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Synthesis and Crystal Structure of $[(Ph_3P)_2(CO)_2(S_2N_2)RuCl]^+AlCl_4^-$. Preparation of Novel S_2N_2 Complexes

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The complex $[(Ph_3P)_2(CO)_2(S_2N_2)RuCl]^+AlCl_4^-$ has been prepared by the reaction of $(Ph_3P)_2(CO)_2RuCl_2$ with $S_2N_2{\cdot}2AlCl_3$, and its structure is determined by single-crystal X-ray analysis. It crystallizes in the monoclinic space group *Cc* with a = 10.365 (1) Å, b = 23.185 (5) Å, c = 18.361 (3) Å, β = 106.06 (1)°, and Z = 4. The structure was refined to R = 0.041, R_w = 0.038 for 3292 reflections with $I \geq 2.0(\sigma(I))$. In the cation the S_2N_2 is coordinated as a monodentate ligand. A considerable degree of bond fixation is observed within the S_2N_2 ring possibly as a result of a relatively strong intramolecular S···Cl interaction of length 2.918 (4) Å. In addition complexes of S_2N_2 with $SnCl_4$, $TiCl_4$, $AlBr_3$, and $BeCl_2$ are prepared by various synthetic routes: the reaction of $S(NSO)_2$ with $TiCl_4$ leads to $S_2N_2{\cdot}TiCl_4$; cleavage of the eight-membered S_4N_4 ring occurs on heating $S_4N_4{\cdot}TiCl_4$ and $S_4N_4{\cdot}2BeCl_2$; S_2N_2 forms 1:1 adducts when it is added to excess $SnCl_4$ or $TiCl_4$. The vibrational spectra of the compounds are discussed.

Introduction

The first complexes with the ligand S_2N_2 were published in 1969 by Patton et al.[2] These were obtained from the reaction of the ligand with the Lewis acids antimony pentachloride and boron trichloride. The X-ray structural analysis of $S_2N_2{\cdot}2SbCl_5$[3] confirmed the proposed[4] cyclic D_{2h} structure of S_2N_2, the respective Lewis acid components of the complexes being attached to the nitrogens. This preparation route has not been further established as a result of the instability of S_2N_2 and the difficulties associated with its handling. In 1980 Thewalt et al.[5] discovered the polymeric $S_2N_2{\cdot}2(CuCl_2{\cdot}CH_3CN)$ from the reaction of S_4N_4 with $CuCl_2$ in acetonitrile. The reaction of S_4N_4 with Al_2Cl_6 in dichloromethane similarly leads to $S_2N_2{\cdot}2AlCl_3$.[6] Herein we report a facile synthetic route for the preparation of bidentate S_2N_2 complexes and for the first time a complex of composition $[(Ph_3P)_2(CO)_2(S_2N_2)RuCl]^+AlCl_4^-$ with a monodentate ligand.

Experimental Section

General Data. All operations were performed strictly under an atmosphere of dry nitrogen, i.e. in a drybox flushed with nitrogen or on a vacuum line. Titanium tetrachloride, tin tetrachloride (E. Merck, Darmstadt, FRG), and aluminum tribromide (Merck-Schuchardt, München, FRG) were distilled and sublimed, respectively, prior to use.

Beryllium dichloride (Fluka AG, Buchs, Switzerland) was used as received. Dicarbonyldichlorobis(triphenylphosphine)ruthenium(II) (Strem Chemicals, Inc.) was dried for 5 h under vacuum before used. Tetrasulfur tetranitride was prepared according to standard methods[7] and recrystallized three times from carbon tetrachloride. Bis(thionylimino)sulfur,[8] disulfur dinitride,[9] $S_2N_2{\cdot}2AlCl_3$,[9] and $S_4N_4{\cdot}TiCl_4$[10] were prepared according to the literature.

Dichloromethane, tribromomethane, and *n*-hexane were refluxed for 3–6 h over P_4O_{10} and sodium, respectively, and distilled prior to use. The spectroscopic measurements were taken as follows: IR spectra as Nujol mulls between CsI plates on a Perkin-Elmer 180; Raman spectra as solids on a 1403 RAMALOG, with the 514.5-nm line of a Spectra-Physics argon laser; mass spectra on a CH 5 Varian MAT (EI, 70 eV). The elemental analyses were performed by Beller, Mikronanalytisches Laboratorium, Göttingen, FRG.

Preparation of $S_2N_2{\cdot}SnCl_4$ (I) from the Reaction of S_2N_2 with $SnCl_4$. A solution of 0.74 g (8 mmol) of S_2N_2 in 80 mL of CH_2Cl_2 was filtered at −20 °C, transferred in a dropping funnel, and added within 30 min to a solution of 10 mL of $SnCl_4$ in 100 mL of CH_2Cl_2. A yellow precipitate was formed, which was filtered off, washed with 2 × 50 mL of CH_2Cl_2 and dried under vacuum: yield 2.7 g (97%); dec pt 146 °C. The infrared spectrum shows bands at 825 s, 805 s, 471 s, 354 vs, 340 s, 338 m, 335 m sh, and 306 vw cm^{-1}. Raman data: 19 m, 44 m, 96 s, 119 m, 140 w, 209 w, 218 w, 224 w, 316 m, 344 s, 355 m, 472 vvw, 619 w sh, 623 vs, 929 m, 1037 m cm^{-1}. The mass spectrum (EI, T = 125 °C) shows peaks at 28 (N_2 43%), 46 (NS, 22%), 64 (S_2, 25%), 92 (S_2N_2, 65%), 120 (Sn, 28%), 155 (SnCl, 24%), 190 ($SnCl_2$ 9%), 225 ($SnCl_3$, 100%), and 260 ($SnCl_4$, 27%). Anal. Calcd for $S_2N_2{\cdot}SnCl_4$: Cl, 40.3; N, 7.9; S, 18.1; Sn, 33.7. Found: Cl, 39.6; N, 7.8; S, 17.3; Sn, 34.3.

