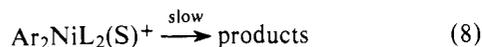


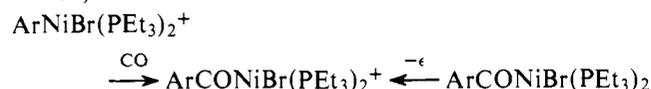
el(III) species using an ESR probe. Moreover, an equilibrium constant of $\sim 10^{-2}$ is deduced by measuring the intensity of the hexachloroiridate absorption with stop-flow techniques in the presence of varying amounts of $o\text{-CH}_3\text{C}_6\text{H}_4\text{NiBr}(\text{PEt}_3)_2$. Quenching the paramagnetic species at -50°C with zinc dust leads to about 50% recovery of the reactant.

A preliminary electrochemical study of $\text{Ar}_2\text{Ni}(\text{PEt}_3)_2$ was examined at a stationary platinum electrode in acetone solution by cyclic voltammetry. A single anodic peak P_1 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 Ar_2NiL_2 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 Ar_2NiL_2 . 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, $\text{Ar}_2\text{NiL}_2(\text{S})^+$.



where $\text{L} = \text{PEt}_3$, $\text{Ar} = o\text{-CH}_3\text{OC}_6\text{H}_4$ and $\text{S} = \text{solvent}$.

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 ($g = 2.16$)



which is identical with that obtained independently by oxidation of the acylnickel(II) complex¹⁵ with Na_2IrCl_6 .¹⁶ A paramagnetic nickel(III) species can also be obtained from bromine oxidation of $\text{ArNiBr}(\text{PEt}_3)_2$. 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

Acknowledgment. We thank Dr. Robert J. Klingler for the electrochemical results and the National Science Foundation for financial support.

