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Configurational Rearrangements in *cis*-M(AA)$_2$X$_2$, *cis*-M(AA)$_2$XY and *cis*-M(AB)$_2$X$_2$ Complexes.
7. The *cis*-M(AA)$_2$XY System – Diastereotopic Probe on AA [1]

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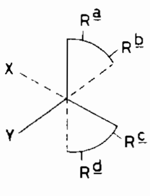
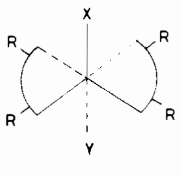
A diastereotopic probe has been incorporated on the terminal A groups in a complex of the type M(AA)$_2$XY to follow the steric course of the configurational rearrangements. Observation of more than one –CH= resonance and one isopropyl methyl spin doublet in the proton nmr spectrum indicates that Ti(dibm)$_2$Cl(OCH$_3$) (dibm = (CH$_3$)$_2$CHCOCHCOCH(CH$_3$)$_2$) in dichloromethane solution exists as the cis *diastereomer. Diastereotopic splitting in the isopropyl methyl proton nmr region reveals that the complex undergoes rearrangement with inversion of the molecular configuration. Approximate rate data at the coalescence temperature for the –CH= group exchange in Ti(dibm)$_2$Cl(OCH$_3$) indicate that stereochemical lability* decreases *as a chloro group in Ti(dibm)$_2$Cl$_2$ is substituted by a methoxy group. The averaging set defining the observed permutations is identified as A'_{13}; this set scrambles all the groups (–CH= and isopropyl methyls) amongst all the nonequivalent sites of the* cis-C_1 *isomer and leads to $\Delta \longleftrightarrow \Lambda$ interconversion. Restricting the rearrangements in the* cis-*Ti(dibm)$_2$Cl(OCH$_3$) complex to a sole reaction pathway suggests that they occur* via *twist motions about two of the four C_3 axes of the octahedral framework.*

Introduction

A complex of the type M(AA)$_2$XY, where X and Y represent different monodentate ligands and AA represents a symmetrical bidentate ligand, may adopt configurations containing *cis* or *trans* X and Y groups. In the enantiomeric *cis* form all four terminal groups of the bidentate ligand are symmetry non-equivalent. Where the bidentate ligand is a 1,3-diketone, the –CH= or –CR= groups in the 2-position of the ring are also nonequivalent. Hence, the *cis* diastereomer would reveal four R group resonances and two –CH= (or –CR=) resonances in the proton nuclear magnetic resonance spectrum, whereas the *trans* diastereomer would reveal a single terminal R group and –CH= (or –CR=) resonance.



cis- Δ(C_1)
[2 -CH=, 4 R]



trans (C_{2v})
[1 -CH= , 1 R]

Compared to the M(AA)$_2$X$_2$ system, the M(AA)$_2$XY complexes have not been the object of many studies even though they can provide greater mechanistic information in the rearrangement processes. The more thoroughly studied complexes in this M(AA)$_2$XY series have been the M(AA)$_2$X(η^5-C$_5$H$_5$) complexes [M = Zr, AA = acac or dpm [2] and X = Cl or Br; M = Hf, AA = acac, and X = Cl] [3, 4]. The solid state structure of Zr(acac)$_2$Cl(η^5-C$_5$H$_5$) is known [5] and, although best visualized using a D$_{2d}$ dodecahedral environment, the solution behaviour of these complexes has been approximated by an octahedral formalism involving a single isomer of C$_1$ symmetry [3, 4]. This is only a formalism for the Zr(IV) and Hf(IV) complexes since the analogous Ti(IV) derivatives exhibit two isomers of C$_1$ symmetry [6, 7]. In the case of the Zr(IV) and Hf(IV) complexes, four acac (and dpm) methyl and two –CH= nmr resonances were observed at ambient temperature, while at elevated temperatures a single methyl and –CH= signal results from a rapid exchange process [3, 4]. Pinnavaia and coworkers [4] have reasoned these exchange processes in terms of twist mechanisms. The phenoxy derivatives M(acac)$_2$(OC$_6$H$_5$)(η^5-C$_5$H$_5$) [M = Zr and Hf] have also been reported [8] and exhibit room-temperature nmr spectra analogous to those of the halo complexes.