Preparation of $S_2N_2{\cdot}TiCl_4$ (II). (a) From the Reaction of S_2N_2 with $TiCl_4$. A solution of 0.8 g (8.7 mmol) of S_2N_2 in 80 mL of CH_2Cl_2 was added dropwise at −10 °C within 30 min to a solution of 10 mL of $TiCl_4$ dissolved in 100 mL of CH_2Cl_2 kept at room temperature. During the addition a yellow precipitate is formed, which was recovered by filtration and washed three times with 30 mL of CH_2Cl_2: yield 2.3 g (94%); dec pt >230 °C. The infrared spectrum of this compound shows bands at 840 vs, 817 s, 626 vvw, 482 m sh, 477 ms, 472 ms, 393 vs br, 361 w sh, 317 w, and 280 vw cm^{-1}. Raman data: 107 m, 135 s, 163 w, 216 vw, 251 vw, 321 ms, 401 vs, 426 m, 626 s, 918 m, 1036 m cm^{-1}. The mass spectrum of the compound (EI, T = 75 °C) shows peaks at 28 (N_2, 100%), 46 (NS, 63%), 64 (S_2, 40%), 92 (S_2N_2, 88%), 153 ($TiCl_3$, 15%), and 188 ($TiCl_4$, 9%). Anal. Calcd for $S_2N_2{\cdot}TiCl_4$: Cl, 50.3; N, 9.9; S, 22.7; Ti, 17.0. Found: Cl, 50.4; N, 9.8; S, 21.7; Ti, 17.0.

(b) From the Reaction of $S(NSO)_2$ with $TiCl_4$. A solution of 10 mL of $TiCl_4$ in 100 mL of CH_2Cl_2 was added with in 30 min under rapid stirring to 2 g (12.8 mmol) of freshly sublimed $S(NSO)_2$ in 80 mL of CH_2Cl_2. At first the reaction mixture turned red-brown, and after a short period of time the color changed to orange. A yellow precipitate was formed slowly. The solid was recovered by filtration, washed three times with 50 mL of CH_2Cl_2, and finally dried under vacuum. On the basis of analytical data and mass and vibrational spectra the compound was identical with $S_2N_2{\cdot}TiCl_4$, prepared from S_2N_2 and $TiCl_4$; yield 3.42 g (95%).

Under identical conditions the reaction of $S(NSO)_2$ with $SnCl_4$ as well as with $SeCl_4$ did not result in the precipitation of the analogous S_2N_2 complexes.

In a series of experiments we investigated whether S_2N_2 can be obtained under ultrahigh vacuum by pyrolysis of $S(NSO)_2$. The temperature of the reaction zone varied from 200 to 400 °C; however, in the cooling trap system only $S(NSO)_2$ was deposited.

(c) By Pyrolysis of $S_4N_4{\cdot}TiCl_4$. *Caution!* $S_4N_4{\cdot}TiCl_4$ as well as the mixture of S_4N_4 and $S_2N_2{\cdot}TiCl_4$ can explode violently. Therefore, the preparations should be carried out behind a protective screen.

Three sealed-off tubes, each one containing 0.6 g of $S_4N_4{\cdot}TiCl_4$, were heated slowly to 125 °C. At this temperature the color of the samples changed within 10 min. The infrared spectrum of the reaction product shows the bands of S_4N_4 and $S_2N_2{\cdot}TiCl_4$. Within 18 h the S_4N_4 was sublimed off under the static vacuum (10^{-3} mbar) at 70–80

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Table I. Spectroscopic Data of S_2N_2 Compounds

compd	IR, cm^{-1}	Raman, cm^{-1}	ref
S_2N_2	785 vs, 476 s		4b
$S_2N_2{\cdot}2SbCl_5$	898 vw, 818 s, 461 s		2a
$S_2N_2{\cdot}TiCl_4$	840 vs, 817 s, 477 ms, 472 ms	626 s, 918 m, 1036 m	this work
$S_2N_2{\cdot}SnCl_4$	825 s, 805 s, 471 s	623 s, 929 m, 1037 m	this work
$S_2N_2{\cdot}2AlCl_3$	887 vs, 850 m, 812 w, 751 m, 722 w, 475 vs	640 s, 904 s, 1103 s	9
$S_2N_2{\cdot}2AlBr_3$	870 vs, 780 w, 733 w, 476 s	629 s, 896 s, 1062 s	this work
$S_2N_2{\cdot}BeCl_2$	877 vs, 734 ms, 710 s, 475 s	655 s, 930 w, 1092 m	this work
$S_2N_2{\cdot}VCl_4$	844 vs, 465 s		10
$[(Ph_3P)_2(CO)_2(S_2N_2)RuCl]^+AlCl_4^-$	860 w, 850 w, 809 vs, 470 s	626, 1004, 1032	this work

°C remaining $S_2N_2{\cdot}TiCl_4$ was identified by vibrational and mass spectra. The yield was quantitative.

