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The Formation of Niobium and Tantalum Oxyalkoxide Derivatives from Niobium and Tantalum Alkoxides and Alkoxychlorides

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The niobium(V) and tantalum(V) oxyalkoxide derivatives $NbO(OMe)_2(OC_6H_4CHO)$, $NbO(OMe)_2[HB(pz)_3]$ *(pz =* $C_3H_3N_2$*),* $NbOCl(OCH_2CCl_3)_2\cdot 2DMSO$ *and* $TaOCl_2(OMe)\cdot 2DMSO$ *have been obtained from the pentaalkoxides or from the alkoxychlorides and characterized by microanalysis, molecular weight measurements, IR and NMR spectroscopy. The structure in solution of these oxo derivatives – all monomeric – which was mainly investigated through low-temperature* ^1H *NMR studies, is discussed.*

Introduction

In a preceding paper [1] we described our investigation into the direct alkoxylation of niobium and tantalum oxychlorides, and concluded that it was far from providing a satisfactory, general route to the metal oxyalkoxides and their derivatives.

The metal pentaalkoxides and mixed alkoxychlorides constitute other possible starting materials for this purpose. Thus, molybdenum oxytrimethoxide was obtained by thermal decomposition of molybdenum pentamethoxide [2]. The controlled hydrolysis of some tantalum pentaalkoxides, $[Ta(OR)_5]_2$ (R = Et, $SiMe_3$) led to highly polymeric oxyalkoxides [3], which were however not isolated and fully characterized. On the other hand, the hydrolysis of $[NbCl_2(OR)_3]_2$ in the presence of bipyridine led to the isolation of the $NbOCl_2(OR)$bipy (R = Et, i-Pr) adducts [4]; but it failed to give the corresponding tantalum compound. The oxyalkoxides $NbO(OR)_3$ and $Nb_2O(OR)_8$ [5] occurred as side products, in poor yields, during the preparation of the pentaalkoxides $Nb(OR)_5$ with crowded alkoxo groups (R = t-Bu and $SiMe_3$).

A possible alternate route to the preparation of oxoalkoxo compounds consists in the exchange of oxygen *versus* chlorine between the mixed metal alkoxychlorides $[NbCl_2(OR)_3]_2$ and an oxo ligand such as dimethylsulfoxide (DMSO) or hexamethylphosphortriamide (HMPA). Indeed, such exchange reactions are well-known for niobium pentahalides [6] and methylniobium tetrahalides [7]. We investigated this route, although in a previous attempt the reaction of $[NbCl_2(OR)_3]_2$ with HMPA led to the unexpected isolation of the dialkoxotrichloroniobium adducts $NbCl_3(OR)_2\cdot$HMPA [8] (R = Me, i-Pr) which result from disproportionation reactions.

We now wish to report the synthesis and characterization of various niobium and tantalum oxyalkoxide and oxyalkoxide chloride adducts, including $NbO(OMe)_2(OC_6H_4CHO)$, $NbO(OMe)_2[HB(pz)_3]$ (pz = $C_3H_3N_2$), $NbOCl(OCH_2CCl_3)_2\cdot 2DMSO$ and $TaOCl_2(OMe)\cdot 2DMSO$.

Experimental

All manipulations were carried out under dry nitrogen using Schlenk-tube techniques. Solvents were dried and purified by standard methods.

Pentamethoxoniobium [9], trimethoxodichloroniobium [8], dimethoxodichlorosalicylatoniobium [10] and potassium tris(pyrazol-yl-1)borate [11] were obtained according to the literature.

NMR spectra were recorded on a C60-HL JEOL spectrometer equipped with a variable temperature attachment and a WH-90 Bruker spectrometer operating in the Fourier transform mode. IR spectra were recorded on a Perkin-Elmer 577 spectrometer on Nujol mulls. Molecular weight data were obtained with a Knauer vapor pressure osmometer. Elemental analyses and mass spectra (MS-30-AEI spectrometer at 70 eV) were carried out by the Service Central de Microanalyse of the C.N.R.S.

