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 (η^5-C_5Me_5)$_2$TiR (R = Me, Et): Insertion versus β-Hydrogen Transfer and Olefin Extrusion. Preparation of the Paramagnetic Titanium Alkoxide, Iminoacyl, Acyl, Vinyl, and Azomethide Complexes (η^5-C_5Me_5)$_2$TiX and Oxidation of These with $PbCl_2$ to the Diamagnetic Tetravalent Derivatives (η^5-C_5Me_5)$_2$Ti(X)Cl

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The paramagnetic, tervalent titanium alkyls Cp^*_2TiR (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 $Me_3CC{\equiv}N$ could an instable adduct $Cp^*_2TiR{\cdot}L$ be isolated. With active-hydrogen-containing substrates HX (X = $O_2C(H)Me_2$, OEt, $C{\equiv}CMe$), Cp^*_2TiX and RH were produced. Polar, unsaturated molecules like $Me_3CN{\equiv}C$, CO, and paraformaldehyde inserted to give $Cp^*_2Ti\{\eta^2\text{-}C(R){=}NCMe_3\}$, $Cp^*_2Ti\{\eta^2\text{-}C(O)R\}$, and $Cp^*_2TiOCH_2R$ for both 1 and 2. Apolar unsaturated substrates did not insert into the Ti—C bond with the exception of $MeC{\equiv}CMe$, which reacted with 1 to produce the vinyl compound $Cp^*_2TiC(Me){=}CMe_2$. A striking difference between 1 and 2 was found in their reaction with CO_2, $Me_3CC{\equiv}N$, $Me_2C{=}O$, and $RC{\equiv}CR^1$ (R, R^1 = Me, Ph). While 1 either gave a normal insertion (CO_2 and $MeC{\equiv}CMe$) or adducts (Me_2CO, $Me_3CC{\equiv}N$) or did not react ($PhC{\equiv}CPh$), 2 lost ethene and gave compounds that appared to be products of insertion into a Ti—H bond, $Cp^*_2TiO_2CH$, $Cp^*_2TiN{=}C(H)CMe_3$, $Cp^*_2TiOC(H)Me_2$, and $Cp^*_2TiC(R){=}C(H)R^1$. Facile β-hydrogen transfer from the ethyl ligands was also observed in the reaction of 2 with olefins $CH_2{=}CHR$ (R = Me, Ph) to give ethene and $Cp^*_2TiCH_2CH_2R$. This reaction is reversible and equilibrium constants could be determined. Ground-state differences between 2 and $Cp^*_2TiCH_2CH_2R$ were found to be 9 (2) (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 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 $Cp^*_2Ti(R)Cl$ after quantitative oxidation with $PbCl_2$. Comparison of spectroscopic 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^x_2MR (Cp^x: η^5-$C_5R_{5-x}H_x$, x = 0–5; R = H, alkyl, aryl) are highly reactive species.[1] 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.[2] Solvent- and salt-free complexes often satisfy their need for electron density by forming (intramolecular) π or agostic interac-

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tions.[3] Some of these compounds are active catalysts for isomerization, hydrogenation, oligomerization, and polymerization of alkenes.[4] Of particular interest is the activation of both aromatic and aliphatic C–H bonds by these complexes.[4,5] This proceeds in a concerted fashion, via a highly polar $[2_s + 2_s]$ transition state, referred to as σ-bond metathesis.[5c] Concerted mechanisms are characteristic for group 3 and lanthanide compounds, which have high M–C dissociation energies[6] and lack low-energy metal electrons. Heteronuclear unsaturated molecules insert into the M–C bond, as is expected for highly polar bonds. Isoelectronic with group 3 and lanthanide metal complexes Cp^*_2MR are monocations $Cp_2M'R^+$ and $Cp^*_2M'R^+$ ($Cp = \eta^5\text{-}C_5H_5$; $Cp^* = \eta^5\text{-}C_5Me_5$; M′ = group 4 element); they show a comparable reactivity.[7]

The group 5 compounds Cp_2MR are 16-electron, d^2 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.[1f,g,8] This raises the activation energy for consecutive reactions. Addition of unsaturated substrate molecules to complexes Cp^*_2MR (M = group 5 element) therefore usually ends in an adduct $Cp^*_2MR{\cdot}S$ (S = $C{\equiv}O$, $MeN{\equiv}C$, etc.).[8] The activation energy for insertion of a coordinated olefin into a Nb—H bond has been determined in $Cp^*_2NbH(CH_2{=}CH_2)$ at 78 kJ·mol^{-1}, a substantial barrier.[9] Another consequence of the presence of the two electrons is the possible destabilization of the alkyl form relative to a hydride-olefin configuration.[9,10] There are no experimental data on the Gibbs energy difference for this process, but calculations indicate that this may be substantial.[9] 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.[6] For vanadium the situation is quite different. The homolytic decomposition of Cp_2VR (R = alkyl) and Cp^*_2VEt to (permethyl)vanadocene at ambient temperatures illustrates that V—C bond dissociation energies are substantially smaller.[11]

The paramagnetic d^1, 15-electron complexes $Cp^{(*)}_2TiR$ represent in a formal sense the intermediate between d^0 and d^2 metallocene derivatives, and a study of their reactivity seems appropriate. Our group has extensively reported on the synthesis and reactivity of Cp_2TiR (R = hydrocarbyl).[12] The majority of these compounds, however, are thermally instable, thus complicating the investigations. Recently, the much more robust pentamethylcyclopentadienyl analogues, Cp^*_2TiR, have become available[13] and preliminary data on the specific aspects of their reactivity have been published.[12,14]

In the first part of this study, the reactivity of Cp^*_2TiMe (1) is reviewed. The compound is an excellent model for investigating Ti–C bond reactivity since it is a prototype alkyl compound Cp^*_2TiR. In the second part the reactivity of the β-hydrogen-containing alkyl Cp^*_2TiEt (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^*_2TiR (R = hydrocarbyl ligand) and Cp^*_2TiX (X = anionic ligand) to tetravalent, diamagnetic complexes $Cp^*_2Ti(R)Cl$ and $Cp^*_2Ti(X)Cl$ by $PbCl_2$[14] 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 Cp^*_2TiMe (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 $Me_3CN{\equiv}C$, CO, CO_2, and but-2-yne, to yield respectively $Cp^*_2TiC(Me){=}NCMe_3$, $Cp^*_2TiC(O)Me$, $Cp^*_2TiO_2CMe$, and $Cp^*_2TiC(Me){=}CMe_2$. With paraformaldehyde insertion and formation of the ethoxide Cp^*_2TiOEt 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), 1 was recovered and polyethene had not been formed. Also internal alkynes ($PhC{\equiv}CPh$, $Me_3SiC{\equiv}CSiMe_3$) do not readily insert into the M—C bond of 1. Only for but-2-yne was insertion observed, to give the vinyl $Cp^*_2TiC(Me){=}CMe_2$. In order to have observable rates, reaction of 1 with but-2-yne had to be carried out in neat alkyne. Active hydrogen-containing substrates HX react under liberation of 1 equiv of

