view of the recent demonstrations of the importance of a sulfur-rich environment about Ni in order to observe both the redox properties[24] and the functionalities[7] appropriate to biological nickel, the ability of our new complexes to bind a fifth anion is important and studies of exchange of I^- for RS^- (and H^-) are in progress.

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Supplementary Material Available: Tables of atom positional parameters for (BME-DACO)Ni^{II} [(Me_2BME-DACO)Ni][I]$_2$ and a crystal packing diagram for [(Me_2BME-DACO)Ni][I]$_2$ (3 pages). Ordering information is given on any current masthead page.

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[22] Mills, D. K.; Farmer, P. J.; Reibenspies, J. H.; Darensbourg, M. Y. To be submitted for publication.

[23] Karlin, K. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1976**, *98*, 6951. A similar tetradentate N_2S_2 donor ligand, *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)-1,3-propanediamine, produced a dimeric iron complex analogous to [(BME-DACO)Fe]$_2$.

[24] Fox, S.; Wang, Y.; Silver, A.; Millar, M. *J. Am. Chem. Soc.* **1990**, *112*, 3218.

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Synthesis and Crystal Structure of a Nine-Coordinate Gadolinium(III) Complex of 1,7,13-Triaza-4,10,16-trioxacyclooctadecane-*N,N',N''*-triacetic Acid

The synthesis of the [18]-N_3O_3 triacetic acid and the crystal structure of its gadolinium(III) complex are described, providing the first 9-coordinate Gd(III) complex in which all donor atoms are derived from the same ligand. There is great interest in the design and synthesis of new ligands for the complexation of Gd(III) as NMR imaging agents.[1-3] Several reports on the parent [18]-N_3O_3 macrocycle (7 in Scheme I) and two derivatives containing noncoordinating pendant substituents on the amino groups have been published.[4,5] However, there is little information about the synthetic routes employed for their preparation. Reported here is the synthesis and study of a new macrocyclic ligand, [18]-N_3O_3 triacetic acid, which forms a 9-coordinate neutral Gd(III) complex.

The synthetic route is shown in Scheme I. Compounds **1-5** were prepared with published procedures[6] or published methods for intermediates employed in the synthesis of macrocyclic and macrobicyclic ligands.[7] In all reaction steps the yields were higher than 80%. [18]-N_3O_3·3HBr (**7**) was obtained by the condensation

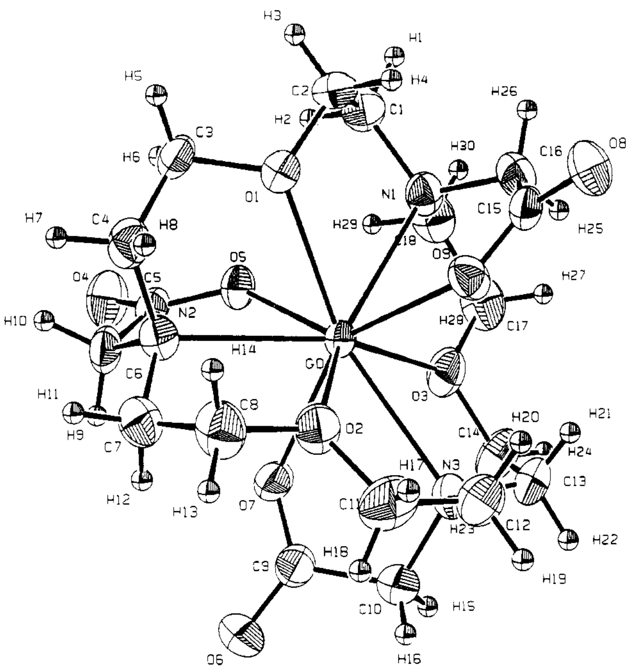

Figure 1. ORTEP diagram of the X-ray crystal structure of $GdC_{18}H_{30}N_3O_9$. Thermal ellipsoids are shown at the 50% probability level.

