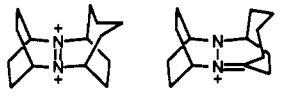
Table I. Results of AM1 Calculations on α-Deprotonated Hydrazine Dications

	species			
	1^{2+}-H_α	3^{2+}-H_α(4)	5^{2+}-H_α(6)	$R_2NRN^+{=}CR_2$[a]
$d(N^+C_\alpha)$, Å	1.435	1.343	1.335	1.334
$f(\Delta d)$[b]	≡0	0.92	0.99_4	≡1.0
N^+C_α twist, deg	79.0	38.2	26.5	2.9
α_{av} at N^+, C_α, deg	115.4, 115.1	119.3, 117.9	119.9, 119.3	120.0, 120.0
$\Delta\Delta H_f(\beta\text{-}\alpha)$,[c] kcal/mol	−28.9	−4.7[d]	+15.9[e]	
rel $\Delta\Delta H_f(\alpha)$ vs neutral,[f] kcal/mol	58.1	26.0	5.9	[≡0]
rel $\Delta\Delta H_f(\alpha)$ vs cation,[g] kcal/mol	66.5	36.2	18.7	[≡0]

[a] R = CH_3. [b] Fractional change in $d(N^+C_\alpha)$ between 1^{2+}-H_α and the acyclic model. [c] $\Delta H_f(X^{2+}\text{-}H_\beta) - \Delta H_f(X^{2+}\text{-}H_\alpha)$, for the most stable β- and α-deprotonation products (which are those derived by proton loss from the largest ring). [d] Products derived by deprotonation at the $(CH_2)_2$ bridges are destabilized by 5.3, 6.6, and 6.8 kcal/mol. [e] Products derived by deprotonation at the $(CH_2)_2$ bridges are destabilized by 1.8, 4.8, and 4.9 kcal/mol. [f] $[\Delta H_f(X^{2+}\text{-}H_\alpha) - \Delta H_f(X^0)]$, minus this quantity for the acyclic model.[4] [g] $[\Delta H_f(X^{2+}\text{-}H_\alpha) - \Delta H_f(X^{\cdot+})]$, minus this quantity for the acyclic model.[4]

facile than for 2^{2+},[4] despite **4** having a calculated twist of 38° at the $N^+{=}C_\alpha$ bond. For 1^{2+}, where the α-deprotonation product is prevented from attaining significant $N^+{=}C$ bonding, the observed β-deprotonation product is calculated to be thermodynamically more favorable than the α-deprotonation product by 28.8 kcal/mol. The most stable of the four β-deprotonation products of 3^{2+}, that derived by deprotonation of the trimethylene bridge, is calculated to be 4.7 kcal/mol thermodynamically more stable than the α-deprotonation product, but the products of these irreversible deprotonations will be determined by kinetics, not thermodynamics of deprotonation.[5]

We have been unable to detect **4** spectroscopically, possibly because of its high reactivity with nucleophiles. It may also be noted in the table that AM1 predicts α-deprotonation of the next higher homologue, 5^{2+} (θ, 64°; $\cos^2\theta$, 0.19), to be more facile than that of 3^{2+} by about 18 kcal/mol and predicts the product **6** to have a 26.5° twist at the $N^+{=}C_\alpha$ bond but little other distortion relative to the acyclic model. 5^{2+} ought to be even more acidic