Preparation of $S_2N_2{\cdot}2AlBr_3$ (III) from the Reaction of S_4N_4 with Al_2Br_6. The reaction of S_4N_4 with 2 equiv of Al_2Br_6 at room temperature in CH_2Cl_2 resulted in $S_2N_2{\cdot}2AlCl_3$ on the basis of a halogen-exchange reaction. Therefore, the reaction was repeated in $CHBr_3$ (11.4 g (61.9 mmol) of S_4N_4 and 66 g (123.8 mmol) of Al_2Br_6 were added successively to 250 mL of $CHBr_3$, and the mixture was stirred for 16 h). For 0.5 h the reaction mixture turned dark red; then the color lightened, and while the mixture was warmed to 50 °C a fine yellow precipitate was obtained, collected on a frit, washed with 3 × 50 mL of $CHBr_3$, and dried for 8 h under vacuum at 60 °C: yield 55 g (71%); mp 155 °C. Anal. Calcd for $S_2N_2{\cdot}2AlBr_3$: Al, 8.6; Br, 76.6; N, 4.6; S, 10.1. Found: Al, 9.1; Br, 76.0; N, 4.3; S, 9.8. The infrared spectrum of the compound shows bands at 870 vs br, 780 w sh, 733 s, 661 w, 476 s, 457 s, 441 vs, 431 vs, and 350 vs cm^{-1}. Raman data: 95 m, 104 m, 195 w, 246 m, 316 s, 441 w, 623 w sh, 629 s, 896 s, 1062 s cm^{-1}. The mass spectrum (EI, T = 120 °C) shows peaks at 32 (S, 35%), 46 (NS, 37%), 64 (S_2, 81%), 79 (Br, 100%), 92 (S_2N_2, 15%), 106 (AlBr, 20%), 111 (SBr, 18%), 128 (S_4, 8%), 138 (AlBrS, 7%), 143 (S_2Br, 73%), 158 (Br_2, 45%), 185 ($AlBr_2$, 94%), 222 (S_2Br_2, 88%), 256 (S_8, 27%), 264 ($AlBr_3$, 73%), and 446 (Al_2Br_5, 42%). Interestingly the mass fragments SBr, S_2Br, and S_2Br_2 are slightly enriched with the heavier isotope ^{81}Br. When treated with CH_2Cl_2, the compound transforms completely into $S_2N_2{\cdot}2AlCl_3$ by halogen exchange.

Formation of $S_2N_2{\cdot}BeCl_2$ (IV) from the Pyrolysis of $S_4N_4{\cdot}2BeCl_2$. *Caution*! The compounds can explode violently on heating. Therefore experiments should be carried out behind a protective screen.

A 1.84-g (10-mmol) sample of S_4N_4 and 1.6 g (20 mmol) of $BeCl_2$ were transformed in 100 mL of CH_2Cl_2 under stirring for 2 h at room temperature. On the basis of analytical data and mass and vibrational spectra, the yellow precipitate proved to be $S_4N_4{\cdot}2BeCl_2$ (yield 85%). In a longer reaction time the red-brown $S_4N_4{\cdot}BeCl_2$ was also isolated. In an attempt to sublime $S_4N_4{\cdot}2BeCl_2$ (6 h at 75–80 °C (10^{-3} mbar)), S_4N_4 collected at the water-cooled cold finger (8 °C), $S_4N_4{\cdot}BeCl_2$ as well as free $BeCl_2$ remained as residue, and S_2N_2 was deposited in the cooling trap.

In each of three sealed-off glass ampules 0.6-g samples of $S_4N_4{\cdot}2BeCl_2$ were slowly heated to 140 °C and kept at this temperature for 30 min. At 110 °C $S_4N_4{\cdot}2BeCl_2$ turned brown; when heated to 130 °C, the samples lightened to a sand-colored powder. On heating of the reaction product under vacuum (80–90 °C (10^{-3} mbar)) for 36 h no volatiles were obtained. The product was washed with 3 × 50 mL of CH_2Cl_2 and dried for 8 h under vacuum; dec pt 230 °C without melting. $S_2N_2{\cdot}BeCl_2$, which the vibrational and mass spectra showed to be contaminated with $S_4N_4{\cdot}BeCl_2$ and $(NS_2^+)_2BeCl_4$, could not be purified further.

The infrared spectrum shows bands at 925 s sh, 911 s, 877 s, 760 m, 734 ms, 710 s, 679 w, 653 w, 624 vs, 586 w, 556 m, 536 w, 475 s, and 340 m cm^{-1}. Raman data: 139 m, 200 s, 229 vs, 558 m, 567 m, 624 w, 655 s, 680 w, 727 w, 881 w, 930 w, 1092 m cm^{-1}. The mass spectrum (EI, T = 75 °C) shows peaks at 46 (NS, 10%), 64 (S_2, 15%), 78 (NS_2, 13%), 92 (S_2N_2, 100%), and 137 (S_3N_3, 15%).

