Reactivity of Tervalent Titanium Compounds (η5-C5Me5)2TiR (R = Me, Et)
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the characterization of tin atoms in cluster molecules.

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Supplementary Material Available: Tables of anisotropic thermal parameters, coordinates of the hydrogen atoms, and complete bond lengths and angles for 2 and 4 (7 pages). Ordering information is given on any current masthead page.

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Reactivity of Tervalent Titanium Compounds ($\eta^5$-C$_5$Me$_5$)$_2$TIR (R = Me, Et): Insertion versus $\beta$-Hydrogen Transfer and Olefin Extrusion. Preparation of the Paramagnetic Titanium Alkoxide, Iminoacyl, Acyl, Vinyl, and Azomethide Complexes ($\eta^5$-C$_5$Me$_5$)$_2$TIX and Oxidation of These with PbCl$_2$ to the Diamagnetic Tetravalent Derivatives ($\eta^5$-C$_5$Me$_5$)$_2$Ti(X)Cl

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The paramagnetic, tervalent alkyls Cp*$_2$TIR (1, R = Me; 2, R = Et) were compared in their behavior toward a range of reactive molecules. These 15-electron, d$^1$ systems appear to be weak Lewis acids, reluctant to form adducts. Only for 1 and Me$_2$CO=CCMe$_2$ could an instable adduct Cp*$_2$Ti[(=O)CO]$_2$Me be isolated. With active-hydrogen-containing substrates HX (X = O$_2$C(H)Me$_2$, OEt, =CMe), Cp*$_2$TiHX and RH were produced. Polar, unsaturated molecules like Me$_2$CN=CCO and paraformaldehyde inserted to give Cp*$_2$Ti[(=O)C(R)=NMe$_3$], Cp*$_2$Ti[(=O)CRC]$_2$R, and Cp*$_2$TIC(H)CH$_2$R for both 1 and 2. Apolar unsaturated substrates did not insert into the Ti=C bond with the exception of MeCdMe, which reacted with 1 to produce the vinyl compound Cp*$_2$TICH(Me)=CMe$_3$. A striking difference between 1 and 2 was found in their reaction with CO$_2$, Me$_2$CO=CCMe$_2$, and RO=CR (R = Me, Ph). While 1 either gave a normal insertion (CO$_2$, Me$_2$CO=CCMe$_2$) or adducts (Me$_2$CO, Me$_2$CC=CCMe$_2$) or did not react (PhC=CCPh), 2 lost ethene and gave compounds that appeared to be products of insertion into a Ti-H bond, i.e., Cp*$_2$TIC-H, Cp*$_2$TIC(H)=CMe$_3$, Cp*$_2$TIC=CHMe$_3$, and Cp*$_2$TIC(R)=C(R)=CR. Facile $\beta$-hydrogen transfer from the ethyl ligand was also observed in the reaction of 2 with olefins CH$_2$=CHR =CHR (R = Me, Ph) to give ethene and Cp*$_2$TIC=CH=CHR. This reaction is reversible and equilibrium constants could be determined.

Ground-state differences between 2 and Cp*$_2$TICH=CH=CHR were found to be 92 kcal mol$^{-1}$ (R = Me) and 72 kcal mol$^{-1}$ (R = Ph). Isoprobe-labeling experiments showed that liberation of ethene and formation of the new insertion products proceed via an intermediate hydride, Cp*$_2$TIC-R. The kinetic preference for insertion of an unsaturated substrate into the Ti-H bond relative to insertion into the Ti=C bond, in combination with a rapid equilibrium between ethene elimination and reinsertion causes 2 to react in most cases as a hydride, and explains the striking difference in reactivity between 1 and 2. The products of 1 and 2 with various substrates were also characterized as their monochloride derivative Cp*$_2$Ti(X)Cl after quantitative oxidation with PbCl$_2$. Comparison of spectroscopic data gives information about the specific coordination of ligand R in both Cp*$_2$TiR and Cp*$_2$Ti(R)Cl and shows that the Lewis acidity of the metal center increases substantially on oxidation to Ti(IV).

Introduction

Early-transition-metal (group 3–5) and lanthanide compounds Cp*$_2$MR (Cp* = $\eta^5$-C$_5$R$_5$, R = H, alkyl, aryl) are highly reactive species. The group 3 and lanthanide derivatives are electronically and sterically very unsaturated 14-electron, d$^0$ systems. They are strong Lewis acids, which leads to coordination of solvent molecules (ethers) and, sometimes, even of salt molecules. Solvent- and salt-free complexes often satisfy their need for electron density by forming (intramolecular) σ or agostic interac-


tions. Some of these compounds are active catalysts for isomerization, hydrogenation, oligomerization, and polymerization of alkenes. Of particular interest is the activation of both aromatic and aliphatic C–H bonds by these complexes. This proceeds in a concerted fashion, via a highly polar $[2, + 2]$ transition state, referred to as σ-bond metathesis. Concerted mechanisms are characteristic for group 3 and lanthanide compounds, which have high C–H dissociation energies and lack low-energy metal–hydrogen vibrations. Heterometallic and lanthanide molecules inserted into the M–C bond, as is expected for highly polar bonds. Isolelectronic with group 3 and lanthanide metal complexes Cp*MR are monocations Cp2M'R+ and Cp*,M'R+ (Cp* = 5-C5Me5; Cp* = 5-C5H5; M' = group 4 element); they show a comparable activity. The group 5 compounds Cp5Pd are 16-electron, d3 systems. The two additional electrons have a distinct effect on their reactivity: a stable adduct can be formed by back-bonding to a ligand with suitable orbitals. This raises the activation energy for consecutive reactions. Addition of unsaturated substrate molecules to complexes Cp*,MR (M = group 5 element) therefore usually ends in an adduct Cp*,MR-S (S = C=O, Me=Me, etc.). The activation energy for insertion of a coordinated olefin into a Nb–H bond has been determined in Cp*,NbH(CH2=CH2) at 78 kJ·mol−1, a substantial barrier. Another consequence of the presence of the two electrons is the possible destabilization of the alkyl form relative to a hydride–olefin configuration. There are no experimental data on the Gibbs energy difference for this process, but calculations indicate that this may be substantial. The activation energy for the reverse process, β-hydrogen elimination, is low. Information on group 5 M–C bond dissociation energies is scarce, but it is assumed that for niobium and tantalum they are probably in the same range as for group 3 M–C bonds. For vanadium the situation is quite different. The homolytic decomposition of Cp5V (R = alkyl) and Cp5V=Et to (permethyl)vanadocene at ambient temperatures illustrates that V–C bond dissociation energies are substantially smaller. The paramagnetic d4, 15-electron complexes Cp*2TiR represent in a formal sense the intermediate between d3 and d2 metallocene derivatives, and a study of their activity seems appropriate. Our group has extensively reported on the synthesis and reactivity of Cp5TiR (R = hydrocyclyl). The majority of these compounds, however, are thermally unstable, thus complicating the investigations. Recently, the much more robust pentamethycyclopentadienyl analogues, Cp*2TiR, have become available and preliminary data on the specific aspects of their reactivity have been published. In the first part of this study, the reactivity of Cp5TiMe (1) is reviewed. The compound is an excellent model for investigating Ti–C bond reactivity since it is a prototype alkyl compound Cp5TiR. In the second part the reactivity of the β-hydrogen-containing alkyl Cp5TiEt (2) is reported. Special interest was taken in a possible involvement of hydride–olefin complexes formed from the alkyl compound in isomerization and substitution reactions. The third part of the study concerns the oxidation of paramagnetic compounds Cp5TiR (R = hydrocyclyl ligand) and Cp5TiX (X = anionic ligand) to tetravalent, diamagnetic complexes Cp5Ti(R)Cl and Cp5Ti(X)Cl by PBU4 and the use of this method to characterize and help identify paramagnetic compounds which are normally not well accessible to conventional NMR spectroscopic methods.

