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Preparation of $S_7X^+MF_6^-$ (X = F, Cl; M = As, Sb) and Vibrational Spectra of the Series S_7X^+ (X = F, Cl, Br, I)[1]

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The salts $S_7F^+MF_6^-$ and $S_7Cl^+MF_6^-$ (M = As, Sb) have been prepared by reaction of $S_8^{2+}(MF_6^-)_2$ with NaF and KCl in liquid SO_2. In comparison to those of the known compounds $S_7Br^+MF_6^-$ and $S_7I^+MF_6^-$, their thermal stabilities are much smaller. The new products have been characterized by analytical and spectroscopic methods. IR and Ra spectra of the complete series $S_7X^+MF_6^-$ (X = F, Cl, Br, I; M = As, Sb) have been recorded and the SX and SS stretching vibrations can be assigned: $\nu(SF) = 804$, $\nu(SCl) = 528$, $\nu(SBr) = 416$, $\nu(SI) = 353$ cm^{-1}; $\nu(SS)$ for the ring system are found in the range 570–330 cm^{-1}.

Introduction

Clearly characterized compounds containing a covalent sulfur–iodine bond are rare.[2] This is due to their thermodynamic instabilities (BE(CF_3S–I) $\simeq$ 203 kJ/mol).[3] Sulfur–iodine compounds generally decompose in exergonic reactions far below room temperature with simultaneous formation of elemental iodine and disulfane species[4,5] (BE(–S–S–) $\simeq$ 320 kJ/mol).[3]

A much greater stability than for iodine sulfanes, such as CF_3SI, is observed for $(C_6H_5)_3CSI$[6,7] and for the sulfur–iodine cations S_7I^+[8-11] and $S_2I_4^{2+}$[2,10,11] prepared by Passmore and co-workers. All these compounds have been studied by X-ray diffraction. The salts $(CH_3)_2SI^+X^-$ ($X^- = SbCl_6^-, AsF_6^-$)[12] and $CF_3CH_3SI^+X^-$ ($X^- = AsF_6^-, SbF_6^-$)[13] have also been isolated and characterized by spectroscopic methods.

To continue our investigations of the sulfur–iodine bond, we attempted to obtain vibrational spectra of $S_7I^+MF_6^-$ (M = As, Sb). Because of the variety of bands in the expected range for ν(SI) between 300 and 400 cm^{-1}, its identification was extremely difficult.

The position of ν(SI) can be established with certainty if the preparation of the still unknown compounds $S_7Cl^+MF_6^-$ and $S_7F^+MF_6^-$ can be carried out and be compared to the frequencies in the well-known compounds $S_7I^+MF_6^-$ and $S_7Br^+MF_6^-$ (M = As, Sb). In this paper we report our investigations in this area.

Experimental Section

Materials and Apparatus. Literature methods were used for the synthesis of $S_4^{2+}(AsF_6^-)_2 \cdot nSO_2$,[14] $S_8^{2+}(MF_6^-)_2$ (M = As, Sb),[15] and $S_7X^+MF_6^-$ (X = Br, I; M = As, Sb).[16] Sulfur dioxide (Bayer AG) was stored over CaH_2. NaF, KCl, KBr, and KI (all from Merck) were dried by heating under vacuum before use.

Standard high-vacuum techniques were employed throughout all preparative procedures; nonvolatile compounds were handled in a dry N_2 atmosphere by using Schlenk techniques. All reactions were carried out in sealed double-arm vessels fitted with Young stopcocks. For separation of insoluble materials, fine-glass filters were placed between the arms of the vessel. Moisture was removed from all surfaces by flaming the vessels several times under vacuum.

Table I. Results of Mole Mass Determinations

compd	obsd values[a]	calcd values	% dev
$S_7F^+SbF_6^-$	496.1	479.2	+3.5
$S_7F^+AsF_6^-$	445.6	432.3	+3.1
$S_7Cl^+SbF_6^-$	515.0	495.6	+3.9
$S_7Cl^+AsF_6^-$	463.1	448.8	+3.2

[a] The observed values are averaged about five independent measurements.

