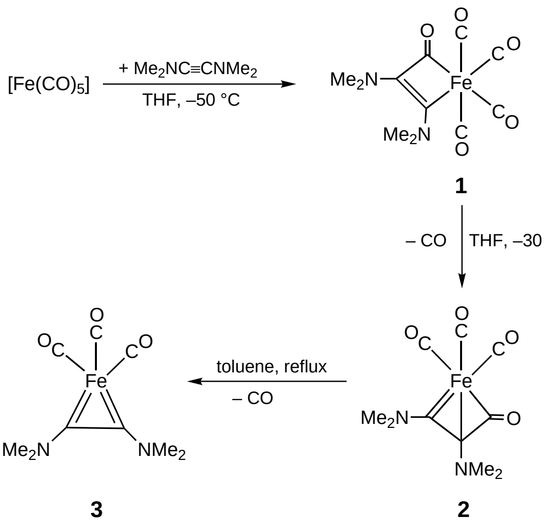
A Reaction Pathway of [Fe(CO)$_5$] with Alkynes via Ferrabicyclobutenones[**]

Alexander C. Filippou[*] and Torsten Rosenauer

Dedicated to Professor Gottfried Huttner
on the occasion of his 65th birthday

Several studies have been carried out on the reactions of [Fe(CO)$_5$] with alkynes since the pioneering work of W. Hübel.[1] These reactions are complex and in general not selective affording a plethora of organometallic complexes and carbocycles.[1, 2] Common products are the tricarbonyl(η^4-cyclopentadienone)iron complexes,[3] which have been widely used in organic synthesis.[4] The reactions of [Fe(CO)$_5$] with alkynes follow a dissociative pathway and need photochemical or high thermal activation because of the large Fe–CO bond dissociation energy.[5] Along this reaction pathway [Fe(CO)$_4$(η^2-alkyne)] complexes have been isolated as thermally sensitive solids.[6] The elementary steps for their conversion into the products remain however unclear. Following our studies on diaminoacetylene complexes[7] we present here the first example for an associative reaction of [Fe(CO)$_5$] with $\mathrm{Me_2N{-}C{\equiv}C{-}NMe_2}$ to afford a ferrabicyclobutenone and its selective C–C coupling and cleavage reactions to give a multitude of novel organoiron compounds.

Thus, treatment of [Fe(CO)$_5$] with $\mathrm{Me_2N{-}C{\equiv}C{-}NMe_2}$ in THF at −50 °C affords a very thermolabile intermediate, which from in situ low-temperature IR and NMR spectroscopy results is suggested to be the ferracyclobutenone **1** (Scheme 1, see Table 1). Complex **1** decarbonylates above about −30 °C to give selectively the ferrabicyclobutenone **2**, which was isolated as an orange, thermally stable solid in 79 % yield (Scheme 1). Complex **2** loses CO either in refluxing toluene or upon melting at 124 °C to afford selectively the red alkyne complex **3** in 95 % yield (Scheme 1, Table 1). Compounds **2** and **3**, are the first fully characterized members of two classes of long sought after complexes (Table 1).[8, 9] The molecular structure of **2** reveals a distorted square-pyramidal complex, in which the C4 and C8 atoms of the ferracycle and two carbonyl ligands (C1–O1, C3–O3) occupy the basal coordination sites (Figure 1).[10] The four-membered ferracycle is puckered (folding angle Fe,C4,C5/Fe,C5,C8 = 133.0°).



Scheme 1.

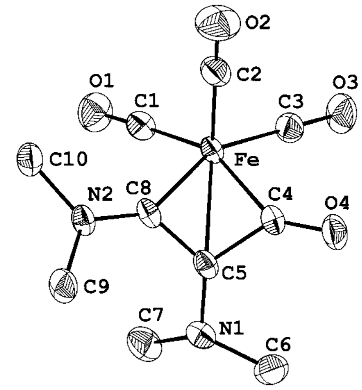


Figure 1. DIAMOND plot of the molecular structure of **2**, hydrogen atoms have been omitted (thermal ellipsoids at the 50 % probability level). Selected bond lengths [Å] and bond angles [°]: Fe-C4 1.933(3), Fe-C5 2.215(2), Fe-C8 1.896(3), C4-C5 1.469(3), C5-C8 1.400(4), C4-O4 1.210(3); C8-Fe-C4 71.91(11), Fe-C4-C5 79.99(15), C4-C5-C8 103.2(2), C5-C8-Fe 82.97(16).

