Communications to the Editor

Synthesis and X-ray Crystal Structure of (1,2,4,5-Tetramethylenebenzene)$Fe_3(CO)_9$: A Metal-Stabilized Disjoint Hydrocarbon

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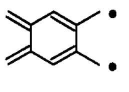
1,2,4,5-Tetramethylenebenzene (TMB), **1**, has attracted considerable recent attention because of its status as a disjoint, non-Kekulé biradical.[1] There has been some discussion concerning the singlet or triplet character of the diradical, but the most recent report provides strong evidence for a singlet ground state.[2] TMB is generated as a transient species via photolysis of ketone **2**, which is obtainable in an overall yield of ≈3%.[3] The possibility had been considered that decarbonylation of **2** might yield tetramethylenebicyclo[2.2.0]hexane, **3**; however, convincing arguments have been advanced which reject this hypothesis.[4] It was, therefore, interesting to note a literature claim that a bis(tricarbonyliron) complex of **3** is apparently isolable from the reaction of tetrabromodurene with $Fe_2(CO)_9$ or $Na_2Fe(CO)_4$.[5] In the absence of unequivocal confirmation of the structure of this complex, we chose to repeat the reported synthesis with a view to obtaining X-ray crystallographic data on the product.



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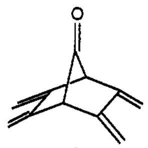

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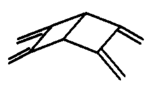

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Accordingly, tetrabromodurene was treated with $Na_2Fe(CO)_4$ in THF (or $Fe_2(CO)_9$ in pentane) and yielded, after chromatographic separation, two new crystalline products. One was identified spectroscopically[6] and crystallographically[7] as the (dimethyl-*o*-xylylene)$Fe(CO)_3$ complex **4**. The X-ray structure (Figure 1) closely resembled that of the parent molecule, **5**, previously synthesized by Roth and Meier[8] and structurally characterized by Batzanov *et al.*[9]

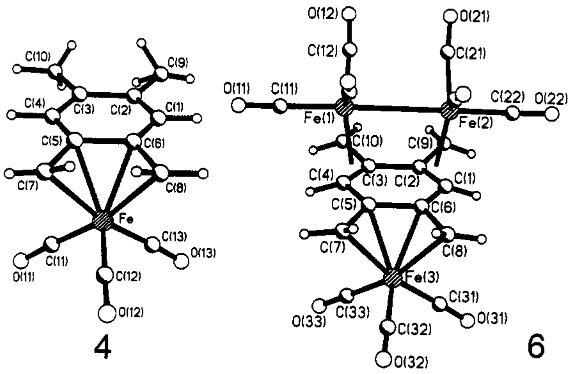
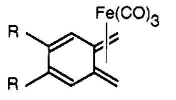
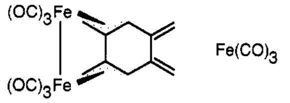


Figure 1. Views of $(C_{10}H_{12})Fe(CO)_3$, **4**, and $(C_{10}H_{10})Fe_3(CO)_9$, **6**, showing the atom numbering system. Selected distances (Å): **4**, C(1)–C(2) 1.349(5), C(2)–C(3) 1.430(4), C(3)–C(4) 1.354(4), C(4)–C(5) 1.426(5), C(5)–C(6) 1.434(4), C(6)–C(1) 1.426(4), C(2)–C(9) 1.507(5), C(3)–C(10) 1.508(6), C(5)–C(7) 1.439(4), C(6)–C(8) 1.430(6). **6**, C(1)–C(2) 1.420(3), C(2)–C(3) 1.463(2), C(3)–C(4) 1.413(3), C(4)–C(5), 1.455(3), C(5)–C(6) 1.421(3), C(6)–C(1) 1.460(3), C(2)–C(9) 1.406(4), C(3)–C(10) 1.418(4), C(5)–C(7) 1.421(3), C(6)–C(8) 1.428(3).



