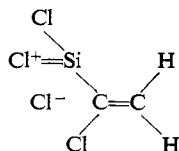


silyl halides¹¹ also reflect a trend toward more positive couplings with increasing halogen substituents. These trends can be interpreted semiquantitatively in terms of changes in s-character of the silicon bonding orbitals combined with changes in Si²⁹-H bond polarity.¹²

The H¹-{H¹} and H¹-{Si²⁹} decoupling results show that the *cis* and *trans* silicon-proton coupling constants and the geminal (J_{III}) coupling constant are all of the same sign in trimethyl- and trichloro- α -chlorovinylsilane. If the reduced Si²⁹C=CH (IA) coupling is assumed to be positive, in conformity with the absolute sign determined for *p*-nitrotoluene,¹³ then the ratio K_{III}/K_{IA} will be negative (J_{IA} is actually negative because of the negative magnetogyric ratio of Si²⁹). Therefore K_{III} and J_{III} are negative in both the α -chlorovinylsilane derivatives. An opposite sign (assumed to be negative for J_{gem} relative to J_{cis} (or J_{trans})) has previously been indicated in monosubstituted vinyl compounds with strongly electronegative substituents.¹⁴

The larger (more negative) value of J_{gem} for the more electronegative trichloro substituent group follows the trends noted for other vinyl compounds.¹⁴ In contrast the magnitudes of the long-range Si²⁹C=CH couplings appear to be anomalous; from electronegativity considerations both the *cis* and *trans* couplings in the trimethyl compound would be expected to have a larger magnitude (more positive) than the corresponding couplings in the trichloro compound, as has, in fact, been observed for the proton-proton coupling constants in trimethyl- and trichlorovinylsilanes.¹⁵ Although a variety of factors can affect the magnitude of long-range coupling constants,^{2,16} it is probable that the "anomalous" silicon couplings arise primarily from hybridization changes of the Si bonding orbitals in much the same manner as for the halosilanes. The magnitude of K_{IA} is therefore sensitive to any change in s-character, α_c^2 , of the Si-C bond and since the chloro groups will undoubtedly increase α_c^2 , compared with CH₃ groups, K_{IA} will be larger (more positive) in the trichloro derivative. Additional contributions from resonance structures such as



and π -bond interaction between Si and C would also act to increase J_I . The present results indicate that the major contribution to J_{IA} and J_{IB} is the contact interaction term and additional contributions from electron-dipole and spin-orbital interactions are not important.^{5b}

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(17) Argonne National Laboratory, Argonne, Ill.

Steven S. Danyluk¹⁷

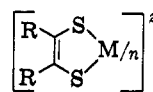
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Received March 6, 1965

New Systems of Complexes Related by Electron-Transfer Reactions

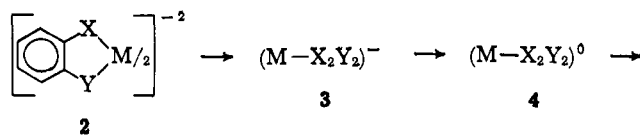
Sir:

Recent investigations in these laboratories have clearly demonstrated that complexes of general type **1** ($R = CN, CF_3, C_6H_5$; $n = 2, 3$) undergo relatively facile one-electron-transfer reactions which can be effected chemically or electrochemically for complexes with $M = Cu, Ni, Co, Pd, Pt$ ($n = 2$),^{1a,b} and V, Cr, Mo, W ($n = 3$)^{1c,d} to yield species with total charge $z = 0, -1, -2$ ($n = 2$), and $0, -1, -2, -3$ ($n = 3$).² For series of bis complexes the existence of electron-transfer reactions has heretofore been confined to those species having the M-S₄ coordination unit. We are investigating the scope of these reactions in bis complexes and report certain results for M-N₄, M-N₂S₂, M-O₂S₂, and M-O₄ complexes which indicate that electron-transfer reactions have a reasonably general occurrence and that oxidative stabilities of complexes of the same general composition and charge type have a marked dependence on the nature of the donor atoms.



