Reactivity of Tervalent Titanium Compounds (η5-C5Me5)2TiR (R = Me, Et)
Luinstra, Gerrit A.; Vogelzang, Johannes; Teuben, Jan H.

Published in:
Organometallics

DOI:
10.1021/om00042a048

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1992

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Download date: 18-01-2019
the characterization of tin atoms in cluster molecules.

Acknowledgment. We acknowledge the support of the Monsanto Co. and the Missouri Research Assistance Act in the form of a postdoctoral fellowship to D.K.S., UM—St. Louis for an IQ Award, and the National Science Foundation for the Grant for the Grant for the NMR spectrometer (CHE-8506671).

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.

OM9200655

Reactivity of Tervalent Titanium Compounds (η5-C5Me5)2TiR (R = Me, Et): Insertion versus β-Hydrogen Transfer and Olefin Extrusion. Preparation of the Paramagnetic Titanium Alkoxide, Iminoacyl, Acyl, Vinyl, and Azomethide Complexes (η5-C5Me5)2TiX and Oxidation of These with PbCl2 to the Diamagnetic Tetravalent Derivatives (η5-C5Me5)2Ti(X)Cl

Gerrit A. Luluistra, Johannes Vogelzang, and Jan H. Teuben*

Groningen Center for Catalysis and Synthesis, Department of Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Received September 13, 1991

The paramagnetic, tervalent titanium alkyls Cp*TiR (1, R = Me; 2, R = Et) were compared in their behavior toward a range of reactive molecules. These 15-electron, d1 systems appear to be weak Lewis acids, reluctant to form adducts. Only for 1 and Me2CO==N could an instable adduct Cp*TiR-L be isolated. With active-hydrogen-containing substrates HX (X = O=C(H)Me2, OEt, C==Me), Cp*TiX and RH were produced. Polar, unsaturated molecules like Me2CN==C, CO, and paraformaldehyde inserted to give Cp*Ti2(C==R)==NCMe3, Cp*Ti2(C==O)R, and Cp*Ti2CH2R for both 1 and 2. Apolar, unsaturated substrates did not insert into the Ti—C bond with the exception of Me2CdMe, which reacted with Cp*Ti2Cl to produce the vinyl compound Cp*Ti(=C(R)==NCMe3)=CMe2. A striking difference between 1 and 2 was found in their reaction with CO2, Me2CO==N, Me2C==O, and ROC==CR (R, R′ = Me, Ph). While 1 either gave a normal insertion (CO2 and Me2CC==Me) or adducts (Me2CO, Me2C==O) or did not react (PhC==CPh), 2 lost ethene and gave compounds that appeared to be products of insertion into a Ti—H bond. Cp*2TiOCH2R for both R (R = Me, Et) and Cp*2TiCH2CH2R. The paramagnetic, tervalent titanium alkyls Cp*TiR (1, R = Me, Et) were compared in their behavior toward a range of reactive molecules. These 15-electron, d1 systems appear to be weak Lewis acids, reluctant to form adducts. Only for 1 and Me2CO==N could an instable adduct Cp*TiR-L be isolated. With active-hydrogen-containing substrates HX (X = O=C(H)Me2, OEt, C==Me), Cp*TiX and RH were produced. Polar, unsaturated molecules like Me2CN==C, CO, and paraformaldehyde inserted to give Cp*Ti2(C==R)==NCMe3, Cp*Ti2(C==O)R, and Cp*Ti2CH2R for both 1 and 2. Apolar, unsaturated substrates did not insert into the Ti—C bond with the exception of Me2CdMe, which reacted with Cp*Ti2Cl to produce the vinyl compound Cp*Ti(=C(R)==NCMe3)=CMe2. A striking difference between 1 and 2 was found in their reaction with CO2, Me2CO==N, Me2C==O, and ROC==CR (R, R′ = Me, Ph). While 1 either gave a normal insertion (CO2 and Me2CC==Me) or adducts (Me2CO, Me2C==O) or did not react (PhC==CPh), 2 lost ethene and gave compounds that appeared to be products of insertion into a Ti—H bond. Cp*2TiOCH2R for both R (R = Me, Et) and Cp*2TiCH2CH2R. This reaction is reversible and equilibrium constants could be determined. Ground-state differences between 2 and Cp*2TiCH2CH2R were found to be 9 (2) R (R = Me) and 7 (2) kJ·mol−1 (R = Ph). Isotope-labeling experiments showed that liberation of ethene and formation of the new insertion products proceed via an intermediate hydride, Cp*2TiH. 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 reinserterion 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*2Ti(R)Cl after quantitative oxidation with PbCl2. Comparison of spectrosopic data gives information about the specific coordination of ligand R in both Cp*2TiR and Cp*2Ti(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*MR (Cp* = η5-C5R5, R = z = 0–5; R = H, alkyl, aryl) are highly reactive species.1 The group 3 and lanthanide derivatives are electronically and sterically very

ununsaturated 14-electron, d2 systems. They are strong Lewis acids, which leads to coordination of solvent molecules (ethers) and, sometimes, even of salt molecules.2 Solvent- and salt-free complexes often satisfy their need for electron density by forming (intramolecular) π or agostic interac-


