ELSEVIER

Journal of Organometallic Chemistry 493 (1995) 101–105

Journal of Organometallic Chemistry

Synthesis and X-ray crystal structure of $(p\text{-}CH_3C_6H_4)_3As=N-S_3N_3$

C.J. Thomas [a,*], R. Cea-Olivares [b], G. Espinosa-Pérez [b], R.W. Turner [c]

[a] *Department of Chemistry, University of Alabama at Birmingham, UAB Station, Birmingham, AL 35294, USA*
[b] *Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, México 04510, DF*
[c] *Department of Chemistry, Florida Agricultural and Mechanical University, Tallahassee, FL 32307, USA*

Received 23 September 1994

Abstract

A 1:2.5 mole ratio reaction of S_4N_4 with (p-tolyl)$_3$As in a solvent mixture of CH_3CN and C_6H_6 at ca. 50 °C gives $(p\text{-}CH_3C_6H_4)_3As{=}N-S_3N_3$ in ca. 75% yield after a two day reaction period. The compound, $(p\text{-}CH_3C_6H_4)_3As{=}N-S_3N_3$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.216(2)$ Å, $b = 11.124(4)$ Å, $c = 12.398(4)$ Å, $\alpha = 76.43(2)°$, $\beta = 83.06(2)°$, $\gamma = 67.09(2)°$, $V = 1137.4(6)$ Å^3, $Z = 2$. The structure is refined to a final R value of 0.047 with $R_w = 0.049$. The As–N bond distance is 1.78 Å while the average S–N ring distance is 1.62 Å.

Keywords: Arsenic; Tertiary arsines; Thiazenes; X-ray diffraction

1. Introduction

In the last decade, a large number of 1-(phosphoranylidene)amino-1N-1,3,5,2,4,6-trithia(5-S^{IV}) triazines of the type, $R_3P{=}N-S_3N_3$ [1–3], $Ph_2(R)P{=}N-S_3N_3$ [4–6], $N_3S_3\text{-}N{=}PR_2-X-R_2P{=}N-S_3N_3$ [7–8] and $N_3S_3\text{-}N{=}PR_2-X-R_2P{=}S$ [7] have been reported in the literature. Although several synthetic routes are available for their isolation [1–8], the reaction between S_4N_4 and a tertiary phosphine serves as one of the most convenient methods [9] for their synthesis in very good yield. The chemical and thermal behaviors of these derivatives have also been studied in some detail [9–12]. The analogous arsenic chemistry is limited only to the synthesis [12,13] X-ray structure [13], and thermal degradation [12] of $Ph_3AsN-S_3N_3$. Pyrolysis [12] of $Ph_3AsN-S_3N_3$ gives $(SN)_x$, an inorganic polymer with interesting optical and conducting properties [14]. 1-(triphenylarsoranylidene)aminotrithiatriazene was initially isolated [13] in low yield by Holt et al. from a 1:1 mole ratio reaction of S_4N_4 with Ph_3As in benzene. The low yield according to the reinvestigation of Chivers et al., is due to the thermal decomposition of $Ph_3AsN-S_3N_3$ to various products at benzene reflux conditions [12]. However the room temperature reaction of S_4N_4 with Ph_3As is very slow and the reaction had to be conducted for three weeks to isolate $Ph_3AsN-S_3N_3$ in 81% yield. Although the same workers reported [12] a twelve hour synthesis of the same compound in 71% yield by allowing $Ph_3As{=}NH$ to react with S_4N_4, the synthesis of $Ph_3As{=}NH$ involves additional steps [15–17].

Based on our experiences on the high yield syntheses of $Ph_2(R)P{=}N-S_3N_3$ (R = C_4H_8N, OC_4H_8N, $C_5H_{10}N$, $CH_3NC_4H_8N$, $C_6H_{12}N$, NC_5H_4) derivatives [4–6] from the reactions of S_4N_4 with $(R)Ph_2P$ at ca. 50 °C, we herein report a convenient high yield synthesis of $R_3AsN-S_3N_3$ (R = phenyl and p-tolyl) in a relatively short reaction period. The p-tolyl derivative is a new compound whose crystal structure is also determined in this study.

