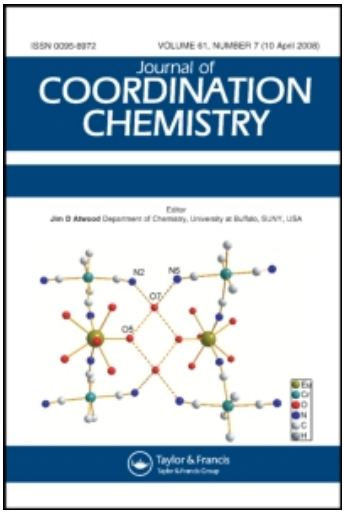

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Synthesis, spectroscopy and structure of *cis,cis,trans*:*N,N;P,P;S,S*-[*bis*(triphenylphosphine)] [*bis*(pyrimidine-2-thiolato)]ruthenium(II)

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Synthesis, spectroscopy and structure of *cis*,*cis*,*trans*:*N*,*N*;*P*,*P*;*S*,*S*-[*bis*(triphenylphosphine)][*bis*(pyrimidine-2-thiolato)]ruthenium(II)

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Reaction of $RuCl_2(PPh_3)_3$ with pyrimidine-2-thione (HpymS) in a 1:2 mol ratio in dry benzene in the presence of triethylamine as base yielded a complex of stoichiometry $[Ru(pymS)_2(PPh_3)_2]$ (**1**). This has been characterized using analytical data and IR, ^1H, ^{13}C and ^{31}P NMR spectroscopy. ^1H NMR confirmed the deprotonation of HpymS. ^{31}P NMR spectra showed a single peak confirming equivalent P atoms. Complex **1** crystallizes in space group $P\bar{1}$ and HpymS acts as a η^2-*N*,*S*-deprotonated bidentate anionic ligand. The coordination geometry around the Ru center is distorted octahedral with *cis* dispositions of P atoms, as well as two N atoms of $pymS^-$ and *trans* S atoms of $pymS^-$. Important bond distances and angles are: Ru–N, 2.119(2), 2.106(2); Ru–S, 2.4256(8), 2.4413(8); and Ru–P, 2.3266(7), 2.3167(7) Å; P(2)–Ru(1)–P(1), 96.07(3); N(21)–Ru(1)–N(11), 83.46(9); and S(1)–Ru(1)–S(2), 153.02(3)°.

Keywords: Pyrimidine-2-thione; Ruthenium; Phosphine; X-ray structure

1. Introduction

Among the heterocyclic thioamides, the simplest prototype, pyridine-2-thione (HpyS, **I**), has been studied in terms of its coordination chemistry and several types of compounds have been reported [1–4]. Pyrimidine-2-thione (HpymS, **II**), on the other hand, has been much less studied. HpyS and HpymS are the thio analogs of nucleobases such as purine and pyrimidine, and as such have biochemical significance. From this laboratory, several complexes of metals with HpyS and its N-oxide have been reported [5–15]. This report concerns complexes of HpymS. Neutral HpymS mainly forms S-bonded complexes [16–22], while deprotonated $pymS^-$ forms S-bonded [23–26], N,S-chelated [27–33], S-bridging-*cum*-N,S-chelated [34], N,S-bridged [35,36] and

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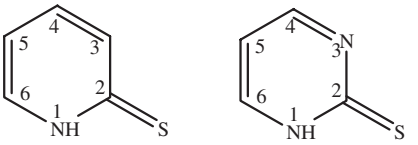
S-bridged-*cum*-N-bridged [37] species. A few tetranuclear and hexanuclear complexes are also known [38,39]. There is increased interest in complexes of HpymS and its derivatives, because several of them find use as antiviral, antimetabolite and antitumor drugs [40–48].



I II

From a survey of the literature we found that the interaction of Ru(II) with HpymS and its derivatives has received scant attention [30,49–51]. In the present work, we report the crystal and molecular structure of $[Ru(PPh_3)_2(pymS)_2]$, which is the first example of its type in the case of HpymS. The solid-state structure is compared with the solution behavior using high-resolution ^1H, ^{13}C and ^{31}P NMR spectroscopy.

