ELSEVIER

Journal of Organometallic Chemistry 485 (1995) 209–213

Journal of Organometallic Chemistry

Dicarbonylbis[2-(diphenylphosphino)-*N,N*-dimethylethanamine]-bis-[μ-(2-methyl)-2-propanethiolato]dirhodium and dicarbonylbis[2-(diphenylphosphino)-*N,N,N*-trimethylethanaminium]-bis-[μ-(2-methyl)-2-propanethiolato]dirhodium tetraphenylborate. Their syntheses, characterization and application as hydrogenation catalyst

Herbert Schumann [a,*], Holger Hemling [a], Nurit Goren [b], Jochanan Blum [b]

[a] *Institut für Anorganische und Analytische Chemie der Technischen Universität Berlin, Straße des 17. Juni 135, D-10623 Berlin, Germany*
[b] *Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel*

Received 26 April 1994

Abstract

$[Rh(CO)_2(\mu\text{-S-t-Bu})]_2$ (**1**) reacts with $[Ph_2PCH_2CH_2NMe_3]^+[BPh_4]^-$ (**2**) as well as with the neutral $Ph_2PCH_2CH_2NMe_2$ (**4**) to give the water soluble cationic dinuclear rhodium complex $[Rh(CO)(Ph_2PCH_2CH_2NMe_3)(\mu\text{-S-t-Bu})]_2^{2+}[BPh_4]_2^{2-}$ (**3**) and the neutral dinuclear complex $[Rh(CO)(Ph_2PCH_2CH_2NMe_2)(\mu\text{-S-t-Bu})]_2$ (**5**), respectively. Both are highly active catalysts for hydrogenation. The NMR spectra of the new compounds and the X-ray crystal structure analysis of **5** are reported and discussed.

Keywords: Rhodium; Phosphine; Catalysis; X-ray diffraction; Hydrogenation

1. Introduction

Although dirhodium complexes with bridging thiolato ligands have been widely used as hydroformylation catalysts under homogeneous [1], heterogeneous [2] and phase transfer conditions [3], only a few cases in which such complexes promote hydrogenation have been reported [4]. Moreover, reinvestigation of hydrogenation of terminal and cyclic olefins by $[Rh(OPMe_3)_2(\mu\text{-S-t-Bu})]_2$ has revealed that part of the dirhodium catalyst cleaves, forming considerable quantities of hydrogen sulfide and mercaptans. In the framework of our recent studies on water soluble dirhodium complexes [5–7] we have now prepared and characterized *cis*-{dicarbonylbis[2-(diphenylphosphino)-*N,N,N*-trimethylethanaminium]bis[μ-(2-methyl)-2-propanethiolato]}dirhodium tetraphenylborate (**3**), a stable and recyclable hydrogenation catalyst that operates in aqueous organic solvents as well as in water.

2. Results and discussion

The synthesis of **3** (eq. 1) and of its neutral analogue, *cis*-{dicarbonylbis[2-(diphenylphosphino)-*N,N*-dimethylethanamine]bis[μ-(2-methyl)-2-propanethiolato]}dirhodium, $[Rh(CO)(Ph_2PCH_2CH_2NMe_2)(\mu\text{-S-t-Bu})]_2$ (**5**) (Eq. 2) was accomplished by interaction of tetracarbonylbis[μ-(2-methyl)-2-propanethiolato]dirhodium (**1**) [8], with the corresponding modified phosphines **2** and **4**.

$$\underset{\mathbf{1}}{[Rh(CO)_2(\mu\text{-S-t-Bu})]_2} + \underset{\mathbf{2}}{2[Ph_2PCH_2CH_2NMe_3]^+[BPh_4]^-} \longrightarrow 2\,CO + \underset{\mathbf{3}}{[Rh(CO)(Ph_2PCH_2CH_2NMe_3)(\mu\text{-S-t-Bu})]_2^{2+}[BPh_4} \qquad (1)$$

---

* Corresponding author.

