

Figure 2. Proposed intermediates in inter-ring η^5, η^5 -haptotropic rearrangements of anionic manganese tricarbonyl complexes of isomeric indeno[1,2-*a*]- and indeno[2,1-*a*]indenes.

version lying in the middle of $C_{5a}-C_{10a}$. For 12 there is a σ_2 plane perpendicular to σ_{xy} , passing through C_4-C_{9a} . In accord with this, nodal properties of two upper occupied, bonding π -MO's of both dianions 11 and 12 cannot be classified relating to the common symmetry element. There is also no common element of symmetry with vacant e and e' orbitals of the $Mn(CO)_3^+$ fragment, retained along the reaction path.

Qualitatively, however, it may be concluded that for the trans anion 11 $\pi(1) + e$, $\pi(1) + e'$, $\pi(2) + e$, and $\pi(2) + e'$ interactions may occur. The first two are strong and stabilize the ground state. While the $Mn(CO)_3^+$ group is moving from one ring to another, only one $\pi(1) + e'$ interaction is retained under the condition that the $Mn(CO)_3^+$ group shifts to the periphery of the system. The intermediate must have the structure 13 (Figure 2). However, with further movement this bonding interaction

disappears. Thus, the inter-ring η^5, η^5 rearrangement as an intramolecular process for complex 6 is completely prohibited.

In the case of cis anion 12 $\pi(1)$ may participate only in one bonding $\pi(1) + e$ interaction, while $\pi(1) + e'$, $\pi(2) + e$, and $\pi(2) + e'$ will be very weak. According to this, bonding of the $Mn(CO)_3^+$ group in complex 9 in the ground state is weakened in comparison with that in 6. In intermediate 14 with rearrangement of complex 9, the $\pi(1) + e$ interaction is lost while $\pi(1) + e'$ becomes very strong.

Therefore, 14 must be more stable than 13. The obligatory withdrawal of the $Mn(CO)_3^+$ group over the ligand contour is not necessary; i.e., as in the case of the cation (pentalene)cyclopentadienyliron¹ the transition on the least motion principle becomes "partially allowed".

The synthesis of the complexes 3-10 and their characteristics have been described.^{19,20}

Acknowledgment. We express our gratitude to the Varian Co. for making available the NMR-VXR-400 spectrometer within the framework of the agreement on scientific-technical cooperation between Moscow University and Varian.

Registry No. 7, 125610-38-0; 8, 125610-39-1; 9, 125610-40-4; 10, 125610-41-5; 11, 65583-99-5; 12, 72866-14-9.

(20) Trifonova, O. I.; Galiullin, R. A.; Kazennova, N. B.; Ustynyuk, Yu. A.; Ustynyuk, N. A.; Kravtsov, D. N.; Piven, V. A. *Metalloorg. Khim.* 1988, 1, 1300-1307.

Unusual Trigonal-Bipyramidal Coordination of Gallium by an Aza Crown Ether. Synthesis and Molecular Structure of $[Ga(CH_3)_2][C_{12}H_{25}N_2O_4][Ga(CH_3)_3]_2$

Baosheng Lee, William T. Pennington, and Gregory H. Robinson*

Department of Chemistry, Clemson University, Clemson, South Carolina 29634-1905

Received January 22, 1990

Summary: Reaction of diaza-18-crown-6, $C_{12}H_{26}N_2O_4$, with trimethylgallium in a toluene/heptane mixture affords the crystalline complex $[Ga(CH_3)_2][C_{12}H_{25}N_2O_4][Ga(CH_3)_3]_2$. The title compound contains two trimethylgallium units and one dimethylgallium unit. The dimethylgallium unit resides within the cavity of the aza crown with the gallium atom bonding to two oxygen atoms and a nitrogen atom in addition to the two methyl carbon atoms. As the gallium atom, the two carbon atoms, and the nitrogen atom constitute a basal plane while the two oxygen atoms of the crown are found to reside above and below the plane (O-Ga-O bond angle $157.2(2)^\circ$), the coordination of the core gallium atom may be described as distorted trigonal bipyramidal.

