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General route to anionic (.eta.4-diene)manganese tricarbonyl complexes. Reactions with electrophiles

Maurice. Brookhart, Seok K. Noh, and Francis J. Timmers

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bridging isocyanides in solution or in the solid state. Clearly a delicate balance of factors allows for the interconversion between ligand arrangements 1 and 2, but the formation of the bridged form 1 clearly demonstrates the ability of all of the rhodium atoms in dpmp-bridged complexes to bind to a single substrate.

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Supplementary Material Available: Tables summarizing the data collection and refinement, atom coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen coordinates (14 pages); a listing of structure factors (18 pages). Ordering information is given on any current masthead page.

A General Route to Anionic (η^4-Diene)manganese Tricarbonyl Complexes. Reactions with Electrophiles

Maurice Brookhart,* Seok K. Noh, and
Francis J. Timmers

Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514

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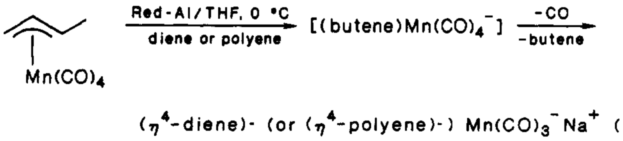
Summary: Reduction of (methallyl)$Mn(CO)_4$ with Red-Al in the presence of substrates containing a conjugated 1,3-diene unit leads to formation of (η^4-diene)$Mn(CO)_3^-$ complexes that can be isolated as stable PPN^+ salts. Substrates examined include 1,3-butadiene, 1,3-cycloheptadiene, 1,3-cyclooctadiene, cycloheptatriene, and cyclooctatetraene. These nucleophilic complexes react readily with electrophiles including H^+, $(CH_3)_3SiOTf$, $(CH_3)_3O^+$, and CO_2 to yield a variety of new manganese tricarbonyl complexes.

(η^4-Diene)iron tricarbonyl complexes have been known for many years and used extensively in synthetic applications.[1] Isoelectronic (η^4-diene)$Mn(CO)_3$ anions have only recently been reported,[2] but the methods of preparation described are not general. We report here a general, convenient synthetic route to (η^4-diene)$Mn(CO)_3^-$ complexes, including the parent complex (η^4-butadiene)$Mn(CO)_3^-$ (1), and selected reactions of these nucleophilic species with electrophiles.

The anionic diene complexes were prepared as shown in eq 1. Reduction of (methallyl)$Mn(CO)_4$ in THF with a 3.4 M solution of sodium bis(2-methoxyethoxy)aluminum hydride in toluene (1 equiv) at 0 °C in the presence of 2 equiv of the diene or polyene leads to formation of the (η^4-diene)- (or (η^4-polyene)-) $Mn(CO)_3^-Na^+$ complexes. Loss of CO and butene occurs; (η^2-butene)$Mn(CO)_4^-$ is a likely intermediate but was not detected.



(1)

Scheme I shows the complexes formed from butadiene, 1,3-cycloheptadiene, 1,3-cyclooctadiene, cycloheptatriene, and cyclooctatetraene. IR spectra of the THF solutions[3] after hydride addition indicate clean conversion to the sodium salts **1a**–**5a**; treatment of these solutions with PPN^+Cl^- results in conversion to the PPN^+ salts **1b**–**5b** which can be precipitated (often as microcrystalline material) by addition of diethyl ether (yields based on $C_4H_7Mn(CO)_4$: **1b** (65%), **2b** (70%), **3b** (40%), **4b** (35%), **5b** (70%).[4]

