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Polyfunctional ligands: carbon-carbon oxidative coupling of $[HC(PPh_2)_2]^-$ and crystal structure of the new tetraphosphine ligand $(Ph_2P)_2CH\text{-}CH(PPh_2)_2$[†]

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Summary – Oxidation of a THF solution of $Li[HC(PPh_2)_2]$ with iodine affords the isomeric products $Ph_2P\text{-}CH{=}PPh_2\text{-}PPh_2{=}CH\text{-}PPh_2$ **2**, $(Ph_2P)_2C{=}PPh_2\text{-}CH_2\text{-}PPh_2$ **4** and $(Ph_2P)_2CH\text{-}CH(PPh_2)_2$ **1**, which result from P-P, P-C and C-C coupling, respectively. The latter pathway has now been established for the first time and the crystal structure of the resulting new chiral tetraphosphine **1** has been determined by X-ray diffraction.

bis(diphenylphosphino)methanide / carbon-carbon coupling / phosphorus ylide / tetraphosphine / chiral ligand

An interesting approach to the synthesis of catalytically relevant (chiral) diphosphine ligands consists of the selective oxidative C-C coupling of monophosphine-derived carbanions. However, this generally requires a multi-step procedure. Typically, BH_3 may be used to protect the phosphine towards water or oxygen, and the borane adduct is reacted with *n*-BuLi to generate a carbanion, which is then C-C coupled by reaction with a Cu(II) reagent. Deprotection of the borane adduct of the resulting diphosphine is finally achieved by treatment with a strong base (*eg*, morpholine or diethylamine) [1].

As part of our studies on the synthesis and coordination properties of polyfunctional phosphine ligands, we recently investigated the behavior of lithium bis(diphenylphosphino)methanide and bis(diphenylphosphino)amide towards various, potentially oxidizing, reagents [2]. Bis(diphenylphosphino)methanide $[Ph_2P\text{-}CH\text{-}PPh_2]^-$ is an anionic ligand in which phosphorus and carbon have the same number of valence electrons and coordination number. Its ambident character, *ie* the possibility of binding to electrophiles through phosphorus or carbon, as in $Ge[HC(PPh_2)_2]_2$ [3], raises interesting questions about its oxidative dimerization : will it occur by P-P, C-P or C-C coupling and will the corresponding products be stable? Related questions may be asked about the isoelectronic anion $[Ph_2P\text{-}N\text{-}PPh_2]^-$, which is obtained by deprotonation of the corresponding diphosphazane ligand. We have recently found that the latter reacts with iodine to give selectively the product of P-P coupling, $Ph_2P\text{-}N{=}PPh_2\text{-}PPh_2{=}N\text{-}PPh_2$, which has a centrosymmetric structure in the solid-state [2]. The reaction behavior of $Li[HC(PPh_2)_2]$ was more complex since products resulting from P-P or P-C coupling were identified. Furthermore, we have now structurally characterized another isomeric product from this reaction and therefore gained a more complete picture of this complex reaction. This new compound is the product of C-C coupling : 1,1,2,2-tetra(diphenylphosphino)ethane $(Ph_2P)_2CH\text{-}CH(PPh_2)_2$ **1**. This finding is particularly significant since this tetraphosphine ligand (i) has never been reported; (ii) was believed to perhaps be sterically too congested to be readily accessible and/or stable; (iii) has probably been formed but not recognized in previous reactions (see below); and (iv) should display a very interesting coordination chemistry.

Two reasonable pathways could account for the formation of the products : metal/halogen exchange or radical intermediates. We favor the latter, where oxidation of $[HC(PPh_2)_2]^-$ would produce first the radical $[HC(PPh_2)_2]^\bullet$, which would then dimerize with formation of a P-P or P-C bond. This would lead to compounds $Ph_2P\text{-}CH{=}PPh_2\text{-}PPh_2{=}CH\text{-}PPh_2$ **2** or $(Ph_2P)_2CH\text{-}PPh_2{=}CH\text{-}PPh_2$ **3** (scheme) which were characterized in $^{31}P\text{-}\{^1H\}$ NMR spectroscopy by their AA′XX′ and AM_2X spin systems, respectively. Compound **3** was only observed at low temperature (−30°C) since rapid formation of the mixed phosphine, ylide isomer $(Ph_2P)_2C{=}PPh_2\text{-}CH_2\text{-}PPh_2$ **4** occurred, as a result of proton migration [2]. In addition, $^{31}P\text{-}\{^1H\}$ NMR resonances appeared at room temperature, which we can

