752 *Inorg. Chem.* **1980**, *19*, 752-755

Contribution from the Department of Chemistry,
The University of North Carolina, Chapel Hill, North Carolina 27514

Intramolecular, Outer-Sphere Electron Transfer in the Mixed-Valence Ion $[(bpy)_2ClRu(Ph_2PCH_2PPh_2)RuCl(bpy)_2]^{3+}$

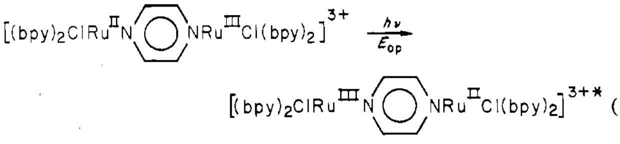
B. PATRICK SULLIVAN and THOMAS J. MEYER*

Received May 17, 1979

The synthesis of the μ-diphosphine-bridged dimer $[(bpy)_2ClRu(Ph_2PCH_2PPh_2)RuCl(bpy)_2]X_2$ (bpy = 2,2′-bipyridine, X = ClO_4 or PF_6) and its mixed-valence form is described. The mixed-valence 3+ ion has a low-intensity intervalence transfer (IT) transition in the near-infrared spectral region. The appearance of the band is of importance since, given the nature of the bridging ligand, it apparently represents an example of an outer-sphere intervalence transfer transition. The solvent dependence of the IT band energy is in agreement with results obtained for intramolecular IT transitions and with a dielectric continuum treatment for the solvent. The appearance of the IT transition allows the mixed-valence ion to act as a useful model for related outer-sphere electron-transfer reactions.

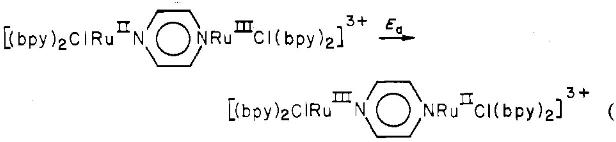
Introduction

Intervalence transfer (IT) absorption bands have been observed in a series of mixed-valence, ligand-bridged ions of ruthenium (e.g., eq 1).[1] From the properties of the bands and the theoretical treatments given by Hush and more recently by Hopfield,[2] it has been possible to deduce the role of solvent polarization and of distance between redox sites in determining the magnitude of the optical (E_{op}, eq 1) and thermal (E_a, eq 2) barriers to intramolecular electron transfer through the bridging ligand. In the mixed-valence dimers, the unsaturated bridging ligands serve to promote electronic interactions by d_π(Ru(II))–π^*(bridge) mixing[3] and the magnitude of the effect can be calculated from the oscillator strengths of the IT bands.[2]



(1)

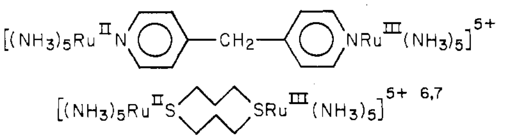
bpy is 2,2′-bipyridine



(2)

The results obtained for mixed-valence ions have been applied by inference to related outer-sphere electron-transfer reactions,[4] but given the information available from IT bands, it would be desirable to observe the transitions directly in outer-sphere systems. There is no requirement that the observation of IT bands be confined to cases where electron transfer occurs through a ligand bridge. One approach which has been successful for outer-sphere systems is to take advantage of Coulombic binding between donor and acceptor sites within an ion pair (eq 3). A second experimental approach is to devise a chemical link between the redox sites which at the same time (a) has a region of saturation so as to minimize electronic coupling through the bridge and (b) constrains the redox sites to be in close contact. Taube and co-workers have in fact reported weak IT bands in the dimers

$$[Ru^{III}(NH_3)_5py,Fe^{II}(CN)_6]^- \xrightarrow[E_{op}]{h\nu} [Ru^{II}(NH_3)_5py,Fe^{III}(CN)_6]^{-*} \quad (3)^5$$



where a continuous region of unsaturation between the metal sites does not exist.

