Alkylation of [N(SPPh₂)(SPPh₂)]⁻, [N(SePPh₂)(SePPh₂)]⁻, and [N(SPPh₂)(SePPh₂)]⁻

Perumal Sekar and James A. Ibers*

Evanston, IL/USA. Northwestern University, Department of Chemistry

Dedicated to Professor Bernt Krebs on the Occasion of his 70th Birthday

Abstract. A facile synthesis is described in which the compounds N(SPPh₂)(CH₃SPPh₂), N(SePPh₂)(CH₃SePPh₂), N(SPPh₂)(CH₃SePPh₂), N(SePPh₂)(NCCH₂SePPh₂), and N(SPPh₂)(NCCH₂SePPh₂) have been obtained in good yield by alkylation of [N(QPPh₂)₂]⁻ (Q = S or Se) or [N(SPPh₂)(SePPh₂)]⁻ with CH₃I or ClCH₂CN in CH₃OH at room temperature. These compounds have been characterized by single-crystal X-ray diffrac-tion and NMR spectroscopic techniques. All five compounds have similar structures in which a CH₃ or NCCH₂ moiety is bonded to an S or preferentially an Se atom of an anion to form a neutral molecule.

Keywords: Alkylation; Facile synthesis; Imidodiphosphinodichalco-genido ligands; Crystal structures

Introduction

In a series of papers in the 1960's *Schmidpeter* and coworkers described the synthesis of "carbon-free chelate rings" of the type $[R_1R_2P(X)N(X)PR_1R_2]^-$, where $R_1 = R_2 =$ Me or Ph and X = Y = S, O, or NH [1−3]. They briefly alluded to the use of these chelates to form metal complexes, but they offered no details beyond melting points [2]. It remained for *Davison* and *Switkes* [4] to synthesize and characterize a number of complexes between these ligands and divalent metals. That work has been followed by numerous reports of metal complexes of such ligands, particularly those of $[N(SPR_2)_2]^-$; a very recent example involves transuranic elements [5]. Surprisingly, very little non-metal reaction chemistry of such ligands has been reported. Reaction of HN(SPPh₂)₂ with X₂ (X = Cl or Br) was shown to afford [N(XPPh₂)₂]X [3]. Methylation of HN(SPPh₂)₂ to afford N(SPPh₂)(CH₃SPPh₂) and [N(CH₃SPPh₂)₂]⁺ was achieved under harsh conditions involving diazomethane [1]. Since that time there appears to be but one report of the methylation of such ligands [6]; in that study it was found that refluxing a 1:1 molar ratio of (CH₃)₃SbCl₂ and K[N(SPPh₂)₂] in toluene for 4 h led to N(SPPh₂)(CH₃SPPh₂) in 58 % yield.

Facile syntheses of $[N(SePR_2)_2]^-$ and $[N(SPR_2)(SePR_2)]^-$ are now available [7−10]. Here we examine the alkylation of $[N(QPPh_2)_2]^-$ (Q = S or Se) and $[N(SPPh_2)(SePPh_2)]^-$.

* Prof. Dr. J. A. Ibers
Department of Chemistry
Northwestern University
2145 Sheridan Rd.
Evanston, IL 60208-3113, USA
E-mail: ibers@chem.northwestern.edu

We describe a facile high-yield reaction that occurs under mild conditions and leads to the alkylation of an S or Se atom of such anions. In particular we demonstrate that alkylation occurs preferentially at the Se atom.

