soluble molecule against which to compare **1**.[15] A $K_i^{HAI} \sim 200$ μM (average of three trials) was obtained for **2**, a factor of 10^4 higher than for the polyvalent liposome system. Liposomes containing no **1** and liposomes containing the methyl ester of **1** were examined by the HAI assay as controls. Neither system inhibited hemagglutination.

These results establish that arrays of SA groups at the surface of liposomes are moderately more effective in inhibiting agglutination of RBCs by influenza virus than are SA groups linked to soluble polymers. More significantly, these SA functionalized liposomes are as good as or better than the best-known natural inhibitors of hemagglutination, the mucins and macroglobulins. We emphasize that the effective inhibition observed with **1** involves only a monosaccharide rather than a complex polysaccharide (i.e., a glycoprotein or ganglioside): this observation makes it unnecessary to synthesize the complex sialyl polysaccharides found in nature. It remains to be established whether this inhibitory activity is due to enhanced binding of SA to viral HA originating in polyvalency and entropic factors or to steric occlusion of the surface of the virus by bound liposome.[16] We will describe studies of the ability of these liposomes to inhibit infectivity of influenza virus in vivo later.

Supplementary Material Available: Experimental data for compounds **1**, **3–7**, and **9–12** (9 pages). Ordering information is given on any current masthead page.

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(15) Compound **1** (in a liposome) and **2** (in solution) have substantially different steric constraints. In the liposome, the Dans group is predicted to be constrained to an area near the lipid bilayer surface and unavailable to interact with HA; in **2**, the Dans group is sterically unconstrained. We have not yet investigated whether the Dans group in either case plays a role in binding. See: Toogood, P. L.; Galliker, P. K.; Glick, G. D.; Knowles, J. R. *J. Med. Chem.* **1991**, *34*, 3138.

(16) *The Effect of Polymers on Dispersion Properties*; Tadros, T. F., Ed.; Academic: London, 1982. Sato, T.; Ruch, R. *Stabilization of Colloidal Dispersions by Polymer Adsorption*; Marcel Dekker: New York, 1980.

$[Pt_2(\mu\text{-}CH_3CO_2\text{-}O,O')_4(H_2O)_2](ClO_4)_2$, a Platinum(III) Dimeric Cation with a Very Short, Compressed, Metal–Metal Bond

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Many metal ions form "lantern-shaped" dimeric complexes in which the metal ions are bridged by four carboxylate anions (e.g., rhodium(II) acetate (**1**)[1]), but no such compound has been characterized with platinum.[2] This is remarkable in view of the existence of complexes in which two platinum(III) atoms are bridged by four sulfate[3-5] (**2**) or hydrogenphosphate[5-7] (**3**) anions. Recently,[8] a Pt(III) compound, **4**, has been prepared in which there are two Pt–CH$_2$C(O)O–Pt bridges as well as two "normal" O,O′-bridging acetate ligands. The question could then be asked, whether a Pt(III) complex analogous to **1** could exist.

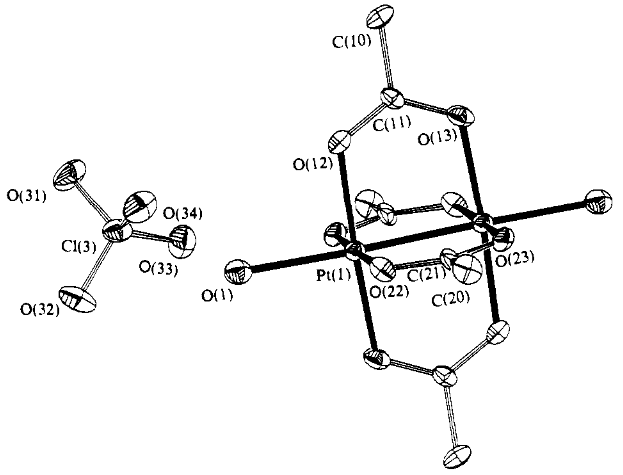
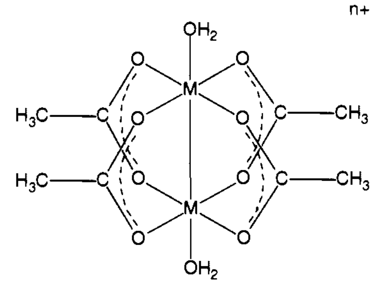