We have prepared the complex $[(bpy)_2ClRu(Ph_2PCH_2PPh_2)RuCl(bpy)_2]^{2+}$ and its corresponding 3+ mixed-valence form. The bridging ligand does include a region of saturation, and calculations based on molecular models indicate that the metal sites are forced to be in close proximity (~7.1 Å) because of the steric constraints imposed by the bridging ligand.[8] In the mixed-valence ion a new transition appears which is assignable to a metal to metal charge-transfer (MMCT) or IT process.

Experimental Section

Measurements. Ultraviolet, visible, and near-infrared spectra were recorded by using either a Cary Model 14 or a Bausch and Lomb Model 210 spectrophotometer. Molar extinction coefficients were obtained from absorbance measurements on at least two different concentrations of complex. Electrochemical measurements were made vs. the saturated sodium chloride calomel electrode (SSCE) at 25 ± 2 °C and are uncorrected for junction potential effects. The $E_{1/2}$ values for reversible couples were calculated from half the difference between E_p values for the anodic and cathodic waves from cyclic voltammetry. $E_{1/2}$ values are used as formal reduction potentials on the assumption that differences in diffusion coefficients for oxidized and reduced species are negligible. The measurements were made by using a PAR Model 173 potentiostat for potential control with a PAR Model 175 universal programmer as a sweep generator for voltammetry measurements. Values for n, where n is the total number of electrons transferred per Ru ion site in exhaustive oxidative electrolyses at constant potential, were calculated after the total area under current vs. time curves for the complete reaction was measured. The reactions were considered complete after the current had fallen to 1% of the initial value. Values of n for the reduction of the oxidized product were calculated on the basis of the same criterion. All coulometry measurements were performed at platinum screen electrodes by using MCB Spectrograde acetonitrile as the solvent and 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the electrolyte. Elemental analyses were performed by Integral Microlabs, Raleigh, N.C.

Materials. TBAH was prepared in accordance with previously published techniques,[9] recrystallized from hot ethanol/water three

---

(1) (a) T. J. Meyer, *Acc. Chem. Res.*, **11**, 94 (1978); (b) H. Taube, *Ann. N.Y. Acad. Sci.*, **313**, 481 (1978); (c) T. J. Meyer, *ibid.*, **313**, 496 (1978).

(2) (a) N. S. Hush, *Prog. Inorg. Chem.*, **8**, 391 (1967); *Electrochim. Acta*, **13**, 1005 (1968); (b) J. J. Hopfield, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 3640 (1974); *Biophys. J.*, **18**, 311 (1977).

(3) E. C. Johnson, R. W. Callahan, R. P. Eckberg, W. E. Hatfield, and T. J. Meyer, *Inorg. Chem.*, **18**, 618 (1979).

(4) R. W. Callahan, F. R. Keene, T. J. Meyer, and D. J. Salmon, *J. Am. Chem. Soc.*, **99**, 1064 (1977).

(5) J. C. Curtis and T. J. Meyer, *J. Am. Chem. Soc.*, **100**, 6284 (1978).

(6) K. Rieder and H. Taube, *J. Am. Chem. Soc.*, **99**, 7891 (1977).

(7) C. A. Stein and H. Taube, *J. Am. Chem. Soc.*, **100**, 1635 (1978).

(8) The calculations were made by assuming Ru–P and C–P distances of 2.3 and 1.9 Å and also that the redox sites are at maximum separation because of electrostatic and steric repulsions.

(9) D. T. Sawyer and J. L. Roberts, "Experimental Electrochemistry for Chemists", Wiley, New York, 1974.

0020-1669/80/1319-0752$01.00/0 © 1980 American Chemical Society

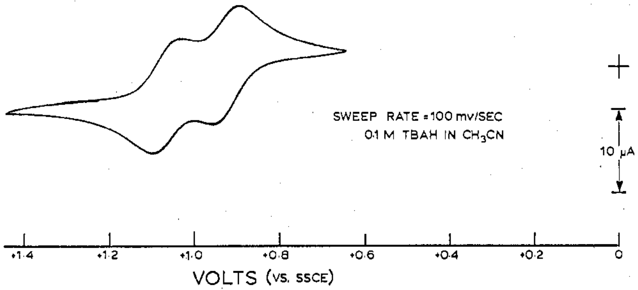


Figure 1. Cyclic voltammetry of a solution containing $[(bpy)_2ClRu(Ph_2PCH_2PPh_2)RuCl(bpy)_2](PF_6)_2$ in CH_3CN with 0.1 M $[N(n\text{-}C_4H_9)_4](PF_6)$ as supporting electrolyte. Potentials are reported vs. the saturated sodium chloride calomel electrode with use of a Pt bead working electrode and a Pt wire auxiliary electrode.