Experimental Section

All manipulations were performed under an inert atmosphere of N₂ with the use of standard Schlenk-line techniques or under Ar in a glove box. Solvents were dried, distilled, and degassed under N₂ before use. CH₂Cl₂ was distilled from P₂O₅; CH₃OH was dried over molecular sieves. CH₃I, ClCH₂CN, and KO'Bu were purchased from Aldrich and used as received. The compounds HN(SPPh₂)₂, HN(SePPh₂)₂, and HN(SPPh₂)(SePPh₂) were prepared according to literature methods [7−10]. NMR data on CH₂Cl₂/CD₂Cl₂ solutions of the products were recorded on either a Mercury 400 MHz spectrometer (³¹P with a 5 mm NMR probe) or an INOVA 400 MHz spectrometer (⁷⁷Se with a 10 mm broad-band NMR probe). ³¹P chemical shifts, in ppm, were recorded at 166.994 MHz and were referenced to an external standard of 85 % H₃PO₄ (set to 0 ppm). ⁷⁷Se chemical shifts, in ppm, were recorded at 76.287 MHz and referenced to an external standard of a saturated solution of Ph₂Se₂ in CD₂Cl₂ (set to 460 ppm). Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Synthesis of N(SPPh₂)(CH₃SPPh₂) (1)

A solution of CH₃I (0.032 mL, 0.5 mmol) in CH₃OH (5 mL) was added slowly to a solution of HN(SPPh₂)₂ (0.225 g, 0.5 mmol) and KO'Bu (0.056 g, 0.5 mmol) in CH₃OH (10 mL). After the mixture was stirred for 10 min, the resultant white precipitate was filtered off, washed with CH₃OH, and dried under vacuum. Clear crystals of [N(SPPh₂)(CH₃SPPh₂)] (**1**) were obtained by recrystallization from CH₂Cl₂ at 0 °C. Yield 0.17 g, 73 %. C₂₅H₂₃NP₂S₂

(463.50 g/mol). calcd.: C 64.8, H 5.00, N 3.02 %; found: C 64.1, H 4.86, N 2.87 %.

^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/CD$_2$Cl$_2$, 25 °C): δ/ppm: 30.0, 43.5 ($^2J_{P-P}$ = 6 Hz).

Synthesis of N(SePPh$_2$)(CH$_3$SePPh$_2$) (2)

N(SePPh$_2$)(CH$_3$SePPh$_2$) was synthesized in a manner similar to that described for the synthesis of **1** but with the addition of HN(SePPh$_2$)$_2$ in place of HN(SPPh$_2$)$_2$. Clear crystals of **2** were obtained by recrystallization from CH$_2$Cl$_2$ at 0 °C. Yield: 0.24 g, 86 %. C$_{25}$H$_{23}$NP$_2$Se$_2$ (557.30 g/mol). calcd.: C 53.9, H 4.16, N 2.51 %; found: C 53.7, H 4.22, N 2.43 %.

^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/CD$_2$Cl$_2$, 25 °C): δ/ppm: 23.5 ($^1J_{P-Se}$ = 405 Hz; $^2J_{P-P}$ = 5 Hz, PSeCH$_3$), 35.5 ($^1J_{P-Se}$ = 715 Hz; $^2J_{P-P}$ = 5 Hz, PSe). **^{77}Se{^{1}H} NMR** (CH$_2$Cl$_2$/CD$_2$Cl$_2$, 25 °C): δ/ppm 142.9 (d, $^1J_{Se-P}$ = 407 Hz, PSeCH$_3$), −145.5 (d, $^1J_{Se-P}$ = 715 Hz, PSe).

Synthesis of N(SPPh$_2$)(CH$_3$SePPh$_2$) (3)

N(SPPh$_2$)(CH$_3$SePPh$_2$) was synthesized in a manner similar to that described for the synthesis of **1** but with the addition of HN(SPPh$_2$)(SePPh$_2$) in place of HN(SPPh$_2$)$_2$. Clear crystals of **3** were obtained by recrystallization from CH$_2$Cl$_2$ at 0 °C. Yield: 0.18 g, 70 %.

C$_{25}$H$_{23}$NP$_2$SSe (510.40 g/mol), calcd.: C 58.8, H 4.54, N 2.74 %: found: C 58.3, H 4.57, N 2.47 %.

