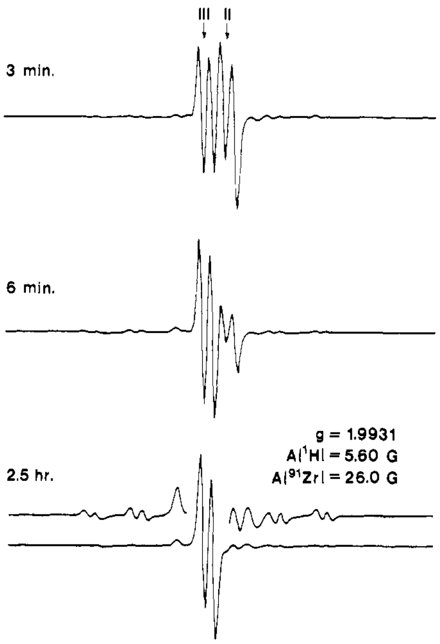

Figure 1. Solution EPR spectra of the photolysis of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ in the presence of PhC≡CPh after 3 min, 6 min, and 2.5 h.

Zr hydrides produced during the photolysis of $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$[17] and $(\eta^5\text{-}C_5H_5)_2Zr(C_6H_5)_2$.[18]

To investigate the chemical reactivity of II, we have photolyzed I in benzene containing either diphenylacetylene, D_2, or PPh_3 and followed the reactions by EPR. For diphenylacetylene, the hydride doublet of II diminishes with the formation of a new paramagnetic Zr–hydride species, III, with $g = 1.9931$, $A(^1H) = 5.6$ G, and $A(^{91}Zr) = 26.0$ G (Figure 1). The EPR spectrum of III may be that of the hydridoacetylene complex, $(\eta^5\text{-}C_5H_4CH_3)_2Zr(H)(PhC{\equiv}CPh)$,[19] which represents a plausible intermediate in the acetylene hydrogenation process.[21] When photolysis of I is performed under a D_2 atomosphere, the hydride doublet is replaced by an "apparent" singlet due to H/D exchange of the Zr–H bond in II. The magnitude of $A(^2D)$, *ca.* $^1/_6$ of $A(^1H)$, is sufficiently small to prevent resolution of the ^2D hyperfine coupling. Further EPR experiments have shown that the H/D exchange process for II is reversible.[22] Finally, for PPh_3 the hydride doublet slowly fades with the appearance of another doublet centered at $g = 1.9977$. The larger hyperfine splitting of the latter is consistent with the formation of a paramagnetic Zr(III)–monophosphine species with $A(^{31}P) = 24.3$ G and $A(^{91}Zr) = 11.3$ G.[23] Analogous spectra are obtained in each case for the corresponding thermal reactions performed at 75 °C. Their spectral features, however, deteriorate upon prolonged heating. Although these EPR studies represent preliminary measurements, they suggest that paramagnetic zirconocene hydride complexes may participate in the chemical reactivity of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$. Work is in progress to determine the stereochemistry of these paramagnetic complexes and to examine further their chemical behavior.

Acknowledgment. We thank the NSF (Grant No. ISP-8011453 and PRM-8011453) for support provided to conduct this research and to purchase an IBM/Bruker ER200D-SRC EPR spectrometer, respectively. Also we acknowledge the support provided by the West Virginia Energy Research Center to acquire a programmable gas chromatograph.

Registry No. I, 77965-67-4; $(\eta^5\text{-}C_5H_4CH_3)_2Zr(C_4(C_6H_5)_4)$, 86508-08-9; $(\eta^5\text{-}C_5H_4CH_3)_2Zr(C_4(C_6H_5)_2H_2)$, 86508-09-0; D_2, 7782-39-0; PPh_3, 603-35-0; phenylacetylene, 536-74-3; diphenylacetylene, 501-65-5.

