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ISOLATION AND ISOMERIZATION OF *anti* AND *syn* ISOMERS OF *trans*-NiRR'L_2, WHERE R, R' = 2-TOLYL, 2,6-DIMETHOXY-3-BROMOPHENYL, OR TRICHLOROVINYL AND L = t-METHYLPHOSPHINES

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Summary

Four types of organonickel(II) complexes, *trans*-Ni(C_6H_4Me-2)$_2L_2$ (**1** and **1'**), *trans*-Ni{C_6H_2Br-3-(OMe)$_2$-2,6}$_2L_2$ (**2** and **2'**), *trans*-Ni(CCl=CCl_2)(C_6H_4Me-2)L_2 (**3**, **3'**, and **3''**), and *trans*-Ni(CCl=CCl_2){C_6H_2Br-3-(OMe)$_2$-2,6}L_2 (**4** and **4'**), (L = PMe_2Ph for **1**–**4**, PMe_3 for **1'**–**4'**, and $PMePh_2$ for **3''**) were obtained as mixtures of *anti* and *syn* isomers with respect to the two unsymmetrically substituted organic ligands. Thermal *anti-syn* isomerizations were observed for some of these complexes **2**, **3**, and **4**, and the equilibrium constants were close to unity.

Introduction

For steric reasons, both *anti* and *syn* isomers of *trans*-NiRR'L_2 complexes, where R and R' are unsymmetrically *o*-substituted phenyl or trichlorovinyl, are expected to be present [1,2], although only the *anti* isomer has been reported for *trans*-Ni(C_6H_4Me-2)$_2$(PMe_2Ph)$_2$ and for *trans*-Ni{C_6H_2Br-3-(OMe)$_2$-2,6}$_2$(PMe_2Ph)$_2$ [3,4]. We report here the reinvestigation and the possibility of *anti-syn* isomerization in the types of complex **1**–**4**, as shown in Scheme 1.

Results and discussion

The complexes **1**–**4** could be prepared essentially by known procedures [1–5]. In each case, the crude product was found to be a mixture of two isomers, as expected, and careful fractional recrystallizations resulted in the separation of pure *anti* and pure *syn* isomers of **1** and **2**, respectively. In both cases the *syn* isomer is the much more soluble, and could be obtained after the separation of the *anti* isomer from the mixture. For **3** and **4**, mixtures of two isomers in a variety of ratios were obtained after recrystallizations. The ^{1}H NMR spectral data for these complexes are shown in

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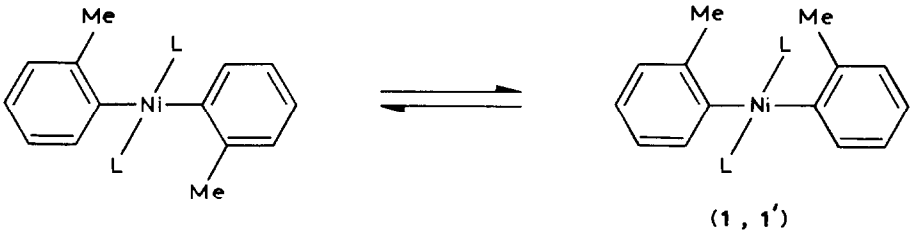
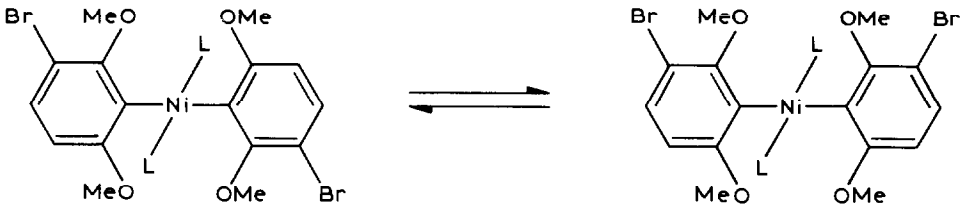
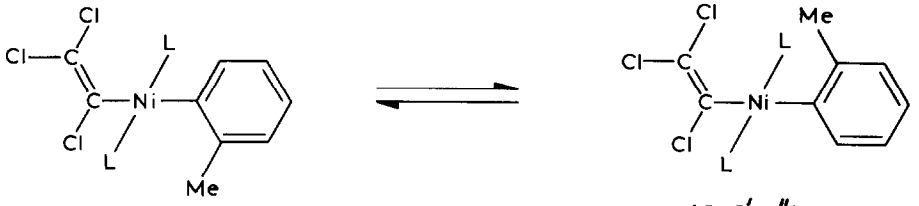


