

The results of our equilibrium and calorimetric studies show (Table I) that the greater stability of the

Table I. Stability Constants, Enthalpy, and Entropy of Formation of the Nickel Complexes of 2,3,2-tet and cyclam at 25.0° and $\mu = 0.1$

Complex	log K_{NiL}	ΔH° , kcal/mol	ΔS° , cal/ (°K mol)
Ni(2,3,2-tet) ²⁺ ^{a, f, g}	15.8	-19.4 ± 0.1 ^{b, h}	7.4
[Ni(2,3,2-tet) (sq planar)] ²⁺ ^c	15.4	-16.8 ± 0.5	14
Ni(cyclam) ²⁺	22.2 ± 0.2 ^{d, i}	-31.0 ± 0.6 ^{e, h, i}	-2

^a Log K_{NiL} is 16.4 in 0.5 M KCl (see footnote f) and is corrected to $\mu = 0.1$ (see footnotes f and g). ^b Determined by calorimetry using the reaction with CN^- and ΔH° for $Ni(CN)_4^{2-}$. ^c Log K , ΔH° , and ΔS° are corrected for the blue \rightleftharpoons yellow equilibrium (ref 7). ^d Determined spectrophotometrically using CN^- and correcting for the $Ni(cyclam)CN^+$ and $Ni(cyclam)OH^+$ complexes.⁹ ^e Determined from the temperature dependence (10.0–40.0°) of the equilibrium constants.⁹ ^f D. C. Weatherburn, E. J. Billo, J. P. Jones, and D. W. Margerum, *Inorg. Chem.*, **9**, 1557 (1970). ^g L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Chem. Soc.*, 5115 (1961). ^h J. J. Christensen, R. M. Izatt, J. D. Hale, R. T. Pack, and G. D. Watt, *Inorg. Chem.*, **2**, 337 (1963). The ΔH° value for $Ni(CN)_4^{2-}$ is interpolated to $\mu = 0.1$ from the tabulated values at ionic strengths of 0.082 and 0.134. ⁱ G. B. Kolski and D. W. Margerum, *Inorg. Chem.*, **7**, 2239 (1968).

macrocyclic complex actually is due to a more favorable change in ΔH° (a difference of -14 kcal/mol) which overcomes a less favorable change in ΔS° (a difference of -16 cal/(°K mol)) for the reaction. Up to this point the effect of ligand solvation has been neglected. In fact, ligand solvation has generally been ignored in the consideration of the thermodynamics of metal complexation reactions. However, for the reaction in eq 1 where the primary solvation (y) of the ligand L is $Ni(H_2O)_x^{2+} + L(H_2O)_y \rightarrow NiL(H_2O)_z^{2+} + (x + y - z)H_2O$ (1) variable, the ΔH° value for the reaction will increase (be less negative) as the enthalpy of solvation of L increases and the ΔS° value will increase as y increases due to the additional H_2O molecules which are released in the reaction.

We propose that ΔH° is much more negative for the complexation of cyclam because this ligand is less solvated by water than is 2,3,2-tet. Cyclam is not able to accommodate as many hydrogen-bonded water molecules with its nitrogen donor atoms because of steric hindrance. However, the primary solvation should be the same for both $Ni(cyclam)^{2+}$ and $Ni(2,3,2-tet)^{2+}$. The result is that for cyclam less enthalpic energy need be expended in breaking hydrogen bonds with the solvent ($\Delta H^\circ \approx 7$ kcal/mol)⁸ and a more favorable ΔH° change is found for reaction 1. It follows that ΔS° must be less positive for the cyclam reaction than for the 2,3,2-tet reaction because fewer water molecules are released from the ligand.

A difference of two in the number of ligand-solvating water molecules (y) accounts for the difference in ΔH° values of the cyclam and 2,3,2-tet reactions. The

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difference in the ΔS° values for the two reactions (16 cal/(°K mol)) is less than would be predicted for the release of two water molecules. This can be attributed to the configurational entropy difference of the ligands and the ΔS° value of +14 cal/(°K mol) for the 2,3,2-tet reaction would be even larger compared to cyclam were it not for the greater loss of configurational entropy of the open-chain ligand.

The postulated ligand solvation effect permits several predictions. The macrocyclic effect should be independent of the metal as long as there is not an unfavorable geometry in the coordination of the metal ion within the macrocycle. Thus, very similar enhancements of the stability constants are found for Cu^{2+} and Ni^{2+} with hexamethyl derivatives of cyclam.⁹ If the solvent is changed to one with weaker primary solvation of the ligand then the importance of the solvation effect will diminish and the relative contribution due to the configurational entropy will increase. Preliminary results support this prediction.¹⁰

The predicted ligand solvation effects are not restricted to macrocyclic ligands but will hold for any ligands where the donor groups are forced to be close to one another or in some way are shielded from solvation. In this respect the terminology of multiple juxtapositional fixedness, although awkward, is appropriate. Thus, the effect of ligand solvation on metal stability constants should be particularly important in biological systems. Obviously, the magnitude of metal ion binding constants to proteins and other biological species may be very much influenced by solvation and could differ from that of smaller, more flexible molecules by very large factors. Finally, there are many small variations in the stability constants of coordination complexes which have been explained by a variety of other postulated effects. These now need to be re-examined in view of the possible magnitude of ligand solvation effects.

