fitting the k_f and k_r data at different $[H^+]$ values to eq 2 and 3, respectively.[16] One notes from the values of k_1 and k_2 (see Table II) that the rates of formation of the binuclear species $(NH_3)_5CoO_2CC_6H_3(X)OAl^{4+}$ are only slightly dependent on the nature of the substituent X on the aromatic ring. The relatively slow rate of complexation of the 3-nitrosalicylato cobalt(III) substrate particularly in the k_2 path presumably reflects that intramolecular hydrogen bonding between the phenolic group and the vicinal NO_2 group makes the cobalt(III)-bound 3-nitrosalicylate ligand less reactive.

A comparison of the values of k_1 and k_2 with the rate data for the formation of monosalicylato Al(III)[6] and mono-5-nitrosalicylato Al(III)[7] complexes via the reactions $Al^{3+} + HL^- \rightarrow AlL^+$ ($k \cong 1$ M^{-1} s^{-1} at 25 °C, $I = 0.1$ M) and $AlOH^{2+} + HL^- \rightarrow AlL^+$ ($k \cong 2 \times 10^3$ M^{-1} s^{-1} at 25 °C, $I = 0.1$ M) reveals that the coordinated ligands react ~10 times slower in the k_1 path and ~100 times slower in the k_2 path. Similar rate differences have also been observed in the complexing of Fe(III) by (oxalato)pentaamminecobalt(III) and (salicylato)pentaamminecobalt(III) substrates.[1,2] Perlmütter-Hayman and Tapuhi[7] reported a value of $<8 \times 10^{-3}$ M^{-1} s^{-1} for the rate constant of the complexation of 5-nitrosalicylic acid with Al(III) at 25 °C and $I = 0.1$ M. The value of k_1 (0.14 M^{-1} s^{-1}) obtained in the present work for the corresponding cobalt(III) substrate reduces to 4.7×10^{-3} M^{-1} s^{-1} at $I = 0$.[17] The values of k_1 for the cobalt(III) substrates are ~100 times smaller than the most recent data for the water-exchange rate constant of $Al(OH_2)_6^{3+}$ ($=k_{ex} = 16$ s^{-1} at 25 °C).[18] A similar observation has been made in the study of the kinetics of complexation of (salicylato)pentaamminecobalt(III) ions with Fe^{3+}, for which $k_1 = 7 \pm 2$ M^{-1} s^{-1} (30 °C, $I = 1.0$ M)[2] and $k_{ex}(Fe(OH_2)_6^{3+}) = 160$ s^{-1} (25 °C).[19] The fact that $k_1 < k_{ex}$ eliminates the simple S_N2 mechanism concept and supports an I mechanism. For the substitution reactions of $Fe(OH_2)_6^{3+}$, the I_a mechanism[1,2,20] has been proposed. Such a possibility cannot be ruled out[21] completely for $Al(OH_2)_6^{3+}$ though, according to Swaddle,[22] substitution at $Al(OH_2)_6^{3+}$ will have more of the I_d character. Much faster substitution reactions for $Al(OH_2)_5(OH)^{2+}$, as observed in the present work, are consistent with the I_d mechanism as has been proposed for $Fe(OH_2)_5(OH)^{2+}$.[1,2,20,23]

The binuclear species $(NH_3)_5CoO_2CC_6H_3(X)OAl^{4+}$ undergo spontaneous dissociation at rates ($k_{-1} = (5.9\text{–}3.8) \times 10^{-3}$ s^{-1}) comparable with the rate of spontaneous dissociation of the monosalicylato Al(III) complex ($k = 7.9 \times 10^{-3}$ s^{-1}; 25 °C, $I = 0.1$ M)[6] and 100 times slower than that of the (salicylato)pentaamminecobalt(III)–Fe(III) complex.[2] So that the nature of the binuclear species could be elucidated, a few trial experiments were also made to see if *p*-nitrophenol could complex with Al(III) under the experimental conditions employed in the present work. There was, however, no spectrophotometric evidence for the interaction of *p*-nitrophenol with Al(III). These facts, therefore, suggest that the binuclear species of Al(III) resemble structurally their (salicylato)aluminum(III) analogues (i.e., the salicylate moieties of the cobalt(III) substrates chelate Al(III) with deprotonation of the phenol group). The opening up of the chelate ring (carboxylate end) is most likely the rate-controlling step in the dissociation. With the assumption[24] that $K_2 = 10^{-6}$ M, the values of the dissociation rate constants (k_{-2}) of $[(NH_3)_5CoO_2CC_6H_3(X)OAlOH]^{3+}$ have been calculated (see Table II). A marked labilizing action of the hydroxo group ($k_{-2}/k_{-1} \cong 10^2$) is also evident in the dissociation reaction of the binuclear species.

