Journal of Organometallic Chemistry, 368 (1989) 23–30
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09789

Reactions of bis(trimethylsilyl)isocyanamine and its isomers with chlorotriphenylphosphonium chloride: evidence for a transient diazomethylenetriphenylphosphorane. Crystal structure of $[Ph_3P\overline{CNN\{C(PPh_3)_2\}NN}][PF_6]_2$

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(Received November 28th, 1988)

Abstract

Triphenylphosphine dichloride reacts with $(Me_3Si)_2C{=}NN$, $Me_3SiN{=}C{=}NSiMe_3$, and metal-coordinated $CN{-}N(SiMe_3)_2$ to give the iminophosphoranes $CN{-}NPPh_3$, $NC{-}NPPh_3$, and $W(CO)_5CN{-}NPPh_3$, respectively, and with free bis(trimethylsilyl)isocyanamine to give a dicationic species containing a tetrazole ring with triphenylphosphonio and bis(triphenylphosphonio)methylide substituents. This latter product can be regarded as a cyclodimerization product of diazomethylenetriphenylphosphorane, $NN{=}C{=}PPh_3$. The structure of the dimer has been established by X-ray crystallography.

We recently described the novel multifunctional synthon, **1**, which combines the structural elements of an α-metallated isocyanide and those of a Wittig reagent [1]. Our understanding of the mechanism of its formation from trimethylsilylmethyl isocyanide (or bis(trimethylsilyl)methyl isocyanide (**2**)) and Appel's reagent [2] (eq. 1), prompted us to make a similar study of the action of $\{PPh_3 + C_2Cl_6\}$ on

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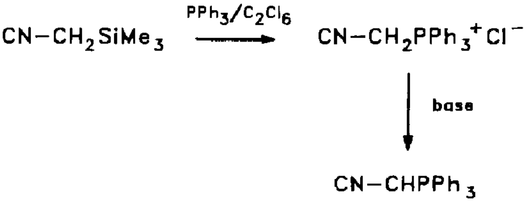
* Reference number with asterisk indicates a note in the list of references.

disilylated isodiazomethane (3) [3,4*], which is a direct *N*-containing analogue of the methyl isocyanide derivative **2**.



$$\begin{tikzcd} CN{-}CH_2SiMe_3 \arrow[r, "PPh_3/C_2Cl_6"] & CN{-}CH_2PPh_3^+Cl^- \arrow[d, "base"] \\ & CN{-}CHPPh_3 \end{tikzcd} \qquad (1)$$

(1)

$CN{-}CH(SiMe_3)_2$ (2)

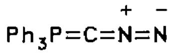
$CN{-}N(SiMe_3)_2$ (3)

Results and discussion

Attack on **3** by the reactive species Ph_3PCl^+ formed in the $\{PPh_3 + C_2Cl_6\}$ system [2] could be expected to occur at the lone pair of the isocyano carbon or that of the amino nitrogen. Blocking of the former site by coordination to a metal gives rise to PN products such as **4**, several of which we previously synthesized from the relevant metal components and free *N*-isocyaniminotriphenylphosphorane [5].

$W(CO)_5{-}CN{-}N{=}PPh_3$

(4)



$Ph_3P{=}C{=}\overset{+}{N}{=}\overset{-}{N}$

(5)

In the case of uncoordinated **3** (as for some dialkyl(isocyano)amines), on the other hand, photoelectron spectroscopy shows the carbon lone pair to be the HOMO [6]. If it is attached at this position, the formal dication PPh_3^{2+} would be likely to induce a drastic reorganization of the molecule, of the type involved in the formation of **1** (eq. 1) [7]; as a result the silyl groups would be expelled from the terminal nitrogen, perhaps giving rise to the unknown and long-sought diazo title compound **5**.

From a 1/1-mixture of **3** and Ph_3PCl_2 (or $PPh_3 + C_2Cl_6$) in tetrahydrofuran, a violet solid **6a** began to separate after ca. 1 h. This solid gave two $^{31}P\{^1H\}$ NMR signals (10.5, 22.5 ppm) in an intensity ratio of ca. 1/2. Replacement of chloride by the non-coordinating PF_6^- gave colourless crystals **6b**, which were used for further identification.