All anionic complexes **1b**–**5b** are cleanly protonated by HBF_4–Me_2O (−78 °C, CH_2Cl_2); weaker acids such as $NH_4^+Cl^-$ also suffice. Complex **1b** yields the neutral butenyl species **6** (95%, orange oil) characterized by an agostic three-center, two-electron Mn–H–C interaction (J_{C-H} = 89 Hz).[5] Complex **6** is stable to temperatures of 120 °C. Two degenerate modes of isomerization can be detected by variable-temperature NMR spectroscopy.[6] These two processes, together with measured $\Delta G^{\ddagger}$'s, are shown in Scheme I; both processes have close analogies.[7] The low-energy process involves "methyl" rotation and averaging of the agostic hydrogen with H_{1S} and H_{1A} while the high-energy process involves end-to-end averaging via the classical diene hydride. The latter process averages the H_{ag}, H_{1S}, H_{1A} set with H_{4A}, H_{5A}; H_3 with H_4; C_1 with C_4; and C_2 with C_3. Protonation of **2b** and **3b** yields the agostic species **7** and **8** which also display degenerate

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(1) (a) Deeming, A. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 4, pp 425–474. (b) Reihln, H.; Gruhl, A.; V. Hessling, G.; Pfrengle, O. *Liebigs Ann. Chem.* **1930**, *482*, 161. (c) Semmelhack, M. F.; Le, H. T. M. *J. Am. Chem. Soc.* **1985**, *107*, 1455. (d) Semmelhack, M. F.; Herndon, J. *Organometallics* **1983**, *2*, 363. (e) Pettit, R.; Emerson, G. F. *Adv. Organomet. Chem.* **1964**, *1*, 1–46.

(2) (a) Lamanna, W.; Brookhart, M. *J. Am. Chem. Soc.* **1981**, *103*, 989. (b) Brookhart, M.; Lamanna, W.; Humphrey, M. B. *J. Am. Chem. Soc.* **1982**, *104*, 2117. (c) Brookhart, M.; Lamanna, M.; Pinhas, A. R. *Organometallics* **1983**, *2*, 638. (d) Brookhart, M.; Lukacs, A. *J. Am. Chem. Soc.* **1984**, *106*, 4161. (e) Timmers, F.; Brookhart, M. *Organometallics* **1985**, *4*, 1365.

(3) **1a**–**3a**: IR (ν_{CO}, THF) 1940 (s), 1840 (s), 1815 (s), 1785 (s) cm^{-1}. **4a**: IR (ν_{CO}, THF) 1940 (s), 1845 (s), 1815 (s), 1790 (m) cm^{-1}. **5a**: IR (ν_{CO}, THF) 1952 (s), 1865 (s), 1840 (s), 1790 (w) cm^{-1}.