Preparation of $[(Ph_3P)_2(CO)_2(S_2N_2)RuCl]^+AlCl_4^-$ (V). An 8.7-g amount (11.5 mmol) of $(Ph_3P)_2(CO)_2RuCl_2$ was added slowly to a suspension of 4.14 g (11.5 mmol) of $S_2N_2{\cdot}2AlCl_3$ in 150 mL of CH_2Cl_2 and stirred for 1 h at room temperature. During the addition of the Ru component, the mixture already turns dark brown. The mixture was refluxed for 2 h and filtered off, and 100 mL of hexane was added to the filtrate. Overnight, 1–10 mm long yellow white crystals formed at −10 °C, which were separated from the mother liquor and dried for 8 h under vacuum: yield 4.7 g after recrystallization from dichloromethane/hexane; dec pt 152 °C. Apart from the bands of the triphenylphosphane and carbonyl ligands the infrared spectrum of the compound shows the following in addition: 860 w, 850 w, 809 vs, 708 s, 470 vs cm^{-1}. In the mass spectrum (EI, T = 155° C) S_2N_2 (m/e = 92, 100%) appears as a new signal. Anal. Calcd for $C_{38}H_{30}P_2RuO_2S_2N_2AlCl_5$ (mol wt 977.98): C, 46.7; H, 3.1; S, 6.6; N, 2.9; Cl, 18.1. Found: C, 45.4; H, 3.2; S, 6.6; N, 3.4; Cl, 18.3. Upon attempts to record the Raman spectrum, the light-sensitive compound decomposed. With a laser capacity of only 10 mW, however, we were able to obtain tiny bands at 626, 1004, and 1032 cm^{-1}, which are assigned to the skeletal vibrations of the S_2N_2 ligand. Yellow-white crystals of V suitable for X-ray diffraction were obtained from dichloromethane/hexane solutions.

Table II. Experimental Details of the X-ray Diffraction Study of $[C_{38}H_{30}N_2O_2P_2S_2ClRu][AlCl_4]$ (V)

Crystal Data	
fw	978.1
space group	*Cc*
unit cell constants (22 ± 1 °C)	
a, Å	10.265 (1)
b, Å	23.185 (5)
c, Å	18.361 (3)
β, deg	106.06 (1)
Z	4
D_{calcd}, g cm^{-3}	1.55
Measurement of Intensity Data	
radiation	Mo Kα
scan mode	ω
2θ angular range, deg	$3 \leqslant 2\theta \leqslant 50$
reflcns measd	3695
abs cor, cm^{-1}	8.36
max transmission	0.358
min transmission	0.303
Structure Refinement	
I observn criterion	$I \geqslant 2.0(\sigma(I))$
no. of reflcns	3292
K (scale factor)	1.3837
g (weighting factor)	0.0002
R	0.041
R_w	0.038

Collection of X-ray Diffraction Data. Experimental work was carried out on a Syntex $P2_1$ diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Crystal data and details of the intensity data collection are given in Table II. Unit cell constants were obtained by least-squares refinement of settings of 15 high-angle reflections $\pm(hkl)$. Intensity data were collected in the ω mode $(+h,+k,\pm l)$ to a maximum 2θ value of 50°. Three control reflections were monitored every 100 reflections. No significant deviations in their intensities were observed. Crystal dimensions were 0.52 × 0.23 × 0.37 mm. Absorption corrections were applied empirically (RSEMP, G.M. Sheldrick) on the basis of azimuthal scan data with ψ intervals of 20° for 15 strong reflections. After reflections with $I = 2.0(\sigma(I))$ had been treated as unobserved, data reduction yielded 3292 independent reflections.

Structure Solution and Refinement of V. The systematic absences indicated the space groups *Cc* or *C*2/*c*, of which the former was confirmed by the successful refinement. The structure was solved by Patterson and difference syntheses and refined by full-matrix least squares with $\sum w\Delta^2$ being minimized. Anisotropic temperature factors were introduced for all nonhydrogen atoms. The phenyl hydrogens were assigned a group isotropic temperature factor and allowed to

Table III. Atom Coordinates and Equivalent Isotropic Temperature Factors ($Å^2 \times 10^3$) with Standard Deviations in Parentheses

