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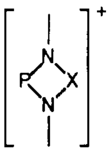
Communications

A Simple Route to the First 1,3-Diaza-2-phosphetine Cations

Although neutral unsaturated four-membered phosphorus heterocycles are attracting increasing interest[1] the corresponding cationic species appear to be rather little known. Up to now, only a few σ^2-phosphorus species (I) have been prepared and fully



I, X = Si<,[2a] Al<,[2b] P–R[2c]

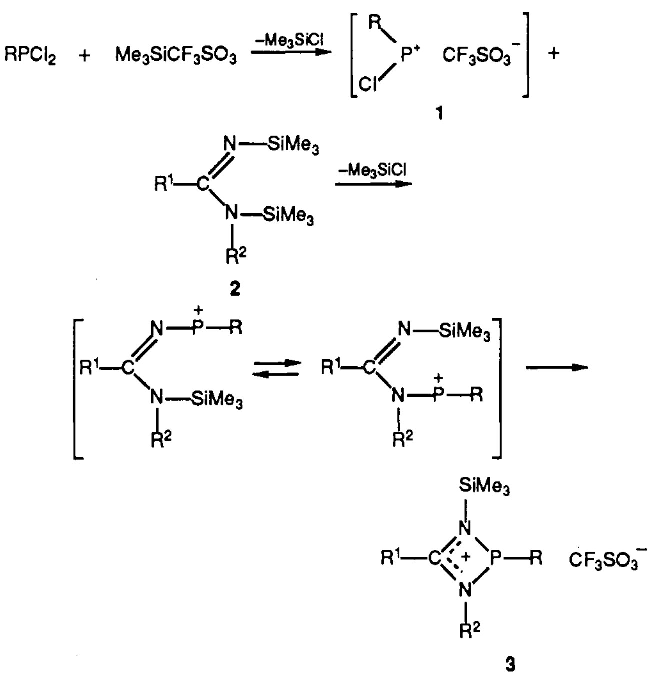
characterized.[2] Therefore, in connection with our investigations on the reactivity of chlorophosphenium salts[3] we are interested in whether a general synthesis of unsaturated cyclic σ^3-phosphorus cations could be developed.

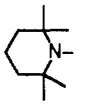
We wish to report now the preparation of 1,3-diaza-2-phosphetine cations of compounds **3a–f**—i.e. stabilized cyclic carbenium species—and the X-ray structure determination of one of them, namely the 1,3-bis(trimethylsilyl)-4-phenyl-2-(diisopropylamino)-1,3-diaza-2-phosphetine cation of **3a**.

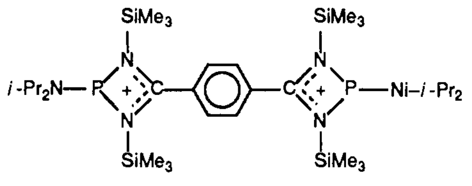
Silylated amidines are versatile reagents toward chlorinated phosphorus compounds, leading either to hexacoordinated phosphorus zwitterionic species[4] or to di- or tricyclic derivatives, as recently demonstrated.[5]

The cations of compounds **3a–f** are prepared in good yield by treating the chlorophosphenium ions **1**—generated in situ by adding (trimethylsilyl)trifluoromethanesulfonate to (diisopropylamino)dichlorophosphine—with *N,N'*-bis- or *N,N,N'*-tris(trimethylsilyl) amidines **2** in dichloromethane[6] (Scheme I).

Scheme I



1–3	a	b	c	d[9]	e
R	*i*-Pr$_2$N	*i*-Pr$_2$N	Et$_2$N	*i*-Pr$_2$N	
R^1	C$_6$H$_5$	*p*-C$_6$H$_4$CH$_3$	C$_6$H$_5$	C$_6$H$_5$	*p*-C$_6$H$_4$CH$_3$
R^2	Me$_3$Si	Me$_3$Si	Me$_3$Si	*t*-Bu	Me$_3$Si



3f[9]

The constitution of the products **3** is substantiated in particular by the position of the signal and the magnitude of the coupling constant for the intracyclic carbon atom in the ^{13}C NMR spectra (δ = 173.76–179.50 ppm, $^2J_{CP}$ = 15.00–20.65 Hz). The following spectroscopic data also suggest structure **3**. The ^{31}P chemical shift (105.9–112.3 ppm) is in good agreement with a λ^3-phosphorus atom and not with a cationic λ^2, which would give signals around +300 ppm.[7] Characteristic C=N and P—N vibrational frequencies were found by infrared spectroscopy: 1640–1665 and 890–910 cm^{-1}, respectively.

