Mesityl- and Pentachlorophenyl-nickel(II) Complexes with the Cyclic Alkoxyvinyl Group or Alkyl(alkoxy)carbene Ligand: the Relative Bronsted Acidity and the Rotational Barrier about the Nickel–Carbon Bønd

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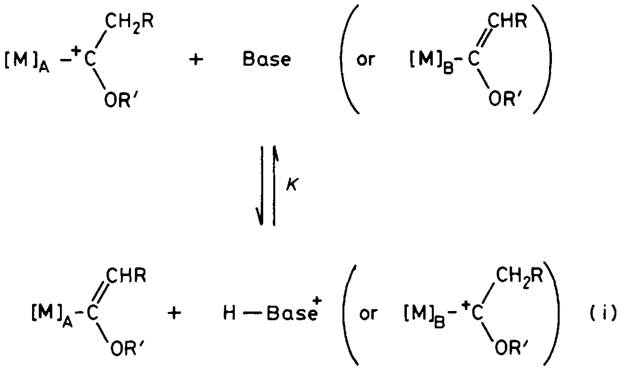
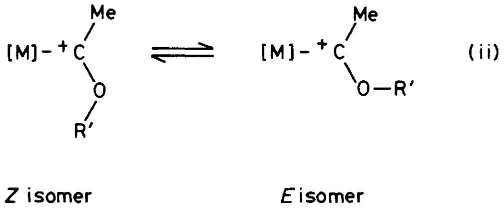
Cyclic α-alkoxyvinylnickel(II) complexes of the types *trans*-$[\mathrm{NiRL_2(\overline{C{=}CHCH_2CH_2O})}]$ and *trans*-$[\mathrm{NiRL_2(\overline{C{=}CHCH_2CH_2CH_2O})}]$ ($\mathrm{R = C_6H_2Me_3}$-2,4,6 or $\mathrm{C_6Cl_5}$ and $\mathrm{L = PMe_3}$ or $\mathrm{PMe_2Ph}$) have been prepared from *trans*-$[\mathrm{NiRL_2X}]$ (X = Cl or Br) and 2,3-dihydro-5-lithiofuran or 2,3-dihydro-6-lithiopyran. Treatment of these complexes with aqueous perchloric acid gives the corresponding cationic cyclic carbene complexes, *trans*-$[\mathrm{NiRL_2(\overline{CCH_2CH_2CH_2O})][ClO_4]}$ and *trans*-$[\mathrm{NiRL_2(\overline{CCH_2CH_2CH_2CH_2O})][ClO_4]}$. The carbene complexes of *trans*-$\mathrm{Ni(C_6H_2Me_3\text{-}2,4,6)L_2}$ have a lower Brønsted acidity than those of *trans*-$\mathrm{Ni(C_6Cl_5)L_2}$ and the barriers to rotation of the cyclic alkoxyvinyl groups and the cyclic alkyl(alkoxy)carbene ligands about the Ni–C bond are lower for the former complexes than for the latter. These results are intepreted in terms of the stronger *trans* influence of the $\mathrm{C_6H_2Me_3}$-2,4,6 group.

WELL characterized organo(alkoxy)carbene complexes are now known for many transition metals.[1-4] We earlier reported the preparation and properties of some organonickel(II) carbene complexes of types *trans*-$[\mathrm{Ni(C_6Cl_5)(PMe_2Ph)_2\{C(OR')CH_2R\}][ClO_4]}$ [5-8] and *trans*-$[\mathrm{Ni(C_6Cl_5)(PMe_2Ph)_2\{C(OR)R''\}][ClO_4]}$ (R″ is an aryl group).[9] Typically, these complexes have fairly rigid bonding and stereochemistries. The former species can be readily and reversibly deprotonated to give α-alkoxyvinyl complexes, *trans*-$[\mathrm{Ni(C_6Cl_5)(PMe_2Ph)_2\{C(OR'){=}CHR\}]}$, and an acid–base equilibrium mixture is obtained on mixing the two types, see equation (i).[5,7,8] Analogous reactions have been observed for the corresponding palladium(II) and platinum(II) complexes.[7,8]