	x/a	y/b	z/c	U_{eq}
Ru(1)	0.0000 (0)	0.1936 (1)	0.2500 (0)	24 (1)
P(1)	−0.0456 (2)	0.0941 (1)	0.2771 (1)	26 (1)
P(2)	0.0590 (2)	0.2896 (1)	0.2137 (1)	27 (1)
C(11)	−0.2081 (8)	0.0833 (3)	0.2992 (4)	35 (4)
C(12)	−0.3222 (8)	0.1072 (4)	0.2510 (5)	42 (4)
C(13)	−0.4475 (9)	0.1001 (4)	0.2625 (6)	54 (5)
C(14)	−0.4602 (10)	0.0676 (5)	0.3243 (5)	57 (6)
C(15)	−0.3459 (10)	0.0400 (4)	0.3698 (5)	56 (6)
C(16)	−0.2228 (10)	0.0487 (4)	0.3579 (5)	48 (5)
C(21)	0.0809 (7)	0.0653 (3)	0.3571 (4)	29 (4)
C(22)	0.1815 (8)	0.0264 (4)	0.3470 (5)	44 (5)
C(23)	0.2837 (10)	0.0087 (4)	0.4085 (5)	51 (5)
C(24)	0.2931 (10)	0.0299 (4)	0.4787 (5)	53 (5)
C(25)	0.1952 (10)	0.0673 (4)	0.4904 (5)	52 (5)
C(26)	0.0914 (9)	0.0854 (3)	0.4296 (4)	39 (4)
C(31)	−0.0593 (7)	0.0438 (3)	0.1989 (4)	28 (3)
C(32)	−0.0037 (8)	0.0543 (3)	0.1385 (4)	36 (4)
C(33)	−0.0268 (9)	0.0159 (4)	0.0795 (5)	45 (5)
C(34)	−0.0987 (10)	−0.0328 (4)	0.0778 (5)	52 (5)
C(35)	−0.1519 (9)	−0.0452 (4)	0.1368 (6)	53 (5)
C(36)	−0.1355 (9)	−0.0075 (4)	0.1968 (5)	45 (5)
C(41)	0.0839 (8)	0.2961 (3)	0.1193 (4)	32 (4)
C(42)	0.0562 (9)	0.3491 (3)	0.0811 (5)	44 (5)
C(43)	0.0773 (10)	0.3552 (4)	0.0110 (5)	53 (5)
C(44)	0.1263 (9)	0.3108 (5)	−0.0236 (5)	54 (5)
C(45)	0.1513 (10)	0.2587 (4)	0.0130 (5)	58 (6)
C(46)	0.1326 (9)	0.2510 (4)	0.0842 (5)	48 (5)
C(51)	0.2133 (8)	0.3179 (3)	0.2775 (5)	36 (4)
C(52)	0.3358 (8)	0.3129 (4)	0.2596 (5)	48 (5)
C(53)	0.4538 (10)	0.3339 (5)	0.3117 (7)	71 (7)
C(54)	0.4490 (12)	0.3583 (5)	0.3770 (7)	76 (7)
C(55)	0.3273 (10)	0.3635 (4)	0.3969 (6)	60 (6)
C(56)	0.2127 (10)	0.3424 (4)	0.3462 (5)	45 (5)
C(61)	−0.0720 (8)	0.3428 (3)	0.2101 (4)	30 (4)
C(62)	−0.0465 (9)	0.3991 (3)	0.2330 (5)	41 (4)
C(63)	−0.1524 (12)	0.4386 (4)	0.2253 (6)	65 (6)
C(64)	−0.2869 (11)	0.4203 (4)	0.1966 (5)	57 (6)
C(65)	−0.3134 (9)	0.3643 (4)	0.1713 (5)	51 (5)
C(66)	−0.2044 (8)	0.3266 (4)	0.1775 (5)	36 (4)
Cl(1)	0.2167 (2)	0.1603 (1)	0.2410 (1)	38 (1)
N(1)	0.1163 (7)	0.2083 (3)	0.3608 (4)	33 (3)
S(1)	0.2826 (2)	0.1953 (1)	0.3996 (1)	48 (1)
N(2)	0.2619 (9)	0.2199 (3)	0.4804 (4)	59 (4)
S(2)	0.1029 (3)	0.2323 (1)	0.4429 (1)	51 (1)
C(1)	−0.0957 (8)	0.1816 (3)	0.1450 (5)	31 (4)
C(1)	−0.1532 (6)	0.1753 (3)	0.0844 (3)	47 (3)
C(2)	−0.1553 (8)	0.2197 (3)	0.2749 (4)	30 (4)
C(2)	−0.2458 (6)	0.2332 (3)	0.2941 (4)	52 (4)
Al(1)	0.4402 (3)	0.1353 (1)	0.0257 (1)	48 (1)
Cl(2)	0.2787 (3)	0.1042 (1)	0.0660 (2)	62 (1)
Cl(3)	0.3617 (3)	0.1579 (1)	−0.0901 (1)	64 (1)
Cl(4)	0.5243 (3)	0.2105 (1)	0.0907 (1)	57 (1)
Cl(5)	0.5941 (3)	−0.0721 (1)	0.5366 (2)	72 (2)

Table IV. Bond Lengths (Å) and Bond Angles (Deg)

Bond Lengths			
P(1)-Ru(1)	2.432 (2)	P(2)-Ru(1)	2.446 (2)
Cl(1)-Ru(1)	2.404 (2)	N(1)-Ru(1)	2.082 (6)
C(1)-Ru(1)	1.926 (8)	C(2)-Ru(1)	1.876 (9)
S(1)-N(1)	1.684 (7)	S(2)-N(1)	1.648 (7)
N(2)-S(1)	1.656 (9)	S(2)-S(1)	2.361 (4)
S(2)-N(2)	1.612 (8)	O(1)-C(1)	1.116 (1)
Bond Angles			
P(2)-Ru(1)-P(1)	173.9 (1)	Cl(1)-Ru(1)-P(1)	86.8 (1)
Cl(1)-Ru(1)-P(2)	88.3 (1)	N(1)-Ru(1)-P(1)	92.6 (2)
N(1)-Ru(1)-P(2)	90.0 (2)	N(1)-Ru(1)-Cl(1)	80.1 (2)
C(1)-Ru(1)-P(1)	89.7 (2)	C(1)-Ru(1)-P(2)	87.4 (3)
C(1)-Ru(1)-Cl(1)	96.3 (3)	C(1)-Ru(1)-N(1)	175.6 (3)
C(2)-Ru(1)-P(1)	91.8 (2)	C(2)-Ru(1)-P(2)	93.7 (2)
C(2)-Ru(1)-Cl(1)	170.2 (2)	C(2)-Ru(1)-N(1)	90.3 (3)
C(2)-Ru(1)-C(1)	93.3 (3)		
S(2)-N(1)-Ru(1)	141.1 (4)	S(2)-N(1)-S(1)	90.2 (3)
N(2)-S(1)-N(1)	87.2 (4)	S(2)-S(1)-N(1)	44.3 (3)
S(2)-S(1)-N(2)	43.0 (3)	S(2)-N(2)-S(1)	92.5 (4)
S(1)-S(2)-N(1)	45.5 (2)	N(2)-S(2)-N(1)	90.0 (4)
N(2)-S(2)-S(1)	44.5 (3)	O(1)-C(1)-Ru(1)	178.7 (8)
S(1)-N(1)-Ru(1)	128.7 (4)		

ride on the corresponding carbon atoms with d(C–H) = 1.08 Å and equal H–C–C angles. The weighting scheme was given by $w = k(\sigma^2(F_o) + 0.0002F_o^2)^{-1}$. Scattering factors for the non-hydrogen atoms were taken from Cromer et al.[11] and for the hydrogen atoms from Stewart et al.[12] No extinction correction was introduced. Computations were performed with SHELX[13] and locally developed programs. The molecule plot was drawn with PLUTO by W. S. S. Motherwell.