times, and vacuum dried at 70 °C for 10 h. Acetonitrile (MCB Spectrograde) was dried over Davison 4-Å molecular sieves for electrochemical experiments and used without drying for spectral measurements. Deuterated solvents were purchased from Stohler Iostope Chemicals. Water was deionized and then distilled from alkaline permanganate. All solvents used for preparations were reagent grade and were used without further purification. $Ph_2PCH_2PPh_2$ was purchased from Strem Chemical Co. and was used as received.

Preparation of $[(bpy)_2ClRu(PPh_2CH_2Ph_2P)RuCl(bpy)_2]X_2$ (X = ClO_4 or PF_6). To 25 mL of deoxygenated absolute ethanol were added 525 mg of *cis*-$(bpy)_2RuCl_2$[12] and 300 mg of $Ph_2PCH_2PPh_2$. The mixture was heated at reflux for 7 h while vigorous magnetic stirring was maintained. At the end of this period the solution was cooled, and 50 mL of a water solution containing a large excess of NH_4PF_6 or $LiClO_4$ was added. The total volume of solution was then reduced to ca. 30 mL on a rotary evaporator. Fifty milliliters of water was added at this point, and the flocculent red-orange precipitate was filtered by suction. The solid was washed with 3 × 50 mL portions of water, followed by 3 × 50 mL portions of Et_2O, and then air-dried. Chromatography was performed on a 40 cm × 350 cm column of alumina packed in 1:2 CH_3CN/C_6H_6. The crude solid was dissolved in a minimum of 1:2 CH_3CN/C_6H_6 and loaded onto the column with a pipet. Elution with 1:2 CH_3CN/C_6H_6, followed by progressive enrichment to 1:1 CH_3CN/C_6H_6, gave a large red-orange band of the complex which was preceded by a small orange band and followed by a lemon yellow band both of which were discarded. The complex was precipitated from CH_3CN with Et_2O to yield a red-orange powdery solid in 60–70% yield. Dark red needles of complex could be grown by making a concentrated CH_3CN solution of the dimer and gently layering Et_2O onto the top of the solution until a slight turbidity was observed followed by cooling at ca. 0 °C for 1–2 days. Elemental analyses were consistent with the dimer formulation.[10]

Results and Discussion

The [2,2] dimer was prepared by heating stoichiometric amounts of $Ph_2PCH_2PPh_2$ (dppm) and *cis*-$Ru(bpy)_2Cl_2$ in absolute ethanol at reflux under N_2 (eq 4). Purification of

$$2[cis\text{-}Ru(bpy)_2Cl_2] + Ph_2PCH_2PPh_2 \xrightarrow[\Delta,\ 8\ h]{EtOH} \underset{[2,2]}{[(bpy)_2ClRu(Ph_2PCH_2PPh_2)RuCl(bpy)_2]^{2+}} + 2Cl^- \quad (4)$$

the crude dimer was achieved by column chromatography of the PF_6^- or ClO_4^- salts on neutral alumina using benzene–acetonitrile mixtures as the eluant solution.

Table I. Electronic Spectra of the Dimers $[(bpy)_2ClRu(Ph_2PCH_2PPh_2)RuCl(bpy)_2]^{n+}$ (n = 2, 3, 4) and of Related Monomeric Complexes

ion[a]	λ_{max}, nm (log ϵ_{max})
$[(bpy)_2ClRu^{II}dppmRu^{II}Cl(bpy)_2]^{2+}$	460 (4.15), 329 (4.13), 294 (4.79), 233 (4.70)
$[(bpy)_2ClRu^{II}(PPh_3)]^+$	454 (3.79), 328 (3.85), 292 (4.60), 231 (4.60)
$[(bpy)_2ClRu^{III}dppmRu^{III}Cl(bpy)_2]^{4+}$	720 (2.63), 605 (2.76), 424 (3.92), 316,[b] 292,[b] 240[b]
$[(bpy)_2ClRu^{III}(PPh_3)]^{2+}$	602 (2.60), 412 (3.74), 313 (4.25), 297 (4.11)
$[(bpy)_2ClRu^{II}dppmRu^{III}Cl(bpy)_2]^{3+}$	729 (2.60), 438 (3.92), 330 (4.12), 317,[b] 293,[b] 240[b]

[a] All PF_6^- salts in CH_3CN solution. [b] ϵ_{max} not measured.

