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Iron carbonyl complexes of isobenzofulvene

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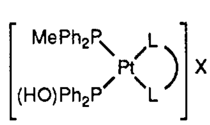
in its anion, **2** and **1** show large differences in phosphinous ^{31}P NMR chemical shift (16.4 ppm) and molar conductance (52 Ω^{-1} cm^2 mol^{-1}), suggesting that the chloride anion in **1** is probably associated with the cation through the acidic proton in P–OH. The interaction of a chloride anion with a coordinated P–OH proton has been reported.[8]



	L–L	X
1	$(CH_2)_2S(O)Me$	Cl
2	$(CH_2)_2S(O)Me$	PF_6
3	S_2CNEt_2	Cl
4	acetylacetonate	Cl

This phase-transfer catalyzed P–C bond cleavage of the dppm is general for other platinum complexes.[9] Treatment of $[Pt(dppm)(S_2CNEt_2)]Cl$ in CH_2Cl_2 with NaOH under PTC conditions gave the ionic compound **3**[10] in 88% yield. Similarly, compound **4**[11] can be formed in 60% yield from [Pt(dppm)(acac)]Cl (acac = acetylacetonate). On the other hand, this P–C bond cleavage is rather specific. Only dppm and not dppe (dppe = $Ph_2P(CH_2)_2PPh_2$) on the platinum is effective, and only one P–methylene bond on a Pt–dppm complex is broken.

While the formation of the Pt–sulfur ylide complex under PTC conditions can proceed in a way similar to the palladium analogy,[2] the hydrolysis of a dppm in Pt–dppm complexes to PPh_2Me and $PPh_2(OH)$ ligands under PTC/OH^- is unknown. A similar but different reaction, the cleavage of a P–C bond in $Pt(dppm)Cl_2$ in liquid ammonia, has been reported.[12] In that reaction, a dppm ligand has been transformed to a methyldiphenylphosphine, PPh_2Me, and a diphenylphosphine oxide anion, PPh_2O^-. The latter is an anionic ligand instead of the neutral diphenylphosphinous acid (PPh_2OH) reported here. If our dppm cleavage products were identical with the known products of the dppm cleavage reaction, we should obtain neutral compounds instead of **1**–**4**. In another reaction, photochemically induced dppm chelate ring expansion followed by hydrolysis has been reported to afford the $PPh_2(OH)$ ligand as one of the products.[13] The hydrolysis product, however, was obtained not by the direct hydrolysis of dppm but rather from an intermediate containing the six-membered chelate ring $\overline{\mathrm{MPOCCP}}$.

To demonstrate that this P–C bond hydrolysis does not have to go through deprotonation of dppm, we substituted the two methylene protons with two methyl groups and found that P–C bond hydrolysis also occurred although at slower rate. The probable pathway for the P–C bond cleavage in Pt–dppm complexes is shown in Scheme I. It is possible that the nucleophilic attack by OH^- at one phosphorus followed by proton abstraction from water would produce the base-catalyzed hydrolysis products. We are currently investigating the factors that will influence the ease of this PT-catalyzed P–C bond hydrolysis and also ylide complex formation when using other sulfonium salts. Not only does this PT-catalyzed novel hydrolysis reaction suggest that dppm is not as stable as we used to think, but this is also a very easy way to convert a bidentate phosphine ligand to two different monodentate phosphines.

Acknowledgment. We thank the National Science Council of Taiwan (Republic of China) for financial support.

Registry No. **1**, 124399-74-2; **2**, 124399-76-4; **3**, 124399-77-5; **4**, 124399-78-6; $Pt(dppm)Cl_2$, 52595-94-5; $[Pt(dppm)(S_2CNEt_2)]Cl$, 124417-99-8; [Pt(dppm)(acac)]Cl, 124418-00-4; $[S(O)Me_3]Cl$, 5034-06-0.

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[8] (a) Sutherland, B. R.; Cowie, M. *Organometallics* **1985**, *4*, 1637. (b) Deraniyagala, S. P.; Grundy, K. R. *Inorg. Chem.* **1985**, *24*, 50. (c) Deraniyagala, S. P.; Grundy, K. R. *Inorg. Chim. Acta* **1984**, *84*, 205.

