

the solid-state structure has been inferred to be similar to that for $\text{Co}_4(\text{CO})_{12}$ (C_{3v}) with an apical $\text{Fe}(\text{CO})_3$ group and a basal Co triangle with three bridging CO and two types of terminal COs.¹³ The solution structure, however, again gave an anomalous ^{13}C spectrum; at -89°C two peaks only (in the ratio of 1:2) were observed even with the high signal-to-noise ratios resulting from ^{13}C enrichment.⁹ The ^{17}O results yielded not only the static structure but also the dynamic processes. At -11°C four peaks characteristic of C_{3v} symmetry were obtained (Figure 3). The narrowest line (70 Hz) at 385.5 ppm is assigned to carbonyls attached to the nonquadrupolar iron. With increase of temperature above -11°C , selective exchange processes are observed. Firstly, broadening of the ^{17}O resonances of the bridging carbonyls (at 494.4 ppm) and one of the terminal Co-CO resonances (at 392.4 ppm) occurs (spectrum at $+42^\circ\text{C}$). This process we take to be the in-plane exchange or merry-go-round process¹⁴ which has previously been observed by ^{13}C NMR studies on several clusters but none of which were based on cobalt. The next stage, involving exchange with the remaining set of carbonyls on cobalt, is indicated by the onset of broadening of the highest field line at 355.8 ppm. Lastly the carbonyls on iron exchange with the others and the totally scrambled spectrum (spectrum at $+107^\circ\text{C}$) is observed. This study demonstrates the utility of ^{17}O studies for metal carbonyl clusters, particularly those which contain quadrupolar metal nuclei which broaden ^{13}C lines and cause loss of ^{13}C signal in some cases.

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(13) The solid-state structure for the trisubstituted derivative $\text{HFeCo}_3(\text{C}_6\text{O})_9[\text{P}(\text{OCH}_3)_3]_3$ has been determined by neutron diffraction to have approximately C_{3v} symmetry with the H atom on the axis below the basal plane. Teller, R. G.; Wilson, R. D.; McMullan, R. K.; Koetzle, T. F.; Bau, R. *J. Am. Chem. Soc.* **1978**, *100*, 3071-3077.

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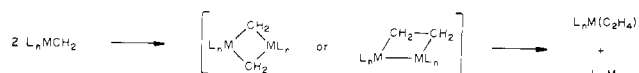
1,3-Dimetallacyclobutanes in Metal-Methylidene Dimerization Reactions

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The attempted synthesis of metal-carbene or -alkylidene complexes often results in formation of olefins or metal-olefin complexes arising from metal-carbene dimerization.^{1a} Decomposition of isolated metal carbenes and alkylidenes also produces olefinic products, presumably through either dimetallacyclic^{1b} or bis(carbenemetal)^{1c} intermediates. Such decompositions have



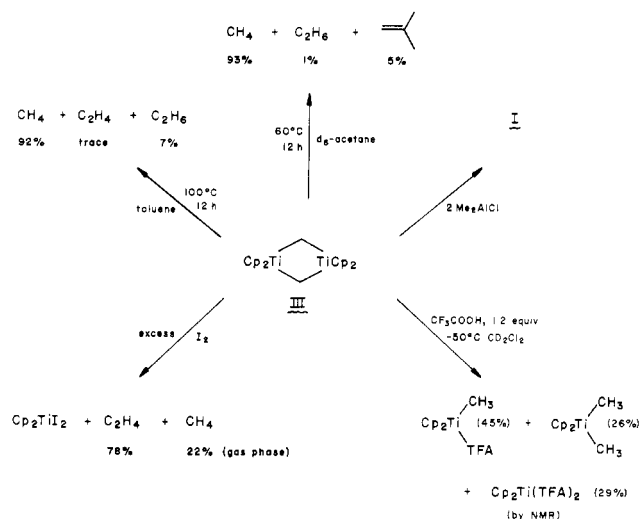
been proposed to be involved in catalyst deactivation in the olefin metathesis reaction² and may serve as models for methylene oligomerization on metal surfaces in the Fischer-Tropsch reaction.³