Results and Discussion

Reactivity of Cp5TiMe (1). The reactivity of 1 can be divided into insertion, acid–base, and adduct formation reactions. Insertion into the Ti–C bond was observed with Me3CN=m, CO, CO2, and but-2-yne, to yield respectively Cp5TiC(Me)=CMe2 in order to have observable rates, reaction of Cp5TiMe (1). This part the reactivity of the β-hydrogen-containing alkyl Cp5TiEt (2) is reported. Special interest was taken in a possible involvement of hydride–olefin complexes formed from the alkyl compound in isomerization and substitution reactions. The third part of the study concerns the oxidation of paramagnetic compounds Cp5TiR (R = hydrocyclyl ligand) and Cp5TiX (X = anionic ligand) to tetravalent, diamagnetic complexes Cp5Ti(R)Cl and Cp5Ti(X)Cl by PBU4 and the use of this method to characterize and help identify paramagnetic compounds which are normally not well accessible to conventional NMR spectroscopic methods.
methane. Treatment of 1 with isobutenoic acid, ethanol, or propyne gave Cp*₂TiOC(Ph)Cl, Cp*₂TiOEt, and Cp*₂TiC(O)Me₃. Reaction with Me₂CC≡N led to an adduct Cp*₂TiMe₂N≡CMe₂. The complex is thermally stable and transfers in solution at room temperature slowly into a mixture of diamagnetic and paramagnetic compounds, apparently due to both insertion and coupling of nitrile ligands. When a solution of the adduct was treated with PbCl₂, Cp*₂Ti(Me)Cl was formed together with Me₂CC≡N. Adduct formation was also found with acetone, but not with weak Lewis bases like trimethylphosphine or triethylamine.

Reactivity of Cp*₂TiEt. IR and NMR spectra indicate that the β-H atoms of the ethyl ligand are involved in an agostic interaction with the metal. The compound is thermally less robust than 1; it decomposes slowly at room temperature (t(1/2 ≈ 45 h, in THF), but decays at unreacted substrates proceeds at such rates that thermal decomposition is always a minor pathway. The reactions can be separated into insertions, acid-base reactions, and olefin extrusion. Insertion into the Ti–C bond of 2 was only observed for Me₂CC≡N, CO, and paraformaldehyde and led to the iminoacyl Cp*₂TiC(=O)Et, the acyl Cp*₂TiC(O)Et, and the alkoxide Cp*₂TiOPr, fully analogous with 1. Other substrates, like CO₂, and alkynes R₃C≡CR, which for reaction with active hydrogen-containing molecules resulted in the liberation of alkane (ethane) as expected for highly polar carbon–carbon bonds. For example, ethanol gave the ethoxide Cp*₂TiOEt, and isobutane the carbonate Cp*₂TiO₂CC(Ph)₂Me₂. The reactions were fast and clean at low temperature (−30 °C). There was no indication for the presence of (intermediate) hydride–olefin species. For instance, dihydrogen was not found, while it would be if a hydride–olefin complex had been present; cf. the methanalysis of Cp*₂NbH(CH₂=CH₂). Reaction of 2 with propyne (equimolar and excess) was not clean. The reaction mixture contained several organic (the dimer 2, methylenetetra-1-en-3-yne was identified) and organometallic compounds, apparently due to both insertion and coupling of alkynes (Ph₂C≡CPh, C₂H₅). In toluene, 2 reacted with internal alkynes R₃C≡CR, which for reaction with the olefin by an incoming ketone carbonyl and thermal decomposition is always a minor pathway. The formation of ethane probably results from an acid-base reaction between them; cf. De Boer, E. J. M.; Teuben, J. H. J. Organomet. Chem. 1978, 153, 65.

Ethene Extrusion from Cp*₂TiEt. The reactivity of 2 is dominated by net β-hydrogen transfer from the ethyl ligand to the substrate and liberation of 1 equiv of ethene. This extrusion proceeds smoothly at room temperature, and 2 appears to react as a protected titanium hydride. Irreversible reactions were observed with heteronuclear unsaturated substrates like Me₂CC≡N, Me₂C≡C=O, and CO₂, and also with internal alkynes R₃C≡CR. Cp*₂TiEt reacted with Me₂CC≡N to yield ethene and the red azomethine complex Cp*₂TiN≡C(H)Me₂. Addition of acetone to 2 (−80 °C) resulted in the liberation of 0.87 mol of gas (95% ethene, 5% ethane) per titanium. The organotitanium product was oxidized with PbCl₂ and analyzed by NMR spectroscopy. The major component (>85%) could be identified as Cp*₂TiOC(H)Me₂Cl. This indicates extrusion of the olefin by an incoming ketone carbonyl function and subsequent insertion into the Ti—H bond. The formation of ethene probably results from an acid-base reaction of 2 with a hydrogen atom of acetone. Reaction of 2 with CO₂ produced Cp*₂TiOC(Ph)₂ and 1 equiv of ethene, as reported before. In toluene, 2 reacted with internal alkynes R₃C≡CR to yield vinyl compounds.

