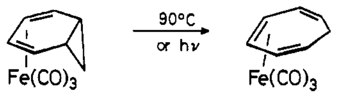
Hz, C-3, -4), 65.9 (^1J = 159.9 Hz, C-2, -5), 15.1 (^1J = 155.0, 156.3 Hz, C-7), 7.8 (^1J = 163.6 Hz, C-1, -6).[15]

The anti configuration of the iron tetracarbonyl group in **3** is deduced from the small shielding of the cyclopropane protons by the metal. The mechanism of the ring opening[9,16] then brings the metal syn to the cyclopropane ring in the norcaradiene complex **4**. This assignment is confirmed by the shielding of the cyclopropane proton H-7s that adsorbs at a 1.0 ppm higher field than the same proton in the trimethylene-bridged norcaradieneiron tricarbonyl[17] with the metal in the anti position.

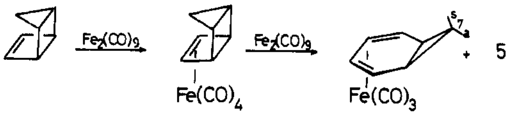
The opening of the bicyclohexene unit in **1** at room temperature with an excess (**5**)[5] diiron nonacarbonyl is unexpected, but it agrees with the proposed mechanism of this process:[9,16] In the rate-determining step a carbonyl group is lost from the tetracarbonyl complex **3** to form the di-η-iron tricarbonyl intermediate which opens readily. The starting dissociation can be activated by heat but also by the "carbonylophile" iron tetracarbonyl that is generated from dissolved $Fe_2(CO)_9$ at room temperature. Accordingly, the isolated tricyclic iron tetracarbonyl complex **3** is transformed into the norcaradiene complex **4** by stirring with diiron nonacarbonyl at room temperature.

At 90.5 °C in benzene solution *syn*-norcaradieneiron tricarbonyl (**4**) cleanly rearranges to cycloheptatrieneiron tricarbonyl (**5**)[5] in a first-order reaction with $k_{90.5} = (2.51 \pm 0.03) \times 10^{-5}$ s^{-1}.



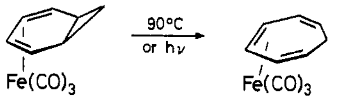
4 5

Treatment of *syn*-tricyclo[3.2.0.0^{2,4}]hept-6-ene (**2**) with diiron nonacarbonyl in the same way as above gives after chromatography with hexane on alumina a 5% yield of the iron tetracarbonyl complex **6**:[13] ^{1}H NMR (C_6D_6) δ 3.32 (s, H-6, -7), 2.57 (d, J = 5 Hz, H-1, -5), 1.65 (d, J = 6 Hz, H-3s), 1.49 (m, H-2, -4), 0.34 (q, J = 6 Hz, H-3a) followed by a mixture (17%) of *anti*-norcaradieneiron tricarbonyl (**7**) and cycloheptatrieneiron tricarbonyl (**5**). After protonation of the latter with 1 equiv of trifluoroacetic acid in benzene solution, filtration over alumina and evaporation of solvent furnishes a 10% yield of pure **7**:[13] ^{1}H NMR (C_6D_6) δ 4.82 (AA′ part of AA′XX′ system, H-3, -4), 3.24 (XX′ part, H-2, -5), 1.0 (m, H-1, -6, -7a), 0.79 (m, H-7s). The proton chemical shifts of **7** are close to those of the *anti*-norcaradieneiron tricarbonyl with a trimethylene bridge[17] and corroborate its structure.



2 6 7

anti-Norcaradieneiron tricarbonyl (**7**) is of similar thermal stability as its syn stereoisomer and opens to cycloheptatrieneiron tricarbonyl (**5**) at 90.5 °C with the first-order rate constant $k_{90.5} = (3.16 \times 0.1)10^{-5}$ s^{-1}.



7 5

The isomerizations of **4** and **7** prove that indeed norcaradiene is less stable than cycloheptatriene also when bonded to the iron tricarbonyl group, but their slow rates rule out either of them as reaction path for the ca. 10^8 times faster 1,3-metal shift in cycloheptatrieneiron tricarbonyl.[6] Irradiation of **4** or **7** in degassed THF solution with a high-pressure mercury lamp through Pyrex also effects their clean rearrangement into **5**.