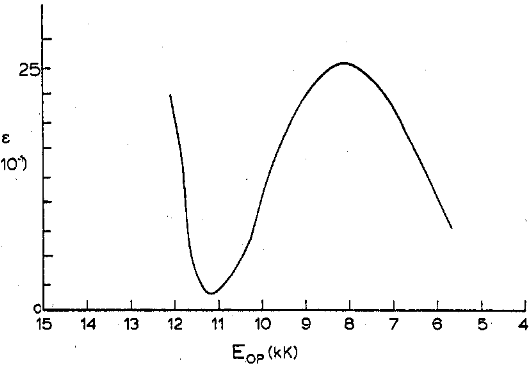


Figure 2. Intervalence transfer band for the ion $[(bpy)_2ClRu^{III}(Ph_2PCH_2PPh_2)Ru^{II}Cl(bpy)_2]^{3+}$ in CH_3CN.

Cyclic voltammetry (see Figure 1) in CH_3CN solution with 0.1 M $[N(n\text{-}C_4H_9)_4](PF_6)$ as supporting electrolyte showed two reversible waves having equal peak currents at $E_{1/2}(1)$ = 0.92 V (ΔE_p = 60 mV) and $E_{1/2}(2)$ = 1.06 V (ΔE_p = 65 mV).[11] Coulometry experiments demonstrated that the complex could be oxidized and reduced reversibly by two electrons without decomposition. From the separation between the redox couples (0.14 V), K_{com} = 230 can be calculated for the comproportionation equilibrium in eq 5. The rather large

$$\underset{[2,2]}{[(bpy)_2ClRu(Ph_2PCH_2PPh_2)RuCl(bpy)_2]^{2+}} + \underset{[3,3]}{[(bpy)_2ClRu(Ph_2PCH_2PPh_2)RuCl(bpy)_2]^{4+}} \overset{K_{com}}{\rightleftharpoons} 2\underset{[2,3]}{[(bpy)_2ClRu(Ph_2PCH_2PPh_2)RuCl(bpy)_2]^{3+}} \quad (5)$$

value of K_{com} is worth noting. In previously studied systems, sizeable values of K_{com} have been found where there is independent evidence for significant electronic coupling.[1b] In the dppm-bridged ion the intensity of the IT band suggests that the resonance energy arising from electronic coupling is small (~0.01 V, see below). This is an important point since it suggests that the magnitude of K_{com} arises primarily from Coulombic repulsion between the charged redox sites and the more favorable solvation energy for the 3+ ion, points that will be discussed in a later publication.

In acetonitrile solution, the UV–visible spectra of the [2,2], [2,3], and [3,3] ions are typical of related monomeric complexes of Ru(II) and Ru(III) (Table I). They include bands

---

(10) For example: Anal. Calcd for $[(bpy)_2RuCl(Ph_2PCH_2PPh_2)ClRu(bpy)_2](ClO_4)_2 \cdot H_2O$: C, 51.45; N, 7.39; H, 4.22. Found: C, 51.14; N, 7.20; H, 4.13. Further support for the dimeric formulation comes from the near identity of the electronic spectra of monomeric analogues such as $[(bpy)_2Ru(PPh_2Me)Cl]^+$ and $[(bpy)_2Ru(PPh_2(CH_2)_3PPh_2)Cl]^+$ which are discussed in ref 12. We have also prepared a series of dimeric diphosphine-bridged species with ligands such as $Ph_2PC{\equiv}CPPh_2$, $Ph_2P(CH_2)_nPPh_2$ (n = 2, 3), and *trans*-$Ph_2PCH{=}CHPPh_2$ whose electrochemistry, electronic spectroscopy, and elemental analyses are consistent with the dimeric formulation. As far as synthesis and characterization, the dppm dimer is not unusual nor unique. The interesting observation of weak intervalence-transfer transitions and electrostatic effects on redox potentials in the homologous series of dimers will be addressed in a separate publication.