Elsevier Science S.A.
SSDI 0022-328X(94)05015-4

$$1 + 2\,\underset{\mathbf{4}}{Ph_2PCH_2CH_2NMe_2} \longrightarrow 2\,CO + \underset{\mathbf{5}}{[Rh(CO)(Ph_2PCH_2CH_2NMe_2)(\mu\text{-S-t-Bu})]_2} \quad (2)$$

Compounds **3** and **5** were characterized by their NMR spectra and elemental analyses. **3** crystallizes from acetonitrile as bright yellow crystals, which start to decompose above 164°C, but melts completely between 179° and 180°C. The ^1H NMR spectrum in $CHCl_3$ shows the expected singlet signals for the t-butyl and the NMe_3-group at 1.15 and 1.60 ppm, respectively besides two unresolved triplets each of the CH_2 groups attached to phosphorus and nitrogen atoms at 1.49 and 1.63 ppm due to the coupling with phosphorus [J(H,P) = 47 and 4.6 Hz, respectively]. The ^{31}P NMR spectrum shows a doublet at 24.75 ppm with J(P, Rh) = 152 Hz.

The neutral complex **5** crystallizes from methanol with two solvent molecules. The crystal structure of the orange crystals of **1** shows both rhodium atoms in a square planar arrangement with the Rh atoms 1.08(6) and 4.23(5) pm out of the planes [S(1)–S(2)–C(1)–P(2)] and [S(1)–S(2)–C(2)–P(2)], respectively (Fig. 1). Both planes make up an angle of 116.47(11)°, resulting in a hinged molecule with both sulfur atoms on top. This bite angle is found to be 113.0(3)° in the corresponding complex $[Rh(CO)(PMe_3)(\mu\text{-}SPh)]_2$ [10]. The phosphine ligands have a *cis*-configuration with respect to the Rh–Rh-axes. The intramolecular distance Rh–Rh is in the same region (310.84(7) pm) as in $[Rh(CO)(PMe_3)(\mu\text{-}SPh)]_2$ (306.1(1) pm), likewise also the Rh–C (180.8(6), 182.0(7) pm), Rh–P (226.2(2), 226.3(2) pm) and Rh–S distances (234.7(2), 236.7(2), 240.3(2), 240.6(2) pm) can be compared with those in $[Rh(CO)(PMe_3)(\mu\text{-}SPh)]_2$ (181.7(9), 181.5(9) pm; 225.6(2), 225.7(2) pm; 237.2(2), 237.9(2), 240.3(2), 239.8(2) pm), [10] and with those in $[Rh_2(CO)_2\{(Ph_2P)_2(CH_2)_4\}(\mu\text{-S-t-Bu})_2]$ (178.9(9), 183.4(7) pm; 226.8(2), 226.9(2) pm; 237.5(2), 234.8(2), 240.4(2), 242.9(2) pm) [11]. The rhodium–sulfur distances differ slightly within the same compounds depending on the position of the sulfur atom in relation to phosphorus. S(2) which is *trans* to both phosphorus atoms is nearer to both Rh atoms than S(1). The angles between sulfur, rhodium and the ligands in *trans*-positions are close to 180°. The angles S(1)–S(2)–C(21) [77.35(7)°] and S(2)–S(1)–C(11) [166.0(8)°] reveal that the tert-butyl group at S(1), *cis* to the phosphine ligands points to an axial position, whereas the second tert-butyl group at S(2), *cis* to both CO ligands is equatorial because of sterical conditions.

There are two molecules of **5** together with four molecules of methanol in the unit cell (Fig. 2). The lone pairs of the nitrogen atoms of both $Me_2NCH_2CH_2$ groups form hydrogen bonds to each CH_3OH molecule. One hydrogen [H(31)] was located at distances of 177(8) pm to N(2) and 105(8) pm to O(30), which correspond very well with common hydrogen bridging bonds in related systems [12]. The distance N(1)–O(40) [277(1) pm] is of the same order of magnitude as the distance N(2)–O(30) [281.3(9) pm], which is also consistent with a hydrogen bridge between N(2) and the second CH_3OH molecule. H(41) could not be located because of disorder of the solvent molecule.

