

high basicities, not only because of their negative charges but also because of the intrinsic basicities of the ligand acetato groups resulting from their inherent tendency (unlike the oxalato groups of **9**) to dechelate readily.^{27,28}

It is also significant that a recent study²⁹ of the first μ -OH bridge cleavage of the heteronuclear di- μ complex ion $[(en)_2Cr(OH)_2Co(en)_2]^{4+}$ fits into the general scheme with the proviso that only the water-catalyzed process contributes. For this complex, k_0 has a value of $\sim 10^{-2} s^{-1}$ at 25 °C, very much more rapid than the corresponding value of $\sim 10^{-5}$ for reactants **4**^{18,19} and **6**,²³ though closely comparable to that for the singly bridged species **7**, for which k_0 is found to have a value³⁰ of about $6 \times 10^{-3} s^{-1}$. A further study³¹ involving the homonuclear di- μ chromium(III) complex ion $[(en)_2Cr(OH)_2Cr(en)_2]^{4+}$ exhibits properties similar to its heteronuclear analogue, with a value for k_0 of $7 \times 10^{-3} s^{-1}$ at 25 °C.

Finally, it should be noted that the limited deuterium solvent isotope effect data obtained in our study are completely consistent with the mechanistic suppositions. As shown in Table I, both the "slow" and "fast" reactions are more rapid in heavy water, the factor being about 2 for the former and 3.5 for the latter. While the proton-catalyzed step described by $k_2[H^+]$ might presumably be somewhat decelerated in D₂O solvent if direct proton transfer is the process involved, this effect is apparently overwhelmed by the positive effect accompanying the proton preequilibration. The predicted factor³² for a protonated intermediate which is a moderately strong acid (see association constant values in Table II, footnoted *c* and *d*) is close to 3, in reasonable agreement with the observed experimental value of 3.5 for the "fast" reaction. For the second μ -OH bond fission (the "slow" reaction), the factor is somewhat smaller, possibly because there is an appreciable isotope effect in the opposite direction, associated with the direct proton transfer in the much slower rate-determining step governed by k_2 .

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References and Notes

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- (13) Diaprep, Inc., Milwaukee, Wis.
- (14) Using the values of the derived constants and eq 2 from ref 3, we calculate values for k_{obs}^* of 0.04, 2.0, 7.7, and 25.5 M⁻¹ s⁻¹ at acidities of 0.008, 0.164, 0.595, and 1.955 M, to be compared with our experimental values of 0.02, 2.0, 8.9, and 22.6 (run no. 7 or 8, 21, 26, and 29).
- (15) (a) This is mathematically identical with eq 2 of ref 3 mentioned in footnote 14 but is in a form more suited to our later analysis of the mechanism. (b) Changing the supporting electrolyte from NaNO₃ to NaClO₄ does slightly accelerate the reaction (cf. run 9 or 10 with 11) but reduction of the ionic strength from 2.0 to 1.0 has little effect (cf. run 6 with 9 or 10). It is possible that use of LiClO₄ rather than NaNO₃ might have been preferable in an acid-dependency study such as this. However, our double-reciprocal plotting procedure favors the low-[H⁺] data, where substitution of Na⁺ for H⁺ is minimal.
- (16) Thacker and Higginson's values³ for k_{obs}^* (25 °C, *I* = 1.0 M (NaClO₄)) are 0.35, 0.135, and 0.047 s⁻¹ at acidities of 0.02, 0.008, and 0.003 M, respectively. Our calculated values according to eq 1 are 0.16, 0.035, and 0.006 s⁻¹ at the same acidities but at *I* = 2.0 M (NaNO₃).
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- (28) However, reactant **8** also shows the $k_2[H^+]$ path, though there are no obvious protonation sites on this species other than the μ -OH bridge. Nevertheless, the activation energy for this process is close to 16 kcal/mol, identical with that for our system, for which a rough average value is obtainable by comparing the data of runs 17, 19, and 23 with those of runs 18, 20, and 24, respectively (Table I), utilizing the Arrhenius equation.
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Thiolato and Selenido Complexes of Rhodium(III)