(11) $E_{1/2} = (E_{p,a} + E_{p,c})/2$ where the potentials were measured vs. the saturated sodium chloride calomel electrode. The ΔE_p values, $\Delta E_p = E_{p,a} - E_{p,c}$ = 60–65 mV, are characteristic of reversible one-electron processes under the experimental conditions used.

assignable to bpy ($\pi^* \leftarrow \pi_b$), π^*(bpy) $\leftarrow$ dπ[Ru(II)], dπ[Ru(III)] $\leftarrow$ pπ(Cl), and dπ[Ru(III)] $\leftarrow$ π_b(bpy) transitions.[12,13] Near-infrared (near-IR) spectra were recorded in CD_3CN. The [2,3] and [3,3] forms were generated in situ by using $Fe(bpy)_3^{3+}$ as a stoichiometric oxidant. Both $Fe(bpy)_3^{2+}$ and $Fe(bpy)_3^{3+}$ are transparent in the region 850–2200 nm. Neither the [2,2] nor [3,3] ions had detectable absorptions in this spectral region, but a band does appear for the mixed-valence ion at 8020 cm^{-1} (1245 nm) with ϵ_{max} 25 $\pm$ 7 M^{-1} cm^{-1} (see Figure 2).

The near-IR band is assignable to the IT transition shown in eq 6. The calculated value of $\Delta\nu_{1/2}$ (the bandwidth at

$$[(bpy)_2ClRu^{II}(Ph_2PCH_2PPh_2)Ru^{III}Cl(bpy)_2]^{3+} \xrightarrow{h\nu} [(bpy)_2ClRu^{III}(Ph_2PCH_2PPh_2)Ru^{II}Cl(bpy)_2]^{3+*} \quad (6)$$

half-height) given by eq 7 is 4.3 × 10^3 cm^{-1} which compares

$$\Delta\nu_{1/2} = (2.31 \times 10^3 \nu_{max})^{1/2} \quad (\text{in cm}^{-1}) \qquad (7)^{2a}$$

well with the experimental value of 4.6 × 10^3 cm^{-1} obtained by doubling the half-bandwidth on the low-energy side of the band. The value also agrees well with values found earlier for related complexes like the pyrazine-bridged dimer in eq 1.

The observation that an IT band appears for the mixed-valence dimer has important implications for related outer-sphere reactions. In an outer-sphere reaction, initial formation of an association complex or ion pair occurs (eq 8) followed by electron transfer within the ion pair (eq 9). Experimentally

$$RuB_2(py)Cl^+ + RuB_2(py)Cl^{2+} \overset{K}{\rightleftharpoons} [Ru^{II}B_2(py)Cl,Ru^{III}B_2(py)Cl]^{3+} \quad (8)$$

$$[Ru^{II}B_2(py)Cl,Ru^{III}B_2(py)Cl]^{3+} \xrightarrow{k_{et}} [Ru^{III}B_2(py)Cl,Ru^{II}B_2(py)Cl]^{3+} \quad (9)$$

$$[Ru^{III}B_2(py)Cl,Ru^{II}B_2(py)Cl]^{3+} \rightarrow RuB_2(py)Cl^{2+} + RuB_2(py)Cl^+ \quad (10)$$

B is 2,2′-bipyridine; py is pyridine

measured rate constants for outer-sphere reactions are the products of two constants, $k_{obsd} = k_{et}K$, and direct information about the electron-transfer step is lost. For the chemically linked, outer-sphere ion, optical electron transfer is observed and the properties of the transition help to reveal the microscopic details of related thermal processes like eq 9. In addition, if the optical transition is outer sphere in nature, its integrated intensity provides a direct experimental probe into the extent of outer-sphere coupling between the redox sites.