1

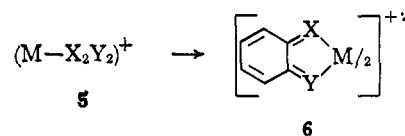
Previous studies have revealed the existence of three-membered electron-transfer series of bis complexes. The present investigation deals with systems in which the metal and, in some cases, the ligand may be oxidized or reduced, thereby generating a five-membered series of complexes represented as



2

3

4



5

6

Reaction of Ni²⁺ and *o*-phenylenediamine in concentrated aqueous ammonia leads to a violet neutral complex,³ diamagnetic and identical with the reaction

(1) (a) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963); (b) *ibid.*, **3**, 814 (1964); (c) *J. Am. Chem. Soc.*, **86**, 2799 (1964); (d) *Inorg. Chem.*, **4**, 55 (1965).

(2) Bis complexes with $R = C_6H_5$, $M = Ni$, and $z = 0, -1, -2$ have also been isolated by others: cf. G. N. Schrauzer and V. Mayweg, *Z. Naturforsch.*, **19b**, 192 (1964); the existence of tris complexes with $R = C_6H_5$, $M = Cr, Mo, W$, $z = 0, -1$ has been demonstrated by J. H. Waters, R. Williams, H. B. Gray, G. N. Schrauzer, and H. W. Finck, *J. Am. Chem. Soc.*, **86**, 4198 (1964).

(3) F. Feigl and M. Fürth, *Monatsh.*, **48**, 445 (1927); Z. Bardodej, *Collection Czech. Chem. Commun.*, **20**, 176 (1955).

product of 1,2-diimino-3,5-cyclohexadiene⁴ and Ni(CO)₄ in ether, which we conclude to be (Ni-N₄)⁰ (**4**, X = Y = NH). Similar reactions afford after considerable purification the analogous (Pd-N₄)⁰, (Pt-N₄)⁰, and (Co-N₄)⁰ (solid, 2.1 B.M.) complexes, all of which represent the intermediate numbers **4** of the (M-N₄)^s electron-transfer series 2-6. Polarography⁵ of (Pt-N₄)⁰ reveals two one-electron reduction and two one-electron oxidation waves with $E_{1/2}$ (v.) = -1.72 (-2 → -1), -1.04 (-1 → 0), +0.21 (0 → 1), +0.77 (+1 → +2). (Ni-N₄)⁰ and (Pd-N₄)⁰ show three of the four possible oxidation-reduction steps, the potentials (v.) for the nickel series being -1.56 (-2 → -1), -0.88 (-1 → 0), +0.19 (0 → +2). Electrochemical reduction of (Ni-N₄)⁰ in DMSO in an e.s.r. cavity gives green (Ni-N₄)⁻ with $\langle g \rangle = 2.0314$ and no hyperfine structure. Reaction of (Ni-N₄)⁰ with 1 or 2 equiv. of I₂ yields, respectively, (Ni-N₄)I (solid, 1.1 B.M., $\langle g \rangle = 2.000$) and (NiN₄)I₂ (diamagnetic, 2:1 electrolyte in DMSO). (Co-N₄)⁰ reacts with 1 equiv. of I₂ to give diamagnetic (Co-N₄)I.

Aerial oxidation of a suspension of bis(*o*-aminothiophenolato)nickel(II) in aqueous NaOH in our hands does not yield the previously claimed⁶ [C₆H₄(NH₂)S]₂NiO₂Ni[S(NH₂)C₆H₄]₂ but rather (Ni-S₂N₂)⁰ (**4**, X = S, Y = NH). This species does not cleanly oxidize but does reduce polarographically in two one-electron steps with $E_{1/2} = -1.04$ (-2 → -1) and -0.19 v. (-1 → 0). Reduction of the blue neutral complex with zinc in pyridine forms green (Ni-S₂N₂)⁻ which has a strong e.s.r. signal (no hyperfine structure) with $\langle g \rangle = 2.0544$. Polarographic reduction of the related neutral complex Ni[SC(C₆H₅)NNH]₂⁷ also produces two one-electron steps with nearly the same potentials as above.