^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/CD$_2$Cl$_2$, 25 °C): δ/ppm 21.8, ($^2J_{P-P}$ = 7 Hz, PS), 44.2 ($^1J_{P-Se}$ = 404 Hz; $^2J_{P-P}$ = 7 Hz, PSe). **^{77}Se{^{1}H} NMR** (CH$_2$Cl$_2$/CD$_2$Cl$_2$, 25 °C): δ/ppm 147.3 (d, $^1J_{Se-P}$ = 403 Hz).

Synthesis of N(SePPh$_2$)(NCCH$_2$SePPh$_2$) (4)

A solution of ClCH$_2$CN (0.032 mL, 0.5 mmol) in CH$_3$OH (5 mL) was added slowly to a solution of HN(SePPh$_2$)$_2$ (0.272 g, 0.5 mmol) and KO^{t}Bu (0.056 g, 0.5 mmol) in CH$_3$OH (10 mL). After the mixture was stirred for 10 min, the resultant white precipitate was filtered off, washed with CH$_3$OH, and dried under vacuum. Clear crystals of **4** were obtained by recrystallization from CH$_2$Cl$_2$ at 0 °C. Yield: 0.19 g, 65 %. C$_{26}$H$_{22}$N$_2$P$_2$Se$_2$ (582.32 g/mol). calcd.: C 53.6, H 3.81, N 4.81 %: found: C 53.4, H 3.58, N 4.68 %.

^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/CD$_2$Cl$_2$, 25 °C): δ/ppm 25.3 ($^1J_{P-Se}$ = 374 Hz; $^2J_{P-P}$ = 7 Hz, PSeCH$_2$CN), 36.9 ($^1J_{P-Se}$ = 709 Hz; $^2J_{P-P}$ = 7 Hz, PSe): **^{77}Se{^{1}H} NMR** (CH$_2$Cl$_2$/CD$_2$Cl$_2$, 25 °C): δ/ppm 295.7 (d, $^1J_{Se-P}$ = 374 Hz, PSeCH$_2$CN), −135.5 (d, $^1J_{Se-P}$ = 708 Hz, PSe).

Synthesis of N(SPPh$_2$)(NCCH$_2$SePPh$_2$) (5)

N(SPPh$_2$)(NCCH$_2$SePPh$_2$) was synthesized in a manner similar to that described for the synthesis of **4** but with the addition of HN(SPPh$_2$)(SePPh$_2$) in place of HN(SePPh$_2$)$_2$. Clear crystals of **5** were obtained by recrystallization from CH$_2$Cl$_2$ at 0 °C. Yield: 0.16 g, 60 %. C$_{26}$H$_{22}$N$_2$P$_2$SSe (535.42 g/mol). calcd.: C 58.3, H 4.14, N 5.23 %: found: C 57.7. H 3.97,N 5.11 %.

^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/CD$_2$Cl$_2$, 25 °C): δ/ppm 22.9 ($^2J_{P-P}$ = 9 Hz, PS), 45.6 ($^1J_{P-Se}$ = 371 Hz; $^2J_{P-P}$ = 9 Hz, PSeCH$_2$CN). **^{77}Se{^{1}H} NMR** (CH$_2$Cl$_2$/CD$_2$Cl$_2$, 25 °C): δ/ppm 299.2 (d, $^1J_{Se-P}$ = 370 Hz).

Single-crystal X-ray diffraction study

Although the crystal structure of N(SPPh$_2$)(CH$_3$SPPh$_2$) (**1**) was determined earlier [6] at 300 K we elected to determine that structure again, this time at 153 K, the temperature used for the collection of data from compounds **2**−**5**. Data were collected on a Bruker Smart 1000 CCD X-ray diffractometer with the program SMART [11] at 153 K with the use of monochromatized Mo Kα radiation (λ = 0.71073 Å). The diffracted intensities generated by a scan of 0.3° in ω were recorded on four sets of 606 frames at φ settings of 0°, 90°, 180°, and 270°, with an additional 50 frames at φ = 0° for detection of possible decay. The exposure times (s/frame) were 5 (for **2**), 10 (for **1**, **3**, and **4**) and 15 (for **5**). Cell refinement and data reduction were carried out with the use of the program SAINT [11]. Face-indexed absorption corrections were made with the program XPREP [12]. Then the program SADABS was employed to make incident beam and decay corrections [11]. The structures were solved by direct methods with the program SHELXS and refined by full-matrix least-squares techniques with the program SHELXL [12]. Hydrogen atoms were generated in calculated positions and constrained with the use of a riding model. The final models involved anisotropic displacement parameters for all non-hydrogen atoms. Selected crystallographic data for compounds **1**−**5** are listed in Table 1 and further crystallographic details may be found in