If electronic coupling is weak, the extent of delocalization of the excess electron from Ru(II) onto Ru(III) in the ground state is given by eq 11 where ν_{max} and $\Delta\bar{\nu}_{1/2}$ are given in cm^{-1}

$$\alpha^2 = 4.2 \times 10^{-4}\epsilon_{max}\Delta\bar{\nu}_{1/2}/\bar{\nu}_{max}d^2 \qquad (11)^{2a}$$

and d in Å. From the properties of the IT band in CD_3CN, $\alpha^2 = 1.3 \times 10^{-4}$ and the resonance energy or electron exchange matrix element, V_{ab}, can be calculated from the first-order perturbation theory result, $V_{ab} = \alpha\bar{\nu}_{max}$, to be V_{ab} = 0.26 kcal/mol (92 cm^{-1}). The value for V_{ab} is an order of magnitude lower than V_{ab} for the ion $[(bpy)_2ClRu^{II}(1,4\text{-pyr})Ru^{III}Cl(bpy)_2]^{3+}$ and is within a factor of 2 of the value found for the outer-sphere ion pair $[(NH_3)_5Ru^{III}(py),Fe^{II}(CN)_6]^-$.[5] Because of the similarities with the ion-pair case and from our previous results comparing related saturated and unsaturated bridging ligands, e.g., *trans*-py-4-CH=CH-4-py vs. py-4-CH$_2$CH$_2$-4-py,[14,17] we conclude that the electronic coupling between redox sites is largely from outer-sphere orbital overlap. The result is important since the magnitude of V_{ab} suggests that electronic coupling between the redox sites may be sufficient that the related outer-sphere electron-transfer reaction in eq 9 is adiabatic in the sense used by Marcus in his semiclassical theory of electron transfer.[15]

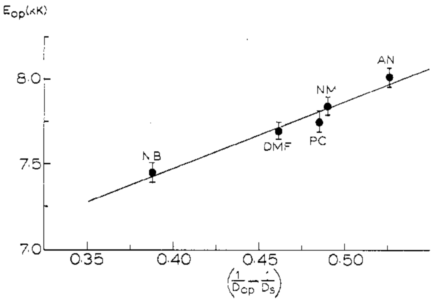
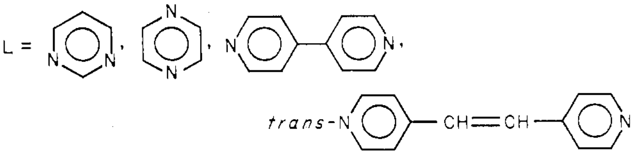


Figure 3. Solvent dependence of the outer-sphere, IT transition in $[(bpy)_2ClRu(Ph_2PCH_2PPh_2)ClRu(bpy)_2]^{3+}$ in the series of perdeuterated solvents, acetonitrile (AN), nitromethane (NM), propylene carbonate (PC), dimethylformamide (DMF), and nitrobenzene (NB). D_{op} is the optical dielectric constant of the solvent, and D_s is the static dielectric constant.

Using the mixed-valence ion, it is possible to investigate the effect of solvent on the energy of the optical transition (E_{op}) and, since $E_{op} = 4E_a$, also the effect of solvent on the activation energy for the thermal transition (E_a). With the assumption of a dielectric continuum model, the dependence of E_{op} on solvent polarization is given by eq 12. In eq 12, χ is the optical

$$E_{op} = \chi = \chi_i + \chi_o = \chi_i + e^2\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{d}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \qquad (12)^{2a}$$

or vertical vibrational barrier to electron transfer which can be partitioned into χ_o, the contribution to χ from solvent polarization effects, and χ_i, which includes the contribution to χ from inner-sphere vibrations as well as all other solvent-independent terms. Included in eq 12 are the radii of the donor (a_1) and acceptor sites (a_2), the distance between the redox sites, d, and D_{op} and D_s which are the optical and static dielectric constants of the medium. In Figure 3 is shown a plot of E_{op} vs. ($1/D_{op} - 1/D_s$) for the mixed-valence ion in a series of perdeuterated solvents. The linearity of the plot shows that good agreement exists between experiment and theory. The intercept, χ_i = 5870 cm^{-1}, is very similar to values found for ions like $[(bpy)_2ClRu(1,4\text{-pyr})RuCl(bpy)_2]^{3+}$ (5710 cm^{-1}),[1,4] and the similarity in values indicates that the vibrational modes of the bridging ligand are not the primary origin of χ_i. The boundary condition on the integration which leads to eq 12 is correct only if $d \geq 2a_1$. A more realistic approach to the charge distribution involved has been given by Cannon,[16] and earlier work on the dimers [(bpy)$_2$ClRu–L–RuCl(bpy)$_2$]$^{3+}$



has shown that the empirical correction $d = d$(calcd) + 0.5

---

(12) B. P. Sullivan, D. J. Salmon, and T. J. Meyer, *Inorg. Chem.*, **17**, 3334 (1978).