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The structure of **3a** has been clearly established by a single-crystal X-ray diffraction study[8] and is illustrated in Figure 1. The four-membered ring is planar. Since the two intracyclic carbon–nitrogen bond lengths are equal (1.35 (1), 1.33 (1) Å) within experimental error and shorter than usual (normal C—N and C═N bonds ~ 1.50 and 1.25 Å, respectively), it is clear that the unsaturation is delocalized along the N–C–N fragment. The result of the delocalization is the opening of the N–C–N angle (106.8°) and therefore the pinching of the ring around phosphorus: to our knowledge, the intracyclic N–P–N angle (73.2°) is the smallest one reported for a four-membered phosphorus heterocycle.

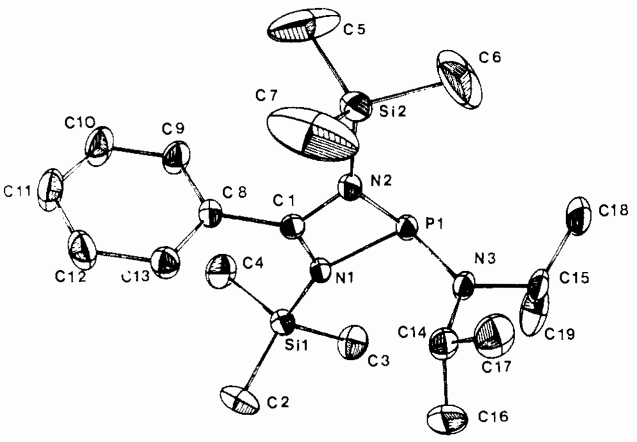
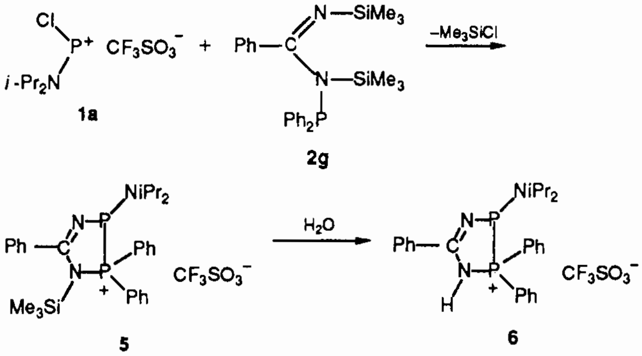


Figure 1. Crystal structure of **3a**. Selected bond lengths (Å) and bond angles (deg): P_1–N_1 = 1.79 (1), P_1–N_2 = 1.788 (9), P_1–N_3 = 1.64 (2), C_1–N_1 = 1.33 (1), C_1–N_2 = 1.35 (1); $N_1P_1N_2$ = 73.2 (5), $C_1N_1P_1$ = 89.8 (6), $C_1N_2P_1$ = 89.5 (6), $N_1P_1N_3$ = 107.1 (5), $N_2P_1N_3$ = 107.3 (5), $N_1C_1N_2$ = 106.1 (9).

Scheme II



The phosphorus–nitrogen distances also reflect the cationic structure of **3a**: the P–N bonds are lengthened from 1.64 (2) (exocyclic P–N) to 1.788 (9) and 1.79 (1) Å (endocyclic P–N) and thus lie at the upper limit of known P–N single-bond lengths.