Table I. Selected Bond Lengths (Å) and Angles (deg) for $GdC_{18}H_{30}N_3O_9$

Gd–O(5)	2.310 (4)	Gd–O(1)	2.609 (3)
Gd–O(9)	2.328 (4)	Gd–N(1)	2.641 (4)
Gd–O(7)	2.341 (3)	Gd–N(2)	2.642 (5)
Gd–O(2)	2.467 (3)	Gd–N(3)	2.686 (4)
Gd–O(3)	2.508 (3)		
N(1)–Gd–N(2)	124.3 (1)	O(7)–Gd–N(3)	64.8 (1)
N(1)–Gd–N(3)	115.7 (1)	O(9)–Gd–N(2)	121.2 (1)
N(2)–Gd–N(3)	119.7 (1)	O(5)–Gd–N(2)	67.6 (1)
O(1)–Gd–N(2)	64.8 (1)	O(2)–Gd–O(3)	130.0 (1)
O(3)–Gd–N(1)	64.0 (1)	O(7)–Gd–O(2)	77.6 (1)
O(2)–Gd–N(2)	66.0 (1)	O(5)–Gd–O(3)	86.7 (1)

Table II. Atomic Coordinates

atom	*x*	*y*	*z*	*B*(eq), Å^2
Gd	0.10900 (2)	0.35741 (2)	0.13772 (1)	2.04 (1)
O(1)	0.1728 (4)	0.5876 (3)	0.1123 (1)	2.9 (1)
O(2)	0.0471 (4)	0.2940 (4)	0.0369 (1)	3.4 (2)
O(3)	0.0189 (4)	0.2709 (4)	0.2244 (1)	3.5 (2)
O(4)	0.5777 (4)	0.3616 (4)	0.2160 (2)	4.4 (2)
O(5)	0.3335 (3)	0.3944 (3)	0.1959 (1)	2.8 (1)
O(6)	0.2333 (4)	−0.0277 (4)	0.0961 (2)	4.5 (2)
O(7)	0.2203 (4)	0.1589 (3)	0.1377 (2)	3.1 (1)
O(8)	−0.2946 (4)	0.6009 (4)	0.1157 (2)	4.4 (2)
O(9)	−0.1176 (4)	0.4585 (3)	0.1087 (1)	3.0 (1)
N(1)	0.0409 (4)	0.5249 (4)	0.2116 (2)	2.8 (2)
N(2)	0.3326 (5)	0.3806 (4)	0.0795 (2)	2.7 (2)
N(3)	−0.0816 (5)	0.1639 (4)	0.1160 (2)	3.2 (2)
C(1)	0.1352 (6)	0.6386 (5)	0.2083 (2)	3.6 (2)
C(2)	0.1220 (6)	0.6828 (5)	0.1481 (3)	3.6 (2)
C(3)	0.3255 (5)	0.6064 (5)	0.1039 (2)	3.0 (2)
C(4)	0.3527 (6)	0.5113 (5)	0.0605 (2)	3.4 (2)
C(5)	0.4612 (5)	0.3683 (4)	0.1820 (2)	2.8 (2)
C(6)	0.4664 (5)	0.3405 (5)	0.1199 (2)	3.0 (2)
C(7)	0.3063 (6)	0.2978 (5)	0.0289 (2)	3.5 (2)
C(8)	0.1497 (7)	0.3114 (6)	−0.0030 (2)	4.0 (3)
C(9)	0.1643 (5)	0.0595 (5)	0.1143 (2)	3.0 (2)
C(10)	−0.0021 (6)	0.0434 (5)	0.1113 (3)	4.2 (3)
C(11)	−0.0769 (7)	0.2169 (6)	0.0156 (3)	4.8 (3)
C(12)	−0.1736 (6)	0.1967 (6)	0.0610 (3)	4.2 (3)
C(13)	−0.1709 (6)	0.1598 (5)	0.1626 (3)	4.1 (3)
C(14)	−0.0700 (7)	0.1584 (6)	0.2193 (3)	4.5 (3)
C(15)	−0.1825 (5)	0.5403 (5)	0.1357 (2)	3.0 (2)
C(16)	−0.1178 (6)	0.5584 (5)	0.1985 (2)	3.4 (2)
C(17)	−0.0020 (7)	0.3472 (6)	0.2728 (2)	4.2 (3)
C(18)	0.0778 (6)	0.4697 (6)	0.2693 (2)	3.9 (2)

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[1] Lauffer, R. C. *Chem. Rev.* **1987**, *87*, 901.