The Fe–C$_\alpha$ bond (Fe–C8 1.896(3) Å) is considerably shorter than the Fe–C$_\beta$ distance (Fe–C5 2.215(2) Å) and compares well with those of metallacyclic iron–carbene complexes.[11] This situation suggests in connection with the coplanar arrangement of the atoms Fe, C8, C5, and N2, the planarity of the C$_\alpha$-bonded amino group (sum of the bond angles at N2 359.6°), the short C8–N2 bond (1.306(4) Å) and the short C5–C8 bond (1.400(4) Å) an extensive π-electron delocalization over the atoms Fe, C8, N2, and C5. The C$_\beta$-bonded amino group is not planar as shown by the sum of the bond angles at N1 of 343.1°, and the C5–N1 bond (1.384(3) Å) is intermediate in length between a C–N single (1.46 Å) and C–N double bond (1.27 Å).[12] The spectroscopic data of **2** also confirm to the solid-state structure (Table 1). Thus, the IR spectrum of **2** in THF displays two characteristic bands at $\tilde{\nu} = 1733$ and 1632 cm^{-1}, which are assigned to the ν(C=O) and ν(C$_\beta$⋯C$_\alpha$⋯N) vibrations, respectively. The ^{13}C{^{1}H} NMR spectrum of **2** (CDCl$_3$, 25 °C) shows a single resonance for the carbonyl ligands at $\delta = 211.4$ suggesting rapid intramolecular CO scrambling and three signals at $\delta = 60.6$, 216.4, and 223.1, which by heteronuclear multiple bond correlation (HMBC) were assigned to the β-, α-, and acyl-carbon atom of the ferrabicycle, respectively. Furthermore, the variable-temperature ^{1}H NMR spectra in CDCl$_3$ (206–298 K) show that complex **2** is fluxional because of hindered rotation of the C$_\beta$-bonded amino group. The activation barrier $\Delta G^{\neq}$ for the site exchange of the methyl groups was calculated to be

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[*] Prof. Dr. A. C. Filippou, Dipl.-Chem. T. Rosenauer
Institut für Chemie
Humboldt-Universität zu Berlin
Brook-Taylor Strasse 2, 12489 Berlin (Germany)
Fax: (+49) 30-2093-6939
E-mail: filippou@chemie.hu-berlin.de

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9.95 kcal mol^{-1} ($T_c = 215$ K, $\Delta\nu = 152$ Hz). In comparison, rotation of the C_α-bonded amino group is frozen even at ambient temperature giving rise to two methyl proton resonance signals at $\delta = 3.33$ and 3.59 ($\Delta G^{\neq} > 14.4$ kcal mol^{-1}).

The coordination geometry of complex **3** can be described as distorted square pyramidal with two CO ligands (C3–O1, C4–O2) and the alkyne carbon atoms occupying the basal coordination sites (Figure 2).[10] Distortion results from the small bite angle of the alkyne ligand (43.8(1)°) and the bending of the apical carbonyl ligand (C5–O3) away from the alkyne moiety (C_m-Fe-C5 114.87°, Figure 2). The short Fe–C_{alkyne} bonds (1.844(3) and 1.845(3) Å), the long $(C-C)_{alkyne}$ bond (1.375(4) Å), the short C_{alkyne}–N bonds (1.318(4) and 1.333(4) Å), and the planarity of the coordinated bis(dimethylamino)acetylene unit provide structural evidence for the presence of a four-electron-donor alkyne ligand with extensive π-electron delocalization.[7] This assignment is supported by the spectroscopic data, such as the IR absorption band of the ν(N$\cdots$C$\cdots$C$\cdots$N) vibration at 1698 cm^{-1}, the downfield-shifted resonance signal for the alkyne carbon atom at $\delta = 193.8$ ppm, and the hindered rotation of the amino groups, which gives rise to two methyl resonance signals in the ^{1}H and ^{13}C{^{1}H} NMR spectra at −79 °C (Table 1).[7] Furthermore the ^{13}C{^{1}H} NMR spectrum of **3** (−79 °C) shows only one carbonyl-carbon resonance at $\delta = 220.5$ ppm indicating a rapid site exchange of the CO ligands on the NMR time scale (Table 1).