Preliminary investigations have shown that the reaction of chlorophosphenium salts with silylated amino compounds of general formula Me_3Si-N-Y:, in which Y is a donor atom, might be a general way for preparing new cyclic cations. Such an observation is exemplified by the reaction of **1a** with the *N,N'*-bis(trimethylsilyl)-*N*-(diphenylphosphino) amidine **2g**: the cationic cyclic five membered ring **5** is thus obtained as two isomers (δ(^{31}P) = +67.40, +43.60 ppm, $^1J_{PP}$ = 354.2 Hz; δ(^{31}P) = +67.70. +44.00 ppm, $^1J_{PP}$ = 354.2 Hz). Mild hydrolysis of **5** led to the NH

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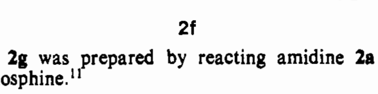
(6) Procedure for **3a**: A mixture of (diisopropylamino)dichlorophosphine (0.487 g, 2.41 mmol) and (trimethylsilyl)trifluoromethanesulfonate (0.536 g, 2.41 mmol) in dichloromethane (15 mL) was treated via syringe with a dichloromethane solution of bis(silyl) amidine **2a** at −70 °C. After 1 h the resulting yellow solution was concentrated, and crystals of **3a** were obtained at −20 °C. Recrystallization from dichloromethane afforded pure **3a** as yellow crystals sensitive to hydrolysis: yield 92%; mp 88–90 °C. **3a**: overall yield 92%; ^{31}P NMR (CD_2Cl_2) δ 111.0; ^{1}H NMR (CD_2Cl_2) δ 0.17 (s, 18 H, Me_3Si), 1.23 (d, $^3J_{HH}$ = 6.63 Hz, 6 H, *Me*$_2$C), 1.42 (d, $^3J_{HH}$ = 6.79 Hz, 6 H, *Me*$_2$C), 3.65 (m, 2 H, *CH*Me$_2$), 7.6 (m, 5 H, Ph); ^{13}C NMR (CD_2Cl_2) δ 0.37 (s, *Me*$_3$Si), 21.78 (s, CH*Me*$_2$), 27.18 (d, $^3J_{CP}$ = 12.76 Hz, CH*Me*$_2$), 47.51 (d, $^2J_{CP}$ = 29.88 Hz, *C*HMe$_2$), 48.01 (d, $^2J_{CP}$ = 7.9 Hz, *C*HMe$_2$), 121.57 (q, $^1J_{CF}$ = 321 Hz, *C*F$_3$SO$_3$), 129.36 (d, $^3J_{CP}$ = 2.99, 1 C), 127.98 (d, $^4J_{CP}$ = 2.55 Hz, 2 C) 129.8 (s, 2 C) and 133.6 (s, 1 C) (C_6H_4), 179.5 (d, $^2J_{CP}$ = 15.6 Hz, *C*═N); ^{29}Si NMR (CD_2Cl_2) δ 14.8 (b s); ^{19}F NMR (CD_2Cl_2) δ −0.2 (s, $CF_3SO_3^-$); IR (CD_2Cl_2) 1656 cm^{-1} (C═N). Anal. Calcd for $C_{20}H_{37}F_3N_3O_3PSSi_2$: C, 44.18; H, 6.86; N, 7.73. Found: C, 44.07; H, 6.84; N, 7.67. **3b**: 95% overall yield; ^{31}P NMR (C_6D_6) δ 112.3; ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 18 H, *Me*$_3$Si), 1.12 (d, $^3J_{HH}$ = 6.70 Hz, 6 H, *Me*$_2$C), 