[2 + 2 + 2] Addition of Diphenylketene to the Reductively Activated Benzene in the Transition Metal Complex [Mn(η^4-C_6H_6)(CO)$_3$]$^-$ To Give a Dihydroisochroman-3-one

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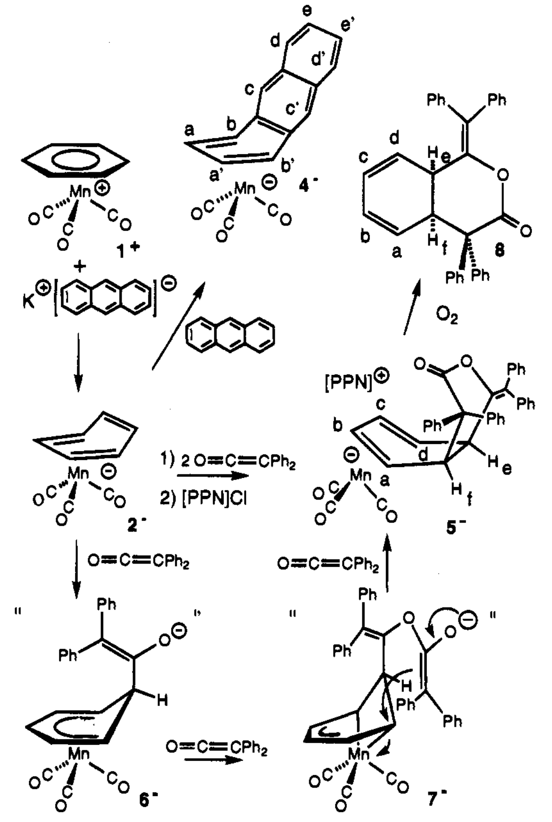
We have previously established that two-electron naphthalenide reduction of the η^6-benzene complex [Mn(η^6-C_6H_6)(CO)$_3$]$^+$ ($\mathbf{1}^+$) results in activation of the benzene with respect to substitution,[1] electrophilic addition,[1] and dimerization.[2] Our proposal that the substitution and addition reactions proceed through an 18-electron η^4-arene complex [Mn(η^4-C_6H_6)(CO)$_3$]$^-$ ($\mathbf{2}^-$) is consistent with our earlier suggestion,[3] confirmed by Wey and Butenschön,[4] that two electron reduction of [Cr(η^6-C_6H_6)(CO)$_3$] gives a reactive complex containing an η^4-benzene ligand.

The formation[2] of the [2 + 2] dimer of $\mathbf{2}^-$ raised the possibility that the uncoordinated double bond in $\mathbf{2}^-$ might participate in cycloaddition reactions. To test this we examined its reaction with diphenylketene; the absence of substituents at the sp carbon of ketenes permits antarafacial approaches to double bonds which may lead to symmetry-allowed [2s + 2a] cycloaddition reactions.[5] Diphenylketene *does* react with $\mathbf{2}^-$, but it gives a [2 + 2 + 2] adduct from which the modified ligand can be recovered in useful yields (see Scheme 1).

We readily established that $\mathbf{2}^-$ prepared by naphthalenide reduction of $\mathbf{1}^+$ reacts with excess diphenylketene, but isolation was initially frustrated by competitive naphthalene substitution to give [Mn(η^4-$C_{10}H_8$)(CO)$_3$]$^-$ ($\mathbf{3}^-$).[1] This was, however, circumvented by preparation of $\mathbf{2}^-$ by potassium anthracenide (KAn) reduction of $\mathbf{1}^+$ in THF; anthracenide is a strong enough reductant (−1.97 V vs SCE in CH_3CN[6]) to convert $\mathbf{1}^+$ to $\mathbf{2}^-$, as established by the consumption of 2 equiv of KAn and the appearance of bands at 1945 (s), 1860 (s), and 1835 (s) cm^{-1} assigned to **K2**, but anthracene substitution of the η^4-benzene ligand is slow and requires ca. 12 h at room temperature to give [Mn(η^4-$C_{14}H_{10}$)(CO)$_3$]$^-$ ($\mathbf{4}^-$). This was isolated as [K(crypt-222)]**4**[7–9] in 72% yield following addition of 1.0 equiv of crypt-222 and recrystallization from CH_2Cl_2/Et_2O (1:4). The rare η^4-coordination mode of the anthracene[10] is established by comparison of its ^{1}H NMR with that of the structurally characterized η^4-naphthalene complex $\mathbf{3}^-$.[1]

