Synthesis and Reactions of Bis(cyclopentadienyl)titanium(IV) Metallocycles

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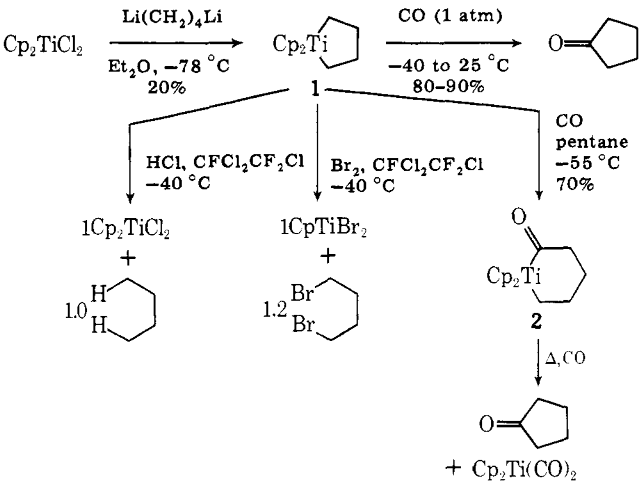
Abstract: 1,4-Tetramethylenebis(cyclopentadienyl)titanium(IV) (**1**) was prepared by reaction between dichlorobis(cyclopentadienyl)titanium(IV) and 1,4-dilithiobutane; it could be isolated at low temperature, but its thermal lability was such that it could be characterized only through its reactions. Compound **1** and the analogous six-membered metallocycle 1,5-pentamethylenebis(cyclopentadienyl)titanium(IV) (**5**) were much more stable than an acyclic titanium alkyl, di-*n*-butylbis(cyclopentadienyl)titanium(IV) (**3**). Thermal decompositions of **3** and **5** appear to take place by unexceptional β-elimination and reduction reactions involving titanium hydrides. These reactions yield, respectively, a mixture of butenes and *n*-butane and a mixture of pentenes and cyclopentane. By contrast, thermal decomposition of **1** (4 h, 0 °C) takes place in part by a path that cleaves a carbon–carbon bond of the titanocyclopentane ring and generates ethylene; 1-butene is the second major product of this decomposition. Carbonylation of **1** yields cyclopentanone; carbonylation of **3**, **5**, and dimethylbis(cyclopentadienyl)titanium(IV) takes place less readily, if at all. These results indicate that the high stability of the titanocyclopentane ring, presumably reflecting suppression of the β-elimination of metal hydride, is accompanied by abnormally high reactivity in carbonylation and in thermal decomposition by carbon–carbon fragmentation. Several functional equivalents of titanocene ($Cp_2TiN_2TiCp_2$, $[Cp_2TiH]_x$, $[Cp_2Ti]_2$, Cp_2TiCl_2 reduced with lithium naphthalenide) react directly with olefins and form titanocyclopentane rings. The best yields in these reactions are obtained using benzonorbornadiene, norbornene, and ethylene.

A dominant decomposition reaction of transition metal alkyls is the β-elimination of a metal hydride moiety.[2] Although this reaction is fundamental to much of transition metal catalysis, its very facility limits the importance of other, potentially valuable, types of reactions, particularly those involving carbon–carbon bond formation and cleavage. We have previously suggested that one way of suppressing the β-hydride elimination reaction is to constrain the M–C–C–H dihedral angle to values far from the optimal 0°. This suggestion was verified by preparing several platinum(II) metallocycles, and establishing that their thermal decomposition is dramatically less rapid than that of acyclic analogues.[3] Here we describe details of the preparation, characterization, and reactions of bis(cyclopentadienyl)titanium(IV) metallocycles, and particularly of 1,4-tetramethylenebis(cyclopentadienyl)titanium(IV), $Cp_2Ti(CH_2)_4$ (**1**). These studies reinforce the suggestion that the chemistry of metallocyclopentanes is significantly different from that of analogous acyclic organometallic compounds, and that an important basis for this difference is suppression of β-hydride elimination.[4]

Scheme I. Preparation and Reactions of $Cp_2Ti(CH_2)_4$ (**1**)



Results

Preparation and Characterization of 1,4-Tetramethylenebis(cyclopentadienyl)titanium(IV) (1). Reaction of a suspension of dichlorobis(cyclopentadienyl)titanium(IV) (Cp_2TiCl_2) with 1,4-dilithiobutane in diethyl ether at −78 °C yields a reaction mixture containing **1** (Scheme I). Its isolation and purification can be accomplished by chromatography over alumina at −40 °C under argon using hexane as eluent; crystallization may be effected by cooling the eluent to −78 °C. Compound **1** is a dark orange crystalline solid, readily soluble in pentane and ethereal solvents, which decomposes thermally in $CFCl_2CClF_2$ solution with a half-life of ca. 0.5 h at 0 °C.

Since the thermal instability of **1** precluded traditional analytical procedures, it was characterized by its reactions. Treatment of chromatographed samples of **1** with HCl (gas) in hexane or $CF_2ClCFCl_2$ yielded Cp_2TiCl_2 and butane in molar ratio 1:1.0; treatment with bromine in the same solvents yielded Cp_2TiBr_2 and 1,4-dibromobutane in molar ratio 1:1.2. The fact that the ratio of titanium-containing products to products derived from the 1,4-tetramethylene moiety is approximately 1.0 in both of these experiments indicates that the compound has stoichiometry $[Cp_2Ti(CH_2)_4]_n$. In what follows, yields are based on the assumption that the reaction of **1** with bromine yields 1,4-dibromobutane quantitatively: viz., that this reaction can be used to assay solutions for the quantity of **1** they contain. The major part of the descriptive chemistry of **1** was carried out by preparing **1** by reaction of 1,4-dilithiobutane with Cp_2TiCl_2, isolating **1** by low-temperature chromatography using procedures outlined in the Experimental Section, and assaying an aliquot by bromination to determine the quantity present. The conversion of Cp_2TiCl_2 to a solution containing **1** was normally ca. 20%.

Two lines of evidence argue that **1** is a monomer containing a five-membered titanocyclopentane moiety, rather than a dimer or higher oligmer having the same empirical composition. First, its thermal stability is much greater than that of acyclic analogues. For example, $Cp_2Ti(CH_2CH_2CH_2CH_3)_2$ (**3**, vide infra) decomposes rapidly at −55 °C, while **1** has appreciable stability at 0 °C. If **1** were a dimer or oligmer containing a ring having more than five members, its thermal stability would be expected to be determined by the rate of β-hydride elimination, and to be approximately the same as that of **3**.[3] The observation that the stability of **1** is qualitatively much greater than that of **3** argues strongly that the 1,4-tetramethylene moiety of **1** is part of a five-membered ring. Second, carbonylation of **1** (CO, 1 atm, warming from −40

Table I. Products of Thermal Decomposition of Metallocyclopentanes[a]

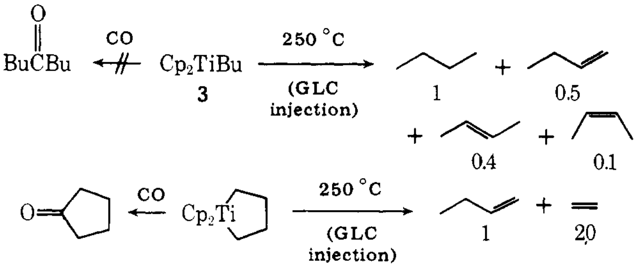
Compound	Temp (°C)	1-Butene/ ethylene[b]
$(C_5H_5)_2Ti(CH_2)_4$ (**1**)	−20	9
	0	4
	250[c]	0.05
$(C_5Me_5)_2Ti(CH_2)_4$	0	(4.5)
	250[c]	(0.4)
$(C_5Me_4Et)_2Ti(CH_2)_4$	0	(6)
	250[c]	(0.6)
$Cp_2Zr(CH_2)_4$	−20	6
	250[c]	2

