Synthesis of Cationic Ruthenium Thioketene Complexes through Intramolecular 1,2-Elimination [1]

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Ruthenium Complexes, Thiocarboxylate, Thioketene, Structure

Halflsandwich thiocarboxylate complexes [CpRu(PR3)2(SC(0)CH2R')] [(PR3)2 = (PPh3)2, Ph3PCH2PPh3 (dppm), Ph3PC2H4PPh3 (dppe); R' = C6H5, 4-C6H4Me, 4-C6H4OMe, 4-C6H4Cl] are obtained from the corresponding thioketene complexes [CpRu(PR3)2SH] and acyl chlorides. The structure of [CpRu(dppm)(SC(O)CH2Ph)] was determined: monoclinic space group P21/c (No. 14), a = 9.229(2), b = 16.680(3), c = 21.447(5) Å, β = 90.751(12)°, Z = 4. Reaction of the thiocarboxylate complexes with the anhydrides of either trifluoroacetic acid or trifluoromethanesulfonic acid gives thioketene complexes [CpRu(dppm) (SC(O)CH2Ph)]PF6. The structure of [CpRu(dppe)(SC(O)CPh2)2]PF6 was determined: monoclinic space group P21/c (No. 14), a = 13.814(5), b = 15.338(2), c = 17.057(7) Å, β = 93.74(2)°, Z = 4.

Introduction

Transition metal complexes of thioketenes have mostly been prepared from stable, isolable thioketenes such as bis (tert-butyl)thioketene or 2,2,6,6-tetramethylcyclohexylidene methanethione [2–5]. As part of a broader investigation into the chemistry of coordinated thiocarboxyl compounds such as thioesters [6], thiolactones [1,7], and thioaldehydes [8] we are particularly interested in complexes of reactive thioketenes which cannot be isolated in the free state. Therefore, we have to rely on a method to produce thioketenes in the protecting coordination sphere of a transition metal. To our knowledge this has been achieved in only a few cases. Stone et al. have obtained bis(trifluoromethylthioketene) complexes of iridium and platinum by metal-induced degradation of a mixture of bis(trifluoromethyl)methylene-substituted trithiolene and tetrathiane (eq. (1)) [9]. Surprisingly, the ketene dimer (x = y = 1) did not react. Werner et al. have reported the addition of sulfur to osmium and rhodium vinylidene complexes which gave a complex of the parent thioketene (eq. (2)) [10]. Rosini and Jones, in an investigation aimed at the cleavage and degradation of thiophene, produced a rhenium thioketene complex by photochemically induced β-hydrogen transfer (eq. (3)) [11]. Here we report on a novel synthetic access to complexes of thioketenes which appears to be of quite general applicability.

Synthesis and Reactions of Ruthenium Thiocarboxylate Complexes

The thiolato complexes 1–3 [12,13] react with acid chlorides at –70 °C to give high yields of the corresponding thiocarboxylate complexes 4–6.

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(eq. (4)). After chromatographic workup the new compounds are isolated as yellow air-stable crystalline materials. Their spectroscopic properties (Table I) are quite straightforward. In the $^1$H NMR spectra the methylene protons give a singlet resonance around 4 ppm, slightly upfield from the Cp resonance at ca. 4.7 ppm. In the $^{13}$C NMR spectra the CH$_2$ group appears as a singlet at 55 ppm while the carbonyl group gives a signal around 205 ppm which is split into a triplet due to coupling with the two phosphorus nuclei. In the infrared spectra a low $v$(C=O) frequency of the carbonyl group attests to the electron donating capability of the [CpRu(PR$_3$)$_2$]$^+$ complex fragment.

