enriched with deuterium only at the 3-*pro-R* position (the 3a-H closest to the lactone ring), indicative of a stereospecific reduction in the biosynthesis of the alkaloid from trigonelline.

Supplementary Material Available: 2D-HETCOR and 2D-COSY of natural dioscorine, with ^{13}C, ^{1}H chemical shifts and ^{1}H-^{1}H couplings; ^{2}H NMR spectrum of enriched dioscorine (5 pages). Ordering information is given on any current masthead page. These data will be provided with requests for reprints.

Crown Thioether Chemistry. Synthesis and Structure of [Bis(1,4,7-trithiacyclononane)rhodium] Tris(triflate): Stabilization of Monomeric Rh(II)

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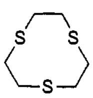
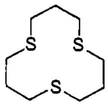
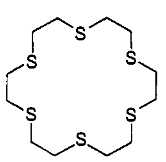
In contrast to the extensive coordination chemistry of Co(II), monomeric Rh(II) complexes have proven elusive by virtue of their propensity for dimerization (e.g., $Rh_2(OAc)_4$) and/or disproportionation to Rh(III) and Rh(I).[1] Recently we have been exploring the coordination chemistry of crown thioethers[2] such as 9S3,[3,4] 18S6,[3-6] and 24S6[7] with a view toward stabilization of



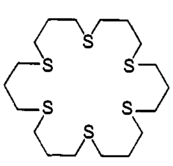
9S3



12S3



18S6



24S6

low oxidation and spin states, in the expectation that the unusual electronic structures induced by these ligands would confer unusual reactivity as well. Thioether complexes of rhodium attract particular interest owing to their potential parallel to industrially important rhodium phosphine complexes. We report herein our synthetic, physical, and structural investigation of $[Rh(9S3)_2]^{3+}$, the first reported homoleptic thioether complex of Rh(III), and its reduction to a rare example of a stable monomeric Rh(II) complex.[1]

Reaction of rhodium(III) triflate (prepared by reaction of $RhCl_3{\cdot}3H_2O$ with silver triflate) with 2 equiv of 9S3[3] in MeOH gives a pale orange solution that upon concentration and cooling deposits colorless needles (yield: 48%). Anal. Calcd for $RhC_{15}H_{24}S_9F_9O_9$: C, 19.78; H, 2.66; found (Oxford microanalytical service) C, 19.44; H, 2.58. ^{1}H NMR (300 MHz, CD_3CN, TMS, δ) 3.52 (m) at room temperature. Recrystallization from MeOH gave crystals suitable for X-ray diffraction measurements.[8]

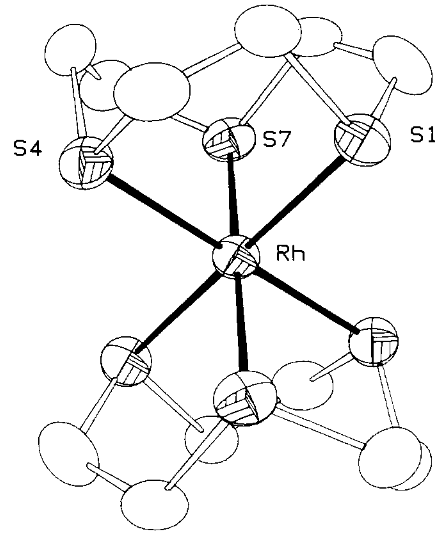


Figure 1. ORTEP drawing of $[Rh(9S3)_2]^{3+}$ cation showing thermal ellipsoids at 50% probability level (hydrogen atoms are omitted for clarity). Atomic numbering of the unique 9S3 ring follows IUPAC nomenclature (i.e., S1, C2, C3, S4, etc.).

The molecular structure of $[Rh(9S3)_2]^{3+}$ (Figure 1) shows a rigorously centrosymmetric RhS_6 coordination sphere in which the metal ion nestles between two 9S3 rings. Two of the unique Rh–S distances are somewhat longer (2.345 (3) and 2.348 (3) Å) than the third (2.331 (2) Å); similar Rh–S bond lengths have been reported for a dimethyl sulfide complex of Rh(III).[9] Interestingly, these distances closely approach those very recently found for $[Ru(9S3)_2]^{2+}$ (in which Ru–S distances range from 2.331 (1) to 2.344 (1) Å),[10] despite the difference in charge between the two complexes. Intraligand dimensions and torsional angles differ insignificantly from those found either in other complexes of this ligand[10,11] or, indeed, in the free ligand itself.[12]