Table 1 Selected crystallographic data for N(SPPh$_2$)(CH$_3$SPPh$_2$) (**1**), N(SePPh$_2$)(CH$_3$SePPh$_2$) (**2**), N(SPPh$_2$)(CH$_3$SePPh$_2$) (**3**), N(SePPh$_2$)(NCCH$_2$SePPh$_2$) (**4**), and N(SPPh$_2$)(NCCH$_2$SePPh$_2$) (**5**)

	1	2	3	4	5
Formula	C$_{25}$H$_{23}$NP$_2$S$_2$	C$_{25}$H$_{23}$NP$_2$Se$_2$	C$_{25}$H$_{23}$NP$_2$SSe	C$_{26}$H$_{22}$N$_2$P$_2$Se$_2$	C$_{26}$H$_{22}$N$_2$P$_2$SSe
Fw	463.50	557.30	510.40	582.32	535.42
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a /Å	14.910(7)	14.997(9)	14.947(5)	9.3712(6)	9.3291(5)
b /Å	8.907(4)	9.047(6)	8.892(3)	10.4474(6)	10.4273(6)
c /Å	18.499(8)	18.600(11)	18.466(7)	13.9259(9)	13.8771(8)
α /deg				84.1700(1)	84.1370(1)
β /deg	108.970(7)	108.980(10)	109.593(6)	77.4970(1)	77.2940(1)
γ /deg				67.9670(1)	67.4640(1)
V /Å^3	2323.3(18)	2372(2)	2312.1(14)	1233.55(13)	1216.07(12)
Z	4	4	4	2	2
T /K	153	153	153	153	153
ρ_{calcd} /(g/cm^3)	1.325	1.561	1.466	1.568	1.462
μ(Mo Kα) /cm^{-1}	3.80	32.65	18.66	31.44	17.78
$R_1(F)^a$	0.046	0.043	0.041	0.022	0.029
$Rw(F^2)^b$	0.133	0.084	0.140	0.069	0.083

^{a} $R_1(F) = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. ^{b} $R_w(F_o^2) = [\Sigma\, w(F_o^2 - F_c^2)^2/\Sigma\, wF_o^4]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (qF_o^2)^2$ for $F_o^2 > 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leq 0$; q = 0.07, 0.03, 0.06, 0.04, 0.04 for **1-5**, respectively.

Table 2 Selected bond distances/Å and angles/deg for N(SPPh₂)(CH₃SPPh₂) (**1**), N(SePPh₂)(CH₃SePPh₂) (**2**), N(SPPh₂)(CH₃SePPh₂) (**3**), N(SePPh₂)(NCCH₂SePPh₂) (**4**), N(SPPh₂)(NCCH₂SePPh₂) (**5**)

	1	2	3	4	5
P=S	1.9654(8)		1.9884(9)		1.9738(6)
P−S(C)	2.0775(8)				
P=Se		2.1136(9)		2.1266(4)	
P−Se(C)		2.224(1)	2.2226(8)	2.2749(4)	2.2716(4)
S−C	1.806(2)				
Se−C					
P(S)−N	1.620(2)		1.618(2)		1.627(1)
P(S(C))−N	1.566(1)				
P(Se)−N		1.613(2)		1.631(1)	
P(Se(C))−N		1.567(2)	1.570(2)	1.583(1)	1.585(1)
N(2)−C(26)ᵃ⁾				1.145(2)	1.144(2)
C(25)−C(26)ᵃ⁾				1.451(2)	1.453(3)
P−N−P	135.4(1)	134.6(1)	134.3(1)	124.02(8)	123.73(9)
N−P−S	120.15(6)		120.23(8)		116.31(5)
N−P−S(C)	120.01(6)				
N−P−Se		119.81(7)		115.67(5)	
N−P−Se(C)		120.14(8)	120.25(8)	113.01(5)	112.62(5)
C(25)−S−P	103.05(7)				
C(25)−Se−P		100.82(9)	100.35(9)	99.14(5)	99.06(5)
N(2)−C(26)−C(25)				177.3(2)	177.7(2)
C(26)−C(25)−Se				110.5(1)	110.8(1)