2. Experimental

2.1. *Materials and techniques*

The starting ruthenium complex, $RuCl_2(PPh_3)_3$ [52], was prepared by refluxing $RuCl_3 \cdot xH_2O$ and PPh_3 in dry ethanol for 5–6 h. HpymS was obtained from Sigma Aldrich Ltd. IR spectra were recorded using KBr pellets on a Pye Unicam SP3-300 spectrophotometer in the 4000–200 cm^{-1} range. Proton NMR spectra were recorded ($CDCl_3$) using a Bruker spectrometer at 200 MHz with TMS as internal reference. ^{13}C NMR spectra were recorded in $CDCl_3$ using a Jeol AL-300 FT spectrometer at 75.45 MHz with TMS as internal reference. ^{31}P NMR spectra were recorded in $CDCl_3$ using the Jeol AL-300 FT instrument at 121.5 MHz with orthophosphoric acid as external reference.

2.2. *Synthesis of [Ru(pymS)$_2$(PPh$_3$)$_2$] (1)*

To a brown solution of $RuCl_2(PPh_3)_3$ (0.050 g, 0.052 mmol) in degassed benzene (25 cm^3) was added a solution of HpymS (0.011 g, 0.104 mmol) in benzene (10 cm^3) along with Et_3N (2 cm^3). The mixture was refluxed under dry and oxygen-free N_2 for 24 h. The color of the solution changed from dark brown to orange–brown. Precipitated $Et_3NH^+Cl^-$ was filtered off and the filtrate concentrated to about one-third of its initial volume. *n*-Hexane (20 cm^3) was added to the filtrate and orange–brown crystals formed after 3 to 4 days. Yield, 65%, m.p. 250–260(d)°C. The complex is soluble in chloroform, dichloromethane and acetone. Anal. Calcd. for $C_{47}H_{39}N_4P_2RuS_2$(%): C, 63.0; H, 4.58; N, 6.26. Found: C, 63.1; H, 4.55; N, 6.24. Main IR peaks (cm^{-1}): ν(C–H) 3180(m), ν(C–C) + ν(C–N), 1560(s), 1480(s); ν(C=S),

1160(m); ν(P–C), 1090(m). Crystals of **1** were grown in dry benzene, and the X-ray crystal structure revealed the presence of lattice benzene.

2.3. *X-ray crystallography*

A brown, prismatic crystal of **1** was mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 25 reflections in the range $17.739 < \theta < 23.967^\circ$ on an Enraf Nonius CAD4 automatic diffractometer [53]. Data were collected at 223 K using Cu Kα radiation ($\lambda = 1.54184$ Å) and the ω-scan technique, and corrected for Lorentz and polarization effects [54]. A semiempirical absorption correction (ψ-scans) was made [55]. The structure was solved by direct methods [56] and subsequent difference Fourier maps, and refined on F^2 by full-matrix least-squares procedures using anisotropic displacement parameters [57]. All hydrogen atoms were included in geometrically idealized positions using appropriate riding models. Atomic scattering factors were taken from the *International Tables for X-ray Crystallography* [58]. Molecular graphics used the programs PLATON [59] and SCHAKAL [60]. Crystallographic data are summarized in table 1. Selected bond lengths and angles are given in table 2.

Table 1. Crystal data and refinement details for **1**.

Empirical formula	$C_{47}H_{39}N_4P_2RuS_2$	D_{calcd} (mg m^{-3})	1.452
M	886.95	μ (mm^{-1})	5.142
T (K)	223(2)	F(000)	910
Crystal system	Triclinic	Crystal size (mm)	0.10 × 0.10 × 0.10
Space group	$P\bar{1}$	2θ range (°) for data collection	5.20–64.98
Unit cell dimensions			
a (Å)	11.0610(8)	Reflections collected	8063
b (Å)	12.2203(14)	Unique reflections	6885 ($R_{int} = 0.0370$)
c (Å)	17.1748(16)	Goodness-of-fit on F^2	1.045
α (°)	69.564(9)	R indices [$I > 2\sigma(I)$]	
β (°)	85.075(7)	R, $wR2$	0.0324, 0.0800
γ (°)	68.943(8)	R, $wR2$ (all data)	0.0390, 0.0830
V (Å^3)	2028.0(3)	Largest diff. peak and hole (eÅ^{-3})	0.489 and −1.079
Z	2		