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Synthesis and Properties of Macrobicyclic Amine Complexes of Rhodium(III) and Iridium(III)

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The macrobicyclic amine complexes $[M(sep)]^{3+}$, $[M(diNOsar)]^{3+}$, $[M(diAMsar)]^{3+}$, and $[M(diAMsarH_2)]^{5+}$ (Scheme I), M = Rh(III) and Ir(III), have been synthesized in moderate (~40%, Ir(III)) to high (90–100%, Rh(III)) yields from $[M(en)_3]^{3+}$ precursors,[1] demonstrating a remarkable degree of regiospecificity for formation of the cage structure. It was anticipated that the rare,[2-4] mononuclear octahedral d^7 Rh(II) and Ir(II) ions might be stabilized, since Co(III) analogues undergo reversible one-electron reductions to substitution inert Co(II) complexes,[5-10] and the d^7 Pt(III) cage complexes are stabilized in the solid state.[11] This expectation has been realized for Rh(II).

The cage complexes were prepared from $[M(en)_3]^{3+}$ ions[12-14] in a similar manner to the cobalt analogues[5-7,10] (Scheme I), except

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[1] sar = sarcophagine = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane; sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane; diNOsar = 1,8-dinitrosarcophagine; diAMsar = 1,8-diaminosarcophagine; $diAMsarH_2$ = 1,8-diammonium sarcophagine; en = 1,2-ethanediamine.

[2] The M(II) oxidation state is normally only observed as a transient intermediate or in spin-paired dimers.[3,4]

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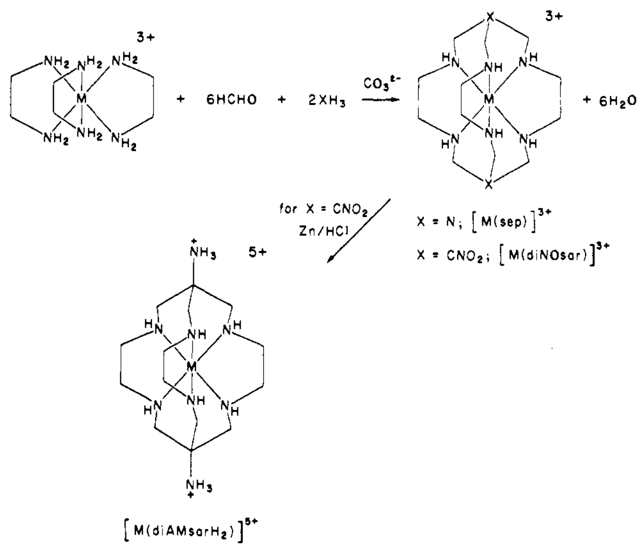
Scheme I



elevated temperatures (Rh, 60 °C; Ir, 90 °C) were required for the quoted yields. Spectral properties (^{1}H and ^{13}C NMR and IR) were characteristic[5-7,10,15] of the highly symmetric (D_3) cage structure.[16] Particularly definitive were the ^{1}H-decoupled ^{13}C NMR specta where only two resonances were observed that correspond to the two sets of six equivalent methylene carbons in the [M(sep)]$^{3+}$ ions. An additional weaker resonance was observed for the apical carbons of the sar cage complexes, having a chemical shift characteristic of the functional group to which it is bonded. An interesting feature of the Rh(III) spectra was the observation of ^{103}Rh–^{13}C coupling at the apical position ($J \sim$ 3–4 Hz), while coupling was not observed for the methylene carbons ($J \leq 0.3$ Hz). A similar trend is observed in the ^{195}Pt–^{13}C coupling for Pt(IV) cage complexes;[11] this point will be discussed in detail elsewhere.[17] ^{1}H NMR spectra of the N-deuterated compexes exhibit AB doublets for the inequivalent axial and equatorial protons of the methylene groups and ABA′B′ multiplets for the ethylene groups. Coupling patterns are readily distinguishable for [M(diNOsar)]$^{3+}$ and [M(sep)]$^{3+}$ ($J_{AB} \sim$ 10–15 Hz);[16] however, [M(diAMsarH$_n$)]$^{(3+n)+}$ ions have the coupling patterns superimposed and the spectra are very pH dependent, due to protonation/deprotonation equilibria involving the apical amines (pK_a 3–4).

