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Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Reactions of the Octaisothiocyanatodirhenate(III) Anion with Tertiary Phosphines. Cleavage of the Rhenium–Rhenium Quadruple Bond

TAYSEER NIMRY and RICHARD A. WALTON*

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The reactions of the salt $(Bu_4N)_2Re_2(NCS)_8$ with monodentate and bidentate tertiary phosphines produce the green complexes $(Bu_4N)_2Re_2(NCS)_8L_2$ which contain dimeric thiocyanate-bridged anions with magnetically dilute rhenium(III) centers. The reactions of the diethylphenylphosphine product with 1,2-bis(diphenylphosphino)ethane, 2,2′-bipyridyl, and 1,10-phenanthroline lead to the breaking of the thiocyanate bridges and the formation of the six-coordinate rhenium(III) monomers $Re(NCS)_3(PEt_2Ph)(B)$, where B = dppe, bpy, or phen. This is the first extensive series of complexes which has been prepared directly from anions of the type $Re_2X_8^{2-}$ (X = Cl, Br, or NCS) where cleavage of the quadruple Re–Re bond is the rule rather than the exception. The reason for this behavior may be due to the fact that the metal–metal bond in $Re_2(NCS)_8^{2-}$ is weaker than that in the related octahalo anions, a conclusion which is based upon differences in the electronic absorption spectra of these species. The complexes of the type $(Bu_4N)_2Re_2(NCS)_8L_2$ which contain monodentate 1,2-bis(diphenylphosphino)ethane (dppe) and bis(diphenylphosphino)methane (dppm) are unstable in acetonitrile solutions due to a very rapid intramolecular attack of the unbound tertiary phosphine groups upon the thiocyanate bridges. This leads to the formation of the yellow monomeric anions $[Re(NCS)_4(dppm)]^-$ and $[Re(NCS)_4(dppe)]^-$, the latter species having been isolated in the solid state as its butylammonium salt. Its properties have been compared to those of the related derivative with triethylphosphine, $(Bu_4N)Re(NCS)_4(PEt_3)_2$, which is also reported here for the first time. The new complexes prepared in the present study have been characterized by infrared, electronic absorption, and x-ray photoelectron spectroscopy and magnetic susceptibility and concentrated range conductance measurements.

Introduction

The reactions of the octahalodirhenate(III) anions $Re_2X_8^{2-}$, where X = Cl or Br, with monodentate tertiary phosphines lead to the formation of either substitution derivatives of the type $Re_2X_6(PR_3)_2$ or the one- or two-electron reduction products $Re_2X_5(PR_3)_3$ or $Re_2X_4(PR_3)_4$.[1] The electronic and molecular structures of these species have attracted much interest[2,3] and studies on the chemical reactivity of these low oxidation state dimers are currently being pursued in our laboratory.[4-6]

While the strong metal–metal bond is more often than not retained in the products which result from reactions of $Re_2X_8^{2-}$, it is becoming increasingly apparent that under quite mild reaction conditions this bond may be disrupted to afford monomeric rhenium species. Thus the reaction of $(Bu_4N)_2Re_2Cl_8$ with ligands as different as thiourea and 1,2-bis(diphenylphosphino)ethane leads to products $(ReCl_3(tu)_3$ and $Re_2Cl_6(dppe)_2$, respectively)[7-9] in which the metal–metal bond is no longer present. More recently we have shown[5] that rhenium(II) complexes of the type $Re_2X_4(PR_3)_4$ may react with carbon monoxide to afford the rhenium(II) monomers $ReX_2(CO)_2(PR_3)_2$. However, in none of these instances is it yet clear why the reactions proceed with disruption of the metal–metal bond while related ones do not. This is in contrast to the photochemical cleavage of the quadruple bond in $Re_2Cl_8^{2-}$ which has recently been achieved[10] by ultraviolet irradiation of acetonitrile solutions of $(Bu_4N)_2Re_2Cl_8$.

In view of the synthetic utility and unique electronic structures of these metal–metal bonded dimers, it is important to establish under what conditions the metal–metal bond order may be changed or the bond completely broken. Accordingly, we are interested in determining which factors associated with the metal–metal bonded dimers favor this particular reaction course.

Little is known about the reactivity of the analogous octaisothiocyanatodirhenate(III) anion, $Re_2(NCS)_8^{2-}$, which was first prepared[11] in 1966 by reacting $(Bu_4N)_2Re_2Cl_8$ with NaSCN in methanol or tetrahydrofuran. It was reported[11] that the addition of triphenylphosphine to the methanol solution of $(Bu_4N)_2Re_2Cl_8$ and NaSCN afforded a green compound which analyzed as $(Bu_4N)_2Re_2(NCS)_8(PPh_3)_2$. This paramagnetic complex was believed not to contain a Re–Re bond. This preliminary report[11] therefore suggests that the behavior of $Re_2(NCS)_8^{2-}$ might be quite different from that exhibited by $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$. We have therefore undertaken a detailed investigation of the reactions of this anion with a number of tertiary phosphines.

Experimental Section

Starting Materials. The salt $(Bu_4N)_2Re_2(NCS)_8$ was prepared as previously described[11] by the reaction of $(Bu_4N)_2Re_2Cl_8$ with NaSCN in acidified tetrahydrofuran solution. Commercial reagents and solvents were used as received. All phosphine ligands were obtained from Strem Chemicals, Inc.

Reaction Procedures. All reactions were carried out in a nitrogen atmosphere and solvents were deoxygenated by purging with N_2 gas for several hours.