The last decade witnessed a proliferation of advances in the chemistry of gallium. Seminal discoveries concerning gallium compounds have found utility in the diagnosis of disease¹⁻³ as well as in the production of semiconductor materials.⁴⁻¹⁰ This laboratory has an interest

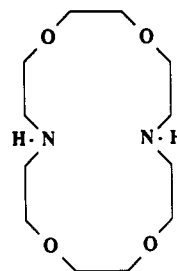


Figure 1. The mixed nitrogen-oxygen donor crown ether diaza-18-crown-6, $C_{12}H_{26}N_2O_4$.

in the chemistry of gallium as it relates to the liquid inclusion compounds known as liquid clathrates, $[M_2R_6X][CE \cdot M']$ ($M = Al, Ga$; $R = \text{alkyl}$; $X = \text{halide}$; $CE = \text{oxygen-based crown ethers}$; $M' = \text{alkali-metal ion}$).¹¹ It

(5) Wells, R. L.; Shafieezad, S.; McPhail, A. T.; Pitt, C. G. *J. Chem. Soc., Chem. Commun.* 1987, 486.

(6) Keyes, R. W. *Science* 1985, 230, 138.

(7) Arif, A. M.; Benac, B. L.; Cowley, A. H.; Geerts, R.; Jones, R. A.; Kidd, K. B.; Power, J. M.; Schwab, S. T. *J. Chem. Soc., Chem. Commun.* 1986, 1453.

(8) Cowley, A. H.; Benac, B. L.; Ekerdt, J. G.; Jones, R. A.; Kidd, K. B.; Lee, J. Y.; Miller, J. E. *J. Am. Chem. Soc.* 1988, 110, 6248.

(9) Cowley, A. H.; Jones, R. A.; Kidd, K. B.; Nunn, C. M.; Westmoreland, D. L. *J. Organomet. Chem.* 1988, 341, C1.

(10) Heaton, D. E.; Jones, R. A.; Kidd, K. B.; Cowley, A. H.; Nunn, C. M. *Polyhedron* 1988, 7, 1901.

(1) Moerlein, S. M.; Welch, M. J.; Raymond, K. N. *J. Nucl. Med.* 1982, 23, 506.

(2) Taliaferro, C. H.; Martell, A. *Inorg. Chim. Acta* 1984, 85, 9.

(3) Green, M. A.; Welch, M. J.; Mathias, C. J.; Fox, K. A. A.; Knabb, R. M.; Huffman, J. C. *J. Nucl. Med.* 1985, 26, 170.

(4) Wells, R. L.; Pitt, C. G.; McPhail, A. T.; Purdy, A. P.; Shafieezad, S.; Hallick, R. B. *Chem. Mater.* 1989, 1, 4.

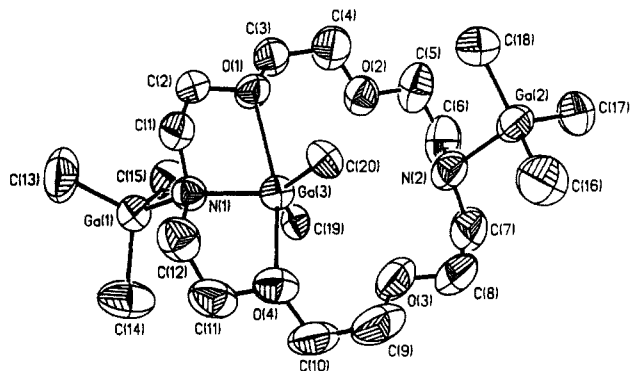
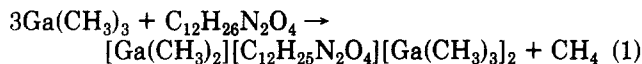