[2] Furmanski, P.; Longley, C. *Cancer Res.* **1988**, *48*, 4604.

[3] Plehwe, W. E.; McRobbie, D. W.; Lerski, R. A.; Kohner, E. M. *Invest. Opthamol. Visual Sci.* **1988**, *29*, 663.

[4] Graf, E.; Lehn, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 5022.

[5] Beer, P. D.; Crowe, D. B.; Main, B. XIVth International Symposium on Macrocyclic Chemistry, June 25-28, 1989, Townsville, Queensland, Australia; Paper P12/T.

[6] Bogatskii, A. V.; Luk'yanenko, N. G.; Kinichenko, T. I. *Zh. Org. Khim.* **1980**, *16*, 1301.

[7] Deitrich, B.; Hosseini, M. W.; Lehn, J. M.; Sessions, R. B. *Helv. Chim. Acta* **1985**, *68*, 289.

[8] Kahwa, I. A.; Folkes, S.; Williams, D. J.; Ley, S. V.; O'Mahoney, C. A.; McPherson, G. L. *J. Chem. Soc., Chem. Commun.* **1989**, 1531.

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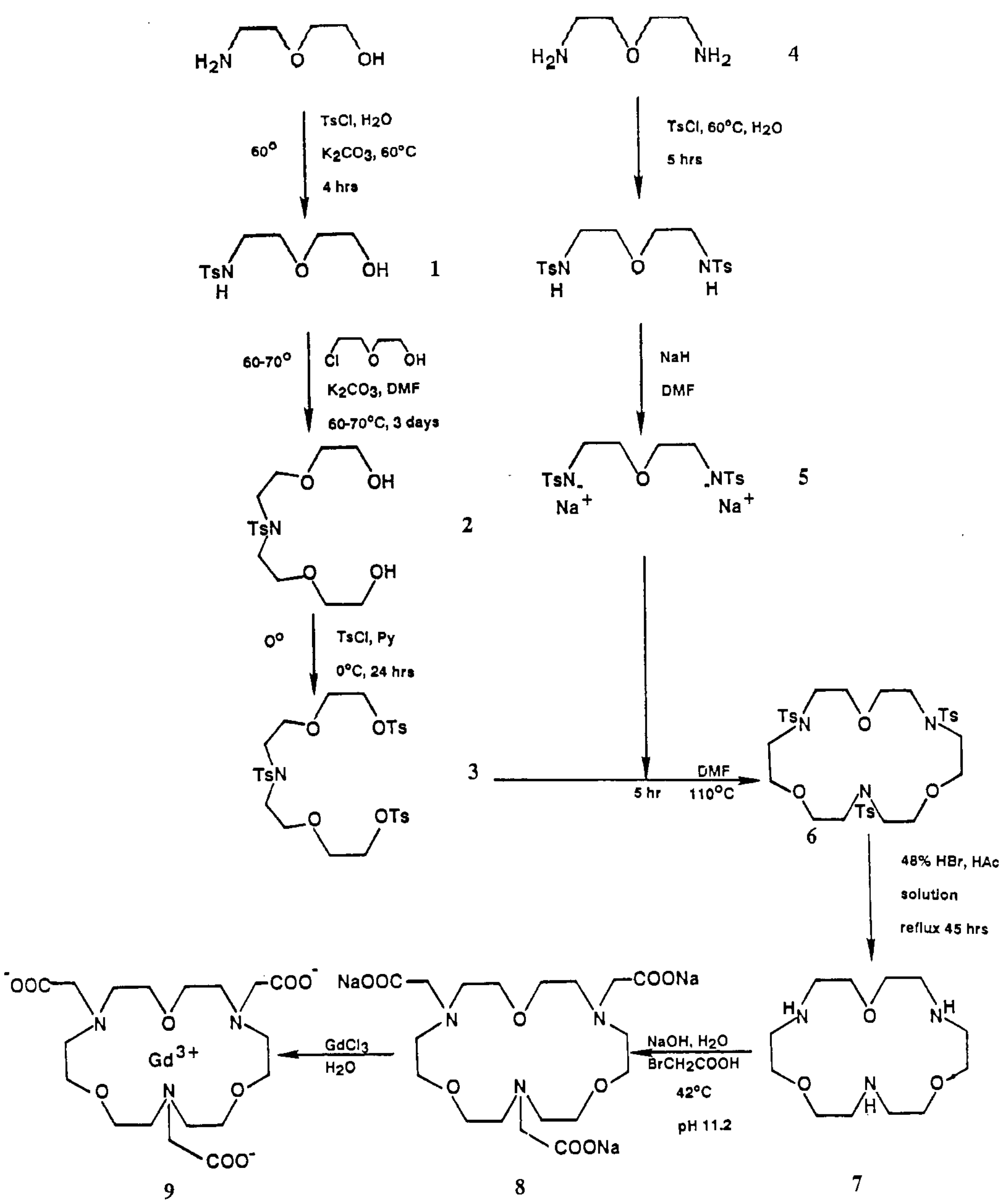
Scheme I



