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PREPARATION OF BIS[2,4-BIS(TRIFLUOROMETHYL)PHENYL]FLUOROPHOSPHINE AND 2,4-BIS(TRIFLUOROMETHYL) PHENYL-[2,6-BIS(TRIFLUOROMETHYL)PHENYL]-FLUOROPHOSPHINE – TWO DISTILLABLE MONOFLUOROPHOSPHINES. STRUCTURE OF *cis*-DICHLORO-BIS[BIS(2,4-BIS(TRIFLUOROMETHYL)PHENYL)FLUOROPHOSPHINO]-PLATINUM(II)

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SUMMARY

Bis[2,4-bis(trifluoromethyl)phenyl]fluorophosphine, 1, and 2,4-bis(trifluoromethyl)phenyl-[2,6-bis(trifluoromethyl)phenyl]fluorophosphine, 2, were found amongst the products of the reaction of 1,3-bis(trifluoromethyl)benzene with *n*-butyllithium, followed by chlorodifluorophosphine. The mixture of 1 and 2 was a stable, distillable oily liquid, which crystallized on standing. The reaction of the mixture of 1 and 2 with dichloro-(η^4-1,5-cyclooctadiene)platinum(II) led to the formation of *cis*-dichloro-bis(bis(2,4-bis(trifluoromethyl)phenyl)fluorophosphino)platinum(II), 3.

The products 1, 2 and 3 were characterized by their ^{1}H-, ^{19}F- and ^{31}P-NMR and mass spectra. The long-range coupling constants ^4J(PF) and ^5J(FF) are discussed. The structure of 3 was confirmed by a single crystal X-ray investigation. 3 crystallizes in the monoclinic space group $C2/c$ with cell constants a = 1331.8(3), b = 2392.5(4), c = 1263.1(2) pm, β = 93.75(2)° and Z = 4 (the complex possesses crystallographic twofold symmetry). The bond lengths Pt-P 221.7, Pt-Cl 232.6, P-F 155.9 pm all lie in the expected range for platinum fluorophosphine complexes.

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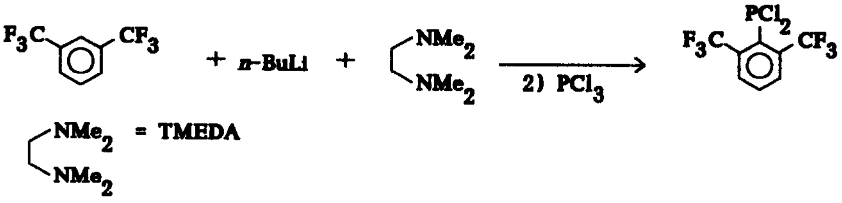
INTRODUCTION

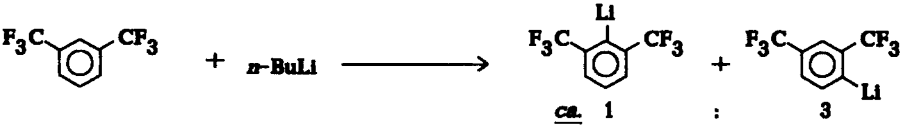
Aryllithium compounds yield aryldifluorophosphines on treatment with chlorodifluorophosphine [1]. For aromatic difluorophosphines bearing an *ortho*-CF_3-group, long-range coupling has been observed [1,2,3,4], for which through-space interactions of the PF_2- and the CF_3-group [2] have been suggested as the cause. Our interest focussed on the long-range couplings of fluorophosphines, and especially on $^4J(PF)$- and $^5J(FF)$-coupling constants.

RESULTS AND DISCUSSION

The following reaction, in which 2,6-bis(trifluoromethyl)phenyllithium is an intermediate, is described in the literature [3] :



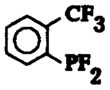
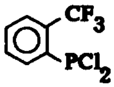
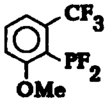
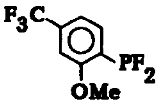
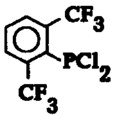
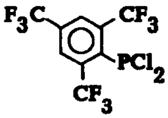
We found that the lithiation reaction without TMEDA yields a ca. 3 : 1 mixture of 2,4- and 2,6-bis(trifluoromethyl)phenyllithium, established by reaction with PF_2Cl.



Treatment of this mixture of isomers with PF_2Cl yields bis[2,4-bis(trifluoromethyl) phenyl]fluorophosphine, **1**, and 2,4-bis(trifluoromethyl)phenyl)-[2,6-bis(trifluoromethyl)phenyl] fluorophosphine, **2** in 38% total yield. The sterically less demanding compound, 2,4-bis(trifluoromethyl)phenyllithium, could react either twice with PF_2Cl or with the expected product, 2,6-bis(trifluoromethyl)phenyldifluorophosphine. The products 1 and 2 were of the same volatility and could not be separated by distillation. The ratio of 1 and 2 was found to be *ca.* 1 : 1 (^{19}F- and ^{31}P-NMR spectra). The ^{19}F- and ^{31}P-NMR data are presented and compared with those of other trifluoromethyl- substituted arylphosphines in Table 1.