Figure 2. View of the $[\text{Ga}(\text{CH}_3)_2][\text{C}_{12}\text{H}_{25}\text{N}_2\text{O}_4][\text{Ga}(\text{CH}_3)_3]_2$ molecule showing the atom-labeling scheme. Thermal ellipsoids show 50% probability levels; hydrogen atoms have been omitted. Selected bond distances (Å) and angles (deg): Ga(1)–N(1) = 2.164 (5); Ga(1)–C(13) = 1.969 (9); Ga(1)–C(14) = 1.982 (9); Ga(1)–C(15) = 2.002 (9); Ga(2)–N(2) = 2.171 (6); Ga(2)–C(16) = 2.007 (9); Ga(2)–C(17) = 1.966 (9); Ga(2)–C(18) = 1.999 (8); Ga(3)–N(1) = 2.024 (5); Ga(3)–C(19) = 1.95 (2); Ga(3)–C(20) = 1.97 (2); Ga(3)–O(1) = 2.450 (5); Ga(3)–O(4) = 2.278 (5); O(1)–Ga(3)–O(4) = 157.2 (2); N(1)–Ga(3)–C(20) = 112.6 (7); N(1)–Ga(3)–C(19) = 112.2 (6); C(19)–Ga(3)–C(20) = 135.2 (9); O(1)–Ga(3)–N(1) = 78.5 (3); O(1)–Ga(3)–C(20) = 86.5 (7); O(1)–Ga(3)–C(19) = 102.4 (7); O(4)–Ga(3)–C(19) = 98.0 (7); O(4)–Ga(3)–C(20) = 86.2 (7); O(4)–Ga(3)–N(1) = 84.5 (2).

has been shown that $[\text{MR}_3]_n[\text{CE}]$ complexes can facilitate the preparation of liquid clathrates in the presence of appropriate alkali-metal salts.^{12–14} Studies in this area have also involved nitrogen-based crown ethers.^{15,16} Importantly, these advances in organoaluminum host–guest chemistry contributed to significant breakthroughs in the organometallic coordination chemistry of aluminum.^{17–22} Although the literature offers a few studies in this area,^{23–26} the organometallic coordination chemistry of gallium has not developed in parallel with that of aluminum. We have endeavored to address this by exploring the organogallium chemistry of the mixed nitrogen–oxygen donor crown ether diaza-18-crown-6 ($\text{C}_{12}\text{H}_{26}\text{N}_2\text{O}_4$)²⁷ (Figure 1). Herein, we

report the synthesis and molecular structure of $[\text{Ga}(\text{C}-\text{H}_3)_2][\text{C}_{12}\text{H}_{25}\text{N}_2\text{O}_4][\text{Ga}(\text{CH}_3)_3]_2$, isolated from the reaction of trimethylgallium with diaza-18-crown-6 (eq 1).²⁸ The



title compound is novel, as it represents the first structural characterization of an organogallium–hetero crown ether complex. Moreover, $[\text{Ga}(\text{CH}_3)_2][\text{C}_{12}\text{H}_{25}\text{N}_2\text{O}_4][\text{Ga}(\text{CH}_3)_3]_2$ is noteworthy, as it contains an unusual pentacoordinate organogallium moiety residing within the cavity of the aza crown. The X-ray crystal structure of $[\text{Ga}(\text{CH}_3)_2][\text{C}_{12}\text{H}_{25}\text{N}_2\text{O}_4][\text{Ga}(\text{CH}_3)_3]_2$ is given in Figure 2.

X-ray intensity data were collected on a Nicolet R3m/V diffractometer by using an $\omega/2\theta$ scan technique with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 21 °C. The title compound crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions $a = 14.344 (4) \text{ \AA}$, $b = 12.122 (3) \text{ \AA}$, $c = 16.552 (3) \text{ \AA}$, $\beta = 95.35 (2)^\circ$, $V = 2866 \text{ \AA}^3$, and $D_{\text{calc}} = 1.37 \text{ g cm}^{-3}$ for $Z = 4$. The dimethylgallium unit was determined to be disordered over two possible sites.²⁹ The non-hydrogen atoms were refined with use of anisotropic thermal parameters. Methylene and methyl hydrogen atoms bonded to full-occupancy carbon atoms were included in the structure factor calculation at idealized positions ($d_{\text{C-H}} = 0.96 \text{ \AA}$); separate isotropic group thermal parameters were refined for the methylene ($U_{\text{iso}} = 0.115 (6) \text{ \AA}^2$) and methyl ($U_{\text{iso}} = 0.18 (1) \text{ \AA}^2$) hydrogen atoms. Hydrogen atoms of the disordered dimethylgallium unit and the two possible sites for the N–H group could not be located by standard Fourier techniques, and these atoms were not included in the model. The structure was solved by direct methods and refined, on the basis of 2857 observed reflections with intensities $I > 3\sigma(I)$, with use of SHELXTL.³⁰ Refinement converged at $R = 0.051$ ($R_w = 0.070$).