(13) G. M. Bryant, J. E. Fergusson, and H. K. T. Powell, *Aust. J. Chem.*, **24**, 257 (1971).

(14) R. W. Callahan, T. J. Meyer, M. J. Powers and D. J. Salmon, *J. Am. Chem. Soc.*, **98**, 6731 (1976).

(15) R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956); **43**, 679 (1965).

(16) R. D. Cannon, *Chem. Phys. Lett.*, **49**, 299 (1977).

(Å) gives excellent agreement with the experimental data.[17] Using the corrected dielectric continuum model, $e = 1$, and calculated[8] values of $d = 7.1$ Å and $a_1 = a_2 = 6.0$ Å for the phosphine-bridged dimer gives a calculated slope of 4080 cm^{-1} for the plot shown in Figure 3. The calculated value is in good agreement with the experimental value of 4000 cm^{-1}.

The properties of the IT band are also consistent with the kinetic results obtained from outer-sphere rate constant measurements. For the reaction in eq 8 and 9, $k_{obsd} = 4.9 \times 10^7$ M^{-1} s^{-1} (in CH_3CN, 25 °C, $I \approx 0$)[4] and $K \approx 0.6$, so that the electron-transfer rate constant within the ion pair is $k_{et} \approx 8 \times 10^7$ M^{-1} s^{-1}. From the quantum mechanical treatments of Duke,[18] Hopfield,[2b] and others,[19] it is possible to calculate rate constants of intramolecular electron transfer from the properties of IT bands.[20] For the intramolecular electron-transfer process, k_{et} is given by eq 13, where $E_{op} \cong 4\Delta G^* = \lambda$ and λ is the free-energy term corresponding to χ. In the high-temperature limit, ν_{et} is given by eq 14. For the dimer,

$$k_{et} = \nu_{et} \exp[-(\Delta G^*/RT)] \tag{13}$$

$$\nu_{et} = \frac{2\pi^{3/2}}{\hbar} V_{ab}^2 \left(\frac{1}{k_B T \lambda} \right)^{1/2} \tag{14}$$

the calculated value for k_{et} using eq 13 is 8.8×10^8 s^{-1} which is in reasonable agreement with the value estimated for the outer-sphere reaction especially given the differences in the distances between redox sites for the two reactions ($d = 6.8$ vs. 13.2 Å).[1,20]

Acknowledgment. Acknowledgments are made to the Materials Research Center of The University of North Carolina under Grant No. DAHC15-73-G9 and to the Army Research Office—Durham under Grant No. DAAG-29-76-G-0135 for support of this research. We also thank Dr. Jerry Walsh for providing a sample of $[Fe(bpy)_3](PF_6)_3$.

Registry No. $[(bpy)_2ClRu(dppm)RuCl(bpy)_2](ClO_4)_2$, 72378-70-2; $[(bpy)_2ClRu(dppm)RuCl(bpy)_2](PF_6)_2$, 72378-72-4; *cis*-$(bpy)_2RuCl_2$, 19542-80-4; $[(bpy)_2ClRu(dppm)RuCl(bpy)_2]^{4+}$, 72390-15-9; $[(bpy)_2ClRu(dppm)RuCl(bpy)_2]^{3+}$, 72478-65-0; $[(bpy)_2ClRu^{II}(PPh_3)]^+$, 50576-57-3; $[(bpy)_2ClRu^{III}(PPh_3)]^{2+}$, 72402-36-9.

---

[17] M. J. Powers, Ph.D. Dissertation, The University of North Carolina, Chapel Hill, N.C., 1977; M. J. Powers and T. J. Meyer, *J. Am. Chem. Soc.*, in press.

[18] C. B. Duke, "Proceedings of the Conference on Tunneling in Biological Systems", in press.