In **6b**, the $^{31}P\{^1H\}$ NMR spectra again show two P resonances (10.6, 22.6 ppm) along with the PF_6 signal at -144.2, with relative intensities of 1/2/2, which indicates the presence of three PPh_3 groups in a +2 charged cation. The $^{13}C\{^1H\}$ NMR spectra show two carbon signals, well separated from the phenyl multiplet, highly characteristic patterns arising from coupling to two equivalent and one single phosphorus species, respectively; this, together with the elementary analysis, suggests that the products are salt-like species made up of two molecules of **5** and Ph_3PX_2 ($X = Cl$ or PF_6).

This interpretation was fully confirmed by an X-ray structural study of **6b**, which showed the dimer to be a tetrazole with a PPh_3^+-substituent attached to the ring

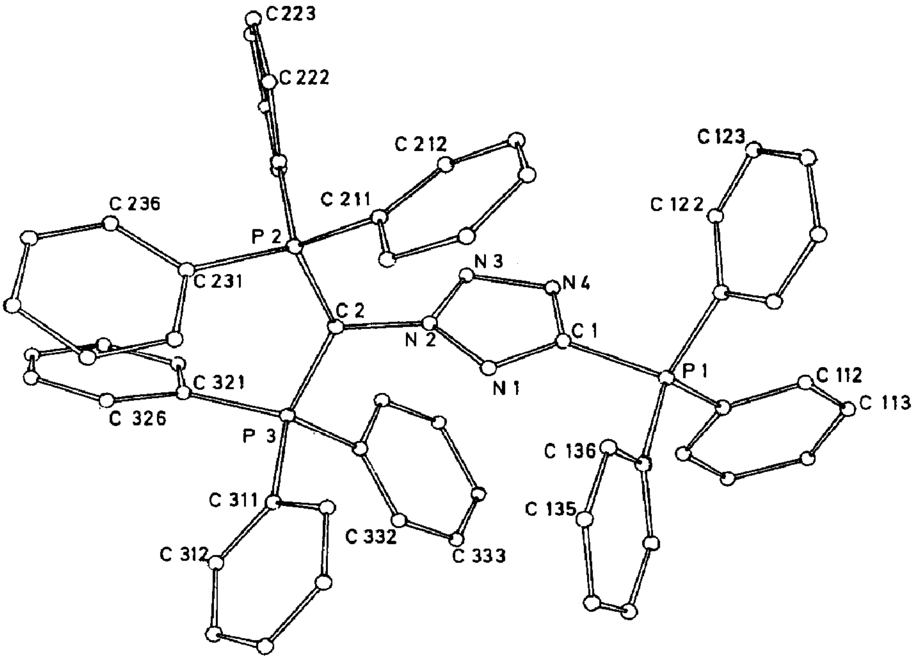
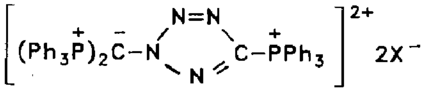


Fig. 1. Perspective view of the dication $[Ph_3P\overline{CNN\{C(PPh_3)_2\}NN}]^{2+}$ of **6b**.

carbon atom and a triphenylphosphoniomethylidenetriphenylphosphorane group bonded to N(2).



(6a) X = Cl

(6b) X = PF_6

The assumption that a cycloaddition takes place between two molecules of **5**, with one of them acting as a 1,3-dipole and the other as a dipolarophile, also receives strong support from a recent report on the chemistry of a stable diamino(halogeno) derivative of **5**, which is dominated by [3 + 2]-cycloaddition reactions [8].

The structure of the dication of **6b** is shown in Fig. 1, values of selected bond lengths and angles are shown in Table 2. All the N–N and N–C distances within the ring are between the values for the corresponding single and double bonds, thus pointing to some aromaticity of the heterocycle. Presumably for steric reasons, the planar CN_4-ring and the C(2), P(2), P(3)-plane of the ylidic substituent at N(2) form a dihedral angle of 76.3(6)° thereby excluding any π-interactions. As a result the C(2)–N(2) distance corresponds to that of a simple single bond.