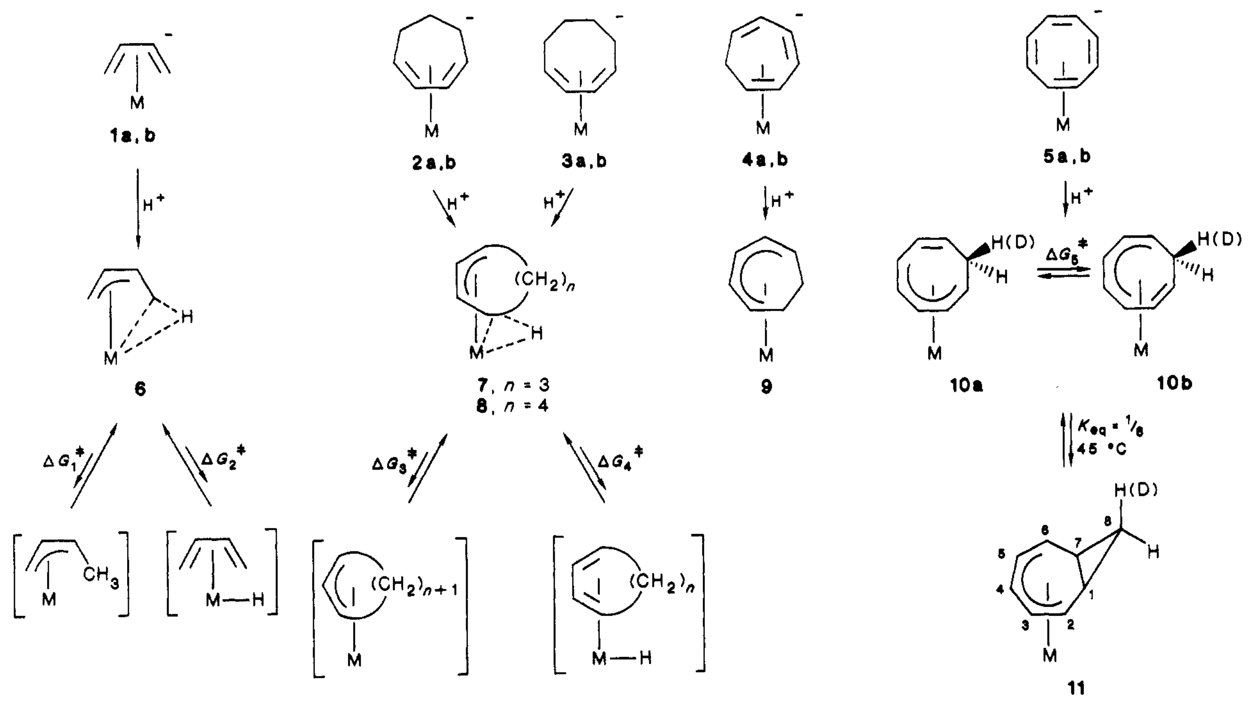
(4) Spectral properties of PPN^+ salts. **1b**: IR (ν_{CO}, THF) 1935 (s), 1838 (s), 1815 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ −0.89 (d, J = 8 Hz, $H_{1a,4a}$), 0.87 (d, J = 7 Hz, $H_{1s,4s}$), 4.68 (m, $H_{2,3}$), 7.3–7.8 (m, PPN^+); ^{13}C NMR (THF-d_8) δ 34.0 (td, J = 152, 6 Hz, $C_{1,4}$), 78.9 (dd, J = 161, 9 Hz, $C_{2,3}$), 130–140 (m, PPN^+), 233.8 (s, CO' s). **2a**: IR (ν_{CO}, THF) 1935 (s), 1938 (s), 1815 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 1.0–1.3 (m, $H_{6n,6x}$), 1.5–1.9 (m, $H_{5,7}$), 2.19 (ddd, $H_{1,4}$), 4.69 (m, $H_{2,3}$), 7.3–7.8 (m, PPN^+); ^{13}C NMR (CD_2Cl_2) δ 27.9 (t, J = 123 Hz, C_6), 28.9 (t, J = 123 Hz, $C_{5,7}$), 52.2 (d, J = 156 Hz, $C_{1,4}$), 84.0 (d, J = 159 Hz, $C_{2,3}$), 130–140 (m, PPN^+), 232.7 (s, CO's). **3b**: IR (ν_{CO}, THF) 1935 (s), 1838 (s), 1815 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 1.0–1.4 (m, $H_{6n,6x,7n,7x}$), 1.88–2.1 (m, $H_{5x,5n,8x,8n}$), 2.45 (m, $H_{1,4}$), 4.75 (m, $H_{2,3}$) 7.3–7.8 (m, PPN^+); ^{13}C NMR (CD_2Cl_2) δ 26.6 (t, $C_{6,7}$), 29.7 (t, $C_{5,8}$), 54.7 (d, $C_{1,4}$), 87.2 (d, $C_{2,3}$), 130–140 (m, PPN^+). **4b**: IR (ν_{CO}, THF) 1935 (s), 1840 (s), 1820 (s) cm^{-1}. ^1H NMR (CD_2Cl_2) δ 2.2 (m, $H_{7x,7n,1}$), 2.53 (m, H_4), 4.5–4.9 (m, $H_{2,3}$), 5.9 (m, H_5), 7.3–7.8 (m, PPN^+); ^{13}C NMR (CD_2Cl_2) δ 32.0 (t, J = 126.5 Hz, C_7), 49.2 (d, J = 147 Hz, C_1), 52.7 (d, J = 146 Hz, C_4), 83.6 (d, J = 161 Hz, C_2), 91.0 (d, J = 160 Hz, C_3), 118.4 (d, J = 152 Hz, C_6), 133.9 (C_5), 130–140 (m, PPN^+), 231.2 (s, CO's). **5a**: IR (ν_{CO}, THF) 1950 (s), 1865 (s), 1840 (s) cm^{-1}; ^1H NMR (THF-d_8) δ 4.84 (s, H_{1-8}), 7.3–7.8 (m, PPN^+); ^{13}C NMR (THF-d_8) δ 94.1 (d, J = 149.5 Hz, C_{1-8}), 130–140 (m, PPN^+), 232.1 (s, CO's). Complex **5a** is fluxional, and all ring hydrogens and ring carbons appear equivalent by NMR down to temperatures of −100 °C. This fluxional behavior is similar to the $(C_8H_8)Fe(CO)_3$ analogue: Kreiter, C. G.; Maasbol, A.; Anet, F. A. L.; Kaesz, H. D.; Winstein, S. *J. Am. Chem. Soc.* **1966**, *88*, 3444. Cotton, F. A.; Davison, A.; Faller, J. W. *Ibid.* **1966**, *88*, 4507. Keller, C. E.; Shoulders, B. A.; Pettit, R. *Ibid.* **1966**, *88*, 4760. Anet, F. A. L.; Kaesz, H. D.; Maasbol, A.; Winstein, S. *Ibid.* **1967**, *89*, 2489. Complexes **1b**, **2b**, **3b**, and **5b** are very air-sensitive in solution. The solids are only moderately air-sensitive and can be handled *briefly* in air. Complex **4b** is thermally unstable and undergoes slow decomposition even at −10 °C both in solution and as a solid.