[19] J. Jortner, *J. Chem. Phys.*, **64**, 4860 (1976); S. G. Christov, *Ber. Bunsenges. Phys. Chem.*, **68**, 358 (1975).

[20] T. J. Meyer, *Chem. Phys. Lett.*, **64**, 417 (1979).

Contribution from the Department of Chemistry,
Texas Christian University, Fort Worth, Texas 76129

Reactions of BCl_3 with Silylamines Containing Si–H Bonds[1]

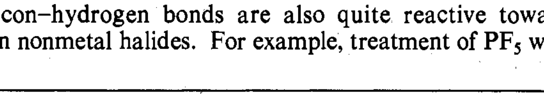
ROBERT H. NEILSON

Received August 28, 1979

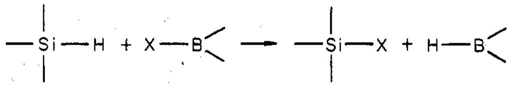
The reactions of BCl_3 with a variety of di- and trisilylamines containing at least one Si–H bond have been investigated. In CH_2Cl_2 solution, the chloro-substituted trisilylamines $(Me_3Si)_2NSiMe_2Cl$ and $Me_3SiN(SiMe_2Cl)_2$ were obtained in high yields from the corresponding Si–H derivatives by chlorination with BCl_3. Depending upon the reaction conditions employed, the *tert*-butylamines *t*-$BuN(SiMe_2H)SiMe_3$ and *t*-$BuN(SiMe_2H)_2$ gave either simple H/Cl exchange products or the (silylamino)boranes $Me_3Si(Me_2SiCl)NB(Cl)H$ (**1**) and $(Me_2SiCl)_2NBH_2$ (**2**) which resulted from an unexpected C–N bond cleavage process. In the case of $Me_3Si(Me_2SiH)NMe$, the trimethylsilyl–nitrogen bond was selectively cleaved to afford another difunctional (silylamino)borane $(Me_2SiCl)(Me)NB(Cl)H$ (**3**). Spectroscopic data for the aminoboranes (**1–3**) and some new silylamines are reported.

Introduction

The cleavage reaction of silicon–nitrogen compounds with boron halides is well documented as an important synthetic method in boron–nitrogen chemistry. With variation of the reaction stoichiometry and the number of Si–N and B–X bonds involved, this process (eq 1) has been used to prepare (silylamino)boranes,[2] diborylamines,[3] borazines,[4] or borazocines.[5]


(1)

Silicon–hydrogen bonds are also quite reactive toward certain nonmetal halides. For example, treatment of PF_5 with Me_3SiH is an effective preparative route to HPF_4.[6] Electronegativity and bond energy considerations suggest that similar exchange reactions (eq 2) can occur between silicon hydrides and boron halides, although only a few examples have been reported.[7]


(2)

In this context, we report here the results of a study in which trichloroborane was allowed to react with some silicon compounds containing both Si–N and Si–H bonds.

Results and Discussion

In a typical experiment, equimolar quantities of BCl_3 and a silylamine were combined at −78 °C in CH_2Cl_2 solution and the mixture was then allowed to warm slowly to room tem-

---

[1] Presented at the Fourth International Meeting on Boron Chemistry, Salt Lake City, Utah, 1979.

[2] (a) Burg, A. B.; Kulijian, E. S. *J. Am. Chem. Soc.* **1970**, *72*, 3103. (b) Barlos, K.; Nöth, H. *Chem. Ber.* **1977**, *110*, 2790.

[3] Nöth, H.; Storch, W. *Chem. Ber.* **1976**, *109*, 884.

[4] Bowser, J. R.; Neilson, R. H.; Wells, R. L. *Inorg. Chem.* **1978**, *17*, 1882.

[5] Neilson, R. H.; Wells, R. L. *Synth. Inorg. Met.-Org. Chem.* **1973**, *3*, 283.

[6] Cowley, A. H.; Braun, R. W. *Inorg. Chem.* **1973**, *12*, 491.

[7] (a) Van Dyke, C. H.; MacDiarmid, A. G. *J. Inorg. Nucl. Chem.* **1963**, *25*, 1503. (b) Vanderwielen, A. J.; Ring, M. A. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 421.

0020-1669/80/1319-0755$01.00/0 © 1980 American Chemical Society