Reductive Dimerization and Thermal Rearrangement of Biphenylene Coordinated to Tricarbonylmanganese

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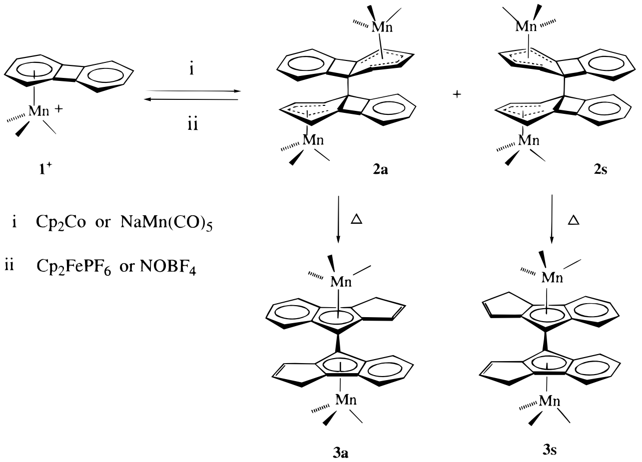
[*N*]-phenylenes are comprised of alternating benzene and cyclobutadiene rings.[1] The unique feature of [*N*]-phenylenes is their strained four-membered rings, which has attracted the attention of theoretical and experimental chemists recently.[2] The parent biphenylene [$(C_6H_4)_2$] was known for many years.[3] Theoretical calculations suggest that biphenylene has a relatively low resonance energy of about 15 kcal/mol,[4] whereas its strain energy is high, about 65 kcal/mol.[5] Thus, previous studies of the activation of biphenylene by iron,[6] cobalt,[7] and nickel[8] group complexes have led to metal insertion into the central ring to form a dibenzo(metallacyclopentadiene) species. It is well-established that arenes are activated toward nucleophiles or chemical reduction by coordination to the $[Cr(CO)_3]$ and $[Mn(CO)_3]^+$ units.[9] We therefore prepared $[(\eta^6\text{-}C_{12}H_8)Mn(CO)_3]^+[BF_4]^-$ ($\mathbf{1}^+BF_4^-$)[10] in 87% yield by direct treatment of biphenylene with $[Mn(CO)_5]^+[BF_4]^-$ [11] in hot CH_2Cl_2. Herein we report that reduction of $\mathbf{1}^+$ affords the dimer $[((\eta^5\text{-}C_6H_4)C_6H_4)Mn(CO)_3]_2$ (**2**), which upon heating rearranges to yield the unprecedented di(benzopentalene) complex $[(\eta^5\text{-}C_5(C_4H_4)(C_3H_4))Mn(CO)_3]_2$ (**3**) (Scheme 1).

Scheme 1



In a typical reaction, a CH_2Cl_2 solution of $\mathbf{1}^+BF_4^-$ (200 mg, 0.53 mmol) and an equimolar solution of cobaltocene were stirred at ambient temperature for 30 min.[12] Two complexes, *syn*-$[((\eta^5\text{-}C_6H_4)C_6H_4)Mn(CO)_3]_2$ (**2s**) and *anti*-$[((\eta^5\text{-}C_6H_4)C_6H_4)Mn(CO)_3]_2$ (**2a**),[13] in an approximate 1:1 ratio were isolated in 82% yield after chromatography on silica gel with a CH_2Cl_2/*n*-hexane (1:4, v/v) eluant. Presumably, initial reduction occurs at the manganese center of $\mathbf{1}^+$ to generate an $[\eta^5\text{-}C_{12}H_8)Mn(CO)_3]$ radical[14] in either enantiomeric form (Chart 1), and cross dimerization of which affords the diastereomers **2s** and **2a**. An alternative pathway via an anion/cation addition route, established for the conversion of $[Mn(CO)_3(\eta^6\text{-}C_6H_6)]^+$ into $[(Mn(CO)_3)]_2(\eta^5,\eta^5\text{-}C_{12}H_{12})$,[15] is also plausible. It is interesting that $Mn(CO)_5^-$ reduces $\mathbf{1}^+$ to give **2(s + a)** and $Mn_2(CO)_{10}$, whereas the organic nucleophiles, $R^- = H^-$, Me^-, and $Me_3CC(O)CH_2^-$, were found to attack $\mathbf{1}^+$ at a bridgehead carbon, forming $((\eta^5\text{-}C_6H_4R)C_6H_4)Mn(CO)_3$.[10] Furthermore, treatment of **2s** (and **2a**) with the oxidizing agent, $(Cp_2Fe)PF_6$ or $NOBF_4$, in CH_2Cl_2 at 25 °C reforms $\mathbf{1}^+$ in high yields

