Coupling of Isoprene and Trimethylenemethane Ligands To Form a Novel Type of 6-Methylene-2-heptene-1,7-diyl Ligand: X-ray Structure of $[Fe(CO)_2\{\eta^3\text{-}(CH_2)_2C\}CH_2CH_2\{\eta^3\text{-}CHC(Me)CH_2\}]$

Luc Girard and Michael C. Baird*

Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

Brian S. Haggerty and Arnold L. Rheingold*

Department of Chemistry, University of Delaware, Newark, Delaware 19716

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Summary: The compound $[Fe(CO)_2\{\eta^3\text{-}(CH_2)_2C\}CH_2CH_2\{\eta^3\text{-}CHC(Me)CH_2\}]$ is formed by treating $[(TMM)Fe(CO)_3]$ (TMM = η^4-trimethylenemethane) with isoprene in the presence of trimethylamine oxide.

We have previously shown that a variety of compounds of the type $(\eta^4\text{-TMM})Fe(CO)_2L$ (η^4-TMM = η^4-$C(CH_2)_3$; L = *t*-BuNC, tertiary phosphines) may be readily prepared by treating the parent tricarbonyl compound $(\eta^4\text{-TMM})Fe(CO)_3$ with L in the presence of trimethylamine oxide.[1] We have now carried out similar reactions of $(\eta^4\text{-TMM})Fe(CO)_3$ with olefins, finding that conjugated diolefins react to form heat- and air-stable products which are a result of very novel coupling of dienes with the TMM ligand.

A solution of $(\eta^4\text{-TMM})Fe(CO)_3$ (formed from 1 g (4.7 mmol) of $Na_2Fe(CO)_4$),[1] isoprene (2 mL, 20 mmol), and $Me_3NO{\cdot}2H_2O$ (5.2 g, 47 mmol) in 40 mL of THF was refluxed for ~16 h. The reaction mixture was then passed through a silica column, and a yellow band of the product, I, was eluted with petroleum ether (bp 30–60 °C). The solvent was removed, and X-ray-quality crystals were obtained by sublimation at 65 °C. The new orange compound, I, has the stoichiometry $(TMM)Fe(CO)_2(isoprene)$, and its IR spectrum (petroleum ether, bp 30–60 °C) exhibits two narrow carbonyl stretching bands, of equal intensity, at 1990 and 1931 cm^{-1}, consistent with the OC–Fe–CO bond angle being about 90°.[2] However, the ^1H and $^{13}C\{^1H\}$ NMR spectra of I indicate clearly that a simple η^2-isoprene complex has not been formed, since no resonances attributable to free olefinic hydrogen or carbon atoms are observed.

Mindful of the report that $(TMM)Fe(CO)_3$ reacts with C_2F_4 to form $[Fe(CO)_3\{\eta^3{:}\eta^1\text{-}(CH_2)_2CCH_2CF_2CF_2\}]$, in which the TMM and C_2F_4 fragments have coupled,[3] we considered but rejected the possibility that the TMM and isoprene had coupled to form the analogous compound $[Fe(CO)_3\{\eta^3{:}\eta^1\text{-}(CH_2)_2C\}CH_2CH_2CH{=}C(Me)CH_2]$, containing the 2-methyl-6-methylene-2-heptene-1,7-diyl ligand. The IR spectrum of I differs from that of the C_2F_4 adduct in that the latter exhibits three carbonyl stretching bands[3] and so, presumably, would the IR spectrum of $[Fe(CO)_3\{\eta^3{:}\eta^1\text{-}(CH_2)_2C\}CH_2CH_2CH{=}C(Me)CH_2]$. Furthermore, the ^1H and ^{13}C NMR spectra of $[Fe(CO)_3(\eta^3{:}\eta^1\text{-}(CH_2)_2C\}CH_2CH_2CH{=}C(Me)CH_2]$ would exhibit free olefinic resonances.