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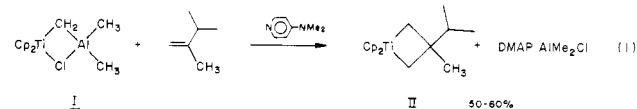
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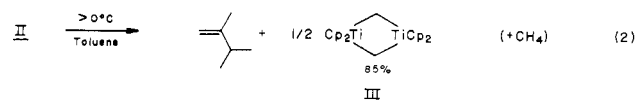
Scheme I



A stable, 1,3-dimetallacyclobutane has now been isolated in good yield from an olefin metathesis system⁴ which is thought to generate a metal methylidene intermediate. As reported previously,⁵ titanacyclobutanes can be isolated from the reaction of I with monosubstituted olefins and Lewis bases. This has proven



to be a general route to numerous other titanacyclobutanes including the one derived from 2,3-dimethyl-1-butene. This complex can be prepared and isolated in moderate yield.⁶ Upon warming deep red saturated solutions of II in aromatic hydrocarbons⁷ above 0°C , the solutions become purple, and purple-red platelets de-

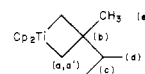


posit.⁸ Monitoring the reaction by ^1H NMR spectroscopy in benzene- d_6 reveals resonances due to the olefin growing in along with two additional singlets at δ 8.72 and 6.22 (area 2:10, re-

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(6) Complex II:



^1H NMR (500.13 MHz, -20°C , CD_2Cl_2 shifts relative to CHDCl_2 at δ 5.320) δ 5.862, 5.851 (Cp-H), 2.777 (d, $J = 9.5$ Hz), 2.047 (d, $J = 9.5$ Hz, H_{CH}), 0.801 (d, $J = 5.5$ Hz, H_β), 0.753 (heptet, $J = 5.5$ Hz, H_γ), 0.701 (s, H_δ); ^{13}C NMR (22.53 MHz, gated decoupled, -30°C , CD_2Cl_2 , shifts relative to CD_2Cl_2 at δ 53.8) δ 111.3, 110.7 (d of m, Cp's), 79.6 (dd, $J = 137$ Hz, C_α), 42.7 (d, $J = 130$ Hz, C_β), 25.1 (q, $J = 124$ Hz, C_γ), 19.4 (q, $J = 124$ Hz, C_δ), 13.4 (s, C_β).

(7) Allowing CD_2Cl_2 solutions of II to warm above 0°C gives rise to other as yet unidentified products.

(8) Typically, 500 mg of I was dissolved in 5 mL of toluene and added to a suspension of 236 mg of DMAP in 6 mL of toluene and 1 mL of 2,3-dimethyl-1-butene at -30°C . This homogeneous red solution was added dropwise to 60 mL of rapidly stirred pentane at 0°C . The resulting suspension was filtered rapidly to remove the $\text{DMAP}\cdot\text{AlMe}_2\text{Cl}$, and the solvent was concentrated in vacuo at -5°C until the solution was saturated in II. The solution was then warmed to room temperature for 8 h, and the purple-red platelets were filtered and washed with hexane to yield 340 mg of III (50% based on I). Other 3,3-disubstituted titanacyclobutanes such as those derived from isobutylene, methylenecyclohexane, 2-methyl-1-butene, and α -methylstyrene also decompose to give III, olefin, and variable amounts of CH_4 .

spectively). A small amount of methane is also observed.

Analytical, spectroscopic, and molecular weight data⁹ along with chemical characterization (Scheme I) suggest that the product is the dimer III. Solutions of III are rapidly oxidized in air but the solid may be handled briefly in air.

Thermolysis of III in toluene (Scheme I) produces mainly methane and some ethylene and ethane. Reactions which require the generation of titanocene, such as the ethylene-producing pathways, are slow and are followed by Cp-H insertion to produce "titanocene".¹⁰ This reluctance to generate the high-energy intermediate Cp₂Ti provides a rationale for the thermal stability of III and the predominance of CH₄ in the decomposition gases. When a more viable leaving fragment is provided, the reaction proceeds as expected. For example, reaction of III with iodine (Scheme I) gives ethylene, Cp₂TiI₂, and some methane.