The activation energy for the reverse process, \( \beta \)-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 in the same range as for group 3 M--C bonds.\(^5\) For vanadium the situation is quite different. The homolytic decomposition of Cp\(_2\)VR (R = alkyl) and Cp\(_2\)VEt to (permethy1)vanadocene at ambient temperatures illustrates that V--C bond dissociation energies are substantially smaller.\(^6\)

The paramagnetic d\(_1\), 15-electron complexes Cp\(_2\)TiR represent in a formal sense the intermediate between d\(_0\) and d\(_2\) metalocene derivatives, and a study of their reactivity seems appropriate. Our group has extensively reported on the synthesis and reactivity of Cp\(_2\)TiR (R = hydrocarbyl).\(^1\)\(^2\) The majority of these compounds, however, are thermally unstable, thus complicating the investigations. Recently, the much more robust penta-methylcyclopentadienyl analogues, Cp\(_2\)TIR, have become available\(^1\)\(^2\) and preliminary data on the specific aspects of their reactivity have been published.\(^1\)\(^2\)

In the first part of this study, the reactivity of Cp\(_2\)TiMe (1) is reviewed. The compound is an excellent model for investigating Ti-C bond reactivity since it is a prototype alkyl compound Cp\(_2\)TiR. In the second part the reactivity of the \( \beta \)-hydrogen-containing alkyl Cp\(_2\)TiEt (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 Cp\(_2\)TiR (R = hydrocarbyl ligand) and Cp\(_2\)TiX (X = anionic ligand) to tetravalent, diamagnetic complexes Cp\(_2\)Ti[R(Cl)\(_2\)] and Cp\(_2\)Ti[Cl\(_2\)] by PbCl\(_2\)\(^1\)\(^4\) and the use of this method to characterize and help identify paramagnetic compounds which are not well accessible to conventional NMR spectroscopic methods.

### Results and Discussion

**Reactivity of Cp\(_2\)TiMe (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 Me\(_2\)CN=C, CO, CO\(_2\), and but-2-yne, to yield respectively Cp\(_2\)Ti(C(Me)=NCMe\(_3\)), Cp\(_2\)Ti(O)Me, Cp\(_2\)TiO\(_2\)Me, and Cp\(_2\)Ti(OMe)\(_2\). With paraformaldehyde insertion and formation of the ethoxide Cp\(_2\)TiOEt was observed. Ethene and higher olefins did not insert into the Ti--C bond of 1. After treatment with ethene (70 bar, 100 °C, 24 h), I was recovered and polyethylene had not been formed. Also internal alkynes (PhC=CPH, Me\(_2\)SiC=C(CH\(_3\))\(_3\)) do not readily insert into the M--C bond of 1. Only for but-2-yne was insertion observed, to give the vinyl Cp\(_2\)TiC(Ph)=CHMe. In order to have observable rates, reaction of 1 with but-2-yne had to be carried out in neat alkane. Active hydride-containing substrates HX react under liberation of 1 equiv of

---


---


methane. Treatment of 1 with isobutenoic acid, ethanol, or propyne gave Cp*₂Ti₂O₂CC(H)Me₂, CP*₂TiOEt, and CP*₂TiCl₂CMe₂. Reaction with Me₂CCN=N led to an adduct CP*₂TiMe₂N=CCMe₂. The complex is thermally instable 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*₃Ti(Me)Cl was formed together with Me₂CC=CN. 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 (t₁/₂ ≈ 45 h, in THF). However, reaction with unsaturated 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 Me₂CB(CMe₃)=NCMe₂, the acyl CP*₃TiC(O)Et, and the alkoxide CP*₃TiOPr, fully analogous with 1. Other substrates, like CO₂, and alkenes RC≡CR, which for 1 gave insertion, led to extrusion of ethene (vide infra). Similar to 1, reaction with active hydrogen-containing molecules resulted in the liberation of alkane (ethane) as expected for highly polar metal–carbon bonds. For example, ethanol gave the ethoxide CP*₃TiOEt, and isobutanoic acid the carboxylate CP*₃TiO₂CC(H)Me₂, 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*₃NbH(CH₂=CH₂). Reaction of 2 with propyne (equimolar and excess) was not clean. The reaction mixture contained several organic (the dimer 2-methylpent-1-en-3-yne was identified) and organometallic compounds, and appeared too complex to analyze.