Results and Discussion

We have been interested in the reaction of S_2N_2 with $SnCl_4$ and $TiCl_4$ and in determining whether S_2N_2 acts as a monodentate or bidentate bridging ligand. According to Patton et al.[2a] the reactions of S_2N_2 with Lewis acids have to be performed so that the S_2N_2 solutions are added to the acid to avoid side reactions. We found that $SnCl_4$ and $TiCl_4$ form with S_2N_2 1:1 adducts, where S_2N_2 acts as a bridging ligand. A new and facile synthesis for S_2N_2 complexes was discovered with use of the precursor $S(NSO)_2$, whose reaction with $TiCl_4$ leads to $S_2N_2{\cdot}TiCl_4$ in a high yield:

$$S(NSO)_2 + TiCl_4 \rightarrow S_2N_2{\cdot}TiCl_4 + SO_2$$

In 1965 Becke-Goehring et al.[14] reported that the reaction of $S(NSO)_2$ with $TiCl_4$ results in the formation of $S_4N_4{\cdot}2TiCl_4$, but a reinvestigation of the procedure, however, shows the product to be in fact $S_2N_2{\cdot}TiCl_4$. $S(NSO)_2$ can be prepared on a large scale, and this leads to easily available complexes of S_2N_2. A ruthenium complex with the S_2N_2 ligand was prepared by the reaction of $(Ph_3P)_2(CO)_2RuCl_2$ with $S_2N_2{\cdot}2AlCl_3$. The elimination of a Cl^- anion with the formation of $AlCl_4^-$ must be the driving force for the change in the coordination of S_2N_2:

$$(Ph_3P)_2(CO)_2RuCl_2 + S_2N_2{\cdot}2AlCl_3 \rightarrow [(Ph_3P)_2(CO)_2(S_2N_2)RuCl]^+AlCl_4^- + {}^1/_2Al_2Cl_6$$

This exchange reaction might become a more general route for the synthesis of transition-metal complexes of S_2N_2.

Formation of the S_2N_2 Ring from the Reaction of S_4N_4 with Lewis Acids. The reactions of S_4N_4 with Lewis acids can result in the cleavage of the S_4N_4 eight-membered ring and the formation of S_2N_2 ring system. This cleavage takes place spontaneously with Al_2Cl_6,[6,9] Al_2Br_6/VCl_4,[10] and $CuCl_2$.[15] When they are heated, the adducts $S_4N_4{\cdot}TiCl_4$ and $S_4N_4{\cdot}2BeCl_2$ are also transformed into the corresponding S_2N_2 compounds according to the equations

$$2S_4N_4{\cdot}TiCl_4 \xrightarrow{\Delta} 2S_2N_2{\cdot}TiCl_4 + S_4N_4$$

$$S_4N_4{\cdot}2BeCl_2 \xrightarrow{\Delta} 2S_2N_2{\cdot}BeCl_2$$

According to the yields we observed for $S_2N_2{\cdot}2AlCl_3$,[9] $S_2N_2{\cdot}2AlBr_3$, $S_2N_2{\cdot}TiCl_4$, and $S_2N_2{\cdot}BeCl_2$, 2 mol S_2N_2 is formed

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Table V. Bonding Parameters of the S_2N_2 Ring Skeleton in S_2N_2 Compounds

compd	S-N, Å	S-S, Å	∠NSN, deg	∠SNS, deg	ref
S_2N_2 (−130 °C)	1.657 (1) 1.651 (1)	2.348^a	89.58 (6)	90.42 (6)	18
$S_2N_2 \cdot 2SbCl_5$	1.616 (7) 1.623 (8)	2.390 (5)	84.9 (4)	95.4 (6)	3
$S_2N_2 \cdot 2(CuCl_2 \cdot CH_3CN)$	1.633 (8) 1.641 (8)	2.410^a	85.2 (5)	94.7 (6)	5
$S_2N_2 \cdot 2AlCl_3$	1.648 (3) 1.644 (3)	2.425^a	85.1 (2)	94.9 (2)	6
$[(Ph_3P)_2(CO)_2(S_2N_2)RuCl]^+AlCl_4^-$	1.684 (7) 1.656 (9) 1.648 (7) 1.612 (8)	2.361 (4)	90.0 (4) 87.2 (4)	92.5 (4) 90.2 (3)	this work

^{a} Calculated by the indicated data.

per mole of S_4N_4. Further investigations of the ring cleavage mechanism are in progress.

Vibrational Spectra. The infrared and Raman spectra—together with the mass spectra and analytical data—are consistent with the S_2N_2 ring system. The skeleton vibrations significantly differ from those of the known S_4N_4 compounds[15] and are in agreement with the results of Bragin and Evans on S_2N_2[4b] (see Table I).