In this system the 1,3- rather than the 1,2-dimetallacyclobutane is favored due to polarization of the Cp₂TiCH₂ moiety and the steric bulk of the Cp ligands.

The use of II as a source of Cp₂TiCH₂ for reaction with unsaturated organic and organometallic substrates appears to be a promising pathway to other metallacyclic and bimetallic methylene bridged systems.

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(9) Anal. Calcd: C, 68.77; H, 6.30. Found: C, 68.88, H, 6.55; ¹³C [1H] (22.53 MHz, shifts relative to CD₂Cl₂ at δ 53.8): δ 235.2 (CH₃), 112.2 (Cp's). ¹J_{C-H} for the CH₂ resonance was measured from the ¹³C satellites in the ¹H spectrum and found to be 126 Hz. IR (benzene-d₆): 2920, 2980 (m, sh). Molecular weight: calculated 384; found 396 ± 30 (cryoscopic in benzene); 427 ± 20 (Signer's method. For a description of the method, see: Clark, E. P. *Ind. Eng. Chem., Anal. Ed.* **1941**, *13*, 820).

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Some Observations Concerning the Temperature Dependence of the Reaction of Ammonia with Water

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Following Alberty and Robinson,¹ we have recently shown that it is possible to account for the heat capacity of activation (ΔC_p^\ddagger) which characterizes the temperature dependence of hydrolytic rate constants by postulating the existence of at least one intermediate between the neutral reactants and ionic products.² The same idea has been applied successfully to the heat capacity changes (ΔC_p^\ominus)

Table I. Equilibrium Data Related to the Ionization of Ammonia in Water at Various Temperatures

<i>T</i> , °C	<i>K_b</i> × 10 ⁵ , ^{a,e} obsd	<i>K_b</i> × 10 ⁵ , ^b calcd	<i>K_b</i> × 10 ⁵ , ^c calcd	<i>K₁</i> × 10, ^{d,f} calcd
0	1.374	1.374	1.374	12.3
5	1.479	1.478	1.478	10.0
10	1.570	1.570	1.570	8.3
15	1.652	1.650	1.650	6.8
20	1.710	1.717	1.717	5.7
25	1.774	1.772	1.772	4.8
30	1.820	1.814	1.814	4.0
35	1.849	1.846	1.846	3.4
40	1.862	1.868	1.868	2.9
45	1.879	1.882	1.882	2.5
50	1.892	1.889	1.889	2.2

^a Taken from ref 18. ^b Calculated from A, B, C and D, solution a, (Table II). ^c Calculated from A, B, C and D, solution b (Table II). ^d Calculated from C and D of solution a, (Table II). ^e For the Wentworth-Deming regression ΔK_b was taken as 0.2% of the observed value of *K_b* (this estimate may be optimistic); ΔT was taken as 0.01 or 0.001. The differing values of ΔT made no difference to the quantities reported in Table II. ^f Khakham reports *K₁* = 0.5 at 25 °C, whereas Moore and Winnill report *K₁* = 0.88 (see also ref 7, p 31).

which characterize the ionization of carboxylic acids by invoking the Eigen intermediate between the aqueous covalent acids and the related ions.³ In this contribution a similar model is applied to the ionogenic reaction between water and ammonia, namely,



where I represents the intermediate.

In contrast to the solvolytic reactions and the carboxylic acid equilibria mentioned above, the notion that an intermediate exists in the ammonia reaction has had a long and interesting history. Such a proposal formed the basis for the work reported by Moore and Winnill^{4,5} early in this century. Their work was reviewed sympathetically in two treatises by Sidgwick^{6,7} although a revised, posthumous edition⁸ of one of them gives a less detailed account of Moore's work. Writing in 1973, Bell⁹ is much less enthusiastic than Sidgwick and claims that Moore and Winnill's work is "based on unverifiable assumptions about the distribution coefficients of the individual species". The related work of Khakham¹⁰ is also dismissed with the added comment that the Russian contribution is in conflict with that of the British investigators. Bell apparently overlooked an important contribution by Patterson¹¹ and co-workers in which all the evidence^{12,13} for the existence of

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