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 Me₂CB(CMe₃)=NCMe₂, and CO₂, and also with internal alkynes R≡CR. CP*₂TiEt reacted with Me₂CC=CN 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 organonitridation product was oxidized with PbCl₂ and analyzed by NMR spectroscopy. The major component (>85%) could be identified as CP*₃TiOC(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 ethane probably results from an acid–base reaction of 2 with a hydrogen atom of acetone. Reaction of 2 with CO₂ produced CP*₂TiO₂CH and 1 equiv of ethene, as reported before. In toluene, 2 reacted with internal alkynes R≡CR to yield vinyl compounds

<table>
<thead>
<tr>
<th>Compd</th>
<th>Assignm</th>
<th>δ (ppm)</th>
<th>Mult.</th>
<th>J(HH) (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP*₃Ti(CH₂CH₂Ph)Cl</td>
<td>Cp*</td>
<td>1.79</td>
<td>s</td>
<td>30</td>
</tr>
<tr>
<td>TI-CH</td>
<td>1.01</td>
<td>ps</td>
<td>t</td>
<td>2</td>
</tr>
<tr>
<td>CH₂Ph</td>
<td>2.65</td>
<td>ps</td>
<td>t</td>
<td>2</td>
</tr>
<tr>
<td>Ph</td>
<td>7.25</td>
<td>m</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>7.07</td>
<td>m</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CP*₃Ti(OEt)Cl</td>
<td>Cp*</td>
<td>1.85</td>
<td>s</td>
<td>30</td>
</tr>
<tr>
<td>OCH₂</td>
<td>4.29</td>
<td>q</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>CH₂</td>
<td>1.20</td>
<td>t</td>
<td>3</td>
<td>7</td>
</tr>
<tr>
<td>CH₂</td>
<td>1.10</td>
<td>d</td>
<td>6</td>
<td>6.3</td>
</tr>
<tr>
<td>CH</td>
<td>5.04</td>
<td>h</td>
<td>1</td>
<td>6.3</td>
</tr>
<tr>
<td>CP*₃Ti[(CH₂)₂H]Cl</td>
<td>Cp*</td>
<td>1.69</td>
<td>s</td>
<td>30</td>
</tr>
<tr>
<td>Me</td>
<td>3.10</td>
<td>s</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>t-Bu</td>
<td>3.31</td>
<td>s</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>CP*₃Ti[(OH)₂Me]Cl</td>
<td>Cp*</td>
<td>1.77</td>
<td>s</td>
<td>30</td>
</tr>
<tr>
<td>Me</td>
<td>2.01</td>
<td>s</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Me</td>
<td>2.72</td>
<td>s</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Me</td>
<td>2.22</td>
<td>q</td>
<td>2</td>
<td>7.2</td>
</tr>
<tr>
<td>CH₂</td>
<td>1.02</td>
<td>t</td>
<td>3</td>
<td>7.2</td>
</tr>
<tr>
<td>CP*₃Ti[(CH₂)₂Me]Cl</td>
<td>Cp*</td>
<td>1.84</td>
<td>s</td>
<td>30</td>
</tr>
<tr>
<td>Me</td>
<td>1.77</td>
<td>sb</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Me</td>
<td>1.73</td>
<td>sb</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Me</td>
<td>0.9</td>
<td>sb</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>CP*₃Ti[(CH₂)₃Me]Cl</td>
<td>Cp*</td>
<td>1.79</td>
<td>s</td>
<td>30</td>
</tr>
<tr>
<td>CH</td>
<td>3.67</td>
<td>q</td>
<td>1</td>
<td>8.1</td>
</tr>
<tr>
<td>CH₂</td>
<td>1.74</td>
<td>m</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>t-CH₃</td>
<td>1.68</td>
<td>dm</td>
<td>3</td>
<td>6.6</td>
</tr>
<tr>
<td>CP*₃Ti[(CH₂)₂Ph]Cl</td>
<td>Cp*</td>
<td>1.80</td>
<td>s</td>
<td>30</td>
</tr>
<tr>
<td>CH₂</td>
<td>2.04</td>
<td>d</td>
<td>3</td>
<td>2.1</td>
</tr>
<tr>
<td>CH</td>
<td>4.86</td>
<td>q</td>
<td>1</td>
<td>2.1</td>
</tr>
<tr>
<td>Ph</td>
<td>7.08</td>
<td>m</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>7.27</td>
<td>m</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CP*₃Ti[(Ph)₂]Cl</td>
<td>Cp*</td>
<td>1.85</td>
<td>s</td>
<td>30</td>
</tr>
<tr>
<td>H</td>
<td>4.65</td>
<td>s</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Ph</td>
<td>6.93</td>
<td>7.26</td>
<td>m</td>
<td>10</td>
</tr>
<tr>
<td>CP*₃Ti[(CH₂)₂Me]Cl</td>
<td>Cp*</td>
<td>1.75</td>
<td>s</td>
<td>30</td>
</tr>
<tr>
<td>t-Bu</td>
<td>1.04</td>
<td>s</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>7.61</td>
<td>s</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

(15) The final product (benzene-d₆, 3 weeks at 50 °C) was identified on the basis of H NMR and IR data as a 1:1 mixture of the insertion product CP*₂TiN=C(H)Me₂ (δ 18.9 ppm, CP*₃, whm 2400 Hz; δ 0.68 ppm, Me and CMe₂, whm 90 Hz) and the nitrile-carbon coupled tetra-titanium azomethide compound (CP*₂TiMe₂N=C(CHMe₂)=Me₂; δ 173 ppm, CP*₃; δ 0.65 ppm, Me). The IR data (νs (C=O) 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, 55.