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methane. Treatment of 1 with isobutanoic acid, ethanol, or propyne gave $Cp^*_2TiO_2CC(H)Me_2$, CP^*_2TiOEt, and $Cp^*_2TiC{\equiv}CMe$.[13b,c] Reaction with $Me_3CC{\equiv}N$ led to an adduct $Cp^*_2TiMe{\cdot}N{\equiv}CCMe_3$. 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.[15] When a solution of the adduct was treated with $PbCl_2$, $Cp^*_2Ti(Me)Cl$ was formed together with $Me_3CC{\equiv}N$. Adduct formation was also found with acetone,[13b] 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.[13b] The compound is thermally less robust than 1; it decomposes slowly at room temperature ($\tau_{1/2} \approx 45$ h, in THF).[16] 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 $Me_3CN{\equiv}C$, CO, and paraformaldehyde and led to the iminoacyl $Cp^*_2TiC(Et){=}NCMe_3$, the acyl $Cp^*_2TiC(O)Et$, and the alkoxide Cp^*_2TiOPr,[17] fully analogous with 1. Other substrates, like CO_2[14a] and alkynes $RC{\equiv}CR$, 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^*_2TiOet, and isobutanic acid the carboxylate $Cp^*_2TiO_2CC(H)Me_2$. 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 methanolysis of $Cp^*_2NbH(CH_2{=}CH_2)$.[9] 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[18]) 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 $Me_3CC{\equiv}N$, $Me_2C{=}O$, and CO_2, and also with internal alkynes $RC{\equiv}CR'$. Cp^*_2TiEt reacted with $Me_3CC{\equiv}N$ to yield ethene and the red azomethine complex $Cp^*_2TiN{=}C(H)CMe_3$. 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 $PbCl_2$ and analyzed by NMR spectroscopy. The major component (>85%) could be identified as $Cp^*_2Ti\{OC(H)Me_2\}Cl$. This indicates extrusion of the olefin by an incoming ketone carbonyl function and subsequent insertion into the Ti—H bond. The formation of ethane propably results from an acid–base reaction of 2 with a hydrogen atom of acetone.[19] Reaction of 2 with CO_2 produced $Cp^*_2TiO_2CH$ and 1 equiv of ethene, as was reported before.[14a] In toluene, 2 reacted with internal alkynes $RC{\equiv}CR^1$ to yield vinyl compounds

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

R^1	K_{eq}	$\Delta G°$ (kJ·mol)	$\Delta\Delta G^a$ (kJ·mol⁻¹)	GS^b (kJ·mol⁻¹)
H	1	0	0	0
Me	$6.5 (5) \times 10^{-5}$	24 (2)	−15	9 (2)
Ph	$3.5 (5) \times 10^{-5}$	25 (2)	−18	7 (2)

[a] Correction for stabilization of free olefins relative to ethene. [b] Relative ground-state energy for complex $Cp^*_2TiCH_2CH_2R$.

Table II. ^1H NMR Data for $Cp^*_2Ti(R)Cl$ Compounds

compd	assgnt	δ (ppm)	mult	I (H)	J(HH) (Hz)
$Cp^*_2Ti(CH_2CH_2Ph)Cl$	Cp*	1.79	s	30	
	Ti—CH_2	1.01	ps t	2	
	CH_2Ph	2.65	ps t	2	
	Ph	7.25	m	4	
		7.07	m	1	
$Cp^*_2Ti(OEt)Cl$	Cp*	1.85	s	30	
	OCH_2	4.29	q	2	7
	CH_3	1.20	t	3	7
$Cp^*_2Ti\{OC(H)Me_2\}Cl$	Cp*	1.85	s	30	
	CH_3	1.10	d	6	6.3
	CH	5.04	h	1	6.3
$Cp^*_2Ti\{C(Me){=}NCMe_3\}Cl$	Cp*	1.69	s	30	
	Me	2.10	s	3	
	t-Bu	1.31	s	9	
$Cp^*_2Ti\{C(Et){=}NCMe_3\}Cl$	Cp*	1.77	s	30	
	CH_2	2.65	q	2	7.5
	CH_2	1.15	t	3	7.5
	t-Bu	1.41	s	9	
$Cp^*_2Ti\{C(O)Me\}Cl$	Cp*	1.75	s	30	
	Me	2.01	s	3	
$Cp^*_2Ti\{C(O)Et\}Cl$	Cp*	1.72	s	30	
	CH_2	2.22	q	2	7.2
	CH_3	1.02	t	3	7.2
$Cp^*_2Ti\{C(Me){=}CMe_2\}Cl$	Cp*	1.84	s	30	
	Me	1.77	sb	3	
	Me	1.73	sb	3	
	Me	0.9	sb	3	
$Cp^*_2Ti\{C(Me){=}C(H)Me\}Cl$	Cp*	1.79	s	30	
	CH	3.67	qq	1	8, 1.8
	c-CH_3	1.74	m	3	
	t-CH_3	1.68	dm	3	6.6
$Cp^*_2Ti\{C(Me){=}C(H)Ph\}Cl$	Cp*	1.80	s	30	
	CH_3	2.04	d	3	2.1
	=CH	4.86	q	1	2.1
	Ph	7.05	m	1	
		7.27	m	4	
$Cp^*_2Ti\{C(Ph){=}C(H)Ph\}Cl$	Cp*	1.85	s	30	
	H	4.65	s	1	
	Ph	6.93–7.26	m	10	
$Cp^*_2Ti\{N{=}C(H)CMe_3\}Cl$	Cp*	1.75	s	30	
	t-Bu	1.04	s	9	
	H	7.61	s	1	

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[15] The final product (benzene-d_6, 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 $Cp^*_2TiN{=}C(Me)CMe_3$ (δ 18.9 ppm, Cp*, whm 2400 Hz; δ 0.65 ppm, Me and CMe_3, whm 90 Hz) and the nitrile–carbon coupled tetravalent titanium azomethide compound $(Cp^*_2TiMe)_2(N{=}C(CMe_3){-}(Me_3C)C{=}N)$ (δ 1.73 ppm, Cp*; δ 1.02 ppm, CMe_3; δ −0.58 ppm, Me). The IR data ($\nu_{C=N}$ 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*, 53.

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[17] The identity of Cp^*_2TiOPr was established by comparison with an authentic sample of this compound prepared from Cp^*_2TiCl and LiOPr. Oxidation with $PbCl_2$ gave $Cp^*_2Ti(OPr)Cl$.

[18] Dimerization of propyne by systems based on permethyltitanocene derivatives has been reported: Akita, M.; Yasuda, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* 1984, *57*, 480.

[19] Hexamethylacetone, 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^*_2TiH and benzophenone. The formation of $Cp^*_2TiOCH(Ph)_2$ could be excluded by comparison with physical data of the compound prepared by salt metathesis between Cp^*_2TiCl and $LiOCH(Ph)_2$.