(5) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

(6) For spectroscopic characterization and analytical data see supplementary material.

(7) (a) Ittel, S. D.; Van-Catledge, F. A.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 6905. (b) Brookhart, M.; Whitesides, T. H.; Crockett, J. M. *Inorg. Chem.* **1976**, *15*, 1550. (c) Howarth, D. W.; McAteer, C. H.; Moore, P.; Morris, G. E. *J. Chem. Soc., Chem. Commun.* **1981**, 506. (d) Brookhart, M.; Cox, K.; Cloke, F. G. H.; Green, J. C.; Green, M. L. H.; Hare, P. M. *J. Chem. Soc., Dalton Trans.* **1985**, 423.

Scheme I[a]

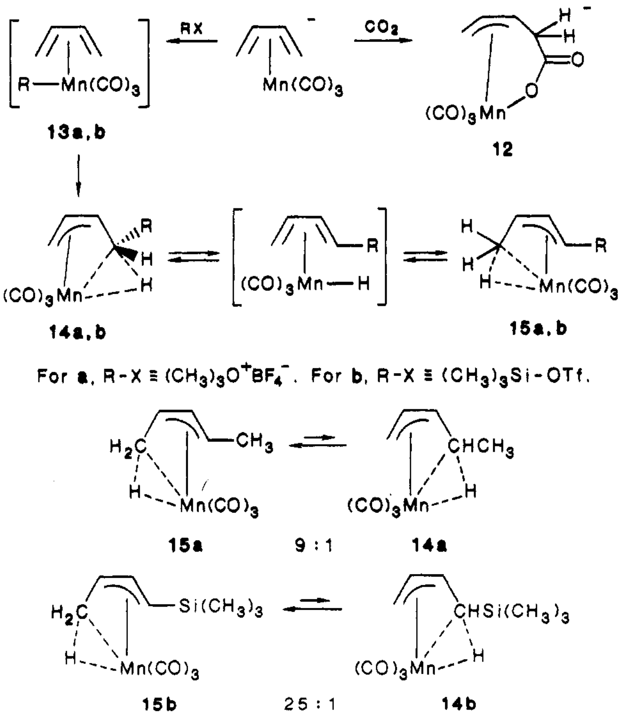


[a] M = Mn(CO)$_3$; **1a**–**5a** counterion = Na$^+$; **1b**–**5b** counterion = PPN$^+$. $\Delta G^\ddagger$'s (kcal/mol): $\Delta G_1^\ddagger = 9.1$, $\Delta G_2^\ddagger = 17.1$, $\Delta G_3^\ddagger$ ($n = 3$) = 9.2, $\Delta G_4^\ddagger$ ($n = 3$) = 16.4, $\Delta G_3^\ddagger < 7.8$, $\Delta G_4^\ddagger > 19.1$, $\Delta G_5^\ddagger = 12.6$.

modes of isomerization similar to those of **6** and other species.[2,5–7] Treatment of **4b** and **5b** with HBF$_4$–Me$_2$O results in protonation of the uncomplexed double bond to generate the known (η^5-cycloheptadienyl)Mn(CO)$_3$[8] (**9**) and (η^5-cyclooctatrienyl)Mn(CO)$_3$[8] (**10**) (a fluxional system, **10a** $\rightleftharpoons$ **10b**, $\Delta G^\ddagger = 12.6$ kcal/mol).[6] Species **10** is in equilibrium via electrocyclic ring closure with the bicyclic species **11** at 45 °C (**10**:**11** = 6 at 45 °C).[6] Results using D$_2$SO$_4$ establish exo attack by D$^+$ (H$^+$).[9] Data are summarized in Scheme I.[10]

Complexes **1**–**5** are quite reactive toward organic electrophiles, and some representative reactions are shown in Scheme II. The stable CO$_2$ adduct **12** is formed rapidly at 25 °C upon exposure to 1 atm of CO$_2$.[11] The methylation and silylation reactions, which yield the agostic species **14** and **15**, may proceed via **13**, but **13** cannot be detected. Carrying out the silylation reactions at low temperatures confirms **14b** as the first-formed agostic species. In both the methyl- and silyl-substituted systems equilibrium favors species **15** (**15a**:**14a** = 9:1, **15b**:**14b** = 25:1). Methylation of (cyclooctatetraene)Mn(CO)$_3^-$ occurs rapidly with CH$_3$I at 25 °C to give the fluxional (*exo*-8-methyl-5-cyclooctatrienyl)manganese tricarbonyl complex, **16** (**16a** $\rightleftharpoons$ **16b**, $\Delta G^\ddagger = 16.1$ kcal/mol). (Stereochemistry has been established by X-ray analysis.)[12] The bicyclic isomer **17** (analogous to **11**) cannot be detected spectroscopically.

Scheme II



These facile reactions of anionic (diene)Mn(CO)$_3$ com-

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(8) King, R. B.; Ackermann, M. N. *Inorg. Chem.* **1974**, *13*, 637. King has reported formation of **10** from reaction of C$_8$H$_8$ with [HMn(CO)$_4$]$_3$ in 6.4% yield. Our ^{1}H NMR data match those reported, but in addition we note equilibration of **10** with bicyclic isomer **11**.

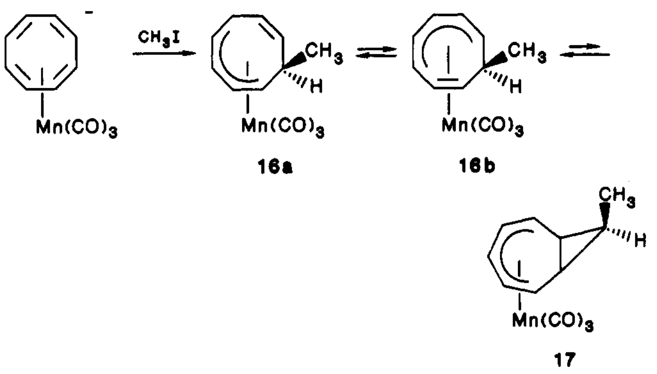
(9) Coupling constant analysis in **11** establishes assignments of exo and endo hydrogens and thus stereochemistry of deuteriation: $J_{gem} = 4.2$ Hz, $J_{H_{exo}-H_{1,7}} = 4.3$ Hz, $J_{H_{endo}-H_{1,7}} = 8.3$ Hz, ^{1}H (toluene-d_8): δ 0.31 (dt, H$_{8n}$), 0.87 (dt, H$_{8x}$), 1.28 (m, H$_{1,7}$).