(17) The identity of CP*₃TiOPr was established by comparison with an authentic sample of this compound prepared from CP*₃TiCl and LiO₂Me. Oxidation with PbCl₂ gave CP*₃Ti(OCl)Pr.

Cp*,TiCl(=CH2CH2R) + CH2=C=CHR \rightleftharpoons Cp*,TiClCH2CH2R + CH2=CHR (1)

1 have been determined for a number of combinations of olefins and alkyl complexes (Table I). Cp*2Et(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 Cp*,TiCH2CH2Ph 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).22 To place the ground states of the alkyl complexes and Cp*,TiCH2CH2R 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 Cp*,TiCH2CH2R. An estimate for this stabilization can be obtained from eq 2. Correction of the observed $\Delta G^\circ$ 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.22

It is tempting to assign the stabilization of 2 to a $\beta$-agostic interaction between the metal and a $\beta$-C-H bond of the ethyl ligand, although the effect is much smaller than the value derived by Brookhart et al.23 from the rotation barrier of the methyl group of the ethyl ligand in Cp*Co(PMe3)CH2CH2CH3 (37 kJ-mol$^{-1}$), which has a $\beta$-agostic C-H bond. However, one has to be careful since in Cp*2Nb(CH2=CHR)(H) (R = H, Me, Ph) similar ground-state differences were found (although smaller in absolute numbers$^{20}$), 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

---

(22) Calculated from eq 2, using the difference in heat of hydrogenation of the olefins and radical formation of the corresponding alkane. 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.


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 Cp\(^*\)TiCl compounds. The IR spectrum of Cp\(^*\)TiCl(\(n\)C\(_2\)H\(_5\)) in 1-hexene is a superposition of the spectra of the two components. No absorptions characteristic for coordinated olefins were found. Also, the \(1\H\) NMR spectrum of Cp\(^*\)TiCl 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 Cp\(^*\)TiCl is slow on the \(1\H\) NMR time scale, since no shift of the resonance of free propene was observed.

**Mechanistic Considerations on Ethene Extrusion from Cp\(^*\)TiEt.** The substrate-induced olefin extrusion from 2 was investigated in detail. The process can follow two routes, either direct transfer of \(\beta\)-hydrogen from the ethyl group to a coordinated substrate or olefin extrusion with intermediate formation of Cp\(^*\)TiH (Scheme I).

**Scheme I**

```
Cp\(^*\)TiCl + \(\text{CH}_2=\text{CH}_2\) \rightarrow Cp\(^*\)Ti=CH\(_2\) + \text{C}_2\text{H}_4
```

This process is demonstrated by a competition experiment. Equimolar amounts of 1 and 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 Cp\(^*\)TiO\(_2\)CH\(_2\).\(^{14a}\) After 1 h, 1 equiv of ethylene (relative to carbon dioxide) had evolved. Oxidation of the reaction mixture with PbCl\(_2\) gave exclusively Cp\(^*\)TiEtCl, no Cp\(^*\)Ti(\text{Et}Cl) was present. This shows the preference of carbon dioxide to insert into the Ti–H bond.

**Oxidation of Cp\(^*\)Ti to Diamagnetic Tetravalent Titanium Derivatives Cp\(^*\)Ti\(_2\)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 \(1\H\) 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. Cp\(^*\)TiCl compounds can be readily converted into their diamagnetic monochloride analogues Cp\(^*\)TiCl(R)Cl by oxidation with PbCl\(_2\) (eq 3).\(^{14b}\) The latter compounds are Cp\(^*\)TiCl + \(\frac{1}{2}\)PbCl\(_2\) (eq 3) 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 Cp\(^*\)TiX and Cp\(^*\)TiCl and reported in this or previous papers.\(^{13}\) In addition to the fact that oxidation to Cp\(^*\)TiCl(R)Cl is very helpful for identification, the method also is an excellent synthetic route to new mixed hydrocarbyl compounds Cp\(^*\)Ti(R)Cl. Experimental procedures and IR spectra are given in the Experimental Part, \(1\H\) and \(13\C\) 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 Cp\(^*\)TiCl with Cp\(^*\)Ti\(_2\)Cl.** Reaction of 1 and 2 with Me\(_2\)CN\(_3\)C gave iminoacyl complexes Cp\(^*\)TiCl(R)Cl = NCCMe\(_3\) (R = Me, \(\nu_{C=\text{N}}\) = 1600 cm\(^{-1}\); R = Et, \(\nu_{C=\text{N}}\) = 1590 cm\(^{-1}\)). Assignment of the coordination mode for the iminoacyl ligand (\(\eta^1\) or \(\eta^2\)) on IR data alone is unreliable, as has been noted before.\(^{27}\) Nowadays there is ample evidence that little correlation exists between the bonding mode of (imino)acyl moieties and spectroscopic data (\(\text{C} = \text{N}\) stretching frequency and \(1\C\) NMR shifts), although conclusions concerning the bonding mode of iminoacyl ligands seem to be valid within a series of homologues.\(^{28}\) So far, only a few structures of titanium iminoacyl compounds have been reported.\(^{27a,29}\) All structures show an \(\eta^2\)-coordinated iminoacyl ligand, which is in general the most favorable coordination mode for coordinatively and electronically unsaturated imido and imido-1 complexes.\(^{27a,30}\) Therefore, it is reasonable to assume that in Cp\(^*\)TiCl(R)Cl = NBR\(^1\) the iminoacyl ligand is \(\eta^2\)-coordinated. This is supported by the spectra of the tetralettantal titanium iminoacyls Cp\(^*\)Ti(C(R)\(_2\))Cl = NCCMe\(_3\)Cl. The \(13\C\) NMR resonance of the iminoacyl