IR spectra were recorded on a Perkin-Elmer Model 580 B spectrometer in a low-temperature cell at 193 K.[17] Samples of S_7X^+ salts were prepared in mixtures of Nujol (Merck, dried over CaH_2) and *n*-hexane (Merck, dried over sodium). The spectra were recorded by using CsBr windows in the range 4000–250 cm^{-1} with a resolution of 2.3 cm^{-1}. Ra spectra of $S_7X^+MF_6^-$ in SO_2 solution at room temperature were run on a Coderg T 800 spectrometer equipped with an Ar^+ laser (Spectra Physics) operating at 514.5 nm and a 850-mW laser power level. The maximum resolution was 5.0 cm^{-1}. All vibrational spectroscopic measurements showed reproducibility within ±5 cm^{-1}.

^{19}F NMR spectra in SO_2 solution at 213 K were recorded on a Bruker AM 300 spectrometer at 282.5 MHz in the range +200 to −200 ppm, positive shifts defined as downfield from the external standard $CFCl_3$. The pulse width was 1.5 μs, and 2048 scans were run for each spectrum; the maximum resolution was 3.4 Hz per data point.

Mass spectra were recorded with IE = 80 eV (Finnigan MAT spectrometer).

Chemical analyses were carried out by ion chromatography and X-ray fluorescence; mole mass determinations, by cryoscopic methods[18] in SO_2 solution. All melting points were measured with an accuracy of ±0.1 K; the reproducibility of the results was within ±3.5%.

Preparative Routes to $S_7X^+MF_6^-$ (X = F, Cl; M = As, Sb). 1. Reactions of $S_8^{2+}(MF_6^-)_2$ (M = As, Sb) with NaF and KCl. All reactions were carried out according to the procedures described by Passmore for the analogous compounds $S_7Br^+MF_6^-$ and $S_7I^+MF_6^-$ (M = As, Sb).

Equimolar amounts of $S_8^{2+}(MF_6^-)_2$ (M = As, Sb) and NaF (KCl) were placed under dry nitrogen in one side of a double arm vessel. After 5–7 mL of SO_2 was condensed onto the solids, the reaction mixtures were stirred for 14 days (4 days) at 218 K (233 K). During the reaction the color of the solutions changed from deep blue to various tones of green. In all cases a yellowish white precipitate was formed; this was identified by Ra spectra as a mixture of S_8 and EMF_6 (E = Na, K; M = As, Sb). The SO_2-soluble products were fritted into the other arm of the vessel, and after the solvent was removed by pumping at 213 K, green solids remained, which were dried under vacuum for 6 h at 213–223 K. The results of the mole mass determinations are summarized in Table I.

Characterization of $S_7X^+MF_6^-$ (X = F, Cl; M = As, Sb). (a) $S_7F^+MF_6^-$ (M = As, Sb). The relative proportions of sulfur and arsenic or antimony were reproducibly 7:1 with a deviation of 2% from the theoretical values.

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Experimental weight determinations of SO_2-soluble ($S_7F^+MF_6^-$) and insoluble (S_8, $NaMF_6$) products confirmed these results (deviations from calculated values ±5%). In the 80-eV mass spectrum of $S_7F^+SbF_6^-$ the following fragments can be identified at 310 K (*m/z*, assignment (%)): 224, S_7^+ (8); 192, S_6^+ (25); 160, S_5^+ (38); 128, S_4^+ (56); 96, S_3^+ (28); 64, S_2^+ (100); 19, F^+ (46); 197, SbF_4^+ (4.3); 178, SbF_3^+ (2.9); 140, SbF^+ (1.9); 121, Sb^+ (1.6).

The ^{19}F NMR spectrum of $S_7F^+MF_6^-$ (M = As, Sb) in SO_2 at 213 K shows in addition to the signal due to the anion ($\delta(AsF_6^-) = -55.33$ ppm; $\delta(SbF_6^-) = -112.22$ ppm) only one sharp singlet at −41.48 ppm ($S_7F^+AsF_6^-$) and −41.26 ppm ($S_7F^+SbF_6^-$), respectively. In each case the peak area ratio is 6:1.