$[\mathrm{M}]_\mathrm{A}$ and $[\mathrm{M}]_\mathrm{B}$ represent different *trans*-$\mathrm{MXL_2}$ moieties

The methyl(alkoxy)carbene complexes exist as an equilibrium mixture of two isomers in solution [equation (ii)] due to hindered rotation about the C(carbene)–O bond † on the ^{1}H n.m.r. time-scale.[5] In the analogous palladium(II) and platinum(II) complexes [7,8] and *trans*-$[\mathrm{Ni(C_6H_2Me_3\text{-}2,4,6)(PMe_2Ph)_2\{C(OMe)Me\}][ClO_4]}$ [10] only the *Z* isomer is present. The rotation of cyclic alkyl(alkoxy)carbene ligands about the C–Ni bond is hindered at low temperatures, where the ligands are oriented perpendicularly to the nickel co-ordination plane.[5,8] In the palladium(II) and platinum(II) complexes, such a hindered rotation could not be observed down to −80 °C.[8]



The nickel complexes exhibit a characteristic weak band attributable to the so-called *d–d* transition in their electronic spectra.[6] The position of alkyl(alkoxy)carbene ligands at the top of the spectrochemical series was interpreted as being due to the presence of Ni–C(carbene) π bonding, whereas the α-alkoxyvinyl groups lie at the lowest position of all the carbon ligands in this series,[5,6] probably because of the optimum σ-bonding polarity in the Ni–C(vinyl) bond.[7,8]

In the present work, we determine the effect on some of the above properties of changing the secondary ligands in nickel α-alkoxyvinyl and alkyl(alkoxy)carbene complexes.

RESULTS AND DISCUSSION

Preparation of Complexes.—Five- and six-membered cyclic α-alkoxyvinyl complexes and alkyl(alkoxy)carbene complexes of four organonickel(II) units, (a)—(d), were prepared according to the reactions shown in Scheme 1 where (a) = *trans*-$\mathrm{Ni(C_6H_2Me_3\text{-}2,4,6)(PMe_3)_2}$, (b) = *trans*-$\mathrm{Ni(C_6H_2Me_3\text{-}2,4,6)(PMe_2Ph)_2}$, (c) = *trans*-$\mathrm{Ni(C_6Cl_5)(PMe_3)_2}$, and (d) = *trans*-$\mathrm{Ni(C_6Cl_5)(PMe_2Ph)_2}$. The analytical, physical, and spectral data for the new organonickel(II) complexes are summarized in Tables 1 and 2. The vinyl complexes of *trans*-$\mathrm{Ni(C_6H_2Me_3\text{-}2,4,6)L_2}$, (1a), (1b), (2a), and (2b), are less stable than

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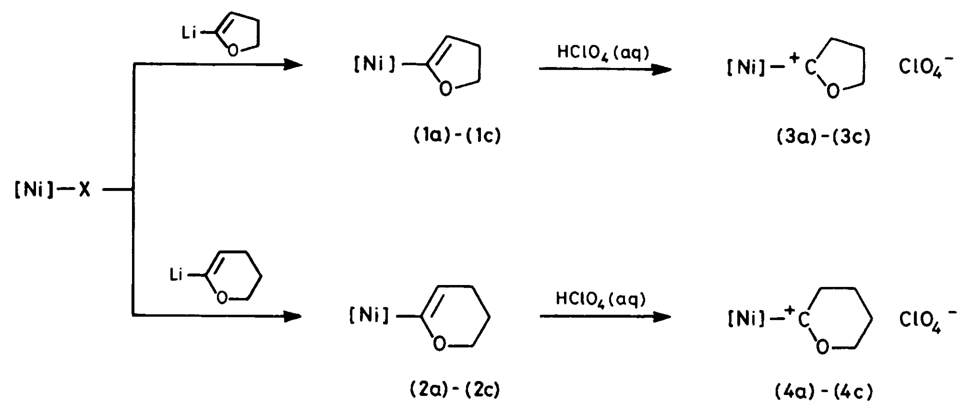
† Throughout this paper, we have omitted to represent the partial double-bond character of the C(carbene)–O bond.