[a] Thermal decompositions were carried out in $CFCl_2CClF_2$ solution at concentrations originally ca. 0.02 M in organometallic compound. [b] The absolute yields of olefins were not measured in instances indicated by parentheses; in other cases, the product balance was greater than 80%. The remaining 1,4-tetramethylene moieties appeared predominantly as a mixture of ethane and butane. Since the ratio of ethane to butane was approximately the same as that of ethylene to butene, these former materials were probably formed by reduction of the latter.[8] [c] Decomposition was carried out by injection directly into a GLC inlet port at 250 °C.

to 25 °C) yields cyclopentanone in 80–90% yield. If **1** were a dimer or oligmer, the carbonyl groups would be expected to join different tetramethylene moieties. The production of cyclopentanone in good yield is consistent with the existence of a titanocyclopentane moiety in **1**.

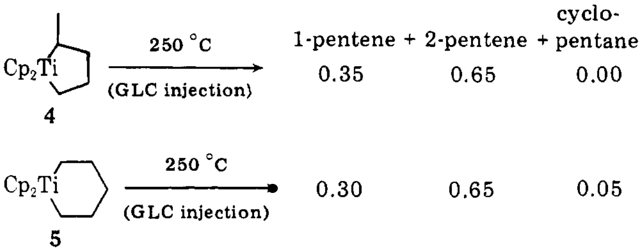
The Thermal Decomposition and Carbonylation Reactions of 1 Produce Different Types of Products Than Do Analogous Reactions of Di-*n*-butylbis(cyclopentadienyl)titanium(IV) (3).

Reaction of *n*-butyllithium and methyllithium with Cp_2TiCl_2 at −78 °C is accompanied by the same color changes observed on reaction with 1,4-dilithiobutane: Cp_2TiMe_2 is easily isolated in 80% yield as a yellow-orange solid which is moderately stable at room temperature;[5,6] Cp_2TiBu_2 (**3**) decomposes rapidly at −50 °C and has been isolated only at −78 °C. It has been possible to examine the products of thermal decomposition of **3** and of the products resulting from its treatment with bromine, hydrochloric acid, and carbon monoxide. Comparison of these products with those observed following analogous reactions of **1** is helpful in identifying reactivity characteristic of the titanocyclopentane ring. Thermal decomposition of **3** is complete in minutes at −50 °C, or very rapidly in the injection port of the GLC at 250 °C. Either decomposition generates, in greater than 80% yield, the 1:1 mixture of *n*-butane and butenes expected[2,7] for initial titanium hydride β-elimination followed by reductive elimination of butane. No ethylene is produced. Reaction of **3** with carbon monoxide does not yield di-*n*-butyl ketone under any conditions we have examined: the butene:butane mixture characteristic of thermal decomposition is again detected. In contrast, thermal decomposition of **1** generates a mixture of ethylene and 1-butene (Table I). Carbonylation of **1** generates a species having an ir absorption (1720 cm^{-1}) expected for a titanium(IV) acyl and assigned to the structure **2.** This carbonylation occurs in good yield at −55 °C in less than 2 h; conversion of **2** to cyclopentanone is rapid (~2 h) at 0 °C.

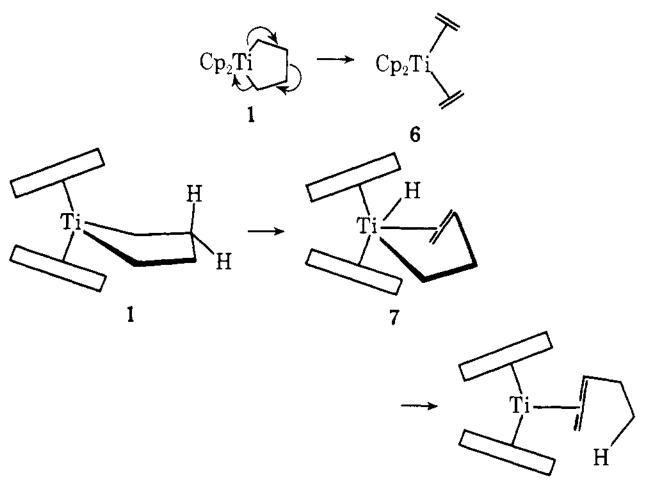


Two aspects of these data deserve comparison. First, the much enhanced thermal stability of **1** relative to **3** is accompanied by a change in the types of hydrocarbon products produced on decomposition: the carbon–carbon fragmentation that converts **1** to ethylene has no counterpart in the decomposition of **3.** Second, this increased stability permits **1** to react with carbon monoxide and generate cyclopentanone. Dibenzylbis(cyclopentadienyl)titanium(IV) and methylbis(cyclopentadienyl)titanium(IV) chloride, in which β-hydride elimination is not possible, also carbonylate;[9] dimethylbis(cyclopentadienyl)titanium(IV) reacts only slowly with carbon monoxide at room temperature. The observation that **1** is significantly more reactive toward carbon monoxide than Cp_2TiMe_2 suggests that the five-membered metallocyclic ring of **1** serves both to suppress β-hydride elimination and to provide a particularly reactive grouping.

The factors influencing the partitioning of the 1,4-tetramethylene unit of **1** between ethylene and 1-butene on thermal decomposition were explored briefly (Table I). Also for comparison, the related metallocycles **4** and **5** were prepared, purified by chromatography, and allowed to decompose thermally. The thermal stabilities of these substances are intermediate between those of **1** and **3.** The products of decomposition varied slightly with temperature, but always consisted predominantly of pentenes. No more than a trace of propylene or ethylene was observed on decomposition of **4.**



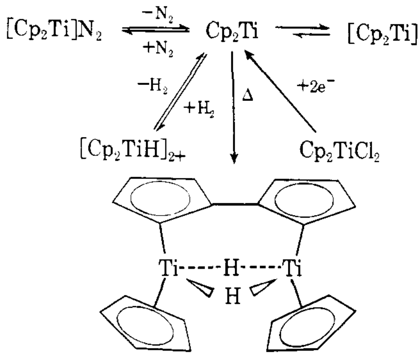
These studies do not provide sufficient evidence to indicate the structural features that promote carbon–carbon cleavage in thermal decomposition of **1** at the expense of the (presumably β-hydride elimination-based) path that leads to butenes.[10] The marked temperature dependence of the yields of hydrocarbons observed on decomposition of **1** is experimentally reproducible, but not easily interpreted. The 1,4-tetramethylenebis(pentaalkylcyclopentadienyl)titanium(IV) species were prepared to test the hypothesis that increased steric bulk in the plane of the cyclopentadienyl rings might inhibit both puckering of the metallocyclopentane ring and transfer of a β-hydrogen from carbon to titanium (**1** → **7**). These materials yield, if anything, less rather than more ethylene than does **1.** Addition of a methyl group to **1** (**4**) inhibits carbon–carbon



fragmentation, perhaps due to a facile β-hydride elimination involving the methyl group. The stability of the related platinocycle is, however, relatively unaffected by the additional methyl group.[3]

Cycloaddition Reactions of Olefins with Functional Equivalents of Titanocene. Two compounds of empirical formula ($\mathrm{C_{10}H_{10}Ti}$) have been called "titanocene" [6,11-18] (Scheme II).