[9] Base hydrolysis of $Pt(dppm)Cl_2$ also occurs under PTC/OH^- conditions. However, more than two hydrolysis products have been observed.

[10] Compound **3**: mp 92–94 °C; IR (KBr) ν(OH) 3400 cm^{-1}; $\Lambda_M = 24$ Ω^{-1} cm^2 mol^{-1}; ^1H NMR ($CDCl_3$) 7.2–7.7 (m), 3.43 and 3.45 (q, $J(H,H) =$ 7 Hz), 2.25 (m, $J(P,H) = 11.2$ Hz, $J(Pt,H) = 40.3$ Hz), 1.13 and 1.15 (t, $J(H,H) = 7$ Hz) ppm; ^{31}P NMR ($CDCl_3$) 41.1 (m, $J(P,P) = 28.7$ Hz, $J(Pt,H) = 3322.3$ Hz), 3.5 (m, $J(P,P) = 28.7$ Hz, $J(Pt,H) = 3633.0$ Hz). Anal. Calcd for $C_{30}H_{34}ClNOP_2S_2Pt$: C, 46.1; H, 4.4; N, 1.8. Found: C, 45.6; H, 4.6; N, 1.7.

[11] Compound **4**: mp 98–100 °C; IR (KBr) ν(OH) 3390 cm^{-1}; $\Lambda_M =$ 9 Ω^{-1} cm^2 mol^{-1}; ^1H NMR ($CDCl_3$) 7.1–7.7 (m), 2.25 (s), 2.45 (m, $J(P,H) = 12.0$ Hz, $J(Pt,H) = 45.0$ Hz), 1.45 (s), 1.65 (s) ppm; ^{31}P NMR ($CDCl_3$) 23.8 (m, $J(P,P) = 32.3$ Hz, $J(Pt,P) = 3647.5$ Hz), 1.2 (m, $J(P,P) = 32.3$ Hz, $J(Pt,P) = 4408.8$ Hz). Anal. Calcd for $C_{30}H_{31}ClO_3P_2Pt$: C, 49.2; H, 4.2. Found: C, 49.4; H, 4.1.

[12] Alcock, N. W.; Bergamini, P.; Kemp, T. J.; Pringle, P. G. *J. Chem. Soc., Chem. Commun.* **1987**, 235.

[13] (a) Al-Jibori, S.; Hall, M.; Hutton, A. T.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 1069. (b) Al-Jibori, S.; Hall, M.; Hutton, A. T.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1984**, 863.

Iron Carbonyl Complexes of Isobenzofulvene

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Summary: Two stable iron carbonyl complexes of isobenzofulvene, a highly reactive molecule, are synthesized and characterized by ^1H NMR, ^{13}C NMR, IR, and MS spectroscopies.

We report the synthesis of the first transition-metal carbonyl complexes of isobenzofulvene (**1**). Isobenzofulvene (IBF) is a highly reactive cross-conjugated isomer of naphthalene that has proven to be unisolable under ordinary conditions.[1] The chemistry of IBF derivatives having substituents on the 1-, 3-, and/or 8-positions has been studied by Warrener,[2-7] Tanida,[8] Hafner,[9,10] and others.[11] Direct identification of **1** has only been achieved through the use of variable-temperature photoelectron spectroscopy (Scheme I). When the flash pyrolysis of **2** was carried out at 800 °C, **1** isomerized to naphthalene; even at very low temperatures, dimerization occurred to form **3**.[12]

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[1] Watson, P. L.; Warrener, R. N. *Aust. J. Chem.* **1973**, *26*, 1725–50.

[2] Paddon-Row, M. N.; Warrener, R. N. *Tetrahedron Lett.* **1974**, 3797–800.

[3] Warrener, R. N.; Collin, G. J.; Hutchison, G. I. *J. Chem. Soc., Chem. Commun.* **1976**, 373.