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Bond lengths			
Ru(1)–N(11)	2.119(2)	P(1)–C(31)	1.835(3)
Ru(1)–N(21)	2.106(2)	P(1)–C(41)	1.847(3)
Ru(1)–P(1)	2.3266(7)	P(1)–C(51)	1.837(3)
Ru(1)–P(2)	2.3167(7)	P(2)–C(61)	1.857(3)
Ru(1)–S(1)	2.4256(8)	P(2)–C(71)	1.841(3)
Ru(1)–S(2)	2.4413(8)	P(2)–C(81)	1.838(3)
Bond angles			
N(11)–Ru(1)–S(1)	67.21(7)	N(11)–Ru(1)–P(1)	170.91(6)
N(11)–Ru(1)–S(2)	92.26(7)	N(11)–Ru(1)–P(2)	90.56(6)
N(21)–Ru(1)–S(1)	92.40(7)	N(21)–Ru(1)–P(1)	90.44(7)
N(21)–Ru(1)–S(2)	67.03(7)	N(21)–Ru(1)–P(2)	172.14(7)
S(1)–Ru(1)–S(2)	153.02(3)	P(2)–Ru(1)–P(1)	96.07(3)
N(21)–Ru(1)–N(11)	83.46(9)		

3. Results and discussion

3.1. *Synthesis and spectroscopy*

Reaction of $RuCl_2(PPh_3)_3$ with neutral HpymS in a 1:2 mol ratio in dry benzene in the presence of triethylamine involved deprotonation of the NH proton and yielded a complex of stoichiometry $[Ru(pymS)_2(PPh_3)_2]$ (**1**). Compound **1** was prepared under dry and oxygen-free N_2 to avoid oxidation of Ru(II) to Ru(III). IR data confirmed deprotonation of HpymS in the complex and the presence of a characteristic peak due to PPh_3, as listed in the experimental section. Proton NMR spectra did not show any signal for the NH proton, supporting coordination of HpymS in the anionic form ($\delta_{NH} = 13.40$(s) ppm, HpymS [23]; table 3). The H(6) proton close to the N(1) nitrogen showed a small upfield shift while H(4) and H(5) protons (table 3) showed larger upfield shifts relative to the free ligand [23]. The *o*-H, *m*-H and *p*-H protons of PPh_3 are clearly resolved; the *o*-H protons exhibit some low-field shift.

In the ^{13}C NMR spectra, the most significant low-field shift occurs for C(2) and this shift is less marked for C(6); C(4) and C(5) are shifted upfield relative to the free ligand (table 3). The ^{13}C NMR data clearly support coordination of N(1) and S atoms to Ru. The *ipso*-carbon of PPh_3 shows a significant low-field shift involving ^{13}C–^{31}P coupling ($J = 19.2$ Hz), while other carbon signals of the ligand are shifted slightly upfield. Finally, ^{31}P NMR spectra show only one peak at $\delta = 46.9$ ppm, with a coordination shift ($\delta_{complex} - \delta_{ligand}$) of 54.1 ppm, revealing the equivalence of phosphorus atoms in the complex and that PPh_3 is coordinating to the Ru atom, in accord with literature data [15]. The data suggest an octahedral structure for **1**, as confirmed by X-ray crystallography.

Table 3. NMR (^1H, ^{13}C, ^{31}P) data (δ, ppm; J, Hz) for **1** and related compounds.

^1H NMR	PPh_3[b]			
	o-H	*m*-H	*p*-H	
1[a]	7.26(t)	7.14(d)	7.06(t)	
PPh_3[b]		7.23(m)[c]		
	H(6)	H(5)	H(4)	N(H)
1	7.3(dd)	6.06(t)	7.9(d)	
	($J_{4,5}$, 3.2)	($J_{4,6}$, 5.1)	(J_5, 4.6)	
HpymS[d]	7.38(m)	6.85(m)	8.29(br)	13.40
	($J_{4,5}$, 4.8)	($J_{4,6}$, 5.4)		
^{13}C NMR	PPh_3[b]			
	C_i	C_o	C_m	C_p
1	135.7(t)	134.0(t)	127.2(t)	128.5(d)
	(J_{C-P}, 19.2)	(J_{C-P}, 5.0)	(J_{C-P}, 4.3)	
PPh_3[b]	132.5	134.2	128.9	129.1
	(J_{C-P}, 10.0)	(J_{C-P}, 19.5)	(J_{C-P}, 10.8)	(9.3)
	C(2)	C(6)	C(4)	C(5)
1	188.1(s)	155.2(s)	153.4(s)	113.1(s)
HpymS[d]	181.4(s)	154.6(s)	158.6(s)	119.1(s)
^{31}P NMR				
	δP	$\Delta\delta$		
1	46.9	54.1		
PPh_3	−7.17			

[a]In $CDCl_3$. [b]From ref. [61]. [c]Not resolved. [d]In DMSO-d_6 [23].