Scheme II. Routes to Titanocene



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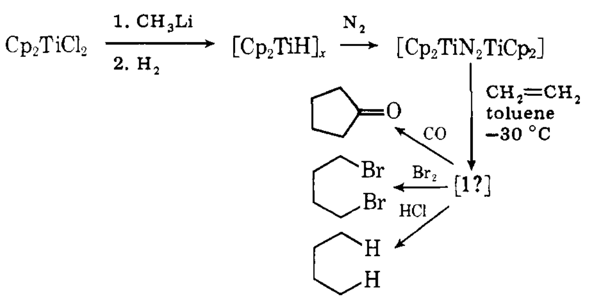
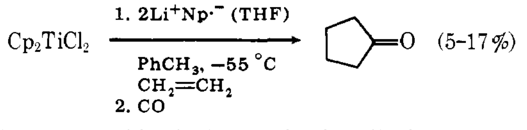
The structure of the less reactive, green, dimeric compound[12,13] has recently been established as **8**.[14] In this paper we refer to bis(cyclopentadienyl)titanium(II), $\mathrm{Cp_2Ti}$, as titanocene. This substance has been well characterized by Brintzinger, et al.[11] In solution, titanocene is preponderantly dimeric and fairly stable at room temperature.[11] Heating to 90 °C in toluene, however, gives almost a quantitative yield of **8**.[11] Titanocene may be generated from its polymeric hydride $(\mathrm{Cp_2TiH})_x$ or its dimeric dinitrogen complex $(\mathrm{Cp_2Ti})_2\mathrm{N_2}$, but the preparations of these compounds are fairly difficult and hazardous since they are pyrophoric.[11] Two-electron reduction of titanocene dichloride using Grignard reagents,[15] sodium sand,[16] sodium naphthalenide,[17] or electrochemical reduction[18] probably yields titanocene, but under the conditions employed it rearranges to **8** or reacts with solvent.[11]

The most straightforward rationalization for production of ethylene from **1** is a pathway of the type suggested by **1** → **6**. It seemed possible that this pathway might be reversible—that is, that ethylene might react with titanocene and form **1**. To test this possibility, a functional equivalent of titanocene, $\mathrm{Cp_2TiN_2TiCp_2}$,[11] was exposed to ethylene at temperatures between −78 and −30 °C (Scheme III). Reaction of the resulting mixture with carbon monoxide, hydrochloric acid, or bromine led to products characteristic of the 1,4-tetramethylene moiety in yields of ca. 10–15%, based on the $[\mathrm{Cp_2Ti}]_2\mathrm{N_2}$ used as a starting material. Although we were never successful in isolating a pure sample of **1** from the reaction of $[\mathrm{Cp_2Ti}]_2\mathrm{N_2}$ with ethylene, the production of moderate yields of products characteristic of **1** strongly implicates it as an intermediate in these reactions. It is, however, possible that other mono- or dititanium organometallic species would show a similar pattern of reactivty, and alternative structures cannot presently be excluded.

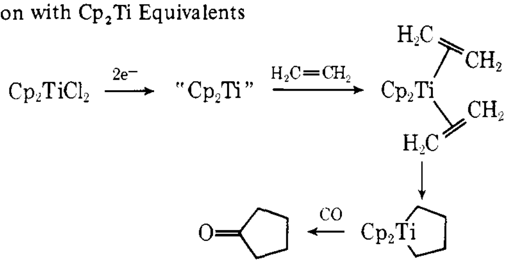
Scheme III. Reaction of Ethylene and "Titanocene" Generates **1**



In principle, any two-electron reduction of $\mathrm{Cp_2TiCl_2}$ might generate a titanium(II) species that could act as an ethylene acceptor.[6] Although $\mathrm{Cp_2TiN_2TiCp_2}$ serves adequately as a source of "titanocene", it is not easily prepared. Accordingly, we spent some effort in trying to find alternative and more convenient procedures for generating the functional equivalent of titanocene from $\mathrm{Cp_2TiCl_2}$ by reduction. The development of a satisfactory reducing agent is made difficult by the requirement that it work rapidly at −30 °C, at which temperature **1** is moderately stable. The alkali metals, alkali metal amalgams, and Na–K alloy reduce $\mathrm{Cp_2TiCl_2}$ to $\mathrm{Cp_2Ti^{II}}$ slowly even at room temperature. Hydridic reducing agents (potassium hydride, Vitride, isobutylmagnesium bromide) were similarly unsatisfactory. Solutions of aromatic anions proved to be efficient reducing agents.[6,17,19] Thus, reaction of a suspension of $\mathrm{Cp_2TiCl_2}$ in toluene with lithium naphthalenide (1.7 M in THF) occurred readily at −55 to −30 °C in the presence of ethylene (1 atm). Carbonylation of the resulting reaction mixture yielded cyclopentanone in 17% yield: the results of several related experiments are summarized in Table II. These experiments, combined with results described earlier, suggest that the failure of this procedure to provide a general route from olefin to ketone is due to poor yields on trapping of titanocene by olefin, rather than to a failure to produce titanocene in the reduction or to unsatisfactory carbonylation (Scheme IV). Reactive olefins (norbornene, benzonobornadiene) are converted in good yields to ketones, based on titanium. Thus, the reduction of $\mathrm{Cp_2TiCl_2}$ to $\mathrm{Cp_2Ti}$ must proceed in satisfactory yields. Previous evidence indicated that carbonylation of **1** to cyclopentanone proceeded in good yield, in agreement with the observation of high yields of ketones from norbornene and benzonorbornadiene. Thus, carbonylation of the metallocycle, once formed, also takes place in good yield. Hence, the yield-determining step for product of ketones is the reaction of titanocene with olefins and formation of metallocyclopentanes. The order of yields—benzonorbornadiene > norbornene > ethylene > 1,7-hexadiene—is that expected if coordination of olefin to metal is important.[20]

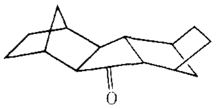
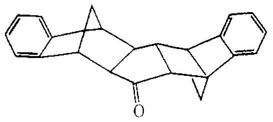
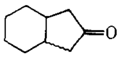


Scheme IV. Conversion of Olefins to Cyclopentanones by Reaction with $\mathrm{Cp_2Ti}$ Equivalents



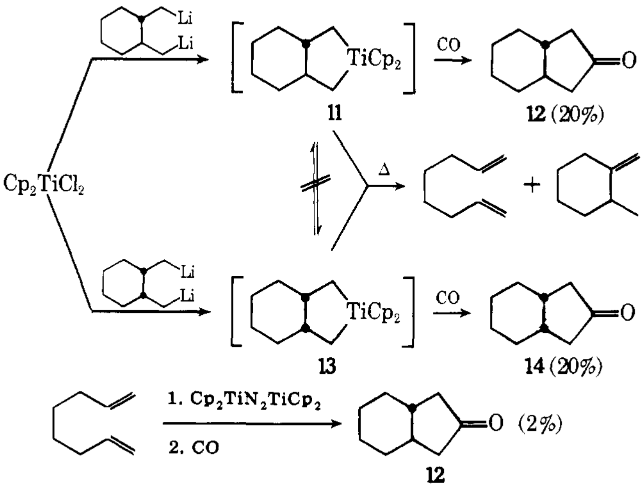
Although 1,7-octadiene does not trap $\mathrm{Cp_2Ti}$ generated by reduction of $\mathrm{Cp_2TiCl_2}$, it does react in low yield with $\mathrm{Cp_2TiN_2TiCp_2}$ (Scheme V). This observation provides an opportunity to check on the rate at which metallocyclopentane and diolefin-metal complex are in equilibrium. Both *cis*- and *trans*-1,2-di(lithiomethyl)cyclohexane react with $\mathrm{Cp_2TiCl_2}$ to give (uncharacterized) metallocyclopentanes, which, in turn, yield the corresponding hexahydroindanones in ca. 20% yield (based on titanium) on carbonylation. The stereochemistry of the cyclohexane ring is completely retained in these transformations: no **14** is obtained from **11**, and no **12** is obtained from **13**. Thus, **11** and **13** do not equilibrate under the reaction conditions (−20 °C, 1 h). Reaction of 1,7-octadiene with $\mathrm{Cp_2TiN_2TiCp_2}$, followed by carbonylation, generates only **12**,