\(^{24}\) Bercaw, J. E.; Davis, R. B.; Wolcanski, P. T. *Organometallics* 1986, 5, 443.

\(^{25}\) This reagent was prepared from Mg and CH\(_2\)\(_3\)Cl\(_3\). Hydrolysis with D\(_2\)O gave CH\(_2\)\(_3\)DO (\(1\C\) NMR) as the only gaseous product. No scrambling of the/qu label had taken place in the Grignard reagent.

carbon atom (R = Me, δ = 231 ppm; R = Et, δ = 228 ppm) is found at low field, as expected for γ²-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 donor 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.

Ink-blue acyl compounds Cp²Ti(C(=O)R)Cl (R = Me, ν_{C-O} = 1590 cm⁻¹; R = Et, ν_{C-O} = 1520 cm⁻¹) were formed from 1 and 2 and 1 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 Cp²TiIC(O)RCl (R = Me, ν_{C-O} = 1590 cm⁻¹; R = Et, ν_{C-O} = 1580 cm⁻¹). The IR spectra of these complexes were identical to those of the corresponding chlorides. The difference in ν_{C-O} is reminiscent of the values for the carbeneoid carbon in Fischer carbene (δ = 500-400 ppm)², suggesting that in Cp²TiIC(O)RCl 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-cm⁻¹ shift to lower field (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 Cp²TiIC(Me=)=CMe₃ yielded the dianionic monochloro vinyl compound Cp²TiIC(Me=)=CMe₃Cl, and the NMR spectra for the compound are characteristic for an acyl derivative discussed before, the relative position of the vinyl and the chloride ligands in the equatorial plane between the cyclopentadienyl rings can explain the isomerism.

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 Cp²TiIC(=CMe)=CMe₂Cl, 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 Cp²TiIC(Me)=CMe₂Cl and Cp²TiIC(Ph)=C(Ph)Cl [from 2 and PhCMe₂Cl and PhCMe₃, respectively] were isolated as single isomers. The oxidation process of the parent compound Cp²Ti(C(=O)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 complexes.

The azomethide complex Cp²TiN=C(H)=CMe₃ has ν_{C=N} at 1680 cm⁻¹, a normal position for early-transition metalketimines. The 'H NMR spectrum shows resonances at δ 22.9 ppm (Cp², 30 H) and δ 1.4 ppm (CMe₃, 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 Cp²TiIC(=C)=CMe₃, obtained from Cp²TiIC(Et-d₅) and Me₆CC≡N). On oxidation to Cp²TiIC(=C)=CMe₃Cl, ν_{C=N} shifts 10 cm⁻¹ to lower frequency, reflecting a slightly stronger donation to the nitrogen atom. The 'H NMR resonance for the azomethide proton is at a characteristic position, 7.6 ppm downfield from TMS.

Concluding Remarks

The reactivity of Cp²TiMe (1) is characteristic for a polar Ti—C bond with a partial positive charge at the metal. Bis(permethycyclopentadienyl)titanium carbyls 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 Cp²TIR do not undergo α-bond metathesis with unactivated hydrocarbons. Apparently, the [2 + 2] transition state for this process cannot be reached. Cp²TIR 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 Cp²TIR. The transition state for migratory insertion (see Cp²NbH(olefin)—>Cp²NbR=O for Ziegler–Natta catalysts is also highly polar, with positive charges developed at the β-carbon in the transition state. Again, the low Lewis acidity of Cp²TIR 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 Cp²TiH, and but-2-yne inserts into the Ti=C bond of Cp²TiMe. The rapid β-hydrogen transfer from Cp²TIR is obviously not the reason for the absence of olefin polymerization activity, since olefin insertion into the Ti=C bond of both Cp²TiMe and Cp²TiEt appeared impossible.

