)
$[Ni(C_6H_2Me_3\text{-}2,4,6)(N_3)(PMe_3)_2]$	III(73)	141 [g]	48.2 (48.5)	8.0 (7.9)	11.3 (11.3)	8.0 (7.9)	2.66 (s, 6 H, *o*-Me), 2.17 (s, 3 H, *p*-Me), 0.70 (t, 18 H, PMe, $[7]_P$); 2 062vs (N_3)
$[Ni(C_6Cl_5)(N_3)(PMe_2Ph)_2]$	III(83)	131—133	42.2 (42.2)	3.6 (3.5)	6.6 (6.7)		1.15 (t, 12 H, PMe, $[8]_P$); 2 070vs (N_3)
$[Ni(CCl{=}CCl_2)(CN)(PMe_3)_2]$	III(70)	143—145	29.2 (29.4)	5.0 (4.9)	3.8 (3.8)	29.0 (29.0)	1.02 (s, 18 H, PMe); 2 117m (CN), 2 108m (CN)
$[Ni(CCl{=}CCl_2)(NCS)(PMe_3)_2]$	III(86)	175—177	27.3 (27.1)	4.7 (4.5)	3.5 (3.5)		0.79 (t, 18 H, PMe, $[8]_P$); 2 100vs (NCS)
$[Ni(C_6H_2Me_3\text{-}2,4,6)(NCS)(PMe_3)_2]$	III(71)	162 [g]	49.6 (49.5)	7.6 (7.5)	3.7 (3.6)	8.3 (8.3)	2.50 (s, 6 H, *o*-Me), 2.14 (s, 3 H, *p*-Me), 0.60 (t, 18 H, PMe, $[7]_P$); 2 090vs (NCS)
$[Ni(C_6Cl_5)(C\equiv CH)(PMe_3)_2]$	IV(61)	120—125 [g]	34.9 (34.7)	4.1 (4.0)		36.3 (36.5)	2.33 (t, 1 H, $C\equiv CH$, $[4]_P$), 0.85 (t, 18 H, PMe, $[8]_P$); 3 286w (CH), 1 958w ($C\equiv C$)
$[Ni(CCl{=}CCl_2)(C\equiv CPh)(PMe_3)_2]$	IV(70)	140 [g]	43.5 (43.4)	5.3 (5.2)		24.3 (24.0)	1.12 (t, 18 H, PMe, $[8]_P$); 2 090s ($C\equiv C$)
$[Ni(CCl{=}CCl_2)(C\equiv CC_6H_4OMe\text{-}p)(PMe_3)_2]$	IV(63)	130 [g]	43.1 (43.2)	5.4 (5.3)		22.6 (22.5)	3.43 (s, 3 H, OMe), 1.17 (t, 18 H, PMe, $[8]_P$); 2 090m ($C\equiv C$)
$[Ni(CCl{=}CCl_2)\{C_6H_3(OMe)_2\text{-}2,6\}(PMe_3)_2]$	V(78)	140—145 [g]	40.2 (40.1)	5.7 (5.7)		22.3 (22.2)	3.48 (s, 3 H, OMe), 3.45 (s, 3 H, OMe), 0.87 (t, 18 H, PMe, $[8]_P$)

[a] All are *trans* isomers. [b] I $[MR(Cl)L_2] + NH_4I$; II $[NiRL_2L']ClO_4 + NH_4I$; III $[NiRXL_2] + NaN_3$, NaCN, or NaNCS; IV $[NiRXL_2] + AgClO_4 + HC\equiv CR' + NEt_3$; V $[NiR(Cl)L_2] + LiR'$; yields are given in parentheses. [c] Calculated values are given in parentheses. [d] Cl, Br, I, and S. [e] In benzene (0.1 mol dm^{-3} solution); s = singlet, t = triplet, tt = triplet of triplets; J_P or J_{Pt} values (Hz) are given in square brackets. [f] Stretching vibrations, in Nujol mull. [g] With decomposition.

complexes in almost the same concentrations, complex (25). In an analogous manner to the above, these results indicate that the bond energy difference between Ni–Cl and Ni–I is larger than that between Pd–Cl and Pd–I, but the latter is comparable with that between Pt–Cl and Pt–I. In these M–X bonds, the d_π–p_π bonding is not a decisive factor, while in the carbene complexes[9] its participation must affect the results for the three different metals.