In our laboratory we have investigated the series of complexes of the type M(acac)$_2$RCl [M = Si, Ge, and Sn; R = CH$_3$ or C$_6$H$_5$] and have shown [9–11],

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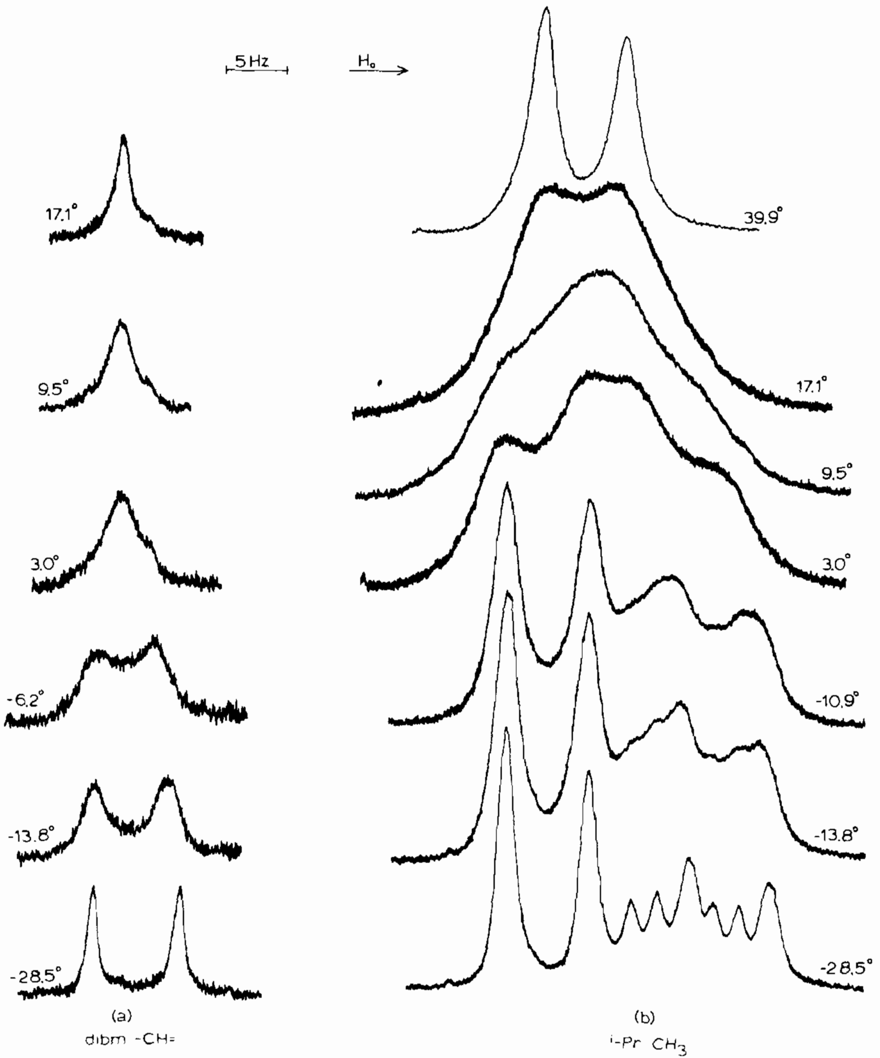

Fig. 1. Temperature dependence of the (a) ring proton (–CH=) and (b) isopropyl methyl resonances of the $Ti(dibm)_2Cl(OCH_3)$ complex in dichloromethane solution, 0.300 *M*.

that these exist as the stereochemically nonrigid *cis* diastereomers. A detailed study of the tin(IV) systems has revealed that rearrangements in this series involve the operation of a twist mechanism [9, 12]. Much less is known about the titanium(IV) derivatives $Ti(AA)_2XY$. The complex $Ti(acac)_2F(OC_2H_5)$ has been generated by ligand exchange reactions and shown to adopt the *cis* geometry [13, 14]. A more general method of preparing and isolating $Ti(acac)_2Cl(OR)$ [$R = CH_3$, C_2H_5, n-C_3H_7, i-C_3H_7, C_3H_5] complexes has recently appeared and all of the complexes studied were found to be the stereochemically nonrigid *cis* diastereomers [15].

We herein establish the operation of enantiomerization processes in complexes of the type $Ti(AA)_2Cl(OR)$ in which a diastereotopic probe has been incorporated on the AA ligand [AA = dibm = $(CH_3)_2CHCOCHCOCH(CH_3)_2$].