A. Reactions of $(Bu_4N)_2Re_2(NCS)_8$ with Tertiary Phosphines. Complexes of the type $(Bu_4N)_2Re_2(NCS)_8L_2$, where L = $P(n\text{-}Pr)_3$, PEt_2Ph, PPh_3, $Ph_2PCH_2PPh_2$, or $Ph_2PCH_2CH_2PPh_2$, were prepared by essentially the same procedure. This involved stirring a suspension of $(Bu_4N)_2Re_2(NCS)_8$ in acidified methanol with an excess of the appropriate tertiary phosphine. The resulting green solid was then separated from the brown mother liquor, washed with ethanol, benzene, diethyl ether, and finally pentane, and then allowed to dry in vacuo for several hours. These products are soluble in acetone, acetonitrile, pyridine, nitrobenzene, and dimethylformamide, slightly soluble in chloroform and tetrahydrofuran, but insoluble in water, ether, benzene, ethanol, and pentane.

(i) $(Bu_4N)_2Re_2(NCS)_8(PEt_2Ph)_2$ (I). A suspension of $(Bu_4N)_2Re_2(NCS)_8$ (1.0 g) in 40 mL of methanol containing a few drops of acetic acid was treated with 2.0 mL of PEt_2Ph. The reaction mixture was stirred at room temperature for 2 h and the insoluble product isolated as described in the preceding paragraph; yield 1.13 g. The product can be recrystallized from acetonitrile and diethyl ether at 0 °C. Anal. Calcd for $C_{60}H_{102}N_{10}P_2Re_2S_8$: C, 43.55; H, 6.23; N, 8.47; S, 15.50; P, 3.74. Found: C, 43.40; H, 6.25; N, 8.66; S, 15.19; P, 4.00; mp 149–151 °C dec.

(ii) $(Bu_4N)_2Re_2(NCS)_8(PPr_3)_2$ (II). A procedure similar to (i) was followed using 0.3 g of $(Bu_4N)_2Re_2(NCS)_8$ and 0.5 mL of PPr_3 in 20 mL of acidified methanol and a reaction time of 0.5 h; yield 0.32 g. Anal. Calcd for $C_{58}H_{114}N_{10}P_2Re_2S_8$: C, 42.4; H, 6.99; N, 8.53. Found: C, 42.20; H, 6.97; N, 8.19; mp 149–151 °C dec.

(iii) $(Bu_4N)_2Re_2(NCS)_8(PPh_3)_2$ (III). The synthesis of this complex was carried out using a slight variation of the method reported by Cotton et al.[11] A mixture of 0.2 g of $(Bu_4N)_2Re_2(NCS)_8$ and 0.2 g of powdered PPh_3 in 20 mL of acidified methanol was stirred for 5 h. The green product was treated as in (i); yield 0.25 g. Recrystallization of this green complex from acetonitrile and ether at 0 °C can be achieved in contrast to the previous report[11] in which a yellow crystalline compound was obtained. Anal. Calcd for $C_{76}H_{102}N_{10}P_2Re_2S_8$: C, 49.44; H, 5.57; N, 7.59. Found: C, 49.15; H, 5.60; N, 7.70; mp 168–170 °C dec.

(iv) $(Bu_4N)_2Re_2(NCS)_8(dppm)_2$ (IV). The general procedure described above was followed using 0.3 g of $(Bu_4N)_2Re_2(NCS)_8$ and 0.2 g of powdered bis(diphenylphosphino)methane (dppm) in 40 mL of acidified methanol solution. The reaction time was 5 h; yield 0.25 g. Anal. Calcd for $C_{90}H_{116}N_{10}P_4Re_2S_8$: C, 51.20; H, 5.60; N, 6.70. Found: C, 51.13; H, 5.76; N, 7.00; mp 143–145 °C dec. A dilute acetonitrile solution of the complex appears to be unstable since it rapidly changes color from green to yellow. Attempts to recover the unchanged complex by adding ether at 0 °C were unsuccessful.

(v) $(Bu_4N)_2Re_2(NCS)_8(dppe)_2$ (V). A longer period of stirring was necessary to obtain the desired product. Thus a mixture of 0.2 g of $(Bu_4N)_2Re_2(NCS)_8$ and 0.2 g of 1,2-bis(diphenylphosphino)ethane (dppe) in 40 mL of acidified methanol was stirred for approximately 20 h. The green compound was filtered off and treated in the usual fashion; yield 0.28 g. Anal. Calcd for $C_{92}H_{120}N_{10}P_4Re_2S_8$: C, 52.15; H, 5.72; N, 6.61. Found: C, 51.33; H, 5.67; N, 6.63; mp 120–123 °C dec.

When this salt was dissolved in acetonitrile, the color of the solution changed from green to yellow in less than 5 min. Evaporation of the solution yielded a yellow solid which was recrystallized by dissolving in benzene and then adding hexane (the green complex is insoluble in benzene). Anal. Calcd for $C_{46}H_{60}N_5P_2ReS_4$: C, 52.15; H, 5.72; N, 6.61. Found: C, 51.88; H, 5.77; N, 6.95. It was subsequently found that dissolution of $(Bu_4N)_2Re_2(NCS)_8(dppe)_2$ in acetonitrile was not the only method of obtaining this complex. Thus, stirring the original reaction mixture for 48 h afforded a yellow insoluble product which after recrystallization from benzene and hexane gave the following microanalyses: C, 52.25; H, 5.77; N, 6.87; mp 182–183 °C.

Although these green and yellow products have very similar microanalyses, the differences in their spectral properties (see Results and Discussion) are consistent with the yellow complex being $(Bu_4N)Re(NCS)_4(dppe)$ (VI).