Table I. Data for Equilibrium 1 (Relative to 2, R = H, 298 K)

<table>
<thead>
<tr>
<th>R₁</th>
<th>Kₛ</th>
<th>ΔG⁰ (kJ·mol⁻¹)</th>
<th>ΔG⁺ (kJ·mol⁻¹)</th>
<th>GS³ (kJ·mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Me</td>
<td>6.5 (8) × 10⁻⁵</td>
<td>24 (2)</td>
<td>−15</td>
<td>9 (2)</td>
</tr>
<tr>
<td>Ph</td>
<td>3.5 (8) × 10⁻⁵</td>
<td>25 (2)</td>
<td>−18</td>
<td>7 (2)</td>
</tr>
</tbody>
</table>

*Correction for stabilization of free olefins relative to ethene. Δ Relative ground-state energy for complex Cp*₂Ti(H)₂H₂.

Table II. ¹H NMR Data for Cp*₂Ti(R)Cl Compounds

<table>
<thead>
<tr>
<th>compd</th>
<th>δ (ppm)</th>
<th>mult</th>
<th>f (H) (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp*₂Ti(CH₃CH₂Cl)</td>
<td>7.05 (m)</td>
<td>1</td>
<td>2.10 (s)</td>
</tr>
<tr>
<td>Cp*₂Ti(OEt)Cl</td>
<td>4.29 (q)</td>
<td>2</td>
<td>1.31 (s)</td>
</tr>
<tr>
<td>Cp*₂TiOC(H)Me₂Cl</td>
<td>1.10 (d)</td>
<td>6</td>
<td>1.85 (s)</td>
</tr>
<tr>
<td>Cp*₂Ti(N=C(Me)=</td>
<td>5.04 (h)</td>
<td>1</td>
<td>2.10 (s)</td>
</tr>
<tr>
<td>Cp*₂Ti(C≡N)Cl</td>
<td>2.65 (q)</td>
<td>2</td>
<td>1.75 (s)</td>
</tr>
<tr>
<td>Cp*₂Ti(C≡N)Me₂Cl</td>
<td>1.15 (t)</td>
<td>3</td>
<td>1.72 (s)</td>
</tr>
<tr>
<td>Cp*₂Ti(C≡N)Me₃Cl</td>
<td>1.41 (s)</td>
<td>9</td>
<td>1.72 (s)</td>
</tr>
<tr>
<td>Cp*₂Ti(C≡N)Me₄Cl</td>
<td>1.02 (t)</td>
<td>3</td>
<td>1.72 (s)</td>
</tr>
<tr>
<td>Cp*₂Ti(CH₃CH₂Cl)</td>
<td>1.84 (s)</td>
<td>30</td>
<td>1.72 (s)</td>
</tr>
<tr>
<td>CH₃</td>
<td>3.67 (q)</td>
<td>1</td>
<td>1.77 (s)</td>
</tr>
<tr>
<td>c-CH₃</td>
<td>1.74 (m)</td>
<td>3</td>
<td>1.73 (s)</td>
</tr>
<tr>
<td>t-CH₃</td>
<td>1.68 (d)</td>
<td>3</td>
<td>1.73 (s)</td>
</tr>
<tr>
<td>CH₂</td>
<td>2.04 (d)</td>
<td>3</td>
<td>1.50 (s)</td>
</tr>
<tr>
<td>CH</td>
<td>2.22 (q)</td>
<td>2</td>
<td>1.50 (s)</td>
</tr>
<tr>
<td>Cp*₂Ti(C≡N)Cl</td>
<td>4.86 (q)</td>
<td>1</td>
<td>1.50 (s)</td>
</tr>
<tr>
<td>Ph</td>
<td>7.05 (m)</td>
<td>1</td>
<td>1.50 (s)</td>
</tr>
<tr>
<td>Cp*₂Ti(PH₃)Cl</td>
<td>7.27 (m)</td>
<td>4</td>
<td>1.50 (s)</td>
</tr>
<tr>
<td>H</td>
<td>4.65 (s)</td>
<td>1</td>
<td>1.50 (s)</td>
</tr>
<tr>
<td>Ph</td>
<td>6.93–7.26 (m)</td>
<td>10</td>
<td>1.50 (s)</td>
</tr>
<tr>
<td>Cp*₂Ti(CH₃CH₂Cl)</td>
<td>1.75 (s)</td>
<td>30</td>
<td>1.50 (s)</td>
</tr>
</tbody>
</table>

(15) The final product (benzene-d₆, 3 weeks at 50 °C) was identified on the basis of ¹H NMR and IR data as a 1:1 mixture of the insertion product Cp*₂Ti(N≡CMe₂)₂Cl (δ 18.9 ppm, Cp*, δ 0.85 ppm, Me and Cp*δ, δ 2040 Hz, MeCl₃, 90 Hz) and the nitrile-carbon coupled tetra-valent titanium azomethide compound (Cp*₂Ti(N=CMe₂)₂Cl (δ 17.23 ppm, Cp*, δ 0.08 ppm, Me). The IR data (ν(C≡N) at 1665 and 1618 cm⁻¹) are compatible with both but do not allow discrimination between them; cf. De Boer, E. J. M.; Teuben, J. H. J. Organomet. Chem. 1978, 153, 65.

(16) Luizatto, G. A.; Teuben, J. H. J. Am. Chem. Soc. 1992, 114, 3361. The identity of Cp*₂TiOPt was established by comparison with an authentic sample of this compound prepared from Cp*₂TiCl and Li₂PtCl₆. Oxidation with PbCl₂ gave Cp*₂TiCl(PtCl₂).


