el(III) species using an ESR probe. Moreover, an equilibrium constant of $\sim 10^{-2}$ is deduced by measuring the intensity of the hexachloroiridate absorption with stop-flow techniques in the presence of varying amounts of o-CH₃C₆H₄NiBr(PEt₃)₂, Quenching the paramagnetic species at -50 °C with zinc dust leads to about 50% recovery of the reactant.

A preliminary electrochemical study of Ar₂Ni(PEt₃)₂ was examined at a stationary platinum electrode in acetone solution by cyclic voltammetry. A single anodic peak P₁ was observed at 0.68 V relative to SCE.¹² The reverse scan exhibited a single cathodic peak P_2 at -0.38 V which is associated with the oxidation observed at P_1 . If the scan is restricted to voltages <0.5 V, the reduction at P_2 is not observed. Therefore, P_2 cannot be due to a primary reduction of Ar_2NiL_2 . The oxidation of Ar₂NiL₂ is irreversible at all scan rates even at -78 °C. However, the current ratio $I_p^{(2)}/I_p^{(1)}$ is independent of the scan rate, and its magnitude, 0.53, though less than the ideal limit of 1.0, is quite large. Thus, P_2 is attributable to the reduction of a major intermediate in the oxidation of Ar₂NiL₂, Furthermore, the lifetime of this intermediate must be comparable with the time scale of the electrochemical measurement. We tentatively propose the following EC mechanism,¹³ in which the cathodic process P_2 corresponds to the reduction of the solvated intermediate, $Ar_2NiL_2(S)^+$.

$$\operatorname{Ar}_{2}\operatorname{NiL}_{2} \xrightarrow{-\epsilon} \operatorname{Ar}_{2}\operatorname{NiL}_{2}^{+}$$
 (6)

$$Ar_2NiL_2^+ + S \xrightarrow{fast} Ar_2NiL_2(S)^+$$
(7)

$$Ar_2NiL_2(S)^+ \xrightarrow{slow} products$$
 (8)

where $L = PEt_3$, Ar, $o-CH_3OC_6H_4$ and S = solvent.

The substitution-lability of the paramagnetic nickel(III) species in eq 714 is also shown in the ready addition of carbon monoxide at -50 °C to afford the acylnickel(III) species (g = 2.16)

 $ArNiBr(PEt_3)_2^+$

$$\rightarrow$$
 ArCONiBr(PEt₃)₂⁺ \leftarrow ArCONiBr(PEt₃)₂

which is identical with that obtained independently by oxidation of the acylnickel(II) complex¹⁵ with Na₂IrCl₆.¹⁶ A paramagnetic nickel(III) species can also be obtained from bromine oxidation of $ArNiBr(PEt_3)_2$. Although it is different from that obtained with Na_2IrCl_6 , having a g value of 2.194 and undergoing a more rapid reductive elimination, it can be converted to the same acylnickel(III) species if phosphine is added in the presence of CO. The pattern of reactivity of halogen toward organometals is similar to that observed in Table I with 1-equiv oxidants. The labilization of alkyl-metal bonds under these conditions has bearing on the mechanism of electrophilic cleavage of transition metal bonds generally, especially in the light of oxidative processes already identified in some cases.¹⁷

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- (5) From 0.050 mmol of Et₂Ni(bipy), the formation of *n*-butane, ethane, and ethylene was 0.024, 0.007, <0.001 mmol from Na₂IrCl₆, 0.025, 0.003, 0 mmol from Br₂, and 0.018, 0.009, and 0.011 mmol from O₂. In addition, 0.034 mmol of EtBr was observed with Br2.
- (6) The yields of di-o-anisyl from 0.070 mmol of (o-CH₃OC₆H₄)₂Ni(PEt₃)₂ was 0.064, 0.063, 0.051, 0.023, 0.038, and 0.043 mmol from Co(TFA)3, Ce(TFA)4, TI(TFA)3, CuBr2, Na2IrCl6, and Br2, respectively. In addition, CuBr2 produced 0.013 mmol of *c*-anisyl bromide and NaIrCl6 produced 0.076 mmol of o-anisyltriethylphosphonium ion.
- (7) (a) From o-CH₃OC₆H₄NiBr(PEI₃)₂ the yields of o-CH₃OC₆H₄PEt₃⁺ were 86, 100, 76, 69, 76, 49, and 0% from K₃Fe(CN)₆, TI(TFA)₃, Na₂IrCl₆, Co(TFA)₃, Ce(TFA)₄, CuBr₂, and Hg(TFA)₂, respectively. (b) The treatment of o-CH₃C₆H₄NIX(PEt₃)₂ with Na₂IrCl₆ afforded o-CH₃C₆H₄PEt₃⁺ in 89, 80, 78, 82, 52, and 80% yields for X = Cl, Br, I, NO₂, CN, and CH₃. In addition, 42% o-tolunitrile and 13% o-xylene were obtained for X = CN and CH₃, respectively
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Manifestations of Sulfur to Sulfur **Through-Space Interactions in Complex Ion Spectra**