of 3 with the disodium salt 5, followed by detosylation with HBr–HOAc aqueous solution. The alkylation of the three nitrogens in the 18-membered ring was effected in aqueous solution with $BrCH_2COONa$ at pH 11.5 to give the amino triacid, 8, trisodium salt. ^1H NMR (D_2O): 3.44 (t, 12 H, $-OCH_2$), 3.03 (s, 6 H, $-CH_2COO$), 2.69 ppm (t, 12 H, $-NCH_2$). ^{13}C NMR (D_2O): 179.6 (–COONa), 67.8 ($-OCH_2$), 57.3 ($-NCH_2COO^-$), 54.3 ppm ($-NCH_2$). Anal. Calcd for $C_{18}H_{30}N_3O_9Na_3 \cdot 1.5H_2O$: C, 40.91; H, 6.30; N, 7.95. Found (Galbraith): C, 41.10; H, 6.35; N, 7.66. The Gd(III) complex was prepared in aqueous solution at pH 7 and was purified with silica gel. Anal. Calcd for $C_{18}H_{30}N_3O_9Gd \cdot 5H_2O$: C, 31.80; H, 5.93; N, 6.18. Found (Galbraith): C, 31.83; H, 5.42; N, 6.26.

Block-shaped crystals of the Gd(III) complex (approximate dimensions 0.30 × 0.30 × 0.40 mm) suitable for an X-ray single-crystal diffraction study were prepared by slow diffusion of 2-propanol into a methanol solution of the complex. The molecular structure[9] showing the atomic numbering scheme is illustrated in Figure 1, and selected interatomic distances (angstroms) and angles (degrees) are given in Table I. Atomic coordinates are listed in Table II.

The crystal structure reveals that this Gd(III) complex has a propeller conformation with no crystallographically imposed symmetry. The gadolinium atom lies within the macrocycle and is 9-coordinate, being bound to three nitrogen atoms, three oxygen atoms of the macrocycle, and three acetate oxygen atoms. The shortest contacts are the Gd–O (acetate) bonds, in the range 2.31–2.34 Å, slightly shorter than the corresponding bond lengths in the 9-coordinate $Gd^{III}EDTA \cdot 3H_2O$ structure.[10] The Gd–O-(ether) bonds are comparable in length to those found in the 9-coordinate dichloro(ethanol)(18-crown-6)gadolinium(III) chloride ether bonds.[11] This is the first example of a 9-coordinate gadolinium(III) complex of a nonadentate ligand in which all