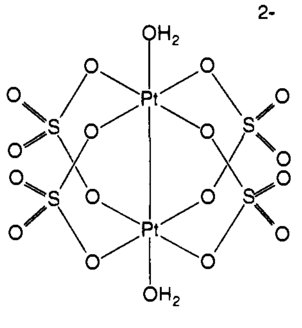
Figure 1. ORTEP diagram of the cation and one of the perchlorate anions of $[Pt_2(\mu\text{-}CH_3CO_2\text{-}O,O')_4(H_2O)_2](ClO_4)_2$, with hydrogen atoms omitted for clarity. Unlabeled atoms are related to those labeled by symmetry.



1 M = Rh, n = 0

5 M = Pt, n = 2

Potassium salts of **2** and **3** have been prepared by reaction of $K_2[Pt(NO_2)_4]$ with sulfuric and phosphoric acid, respectively.[9] A detailed account of the reactions of $K_2[Pt(NO_2)_4]$ with aqueous acetic acid will be published elsewhere.[10] A mixture of platinum(II), platinum(III), and platinum(IV) products was usually obtained, depending on precise reaction conditions. These always contained both acetate and nitrite ligands. However, when a solution of $K_2[Pt(NO_2)_4]$ in a 2:1 mixture (by volume) of glacial acetic acid and 1 M perchloric acid was heated in air, a yellow solid was obtained which was analyzed for $[Pt_2(CH_3CO_2)_4(H_2O)_2](ClO_4)_2$.[11]



2

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(1) Cotton, F. A.; DeBoer, B. G.; LaPrade, M. D.; Pipal, J. R.; Ucko, D. A. *Acta Crystallogr.* **1971**, *B27*, 1664–1671.

(2) Preparation of $[Pt_2(CH_3CO_2)_6]$ has been claimed, by reduction of $K_2[Pt(OH)_6]$ by formic acid in acetic acid suspension. Characterization was by elemental analysis and IR spectroscopy only (Rudyi, R. I.; Cherkashina, N. V.; Mazo, G. Ya; Salyn', Ya V.; Moiseev, I. I. *Izvest. Akad. Nauk SSSR, Ser. Khim.* **1980**, 754–758). Attempts in this laboratory to reproduce this preparation were unsuccessful.

(3) Muraveiskaya, G. S.; Orlova, V. S.; Evstaf'eva, O. N. *Zh. Neorg. Khim.* **1974**, *19*, 1030–1035.

(4) Muraveiskaya, G. S.; Kukina, G. A.; Orlova, V. S.; Evstaf'eva, O. N.; Porai-Koshits, M. A. *Dokl. Akad. Nauk, SSSR* **1976**, *226*, 76–79.

(5) Bancroft, D. P.; Cotton, F. A.; Falvello, L. R.; Han, S.; Schwotzer, W. *Inorg. Chim. Acta* **1984**, *87*, 147–153.

(6) Muraveiskaya, G. S.; Abashkin, V. E.; Evstaf'eva, O. N.; Galovaneva, I. F.; Shchelokov, R. M. *Koord. Khim.* **1980**, *6*, 463–472.

(7) Cotton, F. A.; Falvello, L. R.; Han, S. *Inorg. Chem.* **1982**, *21*, 1709–1710.

(8) Yamaguchi, T.; Sasaki, Y.; Ito, T. *J. Am. Chem. Soc.* **1990**, *112*, 4038–4040.