In polar solvents (THF, MeOH), as well as in water, the ionic complex **3** was shown to catalyze the hydrogenation of C–C double bonds and nitro groups. In a few cases the catalysis could be carried out also in toluene, although at low rates. Optimal results were obtained between 70 and 130°C at 25–45 atm H_2. The results of some typical experiments are summarized in Table 1.

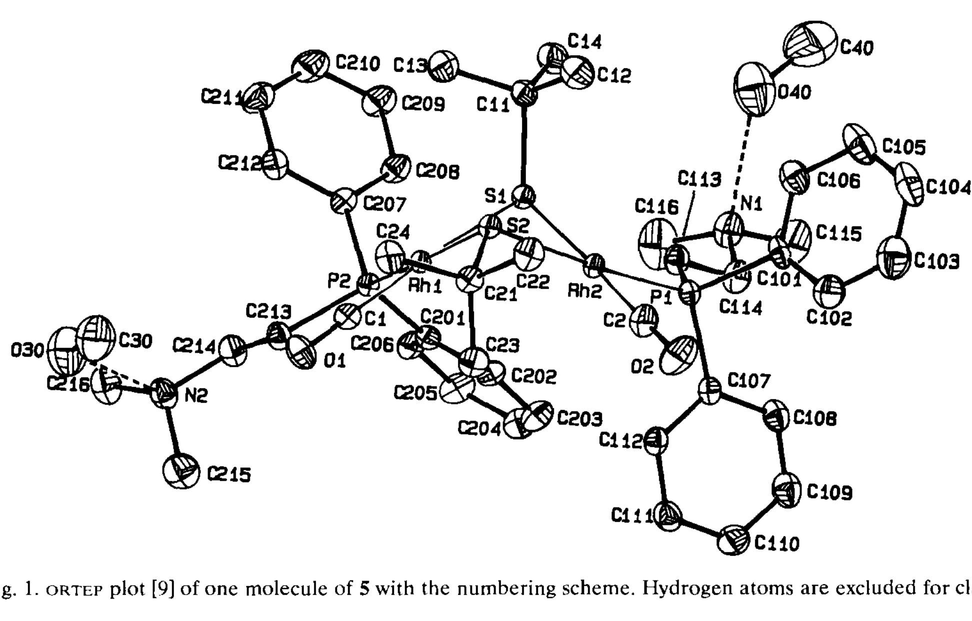

Fig. 1. ORTEP plot [9] of one molecule of **5** with the numbering scheme. Hydrogen atoms are excluded for clarity.

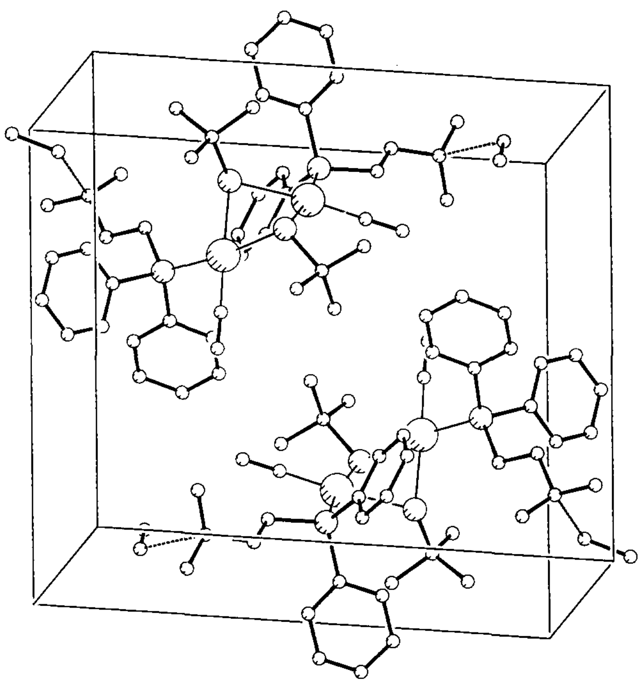

Fig. 2. Arrangement of $[Rh(CO)(Ph_2PCH_2CH_2NMe_2)(\mu\text{-S-t-Bu})]_2(MeOH)_2$ (**5**) in the unit cell.