Sir:

Musker and coworkers^{1,2} have described some remarkable redox characteristics of 1,5-dithiocane. The structural features that facilitate the oxidation of the molecule to a monopositive and to a dipositive ion lead to some rather unexpected effects when the molecule is a ligand, which we report in this paper. A splitting of the ligand to metal charge-transfer band in the visible is observed when the ligand is coordinated to Ru(III); furthermore, a strong intervalence absorption is observed in the Ru(III)-Ru(II) mixed valence complex despite the fact

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Figure 1. Absorption spectra in the near-ultraviolet and visible for complexes of 1,5-dithocane: 1-cm quartz cells, 25 °C, 0.2 M HCl, [Ru] = 3.6×10^{-3} M.



Figure 2. Ligand to metal charge-transfer band in the ruthenium(III) complex of 1.4-dithiane: 1-cm quartz cells, 25 °C, 0.2 M HCl, [Ru] = 5.8×10^{-3} M.

that the metal atoms in the complex are separated by a large number of saturated units. For the purpose of making comparisons, results for 1,4-dithiane as ligand are also described.

The ions pentaammine-1,4-dithianeruthenium(II), I, and pentaammine-1,5-dithiocaneruthenium(II), II, were synthe-



sized by the reaction of a 10-fold excess of ligand with 200 mg of $[(NH_3)_5RuH_2O](PF_6)_2^3$ in 5 mL of deaerated acetone. To each reaction mixture a saturated solution of LiBr in acetone was added after 30 min, whereupon the bromide salt precipitated. This was filtered and redissolved in a minimum of 0.1 M HCl. On adding solid NH₄PF₆, a pale yellow solid formed which was collected. The overall yield in each case was $\sim 50\%$. The binuclear species were produced by the reaction of the mononuclear with a 5% excess of $[Ru(NH_3)_5H_2O](PF_6)_2$ in the minimum volume of acetone needed to provide for a homogeneous reaction system. Analyses were performed on hexafluorophosphate salts, containing ruthenium in the 2+ state. Calcd for $[(NH_3)_5Ru(C_4H_8S_2)](PF_6)_2$: C, 8.06; H, 3.89; N, 11.74; S, 10.75; Ru, 16.96; F, 38.2. Found: C, 8.35; H, 3.89; N, 11.4; S, 10.8; Ru, 17.4; F, 37.8. Calcd for [(NH₃)₅-Ru(C₆H₁₂S₂)](PF₆)₂: C, 11.54; H, 4.36; N, 11.21; S, 10.27; Ru, 16.19; F, 36.5. Found: C, 11.10; H, 4.21; N, 10.59; S, 9.96; Ru, 15.7; F, 36.7. Calcd for $[(NH_3)_5Ru_2(C_4H_8S_2)](PF_6)_4$:



Figure 3. Near-infrared spectra for binuclear complexes. For complexes of 1,4-dithiane: 0.1 M DCl, 2-cm quartz cells, 25 °C, $[Ru] = 10/52 \times 10^{-3}$ M. For complexes of 1,5-dithiocane: 0.1 M DCl, 2-cm quartz cells, 25 °C, $[Ru] = 3.17 \times 10^{-3}$ M. Upper solid line represents the absorbance for [3,3] with 1,5-dithiocane as bridging group. The two [3,3] systems show identical absorption except below 750 nm, where that for the [3,3] based on 1,4-dithiane does not rise as sharply. The apparent residual absorbance registered for the [3,3] species at long wavelength is ascribed to incomplete dissolution of the solid ceric salt which is added (hydrolysis at low acid-ity).

C, 4.48; H, 3.54; N, 13.06. Found: C, 4.32; H, 3.51; N, 12.63. Calcd for $[(NH_3)_5Ru_2(C_6H_{12}S_2)](PF_6)_4$; C, 6.54; H, 3.84; N, 12.77; Ru, 18.36; F, 41.4. Found: C, 6.88; H, 3.80; N, 12.32. Ru, 17.9; F, 40.9.