B. Reactions of $(Bu_4N)_2Re_2(NCS)_8(PEt_2Ph)_2$ with 1,2-Bis(diphenylphosphino)ethane, 2,2′-Bipyridyl and 1,10-Phenanthroline. An identical procedure was followed upon reacting this isothiocyanate salt with each of the bidentate ligands. A reaction mixture comprising 0.2 g of $(Bu_4N)_2Re_2(NCS)_8(PEt_2Ph)_2$ and 0.15 g of the desired ligand in 40 mL of methanol (containing 0.5 mL of acetic acid) was refluxed for 4 h and then allowed to cool slowly to room temperature. The resulting crystalline complex was filtered off, washed with ethanol, diethyl ether, and pentane and then allowed to dry in vacuo for several hours. Yields were usually ~0.15 g.

(i) $Re(NCS)_3(PEt_2Ph)(dppe)$ (VII). Red crystals of the complex began to form shortly after reflux was commenced. Anal. Calcd for $C_{39}H_{39}N_3P_3ReS_3$: C 50.63; H, 4.26; N, 4.54; S, 10.40. Found: C, 50.77; H, 4.11; N, 4.43; S, 10.60; mp 220–223 °C. This complex is soluble in acetone, acetonitrile, benzene, chloroform, tetrahydrofuran, nitrobenzene, and pyridine, slightly soluble in ethanol, but insoluble in methanol, water, ether, and pentane.

(ii) $Re(NCS)_3(PEt_2Ph)(bpy)$ (VIII). The aforementioned general procedure was employed to obtain this dark green crystalline complex. Anal. Calcd for $C_{23}H_{23}N_5PReS_3$: C, 40.45; H, 3.40; N, 10.76. Found: C, 40.35; H, 3.35; N, 10.48; mp 207–208 °C. This complex is much less soluble than its dppe analogue (VII).

(iii) $Re(NCS)_3(PEt_2Ph)(phen)$ (IX). This compound is very similar to VIII in its color and solubility properties. Anal. Calcd for $C_{25}H_{23}N_5PReS_3$: C, 42.59; H, 3.76; N, 9.88; S, 13.56; P, 4.37. Found: C, 42.55; H, 3.64; N, 9.59; S, 12.28; P, 4.61.

C. Synthesis of $(Bu_4N)Re(NCS)_4(PEt_3)_2$ (X). An acetone solution (15 mL) containing 0.2 g of $(Bu_4N)_2Re_2(NCS)_8$ was treated with 0.5 mL of PEt_3. Upon adding the PEt_3, the color of the suspension turned green, presumably due to the formation of $(Bu_4N)_2Re_2(NCS)_8(PEt_3)_2$. Within a few minutes of commencing reflux, the reaction mixture began to turn dark brown, a color which persisted until reflux was stopped after 20 h. The solution was allowed to cool to room temperature and then filtered. Addition of hexane to the filtrate gave a black insoluble material, which was collected and recrystallized from acetone and hexane. The resulting brown-orange solid was washed with hexane and dried in vacuo; yield 0.16 g. Anal. Calcd for $C_{32}H_{66}N_5P_2ReS_4$: C, 42.82; H, 7.43; N, 7.82. Found: C, 42.86; H, 7.48; N, 7.75; mp 180–185 °C. It is soluble in acetone, acetonitrile, tetrahydrofuran, and methanol, slightly soluble in ethanol, and insoluble in benzene, ether, and hexane.

Physical Measurements. Infrared spectra in the region 4000–200 cm^{-1} were recorded as Nujol mulls using a Beckman IR-12 spectrophotometer. Electronic absorption spectra were recorded on Beckman DU-2 and Cary 14 spectrophotometers. X-ray photoelectron spectra were recorded using a Hewlett-Packard 5950A ESCA spectrometer. The aluminum $K\alpha_{1,2}$ line (1486.6 eV) was used as the excitation source. Full details of the experimental procedure are described elsewhere.[12,13] Magnetic susceptibilities were found by the Gouy technique using $Hg[Co(SCN)_4]$ as the calibrant. The measurements were made at only one temperature, approximately 25 °C.

Table I. Isothiocyanato Complexes of Rhenium(III) Derived from the Octaisothiocyanatodirhenate(III) Anion