Several points are worthy of note regarding structure and bonding in $[\text{Ga}(\text{CH}_3)_2][\text{C}_{12}\text{H}_{25}\text{N}_2\text{O}_4][\text{Ga}(\text{CH}_3)_3]_2$. The title compound contains two types of organogallium moieties: one central dimethylgallium unit and two terminal trimethylgallium units. The gallium atoms, Ga(1) and Ga(2), of the terminal trimethylgallium units are found in the usual four-coordinate tetrahedral coordination geometry. However, the central gallium atom, Ga(3), is clearly five-coordinate. Atoms N(1), Ga(3), C(19), and C(20) constitute a basal plane, while the coordination sphere of Ga(3) is completed by O(1) and O(4) residing in

(28) Diaza-18-crown-6 (0.25 g, 0.95 mmol) was allowed to react with trimethylgallium (5 mmol, 0.57 mL) in toluene in a 50-mL reaction vessel in a drybox. The reaction tube was removed from the drybox and heated (130 °C) in an oil bath for 24 h. When the solution was cooled to 0 °C, a multitude of colorless, rectangular, air-sensitive, X-ray-quality crystals deposited on the wall of the reaction vessel in quantitative yield (based on the crown ether); mp = 118–120 °C. ¹H NMR (CDCl_3): δ –0.57 (s, 6 H, $\text{Ga}(\text{CH}_3)_2$), 0.052 (s, 18 H, $\text{Ga}(\text{CH}_3)_3$), 2.30 (s, 1 H, NH), 2.86 (t, 8 H, $\text{OCH}_2\text{CH}_2\text{N}$), 3.59 (s, 8 H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.60 (t, 8 H, $\text{OCH}_2\text{CH}_2\text{N}$). Note: Although the two trimethylgallium units in the title compound are fundamentally inequivalent, the environments about the two gallium atoms are sufficiently similar so as to constitute an unresolvable singlet. In addition, the resonances of these two trimethylgallium units have been found to overlap perfectly with that due to $\text{Si}(\text{CH}_3)_4$. ¹³C NMR (CDCl_3): δ –5.71 (s, 8 C, $\text{Ga}(\text{CH}_3)_2$), 48.21 (s, 4 C, $\text{OCH}_2\text{CH}_2\text{N}$), 66.96 (s, 4 C, $\text{OCH}_2\text{CH}_2\text{O}$), 70.18 (s, 4 C, $\text{OCH}_2\text{CH}_2\text{O}$). Infrared spectrum (cm^{-1} , Nujol): 4431 (s), 3600 (w), 545 (w), 511 (w).

(29) The occupancy of the major site is represented by atoms Ga(3), C(19), and C(20), while the minor site is represented by atoms Ga(3a), C(19a), and C(20a) (a view of the minor conformation is provided in the supplementary material). The group multiplicity of the major component was refined to a value of $m = 0.513 (2)$, and the group multiplicity of the minor component was constrained to be $1 - m$. All other atoms of the molecule for the two possible orientations are so closely overlapped that resolution was not possible.

(30) Sheldrick, G. M. SHELXTL, Crystallographic Computing System, Revision 5.1; Nicolet Instruments Division: Madison, WI, 1986.

(11) Atwood, J. L. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic: London, 1984; Vol. 1, pp 375–405.

(12) Atwood, J. L.; Hrcir, D. C.; Shakir, R.; Dalton, M. S.; Priester, R. D.; Rogers, R. D. *Organometallics* 1982, 1, 1021.

(13) Atwood, J. L.; Elgmal, H.; Robinson, G. H.; Bott, S. G.; Weeks, J. A.; Hunter, W. E. *J. Inclusion Phenom.* 1984, 2, 367.

(14) Robinson, G. H.; Bott, S. G.; Elgmal, H.; Hunter, W. E.; Atwood, J. L. *J. Inclusion Phenom.* 1985, 3, 65.