Electronic spectra of the cage complexes are similar to those of the parent [M(en)$_3$]$^{3+}$ ions. The ligand field transitions (of O_h parentage $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$) for the d^6 ions are observed at ~300 and ~250 nm for Rh(III). For Ir(III), only the lower energy spin-allowed transition occurs at ~250 nm as a shoulder on the more intense charge-transfer band; low-energy spin-forbidden triplet transitions (O_h parentage $^1A_{1g} \rightarrow {}^3T_{1g}$, 400 nm) are also observed.[13,16] The lifetime of the triplet excited state for [Rh(sep)]$^{3+}$ (λ_{max}1.58 μm^{-1}, 2.8 μs, 77 K, crystals) is shorter than those of [Rh(NH$_3$)$_6$]Cl$_3$ (27 μs) and [Rh(en)$_3$]Cl$_3$ (22 μs) under the same conditions.[18]

The Ir(III) cage complexes and [Rh(sep)]$^{3+}$ show no metal-centered reduction processes in aqueous media. However, the electrochemistry of [Rh(sep)]$^{3+}$ in acetone (1.0 M Me$_4$NCF$_3$SO$_3$) parallels that of [Co(sep)]$^{3+}$,[8] where an initial reduction to the M(II) oxidation state is followed by an irreversible two-electron reduction to the metal. The reduction to Rh(II) occurs at −1.8 V vs. the Ag/AgCl/0.1 M LiCl (acetone) reference electrode, which is 1.5 V more negative than its cobalt counterpart in the same medium.[8] The final two-electron step occurs at −2.2 V (cf. −2.0 V for Co(II) → Co(0)). Cyclic voltammetry (CV) and variable frequency phase-sensitive AC polarography indicated the Rh(II) complex was moderately stable and decayed by a first-order process ($t_{1/2} \sim$ 15 ms, 20 °C). Similar experiments on the [Rh(diAMsarH$_2$)]$^{5+}$ and [Rh(diNOsar)]$^{3+}$ complexes indicated that the Rh(III)/Rh(II) couples under similar conditions were reversible even at slow sweep rates (CV); however, the electrochemistry was complicated by prior ligand reductions in both instances.[19] A comparison of the diffusion currents of the rhodium cage complexes (DC polarography) with cobalt cage complexes and coulometric measurements in acetone confirmed the one-electron nature of the Rh(III)/Rh(II) couples. For the iridium complexes, poorly defined oxidation processes occurred at ~+0.9 V vs. SCE in aqueous 1.0 M CF$_3$SO$_3$H (Pt electrode). These were absent for Rh(III) and Co(III) complexes, and are therefore assigned as irreversible oxidations initially to Ir(IV) rather than direct oxidation of the ligands.

Pulse radiolysis of [Rh(sep)]$^{3+}$ ((1–10) × 10^{-4} M) in He-saturated phosphate buffers (0.02 M, pH 6.9, 25 °C) showed pseudo-first-order quenching of the hydrated electron (600 nm), from which a second-order rate constant of 1.4 × 10^{10} M^{-1} s^{-1} was obtained for the production of Rh(II). Its formation coincided with an increase in absorbance at 340 nm, which decayed to the original absorbance by a first-order path (0.5 ± 0,1 s^{-1}, 25 °C). The experiment implies that the powerful reductant, Rh(II), reduces water to regenerate the Rh(III) complex and H$_2$; however, this proposal needs further verification.