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Three routes for the synthesis of dithiolato- and diselenido[difluoro-3,3'-(trimethylenedinitrilo)bis(2-pentanone oximate)borate]rhodium(III) complexes, $(RE)_2[C_2(DO)(DOBF_2)]Rh^{III}$ (*E* = S, Se), have been demonstrated. These are (1) $[C_2(DO)(DOBF_2)]Rh^I + REER$, (2) $[C_2(DO)(DOBF_2)]Rh^I + 2REH$, and (3) $Cl_2[C_2(DO)(DOBF_2)]Rh^{III} + 2RE^-$. These reactions have been expanded to include germanium-bearing sulfur and selenium substituents. The synthesis and physical properties of two hydrosulfidorhodium complexes, $(HS)_2[C_2(DO)(DOBF_2)]Rh^{III}$ and $(SH)(H)[C_2(DO)(DOBF_2)]Rh^{III}$, are also discussed.

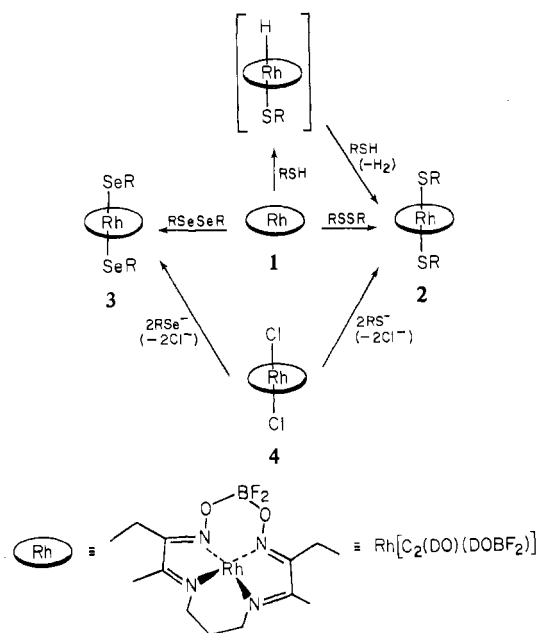
Introduction

We are presently engaged in the synthesis and characterization of compounds comprised of heavy elements covalently bound in a linear array. Our synthetic approach to this problem has centered about the oxidative addition^{1,2} of disulfides and diselenides to a square-planar, macrocyclic rhodium(I) complex. The desired one-dimensional character

of the heavy-atom backbone is ensured by the rigorous geometric demands of the rigidly planar, tetradentate ligand.

The development of one-dimensional materials has been the subject of considerable interest during the past decade. Activity has recently intensified due to the demonstration of highly anisotropic electrical conduction in some of these materials.³ We expect compounds of the type described herein

Scheme I



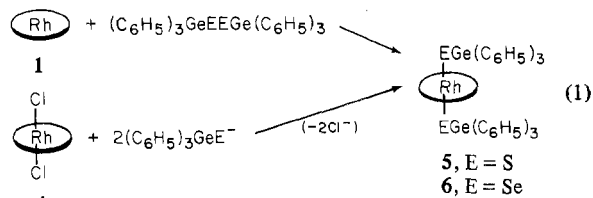
to be of future interest in the area of one-dimensional conductors.

Results and Discussion

For the past decade, it has been our long-range goal to realize the synthesis of a one-dimensional, soluble polymer comprised of a heavy-atom backbone surrounded by organic ligands. Our early work in this area centered about d^8 square-planar complexes which tend to stack in the solid state affording one-dimensional metallic axes.^{4,5} Our next approach employed group 4A (Ge, Sn) metal atom chains with appended transition metal groups.⁶ Rationalization of such a choice comes from the fact that spectral data and calculations⁷ suggest a suitable band gap for germanium chains such that conduction might result upon introduction of electrons from appended, electron-rich transition metal groups. Herein, we report our most recent synthetic approach to this problem.