$Cp^*_2TiC(R){=}C(H)R^1$ and ethene. Reaction with but-2-yne was complete within 0.5 h at room temperature, and $Cp^*_2TiC(Me){=}C(H)Me$ was formed. The process is irreversible: when the vinyl compound was treated with excess ethene (20 bar, 25 °C), compound 2 was not reformed. Also, no reaction was observed when $Cp^*_2TiC(Me){=}C(H)Me$ was dissolved in $Me_3CC{\equiv}N$, although, thermodynamically, there certainly is a driving force for the liberation of but-2-yne and formation of the azomethide complex $Cp^*_2TiN{=}C(H)CMe_3$. Apparently, $Cp^*_2TiC(R){=}C(H)R^1$ does not readily eliminate β-hydrogen. This is quite in contrast to $Cp^*_2Zr\{CH{=}C(H)Me\}_2$[20] and $Cp^*_2ZrR\{C(SiMe_3){=}C(H)Ph\}$,[21] where reversible transfer of β-vinyl hydrogen atoms has been reported. Other alkynes like methylphenylacetylene and diphenylacetylene reacted in a similar way: ethene was liberated, and vinyl compounds formed. The products were characterized as their corresponding monochloride derivatives $Cp^*_2Ti\{C(Me){=}C(H)Ph\}Cl$ and $Cp^*_2Ti\{C(Ph){=}C(H)Ph\}Cl$ (Tables II and III). Reaction of 2 with methylphenylacetylene produces only one of two possible regio isomers. Probably the sterically less crowded $Cp^*_2TiC(Me){=}C(H)Ph$ has been formed (cf. Cp^*_2ScEt where a mixture of isomers was obtained[4c]).

Primary olefins, $R^1CH{=}CH_2$, reacted with 2 but were not polymerized and only replaced ethene. The higher alkyl complexes $Cp^*_2TiCH_2CH_2R^1$ could be transformed back to 2 by reaction with ethene. Cp^*_2TiR complexes with R containing β-hydrogen and α-olefins therefore form true equilibria (eq 1). The equilibrium constants of eq

$$Cp^*_2TiCH_2CH_2R + CH_2{=}CHR^1 \rightleftarrows Cp^*_2TiCH_2CH_2R^1 + CH_2{=}CHR \quad (1)$$

1 have been determined for a number of combinations of olefins and alkyl complexes (Table I). Cp^*_2TiEt (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 $Cp^*_2TiCH_2CH_2Ph$ 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 2 and $Cp^*_2TiCH_2CH_2R$ 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 $Cp^*_2TiCH_2CH_2R$. An estimate for this stabilization can be obtained from eq 2. Correction of the observed $\Delta G°$

$$C_2H_5^{\bullet} + CH_2{=}CHR \rightleftarrows CH_2{=}CH_2 + {}^{\bullet}CH_2CH_2R \quad (2)$$

values for this difference in energy shows that 2 is 7 (2) and 9 (2) $kJ{\cdot}mol^{-1}$ 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]

Table III. ^{13}C NMR Data for $Cp^*_2TiR(Cl)$ Compounds

compd	assgnt	δ (ppm)	mult	$^1J(CH)$ (Hz)
$Cp^*_2Ti(CH_2CH_2Ph)Cl$	$C_5\mathit{Me}_5$	12.54	q	126.6
	C_5Me_5	123.6	s	
	$Ti\mathit{C}H_2$	46.6	t	127.8
	$\mathit{C}H_2Ph$	69.61	t	126.4
	Ph			
	i	149.8	s	
	o	128.37	dd	159.7, 7
	m	127.93	dm	155.4
	p	124.98	dt	158.8, 7
$Cp^*_2Ti(OEt)Cl$	$C_5\mathit{Me}_5$	12.41	q	126.6
	C_5Me_5	124.51	s	
	$\mathit{C}H_2$	75.07	t	139.3
	$\mathit{C}H_3$	20.97	q	124.3
$Cp^*_2Ti\{OC(H)Me_2\}Cl$	$C_5\mathit{Me}_5$	12.55	q	126.4
	C_5Me_5	124.18	s	
	$\mathit{C}H_3$	25.14	q	124.3
	$\mathit{C}H$	77.57	d	131.2
$Cp^*_2Ti\{C(Me){=}NCMe_3\}Cl$	$C_5\mathit{Me}_5$	12.12	q	126.4
	C_5Me_5	118.04	s	
	$\mathit{C}Me_3$	63.47	s	
	$C\mathit{Me}_3$	31.67	q	126.6
	$C\mathit{Me}$	21.58	q	126.4
	$\mathit{C}N$	231	s	
$Cp^*_2Ti\{C(Et){=}NCMe_3\}Cl$	$C_5\mathit{Me}_5$	13.02	q	125.7
	C_5Me_5	118.54	s	
	$\mathit{C}Me_3$	63.80	s	
	$C\mathit{Me}_3$	31.83	q	125.4
	$\mathit{C}H_2$	28.6	t	126.1
	$\mathit{C}H_3$	13.57	q	126.6
	$\mathit{C}N$	228	s	
$Cp^*_2Ti\{C(O)Et\}Cl$	$C_5\mathit{Me}_5$	12.60	q	125.7
	C_5Me_5	124.86	s	
	$\mathit{C}H_2$	52.4	t	126.1
	$\mathit{C}H_3$	10.47	q	128
	$\mathit{C}{=}O$	292.0	s	
$Cp^*_2Ti\{C(Me){=}CMe\}Cl$	$C_5\mathit{Me}_5$	13.05	q	126.6
	C_5Me_5	125.44	s	
	$Ti{-}\mathit{C}$	196.8	s	
	$Ti{-}C{=}\mathit{C}$	121.13	s	
	Me	21.96	q	123.3
		24.51	qq	124, 4
		30.72	qq	124, 4
$Cp^*_2Ti\{C(Me){=}C(H)Me\}Cl$	$C_5\mathit{Me}_5$	12.87	q	126.6
	C_5Me_5	124.6	s	
	C	200.2	s	
	$\mathit{C}H$	119.9	dm	149.6
	$\mathit{C}H_3$	29.40	qd	126, 11
	$\mathit{C}H_3$	16.40	qd	125.4, 6
$Cp^*_2Ti\{C(Me){=}C(H)Ph\}Cl$	$C_5\mathit{Me}_5$	11.93	q	126.4
	C_5Me_5	123.8	s	
	$\mathit{C}H_3$	30.9	q, d	124, 12
	$Ti{-}\mathit{C}$	206.85	s	
	$Ph, {=}\mathit{C}HMe$	139.84	s	
		124.04	dm	158
		masked by solvent		
$Cp^*_2Ti\{C(Ph){=}C(H)Ph\}Cl$	$C_5\mathit{Me}_5$	13.20	q	126.4
	C_5Me_5	126.28	s	
	$Ti{-}\mathit{C}{=}$	204.78	s	
	$Ph, {=}\mathit{CH}$	154.51	s	
		140.06	s	
		128.68	dm	156
		128.55	dm	155
		127.06	dd	152, 6
		124.93	dt	156.2, 7
		124.63	dt	158.8, 7
$Cp^*_2Ti\{N{=}C(H)CMe_3\}Cl$	$C_5\mathit{Me}_5$	12.38	q	126.5
	C_5Me_5	119.4	s	
	$\mathit{C}Me_3$	42.44	s	
	$C\mathit{Me}_3$	27.93	q	126.1
	$\mathit{C}H{=}N$	166.16	d	160

It is tempting to assign the stabilization of 2 to a β-agostic interaction between the metal and a β 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 $Cp^*Co(PMe_3)CH_2CH_3$ (37 $kJ{\cdot}mol^{-1}$), which has a β-agostic C—H bond. However, one has to be careful since in $Cp^*_2Nb(CH_2{=}CHR)(H)$ (R = H, Me, Ph) similar ground-state differences were found (although smaller in absolute numbers[10]), 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

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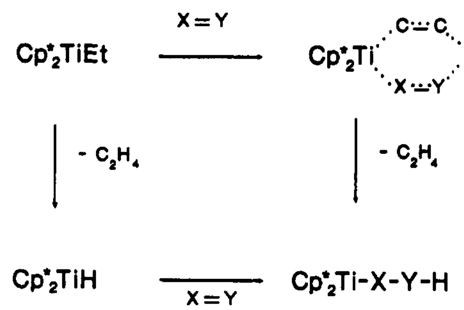
(20) McDade, C.; Bercaw, J. E. *J. Organomet. Chem.* **1985**, *279*, 281.