References and Notes

- (a) P. J. Davidson, M. F. Lappert, and R. Pearce, *Chem. Rev.*, **76**, 219 (1976); (b) R. R. Schrock and G. W. Parshall, *ibid.*, **76**, 243 (1976).
- A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida, and A. Misono, *J. Am. Chem. Soc.*, **90**, 1878 (1968); T. Yamamoto, A. Yamamoto, and S. Ikeda, *Bull. Chem. Soc. Jpn.*, **45**, 1104 (1972).
- (a) The formation of butane when $\text{Et}_2\text{Fe}(\text{bipy})_2$ was treated with I_2 was originally noted by Yamamoto and coworkers.² (b) The iron-containing product was inferred from the iodolysis results.² Further characterization is in progress.
- (a) For preparation and thermolysis, see T. Ikariya and A. Yamamoto, *J. Organomet. Chem.*, **120**, 257 (1976). (b) From 0.043 mmol of $\text{Me}_2\text{Co}^{\text{II}}$ complex, 0.043 mmol of ethane with Na_2IrCl_6 and 0.038 mmol of C_2H_6 , 0.004 mmol of CH_4 , and 0.006 mmol of CH_3Br with Br_2 . The diethyl derivative gives analogous results but is complicated by facile phosphine dissociation as described by T. Ikariya, Y. Nakamura, and A. Yamamoto, *ibid.*, **118**, 101 (1976).
- From 0.050 mmol of $\text{Et}_2\text{Ni}(\text{bipy})_2$, the formation of n -butane, ethane, and ethylene was 0.024, 0.007, <0.001 mmol from Na_2IrCl_6 , 0.025, 0.003, 0 mmol from Br_2 , and 0.018, 0.009, and 0.011 mmol from O_2 . In addition, 0.034 mmol of EtBr was observed with Br_2 .
- The yields of di- o -anisyl from 0.070 mmol of $(o\text{-CH}_3\text{OC}_6\text{H}_4)_2\text{Ni}(\text{PEt}_3)_2$ was 0.064, 0.063, 0.051, 0.023, 0.038, and 0.043 mmol from $\text{Co}(\text{TFA})_3$, $\text{Ce}(\text{TFA})_4$, $\text{Ti}(\text{TFA})_3$, CuBr_2 , Na_2IrCl_6 , and Br_2 , respectively. In addition, CuBr_2 produced 0.013 mmol of o -anisyl bromide and NaIrCl_6 produced 0.076 mmol of o -anisyltriethylphosphonium ion.
- (a) From $o\text{-CH}_3\text{OC}_6\text{H}_4\text{NiBr}(\text{PEt}_3)_2$ the yields of $o\text{-CH}_3\text{OC}_6\text{H}_4\text{PEt}_3^+$ were 86, 100, 76, 69, 76, 49, and 0% from $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{Ti}(\text{TFA})_3$, Na_2IrCl_6 , $\text{Co}(\text{TFA})_3$, $\text{Ce}(\text{TFA})_4$, CuBr_2 , and $\text{Hg}(\text{TFA})_2$, respectively. (b) The treatment of $o\text{-CH}_3\text{OC}_6\text{H}_4\text{NiX}(\text{PEt}_3)_2$ with Na_2IrCl_6 afforded $o\text{-CH}_3\text{OC}_6\text{H}_4\text{PEt}_3^+$ in 89, 80, 78, 82, 52, and 80% yields for $\text{X} = \text{Cl}$, Br , I , NO_2 , CN , and CH_3 . In addition, 42% o -toluonitrile and 13% o -xylene were obtained for $\text{X} = \text{CN}$ and CH_3 , respectively.
- For nickel(III) complexes, see G. Booth and J. Chatt, *J. Chem. Soc.*, 3238 (1965); D. W. Meek, E. C. Alyea, J. K. Stalick, and J. A. Ibers, *J. Am. Chem. Soc.*, **91**, 4920 (1969); A. Wolberg and J. Manassen, *Inorg. Chem.*, **9**, 2365 (1970); R. S. Drago and E. I. Baucorn, *ibid.*, **11**, 2064 (1972); J. G. Mohanty and A. Chakravorty, *ibid.*, **15**, 2912 (1976).
- The 1-equiv oxidation of other alkylmetals by hexachloroiridate(IV) has been established with alkylcobalt(III),^{9a} alkylplatinum(II),^{9b} alkylmercury(II),^{9c} and alkyllead(IV).^{9d} (a) J. Halpern and J. Topich, *Inorg. Chim. Acta*, **20**, L21 (1976); S. N. Anderson, D. H. Ballard, J. Z. Chrzastowski, D. Dodd, and M. D. Johnson, *J. Chem. Soc., Chem. Commun.*, 685 (1972); (b) J. Y. Chen and J. K. Kochi, *J. Am. Chem. Soc.*, **99**, 1450 (1977); (c) J. Y. Chen, H. C. Gardner and J. K. Kochi, *ibid.*, **98**, 6150 (1976); (d) H. C. Gardner and J. K. Kochi, *ibid.*, **97**, 1855 (1975).
- (a) Paramagnetic intermediates may also be involved in the reductive coupling accompanying the oxidation of other organometals such as alkylcopper(I) (G. M. Whitesides, J. San Filippo, Jr., C. P. Casey, and E. J. Panek, *J. Am. Chem. Soc.*, **89**, 5302 (1967); **91**, 4871 (1969)), arylnickel(II) (D. Morrell and J. K. Kochi, *ibid.*, **97**, 7262 (1975)), acylmanganese(I) (C. P. Casey and C. A. Bunnell, *ibid.*, **98**, 436 (1976)), and alkylgold(III) (S. Komiya, T. A. Albright, R. Hoffmann, and J. K. Kochi, *ibid.*, **99**, 8440 (1977)). (b) Homolysis of the paramagnetic intermediate to afford alkyl radicals is also known (see ref 9b-d; for $(\text{CH}_3)_2\text{Co}(\text{DO})(\text{DOH})\text{pn}$, W. T. Tamblin, unpublished results).
- For nickel(I) complexes, see D. G. Holah, A. N. Hughes, B. C. Hui, and K. Wright, *Can. J. Chem.*, **52**, 2990 (1974); M. Aresta, C. F. Nobile, and A. Sacco, *Inorg. Chim. Acta*, **12**, 167 (1975); L. Porri, M. C. Gallazzi, and G. Vitulli, *Chem. Commun.*, 228 (1967). Cf. also M. J. Nilges, E. K. Barefield, R. L. Belford, and P. H. Davis, *J. Am. Chem. Soc.*, **99**, 755 (1977).
- The current function $i_p/v^{1/2}$ for P_1 is independent of the scan rate, v , and is less than that observed for the known one-electron oxidation of ferrocene.
- (a) Compare a similar electrochemical behavior with the dicyanonickel(II) analogue, $\text{trans}(\text{NC})_2\text{Ni}(\text{PEt}_2\text{Ph})_2$; G. Bontempelli, C. Benedetto, and F. Magno, *Anal. Chem.*, **49**, 1005 (1977). (b) Low temperature coulometry at controlled potentials will be examined.
- The rapid solvation of the paramagnetic nickel(III) intermediate in eq 7 suggests that this species prefers to be five coordinate. Indeed, in an analogous situation, the rhodium(III) complexes, $(\text{bipy})_2\text{RhCl}_2^+$ and $(\text{bipy})_3\text{Rh}^{3+}$, upon reduction both rapidly lose one ligand to form the five-coordinate rhodium(II) intermediates, $(\text{bipy})_2\text{RhCl}^+$ and $(\text{bipy})_2\text{Rh}(\text{S})^+$, respectively; G. Kew, K. DeArmond, and K. Hanck, *J. Phys. Chem.*, **78**, 727 (1974).
- Cf. H. F. Klein, *Angew. Chem. Int. Ed. Engl.*, **12**, 402 (1973).
- The variation in yields of coupled products with oxidants (cf. Table I and notes 5, 6, and 7) suggest that the fates of the paramagnetic intermediates may depend on such anation.
- (a) For a recent review, see G. W. Daub, *Prog. Inorg. Chem.*, **22**, 409 (1977). (b) Cf. also V. V. Lalaev and A. P. Belov, *Zh. Obshch. Khim.*, **46**, 2753 (1976).