1.31 (d, $^3J_{HH}$ = 6.7 Hz, 6 H, *Me*$_2$C), 2.28 (s, 3 H, *Me*-C_6H_4), 3.50 (m, $^3J_{HH}$ = 6.7 Hz, 2 H, *CH*Me$_2$), 7.3 (m, 4 H, C_6H_4); ^{13}C NMR (C_6H_6) δ 0.03 (s, *Me*$_3$Si), 21.28 (s, *Me*$_2$CH), 21.54 (s, *Me*-C_6H_4), 26.70 (d, $^3J_{CP}$ = 12.8 Hz, *Me*$_2$CH), 46.74 (d, $^2J_{CP}$ = 30.2 Hz, *C*HMe$_2$), 47.27 (d, $^2J_{CP}$ = 7.5 Hz, *C*HMe$_2$), 120.73 (q, $^1J_{CF}$ = 320.74 Hz, *C*F$_3$SO$_3$), 125.7 (s), 129.8 (s), 143.6 (s) (*C*$_6$H$_4$), 179.27 (d, $^2J_{CP}$ = 15.09 Hz, *C*═N); ^{29}Si NMR (CD_2Cl_2) δ 14.86 (b s); ^{19}F NMR (CD_2Cl_2) δ −0.19 (s, CF_3SO_3); IR (CD_2Cl_2) 1650 cm^{-1} (νC═N). Anal. Calcd for $C_{21}H_{39}F_3N_3O_3PSSi_2$: C, 45.22; H, 7.05; N, 7.53. Found: C, 45.07; H, 7.21; N, 7.42. **3c**: 92% overall yield; ^{31}P NMR (CD_2Cl_2) δ 111.6; ^{1}H NMR (CD_2Cl_2) δ 0.20 (s, 18 H, *Me*$_3$Si), 1.22 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, *Me*CH$_2$N), 1.26 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, *Me*CH$_2$CN), 3.10 (dq, $^3J_{HP}$ = 3.7 Hz, $^3J_{HH}$ = 7.1 Hz, 2 H, CH_2), 3.43 (dq, $^3J_{HP}$ = 15.7 Hz, $^3J_{HH}$ = 7.1 Hz, 2 H, CH_2), 7.60 (m, 5 H, C_6H_5); ^{13}C NMR (CD_2Cl_2) δ −0.16 (s, *Me*$_3$Si), 13.77 (s, *Me*CH2*N*), 15.37 (d, $^3J_{CP}$ = 7.12 Hz, *Me*-CH$_2$N), 38.89 (d,$^2J_{CP}$ = 8.3 Hz, *C*H$_2$N), 44.24 (d, $^2J_{CP}$ = 46.9 Hz, *C*H$_2$N), 121.55 (q, $^1J_{CF}$ = 321 Hz, *C*F$_3$SO$_3$), 128.15 (s), 129.35 (d, $^3J_{CP}$ = 2.70 Hz), 129.73 (s), 133.62 (s) (*C*$_6$H$_4$), 179.2 (d, $^2J_{CP}$ = 15.0 Hz, *C*═N); ^{29}Si NMR (CD_2Cl_2) δ 14.40 (b s); ^{19}F NMR (CD_2Cl_2) δ 0.25 (s, CF_3SO_3); IR (CD_2Cl_2) 1650 cm^{-1} ($\nu_{C═N}$). Anal. Calcd for $C_{18}H_{33}F_3N_3O_3PSSi_2$: C, 41.92; H, 6.45; N, 8.15. Found: C, 41.48; H, 6.39; N, 8.07. **3d**: 85% overall yield; ^{31}P NMR (C_6H_6) δ 105.9; ^{1}H NMR ($CDCl_3$) 0.15 (s, 9 H, *Me*$_3$Si), 1.20 (d, $^3J_{HH}$ = 6.5 Hz, 6 H, *Me*$_2$CH), 1.30 (s, 9 H, *t*-Bu), 1.35 (d, $^3J_{HH}$ = 6.5 Hz, 6 H, *Me*$_2$CH), 3.60 (m, 2 H, Me$_2$C*H*), 7.65 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 0.27 (d, $^3J_{CP}$ = 2 Hz, *Me*$_3$Si), 20.89 (s, *Me*$_2$CH), 21.63 (s, *Me*$_2$CH), 26.40 (d, $^3J_{CP}$ = 12.49 Hz, *Me*$_2$CH), 26.70 (d, $^3J_{CP}$ = 12.30 Hz, *Me*$_2$CH), 30.14 (d, $^3J_{CP}$ = 3.63 Hz, *Me*$_3$C), 46.99 (d, $^2J_{CP}$ = 31.43 Hz, Me$_2$*C*H), 47.94 (d, $^2J_{CP}$ = 9.87 Hz, Me$_2$*C*H), 58.49 (d, $^2J_{CP}$ = 1.818 Me$_3$*C*), 120.73 (q, $^2J_{CF}$ = 320.7 Hz, *C*F$_3$SO$_3$), 174.47 (d, $^1J_{CP}$ = 15.31 Hz, *C*═N); ^{29}Si NMR (CD_2Cl_2) δ 13.70 (d, $^2J_{SiP}$ = 3.05 Hz, Me$_3$Si); ^{19}F NMR (CD_2Cl_2) δ −0.15 (s, CF_3SO_3); IR (CD_2Cl_2) 1652 cm^{-1} ($\nu_{C═N}$). Anal. Calcd for $C_{21}H_{37}F_3N_3O_3PSSi_2$: C, 47.80; H, 7.07; N, 7.96. Found: C, 47.97; H, 7.26; N, 7.89. **3e**: 86% overall yield; ^{31}P NMR ($CDCl_3$) δ 107.95; ^{1}H NMR (CD_2Cl_2) δ 0.06 (s, 18 H, Me$_3$Si), 1.34 (m, 12 H, Me$_2$C), 1.54 (s, 6 H, $(CH_2)_3$), 2.26 (s, 3 H, *Me*C$_6$H$_4$), 7.20 (m, 4 H, C_6H_4); ^{13}C NMR ($CDCl_3$) δ 0.26 (s, Me$_3$Si), 16.24 (s, CH$_2$*C*H$_2$CH$_2$), 21.56 (s, *MeC*$_6$H$_4$), 29.69 (s, *Me*C<), 34.05 (d, $^3J_{CH}$ = 26.50 Hz, *Me*C<), 40.20 (d, *C*H$_2$CH$_2$CH$_2$, $^3J_{CP}$ = 3.05 Hz), 61.66 (d, $^3J_{CP}$ = 33.21 Hz, Me$_2$C), 63.51 (d, $^3J_{CP}$ = 11.32 Hz, Me$_2$*C*), 120.54 (q, $^1J_{CF}$ = 320.74 Hz, *C*F$_3$SO$_3$), 125.81 (s), 128.82 (s), 129.93 (s), 144.30 (s) (*C*$_6$H$_4$), 173.76 (d, $^2J_{CP}$ = 20.65 Hz, *C*═N); ^{29}Si NMR (CD_2Cl_2) δ 14.65 (b s); ^{19}F NMR (CD_2Cl_2) δ −0.05 (s, C*F*$_3$SO$_3$); IR (CD_2Cl_2) 1660 cm^{-1} ($\nu_{C═N}$). Anal. Calcd for $C_{24}H_{43}F_3N_3O_3PSSi_2$: C, 48.22; H, 7.25; N, 7.03. Found: C, 47.97; H, 7.19; N, 7.09. **3f**: 70% overall yield; ^{31}P NMR (C_6D_6) δ 114.1; ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 36 H, Me$_3$Si), 1.24 (d, $^3J_{HH}$ = 6.5 Hz, 12 H, *Me*$_2$C), 1.44 (d, $^3J_{HH}$ = 6.5 Hz, 12 H, *Me*$_2$C), 3.6 (m, 4 H, Me$_2$C*H*), 8.12 (s, 4 H, C_6H_4); ^{13}C NMR ($CDCl_3$) δ 0.66 (s, *Me*$_3$Si), 21.84 (s, CH*Me*$_2$), 27.26 (d, $^3J_{CP}$ = 13 Hz, CH*Me*$_2$), 47.61 (d, $^2J_{CP}$ = 39.6 Hz, *C*HMe$_2$), 48.11 (b s, *C*HMe$_2$), 112.99 (q, $^1J_{CF}$ = 320 Hz, *C*F$_3$SO$_3$), 130.10 (d, J_{CP} = 3.2 Hz), 130.56 (b s), 133.32 (d, $^3J_{CP}$ = 3.2 Hz) (*C*$_6$H$_4$), 177.15 (d, $^2J_{CP}$ = 16.1 Hz, *C*═N); ^{19}F NMR (CD_2Cl_2) δ −0.1 (s, *CF*$_3$SO$_3$); IR (CD_2Cl_2) 1655 cm^{-1} (νC═N). Anal. Calcd for $C_{34}H_{68}F_6N_6P_2S_2Si_4$: C, 40.46; H, 6.79; N, 8.33. Found: C, 40.87; H, 6.49; N, 8.29.