$(Me_3Si)_2C{=}\overset{+}{N}{=}\overset{-}{N}$ (7)

$Me_3Si{-}N{=}C{=}N{-}SiMe_3$ (8)

As well as **3** and its metal complex, the isomers **7** and **8** have also been subjected to the same reactions, and the results further support our view of the reaction path and at the same time extend the synthetic applicability of the exchange of two $SiMe_3$ groups for one PPh_3. Thus, disilylated diazomethane **7** reacts with $\{PPh_3 + C_2Cl_6\}$ to give free *N*-isocyaniminotriphenylphosphorane, which has been observed previously as the coordinated ligand in complex **4**, formed from the tungsten complex of **3**. Under the same conditions, bis(trimethylsilyl)carbodiimide **8** gives an almost quantitative yield of $NC{-}NPPh_3$. The close relationship between this reaction and the chemistry described above is obvious, if **8** is assumed to react via its cyanamide tautomer.

Experimental

All reactions were carried out under purified argon in dried, argon-saturated solvents. The compounds $CNN(SiMe_3)_2$ [3] and $W(CO)_5CNN(SiMe_3)_2$ [9*] were prepared by published procedures, $Me_3SiNCNSiMe_3$ was purchased from Petrarch Systems Inc. (Bristol, England).

Instruments used are: IR: Perkin–Elmer Spectrophotometer IR 983. NMR: JEOL FX 90Q. Analysis (C,H,N): Heraeus CHN-Rapid. Conductivity measurements: Knick Digital–Konduktometer Modell 600. Melting points are uncorrected.

Pentacarbonyl(N-isocyaniminotriphenylphosphorane)tungsten (4)

Triphenylphosphine (0.5 g, 2.0 mmol) and 0.5 g (2.0 mmol) of hexachloroethane were added to a solution of 1.0 g (2.0 mmol) of $W(CO)_5CNN(SiMe_3)_2$ in 100 ml of

Table 1

Crystal data and experimental conditions in data collection and refinement

Formula:	$[(Ph_3P)_2C\overline{NNC(PPh_3)NN}][PF_6]_2 \cdot CH_2Cl_2$
Crystal size:	$0.63 \times 0.32 \times 0.24$ mm^3
Formula wt.:	1241.5
Space group:	*Pbca*, No. 61[a]
Cell constants:	*a* 20.515(6) Å
	b 21.276(7) Å
	c 26.320(8) Å
Number of formula units per cell:	8
Density:	d_{ber} 1.373 g cm^{-3}
Diffractometer:	STOE (Mo-K_α, graphite-monochromatized)
Radiation:	Mo-K_α (λ 0.71069 Å)
Absorption coefficient:	μ(Mo-K_α) 3.0 cm^{-1}
Data range:	$2° \le \theta \le 20°$,
Scan mode:	ω-scan
No. of collected data:	5880
No. of unique data with $F \ge 3\sigma(F_0)$:	2893
No. of parameters refined:	716
Structure solution:	direct methods
Refinement:	least-squares method
Function for minimalisation:	$\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2$
R-value (R_w [b]):	10.3% (6.1%)
Programs:	X-Ray 76, MULTAN 77, ORTEP

[a] International Tables for X-ray Crystallogr., Vol IV, D. Reidel Publishing Company, Boston, 1983.
[b] Weighting scheme: $w = 1/\sigma(I_0)$.

Table 2

Selected bond distances (Å) and angles (°) in **6b**[a]