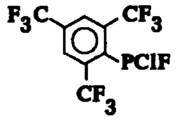
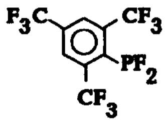
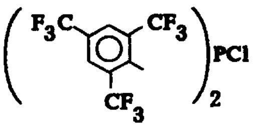
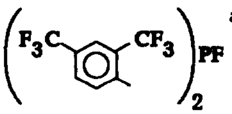
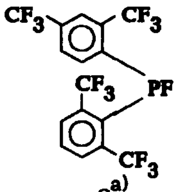
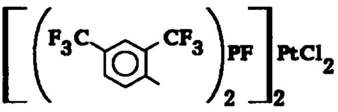
TABLE 1

^{19}F- and ^{31}P-NMR Data of Trifluoromethyl-substituted Arylphosphines

Compound	^{31}P-NMR			^{19}F-NMR		Reference
	δP [ppm]	^{1}J(PF) [Hz]	^{4}J(PF) [Hz]	^{5}J(FF) [Hz]	δF(PF) [ppm]	
	---	-1199	+68.3	+8.3	---	[2]
	---	---	85.2	---	---	[2]
	205.7	1199 (1193)	57 (58)	13	-95.9	[1]
	202.7	1190 (1186)	---	^{6}J(PF) 22	-100.1	[1]
	146.6	---	61.0	---	---	[3]
	144.4	---	61.0	---	---	[4]

(continued)

TABLE 1 (cont.)

Compound	**^{31}P-NMR**			**^{19}F-NMR**		**Reference**
	δP [ppm]	**^{1}J(PF) [Hz]**	**^{4}J(PF) [Hz]**	**^{5}J(FF) [Hz]**	**δF(PF) [ppm]**	
	184.9	1179.6	50.6	---	---	[4]
	187.7	1237.1	46.5	---	---	[4]
	74.2	---	42.0	---	---	[4]
 1	a) 145.0	~930	~64	~6	-190.0	
 2[a)]	a) 155.5	~990	~44	~6; ~21	-191.7	
 3	130.0	954 (957)[b)]	~20	---	-130.5	

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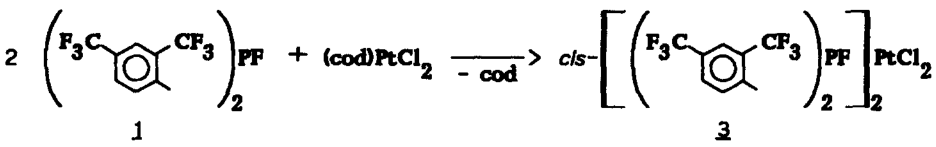
[a] All lines broad; coupling constants are approximate and were taken directly from the spectrum. [b] $|^1{+}^3J(PF)|$; all lines broad.

The reaction of the mixture of **1** and **2** with dichloro-(η^4-cyclooctadiene-1,5) platinum(II) led only to the formation of *cis*-dichloro-bis[bis(2,4-bis(trifluoromethyl)phenyl)-fluorophosphino]platinum(II), **3**.



This reaction was carried out with a ligand to (cod)PtCl$_2$ ratio of 2 : 1 and 4 : 1; in both cases 53% of **3** could be isolated (yield based on (cod)PtCl$_2$). We therefore believe that compound **2** also reacts with (cod)PtCl$_2$, but no mixed complex could be isolated and in the ^{19}F-NMR spectrum no product of this reaction could be identified.

A mass spectrum of **3** was observed at 30°C in spite of its high molecular weight of 1218 g/mole. For all signals in the mass spectrum of **3** a good agreement of the isotopic distribution was found for the calculated and the observed peaks. The molecular peak of **3** is shown in Fig. 1.

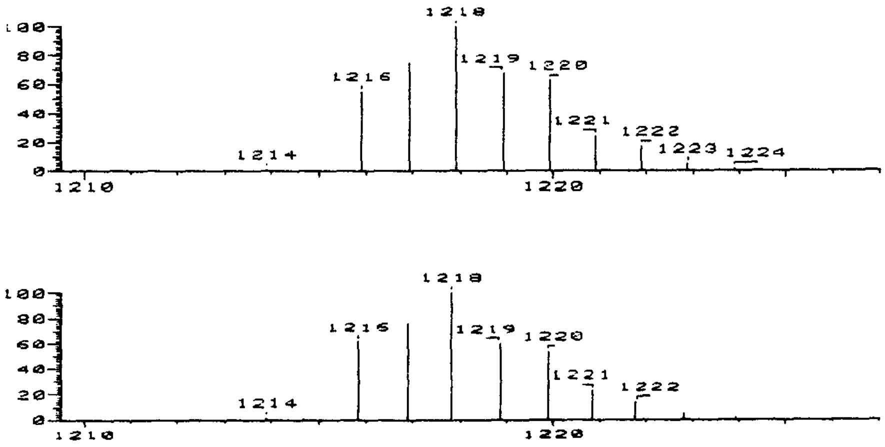
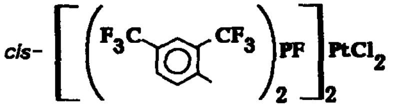


Fig. 1. Molecular peak in the mass spectrum of **3**; observed (below), calculated (above).