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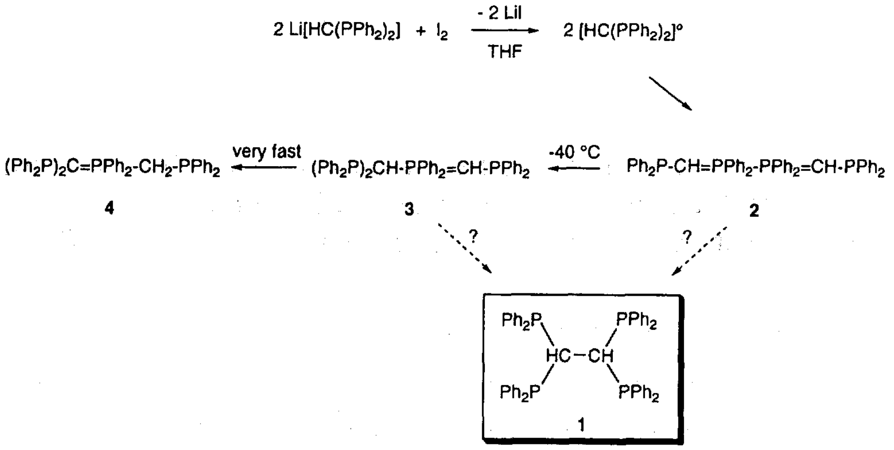
[†] Dedicated to Prof Manfred Regitz on the occasion of his 60th birthday, with our sincere congratulations and warmest wishes.



Scheme

now assign to the new isomer $(Ph_2P)_2CH\text{-}CH(PPh_2)_2$ **1**; they correspond to an AA′BB′ spin system (A, A′ = P(1), P(4); B, B′ = P(2), P(3), see below). The values for the J(PP) coupling constants are fully consistent with the presence of only P^{III} nuclei in this molecule. Inequivalence of the geminal PPh_2 groups would result from hindered rotation about the C(1)-C(2) bond and the population of the various conformers should be temperature-dependent. A related phenomenon has been observed in the phosphine-substituted ylid $Ph_3P{=}C(PPh_2)_2$ [4]. Since the resonances of **1** were not observed in the low temperature spectrum of the reaction mixture, this molecule is not a kinetic product in the oxidative coupling of $[HC(PPh_2)_2]^-$. Whether **1** results from isomerization of **2** or **3** cannot be stated at the moment. Compound **1** was isolated in *ca* 15% yield.

Having now spectroscopically and structurally (see below) identified the long-sought tetraphosphine **1**, it is interesting that we could also detect its presence in the reactions of $Li[HC(PPh_2)_2]$ with $BrCH_2CH_2Br$, CH_2I_2 or PCl_3. In the reactions with the haloalkanes, the ratio **4**/**1** was *ca* 50:50 (based on $^{31}P\text{-}\{^1H\}$ NMR) (but other products were also formed), whereas it was *ca* 60:40 in the latter reaction, in which another product characterized by a $^{31}P\text{-}\{^1H\}$ NMR singlet at −9.2 ppm was also formed. This product may be tris(diphenylphosphino)methane $CH(PPh_2)_3$ [5], which could result from intramolecular substituent exchange [6]. Large amounts of dppm were produced which could be due, at least in part, to hydrogen abstraction from THF. Furthermore, using the haloalkanes as reagents also produced ylids or salts and a separation of these compounds was not accomplished.

It should be noted that our spectroscopic data for **1** are almost identical with those reported by Karsch *et al* [7] for one of the products obtained by oxidation of $Li[HC(PPh_2)_2]$ with $[Cp_2TiCl_2]$, which these authors assigned to **2** (erroneously, we believe). Our own $^{31}P\text{-}\{^1H\}$ NMR data for **2** (δ (THF/C_6D_6, −40°C) : 21.1 and −22.1) are also more consistent than their values (δ (C_6D_6, 20°C) : 1.50 and −8.85) with the presence of both P^{III} and P^{IV} nuclei in the molecule (because of both the chemical shifts and the $^2J(P^{III}P^{IV})$ coupling constant [2]). In view of the reported yields, the $[Cp_2TiCl_2]$-induced coupling of $Li[CH(PPh_2)_2]$ [3] probably represents a more advantageous method to yield **1**. This ligand has the potential of forming metal complexes containing four-membered chelate rings, like bis(diphenylphosphino)methane (dppm), five-membered chelate rings, like 1,2-bis(diphenylphosphino)ethane (dppe), or both like 1,1,2-tris(diphenylphosphino)ethane [8] or even more complex systems. This remains to be explored.