(18) Hexamethyloctetone, lacking acidic hydrogen atoms, did not react with 2, probably for steric reasons. With benzophenone, extrusion of 1 equiv of ethene from 2 was observed but the titanium product, a green-red oil, could not be identified. It is identical to the reaction product of Cp*₂TiCl and benzophenone. The formation of Cp*₂TiOC(H)₂Cl, could be explained by comparison with physical data of the compound prepared by salt metathesis between Cp*₂TiCl and LiOC(H)Cl.)
Cp₅Ti(C(=CH₃)) = C(H)(R) and ethene. Reaction with but-2-yne was complete within 0.5 h at room temperature, and Cp₅Ti(Me)=C(H)Me was formed. The process is irreversible when the vinyl compound was treated with excess ethene (20 bar, 25 °C), compound 2 was not re-formed. Also, no reaction was observed when Cp₅Ti(C(CH₃)=C(H)Me) was dissolved in Me₂CC=CN, although, thermodynamically, there certainly is a driving force for the liberation of but-2-yne and formation of the azomethide complex Cp₅Ti=C(H)Me₂. Apparently, Cp₅Ti(C(=CH₃)) does not readily eliminate β-hydrogen. This is quite in contrast to Cp₅Zr(CH₂C=CH)=C(H)Me₂, and Cp₅Zr(CH₂CMe₃)=C(H)Ph, where irreversible transfer of β-vinyl hydrogen atoms has been reported. Other alkynes like methylphenacylene and diphenylketene reacted in a similar way: ethene was liberated, and vinyl compounds formed. The products were characterized as their corresponding monochloride derivatives Cp₅Ti(CH₂C=CH)Cl and Cp₅Ti(C=CH)Cl (Tables II and III). Reaction of 2 with methylphenacylene produces only one of two possible regio isomers. Probably the sterically less crowded Cp₅TiC(=CH)Me₂ has been formed (cf. Cp₅ScEt where a mixture of isomers was obtained(2)).

Primary olefins, R'CH=CHR₂ reacted with 2 but were not polymerized and only replaced ethene. The higher alkyl complexes Cp₅TiCH₂CH₂R could be transformed back to 2 by reaction with methane. Cp₅TiR complexes with R containing β-hydrogen and α-olefins therefore form true equilibria (eq 1). The equilibrium constants of eq

\[\text{Cp₅TiCH₂CH₂R} + \text{CH₂-CHR} \rightleftharpoons \text{Cp₅TiCH₂CH₂R} + \text{CH₂=CHR} \]

1 have been determined for a number of combinations of olefins and alkyl complexes (Table I). Cp₂TiEt (2) is thermodynamically the most stable alkyl, and eq 1 lies always far to the side of 2. This is also clear from the chemistry of 2 with other olefins. As an example, conversion of 2 to Cp₅TiCH₂CH₂Ph could only be achieved with simultaneous removal of ethene under conditions of dynamic vacuum.

The study of the equilibria enables us to calculate the differences in Gibbs energy for these processes (Table I). To place the ground states of the alkyl complexes 2 and Cp₅TiCH₂CH₂R on a common energy surface, a correction for the contribution of the free olefins has to be made. This is possible when it is realized that hydrogenation of ethene is energetically more favorable than of other olefins, and so one expects 2 to be more stable than Cp₅TiCH₂CH₂R. An estimate for this stabilization can be obtained from eq 2. Correction of the observed ∆G° values for this difference in energy shows that 2 is 7 (2) and 9 (2) kJ·mol⁻¹ more stable for R = Ph and R = Me, respectively. The effects of solvolysis of the species in eq 2 were not considered, but assumed to be negligible. It is tempting to assign the stabilization of 2 to a β-agostic interaction between the metal and a δ C-H bond of the ethyl ligand, although the effect is much smaller than the value derived by Brookhart et al. from the rotation barrier of the methyl group of the ethyl ligand in Cp₅Co(PMe₅)CH₂CH₃ (37 kJ·mol⁻¹), which has a β-agostic C-H bond. However, one has to be careful since in Cp₅Nb(C₂H₅)=C(H)R (R = H, Me, Ph) similar ground-state differences were found (although smaller in absolute numbers(28)), and agostic interactions are here out of the question. The contribution of the agostic interaction in 2 to the relative stabilization of this compound cannot

\[\text{compd} \quad \text{assgnt} \quad \delta \text{C-H} \quad \text{mult} \quad \text{[H]} \]

(22) Calculated from eq 2, using the difference in heat of hydrogenation of the olefins and radical formation of the corresponding alkanes. On both sides of eq 2 the particles are comparable. The overall difference in heat of solvolysis therefore is probably small and can be neglected. Data taken from: CRC Handbook of Chemistry and Physics, 60th ed.; Weast, R. C., Astle, M. J., Eds.; CRC Press: Boca Raton, FL, 1980.

be determined exactly, but it will certainly be small since it will not exceed 10 kJ·mol⁻¹.

There are no indications that olefins form adducts with Cp₂TiR compounds. The IR spectrum of Cp₂Ti(n-C₃H₇) in 1-hexene is a superposition of the spectra of the two components. No absorptions characteristic for coordinated olefins were found. Also, the ¹H NMR spectrum of Cp₂TiPr in the presence of 3 equiv of propene is a superposition of the spectra of individual compounds. This also indicates that the exchange rate for free propene and Cp₂TiPr is slow on the ¹H NMR time scale, since no shift of the resonance of free propene was observed.

Mechanistic Considerations on Ethene Extrusion from Cp₂TiEt. The substrate-induced olefin extrusion from 2 was investigated in detail. The process can follow two routes, either direct transfer of β-hydrogen from the ethyl group to a coordinated substrate or olefin extrusion with intermediate formation of Cp₂TiH (Scheme I). The IR spectrum of Cp₂TiEt from 2 was tested by isotope-labeling experiments. The ¹3C labeled compound Cp₂Ti-¹³CH₂CH₃ was prepared from Cp₂TiCl and IMgCl. Hydrolysis with D₂O gave a 1:1 mixture of labeled ethanes CH₃¹³CH₂ and ¹³CH₃CH₂D. This illustrates that a hydride-olefin configuration is readily accessible at room temperature and that, in addition, rotation of the olefin around the Ti-olefin bond is possible. Moreover, intermolecular exchange of olefins between different molecules of Cp₂TiEt was found as well. Complete scrambling of deuterium between the ethyl ligands was observed within 48 h at room temperature in toluene after mixing 2 and Cp₂TiEt(Et-d₂). This indicates not only that a hydride-olefin configuration is within reach but also that olefin dissociation from 2 can take place to give Cp₂TiH, although the equilibrium lies strongly to the side of the silik Cp₂TiR. This does not necessarily mean that ethene extrusion always proceeds through the formation of a hydride, because substrate coordination could block the coordination site necessary for β-hydrogen elimination and favor a concerted transfer of hydrogen. But since no evidence for a stable olefin adduct of Cp₂TiH has been found and other adducts e.g. with acetone and Me₃CO=NC were very unstable, olefin extrusion is assumed to proceed via Cp₂TiH. This was also concluded for the reaction of β-hydrogen-containing scandium compounds Cp₂ScCH₂CH₃R (R = H, Me, Ph, etc.), which react with but-2-yn to yield Cp₂ScMeCH=CH₂Me and 1 equiv of olefin.¹⁸