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(10) G. F. Smith and D. W. Margerum, to be submitted for publication.

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Rhodium(I) Dithiolene Complexes. Synthesis, Structure, and Dynamic Behavior

Sir:

Studies of Rh(I) complexes have been stimulated by their role in homogeneous catalytic reactions and the related oxidative addition chemistry. To date, the overwhelming majority of these systems are neutral or cationic¹ with few exceptions such as $Rh(CO)_2Cl_2^{-2a}$

(1) See, for example, (a) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1973, p 1018; (b) C. K. Brown and G. Wilkinson, *J. Chem. Soc. A*, 2753 (1970), and references therein; (c) M. Green, T. A. Kuc, and S. H. Taylor, *ibid.*, 2334 (1971); (d) R. R. Schrock and J. A. Osborn, *J. Amer. Chem. Soc.*, **93**, 3089 (1971); (e) L. M. Haines, *Inorg. Nucl. Chem. Lett.*, **5**, 399 (1969); *Inorg. Chem.*, **9**, 1517 (1970).

(2) (a) L. M. Vallarino, *Inorg. Chem.*, **4**, 161 (1965); (b) N. G. Connelly and J. A. McCleverty, *J. Chem. Soc. A*, 1621 (1970).

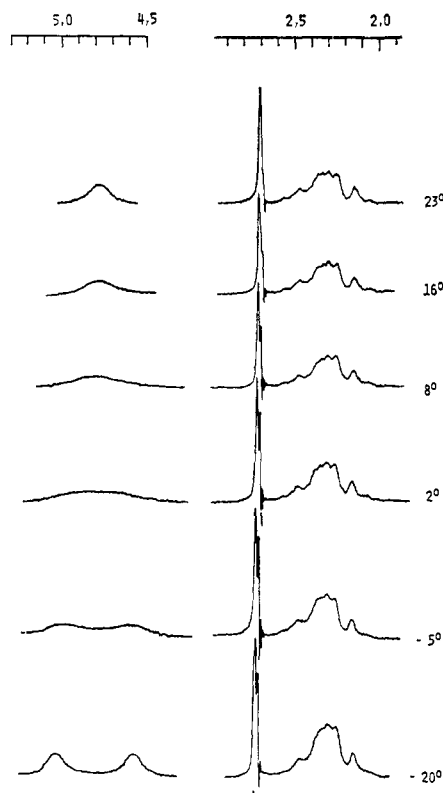


Figure 1. Temperature dependence of the 100-MHz ^1H nmr spectrum of the methylated complex "[Rh(COD)(mnt)(CH₃)]" in CD₂Cl₂.

and Rh(CO)₂(S-S)⁻ where S-S is a bidentate sulfur donor ligand.^{2b} We now report two new Rh(I) anionic complexes, the reactions of these complexes with alkyl halide substrates, and the structures and fluxional behavior of the novel adducts. The observed reaction chemistry implies that the anionic systems have two sites—the Rh(I) ion and the thiolate S donor—for potential attack on common oxidative addition substrates.

The complexes Rh(diene)(mnt)⁻ (diene = 1,5-cyclooctadiene (COD), and norbornadiene (NBD)); mnt = maleonitriledithiolate) are prepared from the corresponding chloro bridged dimers [Rh(diene)(μ-Cl)]₂³ by stoichiometric reaction with Na₂(mnt) in ethanolic hydrazine. Addition of tetra-*n*-butylammonium bromide, followed by solvent evaporation and recrystallization from ethanol-hexane results in yellow crystalline samples of the Rh(I) anions as their (*n*-C₄H₉)₄N⁺ salts.