In short, we have shown that norcaradiene can be frozen out as ligand in a stereoisomeric pair of iron tricarbonyl complexes which may prove a convenient storing form, since methods for its liberation at low temperatures are envisionable.

Acknowledgment. We thank the Fonds der Chemischen Industrie and the Verein der Freunde and Förderer der Universität Köln for unspecified financial support.

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[15] We thank Professor H. Günther, Universität Siegen, for the NMR spectra of **4** and their analysis.

[16] Pinhas, A. R.; Carpenter, B. K. *J. Chem. Soc., Chem. Commun.* **1980**, 15.

[17] Bleck, W.-E.; Grimme, W.; Günther, H.; Vogel, E. *Angew. Chem.* **1970**, *82*, 292. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 303.

High-Field ^{17}O NMR Spectroscopy: Solution Structures and Dynamics of ^{17}O Enriched $Co_4(CO)_{12}$ and $HFeCo_3(CO)_{12}$

S. Aime and D. Osella

Istituto di Chimica Generale ed Inorganica
Università di Torino, Italy

L. Milone

Istituto di Chimica Generale ed Inorganica
Università di Pavia, Italy

G. E. Hawkes and E. W. Randall*

Chemistry Department, Queen Mary College
London, England

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We have combined the advantages of ^{17}O NMR studies of metal carbonyl clusters[1] with the benefits of work at high magnetic field (9.4 T) on ^{17}O enriched samples.[2] This has enabled us to resolve the longstanding problem of the solution structure and dynamics of $Co_4(CO)_{12}$. The solid-state structure determined by X-ray analysis[3] has C_{3v} symmetry (see Figure 1) in which there are four equally populated CO environments (apical, two types of basal terminal, and one type of basal bridging) and two Co environments (apical and basal) in the ratio of 1:3. The structure in solution has presented problems since, although a complete analysis of the infrared spectrum[4] and observation of the ^{59}Co spectrum (two resonances, 1:3)[5,6] are in agreement with the C_{3v} structure, the ^{13}C NMR spectrum[5,7] is anomalous, giving three equally intense signals consistent with a D_{2d} structure.[7,8] This uncertainty has been partially removed by comparison of the exact ^{13}C shift of the single peak produced in the high temperature limiting spectrum,[9] which is consistent with C_{3v} symmetry. Studies based on

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(1) The advantages are that metal carbonyls have narrow ^{17}O lines compared with most organic samples, line widths can be more favorable even than for ^{13}C if a quadrupolar metal is involved, and the temperature range for the study of fluxional dynamics therefore can be extended. Aime, S.; Milone, L.; Osella, D.; Hawkes, G. E.; Randall, E. W. *J. Organomet. Chem.* **1979**, *178*, 171–175.

(2) The instrument was a Bruker WH-400 operating at 9.4 T and 54.25 MHz for ^{17}O. Samples were contained in 10-mm sealed tubes and the $CDCl_3$ solvent provided the ^{2}D lock signal. The combination of high-field and enriched samples gave high sensitivity for a small number of pulses, <1000.

(3) Wei, C. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1966**, *88*, 1821–1822. Carré, R. H.; Cotton, F. A.; Frenz, B. A. *Inorg. Chem.* **1976**, *15*, 380–387.

(4) Bor, G.; Sbrignadello, G.; Noack, K. *Helv. Chim. Acta* **1975**, *58*, 815–833.

(5) Cohen, M. A.; Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 4408–4409.

(6) Lucken, E. A. C.; Noack, K.; Williams, D. F. *J. Chem. Soc. A* **1967**, 148–154.

(7) Evans, J.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W. *J. Am. Chem. Soc.* **1975**, *97*, 1245–1247.

(8) This was proposed also on the basis of infrared studies by: Smith, D. L. *J. Chem. Phys.* **1965**, *42*, 1460–1461.

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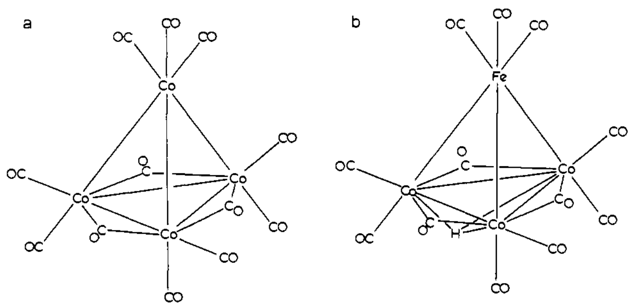

Figure 1. (a) C_{3v} structure for $Co_4(CO)_{12}$. (b) Comparable structure for $HFeCo_3(CO)_{12}$.