$S_7F^+MF_6^-$ (M = As, Sb) decomposes completely in the solid state at room temperature with formation of elemental sulfur within a few minutes and in SO_2 solution within 40 min. Below 233 K it is stable for several months. The solubility of $S_7F^+MF_6^-$ (M = As, Sb) in HF is much less than that in SO_2, and it is insoluble in So_2ClF. Attempts to redissolve solid samples in fresh SO_2 result in decomposition.

(b) $S_7Cl^+MF_6^-$ (M = As, Sb). Relative proportions of chlorine, sulfur, and arsenic or antimony were reproducibly 1:7:1 with a deviation of 3% from the theoretical values.

In an 80-eV mass spectrum of $S_7Cl^+SbF_6^-$ the following fragments were identified at 330 K (*m/z*, assignment (%)): 224, S_7^+ (40); 192, S_6^+ (100); 160, S_5^+ (10); 128, S_4^+ (6); 96, S_3^+ (4); 64, S_2^+ (20); 35, $^{35}Cl^+$ (83); 37, $^{37}Cl^+$ (28); 197, SbF_4^+ (6); 178, SbF_3^+ (17); 140, SbF^+ (4), 121, Sb^+ (32).

$S_7Cl^+MF_6^-$ (M = As, Sb) is stable at room temperature for 30 min as a solid and for 60–80 min in a saturated SO_2 solution. It can be kept below 233 K without decomposition. The solubilities of $S_7Cl^+MF_6^-$ in SO_2, HF, and SO_2ClF are similar to those of $S_7F^+MF_6^-$.

2. Reactions of $S_4^{2+}(AsF_6^-)_2\cdot nSO_2$ ($n < 1$) with NaF and KCl. The reactions were carried out under the same conditions as described above. During the stirring time the color of the solutions changed first rapidly from yellow-gray to deep blue and then to green. Yellowish white precipitates were formed, which were identified as mixtures of S_8, $EAsF_6$ (E = Na, K), and unreacted NaF or KCl. Chemical analysis data and spectra of the isolated solids were identical with those obtained for the salts formed by reactions with S_8^{2+} salts.

Results and Discussion

Formation. Experimental weight and mole mass determinations as well as analytical data show that $S_7F^+MF_6^-$ and $S_7Cl^+MF_6^-$ (M = As, Sb) may be prepared quantitatively in liquid SO_2 at low temperatures according to eq 1.

$$S_8^{2+}(MF_6^-)_2 + EX \xrightarrow{SO_2} S_7X^+MF_6^- + EMF_6 + \tfrac{1}{8}S_8 \quad (1)$$

$$E = Na, K \qquad X = F, Cl \qquad M = As, Sb$$

Reactions of $S_4^{2+}(AsF_6^-)_2\cdot nSO_2$ and NaF or KCl lead to the same products. However, no reaction is observed between either S_8^{2+} or S_4^{2+} salts in SO_2 with KF even at higher temperatures.

Although some examples in the chemistry of chalcogen cations show that evidence of this type may be misleading, it is reasonable to conclude that in all reactions $S_7F^+MF_6^-$ and $S_7Cl^+MF_6^-$ (M = As, Sb) were formed in analogy to the S_7Br^+ and S_7I^+ salts.

The compound $S_8X^+MF_6^-$ (X = F, Cl; M = As, Sb), postulated to be formed in the first step of the reaction, was never found as a final product. In all cases a contraction of the sulfur ring from S_8 to S_7 was observed.

The square-planar S_4^{2+} cation evidently does not react with the halide ions F^- and Cl^-. In all cases $S_8^{2+}(AsF_6^-)_2$ is formed in SO_2 solutions of $S_4^{2+}(AsF_6^-)_2$ and EX (E = Na, K; X = F, Cl) before the reaction starts. This is consistent with former results,[16,19] where an equilibrium between S_8^{2+} and S_4^{2+} cations is postulated.