[4] Russel, R. A.; Vikingur, E. G.; Warrener, R. N. *Aust. J. Chem.* **1981**, *34*, 131–41.

[5] Warrener, R. N.; Evans, D. A. C.; Paddon-Row, M. N.; Russell, R. A. *Aust. J. Chem.* **1982**, *35*, 757–66.

[6] Paddon-Row, M. N.; Watson, P. L.; Warrener, R. N. *Tetrahedron Lett.* **1973**, 1033–6.

[7] Warrener, R. N.; Paddon-Row, M. N.; Russell, R. A.; Watson, P. L. *Aust. J. Chem.* **1981**, *34*, 397–420.

[8] Tanida, H.; Irie, T.; K. Tori, K. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1999–2003.

[9] Hafner, K.; Bauer, W. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 297–9; *Angew. Chem.* **1968**, *80*, 312.

[10] Hafner, K.; Hafner, K. H.; Konig, C.; Kreuder, M.; Ploss, G.; Schulz, G.; Sturm, E.; Vopel, K. H. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 123–34.

[11] Paddon-Row, M. N. *Aust. J. Chem.* **1974**, *27*, 299–313.

[12] Gross, G.; Schulz, R.; Schweig, A.; Wentrup, C. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1021–3.

[13] Morrison, H.; Giacherio, D. *J. Org. Chem.* **1982**, *47*, 1058–63.

[14] Finke, R. G.; Sorrel, T. N. *Org. Synth.* **1979**, *59*, 102–112.

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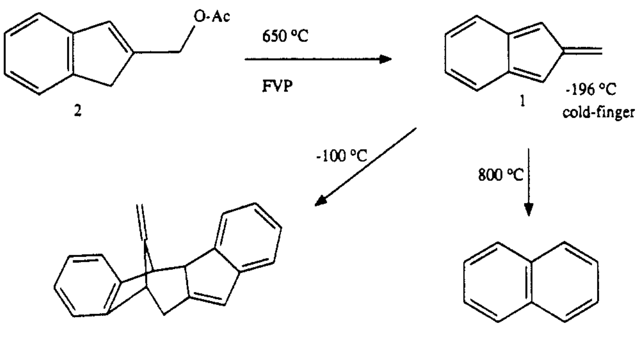
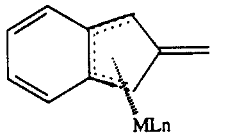
Scheme I. Synthesis and Reactivity of Isobenzofulvene

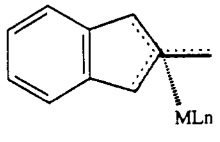


FVP = flash vacuum pyrolysis

Attachment of a four-electron-seeking organometallic unit (e.g., $Fe(CO)_3$ or CoCp) to isobenzofulvene might a priori result in either of the two structures **4** and **5**. In the *o*-xylylene structure (**1**) the benzenoid ring maintains partial aromatic character, whereas aromaticity of the benzenoid ring is maintained in the trimethylenemethane structure (**5**).



4



5

The synthesis of two stable metal carbonyl complexes of isobenzofulvene (**6** and **7**) is shown in Scheme II. Careful chromatography on alumina under nitrogen with hexane as the eluant yielded first an orange and then a maroon band that were isolated and identified by ^1H NMR, ^{13}C NMR, IR, and MS spectroscopies as **6**[15] and **7**,[16] respectively.

Among the evidence supporting the structure **6** rather than its *o*-xylylene-bound isomer are ^1H NMR, ^{13}C NMR, and IR data.

(a) ^1H NMR and ^{13}C NMR resonances for the methylene group of **6** are located at 2.77 and 41.8 ppm, respectively. These transitions occur at fields considerably higher than those observed for free olefinic groups and suggest direct attachment of the CH_2 to iron.