The unfavorable kinetics for insertion into the Ti-C bond in combination with facile olefin dissociation explains the differences in reactivity of 1 and 2. This is illustrated by a competition experiment. Equimolar amounts of 1, 2, and carbon dioxide were stirred in toluene at room temperature. Carbon dioxide is known to insert into the Ti-C bond of 1, and induce olefin elimination in 2 to give Cp₂TiO₂CH₂.²⁴ After 1 h, 1 equiv of ethylene (relative to carbon dioxide) had evolved. Oxidation of the reaction mixture with PbCl₂ gave exclusively Cp₂Ti(Me)Cl, no Cp₂Ti(Et)Cl was present. This shows the preference of carbon dioxide to insert into the Ti-H bond.

Oxidation of Cp₂TiR to Diamagnetic Tetravalent Titanium Derivatives Cp₂Ti(R)Cl. Most products obtained from 1 and 2 are paramagnetic and have typically short proton and electron relaxation times. This results in broad resonances and large chemical shifts in ¹H NMR spectra and in poorly resolved EPR spectra.¹³ These spectroscopic techniques are therefore of limited value for identification of paramagnetic compounds like those studied here. A generally applicable method has been worked out to sidestep these problems of characterization. Cp₂TiR compounds can be readily converted into their diamagnetic monochloride analogues Cp₂Ti(R)Cl by oxidation with PbCl₂ (eq 3).⁴¹ The latter compounds are easily identified by conventional NMR methods. This technique has extensively been applied in this study to demonstrate the presence of ligand R or X in paramagnetic compounds Cp₂TiX and Cp₂TiR obtained from Cp₂TiMe and Cp₂TiEt and reported in this or previous papers.¹³ In addition to the fact that oxidation to Cp₂Ti(R)Cl is very helpful for identification, the method also is an excellent synthetic route to new mixed hydrocarbonyl compounds Cp₂Ti(R)Cl³. Experimental procedures and IR spectra are given in the Experimental Part, ¹H and ¹³C NMR data are in Tables II and III, and a discussion of the spectroscopic properties and other interesting features is presented below.

Comparison of Spectroscopic Data of Cp₂TiR with Cp₂Ti(R)Cl. Reaction of 1 and 2 with Me₃CN=C=C gave iminoacyl complexes Cp₂TiCl(C=N)=CMe₃. Assignment of the coordination mode for the iminoacyl ligand (º or ø) on IR data alone is unreliable, as has been noted before.⁷¹ Nowadays there is ample evidence that little correlation exists between the bonding mode of (imino)acyl moieties and spectroscopic data (C=≡N stretching frequency and ¹³C NMR shifts), although conclusions concerning the bonding mode of iminoacyl ligands seem to be valid within a series of homologues.³⁹ So far, only a few structures of titanium iminoacyl compounds have been reported.²⁷,²⁹ All structures show an ø-coordinated iminoacyl ligand, which is in general the most favorable coordination mode for coordinatively and electronically unsaturated compounds.²⁸,⁹ Therefore, it is reasonable to assume that in Cp₂TiCl(C=N)=CMe₃ the iminoacyl ligand is also ø-coordinated. This is supported by the spectra of the tetravalent titanium iminoacyls Cp₂TiCl(C=N)=CMe₃ and references therein.

1986, 5, 1992

carbon atom (R = Me, δ = 231 ppm; R = Et, δ = 228 ppm) is found at low field, as expected for γ^2-coordination. The IR spectra of the oxidized iminoacyl compounds show ν_C=O (R = Me, 1680 cm⁻¹; R = Et, 1660 cm⁻¹) about 75 cm⁻¹ shifted to higher wavenumbers. This reflects the increase in Lewis acidity of the metal center on oxidation, resulting in stronger donation of the iminoacyl nitrogen lone pair. This increased interaction tends to rehybridize the C and N atoms to become stronger sp in character with resultant stronger C=N bonds and thus higher stretching frequencies.\(^{\text{27a}}\)

The 13C NMR spectrum (recorded at -10 °C) of Cp*,Ti-(C(O)Et)Cl, only the resonances of the major isomer are present in a ratio of 9:37. The isomers probably arise from two carbonyl stretching frequencies in- to obtain a pure sample. The stability of acyl compound Cp*,Ti(C(O)Et)Cl is sufficient to allow full characterization. This increased interaction tends to rehybridize the C and N atoms to become stronger sp in character with resultant stronger sp in character with resultant stronger C=N bonds and thus higher stretching frequencies.\(^{\text{27a}}\)

Blue acyl compounds Cp*₂Ti(C(O)R)Cl (R = Me, ν_C=O = 1690 cm⁻¹; R = Et, ν_C=O = 1520 cm⁻¹) were formed from 1 and 2 equiv of CO at -80 °C. The acyl complexes are thermally labile and start to decompose from about -20 °C. The decomposition pathway is complicated (leading to several compounds) and, until now, poorly understood. Oxidation with PbCl₂ at -20 °C gave the monochloro acyl Cp*₂Ti(C(O)Cl)Cl (R = Me, ν_C=O = 1600 cm⁻¹; R = Et, ν_C=O = 1580, 1600 cm⁻¹). The Cp*₂Ti(C(O)Cl)Cl, have been synthesized by Facchinetti et al.\(^{\text{31}}\) In these complexes (ν_C=O = 1603 cm⁻¹), the γ^2-coordination was established by X-ray structure determination and, by analogy, we assume that the coordination of the acyl fragment in the complexes discussed here is the same. For R = Me the chloride acyl is of marginal thermal stability as well and it was not possible to obtain a pure sample. The stability of acyl compound Cp*₂Ti(C(O)Et)Cl is sufficient to allow full characterization. The presence of two carbonyl stretching frequencies indicates two isomers, and NMR spectra show that they are present in a ratio of 93:7. The isomers probably arise from the fact that two different orientations of the acyl ligand are possible with respect to the chloride ligand (eq 4). In

