

NSCl₂⁻: Thiazyl Dichloride - Aza Analogue of Thionyl Dichloride

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Experimental Section

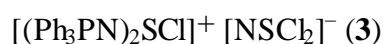
General Remarks: All experiments and manipulations were carried out under argon. Reactions were performed using standard Schlenk techniques. Solvents were freshly distilled, dried and stored under nitrogen. The starting materials (NSCl)₃ and PPh₃NSiMe₃ were prepared according to the literature.^[1] Me₄NCl and Ph₄PCl were purchased from Aldrich and dried in vacuum prior to use. – NMR: Jeol Eclipse 400 (¹⁴N NMR chemical shifts refer to **d**_{CH₃NO₂} = 0.00 and ³¹P NMR shifts to **d**_{H₃PO₄ (85%)} = 0.00). – IR: Nicolet 520 FT-IR (as KBr pellets or in Nujol mulls between CsI windows). – Raman: Perkin Elmer Spectrum 2000R NIR FT. – CHN analyses: Analysator Elementar Vario EL. – Melting points were measured on a Büchi B540. Raman, ¹⁴N NMR and IR data are only listed for the SNCl₂⁻ anion.

[Ph₄P]⁺ [NSCl₂]⁻ (1)

a) A solution of 0.5 g (2.04 mmol) (NSCl)₃ in 15 mL benzene (heated to ca. 50 °C for 2 min) was added in 15 minutes to a slurry of 2.29 g (6.1 mmol, 3 equiv.) Ph₄PCl in 20 mL benzene. The dark green mixture was stirred at ambient temperature for 24 hours. The color changed from green via orange to yellow. The yellow solid was separated and dried under oil pump vacuum for 20 min. Yield: 2.71 g (5.9 mmol, 99 %) – C₂₄H₂₀Cl₂NPS (456.38): calcd. C 63.16, H 4.42, N 3.07, Cl 15.54, S 7.0 %; found C 62.96, H 4.51, N 2.85, Cl 15.6, S 6.62 %. – beginning of decomposition: 140 °C. – Raman (300 mW, RT): $\tilde{\nu}$ = 1339 cm⁻¹(6), 305 (1.5), 295 (2), 223 (2), 161 (2). – IR (Nujol, CsI): $\tilde{\nu}$ = 1338 cm⁻¹ (s), 302 (m), 293 (m), 220 (m). – ¹⁴N NMR (CD₂Cl₂, 28.9 MHz, RT): **d** = 153 ppm (s, $\Delta n^{1/2}$ = 140 Hz).

[Me₄N]⁺ [NSCl₂]⁻ (2)

A solution of 0.5 g (2.04 mmol) (NSCl)₃ in 15 mL dry C₆H₆ was added in ½ hour to a slurry of 0.56 g (5.1 mmol) NMe₄Cl in 15 mL C₆H₆. Alternative solvents: CCl₄ and CH₂Cl₂. The reaction mixture was stirred for 24 hours and the precipitate was separated and dried in oil pump vacuum for 1 hour. The product is an air and moisture sensitive yellow powder. Yield: 0.927 g (4.85 mmol, 95 %) C₄H₁₂Cl₂N₂S (191.13): calcd. C 25.14, H 6.33, N 14.65; found C 25.12, H 6.52, N 14.60. melting range: 90–142 °C – Raman (300 mW, RT): $\tilde{\nu}$ = 1354 cm⁻¹ (10), 278 (1), 241 (1), 211 (1.5), 117 (1.5). – IR (Nujol, CsI plates): $\tilde{\nu}$ = 1355 cm⁻¹ (vs), 262 (m), 247 (m), 217 (m). – ¹⁴N NMR (CD₂Cl₂, 28.9 MHz, RT): **d** = 153 ppm (s, $\Delta\mathbf{n}^{1/2}$ = 140 Hz).



A solution of 0.43 g (1.2 mmol) Ph₃PNSiMe₃ in CCl₄ was added in ½ hour to a green solution of 0.3 g (1.2 mmol, 1 equiv.) (NSCl)₃ in CCl₄ (heated to ca. 50 °C for 2 min). The color changed from dark green to brown. The oily brown mixture is stirred for 12 hours at ambient temperature. The brown oily solid was filtered and washed with benzene. Colorless crystals were obtained from the clear green benzene phase. Yield: 0.088 g (0.12 mmol, 10 %) C₃₆H₃₀Cl₃N₃P₂S₂ (737.09). – Raman (300 mW, RT): $\tilde{\nu}$ = 1339 cm⁻¹ (10), 308 (2), 293 (2), 222 (4), 160 (3). – ³¹P NMR(C₆D₆, 162 MHz, RT): **d** = 26 ppm (s). – ¹⁴N NMR(C₆D₆, 28.9 MHz, RT): **d** = 153 ppm (s, $\Delta\mathbf{n}^{1/2}$ = 140 Hz). .