Table II. In Situ Formation and Carbonylation of Metallocyclopentanes[a]

R_2TiCl_2	Olefin (equiv/equiv Ti)		Product	Yield (%)[b]
Cp_2TiCl_2	Ethylene	(1)	Cyclopentanone	5
		(10)		17
	Norbornene	(1)		24 (18)[c]
		(10)	 9	75
	Benzonorbornadiene	(1)		46 (25)[c]
		(5)	 10	90
	1,7-Octadiene	(10)		0
$(C_5Me_5)_2TiCl_2$	Ethylene	(10)	Cyclopentanone	0
$(C_5Me_4Et)_2TiCl_2$	Ethylene	(10)	Cyclopentanone	0
	Benzonorbornadiene	(5)	**10**	0

[a] All reactions were carried out by reducing the titanium (IV) dichloride in toluene with a solution of lithium naphthalenide in THF at −40 °C in the presence of olefin. [b] All yields were obtained by GLC analysis using internal standard techniques, and are based on titanium. [c] Isolated yield.

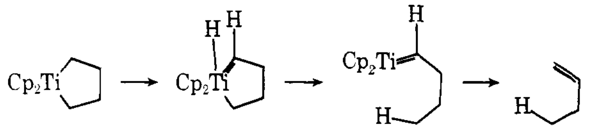
Scheme V. Reactions of Metallocycles Related to 1,7-Octadiene



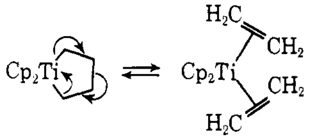
how be it in low yield (ca. 2%) following carbonylation. Thus the metallocycle formed directly from olefin and titanocene also shows no tendency to equilibrate cis and trans isomers of the 1,2-disubstituted cyclohexane ring. Thermal decomposition of **11** and **13** in the absence of carbon monoxide does yield 1,7-octadiene (>50%). The conclusion from these experiments is that the carbon–carbon bond breaking required to convert these metallocyclopentane rings to 1,7-octadiene is a slow process, relative to carbonylation at −40 °C.

Discussion

The reactivity of 1,4-tetramethylenebis(cyclopentadienyl)titanium(IV) (**1**) differs in three characteristic ways from that of di-*n*-butylbis(cyclopentadienyl)titanium(IV) (**3**). First, **1** is much more stable than **3** toward thermal decomposition. The observation that 1,5-pentamethylenebis(cyclopentadienyl)titanium(IV) (**5**) shares some of this stability with **1** suggests that the structural features that determine the thermal stability of these titanium(IV) metallocycles parallel those established for related metallocyclic derivatives of bis(triphenylphosphine)platinum(II).[3] The high stability of Pt(II) and Ti(IV) five- and six-membered metallocycles is compatible with the hypothesis that suppression of the metal β-hydride elimination reaction on constraining the M–C–C–H dihedral angles to values far from the 0 °C that seems to be optimal for metal hydride elimination decreases thermal decomposition rates. Second, **1** is more reactive toward carbon monoxide than either dimethylbis(cyclopentadienyl)titanium(IV) or **5**; the thermal instability of **3** precludes useful direct comparison with **1**. The difference in reactivity of **1** and **5** suggests that the five-membered ring may be sufficiently strained to show enhanced reactivity in reactions that increase coordination of the titanium center (e.g., coordination of carbon monoxide) and (presumably) decrease the C–Ti–C angle. Third, thermal decomposition of **1** takes place in part by a reaction involving carbon–carbon bond cleavage. This reaction apparently has no analogue in decompositions of **3** or **5**. Although the opportunity for this carbon–carbon fragmentation to compete with β-hydride elimination undoubtedly arises in the exceptional slowness of the latter, it is not clear what factors encourage the former. The tacit assumption that the mechanisms of these two reactions are straightforward does not presently rest in any detailed appreciation of their course. Thus, although decomposition of **1** with formation of 1-butene might take place by initial β-hydride elimination, it might also, in principle, occur by initial α-hydride elimination. Loss of α-hydrogen atoms is now well established in organometallic derivatives of metals on the left of the transition series,[21] and this type of decom-

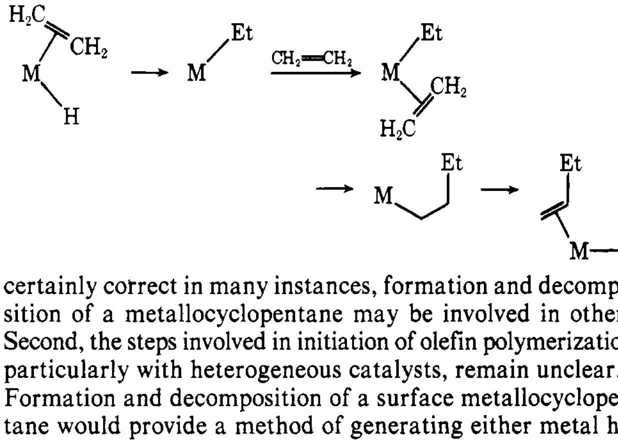


position might serve to explain the insensitivity of the relative rates of production of ethylene and butene to the bulk of substituents on the cyclopentadienyl rings. Distinction between α- and β-hydride paths must wait on further experimental evidence. Formulation of the production of ethylene from **1** as a straightforward reductive elimination reaction is supported by the observation of the reverse reaction, easily rationalized as an oxidative addition. This potentially useful reaction type only works well with reactive olefins (norbornene derivatives,



ethylene), and it is not evident how the system should be modified to increase its rate.