2. Experimental details

All the reactions and subsequent work-ups were performed under N_2 atmosphere. Acetonitrile (Aldrich) was distilled twice over CaH_2 and stored over molecular sieves. Thiophene-free benzene (Aldrich) was dried over metallic sodium and distilled over molecular sieves. S_4N_4 [18] (CAUTION! this should be handled with care [19] as it may explode when sub-

---

[*] Corresponding author. Present address: Department of Chemistry, Southern Methodist University, Dallas, TX 75275, USA.

SSDI 0022-328X(94)05295-6

jected to thermal or physical shock) was synthesized by the reported method. The arsines, Ph_3As and (p-$CH_3C_6H_4)_3As$ were synthesized by the reactions between $As(NMe_2)_3$ [20] and Grignard reagents. (The precise experimental details are provided below.) IR spectra (1600–500 cm^{-1}) were recorded in nujol mull on a Shimadzu IR-460 spectrophotometer. A GE (Nicolet) 300 MHz multinuclear FT-NMR spectrometer operating at 300.1 and 75.5 MHz for ^1H and ^{13}C respectively was used to record the NMR spectra. Data were obtained as 0.1 M $CDCl_3$ solutions of the compounds with Me_4Si as internal reference. UV-visible spectra were obtained on Perkin-Elmer Lambda 6 UV/VIS spectrometer. EI-MS data were recorded by the Direct Insertion Probe technique using a HP5968A GC/MS spectrometer operated at 70 eV. Melting points were determined in sealed capillaries and are uncorrected. Elemental analyses were done at E&R Microanalytical Labotatory, Inc., 96-34 Corona Avenue, Corona, New York.

2.1. Synthesis of R_3As (R = phenyl and p-tolyl)

To a stirred solution of $As(NMe_2)_3$ [20] (0.05 mol) in 100 ml pentane at −78 °C, 0.15 mol of the respective Grignard reagents (R = PhMgCl, p-tolylMgCl) in 100 ml of ether were added over a period of an hour. The reaction mixture was then slowly warmed to room temperature with stirring and then refluxed for 24 h. About 200 ml NH_4Cl solution (degassed for about 6 h) was added at 0 °C with stirring. The organic layer was separated, the aqueous layer was washed with ether (100 ml × 2), and the washings were collected along with pentane. After drying the organic layer with anhydrous Na_2SO_4 for 12 h, it was decanted, solvent was removed by distillation under reduced pressure and the resulting arsine was purified by crystallization using hot ethanol. The yield (Ph_3As, 76%; (p-tolyl)$_3$As, 79%), m.p (Ph_3As, 61 °C; (p-tolyl)$_3$As, 146 °C), IR, ^1H and ^{13}C-NMR data are comparable/identical to the earlier reported values [21,22].