SCHEME 1 [Ni] denotes *trans*-Ni($C_6H_2Me_3$-2,4,6)(PMe_3)$_2$ (a), *trans*-Ni($C_6H_2Me_3$-2,4,6)(PMe_2Ph)$_2$ (b), and *trans*-Ni(C_6Cl_5)(PMe_3)$_2$ (c); X = Cl or Br. Analogous derivatives of *trans*-Ni(C_6Cl_5)(PMe_2Ph)$_2$ (d) have been prepared.[5,8]

those of *trans*-Ni(C_6Cl_5)L_2 (L = PMe_3 or PMe_2Ph), (1c), (1d), (2c), and (2d), and assume a brown colour on storage for 1 month in air at room temperature. In dichloromethane, they remain unchanged for only 1 or 2 d. **CAUTION:** The carbene complexes (3a), (3b), and (4b) decomposed explosively on heating.

TABLE 1

Analytical and physical data for the complexes

Complex	Analysis (%) [a] C	H	Cl [b]	M.p.[c] (θ_c/°C)	$\tilde{\nu}$(C=C) [d]/ cm^{-1}
(1a)	56.8	8.8		117—118	1 550s
	(57.2)	(8.6)			
(1b)	66.2	7.5		98—104	1 546s
	(66.6)	(7.3)			
(1c)	36.4	4.3	33.6	169—170	1 558s
	(36.3)	(4.4)	(33.5)		
(2a)	58.2	9.0		122—123	1 575s
	(58.1)	(8.8)			
(2b)	66.8	7.7		94—95	1 573s
	(67.1)	(7.5)			
(2c)	37.9	4.7	32.5	154—156	1 579s
	(37.6)	(4.6)	(32.6)		
(3a)	45.5	7.2		148	
	(45.7)	(7.1)		130—131	
(3b)	55.7	6.4			
	(55.8)	(6.3)			
(3c)	30.7	3.9	34.1	153—154	
	(30.5)	(3.8)	(33.8)		
(4a)	46.5	7.5	7.2	118—122	
	(46.8)	(7.3)	(6.9)		
(4b)	56.4	6.6		122—126	
	(56.5)	(6.5)			
(4c)	31.9	4.2	32.8	144—145	
	(31.7)	(4.1)	(33.0)		

[a] Calculated values are given in parentheses. [b] The chlorine analyses of some complexes could not be undertaken due to their explosive nature. [c] With decomposition *in vacuo*. [d] In Nujol.

The ^1H n.m.r. spectra of all the nickel complexes show a triplet (1 : 2 : 1) of resonances due to the phosphine methyl protons and are consistent with *trans* square-planar configurations. In accord with the cationic properties of carbene complexes, the resonances of phosphine methyl and carbene oxymethylene protons were in general observed at lower field than those of the corresponding neutral vinyl complexes. Of the $C_6H_2Me_3$-2,4,6 protons, the *m*-H chemical shift clearly distinguished between the cationic (carbene) and the neutral (vinyl) complexes, as found previously for derivatives of *trans*-Ni($C_6H_2Me_3$-2,4,6)L_2.[10,11]

Relative Brønsted Acidity.—The Brønsted acidities of the carbene complexes were determined by ^1H n.m.r. spectroscopy.[7,8] When complexes (1c) and (3d) were mixed in 1 : 1 mole ratio in CD_2Cl_2 the spectrum showed the presence of all four species, (1c), (1d), (3c), and (3d), as expected from the acid–base equilibrium (i). The equilibrium lies slightly in favour of the formation of (1c) and (3d) ($K = 0.45$). When the complexes (1b) and (3d) were mixed the spectrum showed the presence of only (3b) and (1d). Although overlap of resonances between complexes often precluded the determination of accurate equilibrium constants, the order of relative Brønsted acidities of the carbene complexes could be established, as summarized in Scheme 2. This Scheme also includes the results for methyl(methoxy)carbene complexes.[7,10] Apparently, the carbene complexes of *trans*-Ni($C_6H_2Me_3$-2,4,6)L_2 are less acidic than those of *trans*-Ni(C_6Cl_5)L_2, and changing the *cis* tertiary phosphine ligand, PMe_3 or PMe_2Ph, has little effect on the acidity, although the PMe_3 complexes are invariably slightly more acidic than the corresponding PMe_2Ph complexes. The least acidic carbene complex investigated here is (3b), which is as acidic as the piperidinium cation. Thus, its conjugate base, (1b), is as basic as piperidine and hence probably one of the most basic neutral carbon species known.