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(9) Crystal data: $GdC_{18}H_{30}N_3O_9$, monoclinic, space group $P2_1/n$ (No. 14), $a = 9.080$ (9) Å, $b = 10.638$ (4) Å, $c = 23.758$ (4) Å, $\beta = 99.04$ (3)°, $V = 2266$ (2) Å^3, $Z = 4$, $F(000) = 1180$, $D_c = 1.73$ g cm^{-3}, μ(Mo Kα) = 29.89 cm^{-1}. Data were measured at 23 °C on a Rigaku AFC5R rotating-anode diffractometer with graphite-monochromated Mo Kα radiation using ω-scans. The structure was solved by direct methods and refined anisotropically with absorption-corrected data to give $R = 0.029$, $R_w = 0.038$ for 3291 independent observed reflections ($I > 3\sigma(I)$) and 300 variables. During refinement of the complex, three peaks were found in difference Fourier maps that appear to be water molecules of hydration. Located between the complexes, ca. 2.8 Å away, these apparent oxygen atoms have large thermal parameters, and these sites may not be fully occupied. This result is not consistent with the chemical analysis and suggests that the water content of the structure may be variable. Atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and structure amplitudes have been deposited with the Cambridge Crystallographic Data Center.

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donor atoms of the ligand are coordinated to the metal ion. In spite of the fact that the Gd(III) ion is surrounded by ligand donor groups, and the complex does not have a coordinated inner-sphere water molecule, it has been shown to exert moderate relaxivity (1.48 m M^{-1} s^{-1} compared to 2.45 m M^{-1} s^{-1} for Gd^{III}DTPA) of the NMR water signal in the in vitro tests of its potential as an MRI paramagnetic contrast agent.[12]

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Supplementary Material Available: A textual description of the crystallographic study and tables of the crystallographic data, positional parameters, *B*(eq) values, distances, and angles (9 pages); a listing of structure factors (27 pages). Ordering information is given on any current masthead page.

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(10) Templeton, L. K.; Templeton, D. H.; Zalkin, A.; Ruben, H. W. *Acta Crystallogr., Sect. B* **1982**, *38*, 2155.
(11) Forsellini, E.; Benetollo, F.; Bombieri, G.; Cassol, A.; DePaoli, G. *Inorg. Chim. Acta* **1985**, *109* (3), 167.
(12) Wiegers, C. B.; Welch, M. J.; Martell, A. E.; Permen, W. H.; Madsen, S. L.; Sun, Y.; Chen, D. Paper presented at the Ninth Annual Meeting, Society of Magnetic Resonance in Medicine, New York, 1990.

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Surface-Mediated Synthesis of $H_4M_4(CO)_{12}$ (M = Ru, Os) on Hydroxylated Silica

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The surface reactivity with hydrogen of silica-supported $M_3(CO)_{12}$ (M = Ru, Os) has been investigated at atmospheric pressure and temperatures between 25 and 100 °C. Pure $H_4M_4(CO)_{12}$ complexes are selectively obtained and almost quantitatively recovered from the solid sample by solvent extraction. In the case of $H_4Os_4(CO)_{12}$, significative advantages over the conventional synthesis in solution are obtained.

Introduction

Surface organometallic chemistry, particularly concerning the reactivity of transition-metal carbonyl clusters with the surfaces of metal oxides, has been studied in a systematic way.[1] One of the main goals of such studies is to elucidate the elementary steps in surface reactions, hopefully leading to a deeper insight into the mechanism of heterogeneous catalysis.[2] Surface transformations of supported metal clusters can also be regarded as models of sintering processes in heterogeneous systems.

It has been reported, by some of us, that $Rh_4(CO)_{12}$, when physisorbed on silica[3] or alumina,[4] quickly transforms in vacuo into physisorbed $Rh_6(CO)_{16}$. This was the first reported observation of a surface aggregation of a molecular metal cluster to form a new, higher nuclearity species. This surface reactivity could be explained in terms of high surface mobility of the molecular metallic fragments covered with CO, as easily occurring in solution on model compounds.[5] Accordingly, the surface aggregation of $Os^{II}(CO)_n$ or $Ru^{II}(CO)_n$ (n = 2, 3) fragments, covalently linked to the surface of silica, to generate physisorbed $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ has been observed by reductive carbonylation at 250 and 60–80 °C, respectively.[6,7] In the latter reaction, nonnegligible amounts of $Ru_6C(CO)_{17}$ were also formed. Cluster aggregation is often accompanied by incorporation of carbidic carbon atoms, probably deriving from Boudouard reactions.