(b) The carbonyl resonances of (isobenzofulvene)iron tricarbonyl are seen as two singlets at 208.4 and 206.3 ppm, indicating that the iron tricarbonyl moiety is conformationally locked on the ^{13}C NMR time scale. Lillya and Magyar[17] have observed that substituted-TMM iron carbonyl complexes tend to exhibit multiple carbonyl resonances in the ^{13}C NMR spectra due to restricted rotation of the iron tricarbonyl moiety. Extended Hückel calculations performed by Hoffmann, Albright, and Thorn[18] indicate the rotational barrier in $(TMM)Fe(CO)_3$ to be 21–24 kcal/mol. By comparison, Kruczynski and Takats[19] have observed that the carbonyl interchange in (butadiene)iron tricarbonyl has an activation barrier of 9.5 kcal/mol. In contrast to the case for the (isobenzofulvene) iron tricarbonyl complex, ^{13}C NMR spectroscopy shows that the $Fe(CO)_3$ group of (*o*-xylylene)iron tricarbonyl undergoes free rotation as evidenced by a broad single peak at ca. 211 ppm.

(c) An undecoupled ^{13}C NMR spectrum reveals that $^1J(C\text{–}H) = 161$ Hz for the methylene group of **6**; this value compares favorably with that of (trimethylenemethane)iron tricarbonyl, $^1J(C\text{–}H) = 162$ Hz (cf. $^1J(C\text{–}H) = 156$ Hz for ethylene).

(d) Analysis of the AA′BB′ pattern of H(4)–H(7) for **6**[20] and related compounds (Table I) reveals the near-equivalency of J(A–B) and J(A–A′) for **6**, in contrast with the case for the other model compounds. Since vicinal coupling constants directly correlate with bond orders,[21] this indicates little tendency toward bond localization in the benzo ring, consistent with the (trimethylenemethane)iron tricarbonyl structure. A recent crystal structure of (*o*-xylylene)iron tricarbonyl[22] showed bond lengths of 1.36 and 1.42 Å for the double and single bonds in the benzo ring,

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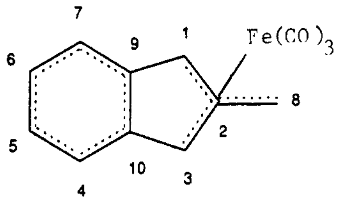
(15) Data for (isobenzofulvene)$Fe(CO)_3$:



red-orange; mp 103–104 °C. ^1H NMR (300 MHz, CD_2Cl_2, δ): 6.87 (m, 2 H, H4,7); 6.66 (m, 2 H, H5,6); 4.61 (s, 2 H, H1,3); 2.77 (s, 2 H, H8); $J(1,4) = 0.0$, $J(3,4) = J(6,7) = 7.4$, $J(5,6) = 7.4$ Hz. ^{13}C NMR (75 MHz, CD_2Cl_2, δ): 208.4 and 206.3 (s, carbonyl); 150.5 (d, $^3J(C9\text{–}H6) = {}^3J(C10\text{–}H5) = 6.65$ Hz, C9,10); 124.9 (dd, $^1J(C\text{–}H) = 161$ Hz, $^3J(C5\text{–}H7) = {}^3J(C6\text{–}H4) = 6.6$ Hz, C5,6); 122.3 (s, C2); 120.0 (dm, $^1J(C\text{–}H) = 162$ Hz, $^3J(C4\text{–}H6) = {}^3J(C7\text{–}H5) \approx {}^3J(C4\text{–}H3) = {}^3J(C7\text{–}H1) =$ ca. 5 Hz, C4,7); 76.0 (dm, $^1J(C\text{–}H) = 178$ Hz, many $^3J(C\text{–}H) = 4\text{–}6$ Hz, C1,3); 41.8 ppm (t, $^1J(C8\text{–}H8) = 161$ Hz, C8). An attached-proton test indicates that the carbons having resonances at 124.9, 120.0, and 76.0 ppm have an odd number of attached protons whereas those carbons having resonances at 208.4, 206.3, 150.5, 122.3, and 41.8 ppm have an even number of attached protons. IR (hexane): $\nu(CO) = 2063, 2002, 1996\ cm^{-1}$. MS ($m/z$ (relative intensity)): 268 (1.1, $M^+ = C_{10}H_8Fe(CO)_3$), 240 (33, $M^+ - CO$), 212 (24, $M^+ - 2\ CO$), 184 (100, $M^+ - 3\ CO$), 128 (93, $M^+ - 3\ CO - Fe$), 56 (27, Fe). Anal. Calcd for $C_{13}H_8O_3Fe$: C, 58.25; H, 3.01; Fe, 20.84. Found: C, 58.72; H, 3.01; Fe, 19.46. The analysis was performed by Galbraith Laboratories Inc., Knoxville, TN.