Preparation of the Complexes

Oxochlorodi(trichloroethoxo)bis(dimethylsulfoxide)niobium(V), $NbOCl(OCH_2CCl_3)_2\cdot 2DMSO$

2,2,2-trichloroethanol (1 ml, 10.2 mmol) was added in the dark to a suspension of $NbCl_5$ (0.24 g, 0.9 mmol) in 8 ml toluene at room temperature. After 15 min stirring, the solvent was removed under vacuum. The crude alkoxychloride was redissolved in 5 ml dry ether. 1 ml (14 mmol) DMSO was added at room temperature and the mixture was stirred for 30 min. Evaporation of the solvent left a yellow oil. Recrystallization in a mixture of toluene and petroleum ether gave white needles, which were again recrystallized in CH_2Cl_2 (350 mg, 65%; m.p. 110–115 °C). *Anal.*: Calcd for $C_8H_{16}Cl_7NbO_5S_2$: C, 16.06; H, 2.69; Cl, 41.57; S, 10.70. Found: C, 15.40; H, 2.75; Cl, 40.80; S, 10.40%. *IR*: 1376, 1347, 1315, 1292, 1260, 1249; 1170; 1125; 1094; 1030, 1024, 1005 (νNb–O–C); 980, 970 (νS=O); 922 (νNb=O); 810, 718 (νC–Cl); 620 (νC–S); 570, 552; 475 (νNb–OR); 415, 380; 318; 280, 250 (νNb–Cl); 218.

Oxodichloromethoxobis(dimethylsulfoxide)tantalum(V), $TaOCl_2(OMe)\cdot 2DMSO$

$TaCl_5$ (2.48 g, 6.77 mmol) was allowed to react with an excess (5 ml) of methanol in dichloromethane. After stirring for 1 h, the solution was evaporated to dryness and the viscous solid was redissolved in 10 ml CH_2Cl_2. 2 ml (28.2 mmol) dimethylsulfoxide was added at room temperature within 15 min. Stirring was maintained 15 min longer, 10 ml of petroleum ether was added, and the reaction mixture was stored at −30 °C. White crystals were filtered off and washed with ether after two days. The mother liquor was stored under refrigeration (−30 °C). After a second filtration, white crystals (1.23 g, 40%; m.p. 131 °C) were obtained. *Anal.*: Calcd for $C_5H_{15}Cl_2O_4S_2Ta$: C, 13.18; H, 3.32; Cl, 15.60; S, 14.05. Found: C, 12.99, H, 3.23; Cl, 14.70; S, 13.63%. *IR*: 1320, 1300, 1260; 1150; 1070, 1025 (νTa–O–C); 992, 958 (νS=O); 947 (νTa=O); 906; 800, 722; 560; 460 (νTa–OR); 344; 320, 265; 240 (νTa–Cl).

Oxodimethoxotris(pyrazol-1-yl)borate niobium(V); $NbO(OMe)_2[HB(pz)_3]$

A solution of potassium trispyrazolylborate (1.25 g, 4.94 mmol) in 15 ml CH_3CN was slowly added to a stirred solution of $NbCl_2(OMe)_3$ (0.62 g, 2.43 mmol) in 15 ml CH_3CN at room temperature. A white precipitate appeared immediately. Stirring was maintained for about 1 h. The KCl precipitate was eliminated by filtration, and the filtrate concentrated to a pasty solid. Addition of a small amount of CH_3CN (~3 ml) produced the formation of white crystals which were removed by filtration and vacuum dried, yielding white crystals (390 mg, 41%, m.p. 140 °C). *Anal.*: Calcd for $C_{11}H_{16}BN_6NbO_3$: C, 34.30; H, 4.19; N, 21.82; B, 2.85. Found: C, 34.60; H, 4.13; N, 22.49; B, 2.93%. *IR*: 2475 (νB–H); 1500, 1300, 1200, 1153, 1124, 1112; 1060, 1048, 984, 970; 920 (νNb=O), 895, 878, 850, 828, 810, 785, 775, 770, 760, 724, 712, 660, 650, 620, 610; 556, 532 (νNb–OMe). *Mass spectrometry* (140 °C) (M = molecular peak, pz = $C_3H_3N_2$): M−½H_2 (16%), M−OMe (100%), M−2OMe (25%), M−pzH (29%), M−pzH−OMe (17%). δ ^{1}H (CD_3CN), 4.20 (OMe), 6.33t (2.1 Hz), 7.83d (2 Hz), 7.96d (2 Hz) ($C_3H_3N_2$ ring).