The single electron of compounds Cp²TIR is not capable of stabilizing adducts. As a consequence, Cp²TiEt

---

(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*2NH2(CH3H).10

The differences in reactivity of 1 and 2 can be explained by kinetic arguments. Insertion of strongly nucleophilic reagents, like C≡O, Me5CN=C=, and CH2=O into the Ti=H bond is observed for both compounds. For these substrates the necessary transition state for insertion can easily be reached. Other unsaturated molecules like olefins, Me5CC=N, acetone, and internal acetylenes do not insert readily. Since β-hydrogen-containing complexes Cp*2TiH are likely to lose olefin, and insertion into the Ti=H bond is much faster than insertion into the Ti=O bond, the reactivity of the Cp*2TiO complexes is completely dominated by net β-hydrogen-transfer reactions. The reactivity of 2 therefore closely resembles that of Cp*2TiH.12,13,15 For the strongly Lewis acidic, d1 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.16 These reactions are not observed for complexes 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*2Ti(C(Me)=NCMe3), Cp*2TiOC(Cp*R), Cp*2TiC(Me)=C(R)Me (R = Me, Et), Cp*2TiC(Me)=NCMe3, Cp*2TiC(O)R, Cp*2TiMeN=NCMe3, and various other unsaturated molecules like olefins, acetylenes and vinylic C–H activations.16 These reactions were distilled and stored over molecular sieves (4 Å) prior to use. Paraffinolysis 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 SP3-300 spectrometer or Varian Infracord 760 infrared spectrophotometer as Nujol mulls between KBr disks. NMR spectra were recorded on a Bruker WH-90 spectrometer. Chemical shifts are expressed in parts per million. 13C NMR spectroscopy was measured using benzene-d6 6 as external reference. Elemental analyses were carried out at the Microanalytical Department of this University. All values given are expressed in parts per million. IR spectra were recorded on a Pye Unicam SP3-300 spectrometer. Chemical shifts are expressed in parts per million.

**1.0 Reaction with Paraffinolysis**

The product of this reaction in pentane was identified as Cp*2TiEt2 after oxidation with PbCl2 to Cp*2Ti(OEt)Cl (vide infra).

**2.0 TiO2**

Cp*2Ti(OEt)Cl 2 (461 mg, 0.30 mmol, and CH2Cl2) (38 mg, 1.30 mmol) were suspended in 10 mL of pentane, and the mixture was stirred overnight. The volatiles were removed in vacuum, and the residue was recrystallized from pentane. Yield: 381 mg of Cp*2TiOPr1. (1.01 mmol, 78%). 1H NMR (90 MHz, benzene-d6, 20 °C): δ 18.4 ppm (Cp*2Ti(OEt)Cl). IR (cm⁻¹): 3080 (w), 3070 (w), 1580 (s), 1450 (m), 1380 (s), 1200 (w), 1150 (w), 1110 (w), 1070 (m), 1020 (s), 960 (m), 910 (m), 840 (w), 770 (w), 750 (vs), 690 (w), 520 (w), 450 (w). Anal. Calcd for Cp*2Ti(OEt)Cl: C, 82.07; H, 8.31; Ti, 9.63. Found: C, 80.95; H, 8.24; Ti, 9.66.

**3.0 TiMeN=NCMe3**

Cp*2TiMeN=NCMe3 1 (350 mg, 0.60 mmol) was dissolved in 10 mL of pentane. Isobutyric acid (0.41 mmol, H, m, whm 1491 (m), 1380 (s), 1245 (m), 1195 (s), 1157 (w), 1060 (w), 1020 (s), 885 (m), 800 (s), 720 (m), 755 (m), 660 (s), 620 (m), 475 (w), 445 (w), 390 (w). MS: parent peak at m/e = 402. Anal. Calcd for Cp*2TiN=NCMe3: C, 74.68; H, 10.42; N, 3.36; Ti, 11.89. Found: C, 75.15; H, 10.42; N, 3.12; Ti, 11.08.

**4.0 TiC(0)Et2**

Cp*2TiC(0)Et2 1 (300 mg, 1.00 mmol) was dissolved in 15 mL of pentane, and Me5CN=C (109 µL, 1.00 mmol) was added to −50 °C. The color of the solution turned yellow-brown. After warming to room temperature, the solution was filtered, concentrated, and cooled to −80 °C. Cp*2TiMeN=NCMe3 was isolated as brown crystals. Yield: 270 mg (0.64 mmol, 64%). 1H NMR (300 MHz, benzene-d6, 22 °C): δ 17.0 ppm (Cp*2TiC(0)Et2), 20 H, whm 2600 Hz, 2.12 (CH2, Me, 12H, whm 180 Hz). IR (cm⁻¹): 2805 (w), 2718 (w), 2228 (m, 90000, 1491 (m), 1238 (s), 1206 (m), 1161 (w), 1115 (w), 1061 (w), 1020 (s), 870 (m), 804 (w), 748 (w), 642 (s). Anal. Calcd for Cp*2TiC(0)Et2: C, 71.09; H, 9.20; Ti, 11.81. Found: C, 70.78; H, 9.18; Ti, 11.92.