ᵃ⁾ The NCCH₂ group is labeled N(2)−C(26)−C(25).

Supporting material. Selected bond distances and angles are listed in Table 2.

Results and Discussion

Syntheses

The compounds N(SPPh₂)(CH₃SPPh₂) (**1**), N(SePPh₂)-(CH₃SePPh₂) (**2**), N(SPPh₂)(CH₃SePPh₂) (**3**), N(SePPh₂)-(NCCH₂SePPh₂) (**4**), and N(SPPh₂)(NCCH₂SePPh₂) (**5**) were obtained in un-optimized yields of greater than 60 % by reaction of the corresponding anion with CH₃I or ClCH₂CN in CH₃OH under very mild conditions, namely with stirring at room temperature for 10 min. Given that these conditions are so mild and that these anions have been involved in an extensive metal chemistry over the past 40+ years, it is surprising that other transformations of these ligands had not been reported. It is also interesting that the comparatively harsh methylation conditions used

previously [6] led to N(SPPh₂)(CH₃SPPh₂) (**1**) rather than to N(CH₃SPPh₂)₂⁺.

NMR Spectroscopy

NMR data for the precursors and for compounds **1**−**5** are presented in Table 3. The ³¹P{¹H} results for N(SPPh₂)(CH₃SPPh₂) (**1**) are in agreement with those obtained earlier [6]. As expected, the ⁷⁷Se{¹H} resonances shift downfield upon alkylation of the Se atom; all ³¹P{¹H} resonances are shifted upfield relative to those in the precursors.

Structures

Figure 1 shows the structure of N(SPPh₂)(CH₃SePPh₂) (**3**) and Figure 2 shows the structure of N(SPPh₂)(NCCH₂SePPh₂) (**5**). The structures of the other compounds are similar to those shown. The figures emphasize the fact that alkylation occurs preferentially at the Se atom rather than at the S atom. This is a manifestation of the increased nucleophilicity of Se over S [13].
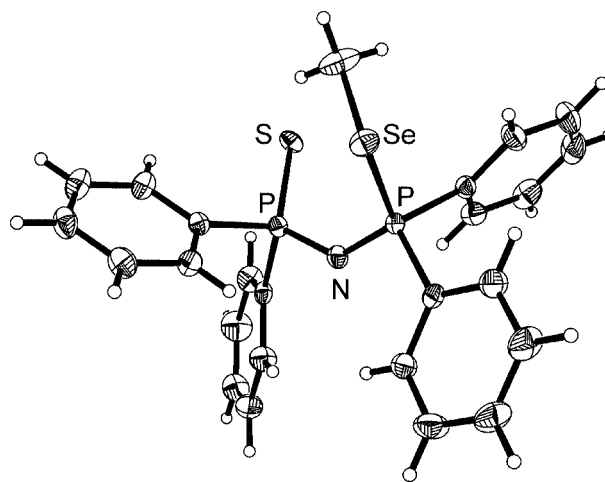

Fig. 1 Molecular structure of N(SPPh₂)(CH₃SePPh₂) (**3**). Here, and in the next figure, the displacement ellipsoids of the non-hydrogen atoms are shown at the 50 % level. The hydrogen atoms are drawn artificially small.