For comparison, when a solution of $Li[CH_2PPh_2]$ and TMEDA in THF was treated with iodine at 0°C, the ^{31}P NMR spectrum of the solution recorded after 1 h at room temperature revealed the formation of *ca* 75% Ph_2PMe and 10% $Ph_2P\text{-}CH{=}PPh_2\text{-}CH_3$ [9]. Signals at −10.3 and −21.7 ppm were tentatively assigned to $CH(PPh_2)_3$ and dppm, respectively, present in *ca* 5% abundance each. An intermolecular transfer of Ph_2P-groups must be involved in this transformation.

Crystal structure of 1

A view of the crystal structure of **1** is shown in figure 1 and a stereoview in figure 2. Selected bond distances and angles are given in table I and all the experimental data are summarized in table II. This molecule is chiral and asymmetric although, when the phenyl groups are neglected, it contains a pseudo C_2 axis passing through the middle of the C(1)-C(2) bond which connects the two $CH(PPh_2)_2$ moieties (fig 3). With a distance of 1.554(7) Å, the C(1)-C(2) single bond is slightly longer than the $C(sp^3)\text{-}C(sp^3)$ distances in the two forms of dppe of 1.516(4) and 1.530(5) Å [10]. This could be due to the presence of four bulky PPh_2 groups in **1**. The C(1)-P(1), C(1)-P(2), C(2)-P(3) and C(2)-P(4) distances range from 1.878(6) to 1.895(5) Å are slightly longer than the $C(sp^3)$-P distances found in dppm (1.848(5) and 1.868(5) Å) [11]. Owing to the stereochemically active lone pairs on phosphorus, the C-P-C angles are all significantly less than the tetrahedral value of 109.5°. The P(1)-C(1)-P(2) and P(3)-C(2)-P(4) angles of 114.0(3) and 117.8(3)°, respectively, are significantly larger than in dppm (106.2(2)°). The NMR spectroscopic data for **1** in solution are consistent with retention of the solid-state structure in solution.

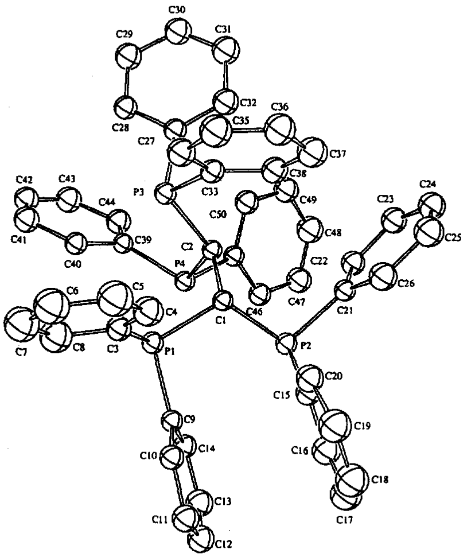


Fig 1. View of the molecular structure of $(Ph_2P)_2CH$-$CH(PPh_2)_2$ in **1** · C_2H_5OH.

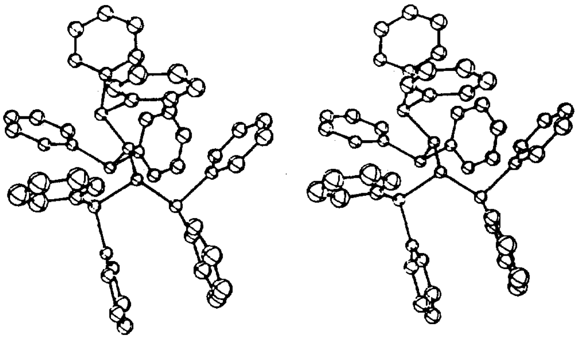


Fig 2. Stereoview of the molecular structure of $(Ph_2P)_2CH$-$CH(PPh_2)_2$ in **1** · C_2H_5OH.