(10) The cationic iron analogue of **10** is known but undergoes rapid and quantitative ring closure to the analogue of **11**, the (bicyclo[5.1.0]-octadienyl)iron tricarbonyl cation: Brookhart, M.; Davis, E. R.; Harris, D. L. *J. Am. Chem. Soc.* **1972**, *94*, 7853.

(11) Hoberg, H.; Jenni, K.; Kruger, C.; Raabe, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*(9), 210 report an analogous CO$_2$ adduct using C$_4$H$_8$Fe(PMe$_3$)$_3$.

(12) Hong, Y.; Noh, S. K; Brookhart, M., to be submitted for publication.

(13) For example **1**–**3** can be protonated with H$_2$O while (diene)iron tricarbonyl complexes require very strong acids with noncoordinating counterions to yield analogous species: See 7b and: Olah, G. A.; Liang, G. A.; Yu, S. H. *J. Org. Chem.* **1976**, *41*, 2227. The neutral iron analogues of **1**–**5** are unreactive to methylating reagents but (butadiene)Fe(CO)$_3$ can be acylated under vigorous conditions: Graf, R. G.; Lillya, C. P. *J. Am. Chem. Soc.* **1972**, *94*, 8282.



plexes with simple organic electrophiles are in marked contrast to isoelectronic neutral (diene)Fe$(CO)_3$ complexes.[12] Such reactivity differences and the ability to directly functionalize the complexed diene or polyene via reactions with electrophiles and to demetalate such complexes[2c,d] makes these manganese complexes potentially useful synthetic complements to the (diene)iron tricarbonyl systems.

Acknowledgment is made to the National Institutes of Health (GM23938) for support of this research.

Supplementary Material Available: Spectroscopic characterization for **6–8**, **10–12**, **14a,b**, **15a,b**, and **16** and analytical data for **1b–3b**, **5b**, **6**, **7**, **10**, **15a,b**, and **16** (6 pages). Ordering information is given on any current masthead page.

Book Reviews

Tailored Metal Catalysts. Edited by Y. Iwasawa. D. Reidel Publishing Co., Dordrecht. 1986. xii + 333 pages. $59.00.

This book is about the chemistry of an increasingly important class of catalysts, metal complexes anchored to solids. H. Hirai and N. Toshima have contributed a well-organized chapter covering the literature of polymer-attached transition-metal complex catalysts, illustrating, for example, the role of the physical properties of the support in influencing the catalyst structure and performance: properly chosen supports can stabilize coordinative unsaturation of metal centers, allow chelation of metal centers with ligands such as phosphines to facilitate control of catalyst selectivity, and allow positioning of catalyst and promoter functions to facilitate their cooperative action. The chapter by Y. Iwasawa concerns transition-metal complexes bonded to metal oxides. The surface chemistry of some of these catalysts is remarkably well-known; the role of silica, for example, as a ligand for supported molybdenum complexes is illustrated with precisely defined structures, with even the Mo–O bond lengths determined by extended X-ray absorption fine structure spectroscopy. R. F. Howe has compiled the literature of catalysts prepared from mononuclear metal carbonyls supported on inorganic solids. Some structurally well-defined species are known, but typically the catalytically active species formed from these precursors are unknown and structurally complex. M. Ichikawa's chapter on supported catalysts derived from metal clusters has some tantalizing information about well-defined surface species, but most of the catalysts are ill-defined and consist of metal aggregates on the supports. Much of this chapter is focused on CO hydrogenation catalysis; the influence of organometallic chemistry on the interpretation of reaction mechanism, even with the supported metal aggregates, is strongly in evidence. The literature of asymmetrically modified nickel catalysts is reviewed by A. Tai and T. Harada. These hydrogenation catalysts consist of optically active compounds implanted on the nickel surface; the nickel activates hydrogen, and the optically active component acts as a stereochemical regulator of the organic reactant.