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(10) The IR, NMR, and crystallographic data agree with those previously reported by Sweigart and co-workers for $\mathbf{1}^+BF4^-$ resulting from substitution of the naphthalene ligand in $[(\eta^6\text{-naphthalene})Mn(CO)_3]^+[BF_4]^-$ by biphenylene. See: Dullaghan, C. A.; Carpenter, G. B.; Sweigart, D. A. *Chem. Eur. J.* **1997**, *3*, 75.

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(12) Cyclic voltammetric investigations of $\mathbf{1}^+BF4^-$ (1 m*M* in CH_3CN) at 25 °C showed an irreversible reduction potential at −896 mV and an irreversible oxidation potential at +1319 mV (vs Ag/AgCl) with Bu_4NPF_6 (0.1 *M*) as supporting electrolyte, a Pt button working electrode, and a Pt wire auxiliary electrode.

(13) The symbols, *syn* and *anti*, indicate the positions of the two phenyl groups in the same and opposite sides of the complex, respectively, with the two central four-membered rings being *trans* to each other. **2s**: mass spectrum (electron impact, EI), *m/z* 582 (M^+), 582−28*n* (*n* = 1−6); IR (*n*-hexane, νCO), 2012 (s), 1960 (s), 1944 (s) cm^{-1}; ^1H NMR (acetone-d_6, 20 °C), δ 3.21 (d, J = 6.9 Hz, 1H), 4.97 (m, 1H), 5.47 (d, J = 2.4 Hz, 2H), 7.15−7.38 (m, 3H), 7.59 (d, J = 7.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (acetone-d_6, 20 °C), δ 59.0, 61.8, 78.3, 83.0, 85.9, 97.4, 119.9, 123.4, 127.4, 130.2, 147.6, 155.5, 223.3 (CO). Anal. Calcd for $C_{30}H_{16}O_6Mn_2$: C, 61.88; H, 2.77. Found: C, 61.80; H, 2.75. **2a**: mass spectrum (EI), *m/z* 582 (M^+), 582−28*n* (*n* = 1−6); IR (*n*-hexane, νCO), 2012 (s), 1960 (s), 1944 (s) cm^{-1}; ^1H NMR (acetone-d_6, 20 °C), δ 4.42 (d, J = 6.6 Hz, 1H), 5.15 (d, J = 4.8 Hz, 1H), 5.36 (t, J = 6.6 Hz, 1H), 5.54 (t, J = 4.8 Hz, 1H), 6.66 (d, J = 7.5 Hz, 1H), 6.95 (d, J = 7.5 Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H), 7.26 (t, J = 7.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (acetone-d_6, 20 °C), δ 60.9, 61.6, 79.2, 84.7, 85.6, 97.9, 119.9, 123.3, 126.6, 130.1, 147.1, 156.5, 223.8 (CO). Anal. Calcd for $C_{30}H_{16}O_6Mn_2$: C, 61.88; H, 2.77. Found: C, 61.76; H, 2.80.

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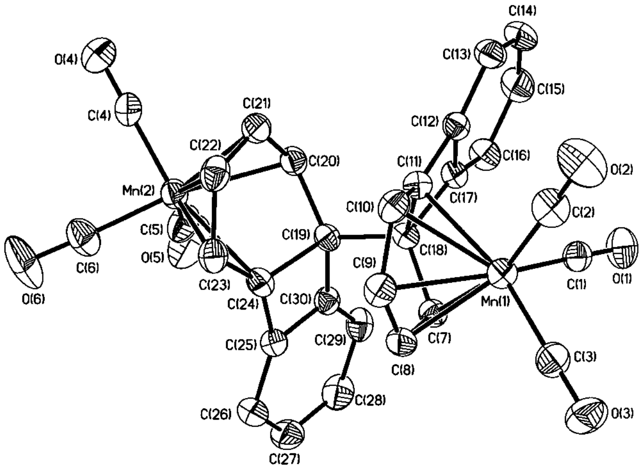
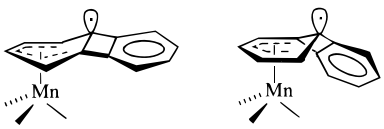


Figure 1. Molecular structure of **2s**. The hydrogen atoms have been artificially omitted for clarity.