(21) Erker, G.; Zwettler, R.; Krueger, C.; Hyla-Kryspin, I.; Gleiter, R. *Organometallics* **1990**, *9*, 524.

(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.

(23) Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 443.

Scheme I



be determined exactly, but it certainly is small since it will not exceed 10 kJ·mol^{-1}.

There are no indications that olefins form adducts with Cp^*_2TiR compounds. The IR spectrum of $Cp^*_2Ti(n$-$C_6H_{13})$ 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 Cp^*_2TiPr 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^*_2TiPr 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 Cp^*_2TiEt. 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 Cp^*_2TiH (Scheme I).[24] The possible formation of Cp^*_2TiH from 2 was tested by isotope-labeling experiments. The ^{13}C labeled compound $Cp^*_2Ti^{13}CH_2CH_3$ was prepared from Cp^*_2TiCl and $IMg^{13}CH_2CH_3$.[25] Hydrolysis with D_2O gave a 1:1 mixture of labeled ethanes $CH_3{}^{13}CH_2D$ and $^{13}CH_3CH_2D$. 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 Cp^*_2TiEt 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 $Cp^*_2Ti(Et$-$d_5)$. This indicates not only that a hydride–olefin configuration is within reach but also that olefin dissociation from 2 can take place to give Cp^*_2TiH, although the equilibrium lies strongly to the side of the alkyl Cp^*_2TiR. 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 Cp^*_2TiR has been found and other adducts e.g. with acetone[13b] and $Me_3CC{\equiv}N$ are very unstable, olefin extrusion is assumed to proceed via Cp^*_2TiH. This was also concluded for the reaction of β-hydrogen-containing scandium compounds $Cp^*_2ScCH_2CH_2R$ (R = H, Me, Ph, etc.), which react with but-2-yne to yield $Cp^*_2ScCMe{=}C(H)Me$ and 1 equiv of olefin.[4c,26]

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 $Cp^*_2TiO_2CH$.[14a] After 1 h, 1 equiv of ethylene (relative to carbon dioxide) had evolved. Oxidation of the reaction mixture with $PbCl_2$ gave exclusively $Cp^*_2Ti(Me)Cl$, no $Cp^*_2Ti(Et)Cl$ was present. This shows the preference of carbon dioxide to insert into the Ti–H bond.

Oxidation of Cp^*_2TiR to Diamagnetic Tetravalent Titanium Derivatives $Cp^*_2Ti(R)Cl$. 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. Cp^*_2TiR compounds can be readily converted into their diamagnetic monochloride analogues $Cp^*_2Ti(R)Cl$ by oxidation with $PbCl_2$ (eq 3).[14b] The latter compounds are

$$Cp^*_2TiR + \tfrac{1}{2}PbCl_2 \rightarrow Cp^*_2Ti(R)Cl + \tfrac{1}{2}Pb \qquad (3)$$

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^*_2TiX and Cp^*_2TiR obtained from Cp^*_2TiMe and Cp^*_2TiEt and reported in this or previous papers.[13] In addition to the fact that oxidation to $Cp^*_2Ti(R)Cl$ is very helpful for identification, the method also is an excellent synthetic route to new mixed hydrocarbyl compounds $Cp^*_2Ti(R)R^1$. Experimental procedures and IR spectra are given in the Experimental Part, ^1H 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^*_2TiR with $Cp^*_2Ti(R)Cl$. Reaction of 1 and 2 with $Me_3CN{\equiv}C$ gave iminoacyl complexes $Cp^*_2TiC(R){=}NCMe_3$ (R = Me, $\nu_{C{=}N}$ = 1600 cm^{-1}; R = Et, $\nu_{C{=}N}$ = 1590 cm^{-1}). Assignment of the coordination mode for the iminoacyl ligand (η^1 or η^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 (C=N stretching frequency and ^{13}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 η^2-coordinated iminoacyl ligand, which is in general the most favorable coordination mode for coordinatively and electronically unsaturated d^0 and d^1 complexes.[27a,30] Therefore, it is reasonable to assume that in $Cp^*_2TiC(R){=}NR^1$ the iminoacyl ligand is also η^2-coordinated. This is supported by the spectra of the tetravalent titanium iminoacyls $Cp^*_2Ti\{C(R){=}NCMe_3\}Cl$. The ^{13}C NMR resonance of the iminoacyl

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[24] Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443.

[25] This reagent was prepared from Mg and $CH_3{}^{13}CH_2I$. Hydrolysis with D_2O gave $CH_3{}^{13}CH_2D$ (^{13}C NMR) as the only gaseous product. No scrambling of the ^{13}C label had taken place in the Grignard reagent.

[26] Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21.

[27] (a) Bochmann, M.; Wilson, L. M. *Organometallics* **1987**, *6*, 2556. (b) Den Haan, K. H.; Luinstra, G. A.; Teuben, J. H. *Organometallics* **1987**, *6*, 1509.

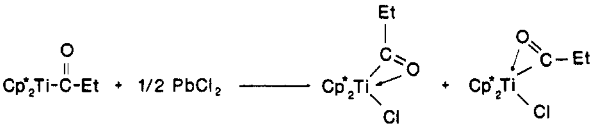
[28] Adams, R. M.; Chodosh, D. F. *J. Am. Chem. Soc.* **1977**, *99*, 6544.

[29] (a) Van Bolhuis, F.; De Boer, E. J. M.; Teuben, J. H. *J. Organomet. Chem.* **1979**, *170*, 299. (b) Chamberlain, L. R.; Durfee, D. L.; Fanwick, P. E.; Kobriger, L.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E.; Wang, R. *J. Am. Chem. Soc.* **1987**, *109*, 390.

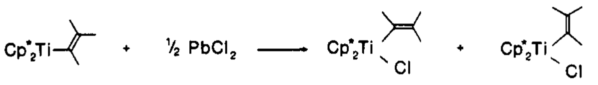
[30] Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059 and references therein.

carbon atom (R = Me, δ = 231 ppm; R = Et, δ = 228 ppm) is found at low field, as expected for η^2-coordination.[28] The IR spectra of the oxidized iminoacyl compounds show $\nu_{C=N}$ (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.[27a]