These results establish that it is possible to form titanocyclopentanes by oxidative cycloaddition of two olefins and one titanium atom. It remains to be established whether this path is common or extraordinary in transition metal catalysis. Related stoichiometric reactions have been observed previously in reactions between other metals and reactive olefins,[22] but the possible intermediacy of metallocyclic species in useful catalytic processes has not been investigated. Three types of reactions particularly warrant attention. First, the variety of reactions in which transition metals catalyze the conversion of ethylene to 1-butene are presently believed to involve metal hydrides as intermediates.[23] Although this formulation is certainly correct in many instances, formation and decomposition of a metallocyclopentane may be involved in others. Second, the steps involved in initiation of olefin polymerization, particularly with heterogeneous catalysts, remain unclear.[24] Formation and decomposition of a surface metallocyclopentane would provide a method of generating either metal hydride or metal alkyl centers directly from olefins. Third, it is possible to write mechanisms for olefin metathesis that involve metallocyclic intermediates.[25] Although current attention is focused on the probable intermediacy of metal-carbene complexes in these reactions,[26] at least one reaction, probably involving an intermediate tungsten metallocycle, has yielded results of the type expected for metathesis.[25] In the work reported here, examination of the reactions of 1,7-octadiene with titanocene showed no suggestion of metathesis-like rearrangements of the carbon skeleton. Titanium is not, however, a component of active metathesis catalysts.[17]



Experimental Section

General Methods. All reactions involving organometallic compounds were carried out under welding grade argon using standard techniques for handling air-sensitive compounds.[28,29] Diethyl ether was distilled from lithium aluminum hydride. Toluene and 2,2,4-trimethylpentane were distilled from calcium hydride after refluxing for 12 h. Pentane and hexane were washed free of olefins with concentrated sulfuric acid and distilled from a suspension of sodium benzophenone ketyl. Tetrahydrofuran was distilled from a solution of sodium benzophenone dianion. All distillations were carried out under argon. $CF_2ClCFCl_2$ was purged with argon or degassed under high vacuum before use. NMR spectra were run on Varian T-60 or Hitachi Perkin-Elmer R20B (60 MHz) and R22 (90 MHz) spectrometers. Infrared spectra were measured with a Perkin-Elmer Model 567 instrument. Standard, tightly stoppered, sodium chloride solution ir cells proved satisfactory for air-sensitive compounds if the spectra were taken promptly. GLC analyses were performed on a Perkin-Elmer Model 990 instrument, equipped with a flame ionization detector. Dicyclopentadienyltitanium dichloride was obtained from Alfa Inorganics and used without further purification. Ethylene was obtained from Matheson (C. P. grade). Other chemicals were reagent grade and used without further purification. Liquid reagents to be added to air-sensitive solutions were first purged with argon.

1,4-Dilithiobutane and 1,5-Dilithiopentane. A solution of 1,4-dichlorobutane (11.0 ml; 0.10 mol) in 50 ml of diethyl ether was added in drops over a period of 2 h to 100 ml of ether containing 2.8 g (0.40 mol) of lithium (1% Na) wire at 0 °C. The reaction was stirred at 0 °C for 24 h. The solution was freed of suspended solids by centrifugation and stored in a Schlenk tube at −20 °C. If kept at this temperature, the reagent had a useful life of 3-4 weeks. The concentration of "RLi" was 1.2 N (90% yield) with 0.02 N residual base by dibromoethane double titration.[30] GLC analysis of aliquots of the solution obtained from this organolithium reagent following reaction with dibromoethane indicated that most of the RLi titer was present as dilithium reagent. Cyclobutane was the principal by-product of the reaction, along with smaller amounts of butane and butene. No ethylene was observed. Much less satisfactory results were obtained using either low-sodium lithium or 1,4-dibromobutane.

1,5-Dilithiopentane was prepared in an analogous manner in 85% yield.

1,4-Tetramethylenebis(cyclopentadienyl)titanium(IV) (1). A suspension of Cp_2TiCl_2 (0.50 g; 2.0 mmol) was rapidly stirred in 20 ml of diethyl ether at −78 °C. A solution of 1,4-dilithiobutane (2.2 mmol) in ether was added rapidly by syringe. The solution was gradually warmed with vigorous stirring to −45 °C and maintained at this temperature until all the dichloride had dissolved (1.5 h). Methanol (50 μl) was added to destroy excess alkyllithium reagent. Removal of the solvent at −40 °C (0.05 Torr) left a red-brown residue which was triturated with 10 ml of hexane at −40 °C to give an orange-brown solution. The extract was then transferred by cannula to a dry 5-cm column of alumina (Woelm, activity grade I) which had been thoroughly flushed with argon. This column was provided with a cooling jacket, and maintained at −40 °C. The residue was triturated with two further 5-ml aliquots of hexane, and these were also transferred to the column. The column was eluted with hexane (pentane, 2,2,4-trimethylpentane (isooctane), and $CFCl_2CF_2Cl$ (mp −37 °C) were also satisfactory eluting solvents for the chromatography), and a bright orange band was collected as it eluted. Cooling the resulting dark orange-red solution to −78 °C gave dark orange needles which discolored if warmed above −30 °C. The solution showed no decomposition after 48 h at −78 °C. Compound **1** has a sharp singlet in the NMR spectrum (60 MHz; 0 °C) at δ 6.20 when dissolved in $CFCl_2CF_2Cl$. The methylene region was obscured by residual traces of ether and hexane. If the sample was allowed to stand at 0 °C, light tan solids precipitated from solution and the NMR singlet decreased to half its original value in 0.5 h.

The thermal and oxidative instability of **1** precluded microanalysis. Instead, it was possible to estimate the ratio of Cp_2Ti to 1,4-tetramethylene moieties by examining the products derived from **1**. Treatment of a $CFCl_2CF_2Cl$ solution of **1** with bromine, followed by GLC analysis, permitted an estimation of the quantity of 1,4-dibromobutane formed; cooling the solution to −20 °C, separating the dark red precipitate by filtration, and washing it with cold hexane isolated the Cp_2TiBr_2 (characterized by decomposition temperature and NMR ($CDCl_3$) δ 6.70 (s), with no detectable impurities). The molar ratio of these materials was 1,4-$C_4H_8Br_2$:Cp_2TiBr_2 = 1.2:1.0. Similarly, following treatment with anhydrous HCl, analysis for butane and Cp_2TiCl_2 (characterized by decomposition temperature and NMR ($CDCl_3$) δ 6.57 (s) with no detectable impurities) gave the ratio C_4H_{10}:Cp_2TiCl_2 = 1.0:1.0. Carbonylation of a solution of **1** in $CFCl_2CF_2Cl$ by allowing the solution to warm to ambient from −40 °C over several hours under 1 atm of CO yielded cyclopentanone (0.8-0.9 equiv, based on the assumption that the reaction of **1** with Br_2 yielding 1,4-dibromobutane is quantitative).

Di-*n*-butylbis(cyclopentadienyl)titanium(IV) (3). A suspension of Cp_2TiCl_2 (0.50 g; 2.0 mmol) was rapidly stirred in 5 ml of diethyl ether at −78 °C. A solution of *n*-butyllithium (2.0 mmol) in ether was added rapidly by syringe, and stirring was continued at −78 °C for 1 h. Methanol (50 μl) was injected to destroy any unreacted lithium reagent. Removal of the solvent at −78 °C (0.01 Torr) for 2 h left an orange sludge. The product was chromatographed by a procedure analogous to that used for **1** with isooctane as the eluting solvent while maintaining the column at −70 to −78 °C. A clear orange solution was obtained, and although it readily decomposed to a tan precipitate at −50 °C, no change in appearance had occurred after standing for 24 h at −78 °C.

The thermal and oxidative instability of **3** necessitated its characterization through its reaction products. Treatment of the isooctane solution of **3** with bromine, followed by GLC analysis, permitted an estimation of the quantity of 1-bromobutane formed; the dark red precipitate of Cp_2TiBr_2 was separated by filtration and washed with pentane: its NMR spectrum ($CDCl_3$) showed a singlet at δ 6.70, and impurities (5-10%) δ 1.0-1.6. The molar ratio of these materials was C_4H_9Br:Cp_2TiBr_2 = 1.9:1.0. Similarly, following treatment with anhydrous HCl, analysis for butane and Cp_2TiCl_2 (NMR ($CDCl_3$)

δ 6.57 (s), no detectable impurities) yielded the ratio C_4H_{10}:Cp_2TiCl_2 = 2.0:1.0. Attempts to carbonylate **3** gave less than 0.01 equiv of dibutyl ketone by GLC analysis owing to the rapid decomposition of **3** at normal carbonylation temperatures (−50 °C).