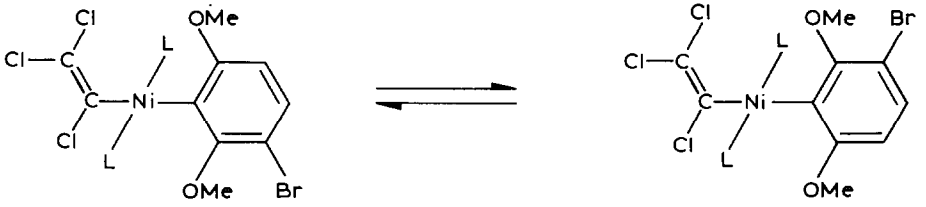
(1 , 1′)



(2 , 2′)



(3, 3′, 3″)



(4 , 4′)

Anti isomer

Syn isomer

(L = PMe_2Ph for 1–4 , PMe_3 for 1′–4′ , and $PMePh_2$ for 3″)

SCHEME 1

Table 1, the assignment of each resonance being straightforward. Although the *anti* or *syn* conformations of **1** and **2** can be distinguished easily by the PMe proton resonance pattern [3], those of the other complexes remain undetermined. The analogous PMe_3 complexes **1′–4′**, shown in the Scheme, were prepared in a similar manner, and their ^1H NMR spectra (Table 1) again showed the presence of two isomers. The two Me-2 proton resonances of **1′** strongly overlap, and estimation of the relative *anti-syn* ratio was difficult. The ratios in the other complexes **2′–4′**, after recrystallizations, remained 50 : 50 or differed only slightly from this. The $PMePh_2$ complex **3″** was isolated as ca. 30 : 70–20 : 80 mixtures of two isomers, with the two Me-2 proton resonances appearing very close together in the ^1H NMR spectrum.

The ^1H NMR spectra of the *anti* or *syn* isomers of **1–4** varied on heating their benzene solutions in evacuated NMR tubes. Heating a solution of **1**(*anti*) at 81 °C for 10 h resulted in a partial decomposition, but the spectrum showed the formation of the *syn* isomer with consumption of the *anti* isomer, giving a relative *anti* : *syn* ratio of ca. 80 : 20. A solution of **1**(*syn*) also gave a mixture of two isomers on being heated. A solution of **2** maintained homogeneity during a longer heating period, and the spectra showed the formation of the other isomer, with little decomposition. Analogous isomerizations were observed for **3** and **4**, using solutions of different isomer ratios. On heating the PMe_3 complexes **2′–4′** retained an isomer ratio close to 50 : 50 (± 5), or decomposed on further heating, and the $PMePh_2$ complex **3″** was thermally the most unstable.

The isomerization of **2** is catalyzed by carbon monoxide, probably by a mechanism including PMe_2Ph–CO ligand exchange [5,6]. Thus, when a solution of the *anti* or *syn* isomer was kept under carbon monoxide (1 atm.) at room temperature for ca. 1 h, the ^1H NMR spectrum of a ca. 50 : 50 isomer mixture was obtained from both

TABLE 1

^1H NMR SPECTRAL DATA FOR ORGANONICKEL(II) COMPLEXES, *trans*-$NiRR'L_2$ [a]

Complex	Chemical shifts (δ, p.p.m.); in C_6H_6 at 23 °C
1(*anti*)	2.18(s, Me-2), 0.98(t)[7] and 0.69(t[7], PMe)
1(*syn*)	2.50(s, Me-2), 0.81(t[7], PMe)
1′	2.69(s, Me-2), 0.56(t[7], PMe)
1′ [b]	2.64(s) and 2.61(s, Me-2), 0.75(t)[7] and 0.74(t[7], PMe)
2(*anti*)	4.16(s, OMe-2), 2.98(s, OMe-6). 1.07(t)[7] and 0.80(t[7], PMe)
2(*syn*)	4.11(s, OMe-2), 3.03(s, OMe-6), 0.94(t[7], PMe)
2′	4.40(s) and *4.21(s*, OMe-2), *3.35(s)* and 3.29(s, OMe-6), *0.61(t)[7]* and 0.57(t[7], PMe)
3	2.27(s) and *2.12(s*, Me-2), *1.10(t)[7]*, 1.08(t)[7], 1.07(t)[7], and *1.04(t[7]*, PMe)
3′	2.62(s) and 2.55(s, Me-2), 0.73(t[7.5], PMe)
3″	2.38(s) and *2.34(s* Me-2), 1.37(t)[7] and *1.31(t[7]*, PMe)
4	4.26(s) and *4.18(s*, OMe-2), *3.04(s)* and 3.02(s, OMe-6), *1.24(t)[7.5]*, 1.19(t)[7.5], 1.10(t)[7.5], and *1.03(t[7.5]*, PMe)
4′	4.38(s) and *4.21(s*, OMe-2), *3.27(s)* and 3.21(s, OMe-6), 0.76(t[8], PMe)