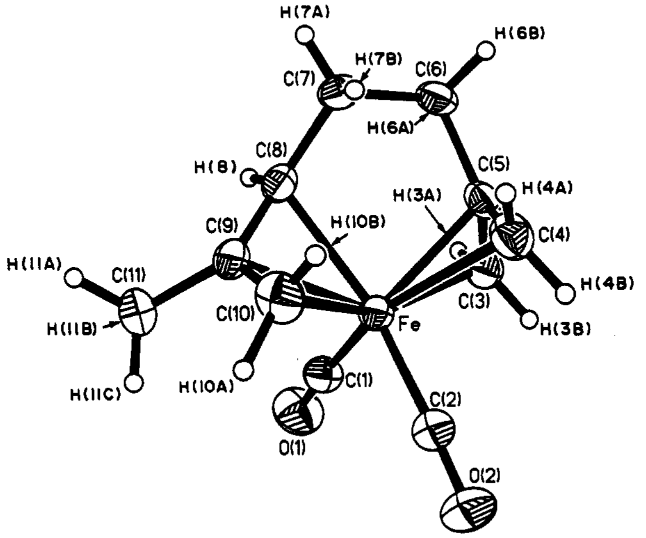
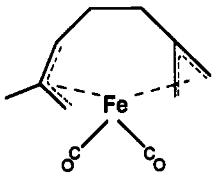
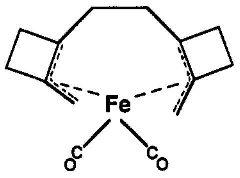


Figure 1. ORTEP drawing and labeling scheme for I. Ellipsoids are drawn at 35% probability; hydrogens are at a fixed radius for clarity. Values of selected interatomic distances (Å) and angles (deg) are as follows: Fe–C(1) = 1.754 (4), Fe–C(2) = 1.780 (4), Fe–C(3) = 2.125 (4), Fe–C(4) = 2.209 (4), Fe–C(5) = 2.090 (4), Fe–C(8) = 2.139 (4), Fe–C(9) = 2.094 (4), Fe–C(10) = 2.135 (4); C(1)–Fe–C(2) = 92.0 (2).

We therefore considered a compound in which the same ligand would coordinate to the iron in an $\eta^3{:}\eta^3$-diallylic fashion, denoted schematically as A and readily derived from the above-mentioned $\eta^3{:}\eta^1$ species by loss of one CO.



A



B

Consistent with this structure, all 11 non-methyl hydrogen atoms are nonequivalent, as are both carbonyl groups and all nine carbon atoms of the TMM and isoprene moieties. A *J*-modulated spin-echo experiment[4] indicated that I contains one CH_3, five CH_2, one CH, and two quaternary carbon atoms, compatible with A, and we note that the carbonyl stretching bands of I are almost identical with those of the rather similar compound B[5] (1991, 1935 cm^{-1}). The ^1H resonances of I were found to exhibit only first-order coupling patterns at 400 MHz, and thus it was readily possible to combine selective decoupling, COSY, HETCOR, and NOE difference experiments[4] to assign the

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(1) Girard, L.; MacNeil, J. H.; Mansour, A.; Chiverton, A. C.; Page, J. A.; Fortier, S.; Baird, M. C. *Organometallics* 1991, *10*, 3114.

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(5) King, R. B.; Harmon, C. A. *J. Am. Chem. Soc.* 1976, *98*, 2409.

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resonances of all of the proton and proton-bearing carbon atoms.[6]

The NOE difference experiments were especially informative, as irradiation of the resonance of H(4A) resulted in enhancement of the intensity of the resonance of H(10B); since these two H atoms are at opposite ends of the organic ligand, the result suggests a structure in which the diallylic ligand wraps around the metal atom. This conclusion was supported by molecular mechanics (MMX[7]) calculations and subsequently confirmed by X-ray crystallographic analysis.[8]

The structure of I (Figure 1) contains two mutually cis carbonyl groups, the C(1)–Fe–C(2) bond angle being 92.0 (2)°. The hydrocarbon framework is coordinated to the iron via the two η^3-allyl groups C(3)–C(5) and C(8)–C(10), involving the former TMM and isoprene constituents, respectively. The Fe–C(4) bond is marginally longer than the other iron–allyl bonds, but all are typical of (η^3-allyl)iron compounds in general.[9] Interestingly, I is much more thermally stable than is $Fe(CO)_2(\eta^3\text{-allyl})_2$,[10] which is reported to reductively eliminate diallyl at above room temperature. Presumably the ethylene backbone joining the two η^3-allylic fragments prevents intramolecular rearrangement to the orientation necessary for coupling and decoordination, although an oscillatory motion involving rotation about the C(6)–C(7) bond and comcomitant mutual reorientation of the two η^3-allyl–iron linkages seems likely since the resonances of H(6A,B) and H(7A,B) exhibit temperature-dependent chemical shifts.