Ink-blue acyl compounds $Cp^*_2TiC(O)R$ (R = Me, $\nu_{C=O}$ = 1530 cm^{-1}, R = Et, $\nu_{C=O}$ = 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 $PbCl_2$ at −20 °C gave the monochloride acyls $Cp^*_2Ti\{C(O)R\}Cl$ (R = Me, $\nu_{C=O}$ = 1600 cm^{-1}; R = Et, $\nu_{C=O}$ = 1590, 1660 cm^{-1}). The Cp homologues, $Cp_2Ti\{C(O)R\}X$, have been synthesized by Facchinetti et al.[31] In these complexes ($\nu_{C=O}$ = 1603 cm^{-1}), the η^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 the ^{13}C NMR spectrum (recorded at −10 °C) of $Cp^*_2Ti\{C(O)Et\}Cl$, only the resonances of the major isomer are well enough resolved to allow an unambiguous assignment (Table III). The signal for the acylic carbon atom is strongly shifted to 292 ppm. This large shift to low field is reminiscent of the values for the carbenoid carbon in Fischer carbenes ($\delta \approx$ 300–400 ppm[32]), suggesting that in $Cp^*_2Ti\{C(O)R\}Cl$ 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-cm^{-1} shift (140 cm^{-1} for one of the isomers) to higher wavenumbers of the $\nu_{C=O}$, analogous to what was found for iminoacyl compounds. $PbCl_2$ oxidation of $Cp^*_2TiC(Me)=CMe_2$ yielded the diamagnetic monochloride vinyl compound $Cp^*_2Ti\{C(Me)=CMe_2\}Cl$, 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 before, the relative position of the vinyl and the chloride ligands in the equatorial plane between the cyclopentadienyl rings can explain the isomerism (eq 5).



(4)



(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 $Cp^*_2Ti\{CMe=C(H)Me\}Cl$, obtained from 2 and but-2-yne and subsequent oxidation with $PbCl_2$, appeared to be a mixture of two isomers (5:2) as well, but the homologues $Cp^*_2Ti\{C(Me)=C(H)Ph\}Cl$ and $Cp^*_2Ti\{C(Ph)=C(H)Ph\}Cl$ (from 2 and PhC≡CMe and PhC≡CPh, respectively) were isolated as single isomers. The oxidation process of the parent compound $Cp^*_2TiC(R)=C(H)R'$ 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 $Cp^*_2TiN=C(H)CMe_3$ has $\nu_{C=N}$ at 1680 cm^{-1}, a normal position for early-transition-metal ketimines.[33] The ^1H NMR spectrum shows resonances at δ 22.9 ppm (Cp*, 30 H) and δ 1.4 ppm (CMe_3, 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 $Cp^*_2TiN=C(D)CMe_3$, obtained from $Cp^*_2Ti(Et\text{-}d_5)$ and $Me_3CC\equiv N$). On oxidation to $Cp^*_2Ti\{N=C(H)CMe_3\}Cl$, $\nu_{C=N}$ 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 downfield from TMS.[33a]

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 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 Cp^*_2TiR do not undergo σ-bond metathesis with unactivated hydrocarbons. Apparently, the $[2_s + 2_s]$ transition state for this process cannot be reached.[4c,34] Cp^*_2TiR 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^*_2TiR. The transition state for migratory insertion (see $Cp^*_2NbH(olefin) \rightarrow Cp^*_2NbR$[10]) 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^*_2TiR 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^*_2TiR is obviously not the only factor responsible 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^*_2TiR is not capable of stabilizing adducts. As a consequence, Cp^*_2TiEt

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(**2**) is an alkyl and not a hydride–olefin complex. This is also expressed in its reactivity. Reactions of **2** with Brøndsted acids, like alcohols, do not lead to dihydrogen formation, as was observed for $Cp^*_2NbH(C_2H_4)$.[10]

The differences in reactivity of **1** and **2** can be explained by kinetic arguments. Insertion of strongly nucleophilic reagents, like C≡O, $Me_3CN{\equiv}C$, and $CH_2{=}O$ 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, $Me_3CC{\equiv}N$, acetone, and internal acetylenes do not insert readily.[35] 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.[12,13b] For the strongly Lewis acidic, d^0, 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.[4c,26] 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), $Cp^*_2TiC(Me){=}NCMe_3$, $Cp^*_2TiC(O)R$, $Cp^*_2TiO_2CR$, $Cp^*_2TiC(Me){=}C(R)Me$ (R = H, Me), $Cp^*_2TiC{\equiv}CMe$, and $Cp^*_2TiMe.O{=}CMe_2$ have been described in earlier papers.[13] $PbCl_2$ (Merck-Schuchardt) was stored in an oven at 150 °C. Gases were used without further purification. $Me_3CN{\equiv}C$, $Me_3CC{\equiv}N$, acetone, alcohols, styrene, phenylmethylacetylene, 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 SP3-300 or Bruker IFS-88 spectrophotometer as Nujol mulls between KBr disks. NMR spectra were recorded on a Bruker WH-90 or Varian VXR-300 spectrometer. Chemical shifts are reported in ppm and referenced to residual protons in deuterated solvents (benzene-d_6 δ 7.15 ppm, THF-d_8 δ 3.57 ppm, and toluene-d_8 δ 7.02 ppm for ^1H NMR spectroscopy and benzene-d_6 δ 127.96 ppm for ^{13}C NMR spectroscopy). Gas chromatography was performed on an HP-5890A apparatus using a Porasil B packed column. Quantitative gas determinations were done using a Toepler 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.

$Cp^*_2TiC(Et){=}NCMe_3$. **2** (681 mg, 1.96 mmol) was dissolved in 10 mL of pentane. $Me_3CN{\equiv}C$ (200 μL) was added at −80 °C. The color changed to blue on warming to room temperature. No gas evolution was observed. After stirring for 0.5 h, the volatiles were removed in vacuum to remove the excess $Me_3CN{\equiv}C$. The residue was recrystallized from pentane. Yield: 605 mg of $Cp^*_2TiC(Et){=}NCMe_3$ (1.41 mmol, 72%) as blue crystals. ^1H NMR (300 MHz, benzene-d_6, 20 °C): δ 20.93 ppm (Cp*, 30H, whm 8200 Hz), −0.11 (CMe_3, whm 250 Hz), −0.72 (Et, whm 360 Hz). MS: parent peak at *m/e* = 429. EPR (pentane, −80 °C): *g* 1.986 (t), a_N 2.1 G (Δ*H* 1.8 G). IR (cm^{-1}): 2720 (w), 1590 (m), 1490 (w), 1375 (s), 1360 (m), 1295 (w), 1290 (w), 1270 (w), 1215 (w), 1190 (s), 1105 (w), 1020 (sb), 930 (w), 915 (w), 665 (w), 550 (w). Anal. Calcd for $C_{27}H_{44}NTi$: C, 75.32; H, 10.30; N, 3.25; Ti, 11.13. Found: C, 75.15; H, 10.42; N, 3.12; Ti, 11.08.

$Cp^*_2TiN{=}C(H)CMe_3$. **2** (366 mg, 1.05 mmol) was dissolved in 10 mL of pentane. $Me_3CC{\equiv}N$ (0.115 mL, 1.10 mmol) was added at room temperature. After stirring for 2 h, the volatiles were removed in vacuum and the residue was recrystallized from 5 mL of pentane. Yield: 304 mg (0.76 mmol, 72%) of $Cp^*_2TiN{=}C(H)CMe_3$ as dark red crystals. ^1H NMR (90 MHz, benzene-d_6, 20 °C): δ 22.9 ppm (Cp*, 30 H, whm 1730 Hz), 1.40 (*t*-Bu, 9 H, whm 70 Hz). IR (cm^{-1}): 3340 (vw), 2950 (vs), 2890 (vs), 2850 (vs), 2720 (m), 2700 (w), 2620 (m), 1750 (w), 1678 (vs), 1480 (m), 1450 (s), 1420 (m), 1385 (m), 1375 (s), 1331 (m), 1245 (w), 1195 (s), 1157 (w), 1060 (w), 1020 (s), 885 (m), 800 (s), 820 (m), 755 (m), 660 (s), 620 (w), 475 (w), 445 (vs), 390 (w). MS: parent peak at *m/e* = 402. Anal. Calcd for $C_{25}H_{40}TiN$: C, 74.60; H, 10.02; Ti, 11.90. Found: C, 74.80; H, 9.91; Ti, 12.40.