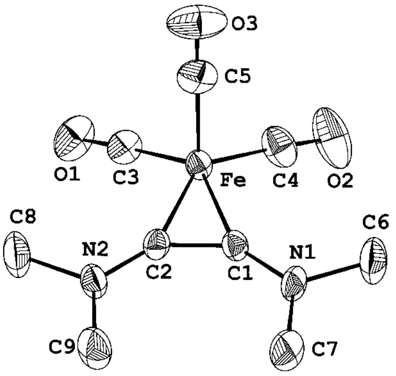
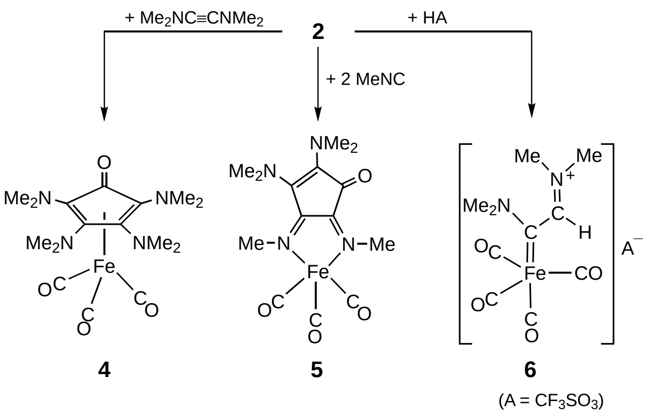


Figure 2. DIAMOND plot of the molecular structure of **3**, hydrogen atoms have been omitted (thermal ellipsoids at the 50% probability level). Selected bond lengths [Å] and bond angles [°]: Fe-C1 1.845(3), Fe-C2 1.844(3), Fe-C3 1.773(4), Fe-C4 1.785(4), Fe-C(5) 1.787(4), C1-C2 1.375(4), C1-N1 1.318(4), C2-N2 1.333(4); C1-Fe-C2 43.76(14), C3-Fe-C4 98.98(18), C3-Fe-C5 99.68(16), C4-Fe-C5 98.96(18), C_m-Fe-C5 114.87 (C_m denotes the midpoint of the alkyne C–C bond).

Complex **2** is a useful reactive starting material undergoing a variety of selective reactions with nucleophiles.[13] Thus, treatment of **2** with $Me_2N-C\equiv C-NMe_2$ in THF at −50 °C affords selectively the yellow cyclopentadienone complex **4** (Scheme 2, Table 1),[3d] which provides for the first time experimental evidence for the key role that ferrabicyclobutenons can play in iron-centered [2+2+1] cycloaddition reactions.[1, 3, 4] Another example of the high reactivity of **2** is the fast reaction with methyl isocyanide (MeNC) in THF at −10 °C to yield, after double isocyanide insertion, the very air-sensitive, black 1,4-diaza-1,3-diene complex **5**, in which $Me_2N-C\equiv C-NMe_2$, one carbon monoxide, and two isocyanide molecules have been C–C coupled to give a rare 4,5-diimino-2-cyclopentene-1-one ligand (Scheme 2, Table 1).[14] Complex **5** adopts a coordination geometry between trigonal bipyramidal and square pyramidal, the carbonyl ligand C7–O3 being the pivot group (Figure 3).[10] The 1,4-diaza-1,3-diene (DAD) ligand in **5** reveals similar bonding parameters to those of the few other structurally characterized $[(DAD)Fe(CO)_3]$ complexes.[15]



(A = CF$_3$SO$_3$)

Scheme 2.