No.	Complex	Medium[a]	Electronic absorption maxima (2000–400 nm), nm[b]	Infrared spectra, ν(C–N), cm^{-1}	Magnetic moment, μ_{eff}, μ_B
I	$(Bu_4N)_2(NCS)_8(PEt_2Ph)_2$	A	~850 sh, 750, 625, 450 sh, 410	2120 m, 2070 vs, 2048 vs, 2025 sh	1.9
		B	810 sh, 735 (1870), 615 (1160), 440 sh, 410 (95 000)		
II	$(Bu_4N)_2Re_2(NCS)_8(PPr_3)_2$	A	885 sh, 740, 620, ~450 sh, 415	2110 w, 2070 vs, 2020 vs, 2015 vs	1.8
		B	830, 735 (900), ~615 br (620), 430 sh, 405 (108 000)		
III	$(Bu_4N)_2Re_2(NCS)_8((PPh_3)_2$	A	~850 sh, 750, 650 sh, ~460 sh, 435	2110 m, 2065 vs, 2040 vs, 2020 vs	2.6
		B	810 sh, 740, 615, 450 sh, 420		
IV	$(Bu_4N)_2Re_2(NCS)_8(dppm)_2$	A	~850 sh, 755, ~645, ~460 sh, 420	2110 w, 2070 vs, 2045 vs, 2025 vs	
		B	453 (29 100), 400 (23 200)		
V	$(Bu_4N)_2Re_2(NCS)_8(dppe)_2$	A	~900 sh, 750, 650, 460 sh, 430	2110 w, 2065 vs, 2040 vs, br	
		B	448 (55 600), 380 sh		
VI	$(Bu_4N)Re(NCS)_4(dppe)$	A	~650 sh, w, ~480 sh, 450, 405 sh	2080 vs, 2055 vs, 2025 vs	
		B	448, 380 sh		
VII	$Re(NCS)_3(PEt_2Ph)(dppe)$	A	555, 475	2080 vs, 2020 vs, 1995 vs, br	2.7
		B	545 (20 600), 468 (41 100)		
VIII	$Re(NCS)_3(PEt_2Ph)(bpy)$	A	800 sh, 625, 575 sh, ~450 br	2065 vs, 2028 vs, 1995 vs	2.5
		B	582, 442, ~400 sh		
IX	$Re(NCS)_3(PEt_2Ph)(phen)$	A	~800 sh, w?, 600, ~500 sh, 465	2075 vs, 2035 vs, 2000 vs, br	
		B	580 (1550), 440 (6200), 405 sh		
X	$(Bu_4N)Re(NCS)_4(PEt_3)_2$	A	~600 sh, 510, 410	2060 vs, 2040 vs	
		B	500 (3920), 400 (13 800)		

[a] A = diffuse reflectance; B = acetonitrile. [b] Molar extinction coefficients are given in parentheses (these values are calculated relative to the baseline at ~1200 nm where there is no significant absorption).

Corrections for the ligand diamagnetism were estimated from Pascal's constants. Conductivity measurements were carried out using an Industrial Instruments bridge, Model RC 16B2.

Analytical Procedures. Elemental microanalyses were performed by Dr. C. S. Yeh of the Purdue University microanalytical laboratory.

Results and Discussion

Although it has been some 10 years since salts of the $Re_2(NCS)_8^{2-}$ anion were first isolated and characterized, a study of their behavior toward Lewis bases is restricted to only one reaction. Thus, Cotton and co-workers[11] reported that the addition of triphenylphosphine to a solution containing $Re_2(NCS)_8^{2-}$ (generated in situ by stirring $(Bu_4N)_2Re_2Cl_8$ with NaSCN in methanol) gave a green complex with the unusual stoichiometry $(Bu_4N)_2Re_2(NCS)_8(PPh_3)_2$. Recent developments in the chemistry of the octahalodirhenate(III) anions[1,2,4,5] have led us to reinvestigate this reaction and extend our study to include a number of other tertiary phosphines.

The reactions between $(Bu_4N)_2Re_2(NCS)_8$ and tertiary phosphines, in which green complexes of stoichiometry $(Bu_4N)_2Re_2(NCS)_8L_2$ are formed, appear to be quite general since both monodentate and bidentate phosphines react in this same fashion. These complexes (I–V), together with species which are derived therefrom (compounds VI–X), are listed in Table I, along with pertinent details of their infrared and electronic absorption spectra and magnetic properties.

(a) Electronic and Infrared Absorption Spectra. The green complexes I–V possess strikingly similar solid-state electronic absorption spectra (Table I), the most dominant spectral feature being a broad band envelope, centered between 735 and 755 nm, which contains three components (Figure 1). These spectra are quite different from that of the $Re_2(NCS)_8^{2-}$ anion,[11] which has no absorption present between 700 and 800 nm but which instead displays an intense band at ~1100 nm. The complexes with monodentate tertiary phosphines (I–III) dissolve in acetonitrile to form green solutions which have very similar electronic spectra to those of the solid complexes.[14] Accordingly, it is clear that these species retain their identity in solution. In contrast to this, acetonitrile solutions of $(Bu_4N)_2Re_2(NCS)_8(dppm)_2$ and $(Bu_4N)_2Re_2(NCS)_8(dppe)_2$ quickly changed color from green to yellow and were found to possess spectra quite different from those of the other complexes. In particular, the band centered around 750 nm is absent and in the region between 400 and 2000 nm the only absorptions are at ~450 and 400 nm. These latter spectral features are identical with those exhibited by the yellow complex $(Bu_4N)Re(NCS)_5(dppe)$, which while possessing an identical stoichiometry to that of complex V is structurally different (see later).

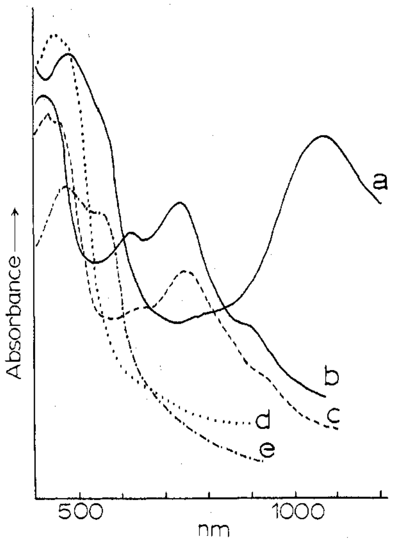


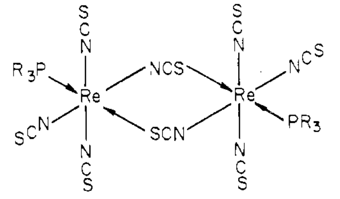
Figure 1. Diffuse-reflectance spectra (400–1200 nm) of (a) $(Bu_4N)_2Re_2(NCS)_8$, (b) $(Bu_4N)_2Re_2(NCS)_8(PPr_3)_2$, (c) $(Bu_4N)_2Re_2(NCS)_8(dppe)_2$, (d) $(Bu_4N)Re(NCS)_4(dppe)$, and (e) $Re(NCS)_3(PEt_2Ph)(dppe)$.