The complexes react with CH₃I and C₆H₅CH₂X (X = Br, I) in ethanol to yield neutral adducts with analyses corresponding to the general formula Rh(diene)(mnt)R. The ^1H nmr spectrum of Rh(COD)(mnt)(CH₃) at ambient room temperature exhibits three resonances assigned to a methylene multiplet at δ 2.3, a methyl singlet at δ 2.68 and a broad vinyl resonance at δ 4.75. Upon cooling, the vinyl resonance broadens, collapses, and separates into two distinct multiplets at δ 4.99 and 4.53, while the methyl resonance changes from a singlet to a closely spaced doublet ($J_{\text{Rh-H}} \approx 1.5$ Hz). Figure 1 shows the temperature dependence of the ^1H nmr spectrum of Rh(COD)(mnt)(CH₃) down to -20°; the spectrum remains invariant from -20 to -80° at which

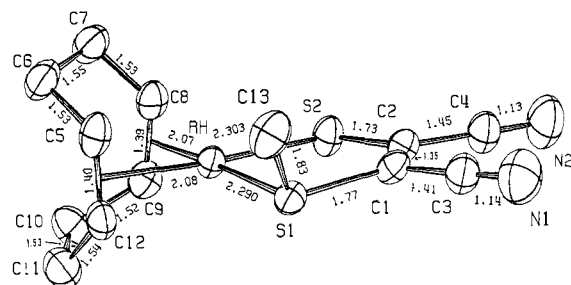


Figure 2. A perspective view of the structure of Rh(COD)(CH₃-mnt). The estimated standard deviations in the bond lengths are: Rh-S, 0.002; S-C, 0.005; Rh-C, 0.005; C-C, 0.007 Å. Some important bond angles with esd's in parentheses are: S1-Rh-S2, 87.48 (7); Rh-S1-C13, 114.7 (2); Rh-S1-C1, 105.0 (2); Cl-S1-C13 102.6(2); Rh-S2-C2, 103.2(2)°.

point precipitation of the complex causes a loss in resolution. Similar dynamic behavior is also noted with Rh(COD)(mnt)(C₆H₅CH₂) and with Rh(NBD)(mnt)(C₆H₅CH₂). Reactions of the Rh(I) anions with SO₂ and C₆H₅HgCl are also observed. The SO₂ adducts are reversibly formed. The reaction involving C₆H₅HgCl results in a complex whose stoichiometry most closely resembles the neutral phenylmercury adduct; however, insolubility and lack of volatility have hindered more extensive characterization.

For the purpose of explaining the variable temperature nmr spectra of the alkyl adducts, the structure of Rh(COD)(mnt)(CH₃) was determined by X-ray methods: (crystal data) $a = 14.78$ (1), $b = 10.69$ (1), $c = 9.20$ (1) Å; $\beta = 106.09$ (5)°; $V = 1397$ Å³; space group, $P2_1/a - C_{2h}^5$; $\rho_{\text{exptl}} = 1.75$ (2), $\rho_{\text{calcd}} = 1.75$ g/cm³ for $Z = 4$; $\mu(\text{Mo K}\alpha) = 14.67$ cm⁻¹. Intensity data were collected by the θ - 2θ scan technique on a computer-controlled diffractometer using Mo K α radiation. The structure was solved by standard heavy atom methods, and refined by least squares to discrepancy indices R and R' of 0.032 and 0.045, respectively, for 2127 reflections above 2σ . In the refinements all nonhydrogen atoms were allowed to vibrate according to an anisotropic thermal model. Hydrogen atoms were located and included in the final cycles as fixed contributions with isotropic temperature factors. Final positional and thermal parameters for the structure are available.⁴

The structure determination reveals that the complex is methylated at one of the sulfur donor atoms rather than at the rhodium. The methylated complex thus remains a four-coordinate d⁸ system, and a perspective view of the molecule is shown in Figure 2. Despite the alkylation of one of the sulfur donor atoms, the two Rh-S distances are nearly equal with the Rh-S(CH₃) distance being slightly shorter (see Figure 2). The two S-C distances of the mnt ligand, however, are significantly different reflecting the partial multiple bond character in the carbon-thiolate sulfur bond. The COD ligand adopts a conformation such that the metal diolefin chelate unit possesses only approximate C₂ symmetry with torsional angles about the bonds of the methylene C atoms averaging 93.7 (9), 33.4 (10), and 41.8 (10)°. The methylated sulfur is pyramidal with the methyl group 1.42 Å out of the coordination plane.

(3) (a) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957); (b) E. W. Abel, M. A. Bennett, and G. Wilkinson, *ibid.*, 3178 (1959).

(4) See paragraph at end of paper regarding supplementary material.

The four vinyl protons of the COD ligand are thus nonequivalent in the static structure (two cis to the methylated sulfur and two trans, two above the coordination plane and two below).