Reductions of Rh(III) amine complexes are normally irreversible processes.[20,21] The Rh(II) intermediates dimerize, disproportionate and/or undergo further rapid reductions to square-planar Rh(I) species, which subsequently react with solvent and electrode.[21] The expectation that the cage structures would stabilize Rh(II) has been realized; even so, they are powerful reductants. The very negative reduction potentials of the Rh(III) cage complexes was not unexpected, since Rh(III) complexes are normally more difficult to reduce than their Co(III) counterparts[20] and the preferred cavity size constraints would tend to destabilize the larger Rh(II) ion further. Both factors are more pronounced for Ir(II) in agreement with the experimental observations. The differences also reflect the ionization potentials for the triad. We hope to stabilize the M(II) oxidation states further by synthesizing cage complexes with larger cavity sizes.

The regiospecificity for the syntheses is fairly remarkable since the formation of the ligands involves the condensation of 11 molecules to form the 14-membered rings of the macrobicycles. Such condensations would be expected to occur only in yields of a fraction of a percent, at best, in the absence of a metal ion template. Moreover, if chiral [Rh(en)$_3$]$^{3+}$ is used,[22] chiral cage complexes are obtained in ~100% chemical and chiral yields (despite the seven centers of chirality).

Acknowledgment. We thank Lektor F. Galsbøl for making results available prior to publication and for a generous gift of

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(16) [Rh(sep)]Cl$_3$·H$_2$O: Anal. (C$_{12}$H$_{32}$Cl$_3$N$_8$ORh) C, H, Cl, N, Rh; ^{13}C NMR (D$_2$O, downfield shifts vs. dioxane as internal standard) −12.3 (en), +2.0 (cap); Vis/UV (0.1 M HCl) ϵ_{296}^{max} 309 M^{-1} cm^{-1}, ϵ_{244}^{max} sh. [Rh(diNOsar)]Cl$_3$·H$_2$O: Anal. (C$_{14}$H$_{32}$Cl$_3$N$_8$O$_5$Rh) C, H, Cl, N, Rh. ^{13}C NMR (D$_2$O) +24.6 (C, cap, $J_{^{103}Rh}$ 3.36 Hz) −9.1 (CH$_2$, cap), −10.1 (CH$_2$, en); Vis/UV (0.1 M HCl) ϵ_{297}^{max} 553, ϵ_{252}^{max} 347. [Rh(diAMsarH$_2$)]Cl$_5$·3.5H$_2$O: anal. (C$_{14}$H$_{43}$Cl$_5$N$_8$O$_{3.5}$Rh) C, H, Cl, N, Rh; ^{13}C NMR (0.1 M DCl) −6.7 (C, cap, $J_{^{103}Rh}$ 4.15 Hz), −10.1 (CH$_2$, en), −13.0 (CH$_2$, cap); Vis/UV (0.1 M HCl) ϵ_{299}^{max} 511, ϵ_{251}^{max} 360. [Rh(diAMsar)]$^{3+}$: ^{13}C NMR (D$_2$O, pD ~7) −6.4 (C, cap, $J_{^{103}Rh}$ 3.42 Hz), −9.2 (CH$_2$, cap), −10.2 (CH$_2$, en). [Ir(sep)]Cl$_3$·2H$_2$O: anal. (C$_{12}$H$_{34}$Cl$_3$N$_8$O$_2$Ir) C, H, N; ^{13}C NMR (D$_2$O) + 3.6 (CH$_2$, cap), −10.0 (CH$_2$ en); Vis/UV (0.1 M HCl) ϵ_{244}^{max} 290 sh. [Ir(diNOsar)]Cl$_3$·2H$_2$O: anal. (C$_{14}$H$_{34}$Cl$_3$N$_8$O$_6$Ir) C, H, Cl, N; ^{13}C NMR (D$_2$O) ~+30 (C, cap), −7.7 (CH$_2$, en), −10.8 (CH$_2$, cap); Vis/UV (0.1 M HCl) ϵ_{375}^{max} 40, ϵ_{246}^{max} 486 sh. [Ir(diAMsarH$_2$)]Cl$_5$: ^{13}C NMR (0.1 M DCl) −4.1 (C, cap), −7.7 (CH$_2$, en), −11.2 (CH$_2$, cap); Vis/UV (0.1 M HCl) ϵ_{248}^{max} 473 sh. [Ir(diAMsar)]$^{3+}$: ^{13}C NMR (D$_2$O) −4.1 (C, cap), −7.8, (CH$_2$, en), −7.1 (CH$_2$, cap).