Table 3 Selected NMR data for compounds **1**−**5** and precursors

| Compound	³¹P{¹H} / ppm	¹J_{P-Se} /Hz	⁷⁷Se{¹H} / ppm	¹J_{Se-P} / Hz	²J_{P-P} / Hz	Reference
HN(SPPh₂)₂	56.9					Ref. [7]
HN(SePPh₂)₂	52.3	790	−162.8	790	25	Ref. [8]
HN(SPPh₂)(SePPh₂)	56.9, 52.5	790	−160.2	790	4.6	Ref. [10]
N(SPPh₂)(CH₃SPPh₂) (**1**)	30.0, 43.5				6	This work
N(SePPh₂)(CH₃SePPh₂) (**2**)	23.5, 35.5	405 (PSeCH₃)	142.9	407	5	This work
		715 (PSe)	−145.5	715		
N(SPPh₂)(CH₃SePPh₂) (**3**)	21.8, 44.2	404	147.3	403	7	This work
N(SePPh₂)(NCCH₂SePPh₂) (**4**)	25.3, 36.9	374 (P-SeCH₂CN)	295.7	374	7	This work
		709 (P-Se)	−135.5	708		
N(SPPh₂)(NCCH₂SePPh₂) (**5**)	22.9, 45.6	371	299.2	370	9	This work
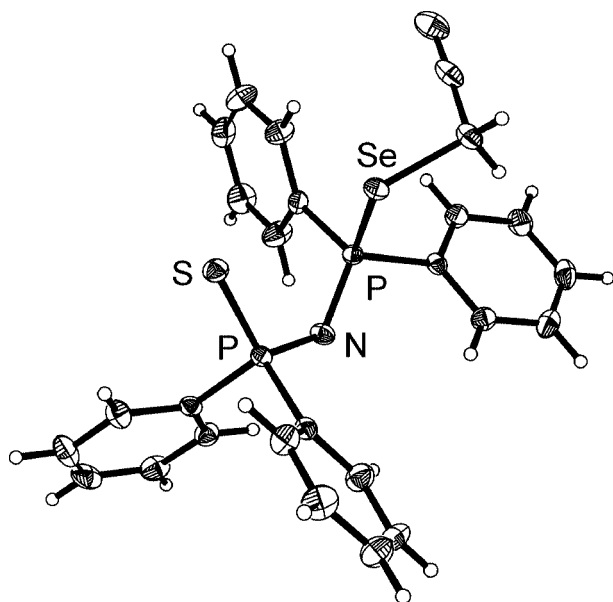
Fig. 2 Molecular structure of N(SPPh$_2$)(NCCH$_2$SePPh$_2$) (**5**).

Table 4 Selected bond distances/Å and P−N−P angle/deg for the precursors and related compounds

	HN(SPPh$_2$)$_2$[a),b)]	HN(SPPh$_2$)$_2$[c)]	HN(SePPh$_2$)$_2$[d)]	HN(SP^{i}Pr$_2$)(SePPh$_2$)[e)]
P=S	1.950(1)	1.950(1)		1.966(1)
	1.936(1)	1.937(1)		
P=Se			2.101(1)	2.0971(8)
			2.085(1)	
P−N	1.671(2)	1.672(2)	1.678(4)	1.686(2)
	1.684(2)	1.683(2)	1.686(3)	1.686(2)
P−N−P	132.6(1)	132.7(1)	132.3(2)	135.6(2)

[a)] Ref [14]; [b)] The crystal structure of this compound was also determined in Ref. [15], but it contains atypical distances and therefore the results are ignored here; [c)] Ref [16]; [d)] Ref [8]; [e)] Ref [17].