Reaction of *o*-C₆H₄OS⁻² and M⁺² in 50% aqueous ethanol has resulted in the isolation of [(C₆H₅)₄As]₂(M-O₂S₂) (**2**, X = O, Y = S, M = Cu, Ni, Co, Pd). These reduced members of the (M-O₂S₂)^s series can be oxidized; e.g., polarographic oxidation of red diamagnetic (Ni-O₂S₂)⁻² shows $E_{1/2} = -0.42$ (-2 → -1) and +0.38 v. (-1 → 0). Oxidation of (Ni-O₂S₂)⁻² with air in ethanol-nitromethane produces deep green solutions from which salts of (Ni-O₂S₂)⁻ can be isolated. This monoanion in DMF-CHCl₃ has $\langle g \rangle = 2.083$ (solution) and $g_1 = 2.017$, $g_2 = 2.036$, $g_3 = 2.191$ (glass, ~100°K.) indicating rhombic symmetry of the ligand field and an electronic configuration possibly similar to that deduced from the e.s.r. studies for [NiS₄C₄R₄]⁻.^{1a,b,8}

(4) R. Willstätter and A. Pfannensteil, *Ber.*, **38**, 2348 (1905).

(5) All polarographic data were obtained relative to s.c.e. at 25° in dimethyl sulfoxide solution containing 0.1 M (*n*-C₃H₇)₄NClO₄ as supporting electrolyte.

(6) W. Hieber and R. Brück, *Z. anorg. allgem. Chem.*, **269**, 13 (1952).

(7) K. A. Jensen and J. F. Miguel, *Acta Chem. Scand.*, **6**, 189 (1952).

The intermediate members **4** in the (Ni-O₄)^s electron-transfer series have been obtained in two cases by treating the stable *o*-quinones, 3,5-di-*t*-butyl-*o*-quinone, and tetrachloro-*o*-quinone, with Ni(CO)₄ in hexane. Neutral paramagnetic bis complexes⁹ are obtained which are insufficiently stable in solution for polarography. However, reaction of Ni⁺² and C₆H₄O₂⁻² or C₆Cl₄O₂⁻² forms the dianions (Ni-O₄)⁻² and [Ni(C₆Cl₄O₂)₂]⁻² which have been isolated as diamagnetic tetra-*n*-propylammonium salts. The former exhibits two one-electron oxidations at -0.29 (-2 → -1) and +0.46 v. (-1 → 0). The latter oxidizes in an apparent two-electron step at +0.17 v. and in addition shows the (0 → +1) oxidation at +0.78 v. Reaction of [Ni(C₆Cl₄O₂)₂]⁻² and [Ni(C₆Cl₄O₂)₂]⁰ in dichloromethane yields [Ni(C₆Cl₄O₂)₂]⁻ isolated as the paramagnetic (3.80 B.M., solid, 3.88 B.M., dichloromethane) tetra-*n*-propylammonium salt. Previous isolation¹⁰ of salts of cations analogous to **6** together with these results substantiates the existence of all five members of the (Ni-O₄)^s series.

(M-S₄)⁻ complexes have been isolated from reaction in air of toluene-3,4-dithiol and M⁺².¹¹ As expected from previous work^{1a,b} these complexes show evidence of a three-member series **2**, **3**, **4**; e.g., the potentials for the nickel system are -0.51 (-2 → -1) and +0.45 v. (-1 → 0).

The half-wave potential data clearly indicate that the stability to oxidation for complexes of a given metal, e.g., Ni(II), in the step -2 → -1 is a strong function of the donor atom set, the stability order being O₄ > O₂S₂ > S₄ > N₂S₂ > N₄. Whether or not this order is that of the oxidative stabilization of Ni(III) in **3** is currently being investigated. Detailed accounts of the preparation, properties, and electronic studies of these systems of complexes will be presented subsequently.

(8) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 4580 (1964); for a different interpretation of the electronic structures of these complexes based on a semiempirical MO treatment of the electronic spectra, see S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *ibid.*, **86**, 4594 (1964).

(9) At present it cannot be stated with certainty that these complexes have the structure implied in **4** or whether they have the sandwich-type structure of bis(duroquinone)nickel: G. N. Schrauzer and H. Thyret, *ibid.*, **82**, 6420 (1960); *Z. Naturforsch.*, **16b**, 352 (1961). The observed strong reduction of the carbonyl frequencies (~160 cm.⁻¹) in the complexes is anticipated for either structure.

(10) P. J. Crowley and H. M. Haendler, *Inorg. Chem.*, **1**, 904 (1962).

(11) H. B. Gray and E. Billig, *J. Am. Chem. Soc.*, **85**, 2019 (1963).

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