$Cp^*_2TiC(Ph){=}C(H)Ph$. **2** (328 mg, 0.94 mmol) and diphenylacetylene (168 mg, 0.94 mmol) were dissolved in 10 mL of ether, and the vessel was evacuated. After stirring for 2 days, the solution was concentrated to about 2 mL and cooled to −80 °C. Black crystals separated; yield 204 mg of $Cp^*_2TiC(Ph){=}C(H)Ph$ (0.410 mmol, 43%). ^1H NMR (300 MHz, benzene-d_6, 20 °C): δ 18 ppm (Cp*, Ph, whm 10 kHz). IR (cm^{-1}): 3080 (w), 3070 (w), 2720 (w), 1590 (s), 1560 (w), 1480 (s), 1380 (s), 1200 (w), 1150 (w), 1110 (w), 1070 (m), 1020 (s), 960 (w), 910 (m), 840 (w), 770 (m), 750 (vs), 690 (vs), 520 (w), 450 (w), 420 (w). Anal. Calcd for $C_{34}H_{41}Ti$: C, 82.07; H, 8.31; Ti, 9.63. Found: C, 80.95; H, 8.24; Ti, 9.66.

Reaction of 1 with Paraformaldehyde. The product of this reaction in pentane was identified as Cp^*_2TiOEt after oxidation with $PbCl_2$ to $Cp^*_2Ti(OEt)Cl$ (vide infra).

Cp^*_2TiOPr. **2** (451 mg, 1.30 mmol) and $(CH_2O)_n$ (39 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 purple residue was recrystallized from pentane. Yield: 381 mg of Cp^*_2TiOPr (1.01 mmol, 78%). ^1H NMR (90 MHz, benzene-d_6, 20 °C): δ 18.4 ppm (Cp*, 30 H, whm 2900 Hz) 1.75 (Pr, 7 H, m, whm 170 Hz). IR (cm^{-1}): 2720 (w), 1130 (vs), 1100 (m), 1020 (s), 1000 (w), 880 (w), 800 (w), 620 (w), 600 (s), 550 (w), 420 (m). Anal. Calcd for $C_{23}H_{37}TiO$: C, 73.19; H, 9.88; Ti, 12.69. Found: C, 72.90; H, 9.80; Ti, 12.86.

$Cp^*_2TiO_2CC(H)Me_2$. **2** (208 mg, 0.60 mmol) was dissolved in 10 mL of pentane. Isobutyric acid (55 μL, 0.60 mmol) was added. Gas evolution immediately started, and the color changed to blue. The solvent and other volatile components were removed in vacuum, and the residue was extracted with pentane. The extracts were concentrated and kept at −80 °C. Blue crystals precipitated and were isolated. Yield: 191 mg of $Cp^*_2TiO_2C(H)Me_2$ (0.47 mmol, 78%). IR (cm^{-1}): 2720 (w), 1520 (bs), 1295 (s), 1160 (m), 1120 (w), 1095 (w), 1060 (w), 1020 (s), 930 (s), 850 (s), 800 (w), 760 (w), 440 (w). Anal. Calcd for $C_{24}H_{37}TiO_2$: C, 71.09; H, 9.20; Ti, 11.81. Found: C, 70.78; H, 9.18; Ti, 11.92.

$Cp^*_2TiMe{\cdot}N{\equiv}CCMe_3$. **1** (350 mg, 1.00 mmol) was dissolved in 15 mL of pentane, and $Me_3CC{\equiv}N$ (109 μL, 1.00 mmol) was added at −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. $Cp^*_2TiMe{\cdot}N{\equiv}CCMe_3$ was isolated as brown crystals. Yield: 270 mg (0.64 mmol, 64%). ^1H NMR (200 MHz, benzene-d_6, 22 °C): δ 17.0 ppm (Cp*, 30 H, whm 2600 Hz), 1.21 (*t*-Bu, Me, 12H, whm 180 Hz). IR (cm^{-1}): 2805 (w), 2718 (w), 2228 (m, $\nu_{C{\equiv}N}$), 1491 (m), 1238 (s), 1206 (m), 1161 (w), 1115 (w), 1061 (w), 1020 (s), 870 (m), 804 (w), 642 (w), 432 (s). Anal. Calcd for $C_{26}H_{42}NTi$: C, 74.98; H, 10.16; N, 3.36; Ti, 11.50. Found: C, 74.95; H, 10.14; N, 3.25; Ti, 11.54.

$Cp^*_2Ti\{C(O)Me\}Cl$. **1** (243 mg, 0.73 mmol) was dissolved in 10 mL of pentane. At −80 °C 1 equiv of CO was admitted. The reaction mixture was allowed to warm to −20 °C. The color gradually changed from green to blue. At −20 °C $PbCl_2$ (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). Crystallization at −80 °C gave 68 mg of $Cp^*_2Ti\{C(O)Me\}Cl$ (0.17 mmol, 23%) as green crystals. IR (cm^{-1}): 2720 (w), 1600 (vs), 1310 (m), 1070 (m), 1020 (m), 850 (w), 790 (m), 560 (w). The compound is thermally very unstable, it decomposes within days (even in the solid state) at −35 °C.

$Cp^*_2Ti\{C(O)Et\}Cl$. **2** (166 mg, 0.48 mmol) was dissolved in 10 mL of ether, and the solution was cooled to −80 °C. CO (1

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[35] An intermediate case seems to be formed by CO_2, but a competition experiment clearly demonstrated the kinetic advantage that insertion into a Ti-H bond has over insertion into a Ti-C bond.

equiv) was admitted, and the reaction mixture slowly warmed to −30 °C. After 0.5 h at this temperature the ink-blue solution was evacuated to remove traces of CO, and $PbCl_2$ (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 $Cp^*_2Ti\{C(O)Et\}Cl$ 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), 1660 (m), 1590 (vs), 1480 (m), 1440 (w), 1420 (m), 1365 (vs), 1280 (w), 1110 (w), 1060 (s), 1020 (s), 830 (s), 660 (w), 400 (w). Anal. Calcd for $C_{23}H_{35}TiClO$: C, 67.23; H, 8.58; Ti, 11.66; Cl, 8.63. Found: C, 66.86; H, 8.73; Ti, 11.58; Cl, 8.38.