With respect to the oxidative addition reaction, the [difluoro-3,3'-(trimethylenedinitrilo)bis(2-pentanone oximate)borate]rhodium(I) complex **1**, $\text{Rh}[\text{C}_2(\text{DO})(\text{DOBF}_2)]$, is the most reactive neutral, d^8 complex yet isolated. Alkyl halides and tosylates generally undergo the addition by an $\text{S}_{\text{N}}2$ mechanism.⁸ Presently, we report that disulfides and diselenides oxidatively add to $\text{Rh}[\text{C}_2(\text{DO})(\text{DOBF}_2)]$. Treatment of the Rh(I) complex **1** with organic disulfides in THF affords the corresponding dithiolato complexes of $[\text{C}_2(\text{DO})(\text{DOBF}_2)]\text{Rh}^{\text{III}}$, **2** (Scheme I). Organic diselenides react in an analogous fashion, affording diselenido complexes of $[\text{C}_2(\text{DO})(\text{DOBF}_2)]\text{Rh}^{\text{III}}$, **3**. The oxidative addition of disulfides^{9,10} and diselenides¹⁰ to other low-valent transition metal complexes has been previously reported. The same dithiolato complexes **2** are formed in the reaction of the rhodium(I) complex **1** with 2 equiv of thiol.¹¹ Although we have not rigorously demonstrated its formation, hydrogen is presumed to be the other product from the reaction. It is likely that this reaction involves an intermediate (thiolato)(hydrido)rhodium(III) complex which forms upon attack of $\text{Rh}[\text{C}_2(\text{DO})(\text{DOBF}_2)]$ by the first equivalent of thiol. This intermediate and a second equivalent of RSH could then form the final observed product. A third general synthetic route to complexes **2** and **3** involves the reaction of dichloro[difluoro-3,3'-(trimethylenedinitrilo)bis(2-pentanone oximate)borate]rhodium(III), **4**, $[\text{C}_2(\text{DO})(\text{DOBF}_2)]\text{RhCl}_2$, with alkyl or aryl thiolates and selenides, respectively.

These general reactions have been expanded to include germanium-bearing sulfur and selenium substituents. Treatment of the Rh(I) complex **1** with bis(triphenylgermanium) disulfide in THF affords the oxidative addition adduct $(\text{Ph}_3\text{GeS})_2[\text{C}_2(\text{DO})(\text{DOBF}_2)]\text{Rh}^{\text{III}}$, **5** (eq 1). This

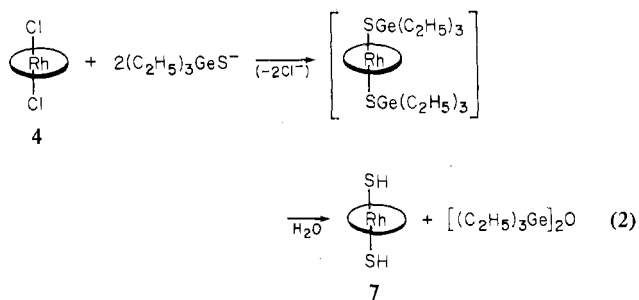


same compound is formed in the reaction of the dichloro complex **4** with sodium triphenylgermanium sulfide in acetonitrile.

The previously unknown bis(triphenylgermanium) diselenide was synthesized by treatment of triphenylgermanium bromide with sodium selenide followed by oxidation with methane sulfonyl chloride. Oxidative addition of $(\text{C}_6\text{H}_5)_3\text{GeSeSeGe}(\text{C}_6\text{H}_5)_3$ to $\text{Rh}[\text{C}_2(\text{DO})(\text{DOBF}_2)]$, **1**, resulted in $(\text{Ph}_3\text{GeSe})_2[\text{C}_2(\text{DO})(\text{DOBF}_2)]\text{Rh}^{\text{III}}$, **6** (eq 1). The diselenido complex **6** also can be formed by treating $[\text{C}_2(\text{DO})(\text{DOBF}_2)]\text{RhCl}_2$, **4**, with sodium triphenylgermanium selenide in acetonitrile.

A three-dimensional x-ray diffraction study¹² of $(\text{PhSe})_2[\text{C}_2(\text{DO})(\text{DOBF}_2)]\text{Rh}^{\text{III}}$, **3** ($\text{R} = \text{C}_6\text{H}_5$), revealed the expected structural features. The complex displays octahedral geometry about the rhodium, which lies in the center of the plane of the four nitrogen atoms of the macrocycle. The phenyl selenido ligands occupy the two remaining trans positions.