2.2. Synthesis of R_3AsN–S_3N_3 (R = phenyl and p-tolyl)

To a stirred solution of R_3As (6.25 mmol) in 30 ml 1:1 mixture of C_6H_6 and CH_3CN, S_4N_4 (2.5 mmol) was added all at once at room temperature. The reaction mixture was then warmed to ca. 50 °C with stirring at this temperature for about 2 days. Orange red color formation with the slow disappearance of S_4N_4 was noticed. The reaction mixture was then concentrated to half its original volume and cooled in the refrigerator for a day to give red microcrystals, which were then recrystallized from a mixture of warm C_6H_6–CH_3CN (1:1, 20 ml) to obtain red rectangular crystals of $R_3As{=}N{-}S_3N_3$ (R = Ph, p-$CH_3C_6H_4$) in 75–80% yield. Apart from C, H, N and As analyses, the m.p (142 °C dec.), IR, UV-VIS of $Ph_3As{=}N{-}S_3N_3$ is very close to the reported values [12]. ^1H-NMR (δ) PPM: 7.75 (*ortho*), 7.51 (*meta*), 7.54 (*para*); $^3J\{H{-}H\}$ = 8 Hz. ^{13}C-NMR (δ) PPM: 132.63 (C1), 132.59 (C2, 6), 129.21 (C3, 5), 129.84 (C4). The new compound, (p-tolyl)$_3As{=}N{-}S_3N_3$ (Found: C, 50.57; H, 4.18; N, 11.31; As, 15.19% Calcd for $C_{21}H_{21}N_4S_3As$: C, 50.40; H, 4.20; N, 11.20; As, 15.00%) melted at 149 °C with decomposition. λ_{max} nm^{-1} ($CHCl_3$): 488 and 338 (4.15×10^3 and 3.6×10^3); IR (nujol): 1585(w), 1475(sh), 1300(w), 1248(m), 1205(w), 1192(m), 1160(w), 1118(w), 1080(s), 1030(w), 1012(m), 982(s), 960(vs), 918(vs), 841(vw), 800(s), 735(vs), 722(sh), 685(w) and 650(s) cm^{-1}; ^1H-NMR (δ) PPM: 7.59 (*ortho*), 7.57 (*meta*), 2.41 (CH_3), ^{13}C-NMR (δ) PPM: 126.64 (C1), 132.44 (C2, 6), 129.86 (C3, 5), 143.16 (C4), 21.64 (CH_3). Filtrate on work-up gave arsine sulfides, $R_3As = S$ and unreacted arsines, R_3As.

2.3. X-ray analysis of (p-tolyl)$_3As{=}N{-}S_3N_3$

A red colored, rectangular shaped crystal grown from a mixture of C_6H_6 and CH_3CN solution was

Table 1

Crystallographic data [a] for (p-$CH_3C_6H_4)_3As{=}NS_3N_3$

Formula	$C_{21}H_{21}AsN_4S_3$
Fw	500.5
Cryst syst	Triclinic
Space group	$P\bar{1}$
a(Å)	9.216(2)
b(Å)	11.124(4)
c(Å)	12.398(4)
α(°)	76.43(2)
β(°)	83.06(2)
γ(°)	67.09(2)
V(Å^3)	1137.4(6)
Z	2
D calcd (g cm^{-3})	1.461
Abs coeff (mm^{-1})	1.785
Cryst dmns (mm)	0.34×0.30×0.80
Scan type	$\theta/2\theta$
Scan speed in ω	8.0, 30.0
Deg min^{-1}, min, max}	3.0, 50.0
2θ range (°)	
Data collected	4196
$T(K)$	293
Decay (%)	4
no. of obsd rfln, $I > 3.0\ \sigma(I)$	3175
No. of params refined	262
GOF	1.15
R [b]	0.0467
R_w	0.0491
$\Delta\rho$ max, min, (eÅ^{-3})	+0.61, −0.84
weig sch. (w^{-1})	$\sigma^2\ (F_0)+(99.0008)F_0^2$

[a] Graphite-monochromatized Mo-Kα radiation, λ = 0.71073Å.

[b] $R = \Sigma \| F_0 | - | F_c \| / \Sigma | F_0 |$; $R_w = [\Sigma w[F_0 - F_c)^2 / \Sigma w(F_0)^2]^{1/2}$; $w = 1/[\sigma^2(F_0) + k(F_0)^2]$.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$)