(15) Robinson, G. H.; Rae, A. D.; Campana, C. F.; Byram, S. K. *Organometallics* 1987, 6, 1227.

(16) Robinson, G. H.; Zhang, H.; Atwood, J. L. *J. Organomet. Chem.* 1987, 331, 153.

(17) Robinson, G. H.; Sangokoya, S. A. *J. Am. Chem. Soc.* 1987, 109, 6852.

(18) Robinson, G. H.; Sangokoya, S. A.; Moise, F.; Pennington, W. T. *Organometallics* 1988, 7, 1887.

(19) Robinson, G. H.; Sangokoya, S. A. *J. Am. Chem. Soc.* 1988, 110, 1494.

(20) Sierra, M. L.; de Mel, V. S. J.; Oliver, J. P. *Organometallics* 1989, 8, 2486.

(21) Leman, J. T.; Barron, A. R. *Organometallics* 1989, 8, 1828.

(22) Healy, M. D.; Barron, A. R. *J. Am. Chem. Soc.* 1989, 111, 398.

(23) See for example: Robinson, G. H.; Hunter, W. E.; Bott, S. G.; Atwood, J. L. *Organomet. Chem.* 1987, 326, 9 and references cited therein.

(24) Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* 1974, 52, 2206.

(25) Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* 1975, 53, 58.

(26) Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* 1975, 53, 753.

(27) The IUPAC name for this mixed nitrogen–oxygen donor crown ether is 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane. Albeit somewhat less formal and akin to the trivial nomenclature often employed for crown ethers, the macrocycle is also referred to as 4,13-diaza-18-crown-6. We refer to this macrocyclic ligand simply as diaza-18-crown-6.

axial positions on either side of the N-Ga-C₂ basal plane. As the O(1)-Ga(3)-O(4) bond angle is 157.2 (2)°, the coordination environment about Ga(3) may be described as distorted trigonal bipyramidal. It is interesting to note that the Ga(3)-N(1) bond distance of 2.024 (5) Å is noticeably shorter than the terminal Ga-N bond distances of 2.164 (5) and 2.171 (6) Å for Ga(1)-N(1) and Ga(2)-N(2), respectively. The Ga-O bond distances are 2.450 (5) and 2.278 (5) Å for Ga(3)-O(1) and Ga(3)-O(4), respectively. These Ga-O bond distances in the title compound are exceedingly long and, when compared to those in other organogallium-oxygen compounds,²³ must be considered among the longest reported. Furthermore, considering the great affinity that gallium has for oxygen, in addition to the fact that the aza crown contains twice as many oxygen atoms as nitrogen atoms, it is interesting to note that the trimethylgallium units preferred nitrogen over oxygen. The conformation of the crown in [Ga(CH₃)₂][C₁₂H₂₆N₂O₄][Ga(CH₃)₃]₂ is also noteworthy. The conformation of dibenzo-18-crown-6 in [Ga(CH₃)₃]₂[dibenzo-18-crown-6]²³ was observed to be exodentate. Indeed, the conformation of crown ethers is predominantly found to be exodentate in group 13 metal-crown ether complexes. However, the conformation of diaza-18-crown-6 in the title compound is determined to be endodentate. This may be regarded as a consequence of the stabilizing influence of the central dimethylgallium unit as well as N-H...O hydrogen bonding

present in the compound.³¹ From a comparison of other pentacoordinate organogallium moieties,^{24-26,32,33} it appears that trigonal bipyramidal is the preferred mode of coordination geometry. Forthcoming studies from this laboratory will further examine factors affecting the organometallic coordination chemistry of gallium.

Acknowledgment. We are grateful to the National Science Foundation for support of this work to G.H.R. (Grant No. RII-8520554).

Registry No. [Ga(CH₃)₂][C₁₂H₂₆N₂O₄][Ga(CH₃)₃]₂, 126876-15-1; Ga(CH₃)₃, 1445-79-0; C₁₂H₂₆N₂O₄, 23978-55-4.