Experimental

The $Ti(dibm)_2Cl_2$ complex was available from an earlier study [16]. Dichloromethane, pyridine, hexane and methanol were reagent grade and were dried over CaH_2 just prior to use. Manipulation of the chemicals and the reaction were carried out under a dry inert nitrogen atmosphere in a glove bag.

The chloromethoxybis(2,6-dimethyl-3,5-heptanedionato)titanium(IV) complex, $Ti(dibm)_2Cl(OCH_3)$, was prepared by a procedure analogous to that reported by Thompson and coworkers [15]. Thus to an orange-red solution of 4.39 g (10.2 mmol) of $Ti(dibm)_2Cl_2$ in ~40 ml of dichloromethane was added 0.85 ml (0.84 g; 10.6 mmol) of pyridine to yield a green-yellow solution. Addition of 0.45 ml (0.36 g; 11.1 mmol) of methanol gave an orange-yellow solution, which on stirring deposited a white solid. The solution was concentrated to half its original volume and subsequently 20 ml of hexane was added. The white solid was collected, washed with hexane, and dried *in vacuo*. The filtrate was further concentrated and ~80 ml of hexane added prior to storing the solution for several hours in the freezer (~0 °C). A small amount of white solid was filtered out and the solvent stripped from the filtrate to give a viscous orange liquid, which was then dissolved in 20 ml of hexane and again the solution was stored in the freezer. The resulting yellow-orange solid was collected and dried *in vacuo*; yield 2.70 g (62%). This crude product was further recrystallized from hexane at low temperature (~–10 °C); mp 43–45 °C. The purity of $Ti(dibm)_2Cl(OCH_3)$ was further verified by infrared and proton nmr spectroscopy. The white solid was identified as the pyridinium chloride salt (mp 142–146 °C; 139–145 °C [15]).

The proton nmr spectral techniques employed were the same as those used in our previous studies [16].

Results and Discussion

Nmr Spectra

For a *cis*-$M(dibm)_2XY$ complex undergoing rearrangements with enantiomerization, eight isopropyl methyl spin doublets and two –CH= proton nmr resonances are expected under slow exchange conditions. Figure 1 illustrates the temperature dependence of the –CH= and isopropyl methyl proton signals of the $Ti(dibm)_2Cl(OCH_3)$ complex in dichloromethane solution. Below *ca.* –5 °C, two –CH= proton resonances are observed, which, on raising the temperature, collapse to a singlet as a result of a rapid exchange process which scrambles the two –CH= protons between the two symmetry nonequivalent sites. The isopropyl methyl nmr region is more revealing. At ambient temperature, the nmr spectrum reveals a single spin doublet; on cooling, this doublet broadens until a structureless resonance remains at ~10 °C. Further cooling causes the appearance of two broad doublets by –10 °C and eventually four doublets are discernible at –30 °C. These observations indicate that $Ti(dibm)_2Cl(OCH_3)$ exists solely as the *cis* diastereomer.

In our earlier study on the configurational rearrangements in the organotin(IV) chelates $(CH_3)ClSn(acac)_2$ and $(C_6H_5)ClSn(acac)_2$ we assigned [9] the two lowfield acac methyl signals to the unique acetylacetonate methyl groups *trans* to, and equatorial with, the two monodentate ligands X and Y (*vide supra*). By analogy with this, we also assign the lowest-field isopropyl methyl doublet to those isopropyl methyl groups in the equatorial plane and *trans* to the chloro and methoxy groups. The four axial isopropyl methyl groups comprise the three less intense upfield spin doublets. The nmr resonance pattern at –30 °C is therefore described as four spin doublets with relative intensity 4:1:1:2 and accounts for all eight isopropyl methyl groups in this *cis*-$Ti(dibm)_2Cl(OCH_3)$ complex. No change in this resonance pattern occurs on cooling to –60 °C except for slight broadening of the signals. The lack of resolution of all the spin doublets has also been observed before for the $M(dibm)_2Cl_2$ complexes [M = Sn, Ti, Ge) [16], the nmr spectra of which show three spin doublets (rather than four) with relative intensity 2:1:1. We attribute these observations to an accidental chemical shift degeneracy of some of the spin doublets, and conclude that diastereotopic splitting is observed in the *cis*-$Ti(dibm)_2Cl(OCH_3)$ complex and that rearrangements involve enantiomerization. In the event that only exchange without enantiomerization occurred in this complex the nmr spectra would have revealed four spin doublets of equal intensity.