(7) See for example: Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367.

(8) **3a**: monoclinic $P2_1/n$, a = 10.748 (5) Å, b = 18.051 (9) Å, c = 15.436 (6) Å, β = 92.58 (7)°, Z = 4, ρ_{calcd} = 1.207 g·cm^{-1}, R = 0.073, R_w = 0.079 [Mo Kα, λ = 0.7107 Å, 4357 unique reflections, 3124 reflections with $I > 3\sigma(I)$, anisotropic temperature factors, hydrogen atoms only positioned and introduced in the calculations, 301 refined parameters, only Lorentz–polarization corrections, no absorption corrections because of the small value, 2.75 cm^{-1}, of the absorption coefficient]. This structure was solved by using SDP (structure determination package of Enraf-Nonius).

(9) Compounds **3d** and **3f** were prepared respectively from the new amidine **2d** and bis(amidine) **2f**.[11]



2f

Amidine **2g** was prepared by reacting amidine **2a** with chlorodiphenylphosphine.[11]

derivative **6**[10] (only one compound detectable because of the fast hydrogen exchange between the two nitrogen atoms) (Scheme II).

Registry No. **1a**, 122271-86-7; **2a**, 24261-90-3; **2b**, 117357-77-4; **2d**, 122271-81-2; **2f**, 117357-84-3; **2g**, 122271-82-3; **3a**, 122271-68-5; **3b**, 122271-70-9; **3c**, 122271-72-1; **3d**, 122271-74-3; **3e**, 122271-76-5; **3f**, 122271-78-7; **5** (isomer 1), 122271-84-5; **5** (isomer 2), 122271-85-6; **6**, 122271-80-1; *i*-Pr_2NPCl_2, 921-26-6; Et_2NPCl_2, 1069-08-5; (2,2,6,6-tetramethyl-1-piperidinyl)phosphonous dichloride, 64945-24-0; chlorodiphenylphosphine, 1079-66-9; (trimethylsilyl)trifluoromethanesulfonate, 27607-77-8.

Supplementary Material Available: Tables listing bond lengths, bond angles, positional and anisotropic thermal parameters, and derived H atom coordinates for **3a** (13 pages); a table of calculated and observed structure factors (15 pages). Ordering information is given on any current masthead page.

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[10] **6**: ^{31}P NMR (C_6D_6) δ 54.1, 49.9 ($^1J_{PP}$ = 308.8 Hz); ^1H NMR ($CDCl_3$) δ 1.30 (d, $^3J_{HH}$ = 6.5 Hz, 12 H, *Me*$_2$CH), 3.01 (m, 2 H, Me$_2$*C*H), 7.61 (m, 15 H, C_6H_5), 10.36 (t, $^2J_{HP}$ = $^3J_{HP}$ = 10.36 Hz, 1 H, >NH); ^{13}C NMR ($CDCl_3$) δ 24.20 (s, *Me*$_2$CH), 47.91 (s, Me$_2$*C*H), 120.73 (q, $^1J_{CF}$ = 319.9 Hz, *C*F_3SO_3), 128 (m, C_6H_5), 176.06 (dd, $^2J_{CP}$ = 8.36 Hz, $^2J_{CP}$ = 8.31 Hz, *C*–C_6H_5); IR ($CDCl_3$) 1670 cm^{-1} (νC=N).

[11] Roques, C.; Mazières, M. R.; Majoral, J. P.; Sanchez, M. Unpublished results.