In order to compare the new thiocarboxylate complexes 4–6 to the similar thiolate complexes [CpRu(PR$_3$)$_2$(SR')] [8,14] a few reactions have been carried out. Thus, substitution of triphenylphosphine for CO in 4a (eq.(5)) requires considerably harsher conditions (50 °C, 4 h) than a similar ligand exchange in the corresponding thiolate complexes (20 °C, 3 h) [14]. The carbonyl complex 8 can also be synthesized from the thiolate derivative 7 (eq.(5)). 8 was isolated as a highly stable, off-white crystalline powder. In the infrared spectrum of 8 the carboxylate-CO vibration is shifted to higher wavenumbers compared to 4–6 (Table I) which demonstrates that the decreased electron density at the metal is transmitted all the way to the carboxylate function. Vice versa, the vibration of the metal-bound CO is found also at higher wavenumber compared to analogous thiolate complexes [CpRu(CO)(PPh$_3$)(SR')] [14]. The two methylene protons are diastereotopic and give a narrow AB-system in the proton NMR spectrum. The $^{13}$C resonances of the two CO groups are very close in chemical shift but can

Table I. Important spectroscopic data of the thiocarboxylate complexes 4–6 and 8.

<table>
<thead>
<tr>
<th>No.</th>
<th>IR (Nujol) ($v$(CO) (cm$^{-1}$))</th>
<th>$^1$H NMR (C$_6$D$_6$)</th>
<th>$^{13}$C-NMR (C$_6$D$_6$)</th>
<th>$^3$P-NMR (C$_6$D$_6$)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CH$_2$</td>
<td>CH$_3$</td>
<td>CH$_2$</td>
</tr>
<tr>
<td>4a</td>
<td>1610</td>
<td>4.67</td>
<td>4.24</td>
<td>82.8</td>
</tr>
<tr>
<td>4b</td>
<td>1601</td>
<td>4.68</td>
<td>4.25</td>
<td>83.0</td>
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<tr>
<td>4c</td>
<td>1598</td>
<td>4.69</td>
<td>4.22</td>
<td>83.0</td>
</tr>
<tr>
<td>4d</td>
<td>1606</td>
<td>4.67</td>
<td>4.06</td>
<td>83.0</td>
</tr>
<tr>
<td>5a</td>
<td>1600</td>
<td>4.91</td>
<td>3.85</td>
<td>80.4</td>
</tr>
<tr>
<td>5b</td>
<td>1625</td>
<td>4.92</td>
<td>3.85</td>
<td>80.4</td>
</tr>
<tr>
<td>5c</td>
<td>1627</td>
<td>4.93</td>
<td>3.82</td>
<td>80.5</td>
</tr>
<tr>
<td>5d</td>
<td>1601</td>
<td>4.90</td>
<td>3.69</td>
<td>80.5</td>
</tr>
<tr>
<td>6a</td>
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<td>4.79</td>
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<td>6b</td>
<td>1624</td>
<td>4.82</td>
<td>3.79</td>
<td>82.1</td>
</tr>
<tr>
<td>6c</td>
<td>1595</td>
<td>4.81</td>
<td>3.76</td>
<td>82.1</td>
</tr>
<tr>
<td>6d</td>
<td>1620</td>
<td>4.78</td>
<td>3.66</td>
<td>82.0</td>
</tr>
<tr>
<td>8</td>
<td>1636$^a$</td>
<td>4.81</td>
<td>4.23$^b$</td>
<td>87.0</td>
</tr>
</tbody>
</table>

$^a$v(Ru–CO) 1961 (vs); $^b$AB-System, $^3$J(H–H) 13.4 Hz; $^c$Ru–CO 204.6 ppm, $^3$J(P–C) 19.1 Hz.
readily be distinguished by their rather different P–C couplings.

An unsuccessful attempt was made to alkylate 6a using methyl iodide, while methyl tosylate or triethyl oxonium hexafluorophosphate were both electrophilic enough to convert 5a into the thioether complexes 9a,b (eq. (6)). The site of alkylation – sulfur rather than oxygen – is apparent from the 1H and 13C NMR signal of the group R. Taken together these reactions attest to both a reduced nucleophilicity and a reduced π-donor ability of the thiocarboxylate ligand.