Kinetic Analysis

No detailed lineshape analysis of the –CH= group exchange was carried out; an approximate rate constant was calculated at the coalescence temperature (T_c) for –CH= group exchange from the expression $k_{T_c} = \pi\delta\nu/\sqrt{2}$ [17], where $\delta\nu$ (in Hz) is the chemical shift separation of the two –CH= proton resonances in the slow exchange limit. For the $Ti(dibm)_2Cl(OCH_3)$ complex, $\delta\nu$ was not constant in the slow exchange region; consequently the observed value at the lowest measured temperature ($\delta\nu = 7.92$ Hz at –60.4 °C) was used. This yields a k_{Tc} of ~18 sec^{-1} at 0 °C. It is instructive to compare the nonrigidity of this $Ti(dibm)_2Cl(OCH_3)$ complex with that of $Ti(dibm)_2Cl_2$ and $Ti(dibm)_2(OCH_3)_2$ to estimate what effect substitution of a Cl group by an alkoxy group has on the rate of the exchange processes. The rate constant at 0 °C for $Ti(dibm)_2Cl_2$ is ~200 sec^{-1} [16]. The corresponding $k_{0\,°C}$ for $Ti(dibm)_2(OCH_3)_2$ may be estimated from the data for $Ti(acac)_2(OCH_3)_2$ [18] and from the realization that bidentate ligand labilization is faster in dibm complexes *vs.* acac complexes by nearly a factor of two [16]; this yields a rate constant of ~13 sec^{-1}. Evidently, replacement of a chloride in $Ti(dibm)_2Cl_2$ by an OR group *decreases* the stereochemical labilization of the bidentate dibm ligand. This decrease in lability is also evident in the rearrangements in $Ti(acac)_2Cl_2$, $k_{25\,°C}$ = 670 sec^{-1} [19], compared to $Ti(acac)_2(OCH(CH_3)_2)_2$, $k_{25\,°C}$ = 8.9 sec^{-1} [20], and more dramatically evident in $Ti(dpm)_2Cl_2$ ($k_{25\,°C}$ = 3500 sec^{-1}) [21] *versus* $Ti(dpm)_2(OR)_2$ ($k_{25\,°C}$ = 0.02–19.7 sec^{-1}) where R is $CH_2C_6H_5$, $CH_2CH(CH_3)_2$, and $C(CH_3)_2C_6H_5$ [20]. *In contrast,* replacement of a chloride in $Sn(acac)_2Cl_2$ by a phenyl or a methyl group significantly *increases* the stereochemical lability of the acetylacetonate complexes. These variations must be due to variations in some electronic property of the alkyl and aryl groups *versus* alkoxy groups.

Permutational and Mechanistic Remarks

A permutational and mechanistic analysis of possible rearrangements within a *cis*-$M(AA)_2XY$ system has been presented earlier [22, 23]. Consulting Table V of ref. 22, which lists the expected changes in signal multiplicities for the various averaging sets, reveals that no averaging set will predict the collapse of the diastereotopic terminal groups of the AA ligand to a *single* doublet. The minimum number of doublets predicted is two, generated by averaging sets A'_6 and A'_{13}. In the present case, the extra provision of nonequivalent –CH= groups allows a more definite exclusion of certain averaging sets. Also, inasmuch as the isopropyl methyl resonances and –CH= signals coalesce over the same temperature region, exchange of terminal A groups and –CH= groups must be intimately connected; that is, they both originate from the same molecular motion [see also ref. 9].

To the extent that –CH= groups are exchanged (2 signals → 1 signal), the following averaging sets can be eliminated on the basis of Table V (see ref. 22): A'_1, A'_2, A'_3, A'_5, A'_8, A'_9, A'_{10}, and A'_{12}. With the assumption that observation of a single isopropyl methyl doublet results from overlap of two doublets and since multiplicity changes of 4 → 1 have been observed for a number of *cis*-$Ti(acac)_2Cl(OR)$ complexes [15], the A'_4, A'_7, A'_{11} and A'_{14} averaging sets may also be discarded. Only averaging sets A'_6 and A'_{13} remain. The sole difference between these two averaging sets is that A'_{13} allows for $\Delta \longleftrightarrow \Lambda$ interconversions. Since diastereotopic splitting is observed in the low temperature nmr spectra of the *cis*-$Ti(dibm)_2Cl(OCH_3)$ complex (Fig. 1), the exchange process involves inversion of the molecular configuration (*vide supra*). Thus, only averaging set A'_{13} remains to explain the permutation of nonequivalent groups within the *cis*-$Ti(dibm)_2Cl(OCH_3)$ complex.

