Reductive Dimerization and Thermal Rearrangement of Biphenylene Coordinated to Tricarbonylmanganese

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[N]-phenylenes are comprised of alternating benzene and cyclobutadiene rings. 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 [(C₆H₄)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 nickel⁸ 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 $[(\eta^6-C_{12}H_8)Mn(CO)_3]^+[BF_4]^-(1^+BF_4^-)^{10}$ 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 $[((\eta^5-C_6H_4)C_6H_4)Mn(CO)_3]_2$ (2), which upon heating rearranges to yield the unprecedented di(benzopentalene) complex $[(\eta^5-C_5(C_4H_4)(C_3H_4))Mn(CO)_3]_2$ (3) (Scheme 1).

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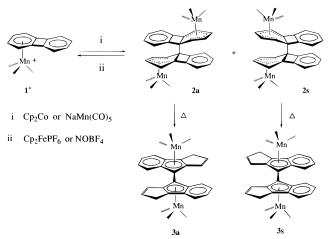
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(10) The IR, NMR, and crystallographic data agree with those previously reported by Sweigart and co-workers for 1^+BF4^- resulting from substitution of the naphthalene ligand in $[(\eta^6$ -naphthalene)Mn(CO)₃] $^+$ [BF4] $^-$ by biphenylene. See: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

Scheme 1



In a typical reaction, a CH₂Cl₂ solution of 1⁺BF₄⁻ (200 mg, 0.53 mmol) and an equimolar solution of cobaltocene were stirred at ambient temperature for 30 min. 12 Two complexes, syn-[((η^5 - $C_6H_4)C_6H_4)Mn(CO)_3]_2$ (2s) and anti-[((η^5 - $C_6H_4)C_6H_4)Mn(CO)_3]_2$ (2a),13 in an approximate 1:1 ratio were isolated in 82% yield after chromatography on silica gel with a CH₂Cl₂/n-hexane (1:4, v/v) eluant. Presumably, initial reduction occurs at the manganese center of $\mathbf{1}^+$ to generate an $[\eta^5\text{-}C_{12}H_8)Mn(CO)_3]$ radical¹⁴ 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 $[Mn(CO)_3(\eta^6-C_6H_6)]^+$ into $[(Mn(CO)_3)]_2(\eta^5,\eta^5-C_{12}H_{12}),^{15}$ is also plausible. It is interesting that $Mn(CO)_5^-$ reduces 1^+ to give $2(s)_5^-$ + a) and Mn₂(CO)₁₀, whereas the organic nucleophiles, R⁻ = H⁻, Me⁻, and Me₃CC(O)CH₂⁻, were found to attack 1⁺ at a bridgehead carbon, forming $((\eta^5\text{-}C_6H_4R)C_6H_4)Mn(CO)_3.^{10}$ Furthermore thermore, treatment of 2s (and 2a) with the oxidizing agent, (Cp₂-Fe)PF₆ or NOBF₄, in CH₂Cl₂ at 25 °C reforms 1⁺ in high yields

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(12) Cyclic voltammetric investigations of 1+BF4- (1 mM in CH₃CN) at 25 °C showed an irreversible reduction potential at -896 mV and an irreversible oxidation potential at +1319 mV (vs Ag/AgCl) with Bu₄NPF₆ (0.1 M) as supporting electrolyte, a Pt button working electrode, and a Pt wire auxiliary electrode.

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⁺), 582–28n (n = 1–6); IR (n-hexane, ν CO), 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); ¹³C{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 C₃₀H₁₆O₆Mn₂: C, 61.88; H, 2.77. Found: C, 61.80; H, 2.75. **2a**: mass spectrum (EI), m/z 582 (M⁺), 582–28n (n = 1–6); IR (n-hexane, VCO), 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); 13 C 1 H} 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 C₃₀H₁₆O₆Mn₂: C, 61.88; H, 2.77. 147.1, 156.5, 223.8 (CO). Anal. Calcd for C₃₀H₁₆O₆Mn₂: C, 61.88; H, 2.77. Found: C, 61.76; H, 2.80.

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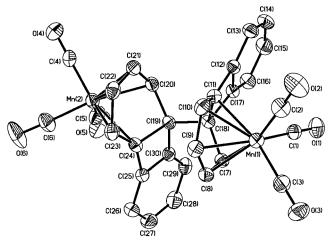


Figure 1. Molecular structure of 2s. The hydrogen atoms have been artificially omitted for clarity.

Chart 1



(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, $1.36 \pm 0.02 \text{ Å}$.

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- $[(\eta^5-C_5(C_4H_4)(C_3H_4))Mn(CO)_3]_2$ (3s) and anti- $[(\eta^5-C_5(C_4H_4)-C_5(C_4H_4))]_2$ (C₃H₄))Mn(CO)₃]₂ (3a), ¹⁹ respectively, in 71% yield after purification by TLC on silica gel eluting with CH₂Cl₂/n-hexane (1:4, v/v). In this reaction the organic ligand has rearranged to form a di(benzopentalene) species,20 and the 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 HMn(diene)(CO)₃ inter-

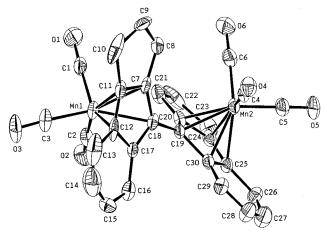


Figure 2. Molecular structure of 3s. The hydrogen atoms have been artificially omitted for clarity.

Scheme 2

mediate has been proposed to account for the hydrogen migration in (η⁵-cyclohexadienyls)Mn(CO)₃.²¹ Nevertheless, a concerted process via a C-C bond migration, a [1,4]-hydrogen shift, and slippage of the 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 pentalenes²² 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 $(N \ge 3)$ which are applicable to organic synthesis.23 Further investigation is in progress in our laboratory.

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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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C45. (18) The ring strain is evidenced by the bond angles in **2s**: C7–C18–C11 = $102.3(3)^\circ$, C20–C19–C24 = $101.7(3)^\circ$, C11–C18–C17 = $83.9(2)^\circ$, and C24–C19–C30 = $83.9(2)^\circ$ by comparing with those angles in free biphenylene (122.6° and 90°) and in 1^+ (122.3° and 89.3°). (19) **3s**: mass spectrum (E1), m/z 582 (M⁺), 582-28n (n=1-6); IR (n-hexane, ν CO), 2016 (s), 1948 (vs) cm⁻¹; ¹H 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 $C_{30}H_{16}O_6Mn_2$: C, 61.88; H, 2.77. Found: C, 61.66; H, 2.83. **3s**: mass spectrum (E1), m/z 582 (M⁺), 582-28n (n=1-6); IR (n-hexane, ν CO), 2016 (s), 1950 (vs) cm⁻¹; ¹H 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), 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).

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