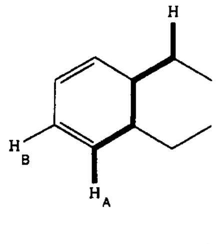
(16) Data for (isobenzofulvene)$Fe_2(CO)_6$: wine red; mp 175–177 °C. ^1H NMR (300 MHz, CD_2Cl_2, δ): 7.48 (m, 2 H, H4,7); 7.21 (m, 2 H, H5,6), 4.92 (s, 2 H, H1,3), 1.98 (s, 2 H, H8). ^{13}C NMR (75 MHz, CD_2Cl_2, δ): 127.6, 124.8 (c4,5 and C6,7); 70.0 (C1,3); −2.3 (C8). IR (KBr pellet): $\nu(CO) = 2077, 2019, 1986, 1971, 1951, 1907, 1882$ (sh) cm^{-1}; aromatic CH out-of-plane bending 862, 750, 622, 599, 572, 498 cm^{-1}. IR (CH_2Cl_2 deposited film): $\nu(CO) = 2083, 2021, 1982, 1970, 1951, 1906, 1880\ cm^{-1}$. MS ($m/z$ (relative intensity)): 408 (0.7, $M^+ = C_{10}H_8Fe_2(CO)_6$), 380 (2.7, $M^+ - CO$), 352 (4.9, $M^+ - 2\ CO$), 324 (9.0, $M^+ - 3\ CO$), 296 (25, $M^+ - 4\ CO$), 268 (46, $M^+ - 5\ CO$), 240 (57, $M^+ - 6\ CO$), 184 (76, $M^+ - 6\ CO - Fe$), 128 (100, $(C_{10}H_8)^+$), 112 (31, Fe_2^+).

(17) Magyar, E. S.; Lillya, C. P. *J. Organomet. Chem.* **1976**, *116*, 99–102.

(18) Hoffmann, R.; Albright, T. A.; Thorn, D. L. *Pure Appl. Chem.* **1978**, *50*, 1–9.

(19) Kruczynski, L.; Takats, J. *J. Am. Chem. Soc.* **1974**, *96*, 932–4; *Inorg. Chem.* **1976**, *15*, 3140–7.

(20) Close examination of the ^1H NMR spectrum of **6** reveals that the low-field aromatic resonances are broadened relative to those at high field. These low-field resonances are assignable to H4 and H7 (the A, A′ protons)



because these nuclei may interact with H1 and H3, respectively, via an optimal five-bond coupling path. H5 and H6 (the B, B′ protons) cannot interact with any nuclei outside the confines of the benzo moiety; hence, resonances arising from the H5 and H6 nuclei should be better resolved than those attributable to H1 and H3. We have observed that a similar broadening of the low-field multiplet also occurs in (*o*-xylylene)iron tricarbonyl.

(21) Smith, W. B.; Watson, W. H.; Chiranjeevi, S. *J. Am. Chem. Soc.* **1967**, *89*, 1438–40.

(22) Batsanov, A. S.; Zol'nikova, G. P.; Struchkov, Y. T.; Kritskaya, I. I. *Koord. Khim.* **1987**, *13*, 1551–3; *Chem. Abstr.* **1988**, *108*, 29808d.

