

Communications to the Editor

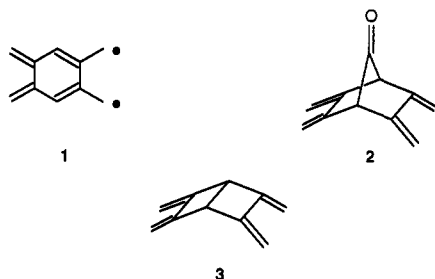
Synthesis and X-ray Crystal Structure of (1,2,4,5-Tetramethylenebenzene)Fe₃(CO)₉: A Metal-Stabilized Disjoint Hydrocarbon

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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 Fe₂(CO)₉ or Na₂Fe(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.



Accordingly, tetrabromodurene was treated with Na₂Fe(CO)₄ in THF (or Fe₂(CO)₉ in pentane) and yielded, after chromatographic separation, two new crystalline products. One was identified spectroscopically⁶ and crystallographically⁷ as the (dimethyl-*o*-xylylene)Fe(CO)₃ complex **4**. The X-ray structure

(1) (a) Reynolds, J. H.; Berson, J. A.; Scaiano, J. C.; Berinstein, A. B. *J. Am. Chem. Soc.* **1992**, *114*, 5866 and references therein. (b) Roth, W. R.; Langer, R.; Ebbrecht, T.; Beitatz, 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.; Berinstein, 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**: ¹H NMR (500 MHz, CD₂Cl₂) 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}); ¹³C NMR (125.7 MHz, CDCl₃) 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) (C₁₀H₁₂)⁺; IR (CH₂Cl₂) ν_{CO} 2051, 1982 cm⁻¹.

(7) Crystal data for **4** at 27 °C: monoclinic, space group *P2₁/n*, *a* = 13.619(2) Å, *b* = 5.8150(10) Å, *c* = 17.006(2) Å, β = 113.44°, *V* = 1235.7(3) Å³, *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*| ≥ 4σ_{*F*}.

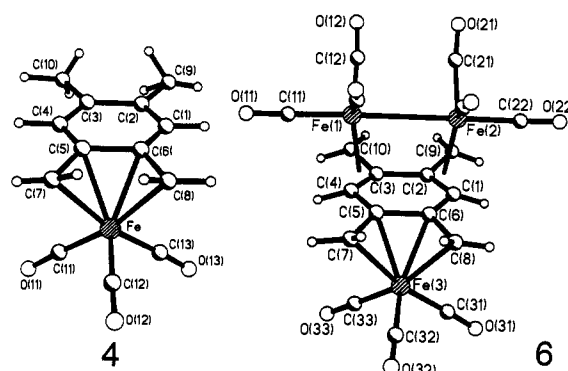
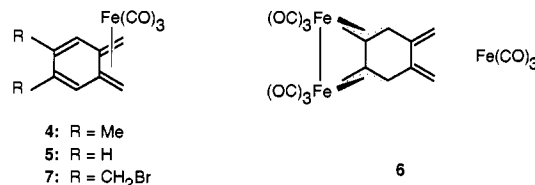


Figure 1. Views of (C₁₀H₁₂)Fe(CO)₃, **4**, and (C₁₀H₁₀)Fe₃(CO)₉, **6**, showing the atom numbering system. Selected distances (Å): **4**, C(1)–C(2) 1.349(5), C(2)–C(3) 1.430(4), C(3)–C(4) 1.354(4), C(4)–C(5) 1.426(5), C(5)–C(6) 1.434(4), C(6)–C(1) 1.426(4), C(2)–C(9) 1.507(5), C(3)–C(10) 1.508(6), C(5)–C(7) 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).

(Figure 1) closely resembled that of the parent molecule, **5**, previously synthesized by Roth and Meier⁸ and structurally characterized by Batzanov *et al.*⁹



The mass spectrum of the second product, **6**, yielded the molecular formula (C₁₀H₁₀)Fe₃(CO)₉,¹⁰ and the X-ray crystal structure¹¹ (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 [η³:η³-(OC)₃Fe-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)Fe₂(CO)₆ structural motif has previously been char-

(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**: ¹H NMR (500 MHz, CD₂Cl₂) 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}); ¹³C NMR (125.7 MHz, CDCl₃) 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) (C₁₀H₁₀)⁺. IR (CH₂Cl₂) 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, β = 99.37(3)°, *V* = 4104.4(15) Å³, *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*| ≥ 4σ_{*F*}.

acterized in a number of molecules,¹² and the geometric parameters of this fragment in **6** lie within the normal ranges. The C₁₀ 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 Fe₂(CO)₆ and Fe(CO)₃ units bind to opposite faces of the TMB ligand. The methylene groups are twisted; the CH₂(9) and CH₂(10) fragments rotate outward by ≈26°, while the CH₂(7) and CH₂(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 Fe₂(CO)₆ fragment¹⁴ to TMB leaves an exocyclic diene unit poised to react with an Fe(CO)₃ source,

(12) (a) Cotton, F. A.; DeBoer, B. G.; Marks, T. J. *J. Am. Chem. Soc.* **1971**, *93*, 5069. (b) Howell, J. A. S.; Lewis, J.; Matheson, T. W.; Russell, D. R. *J. Organomet. Chem.* **1975**, *99*, C55. (c) Begley, M. J.; Puntambekar, S. G.; Wright, A. H. *J. Chem. Soc., Chem. Commun.* **1987**, 1251. (d) Morita, N.; Kabuto, C.; Asao, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1677.

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

(14) The frontier orbitals of the Fe₂(CO)₆ fragment have been fully discussed previously: Thorn, D. L.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 126.

yielding a (diene)Fe(CO)₃ product. The experimental process, however, almost certainly occurs by initial formation of the [bis(bromomethyl)-*o*-xylylene](η⁴-Fe(CO)₃), **7**, which possesses two contiguous allyl bromide functionalities appropriate for the generation of (TMB)Fe₃(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.