This book covers the literature through 1982, with a few references to later work. It is an important source of ideas and a stimulating account that justifies the use of the term "tailored catalysts". There are still only a few supported transition-metal catalysts that have truly been designed, and most of these are simple analogues of soluble molecular catalysts. Nonetheless, the knowledge of these is developing rapidly, and there are compelling prospects for "tailored" surface species with new structures and unique catalytic properties (such as multinuclear metal assemblies and uniquely sized metal aggregates). Wider recognition of these prospects will strengthen the role of organometallic chemistry in surface catalysis.

B. C. Gates, *University of Delaware*

Metal Clusters in Catalysis (Studies in Surface Science and Catalysis. 29.). Edited by B. C. Gates, L. Guczi, and H. Knözinger. Elsevier, Amsterdam. 1986. xxvii + 648 pp. $84.75.

Metal cluster chemistry has been developed at least in part because of the potential offered for improved catalysts, either homogeneous or heterogeneous. The stated purpose of this monograph is "to give a thorough and critical evaluation of the literature and prospects of metal clusters in catalysis". In large part that goal has been achieved.

Part I concerns molecular cluster chemistry. Short chapters by G. L. Geoffroy review syntheses (18 pages, 60 references) and structures (11 pages, 8 references). Missing is any discussion of the theories of bonding and structure in larger clusters, but references to comprehensive reviews are given. Thermochemistry and energies of metal–metal and metal–ligand bonds are tabulated by J. A. Connor (8 pages, 26 references). A chapter on reactivities of metal clusters (G. Lavigne and H. D. Kaesz, 40 pages, 168 references) emphasizes reactions of molecular clusters which have some relevance to catalysis. Concluding this part is a chapter on homogeneous catalysis (28 pages, 116 references) by L. Markô and A. Vizi-Orosz; although many examples of cluster catalysis are reviewed, the authors note that in most cases it is difficult to prove that the catalyst is actually a cluster. Part I will be of value to readers who are not active in molecular cluster chemistry, but the brevity of the chapters and the fact that most references are pre-1984 makes the section less valuable to researchers in the area.

Part II addresses the primary topic of the volume, supported metal clusters. This section begins with general chapters on methods of characterization of supported clusters: vibrational (38 pages, 155 references), optical (12 pages, 36 references), and magnetic resonance spectroscopy (18 pages, 82 references) and thermoanalytical methods (4 pages, 12 references) by H. Knözinger, photoelectron (9 pages, 40 references) and Mössbauer specroscopy (9 pages, 17 references) by L. Guczi, and X-ray absorption spectroscopy (27 pages, 29 references) by R. F. Pettifer. Next the preparation and characterization of supported metal clusters are presented: a thorough review of deposition of metal clusters in matrices by metal atom vaporization (G. A. Ozin and M. P. Andrews, 86 pages, 151 references), clusters supported in zeolites (P. A. Jacobs, 51 pages, 198 references), molecular metal clusters supported on polymers or chemically modified oxides (B. C. Gates, 9 pages, 42 references), and clusters on unfunctionalized oxides (R. Psaro and R. Ugo, 59 pages, 277 references). This part concludes with chapters on the use of supported clusters for alkene conversions (Gates, 10 pages, 20 references), hydrogenolysis and skeletal isomerization of hydrocarbons (G. Maire, 19 pages, 56 references), CO reduction (Knözinger and Gates, 13 pages, 52