	x	y	z	$U_{(eq)}$ [a]
As(1)	−2395(1)	1753(1)	−2783(1)	42(1)
S(1)	−537(2)	3378(1)	−3045(1)	56(1)
N(2)	611(5)	1970(5)	−2250(4)	62(2)
S(3)	1661(2)	2151(2)	−1386(2)	86(1)
N(4)	684(7)	3338(6)	−749(5)	87(3)
S(5)	−1017(3)	4402(2)	−1105(2)	89(1)
N(6)	−1715(6)	4311(5)	−2170(4)	69(2)
N(7)	−1639(5)	2939(4)	−3599(4)	55(2)
C(1)	−4155(5)	2008(5)	−3614(4)	44(2)
C(2)	−4777(7)	1043(6)	−3459(5)	72(3)
C(3)	−6016(8)	1225(7)	−4104(6)	81(3)
C(4)	−6666(6)	2381(6)	−4875(4)	52(2)
C(5)	−6051(7)	3339(6)	−4994(5)	64(3)
C(6)	−4809(6)	3174(5)	−4373(5)	60(2)
C(7)	−8006(7)	2549(7)	−5554(5)	70(3)
C(8)	−956(5)	−59(5)	−2751(4)	43(2)
C(9)	−1143(6)	−1109(5)	−1989(4)	53(2)
C(10)	−146(7)	−2412(5)	−2043(5)	61(2)
C(11)	1034(7)	−2653(5)	−2860(5)	61(2)
C(12)	1228(6)	−1585(6)	−3605(5)	61(2)
C(13)	249(6)	−280(5)	−3559(4)	51(2)
C(14)	2097(8)	−4076(6)	−2947(7)	90(3)
C(15)	−3143(5)	1946(5)	−1305(4)	43(2)
C(16)	−2161(6)	1371(5)	−420(4)	54(2)
C(17)	−2734(6)	1547(6)	637(4)	59(2)
C(18)	−4315(6)	2316(6)	831(4)	60(3)
C(19)	−5276(7)	2878(7)	−64(5)	84(3)
C(20)	−4718(6)	2702(6)	−1124(5)	68(3)
C(21)	−4933(8)	2516(8)	1974(5)	89(4)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

mounted on a Siemens P_4 diffractometer. Final unit-cell parameters were obtained by a least squares fit of 28 accurately centered reflections measured in the ranges of $10.28° \leq 2\theta \leq 26.03°$. The pertinent crystallographic data are summarized in Table 1. Intensity data were collected in the ranges of $3° \leq \theta \leq 50°$ using Mo Kα radiation at 293 °K. These data were corrected for Lorentz-polarization effects. The structure was solved by direct methods and refined by full-matrix least-squares using anisotropic thermal parameters for all non-hydrogen atoms. The H atoms were placed geometrically at idealized positions and constrained to ride on bonded C atoms with a fixed isotropic temperature factor, $U = 0.06$ Å^2 and C–H distances of 0.096 Å. The structure was refined by SHELXTL-PLUS PC version [23]. The final atomic coordinates, and selected bond angles and bond lengths are listed in Tables 2 and 3.

3. Results and discussion

In 1964 Tzschach and Lange reported that As–N bond cleavage occurs when excess grignard reagent is present in the preparation of $R_2As(NMe_2)$ and $RAs(NMe_2)_2$ from $Cl_2As(NMe_2)$ and $ClAs(NMe_2)_2$ respectively [24]. We have recently explored this as a viable synthetic route to twelve different heteroleptic tertiaryarsines, Me_2AsR by allowing Me_2AsNMe_2 to react with the appropriate grignard reagents [25]. However, this method is not very convenient for the synthesis of homoleptic tertiary arsines, R_3As with sterically bulky R groups [22] such as ^{t}Bu-, Me_3SiCH_2-, mesityl- etc., although phenyl and p-tolyl derivatives are readily isolated in good yield. The reaction between an aminoarsine and Grignard reagent can be represented by the following equation.

$$As(NMe_2)_3 + 3RMgCl \rightarrow R_3As + 3\text{“}(Me_2N)MgCl\text{”} \qquad (1)$$

However, we have not made any effort to isolate the magnesium amides.

As reported by Chivers et al. [12], the reaction of S_4N_4 with R_3As (R = Ph) is extremely slow (3 weeks) at room temperature, although the corresponding reactions with tertiary phosphines are over within hours [1–6]. However, the benzene or acetonitrile reflux reactions produced only the thermally degraded [12] products of $Ph_3E{=}N{-}S_3N_3$(E = P, As). We have observed earlier that $(R)Ph_2P{=}N{-}S_3N_3$ compounds can be produced in very good yield when the reactions of S_4N_4 with $(R)Ph_2P$ were carried out at about 45–50 °C. When the same conditions were applied to the tertiary arsine systems, the reaction period was reduced from three weeks to two days with the isolation of $R_3As{=}N{-}S_3N_3$(R = phenyl, p-tolyl) in 75–80% yield. Since arsine sulfides have been isolated from the study, the reaction between S_4N_4 and R_3As seems to pro-