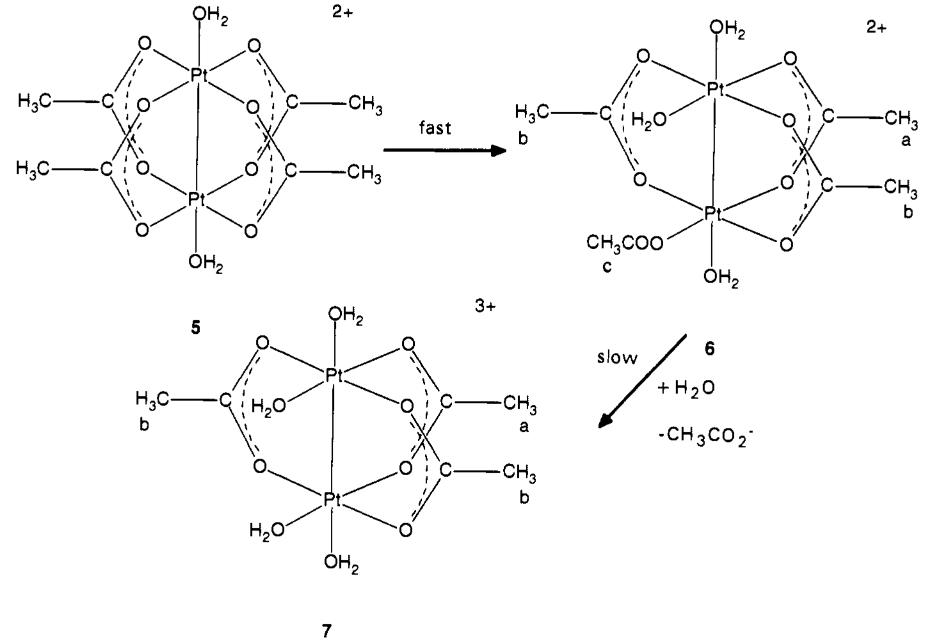
(9) We have found that O_2 is also necessary in these reactions.

(10) Appleton, T. G.; Barnham, K. J.; Byriel, K. A.; Hall, J. R.; Kennard, C. H. L.; Mathieson, M. T.; Penman, K. G., to be submitted for publication.

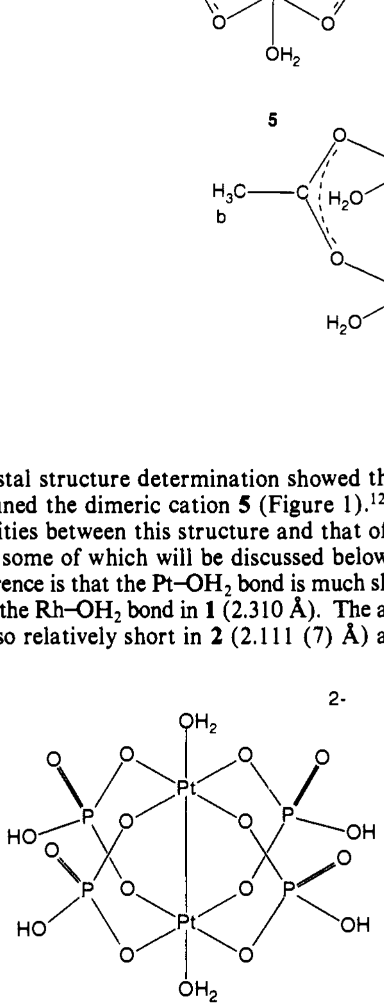
(11) CAUTION: in two separate incidents, very small quantities of the solid have decomposed violently. The compound should be handled in small quantities only and treated with respect. An analogous reaction with CF_3SO_3H gives the trifluoromethanesulfonate salt.

0002-7863/92/1514-7305$03.00/0

Scheme I

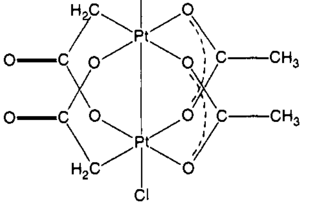


X-ray crystal structure determination showed that the compound contained the dimeric cation **5** (Figure 1).[12] There are close similarities between this structure and that of the neutral molecule **1**,[1] some of which will be discussed below. The most obvious difference is that the Pt–OH_2 bond is much shorter (2.167 (12) Å) than the Rh–OH_2 bond in **1** (2.310 Å). The axial Pt–OH_2 bonds are also relatively short in **2** (2.111 (7) Å) and **3** (2.161 (13) Å).[5]