Oxodimethoxosalicylaldehydoniobium(V), $NbO(OMe)_2(OC_6H_4CHO)$

Salicylaldehyde (780 mg, 6.4 mmol) was added at room temperature to a stirred solution of 1.45 g (5.8 mmol) of niobium pentamethoxide in 10 ml dry ether at room temperature. A slight gaseous evolution occurred. The reaction mixture was stirred for 30 min, and finally refluxed for about 10 min. The solvent was removed under vacuum. The residue was washed with petroleum ether and recrystallized in toluene. Orange crystals were obtained (1.5 g, 90%; m.p. 130 °C, dec. 170 °C). *Anal.*: Calcd for C_9H_{11}-NbO_5: C, 36.98; H, 3.79; Nb, 31.85. Found: C, 35.62; H, 3.37; Nb, 31.5%. *IR*: 1618, 1600 (νCO); 1545 (νC=C); 1284, 1213; 1125, 1030 (νNb–O–C); 934 (νNb=O); 911; 800, 760; 666, 624; 566, 497 (νNb–OR); 420, 345, 333.

The various compounds are insoluble in aliphatic hydrocarbons, slightly soluble in toluene or chloroform, more soluble in acetonitrile.

Results and Discussion

Synthesis and Characterisation

Molybdenum oxytrimethoxide was obtained by thermal decomposition of the corresponding pentamethoxide [2]. Our attempts to obtain $MO(OMe)_3$ (M = Nb or Ta) by a similar route were hindered by the high thermal stability of niobium and tantalum pentamethoxides (no decomposition was observed up to 250 °C). The only instance in which we obtained a well defined compound from $[Nb(OMe)_5]_2$ was its reaction with salicylaldehyde. The reaction was monitored by ^{1}H NMR in toluene at −50 °C. The peaks corresponding to dimethylether (δ = 3.33 ppm) and methanol (δ = 5.90 and 2.92 ppm) appeared after a few minutes, while a new single peak developed for the Nb–OCH_3 group (δ = 3.83). The crystalline product obtained from the orange solution corresponds to the $NbO(OMe)_2\cdot OC_6H_4CHO$ adduct. The reaction between $[Ta(OMe)_5]_2$ and salicylaldehyde in toluene proceeds differently (as only methanol, and no dimethyl ether, could be detected). However, only polymeric ill-defined products could be obtained.

Oxygen *vs.* chlorine exchange reactions between $[NbCl_2(OR)_3]_2$ and an oxo ligand such as DMSO or HMPA were expected to offer an alternate route to the desired oxyalkoxides. We found, however, that halide–alkoxide exchange reactions are often prevented by the high lability of the niobium alkoxo bond, resulting in the formation of redistribution products and the elimination of ethers [8]. When for example $[NbCl_2(OMe)_3]_2$ or $NbCl_2(OMe)_2(OC_6H_4CHO)$ was allowed to react with more than one equivalent of DMSO or HMPA (L), the formation of $NbOCl_3 \cdot 2L$ was strongly favored, even at low temperatures –40 °C) and no pure oxyalkoxides could be isolated. The ether elimination could however be reduced when the alkoxo group was a 2,2,2-trichloroethoxo group, and the $NbOCl(OCH_2CCl_3)_2 \cdot 2DMSO$ adduct could thus be obtained in good yield. A similar exchange reaction between $[TaCl_2(OMe)_3]_2$ and DMSO led to the isolation of $TaOCl_2(OMe) \cdot 2DMSO$, probably as a consequence of the non-existence of the $TaOCl_3 \cdot 2DMSO$ adduct [6]. This compound is the first reported tantalum oxyalkoxochloride.

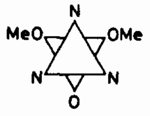
Moreover, chlorine substitution reactions on $[NbCl_2(OMe)_3]_2$ provided an unexpected route to oxyalkoxide by ether elimination. Thus, $NbO(OMe)_2[HB(pz)_3]$ (pz = $C_3H_3N_2$) was isolated by treating $[NbCl_2(OMe)_3]_2$ with the potassium tris(pyrazol-1-yl)borate salt in acetonitrile.