Table 3
Selected bond lengths (Å) and bond angles (°) with estimated standard deviations in parentheses

Bond distances			
S(1)–N(2)	1.668(4)	S(1)–N(7)	1.567(6)
S(1)–N(6)	1.674(5)	As(1)–N(7)	1.779(5)
S(3)–N(2)	1.621(6)	As(1)–C(1)	1.919(5)
S(3)–N(4)	1.604(7)	As(1)–C(8)	1.929(4)
S(5)–N(4)	1.590(6)	As(1)–C(15)	1.908(5)
S(5)–N(6)	1.577(7)	C(11)–C(14)	1.524(8)
C(4)–C(7)	1.505(9)	C(8)–C(21)	1.495(9)
Av. C–C in benzene ring C(1) to C(6)	1.377		
Av. C–C in benzene ring C(8) to C(13)	1.387		
Av. C–C in benzene ring C(15) to C(20)	1.383		
Bond angles			
N(7)–As(1)–C(1)	102.6(2)	N(7)–As(1)–C(8)	112.4(2)
C(1)–As(1)–C(8)	106.1(2)	N(7)–As(1)–C(15)	118.0(2)
C(1)–As(1)–C(15)	107.9(2)	C(8)–As(1)–C(15)	109.0(2)
N(2)–S(1)–N(6)	105.9(2)	N(2)–S(1)–N(7)	104.1(2)
N(6)–S(1)–N(7)	105.2(3)	S(1)–N(2)–S(3)	115.5(3)
N(2)–S(3)–N(4)	112.9(3)	S(3)–N(4)–S(5)	123.0(5)
N(4)–S(5)–N(6)	117.7(3)	S(1)–N(6)–S(5)	119.9(3)
As(1)–N(7)–S(1)	118.7(3)		

ceed in a similar manner to that of the phosphine/S_4N_4 systems [5] and can be represented as in Eq. (2).

$$2R_3As + S_4N_4 \rightarrow R_3As{=}N{-}S_3N_3 + R_3As{=}S \qquad (2)$$

The low reactivity of tertiary arsines towards S_4N_4 at room temperature in comparison to the respective phosphines can be acertained to their relatively low nucleophilicity. It is also noticed that no 1,5-$(R_3AsN)_2S_4N_4$ and $(R_3AsN)_3S^+S_4N_5^-$ could be isolated from this study, although some tertiary phosphines do yield the respective derivatives in their reactions with S_4N_4 [2–5].

Electron impact mass spectra of the title compounds gave molecular ion peaks of intensity less than 1%. Irrespective of the nature of the phosphine substituents, all of the $\equiv P{=}N{-}S_3N_3$ (about twenty compounds are known today) have a typical UV-visible absorption [1–8] at 480 ± 2 nm and 330 ± 2 nm, due to $\pi^* \rightarrow \pi^*$ transitions [26]. However, for both the arsenic derivatives, the values are about 8–10 nm higher, which suggests that the $\pi^* \rightarrow \pi^*$ gap in $R_3As{=}N{-}S_3N_3$ compounds are slightly altered owing to the presence of arsenic atoms.

In the ^{1}H-NMR spectrum of Ph_3As, all of the protons in the phenyl rings are identical (7.32 PPM) [21], while in the $Ph_3As{=}N{-}S_3N_3$ compound, the *ortho*, *meta* and *para* protons are not only non-identical but their chemical shift values are also shifted toward the downfield region with respect to the parent. The *ortho* protons are more deshielded in comparison to *meta* and *para*, which could be explained in terms of the anisotropic deshielding effect of the arsenic–nitrogen double bond. Similar situations have been reported [5,27] in the case of $(R)Ph_2P{=}X$ (X = O, S, N–R) and also in the case of aromatic carbonyls. The *p*-tolyl derivative shows a similar trend.