**5.0 TiMeN=NCMe3**

Cp*2TiMeN=NCMe3 1 (350 mg, 1.00 mmol) was dissolved in 15 mL of pentane, and Me5CN=C (109 µL, 1.00 mmol) was added to −50 °C. The color of the solution turned yellow-brown at once. After warming to room temperature, the solution was filtered, concentrated, and cooled to −80 °C. Cp*2TiMeN=NCMe3 was isolated as brown crystals. Yield: 270 mg (0.64 mmol, 64%). 1H NMR (300 MHz, benzene-d6, 22 °C): δ 17.0 ppm (Cp*2TiMeN=NCMe3), 20 H, whm 2600 Hz, 2.12 (CH2, Me, 12H, whm 180 Hz). IR (cm⁻¹): 2805 (w), 2718 (w), 2228 (m, 90000, 1491 (m), 1238 (s), 1206 (m), 1161 (w), 1115 (w), 1061 (w), 1020 (s), 870 (m), 804 (w), 748 (w), 642 (s). Anal. Calcd for Cp*2TiMeN=NCMe3: C, 71.09; H, 9.20; Ti, 11.81. Found: C, 74.95; H, 10.14; N, 3.25; Ti, 11.54. **6.0 TiC(0)Me**

Cp*2TiC(0)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 from green to blue. At −20 °C PbCl2 (101 mg, 0.37 mmol) was added. The color changed to green, and after stirring for 0.5 h the solution was filtered (at −20 °C) and recrystallized at −80 °C 25% of Cp*2TiC(0)MeCl (0.17 mmol, 23%) as green crystals. IR (cm⁻¹): 2720 (w), 1600 (vs), 1310 (m), 1070 (m), 1020 (m), 850 (w), 790 (m), 600 (w). The compound is thermally very unstable, it decomposes within days (even in the solid state) at −35 °C.

**7.0 TiC(0)EtCl**

Cp*2TiC(0)EtCl 2 (166 mg, 0.48 mmol) was dissolved in 10 mL of ether, and the solution was cooled to −80 °C. CO (1
Luinstra et al.

1. Introduction

A typical experiment is described. Cp*₂TiEt (79 mg, 0.279 mmol) was dissolved in 2 mL of toluene, and the vessel was evacuated. Me₅CO=N (1 equiv) was condensed into the vessel. Upon melting, a yellow precipitate formed. Slowly warming the mixture to room temperature resulted in a dark red solution. The gas was collected (0.53 mol/L) and analyzed with GC: ethene (100%). The remaining solution was evaporated to dryness and the residue identified as Cp*₂TiCN. IR and 1H NMR analysis.

2. 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. After 1 h, the styrene was evaporated to dryness, and the solution was dissolved in 10 mL of pentane. Methylphenylacetylene (84 μL, 0.38 mmol) was dissolved in 10 mL of pentane. 2-Propanol (30 μL, 0.38 mmol) was added. Gas evolution immediately started, and the color changed to purple. After stirring for 10 min, PbCl₂ (53 mg, 0.19 mmol) was added. The solution turned red. After stirring for 0.5 h, the solution was filtered, concentrated, and cooled to -80 °C. Orange crystals of Cp*₂TiN≡C(H)MeCl separated. Yield: 87 mg (0.21 mmol, 56%). IR (cm⁻¹): 2550 (w), 2350 (m), 1680 (m), 1570 (s), 1230 (m), 1150 (s), 1050 (m), 950 (s), 800 (s), 750 (s), 670 (s), 570 (m), 470 (w), 390 (m), 360 (s). Anal. Calcd for C₇H₇NCl: C, 75.71; H, 8.35; N, 4.67; Cl, 10.28. Found: C, 75.56; H, 8.41; N, 4.73; Cl, 10.25.

3. Quantitative Determination of Gases

The reaction mixture turned red during stirring at -80 °C. Dark red crystals of Cp*₂TiN≡C(H)MeCl separated. Yield: 114 mg (0.26 mmol, 40%). IR (cm⁻¹): 2720 (m), 2700 (w), 1670 (s), 1570 (s), 1480 (m), 1360 (s), 1230 (w), 1200 (s), 1090 (s), 900 (s), 800 (s), 750 (s), 660 (s), 430 (m). Anal. Calcd for C₁₀H₁₄NCl: C, 66.86; H, 8.21; Cl, 8.10; N, 3.20. Found: C, 65.84; H, 8.23; Cl, 8.17; N, 3.12.

Cp*₂Ti(NEt₃)-Cl. A mixture of 1 (315 mg, 0.94 mmol) and (CH₂O)₃ (28 mg, 0.95 mmol) was suspended in 5 mL of pentane. After stirring overnight, the reaction mixture was evaporated to dryness. The purple residue was dissolved in 10 mL of ether, and PbCl₂ (131 mg, 0.47 mmol) was added. The solution turned red and was filtered after stirring for 0.5 h. Crystalization at -80 °C yielded 36.3 mg (0.09 mmol, 57%) of Cp*₂Ti(C(Ph)=C(H)Ph)Cl. IR (cm⁻¹): 2720 (m), 1590 (m), 1455 (s), 1280 (w), 1150 (w), 1050 (s), 1000 (m), 950 (s), 800 (s), 700 (s), 600 (w). Anal. Calcd for C₁₄H₁₄Cl: C, 66.19; H, 6.96; Cl, 16.31. Found: C, 66.15; H, 6.89; Cl, 16.34.