The close similarity of the solid-state electronic absorption spectra of complexes I–V is very strong evidence in support of their possessing identical structures. This is further reflected by the similarity of their infrared spectra in the ν(C–N) region (Table I). Unfortunately, the complexity of the infrared spectra arising from the presence of butylammonium cations and phosphine ligands precludes an assignment of the related ν(C–S) and δ(N–C–S) modes of coordinated thiocyanate and therefore prevents us using an infrared criterion[15] to identify the mode of thiocyanate bonding. However, there is indirect evidence to support the presence of terminal M–NCS units in these complexes. First, there is now little doubt that the

$Re_2(NCS)_8^{2-}$ anion starting material contains N-bonded thiocyanate.[11,15] Furthermore $(Bu_4N)_2Re_2(NCS)_8(PEt_2Ph)_2$ is readily converted into the monomeric complex $Re(NCS)_3(PEt_2Ph)$ (dppe) (see later), for which a single-crystal x-ray structure analysis[16] has revealed the exclusive presence of N-bound thiocyanate ligands.

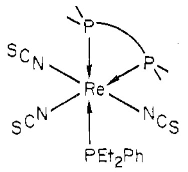
(b) Conductance Studies. In an earlier study,[11] we investigated the equivalent conductances of acetonitrile solutions of $(Bu_4N)_2Re_2Cl_8$, $(Bu_4N)_2Re_2(NCS)_8$, and $(Bu_4N)_2Re_2(NCS)_8(PPh_3)_2$. By making measurements over a concentration range and plotting $\Lambda_0 - \Lambda_e$ against $c_e^{1/2}$, we were able to show that all three complexes behave as 2:1 electrolytes.[17] In the present study we have confirmed that $(Bu_4N)_2Re_2(NCS)_8(PPh_3)_2$ shows behavior typical of a 2:1 electrolyte, as does its diethylphenylphosphine analogue I.[18] For these two complexes, plots of $\Lambda_0 - \Lambda_e$ against $c_e^{1/2}$ were linear and closely similar to that expected for a typical 2:1 electrolyte.[16b] Extension of these studies to the dppm and dppe complexes IV and V were thwarted by their reactivity in acetonitrile. In contrast to the behavior of complexes I and III, the species containing monomeric anions, $(Bu_4N)Re(NCS)_4$(dppe) and $(Bu_4N)Re(NCS)_4(PEt_3)_2$ (complexes VI and X), gave $\Lambda_0 - \Lambda_e$ vs. $c_e^{1/2}$ plots whose slopes were approximately half that expected for a 2:1 electrolyte, behavior which is consistent with their formulation as 1:1 electrolytes.[18]

(c) Structural Conclusions Concerning $(Bu_4N)_2Re_2(NCS)_8L_2$. Having established the spectral similarity of the complexes I–V, and their formulation as salts of dimeric anions, we are now in a position to consider further their electronic and molecular structures. In contrast to the diamagnetic $Re_2(NCS)_8^{2-}$ anion,[11] a species containing a rhenium–rhenium quadruple bond with a $\sigma^2\pi^4\delta^2$ ground-state configuration,[19] complexes I–III were found to be paramagnetic with magnetic moments which are characteristic of magnetically dilute rhenium(III) complexes.[20] The values reported in Table I are calculated per rhenium atom and are considered accurate to at least $\pm 0.2\ \mu_B$. Although the moment for the triphenylphosphine complex III is a little higher than that usually found for magnetically dilute phosphine complexes of rhenium(III) (1.6–2.1 μ_B),[20] it is similar to the values for the monomeric isothiocyanato complexes VII and VIII, which are authentic magnetically dilute complexes of rhenium(III). The paramagnetic behavior of I–III clearly rules out the presence of a metal–metal bonded structure which is in any way related to that of $Re_2(NCS)_8^{2-}$ and substantiates our earlier tentative suggestions[11] concerning the structure of $(Bu_4N)_2Re_2(NCS)_8(PPh_3)_2$, namely, that it contains a dimeric anion with a thiocyanate-bridged structure **1**. This structure requires that in the case of the dppm and dppe derivatives IV and V, the potentially bidentate phosphines are bound in a monodentate fashion. This is not unreasonable since we have recently isolated and characterized the rhenium(IV) complex *trans*-$ReCl_4(dppm)_2$ which contains monodentate dppm.[21] Although the related dppe derivative was not prepared, we did obtain the analogous complex of the mixed arsenic–phosphorus ligand $Ph_2PCH_2CH_2AsPh_2$(arphos), i.e., *trans*-$ReCl_4(arphos)_2$.



1

(d) Reactions of $(Bu_4N)_2Re_2(NCS)_8L_2$. Structure **1** suggests that complexes I–V should provide a direct synthetic route into monomeric derivatives of rhenium(III) thiocyanate, through splitting of the thiocyanate bridges. The existence of such reactions would in turn be support for this structural formulation. In the reactions of $(Bu_4N)_2Re_2(NCS)_8(PEt_2Ph)_2$ with the bidentate ligands dppe, bpy, and phen, we find that the six-coordinate complexes VII–IX are formed in high yield through bridge-splitting reactions. These paramagnetic complexes possess very similar electronic absorption spectra and infrared spectra in the ν(C–N) region (Table I) and they dissolve in acetonitrile to afford solutions which are essentially nonconducting (Λ_e = 5–7 Ω^{-1} cm^2 for $c_e \approx 10^{-3}$ M). The dppe complex VII is monomeric in benzene (mol wt found 918, calcd 925) and a single-crystal x-ray structure analysis, which is currently in progress,[16] has shown that it possesses the octahedral structure **2**. The related rhenium(III) complexes VIII and IX presumably possess structures related to that of **2** in view of the close similarity of their spectral and magnetic properties to those of VII.