Passmore and co-workers[14] have already predicted and explained the instability of $S_7F^+MF_6^-$ and $S_7Cl^+MF_6^-$ (M = As, Sb) in comparison to S_7Br^+ and S_7I^+ salts on the basis of the greater thermodynamic stability of the disproportionation products S_nX_2 and SX_3^+ (X = F, Cl). Our spectroscopic investigations of the decomposition products confirm the formation of $SX_3^+MF_6^-$ (X = F, Cl; M = As, Sb). S_7F^+ and S_7Cl^+ cations were only formed over long reaction periods at low temperatures; in contrast to the iodo- and bromosulfur cations, their thermal stabilities were much smaller. This behavior agrees well with the concept of hard and soft acids and bases of Pearson.[20,21] The S_8^{2+} cation may be regarded as a soft acid; because of the increasing hardness of the halide ions from I^- to F^-, the thermal stability of products formed by reaction with the same soft acid decreases in the same series. The applicability of this concept leads to the conclusion that the preparation of stable cyclic sulfur cations with exocyclic ligands should be possible by reacting S_8^{2+} salts with soft bases.[22]

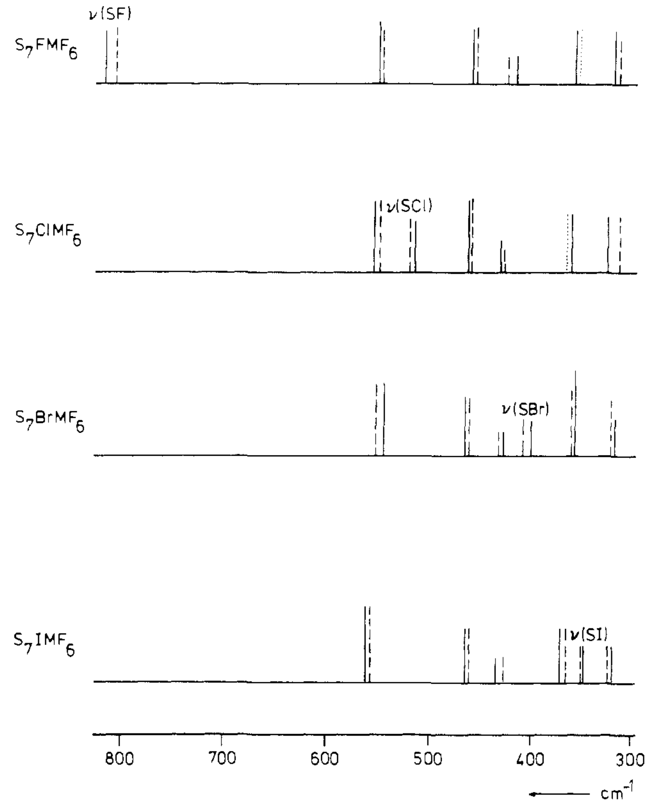

Figure 1. Relative positions and intensities of ν(SS) and ν(SX) in the IR spectra of $S_7X^+MF_6^-$ (X = F, Cl, Br, I; M = As, Sb): (—) SbF_6^-; (- - -) AsF_6^-; (···) covered by $\delta(AsF_6^-)$.

Discussion of the Spectroscopic Series $S_7X^+MF_6^-$ (X = F, Cl, Br, I; M = As, Sb). Although the crystal structures of $S_7I^+SbF_6^-$ and S_7Br^+ salts were already known, no accurate spectroscopic data had been obtained until now. For conclusive proof of the existence of the very unstable S_7X^+ cations (X = F, Cl), we need the comparison of the complete spectroscopic series $S_7X^+MF_6^-$ (X = F, Cl, Br, I; M = As, sb) with the isoelectronic and isostructural S_7O, prepared by Steudel and co-workers.[23]

IR and Ra data of $S_7X^+MF_6^-$ (X = F, Cl, Br, I; M = As, Sb) are summarized in Table II. The bands of the anions were found in all cases within the expected range. As shown in Figure 1, all IR spectra show five bands between 570 and 330 cm^{-1} that can be assigned to ν(SS) of the S_7 ring. While Steudel observes all SS stretching vibrations in the Ra spectrum, the IR spectrum of S_7O[24] shows only the five bands that are observed for the S_7X^+ cations.