The formation of I presumably involves initial coordination of the unsubstituted end of the isoprene, since trimethylamine oxide is required for the reaction to occur. Details of the subsequent coupling step are not obvious, but we note several apparently similar, photochemically induced coupling reactions of C_2F_4 to coordinated TMM[3] and η^4-diene ligands[11] and of conjugated dienes to pentadienyl ligands.[12] Preliminary investigations of reactions of $(TMM)Fe(CO)_3$ with 2,3-dimethyl-1,3-butadiene and 1,3-butadiene suggest that the former yields a compound analogous to I while the latter yields a tricarbonyl compound, not yet identified.

Acknowledgment. Financial support from the Natural Sciences and Engineering Research Council (operating and equipment grants to M.C.B.) and Queen's University (graduate fellowship to L.G.) made this research possible.

Supplementary Material Available: Complete tables of atomic positional and thermal parameters, bond lengths and angles, and anisotropic thermal parameters for I (5 pages). Ordering information is given on any current masthead page.

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[6] See Figure 1 for the numbering scheme. ^{13}C NMR resonances (C_6D_6): δ 219.2 (CO), 216.5 (CO), 123.5 (C(5) or C(9)) 109.5 (C(9) or C(5)), 76.7 (C(8)), 64.0 (C(4)), 45.3 (C(3)), 45.2 (C(10)), 39.1 (C(6)), 32.1 (C(7)), 27.4 (C(11)). ^1H NMR resonances (C_6D_6): δ 3.16 (d, H(3A)), 3.07 (dd, H(10A)), 3.04 (dd, H(8)), 2.76 (br s, H(10B)), 2.24 (d, H(4A)), 2.18 (br s, H(3B)), 2.15 (br s, H(4B)), 2.07 (dd, H(6B)), 1.79 (dddd, H(6A)), 1.49 (s, H(11A,B,C)), 1.36 (ddd, H(7A)), 0.66 (dddd, H(7B)); $J_{3A-4A} = 3.3$, $J_{4B-6A} = 1.5$, $J_{6A-6B} = 12.2$, $J_{6A-7A} = 4.8$, $J_{6A-7B} = 14.2$, $J_{6B-7B} = 5.0$, $J_{7A-7B} = 13.2$, $J_{7A-8} = 6.3$, $J_{7B-8} = 10.8$, $J_{8-10A} = 1.5$, $J_{10A-10B} = 1.5$ Hz.

[7] Available as PCMODEL from Serena Software, Bloomington, IN. See: Gajewski, J. J.; Gilbert, K. E.; McKelvey, J. *Adv. Mol. Model.* 1990, 2, 65.

[8] Crystal Data: $C_{11}H_{14}FeO_2$, $M_r = 234.06$, monoclinic, space group $P2_1/c$, $a = 8.8800$ (12) Å, $b = 8.9197$ (12) Å, $c = 13.5091$ (17), $\beta = 95.642$ (11)°, $V = 1064.82$ (24) Å^3, $Z = 4$, $D_c = 1.460$ g cm^{-3}, $F(000) = 488$, μ(Mo Kα) = 13.86 cm^{-1}, $R = 0.0401$ ($R_w = 0.0466$) for 2440 observed data (298 K, Wyckoff ω scans, $2\theta \leq 55°$, $F \geq 4\sigma(F)$). Data were collected using a Siemens P4 diffractometer (298 K, Mo Kα radiation, $\lambda = 0.71073$ Å). The data were corrected for Lorentz and polarization effects, and the structures were solved using direct methods (SHELXTL PLUS program). Complete details will be published in a full paper.

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Oxidative Addition of Germanium–Germanium and Germanium–Chlorine Bonds to $Pt(PEt_3)_3$ and Unexpected Germylene Generation from the Resulting Bis(chlorogermyl)platinum Complex

Hiroshi Yamashita, Toshi-aki Kobayashi, and Masato Tanaka*
National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305, Japan

John A. Samuels and William E. Streib
Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

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Summary: Reactions of $ClMe_2GeGeMe_2Cl$ and Me_2GeCl_2 with $Pt(PEt_3)_3$ proceeded to give *cis*-/*trans*-$(ClMe_2Ge)_2Pt(PEt_3)_2$ (**1**) and *trans*-$(ClMe_2Ge)PtCl(PEt_3)_2$ (**2**), respectively. The structure of *cis*-**1** was determined by crystallography. Thermolysis of a cis/trans mixture of **1** afforded **2** with release of dimethylgermylene, which could be trapped by benzil to give a 1,3-dioxa-2-germa-4-cyclopentene species.

In view of the growing interest in group 14 metal-based materials and reagents,[1] understanding of the reactivities

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