3

The Pt–Pt bond length in **5**, 2.3905 (14) Å, is the shortest yet reported (cf., 2.451 (1) Å in **4**,[8] 2.461 (1) Å in **2**, 2.487 (2) Å in **3**,[5] and the Rh–Rh distance in **1**, 2.3855 (5) Å[1]). We suggest that the optimum length for a Pt(III)–Pt(III) single bond in a "lantern structure" (when the axial ligands are water) is close to that in **2**, but that the bond is flexible enough to be stretched or compressed in response to the geometrical demands of the bridging ligands. The structure of **2** shows little sign of strain. The Pt–Pt–O (sulfate) angles average 89.9 (1)°,[5] and each Pt atom is, within experimental error, coplanar with the plane of the four sulfate oxygen atoms to which it is bound.[13] In **5**, it appears that the constraints provided by the four acetate bridges compress the Pt–Pt bond so that it is 0.07 Å shorter than this optimum length. There are small but significant signs of strain in the complex. The Pt–Pt–O (acetate) angles are all slightly less than 90° (average 88.2 (3)°), so that each Pt atom is displaced slightly from the best-fit plane through the four acetate O-atoms bound to it, away from the other Pt atom (by 0.064 (7) Å).[14]



4

Aqueous solutions of the anions **2** and **3**, and their axially-substituted derivatives, are quite stable and have been subjected to study by a variety of spectroscopic techniques.[15-17] By contrast, ^1H NMR spectra in D_2O[18] showed that **5** was rapidly converted to **6**, with only three acetate bridges (complete within 5 min) followed by a much slower displacement of monodentate acetate by water to give **7** (complete within 2 h) (Scheme I). The breaking of one bridge in **5** allows some tilting of the PtO_4 planes with respect to each other and, probably, some lengthening of the Pt–Pt bond, relieving the strain that exists in **5**. The product **7** was quite stable in solution (δ_{Pt} +1320 relative to $PtCl_6^{2-}$; cf., +1756 for **2**[15]).

The structure of **1** also shows signs of strain: The average Rh–Rh–O (acetate) angle is 88.07 (26)°,[1] and each rhodium atom is displaced 0.069 (2) Å from the plane of the four acetate oxygen

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(12) The compound crystallizes in the monoclinic space group $P2_1/c$, with a = 8.113 (4) Å, b = 8.279 (2) Å, c = 14.892 (7) Å, β = 101.16 (2)°, V = 981.4 (7) Å^3, Z = 2. With the use of 1553 unique reflections ($I > 2.5\sigma(I)$) collected at room temperature with Mo K_α (λ = 0.71073 Å) radiation up to 2θ = 50° on a Enraf-Nonius CAD4 diffractometer. The structure was solved by the Patterson heavy-atom method. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms were fixed in idealized positions. The final R value was 0.038.

(13) From data given in ref 5, each Pt atom is calculated to be 0.007 (17) Å from the plane of the four sulfate O-atoms bound to it.

(14) The Pt–Pt bond in **3** could then be regarded as slightly "stretched". Most differences between the structures of **2** and **3** are too small to be significant, but all of the Pt–Pt–O (hydrogen phosphate) angles in **3** are slightly greater than 90° (av 90.8 (1)°).

(15) Appleton, T. G.; Hall, J. R.; Neale, D. W.; Ralph, S. F. *Inorg. Chim. Acta* **1983**, *77*, L149–L151. Appleton, T. G.; Hall, J. R.; Neale, D. W. *Inorg. Chim. Acta* **1985**, *104*, 19–31.

(16) Newman, R. A.; Martin, D. S.; Dallinger, R. F.; Woodruff, W. H.; Stiegemann, A. E.; Che, C.-M.; Schaefer, W. P.; Miskowski, V. M.; Gray, H. B. *Inorg. Chem.* **1991**, *30*, 4647–4654.

(17) Shin, Y.-K.; Miskowski, V. M.; Nocera, D. G. *Inorg. Chem.* **1990**, *30*, 2308–2313.

(18) ^1H NMR spectra (with labels as in Scheme I): for **6**, H_a 2.32, H_b 2.14, H_c 1.96 ppm; for **7**, H_a 2.29, H_b 2.14 ppm.

atoms, away from the other rhodium atom.[19] It is stable in aqueous solution but does react readily with H_2SO_4 and H_3PO_4 to give sulfate- and dihydrogen phosphate-bridged complexes, respectively.[20,21] The Rh–Rh distance in the dihydrogen phosphate is 2.485 (1) Å, longer than in **1**, and identical to the Pt–Pt distance in **3**.[22]

Acknowledgment. We thank the Australian Research Council for financial support.