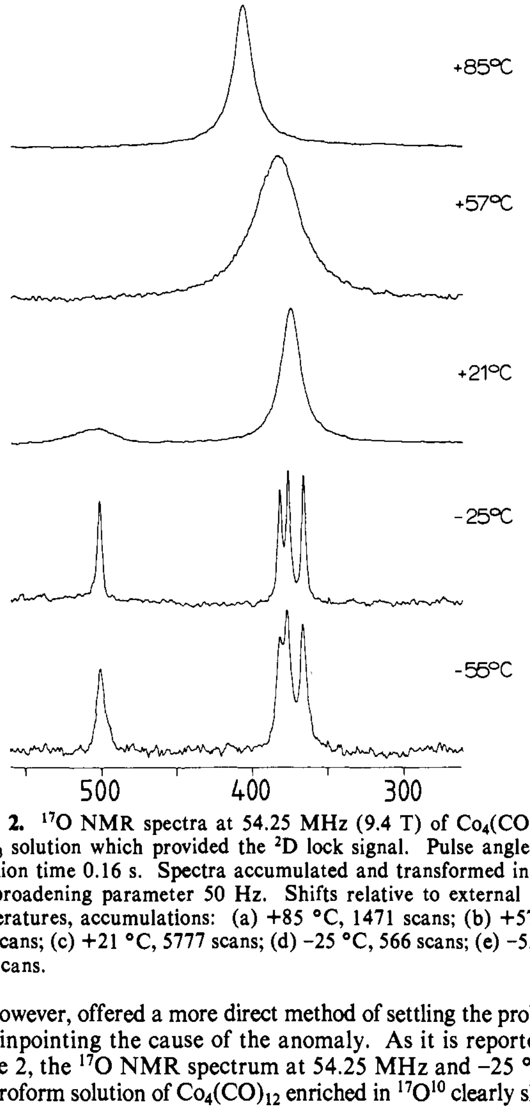

Figure 2. ^{17}O NMR spectra at 54.25 MHz (9.4 T) of $Co_4(CO)_{12}$ in $CDCl_3$ solution which provided the ^2D lock signal. Pulse angle 90°, repetition time 0.16 s. Spectra accumulated and transformed in 8 K. Line broadening parameter 50 Hz. Shifts relative to external H_2O. Temperatures, accumulations: (a) +85 °C, 1471 scans; (b) +57 °C, 1246 scans; (c) +21 °C, 5777 scans; (d) -25 °C, 566 scans; (e) -55 °C, 1452 scans.

^{17}O, however, offered a more direct method of settling the problem and pinpointing the cause of the anomaly. As it is reported in Figure 2, the ^{17}O NMR spectrum at 54.25 MHz and -25 °C of a chloroform solution of $Co_4(CO)_{12}$ enriched in ^{17}O[10] clearly shows four CO resonances with shifts of 501.2, 381.5, 375.9, and 365.8 ppm (relative to water as external reference). The C_{3v} structure is thus confirmed. There are two interesting NMR features of general importance. Firstly the bridging CO gives a low field ^{17}O resonance which has a shift difference from the nearest resonance produced by a terminal CO of nearly 119.7 ppm. This is significantly larger than the corresponding ^{13}C shift difference of 47.7 ppm and renders ^{17}O work even more useful than ^{13}C work is for fluxional studies. Secondly, the line of the bridging carbonyls is relatively narrow (190 Hz), being nearly as narrow as the terminal carbonyl lines (~160 Hz) and much narrower than the resonances of organic ketones which can be as broad as 0.5–1.0 kHz. This observation means that the promise of high-resolution ^{17}O studies of terminal COs can now be extended to the bridging COs and hence to the study of fluxional processes involving both. The line widths of $Co_4(CO)_{12}$ are, however, greater than those observed for mononuclear metal carbonyls,[1] and progressive broadening at low temperatures due to the increased quadrupole relaxation of ^{17}O is observed (see spectrum at -55 °C in Figure 2).[11] Nevertheless this broadening is insufficient to prevent the full resolution of the four resonances in the slow exchange limit. The advantage here of the large shifts arising from the combined use of a high magnetic field and ^{17}O as the observing nucleus, giving a 6.4-kHz separation of bridging and terminal resonances, is clear. Increase of the temperature of the sample yields spectra which show broadening due to exchange. The nature of the broadening is nonselective and is therefore consistent with the suggestion that the T_d structure is involved in the exchange mechanism as suggested earlier by Cotton in the seminal paper that predicted the whole phenomenon of carbonyl scrambling.[12] The sharpening as the high temperature limit is approached is shown in the spectrum at +85 °C where the single line has a shift of 402.8 ppm compared to the calculated average of the four lines which gives a value of 406.1 ppm. The success of this study led us to investigate the related compound $HFeCo_3(CO)_{12}$ for which