2

The tendency for the thiocyanate bridges of I–V to be disrupted is apparent upon examination of the solution properties of these complexes in acetonitrile. While these solutions appear to be unstable and their green color changes to yellow-orange, the period over which this change takes place varies considerably. The solutions of IV and V undergo a color change in less than 5 min, whereas the others require several hours for this change to be apparent. Of significance is the fact that we were able to isolate a yellow-orange solid VI by the addition of diethyl ether to a cold acetonitrile solution of V while our attempts to isolate pure crystalline complexes from solutions of the other compounds have failed. The complex VI has an elemental microanalysis identical with that of V, yet it has a quite different color, melting point and electronic absorption spectrum and behaves as a 1:1 electrolyte in acetonitrile. Accordingly, it is apparent that the dimeric $[Re_2(NCS)_8(dppe)_2]^{2-}$ anion has been converted to monomeric six-coordinate $[Re(NCS)_4(dppe)]^-$. The solution electronic spectra of IV and V are very similar and V is in turn identical with both the solid-state and solution spectra of VI. Although we were unable to isolate the related dppm complex $(Bu_4N)Re(NCS)_4$(dppm), it is clear that such a species is at least present in solution.

The difference between the rapid rate at which IV and V react and the sluggish decomposition of I–III is almost certainly a consequence of the possibility of rapid intramolecular attack on the thiocyanate bridges by the unbound phosphine donor sites of the *monodentate* dppm and dppe ligands. Such a mechanism cannot occur with the complexes I–III derived as they are from monodentate phosphines. In the latter cases, the formation of $(Bu_4N)Re(NCS)_4(PR_3)_2$ would first require phosphine dissociation to occur through prior decomposition of a portion of the dissolved complex before the free phosphine concentration was sufficient to permit attack at the thiocyanate bridges. Support for this mechanism is provided by the two following observations. First, the reaction of $(Bu_4N)_2Re_2(NCS)_8$ with an excess of triethylphosphine afforded the orange complex $(Bu_4N)Re(NCS)_4(PEt_3)_2$ (X) via the green intermediate $(Bu_4N)_2Re_2(NCS)_8(PEt_3)_2$ only after a fairly long reflux period. This complex has a relatively simple electronic absorption spectrum which resembles in its main features the spectra of $(Bu_4N)Re(NCS)_4$(dppe) and the monomeric derivatives VII–IX. This reaction establishes that

Table II. X-Ray Photoelectron Spectra of Isothiocyanato Complexes of Rhenium(III)[a]

No.	Complex	Re 4f$_{5/2}$	Re 4f$_{7/2}$	S 2p$_{1/2}$	S 2p$_{3/2}$	N 1s	P 2p	C 1s
I	$(Bu_4N)_2Re_2(NCS)_8(PEt_2Ph)_2$	44.1	41.7 (1.2)	163.2 sh	162.3 (1.3)	401.9, 398.4		~286.0 sh; 284.6
II	$(Bu_4N)_2Re_2(NCS)_8(PPr_3)_2$	44.1	41.6 (1.2)	~163.1 sh	162.1 (1.2)	402.0, 398.4		285.9 sh; 284.6
III	$(Bu_4N)_2Re_2(NCS)_8(PPh_3)_2$	44.5	42.1 (1.1)	~163.2 sh	162.1 (1.4)	402.4, 398.7		~286.2 sh; 284.9
IV	$(Bu_4N)_2Re_2(NCS)_8(dppm)_2$	44.3	41.8 (1.4)	163.2 sh	162.3 (1.3)	402.0, 398.5	131.0 (2.1)	~286.0 sh; 284.7
V	$(Bu_4N)_2Re_2(NCS)_8(dppe)_2$	44.3	41.8 (1.2)	*b*	162.4 (1.4)	~402.1, 398.5	131.1 (1.9)	~285.8 sh; 284.7
VI	$(Bu_4N)Re(NCS)_4(dppe)$	44.5	42.1 (1.3)	163.5	162.4 (1.1)	402.3, 398.6	131.3 (1.8)	~286.4; 284.9
VII	$Re(NCS)_3(PEt_2Ph)(dppe)$	44.1	41.7 (1.2)	163.2	162.3 (1.1)	..., 398.5	130.9 (1.7)	*b*; 284.6
VIII	$Re(NCS)_3(PEt_2Ph)(bpy)$	44.4	41.8 (1.3)	163.3	162.2 (1.0)	400.2, 398.4	130.9 (1.7)	~285.9 sh; 284.7
IX	$Re(NCS)_3(PEt_2Ph)(phen)$	44.3	41.9 (1.4)	163.2	162.1 (1.0)	400.1, 398.4		*b*; 284.8

[a] All spectra are referenced to the carbon 1s binding energy of graphite taken as 284.0 eV; full-width half-maximum values (fwhm) of Re 4f$_{7/2}$, S 2p$_{3/2}$, and P 2p peaks are given in parentheses. [b] Not observed.

monodentate phosphines can indeed convert the green dimeric anion to the yellow-orange monomeric species. Second, we have found that the addition of a few drops of diethylphenylphosphine to an acetonitrile solution of I hastened its conversion to an orange species. The electronic absorption spectrum of this solution (maxima at 505 and 405 nm) is almost identical with that of $(Bu_4N)Re(NCS)_4(PEt_3)_2$ (Table I), thereby identifying the absorbing species as $[Re(NCS)_4(PEt_2Ph)_2]^-$ or some closely related entity.