Supplementary Material Available: A summary of the data collection and refinement, plots of molecules, and tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters (12 pages); a listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

(31) Although not included in the model, hydrogen atoms placed in idealized positions for either the major (atom N(2)) or minor (atom N(1)) disorder component site are involved in bifurcated hydrogen bonding with atoms O(2) and O(3) of the major component or atoms O(1) and O(4) of the minor component. This interaction is characterized by N...O distances ranging from 2.85 to 2.90 Å, H...O distances ranging from 2.48 to 2.51 Å, N-H...O angles ranging from 104 to 107°, and O...H...O angles of 136°.

(32) Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* 1976, 54, 1278.

(33) Reger, D. L.; Knox, S. J.; Lebiada, L. *Inorg. Chem.* 1989, 28, 3093.

Fully Regioselective Catalytic Carbonylation of Acrylic Derivatives: Synthesis of Methylmalonic Acid by Iron Pentacarbonyl Catalyzed Hydrocarboxylation of Acrylic Acid

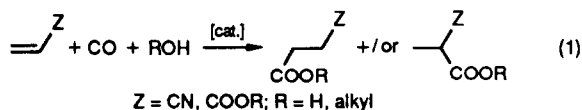
Jean-Jacques Brunet* and Elisabeth Passelaigue

Laboratoire de Chimie de Coordination du CNRS, Unité No. 8241 liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique, 205 route de Narbonne, 31077 Toulouse Cedex, France

Received March 20, 1990

Summary: The catalytic, fully regioselective hydrocarboxylation of acrylic acid to methylmalonic acid is reported for the first time. This reaction, which involves Fe(CO)₅ as catalyst precursor in the presence of Ca(OH)₂ in a H₂O-iPrOH mixture as solvent, is brought about at 70 °C under atmospheric carbon monoxide pressure.

The catalytic oxacarbonylation of olefins with carbon monoxide and alcohols or water in the presence of transition metals has been known to occur since 1940.¹ Since that time, a great deal of work has been devoted to the designing of systems for the precise control of the regioselective oxacarbonylation of α-olefins.² However, acrylic derivatives (eq 1) have been given far less attention.



The hydroesterification of acrylonitrile in the presence of base-promoted cobalt catalyst systems can be selectively

(>92%) directed either to 2- or to 3-cyanopropionates by the appropriate choice of the base promoter and process conditions.³

In contrast, no catalytic oxacarbonylation of acrylates or acrylic acid at the α-position has been reported so far. In the case of ethyl acrylate, only cobalt-catalyzed reactions leading to diethyl succinate have been reported.^{4,5} Similarly, in the case of acrylic acid itself, only a nickel-catalyzed hydrocarboxylation to succinic acid has been known.⁶ No catalytic carbonylation to methylmalonic acid (MMA) or its derivatives has been reported so far.

Interestingly, however, Takegami et al.,⁷ and later Collman et al.,⁸ reported that the stoichiometric addition of NaHFe(CO)₄ to methyl acrylate, in THF, was highly regioselective, leading to an alkyltetracarbonylferrate (isolated as the PPN⁺ salt) with the iron moiety linked α to the methoxycarbonyl group. Both groups, however, observed that the addition was strongly inhibited by a

(3) Pesa, F.; Haase, T. *J. Mol. Catal.* 1983, 18, 237.

(4) Matsuda, A. *Bull. Chem. Soc. Jpn.* 1969, 42, 571.

(5) Reuvers, J. G.; Richter, W.; Kummer, R. Ger. Offen. DE. 3,332,018, 1985; *Chem. Abstr.* 1985, 103, 177968.

(6) Reppe, W. U.S. Patent 2,604,490, 1952; *Chem. Abstr.* 1953, 47, 5603.

(7) Mitsudo, T. A.; Watanabe, Y.; Yamashita, M.; Takegami, Y. *Chem. Lett.* 1974, 1385.

(8) Collman, J. P.; Finke, R. G.; Matlock, P. L.; Wahren, R.; Komoto, R. G.; Brauman, J. I. *J. Am. Chem. Soc.* 1978, 100, 1119.

(1) Wender, I.; Pino, P. *Organic Synthesis via Metal Carbonyls*; Wiley: New York, 1977; Vol. II.

(2) Falbe, J. *New Syntheses with Carbon Monoxide*; Springer-Verlag: New York, 1980.