Scheme II. Synthesis of Iron Carbonyl Complexes of Isobenzofulvene

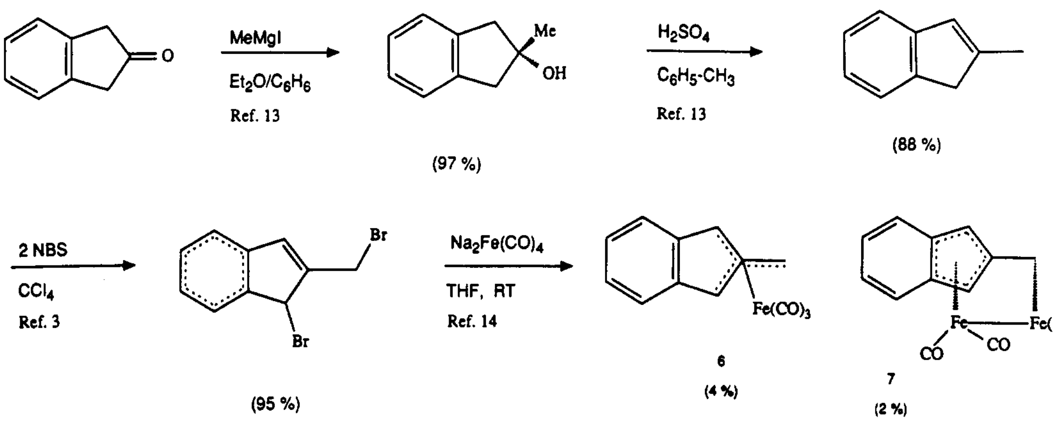
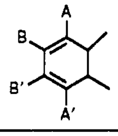
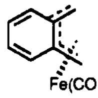
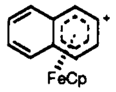
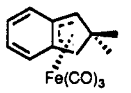
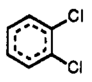
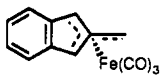


Table I. Analysis of the AA′BB′ Pattern of Symmetrically Ortho-Disubstituted Benzo Rings



	δ(A)	δ(B)	J_{AB}, Hz	$J_{BB'}$, Hz	$J_{AB'}$, Hz	$J_{AA'}$, Hz	ref
	5.68	5.79	9.66	5.06 ΔJ = 4.6	1.03	1.13	28
	7.50	7.40	8.40	5.70 ΔJ = 2.7	1.0	0	this work
	8.12	7.88	8.63	6.16 ΔJ = 2.47	1.24	0.09	29
	7.6	7.3	8.62	6.64 ΔJ = 1.98	0.98	1.07	30
	7.23	6.98	8.1	7.5 ΔJ = 0.6	1.5	0.3	31
	6.87	6.66	7.4	7.3 ΔJ = 0.1	1.0	0	this work

consistent with the comparatively large ΔJ of 2.7 Hz.

(e) The carbonyl stretching vibrations of 6, located at 2062, 2004, and 1989 cm^{-1}, are at frequencies higher than those of (*o*-xylylene)iron tricarbonyl,[23] which occur at 2054 and 1985 cm^{-1} (hexane solution), but are similar to those of (phenyltrimethylenemethane)iron tricarbonyl:[24] 2061, 1993 cm^{-1}.

IR data for 7 indicate the presence of six terminally bound carbonyl ligands. MS data are confirmatory, showing sequential loss of six carbon monoxide fragments from the parent ion. The same fragmentation pattern is observed for the diiron hexacarbonyl complex of benzofulvene.[25] The relatively intense Fe_2^+ peak at m/z = 112 suggests that the two iron nuclei in 7 are presumably

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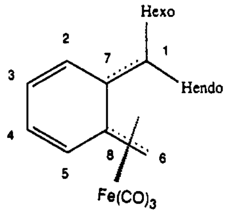
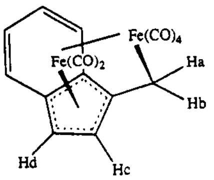
(23) Data for (*o*-xylylene)iron tricarbonyl:



yellow; mp 38–39 °C. ^{1}H NMR (300 MHz, CD_2Cl_2, δ): 0.22 (d, H_{endo}); 2.44 (d, H_{exo}); 7.42 (m, H3,4); 7.52 (m, H2,5); $J(H_{endo}-H_{exo})$ = 3.2 Hz, J(2,3) = J(4,5) = 8.4 Hz, J(3,4) = 5.7 Hz, J(2,4) = J(5,3) = 1.0 Hz. ^{13}C NMR (75 MHz, CD_2Cl_2, δ): ca. 211 (br s, carbonyl); 132.9 (d m, ^1J(C–H) = 164 Hz and possibly two ^3J(C–H) = ca. 4–6 Hz, C2,5); 129.2 (dd, ^1J(C–H) = 162 Hz, ^3J(C3–H5) = ^3J(C4–H2) = 8.3 Hz, C3,4); 100.6 (m, several ^3J(C–H) = ca. 4–7 Hz, C7,8); 38.3 (t, ^1J(C–H) = 158 Hz, C1,6). The central line of the triplet at 38.3 ppm is slightly broadened relative to those on either side of it, indicating that $^1J(C-H_{exo})$ and $^1J(C-H_{endo})$ have similar but not identical values. For the original synthesis, see: Roth, W. R.; Meier, J. D. *Tetrahedron Lett.* **1967**, *22*, 2053–8.

(24) Ehrlich, K.; Emerson, G. F. *J. Am. Chem. Soc.* **1972**, *94*, 2464–70.

(25) Moriarty, R. M.; Chen, K.; Flippen, J. *J. Am. Chem. Soc.* **1973**, *95*, 6489–90. Data for (benzofulvene)diiron hexacarbonyl:



^{1}H NMR (δ): 2.21 ("quartet", H_a, H_b, J = 13.1 Hz); 3.80 (d, H_c, J_{cd} = 2.8 Hz); 5.66 (d, H_d), 7.20 (m, aromatic, 4 H). Note that the H_a, H_b quartet is undoubtedly made up of two sets of resonances, each of which is a doublet. IR: ν(CO) = 2060, 2000–1960 cm^{-1}. MS (m/e): 407 (M^+), 380, 352, 324, 296, 268, 240 (corresponding to loss of CO).

bonded.[26] ^1H NMR and ^{13}C NMR resonances for the methylene group of 7 are located at 1.98 and −2.3 ppm, respectively. These values compare favorably with those for the (benzofulvene)- and (fulvene)diiron hexacarbonyl complexes.[25,27]

Our current work includes efforts to improve the yields of **6**, a crystal structure, and chemical studies. We will report on these in due course.

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Registry No. **6**, 124511-84-8; **7**, 49596-01-2; 2,3-dihydro-1*H*-inden-2-one, 49596-01-2; 2-methyl-2,3-dihydro-1*H*-inden-2-ol, 33223-84-6; 2-methyl-1*H*-indene, 2177-47-1; 3-bromo-2-bromomethyl-1*H*-indene, 60858-22-2; [η^4-5,6-bis(methylene)-1,3-cyclohexadiene]tricarbonyliron, 12181-95-2.

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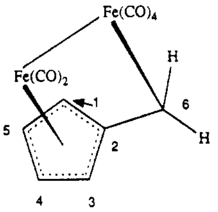

^1H NMR (C_6D_6, δ): 1.85 (s, CH_2); 4.01 (t, H1,3); 4.93 (t, H5,4). ^{13}C NMR (δ): 212.8 (CO); 94.5 (C2); 84.2 (C4,5); 75.6 (C1,3); −3.1 (C6). IR (cyclohexane): ν(CO) = 2077, 2014, 2004, 2000, 1981, 1950 cm^{-1}.

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Synthesis and Characterization of the Chiral Cluster $Fe_3(CO)_9[\eta^3\text{-}B(H)C(H)C(Me)]$. An Unambiguous Example of a Transition-Metal–Main-Group Six-Atom Cluster

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Summary: The synthesis and structural characterization of the first example of a boracyclopropene ring coordinated to a trimetal fragment, $Fe_3(CO)_9[C^3\text{-}B(H)C(H)C(Me)]$, I, are described. The compound constitutes an example of a cluster containing three transition metals that can only be reasonably considered as a six-atom cluster containing three iron, two carbon, and one boron atoms. This particular derivative of the cluster core also constitutes an example of a chiral cluster.