Table I. Selected Bond Distances (Å) and Angles (deg) in $(Ph_2P)_2CH$-$CH(PPh_2)_2 \cdot CH_3CH_2OH$ (**1** · CH_3CH_2OH).

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Atom 3	Angle
P1	C1	1.878(5)	C1	P1	C3	105.2(3)
P1	C3	1.821(7)	C1	P1	C9	106.6(3)
P1	C9	1.807(6)	C3	P1	C9	102.5(3)
P2	C1	1.883(6)	C1	P2	C15	103.8(3)
P2	C15	1.827(7)	C1	P2	C21	101.6(2)
P2	C21	1.848(6)	C15	P2	C21	101.2(3)
P3	C2	1.878(6)	C2	P3	C27	104.5(3)
P3	C27	1.854(6)	C2	P3	C33	101.6(3)
P3	C33	1.828(7)	C27	P3	C33	100.0(3)
P4	C2	1.895(5)	C2	P4	C39	108.0(3)
P4	C39	1.808(6)	C2	P4	C45	102.3(2)
P4	C45	1.831(6)	C39	P4	C45	101.7(3)
C1	C2	1.554(7)	P1	C1	P2	114.0(3)
			P1	C1	C2	106.9(3)
			P2	C1	C2	109.0(4)
			P3	C2	P4	117.8(3)
			P3	C2	C1	107.2(4)
			P4	C2	C1	107.7(3)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table II. X-ray experimental data for $(Ph_2P)_2CH$-$CH(PPh_2)_2 \cdot CH_3CH_2OH$ (**1** · CH_3CH_2OH).

Formula	$C_{50}H_{42}P_4 \cdot CH_3CH_2OH$
Molecular weight	812.9
Color	colorless crystals
Crystal system	monoclinic
a(Å)	17.842(5)
b(Å)	23.104(7)
c(Å)	10.675(3)
β(deg)	90.87(2)
Volume(Å^3)	4 400.0
Z	4
Dcalc (gcm^{-3})	1.227
Wavelength (Å)	1.5418
μ (cm^{-1})	18.727
Space group	$P2_1/n$
Diffractometer	Philips PW1100/16
Crystal dim (mm)	0.35 × 0.30 × 0.20
Temperature	20°C
Radiation	Cu$K\alpha$ graphite monochromated
Mode	$\theta/2\theta$ flying step-scan
Scan speed (degs^{-1})	0.020
Step width (deg)	0.04
Scan width (deg)	1.10 + 0.14tg(θ)
Octants	$\pm h + k + l$
θ min/max (deg)	3/52
Data collected	5 327
Data with $I > 3\sigma(I)$	3 156
Number of variables	499
Abs min/max	0.76/1.32
R(F) ; Rw(F)	0.059; 0.083
p	0.08
Largest peak in final diff (eÅ^{-3})	0.05
GOF	1.695

Experimental section

General procedures

All reactions were performed in Schlenk-type flasks under nitrogen. Solvents were purified and dried under nitrogen. Infra-red spectra were recorded in the 4000-400 cm^{-1}range on a Perkin-Elmer 398 spectrophotometer or Bruker IFS66 FTIR. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a FT Bruker AC 300 instrument.

Synthesis of 1,1,2,2-tetrakis(diphenylphosphino)ethane $(Ph_2P)_2CH$-$CH(PPh_2)_2$ 1

Compound **1** was obtained by oxidation of a THF solution of Li[HC(PPh_2)$_2$] with iodine, in *ca* 10-15% yield based on the integration of the ^{31}P NMR resonances of the reaction mixture. The crude product was extracted with Et_2O, leaving a pure solid of $(Ph_2P)_2C{=}PPh_2$-CH_2-PPh_2 **4**. Precipitation of the extract with *n*-hexane and repetititon of this procedure finally led to recrystallization of small amounts of **1**.

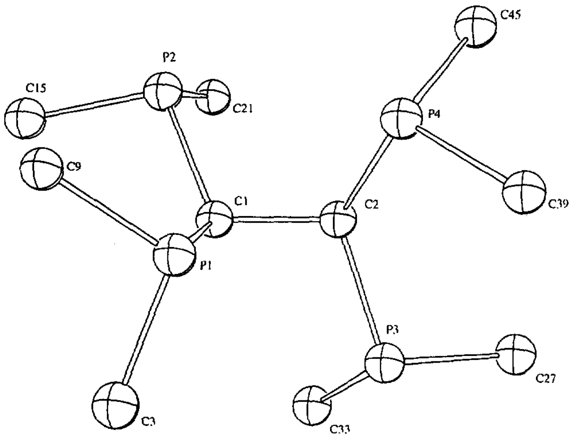


Fig 3. View of the molecular structure of $(Ph_2P)_2CH$-$CH(PPh_2)_2$ in **1** · C_2H_5OH, only the aromatic ipso carbon atoms are represented.