Bond distances			
C1–N1	1.33(2)	C1–N4	1.33(2)
C1–P1	1.76(1)	C2–P2	1.70(1)
C2–P3	1.78(1)	C2–N2	1.45(1)
N1–N2	1.34(1)	N2–N3	1.34(2)
N3–N4	1.35(2)		
P1–C111	1.79(1)	P1–C121	1.77(1)
P1–C131	1.80(1)	P2–C211	1.78(1)
P2–C221	1.81(1)	P2–C231	1.80(1)
P3–C311	1.81(1)	P3–C321	1.82(1)
P3–C331	1.77(1)		
C111–C112	1.34(2)	C121–C122	1.36(2)
C112–C113	1.37(2)	C122–C123	1.32(2)
C113–C114	1.34(2)	C123–C124	1.36(3)
C114–C115	1.42(3)	C124–C125	1.30(3)
C115–C116	1.30(2)	C125–C126	1.30(3)
C116–C111	1.37(2)	C126–C121	1.33(2)
C131–C132	1.35(2)	C211–C212	1.33(2)
C132–C133	1.36(2)	C212–C213	1.33(2)
C133–C134	1.35(2)	C213–C214	1.34(3)
C134–C135	1.39(2)	C214–C215	1.33(2)
C135–C136	1.39(2)	C215–C216	1.46(2)
C136–C131	1.37(2)	C216–C211	1.37(2)
C221–C222	1.40(2)	C231–C232	1.37(2)
C222–C223	1.36(2)	C232–C233	1.36(2)
C223–C224	1.38(2)	C233–C234	1.36(2)
C224–C225	1.32(2)	C234–C235	1.35(2)
C225–C226	1.32(2)	C235–C236	1.29(2)
C226–C221	1.34(2)	C236–C231	1.36(2)
C311–C312	1.36(2)	C321–C322	1.33(2)
C312–C313	1.34(2)	C322–C323	1.35(2)
C313–C314	1.43(2)	C323–C324	1.27(2)
C314–C315	1.33(2)	C324–C325	1.33(2)
C315–C316	1.37(2)	C324–C326	1.35(2)
C316–C311	1.39(2)	C326–C321	1.37(2)
C331–C332	1.36(2)		
C332–C333	1.34(2)		
C333–C334	1.31(3)		
C334–C335	1.45(3)		
C335–C336	1.37(2)		
C336–C331	1.40(2)		
P4–F41	1.45(1)	P5–F51	1.48(1)
P4–F42	1.50(1)	P5–F52	1.46(1)
P4–F43	1.41(2)	P5–F53	1.56(1)
P4–F44	1.36(2)	P5–F54	1.51(1)
P4–F45	1.42(2)	P5–F55	1.45(1)
P4–F46	1.48(2)	P5–F56	1.47(1)

Table 2 (continued)

Bond angles			
N1–C1–N4	114(1)	C1–N4–N3	105(1)
C1–N1–N2	102(1)	N1–N2–N3	112(1)
C2–N2–N1	124(1)	C2–N2–N3	123(1)
N2–N3–N4	106(1)	P2–C2–P3	133(1)
P2–C2–N2	113(1)	P3–C2–N2	114(1)
P1–C1–N4	125(1)	P1–C1–N1	121(1)
C1–P1–C111	107(1)	C2–P2–C211	107(1)
C1–P1–C121	106(1)	C2–P2–C221	111(1)
C1–P1–C131	106(1)	C2–P2–C231	112(1)
C111–P1–C121	111(1)	C211–P2–C221	107(1)
C111–P1–C131	113(1)	C211–P2–C231	112(1)
C121–P1–C131	113(1)	C221–P2–C231	107(1)
C2–P3–C311	115(1)		
C2–P3–C321	110(1)		
C2–P3–C331	105(1)		
C311–P3–C321	108(1)		
C311–P3–C331	104(1)		
C321–P3–C331	113(1)		

[a] Estimated standard deviation is given in parentheses for the last significant figures.

THF. After 18 h the solvent was removed, and the residue washed with petroleum ether, then recrystallized from CH_2Cl_2/petroleum ether. The product **4** (1.1 g, 88%) was identified by comparison with an authentic sample prepared from $W(CO)_5(THF)$ and $CNNPPh_3$ [5]. Anal. Found: C, 46.41; H, 2.66; N, 4.48. $C_{24}H_{15}N_2O_5PW$ (626.22) calcd.: C, 46.03; H, 2.41; N, 4.47%.

*[(5-Triphenylphosphoniotetrazol-2-yl)triphenylphosphoranylidene]methyltriphenylphosphonium chloride (**6a**)*

A 200-ml Schlenk tube was flushed with argon and charged with 100 ml of purified anhydrous THF, 1.5 g (8.0 mmol) of $CNN(SiMe_3)_2$, 3.1 g (12.0 mmol) of triphenylphosphine, and 2.8 g (12.0 mmol) of hexachloroethane. The solution was stirred at room temperature for 18 h during which a violet solid separated. This was filtered off, washed with 20 ml of diethyl ether, and dried in vacuo. Recrystallization from CH_2Cl_2/ether gave 3.2 g (85%) of a pale yellow solid (m.p. 162° C, dec.). Anal.: Found. C, 67.31; H, 5.18; N, 5.81. $C_{56}H_{45}Cl_2N_4P_3 + \frac{1}{2}CH_2Cl_2$ (980.30) calcd.: C, 69.23; H, 4.73; N, 5.71%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 22.5 [$C(PPh_3)_2$]; 10.5 [$CPPh_3$]. Λ_M (CH_3NO_2): 98 $cm^2\ \Omega^{-1}\ mol^{-1}$.