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 obtained on a JEOL model JNM-FX-90Q spectrometer operating in the Fourier-transform mode at 36.2 MHz, using H_3PO_4 as external standard. I.r. spectra were recorded on a Hitachi 215 spectrophotometer.

The following complexes were prepared as described previously: *trans*-$[Ni(CCl{=}CCl_2)(Cl)L_2]$ (L = PMe_3,[10] PMe_2Ph,[6] and $PMePh_2$[10]), *trans*-$[Ni(CCl{=}CCl_2)X(PMe_2Ph)_2]$ [X = $C{\equiv}CPh$,[8] $C{\equiv}CC_6H_4OMe$-*p*,[8] and $C_6H_3(OMe)_2$-2,6[7]], *trans*-$[Ni(C_6Cl_5)(Cl)L_2]$ (L = PMe_3,[11] PMe_2Ph,[3] $PMePh_2$,[4] and PPh_3[2]), *trans*-$[Ni(C_6Cl_5)X(PMe_2Ph)_2]$ (X = I,[3] NCS,[20] $C{\equiv}CH$,[5] and $C{\equiv}CPh$[5]), *trans*-$[Ni(C_6H_2Me_3\text{-}2,4,6)Br(PMe_3)_2]$,[10] *trans*-$[Ni(C_6H_2Me_3\text{-}2,4,6)X(PMe_2Ph)_2]$ (X = Cl,[8] Br,[3] I,[3] N_3,[8] and NCS[3]), *trans*-$[M(C_6Cl_5)Cl(PMe_2Ph)_2]$ (M = Pd and Pt).[9] New complexes are listed in Table 3, together with the methods of preparation. The starting complexes used for method II were as follows: *trans*-$[Ni(CCl{=}CCl_2)(PMePh_2)_2(NC_5H_3Me_2\text{-}3,5)]ClO_4$,[10] *trans*-$[Ni(C_6H_2Me_3\text{-}2,4,6)(PMe_3)_2(NC_5H_4Me\text{-}3)]ClO_4$,[10] *trans*-$[Ni(C_6Cl_5)(PMe_3)_2(NCMe)]ClO_4$ (see below), and *trans*-$[Ni(C_6Cl_5)(PMePh_2)_2(NCMe)]ClO_4$.[20]

trans-$[Ni(C_6Cl_5)(PMe_3)_2(NCMe)]ClO_4$.—A solution of *trans*-$[Ni(C_6Cl_5)Cl(PMe_3)_2]$ (2.48 g, 5 mmol) in benzene (50 cm^3) was added dropwise to a solution of silver perchlorate (1.04 g, 5 mmol) in benzene (50 cm^3). The silver chloride precipitate was removed by filtration to give an orange-brown solution, to which was added an excess of acetonitrile (2.5 cm^3) with stirring, followed by n-hexane (50 cm^3). The resulting yellow precipitate was separated by filtration, and dried *in vacuo*, yield *ca.* 90%, m.p. 200—205 °C (decomp.) (Found: C, 28.4; H, 3.6; Cl, 34.7; N, 2.3. $C_{14}H_{21}Cl_6NNiO_4P_2$ requires C, 28.0; H, 3.5; Cl, 35.4; N, 2.3%). ^1H n.m.r. (CH_2Cl_2): δ 2.58 (s, 3 H, CMe) and 1.23 p.p.m. (t, 18 H, PMe, J_P = 8 Hz).

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