Since acidity is related to the difference in free-energy between the acid and its dissociated system, the lower acidity of the carbene complexes of *trans*-Ni($C_6H_2Me_3$-2,4,6)L_2 may be attributed to one of the following properties: (*i*) the $C_6H_2Me_3$-2,4,6 group induces a larger partial negative charge on the *trans* alkoxyvinyl group to destabilize the complex (*trans* influence); (*ii*) the $C_6H_2Me_3$-2,4,6 group increases the π-donor ability of the nickel in order to stabilize the Ni–C(carbene) bond through d_π–p_π bonding; or (*iii*) a combination of these two. The i.r. spectra (Table 1) of alkoxyvinyl complexes of *trans*-Ni($C_6H_2Me_3$-2,4,6)L_2, (1a), (1b), (2a), and (2b), showed the ν(C=C) band at a lower frequency than that of the *trans*-Ni(C_6Cl_5)L_2 complexes, (1c), (1d),[8] (2c), and

TABLE 2

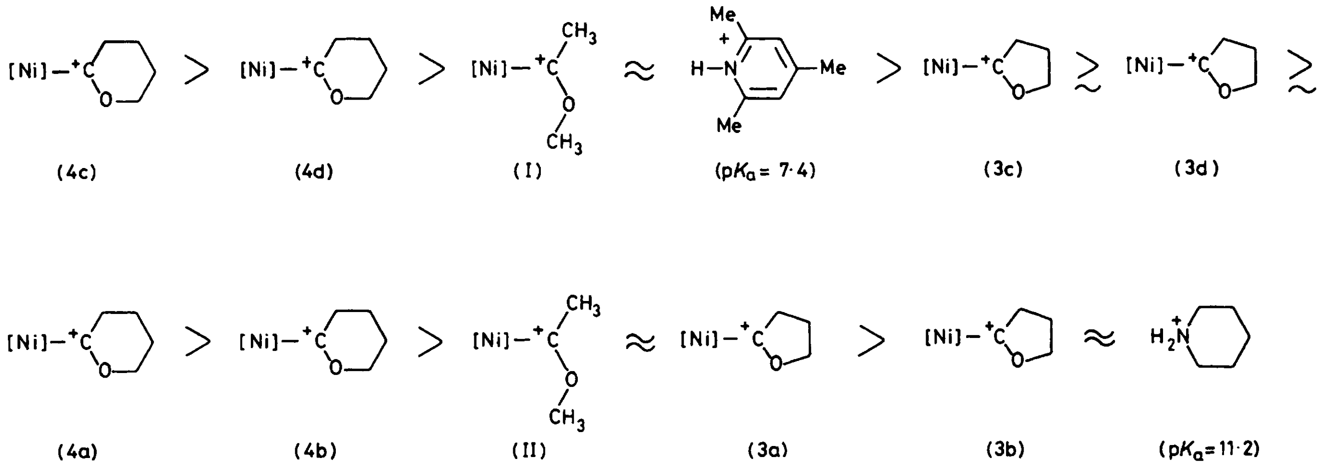
Hydrogen-1 n.m.r. spectral data for the complexes [a, b]