1,5-Pentamethylenebis(cyclopentadienyl)titanium(IV) (5) was prepared by a procedure analogous to that used for **1**, substituting 1,5-dilithiopentane for 1,4-dilithiobutane. Column chromatography using $CFCl_2CF_2Cl$ or isooctane as eluting solvents gave a dark orange solution. After standing for 30 min at −45 °C a small amount of yellow precipitate had formed. Bromine and HCl quenches of these solutions gave the ratios 1,5-$C_5H_{10}Br_2$/Cp_2TiBr_2 = 0.7 and C_5H_{12}/Cp_2TiCl_2 = 1.5. Both of the isolated titanocene products had decomposition points that were lower and broader than authentic samples. Carbonylation of solutions of **5** gave less than a 1% yield of cyclohexanone by GLC analysis.

1-Methyl-1,4-tetramethylenebis(cyclopentadienyl)titanium(IV) (4) was prepared by a procedure analogous to that used for **1**, substituting 1,4-dilithiopentane for 1,4-dilithiobutane. Column chromatography using isooctane as eluting solvent gave an orange-brown solution that slowly decomposed at −45 °C. Bromine and HCl quenches of the solution gave 1,4-dibromopentane and pentane, respectively, but the reactions were not clean and the resulting titanocene products were very impure.

Carbonylations of 1, 3, and 5. Chromatographed solutions of these compounds (ca. 0.02 M) were prepared as described above. They were stirred under 1 atm of CO at −50 °C and allowed to warm to room temperature over several hours with stirring. Yields of ketone products were determined by GLC analysis using internal standard techniques. **1** yielded 0.8–0.9 equiv of cyclopentanone, while **3** and **5** gave less than 0.01 equiv of dibutyl ketone and cyclohexanone, respectively.

1,4-Tetramethylenebis(cyclopentadienyl)zirconium (IV) was prepared and chromatographed by a procedure analogous to that used for **1** substituting Cp_2ZrCl_2 (0.58 g; 2.0 mmol) for Cp_2TiCl_2. Chromatographing the yellow reaction mixture with $CFCl_2CF_2Cl$ gave a clear, colorless solution that was ca. 0.02 M in product. Warming the solution to room temperature resulted in a white precipitate and a hydrocarbon mixture containing 15% ethylene and 85% butenes. Thermolysis of the chromatographed solution at 250 °C gave 30% ethylene and 70% butenes. Bromination gave 1,4-dibromobutane, but the Cp_2ZrBr_2 could not be isolated. Treatment with anhydrous HCl gave butane and Cp_2ZrCl_2 (isolated by filtration; mp 239–240 °C), but the reaction was not clean enough to obtain a ratio of butane to Cp_2ZrCl_2. Carbonylation of solutions of $Cp_2Zr(CH_2)_4$ before chromatography gave only a 2% yield of cyclopentanone.

Thermal Decomposition of 1, 3, 4, 5, and $Cp_2Zr(CH_2)_4$. Chromatographed solutions of these compounds were prepared as described above. They were decomposed at 250 °C by injecting samples of the cold solutions directly into the gas chromatograph. Pentane and hexane were used as internal standards to determine the product balance (80–95%) and yields of hydrocarbons. Solutions of **1** were decomposed at 0 and −20 °C by fitting the tubes with new serum stoppers and storing them at 0 °C for several hours and at −20 °C for several days. Subsequent analyses gave the same results, indicating complete decomposition. The samples were cooled to −40 °C before GLC analysis, and the product balances were within 10% of that for the 250 °C decomposition. The data obtained in these decompositions are summarized in Table I.

Thermal Decomposition of $(C_5Me_5)Ti(CH_2)_4$. Bis(pentamethylcyclopentadienyl)titanium(IV) dichloride[11,31] (97 mg; 0.25 mmol) was slurried in 3 ml of ethyl ether at −78 °C. A solution of 1,4-dilithiobutane (0.28 mmol) in ether was added rapidly by syringe. The mixture was gradually warmed to −45 °C with stirring and maintained at this temperature for 1 h, giving an orange-brown solution. Methanol (50 μl) was injected to destroy the excess lithium reagent. Removing the solvent at −40 °C (0.1 Torr) and triturating the resulting brown solids with 3 ml of $CFCl_2CF_2Cl$ gave a dark orange solution. Samples of the cold solution were injected directly into the gas chromatograph to decompose at 250 °C. The reaction tube was then fitted with a new serum stopper and stored at 0 °C for several hours and the decomposition was judged complete when two successive analyses gave the same result. The samples were cooled to −40 °C for GLC analysis, and no significant loss of gases was observed. The ethylene to butene ratio was unaffected by chromatographing the solution through alumina.

$(C_5Me_4Et)_2Ti(CH_2)_4$ was prepared and decomposed by the same procedure from $(C_5Me_4Et)_2TiCl_2$.

The yields of hydrocarbons found in these experiments are summarized in Table I.

Reaction of Cp_2TiMe_2 with Carbon Monoxide. A 0.1 M solution of Cp_2TiMe_2 in $CF_2ClCFCl_2$ was stirred at 25 °C under 10 atm of CO. At intervals the solution was examined by NMR. The spectrum of Cp_2TiMe_2 ($CF_2ClCFCl_2$), δ 6.10 (s, 10 H), 0.02 (s, 6 H), was observed to decline only slightly after several hours. No evidence for an acyl complex could be found at any time. At lower temperatures no observable reaction took place.

Isolation of 2 in the Carbonylation of 1. A pentane solution of **1** (0.8 mmol by Br_2 quench) was stirred for 2 h under 1 atm of carbon monoxide at −55 °C. A yellow-brown solid separated from solution. The solid was washed once with cold pentane, then dissolved in a minimum amount of toluene at 0 °C. Pentane was added slowly until a slight cloudiness persisted. A yellow solid crystallized when the solution was slowly cooled to −60 °C. After 2 h the solution was discarded and the solid washed with pentane and dried under a stream of argon at 0 °C, yielding 0.16 g (75%) of **2:** NMR (CD_2Cl_2) δ 6.25 (s, 10 H, Cp), 2.5–1.0 (m, 8 H, $(CH_2)_4$). An ir spectrum of the same solution had a strong band at 1720 cm^{-1} which gradually disappeared at 35 °C to be replaced by a broad band centered at 1740 cm^{-1}. The carbonyl band of cyclopentanone is at 1745 cm^{-1}. The Cp resonance at 6.25 disappeared at a similar rate and a half-life of 15 min at 35 °C can be estimated. Analysis of the resultant solution by GLC showed cyclopentanone to be present. Solid **2** decomposed completely when left at 25 °C for 24 h. In solution **2** is extremely sensitive to oxygen.

$[Cp_2TiH]_x$ was prepared by the procedure of Brintzinger et al.[11] **$Cp_2TiN_2TiCp_2$** was prepared by stirring a toluene or diethyl ether solution of $[Cp_2TiH]_x$ under nitrogen at −20 °C for several hours.[11] In general, $[Cp_2Ti]_2$ and its hydride precursor must be handled under rigorously O_2-free conditions for the reactions to succeed. As previously reported,[11] the hydride is pyrophoric. One sample ignited in a flask due to a small air leak. No problems were encountered with the residues of the reactions reported here, but caution is recommended with all reactions involving organotitanocene species.