We next focus attention on the most probable physical process(es) which generates the unique set of permutations of nonequivalent groups known as averaging set A'_{13}. Details of the physical processes have been given elsewhere [23].

The analysis in Table I of ref. 23 demonstrates that averaging set A'_{13} may be generated by twist motions about the $C_3(i')$ and $C_3(i''')$ axes of the octahedral framework. The analysis [23] also reveals that a bond rupture process proceeding *via* trigonal bipyramidal (TBP) axial and equatorial intermediates [12] cannot accomodate averaging set A'_{13}. However, TBP intermediates can rearrange intramolecularly to another TBP intermediate which may afford averaging set A'_{13} on reattachment of the dangling ligand. This rearrangement could occur by a pseudorotation process about each of the three metal ligand bonds in the trigonal plane of the TBP intermediate [12]. TBP-axial intermediates yield only TBP-equatorial intermediates after pseudorotation while TBP-equatorial intermediates generate a mixture of TBP-axial and -equatorial intermediates. However, owing to the extensive ligand motion involved in the pseudo-rotation pathway, it does not present an attractive energetic pathway for configurational rearrangements in the *cis*-$Ti(dibm)_2Cl(OCH_3)$ complex.

A bond rupture process occurring *via* square pyramidal (SP) axial intermediates (Table I of ref. 23) formed and decaying to products *via* the primary process [24] will generate the A'_{13} set. However, this result obtains only if attack of the dangling end of the 'monodentate' AA ligand occurs at just one basal position. *A priori*, attack is not expected to be equally probable at all four positions as the basal plane is defined by dissimilar atoms (O_{acac}, O_{CH_3}, Cl). Indeed, it would be highly unlikely for the attacking ligand end to so effectively discriminate against certain ligand atoms to generate only the averaging set A'_{13}. On this basis, bond rupture through SP intermediates is not considered a viable pathway for rearrangements in $Ti(dibm)_2Cl(OCH_3)$.

If we restrict the rearrangement process taking place in the *cis*-$Ti(dibm)_2Cl(OCH_3)$ complex to a single physical pathway, the above discussion leads us to conclude that rearrangements occur predominantly *via* twist motions about the nearly identical $C_3(i')$ and/or $C_3(i''')$ threefold rotation axes. Where direct permutational evidence has been lacking for rearrangements, mechanisms have generally been inferred from the magnitudes of frequency factors (or entropies of activation) and/or activation energies [24, 25]. It is tempting to extend our conclusion for the *cis*-$Ti(dibm)_2Cl(OCH_3)$ complex to the rearrangements in the $Ti(AA)_2X_2$ complexes (AA = acac or dpm; X = halide, alkoxy, phenoxy), which exchange terminal A groups *via* a process with negative activation entropies [18, 19, 21, 26, 27]; this requires that the latter type of complexes also rearrange *via* a twist mechanism. Wilkie and coworkers [28, 29] have recently suggested that rearrangements in the $M(acac)_2X_2$ complexes (M = Ti, Sn; X = F, Cl, Br, I) take place *via* a bond rupture process on the basis of the relative *trans* effect of the halides and on a correlation between the rate data and M–O stretching frequencies. Unfortunately, their data is equivocal with regard to distinguishing a physical pathway for the rearrangement processes, since, even in the twist motions, stretching of the bonds must occur prior to twisting.

Finally, we wish to stress here that our conclusion above is based on the existence of a single permutational averaging set for rearrangements in the *cis*-Ti(dibm)$_2$Cl(OCH$_3$) complex and a single physical process accounting for the A$'_{13}$ set. Unfortunately also, any linear combination of averaging sets (and hence physical processes) which effect –CH= exchange, isopropyl methyl group exchange and $\Delta \longleftrightarrow \Lambda$ interconversions cannot be precluded by our observations.

Acknowledgement

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