Complex	P–Me	*o*-Me	*m*-H	*p*-Me	OCH_2	C=CH or $^+CCH_2$	Other CH_2 protons
(1a)	0.98 (t) [6.9]	2.48 (s)	6.46 (s)	2.10 (s)	3.97 (t) [8.8]	4.48 (br)	*ca.* 2.37 (m) [c]
(1b)	1.15 (t) [7.1]	2.27 (s)	6.47 (s)	2.15 (s)	3.74 (t) [9.5]	4.28 (qnt) [2.3] [d]	*ca.* 2.25 (m) [c]
(1c)	1.07 (t) [7.6]				4.08 (t) [9.0]	4.55 (m)	2.43 (m)
(2a)	0.99 (t) [6.8]	2.45 (s)	6.48 (s)	2.12 (s)	3.87 (t) [4.9]	4.27 (qnt) [3.0] [d]	1.69—1.97 (m)
(2b)	1.22 (t) [6.5]	2.30 (s)	6.45 (s)	2.14 (s)	3.44 (t) [5.1]	3.98 (br)	1.54 (m), 1.73 (br)
(2c)	1.12 (t) [7.5]				3.88 (t) [5.0]	4.32 (t) [3]	1.68—2.04 (m)
(3a)	1.05 (t) [8.0]	2.48 (s)	6.68 (s)	2.16 (s)	5.26 (t) [7.7] [e]	3.63 (m)	2.15 (qnt) [7.5] [e]
(3b)	1.34 (t) [7.7]	2.62 (s)	6.74 (s)	2.23 (s)	4.54 (t) [7.5]	2.45 (t) [7.5]	1.03 (qnt) [7.5]
(3c)	1.20 (t) [8.9]				5.34 (t) [7.8] [e]	3.78 (tt) [7.5] [f] [2.9] [g]	2.25 (qnt) [7.5]
(4a)	1.06 (t) [8.3]	2.47 (s)	6.64 (s)	2.17 (s)	4.95 (t) [4.8]	3.49 (m)	1.71—2.09 (m)
(4b)	1.32 (t) [8.2]	2.64 (s)	6.74 (s)	2.22 (s)	4.24 (t) [5.3]	2.47 (m)	0.67 (qnt) [6.4], 1.11 (qnt) [6.4]
(4c)	1.24 (t) [8.3]				5.09 (t) [4.9]	3.60 (m)	1.78—2.13 (m)

[a] Chemical shift (δ, p.p.m.) in CH_2Cl_2 or CD_2Cl_2 at 23 °C. The coupling constants (J_P or J_H, Hz) are given in square brackets. s = Singlet, t = triplet, qnt = quintet, m = multiplet, tt = triplet of triplets, br = broad. [b] Data for (1d), (2d), (3d), and (4d) are given in ref. 8. [c] Overlapped with other resonance. [d] $J_P \approx J_H$. [e] Data for $CDCl_3$ solution. [f] J_H. [g] J_P.

(2d)[8] respectively, although the difference in each case was small. These results tend to support features (*i*) or (*iii*) above, although a comparison of the rotational barriers of the cyclic alkoxyvinyl groups and the cyclic carbene ligands is more informative.

Rotational Barriers of Cyclic Alkoxyvinyl and Alkyl(alkoxy)carbene Ligands.—The barriers to rotation (Δ*G*‡) of these ligands about the C–Ni bond were obtained from the temperature-dependent ^1H n.m.r. spectra of the *ortho*-methyl protons of the $C_6H_2Me_3$-2,4,6 group and/or the methyl protons of the PMe_2Ph ligands. The results are summarized in Table 3.



SCHEME 2 Relative Brønsted acidity of cationic carbene complexes. For definition of [Ni] see caption to Scheme 1; (d) = *trans*-$Ni(C_6Cl_5)(PMe_2Ph)_2$; [Ni] = (d) for complex (I) and (b) for (II)