Registry No. Al, 7429-90-5; $[(NH_3)_5CoO_2CC_6H_4OH]^{2+}$, 30931-74-9; $[(NH_3)_5CoO_2CC_6H_3(5\text{-}NO_2)OH]^{2+}$, 56295-01-3; $[(NH_3)_5CoO_2CC_6H_3(3\text{-}NO_2)OH]^{2+}$, 60552-07-0.

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(16) k_f and k_r were weighted as $1/\sigma^2(S)$ and $1/\sigma^2(I)$, respectively.

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Contribution from the Department of Chemistry,
Texas Woman's University, Denton, Texas 76204

Improved Method for the Preparation of Pentafluorosulfur Bromide

Rahim Rahbarnoohi and Lewis C. Sams*

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Pentafluorosulfur bromide is a particularly attractive reagent for the addition of the SF_5 group into other compounds,[1-4] but its use is limited because its synthesis is inefficient. Procedures for its synthesis have been described by Merrill[1] (low yield) and by Cohen and MacDiarmid[5] (low conversion). Kovacina, Berry, and Fox[6] described a procedure in which the bromine, recovered from the reaction with S_2F_{10}, was returned to the reactor with additional S_2F_{10}, giving yields that increased from 46% in the first reaction to above 80% in the fourth and further reactions.

In this note we report two simple modifications of the Kovacina, Berry, and Fox method that will permit yields of high-purity SF_5Br exceeding 80% (based on S_2F_{10} charged) from the first synthesis, thereby eliminating the necessity of having low yields in the first three reactions. Using the Fox fractionation procedure (traps at −78, −116, and −196 °C) we found from the ^{19}F NMR spectra that SF_5Br was distributed among three collection traps, indicating that improvements need to be made in the fractionation procedure. Our improvements allow SF_5Br to be isolated in 85% yield in the first synthesis.

The S_2F_{10} and purified bromine were obtained from Professor G. Gard of Portland State University and J. T. Baker Chemical Co., respectively. The ^{19}F NMR spectra were obtained with a Varian EM-390 NMR spectrometer operated at 85 MHz with SF_6 as the reference.

In the repetition of Fox's procedure 10 mmol of S_2F_{10} and 100 mmol of Br_2 were heated in a 300-mL Monel cylinder at 150 °C for 16 h. The cylinder was evacuated while being held at liquid-nitrogen temperature, the liquid nitrogen was poured out of the Dewar, and the cool Dewar was placed around the cylinder. The trap-to-trap fractionation (−78, −116, and −196

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Table I

Data Reported[6]		
−78 °C	−116 °C	−196 °C
Br_2	SF_5Br, Br_2	SF_6, SF_5, SOF_2, SiF_4, S_2F_{10}
Data Obtained by Following the Reported Procedure[6]		
−78 °C	−116 °C	−196 °C
Br_2, SF_5Br, S_2F_{10}	SF_5Br, Br_2	SF_4, SF_5Br, SF_6
Data Obtained in the Modified Procedure		
−68 °C[a]	−116 °C	−196 °C
Br_2, S_2F_{10}	SF_5Br, Br_2	SF_6, SF_4

[a] Pyrex beads used in the trap.

°C) was carried out with continuous pumping for 4 h. The yield we obtained was 45%. After the reaction was repeated five times (with use of recovered bromine with 10 mmol of S_2F_{10} each time), the yield increased to 75%. The ^{19}F NMR spectroscopy showed the presence of large amounts of SF_5Br and unreacted S_2F_{10} in the −78 °C trap. Fox had stated that this trap contained only bromine. There was also some SF_5Br found in the −196 °C trap as detected by NMR signals at −5 and −88 ppm[7] with respect to SF_6.

The reaction was repeated with 10 mmol of S_2F_{10} and 100 mmol of Br_2 (150 °C, 16 h). The conditions of the fractionation were changed by (a) increasing the temperature of the first trap to −63 °C in order to allow a better transfer of SF_5Br from the first to second trap and (b) using glass beads in order to increase the surface area of the traps at −63 and −116 °C to prevent escape of Br_2 from the first into the second and of SF_5Br from the second into the third trap. The NMR spectra of the contents of the traps at −63 and −196 °C showed no presence of SF_5Br. SF_5Br was found only in the −116 °C trap, along with small amounts of bromine. Purification of SF_5Br from traces of bromine was completed by addition of a few milliliters of mercury to the SF_5Br trap at 0 °C.[6]

Table I compares the compounds in each trap for each method.