Supplementary Material Available: Preparative details, tables of atomic coordinates, thermal parameters, bond distances and angles (6 pages); a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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(19) Calculated from data in ref 1.

(20) Baranovskii, I. B.; Chalisova, N. N.; Mazo, G. Ya *Zh. Neorg. Khim.* **1979**, *24*, 3395–3396.

(21) Baranovskii, I. B.; Abdullaev, S. S.; Shchelokov, R. N. *Zh. Neorg. Khim.* **1979**, *24*, 3149.

(22) Dikaneva, L. M.; Sadikov, G. G.; Porai-Koshits, M. A.; Baranovskii, I. B.; Abdullaev, S. S. *Zh. Neorg. Khim.* **1980**, *25*, 875.

A Highly Catalytic System for the Direct Oxidation of Lower Alkanes by Dioxygen in Aqueous Medium. A Formal Heterogeneous Analog of Alkane Monooxygenases

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Methane is the most abundant and the least reactive member of the hydrocarbon family (C–H bond energy: 104 kcal/mol). Ethane comes second in both categories. Hence, C–H activation leading to catalytic oxidation of these hydrocarbons is one of the most challenging chemical problems, in addition to being of great practical importance. In terms of oxidants, dioxygen (O_2) is clearly the most desirable oxidant due to its ready availability and high reduction potential. However, we are unaware of *any* report of a highly catalytic system for the direct oxidation of these two alkanes by dioxygen at low to moderate temperatures (≤100 °C).[1] Herein, we describe a system that achieves this goal in aqueous medium. *For example, starting with ethane, it is possible to form acetic acid whose concentration exceeds 0.5 M!* The system involves a metal catalyst (palladium) and a coreductant (carbon monoxide). The metal serves as the catalyst for *three* reactions in tandem resulting eventually in the oxidation of the alkane and the coreductant and the reduction of dioxygen (Scheme I).

Scheme I

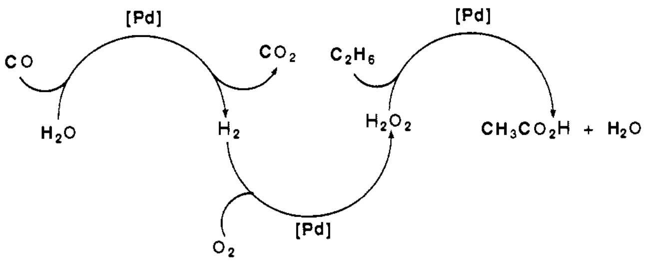

Table I. Oxidation of Ethane[a]

temp, °C	yield,[b] mmol (turnover = mmol of product/mmol of surface metal atoms[c])		
	CH_3CO_2H	HCO_2H	CH_3CH_2OH
70	0.53 (221)	0.12 (50)	0.035 (15)
85	2.55 (1063)	1.43 (596)	
100	2.73 (1138)	0.24 (100)	
110	0.88 (367)	0.16 (67)	
100[d]	<0.001		
100[e]	0.006		
95[f]	0.30	0.30	
95[g]	0.40 (88)	0.11 (24)	
95[h]	0.13		

[a] Typical conditions: 40 mg of 5% palladium on carbon (60 μmol of surface Pd atoms/g of catalyst); 5 mL of 0.1 M DCl in D_2O; CH_3CH_3, 500 psi; CO, 100 psi; O_2, 100 psi; time, 20–24 h. The reactions were run in 140-mL stainless steel bombs equipped with glass liners. Approximately 180 mmol of CH_3CH_3 was present in the initial gas mixture. [b] Yields determined independently by ^1H NMR and GC. [c] Amount of surface metal atoms in catalyst sample determined from dihydrogen chemisorption studies. [d] CO was not added. [e] DCl was not added. [f] 10.6 mg of palladium black was used. [g] 40 mg of 5% palladium on alumina (114 μmol of surface Pd atoms/g of catalyst) was used. [h] 50 mg of 5% platinum on carbon was used.