We believe that the barrier to rotation results from the steric hindrance between the vinyl group or the carbene ligand and the tertiary phosphine ligands at the *cis* positions.[11] This assumption explains the smaller Δ*G*‡ values for the five-membered cyclic carbene complexes, (3a), (3b), and (3d), than those for the corresponding six-membered cyclic carbene complexes, (4a), (4b), and (4d) respectively, as well as the smaller values for the PMe_3 complexes, (2a), (3a), and (4a), than those for the PMe_2Ph complexes, (2b), (3b), and (4b) respectively. On changing the *trans* phenyl group from C_6Cl_5 to $C_6H_2Me_3$-2,4,6, a decrease in the value of Δ*G*‡ was observed for both the vinyl and the carbene complexes [(2b) *vs.* (2d), (3b) *vs.* (3d), and (4b) *vs.* (4d)]. The lower barrier for (2b) than (2d) is in accord with the stronger inductive effect (*trans* influence) of the $C_6H_2Me_3$-2,4,6 group, which should cause an elongation of the *trans* Ni–C(vinyl) bond. The analogous trend observed for the carbene complexes suggests that features (*i*) or (*iii*) (see above) are responsible for the lower acidity of carbene complexes of *trans*-$Ni(C_6H_2Me_3\text{-}2,4,6)L_2$. The rotational barrier for carbene complexes is always higher than that for the corresponding vinyl complexes. This is in accord with the presence of d_π–p_π bonding in the Ni–C(carbene) bond, and supports case (*iii*).

It now seems possible to explain why *trans*-[Ni$(C_6Cl_5)(PMe_2Ph)_2\{C(OMe)Me\}][ClO_4]$ exists as an equilibrium mixture of two isomers (*Z* and *E*), while *trans*-[Ni$(C_6H_2Me_3\text{-}2,4,6)(PMe_2Ph)_2\{C(OMe)Me\}][ClO_4]$ exists only in the form of the *Z* isomer. We assume that the carbene methyl group exerts greater steric hindrance than the nickel atom in relation to the methoxy-methyl group, that the Ni–C(carbene) bond in the $C_6H_2Me_3$-2,4,6 complex is sufficiently long to allow the carbene ligand to assume the *Z* form, but that the corresponding bond in the C_6Cl_5 complex is so short that it causes a considerable steric interaction between the nickel atom and the methoxy-methyl group. This argument contrasts with that of Cross and co-workers,[12] who studied *cis*-[$PtCl_2(PMe_2Ph)\{C(OEt)CH_2Ph\}$] (*Z* isomer) and deduced the possibility of a Pt • • • H (of OCH_2) bonding interaction, in which the platinum atom was electrophilic. If such a situation existed in our methyl(methoxy)carbene complexes the proportion of the *Z* isomer in *trans*-Ni(C_6Cl_5)L_2 would have been greater than that in *trans*-Ni($C_6H_2Me_3$-2,4,6)L_2.

TABLE 3

Barriers to rotation of cyclic alkoxyvinyl and alkyl(alkoxy)-carbene ligands about the C–Ni bond to *trans*-$NiRL_2$

Complex	Coalescence temperature/K	$\Delta G^{\ddagger}{}_{T_c}$/ kcal mol^{-1} [a]
(1a)	<190	
(1b)	<190	
(1d)	≲193 [b]	
(2a)	201 [c]	10.5
(2b)	217 [c]	10.6
(2d)	234 [b]	11.8 [d]
(3a)	216 [c]	10.7
(3b)	227 [b,c]	11.2
(3d)	243 [b]	12.0 [e]
(4a)	258 [c]	12.8
(4b)	262 [b]	13.2
	267 [c]	13.3
(4d)	288 [b]	14.4 [d]

[a] 1 cal = 4.18 J. [b] Coalescence temperature of P–CH_3 resonance of PMe_2Ph ligands. [c] Coalescence temperature of *o*-CH_3 resonance of $C_6H_2Me_3$-2,4,6 group. [d] From ref. 8. [e] This value is more accurate than that quoted in ref. 5 (11.7 kcal mol^{-1}).