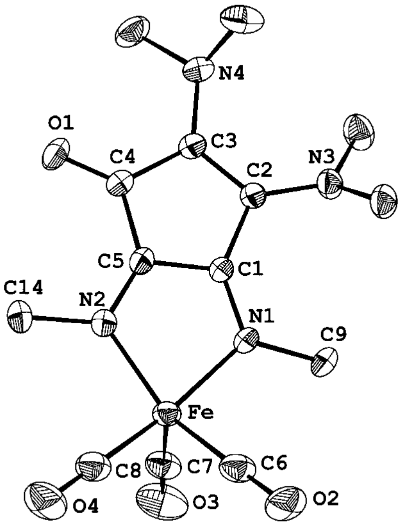


Figure 3. DIAMOND plot of the molecular structure of **5**, hydrogen atoms have been omitted (thermal ellipsoids at the 50% probability level). Selected bond lengths [Å] and bond angles [°]: Fe-N1 1.963(2), Fe-N2 1.928(2), C1-N1 1.316(3), C5-N2 1.318(3), C1-C2 1.487(3), C2-C3 1.391(3), C3-C4 1.487(3), C4-C5 1.487(3), C1-C5 1.412(3), N1-C9 1.470(3), N2-C14 1.473(3), C2-N3 1.367(3), C3-N4 1.391(3); N1-Fe-N2 81.64(9), N1-Fe-C8 165.96(10), N2-Fe-C6 147.94(11).

Complex **2** also reacts with electrophiles as shown by the C–C bond cleavage reaction with CF_3SO_3H in CH_2Cl_2 at 20 °C to afford selectively the orange-yellow aminocarbene complex **6** (Scheme 2, Table 1). Compound **6** is the first reported carbene complex bearing an electron-withdrawing iminium group at the carbene-carbon atom. An almost orthogonal orientation of the carbene-ligand plane (Figure 4; Fe,C5,N1,C8) and the plane of the iminium group

Table 1. Selected analytical data of complexes **1**–**6**.[a]

$[\mathrm{Fe(CO)_5}]$: IR: $\tilde{\nu} = 2019$ (s), 1993 cm^{-1} (vs) ($\nu(\mathrm{C{\equiv}O})$).

1: IR (THF, –50 °C): $\tilde{\nu} = 2086$ (w), 2034 (s), 2014 cm^{-1} (vs) ($\nu(\mathrm{C{\equiv}O})$); ^{1}H NMR ([D$_8$]THF, –50 °C, 300.1 MHz): $\delta = 2.50$ (s, 6H, C$_\beta$-NMe_2), 3.39 ppm (broad s, 6H, C$_\alpha$-NMe_2); ^{13}C{^{1}H} NMR ([D$_8$]THF, –50 °C, 75.5 MHz): $\delta = 44.6$ (C$_\beta$-NMe_2), 46.0 (broad s, C$_\alpha$-NMe_2), 126.6 (C_β), 170.3, 172.0 (C=O, C_α), 204.7 (1 × $C{\equiv}$O), 208.2 (1 × $C{\equiv}$O), 212.8 ppm (2 × $C{\equiv}$O).

2: IR: $\tilde{\nu} = 2035$ (vs), 1963 (vs, sh), 1955 (vs) ($\nu(\mathrm{C{\equiv}O})$), 1733 (m) ($\nu(\mathrm{C{=}O})$), 1632 cm^{-1} (m) ($\nu(\mathrm{C\overset{\cdots}{-}C\overset{\cdots}{-}N})$); ^{1}H NMR (CDCl$_3$): $\delta = 2.08$ (s, 6H, C$_\beta$-NMe_2), 3.33 (s, 3H, C$_\alpha$-NMe_A), 3.59 ppm (s, 3H, C$_\alpha$-NMe_B); ^{13}C{^{1}H} NMR (CDCl$_3$): $\delta = 40.4$ (C$_\beta$-NMe_2), 43.8 (C$_\alpha$-NMe_A), 46.6 (C$_\alpha$-NMe_B), 60.6 (C_β), 211.4 (3 × $C{\equiv}$O), 216.4 (C_α), 223.1 ppm (C=O).