Selected bond distances and angles are presented in Table 2. The distances and angles for compound **1** do not differ significantly from those found earlier [6]. As a point of reference Table 4 lists some comparative distances for the precursors HN(SPPh$_2$)$_2$, HN(SePPh$_2$)$_2$, and HN(SP^{i}Pr$_2$)(SePPh$_2$). (Note that there is S/Se disorder in the solid-state structure of HN(SPPh$_2$)(SePPh$_2$) and hence no useful metrical data are available [10].) The P=S and P=Se distances in the current structures are about 0.02 Å shorter than in the precursors. Similarly, the corresponding P−N distances are about 0.04 Å shorter. Whereas both P−N distances in the precursors are of equal length they are not in the present compounds owing to the general asymmetry that results from alkylation of one chalcogen. This alkylation results in the lengthening of the P−S bond by about 0.1 Å and the shortening of the corresponding P−N bond by about 0.05 Å. Alkylation with CH$_3$ has minimal effect on the P−N−P angle but alkylation with NCCH$_3$ results in a decrease of this angle by about 10°.

Supporting material

CIF format crystallographic files for [N(SPPh$_2$)(CH$_3$SPPh$_2$)] (**1**), [N(SePPh$_2$)(CH$_3$SePPh$_2$)] (**2**), [N(SPPh$_2$)(CH$_3$SePPh$_2$)] (**3**), [N(SePPh$_2$)(NCCH$_2$SePPh$_2$)] (**4**), and [N(SPPh$_2$)(NCCH$_2$SePPh$_2$)] (**5**) have been deposited with the Cambridge Crystallographic Data Center, CCC Nos. 689663-689667, respectively. Copies may be obtained free of charge from The Director, CCC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: **deposit@ccdc.cam.ac.uk** or **http://www.ccdc.cam.ac.uk**).

References

[1] A. Schmidpeter, H. Groeger, *Z. Anorg. Allg. Chem.* **1966**, *345*, 106−118.

[2] A. Schmidpeter, R. Böhm, H. Groeger, *Angew. Chem., Int. Ed. Engl.* **1964**, *76*, 704.

[3] A. Schmidpeter, H. Groeger, *Chem. Ber.* **1967**, *100*, 3979−3991.

[4] A. Davison, E. S. Switkes, *Inorg. Chem.* **1971**, *10*, 837−842.

[5] A. J. Gaunt, S. D. Reilly, A. E. Enriquez, B. L. Scott, J. A. Ibers, P. Sekar, K. I. M. Ingram, N. Kaltsoyannis, M. P. Neu, *Inorg. Chem.* **2008**, *47*, 29−41.

[6] I. Ghesner, A. Soran, C. Silvestru, J. E. Drake, *Polyhedron* **2003**, *22*, 3395−3401.

[7] F. T. Wang, J. Najdzionek, K. L. Leneker, H. Wasserman, D. M. Braitsch, *Synth. React. Inorg. Met. Org. Chem.* **1978**, *8*, 119−125.

[8] P. Bhattacharyya, J. Novosad, J. Phillips, A. M. Z. Slawin, D. J. Williams, J. D. Woollins, *J. Chem. Soc., Dalton Trans.* **1995**, 1607−1613.

[9] P. Bhattacharyya, A. M. Z. Slawin, D. J. Williams, J. D. Woollins, *J. Chem. Soc., Dalton Trans.* **1995**, 2489−2495.

[10] P. Sekar, J. A. Ibers, *Inorg. Chim. Acta* **2001**, *319*, 117−122.

[11] Bruker. SMART Version 5.054 Data Collection and SAINT-Plus Version 6.45a Data Processing Software for the SMART System; Bruker Analytical X-ray Instruments, Inc., Madison, WI, USA, 2003.

[12] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112−122.

[13] R. G. Pearson, H. Sobel, J. Songstad, *J. Am. Chem. Soc.* **1963**, *85*, 319−326.

[14] H. Nöth, *Z. Naturforsch.* **1982**, *37b*, 1491−1498.

[15] P. B. Hitchcock, J. F. Nixon, I. Silaghi-Dumitrescu, I. Haiduc, *Inorg. Chim. Acta* **1985**, *96*, 77−80.

[16] S. Husebye, K. Maartmann-Moe, *Acta Chem. Scand. Ser. A* **1983**, *37*, 439−441.

[17] P. Sekar, J. A. Ibers, *Inorg. Chem.* **2003**, *42*, 6294−6299.