Scheme 1



The diphenylketene addition product can be isolated following reaction of 2.4 equiv (0.31 g, 1.60 mmol) of diphenylketene at −78 °C with $\mathbf{2}^-$ freshly prepared by reduction of a slurry of **1**PF_6 (0.22 g, 0.61 mmol) in 25 mL of THF with 2.2 equiv of KAn at −78 °C. The stirred mixture was allowed to warm until it became homogeneous (ca. −10 to 0 °C). The solvent was removed under vacuum, and after washing with Et_2O to remove anthracene the bright orange powder was metathesized with [PPN]Cl (0.35 g, 0.61 mmol; PPN$^+$ = [Ph_3PNPPh_3]$^+$) in THF overnight at room temperature. The solvent was removed and the product was recrystallized from CH_2Cl_2 by addition of *n*-pentane to give a 74% yield of yellow crystals of PPN[Mn{η^4-$C_6H_6CPh_2C({=}O)OC({=}CPh_2)$}(CO)$_3$]·2$CH_2Cl_2$ ([PPN]**5**·2CH_2Cl_2;[8,11] 0.59 g, 0.45 mmol).

A single-crystal X-ray diffraction study[12] established that $\mathbf{5}^-$ is an anion (Figure 1) in which 2 equiv of diphenylketene has

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[1] Thompson, R. L.; Lee, S.; Rheingold, A. L.; Cooper, N. J. *Organometallics* **1991**, *10*, 1657.

[2] (a) Thompson, R. L.; Geib, S. J.; Cooper, N. J. *J. Am. Chem. Soc.* **1991**, *113*, 8961. (b) Lee, S.; Thompson, R. L.; Lovelace, S.; Arford, D.; Weber, S. G.; Cooper, N. J. Manuscript submitted.

[3] (a) Leong, V. S.; Cooper, N. J. *J. Am. Chem. Soc.* **1988**, *110*, 2644. (b) Corella, J. A., II; Cooper, N. J. *J. Am. Chem. Soc.* **1990**, *112*, 2832.

[4] Wey, H. G.; Butenschön, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1444.

[5] (a) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; Chapter 11. (b) Tidwell, T. T. *Ketenes*; John Wiley: New York, 1995.

[6] (a) Parker, V. D. *J. Am. Chem. Soc.* **1976**, *98*, 98. (b) Similar values have been reported in DMF and dioxane: Hoytink, G. J. *Adv. Electrochem. Electrochem. Eng.* **1970**, *7*, 221.

[7] Crypt-222 is an abbreviation for the cryptand 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane.

[8] There are [K(crypt-222)]$^+$ or PPN+ resonances of appropriate intensities in NMR spectra of all anionic species. Microanalyses: Dornis u. Kolbe, Mülheim, Germany. Scheme 1 shows numbering schemes for NMR assignments. Multiplicities describe the appearance of peaks in fully coupled spectra; coupling patterns for $\mathbf{5}^-$ and **8** were established by sequential narrow band decoupling of all coupled nuclei and are consistent with the assignments even if no *J* value is quoted; averaged values are reported for overdetermined coupling constants.

[9] [K(crypt-222)]**4**: IR ($\nu_{C{\equiv}O}$ only, THF) 1945 (s), 1860 (s), 1840 (s) cm^{-1}; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.08 (m, 2H, H_e, H_e'), 6.88 (m, 2H, H_d, H_d'), 6.36 (s, 2H, H_c, H_c'), 5.64 (m, 2H, H_a, H_a'), 2.80 (m, 2H, H_b, H_b'). Anal. Calcd for $C_{35}H_{46}KMnN_2O_9$: C, 57.37; H, 6.33; N, 3.82. Found: C, 57.40; H, 6.58; N, 3.75.

[10] (a) Klein, H.-F.; Ellrich, K.; Lamac, S.; Lull, G.; Zsolnai, L.; Huttner, G. *Z. Naturforsch.* **1985**, *B40*, 1377. (b) Protasiewicz, J. D.; Bianconi, P. A.; Williams, I. D.; Liu, S.; Rao, Ch. P.; Lippard, S. J. *Inorg. Chem.* **1992**, *31*, 4134. (c) Boese, R.; Stanger, A.; Stellberg, P.; Shazar, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1475.