Cp*₂Ti(H)PhCl. 2 (143 mg, 0.42 mmol) in 10 mL of pentane was treated with diphenylacetylene (37 mg, 0.42 mmol) as above. After 2 days PbCl₂ (58 mg, 0.21 mmol) was added. The color turned red, and after stirring for 0.5 h, the solution was filtered. The red solution was extracted with 10 mL of ether. The remaining solution was concentrated and kept at 0 °C to yield 99 mg (0.18 mmol, 44%) of Cp*₂Ti(Ph)Cl. IR (cm⁻¹): 3070 (w), 3030 (w), 3000 (w), 2720 (w), 1580 (m), 1570 (m), 1540 (s), 1480 (m), 1450 (w), 1380 (s), 1140 (w), 1060 (w), 1020 (m), 910 (m), 870 (w), 790 (w), 770 (w), 750 (s), 700 (s), 680 (s), 650 (w). Anal. Calcd for C₁₅H₁₅Cl: C, 76.77; H, 6.15; Cl, 16.61. Found: C, 76.72; H, 6.16; Cl, 16.58.

Cp*₂Ti(Ph)PhCl. 2 (253 g, 0.73 mmol) was dissolved in 2 mL of pentane. After several freeze-thaw cycles with a Teflon pump in a calibrated volume (110.0 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 by 1H NMR spectroscopy: Cp*₂Ti(Ph)PhCl = Cp*₂Ti(Ph)PhCl. A gas data equilibrium K was calculated, assuming that Cp*₂TiPPh and Cp*₂TiPhCl are equally reactive toward PbCl₂.

Experimental Procedure. 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. CO (0.11 mmol) was added at room temperature, and the mixture was stirred for 1 h. The color changed to blue. The gas cycle was repeated with a Teflon pump in a calibrated volume (110.0 mL) containing 100% of ethene. The remaining solution was evaporated to dryness, and the residue was dissolved in benzene-d₆ and oxidized with PbCl₂. After filtration and crystallization at -80 °C, 157 mg (0.34 mmol, 47%) of Cp*₂Ti(CH₂CH₂Ph)Cl was isolated as red crystals. IR (cm⁻¹): 2720 (w), 1580 (m), 1490 (m), 1455 (w), 1380 (s), 1280 (w), 1150 (w), 1070 (m), 1060 (m), 1020 (w), 750 (vs), 700 (v), 590 (w), 410 (m).
Thermal and Photoassisted Ring Opening of Thietane In a Triosmium Cluster Complex

Richard D. Adams* and Michael P. Pompeo
Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

Received January 17, 1992

UV irradiation of Os3(CO)10[S(CH2)2]1, produced decarboxylation and formation of two isomers, Os3(CO)10[S(CH2)2CH]2, and Os3(CO)10[S(CH2)2CH-CH]2(μ-H)3, by C-S bond cleavage and opening of the thietane ring. Compound 2 contains a thiatetrametacycloheptane ring system that was formed by insertion of an osmium atom into one of the C-S bonds. Compound 3 contains a 2-propenonitridolato 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 Os3(CO)10[S(CH2)2CH]2(μ-H)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 allylidyne carbon. Compound 3 was also formed in the reaction of thietane with Os3(CO)10(NCMe)6 at 25 °C. Compound 2 adds phosphines by opening the cluster to yield the adducts Os3(CO)10(S(CH2)2)L(5, L = PPh3; 6, L = PMe2Ph). At 97 °C, 5 and 6 undergo β-elimination involving the metallacycle to yield the complexes Os3(CO)10[S(CH2)2CH]2(μ-H)7, L = PPh3; 8, L = PMe2Ph) 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/c, a = 9.020 (2), b = 11.752 (3), c = 13.7000 (4) A, β = 94.21 (2)°, Z = 4, 1947 reflections, R = 0.038. For 2: space group P21/c, a = 11.750 (3), b = 12.623 (2), c = 13.242 (5), β = 100.79 (2)°, Z = 4, 2423 reflections, R = 0.055. For 4: space group P1, a = 5.5830 (9), b = 12.999 (2), c = 6.4810 (6), A, α = 92.23 (1)°, β = 110.370 (8)°, γ = 74.165 (9)°, Z = 2, 1266 reflections, R = 0.027. For 6: space group P21/c, n = 10.536 (2), A, b = 18.131 (3), c = 14.174 (2), β = 99.57 (1)°, Z = 4, 2780 reflections, R = 0.024. For 7: space group P1, a = 10.341 (1), b = 17.584 (4), c = 9.736 (2), α = 95.35 (2)°, β = 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 thiocarbonates 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 hydrodesulfurization reactions.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 thiocarbonates3 A and thietanes−10 B and their derivatives by transition-metal carbonyl cluster complexes.