[a] The coupling constants J(P) (Hz) are given in square brackets: s, singlet; t, triplet; those data assignable to the different isomer are shown in italics. [b] CH_2Cl_2 solution.

isomers. An analogous result was observed for **4**, but the complexes **1** and **3** decomposed under carbon monoxide. These equilibrations with a value of K of unity suggest that the non-bonded steric interaction between the *o*-substituents on the different organic ligands is either not present or is negligibly small. X-ray molecular structures of the related complexes, *trans*-Ni{C_6HX_2-3,5-$(OMe)_2$-2,6}$_2$$(PMe_2Ph)_2$ (X = H or Br), are in accord with these observations [7].

The observations of thermal isomerization are surprising in a sense, since molecular models suggest that the rotation of these organic ligands about the Ni–C bond should be severely restricted by the presence of *cis*-t-phosphine ligands, as Miller et al. [1] described. For the isomerizations to occur, the t-phosphine ligands or the organic ligands must be highly distorted from their normal conformations, or the phosphine ligand–metal bond must dissociate to give a 3- or 2-coordinated intermediate. The following observation seems to suggest the last possibility: the ^1H NMR spectrum of a 50 : 50 mixture of **2**(*syn*) and **2′**(*anti* + *syn*), heated in benzene at 65°C for 60 h, showed new resonances assignable to the 6-OMe protons of the mixed ligand complex, *trans*-Ni{C_6H_2Br-3-$(OMe)_2$-2,6}$_2$$(PMe_3)(PMe_2Ph)$ (**2″**), at δ 3.21 and 3.16, as well as those of **2**(*anti*). The ratio of **2** : **2′** : **2″** was 38 : 41 : 21, and the *anti* : *syn* ratios were 40 : 60 for **2** and 50 : 50 for **2′** and **2″**.

The isomerization rates of **2**, **3**, and **4** were measured under a variety of conditions, and the first order rate constants were calculated assuming a value for the equilibrium constant for **3** of unity. The results are summarized in Table 2. Putting these values into the Eyring equation yielded the following activation parameters: for **2**, E_a 28.3 kcal/mol ($r = -0.9948$), $\Delta S^{\ddagger}_{329}$ −1.2 e.u.; for **3**, E_a 21.6 kcal/mol ($r = -0.9995$), $\Delta S^{\ddagger}_{329}$ −13.4 e.u.; for **4**, E_a 23.2 kcal/mol ($r = -0.9898$), $\Delta S^{\ddagger}_{329}$ −15.2 e.u. The $\Delta S^{\ddagger}$ value for **2** was quite small and negative, and the rate hardly varied for solutions containing free PMe_2Ph ligand or polar solvent (Table 2). Accordingly, it also seems possible that the isomerization proceeds while retaining the four coordinated configuration. The $\Delta S^{\ddagger}$ values for **3** and **4** were more negative, the rate for solution containing free PMe_2Ph ligand again hardly varied, and the E_a values were lower than that of **2**. So, we believe that the trichlorovinyl group rotates faster than 2-tolyl and 2,6-dimethoxy-3-bromophenyl groups.

TABLE 2

RATES OF *anti-syn* ISOMERIZATION IN C_6H_6

2		**3**		**4**	
T(°C)	k ($\times 10^6$) (sec^{-1})	T(°C)	k ($\times 10^6$) (sec^{-1})	T(°C)	k ($\times 10^6$) (sec^{-1})
56	1.39	25	2.905	39.5	0.384
64	5.71	35	10.6	55	4.64
81	30.6	40	17.45	64	6.92
87	88.4	56	100	79.5	30.3
100	237	65	219	85.5	59.3
64 [a]	7.71	55 [a]	111	64 [a]	4.09
65 [b]	7.11				
65 [c]	4.71				

[a] Free PMe_2Ph was added: $PMe_2Ph/2 = 1.7$, $PMe_2Ph/3 = 1.4$, $PMe_2Ph/4 = 2.1$. [b] In C_6H_6/CD_3CN(2:1). [c] In $C_6H_6/(CD_3)_2CO$ (2:1).