*[(5-Triphenylphosphonio-tetrazol-2-yl)triphenylphosphoranylidene]methyltriphenylphosphonium hexafluorophosphate (**6b**)*

A solution of 1.0 g (1.1 mmol) of **6a** in 100 ml of water was filtered into a solution of 0.2 g (1.2 mmol) of NH_4PF_6 in 100 ml of water. The white precipitate which separated immediately was recrystallized from CH_2Cl_2/ether to give colourless crystals, m.p. 240° C, dec. Anal.: Found: C, 58.06; H, 4.17; N, 4.82. $C_{56}H_{45}F_{12}N_4P_5$ (1156.85) calcd.: C, 58.14; H, 3.92; N, 4.84%. ^1H NMR (CD_2Cl_2): δ 7.54 [m, Ph]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 152.0 [d, $CPPh_3$, $^1J(PC)$ 133 Hz]; 136–112 [C_6H_5]; 38.7 [t, $C(PPh_3)_2$, $^1J(PC)$ 130 Hz]. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 22.6 [$C(PPh_3)_2$]; 10.6 [$CPPh_3$]; −144.2 [sept., PF_6, $^1J(PF)$ 710 Hz]. Λ_M (CH_3NO_2): 71 $cm^2\ \Omega^{-1}\ mol^{-1}$.

Table 3

Fractional coordinates ($\times 10^4$) with e.s.d.'s in parentheses

Atom	x	y	z	Atom	x	y	z
P1	0145(2)	5337(1)	3785(1)	C211	2207(6)	6606(5)	4329(4)
P2	2854(2)	6055(2)	4410(1)	C212	1733(7)	6680(6)	4667(5)
P3	2982(2)	4765(1)	3805(1)	C213	1234(10)	7075(9)	4609(7)
P4	0123(2)	3067(2)	2226(2)	C214	1150(9)	7414(8)	4183(8)
P5	3156(2)	3428(2)	5868(2)	C215	1568(7)	7341(7)	3804(5)
F41	−0293(5)	3593(4)	2362(6)	C216	2120(6)	6916(7)	3876(5)
F42	0553(8)	2498(5)	2180(7)	C221	3005(6)	5987(6)	5086(4)
F43	−0347(8)	2747(7)	1935(6)	C222	3046(8)	6538(6)	5374(6)
F44	0442(12)	3367(8)	1841(7)	C223	3191(7)	6505(6)	5879(5)
F45	0558(9)	3332(9)	2584(9)	C224	3267(7)	5925(7)	6109(5)
F46	−0144(15)	2699(7)	2653(6)	C225	3187(7)	5420(6)	5824(5)
F51	2769(5)	3850(5)	5536(4)	C226	3059(6)	5439(5)	5331(4)
F52	2680(5)	2918(5)	5882(4)	C231	3598(5)	6322(5)	4117(4)
F53	3707(5)	3933(4)	5852(4)	C232	3636(6)	6391(5)	3600(4)
F54	3589(5)	3042(5)	6211(4)	C233	4191(7)	6605(6)	3380(6)
F55	2862(5)	3761(4)	6294(3)	C234	4721(7)	6728(7)	3673(7)
F56	3520(8)	3132(5)	5449(4)	C235	4678(7)	6647(8)	4182(5)
N1	1454(6)	5359(4)	3858(3)	C236	4144(5)	4658(6)	4387(4)
N2	1895(5)	5271(5)	4228(4)	C311	3041(6)	4918(6)	3130(4)
N3	1619(7)	5095(5)	4668(4)	C312	3475(6)	4593(6)	2843(5)
N4	0970(6)	5065(6)	4579(5)	C313	3451(7)	4660(8)	2338(5)
C1	0898(6)	5245(6)	4099(6)	C314	3031(8)	5104(10)	2092(5)
C2	2589(5)	5360(5)	4166(4)	C315	2615(8)	5404(6)	2394(5)
C111	−0313(5)	4631(6)	3886(4)	C316	2608(6)	5339(6)	2912(4)
C112	−0029(7)	4073(6)	3797(5)	C321	3797(5)	4617(5)	4051(5)
C113	−0400(8)	3540(7)	3843(6)	C322	3907(6)	4234(7)	4439(5)
C114	−1035(9)	3559(8)	3968(7)	C323	4517(7)	4165(9)	4627(7)
C115	−1307(8)	4157(9)	4075(6)	C324	5012(7)	4430(8)	4428(5)
C116	−0950(6)	4658(7)	4045(5)	C325	4921(6)	4853(7)	4061(5)
C121	−0245(6)	5991(6)	4071(5)	C326	4323(6)	4938(6)	3856(4)
C122	−0225(7)	6072(8)	4585(6)	C331	2467(5)	4101(5)	3848(4)
C123	−0498(8)	6569(8)	4793(6)	C332	2167(6)	3833(7)	3444(5)
C124	−0835(13)	6991(11)	4505(7)	C333	1750(10)	3349(9)	3494(9)
C125	−0862(14)	6893(13)	4018(8)	C334	1569(10)	3101(10)	3927(10)
C126	−0577(7)	6413(7)	3806(5)	C335	1896(7)	3345(7)	4373(6)
C131	0344(5)	5471(5)	3128(4)	C336	2322(7)	3838(7)	4324(4)
C132	0292(7)	4995(7)	2791(5)	C3[a]	2649(13)	7608(13)	2142(10)
C133	0472(7)	5089(7)	2301(6)	Cl1[a]	2593(5)	7099(3)	2505(2)
C134	0745(7)	5636(6)	2149(5)	Cl2[a]	2208(5)	8165(4)	2193(3)
C135	0786(7)	6136(7)	2487(5)				
C136	0604(6)	6039(6)	2992(4)				