5^{2+} **6**

than 3^{2+} and **6** (which contains a *trans*-cyclooctene structure) to be isolable. Neutral **5** was prepared by addition of 1,3-cyclohexadiene to protonated 7,8-diazabicyclo[4.2.2]dec-7-ene followed by hydrogenation and deprotonation.[6] In contrast to 1^{2+} and 3^{2+}, dication 5^{2+} (bridgehead signals: ^1H NMR δ 6.03 and 5.91; ^{13}C NMR δ 82.5 and 81.6)[6] decomposes slowly in CD_3CN even at −38 °C to produce cation **6**, which was isolated as the hexafluorophosphate salt in 83% yield after an ether quench. **6**-PF_6 shows three bridgehead ^1H NMR signals at δ 4.47, 3.79, and 3.61, an olefinic ^{13}C NMR C_q at 175.6 and bridgehead CH at 66.6, 55.7, and 53.9, weak IR absorptions at 1608 and 1571 cm^{-1}, and UV bands at 298 (ε 4360) and 210 (ε 3700).[6] The spectroscopic effects of twisting at neutral N=C bonds have received considerable study from the extensive matrix isolation work reported on bridgehead imines generated from bicyclic bridgehead azides.[7] We believe **6** to be the first twisted $N^+{=}C$ species to be reported. Electrochemical measurements of the kinetics of deprotonation of tetraalkyldiazenium dications and the use of their α-deprotonation products for the preparation of substituted hydrazines will be reported in due course.

Acknowledgment. We thank the National Institutes of Health for financial support of this work under GM-29549, the National Science Foundation for grants supporting the spectroscopic and computational equipment, and Timothy Clark for the computer programs employed.

Supplementary Material Available: Experimental procedures for the preparation of $3^{2+}(PF_6^-)_2$ and $6^+PF_6^-$ and a listing of NMR spectral data for $5^{2+}(PF_6^-)_2$ determined from mixtures with **6** (4 pages). Ordering information is given on any current masthead page.

(4) Meaningful comparisons of heats of formation for compounds of different empirical formulas and strain are always a problem. The last two rows of the table tabulate the difference in ΔH_f for the α-deprotonated dication and the neutral compound and the radical cation, respectively, with the proper quantity for the acyclic model subtracted, which gives an indication of the effects imposed by the polycyclic structure. Neither set of numbers provides a perfect comparison because of significant differences in bonding at the nitrogens between the different compounds. We note that the differences between the entries for 1^{2+}-H_α and 3^{2+}-H_α are 32.1 and 30.3, respectively, while those between 3^{2+}-H_α and 5^{2+}-H_α are 20.1 and 17.5, respectively, which are rather similar, despite the differences in the magnitudes of the numbers depending upon whether comparisons were made with the neutral hydrazines or their radical cations.

(5) A referee suggested that examination of charges at the protons or s-orbital coefficients in the LUMO might reflect the large changes in α-proton kinetic acidities. Neither does. Higher charge is calculated at the bridgehead hydrogens of the [222] rings of both 3^{2+} and 5^{2+} than is calculated at the larger ring, in contradiction to the experimental site of α-deprotonation. The LUMOs are π^*(NN) and have vanishingly small coefficients at the bridgehead hydrogens. The structural changes undergone upon deprotonation are apparently too large to make the dication a good enough model for the deprotonation transition state for such approximations to work.

(6) See supplementary material.

(7) For a recent review, see: Warner, P. M. *Chem. Rev.* **1989**, *89*, 1067.

The Redox Chemistry of $(n\text{-}Bu_4N)_2[Os_2Cl_8]$: Low-Temperature Spectroelectrochemical Characterization of $[Os_2Cl_8]^-$ and Voltammetric Evidence for $[Os_2Cl_8]^0$

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The nature of metal–metal-bonded systems is of particular and enduring interest.[1] Face-to-face complexes of form $[M_2X_8]^{n-}$ (M = Cr, Mo, W, Tc, Re, Os; X = Cl, Br) allow comparisons of the unsupported M–M multiple bond according to periodic trends and as a function of the varying electronic occupancy of the binuclear $\sigma\pi\delta\delta^*\pi^*\sigma^*$ orbital manifold. The maximal, quadruple bond occurs for eight-electron (8e) systems, typified by $[Re_2Cl_8]^{2-}$. So far, $[Tc_2Cl_8]^{2-}$ and $[Tc_2Cl_8]^{3-}$ represent the only octahalide isolated and structurally characterized in two oxidation states.[2] However, $[Re_2Cl_8]^{3-}$, which is more reactive than $[Tc_2Cl_8]^{3-}$, was recently characterized in solution by generation from $[Re_2Cl_8]^{2-}$ in an

* To whom correspondence should be addressed.