Both bridged and monodentate transition metal thiols are extremely rare. Only a very few such complexes have been reported.¹³ The novel complex $(\text{HS})_2[\text{C}_2(\text{DO})(\text{DOBF}_2)]\text{Rh}^{\text{III}}$, **7**, was formed in high yield as the unexpected product from the reaction of the dichloro complex **4** with an excess of sodium triethylgermanium sulfide in acetonitrile. The dithiol complex **7** is presumed to result from the hydrolysis of the expected $(\text{Et}_3\text{GeS})_2[\text{C}_2(\text{DO})(\text{DOBF}_2)]\text{Rh}^{\text{III}}$ (eq 2).



$[\text{C}_2(\text{DO})(\text{DOBF}_2)]\text{Rh}(\text{SH})_2$, **7**, is indefinitely air stable in the solid state, although air stable in solution for only a period of hours. The complex exhibits a very weak ν_{SH} at 2580 cm^{-1} , characteristic of organic thiols. The NMR spectrum in CD_3CN exhibits a single broadened peak at $\delta -1.55$ ppm assigned to the SH ligands. The thiol protons are exchangeable with H_2O and D_2O at a rate which is slow on the NMR time scale. This exchange provides a rationalization for the broadened singlet observed for the thiol protons rather than the doublet which might have been expected (^{103}Rh , $S = 1/2$) in the absence of exchange.

A rhodium monothiol was prepared by adding 1 equiv of hydrogen sulfide to the rhodium(I) complex **1** (eq 3). This

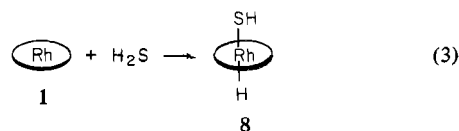


Table I. Preparation and Characterization of $[C_2(DO)(DOBF_2)]Rh(ER)_2$ Complexes; E = S, Se

$[C_2(DO)(DOBF_2)]-$ $Rh(ER)_2$				Analysis, %																
No.	E	R	Prepn ^{a,b} (% yield)	IR freq, ^c cm^{-1}	Calcd					Found										
					C	H	N	S	Se	C	H	N	S	Se						
2a	S	CH ₃	A (85)		35.25	5.53	10.92	12.51			35.20	5.49	10.76							
			B (33)													34.90	5.38	10.73		
			C (76)																	
2b	S	C ₆ H ₅	A (75)	ν_{Ph} 3030, 1425, 740	47.18	5.08	8.82	10.07			46.88	5.10	8.62							
			B (87)													46.85	5.14	8.71	9.91	
			C (65)																	
2c	S	CH ₃ C=O	A (63)	ν_{CO} 1620	35.93	4.97	9.86	11.28			35.55	4.79		11.41						
			B (45)													35.37	4.93	9.80		
			C (55)																	
2d	S	<i>p</i> -C ₆ H ₅ NH ₂	A (84)	ν_{NH} 3450, 3340, 3200 ν_{N-Ph} 1275	45.10	5.14	12.60	9.63			44.62	5.28	12.21	9.38						
3a	Se	CH ₃	A (52) C (42)		29.73	4.66	9.25			26.06	29.75	4.55	9.02		26.28					
3b	Se	C ₆ H ₅	A (62)	ν_{Ph} 3020, 1420, 740	41.12	4.42	7.67			21.63	41.14	4.38	7.52		21.60					
5	S	Ge(C ₆ H ₅) ₃	A (33)	ν_{Ph} 3020, 1420, 725	53.99	4.81	5.14	5.88			53.54	4.84		5.91						
			C (55)													54.06	4.89	5.09	5.95	
6	Se	Ge(C ₆ H ₅) ₃	A (58)	ν_{Ph} 3040, 1430, 735	49.71	4.43	4.73			13.34	49.29	4.38	4.99		13.11					
			C (40)													49.08	4.40	4.77	13.8	

^a A = $Rh[C_2(DO)(DOBF_2)] + REER$ (E = S, Se); B = $Rh[C_2(DO)(DOBF_2)] + 2RSH$; C = $[C_2(DO)(DOBF_2)]RhCl_2 + 2RE^-$ (RE = NaER), REH + N(CH₂CH₃)₃ (E = S, Se). ^b Isolated yields. ^c All of the complexes exhibit the following infrared stretching frequencies characteristic of the macrocyclic ligand: ν_{CN} 1600, 1525 cm^{-1} ; ν_{NO} 1120 cm^{-1} ; ν_{BO} 1170, 810 cm^{-1} ; ν_{BF} 1005 cm^{-1} . All IR spectra were obtained as KBr pellets.

reaction was carried out in tetrahydrofuran, a solvent in which the resulting (HS)(H)[C₂(DO)(DOBF₂)]Rh^{III}, **8**, is insoluble. The expected ν_{SH} in the monothiol **8** is apparently too weak to be detected. The rhodium hydride stretch appears as a strong band at 1910 cm^{-1} . Compound **8** is unstable in solution, reverting back to **1** via reductive elimination of hydrogen sulfide.