Moreover, additional single bands were observed for each cation in the expected ranges of ν(SX) (X = F, Cl, Br, I). The comparison of the spectroscopic data provides an assignment for ν(SI) in S_7I^+ salts. The value 353 cm^{-1} (351 cm^{-1} for the SbF_6^- salt) is consistent with that found for ν(SI) in other iodosulfonium

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Table II. IR and Ra[a] Frequencies of S_7XMF_6 (X = F, Cl, Br, I; M = As, Sb) and of S_7O[b] in cm^{-1}[c]

S_7F^+				S_7Cl^+				S_7Br^+		S_7I^+		S_7O		
AsF_6^-		SbF_6^-		AsF_6^-		SbF_6^-		AsF_6^-	SbF_6^-	AsF_6^-	SbF_6^-			
Ra	IR	Ra	IR	Ra	IR	Ra	IR	IR	IR	IR	IR	Ra	IR	assgnt
678 (vs)	700 (s)			675 (vs)	705 (s)			704 (s)		700 (vs)				$\nu(AsF_6^-)$
582 (vw)														$\nu(AsF_6^-)$
375 (s)	395 (vs)			378 (s)	393 (vs)			394 (vs)		399 (vs)				$\delta(AsF_6^-)$
		655 (vs)	667 (vs)			655 (vs)	661 (vs)		662 (vs)		660 (s)			$\nu(SbF_6^-)$
		585 (vw)												$\nu(SbF_6^-)$
		280 (vs)	284 (vs)			281 (vs)	284 (vs)		284 (vs)		284 (vs)			$\delta(SbF_6^-)$
562 (m)	561 (ms)	560 (m)	565 (m)	563 (m)	564 (ms)	557 (m)	568 (ms)	567 (ms)	561 (ms)	571 (ms)	575 (ms)	575 (m)	570 (ms)	$\nu(SS)$
												534 (w)	n.o.	
475 (ms)	468 (m)	468 (m)	470 (m)	467 (ms)	471 (ms)	460 (m)	474 (ms)	472 (m)	474 (m)	470 (m)	472 (m)	517 (m)	496 (m)	
420 (m)	440 (w)	420 (mw)	431 (w)	425 (m)	440 (m)	425 (m)	442 (mw)	441 (w)	438 (w)	436 (w)	443 (w)	402 (w)	425 (w)	
365 (m)	370 (sh)*	366 (m)	373 (m)	362 (w)	376 (sh)*	360 (m)	373 (m)	368 (sh)*	362 (s)	374 (sh)*	380 (m)	372 (w/m)	371 (ms)	
												345 (m)	n.o.	
325 (ms)	328 (mw)	323 (m)	332 (m)	n.o.	325 (m)	321 (m)	336 (m)	330 (m)	329 (m)	335 (mw)	330 (mw)	325 (vs)	332 (m)	
295 (s)		*		300 (m)		296 (ms)						292 (s)		$\delta(SS)$
270 (mw)		270 (sh)*		265 (mw)		268 (sh)*						281 (m)		
225 (ms)		228 (s)		221 (ms)		220 (m)						232 (s)		
204 (m)												209 (w)		
187 (ms)		185 (ms)		185 (ms)		200 (s)						193 (m)		
155 (s)		155 (s)				161 (ms)						165 (s)		
143 (m)		145 (s)		145 (s)		140 (m)						158 (m)		
												129 (w–m)		
												1113 (vw)		
												1102 (w)	1105 (ms)	$\nu(SO)$
												1098 (vw)		
800 (w)	804 (m)	799 (w)	810 (m)											$\nu(SF)$
				535 (ms)	528 (m)	532 (ms)	526 (m)							$\nu(SCl)$
								416 (mw)	405 (mw)					$\nu(SBr)$
										353 (mw)	351 (mw)			$\nu(SI)$

[a] Measured in 8-mm tubes; in SO_2 solution at room temperature. [b] Solid-state measurement. [c] Asterisks indicate the frequency is obscured by vibrations of the anion.

cations, e.g. 395 cm^{-1} for $CH_3CF_3SI^+AsF_6^-$[13] or 332 cm^{-1} in $(CH_3)_2SI^+AsF$.[12] The Ra frequencies of $S_7X^+MF_6^-$ confirm the results of the IR data (Table II) and are in good agreement with the Ra spectrum of solid S_7O.