Investigation of I by cyclic voltammetry gave a reversible wave at +525 mV vs. NHE (0.1 M HCl, 25 °C). A solution containing I shows absorption similar to that of II (see Figure 1), but, on oxidation to the 3+ state by 1 equiv of Ce(IV) in 0.2 M HCl, a band appears in the visible region (see Figure 2) at 429 nm ($\epsilon 2.6 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$). A band in this region is also observed in a similarly oxidized solution of $[(NH_3)_5$ -RuS(CH₃)₂]³⁺⁴ (λ_{max} 452 nm (ϵ 3.0 × 10² M⁻¹)).⁵ Cyclic voltammetry on II, under the conditions specified for I, gave a reversible wave at 475 mV and an oxidation wave at 1050 mV, the corresponding reduction wave being of very small amplitude. On oxidation to the 3+ state as above, the absorption spectrum shown in Figure 1 results. In addition to a band at 460 nm ($\epsilon 1.7 \times 10^2 \,\mathrm{M}^{-1} \,\mathrm{cm}^{-1}$), there is now a second band at 655 nm ($\epsilon 2.5 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$). On substituting the trans ammonia by isonicotinamide, and oxidizing the 2+ complex with $Fe(o-phen)_3^{3+}$ in acetone, the long wavelength band is shifted to 772 nm and is much diminished in intensity ($\epsilon 25 \text{ M}^{-1} \text{ cm}^{-1}$). The value of $E_{\rm f}$ for the 3+/2+ couple based on the trans isonicotinamide complex is 725 mV.

When I is converted to a binuclear species, the resultant complex shows reversible cyclic voltammetric waves, at 558 and at 653 mV. These values lead to 40 as the conproportionation constant corresponding to the reaction [2,2] + [3,3]= 2[3,2]. The mixed valence species was produced in 0.1 M DCI using a solid Ce(IV) salt as oxidant. The [3,2] species shows a band in the visible (λ_{max} 429 nm (ϵ 4.6 \times 10² M⁻¹ cm⁻¹)) and a band in the near infrared region (λ_{max} 972 nm $(\epsilon 6 \text{ M}^{-1} \text{ cm}^{-1}, f 0.17 \times 10^{-3}))$. The binuclear ion based on II shows a single broad cyclic voltammetric wave with an abnormally large peak to peak separation (100 mV) at 503 mV. Apparently, the two stages of oxidation are poorly resolved, so that the conproportionation constant is ~ 10 . In a half-oxidized sample of the [2,2], where the concentration of [3,2] is at a maximum, a single band appears in the visible (λ_{max} 515 nm ($\epsilon 4.6 \times 10^2 \,\mathrm{M^{-1} \, cm^{-1}}$)) and a band appears in the nearinfrared region (λ_{nm} 1180 nm (ϵ based on total ruthenium, 75 $M^{-1} \text{ cm}^{-1}, f 2.00 \times 10^{-3})).$

Two of the observations made on the complexes of the dithiocane compound are indicative of significant through-space interaction between the sulfur atoms. The extra band at long wavelength observed for the 3+ ion derived from II can be understood as ligand to metal charge transfer from the antibonding orbital resulting from the interaction of sulfur lone pairs, and the other as ligand to metal from the complementary

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bonding orbital. That the long wavelength band is correctly assigned as ligand to metal charge transfer is indicated by the shift produced on substituting *trans*-NH₃ by isonicotinamide. Taking into account the increase in reduction potential attending this change the new band position is calculated as 750 nm, to be compared with the observed 772 nm. The observations made on replacing NH₃ trans to sulfur by isonicotinamide demonstrate that the intensity of long wavelength band in the complex of the eight-membered ring is very sensitive to this change. The lone-pair interactions are also very sensitive to substitution on the sulfur atoms. Thus, both binuclear species, ([3,2] and [3,3]) show only a single band in the visible, the positions being nearly the same for both. For the [3,3] species, λ_{max} is registered at 510 nm with ϵ 7.0 × 10² M⁻¹ cm⁻¹. The diminution in the splitting in the binuclear complexes can be ascribed to the contraction of the sulfur orbitals by the cationic charges and, on this basis, the position of the single band can be taken as an approximate measure of the center of gravity of the orbitals when they are unaffected by the lone pair interactions.