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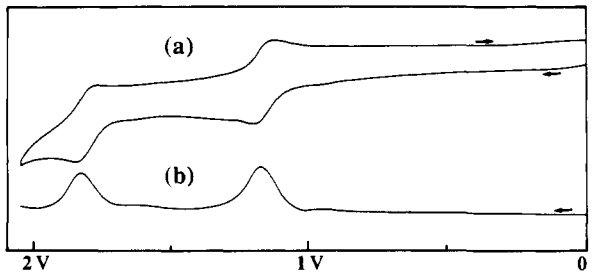

Figure 1. Voltammetry of $(n\text{-}Bu_4N)_2[Os_2Cl_8]$ in *n*-PrCN at 235 K, vs Ag/AgCl: (a) cyclic dc scan, 100 mV/s; (b) linear ac scan, 20 mV/s.

Scheme I

$$[Os_2Cl_8]^0 \rightleftharpoons [Os_2Cl_8]^{1-} \rightleftharpoons [Os_2Cl_8]^{2-} \rightleftharpoons \{[Os_2Cl_8]^{3-}\}$$

8e 9e 10e 11e

optical spectroelectrochemical cell.[3] The electronic absorption spectra of these 8e and 9e group 7 ions are very informative, especially in the near-infrared and visible region where δ/δ^*, π/δ^* and δ^*/π^* transitions are expected.[3,4] Further reduction to $[Re_2Cl_8]^{4-}$ (10e, bond order 3) seems out of reach, but we now report complementary electrochemical studies of 10e $[Os_2Cl_8]^{2-}$, according to Scheme I, and describe the optical spectrum of hitherto unknown $[Os_2Cl_8]^{1-}$.

Voltammetry of $[Os_2Cl_8]^{2-}$ at room temperature in both CH_2Cl_2 and butyronitrile (*n*-PrCN) reveals only an irreversible (ec)[3a] reduction and a similarly irreversible oxidation, much as described by Walton.[5] However, at 235 K one-electron oxidation of $[Os_2Cl_8]^{2-}$ is fully reversible and a second reversible oxidation is revealed at extreme potential.[6] In $n\text{-}Bu_4NPF_6/n$-PrCN solution, the $[Os_2Cl_8]^{2-/1-}$ couple occurs at 1.19 V, while the $[Os_2Cl_8]^{1-/0}$ couple occurs at 1.82 V vs Ag/AgCl (Figure 1). In CH_2Cl_2 the couples are similarly spaced at 1.35 and 2.05 V, respectively. The second oxidation wave (dc cyclic mode) is well resolved in rigorously dry *n*-PrCN but rides on the solvent oxidation front in CH_2Cl_2. By ac voltammetry, this couple is clearly defined as a reversible one-electron step in both solvents. Accordingly, the electrode product is identified as the previously undetected, neutral, quadruply-bonded diosmium(IV) complex, isoelectronic with $[Re_2Cl_8]^{2-}$, and is evidently stable at least on the voltammetric time scale. In contrast, the one-electron reduction near −1.0 V remains irreversible even at 215 K. We note that in transient 11e $[Os_2Cl_8]^{3-}$ the formal bond order declines to 2.5 through population of the antibonding π^* level.