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$[Ir(en)_3]^{3+}$, the ANU Microanalytical and NMR Services, the Department of Chemistry, the University of Melbourne for use of facilities, and the U.S.-Australia Program for Cooperation in Science for support to carry out the pulse radiolysis studies at Argonne.

Registry No. $[Rh(sep)]Cl_3$, 86372-67-0; $[Rh(diNOsar)]Cl_3$, 86372-68-1; $[Rh(diAMsarH_2)]Cl_5$, 86372-69-2; $[Rh(diAMsar)]^{3+}$, 86372-73-8; $[Ir(sep)]Cl_3$, 86372-70-5; $[Ir(diNOsar)]Cl_3$, 86372-71-6; $[Ir(diAMsarH_2)]Cl_5$, 86372-72-7; $[Ir(diAMsar)]^{3+}$, 86409-32-7; $[Ir(en)_3]^{3+}$, 41673-42-1; $[Rh(en)_3]^{3+}$, 16786-61-1; HCHO, 50-00-0; NH_3, 7664-41-7; H_3CNO_2, 75-52-5.

Rates of Chelate Ring Closure in Five-Coordinate Metal Carbonyl Intermediates[1]

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Photochemical reactions of (chelate)$M(CO)_4$ complexes (M = Cr, Mo, W) have been found to proceed via chelate ring-opening[2] or carbonyl loss[1-3] depending upon the irradiating wavelength and the identity of the chelating ligand. In several instances, rates of bimolecular reactions of Lewis bases with five-coordinate intermediates formed via carbonyl loss in these and related complexes have been determined.[1,3] We wish to report studies of $(\eta^2\text{-NP})M(CO)_4$ (NP = 1-(diphenylphosphino)-2-(diethylamino)ethane; M = Cr, Mo) employing pulsed laser flash photolysis, for which evidence supports chelate ring opening as the predominant photolytic pathway and which provides what are to our knowledge the first rates for unimolecular chelate ring closure in a metal carbonyl intermediate.

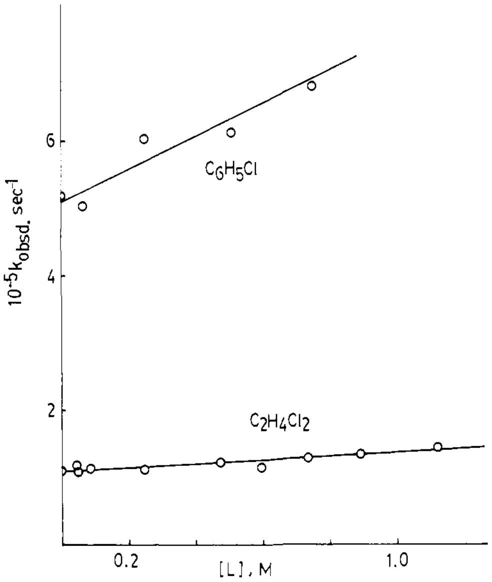

Figure 1. Plots of k_{obsd} vs. [L] for reaction of $[(\eta^1\text{-NP})Cr(CO)_4]$ with triisopropyl phosphite in 1,2-dichloroethane and chlorobenzene at 22 °C.