The formation of oxyalkoxides was confirmed in all cases by the presence of a νM=O stretching frequency in the IR of the solid state. The coordination of salicylaldehyde through its carbonyl group is reflected by the lowering of the νC=O frequency by 60 cm^{-1} in $NbO(OMe)_2(OC_6H_4CHO)$ with respect to the free ligand [12]. The spectra of the dimethylsulfoxide adducts show the νS=O absorption at 980 and 970 cm^{-1} for $NbOCl(OCH_2CCl_3)_2 \cdot 2DMSO$ and at 992 and 958 cm^{-1} for $TaOCl_2(OMe) \cdot 2DMSO$ compared to 1040 cm^{-1} in the free ligand. The splitting of the S=O vibrations suggests that the two ligands occupy *cis* positions [13] (see NMR). The metal–alkoxo vibrations were found between 600 and 525 cm^{-1}, depending on the nature of the alkoxo group and on the other ligands surrounding the metal [14], while the metal–chlorine stretching frequencies were observed at 380 and 318 cm^{-1} for $NbOCl(OCH_2CCl_3)_2 \cdot 2DMSO$ and at 320 and 265 cm^{-1} for $TaOCl_2(OMe) \cdot 2DMSO$.

Molecular Constitution in Solution

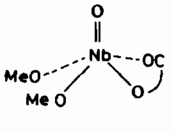
Structural information in solution was essentially obtained through variable temperature NMR spectroscopy and vapor pressure osmometry. It was shown that early transition metal derivatives, well defined in the solid state, can give complex mixtures when put in solution [15]. Thus for instance, the molecular constitution of *mer*-$NbOCl_3 \cdot 2HMPA$ consists of complex mixtures of monomeric species having ligand:metal stoichiometries of 1, 2 and 3, and for each stoichiometry, of various isomers in equilibrium with each other and with the free ligand.

The number of geometrical isomers [for instance, 3 and 6 octahedral isomers respectively for $NbOCl_3 \cdot 2HMPA$ and $NbOCl_2(OMe) \cdot 2HMPA$ [15]] was expected to be reduced when chelating ligands were present. $NbO(OMe)_2[HB(pz)_3]$ was found to be monomeric in acetonitrile (M found 405, calcd 383). The proton spectra in acetonitrile exhibit a single methoxo resonance (δ = 4.20 ppm) and only one type of pyrazolyl rings. They are independent of the temperature (–45 to +60 °C) and of the dilution. All these data are consistent with the presence in solution, of a single molecular species with a hexacoordinated niobium having equivalent methoxo groups, and in which the trispyrazolylborate ligand behaves as a tridentate ligand. Facial isomer A in which the methoxo groups are *trans* to a pyrazolyl ring is in accordance with this.

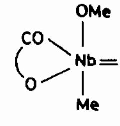


A

The ^1H spectra of $NbO(OMe)_2(OC_6H_4CHO)$ (0.02 molar in toluene) also show only a single sharp peak (δ = 4.20 ppm) for the methoxo groups, even at –85 °C. This is compatible either with a magnetically equivalent environment of these groups or with their stereolability on the NMR time-scale. Molecular weight data in benzene support the existence of a monomeric species (M found 340, calcd 292) in which the metal would be pentacoordinated. Pentacoordinated niobium(V) compounds are rare, although a few species in which the metal presents, in the solid state, a square pyramidal or trigonal bipyramidal environment have been reported [16]. Theoretical considerations have led to the prediction that a bipyramidal trigonal geometry should be more stable for compounds having a d° configuration [17]; it is also the only kind actually recognized so far for niobium(V) derivatives in solution [18]. In the case of $NbO(OMe)_2(OC_6H_4CHO)$ a rigid square pyramidal geometry with the oxo group in the apical position (isomer B) would result in non-equivalent methoxo groups as a consequence of the dissymetry of the salicylaldehydo group. The observed spectra are therefore more consistent with a bipyramidal trigonal environment of the metal with the OMe groups occupying apical positions (isomer C):



B



C

The NMR spectra of $NbO(OMe)_2(OC_6H_4CHO)$ in a polar solvent such as acetonitrile are more complex. At –40 °C two pairs of sharp signals are found for the methoxo region (δ_b: 4.73; δ_c: 4.60 ppm, 1:1; δ_a: 4.78; δ_d: 4.62 ppm, 1:1). Inspection of peak area