3: yield 95 %, red solid, m.p. 71 °C. IR: $\tilde{\nu} = 2011$ (s), 1927 (vs) ($\nu(\mathrm{C{\equiv}O})$), 1698 cm^{-1} (m) ($\nu(\mathrm{N\overset{\cdots}{-}C\overset{\cdots}{-}C\overset{\cdots}{-}N})$); ^{1}H NMR ([D$_8$]toluene, –79 °C): $\delta = 1.93$ (s, 6H, 2 × NMe_A), 2.95 ppm (s, 6H, 2 × NMe_B); ^{13}C{^{1}H} NMR ([D$_8$]toluene, –79 °C): $\delta = 45.1$ (2 × NMe_A), 47.1 (2 × NMe_B), 193.8 (2 × C_{alkyne}), 220.5 ppm (3 × $C{\equiv}$O).

4: yield 89 %, yellow solid, m.p. 101 °C. IR: $\tilde{\nu} = 2030$ (s), 1959 (vs) ($\nu(\mathrm{C{\equiv}O})$), 1638 cm^{-1} (m) ($\nu(\mathrm{C{=}O})$); ^{1}H NMR (CDCl$_3$): $\delta = 2.74$ (s, 12H, 2 × NMe_2), 2.79 ppm (s, 12H, 2 × NMe_2); ^{13}C{^{1}H} NMR (CDCl$_3$): $\delta = 41.8$ (2 × NMe_2), 43.8 (2 × NMe_2), 97.9 (2 × C-NMe$_2$), 108.8 (2 × C-NMe$_2$), 159.4 (C=O), 211.6 ppm (3 × $C{\equiv}$O).

5: yield 78 %, black solid, m.p. 93 °C (decomp.). IR: $\tilde{\nu} = 2015$ (vs), 1941 (vs) ($\nu(\mathrm{C{\equiv}O})$), 1670 (m), 1565 (m), 1533 (w), 1505 cm^{-1} (m) ($\nu(\mathrm{C{=}O})$, $\nu(\mathrm{C{=}C})$, $\nu(\mathrm{C{=}N})$); ^{1}H NMR (C$_6$D$_6$): $\delta = 2.03$ (s, 6H, NMe_2), 2.51 (s, 6H, NMe_2), 3.54 (s, 3H, NMe), 3.97 ppm (s, 3H, NMe); ^{13}C{^{1}H} NMR (C$_6$D$_6$): $\delta = 41.3$ (2C, NMe_2), 42.9 (2C, NMe_2), 45.9 (1C, NMe), 47.3 (1C, NMe), 145.6 (1C, C_{ring}), 147.6 (1C, C_{ring}), 148.4 (1C, C_{ring}), 163.9 (1C, C_{ring}), 181.3 (1C, C_{ring}), 216.5 ppm (3 × $C{\equiv}$O).

6: yield 85 %, orange-yellow solid, m.p. 106 °C (decomp.). IR: $\tilde{\nu} = 2053$ (s), 1984 (m), 1951 (vs), 1944sh ($\nu(\mathrm{C{\equiv}O})$), 1672 (w), 1589 cm^{-1} (w) ($\nu(\mathrm{C{=}N})$); ^{1}H NMR (CD$_2$Cl$_2$): $\delta = 3.37$(s, broad, 6H, NMe_2), 3.72 (s, 3H, NMe_A), 3.89 (s, 3H, NMe_B), 8.84 ppm (s, 1H, CH); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): $\delta = 44.1$ (very broad, NMe_2), 48.9 (NMe_A), 51.7 (NMe_B), 150.0 (C(H)NMe$_2$), 211.6 (4 × $C{\equiv}$O), 239.6 ppm (Fe=C).