Chart 1



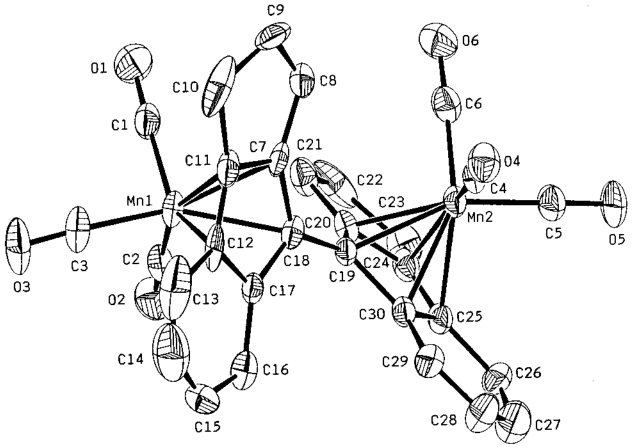
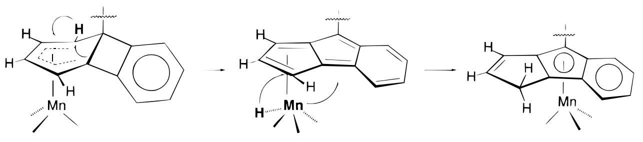


Figure 2. Molecular structure of **3s**. The hydrogen atoms have been artificially omitted for clarity.

Scheme 2



(70−75%) after purification. Reductive dimerization of ligated arenes is well documented,[9c,16] while the reversed oxidative C−C cleavage of their dimers is seldom recorded.[17]

The ORTEP diagram of **2s** is shown in Figure 1. The structure consists of a discrete molecule with each manganese atom bonded to three terminal carbonyls and a cyclohexadienyl group. The pentadienyl units (C7−C11 and C20−C24) and the benzocyclobutane units (C11−C18 and C19, C24−C30) are each planar to within 0.04 Å. The bridging C18 and C19 atoms are displaced from the pentadienyl planes exo to Mn. The dihedral angles between the (C7−C11) and (C7, C18, C11) planes is 41.5°, and between the (C7, C18, C11) and (C11, C12, C17, C18) planes is 51.3°. The pentadienyl carbons are bonded to the manganese atoms asymmetrically, with the Mn−C distances in the range 2.275(3)−2.130(4) Å to Mn1 and 2.307(3)−2.113(3) Å to Mn2. The benzene C−C bonds are delocalized, 1.36 ± 0.02 Å.

It is apparent that the central rings in **2** remain strained.[18] Thus, heating **2s** and **2a** in refluxing *n*-octane (125 °C) affords *syn*-[(η^5-$\mathrm{C_5(C_4H_4)(C_3H_4)}$)$\mathrm{Mn(CO)_3}$]$_2$ (**3s**) and *anti*-[(η^5-$\mathrm{C_5(C_4H_4)(C_3H_4)}$)$\mathrm{Mn(CO)_3}$]$_2$ (**3a**),[19] respectively, in 71% yield after purification by TLC on silica gel eluting with $\mathrm{CH_2Cl_2}$/*n*-hexane (1:4, v/v). In this reaction the organic ligand has rearranged to form a di(benzopentalene) species,[20] and the $\mathrm{Mn(CO)_3}$ groups have shifted to bind the middle cyclopentadienyl rings. Compounds **3s** and **3a** are not interconvertible. The regiospecific and stereospecific conversion from **2** to **3** implies a metal-mediated pathway (Scheme 2). The involvement of an $\mathrm{HMn(diene)(CO)_3}$ intermediate has been proposed to account for the hydrogen migration in (η^5-cyclohexadienyls)$\mathrm{Mn(CO)_3}$.[21] Nevertheless, a concerted process via a C−C bond migration, a [1,4]-hydrogen shift, and slippage of the $\mathrm{Mn(CO)_3}$ group cannot be excluded at this stage.