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Synthesis and Structural Characterization of Metallacarborane Poly(pyrazolyl)borate Complexes

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The mixed-ligand poly(1-pyrazolyl)borate–dicarbollide metallacarborane complexes *closo*-3-{η^3-HB(pz)$_3$}-3,1,2-RhC$_2$B$_9$H$_{11}$ (**3a**), *closo*-2-(η^3-HB(pz)$_3$)-2,1,7-RhC$_2$B$_9$H$_{11}$ (**3b**), and [*closo*-3-(η^2-Ph$_2$B(pz)$_2$)-3,1,2-NiC$_2$B$_9$H$_{11}$]$^-$ ([**5**]$^-$) (pz = 1-pyrazolyl) have been prepared and characterized by a combination of spectroscopic techniques, elemental analysis, and X-ray crystallography. Complex **3a** crystallizes in the space group $P2_1$ with a = 8.874 (1) Å, b = 10.786 (1) Å, c = 10.604 (1) Å, β = 109.284 (3)°, V = 960 Å^3, and Z = 2. Data were collected to a maximum of 2θ = 55°, giving 2322 unique reflections. The final discrepancy index was R = 0.042 (R_w = 0.054) for 1969 independent reflections. Complex **3b** crystallizes in the space group $C2/c$ with a = 14.830 (2) Å, b = 27.059 (3) Å, c = 20.298 (2) Å, β = 108.907 (3)°, V = 7706 Å^3, and Z = 16. Data were collected to a maximum of 2θ = 50°, giving 4672 unique reflections. The final discrepancy index was R = 0.048 (R_w = 0.063) for 3525 independent reflections. Compound [NMe$_4$][**5**] crystallizes in the space group $P2_1/a$ with a = 17.437 (6) Å, b = 9.631 (3) Å, c = 19.695 (4) Å, β = 92.271 (8)°, V = 3305 Å^3, and Z = 4. Data were collected to a maximum of 2θ = 45°, giving 4332 unique reflections. The final discrepancy index was R = 0.082 (R_w = 0.091) for 1585 independent reflections. The anion [**5**]$^-$ is oxidized by ferric chloride to the neutral species *closo*-3-(η^2-Ph$_2$B(pz)$_2$)-3,1,2-NiC$_2$B$_9$H$_{11}$ (**6**). NMR spectral data for **3a**, **3b**, and [**5**]$^-$ indicate fluxional solution behavior such that pyrazole ring environments are equilibrated on the NMR time scale. Complex [**5**]$^-$ exhibits an unusual carborane cage distorion resulting from an intramolecular influence of the axial phenyl group of the [η^2-Ph$_2$B(pz)$_2$]$^-$ ligand.

Introduction

The poly(pyrazolyl)borate[2] and dicarbollide[3] ligands were perhaps the most significant new ligand types to be introduced in the 1960s; large subareas of coordination and organometallic chemistry have now developed around each of these ligand systems. Despite the extensive and parallel development of the transition-metal chemistry involving each of these ligand types, no examples of metal complexes containing both dicarbollide and poly(pyrazolyl)borate ligands bound to the same metal center have previously been reported. Herein we report the synthesis and structural characterization of the first mixed-ligand sandwich complexes that contain both of these boron-supported ligand systems.