[a] Correct elemental analyses were obtained for complexes **2**–**6**. IR spectra were recorded with a Bruker IFS-55 spectrometer in THF at ambient temperature unless otherwise stated. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AM-300 spectrometer in solution at 25 °C unless otherwise stated.

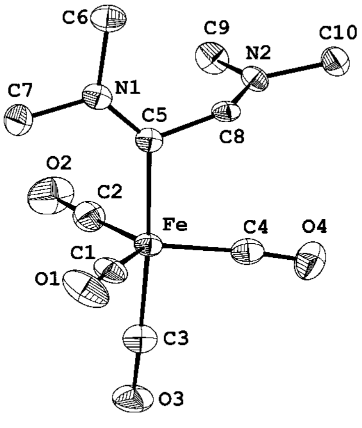


Figure 4. DIAMOND plot of the structure of the cation in **6**, hydrogen atoms have been omitted (thermal ellipsoids at the 50 % probability level). Selected bond lengths [Å] and bond angles [°]: Fe-C5 1.978(6), C5-N1 1.284(9), C5-C8 1.484(9), C8-N2 1.284(8); C5-C8-N2 123.8(6).

(C8,N2,C9,C10), is observed in the trigonal-bipyramidal complex cation (dihedral angle = 83.9°).[10]

It is not only the unique reaction pathway of $[\mathrm{Fe(CO)_5}]$ with $\mathrm{Me_2N{-}C{\equiv}C{-}NMe_2}$ to give the novel ferrabicyclobutenone **2** and the experimental evidence that this type of complexes can be the key intermediate in the iron-mediated cyclization of alkynes to cyclopentadienones that merits consideration, but also the diverse reactivity of **2** which provides access to a multitude of new organoiron compounds. Compound **2** is a useful starting material for a multitude of electron-rich ferracycles, which react with electrophiles to give π-electron delocalized systems.

Experimental Section

2: A solution of $[\mathrm{Fe(CO)_5}]$ (2.07 g, 10.56 mmol) in THF (90 mL) was treated at –78 °C with $\mathrm{Me_2N{-}C{\equiv}C{-}NMe_2}$ (0.79 g, 7.04 mmol). The mixture was allowed to warm to room temperature within 3 h and stirred for 1 h. Completion of the reaction was confirmed by IR spectroscopy. The resulting orange solution was evaporated to dryness and the dirty orange residue washed with cold pentane (0 °C; 3 × 10 mL) to remove traces of **4**. The solid was extracted with diethyl ether and the extract filtered to remove some insoluble green material. The filtrate was evaporated to dryness to give complex **2** as an orange, microcrystalline solid. Yield 1.564 g (79 % from $\mathrm{Me_2N{-}C{\equiv}C{-}NMe_2}$), m.p. 124 °C (decarbonylation to **3**); elemental analysis calcd (%) for $\mathrm{C_{10}H_{12}FeN_2O_4}$ (280.06): C 42.89, H 4.32, N 10.00; found: C 42.79, H 4.41, N 9.71; EI-MS (70 eV): m/z: 280 $[M]^+$, 252 $[M-\mathrm{CO}]^+$, 224 $[M-2\,\mathrm{CO}]^+$, 196 $[M-3\,\mathrm{CO}]^+$, 168 $[M-4\,\mathrm{CO}]^+$, 112 $[\mathrm{Me_2NC{\equiv}CNMe_2}]^+$.

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[7] A. C. Filippou, B. Lungwitz, G. Kociok-Köhn, *Eur. J. Inorg. Chem.* **1999**, 1905–1910, and references therein.

[8] To date complexes analogous to **2** have only been postulated as intermediates in metal-centered alkyne–CO coupling reactions: a) T. Mao, Z. Zhang, J. Washington, J. Takats, R. B. Jordan, *Organometallics* **1999**, *18*, 2331–2341; b) M. Barrow, N. L. Cromhout, A. R. Manning, J. F. Gallagher, *J. Chem. Soc. Dalton Trans.* **2001**, 1352–1358.