The yield that we obtained in our method was about 85% for SF_5Br and was not dependent on reusing the bromine or removal of a deleterious contaminant from the bromine, as suggested by Kovacina, Berry, and Fox.[6]

Registry No. SF_5Br, 15607-89-3; S_2F_{10}, 5714-22-7; Br_2, 7726-95-6.

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Contribution from the Istituto di Chimica Generale, Università di Pisa, 56100 Pisa, Italy, and the Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffrattometrica CNR, Università di Parma, 43100 Parma, Italy

Thiobenzophenone η^2-C,S Bonded to Vanadocene: A Precursor in Desulfurization Reactions

Marco Pasquali, Piero Leoni, Carlo Floriani,*
Angiola Chiesi-Villa, and Carlo Guastini

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The organometallic chemistry of thioketones has undergone a substantial recent development by Alper and his group.[1] Thioketones have been used as model substrates for studying the desulfurization reaction and for testing the thiophilicity of low-valent metal complexes.[1-5] The activation of the thiocarbonyl function depends on the interaction mode in a preliminary step of the >C=S unit with the metal. Thioketones, usually, coordinate to a metal center by using the lone pairs on the sulfur atom,[3] while a unique thioketone η^2-C,S bonded to a molybdenum complex was very recently structurally identified.[1] The ortho metalation of aromatic thioketones, occurring with a transformed[4] or retained[5] thiocarbonyl function and the desulfurization reaction,[6,7] producing carbenes, can be considered as the step following the preliminary thioketone–metal interaction.

We decided to use vanadocene, $(cp)_2V$ (cp = η^2-C_5H_5), in the reaction with a thioketone function, since vanadocene adds as a carbene-like species to a variety of organic functions and small molecules.[8] Vanadocene produces a remarkable change in the chemical properties of the metal-bonded unit by a significant electron transfer from the metal to the functional group.

The present report concerns the reaction occurring between vanadocene and thiobenzophenone leading to a η^2-C,S metal-anchored thiocarbonyl function. The thermal decomposition of such a complex generates a sulfur-containing vanadium complex and diphenylfulvene.

Experimental Section

All the reactions described were carried out under an atmosphere of purified nitrogen. Solvents were purified by standard methods. Tetracarbonyl(η^5-cyclopentadienyl)vanadium(I),[9] bis(η^5-cyclopentadienyl)vanadium(II),[10] and thiobenzophenone[11] were prepared as in the literature. IR spectra were measured with a Perkin-Elmer 283 spectrometer. Magnetic measurements were made with a Faraday balance.

Synthesis of $[(cp)_2V(Ph_2CS)]$ (II). A toluene (15 mL) solution of vanadocene (0.55 g, 3.04 mmol) was reacted with thiobenzophenone (0.68 g, 3.43 mmol). The color of the solution changed rapidly from deep violet to deep red. The solution gave on standing for 12 h dark red crystals of $[(cp)_2V(Ph_2CS)]$ (0.65 g, 56%). The solid is very sensitive to air. Anal. Calcd for $[(cp)_2V(Ph_2CS)]$, $C_{23}H_{20}VS$: C, 72.82; H, 5.27; S, 8.44. Found: C, 72.92; H, 5.22; S, 8.20. The magnetic moment is 1.74 μ_B at 292 K.

Reaction of Complex II with Methyl Iodide. An *n*-hexane (50 mL) suspension of complex II (1.29 g, 3.40 mmol) was reacted with methyl iodide (2.0 mL, 32.0 mmol). When the mixture was heated for 10 min at 50 °C, $(cp)_2VI$[12] was formed as a maroon-green solid in almost quantitative yield. A toluene solution of II reacted with I_2 gave in quantitative yield (ca. 90%) $(cp)_2VI_2$.[8]

Thermal Decomposition of Complex II. A toluene (30 mL) solution of complex II (1.05 g, 2.77 mmol) was heated at 100 °C for 4 h. The color of the solution changed to maroon, and a brown microcrystalline solid was formed (0.19 g, 46% yield). Anal. Calcd for $[cpVS]_n$,

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* To whom correspondence should be addressed at the Università di Pisa.

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