Since only two vinyl resonances are observed in the low temperature spectrum down to -80° , we suggest that two dynamic processes are occurring in solution which equilibrate pairs of vinyl protons with only one of these processes observed on the nmr time scale in the present study. Possible averaging processes include: (a) inversion at the pyramidal sulfur;⁵ (b) twofold twist of one chelate ring going through a tetrahedral transition state; (c) dissociation of a Rh-olefin bond, rotation of the diolefin, and recombination; and (d) a process similar to (c) in which the Rh-S(CH₃) bond cleaves. Because of the loss of methyl proton-rhodium coupling in going from -20° to room temperature, we tend to favor (d) as the observed process with inversion at sulfur (a) as the rapid equilibrating process which we are unable to freeze out on the nmr time scale. However, (b) cannot be ruled out as the observed process because of coalescence temperatures of 0 and -50° for Rh(COD) (C₆H₅CH₂-mnt) and Rh(NBD)(C₆H₅CH₂-mnt), respectively. In the twofold twist mechanism, steric interactions between the diene and the sulfur donor ligands should be reduced for the NBD complex and thus lead to the observed lower barrier for equilibration in that system. The low activation energy implicit in our assumption about inversion at sulfur seems reasonable since the transition state for process (a) should be stabilized by a delocalized dithiolene resonance structure. In addition, the solid state structure of Rh(COD) (CH₃-mnt) shows the alkylated sulfur to be slightly less pyramidal than those found in other metal complexes.⁶ The magnitude of $J_{\text{Rh-H}}$ in the present case is similar to that found in structurally related systems.⁷ Further studies including detailed spectral analyses will be reported.

Alkylation of dithiolate sulfur atoms has been observed previously.⁸ In the present study the adduct complexes remain as d⁸ Rh(I) systems potentially capable of undergoing oxidative addition reactions. The thiolate S donor lone pairs function as nucleophiles in attack on oxidative addition substrates and thus raise the possibility of utilizing such ligand lone pairs in certain multi-step, metal complex promoted reactions.

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(6) To assess the pyramidal nature of the alkylated sulfur in this system, we have summed the three bond angles about S(1) and compared that sum with trivalent sulfur in other systems. The larger the sum, the greater the s character in the sulfur σ -bonding orbitals and the closer the sulfur is to the 360° value for a planar, trigonal atom. The values for representative systems are as follows: 322° (present case); 316° in Re₂Cl₅(CH₃SCH₂CH₂SCH₃)₄ [M. J. Bennett, F. A. Cotton, and R. A. Walton, *Proc. Roy. Soc., Ser. A*, **303**, 175 (1968)]; 315° in Ni(TSP)Cl⁺ (L. P. Haugen and R. Eisenberg, *Inorg. Chem.*, **8**, 1072 (1969)); 310° in (CH₃)₂(C₆H₅)S⁺ (A. Lopez-Castro and M. R. Truter, *Acta Crystallogr.*, **17**, 465 (1964)).

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(9) Alfred P. Sloan Foundation Fellow, 1972-1974.

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Supplementary Material Available. The table of final positional and thermal parameters for the structure will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-4994.

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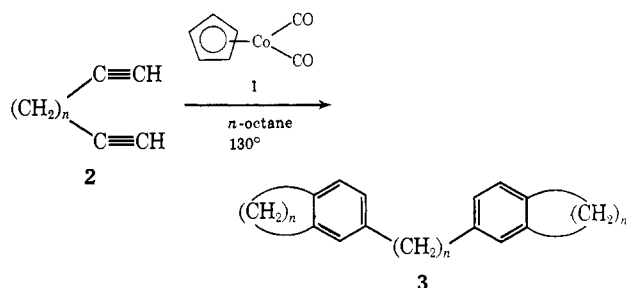
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A One-Step Synthesis of Benzocyclobutenes Involving Cooligomerization of Linear Mono- and Diacetylenes Catalyzed by η^5 -Cyclopentadienylcobalt Dicarboxyl

Sir:

We wish to report that commercially available η^5 -cyclopentadienylcobalt dicarbonyl (η^5 -C₅H₅Co(CO)₂) (**1**) reacts catalytically with linear 1, *m*-diacetylenes to produce, in good to moderate yield, trimers the formation of which involves the interaction of six acetylene functions. The product-forming intermediates in these reactions can be intercepted either by other acetylenes, leading to a versatile one-step synthesis of benzocyclobutenes, or by nitriles, leading to complex pyridines.

Our first observation was made in the reaction of 1,5-hexadiyne (**2**, $n = 2$) with **1** in refluxing *n*-octane (con-



ditions similar to those described by King and Efraty¹ and by Macomber²). Chromatography of the reaction mixture gave a product (45% yield) containing neither acetylene, carbonyl, nor metal, the spectral data of which were consistent with benzocyclobutene structure **3** ($n = 2$). This material was identical with the sample of **3** ($n = 2$) reported earlier as having been isolated in 13% yield on reaction of **2** with a Ziegler-Natta catalyst.³

The reaction is apparently general for linear terminal diacetylenes. Compounds **2** ($4 \geq n \geq 2$) all produce **3** in reasonable yield along with only trace amounts of colored by-products, easily removed by column chromatography. The reaction is even cleaner when carried out catalytically; a 1:20 mole ratio of **1** to **2** leads to comparable yields of **3** in better purity and at about the same rate.

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(2) R. S. Macomber, *J. Org. Chem.*, **38**, 816 (1973).

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