Notably, both the tris(1-pyrazolyl)borate ([RB(pz)$_3$]$^-$, pz = 1-pyrazolyl) and the isomeric dicarbollide ([*nido*-C$_2$B$_9$H$_{11}$]$^{2-}$) ligands bear a relationship to the cyclopentadienide ([C$_5$H$_5$]$^-$) ligand in so far as each of these ligands is capable of functioning as a six-electron donor in coordination compounds. Thus, either of these ligands may be used to form symmetrical bis(ligand) transition-metal complexes. However, these ligands differ from the cyclopentadienide ligand and from each other in important respects; the [RB(pz)$_3$]$^-$ ligands are uninegative σ-donors, whereas the [*nido*-C$_2$B$_9$H$_{11}$]$^{2-}$ ligands are dinegative π-donors. The dicarbollide ligands are also capable of functioning as formal four-electron π-donors in the "slipped" bonding mode,[3b] and hence may be compared with the [RB(pz)$_3$]$^-$ ligands, which exhibit the η^2-σ-bonding mode, as well as with the bidentate σ-donor bis(1-pyrazolyl)borate ([R$_2$B(pz)$_2$]$^-$) ligands.[2] The mixed-ligand sandwich complexes described herein represent the first examples of formal 18-electron, d^6 and d^8 metal *closo*-(η-R$_n$B(pz)$_{4-n}$)M(C$_2$B$_9$H$_{11}$) (n = 1, 2) species. Considering the great structural versatility of each of these ligand systems, innumerable other possibilities exist for mixed poly(pyrazolyl)borate–metallacarborane complexes.

Results and Discussion

Synthesis of Tris(1-pyrazolyl)borate Metallacarborane Complexes. Initial attempts to prepare mixed poly(1-pyrazolyl)borate–dicarbollide transition-metal complexes by direct reactions of the ligands and metal salts were unsuccessful due to the formation of symmetrical bis(ligand) complexes. For example, attempts to directly prepare the unsymmetrical cobalt complex *closo*-3-(η^3-HB(pz)$_3$)-3,1,2-CoC$_2$B$_9$H$_{11}$ resulted in a high yield of an orange crystalline salt composed of the symmetrical cationic[4] and anionic[3] cobalt sandwich complexes, as shown in eq 1. This

$$\begin{aligned}&2\mathrm{Na_2}[\textit{nido}\text{-}7,8\text{-}\mathrm{C_2B_9H_{11}}] + 2\mathrm{K}[\mathrm{HB(pz)_3}] + 3\mathrm{CoCl_2} \rightarrow \\ &[\mathrm{Co}(\eta^3\text{-}\mathrm{HB(pz)_3})_2]^+[\textit{commo}\text{-}3,1,2\text{-}\mathrm{Co}(3,1,2\text{-}\mathrm{C_2B_9H_{11}})_2]^- + \\ &\mathrm{Co} + 4\mathrm{NaCl} + 2\mathrm{KCl} \quad (1)\end{aligned}$$

salt was identified by a combination of NMR and IR spectroscopy and by a single-crystal X-ray analysis. This result was not unexpected since the formation of symmetrical bis(ligand) complexes is characteristic of the tris(1-pyrazolyl)borate ligand as a result of its excellent chelating ability.[2] Nevertheless, these results indicated that less direct methods were necessary to achieve the desired syntheses of unsymmetrical metal complexes containing both dicarbollide and poly(pyrazolyl)borate ligands.

The rhodacarborane complexes *closo*-3,3-(PPh$_3$)$_2$-3-Cl-3,1,2-RhC$_2$B$_9$H$_{11}$ (**1**) and *closo*-2-(PPh$_3$)-2-Cl-2,1,7-RhC$_2$B$_9$H$_{11}$ (**2**) are excellent precursors for species that contain the [3,1,2-RhC$_2$B$_9$H$_{11}$] and [2,1,7-RhC$_2$B$_9$H$_{11}$] metallacarborane moieties, respectively. These structurally characterized complexes are readily prepared derivatives of the corresponding rhodacarborane hydride species *closo*-3,3-(PPh$_3$)$_2$-3-H-3,1,2-RhC$_2$B$_9$H$_{11}$ and *closo*-2,2-

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