Spectroelectrochemical characterization of $[Os_2Cl_8]^{1-}$ from 4000 to 50000 cm^{-1} was achieved using a cryostatic optically transparent thin-layer electrode (OTTLE) cell, as described elsewhere.[7] In CH_2Cl_2 solution at 233 K, oxidation of $[Os_2Cl_8]^{2-}$ at 1.55 V leads to growth of a new low-energy charge-transfer envelope (Cl π to Os_2 δ^*) with a maximum at 23000 cm^{-1} (Figure 2a). Simultaneously, the dianion band at 14000 cm^{-1} collapses while two weak bands emerge at 17750 and 10200 cm^{-1}, together with a highly structured feature at 4600 cm^{-1} (ϵ = 1000 M^{-1} cm^{-1}) unequivocally assigned to the $\delta \rightarrow \delta^*$ transition (Figure 2b). The prominent vibronic coupling to the Os–Os stretch, even in the solution absorption spectrum, is characteristic of $[M_2X_8]^{n-}$ species

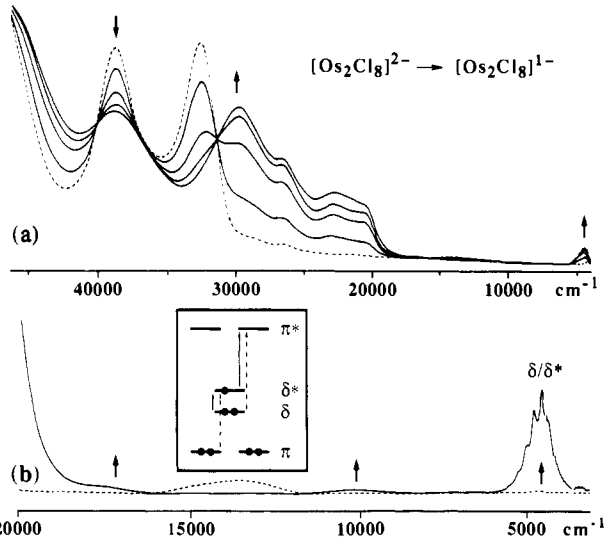

Figure 2. Spectroelectrochemical oxidation of $[Os_2Cl_8]^{2-}$ in CH_2Cl_2 at 223 K. (a) Progressive, fully reversible oxidation to $[Os_2Cl_8]^{1-}$. The dashed line is $[Os_2Cl_8]^{2-}$, prior to electrolysis. (b) Expansion showing three visible/near-IR bands for $[Os_2Cl_8]^{1-}$. Inset: Low-energy transitions within the frontier valence-orbital manifold (drawn to scale;[10] the σ^2 level lies much lower and has been omitted). Dashed arrows represent orbitally forbidden transitions.

with $\sigma^2\pi^4\delta$ and $\sigma^2\pi^4\delta^2\delta^*$ ($S = {}^1/_2$) configurations.[8]

The distinctive δ/δ^* band is an important index of M–M interaction. Firstly, it proves that $[Os_2Cl_8]^{1-}$ approaches the eclipsed conformation. Secondly, the 4600-cm^{-1} band directly reflects the energy gap between the δ and δ^* orbitals, shown here to diminish sharply in $[Os_2Cl_8]^{1-}$ compared to the lower-valent $[Tc_2Cl_8]^{3-}$ and $[Re_2Cl_8]^{3-}$ systems, where the band is centered at 6800 and 6950 cm^{-1}, respectively.[3a,9] An earlier suggestion[10] that the δ–δ^* separation in $[M_2X_8]^{n-}$ species is roughly constant, regardless of the identity of M, evidently should not be extended to systems of differing valency. Thirdly, the existence of weaker M–M bonding *overall* in $[Os_2Cl_8]^{1-}$ compared to isoelectronic $[Re_2Cl_8]^{3-}$ is confirmed by the observed Frank-Condon progression on the δ/δ^* band, which is 220 cm^{-1} for $\nu_{(Os-Os)7+}$ and 270 cm^{-1} for $\nu_{(Re-Re)5+}$.