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. Infrared spectra were recorded on a Hitachi 215 spectrophotometer. The reagents *trans*-[$Ni(C_6H_2Me_3$-2,4,6)$(PMe_3)_2Br$] [11] and *trans*-[$Ni(C_6H_2Me_3$-2,4,6)$(PMe_2Ph)_2Br$] [10] were prepared as described previously.

trans-[$Ni(C_6Cl_5)(PMe_3)_2Cl$].—An ethereal solution of pentachlorophenyl-lithium [13] was prepared from hexachlorobenzene (5.70 g, 20 mmol) and a 15% n-hexane solution of n-butyl-lithium (12.5 cm^3, 20 mmol) in dry diethyl ether (200 cm^3). The two reagents were mixed at *ca.* −15 to −20 °C under a nitrogen atmosphere to give a pale yellow solution, to which was added *trans*-[$NiCl_2(PMe_3)_2$] (5.64 g, 20 mmol) in small portions at −60 °C. The mixture was allowed to warm to room temperature over 2.5 h, and was then stirred continuously for 1 h. The solvent was evaporated and the residue extracted with dichloromethane–water containing ammonium chloride. The dichloromethane extract was washed repeatedly with water. The volatile materials were removed under reduced pressure and the residue was recrystallized from acetone or ethanol to give brown crystals of the product; yield 6.84 g (69%), m.p. 235 °C (decomp.) (Found: C, 29.2; H, 3.9; Cl, 42.8. $C_{12}H_{18}Cl_6NiP_2$ requires C, 29.1; H, 3.7; Cl, 42.9%); ^{1}H n.m.r. (CH_2Cl_2), δ 1.09 p.p.m. (t, PMe, J_P 8.3 Hz). The complex crystallized very slowly from solution and often as poorly formed crystals, in spite of the analytical and spectroscopic purity. It is reasonably stable in a variety of organic solvents in air.

All the following preparations were carried out under a nitrogen atmosphere, unless otherwise noted.

trans-[$Ni(C_6H_2Me_3$-2,4,6)$(PMe_3)_2(C{=}CHCH_2CH_2O)$], (1a).—To an ethereal suspension of the lithium reagent, $Li{-}C{=}CHCH_2CH_2O$, prepared from 2,3-dihydrofuran (0.28 g, 4 mmol) and a 15% n-hexane solution of n-butyl-lithium (2.5 cm^3, 4 mmol) in dry diethyl ether (5 cm^3) at 0 °C, was added a dry diethyl ether (15 cm^3) solution of *trans*-[$Ni(C_6H_2Me_3$-2,4,6)$(PMe_3)_2Br$] (0.820 g, 2 mmol) at −50 °C. The mixture was warmed to −15 °C over 1 h to give a clear yellow solution, which was washed repeatedly with cold water containing ammonium chloride. The solvent was removed under reduced pressure, and the residual yellow solid was recrystallized from methanol without heating above 40 °C to give yellow crystals of (1a); yield 0.479 g (60%).

trans-[$Ni(C_6H_2Me_3$-2,4,6)$(PMe_2Ph)_2(C{=}CHCH_2CH_2O)$], (1b).—This complex was prepared in 45% yield in a manner similar to (1a) using *trans*-[$Ni(C_6H_2Me_3$-2,4,6)$(PMe_2Ph)_2Br$] (0.534 g, 1 mmol) dissolved in dry benzene (10 cm^3)–diethyl ether (10 cm^3), and was recrystallized from diethyl ether (3 cm^3)–ethanol (10 cm^3).

trans-[$Ni(C_6Cl_5)(PMe_3)_2(C{=}CHCH_2CH_2O)$], (1c).—This complex was prepared in 58% yield in a manner similar to (1a) using *trans*-[$Ni(C_6Cl_5)(PMe_3)_2Cl$] (1.48 g, 3 mmol) dissolved in dry benzene (15 cm^3)–diethyl ether (15 cm^3), and was recrystallized in air from acetone (20 cm^3)–methanol (15 cm^3).