There are six vibrational fundamentals for the D_{2h} structure of S_2N_2. The symmetry species are 2 A_{1g} + B_{1g} + B_{1u} + B_{2u} + B_{3u}. Three of them (2 A_{1g} + B_{1g}) are only Raman active the others are active only in the infrared.[16]

The broad system in the range of 785–900 cm^{-1} in the infrared spectra of the complexes and S_2N_2 itself (Table I) is assigned to the B_{3u} ν(S–N) stretching mode while the 461–477-cm^{-1} bands are assigned to the B_{2u} ν(S–N). In the bidentate coordinated S_2N_2 complexes the B_{3u} ν(S–N) is shifted 20–110 cm^{-1} to higher frequencies. The shift is smaller in the monodentate Ru complex (although weak bands at 850 and 860 cm^{-1} occur in the infrared). The Raman-active vibrations in the spectra cannot be assigned without a force field calculation. Since, according to the vibrational spectra, the S_2N_2 ring is bidentate in the 1:1 adducts with $SnCl_4$, $TiCl_4$, VCl_4, and $BeCl_2$, the metal atoms must display the coordination number 6 (Sn, Ti, and V) and 4 (Be), hence the structure of these complexes should be a polymeric chain of alternating S_2N_2 and Lewis acid units. As regards the molecule $S_2N_2 \cdot SnCl_4$, the coordination geometry of the Sn atoms is considered to be a distorted octahedron with the symmetry C_{2v} according to the vibrational spectra. The infrared spectrum shows three bands in the Sn–Cl stretching region. A coincidence between the 354-cm^{-1} band in the infrared and the 355-cm^{-1} band in the Raman spectra is to be considered.[17] As regards the other complexes, it is not to be seen from the spectra whether the S_2N_2 ligands are coordinated cis or trans.

Description of the Structure of $[(Ph_3P)_2(CO)_2(S_2N_2)RuCl]^+AlCl_4^-$. Interatomic distances are given in Table III and bond angles in Talbe IV. The structure of the cation is presented in Figure 1. The coordination geometry about the Ru atom may be described as a highly distorted octahedron. The coordinated S_2N_2 is efficiently protected sterically by the bulky triphenylphosphine ligands. It lies in the plane of the octahedron defined by Ru1, N1, C1, C2, and Cl1. In contrast to free S_2N_2 and all those complexes that have been structurally characterized (Table V), a marked degree of bond fixation is observed for the S_2N_2 ring in the Ru complex. Whereas N1–S2 and N2–S1 are similar in length to the bond distances observed in free S_2N_2,[18] N1–S1 is markedly longer (1.684 Å) and N2–S2 markedly shorter (1.612 Å). In this context it is interesting to note that a remarkably short intramolecular S···Cl contact of length 2.918 (4) Å is to be observed between S1 and Cl1 (sum of the van der Waals radii 3.75 Å). This secondary bond is associated with a widening of the S2–N1–Ru1 angle to 141.1 (4)° and a narrowing of the S1–N1–Ru1 angle to 128.7 (4)°. The bond angle N1–Ru1–Cl1 has a value of 80.1 (2)°. Short albeit somewhat longer intramolecular S···Cl interactions of length 3.056 Å were also observed in $S_2N_2 \cdot 2AlCl_3$.[6] In this case, however, both S atoms are involved in identical interactions and the ring S–N distances are very similar to one another (the molecule $S_2N_2 \cdot AlCl_3$ contains a crystallographic center of symmetry). S–N–Al angles of 142.6 (2) and 122.5 (2)° are associated with the interaction.

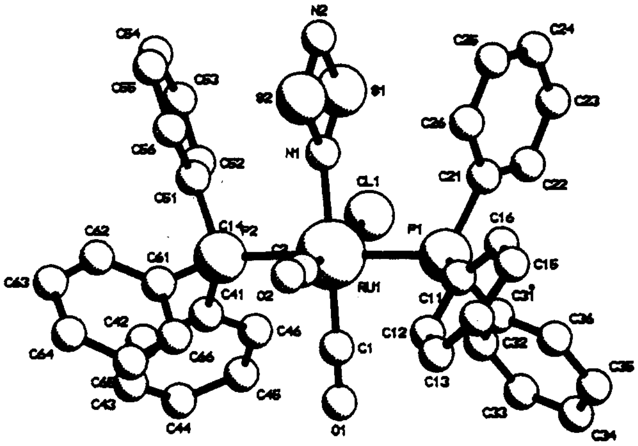

Figure 1. Perspective view of the structure of the cation $[(Ph_3P)_2(CO)_2(S_2N_2)RuCl]^+$.

Whereas S1 in the Ru complex is not involved in any short intermolecular contacts to Cl1 of a neighboring cation or to the Cl atoms of the $AlCl_4^-$ anion, the structure does display two short intermolecular S2···Cl contacts with the anion. The strength of these interactions is, however, much weaker than for the S1···Cl1 interaction: S2···Cl3 = 3.487 Å, S2···Cl4 = 3.315 Å. These findings suggest that a plausible explanation for the degree of bond fixation observed in the S_2N_2 ring of the Ru complex may be sought in terms of the S1···Cl1 interaction.

On the basis of the difference between the Ru–C distances (Ru1–C1 = 1.926 (8) Å, Ru1–C2 = 1.876 (9) Å), it may be assumed that the donor capability of the S_2N_2 ligand to the central Ru atom is weaker than that of the chlorine ligand (trans to C2).

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Registry No. I, 87861-56-1; II, 87861-57-2; III, 87861-58-3; IV, 87861-59-4; V, 87861-61-8; $S_4N_4\cdot TiCl_4$, 87800-10-0; $(Ph_3P)_2(CO)_2RuCl_2$, 14564-35-3; $S_2N_2\cdot 2AlCl_3$, 82571-22-0; $S(NSO)_2$, 13840-74-9; S_4N_4, 28950-34-7.