The activation of H_2 via incorporation into supported molecular clusters has been also observed. The chemisorbed cluster anion $[HRuOs_3(CO)_{13}]^-$ easily transforms to $[H_3RuOs_3(CO)_{12}]^-$ in the presence of CO and H_2.[8]

In other words, metal carbonyl clusters often show a controlled and unexpectedly easy reactivity when supported onto the surface of inorganic oxides. A new approach to the highly selective synthesis of organometallic cluster compounds via "surface-mediated" gas–solid reactions is thus offered.[9,10]

In this context, we now wish to report the selective synthesis of $H_4M_4(CO)_{12}$ species from physisorbed $M_3(CO)_{12}$ (M = Ru, Os) clusters on the surface of silica.

Experimental Section

$Os_3(CO)_{12}$,[11] $H_4Os_4(CO)_{12}$,[12] $Ru_3(CO)_{12}$,[13] and $H_4Ru_4(CO)_{12}$[12] were

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[‡] On leave from the University of Ottawa, Ottawa, Canada.

(1) Basset, J. M.; Choplin, A. *J. Mol. Catal.* **1983**, *21*, 95. Psaro, R.; Ugo, R. In *Metal Clusters in Catalysis*; Gates, B. C., Knözinger, H., Guczi, L., Eds.; Elsevier: Amsterdam, 1986; p 427. Lamb, H. H.; Gates, B. C.; Knözinger, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1127.
(2) *Surface Organometallic Chemistry: Molecular Approaches to Surface Catalysis*; Basset, J. M., Gates, B. C., Candy, J. P., Choplin, A., Quignard, F., Leconte, M., Eds.; Kluwer: Dordrecht, The Netherlands 1988. Gates, B. C.; Lamb, H. H. *J. Mol. Catal.* **1989**, *52*, 1. Basset, J. M.; Candy, J. P.; Choplin, A.; Santini, C.; Theolier, A. *Catal. Today* **1989**, *6*, 1.
(3) Theolier, A.; Smith, A. K.; Leconte, M.; Basset, J. M.; Zanderighi, G. M.; Psaro, R.; Ugo, R. *J. Organomet. Chem.* **1980**, *191*, 415.
(4) Bilhou, J. L.; Bilhou-Bougnol, V.; Graydon, W. F.; Basset, J. M.; Smith, A. K.; Zanderighi, G. M.; Ugo, R. *J. Organomet. Chem.* **1978**, *153*, 73. Smith, A. K.; Hugues, F.; Theolier, A.; Basset, J. M.; Ugo, R.; Zanderighi, G. M.; Bilhou, J. L.; Bilhou-Bougnol, V.; Graydon, W. F. *Inorg. Chem.* **1979**, *18*, 1395.
(5) Chini, P.; Martinengo, S. *Inorg. Chim. Acta* **1969**, *3*, 315.
(6) Dossi, C.; Fusi, A.; Grilli, E.; Psaro, R.; Ugo, R.; Zanoni, R. *Catal. Today* **1988**, *2*, 585.
(7) Zanderighi, G. M.; Dossi, C.; Ugo, R.; Psaro, R.; Theolier, A.; Choplin, A.; D'Ornelas, L.; Basset, J. M. *J. Organomet. Chem.* **1985**, *296*, 127.
(8) Scott, J. P.; Budge, J. R.; Rheingold, A. L.; Gates, B. C. *J. Am. Chem. Soc.* **1987**, *109*, 7736.
(9) Lamb, H. H.; Gates, B. C. *J. Chem. Soc., Chem. Commun.* **1986**, 821.
(10) Fung, A. S.; Tooley, P. A.; Kelley, M. J.; Gates, B. C. *J. Chem. Soc., Chem. Commun.* **1988**, 371.
(11) Johnson, B. F. G.; Lewis, J. *Inorg. Synth.* **1976**, *13*, 92.
(12) Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3942.

0020-1669/90/1329-4368$02.50/0