$Cp^*_2Ti\{C(Me){=}NCMe_3\}Cl$. $Cp^*_2TiC(Me){=}NCMe_3$ (1.08 mmol) was dissolved in 10 mL of ether, and $PbCl_2$ (149 mg, 0.54 mmol) was added at room temperature under stirring. The solution turned yellow and was filtered after 0.5 h. The filtrate was cooled (−80 °C), and 305 mg of $Cp^*_2Ti\{C(Me){=}NCMe_3\}Cl$ (0.67 mmol, 51%) separated as yellow crystals. IR (cm^{-1}): 2700 (w), 1680 (s), 1490 (m), 1460 (w), 1390 (w), 1370 (s), 1225 (w), 1210 (w), 1185 (s), 1070 (s), 1020 (m), 940 (w), 800 (w), 740 (w), 650 (w), 420 (w). Anal. Calcd for $C_{26}H_{42}TiNCl$: C, 69.09; H, 9.37; Ti, 10.60; N, 3.10; Cl, 7.84. Found: C, 68.93; H, 9.28; Ti, 10.66; N, 3.01; Cl, 8.17.

$Cp^*_2Ti\{C(Et){=}NCMe_3\}Cl$. $Cp^*_2TiC(Et){=}NCMe_3$ (282 mg, 0.65 mmol) and $PbCl_2$ (19 mg, 0.33 mmol) were suspended in 10 mL of ether. The color changed to yellow. After stirring for 0.5 h, the solution was filtered and concentrated. Crystalization at −80 °C yielded 154 mg of $Cp^*_2Ti\{C(Et){=}NCMe_3\}C$ (0.33 mmol, 51%) as yellow crystals. IR (cm^{-1}): 2720 (w), 1660 (vs), 1490 (w), 1460 (m), 1390 (w), 1370 (s), 1220 (m), 1190 (s), 1070 (m), 1020 (m), 950 (w), 900 (m), 800 (w), 620 (w), 540 (w), 405 (w). Anal. Calcd for $C_{27}H_{44}ClNTi$: C, 69.59; H, 9.52; Ti, 10.26. Found: C, 69.33; H, 9.37; Ti, 10.35.

$Cp^*_2Ti\{C(Me){=}CMe_2\}Cl$. $Cp^*_2TiC(Me){=}CMe_2$ (0.44 mmol) was dissolved in 5 mL of ether, and $PbCl_2$ (62 mg, 0.22 mmol) was added. The reaction mixture turned red during stirring at room temperature. After 0.5 h the solution was filtered and the filtrate cooled to −80 °C. Yield: 57 mg (0.14 mmol, 19%) of $Cp^*_2Ti\{C(Me){=}CMe_2\}Cl$ as red crystals. IR (cm^{-1}): 2720 (w), 1630 (w), 1470 (m), 1370 (s), 1260 (w), 1200 (w), 1090 (m), 1020 (s), 800 (w), 580 (vw), 410 (w).

$Cp^*_2Ti\{C(Me){=}C(H)Me\}Cl$. $Cp^*_2TiC(Me){=}C(H)Me$ (57.8 mg, 0.16 mmol) and $PbCl_2$ (22 mg, 0.08 mmol) were suspended in 5 mL of ether. The color immediately changed to red. After stirring for 0.5 h, the solution was filtered. Crystallization at −80 °C yielded 36.3 mg (0.09 mmol, 57%) of $Cp^*_2Ti\{C(Me){=}C(H)Me\}Cl$. IR ($cm^{-1}$): 2720 (w), 1490 (s), 1440 (m), 1375 (vs), 1100 (w), 1060 (w), 1020 (s), 960 (w), 810 (m), 800 (m), 420 (w). Anal. Calcd for $C_{24}H_{37}ClTi$: C, 70.50; H, 9.12. Found: C, 68.24; H, 8.88.

$Cp^*_2Ti\{C(Me){=}C(H)Ph\}Cl$. **2** (237 mg, 0.68 mmol) was dissolved in 10 mL of pentane. Methylphenylacetylene (84 μL, 0.68 mmol) was added. The color of the solution remained brownish. After stirring for 2 days under static vacuum, $PbCl_2$ (95 mg, 0.34 mmol) was added. The pentane was exchanged for 10 mL of ether, and after filtration and crystallization at −80 °C 123 mg of $Cp^*_2Ti\{C(Me){=}C(H)Ph\}Cl$ (0.26 mmol, 38%) was isolated. IR (cm^{-1}): 2720 (w), 1590 (m), 1570 (w), 1550 (m), 1540 (w), 1490 (s), 1450 (m), 1380 (vs), 1180 (w), 1120 (w), 1080 (m), 1060 (m), 1020 (s), 980 (w), 900 (w), 870 (w), 750 (s), 700 (s), 550 (w), 420 (w).

$Cp^*_2Ti\{C(Ph){=}C(H)Ph\}Cl$. **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 $PbCl_2$ (58 mg, 0.21 mmol) was added. The color turned red, and after stirring for 0.5 h, the solution was filtered. The residue was extracted with 10 mL of ether. The solution was concentrated and kept at −80 °C to yield 99 mg (0.18 mmol, 44%) of $Cp^*_2Ti\{C(Ph){=}C(H)Ph\}Cl$ as dark red crystals. IR (cm^{-1}): 3070 (w), 3030 (w), 3000 (w), 2720 (w), 1590 (m), 1545 (w), 1480 (m), 1460 (m), 1380 (s), 1140 (w), 1060 (w), 1020 (m), 910 (m), 870 (w), 790 (w), 770 (w), 750 (s), 700 (s).

$Cp^*_2Ti(CH_2CH_2Ph)Cl$. **2** (253 g, 0.73 mmol) was dissolved in 2 mL of styrene. After several freeze–thaw cycles to remove ethene and after the solution had turned green, $PbCl_2$ (101 mg, 0.36 mmol) was added. The color changed to red. After stirring for 1 h, the styrene was exchanged for 25 mL of ether. After filtration and crystallization at −80 °C, 157 mg (0.34 mmol, 47%) of $Cp^*_2Ti(CH_2CH_2Ph)Cl$ was isolated as red crystals. IR (cm^{-1}): 2720 (w), 1580 (m), 1490 (m), 1455 (w), 1380 (s), 1260 (w), 1150 (w), 1120 (m), 1070 (m), 1060 (m), 1020 (w), 750 (vs), 700 (vs), 590 (w), 410 (m).

$Cp^*_2Ti\{N{=}C(H)CMe_3\}Cl$. $Cp^*_2TiN{=}C(H)CMe_3$ (0.65 mmol) and $PbCl_2$ (90 mg, 0.32 mmol) were suspended in 10 mL of ether. The color of the solution turned reddish-yellow. After stirring for 0.5 h, the solution was filtered and cooled to −80 °C. Dark red crystals of $Cp^*_2Ti\{N{=}C(H)CMe_3\}Cl$ separated. Yield: 114 mg (0.26 mmol, 40%). IR (cm^{-1}): 2760 (m), 2720 (w), 2620 (w), 1670 (vs), 1630 (w), 1480 (m), 1420 (m), 1380 (w), 1360 (s), 1320 (w), 1310 (w), 1240 (m), 1200 (s), 1060 (w), 1020 (s), 890 (m), 800 (w), 750 (w), 660 (s), 590 (w), 430 (m). Anal. Calcd for $C_{25}H_{40}TiClN$: C, 68.56; H, 9.21; Ti, 10.94; Cl, 8.10; N, 3.20. Found: C, 68.64; H, 9.23; Ti, 10.96; Cl, 8.17; N, 3.12.