Although the hydrogenations do not take place under ambient conditions pressure was found to have only a marginal effect on the catalyses, but the rates depend substantially on the nature of the substrate, the reaction temperature and the solvent. For instance, the allylic alcohols are reduced considerably faster than the other unsaturated compounds listed in Table 1. Comparison of experiments 2 and 4 reveals that the rates in THF are higher than in water. The rate enhancement at elevated temperature is demonstrated in experiments 4 and 5. It is notable that even at 130°C, the 3-octanol is the sole product. No contamination of 3-octanone has been detected in these experiments, although other thiolato-bridged dirhodium complexes had been shown to be efficient isomerization catalysts of the allylic alcohol [13]. For some substrates (styrene, acrolein) the hydrogenation cannot be conducted above 75°C because of enhanced polymerization that prevails at higher temperatures. Nitro groups are reduced smoothly to the corresponding amines. Dinitrobenzene forms exclusively phenylenediamine free of any nitroaniline.

Table 1
Hydrogenation of same unsaturated compounds in the presence of **3** [a]

Expt.	Substrate	Solvent	Reaction temperature (°C)	Reaction time (h)	Yield (%)
1	allyl alcohol	H_2O	70	2	100
2	1-octen-3-ol	H_2O	70	2.5	17
3	1-octen-3-ol	H_2O	120	5	97
4	1-octen-3-ol	THF	70	1	90
5	1-octen-3-ol	THF	130	0.3	98
6	maleic acid	H_2O [b]	120	6	40
7	itaconic acid	THF	125	7	45
8	acetamino cinnamic acid	MeOH [c]	130	8.5	46
9	styrene	THF	75	10	93
10	nitrobenzene	THF	130	6	90
11	1,3-Dinitrobenzene	THF [b]	130	9	97 [d]

[a] Reaction conditions: 4 mmoles of substrate, 1.36×10^{-2} mmol of **3**, 1 ml solvent, 25–45 atm H_2; the THF and MeOH includes 4–6% H_2O.

[b] 2 ml of solvent.

[c] 6 ml of solvent.

[d] 1,3-Phenylenediamine.

When the reaction mixtures are worked up under exclusion of air, the catalyst can be recycled. Thus, when in experiment 3 the solvent and product are removed from the reaction vessel by vacuum distillation, the residual complex can be used over and over again without loss of activity.

Although **3** is modified during the hydrogenation process, neither H_2S nor low boiling mercaptans could be detected in the reaction mixture of 1-octen-3-ol and H_2. Therefore, we propose that the catalyst retains its dinuclear structure during the catalytic process. Support for this hypothesis was found in the mass spectra of pyrolyzed **3** under electron impact (70eV, 200°C) before and after applications of the catalyst. Both spectra consist of similar fragments of $m/z > 500$ that cannot result from mononuclearic species.

The neutral complex **5** could also be used as a catalyst for some hydrogenation processes. It proved as efficient as **3** for the hydrogenation of 1-octen-3-ol in THF (the substrate was converted into 97% of 3-octanol within 2.5 h at 70°C and to 96% within 1 h at 130°C) but was practically inactive in water, toluene and in a biphasic system of water and toluene.