[a] Population 0.8 (solvent).

X-Ray crystal structure determination of ***6b*** *(See Table 1).*

$C_{56}H_{45}F_{12}N_4P_5 \cdot CH_2Cl_2$, $M = 1241.5$, orthorhombic, space group *Pbca*, a 20.515(6), b 21.276(7), c 26.320(8) Å, U 11488.2 Å^3, $Z = 8$, D_c 1.373 g cm^{-3}, μ 3.0 cm^{-1} for Mo-K_α radiation (λ 0.71069 Å). Of 5880 reflections measured at room temperature on a STOE diffractometer with $4 \leq 2\theta \leq 40°$, 2893 were unique with $F > 3\sigma(F)$. The structure was solved by direct methods (MULTAN) and the model completed through a combination of Fourier difference maps and least-squares refinements (X-RAY 76). Hydrogen atoms were placed in idealized positions (C–H 0.95 Å) and were not refined. Final R and R_w ($w = \sigma^{-1}(I_0)$) values were 0.103 and 0.061, respectively. The selected bond lengths and bond angles are given in Table 2 and Table 3 *.

Cyaniminotriphenylphosphorane

Triphenylphosphine (2.1 g, 8.1 mmol) and 1.9 g (8.1 mmol) of hexachloroethane were added to a solution of 1.5 g (8.1 mmol) of bis(trimethylsilyl)carbodiimide in 100 ml of THF. The mixture was stirred for 18 h, and the precipitate then filtered off, washed three times with 10 ml portions of ether, and recrystallized from CH_2Cl_2/ether to give 2.1 g (86%) of the pure product; m.p. 196 °C (lit. [10]: 196 °C). Anal.: Found: C, 75.34; H, 4.93; N, 9.60. $C_{19}H_{15}N_2P$ (302.32) calcd.: C, 75.49; H, 5.00; N, 9.27%.

Acknowledgement

We thank the Fonds der Chemischen Industrie for financial support.

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* Further details of the structure are available on request from the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2, West Germany, on quoting the depository number CSD 53658, the authors, and the full journal citation.