Table III. Positional parameters with ESD's for the non-hydrogen atoms of **1** · CH_3CH_2OH.

Atom	x	y	z	B (Å^2)
P1	0.25263(8)	0.28754(6)	0.3776(1)	4.84(3)
P2	0.33130(8)	0.32757(6)	0.6297(1)	4.93(3)
P3	0.40900(8)	0.20365(6)	0.3389(2)	4.95(3)
P4	0.29032(7)	0.18584(6)	0.5612(1)	4.80(3)
C1	0.3420(3)	0.2920(2)	0.4723(5)	4.2(1)
C2	0.3700(3)	0.2289(2)	0.4920(5)	4.3(1)
C3	0.2762(3)	0.3147(2)	0.2230(5)	5.6(1)
C4	0.3335(4)	0.3510(3)	0.1931(6)	8.2(2)
C5	0.3477(5)	0.3678(4)	0.0709(7)	11.5(2)
C6	0.3025(5)	0.3482(4)	−0.0204(8)	13.7(3)
C7	0.2444(5)	0.3153(4)	0.0035(7)	12.8(3)
C8	0.2309(5)	0.2956(3)	0.1287(6)	9.6(2)
C9	0.1917(3)	0.3435(2)	0.4363(5)	4.8(1)
C10	0.1809(3)	0.3975(3)	0.3790(5)	5.7(1)
C11	0.1314(3)	0.4370(3)	0.4290(6)	7.0(2)
C12	0.0928(3)	0.4245(3)	0.5339(7)	8.0(2)
C13	0.1013(4)	0.3719(3)	0.5893(6)	8.4(2)
C14	0.1498(3)	0.3307(3)	0.5414(6)	6.1(1)
C15	0.3229(3)	0.4045(3)	0.5924(5)	5.9(1)
C16	0.2749(4)	0.4365(3)	0.6648(6)	8.2(2)
C17	0.2663(5)	0.4961(3)	0.6451(8)	10.5(2)
C18	0.3062(6)	0.5234(3)	0.5599(8)	12.6(3)
C19	0.3533(5)	0.4937(3)	0.4867(8)	10.1(2)
C20	0.3632(4)	0.4330(3)	0.5015(6)	7.3(2)
C21	0.4281(3)	0.3242(2)	0.6931(5)	4.8(1)
C22	0.4450(3)	0.2781(3)	0.7724(6)	6.1(1)
C23	0.5153(3)	0.2692(3)	0.8232(6)	7.3(2)
C24	0.5698(3)	0.3091(3)	0.8016(7)	7.9(2)
C25	0.5556(4)	0.3556(3)	0.7288(8)	9.4(2)
C26	0.4834(4)	0.3635(3)	0.6743(7)	7.8(2)
C27	0.4661(3)	0.1392(2)	0.3804(5)	5.5(1)
C28	0.4485(3)	0.0886(2)	0.3190(6)	5.9(1)
C29	0.4932(4)	0.0407(3)	0.3333(7)	7.7(2)
C30	0.5553(4)	0.0424(3)	0.4113(8)	8.5(2)
C31	0.5730(4)	0.0915(3)	0.4723(7)	8.4(2)
C32	0.5285(3)	0.1405(3)	0.4575(7)	7.4(2)
C33	0.4834(3)	0.2565(2)	0.3136(5)	5.5(1)
C34	0.4983(3)	0.2702(3)	0.1903(6)	7.0(2)
C35	0.5540(4)	0.3089(3)	0.1600(7)	8.9(2)
C36	0.5954(4)	0.3346(3)	0.2515(7)	9.0(2)
C37	0.5810(4)	0.3233(3)	0.3763(7)	8.5(2)
C38	0.5259(3)	0.2838(3)	0.4065(6)	6.5(2)
C39	0.2782(3)	0.1207(2)	0.4692(5)	5.0(1)
C40	0.2585(3)	0.1256(2)	0.3412(6)	6.1(2)
C41	0.2411(3)	0.0754(3)	0.2716(7)	7.9(2)
C42	0.2401(4)	0.0221(3)	0.3257(8)	8.8(2)
C43	0.2577(4)	0.0170(3)	0.4482(9)	9.6(2)
C44	0.2767(4)	0.0661(3)	0.5192(7)	7.3(2)
C45	0.3330(3)	0.1573(2)	0.7056(5)	5.1(1)
C46	0.2980(3)	0.1727(3)	0.8161(6)	6.5(2)
C47	0.3302(4)	0.1568(3)	0.9326(6)	8.4(2)
C48	0.3962(4)	0.1256(3)	0.9326(7)	9.2(2)
C49	0.4295(4)	0.1107(3)	0.8258(6)	8.0(2)
C50	0.3986(4)	0.1253(3)	0.7128(6)	6.7(2)
C51	−0.0060(6)	0.0263(5)	0.752(1)	7.5(3)*
C52	0.0510(8)	0.0033(7)	0.641(2)	11.6(4)*
O	0.0553(9)	0.0311(7)	0.529(2)	21.1(6)*

