Some Labile *cis*-Dialkoxybis(acetylacetonato)titanium Compounds

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THE octahedral complexes $\mathrm{Ti(acac)_2X_2}$ may exist as *trans*- or *cis*- (enantiomorphic) isomers. Proton magnetic resonance studies on the dialkoxides (X = OR) in cyclohexane suggest that the *cis*-isomers are the more stable. The di-t-butoxide ($\mathrm{X = OBu^t}$) gave two equal signals separated by 6·2 c./sec. for the resonance of the acac-methyl protons. Single resonances were given by the other two types of proton present. Inspection of structural models shows that the acac-methyl protons are all equivalent in the *trans*-isomer but in a *cis*-enantiomorph the methyl groups on an acac-group are distinguishable. Other dialkoxides (X = OMe, OEt, etc.) gave single acac-methyl resonances which broadened at lower temperatures and eventually split into equal doublets. Thus it appears that the bisacetylacetonatotitanium dialkoxides exist in solution as *cis*-isomers which fairly rapidly isomerize. Some relevant n.m.r. data on various $\mathrm{Ti(acac)_2X_2}$ are given in the Table. From comparison of the temperatures at which the acac-methyl proton doublets coalesce in these compounds it seems that electron-withdrawing groups promote lability whereas bulky groups oppose it.

The *trans*-isomer of the neopentylglycollate ($\mathrm{X_2 = O{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}O}$) cannot exist and the isomerisation must involve racemization. In the other compounds a *cis–trans*-isomerization cannot be excluded but we believe that racemization is more likely. It is hoped that the activation energies and entropies of activation for these isomerizations (now being determined) may suggest a mechanism (preliminary results suggest $E_a \sim 8$—12 kcal./mole).

Steric considerations would favour the stability of the *trans*-isomer but the results show that even with the bulky t-butoxide groups the *cis*-isomers are more stable. This suggests that electronic factors are responsible for the stability of the *cis*-isomers. We suggest that π-bonding (p_π oxygen $\rightarrow d_\pi$ metal) is a significant factor because in the *cis*-complex all three d_ε orbitals of titanium will be involved whereas in the *trans*-complex only two of the d_ε orbitals can participate.

Nuclear magnetic resonance data for $\mathrm{Ti(acac)_2X_2}$

	Chemical shift* of acac protons		Coalescence†
X	$=$CH$-$	$-\mathrm{CH_3}$ (av.)	Temp. (°c)
OMe	$-325{\cdot}5$	$-112{\cdot}5$	13·0
OEt	$-324{\cdot}5$	$-111{\cdot}5$	22·0
$\mathrm{OCH_2{\cdot}CF_3}$	$-335{\cdot}0$	$-115{\cdot}0$	$-22{\cdot}0$
$\mathrm{OPr^i}$	$-324{\cdot}0$	$-110{\cdot}0$	32·0
$\mathrm{OBu^n}$	$-324{\cdot}2$	$-111{\cdot}9$	21·0
$\mathrm{OBu^t}$	$-322{\cdot}3$	$-109{\cdot}8$	53·0
$\frac{1}{2}(\mathrm{O{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}O})$	$-330{\cdot}0$	$-112{\cdot}0$	$-42{\cdot}0$
Cl	$-363{\cdot}0$	$-130{\cdot}0$	$-25{\cdot}0$

* In c./sec. relative to tetramethylsilane at 60 Mc./sec. in cyclohexane (X = Cl in methylene chloride).

† In methylene chloride or carbon tetrachloride solution.

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