Crystal and Molecular Structure of [CpRu(dpmm)(SC(O)CH3Ph)] (5a)

Details of the structure determination are collected in Table II and in the Experimental Section. Important bond distances and angles are listed in Table III, a view of the molecule is shown in Fig. 1. The geometry of the [CpRu(dpmm)] part of the molecule is, as expected, almost identical to that of other compounds containing this grouping [8,15]. The Ru–S distance (238.2 pm) equals those in the thioether complex [CpRu(dpmm)(SC6H5C6H4Cl)]+ (236.3 pm) [8] or in the metal thiolate [CpRu(dpmm)(SCH2C6H5F)] (239.5 pm) [16]. The two dihedral angles P(1)–Ru–S–C(71) and P(2)–Ru–S–C(71) are rather unequal. The SC(O)–CH3Ph ligand apparently assumes an orientation which minimizes the antibonding interaction of the lone pairs at sulfur and both filled frontier orbitals a’ and a” of the halfsandwich complex [17]. The S–C(71) distance in 5a is 8.4 pm shorter than in the benzyl thiolate complex mentioned.
above [16] which corresponds exactly to the difference of covalent radii of sp² and sp³ carbon. Thus, while both the IR data and the reactivity point to a major contribution of resonance form B this is not borne out in the structures of these thiocarboxylate complexes.

\[
\text{[Ru]}^\text{S/C} \quad \text{[Ru]}^\text{S/C=CHR}
\]

\(A\) \(B\)

**Synthesis of Ruthenium Thioketene Complexes**

Among the numerous routes to thioketenes simple 1,2-elimination reactions have found surprisingly little attention [18]. After such a strategy had been successfully employed for the synthesis of ruthenium sulfine complexes [19] we tried to acylate the thiocarboxylate complexes \(5\text{a–d}\) at oxygen using trifluoroacetic acid anhydride. The desired thioketene complexes \(10\text{a–d}\) were indeed obtained, albeit in only moderate yield. A major side product was the trifluorothioacetate complex \(11\) which apparently arises from competing electrophilic attack at sulfur (eq. (7)). This problem can readily be overcome by using the anhydride of trifluoromethane sulfonic acid as an electrophile. After addition of \(\text{NH}_4\text{PF}_6\) the thioketene complexes are isolated as stable, orange-brown crystalline materials.

Mechanistically, the formation of the C=C double bond certainly involves acylation at oxygen followed by intramolecular 1,2-elimination (eq. (8)). When the reaction is carried out at low temperature a transient color change to dark red is observed which might be due to either the anhydride or the \(\eta^1\)-thioketene intermediate - among the thioester and thioaldehyde complexes the \(\eta^1\) isomers are also consistently more deeply colored [6,8]. \(\eta^1\text{(S)}\)-coordinated thioketene complexes with electron-poor transition metal fragments such as [M(CO)]₅ (M = Cr, W) or [CpMn(CO)]₂ have been obtained previously [3]. Thioaldehyde complexes \([\text{CpRu(P}_3\text{)}(\text{S=CHPh})]^+\) normally occur as \(\eta^1\text{(S)}\)-isomers; rapidly equilibrating \(\eta^1/\eta^2\)-mixtures are formed only with sterically less demanding, strongly donating PR₃ ligands such as PMe₃ or Me₂PC₂H₂PMe₂(dmpe). The side-on coordination of the C=S group in the final products \(10\text{a–d}\) is apparent from the non-equivalence of the two phosphorus nuclei as well as from the high-field shift of the thiocarbonyl carbon atom (ca. 110 ppm upfield from free thioketenes) [18] and its strong coupling to one of the phosphorus nuclei (Table IV). We have not found any spectroscopic evidence for the presence of the corresponding \(\eta^1\)-isomers in solution.

Table IV. Important spectroscopic data of the thioketene complexes \(10\text{a–d}\).

<table>
<thead>
<tr>
<th>No.</th>
<th>(^1\text{H} \text{NMR (acetone-d₆)})</th>
<th>(^{13}\text{C} \text{NMR (acetone-d₆)})</th>
<th>(2\text{J(P–C)})</th>
<th>(\text{SCC})</th>
<th>(3\text{J(P–C)})</th>
<th>(3\text{P NMR (acetone-d₆)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10\text{a})</td>
<td>5.71 6.22 3.2</td>
<td>91.4 158.9 11.1</td>
<td>119.5 6.8</td>
<td>0.1</td>
<td>-8.8</td>
<td>96</td>
</tr>
<tr>
<td>(10\text{b})</td>
<td>5.78 6.20 3.2a</td>
<td>92.0 158.5 10.1</td>
<td>120.0 7.0b</td>
<td>0.2</td>
<td>-8.6</td>
<td>96</td>
</tr>
<tr>
<td>(10\text{c})</td>
<td>5.77 6.16 3.2c</td>
<td>91.8 157.5 10.8</td>
<td>119.6 7.0d</td>
<td>0.4</td>
<td>-8.6</td>
<td>96</td>
</tr>
<tr>
<td>(10\text{c})</td>
<td>5.82 6.26 3.2</td>
<td>91.1 161.9 11.1</td>
<td>118.9 7.0</td>
<td>-0.3</td>
<td>-9.0</td>
<td>97</td>
</tr>
</tbody>
</table>