4: R = Me
5: R = H
7: R = CH_2Br



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The mass spectrum of the second product, **6**, yielded the molecular formula $(C_{10}H_{10})Fe_3(CO)_9$,[10] and the X-ray crystal structure[11] (Figure 1) revealed the molecule to be a metal-stabilized 1,2,4,5-tetramethylenebenzene complex. The TMB ligand in **6** possesses two allyl moieties spanned by an $[\eta^3:\eta^3\text{-}(OC)_3Fe\text{-}Fe(CO)_3]$ fragment while the remaining two exocyclic methylenes are coordinated to a single $Fe(CO)_3$ unit, as in **4**. The bis(allyl)$Fe_2(CO)_6$ structural motif has previously been char-

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(1) (a) Reynolds, J. H.; Berson, J. A.; Scaiano, J. C.; Berinstain, A. B. *J. Am. Chem. Soc.* **1992**, *114*, 5866 and references therein. (b) Roth, W. R.; Langer, R.; Ebbrecht, T.; Beitat, A.; Lennartz, H.-W. *Chem. Ber.* **1991**, *124*, 2751 and references therein. (c) Du, P.; Hrovat, D. A.; Borden, W. T.; Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 5072.

(2) Reynolds, J. H.; Berson, J. A.; Kumashiro, K. K.; Duchamp, J. C.; Zilm, K. W.; Scaiano, J. C.; Berinstain, A. B.; Rubello, A.; Vogel, P. *J. Am. Chem. Soc.* **1993**, *115*, 8073.

(3) Rubello, A.; Vogel, P. *Helv. Chim. Acta* **1988**, *71*, 1268.

(4) Liu, R.; Zhou, X.; Hinton, J. *J. Am. Chem. Soc.* **1992**, *114*, 6925.

(5) (a) Khan, S. M. A.; Ullah, S. S. *Ind. J. Chem.* **1985**, *24A*, 607. (b) Khan, S. M. A.; Ullah, S. S. *Ind. J. Chem.* **1987**, *26A*, 831.

(6) **4**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.22 (s, 2H, $H_{1,4}$), 2.41 (d 3 Hz, 2H, *exo*-$H_{7,8}$), 2.30 (s, 6H, $Me_{9,10}$), 0.22 (d 3 Hz, 2H, *endo*-$H_{7,8}$); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 213 (CO), 130.5 ($C_{1,4}$), 35.1 ($C_{7,8}$), 20.4 ($C_{9,10}$ Me's); mass spectrum, *m/z* 272 (9) $(M)^+$, 244 (22) $(M - CO)^+$, 216 (22) $(M - 2CO)^+$, 188 (100) $(M-3CO)^+$, 160 (15) $(M-2CO-Fe)^+$, 132 (21) $(C_{10}H_{12})^+$; IR (CH_2Cl_2) ν_{CO} 2051, 1982 cm^{-1}.

(7) Crystal data for **4** at 27 °C: monoclinic, space group $P2_1/n$, $a = 13.619(2)$ Å, $b = 5.8150(10)$ Å, $c = 17.006(2)$ Å, $\beta = 113.44°$, $V = 1235.7(3)$ Å^3, $Z = 4$, $d_{calc} = 1.462$ g cm^{-3}. A total of 4189 with 3154 independent reflections were collected on a Siemens P4 diffractometer using graphite-monochromated Mo Kα radiation. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least squares; $R(F) = 0.038$ based on 2094 reflections with $|F| \geq 4\sigma F$.

(8) Roth, W. R.; Meier, J. D. *Tetrahedron Lett.* **1967**, 2053.

(9) Batsanov, A. S.; Zol'nikova, G. P.; Struchkov, Yu. T.; Kritskaya, I. *Koord. Khim.* **1987**, *13*, 1551.