3.2. *Crystal structure of 1*

The atom numbering scheme for **1** is shown in figure 1. In the complex, both PPh_3 and $pymS^-$ ligands occupy *cis* positions. Ru(II) is bonded to two P atoms, two exocyclic S atoms and two N(1) atoms, and the geometry is octahedral. The two S atoms are nearly *trans* with an S(1)–Ru(1)–S(2) angle of 153.02°, quite close to that (154.7°) observed in $Ru(pyS)_2(PPh_3)_2$, **2** (pyS = pyridine-2-thiolate) [51]. [$Ru(pyS)_2$(diphosphane)] complexes [diphosphane = dppe, $Ph_2P(CH_2)_2PPh_2$, **3**; dppp, $Ph_2P(CH_2)_3PPh_2$, **4**; and dppb, $Ph_2P(CH_2)_4Ph_2P(CH_2)_2PPh_2PPh_2$, **5**] show S–Ru–S angles in the range 153.9–155.6° [13–15].

The *cis* nitrogen atoms of **1** make an N(21)–Ru–N(11) angle of 83.46°, and this is close to that (80.9°) in compound **2**. P(2)–Ru(1)–P(1) (96.07°) subtended by the PPh_3 ligands in **1** is slightly smaller than that (96.8°) of **2**. In [$Ru(pyS)_2$(diphosphane)] complexes, the N–Ru–N and P–Ru–P bond angles vary in inverse fashion with the bite angle of the diphosphane. The bite angle, N–Ru–S, remains constant, *ca* 67° for HpymS and HpyS ligands, for a series of complexes, as shown in table 4.

Ru–P distances (2.327, 2.318 Å) in **1** are similar to those (2.332, 2.319 Å) of **2** [51]. This shows that P atoms of the PPh_3 ligands bind equally strongly in both cases.

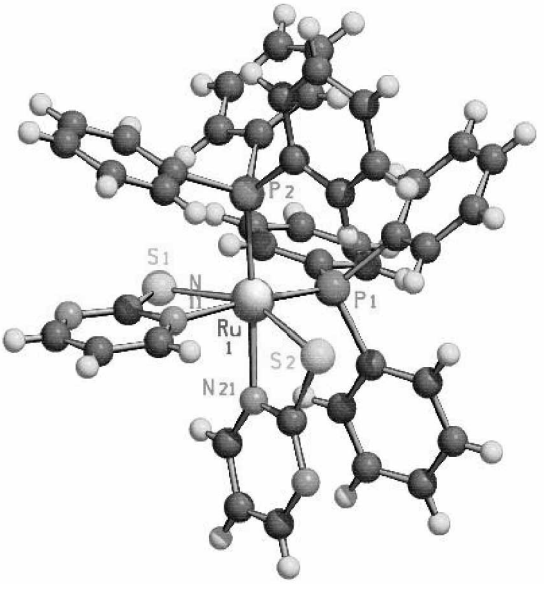


Figure 1. Structure of **1** with the atom numbering scheme.

Table 4. Comparison of bond lengths (Å) and angles (°) of **1** with those of other complexes.

	Ru–N	Ru–S	Ru–P	S–Ru–S	N–Ru–N	P–Ru–P	N–Ru–S	Ref.
1	2.112	2.433	2.321	153.02	83.46	96.07	67.2	This work
2	2.124	2.436	2.326	154.7	80.9	96.8	67.0	[53]
3	2.134	2.421	2.248	155.0	87.5	84.1	67.3	[14]
4	2.131	2.421	2.277	153.9	84.5	90.7	67.5	[15]
5	2.143	2.422	2.276	155.6	82.3	94.3	67.0	[13]

The distances are slightly longer than in [Ru(pyS)$_2$(diphosphane)] complexes [13–15], but somewhat smaller than shown by related complexes reported in the literature [62,63]. The Ru–N bond distance of 2.112 Å in **1** is somewhat shorter than in **2** (2.123 Å) [51]. Ru–S in **1** is 2.433 Å, similar to that in **2** (2.435 Å).

Supplementary material

Full details have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 244843. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk; or http://www.ccdc.cam.ac.uk).