\(\text{a Aryl–CH₃ 2.22 (s); b Aryl–CH₃ 21.0; c Aryl–OCH₃ 3.71 (s); d Aryl–OCH₃ 55.4.}\)
Crystal and Molecular Structure of [CpRu(dppm)(η²-S=C=CHPh)]PF₆ (10a)

Details of the structure determination are collected in Table II and in the Experimental Section. Important bond distances and angles are listed in Table V, a view of the cation of 10a is shown in Fig. 2. The geometry of the [CpRu(dppm)] part of the cation is similar to that of 5a. The small decrease (2°) of the P(1)-Ru-P(2) angle as well as the remarkable increase of the average Ru-P distance (6 pm) are forced by the formal increase of the coordination number. The two angles C(1)-Ru-P(1) and C(1)-Ru-P(2) are rather different which explains why in the ¹³C-NMR spectra C(1) is coupled only to one of the phosphorus nuclei. The S-C(1) distance is roughly 10 pm greater than in free 2,2,6,6-tetramethylcyclohexyldene-methanethione [20] or its η¹-[CpMn(CO)₂] complex [3], but slightly smaller than in d⁶-halssandwich η²-thioketene complexes of cobalt or rhodium [5,10]. This indicates that the d⁶-cations of this work have less back-bonding capability.

Conclusions

The acylation-elimination route outlined in this study provides an efficient access to cationic d⁶-complexes of thioketenes. Spectroscopic and structural data seem to suggest that there is only limited back-donation of electrons from the metal into the cumulated π*-system. As a consequence we expect thioketene complexes of this type to undergo nucleophilic addition reactions and cycloadditions similar to those of the analogous ruthenium and rhenium thioaldehyde complexes [8].

Experimental Section

All experiments were carried out in Schlenk tubes under an atmosphere of nitrogen using suitably purified solvents. The thiolato complexes 1-3 and 7 were obtained as described previously [12,13], all other reagents were used as purchased.

IR: Perkin-Elmer 283; NMR: Bruker AM X 400 (¹H, 400 MHz, TMS; ¹³C, 100 MHz, TMS; ³¹P, 162 MHz, H₃PO₄). Melting or decomposition points were determined by differential scanning calorimetry (DSC).

[CpRu(PR₃)₂(SC(O)CH₂R')]/(4-6)

To a solution of thiocarbonyl complexes 1-3 (0.20 mmol) in THF (8 ml) is slowly added at -70°C a solution of acyl chloride (0.20 mmol) in THF (5 ml). (In the synthesis of the bis(triphenylphosphine) complexes 4a-d free triphenylphosphine (100 mg, 0.40 mmol) has to be added to the reaction mixture in order to suppress decomposition into [CpRu(PPh₃)₂Cl].) The mixture is allowed to warm to room temperature while the solvent is stripped under vacuum. The dry residue is taken up in a minimum amount of THF, transferred onto a silica column (20 cm) and chromatographed using THF/Et₂O 1:2 as eluent. The broad yellow zone contains the thiocarboxylate complex which is isolated by evaporation of the solvent and crystallization from benzene/hexane.

4a: Yield 155 mg (92%), yellow crystalline powder, m.p. 82°C.
C₄₀H₄₂OP₂RuS (842.0)
Calcd C 69.90 H 5.03 S 3.81%.
Found C 70.11 H 5.31 S 3.65%.

4b: Yield 134 mg (78%), yellow crystalline powder, m.p. 117 °C. This compound contained a contamination which we were unable to remove.

C₅₀H₄₄O₇P₂RuS (856.0)
Calcd C 70.16 H 5.18 S 3.75%.
Found C 71.74 H 5.36 S 2.87%.