The ORTEP diagram of **3s** is shown in Figure 2. Each manganese atom is linked to three terminal carbonyls and a cyclopentadienyl ligand. The two benzopentalene units C7−C18 and C19−C30 are each planar, with the averaged atomic displacement from plane being 0.04 Å, and the dihedral angle between the two planes is 53.5°. The C19−C20 length is 1.484(9) Å, characteristic of *sp*^{2} C−C single bonds. The cyclopentadienyl carbons are bonded to the manganese atom about equally, being 2.17 ± 0.02 Å. The short C8−C9 (1.34(1) Å) and C21−C22 (1.41(1) Å) lengths could indicate the positions of C−C double bonds in the external cyclopentadiene rings. The benzene C−C distances are localized, ranging from 1.30(2) through 1.45(1) Å, implying little aromaticity of the rings.

In summary, the transformation from **1**$^+$ to **3** is of interest within the context of the chemistry of phenylenes[1,2] and pentalenes[22] and of the ability of a transition-metal center to promote these reactions. It may provide an attractive general strategy for the activation of larger [*N*]-phenylenes ($N \geq 3$) which are applicable to organic synthesis.[23] Further investigation is in progress in our laboratory.

Acknowledgment. This research was supported by the National Science Council of Taiwan.

Supporting Information Available: Complete tables of crystallographic data, positional parameters, anisotropic thermal parameters, bond angles, and bond distances of **2s** and **3s** (14 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(18) The ring strain is evidenced by the bond angles in **2s**: C7−C18−C11 = 102.3(3)°, C20−C19−C24 = 101.7(3)°, C11−C18−C17 = 83.9(2)°, and C24−C19−C30 = 83.9(2)° by comparing with those angles in free biphenylene (122.6° and 90°) and in **1**$^+$ (122.3° and 89.3°).

(19) **3s**: mass spectrum (EI), *m*/*z* 582 ($\mathrm{M^+}$), 582−28*n* (*n* = 1−6); IR (*n*-hexane, νCO), 2016 (s), 1948 (vs) $\mathrm{cm^{-1}}$; ^{1}H NMR (acetone-d_6, 20 °C), δ 3.85 (s, 4H), 6.84 (br, 2H), 7.00−7.50 (m, 8H), 7.92 (d, *J* = 9.0 Hz, 2H). Anal. Calcd for $\mathrm{C_{30}H_{16}O_6Mn_2}$: C, 61.88; H, 2.77. Found: C, 61.66; H, 2.83. **3s**: mass spectrum (EI), *m*/*z* 582 ($\mathrm{M^+}$), 582−28*n* (*n* = 1−6); IR (*n*-hexane, νCO), 2016 (s), 1950 (vs) $\mathrm{cm^{-1}}$; ^{1}H NMR (acetone-d_6, −60 °C), δ 3.79 (s, 2H), 3.86 (s, 2H), 6.51 (d, *J* = 4.5 Hz, 1H), 6.69 (d, *J* = 4.8 Hz, 1H), 6.95 (d, *J* = 4.8 Hz, 1H), 7.10 (d, *J* = 5.1 Hz, 1H), 7.22 (t, *J* = 7 Hz, 1H), 7.37 (t, *J* = 6.9 Hz, 1H), 7.44 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.95 (d, *J* = 8.7 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 8.13 (d, *J* = 8.7 Hz, 1H).

(20) Flash vacuum pyrolysis of organic biphenylene (900 °C/0.02 Torr) has been shown to yield benzopentalene, which dimerizes readily and adds cyclopentadiene above −70 °C. See: Brown, R. F. C.; Choi, N.; Coulston, K. J.; Eastwood, F. W.; Wiersum, U. E.; Jenneskens, L. W. *Tetrahedron Lett.* **1994**, *35*, 4405.

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