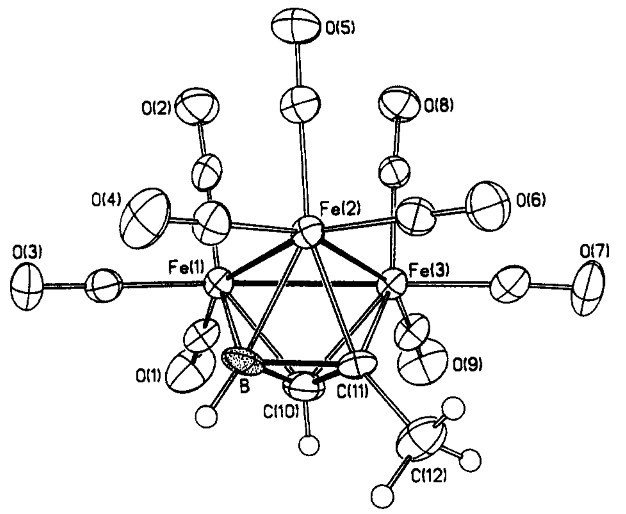

Figure 1. Structure and labeling scheme of $Fe_3(CO)_9[\eta^3\text{-}B(H)C(H)C(Me)]$, I. Atoms are shown as 30% thermal ellipsoids except hydrogen atoms, which are drawn at a fixed radius. One of two crystallographically independent but chemically similar molecules is shown.

The relationship between main-group and transition-metal clusters is expressed in the electron-counting formalism that has been developed over the past 10 or 15 years.[1] Although the reality of these rules lies in their usefulness, the study of compounds containing both transition-metal and main-group atoms in a contiguous network serves to emphasize similarities and differences in bonding of homonuclear clusters of atoms with and without d valence orbitals. However, in these mixed main group–metal systems an ambiguity often arises in the sense that a molecule containing *n* metal atoms and *m* main-group atoms can be equally well considered as an *n* + *m* atom cluster or an *n* atom cluster with a η^m ligand. Herein we report the characterization of a molecule that can only be reasonably considered a six-atom cluster containing equal numbers of main-group and transition-metal atoms.

The new compound was prepared via a developing method[2] for the synthesis of metallaboranes and metallacarboranes via the reaction of organometallic compounds, particularly those containing negatively charged ligands, with boranes. Specifically, the new cluster was synthesized from the reaction of $[Fe(Py)_6][Fe_4(CO)_{13}]$[3] with $BH_2Br\cdot SMe_2$ in toluene at 75 °C for 2 h. After removal of toluene under reduced pressure, protonation of the residues with CF_3COOH and hexane was followed by low-temperature chromatography. Fractional crystalization of the second band (brown) containing mainly $[HFe_4(CO)_{12}C]BH_2$[4] gave bright red crystals of a new compound in about 5% yield. The spectroscopic data[5] indicate that the compound can be formulated as $Fe_3(CO)_9[\eta^3\text{-}B(H)C(H)C(Me)]$, I. Our approach usually produces compounds with either reduced

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(5) IR (hexane, cm^{-1}) 2560 w (BH), 2090 m, 2040 vs, 2035 vs, 2020 s, 2005 m, 1985 w (sh) (CO); ^{11}B NMR (hexane, 20 °C) δ, 58.2 (d, J_{B-H} = 177 Hz); ^1H NMR (CD_2Cl_2, 20 °C) δ 7.82 (s, CH, 1 H), 6.02 (q, $J_{B-H} \approx 190$ Hz, 1 H), 2.53 (s, CH_3, 3 H); ^{13}C NMR (CD_2Cl_2, 20 °C, {^1H}) δ 210.4, 209.5, 209.3 (s, 9 CO), 187.5 (s, CMe), 164.4 (s, CH), 40.8 (s, CMe); MS (EI) P^+ = 472 (−9CO); $^{56}Fe_3{}^{12}C_{12}{}^{16}O_9{}^{11}B_1{}^1H_5{}^+$, 471.8087 obsd, 471.8078 calcd.

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