Electrochemical studies of $[Rh(9S3)_2]^{3+}$ reveal an extraordinary result. Cyclic voltammetry in $MeNO_2$ on a glassy carbon electrode (Figure 2) shows *two quasi-reversible one-electron processes* at −309 and −721 mV versus SCE (ΔE_{pp} = −71 and −98 mV, respectively; ν = 50 mV/s). Controlled potential coulometry establishes that both processes entail transfer of one-electron (n = 1.05 and 0.97, respectively). Preparative electrolysis at −500 mV affords a straw-colored solution that exhibits an EPR spectrum (at 298 K) with g = 2.046 without resolved ^{103}Rh (I = 1/2, 100%)

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† Inorganic Chemistry Laboratory.

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(2) The following abbrevations are used: 9S3, trithia-9-crown-3, 1,4,7-trithiacyclononane; 18S6, hexathia-18-crown-6, 1,4,7,10,13,16-hexathiacyclooctadecane; 24S6, hexathia-24-crown-6, 1,5,9,13,17,21-hexathiacyclotetracosane.

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(8) Crystal data: $RhC_{15}H_{24}S_9F_9O_9$, fw = 910.83, monoclinic, space group *C2/c* (no. 15), a = 18.638 (6) Å, b = 10.643 (3) Å, c = 16.075 (2) Å, β = 105.93 (2)°, V = 3066.1 Å^3, Z = 4, d_{calcd} = 1.97 g/cc. A crystal (0.1 mm × 0.1 mm × 0.4 mm) was sealed in an X-ray capillary for crystallographic studies. An Enraf Nonius CAD4 diffractometer with Cu Kα radiation (1.5418 Å) was used for collection of 4021 data with $2\theta \leq 140°$. The 1547 reflections with $I > 3\sigma(I)$ remaining after data reduction and averaging of equivalent reflections were used in subsequent calculations. Three standard reflections that were measured every hour showed no decay. Calculations were performed with the CRYSTALS crystallographic programs on a VAX 11/750 computer, with atomic scattering factors from the usual source. An empirical absorption correction was applied. The Rh atom was found from a three-dimensional Patterson map, and the remaining non-hydrogen atoms were found by Fourier syntheses. Approximately half of the hydrogen atoms were also found; all hydrogen atoms were included at calculated positions, and a group isotropic thermal parameter was refined. Full-matrix least-squares refinement converged to R = 6.84% (R_w = 8.65%) for 199 parameters. One of the triflate groups is disordered across a twofold axis; it was refined as two molecules each with half occupancy. The highest peak in the final difference map was 1.3 e/Å^{-3} and was found next to the disordered triflate.

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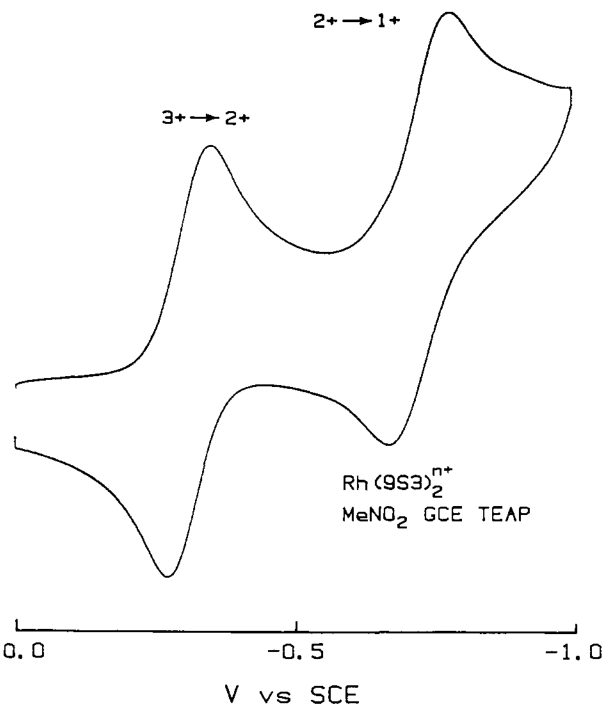

Figure 2. Cyclic voltammogram of $[Rh(9S3)_2](CF_3SO_3)_3$ in $MeNO_2$ (0.1 M Et_4NClO_4) at a glassy carbon electrode (scan rate 50 mV/s).