Our results on the oxidation of ethane are summarized in Table I. Both carbon monoxide and an acidic solution were clearly necessary since little or no oxidation of ethane occurred in their absence. Although Pd on carbon was the most active catalyst examined, other forms of metallic Pd, as well as metallic Pt, were also effective. The following pieces of evidence support the mechanism shown in Scheme I. The use of ^{13}CO resulted in the formation of $^{13}CO_2$ as the *only* ^{13}C-containing product (as determined by ^{13}C NMR). Water was also necessary since no oxidation was observed in a dry CH_3NO_2/CF_3CO_2H mixture (however, vide infra). The above observations were consistent with a metal-catalyzed water gas shift reaction.[2] It was possible to bypass this first catalytic reaction by replacing carbon monoxide with dihydrogen (H_2). In the latter instance it was possible to run the reaction in a nonaqueous medium as shown in eq 1.

$$\text{CH}_3\text{CH}_3\ (350\ \text{psi}) + \text{H}_2\ (100\ \text{psi}) + \text{O}_2\ (100\ \text{psi}) \xrightarrow[\text{CH}_3\text{NO}_2\ (3\ \text{mL})/\text{CF}_3\text{CO}_2\text{H}\ (0.08\ \text{mL}),\ 85\ ^\circ\text{C},\ 12\ \text{h}]{5\%\ \text{Pd/C}\ (50\ \text{mg})} \text{CH}_3\text{CO}_2\text{H}\ (0.46\ \text{mmol}) + \text{HCO}_2\text{H}\ (0.26\ \text{mmol}) \quad (1)$$

The second catalytic reaction involved the formation of hydrogen peroxide from dihydrogen and dioxygen and has been reported previously in a patent.[3] This reaction occurred only under acidic conditions. That hydrogen peroxide was formed in our system starting with carbon monoxide and dioxygen in the presence of water was verified by running the reaction in the absence of alkane. Titration of the resultant solution with a standard solution of $KMnO_4$ indicated a hydrogen peroxide concentration of 0.002 M. In an independent experiment we observed the slow Pd-catalyzed oxidation of ethane to ethanol, acetic acid, and formic acid by hydrogen peroxide at 30 °C. A lower reaction temperature was chosen in order to avoid the observed metal-catalyzed decomposition of hydrogen peroxide to water and dioxygen. It was this latter undesirable reaction that made carbon monoxide a more effective coreductant than dihydrogen. Starting with carbon

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(1) Examples of high-temperature oxidations and/or oxidations with significantly lower turnovers: (a) Baerns, M.; van der Wiele, K.; Ross, J. R. H. *Catal. Today* **1989**, *4*, 471. (b) Pitchai, R.; Klier, K. *Catal. Rev.—Sci. Eng.* **1986**, *28*, 13. (c) Kung, H. H. *Stud. Surf. Sci. Catal.* **1989**, *45*, 200. (d) Hunter, N. R.; Gesser, H. D.; Morton, L. A.; Yarlagadda, P. S.; Fung, D. P. C. *Appl. Catal.* **1990**, *57*, 45. (e) Burch, R. B.; Squire, G. D.; Tsang, S. C. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 3561. (f) Kowalak, S.; Moffat, J. B. *Appl. Catal.* **1988**, *36*, 139. (g) Stolarov, I. P.; Vargaftik, M. N.; Sishkin, D. I.; Moiseev, I. I. *J. Chem. Soc., Chem. Commun.* **1991**, 938. (h) Vargaftik, M. N.; Stolarov, I. P.; Moiseev, I. I. *J. Chem. Soc., Chem. Commun.* **1990**, 1049. (i) Herron, N. *New J. Chem.* **1989**, *13*, 761. (j) Lyons, J. E.; Ellis, P. E.; Durante, V. A. *Stud. Surf. Sci. Catal.* **1991**, *68*, 99. The reaction conditions and rates described in the last paper come closest to our system.

(2) Reviews: (a) Thomas, C. L. *Catalytic Processes and Proven Catalysts*; Academic: New York, 1970; p 104. (b) Happel, J. *Catal. Rev.* **1972**, *6*, 221. (c) Laine, R. M.; Wilson, R. B. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; D. Reidel: Dordrecht, 1984; p 217. (d) Ford, P. C. *Acc. Chem. Res.* **1981**, *14*, 31.

(3) Gosser, L. W. U.S. Patent, 4,681,751, 1987.