Reaction of $[Cp_2Ti]_2$ with Ethylene. The gray-green hydride $(Cp_2TiH)_x$[11] (107 mg; 0.60 mmol) was stirred in toluene at −78 °C. Ethylene (35 ml; 1.2 mmol) was added by syringe and the solution was warmed to −35 °C. The solid dissolved as the reaction was stirred for 3 h at this temperature. The argon atmosphere was replaced by one of carbon monoxide, and the reaction mixture was allowed to warm to room temperature over several hours. After 12 h a 12% yield (based on $(Cp_2TiH)_x$) of cyclopentanone was detected in solution by GLC. If an HCl quench was substituted for the carbon monoxide, a similar yield of butane was obtained.

Reaction of $Cp_2TiN_2TiCp_2$ with Ethylene. A dark-blue solution of $Cp_2TiN_2TiCp_2$ was prepared[11] from 1 mmol of $(Cp_2TiH)_x$ and 15 ml of toluene or ethyl ether. Ethylene (50 ml; 2 mmol) was introduced at −78 °C after the nitrogen atmosphere had been replaced by argon. The reaction was allowed to warm to −30 °C whereupon it changed to a green-brown color. After 1 h, aliquots were allowed to react with HCl, CO, and Br_2 for GLC analysis. Butane, cyclopentanone, and 1,4-dibromobutane were obtained in 10–15% yield based on $(Cp_2TiH)_x$. The bromine quench was not used in toluene because the retention times of 1,4-dibromobutane and benzyl bromide are similar.

Reduction of Cp_2TiCl_2 with Lithium Naphthalenide in the Presence of Ethylene. A solution of lithium naphthalenide was prepared by stirring a 2 M solution of naphthalene in tetrahydrofuran with a slight excess of lithium wire. During the first hour the exothermic reaction was cooled occasionally with an ice bath to maintain the temperature at 25 °C or below. After five additional hours, the titer, typically 1.7 M, was determined[32] by quenching an aliquot with deoxygenated water and titrating with standard HCl.

Bis(cyclopentadienyl)titanium dichloride (0.25 g; 1.0 mmol) was suspended in 15 ml of toluene at −50 °C by rapid stirring under an ethylene atmosphere. Lithium naphthalenide (2.1 mmol) was added in drops over 15 min. Most of the Cp_2TiCl_2 dissolved during this period. The remainder dissolved during an additional 30 min of stirring at −40 °C. The ethylene atmosphere was replaced by carbon monoxide and the reaction mixture was allowed to warm to room temperature over 4–5 h. After 6 h at 25 °C, 0.17 mmol of cyclopentanone was present. A more prolonged reaction at 50 °C did not increase the yield.

Reduction of Cp_2TiCl_2 in the Presence of Norbornene. Bis(cyclopentadienyl)titanium dichloride (0.25 g; 1.0 mmol) and norbornene (0.20 g; 2.1 mmol) were stirred in 10 ml of toluene at −50 °C. Lithium naphthalenide (1.2 ml of a 1.7 M solution) was added dropwise over 15 min and the reaction was warmed to −30 °C. After 30 min of additional stirring the solution was carbonylated by allowing it to warm slowly to 25 °C under 1 atm of CO. Only one product was detected by GLC with the same retention time as the ketone dimer **9** produced in the reaction of norbornene with $Fe(CO)_5$.[33] A 24% yield was measured using octadecane as an internal standard. Pentane (30 ml) was added and the reaction mixture shaken in air with 1 M HCl until the red color had discharged and no more solids precipitated. After filtration, the solution was dried over Na_2SO_4. Removing the solvent at reduced pressure left a yellow oil, which subsequently solidified. The ketone dimer **9** was isolated by preparative TLC on silica gel on elution with hexane:ethyl acetate (9:1). The pure compound was the exo,trans,exo ketone dimer;[33] NMR ($CDCl_3$) δ 2.35 and 2.16 (m, 4 H, bridgehead), 1.93 and 1.70 (d, 4 H, J = 7.5 Hz, cyclopentanone), 1.5–1.1 (m, 8 H, $-CH_2CH_2-$), 1.04 (m, 4 H, bridge). Mass spectral analysis gave a parent ion at m/e 216.

Use of a tenfold excess of norbornene (2.1 g, 21 mmol) in conditions similar to those reported above produced a yield of ketone dimer of 75%, based on Cp_2TiCl_2. When the reaction solution was heated to 75 °C for 15 h under carbon monoxide, no increase in the yield of ketone was observed.

Reduction of Cp_2TiCl_2 with Lithium Naphthalenide in the Presence of Benzonorbornadiene. Benzonorbornadiene[34] (0.14 g, 1.0 mmol), Cp_2TiCl_2 (0.13 g; 0.50 mmol), and $CH_3(CH_2)_{30}CH_3$ (90 mg, GLC internal standard) were dissolved in ca. 10 ml of dry toluene under argon. The mixture was cooled to −40 °C and a THF solution of lithium naphthalenide (1.1 mmol) was added slowly by syringe. After stirring for 1 h at −40 °C, the argon atmosphere was replaced with carbon monoxide, and the reaction mixture was allowed to warm to room temperature over several hours. The mixture was analyzed by GLC. Removal of the solvent and preparative TLC (silica gel, 1EtOAc:9hexane) afforded a fraction with R_f 0.32–0.44. Recrystallization from ether gave a white powder identified as the exo, trans,exo dimer (41 mg; 26%) on the basis of mp 224–225 °C (lit.[34] mp 223–224 °C): ir 1725 cm^{-1} (lit.[34] 1722 cm^{-1}), NMR (CCl_4) δ 1.60 (m, 4 H), 2.13 (d, J = 8 HZ= 2 H), 245 (d, J = 8 Hz, 2 H), 3.35 (s, 2 H), 3.53 (s, 2 H), 7.10 (m, 8 H). The yield of this ketone in the reaction mixture before workup was determined to be 48% by GLC. Repetition of the experiment using a fivefold excess of benzonorbornadiene raised the yield to ca. 90%.

***trans*-1,2-Bis(chloromethyl)cyclohexane.** In a flame-dried flask under nitrogen was placed *trans*-1,2-bis(hydroxymethyl)cyclohexane[35] (6.2 g, 50 mmol) and 50 ml of reagent carbon tetrachloride. Tri-*n*-butylphosphine (32 g, 110 mmol) was added over a 45-min period with stirring at room temperature. The solution was refluxed for 15 h. Examination of the resulting reaction mixture by NMR showed no residual OH absorption. A flash distillation followed by a fractional distillation afforded 3.8 g (41%) of the trans dichloride: bp (15 Torr) ~120 °C; density 1.14 g/ml; NMR ($CDCl_3$) δ 3.62 (m, 4 H), 1.0–2.2 (m, 10 H). GLC analysis suggested that this material was >98% one component.

cis-1,2-Bis(chloromethyl)cyclohexane was prepared using a similar procedure, bp (15 Torr) ~112 °C; density 1.14 g/ml; NMR ($CDCl_3$) δ 3.50 (d, 4 H), 1.0–2.4 (m, 10 H).

1,2-Bis(lithiomethyl)cyclohexanone. This cis and trans dilithium reagents were prepared in diethyl ether using a procedure analogous to that for the preparation of 1,4-dilithiobutane, except that high-sodium (1% Na) lithium dispersion (Foote Mineral Co.) was used instead of lithium wire. Typical yields for conversion of CH_2Cl to CH_2Li groups were 50%.