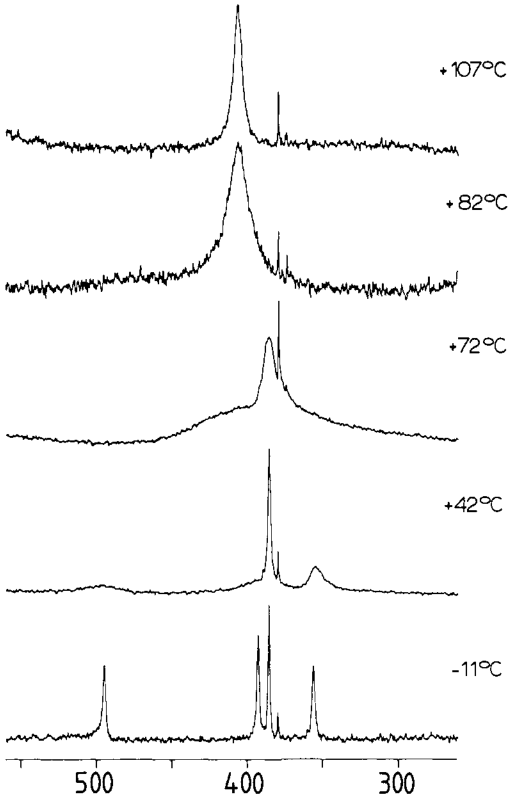

Figure 3. ^{17}O NMR spectra at 54.25 MHz (9.4 T) of $HFeCo_3(CO)_{12}$. Conditions as in Figue 2 except line broadening parameter 25 Hz; (a) toluene-d_8 solution, +107 °C, 5345 scans; (b) toluene-d_8, +82 °C, 21 938 scans; (c) $CDCl_3$ solution, +72 °C, 28 789 scans; (d) $CDCl_3$, +42 °C, 6983 scans, and (e) $CDCl_3$, -11 °C, 1000 scans. Peaks marked with an asterisk are impurity peaks.

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(9) At -66 °C the observed ^{13}C shifts are 242.6, 195.6, and 192.5 ppm. The observation of the single peak of the collapsed spectrum at high temperature required the use of a high viscosity solvent to offset the quadrupole broadening and yielded a shift of 206.1 ppm. This is consistent with a value of 206.6 ppm calculated from a weighting of 1:2:1 for the three peaks observed at low temperature (or 205.8 ppm with the 1:1:2 weighting) which would be appropriate for an accidental degeneracy of two terminal resonances. The intensity anomaly in the low temperature limit, however, remains. See: Aime, S.; Milone, L.; Poli, A.; Osella, D. *Inorg. Chim. Acta* **1978**, *30*, 45–49.

(10) Enrichment was accomplished by stirring the unenriched compound in hexane in the presence of 36% ^{17}O enriched CO gas at <1-atm pressure for 3 days at about 30 °C. The ^{17}O enriched CO was supplied by Prochem.

(11) The lowest field line at 501.2 ppm relative to water has the following line widths at half-height: 190 Hz at -25 °C, 240 Hz at -38 °C, and 325 Hz at -60 °C. The highest field line gives the sequence 162, 180, and 260 Hz for the same temperatures.

(12) Cotton, F. A. *Inorg. Chem.* **1966**, *5*, 1083–1085.

the solid-state structure has been inferred to be similar to that for $Co_4(CO)_{12}$ (C_{3v}) with an apical $Fe(CO)_3$ 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 °C). This process we take to be the in-plane exchange or merry-go-round process[14] 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 °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.

Acknowledgment. We are grateful to C.N.R. for support (Grant 8000334) and the University of London and S.R.C. for the use of the Bruker WH-400 at Queen Mary College under the ULIRS scheme.