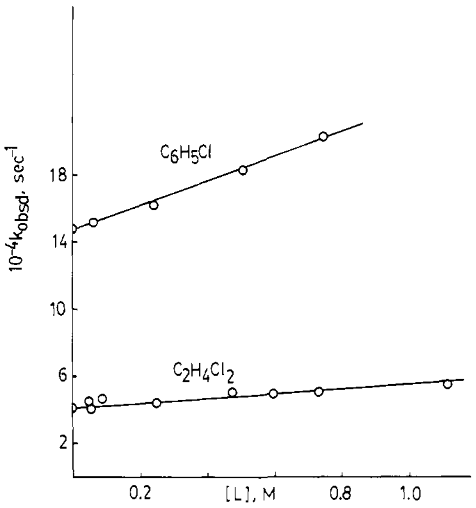

Figure 2. Plots of k_{obsd} vs. [L] for reaction of $[(\eta^1\text{-NP})Mo(CO)_4]$ with triisopropyl phosphite in 1,2-dichloroethane and chlorobenzene at 22 °C.

Table I. Rate Constants for Reactions of $[(\eta^1\text{-NP})M(CO)_4]$ Intermediates[a]

M	solvent	$10^{-4}k_1$, s^{-1}	$10^{-4}k_2$, M^{-1} s^{-1}
Cr	DCE	10.9 (2)	2.7 (3)
Cr	CB	52 (2)	22 (4)
Mo	DCE	4.2 (1)	1.1 (2)
Mo	CB	14.6 (1)	7.4 (2)

[a] Numbers in parentheses: error limits at the 95% confidence level.

The $(\eta^2\text{-NP})Mo(CO)_4$ substrates, synthesized by means of published methods,[4] were irradiated at 22 °C by employing a Q-switched Nd:YAG laser (355-nm irradiating frequency, 11-ns FWHI) in Ar-bubbled 1,2-dichloroethane (DCE) or chlorobenzene (CB) containing various concentrations of triisopropyl phosphite (L) as "trapping agent". The decay of the intermediate thus produced was monitored at 475 nm for M = Cr and 420 nm for M = Mo to afford the pseudo-first-order rate constants, k_{obsd}. Figures 1 and 2 exhibit plots of k_{obsd} vs. [L] for both metals and solvents. These data are consistent with the rate law

$$-d[Int]/dt = k_1[Int] + k_2[Int][L] \qquad (1)$$

and with overall mechanism illustrated in the scheme. It is especially significant to note that values of k_{obsd} obtained in the absence of L very closely approximate those obtained through extrapolation of plots of k_{obsd} vs. [L] to [L] = 0, as is expected for a unimolecular ring-closure pathway. Separate studies, involving irradiation of the substrate (M = Mo) at 22 °C employing the 366-nm Hg line (Hanovia 400-W medium-pressure Hg lamp), demonstrated that the Mo-N bond is broken during the ring-opening process and that no Mo-CO bond fission takes place. The sole reaction product was found to be *cis*-$(\eta^1\text{-NP})(L)Mo(CO)_4$, identified through its carbonyl stretching spectrum (ν_{CO} 2017 (m), 1915 (ms), 1895 (s), 1880 (s); DCE solvent).[5]

Rates of reaction (Table I) differ significantly in DCE and CB, suggesting solvation of the ring-opened intermediate, with subsequent solvent displacement during ring closure or attack at the solvated intermediate by L. The relative rates of both reaction pathways suggest greater solvent-intermediate interaction for the

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[5] These frequencies compare very favorably to those for closely related *cis*-$L_2Mo(CO)_4$ complexes containing two ligands coordinating through P, such as, (diphos)$Mo(CO)_4$, ν_{CO} (in DCE) 2020 (m), 1919 (s), 1907 (s), 1881 (s), ref 4, but are significantly different from those for the corresponding complexes containing one N and one P donor atom, expected if Mo-P bond fission takes place. Carbonyl stretching frequencies, DCE solvent, for (N-P)$Mo(CO)_4$ are 2010 (m), 1894 (vs, br), 1844 cm^{-1}.

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