Our voltammetric and spectroelectrochemical investigation of structurally contrasting $[Re_2Cl_8]^{n-}$ and $[Re_2Cl_9]^{(n+1)-}$ revealed oxidation-state-dependent interconversions between dirhenium octa- and nonahalide stoichiometries.[3a] Electrogenerated $[Re_2Cl_8]^{1-}$ rearranges readily to $[Re_2Cl_9]^{1-}$, although this step is suppressed at 220 K and below. Though having the same charge and formal bond order (3.5) as $[Re_2Cl_8]^{1-}$, $[Os_2Cl_8]^{1-}$ cleaves above 245 K in the OTTLE cell, forming $[Os^{V}Cl_6]^{1-}$ (1 mol)[11] and chloride-depleted byproducts. We associate the different behavior with electron count; diamagnetic $[Re_2Cl_9]^{1-}$ is stabilized by significant metal–metal bonding ($\sigma^2\pi^4$), whereas $[Os_2Cl_9]^{1-}$ is believed to have a weaker M–M interaction, through the population of antibonding orbitals ($\sigma^2\pi^4\pi^{*2}$).[12] Similarly, the only known route[13] to $[Os_2Cl_9]^{n-}$ involves reductive expulsion of Cl^- from

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(6) $(n\text{-}Bu_4N)_2[Os_2Cl_8]$ was prepared as described elsewhere.[5] Solvents were freshly distilled and degassed. The supporting electrolyte was $[n\text{-}Bu_4N][BF_4]$ (0.15 M in *n*-PrCN, 0.5 M in CH_2Cl_2) purged with N_2. All measurements were carried out with a Princeton Applied Research 170 potentiostat, vs a Ag/AgCl reference electrode such that the ferrocene/ferricinium redox couple was located at 0.55 V in both solvents.

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(11) $[OsCl_6]^{2-}$ cannot exist at the prevailing potential, 1.5 V. $[OsCl_6]^{1-}$ was identified by its visible spectrum, and by subsequent conversion at 1.20 V to equally recognizable $[OsCl_6]^{2-}$.

(12) For $[Os_2Br_9]^{1-}$,[13] μ_{eff} (per Os atom) = 1.4 μ_B at room temperature and 0.4 μ_B at 20 K, little different from $[OsBr_6]^{2-}$ (D. G. Humphrey, Ph.D. Dissertation, ANU, 1992. G. A. Heath, D. G. Humphrey, K. S. Murray, to be published).

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$[Os_2Cl_{10}]^{2-}$, rather than Cl_2 oxidation of the octahalide which serves well[14] for the synthesis of $[Re_2Cl_9]^{1-}$.

Corresponding studies on $[Os_2Br_8]^{2-}$, in CH_2Cl_2 at 235 K, reveal successive one-electron oxidations at 1.35 and 2.03 V. The δ/δ^* band for $[Os_2Br_8]^{1-}$ is found at 4630 cm^{-1}, and the associated vibronic progression is 225 cm^{-1}. Efforts are continuing to isolate or further characterize these highly reactive molecules. The present results confirm the value of pursuing periodic relationships in binuclear heavy element chemistry through low-temperature voltammetry and spectroelectrogeneration.

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Enantioselective Polymerizations of Achiral Isocyanides. Preparation of Optically Active Helical Polymers Using Chiral Nickel Catalysts

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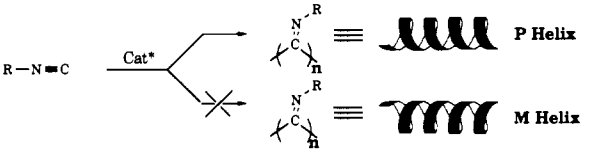
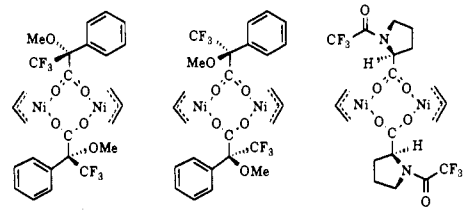
The issue of stereochemistry in macromolecules has received a wide range of treatment, both experimental and theoretical.[2] Pioneering work with vinyl and other addition polymers utilizing chiral catalysts and initiators as well as optically active monomers has led to the development of a new dimension of organic stereochemistry.[3] The helical motif is a fine example of stereochemistry commonly found in polymers yet which is quite rare in small-molecule chemistry.[4] Polymers which maintain stable helical conformations in solution, namely, polyisocyanides,[5] poly(triarylmethacrylates),[6] and chloral oligomers,[7] have received much attention since they can possess optical activity due solely to main chain conformations (atropisomers). Consequently, helix-sense-selective preparations of these polymers have been an important goal in this field.