The second observation which is significant for the issue of through-space interaction is the much higher intensity recorded for the intervalence transition of the mixed valence complex based on the eight-membered ring compared to the six-membered ring (see Figure 3). Effects transmitted through the σ -bond systems are expected to be much weaker in the former than in the latter case, and thus the higher intensity observed for the former suggests a through-space mechanism for the interaction in the case of the eight-membered ring. Presumably, the stable conformation of the eight-membered ring allows for better overlap of the sulfur lone pairs than is the case for the six-membered ring.

If the general correlation between rates of intramolecular electron transfer (Ru(II)-Co(III)) and the intensity of the intervalence transition for the Ru(III)-Ru(II) mixed valence molecules with the same bridging groups^{6,7} carries over to the present system, the results suggest that the through-space contact in the eight-membered ring is sufficient to provide for virtually adiabatic electron transfer between the metal ions.

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Preparative Nucleophilic Substitution with "Betylates". Substrate Phase Transfer and Substrate-Reagent Ion-Pair Reactions^{1,2}

Sir:

We wish to point to the synthetic value of ammonioalkanesulfonate esters ("betylates")³ as intermediates in the

$$ROH \rightarrow ROSO_{2}(CH_{2})_{n}N^{+}Me_{2}R'X^{-}$$

$$1 (n = 2; R' = Me \text{ or } H)$$

$$Nu^{-} \downarrow (\text{or } Nu)$$

$$RNu + \overline{O}_{3}S(CH_{2})nN^{+}Me_{2}R'$$

$$2 \qquad (1)$$

and at the same time to call attention to two useful ways of facilitating reaction between a lipophilic substrate and a hydrophilic reagent. As may be seen from Table I, betylates work well with a remarkably wide array of nucleophiles, substrates, and solvent systems; the procedures are characterized by mild conditions, easy workup, and the formation of clean products with generally good yields.⁴ Noteworthy are (a) the use of an aqueous medium with substrates bearing large hydrophobic alkyl groups (e.g., 1-docosyl), and (b) the formation of the corresponding esters with such feeble nucleophiles as perchlorate and triflate anions.

[2]Betylates (1, n = 2) are made^{4,5} from the alcohol via the ethenesulfonate ester (3) in overall yields of ~90-95%. In a homogeneous system (acetone:H₂O) [2]betylates are about as reactive to nucleophiles (e.g., N₃⁻) as trifluoroethanesulfonates,⁶ but in an aqueous suspension or a CH₂Cl₂:H₂O system [2] betylates react as much as 10⁵ times more quickly. One specific limitation of the [2] betylate grouping stems from the ease with which bases convert it back to ethenesulfonate (3), sometimes followed by Michael addition to form 4.

$$\begin{array}{ccc} \operatorname{ROSO_2CH_2CH_2N^+R'_3} & \xrightarrow{\text{base}} \operatorname{ROSO_2CH} = & \operatorname{CH_2} + \operatorname{R'_3N} \\ & X^- & 3 \\ 1(n=2) & & & & \\ & & & \operatorname{ROSO_2CH_2CH_2Nu} \\ & & & & 4 \end{array}$$

[3] Betylates (1, n = 3), however (which are obtained as shown⁷ in Scheme I), show no tendency to eliminate the trialkylammonio group under such conditions and are converted in good yields to the substitution products with both basic and nonbasic nucleophiles. [3] Betylates react about 10 times more slowly than [2] betylates.

In addition to providing what we believe to be a useful and general synthetic procedure, the reactions of betylates illustrate two powerful methods for dealing with the general synthetic problem of inducing reaction between a lipophilic substrate and a hydrophilic reagent.⁹ One method, "substrate phase transfer", has three logically distinct steps, (i) attachment of a hydrophilic group to the original substrate (ROH \rightarrow 1, in the present case), (ii) reaction in an aqueous medium, and (iii) removal of the hydrophilic group. In practice these conceptual steps need not be separate processes, steps ii and iii in the present examples occur in the same reaction. Solid-liquid

Scheme I

 $ROH + \underbrace{\overset{SO_2}{\overset{\bullet}{\underset{N}{\longrightarrow}}}}_{5 \text{ FSO}_3^-} \overset{Me}{\underset{Me}{\xrightarrow{\text{Et}_3N}}} ROSO_2CH_2CH_2CH_2NMe_2} \underbrace{\overset{Me}{\underset{Me}{\xrightarrow{\text{Me}}}}_{MeX \text{ or } HX}$

 $X = FSO_{1}$ MeOSO₃, or Br 1 (n = 3, R' = Me or H)(>80% from ROH)

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