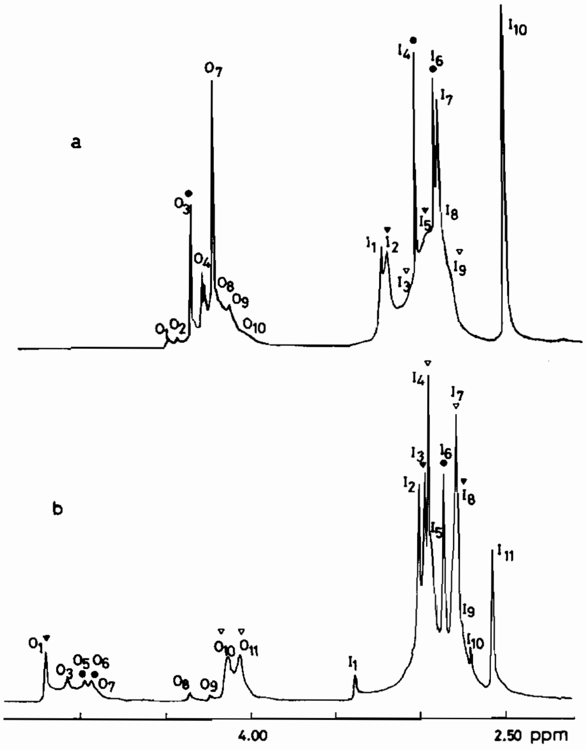
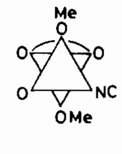


Fig. 1. Proton NMR spectra (0.12 molar in CD$_3$CN, –40 °C; alkoxo and ligand region) of: a) TaOCl$_2$(OMe)·2DMSO: $\delta l_1 = 3.24$, $\delta l_2 = 3.19$, $\delta l_3 = 3.06$, $\delta l_4 = 3.03$, $\delta l_5 = 2.96$, $\delta l_6 = 2.96$, $\delta l_7 = 2.89$, $\delta l_8 = 2.87$, $\delta l_9 = 2.87$, $\delta l_{10} = 2.51$; $\delta o_1 = 4.47$, $\delta o_2 = 4.42$, $\delta o_3 = 4.34$, $\delta o_4 = 4.27$, $\delta o_5 = 4.26$, $\delta o_6 = 4.23$, $\delta o_7 = 4.22$, $\delta o_8 = 4.17$, $\delta o_9 = 4.11$, $\delta o_{10} = 4.06$ ppm. b) NbOCl(OCH$_2$CCl$_3$)$_2$·2DMSO: $\delta l_1 = 3.38$, $\delta l_2 = 2.98$, $\delta l_3 = 2.94$, $\delta l_4 = 2.93$, $\delta l_5 = 2.91$, $\delta l_6 = 2.83$, $\delta l_7 = 2.77$, $\delta l_8 = 2.76$, $\delta l_9 = 2.73$, $\delta l_{10} = 2.68$, $\delta l_{11} = 2.55$; $\delta o_1 = 5.20$, $\delta o_2 = 5.14$, $\delta o_3 = 5.06$, $\delta o_4 = 4.98$, $\delta o_5 = 4.96$, $\delta o_6 = 4.92$, $\delta o_7 = 4.90$, $\delta o_8 = 4.34$, $\delta o_9 = 4.22$, $\delta o_{10} = 4.13$, $\delta o_{11} = 4.05$ ppm. (●, △, ▲ indicate resonance corresponding to the same molecular species).

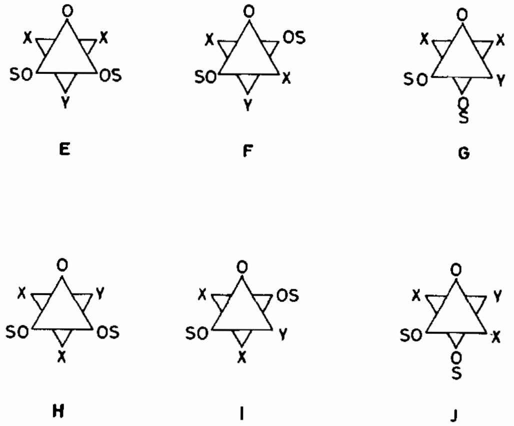
variations in terms of dilution (0.6 to 0.01 ml^{-1}) suggests the existence of at least two molecular species, one (resonances a and d) always being strongly predominant (~90% of the total peak area). The coordination of an additional molecule of acetonitrile by the metal which would then satisfy its tendency to hexacoordination is very likely, and is supported by the small shift observed for the νC≡N stretching frequency in the infra-red (≅7 cm^{-1}); but all attempts to isolate the presumed complex from its solution failed. Among the seven geometrical isomers which would be possible in the hypothesis of the formation of octahedral species, only isomer D in which the OR occupy *trans* and equivalent positions can be excluded on the basis of the spectral ^{1}H data.