Transition metal thiols constitute a unique class of compounds whose synthetic utility has not yet been explored. We expect these complexes to prove useful as synthetic intermediates.

Experimental Section

All reactions were performed under a nitrogen atmosphere. Nitrogen (Liquid Carbonic) was further purified by passage through a BASF catalyst in the standard fashion. Tetrahydrofuran and acetonitrile were distilled from calcium hydride just prior to use. Benzene was distilled from Red-al, a 70% solution of sodium bis-(2-methoxyethoxy)aluminum hydride in benzene (Aldrich). All other solvents, unless otherwise noted, were of reagent grade and used without further purification.

Commercial triethylamine, dimethyl disulfide, thioacetic acid, benzenethiol, and methanesulfonyl chloride were all distilled prior to use and stored over 4A Linde molecular sieves. Gaseous methyl mercaptan and hydrogen sulfide were dried by passage through 3A Linde molecular sieves. Diphenyl disulfide was twice recrystallized from hot/cold absolute ethanol and dried under vacuum for 24 h. Technical grade 4-aminophenyl disulfide (Aldrich) was recrystallized from hot benzene/hexane to a constant melting point of 75–77 °C. Commercial dimethyl diselenide (Alfa, Ventron), diphenyl diselenide (Eastman Kodak), sodium selenide (Alfa, Ventron), and triphenylgermanium bromide (Alfa, Ventron) were used as obtained without further purification. Acetyl sulfonyl chloride,¹⁴ methaneselenol,¹⁵ sodium methyl selenide,¹⁵ bis(triphenylgermanium) disulfide¹⁶, sodium triphenylgermaniumthiol,¹⁶ and triethylgermaniumthiol¹⁷ were prepared as previously described. The preparations of $Rh[C_2(DO)(DOBF_2)]$ and $[C_2(DO)(DOBF_2)]RhCl_2$ were described^{8a} in an earlier paper of this series.

Elemental analyses were performed by the microanalytical laboratory of the Stanford University Department of Chemistry. Infrared spectra were recorded on a Perkin-Elmer Model 457 grating spectrometer. Nuclear magnetic resonance spectra were recorded on a Varian T-60 instrument and chemical shifts are reported relative to tetramethylsilane (δ 0.0).

Table I summarizes the methods of preparation and the characterization of the $[C_2(DO)(DOBF_2)]Rh(ER)_2$ complexes (E = S, Se) reported herein.

Acetyl Disulfide. To freshly distilled acetyl sulfonyl chloride (3.67 g, 33 mmol) was added dropwise thioacetic acid (2.53 g, 33 mmol). After the exothermic reaction subsided, the mixture was heated to 80–100 °C for 2 h. The reaction mixture was twice distilled in vacuo and the fraction with bp 100–110 °C (15 mm) was collected as a very pale yellow liquid (3.2 g, 64%).

Sodium Triphenylgermanium Selenide. To a suspension of 2.0 g (16 mmol) Na₂Se in 30 ml of absolute ethanol was added dropwise a solution of 2.0 g (5.2 mmol) of triphenylgermanium bromide in 30 ml of benzene. After 15 min of additional stirring, the solvent was removed under vacuum (0.01 mm) and the resulting residue extracted with hot benzene and filtered. The filtrate was used as a solution without further purification.

Bis(triphenylgermanium) Diselenide. A solution of sodium triphenylgermanium selenide in benzene was treated with an excess of methanesulfonyl chloride. An immediate reaction occurred with the precipitation of an orange powder. Recrystallization from benzene afforded orange crystallites, mp 140–171 °C dec. Spectral data: IR (KBr pellet) ν_{Ph} 3060, 1480, 1430, 1090, 730, 695 cm^{-1} , ν_{Se-Ge} 290 cm^{-1} ; NMR (CCl₄) δ 7.4 (m). Anal. Calcd for C₃₆H₃₀Ge₂Se₂: C, 56.47; H, 3.95; Se, 20.62. Found: C, 56.38; H, 3.90; Se, 19.94.