3.1. Crystal structure of (p-$CH_3C_6H_4)_3AsN{-}S_3N_3$

The structure of the molecule is shown in Fig. 1. The important bond distances and bond angles are listed in Table 3. The orientations of the three *p*-tolyl groups and the $N{-}S_3N_3$ group around the As atom are shown in Fig. 1. The arsenic atom in the molecule has a tetrahedral geometry with an average NAsC/CAsC bond angle of 109.3(2) Å. The most interesting feature of this molecule is that the As–N bond distance (1.779(5) Å) is closer to the double bond distance (1.742(6)–1.771(6) Å; av: 1.758(4) Å) reported for $(Ph_2AsN)_3$ by Krannich et al. [28], whereas in the reported crystal structure [13] of $Ph_3AsN{-}S_3N_3$, the As–N distance (1.837(2) Å) is close to the single bond length (1.870(4) Å) [29]. This suggests that in (*p*-tolyl)$_3AsN{-}S_3N_3$, the back donation of the lone pair of electrons from the exocyclic nitrogen atom to the 4d orbitals of the arsenic atom is more effective than that in $Ph_3As{=}N{-}S_3N_3$. As a result of this, the bonding interaction between the exocyclic N to S in the *p*-tolyl derivative (1.567(5) Å) is slightly weaker than that in the phenyl (1.554(5) Å) [13] derivative. The $-S_3N_3$ ring has a puckered conformation in which the tricoordinate sulfur atom is slightly above the plane constituted by N(2), S(3), N(4), S(5) and N(6) atoms. The endocyclic S–N distances are in the comparable range of the S–N distances reported for several cyclic S–N compounds [1,6,13,30].

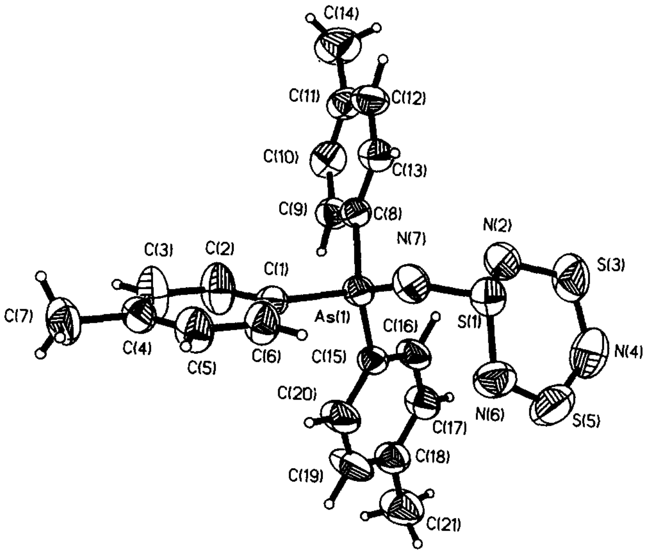

Fig. 1. A perspective view of $(p\text{-}CH_3C_6H_4)_3As{=}N{-}S_3N_3$ showing the atom numbering scheme. The thermal ellipsoids are of 40% probability level.

4. Summary

This study provides a relatively quick and high yield synthesis for $R_3As{=}N{-}S_3N_3$ (R = Ph and *p*-tolyl) compounds. The X-ray crystal structure of the *p*-tolyl derivative reveals that the As–N bond distance is closer to the arsenic–nitrogen double bond distance, unlike in the reported phenyl derivative [13].

Acknowledgements

Professor C.L. Watkins, Department of Chemistry, University of Alabama at Birmingham, Birmingham, Alabama, is acknowledged for the ^{1}H and ^{13}C-NMR spectra. Professor L.K. Krannich, Chairman of the same department is also thanked for his interest and encouragement in this work.

Supplementary material available

Listing of structure factors, complete list of bond angles and bond lengths, anisotropic displacement coefficents and H- atom coordinates are deposited to the editor. Ordering information is given on any current masthead page.

References

[1] A.J. Elias, M.N.S. Rao and B. Varghese, *Polyhedron*, *9* (1990) 1433.