Experimental

^{1}H NMR spectra were obtained on a JEOL-PS-100 spectrometer, using $SiMe_4$ or $Me_3SiOSiMe_3$ (δ 0.13) as internal standard. Melting points and analytical data are given in Table 3.

trans-Ni(C_6H_4Me-2)$_2$(PMe_2Ph)$_2$, (1)

All operations were carried out under argon, unless otherwise stated. An ethereal solution of 2-tolyllithium was prepared from 2-bromotoluene (1.2 ml, 10 mmol) and a 15% hexane solution of butyllithium (6.3 ml, 10 mmol) in diethyl ether (25 ml). It was added dropwise to a suspension of $NiCl_2(PMe_2Ph)_2$ (1.42 g, 3.5 mmol) in diethyl ether (35 ml) at 0°C. The mixture was stirred for 1 h at 0°C to give a dark solution, which was washed with cold water containing ammonium chloride and then repeatedly with cold water, and it was then filtered using a cylindrical filtering paper. Volatile materials were removed under reduced pressure, and the residue was dissolved in methanol (30 ml). To this solution was added water (ca. 10 ml) at 0°C, with vigorous stirring. The resultant precipitate was filtered off quickly in air, to give a yellow solid in 0.9–1.0 g yield. It was dissolved in methanol (40 ml) at 40°C under argon, the solution was filtered if turbid, and the filtrate was cooled to −15°C to give yellow crystals (0.1–0.3 g). The ^{1}H NMR spectrum showed that this product was almost the pure *anti* isomer of **1**. (The small amount of the *syn* isomer present could be removed by recrystallization from acetone.) Water (ca. 10 ml) was added to the methanol filtrate until it became slightly turbid at room temperature. It was

TABLE 3

ANALYTICAL AND PHYSICAL DATA FOR THE COMPLEXES [a]

Complex [b]	M.p. (°C)	Analysis (%) [c]		
		C	H	Cl + Br
1 (*anti*)	148–151 [d]	69.4	7.05	
1 (*syn*)	120–121	69.4	7.0	
		(69.7)	(7.0)	
1′	169 [e]	61.0	8.3	
		(61.1)	(8.2)	
2 (*syn*)	136–138	50.2	5.0	21.0
		(50.1)	(5.0)	(20.8)
2′ (47:53)	195–196 [e]	41.3	5.35	25.1
		(41.1)	(5.3)	(24.85)
3 (25:75)	127–128	54.0	5.35	19.0
3 (60:40)	122.5–123.5	53.9	5.3	
		(53.9)	(5.25)	(19.1)
3″ (20:80)	142–143 [e]	61.5	5.0	15.8
		(61.8)	(5.0)	(15.6)
4 (76:24)	88–89	45.7	4.6	26.9
4 (13:87)	99–100	45.95	4.6	26.9
		(45.8)	(4.4)	(27.3)
4′ (54:46)	163–165 [e]	34.6	4.8	33.3
		(34.5)	(4.7)	(33.4)

[a] Data for **2**(*anti*) and **3′** have been reported in refs. [4] and [2], respectively. [b] Isomer ratio is given in parentheses. [c] Calculated values are given in parentheses. [d] Reported value, 148–145°C in ref. [3]. [e] Decomp.

warmed to ca. 40°C, to give a clear solution, and was then cooled to give yellow crystals (0.3–0.4 g) of **1**(*syn*). A small amount of the *anti*-isomer, if present, could be removed by recrystallization from methanol.

trans-Ni(C_6H_4Me-2)$_2$(PMe_3)$_2$, (1')

This complex was prepared, using $NiCl_2(PMe_3)_2$ (0.986 g, 3.5 mmol), in ca. 35% yield after careful recrystallizations from methanol or acetone-methanol, in a manner similar to **1**.

trans-Ni{C_6H_2Br-3-$(OMe)_2$-2,6}$_2$(PMe_2Ph)$_2$, (2)

To a solution of *trans*-Ni{$C_6H_3(OMe)_2$-2,6}$_2$(PMe_2Ph)$_2$ [4,5] (1.22 g, 2 mmol) in acetone (100 ml) was added dropwise (ca. 20 min) a solution of *N*-bromosuccinimide (0.712 g, 4 mmol) in acetone (40 ml). The solvent was removed under reduced pressure, the residue was washed with cold methanol, and recrystallized from acetone (100 ml), dissolving at 40°C and cooling to −15°C to give orange crystals of **2**(*anti*) (0.541 g, 35%). The solvent of the filtrate was removed under reduced pressure, and the residue was recrystallized from ethanol (65 ml) between 40 and 0°C to give orange crystals of **2**(*syn*) (0.427 g, 28%).