[11] [PPN]**5**·2CH_2Cl_2: IR ($\nu_{C{\equiv}O}$ and $\nu_{C{=}O}$ only, CH_2Cl_2) 1940 (s), 1830 (s, br), and 1760 (m) cm^{-1}; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 6.4–7.3 (m, 20H, 4 Ph), 4.83 (m, 1H, H_b), 4.73 (m, 1H, H_c), 3.52 (dd, J_{He-Hf} = 10.3 Hz, J_{He-Hd} = 2.5 Hz, 1H, H_e), 3.17 (dd, 1H, J_{Hf-He} = 10.3 Hz, J_{Hf-Ha} = 3.6 Hz, H_f), 2.23 (m, J_{Ha-Hb} = 6.1 Hz, J_{Ha-Hc} = 2.4 Hz, 1H, H_a), 1.86 (m, 1H, H_d); ^{13}C NMR (125 MHz, CD_3CN) δ 233.0 (s, CO), 172.0 (s, C=O), 152.8 (s, =CO), 144–126 (m, Ph), 119.7 (s, =CPh_2), 81.1 and 79.8 (each d, $^1J_{CH}$ = 166, 167 Hz, C_b, C_c), 64.1 (s, CPh_2), 56.0 and 53.8 (each d, $^1J_{CH}$ = 156, 161 Hz, C_a, C_d), 48.1 and 41.9 (each d, $^1J_{CH}$ = 138, 124 Hz, C_eC_f). Anal. Calcd for $C_{75}H_{60}Cl_4MnNO_3P_2$: C, 68.56; H, 4.60; N, 1.07. Found: C, 68.25; H, 4.70; N, 1.25.

[12] Crystal data for [PPN]**5**·2CH_2Cl_2: monoclinic space group $P2_1/n$, $Z = 4$, $a = 10.251$ (3) Å, $b = 36.013(9)$ Å, $c = 17.987$ (6) Å, $\beta = 94.88(2)^\circ$, $d_{calcd} = 1.319$ Mg m^{-3}, $\mu = 0.462$ mm^{-1}, $\lambda = 0.710\,73$ Å. Of the 8671 reflections measured in the range $4.0^\circ < 2\theta < 45.0^\circ$, 8105 unique reflections were used in the structure solution by direct methods. Refinement on F^2 converged at $R = 5.37\%$, $wR_{F^2} = 13.24\%$, with GOF = 0.834. Details will be published elsewhere.

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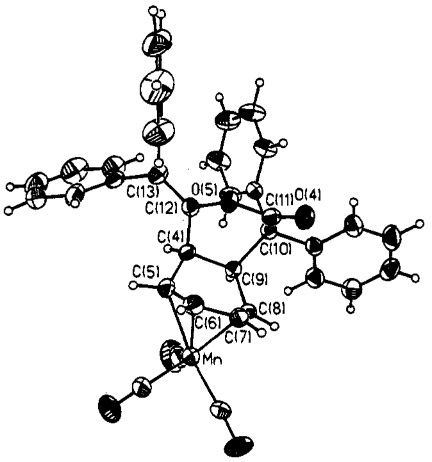

Figure 1. Molecular structure of [Mn{η^4-$C_6H_6CPh_2C(=O)OC(=CPh_2)$}$(CO)_3$]$^-$ (35% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Mn−C(5) = 2.125(5), Mn−C(6) = 2.057(5), Mn−C(7) = 2.068(5), Mn−C(8) = 2.139(5), C(4)−C(5) = 1.524(6), C(4)−C(9) = 1.554(6), C(4)−C(12) = 1.495(6), C(5)−C(6) = 1.409(6), C(6)−C(7) = 1.393(6), C(7)−C(8) = 1.411(6), C(8)−C(9) = 1.510(6), C(9)−C(10) = 1.572(6), C(10)−C(11) = 1.533(6), C(12)−C(13) = 1.342(6), C(11)−O(4) = 1.190(5), C(11)−O(5) = 1.373(5), C(12)−O(5) = 1.397(5); C(5)−C(4)−C(12) = 108.0(4), C(8)−C(9)−C(10) = 112.6(4), C(11)−O(5)−C(12) = 119.7(4), O(5)−C(11)−C(10) = 113.7(4).

been added to the activated benzene in **2**$^-$ to give a bicyclic lactone complex.

We did not anticipate that diphenylketene would give a bis-adduct with **2**$^-$, but this stoichiometry and the exo stereochemistry can be accounted for by a sequence (Scheme 1) in which the first ketene molecule adds as an electrophile to give a cyclohexadienyl complex **6**$^-$. Addition of a second ketene would then give **7**$^-$, which could give the observed product by ring closure.

A polar two-step addition has precedent in the addition of ketenes to imines; it has been known since Staudinger's early reports that these can result in 2:1 adducts as well as the better known[5b] 1:1 β-lactam adducts, and it has been demonstrated[13] that the 2:1 adducts are dihydrooxazinones formed by a mechanism in which the analog of **6**$^-$ is a zwitterion stabilized by the ability of nitrogen to be oxidized from N(III) to N(V). Formation of **6**$^-$ should be even more favorable, since it involves the facile oxidation of Mn(−I) to Mn(I).