T. T. Tsou, J. K. Kochi*

Department of Chemistry, Indiana University
Bloomington, Indiana 47401
Received November 16, 1977

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 monocationic and to a dicationic 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

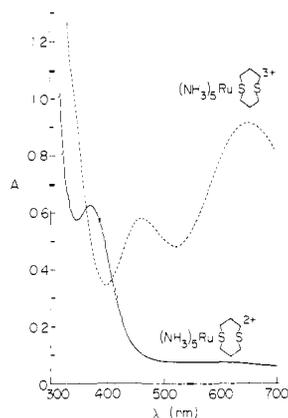


Figure 1. Absorption spectra in the near-ultraviolet and visible for complexes of 1,5-dithiocane: 1-cm quartz cells, 25 °C, 0.2 M HCl, [Ru] = 3.6×10^{-3} M.

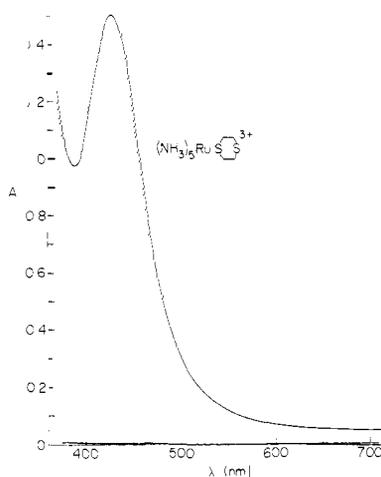
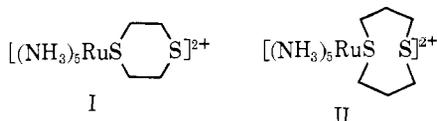


Figure 2. Ligand to metal charge-transfer band in the ruthenium(III) complex of 1,4-dithiane: 1-cm quartz cells, 25 °C, 0.2 M HCl, [Ru] = 5.8×10^{-3} M.

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 $[(\text{NH}_3)_5\text{RuH}_2\text{O}](\text{PF}_6)_2^3$ 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 NH_4PF_6 , a pale yellow solid formed which was collected. The overall yield in each case was ~50%. The binuclear species were produced by the reaction of the mononuclear with a 5% excess of $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}](\text{PF}_6)_2$ 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 $[(\text{NH}_3)_5\text{Ru}(\text{C}_4\text{H}_8\text{S}_2)](\text{PF}_6)_2$: 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 $[(\text{NH}_3)_5\text{Ru}(\text{C}_6\text{H}_{12}\text{S}_2)](\text{PF}_6)_2$: 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 $[(\text{NH}_3)_5\text{Ru}_2(\text{C}_4\text{H}_8\text{S}_2)](\text{PF}_6)_4$:

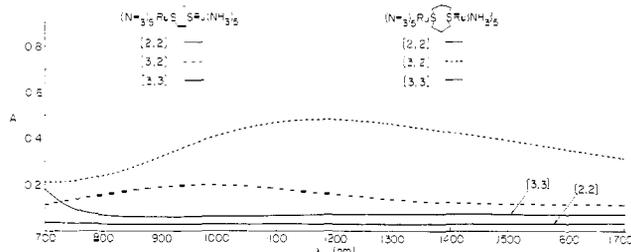


Figure 3. Near-infrared spectra for binuclear complexes. For complexes of 1,4-dithiane: 0.1 M DCl, 2-cm quartz cells, 25 °C, [Ru] = $10/52 \times 10^{-3}$ M. For complexes of 1,5-dithiocane: 0.1 M DCl, 2-cm quartz cells, 25 °C, [Ru] = 3.17×10^{-3} M. Upper solid line represents the absorbance for [3,3] 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 acidity).

C, 4.48; H, 3.54; N, 13.06. Found: C, 4.32; H, 3.51; N, 12.63. Calcd for $[(\text{NH}_3)_5\text{Ru}_2(\text{C}_6\text{H}_{12}\text{S}_2)](\text{PF}_6)_4$: 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 $[(\text{NH}_3)_5\text{RuS}(\text{CH}_3)_2]^{3+}$ ($\lambda_{\text{max}} 452 \text{ nm}$ ($\epsilon 3.0 \times 10^2 \text{ M}^{-1}$)).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 ($\epsilon 1.7 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$), 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 $\text{Fe}(o\text{-phen})_3^{3+}$ 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_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 DCl using a solid Ce(IV) salt as oxidant. The [3,2] species shows a band in the visible ($\lambda_{\text{max}} 429 \text{ nm}$ ($\epsilon 4.6 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$)) and a band in the near infrared region ($\lambda_{\text{max}} 972 \text{ nm}$ ($\epsilon 6 \text{ M}^{-1} \text{ cm}^{-1}$, $f 0.17 \times 10^{-3}$)). 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 ($\lambda_{\text{max}} 515 \text{ nm}$ ($\epsilon 4.6 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$)) and a band appears in the near-infrared region ($\lambda_{\text{nm}} 1180 \text{ nm}$ (ϵ based on total ruthenium, $75 \text{ M}^{-1} \text{ cm}^{-1}$, $f 2.00 \times 10^{-3}$)).

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