trans-Ni{C_6H_2Br-3-$(OMe)_2$-2,6}$_2$(PMe_3)$_2$ (2')

This complex was prepared in a manner similar to **2** using *trans*-Ni{$C_6H_3(OMe)_2$-2,6}$_2$(PMe_3)$_2$ [5] (0.97 g, 2 mmol) in 50–65% yield. The isomer ratio was 50 : 50–46 : 54 after recrystallization from acetone, acetonitrile, or acetone/methanol.

trans-Ni(CCl=CCl_2)(C_6H_4Me-2)(PMe_2Ph)$_2$, (3)

An ethereal solution of 2-tolyl-lithium (4 mmol) was added dropwise to a solution of *trans*-Ni(CCl=CCl_2)Cl(PMe_2Ph)$_2$ [4] (1.0 g, 2 mmol) in dry diethyl ether (40 ml) under argon at 0°C. The mixture was stirred for 1 h at room temperature. Diethyl ether (40 ml) was added, the solution was washed with water repeatedly, and then the solvent was removed under reduced pressure. The residue was recrystallized from methanol (100 ml) to give yellow micro crystals (0.643 g, 58%; m.p. 124–125°C). Water (20 ml) was added to the filtrate, the mixture was cooled, and the resultant precipitate (0.150 g, 13%; m.p. 115–117°C) was separated by filtration. The ^1H NMR spectra showed that the first product was a 40 : 60 mixture of the two isomers of **3** and that the second was a 75 : 25 mixture. Recrystallization of the first product (0.615 g) from cold 1 : 1 acetone-methanol (40 ml) gave a fraction (0.288 g; m.p. 127–128°C; 25 : 75 mixture). Recrystallization of the 75 : 25 mixture from methanol gave a 70 : 30 mixture (m.p. 119–121°C).

trans-Ni(CCl=CCl_2)(C_6H_4Me-2)(PMe_3)$_2$, (3')

Preparation of this complex has been reported previously [2]. It was a 55 : 45 mixture of the two isomers. Recrystallization of this sample (0.5 g) from 1 : 3 acetone-methanol (40 ml) gave fractions containing the isomers in the ratios 65 : 35 (0.09 g), 60 : 40 (0.08 g), and 55 : 45 (0.15 g).

trans-Ni(CCl=CCl_2)(C_6H_4Me-2)($PMePh_2$)$_2$, (3'')

This complex was prepared in a manner similar to **3** by mixing *trans*-Ni(CCl=CCl_2)Cl($PMePh_2$)$_2$ [2] (0.625 g, 1 mmol) and 2-tolyllithium at 0°C and by

stirring overnight at room temperature. It was recrystallized below room temperature by dissolving in acetone (20 ml), followed by the addition of methanol (40 ml) and by concentration under reduced pressure, to give microcrystals (0.308 g, 45%; m.p. 136–137°C (decomp) of a 30 : 70 mixture of the two isomers). Repeated recrystallization gave a fraction containing a 20 : 80 mixture of the two isomers.

trans-Ni(CCl=CCl$_2$){C$_6$H$_2$Br-3-(OMe)$_2$-2,6}(PMe$_2$Ph)$_2$, (4)

To a solution of *trans*-Ni(CCl=CCl$_2$){C$_6$H$_3$(OMe)$_2$-2,6}(PMe$_2$Ph)$_2$ [4] (1.205 g, 2 mmol) in acetone (50 ml) was added, at 0°C, a solution of *N*-bromosuccinimide (0.356 g, 2 mmol) in acetone (20 ml). The solvent was removed under reduced pressure, and the residue was crystallized from methanol (100 ml) to give a mixture of two kinds of crystals, fine yellow needles and orange cubes (0.620 g). Addition of water to the filtrate produced two yellow precipitates (0.62 g), which were a 68 : 32 and a 48 : 52 mixture of the two isomers of **4**, respectively, and their recrystallization from methanol resulted in the formation of similar mixtures with a variety of isomer ratios.

trans-Ni(CCl=CCl$_2$){C$_6$H$_2$Br-3-(OMe)$_2$-2,6}(PMe$_3$)$_2$, (4')

This complex was prepared in a manner similar to **4**, using *trans*-Ni(CCl=CCl$_2$){C$_6$H$_3$(OMe)$_2$-2,6}(PMe$_3$)$_2$ [6] (0.478 g, 1 mmol), in ca. 70% yield after recrystallization from methanol. The isomer ratio did not vary from 54 : 46 after repeated recrystallizations.

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