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(13) The solid-state structure for the trisubstituted derivative $HFeCo_3(CO)_9[P(OCH_3)_3]_3$ 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.

(14) Cotton, F. A.; Hanson, B. E. In "Rearrangements in ground and excited state"; Academic Press: New York, 1980; Vol. 2, pp 379-421.

1,3-Dimetallacyclobutanes in Metal-Methylidene Dimerization Reactions

Kevin C. Ott and Robert H. Grubbs*

Contribution No. 6464, Laboratories of Chemistry
California Institute of Technology
Pasadena, California 91125

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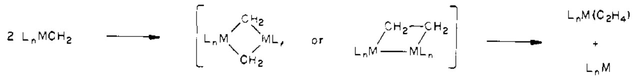
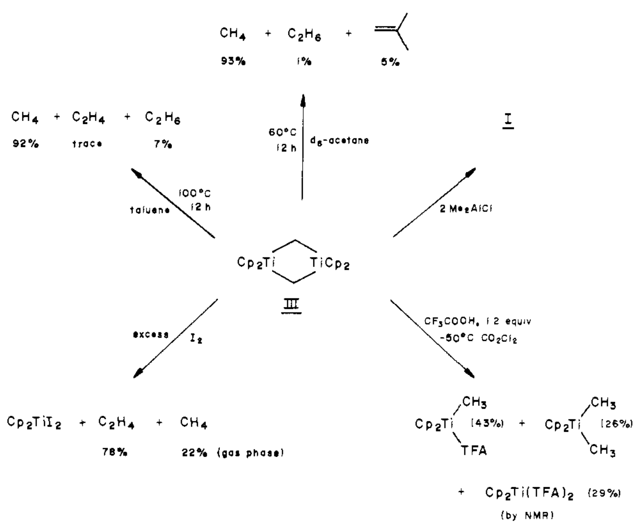
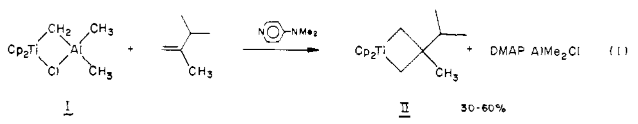
The attempted synthesis of metal-carbene or -alkylidene complexes often results in formation of olefins or metal-olefin complexes arising from metal-carbene dimerization.[1a] Decomposition of isolated metal carbenes and alkylidenes also produces olefinic products, presumably through either dimetallacyclic[1b] or bis(carbenemetal)[1c] intermediates. Such decompositions have been proposed to be involved in catalyst deactivation in the olefin metathesis reaction[2] and may serve as models for methylene oligomerization on metal surfaces in the Fischer-Tropsch reaction.[3]



Scheme I

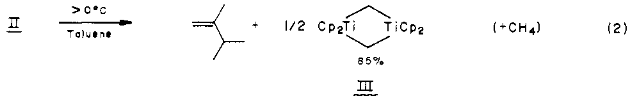


A stable, 1,3-dimetallacyclobutane has now been isolated in good yield from an olefin metathesis system[4] which is thought to generate a metal methylidene intermediate. As reported previously,[5] titanacyclobutanes can be isolated from the reaction of I with monosubstituted olefins and Lewis bases. This has proven



(1)

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 hydrocarbons[7] above 0 °C, the solutions become purple, and purple-red platelets deposit.[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-



(2)

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(1) (a) Fischer, E. O.; Plabst, D. *Chem. Ber.* **1974**, *107*, 3326. (b) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389. (c) Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 895.

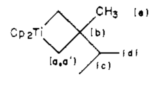
(2) Grubbs, R. H.; Hoppin, C. R. *J. Chem. Soc., Chem. Commun.* **1977**, 634.

(3) See, for example: Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61.

(4) Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 5074.

(5) Lee, J. B.; Howard, T. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876.

(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, $H_{a,a'}$), 0.801 (d, J = 5.5 Hz, H_d), 0.753 (heptet, J = 5.5 Hz, H_c), 0.701 (s, H_e); ^{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_a), 42.7 (d, J = 130 Hz, C_c), 25.1 (q, J = 124 Hz, C_e), 19.4 (q, J = 124 Hz, C_d), 13.4 (s, C_b).

(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 rapidily stirred pentane at 0 °C. The resulting suspension was filtered rapidly to remove the DMAP·$AlMe_2Cl$, 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.

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