Scheme I



In the polyisocyanides, polymers with sterically bulky substituents have been resolved using chiral chromatography[5b,f] and helix-sense-selective polymerizations have been attempted using optically active end groups.[8] These attached chiral end groups produce diastereomeric polymers (due to the chirality of the helix and the end group) as opposed to purely enantiomeric polymers. We would like to prepare enantiomeric polyisocyanides using a chiral catalyst (Scheme I) in order to study properties of the helix in the absence of any chiral side or end groups. Successful asymmetric induction of this type requires that there be a high helical inversion barrier associated with the polymer, so that racemization of a kinetically controlled helix sense will not be possible.[9] We now report the use of chiral catalysts (*R*)-(−)-$[(\eta^3\text{-}C_3H_5)Ni(O_2CC^*(OCH_3)(C_6H_5)CF_3)]_2$ (**R-I**), (*S*)-(+)-$[(\eta^3\text{-}C_3H_5)Ni(O_2CC^*(OCH_3)(C_6H_5)CF_3)]_2$ (**S-I**), and (*S*)-(−)-$[(\eta^3\text{-}C_3H_5)Ni(O_2CC^*HN(CH_2CH_2CH_2)C(O)CF_3)]_2$ (**S-II**) for the enantioselective polymerization of achiral *tert*-butyl isocyanide (**III**) and diphenylmethyl isocyanide (**IV**) to yield optically active, enantiomerically enriched samples of poly(*tert*-butyl isocyanide) (poly(**III**)) and poly(diphenylmethyl isocyanide) (poly(**IV**)).

We designed our optically active catalyst around the complex, $[(\eta^3\text{-}C_3H_5)Ni(OC(O)CF_3)]_2$, which promotes the homogeneous, living polymerization of select isocyanides.[10] Subsequent modification of this catalyst with an optically active ligand would lead to our desired chiral catalyst. Addition of chiral donors (e.g., phosphines) was ruled out due to the very high ligand strength of isocyanides and inevitable dissociation of any optically active donor under polymerization conditions.[11] Our approach therefore was the incorporation of optical activity into the anionic carboxylato ligand which, due to high Coulombic attractions, would not be expected to dissociate in organic solvents (e.g., toluene). Consequently, we prepared the optically active compounds **R-I**, **S-I**, and **S-II** from commercially available, optically pure carboxylic acids. Note that, while these compounds are dimeric, they are readily cleaved into monometallic catalytic species by high ligand concentrations present under polymerization conditions.[10]



R-I **S-I** **S-II**

To verify whether the chiral pendant groups do indeed affect the stereochemistry at the active catalytic site, we separately polymerized both enantiomers of a chiral monomer (1-phenylethyl isocyanide, **S-V** and **R-V**), using either **S-I**, **R-I**, or **S-II** while monitoring the reaction kinetics. **R-I** polymerizes **S-V** and **R-V** under O_2[10] at 298 K to yield the rate constants (rate = k[catalyst]) $k_R = 6.2\ (2) \times 10^{-3}\ s^{-1}$ and $k_S = 14.6\ (2) \times 10^{-3}\ s^{-1}$ with $k_S/k_R = 2.3\ (5)$. Conversely, **S-I** polymerizes **S-V** and **R-V** under O_2 at 298 K to yield the rate constants $k_R = 15.4\ (2) \times 10^{-3}\ s^{-1}$ and

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