4c: Yield 143 mg (82%), yellow crystalline powder, m.p. 124 °C.

C₅₀H₄₄O₂P₂RuS (872.0)
Calcd C 68.87 H 5.09 S 3.68%.
Found C 68.66 H 5.09 S 3.75%.

4d: Yield 131 mg (75%), yellow crystalline powder, m.p. 168 °C.

C₅₀H₄₄ClO₇P₂RuS (876.4)
Calcd C 68.66 H 5.09 S 3.75%.
Found C 68.66 H 5.09 S 3.75%.

5a: Yield 126 mg (90%), yellow crystalline powder, m.p. 152 °C.

C₃₂H₂₇O₂PRuS (607.7)
Calcd C 63.25 H 4.48 S 5.28%.
Found C 63.24 H 4.46 S 5.27%.

[CpRu(CO)(PPh₃)(SC(O)CH₂Ph)]PF₆ (9a)

To a solution of 5a (35 mg, 0.05 mmol) in acetone (2 ml) is added methyltosylate (466 mg, 2.50 mmol) and NH₄PF₆ (8.2 mg, 0.05 mmol). After 2 h the mixture is evaporated to dryness, the residue extracted with a minimum amount of dichloromethane, and the product precipitated with hexane. Yield 12 mg (27%), red-brown crystalline powder.

[1H NMR (CD₂Cl₂): 1.85 (s, CH₃), 3.12 (s, CH₂), 4.96 (s, CH₃), 4.84 (dt, J(H–H) 15.0 Hz, J(P–H) 11.2 Hz, PCH₂P), 4.99 (dt, J(H–H) 15.0 Hz, J(P–H) 10.4 Hz, PCH₂P).] ³¹P NMR (CD₂Cl₂): 5.1 (s).

[CPRu(dpmp)(EtSC(O)CH₂Ph)]PF₆ (9b)

To a solution of 5a (35 mg, 0.05 mmol) in dichloromethane (2 ml) is added [Et₃O]PF₆ (11 mg, 0.045 mmol) at 0 °C. After 2 h the mixture is...
worked up as described above for 9a. Yield 13.5 mg (31%), yellow crystalline powder.

$^1$H NMR (CD$_2$Cl$_2$): 0.64 (t, J(H—H) 7.2 Hz, CH$_3$), 2.27 (q, J(H—H) 7.2 Hz, CH$_3$), 3.08 (s, CH$_2$), 4.96 (s, C$_5$H$_5$), 4.88 (dt, J(H—H) 16.6 Hz, J(P—H) 10.5 Hz, PCH$_3$P), 4.92 (dt, J(H—H) 18.8 Hz, J(P—H) 11.2 Hz, PCH$_2$P). $^{31}$P NMR (CD$_2$Cl$_2$): 5.0 (s).

$[\text{CpRu(dppm)}(\eta^2 - S=C=CHR)]PF_6$ (10a–d)

A solution of thiocarboxylate complex 5a–d (0.10 mmol) and NH$_4$PF$_6$ (20 mg, 0.12 mmol) in dichloromethane (1 ml) is treated at $-70 \degree C$ with trifluoromethanesulfonic acid anhydride (28 mg, 0.19 mmol). A color change from yellow to deep red is observed immediately. After 15 min the crude product is precipitated by adding cold hexane, washed repeatedly with hexane and diethyl ether, and carefully dried under vacuum. Further purification is effected by chromatography over a short (10 cm) silica column using dichloromethane/acetone 50:1 as eluent.

10a: Yield 59 mg (71%) yellow-orange crystalline powder, m.p. 200 °C (dec).

$C_{38}H_{32}F_2P_2RuS$ (829.7)
Calcd $C$ 55.01 H 4.01 S 3.86%,
Found $C$ 54.86 H 4.09 S 3.93%.

10b: Yield 53 mg (63%), yellow-orange crystalline powder, m.p. 144 °C (dec).

$C_{39}H_{33}F_2P_2RuS$ (843.8)
Calcd $C$ 55.52 H 4.18 S 3.80%,
Found $C$ 55.50 H 4.42 S 3.40%.

10c: Yield 58 mg (68%) yellow-orange crystalline powder, m.p. 155 °C (dec).