trans-[$Ni(C_6H_2Me_3$-2,4,6)$(PMe_3)_2(C{=}CHCH_2CH_2CH_2O)$], (2a).—To a solution of 2,3-dihydropyran (1.54 g, 18.3 mmol) in dry diethyl ether (10 cm^3) containing *NNN′N′*-tetramethylethylenediamine (1 cm^3) was added a 15% n-hexane solution of n-butyl-lithium (9.3 cm^3, 15 mmol) at 0 °C. The mixture was stirred at room temperature overnight to give a white-orange suspension. A solution of *trans*-[$Ni(C_6H_2Me_3$-2,4,6)$(PMe_3)_2Br$] (5 mmol) in dry benzene (15 cm^3) was added at −10 °C. The mixture was allowed to warm to 0 °C over 2 h, and was washed repeatedly with cold water containing ammonium chloride. The organic layer was separated, the solvents were evaporated under reduced pressure, and the residue was recrystallized from diethyl ether (15 cm^3)–methanol (50 cm^3) without heating above 40 °C to give yellow crystals of (2a); yield 1.411 g (68%).

trans-[$Ni(C_6H_2Me_3$-2,4,6)$(PMe_2Ph)_2(C{=}CHCH_2CH_2CH_2O)$], (2b).—This complex was prepared in 43% yield in a manner similar to (2a) using *trans*-[$Ni(C_6H_2Me_3$-2,4,6)$(PMe_2Ph)_2Br$] (5 mmol).

trans-[$Ni(C_6Cl_5)(PMe_3)_2(C{=}CHCH_2CH_2CH_2O)$], (2c).—This complex was prepared in 62% yield in a manner similar to (2a) using *trans*-[$Ni(C_6Cl_5)(PMe_3)_2Cl$] (3 mmol). It could be recrystallized in air from acetone (20 cm^3)–methanol (20 cm^3).

trans-[$NiRL_2(CCH_2CH_2CH_2O)$][ClO_4], (3a), (3b), (3c), *and* *trans*-[$NiRL_2(CCH_2CH_2CH_2CH_2O)$][$ClO_4$], (4a), (4b), (4c).—To a solution of (1a) (0.399 g, 1 mmol) in diethyl ether (10 cm^3), was added dropwise 60% aqueous perchloric acid (*ca.* 0.05 cm^3) with stirring at 0 °C. The resulting yellow precipitate was recrystallized from ethanol to give yellow crystals of (3a); yield 0.260 g (52%). Complexes (3b), (3c), (4a), (4b), and (4c) were prepared in 56, 76, 34, 57, and 62% yields respectively, in a similar manner but using (1b), (1c), (2a), (2b), and (2c), respectively as reagent.

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REFERENCES

[1] D. J. Cardin, B. Çetinkaya, and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545.

[2] F. A. Cotton and C. M. Lukehart, *Prog. Inorg. Chem.*, 1972, **16**, 487.

[3] E. O. Fischer, *Pure Appl. Chem.*, 1972, **30**, 353.

[4] D. J. Cardin, B. Çetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, 1973, **2**, 99.

[5] K. Oguro, M. Wada, and R. Okawara, *J. Organomet. Chem.*, 1978, **159**, 417.

[6] M. Wada, S. Kanai, R. Maeda, M. Kinoshita, and K. Oguro, *Inorg. Chem.*, 1979, **18**, 417.

[7] M. Wada and Y. Koyama, *J. Organomet. Chem.*, 1980, **201**, 477.

[8] M. Wada and Y. Koyama, *J. Organomet. Chem.*, 1981, **209**, 115.

[9] M. Wada, N. Asada, and K. Oguro, *Inorg. Chem.*, 1978, **17**, 2353.

[10] M. Wada, K. Oguro, and Y. Kawasaki, *J. Organomet. Chem.*, 1979, **178**, 261.

[11] M. Wada and K. Sameshima, *J. Chem. Soc., Dalton Trans.*, 1981, 240.

[12] G. A. Anderson, R. J. Cross, L. Manojlović-Muir, K. W. Muir, and R. A. Wales, *J. Chem. Soc., Dalton Trans.*, 1979, 684.

[13] M. D. Rausch, F. E. Tibbets, and H. B. Gordon, *J. Organomet. Chem.*, 1966, **5**, 493.