Bis(methanethiolato)[difluoro-3,3'-(trimethylenedinitrilo)bis(2-pentanone oximate)borate]rhodium(III) (2a). Method A. To a solution of $Rh[C_2(DO)(DOBF_2)]$, **1** (100 mg, 0.239 mmol), in 10 ml of THF was added via syringe an excess of dimethyl disulfide (50 μ l, 0.56 mmol). A pale orange solution with a deep red precipitate formed immediately. After 10 min of stirring, the product was collected by filtration and washed with diethyl ether. Recrystallization from acetonitrile afforded red crystals (103 mg, 85%); mol wt calcd for C₁₅H₂₈BF₂N₄O₂RhS₂, 512; found, 506 in dichloromethane (by osmometry).

Method B. Methanethiol was bubbled through a solution of $Rh[C_2(DO)(DOBF_2)]$ (100 mg, 0.239 mmol) in 10 ml of THF. After 30 min, a red precipitate formed, was collected by filtration, and washed with diethyl ether. Recrystallization from acetonitrile afforded red crystals (40 mg, 33%).

Method C. Methanethiol was bubbled through a solution of $[C_2(DO)(DOBF_2)]RhCl_2$, **4** (25 mg, 0.051 mmol), and triethylamine (70 μ l, 0.50 mmol) in 5 ml of acetonitrile for 20 min. The solvent was removed under reduced pressure and the resulting residue crystallized from acetonitrile affording red crystals (20 mg, 76%).

Thiolato complexes **2b–2d** and **5** and selenido complexes **3a**, **3b**, and **6** were prepared employing similar procedures (Table I).

Bis(hydrosulfido)[difluoro-3,3'-(trimethylenedinitrilo)bis(2-pentanone oximate)borate]rhodium(III) (7). To a solution of $[C_2(DO)(DOBF_2)]RhCl_2$, **4** (100 mg, 0.205 mmol), in 10 ml of CH₃CN was added a solution of sodium triethylgermaniumthiol (175 mg, 0.81 mmol) in 2 ml of methanol. The color of the solution rapidly changed from

yellow to orange with precipitation of a colorless solid. After being stirred for 4 h, the mixture was filtered. The solvent was removed from the orange filtrate under reduced pressure. The resulting orange solid was then washed with 2×10 ml of diethyl ether, 3×10 ml of water, 1 ml of absolute ethanol, and finally 2×10 ml of diethyl ether. The resulting bright orange solid (75 mg, 76%) was recrystallized from acetonitrile under a nitrogen atmosphere affording orange crystallites. Spectral data: IR (KBr pellet) ν_{SH} 2580 cm^{-1} , ν_{CN} 1600, 1530 cm^{-1} , ν_{NO} 1115 cm^{-1} , ν_{BO} 810 cm^{-1} , ν_{BF} 995 cm^{-1} ; NMR (CD_3CN) δ -1.55 (br s, 2 H), δ 1.10 (t, $J = 8$ Hz, 6 H), δ 2.40 (s, 6 H), δ 2.45 (m, 2 H), δ 2.80 (q, $J = 8$ Hz, 4 H), δ 4.1 (br t, 4 H). Anal. Calcd for $\text{C}_{13}\text{H}_{24}\text{BF}_2\text{N}_4\text{O}_2\text{RhS}_2$: C, 32.24; H, 5.00; N, 11.57; S, 13.24. Found: C, 32.29; H, 5.04; N, 11.47; S, 13.01.

(Hydrosulfido)(hydrido)[difluoro-3,3'-(trimethylenedinitrilo)bis-(2-pentanone oximato)borate]rhodium(III) (8). Hydrogen sulfide was bubbled through a solution of $\text{Rh}[\text{C}_2(\text{DO})(\text{DOBF}_2)]_2$ (1 (100 mg, 0.239 mmol), in 10 ml of THF. The orange precipitate which formed immediately was collected by filtration and washed with diethyl ether (70 mg, 65%). Spectral data: IR (KBr pellet) $\nu_{\text{Rh-H}}$ 1910 cm^{-1} , ν_{CN} 1590, 1520 cm^{-1} , ν_{NO} 1115 cm^{-1} , ν_{BO} 1165, 810 cm^{-1} , ν_{BF} 990 cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_{24}\text{BF}_2\text{N}_4\text{O}_2\text{RhS}$: C, 34.54; H, 5.36; N, 12.40; S, 7.09. Found: C, 34.41; H, 5.36; N, 12.19; S, 7.26.