3. Experimental details

3.1. General

The preparation of the rhodium complexes was performed in an atmosphere of dry, oxygen-free argon. All solvents were dried over sodium and benzophenone and distilled prior to use. **1** was prepared from $[Rh(CO)_2(\mu\text{-}Cl)]_2$ and t-BuSH (Aldrich) following the procedure of Kalck and Poilblanc [14], **4** and $[Ph_2P(O)CH_2CH_2NMe_3]^+[I]^-$ by the method of Smith and Baird [15]. Elemental analyses were performed on a Perkin-Elmer Series II CHNS/O Analyzer 2400, NMR data were recorded on a Bruker WP 80 (80 and 36.4 MHz) and AMX 400 (400 MHz) in sealed tubes.

*3.2. 2-(Diphenylphosphino)-N,N,N-trimethylethanaminium iodide (**6**)*

By the method described by Smith and Baird [15] 2 g (4.8 mmol) of $[Ph_2P(O)CH_2CH_2NMe_3]^+I^-$ was reacted under exclusion of air with 3.25 g (24 mmol) of $HSiCl_3$ to give 0.96 g (51%) of pure **6**. M.p.: 195–196.5°C (194–196°C [15]) (from $MeCN/Et_2O$). ^1H-NMR (CD_3OD 80 MHz): δ 3.14 (s, 9H, CH_3), 7.40 (m, 10H, ArH), the CH_2CH_2 protons cannot be clearly detected at this resolution. $^{13}C\{^1H\}$NMR (CD_3OD 20 MHz): δ 22.87 (d, $J = 16$ Hz), 53.5 (s), 65.8 (d, $J = 36$ Hz), 137.65 (d, $J = 13$ Hz), 133.90 (d, $J = 7$ Hz), 136.57 (s). $^{31}P\{^1H\}$NMR (CD_3OD 36.4 MHz): $\delta - 18.9$ (s). Anal. Found: C, 50.07, H, 5.53, N, 4.06. $C_{17}H_{23}INP$ (399.06) calcd.: C, 51.14, H, 5.81, N, 3.51%.

*3.3. 2-(Diphenylphosphino)-N,N,N-trimethylethanaminium tetraphenylborate (**2**) [15]*

Compound **6** was converted in quantitative yield into **2** by interaction with an equimolar amount of $NaBPh_4$ in aqueous MeOH. Anal. Found: C, 83.01, H, 7.43, N, 2.19. $C_{41}H_{43}BNP$ (591.32) calcd.: C, 83.20, H, 7.33, N, 2.37%.

*3.4. Preparation of **3***

Into a solution of 200 mg (0.4 mmol) of **1** [8] in 6 ml of degassed MeOH was syringed under Ar atmosphere a solution of 473 mg (0.8 mmol) of **2** in 4 ml of the same solvent. The solvent was removed under reduced pressure and the orange-yellow residue washed with pentane. Crystallization from acetonitrile gave pure **3** as bright yellow crystals (553 mg; 85% yield). M.p.: 179–180°C (dec.; starts to darken > 164°C); ^1H-NMR ($CDCl_3$ 400 MHz): δ 1.15 (s, 18H, CH_3), 1.49 (two unresolved t, 4H, J(H,P) = 47 Hz, CH_2P), 1.60 (s, 18H, CH_3), 1.63 (two unresolved t, 4H, J(H,P) = 4.6 Hz, CH_2N), 6.80–7.63 (m, 60H, ArH); $^{31}P\{^1H\}$NMR ($CDCl_3$ 162 MHz): δ 24.74 (d, J(P,Rh) = 152 Hz). Anal. Found: C, 67.98, H, 6.81, N, 2.01. $C_{92}H_{104}B_2N_2O_2P_2Rh_2S_2$ (1622.53) calcd.: C, 68.04, H, 6.46, N, 1.73%.