hyperfine splitting (line width = 40 G). Frozen solutions (77 K) yield rhombic spectra with $g_1 = 2.085$, $g_2 = 2.042$, and $g_3 = 2.009$, where g_1 reveals ^{103}Rh ($I = 1/2$, 100%) hyperfine splitting of 12 × 10^{-4} cm^{-1}. In a situation analogous to that recently found for the isoelectronic complex $[Co(9S3)_2]^{2+}$,[4,5] the g value pattern of $[Rh(9S3)_2]^{2+}$ (g_1, $g_2 > 2$; $g_3 \approx 2$) probably reflects a d_{z^2} ground state, consistent with axial elongation of this Jahn-Teller active d^7 ion.

The exceptional stability of $[Rh(9S3)_2]^{2+}$ with respect to disproportionation ($K_{disp} = 10^{-7}$, calculated from $E(Rh^{III}/Rh^{II}) - E(Rh^{II}/Rh^{I})$) apparently derives from both the electronic and steric properties of this crown thioether. Thioethers generally stabilize low oxidation states by virtue of their π-acidity. Thus $[Cu(SR_2)_6]^{2+}$ complexes, for example, have the highest redox potentials known for the (Cu^{II}/Cu^{I}) couple of this element.[3,13] Hence 9S3 presumably electronically destabilizes Rh(III) with respect to Rh(II) and Rh(I). On the other hand, the rigid conformation of 9S3 ensures that any bis complex of this ligand has six thioether groups in close proximity to the metal. The imposition of a six-coordinate environment would tend to destabilize Rh(I), which usually adopts square planar coordination geometry. These cross-cutting effects evidently suffice to buckle the free energy profile such that Rh(II) is no longer at a relative maximum with respect to Rh(III) and Rh(I) but rather a relative minimum. At the same time, 9S3 apparently inhibits the usually rapid dimerization of Rh(II); EPR and electrochemical studies show that $[Rh(9S3)_2]^{2+}$ decays (presumably by dimerizing) with a half-life greater than 0.5 h.

Further studies addressing the generality of this unusual stabilization as well as the reactivity of the resulting novel species will be reported shortly.

Acknowledgment. We are grateful to Richard Brownsword for experimental assistance. Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society and to the Science and Engineering Research Council (U.K.) for support of this research.

Supplementary Material Available: Tables S1-S6 listing crystallographic details, final atomic coordinates, bond lengths and angles, hydrogen atomic coordinates, anisotropic thermal parameters for non-hydrogen atoms, and torsional angles (5 pages); tables of observed and calculated structure factors (8 pages). Ordering information is given an any current masthead page.

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Photochemistry of Titanacyclobutanes. Evidence for a Metal-Centered 1,4-Biradical Intermediate

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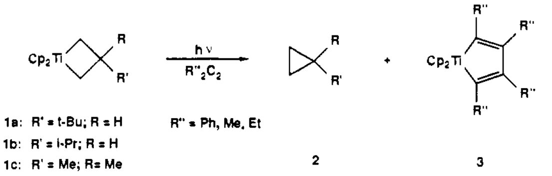
Metallacycles are key intermediates in organometallic chemistry and catalysis as well as useful reagents for organic synthesis.[1] Despite numerous studies on the preparation and thermal chemistry of these complexes, few photochemical investigations have been reported.[2,3] In this paper, we report photochemical studies of the bis(cyclopentadienyl)titanacyclobutanes **1**.[4] Photochemical activation of **1** results in clean reductive elimination to form cyclopropanes and titanocene which can be trapped by a number of added reagents. Stereochemical studies strongly suggest a stepwise mechanism in which the primary photochemical step involves metal-carbon bond homolysis to produce a metal-centered 1,4-biradical intermediate.

Photolysis of the d^0, 16-electron titanacyclobutanes[5] **1** in aromatic, hydrocarbon, or ether solvents in the presence of disubstituted acetylenes[6a] produces cyclopropane[6b] **2** and the bis(cyclopentadienyl)titanacyclopentadiene[6c] **3** (independent of irradiation wavelength over range 250-550 nm). The mass balance



(1)

between the products (cyclopropane and **3**) and starting material **1** is essentially quantitative (>95% by NMR). This photochemically induced reductive elimination[8] contrasts with the well-

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