$C_{39}H_{33}F_2OP_2RuS$ (859.8)
Calcd $C$ 54.48 H 4.10 S 3.73%,
Found $C$ 54.28 H 4.20 S 3.96%.

10d: Yield 56 mg (65%) yellow-orange crystalline powder, m.p. 154 °C (dec).

$C_{38}H_{32}ClF_2P_2RuS$ (864.2)
Calcd $C$ 52.82 H 3.73 S 3.71%,
Found $C$ 52.71 H 3.71 S 3.55%.

When the same reaction is carried out with trifluoroacetic acid anhydride a larger amount of $[\text{CpRu(dppm)}(\text{SC(O)CF}_3)]$ (11) is produced. 11 appears in the chromatographic work up as a first yellow band. The yields of the thioketene complexes drop to ca. 35%.

11: Yield ca. 50%, yellow crystalline powder, m.p. 215 °C.

$C_{32}H_{27}F_3OP_2RuS$ (679.4)
Calcd $C$ 56.55 H 4.00 S 4.72%,
Found $C$ 56.58 H 4.29 S 4.87%.

IR (Nujol) 1607 cm$^{-1}$ (CO). $^1$N NMR (acetone-d$_6$): 11.2 Hz, PCH$_2$), 2.27 (q, J(H—H) 7.2 Hz, CH$_2$), 3.08 (s, CH$_2$), 4.96 (s, C$_5$H$_5$), 4.88 (dt, J(H—H) 16.6 Hz, J(P—H) 10.5 Hz, PCH$_3$P), 4.92 (dt, J(H—H) 18.8 Hz, J(P—H) 11.2 Hz, PCH$_2$P). $^{31}$P NMR (acetone-d$_6$): 5.0 (s).

X-ray structure determination of $[\text{CpRu(dppm)}(\eta^2 - S=C=CHR)]PF_6$ (10a)

Clear yellow prisms suitable for structure determination were obtained from a benzene/heptane solution. 25 centered reflections from a crystal of the dimensions given in Table II gave a monoclinic unit cell. Data were collected from one fourth of the reflection sphere in the range $2 \degree < \theta < 24 \degree$ (Enraf-Nonius CAD 4 diffractometer, MoK$_\alpha$ radiation, graphite monochromator, filter factor 15.4). An empirical absorption correction based on the counts of 9 reflections was applied. The structure was solved by the heavy atom method (program SHELXS86) [21] in the space group P2$_1$/c (No. 14). H atoms were included in idealized positions. Least-squares cycles using the SHELXL93 [22] program package led to the R values given in Table II. The 5 highest maxima of the final difference Fourier map were between 0.26 and 0.19 e A$^{-3}$. Further details of the structure determination may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD 405579, the names of the authors and the journal citation.

X-ray structure determination of $[\text{CpRu(dppm)}(\eta^2 - S=C=CHPh)]PF_6$ (10a)

Clear brownish-yellow crystals suitable for X-ray work were obtained from a dichloromethane/diethyl ether solution. 25 centered reflections from a crystal of the dimensions given in Table II gave a monoclinic unit cell. Data were collected from one fourth of the reflection sphere in the range $2 \degree < \theta < 23 \degree$ (Enraf-Nonius CAD 4 diffractometer, MoK$_\alpha$ radiation, graphite monochromator, filter factor 16.4). An empirical absorption correction based on the counts of 9 reflections was applied. The structure was solved by the Patterson method (program SHELXS86) [21] in the space group P2$_1$/b (No. 10) with $\alpha=13.39$, $b=16.00$, $c=13.88$ Å, $\beta=90$. H atoms were included in idealized positions. Least-squares cycles using the SHELXL93 [22] program package led to the R values given in Table II. The 5 highest maxima of the final difference Fourier map were between 0.29 and 0.19 e A$^{-3}$. Further details of the structure determination may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD 405579, the names of the authors and the journal citation.
P2_1/c (No. 14). All hydrogen atoms were located and refined isotropically. Least-squares cycles using the SHELXL93 [22] program package led to the R values given in Table II. The 5 highest maxima of the final difference Fourier map were below 0.28 Å⁻³.

Further details of the structure determination may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD 405580, the names of the authors and the journal citation.

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