[9] To date $[\mathrm{M(CO)_3}(\eta^2\text{-alkyne})]$ species (M = Fe, Ru, Os) have only been suggested as intermediates to account for the increased reactivity of the complexes $[\mathrm{M(CO)_4}(\eta^2\text{-alkyne})]$ in carbonyl substitution reactions: a) ref. [5]; b) S. A. Decker, M. Klobukowski, *J. Am. Chem. Soc.* **1998**, *120*, 9342–9355.

[10] Crystal structure determination of **2**: $\mathrm{C_{10}H_{12}FeN_2O_4}$, $M_r = 280.06$; orange crystals from diethyl ether upon cooling from 20 → –78 °C, monoclinic, space group $P2_1/c$, $a = 8.7893(10)$, $b = 9.359(3)$, $c = 15.2880(14)$ Å, $\alpha = \gamma = 90$, $\beta = 98.530(8)°$, $V = 1243.6(4)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.496$ g cm^{-3}, $T = 180(2)$ K, $2\theta_{\max} = 65.8°$, $\mu = 1.216$ mm^{-1}, $F(000) = 576$, 5571 reflections, 2180 unique reflections, 154 parame-

ters, GOF = 1.081, $R_1 = 0.0463$ [$I > 2\sigma(I)$], w$R_2 = 0.1350$, min./max. residual electron density -0.989/0.599 e Å^{-3}. Crystal structure determination of **3**+**4**: $C_9H_{12}FeN_2O_3$, $M_r = 252.05$ (**3**), $C_{16}H_{24}FeN_4O_4$, $M_r = 392.24$ (**4**); orange cocrystals of **3** and **4** (molar ratio 1/1: chromatographic work-up of the product mixture of the reaction of [$Fe_2(CO)_9$] with $Me_2N-C\equiv C-NMe_2$ containing the complexes **2**, **3**, **4** and [$Fe_2(CO)_6(\mu\text{-}CNMe_2)_2$] led to a fraction containing **3** and **4** from which the cocrystals were grown from a pentane solution upon cooling from 20 → −30 °C), triclinic, space group $P\bar{1}$, $a = 8.831(2)$, $b = 8.944(2)$, $c = 21.354(5)$ Å, $\alpha = 97.26(3)$, $\beta = 95.31(3)$, $\gamma = 113.20(3)°$, $V = 1519.0(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.409$ g cm^3, $T = 160(2)$ K, $2\theta_{max} = 52.48°$, $\mu = 1.005$ mm^{-1}, $F(000) = 672$, 13771 reflections, 5573 unique reflections, 361 parameters, GOF = 1.008, $R_1 = 0.0461[I > 2\sigma(I)]$, $wR_2 = 0.1311$, min./max. residual electron density −0.504/0.524 e Å^{-3}. Crystal structure determination of **5**: $C_{14}H_{18}FeN_4O_4$, $M_r = 362.17$; violet crystals from pentane upon cooling from 20 → −78 °C, triclinic, space group $P\bar{1}$, $a = 8.6326(12)$, $b = 10.222(2)$, $c = 11.114(3)$ Å, $\alpha = 113.15(2)$, $\beta = 105.499(17)$, $\gamma = 99.58(3)°$, $V = 827.2(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.454$ g cm^{-3}, $T = 180(2)$ K, $2\theta_{max} = 53.9°$, $\mu = 0.936$ mm^{-1}, $F(000) = 376$, 5758 reflections, 3512 unique reflections, 209 parameters, GOF = 1.068, $R_1 = 0.0451[I > 2\sigma(I)]$, $wR_2 = 0.1324$, min./max. residual electron density −0.631/0.685 e Å^{-3}. Crystal structure determination of **6**: $C_{11}H_{13}F_3FeN_2O_7S$, $M_r = 430.14$; yellow crystals upon diffusion of diethyl ether in THF at 20 °C, triclinic, space group $P\bar{1}$, $a = 6.6594(17)$, $b = 10.490(3)$, $c = 12.988(4)$ Å, $\alpha = 102.87(4)$, $\beta = 100.02(3)$, $\gamma = 95.78(3)°$, $V = 861.8(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.658$ g cm^{-3}, $T = 180(2)$ K, $2\theta_{max} = 50.48°$, $\mu = 1.062$ mm^{-1}, $F(000) = 436$, 5674 reflections, 2892 unique reflections, 226 parameters, GOF = 1.109, $R_1 = 0.0776[I > 2\sigma(I)]$, $wR_2 = 0.2197$, min./max. residual electron density −0.725/1.778 e Å^{-3}. Instruments: STOE STADI-4 four-circle diffractometer with scintillation counter (**2** and **5**) and STOE-IPDS diffractometer with area detector (**3** and **6**) at $\lambda(Mo_{K\alpha}) = 0.71073$ Å. CCDC-181665–181668 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[13] Additional evidence for the Lewis acidic character of **2** is the formation of adducts with Lewis bases such as PMe_3. The resulting octahedral ferracyclobutenones *mer*/*fac*-[$Fe(CO)_3PMe_3(\eta^1{:}\eta^1\text{-}C(NMe_2)C(NMe_2)C(O))$] are related to **1**: T. Rosenauer, A. C. Filippou, unpublished results.