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References

[1] E.S. Raper, *Coord. Chem. Rev*. **61**, 115 (1985).
[2] E.S. Raper, *Coord. Chem. Rev*. **153**, 199 (1996).
[3] E.S. Raper, *Coord. Chem. Rev*. **129**, 91 (1994).
[4] E.S. Raper, *Coord. Chem. Rev*. **165**, 475 (1997).
[5] T.S. Lobana, P.K. Bhatia, *J. Sci. Indian Res*. **48**, 394 (1989).
[6] D.C. Povey, G.W. Smith, T.S. Lobana, P.K. Bhatia, *J. Crystallogr. Spectrosc. Res*. **21**, 9 (1991).
[7] T.S. Lobana, P.K. Bhatia, *Indian J. Chem*. **30A**, 877 (1991).
[8] T.S. Lobana, P.K. Bhatia, *Indian J. Chem*. **29A**, 1225 (1990).
[9] T.S. Lobana, P.K. Bhatia, E.R.T. Tiekink, *J. Chem. Soc., Dalton Trans*. 749 (1989).
[10] T.S. Lobana, P.K. Bhatia, *J. Chem. Soc., Dalton Trans*. 1407 (1992).
[11] T.S. Lobana, S. Paul, *Transition Met. Chem*. **21**, 300 (1996).
[12] T.S. Lobana, E. Horn, E.R.T. Tiekink, R. Singh, *J. Crystallogr. Spectrosc. Res*. **21**, 205 (1991).
[13] T.S. Lobana, E. Horn, E.R.T. Tiekink, R. Singh, *Z. Kristallogr*. **205**, 291 (1993).
[14] T.S. Lobana, R. Singh, *Polyhedron* **14**, 907 (1995).
[15] T.S. Lobana, R. Verma, R. Singh, A. Castineriras, *Transition Met. Chem*. **23**, 25 (1998).
[16] C. Leconite, S. Skoulika, P. Aslanidis, P. Karagiannidis, S. Papastefanou, *Polyhedron* **8**, 1103 (1989).
[17] P. Karagiannidis, S.K. Hadjikakou, P. Aslanidis, A. Hountas, *Inorg. Chim. Acta* **178**, 27 (1990).
[18] Z. Popavic, G. Pavlovic, D.M. Calogovic, Z. Solidin, M. Rajic, D.V. Topic, D. Kovacek, *Inorg. Chim. Acta* **306**, 142 (2000).
[19] M. Kubicki, S.K. Hadjikakau, M.N. Xanthopoulou, *Polyhedron* **20**, 2179 (2001).
[20] P. Aslanidis, P.J. Cox, S. Divanidis, A.C. Tsipis, *Inorg. Chem*. **41**, 6875 (2002).
[21] P.J. Cox, P. Aslanidis, P. Karagiannidis, S. Hadjikakau, *Inorg. Chim. Acta* **310**, 268 (2000).
[22] P. Aslanidis, S.K. Hadjikakau, P. Karagiannidis, M. Gdaniec, Z. Kasturkiewicz, *Polyhedron* **12**, 2221 (1993).
[23] P.D. Cookson, E.R.T. Tiekink, *J. Chem. Soc., Dalton Trans*. 259 (1993).
[24] J.-D. Shi, L.-J. Chen, X.-Y. Huang, D.-X. W, B.-S. Kang, *J. Organomet. Chem*. **535**, 17 (1997).
[25] L. Petrilli, F. Caruso, E. Rivarola, *Main Group Metal Chem*. **6**, 17 (1994).
[26] S.K. Hadjikakau, M. Kubicki, *Polyhedron* **19**, 2231 (2000).
[27] F.A. Cotton, W.H. Ilsley, *Inorg. Chem*. **20**, 614 (1981).
[28] R. Castro, M.L. Duran, G. Vazquez, J.A. Romero, J. Sousait, A. Castenerias, W. Hiller, J. Straehle, *Z. Naturforsch. B., Chem. Sci*. **47**, 1067 (1992).
[29] P.K. Baker, M.E. Harman, S. Hughes, M.B. Hursthouse, K.M. Abdul Malik, *J. Organomet. Chem*. **498**, 257 (1995).