\[
\text{Cp}^*\text{Ti}^+\cdot\text{C}^\equiv\text{O} + \frac{1}{2} \text{PbCl}_2 \rightarrow \text{Cp}^*\text{Ti}^+\cdot\text{C}^\equiv\text{O} + \text{PbCl}^+\cdot\text{Cl}^{-} \tag{4}
\]

the 13C NMR spectrum (recorded at -10 °C) of Cp*₂Ti(C(O)OEt)Cl, only the resonances of the major isomer are well resolved. The signal for the acyl carbon atom is strongly shifted to 292 ppm. A large shift to low field is reminiscent of the values for the carbonyl carbon in Fischer carbines (δ = 500-400 ppm), suggesting that in Cp*₂Ti(C(O)Cl)Cl the acyl carbon atom has carbene character. Increasing the oxidation state of titanium to Ti(IV) enhances the Lewis acidity of the metal center and results in a 70-7 cm⁻¹ shift (140 cm⁻¹ for one of the isomers) to higher wavenumbers of the ν_C=O, analogous to what was found for iminoacyl compounds. PbCl₂ oxidation of Cp*₂Ti(C(O)Me)Cl yielded the diamagnetic monochloro vinyl compound Cp*₂Ti(C(O)Me)Cl, and the NMR spectra (Tables II and III) confirm the insertion of but-2-yne into the M-C bond of 1. According to the 1H NMR spectrum the compound is present as a mixture of two isomers (3:2 ratio) and we assume that, analogous to the acyl derivatives discussed above, the relative position of the vinyl and the chloride ligands in the equatorial plane between the cyclopentadienyl rings can explain the isomerism (eq 5).

\[
\text{Cp}^*\text{Ti}^+\cdot\text{C}^\equiv\text{O} + \frac{1}{2} \text{PbCl}_2 \rightarrow \text{Cp}^*\text{Ti}^+\cdot\text{C}^\equiv\text{O} + \text{PbCl}^+\cdot\text{Cl}^{-} \tag{5}
\]

Rotation of the vinyl ligand around the Ti-C bond appears to be hindered, but this is not a surprise in very congested molecules like these. The vinyl compound Cp*₂TiCl(C(H)Me)Cl, obtained from 2 and but-2-yne and subsequent oxidation with PbCl₂, appeared to be a mixture of two isomers (5:2) as well, but the homologues Cp*₂TiCl(C(H)Ph)Cl and Cp*₂TiCl(C(H)Me)Cl (from 2 and PhC=Me and PhC=OPh, respectively) were isolated as single isomers. The oxidation process of the parent compound Cp*₂TiCl(R)=C(H)R' appears to be regioselective in these cases, since it is unlikely that rotation of the vinyl ligand is less hindered in these compounds.

The azomethide complex Cp*₂TiN=CH(Me)Cl has ν_C=O at 1680 cm⁻¹, a normal position for early-transition metal ketimines.\(^{\text{33}}\) The 1H NMR spectrum shows resonances at δ 22.9 ppm (Cp*, 30 H) and δ 1.4 ppm (CMe₂, 9 H), but the resonance of the hydrogen atom at the β position is not observed. The EPR spectrum shows four signals due to two hyperfine couplings, one for the nitrogen atom of 2.5 G and one for the azomethide proton of 2.5 G (assigned by comparison with Cp*₂TiN=C(D)MeCl, obtained from Cp*₂Ti(Et-d₅) and Me₂CC≡D). On oxidation to Cp*₂TiN=C(H)MeCl, ν_C=O shifts 10 cm⁻¹ to lower frequency, reflecting a slightly stronger donation to the stronger (Lewis) acidic tetravalent titanium and the 1H NMR resonance for the azomethide proton is at a characteristic position, δ 7.6 ppm, different from TMS.\(^{\text{33b}}\)

**Concluding Remarks**

The reactivity of Cp*₂TiMe (1) is characteristic for a polar Ti-C bond with a partial positive charge at the metal. Bis(permethylcyclopentadienyl)titanium carbonyls are weaker Lewis acids than their scandium analogues; they do not complex salt molecules nor form stable adducts with Lewis bases. One consequence of the reduced Lewis acidity is that compounds Cp*₂TiCl do not undergo σ-bond metathesis with unactivated hydrocarbons. Apparently, the [2 + 2₁] transition state for this process cannot be reached.\(^{\text{34}}\)\(^{\text{34}}\) Cp*₂TiCl complexes are not capable of inducing sufficient positive charge on a hydrogen atom of an unactivated C-H bond for transfer of a proton to a leaving group R. This transition state is only reached for polar substrates like acids, primary alkynes, or alcohols. Olefins are not polymerized by Cp*₂TiCl. The transition state for migratory insertion (see Cp*₂NbH(olefin) → Cp*₂Nb=O(olefin) for Ziegler–Natta catalysts is also highly polar, with positive charge developed at the β-carbon in the transition state. Again, the low Lewis acidity of Cp*₂TiCl compounds seems crucial, since there are no apparent steric constraints for insertion of olefins into the Ti-C bond: olefins readily insert into the Ti-H bond of Cp*₂TiH, and but-2-yne inserts into the Ti-C bond of Cp*₂TiMe. The rapid β-hydrogen transfer from Cp*₂Ti is obviously not the reason for the absence of olefin polymerization activity, since olefin insertion into the Ti-C bond of both Cp*₂TiMe and Cp*₂TiEt appeared impossible.

The single electron of compounds Cp*₂TiCl is not capable of stabilizing adducts. As a consequence, Cp*₂TiCl


\(^{\text{34}}\) Crabtree, R. H. Chem. Rev. 1985, 85, 245.
![Image](https://example.com/image.png)

(2) is an alkyl and not a hydride-olefin complex. This is also expressed in its reactivity. Reactions of 2 with Brensted acids, like alcohol, do not lead to dihydrogen formation, as was observed for Cp*₂NBH(C₅H₄).¹⁰

The differences in reactivity of 1 and 2 can be explained by kinetic factors. Insertion of strongly nucleophilic reagents, like C=O, Me₃CN=O, and CH₃=O into the Ti⋯C bond is observed for both compounds. For these substrates the necessary transition state for insertion can easily be reached. Other unsaturated molecules like olefins, Me₂CC=N, acetone, and internal acetylenes do not insert readily.⁵ Since β-hydrogen-containing complexes Cp*₂TiR are liable to lose olefin, and insertion into the Ti⋯H bond is much faster than insertion into the Ti⋯C bond, the reactivity of the Cp*₂TiR compounds is completely dominated by net β-hydrogen-transfer reactions. The reactivity of 2 therefore closely resembles that of Cp*₂TiH.¹²,¹³ For the strongly Lewis acidic,¹α group 3 and lanthanide element compounds Cp*₂MR, β-hydrogen elimination, although kinetically within reach, normally competes with other pathways like β-alkyl eliminations and allylic and vinylic C=H activations.⁵,⁶ These reactions are not observed for compounds Cp*₂TiR, resulting in relatively simple reactivity patterns.