Crystal Structure Analysis of 3: C₃₆H₃₀Cl₃N₃P₂S₂ · C₆H₆, *M* = 815.193, crystal size: 0.25 × 0.10 × 0.02 mm, colorless platelet, monoclinic, space group *P*2₁/*c*, *a* = 22.373(2), *b* = 9.4108(7), *c* = 20.030(3) Å, **b** = 108.460(13), *V* = 4000.3(7) Å³, *Z* = 4, *d*_{calcd.} = 1.3536(2) g · cm⁻³, μ = 0.448 mm⁻¹, *F*(000) = 1688. Stoe IPDS image-plate area detector, Mo-*K*_α, **I** = 0.71073 Å, *T* = 200(3) K, **q**range = 1.92 to 22.26° in -23 ≤ *h* ≤ 23, -9 ≤ *k* ≤ 10, -21 ≤ *l* ≤ 15, reflections collected: 12023, independent reflections: 4785 (*R*_{int} = 0.1175), observed reflections: 2106 (*F* > 4σ(*F*)). Structure solution program: SHELXS-97 (G. M. Sheldrick, University of Göttingen, Germany, 1997), direct methods, final *R* indices [*F* > 4σ(*F*)]: *R*1 = 0.0398, *wR*2 = 0.0736 (all data), GOF on *F*² = 0.629, largest difference peak/hole: 0.210, -0.248 e Å⁻³, program used: SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany, 1997).

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-152427. Copies of the data can be obtained free of charge on

application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

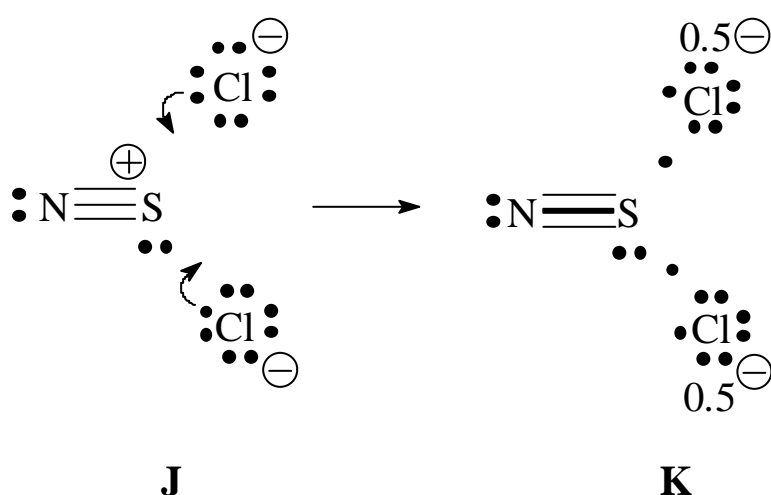
Computational Details

Computations have been carried out on SN^+ , NSCl , NSCl_2^- and OSCl_2 using the Gaussian98 program package.^[2] Full geometry optimizations were performed at two different correlated levels of theory, CCSD(t) and density functional (B3LYP).^[3] All stationary points were characterized by a frequency analysis at both the B3LYP and the CCSD(t) level. Several all electron basis sets were applied, including 6-311+G(3df) and the Dunning correlation consistent cc-PVTZ and cc-PV5Z basis sets^[4] augmented by diffuse functions.^[5] As the geometries are rather sensitive to the applied basis sets and methods, higher level computations using large basis sets are more realistic.

The potential energy scan of the $\text{Cl} + \text{NSCl}$ reaction was calculated using the 6-311+G(3df) basis set at B3LYP. The energy was calculated as a function of the Cl-S distance in 0.1 Å steps.

NBO analysis and Mulliken population analysis were carried out to investigate the bonding in all molecules (B3LYP/6-311+G(3df)).

Figure Increased valence representation (**K**) of NSCl_2^- derived from concerted one electron delocalization (**J**).



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- [4] a) D. E. Woon, T. H. Dunning, *J. Chem. Phys.* **1993**, *98*, 1358–1371;
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- [5] B3LYP/aug-cc-pvTZ: d(SN) = 1.453, d(SCl) = 2.503 Å; <(NSCl) = 114.0, <(ClSCl) = 104.0°; B3LYP/aug-cc-pv5Z: d(SN) = 1.443, d(SCl) = 2.485 Å; <(NSCl) = 114.3, <(ClSCl) = 102.9°.