Articles

Contribution from the Guelph-Waterloo Centre for Graduate Work in Chemistry,
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Reduction of Oxygen- and Sulfur-Bonded (Thiocarbamato)pentaamminecobalt(III) Complexes by Chromium(II)

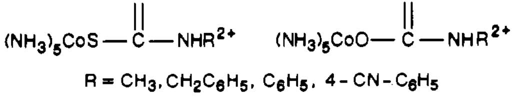
Robert J. Balahura,* Michael Johnson, and Tim Black

Received October 5, 1988

The chromium(II) reduction of several S- and O-bonded (thiocarbamato)pentaamminecobalt(III) complexes has been studied. For $(NH_3)_5CoSCONHR^{2+}$ (R = CH_3, C_6H_5, $CH_2C_6H_5$, 4-CN-C_6H_4) the reductant attacks at the remote oxygen atom, giving the rate constants 6.5×10^4, 3.5×10^4, 4.0×10^4, and 2.2×10^4 M^{-1} s^{-1}, respectively, at T = 25 °C and I = 1.0 M ($LiClO_4$). The O-bonded chromium(III) product formed in the reduction step isomerizes with $k_{obs} = k[H^+]$, where k = 41 M^{-1} s^{-1} for R = CH_3 and k = 14 M^{-1} s^{-1} for R = C_6H_5 and $CH_2C_6H_5$. The O-bonded complexes $(NH_3)_5CoOCSNHR^{2+}$ (R = CH_3, $CH_2C_6H_5$) are reduced by attack at the remote S with the rate constants 68 and 55 M^{-1} s^{-1} at 25 °C and I = 1.0 M ($LiClO_4$). The facile electron transfer in the S-bonded cobalt(III) complexes is attributed to a structural trans effect.

Introduction

Redox reactions between Co(III) complexes containing low-valent coordinated sulfur and Cr(II) are "unusually" facile.[1,2] For example, thiolate complexes are reduced 100–1000 times more rapidly than the corresponding alkoxy species. The nature of this rate enhancement is not well-understood, although it has been suggested that it arises from a sulfur-induced structural trans effect (STE).[3] This explanation has been supported by X-ray data, which show a lengthening of the bond trans to the coordinated sulfur atom.[3-5] In an attempt to probe the electron-mediating ability of sulfur, both coordinated and remote, we report here the reduction of several S- and O-bonded thiocarbamato complexes of pentaamminecobalt(III) by Cr(II):



$$(NH_3)_5CoS-\overset{\overset{\displaystyle O}{\|}}{C}-NHR^{2+} \qquad (NH_3)_5CoO-\overset{\overset{\displaystyle S}{\|}}{C}-NHR^{2+}$$

R = CH_3, $CH_2C_6H_5$, C_6H_5, 4-CN-C_6H_5

Experimental Section

Organic starting materials and solvents were of reagent grade and were used without further purification (Eastman Kodak, Aldrich). Purification of complexes was carried out by chromatography on CM-Sephadex C-25 or SP Sephadex in the Na^+ form (Sigma) in a cold room held at 5 °C.

Stock solutions of lithium perchlorate prepared from the anhydrous material (G. Frederick Smith) were filtered by using a 0.6 μm Millipore filter. Triplicate portions of this solution were standardized by titration of hydrogen ions released from the strong-acid ion-exchange resin Amberlite IR 120(H). Perchloric acid solutions were prepared from doubly distilled $HClO_4$ (G. Frederick Smith) and standarized with NaOH. Chromium(II) solutions were prepared and analyzed by standard methods. Water used in this study was from a Millipore ion-exchange system.

UV–visible spectra were obtained with a Beckman Acta (III) spectrophotometer. NMR spectra were recorded with a Varian HA 100 or Bruker WH-400 spectrometer. Chemical shifts are given relative to tetramethylsilane (TMS).

Preparation of Complexes. The S-bonded complexes were synthesized by the general procedure described previously.[6] All analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario, Canada.

Pentaammine(*N*-methylthiocarbamato-*S*)cobalt(III) Perchlorate. Anal. Calcd for $[Co(NH_3)_5SCONH(CH_3)](ClO_4)_2$: C, 5.55; H, 4.42; N, 19.41. Found: C, 5.50; H, 4.38; N, 18.89.

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