$Cp^*_2Ti(OEt)Cl$. A mixture of **1** (315 mg, 0.94 mmol) and $(CH_2O)_n$ (28 mg, 0.95 mmol) was suspended in 8 mL of pentane. After stirring overnight, the reaction mixture was evaporated to dryness. The purple residue was dissolved in 10 mL of ether, and $PbCl_2$ (131 mg, 0.47 mmol) was added. The solution turned red and was filtered after stirring for 0.5 h. Crystallization at −80 °C yielded 178 mg of $Cp^*_2Ti(OEt)Cl$ (0.40 mmol, 42%) as orange-red needles. IR (cm^{-1}): 2720 (w), 1330 (m), 1090 (vs), 1050 (vs), 1020 (s), 890 (s), 800 (w), 560 (s), 400 (w). Anal. Calcd for $C_{22}H_{35}TiClO$: C, 66.25; H, 8.84; Ti, 12.01; Cl, 8.89. Found: C, 66.24; H, 8.77; Ti, 12.10; Cl, 9.13.

$Cp^*_2Ti\{OC(H)Me_2\}Cl$. **2** (121 mg, 0.38 mmol) was dissolved in 10 mL of ether. 2-Propanol (30 μL, 0.38 mmol) was added. Gas evolution immediately started, and the color changed to purple. After stirring for 10 min, $PbCl_2$ (53 mg, 0.19 mmol) was added. The color changed to red. After stirring for 0.5 h, the solution was filtered, concentrated, and cooled to −80 °C. Orange crystals of $Cp^*_2Ti\{OC(H)Me_2\}Cl$ separated: 87 mg (0.21 mmol, 56%). IR (cm^{-1}): 2720 (w), 1350 (m), 1320 (m), 1150 (m), 1115 (s), 1060 (w), 1020 (m), 980 (s), 850 (m), 570 (m), 470 (w), 400 (w). Anal. Calcd for $C_{23}H_{37}TiClO$: C, 66.91; H, 9.03; Ti, 11.60. Found: C, 66.13; H, 8.93; Ti, 11.22.

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. $Me_3CC{\equiv}N$ (1 equiv) was condensed into the vessel. Upon melting, a yellow precipate formed. Slowly warming the mixture to room temperature resulted in a dark red solution. The gases were collected (0.93 mol/Ti) and analyzed with GC: ethene (100%). The remaining solution was evaporated to dryness and the residue identified as $Cp^*_2TiN{=}C(H)CMe_3$ (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 waterbath 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%.

$Cp^*_2TiCH_2CH_2Ph$ (57 mg, 0.13 mmol) was dissolved in 14.00 mL of toluene in a two-compartment vessel, interconnected by a Teflon valve. The second compartment (volume 14.00 mL) contained $PbCl_2$. Propene gas was added (0.58 mmol). The mixture was stirred for 24 h at 25 °C. The mixture was transferred to the other compartiment (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: $Cp^*_2Ti(CH_2CH_2Ph)Cl/Cp^*_2Ti(Pr)Cl = 0.76$. From these data equilibrium K was calculated, assuming that Cp^*_2TiPr and $Cp^*_2TiCH_2CH_2Ph$ are equally reactive toward $PbCl_2$.

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. CO_2 (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 Toepler 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-d_6 and oxidized with $PbCl_2$. After

Organometallics 1992, *11*, 2281–2289 2281

filtration, the resulting mixture was analyzed by ^{1}H NMR spectroscopy: $Cp^*_2Ti(Me)Cl$ (δ 1.78 ppm (Cp^*), 0.23 (Me)), the reaction product of $Cp^*_2TiO_2CH$ and $PbCl_2$ is insoluble.

Deuterium Scrambling between Cp^*_2TiEt and $Cp^*_2Ti(Et\text{-}d_5)$. Cp^*_2TiEt (61 mg, 0.17 mmol) and $Cp^*_2Ti(Et\text{-}d_5)$ (60 mg, 0.17 mmol) were dissolved in 2 mL of toluene, and the solution was stirred for 48 h under vacuum. D_2O was condensed into the vessel at −196 °C, and the mixture warmed to room temperature. The evolved ethane was collected with a Toepler pump (0.26 mmol, 77%) and subsequently analyzed with MS (*m*/*e* (int (%))): 36 (3.5, C_2D_6), 35 (17.5, C_2D_5H), 34 (55.5, $C_2D_4H_2$), 33 (53, $C_2D_3H_3$).

Scambling in $Cp^*_2Ti^{13}CH_2CH_3$. Cp^*_2TiCl (600 mg, 1.70 mmol) was dissolved in 20 mL of ether, and 6.0 mL of a 0.28 M solution of $CH_3{}^{13}CH_2MgI$ (1.68 mmol) was syringed in. After stirring for 1 h, the volatiles were removed in vacuum and the brown residue was extracted with pentane. After crystallization at −80 °C brown crystals were collected: 364 mg (1.05 mmol, 62%). A sample was dissolved in toluene, and DCl was added. The formed ethane was collected in $CDCl_3$ and analyzed by ^{13}C NMR: 1:1 mixture of $CH_3{}^{13}CH_2D$ and $^{13}CH_3CH_2D$.

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Thermal and Photoassisted Ring Opening of Thietane in a Triosmium Cluster Complex

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UV irradiation of $Os_3(CO)_{11}[S(CH_2)_3]$, **1**, produced decarbonylation and formation of two isomers, $Os_3(CO)_{10}[\mu\text{-}S(CH_2)_2CH_2]$, **2**, and $Os_3(CO)_{10}[\mu\text{-}SCH_2CH{=}CH_2](\mu\text{-}H)$, **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 ligand. When heated to 97 °C, **2** was converted to **3** by a β-elimination reaction and $Os_2(CO)_6[\mu\text{-}SCH_2CH_2CH](\mu\text{-}H)$, **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 alkylidene carbon. Compound **3** was also formed in the reaction of thietane with $Os_3(CO)_{10}(NCMe)_2$ at 25 °C. Compound **2** adds phosphines by opening the cluster to yield the adducts $Os_3(CO)_{10}[\mu\text{-}S(CH_2)_2](L)$ (**5**, L = PPh_3; **6**, L = PMe_2Ph). At 97 °C, **5** and **6** undergo β-elimination involving the metallacycle to yield the complexes $Os_3(CO)_9[\mu\text{-}SCH_2CH{=}CH_2](L)(\mu\text{-}H)$ (**7**, L = PPh_3; **8**, L = PMe_2Ph) 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 $P2_1/c$, a = 9.020 (2) Å, b = 11.673 (3) Å, c = 19.7000 (4) Å, β = 94.21 (2)°, Z = 4, 1947 reflections, R = 0.038. For **2**: space group $P2_1$, a = 11.750 (3) Å, b = 12.623 (2) Å, c = 13.242 (5) Å, β = 100.79 (2)°, Z = 4, 2423 reflections, R = 0.055. For **4**: space group $P\bar{1}$, a = 8.5830 (9) Å, b = 12.999 (2) Å, c = 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 $P2_1/n$, a = 10.536 (2) Å, b = 18.131 (3) Å, c = 14.174 (2) Å, β = 99.57 (1)°, Z = 4, 2780 reflections, R = 0.024. For **7**: space group = $P\bar{1}$, a = 10.341 (1) Å, b = 17.584 (4) Å, c = 9.736 (2) Å, α = 98.35 (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 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 hydrodesulfurization 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 thiirane[3] A and thietane[4–10] B and their derivatives by transition-metal carbonyl cluster complexes.

A

B

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