*3.5. Preparation of **5***

In the manner described for the preparation of **3**, the tetracarbonyl complex **1** was reacted with 2-(diphenylphosphino)-*N,N*-dimethylethanamine (**4**) to give **5** in 43% yield. M.p.: 170–180° (dec.). ^1H-NMR (CD_3OD 80 MHz): δ 1.72 (s, 18H, CCH_3), 3.15 (s, 12H, NCH_3), 7.5 (m, 28H, ArH), the CH_2CH_2 protons cannot be clearly detected at this resolution. $^{31}P\{^1H\}$NMR (CD_3OD 36.4 MHz): δ 28.71 (d, J(P,Rh) = 167 Hz). Anal. Found: C, 52.03, H, 5.97, N, 2.46. $C_{42}H_{58}N_2O_2P_2Rh_2S_2$ (954.15) calcd.: C, 52.82, H, 6.13, N, 2.94%.

3.6. General hydrogenation procedure

Typically, a mixture of 4 mmol of the substrate, 22.5 mg (1.36×10^{-2} mmol) of **3** and 1 ml of degassed solvent (THF, MeOH or H_2O) was placed under exclusion of air in a glass-lined mini autoclave provided with a magnetic stirrer. The sealed autoclave was purged with argon and charged with 30 atm H_2. The reaction vessel was placed in an oil bath thermostated at 120°C. After the desired time, the autoclave was cooled and the mixture extracted several times with chloroform, dried and analyzed by ^1H NMR or by gas chromatography.

When recycling of the catalyst was desired, the autoclave was connected to a distillation apparatus fitted with a dry ice-acetone collector and the mixture distilled under reduced pressure. The distillate was analyzed as above and the autoclave was recharged with a fresh solution of 4 mmol of substrate.

*3.7. X-ray structure determination of **5***

A suitable crystal of **5** was obtained by recrystallization from MeOH. The crystallographic data are given in [16]. Data collection was carried out with an Enraf-Nonius CAD-4 automatic diffractometer, controlled by a Micro-VAX II computer and fitted with low-temperature equipment. The cell parameters were obtained from the angles of 25 reflections in the range of $20° < 2\Theta < 30°$. Due to some problems with the low-temperature device the crystal was exposed to air for a short time during measurement, and a sudden loss of intensity (41%) was observed. Therefore the data were split into two parts. The data sets were corrected for Lorentz and polarization effects [17], scaled with SHELX 76 [18] and merged. Consequently the overall total loss of intensity was 1.4% for the merged data sets. The position of the rhodium atom was determined from a three dimensional Patterson synthesis. Refinements in space group $P\bar{1}$ were successful. The calculated difference Fourier map revealed all missing carbon, sulphur, nitrogen, oxygen, phosphorus and hydrogen atoms. The hydrogen positions were calculated isotropically (except for the hydrogen-bonding in $N(CH_3)_3$). Several least squares cycles minimized the quantity $\Sigma w(|F_o| - |F_c|)$. Atomic scattering factors and anomalous dispersion terms for all nonhydrogen atoms were taken from [19,20]. Scattering factors for hydrogen were taken from [21]. Data reduction was performed using the SDP software package [22]. All other calculations were undertaken with SHELX 76 [18].

Acknowledgements

We thank the German-Israeli Foundation for Scientific Research and Development (GIF), the Deutsche

Forschungsgemeinschaft (DFG) and the Exchange Program between the Technical University of Berlin and the Hebrew University of Jerusalem for financial support of this study, and Degussa, Hanau for the valuable gift of rhodium chloride.

References and notes

[1] See e.g., P. Kalck, *Organomet. Org. Synth.*, (1988) 297 and references cited therein.

[2] P. Kalck, F. Serein-Spirau, A. Thorez, Fr. Demande Fr. 2, 634, 209 (1988/1990); *Chem. Abstr. 113* (1990) 190469 g.

[3] P. Kalck, P. Escaffre, F. Serein-Spirau, A. Thorez, B. Besson, Y. Collenille and R. Perron, *New J. Chem. 72* (1988) 687.

[4] See e.g., P. Kalck, R. Poilblanc, R.-P. Martin, A. Rovera and A. Gaset, *J. Organomet. Chem., 195* (1980) C9.