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as : $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

IR (KBr) : 3 048s, 1 582s, 1 476vs, 1 431vs, 1 258s, 1 181s, 1 090vs, 1 023s, 998s, 739vs, 692vs, 622s, 611s, 538vs, 506vs, 481vs cm^{-1}.

^{1}H NMR ($CDCl_3$, 300.13 MHz, TMS) : δ 8.2-6.6 (Ph, m, 40H), 4.0-3.7 (CH, m, 2H).

^{13}C NMR ($CDCl_3$, 75.5 MHz, TMS) : δ 137.8-127.5 (Ph, m), 36.4 (CH, m).

^{31}P NMR ($CDCl_3$, 121.5 MHz, H_3PO_4) : δ 0.6 (P_A), −8.6 (P_B) ppm, AA'BB'-system, N = 94.0, calculated couplings under the assumption that $J_{BB'} = 0$: $J_{AA'} = \pm 84.9$ Hz, $J_{AB} = \pm 88.0$ Hz, $J_{AB'} = \pm 3.1$ Hz.

These values are very similar to those found by Karsch *et al* [7] for a product resulting from the oxidation of $[Ph_2P$-CH-$PPh_2]^-$ with $[Cp_2TiCl_2]$. These authors attributed them to the P-P coupling product $Ph_2PCH{=}PPh_2$-PPh_2-$CH{=}PPh_2$, but the present data strongly suggest that this assignment was incorrect.

X-Ray structure determination

Suitable single crystals of **1** · C_2H_5OH were obtained by slow diffusion of hexane into a EtOH solution at −4°C. A single crystal was mounted on a rotation-free goniometer head. Systematic searches in reciprocal spaces using Philips PW1100/16 automatic diffractometer showed that the crystal belong to the monoclinic system (table II). Quantitative data were obtained at room temperature using monochromatic Mo$K\alpha$ radiation source (λ = 1.5418 Å). The resulting data-set was transferred to a VAX computer, and for all subsequent calculations the Enraf-Nonius Molen/VAX package [12] was used. Three standard reflections measured every hour during the entire data collection periods showed 34% decay due to progressive loss of the solvent molecule. Linear time-dependent decay corrections were applied. The raw data were converted to intensities and corrected for Lorentz, polarization and absorption factors, the latter computed from psi scans of 4 reflections. After refinement of the heavy atoms, difference-Fourier maps revealed maxima of residual electronic density close to the positions expected for hydrogen atoms; they were introduced in structure factor calculations as fixed contributors (C-H = 0.95 Å) with isotropic temperature factors such as $B(H) = 1.3\ B_{eqv}(C)$ Å^2. Full least-squares refinements on F ; $\sigma^2(F^2) = \sigma^2_{counts} + (pI)^2$. A final difference map revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients come from reference [13]. Atomic coordinates are given in table III.

Supplementary material data (H-atom coordinates, thermal parameters, and remaining bond distances and angles) have been deposited with the British Library, Document Supply, Centre at Boston Spa, Wetherby, West Yorkshire, LS23, 7BQ, UK as supplementary publication N° = SUP 90387 and are available on request from the Document Supply Centre.

Acknowledgements

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