Preparation and Carbonylation of 11. Bis(cyclopentadienyl)titanium dichloride (0.13 g; 0.50 mmol) was stirred in 10 ml of ether at −78 °C, and *trans*-1,2-bis(lithiomethyl)cyclohexane (0.55 mmol) in ether was added by syringe. The mixture was stirred for 5 h with slow warming to −20 °C to give a dark orange solution. Thermolysis of an aliquot by injection into the inlet of the GLC at 250 °C gave a substantial amount of 1,7-octadiene. The solution was cooled to −50 °C, placed under an atmosphere of CO, and allowed to warm to room temperature over several hours. GLC analysis using tetradecane as an internal standard gave a 20% yield (based on Ti) of isomerically pure *trans*-hexahydroindan-2-one (**9**).[36] Compound **13** was prepared and carbonylated by the same procedure to give a 20% yield of *cis*-hexahydroindan-2-one (**14**).[36]

Reaction of $[Cp_2Ti]_2$ with 1,7-Octadiene. This reaction was carried out using $(Cp_2TiH)_x$ (107 mg, 0.60 mmol) and 1,7-octadiene (0.11 ml, 0.72 mmol) in toluene, using a procedure analogous to that described for the reaction of $[Cp_2Ti]_2$ with ethylene. The only identified ketonic product was *trans*-hexahydroindan-2-one (**12**), ir 1742 cm^{-1}; the cis-isomer **14** and hexahydroindan-1-one could not be detected in the GLC trace, and, if present, were formed in yields less than 0.5%.

Reductions of zirconocene dichloride in the presence of ethylene and norbornene were conducted in a fashion analogous to those of titanocene dichloride. Ethylene gave only 1% cyclopentanone. The yield of the ketone dimer was 5% with a stoichiometric amount of norbornene and 8% when a tenfold excess was used. These yields are based on Cp_2ZrCl_2.

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Mechanism of the Quenching of the Emission of Substituted Polypyridineruthenium(II) Complexes by Iron(III), Chromium(III), and Europium(III) Ions

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Abstract: The series of complexes RuL_3^{2+}, where L is a bipyridine or phenanthroline derivative, has been used to investigate the mechanism of the quenching of $*RuL_3^{2+}$, the luminescent excited state of RuL_3^{2+}, by iron(III), chromium(III), and europium(III) in aqueous solutions at 25 °C. The quenching rate constants k_q were obtained from emission intensity and emission lifetime studies. In the iron(III)-$*RuL_3^{2+}$ systems flash-photolysis experiments showed that RuL_3^{3+} and iron(II) are produced in the quenching reaction. The steady-state levels of these products under continuous irradiation were determined as a function of iron(III) concentration and light intensity. In addition, the rate constants k_t for the thermal back-reaction of RuL_3^{3+} and iron(II) to re-form the starting species RuL_3^{2+} and iron(III) have been measured using flash-photolysis and stopped-flow techniques. The rate constants k_q and k_t are a function of excited state and ground state RuL_3^{3+}/RuL_3^{2+} potentials, respectively. Furthermore, the rate constants are, for the most part, in accord with the steady-state levels of RuL_3^{3+} and iron(II) produced under continuous illumination. Thus it is concluded that the mechanism of quenching by iron(III) is predominantly electron transfer in nature. The rate constants for the $*RuL_3^{2+}$-Eu(III) reactions vary more than two orders of magnitude on changing L. As the highest rate constants are observed for the ruthenium complexes with lowest reduction potentials, electron-transfer quenching is indicated and this hypothesis is supported by the results of flash-photolysis experiments. In sharp contrast, the lower than diffusion-controlled rate constants for the quenching of $*RuL_3^{2+}$ by chromium(III) are insensitive to the nature of L and do not follow the pattern expected from the redox potential of the ruthenium complex. In these systems, the quenching is ascribed to energy transfer in which ground state RuL_3^{2+} and the $^4T_{2g}$ and/or ^2E_g chromium(III) excited states are produced.

The quenching of the luminescence of tris(2,2′-bipyridine)ruthenium(II) by metal complexes is currently under active investigation.[1] Depending upon the system, the dynamic quenching of the ruthenium(II) emission may involve either oxidation (eq 1)[2–6] or reduction (eq 2)[7] of the excited state ($*Ru(bpy)_3^{2+}$) by the quencher (Q). Energy-transfer quenching also offers a pathway for deactivation of the excited state in some systems (eq 3).[8,9]

$$*Ru(bpy)_3^{2+} + Q \rightarrow Ru(bpy)_3^{3+} + Q^- \qquad (1)$$

$$*Ru(bpy)_3^{2+} + Q \rightarrow Ru(bpy)_3^{+} + Q^+ \qquad (2)$$

$$*Ru(bpy)_3^{2+} + Q \rightarrow Ru(bpy)_3^{2+} + Q^* \qquad (3)$$

Moreover, as has been pointed out,[1,10] energy transfer (eq 3) may also give rise to the electron-transfer products formed in eq 1 or 2. Conversely, the electron-transfer products generated in eq 1 or 2 may undergo subsequent reaction to yield the energy-transfer products of eq 3. Therefore the detection of electron-transfer products in flash-photolysis experiments[3] does not necessarily discriminate between primary electron-transfer and energy-transfer quenching mechanisms. In these instances, consideration of the relative reactivities of ground and excited donors and quenchers may make it possible to distinguish between the two mechanisms.

The series of luminescent polypyridineruthenium(II) complexes RuL_3^{2+} (L a 2,2′-bipyridine or 1,10-phenanthroline derivative) presents a useful probe for ascertaining the relative importance of electron-transfer and energy-transfer quenching mechanisms. The absorption and emission spectra of the complexes are nearly identical,[11,12] making it likely that the rates of energy-transfer quenching with a given acceptor Q will be constant for this series.[13] On the other hand, the redox potentials of the complexes in this series may be varied by changing the substituents on the ligands[11,14] and the rates of electron-transfer quenching reactions with a given oxidant or reductant Q should reflect the differences in driving force in a known manner.[15,16]

In the present work, this series of complexes has been used to further probe the mechanism of the quenching of RuL_3^{2+} by Fe^{3+} ions. In this system it was observed that relatively high steady-state levels of $Ru(bpy)_3^{3+}$ and Fe^{2+} accumulate when solutions of $Ru(bpy)_3^{2+}$ and Fe^{3+} are continuously illuminated. Recently it was shown that the quenching of the $Ru(bpy)_3^{2+}$ emission by Fe^{3+} ions can be interpreted in terms of the electron-transfer scheme shown in eq 4–6.[3,17]

$$Ru(bpy)_3^{2+} \underset{k_0}{\overset{h\nu}{\rightleftharpoons}} *Ru(bpy)_3^{2+} \qquad (4)$$

$$*Ru(bpy)_3^{2+} + Fe^{3+} \xrightarrow{k_{el}} Ru(bpy)_3^{3+} + Fe^{2+} \qquad (5)$$

$$Ru(bpy)_3^{3+} + Fe^{2+} \xrightarrow{k_t} Ru(bpy)_3^{2+} + Fe^{3+} \qquad (6)$$

Here k_{el} is the second-order rate constant for the production of free $Ru(bpy)_3^{3+}$ and Fe^{2+} from the reaction of $*Ru(bpy)_3^{2+}$ with Fe^{3+} and k_t is the second-order rate constant for the back (thermal) electron transfer between $Ru(bpy)_3^{3+}$ and Fe^{2+}. In this interpretation, the steady-state levels of $Ru(bpy)_3^{3+}$ and