[5] W. Baidossi, N. Goren, J. Blum, H. Schumann and H. Hemling, *J. Mol. Catal., 85* (1993) 153.

[6] I. Amer, H. Schumann, V. Ravindar, V. Baidossi, N. Goren and J. Blum,*J. Mol. Catal., 85* (1993) 163.

[7] H. Schumann, H. Hemling, V. Ravindar, Y. Badrieh and J. Blum, *J. Organomet. Chem., 469* (1994) 213.

[8] P. Kalck, F. Senocq, M. Siani and A. Thorez, *J. Organomet. Chem., 350* (1988) 77.

[9] C.K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, 1976.

[10] J.J. Bonnet, P. Kalck and R. Poilblanc, *Inorg. Chem., 16* (1977) 1514.

[11] P. Kalck, C. Randrianalimanana, M. Ridmy, A. Thorez, H. tomDieck and J. Ehlers, *New J. Chem., 12* (1988) 679.

[12] H.J. Simpson, Jr. and R.E. Marsh, *Acta Cryst., 20* (1966) 550.

[13] See e.g., H. Schumann, G. Cielusek, S. Jurgis, E. Hahn, J. Pickardt, J. Blum, Y. Sasson and A. Zoran, *Chem. Ber., 117* (1984) 2825.

[14] P. Kalck and R. Poilblanc, *Inorg. Chem., 14* (1977) 2779.

[15] R.T. Smith and M.C. Baird, *Inorg. Chim. Acta, 62* (1982) 135.

[16] Crystallographic data of **5**: Formula: $C_{42}H_{58}N_2O_2P_2Rh_2S_2(CH_3OH)_2$; molecular mass: 1018.92 g/mol; crystal size: $0.15 \times 0.1 \times 0.1$ mm^3; cell parameters: $a = 1107.89(17)$, $b = 1421.57(14)$, $c = 1697.40(14)$ pm, $\alpha = 85.27(2)°$, $\beta = 75.058(16)°$, $\gamma = 75.923(19)°$; cell volume: 2504.6(8) 10^{-30} m^3; space group: triclinic, $P\bar{1}$; $Z = 2$; calculated density: 1.351 g/cm^3; linear absorption coefficient: 8.3 cm^{-1}; $F(000)$: 1056; radiation: Mo Kα, $\lambda = 71.069$ pm; monochromator: graphite crystal; experimental temperature: 165 K; range: $1° < 2\Theta < 50°$; hkl boundaries: $0 \rightarrow 13$, $-16 \rightarrow 16$, $-20 \rightarrow 20$; scan technique: ω-2Θ; scan time: variable, max. 45 s; scan angle: $(0.70 + 0.35 \tan \Theta)°$; aperture: 2.0 mm; total number of measured reflections: 9945; unique reflections: 8008 ($R_{int} = 0.0166$); observed reflections with $F_o > 4\sigma(F_o)$: 6484; corrections for Lorentz-, polarization n-effects; max. shift/error (Δ/σ): 0.001; residual electron density: max. 2.589, min. -0.540 eÅ^{-3}; number of refined parameters: 527; $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | = 0.0400$. Further details of the structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany upon quoting the depository number (CSD 58403), the authors names and the full citation of the journal.

[17] D. Walker and D. Stewart, *Acta Crystallogr. A39* (1983) 159.

[18] G.M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, UK, 1976.

[19] D.T. Cromer and J.B. Mann, *Acta Crystallogr., A24* (1968) 321.

[20] D.T. Cromer and D. Liberman, *J. Chem. Phys., 53* (1970) 1891.

[21] R.F. Steward, E.R. Davidson and W.T. Simpson, *J. Chem. Phys., 42* (1965) 3175.

[22] B.N. Frenz, SDP-PLUS Structure Determination Package, Version 3.0, Enraf-Nonius, Delft, 1985.