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Registry No. 1, 53335-25-4; 2a, 61129-06-4; 2b, 61129-07-5; 2c, 61129-08-6; 2d, 61193-32-6; 3a, 61129-09-7; 3b, 60224-27-3; 4, 61129-11-1; 5, 61129-10-0; 6, 61129-12-2; 7, 61193-33-7; 8, 61129-13-3; acetyl disulfide, 505-73-7; sodium triphenylgermanium selenide, 61104-43-6; $\text{Ge}(\text{C}_6\text{H}_5)_3\text{SeSeGe}(\text{C}_6\text{H}_5)_3$, 61104-44-7; CH_3SSCH_3 , 624-92-0; $\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5$, 882-33-7; *p*- $\text{C}_6\text{H}_5\text{NH}_2\text{SS-}p$ - $\text{C}_6\text{H}_5\text{NH}_2$, 722-27-0; $\text{CH}_3\text{SeSeCH}_3$, 7101-31-7; $\text{C}_6\text{H}_5\text{SeSeC}_6\text{H}_5$, 1666-13-3; $\text{Ge}(\text{C}_6\text{H}_5)_3\text{SSGe}(\text{C}_6\text{H}_5)_3$, 61104-37-8; acetyl sulfonyl chloride, 18369-83-0; thioacetic acid, 507-09-5; Na_2Se , 1313-85-5; triphenylgermanium bromide, 3005-32-1.

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Pentacoordinate Nickel(II) Complexes of Monodentate Ligands. Complexes of Trimethylstibine

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Five new complexes of nickel(II) and trimethylstibine, $\text{NiX}_2(\text{SbMe}_3)_3$ ($\text{X} = \text{Cl, Br, I, CN, SbMe}_3$), have been synthesized and characterized. To our knowledge, these are the first examples of stable Ni(II) complexes containing Ni-Sb bonds in which neither steric nor chelating properties of the ligand can be responsible for the observed stability. Except $[\text{Ni}(\text{SbMe}_3)_5](\text{BF}_4)_2$ which is a 2:1 electrolyte, they are molecular, diamagnetic complexes. On the basis of their variable-temperature electronic spectra in the solid state and in solution in organic solvents, they have been assigned a trans trigonal-bipyramidal structure (D_{3h} symmetry). The two ligand field bands attributed to the allowed ${}^1A'_1 \rightarrow {}^1E'$ and the symmetry-forbidden ${}^1A'_1 \rightarrow {}^1E''$ transition are present for all complexes. At low temperature, improved resolution of the spectra is marked by an increase in symmetry and in the extinction coefficient of the lower energy ligand field band. The stability of the complexes follows the order $\text{I} > \text{Br} > \text{SbMe}_3 \gg \text{CN} > \text{Cl}$. Only the first three derivatives have been isolated in the solid state. $[\text{Ni}(\text{SbMe}_3)_5](\text{BF}_4)_2$ represents one of the few Ni(II) pentacoordinate complexes with five identical ligands. They are all dissociated in solution at room temperature, even in the presence of excess SbMe_3 , but they are stable at low temperature. However no tetracoordinate species have been obtained. The particular influence of SbMe_3 in stabilizing pentacoordinate Ni(II) complexes is discussed by comparison with trimethylphosphine from the point of view of steric and electronic factors (polarizability and σ - and π -bonding abilities) of the ligands.

Introduction

It is well-known that monodentate tertiary phosphines, phosphites, and phosphonites readily form pentacoordinate low-spin complexes of the type NiX_2L_3 ($\text{X} = \text{halide or}$

pseudohalide) with nickel(II).¹ However, the kinetic and thermodynamic stabilities of these complexes, as well as their stereochemistries which depend on both electronic and steric effects, are not yet fully understood.

In recent years, particular attention has been focused on the geometrical structure and characterization of these complexes, in order to determine their preferred geometry: the trigonal

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