Supplementary Material Available: Listings of anisotropic temperature factors for non-hydrogen atoms, isotropic temperature factors and atom coordinates for hydrogen atoms, and observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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Dealkylation of *N*-Methyl-5,10,15,20-tetraphenylporphine by Palladium(II) in Acetonitrile, Dimethyl Sulfoxide, and Dimethylformamide

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Kinetics data for the dealkylation of *N*-methyl-5,10,15,20-tetraphenylporphyrin by palladium(II) have been obtained in acetonitrile, dimethyl sulfoxide, and dimethylformamide solutions. The data are consistent with a general mechanism involving ion-dipole association of a solvated Pd(II) complex with the free base *N*-methylporphyrin followed by a series of ligand dissociation and bond formation equilibria and a terminal step involving nucleophilic displacement of the *N*-methyl group. The rate-determining step and the ability of the solvent itself to act as the nucleophile, however, differ in these three solvents. In acetonitrile, rapid formation of an *N*–methylporphyrin complex of Pd(II) ($Pd(N\text{-}CH_3TPP)^+$) is indicated by visible absorption spectroscopy. The overall formation of (tetraphenylporphinato)palladium(II) (PdTPP) is only affected slightly by the concentration of Pd(II) and is first order in the concentration of added nucleophile, di-*n*-butylamine. At [Pd(II)] = 0.010 M, $\Delta H^\ddagger = 14.0 \pm 0.4$ kcal/mol and $\Delta S^\ddagger = -23.2 \pm 1.2$ cal/(mol K). In Me_2SO, an intermediate that does not correspond spectrally to $Pd(N\text{-}CH_3TPP)^+$ is $\Delta S^\ddagger$ 2 orders of magnitude faster than the formation of PdTPP. The activation parameters for the second process are $\Delta H^\ddagger = 19.1 \pm 0.3$ kcal/mol and $\Delta S^\ddagger = -12.3 \pm 0.4$ cal/(mol K). In contrast for the reactions in CH_3CN and Me_2SO, in DMF isosbestic points indicated conversion of $N\text{-}CH_3HTPP$ to PdTPP without appreciable accumulation of any intermediate. Both Me_2SO and DMF act as nucleophiles in the dealkylation of $N\text{-}CH_3HTPP$ in the presence of Pd(II).

Introduction

In this report we discuss the formation of (tetraphenylporphinato)palladium(II) from *N*-methyl-5,10,15,20-tetraphenylporphine (Figure 1) and Pd(II) in acetonitrile, dimethyl sulfoxide, and dimethylformamide. These dealkylation reactions are of interest for several reasons. Several years ago Fawwaz and co-workers found that the rejection of transplanted tissue in small animals could be controlled by administration of ^{109}Pd hematoporphyrin IX,[1] but experimentation with larger animals was prevented because the traditional route for the preparation of Pd(II) complexes of porphyrins[2] is too time consuming and only about 15% of the initial activity of the ^{109}Pd is present in the product. We have shown that ^{109}Pd hematoporphyrin IX can be synthesized with about 80% retention of activity in a simple, rapid procedure using *N*-methylhematoporphyrin IX as starting material.[3] Since this reaction takes place in dimethyl sulfoxide, we were interested in elucidating its mechanism. In addition, we have investigated dealkylation reactions involving Cu(II), Ni(II), Mn(II), and Zn(II) in acetonitrile and concluded that the stability of the final dealkylated porphyrin complex rather than the size or Lewis acidity of the metal ion determines the relative rate of dealkylation.[4] The dealkylation reaction with Pd(II), a relatively large ion that forms very stable porphyrin complex,[5] would be a good test of this conclusion. The third solvent, dimethylformamide, was chosen because it is one of the few solvents in which kinetic studies for the formation of porphyrin complexes with a significant number of metal ions show second-order behavior.[6,7] If formation of the *N*-methylporphyrin complex of Pd(II) were to be rate determining in the dealkylation reaction, the formation rate could be compared with those of other metal ions.[7]

Experimental Section

N-Methyl-5,10,15,20-tetraphenylporphine was prepared as previously described,[8] with the exception that methyl trifluoromethanesulfonate was substituted for the methyl fluoromethanesulfonate, which is reported to be more toxic. It was chromatographed on alumina, recrystallized, and showed appropriate spectral properties.[8] Acetonitrile was stirred overnight with 4-Å molecular sieves (Davison) and CaH_2 and filtered. After being stirred overnight with P_2O_5, it was refluxed for 1 h, distilled, and stored over molecular sieves. Dimethylformamide was stirred with BaO for 2 h under N_2 and distilled from BaO into a receiver containing 4-Å molecular sieves. No dimethylamine or formic acid was evident in the ^1H NMR spectrum of the distillate. Dimethyl sulfoxide was stirred with BaO for 30 min, distilled under vacuum, and stored over molecular sieves. Di-*n*-butylamine was stored over KOH pellets and CaH_2 for 2 dys, filtered, and fractionally distilled into a receiver containing molecular sieves. The 2,6-lutidine and 2,6-di-*tert*-butylpyridine were refluxed with BaO and distilled. The 2,2,6,6-tetramethylpiperidine was used as received from Aldrich Chemical Co.

The Pd(II) stock solutions were prepared by dissolving $Pd(NO_3)_2\cdot xH_2O$ (Alfa Ventron) in the appropriate solvent, filtering through

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