(e) X-Ray Photoelectron Spectra (XPS). This investigation seemed appropriate in view of our previous studies on the XPS of salts of the $Re_2(NCS)_8^{2-}$ and $Re(NCS)_6^{2-}$ anions[22] and our current interest[23] in the possibility of using this spectroscopic technique to distinguish different modes of thiocyanate bonding. The core electron binding energies of the complexes in question are presented in Table II. First we note that the Re 4f binding energy spectra are consistent with the presence of rhenium(III).[22] If we internally reference the Re 4f binding energies given in Table II and those reported in ref 22 to the same internal standard, namely, a value of 285.0 eV for the C 1s energy of Bu_4N^+ and/or the organic phosphine and amine ligands, we find that the Re 4f energies of complexes I–IX are less than those of $(Bu_4N)_2Re(NCS)_6$ and $(Bu_4N)_2Re_2(NCS)_8$ by ~1.6 and ~1.0 eV, respectively. The lowering of the Re 4f binding energies relative to $(Bu_4N)_2Re_2(NCS)_8$ is probably due to the increase of the coordination number of 6 in the phosphine complexes which leads to a decrease in the positive charge at the metal centers.

The S 2p$_{3/2}$ and N 1s (398.5 eV) energies of thiocyanate are very similar to those of other complexes which contain either N-bonded or S-bonded thiocyanate.[23] However, one difference which we do note within the group of complexes reported here is that while the S 2p binding energy spectra of complexes VI–IX exhibit a well-resolved S 2p$_{1/2,3/2}$ doublet, this resolution is much less apparent in complexes I–V which contain both terminal Re–NCS and bridging Re–NCS–Re units. While differences between the S 2p binding energies of thiocyanate in these two different bonding modes are small,[23] if both structural units are present in the *same* complex they are likely to lead to a slight broadening of the S 2p doublet and loss in resolution of the 2p$_{1/2,3/2}$ components, as we have observed.

(f) Comments on the Different Reactivities of $Re_2X_8^{2-}$ (X = Cl or Br) and $Re_2(NCS)_8^{2-}$. Our earlier study[11] on the substitution of chloride by thiocyanate and that by Hendriksma,[24] who subsequently investigated the related selenocyanate system, clearly showed that the quadruple Re–Re bond could survive in an $[Re_2N_8]$ environment. The important question which now arises concerns the reasons why the reactions of $Re_2(NCS)_8^{2-}$ with tertiary phosphines lead to the immediate disruption of this metal–metal bond. There is no evidence for the formation of intermediates such as $Re_2(NCS)_6(PR_3)_2$ and reduced complexes $Re_2(NCS)_4(PR_3)_4$ analogous to the related chloride and bromide derivatives of these types.[1] While the reactions of $Re_2X_8^{2-}$ (X = Cl or Br) and $Re_2(NCS)_8^{2-}$ with tertiary phosphines may of course proceed by quite different reaction mechanisms,[25,26] we also believe that in $Re_2(NCS)_8^{2-}$ the metal–metal bond is significantly weaker than in $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$ thereby leading to its cleavage upon reaction with phosphines. Our reason for proposing this possibility stems from a reconsideration of our earlier analysis of the electronic absorption spectrum of $Re_2(NCS)_8^{2-}$.[11] In contrast to $Re_2X_8^{2-}$ and $Re_2X_6(PR_3)_2$ which exhibit their $\delta \rightarrow \delta^*$ transitions at ca. 700 nm,[1,27-29] this electronic transition is located at a much lower energy in $Re_2(NCS)_8^{2-}$ (ca. 1000 nm). Furthermore, the other electronic absorption bands associated with this anion (520 (sh) and 460 nm)[11] are likewise at lower energies than the related bands in the spectra of $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$,[27-29] implying that the metal–metal bond is weaker in $Re_2(NCS)_8^{2-}$. Coordination of ligands such as tertiary phosphines, perhaps as metal–metal bonded intermediates of the type $[Re_2(NCS)_8L_2]^{2-}$ which contain axially bound L, is presumably sufficient to so further weaken the metal–metal bond that conversion to thermodynamically favored six-coordinated complexes takes place. The reactions of tertiary phosphines with $(Bu_4N)_2Re_2(NCS)_8$ therefore provide the first examples where cleavage of the quadruple Re–Re bond is the rule rather than the exception.

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Registry No. I, 63848-83-9; II, 63848-81-7; III, 15213-70-4; IV, 63848-77-1; V, 63848-79-3; VI, 63848-75-9; VII, 63848-73-7; VIII, 63848-72-6; IX, 63848-71-5; X, 63848-70-4; $(Bu_4N)_2Re_2(NCS)_8$, 16591-28-9.