Experimental Part

All operations were performed under an inert atmosphere using Schlenk, vacuum-line, or glovebox techniques. Solvents (THF, ether, pentane) were distilled from Na/K alloy prior to use. Experimental procedures for the preparation of Cp*₂TiR (R = Me, Et), Cp*₂TiCl(Me)=NCMe₂, Cp*₂TiCl(O)R, Cp*₂TiO₂CR₂, and Cp*₂Ti=NC(Me)=CR(Me)=NC(Me)=CR(Me)=NC(Me)=CR(Me)=NC(O)=Me have been described in earlier papers.¹³ PhCl₃ (Merck-Schuchardt) was stored in an oven at 150 °C. Gases used were further purification. Me₂CC=N, Me₂CC=O, acetonitrile, alcohols, styrene, phenylmethacrylène, and i-PrCOOH were distilled and stored over molecular sieves (4 Å) prior to use. Paraformaldehyde was sublimed; benzophenone and diphenylacetylene were recrystallized from ether. Reaction of Cp*₂TiR with various substrates was carried out at room temperature unless stated otherwise. IR spectra were recorded on a Pye Unicam SP-1100S or BrukerIFS-88 spectrophotometer as Nujol mulls between KBr disks. NMR spectra were recorded on a Bruker WM-90 or Varian VXR-300 spectrometer. Chemical shifts are reported in ppm and referenced to residual protons in deuterated solvents (benzene-d₆ δ 7.15 ppm, THF-d₈ δ 3.57 ppm, and toluene-d₈ δ 7.02 ppm for 'H NMR spectroscopy and benzene-d₆ δ 127.96 ppm for ¹³C NMR spectroscopy). Gas chromatography was performed on an HP-5890A apparatus using a Porasil B packed column. Quantitative gas determinations were done using a Teepel pump. EPR spectra of pentane solutions were recorded at −80 °C on a Varian E4 spectrometer, using DPPH (g = 2.0037) as external reference. Elemental analyses were carried out at the Microanalytical Department of this University. All values given are the average of at least two independent determinations.

Cp*₂Ti(ET)=NCMe₂. 2 (681 mg, 1.96 mmol) was dissolved in 10 mL of pentane. Me₂CN=O (200 mL) was added at −80 °C. The mixture chromatographed blue on room temperature. No gas evolution was observed. After stirring for 0.5 h, the volatiles were removed in vacuum to remove the excess Me₂CN=O. The residue was recrystallized from pentane. Yield: 605 mg of Cp*₂Ti(ET)=NCMe₂ (1.41 mmol, 72%) as blue crystals.

¹'H NMR (300 MHz, benzene-d₆, 20 °C): δ 19.12 ppm (Cp*, Me), 118.97 ppm (Cp*, H), 142.20 ppm (Cp*, C), 152.34 ppm (Cp*, C), 164.84 ppm (Cp*, C), 196.17 ppm (Cp*, C). IR (cm⁻¹): 2720 (w), 2920 (m), 3050 (w), 3400 (w). Anal. Calcd for Cp*₂Ti(ET)=NCMe₂: C, 67.90; H, 10.41; N, 3.25; Ti, 11.57. Found: C, 67.85; H, 10.45; N, 3.30; Ti, 11.60.

Cp*₂TiCl(CO)MeCl. 1 (243 mg, 0.73 mmol) was dissolved in 10 mL of pentane. At −80 °C 1 equiv of CO was added. The reaction mixture was allowed to warm to −20 °C. The color gradually changed to green from blue. At −20 °C Pbc1 (101 mg, 0.37 mmol) was added. The color changed to green, and after stirring for 0.5 h the solution was filtered (0.45 μm). The filtrate was crystallized at −80 °C to give 68 mg of Cp*₂TiCl(CO)MeCl (0.17 mmol, 23%) as green crystals. IR (cm⁻¹): 2720 (w), 1600 (s), 1310 (m), 1070 (m), 1020 (m), 850 (w), 790 (m). The compound is thermally very unstable, it decomposes within days (even in the solid state) at −35 °C.

Cp*₂TiCl(CO)EtCl. 2 (166 mg, 0.48 mmol) was dissolved in 10 mL of ether, and the solution was cooled to −90 °C. CO (1...
equil) was admitted, and the reaction mixture slowly warmed to 30 °C. After 0.5 h at this temperature the ink-blue solution was evaporated to remove traces of CO, and PbCl₂ (66.3 mg, 0.24 mmol) was added. The temperature was raised to 0 °C. After stirring for 2 h, the ether solution was filtered, concentrated, and cooled to −90 °C. Green crystals of Cp*₂Ti(CO)EtCl separated and were isolated at 0 °C: 99 mg (0.24 mmol, 51%). The compound is thermally unstable and decomposes at room temperature in about 1 h.

IR (cm⁻¹): 2720 (w), 2700 (w), 1660 (m), 1590 (v), 1490 (m), 1460 (w), 1400 (v), 1370 (s), 1220 (m), 1210 (w), 1185 (s), 1070 (s), 1020 (m), 940 (w), 740 (w), 650 (m), 420 (w). Anal. Calcd for C₆₃H₇₆O₂: C, 66.91; H, 6.03; Ti, 11.60. Found: C, 66.13; H, 6.93; Ti, 11.84.

Cp*₂Ti(CO)EtCl was dissolved in 2 mL of styrene. After several freeze-thaw cycles to remove solvent, the mixture was stirred for 0.5 h, the styrene was exchanged for 25 mL of ether. After filtration and crystallization at −80 °C, 178 mg of Cp*₂Ti(CO)EtCl (0.40 mmol, 42%) as orange-red needles. IR (cm⁻¹): 2720 (w), 1330 (m), 1090 (m), 1070 (m), 1060 (m), 1020 (m), 990 (w), 900 (m), 820 (m), 540 (w), 405 (w). Anal. Calcd for C₆₃H₇₆C₁O₂: C, 66.25; H, 6.84; Ti, 12.01; Cl, 8.89. Found: C, 66.24; H, 8.77; Ti, 12.10; Cl, 8.13.