(10) **6**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 4.04 (s, 2H, $H_{1,4}$), 2.08 (d 3 Hz, 2H, *exo*-$H_{7,8}$), 1.79 (d 3 Hz, 2H, *exo*-$H_{9,10}$), 1.75 (d 3 Hz, 2H, *endo*-$H_{9,10}$), –0.09 (d 3 Hz, 2H, *endo*-$H_{7,8}$); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 215, 213 (CO), 60.9 ($C_{1,4}$), 37.3, 32.1 ($C_{7,8}$, $C_{9,10}$); mass spectrum, *m/z* 550 (6) $(M)^+$, 522 (20) $(M - CO)^+$, 494 (16) $(M - 2CO)^+$, 466 (16) $(M - 3CO)^+$, 438 (10) $(M - 4CO)^+$, $(M - 2CO - Fe)^+$, 410 (30) $(M - 5CO)^+$, $(M - 3CO - Fe)^+$, 382 (68) $(M - 6CO)^+$, $(M - 4CO - Fe)^+$, 354 (32) $(M - 7CO)^+$, $(M - 5CO - Fe)^+$, 326 (32) $(M - 8CO)^+$, $(M - 6CO - Fe)^+$, 298 (66) $(M - 9CO)^+$, $(M - 7CO - Fe)^+$, 270 (40) $(M - 6CO - 2Fe)^+$, 242 (40) $(M - 9CO - Fe)^+$, $(M - 7CO - 2Fe)^+$, 130 (100) $(C_{10}H_{10})^+$. IR (CH_2Cl_2) ν_{CO} 2069 (w), 2050 (vs), 2027 (s), 2006 (m), 1992 (w), 1982 (w) cm^{-1}.

(11) Crystal data for **6** at 27 °C: monoclinic, space group $C2/c$, $a = 28.116(6)$ Å, $b = 11.072(2)$ Å, $c = 13.363(3)$ Å, $\beta = 99.37(3)°$, $V = 4104.4(15)$ Å^3, $Z = 8$, $d_{calc} = 1.780$ g cm^{-3}. A total of 6915 with 5973 independent reflections were collected on a Siemens P4 diffractometer using graphite-monochromated Mo Kα radiation. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least squares; $R(F) = 0.034$ based on 4324 reflections with $|F| \geq 4\sigma F$.

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acterized in a number of molecules,[12] and the geometric parameters of this fragment in **6** lie within the normal ranges. The C_{10} skeleton in **6** is not flat but instead tends toward a "chaise longue" conformation, and in each case the metallic fragment is *endo*; that is, the $Fe_2(CO)_6$ and $Fe(CO)_3$ units bind to opposite faces of the TMB ligand. The methylene groups are twisted; the $CH_2(9)$ and $CH_2(10)$ fragments rotate outward by ≈26°, while the $CH_2(7)$ and $CH_2(8)$ fragments turn inward by ≈40°.

To place these results in perspective, we note that, in their pioneering investigations,[3] Rubello and Vogel not only synthesized the precursor ketone **2** but also prepared a series of iron and rhodium complexes.[13] However, attempted decarbonylation of these latter molecules did not yield metal complexes of TMB, but led only to decomposition. EHMO calculations show that coordination of the $Fe_2(CO)_6$ fragment[14] to TMB leaves an exocyclic diene unit poised to react with an $Fe(CO)_3$ source, yielding a (diene)$Fe(CO)_3$ product. The experimental process, however, almost certainly occurs by initial formation of the [bis(bromomethyl)-*o*-xylylene](η^4-$Fe(CO)_3$), **7**, which possesses two contiguous allyl bromide functionalities appropriate for the generation of (TMB)$Fe_3(CO)_9$, **6**. The liberation of the free TMB ligand from **6** and the elucidation of its chemistry are the focus of current investigations.

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Supplementary Material Available: Details on the syntheses and crystal structure data of **4** and **6**, atom coordinates, thermal parameters, and bond distances and angles (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(13) Rubello, A.; Vogel, P. *Helv. Chim. Acta* **1989**, *72*, 158.

(14) The frontier orbitals of the $Fe_2(CO)_6$ fragment have been fully discussed previously: Thorn, D. L.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 126.