The various species present are in dynamic equilibrium, as shown by the coalescence of all the signals at 80 °C ($\Delta G^{\neq} = 70 \pm 6$ KJ mol^{-1}).



D

TaOCl$_2$(OMe)·2DMSO (M exp. 490, calcd 455 – compound 1) and NbOCl(OCH$_2$CCl$_3$)$_2$·2DMSO (M exp. 610, calcd 597 – compound 2) are both monomeric, which implies hexacoordinated metal atoms. Six geometrical isomers (scheme 1) are then expected for compounds 1 and 2. Three isomers (G, H and 6) present non-equivalent ligand sites and should give doublets of equal area in the NMR spectra. Furthermore, for compound 2, isomers G, H and I display different environments for the two trichloroethoxo groups. As a result, and if all isomers were present in solution, the ^{1}H NMR should exhibit 9 ligand peaks and 6 alkoxo resonances for compound 1, 9 ligand peaks and also 9 alkoxo resonances for compound 2.



SO = OSMe$_2$ for compound 1 X = Cl Y = OMe
2 X = OCH$_2$CCl$_3$ Y = Cl

The low temperature (–40 °C) ^{1}H spectra of compound 1 (Fig. 1a) in a 0.12 molar acetonitrile solution exhibits no less than 10 signals for the methoxo groups (4.47 to 4.06 ppm) and at least 10 peaks for the ligand (3.24 to 2.51 ppm). The addition of an excess of DMSO allowed the attribution of the most shielded ligand peak (2.51 ppm) to the free ligand (22% of the total DMSO resonances area) showing that the complex is partially dissociated in solution, which may account for the four extra alkoxo resonances in the spectra of TaOCl$_2$(OMe)·2DMSO. Dilution experiments show the presence of at least 6 distinct DMSO adducts, three of which have non-equivalent ligands (3 couples of peaks, l_4, l_6; l_2, l_5 and l_3, l_9 with similar areas). The predominant tantalum species (23%) correspond to $l_4 = 3.03$; $l_6 =$

2.92 ppm and O_3 = 4.43 ppm. On the basis that the isomers in which the oxo ligand are *trans* to the best π-donors are usually the most stable [19] we favor isomer H as the most abundant isomer of $TaOCl_2(OMe) \cdot 2DMSO$.

A comparable analysis applies to compound 2, whose spectra (Fig. 1b) at –40 °C, in a 0.12 molar acetonitrile solution, present 11 ligand resonances ranging from 3.38 to 2.55 ppm and at least 11 distinct trichloroethoxo groups (5.20 to 4.05 ppm). The addition of an excess of DMSO shows that the extent of dissociation reactions is low (free DMSO at 2.55 ppm, 8%). On the other hand, the presence of 11 ligand resonances could mean* that the dissociation reactions of $NbOCl(OCH_2CCl_3)_2 \cdot 2DMSO$ proceed through 1:1 metal DMSO adducts (in which the metal would be pentacoordinated or more probably hexacoordinated, the second ligand being acetonitrile). Quantitative analysis of the spectra shows the presence of at least 7 different molecular species. The most abundant (24% of all metal species) corresponds to an octahedral isomer presenting non-equivalent ligand sites (resonances l_4 and l_7), but also two different alkoxo groups (O_{10} and O_{11}). Isomers G and H may account for these observations, the latter being expected to be the most stable.

The coalescence of all the signals at high temperature shows that the various species detected in the acetonitrile solutions of $TaOCl_2(OMe) \cdot 2DMSO$ and $NbOCl(OCH_2CCl_3)_2 \cdot 2DMSO$ are all in dynamic equilibrium on the NMR time-scale.

The preceding NMR data show that well-defined solids may consist of a complex mixture of various geometrical isomers of diverse stoichiometries in rapid dynamic equilibrium with the free ligand. This behaviour appears to be a particularity of early transition metal derivatives.

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*The asymmetry of some isomers may result in the diastereotopy of the methine protons of the trichloroethoxo group, which are – at least in principle – anisochronous and should appear as an AB spectrum; but this effect appears to be smaller than the effect of the ligand in *trans*.