[2] A.J. Elias and M.N.S. Rao, *Inorg. Chim. Acta.*, *164* (1989) 45.

[3] J. Bojes, T. Chivers, A.W. Cordes, G. Maclean and R.T. Oakley, *Inorg. Chem.*, *20* (1981) 16.

[4] C.J. Thomas and M.N.S. Rao, *J. Chem. Soc., Dalton Trans.*, (1988) 1445.

[5] C.J. Thomas and M.N.S. Rao, *Heteroatom Chemistry*, *3* (1992) 321.

[6] C.J. Thomas, K.K. Bhandary, L.M. Thomas, S.E. Senadhi and S. Vijay-Kumar, *Bull. Chem. Soc. Jpn.*, *66* (1993) 1830.

[7] C.J. Thomas and M.N.S. Rao, *Z. Anorg. Allg. Chem.*, *619* (1993) 433.

[8] I. Rupert, V. Bastian and R. Appel, *Chem. Ber.*, *107* (1974) 3426.

[9] C.J. Thomas and M.N.S. Rao, *Z. Anorg. Allg. Chem.*, *615* (1992) 149 and the references cited therein.

[10] C.J. Thomas and M.N.S. Rao, *Ind. J. Chem., Sect. A 29* (1990) 450.

[11] S.W. Liblong, R.T. Oakley, A.W. Cordes and M.C. Noble, *Can. J. Chem.*, *61* (1983) 2063.

[12] T. Chivers, A.W. Cordes, R.T. Oakley and P.N.Swepston, *Inorg. Chem.*, *20* (1981) 2377.

[13] E.M. Holt and K.J. Watson, *J. Chem. Soc., Dalton Trans.*, (1977) 514 and references cited therein.

[14] M.M. Labes, P. Love and L.F. Nichols, *Chem. Rev.*, *79* (1979) 1 and references cited therein.

[15] R. Appel and O. Wagner, *Z. Anorg. Allg. Chem.*, *72* (1960) 209.

[16] B.W. Ross and W.B. Marzi, *Chem. Ber.*, *108* (1975) 1518.

[17] W. Richter, Y. Yamamoto and H. Schmidbaur, *Chem. Ber.*, *110* (1977) 1312.

[18] M. Villena-Blanco and W.L. Jolly, *Inorg. Synth.*, *9* (1967) 98.

[19] A.J. Banister, *Inorg. Synth.*, *17* (1977) 197.

[20] K. Modritzer, *Chem. Ber.*, *92* (1959) 2637.

[21] D.K. Srivastava, L.K. Krannich and C.L. Watkins, *Inorg. Chem.*, *29*, (1990) 3502.

[22] C.J.Thomas, L.K. Krannich and C.L. Watkins, *Polyhedron*, *12* (1993) 89.

[23] G.M. Sheldrick, *Structure Determination Software Programs*, Siemens X-ray Analytical Instrument Corp, Madison, WI, 1991.

[24] A. Tzschach and W. Lange, *Z. Anorg. Allg. Chem.*, *326* (1964) 280.

[25] C.J. Thomas, L.K. Krannich, and C.L. Watkins, *Synth. React. Inorg. Met-org. Chem.*, *22* (1992) 461.

[26] (a) J.W. Walula, T. Chivers, R.T. Oakley and J. Michl, *Inorg. Chem.*, *21* (1982) 832; (b) T. Chivers and R.T. Oakley, *Top. Curr. Chem.*, *102* (1982) 117.

[27] W. Kemp *Organic Spectroscopy*, ELBS/Macmillan, London, 1982. pp. 76–152.

[28] L.K. Krannich, U. Thewalt, W.J. Cook, S.R. Jain and H.H. Sisler, *Inorg. Chem.*, *12* (1973) 2304.

[29] J. Weiss and W. Eisenhuth, *Z. Anorg. Allg. Chem.*, *350* (1967) 9.

[30] T. Mohan, C.J. Thomas, M.N.S. Rao, G. Aravamudan, A. Meetsma and J.C. van de Grampel, *Heteroatom Chemistry*, *5* (1994) 19.