[30] K. Yamanari, T. Nazoki, A. Fuyuhiro, Y. Kushi, S. Kaizaki, *J. Chem. Soc., Dalton Trans*. 2851 (1996).
[31] P.G. Hua, Z. Zo-Tas, H.L. Ren, J. Huaxue, *Chin. Acad. Sci. Str. Matter* **17**, 334 (1998).
[32] C. Wycliff, D.S. Bharathi, A.G. Samuelson, M. Nethaji, *Polyhedron* **18**, 949 (1999).
[33] J. Romero, M.L. Duran, A. Rodriguez, J.A. Garcia-Vazaquez, A. Sousa, D.J. Rose, J. Zubieta, *Inorg. Chim. Acta* **274**, 131 (1998).
[34] J. Romero, J.A. Garcia-Vazaquez, A. Sousa, Y. Chang, J. Zubieta, *Polyhedron* **15**, 2741 (1996).
[35] D.M.L. Goodgame, R.W. Rollins, A.C. Spapski, *Inorg. Chim. Acta* **83**, L11 (1984).
[36] D.M.L. Goodgame, A.M.Z. Slawin, D.J. Williams, P.W. Zard, *Inorg. Chim. Acta* **148**, 5 (1988).
[37] K. Yamanari, I. Fukuda, A. Fuyuhiro, Y. Kushi, S. Yamamoto, N. Kobuta, T. Fukuo, R. Arakawa, *J. Chem. Soc., Dalton Trans*. 2131 (2000).
[38] D.M.L. Goodgame, G.A. Leach, A.C. Skapski, K.A. Woode, *Inorg. Chim. Acta* **31**, L375 (1978).
[39] S. Kitagawa, Y. Nozaka, M. Munakata, S. Kawata, *Inorg. Chim. Acta* **197**, 169 (1992)
[40] J.A. Carbon, L. Hung, D.S. Jones, *Proc. Natl Acad. Sci. USA* **53**, 979 (1965).
[41] R.K. Robins, *J. Med. Chem*. **7**, 186 (1964).
[42] W.R. Trotter, *Nature (London)* **164**, 63 (1949).
[43] E.B. Astwood, A. Bissell, A.M. Hughes, *Endocrinology* **37**, 456 (1945).
[44] J.A. Carbon, H. David, M.H. Studier, *Science* **161**, 1146 (1968).
[45] V.N. Krisnamurthy, K.V.N. Rao, P.L.N. Rao, H.B. Prophulla, *J. Pharmacol. Chemother*. **31**, 1 (1967).
[46] R. Truhaut, M. de Clercq, *Rev. Fr. Etud. Clin. Biol*. **7**, 68 (1962).
[47] R.N. Lindsay, H. Nakagawa, P.P. Cohen, *Endocrinology* **76**, 728 (1965).
[48] C.K. Mirabelli, R.K. Johnson, C.M. Sung, L.F. Faucette, K. Muirhead, S.T. Crooke, *Cancer Res*. **45**, 32 (1986).
[49] R. Dilshad, K.M. Hanif, M.B. Hursthouse, S.E. Kabir, K.M.A. Malik, E. Rosenberg, *J. Organomet. Chem*. **585**, 100 (1999).
[50] Y.K. Au, K.K. Cheung, W.T. Wong, *Inorg. Chim. Acta* **228**, 267 (1995).
[51] S.R. Flectcher, A.C. Skapski, *J. Chem. Soc., Dalton Trans*. 635 (1972).
[52] J. Chatt, R.G. Hayter, *J. Chem. Soc*. 896 (1961).
[53] B.V. Nonius, *CAD4–Express Software, Version 5.1/1.2* Enraf Nonius, Delft, the Netherlands (1990).
[54] M. Kretschmar, *GENHKL: Program for the Reduction of CAD4 Diffractometer Data* University of Tübingen, Germany (1997).
[55] A.C.T. North, D.C. Phillips, F.S. Mathews, *Acta Cryst*. **A24**, 315 (1968).
[56] G.M. Sheldrick, *Acta Cryst*. **A46**, 467 (1990).
[57] G.M. Sheldrick, *SHELXL 97: Program for the Refinement of Crystal Structures* University of Göttingen, Germany (1997).
[58] A.J.C. Wilson, *International Tables for X-ray Crystallography* Kluwer, Dordrecht, the Netherlands (1995).
[59] A.L. Speck, *PLATON: A Multipurpose Crystallographic Tool* Utrecht University, the Netherlands (2003).
[60] E. Keller, *SCHAKAL* 97*: A Computer Program for the Graphic Representation of Molecular and Crystallographic Models* University of Freiburg, Germany (1997).
[61] T.S. Lobana, A. Castineiras, *Polyhedron* **21**, 1603 (2002).
[62] C. Landgrafe, W.S. Sheldrick, *J. Chem. Soc., Dalton Trans*. 989 (1996).
[63] R. Cini, A. Cinquantini, M. Sabat, L.G. Marzilli, *Inorg. Chem*. **24**, 3903 (1985).