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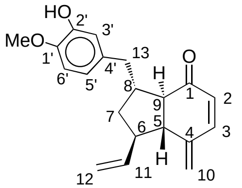
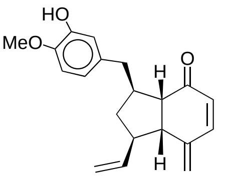
Total Synthesis of (±)-Otteliones A and B**

Goverdhan Mehta* and Kabirul Islam

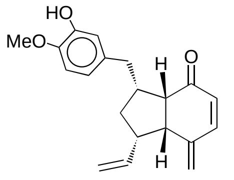
The isolation of the two diastereomeric otteliones A and B from the widely occurring but little studied fresh water plant *Ottelia alismoides*, and the determination of their structures, which include a unique 4-methylenecyclohex-2-enone substructure, was reported in 1998.[1] Collaborative efforts between US and Egyptian scientists, who employed high-field NMR spectroscopy techniques and modeling studies, led to the stereostructure **1** for ottelione B. However, the structure of ottelione A could not be assigned unambiguously, and both **2a** and **2b** were considered as likely formulations, the former being more likely.[1] In 2000, scientists at Rhône-Poulenc Rohrer reinterpreted[2] the NMR spectroscopic data and proposed an alternate stereostructure **2c** for ottelione A (RPR 112378). Otteliones have attracted much attention as they exhibit remarkable, broad-ranging biological activity.[1–4] Chinese scientists have reported the antitubercular effect of extracts of *Ottelia alismoide*s, which is rich in otteliones, and have shown in clinical trials that two cases of bilateral tuberculosis of the cervical lymph gland were cured in three months.[3] At the National Cancer Institute, in vitro screening against a panel of 60 human cancer cell lines showed that otteliones exhibited cytotoxicity at nM–pM levels.[1, 4] More recent results have shown that ottelione A is an efficient inhibitor of tubulin polymerization ($IC_{50} = 1.2$ μM) and is able to disassemble preformed microtubules in a manner reminiscent of the colchicines, vinblastine, and vincristine.[2] The cytotoxicity of otteliones can be attributed to the presence of



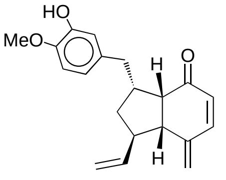
1



2a



2b



2c

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[*] Prof. G. Mehta, K. Islam
Department of Organic Chemistry, Indian Institute of Science
Bangalore-560012 (India)
Fax: (+91) 80-360-0936
E-mail: gm@orgchem.iisc.ernet.in

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