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contaminant. Also, the molar extinction coefficients previously reported for $(Bu_4N)_2Re_2(NCS)_8(PPh_3)_2$ (see Table III of ref 11) should be increased by a factor of 2, since these values were calculated[11] for the monomeric formulation.
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Contribution from the Department of Chemistry, University of California,
and the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

A Kinetic Study of the Hydrolysis of 2-Germaacetate in Neutral and Alkaline Solutions

DUCK J. YANG and WILLIAM L. JOLLY*

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In neutral and alkaline solutions, the 2-germaacetate ion decomposes to give germane and bicarbonate (or carbonate): $GeH_3CO_2^- + H_2O \rightarrow GeH_4 + HCO_3^-$. The rate of this decarboxylation is pH independent and is first order in the germaacetate ion. The rate constant at 60 °C and ionic strength 1.0 is 1.62×10^{-5} s^{-1}; the activation energy is 28.6 kcal/mol. In strongly alkaline solutions (especially at hydroxide concentrations above 1 M), a second decomposition reaction, producing hydrogen and the insoluble brown polymer $H_2Ge_2O_3 \cdot xH_2O$, competes with the decarboxylation: $2GeH_3CO_2^- + 2OH^- + (3 + x)H_2O \rightarrow 6H_2 + H_2Ge_2O_3 \cdot xH_2O + 2CO_3^{2-}$. The rate of the latter reaction is first order in germaacetate ion and is inversely proportional to the Hammett acidity function h_-, i.e., first order in hydroxide ion; $-d \ln (GeH_3CO_2^-)/dt = k(OH^-)$. At 60 °C, $k = 2.0 \times 10^{-5}$ M^{-1} s^{-1}; the activation energy is 20.8 kcal/mol. Probable mechanisms of the reactions are discussed.

Introduction

It has previously been shown that hot aqueous solutions of potassium 2-germaacetate decompose to give germane and bicarbonate.[1] In this study we investigated the kinetics of the reaction from pH 6 to pH ~15 in the temperature interval 45–75 °C to obtain information regarding the mechanism of the reaction and to allow comparison with similar data for the decarboxylation of organic carboxylates. We discovered that a second decomposition reaction (involving the formation of hydrogen and a brown precipitate) occurs concurrently in the strongly alkaline solutions. We identified the products, established the stoichiometry, and studied the kinetics of this reaction.

Experimental Section

General Information. Manipulations were carried out using a vacuum line or a nitrogen-filled glovebag. Commercial 1,2-dimethoxyethane was dried with potassium hydroxide, filtered, refluxed with sodium metal, and then distilled. Germane gas from the Matheson Co. (minimum purity 99.8%) was used without further purification. The identification of reaction products was aided by infrared spectrometry with a Perkin-Elmer Infracord spectrometer (Model 337) and by mass spectrometry with a Finnigan Instruments Corp. quadrupole mass spectrometer.

Preparation and Analysis of GeH_3CO_2K. A solution of potassium germyl in 1,2-dimethoxyethane was prepared by a method similar to that of Dreyfuss and Jolly.[2] The solution of $KGeH_3$ was stirred and shaken under approximately 1 atm pressure of carbon dioxide in an ice bath. After about 2 h, when the pressure in the closed system had become constant, the precipitated product was collected by suction filtration on a frit.

A 1.228-mmol sample of GeH_3CO_2K was heated in a sealed tube at 510 °C for 24 h. The pyrolysis products were analyzed as described by Kuznesof and Jolly.[1] Sample purity was calculated on the basis of the reaction $2GeH_3CO_2K \rightarrow 3H_2 + CO + 2Ge + K_2CO_3$. The purity was 97.0% based on the total amount of noncondensable gas (collected 2.382 mmol, theory 2.456 mmol), and 99.0% based on the carbon dioxide liberated upon acidification of the residue (collected 0.608 mmol, theory 0.614 mmol).

A 1.016-mmol sample of GeH_3CO_2K was treated with 100 mL of 1 M NaOH in a Teflon-lined reaction vessel at 60 °C for 100 h. Germane gas (0.368 mmol) was isolated from the volatile products. Germanium in the solution was analyzed by the mannitol method[3] after treatment with acid and peroxide to ensure that all the germanium was in the +4 oxidation state. The solution was found to contain 0.631 mmol of Ge. The total Ge found, 0.999 mmol, corresponds to a purity of 98.3%.

Chemical Analysis of the Dark Brown Compound. A dark brown precipitate was obtained by heating a solution of GeH_3CO_2K in 7 M NaOH at 75 °C for 1 h. The material was centrifuged and washed with degassed distilled water until the wash water was neutral. The sample was kept for several days at 0 °C in an evacuated system containing Drierite. The dehydrated sample was observed to be darker in color than the original wet sample. The reducing power per gram of sample was determined by treatment with a known excess of triiodide (under argon in the dark) followed by titration with standard thiosulfate solution, and the number of moles of germanium per gram of sample was measured by the mannitol method.[3] The reducing power per gram of sample was found to be 20.77 and 20.70 mequiv/g, average 20.74 mequiv/g. The number of millimoles of germanium per gram of sample was found to be 10.54, 10.86, and 10.84 mmol/g, average 10.75 mmol/g.

Alkali-digested germanous hydroxide was prepared by digestion of fresh germanous hydroxide[4] in 7 M NaOH at 75 °C for 1 h, followed by the same purification as described for the dark brown compound. Nujol mull infrared spectra of the dried dark brown compound and of alkali-digested germanous hydroxide are shown in Figure 1.

Procedure for Kinetic Study. A solution of GeH_3CO_2K (ca. 10^{-2} M in a buffer solution) was prepared at 0 °C. The ionic strength of the solutions in the pH range 6–14 was adjusted to $\mu = 1.0$ by appropriate addition of potassium chloride. The solution was placed in a flask with a magnetic stirring bar and connected to a vacuum line by means of a glass joint attached to a stopcock. The flask was evacuated while stirring the solution at 0 °C, and the solution was then warmed to the reaction temperature in a thermostated (±0.1 °C) oil bath. At measured intervals the volatile reaction products which formed in the 20-mL space over the solution in the reaction