Our report[3b] of the carboxylation of $[Cr(\eta^4\text{-}C_6H_6)(CO)_3]^{2-}$ provides some precedent for addition of the first ketene molecule to the arene ligand in **2**$^-$, since both reactions involve heteroallene addition to a reductively activated η^4-benzene. There is a sharp contrast between the endo stereochemistry observed for carboxylation in the Cr system and the exo stereochemistry required (by the configuration of **5**$^-$) for the initial ketene addition to **2**$^-$, but this change is reasonable. The endo stereochemistry in the Cr system reflects a metal-mediated pathway for carboxylation, and the less basic nature of the metal in monoanionic **2**$^-$ could result in a switch to direct electrophilic addition to the arene ring.

The proposed mechanism is consistent with several characteristics of the reaction, including the exo stereochemistry and the experimental observation that the reaction involves the ketene monomer and not its dimer; the dimer reacts with **2**$^-$, but gives a different and as yet uncharacterized organometallic product. We have also obtained some evidence for an intermediate 1:1 adduct by establishing that reaction of **2**$^-$ with 1 equiv of diphenylketene leads to the anthracene complex **4**$^-$ in 73% isolated yield (rather than **5**$^-$ in a reduced yield). The formulation of **6**$^-$ (and of **7**$^-$) must, however, remain speculative at this point.

The dihydroisochroman-3-one ligand in **5**$^-$ has not previously been reported and presents an interesting array of functionalities derived in a straightforward manner from benzene. The ligand was easily removed by oxidation of K**5** prepared from 0.23 g (0.64 mmol) of **1**PF_6 in THF (50 mL) with O_2 at room temperature overnight. The solvent was removed from the bright yellow filtered solution under vacuum, and the solid was washed with toluene. The product was crystallized from a minimum amount of ethanol to give 0.22 g (0.47 mmol = 73%) of white microcrystalline 4a,8a-dihydro-4,4-diphenyl-1-(diphenylmethylidene)isochroman-3-one (**8**)[8,14] (Scheme 1), which was characterized by HRMS, an IR lactone absorption at 1765 cm^{-1}, and comparison of its ^{1}H NMR spectrum with that of **5**$^-$ (the terminal protons of the diene shift, as expected,[1,2a] 3−4 ppm downfield following decomplexation, while the distinctive >10 Hz coupling between the vicinal protons at the ring junction is retained).

The isolation of **5**$^-$ from the reaction of diphenylketene with **2**$^-$, together with our earlier observation that reduction of **1**$^+$ can give a dimer containing a ligand which is a [2 + 2] dimer of benzene,[2] suggests that reductive activation of the benzene in **1**$^+$ may provide access to a range of unusual cycloaddition reactions of benzene. Since simple oxidation releases the ligand from **5**$^-$, and since **1**$^+$ and substituted derivatives are readily available,[15] such reactions could be valuable additions to the known reactions of arenes. Further experiments are under way to explore the range and applications of the cycloaddition reactions.

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(13) (a) Martin, J. C.; Brannock, K. C.; Burpitt, R. D.; Gott, P. G.; Hoyle, V. A., Jr. *J. Org. Chem.* **1971**, *36*, 2211. (b) Pratt, R. N.; Taylor, G. A.; Proctor, S. A. *J. Chem. Soc. C* **1967**, 1569.

(14) **8**: 1H NMR (300 MHz, CD_2Cl_2): δ 7.5−7.1 (m, 18 H, 2Ph + *o,m*-2Ph′), 6.39 (m, 2 H, p-2Ph′), 6.02 (ddd, J_{Hc-Hd} = 9.8 Hz, J_{Hc-Hb} = 5.1 Hz, J_{Hc-He} = 2.4 Hz, 1H, H_c), 5.99 (dd, J_{Hb-Ha}, = 9.3 Hz, J_{Hb-Hc} = 5.1 Hz, 1H, H_b), 5.55 (dd, J_{Hd-Hc} = 9.8 Hz, J_{Hd-He} = 2.2 Hz, 1H, H_d), 5.20 (dd, 1H, J_{Ha-Hb} = 9.3 Hz, J_{Ha-Hf} = 5.9 Hz, H_a), 4.49 (dt, J_{He-Hf} = 11.1 Hz, J_{He-Hd} = 2.2 Hz, J_{He-Hc} = 2.4 Hz,1H, H_e), 3.60 (dd, 1H, J_{Hf-He} = 11.1 Hz, J_{Hf-Ha} = 5.9 Hz, H_f); HRMS calcd for $C_{34}H_{26}O_2$ 466.1933, obsd 466.1928.

(15) Jackson, J. D.; Villa, S. J.; Bacon, D. S.; Pike, R. D.; Carpenter, G. B. *Organometallics* **1994**, *13*, 3972 and references therein.