Quantitative Determination of Gases. A typical experiment is described. Cp*₂TiEt (79 mg, 0.279 mmol) was dissolved in 2 mL of toluene, and the vessel was evacuated. Me₂CO·N≡N (1 equiv) was condensed into the vessel. Upon melting, a yellow precipitate formed. Slowly warming the mixture to room temperature resulted in a red dark solution. The gases were collected (0.13 mmol) and analyzed with GC: ethene (100%). The remaining solution was evaporated to dryness and the residue identified as Cp*₂Ti≡N≡C(H)Me₂ (IR and ¹H NMR analysis).

Determination of Equilibrium Constants for Olefin-Exchange Reactions with 2 (Eq 1). Cp*₂TiEt (181 mg, 0.52 mmol) was dissolved in 2.00 mL of styrene in a calibrated volume (106.1 mL) and the vessel evacuated on a vacuum line. The mixture was stirred in a water bath at 25 °C until the pressure did not change over a 0.5 h period. The final pressure was 33 mmHg. In a separate experiment it was found that 5.8 μmol of ethylene dissolves in 2 mL of styrene at this pressure and temperature. From these data the equilibrium constant was calculated. Measurements were reproducible within 10%.

Cp*₂TiH₂C₂H₅Ph (56 mg, 0.13 mmol) was dissolved in 14.00 mL of toluene in a two-compartment vessel, interconnected with a Teflon valve. The second compartment (volume 14.00 mL) contained PbCl₂. Propene gas was added (0.58 mmol). The mixture was stirred for 24 h at 25 °C. The mixture was transferred to the other compartment (volume 14.00 mL) and the valve closed. The remaining propene in the vessel was collected (0.46 mmol). The oxidized mixture was analyzed with ¹H NMR spectroscopy: Cp*₂TiH₂C₂H₅Ph = Cp*₂TiH₁C₂H₄Ph + 1 mole of propene. The equilibrium constant K was calculated, assuming that Cp*₂TiPh and Cp*₂TiH₂C₂H₅Ph are equally reactive toward PbCl₂.

Competition Experiment. Cp*₂TiMe (39 mg, 0.12 mmol) and Cp*₂TiEt (37 mg, 0.11 mmol) were dissolved in 2 mL of toluene, and the vessel was evacuated. CO₂ (0.11 mmol) was added at room temperature, and the mixture was stirred for 1 h. The color changed to blue. The gases were collected with a Teflon pump in a calibrated volume: 0.11 mmol (GC: 100% ethene). The remaining solution was evaporated to dryness, and the residue was dissolved in benzene-d₆ and oxidized with PbCl₂. After reaction...
Thermal and Photoassisted Ring Opening of Thietane in a Triosmium Cluster Complex

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UV irradiation of Os₆(CO)₁₀[μ-S(CH₂)₂]₅, 1, produced decarbonylation and formation of two isomers, Os₆(CO)₁₀[μ-S(CH₂)₂CH₂]₂, 2, and Os₆(CO)₁₀[μ-SCH₂CH₂CH₃]₂(μ-H)₃, 3, by C-S bond cleavage and opening of the thietane ring. Compound 2 contains a thiametallacyclopentane ring system that was formed by insertion of an osmium atom into one of the C-S bonds. Compound 3 contains a 2-propenethiolato ligand and bridging hydride ligand formed by a combination of C-S and C-H bond cleavage at the 3-position of the thietane ring. When heated to 70 °C, 2 was converted to 3 by a β-elimination reaction and Os₆(CO)₁₀[μ-SCH₂CH₂CH₃]₂(μ-H)₄, 4, by a fragmentation of the cluster. Compound 4 has only two metal atoms, and these are bridged by the sulfur atom, a hydride ligand, and an alkylidene carbon. Compound 3 was also formed in the reaction of thietane with Os₆(CO)₁₀(NCMe)₆ at 25 °C. Compound 2 adds phosphines by opening the cluster to yield the adducts Os₆(CO)₁₀[μ-S(CH₂)₂](L)₅ (5, L = PPh₃; 6, L = PMe₃Ph). At 97 °C, 5 and 6 undergo β-elimination involving the metalacycle to yield the complexes Os₆(CO)₁₀[μ-SCH₂CH₂CH₃]₂(μ-H)⁷ (7, L = PPh₃; 8, L = PMe₃Ph) which are simply phosphine-substitution derivatives of 2. Compounds 1, 2, 4, 6, and 7 were characterized by single-crystal X-ray diffraction analysis. For 1: space group P2₁/a, α = 9.020 (2) Å, β = 11.750 (3) Å, γ = 13.242 (5) Å, Z = 16, 1497 reflections, R = 0.048. For 2: space group P2₁/a, α = 11.750 (3) Å, β = 12.623 (2) Å, γ = 13.242 (5) Å, β = 100.79 (2)°, Z = 4, 2423 reflections, R = 0.056. For 4: space group P1, α = 5.5830 (9) Å, β = 12.999 (2) Å, γ = 6.4810 (6) Å, α = 92.23 (1)°, β = 110.370 (8)°, γ = 74.165 (9)°, Z = 2, 1266 reflections, R = 0.027. For 6: space group P2₁/a, α = 10.536 (2) Å, β = 18.131 (3) Å, α = 14.174 (2) Å, γ = 99.57 (1)°, Z = 4, 2780 reflections, R = 0.024. For 7: space group P1, α = 10.341 (1) Å, β = 17.854 (4) Å, γ = 93.14 (1)°, γ = 84.39 (2)°, Z = 2, 3247 reflections, R = 0.038.

Introduction

Studies of the coordination and reactivity of organosulfur ligands in metal complexes have attracted much attention recently.1 The transformations of cyclic thioethers such as thiophenes in organometallic complexes and on metal surfaces have been widely studied in an effort to develop an understanding of the mechanisms of the metal-catalyzed hydrosulfurization reaction.2 The cleavage of C-S bonds is a key step in this process. We have been investigating the ring opening of the strained-ring thioethers thiirane3 A and thietane4-10 B and their derivatives by transition-metal carbonyl cluster complexes.