The structure of compound 3



3

was confirmed by an X-ray investigation. The conformation is *cis* and the coordination geometry is square planar. The molecule (Fig. 2) possesses crystallographic twofold symmetry (the Pt-atom lies on the axis 1/2, *y*, 3/4).

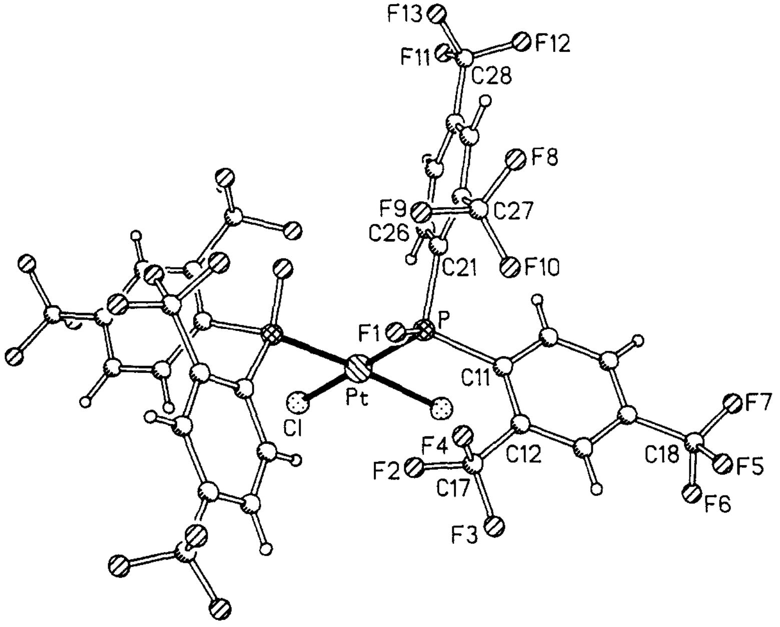
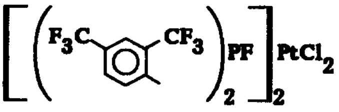


Fig. 2. The molecule of complex 3 in the crystal, showing the numbering of the asymmetric unit. Radii are arbitrary. Selected bond lengths [pm] and angles [°]: Pt-P 221.7(1), Pt-Cl 232.6(1), P-F(1) 155.9(2), P-C(11) 181.9(3), P-C(21) 181.6(3), P-Pt-Cl 176.3(1), P-Pt-P(I) 92.9(1), Cl-Pt-P(I) 89.4(1), Cl-Pt-Cl(I) 88.5(1), Pt-P-F(1) 112.2(1), Pt-P-C(11) 118.0(1), Pt-P-C(21) 105.2(1), F(1)-P-C(11) 104.5(1), F(1)-P-C(21) 103.6(1), C(11)-P-C(21) 105.2(1). Symmetry operator (I) : 1 - *x*, *y*, 1.5 - *z*.

The bond lengths Pt-P 221.7(1), Pt-Cl 232.6(1), P-F 155.9(2) pm all lie in the expected range for platinum fluorophosphine complexes [5]. The bond lengths P-C and P-F are shorter than in the square planar complex *trans*-(*tert*-$Bu_2PF)_2NiBr_2$ [6] (see Table 2). This may be due to the difference in electronegativity of the organic group and the metal centre and also because **3** is *cis*.

TABLE 2

Bond Lengths [pm] and Angles [°] in Monofluorophosphines and their Complexes

	r(P-C)	r(P-F)	r(P-M)	<(C-P-F)
tert-Bu_2PF	185.9(6)	161.9(7)	---	96.0(2)
Lit. [9]				
trans-(*tert*-$Bu_2PF)_2NiBr_2$	186(1)	157.9(7)	223.2(3)	97.3(5)
Lit. [6]	188(1)			97.9(5)
cis-  **3**	181.9(3) 181.6(3)	155.9(2)	221.7(1)	104.5(1) 103.6(1)

In reference [2] the strong long-range couplings $^4J(PF)$ and $^5J(FF)$ (see Table 1) were attributed to through-space interactions between the lone pair of phosphorus and the CF_3-group. In the case of two CF_3-groups *ortho* to phosphorus these couplings were smaller (see Table 1), and significantly smaller for **3**. We agree with the view expressed in reference [2] that lone-pair interactions are the main factor for the long-range couplings, because the lone pair is unavailable in **3** and cannot interact in the same way with two *ortho*-CF_3-groups in the 2,6-disubstituted derivatives as with one *ortho*-CF_3-group. The through-space interactions are therefore not solely a consequence of the relatively short non-bonded distances FP---CF_3, as observed in **3** (P---C(17) 330 pm; P---C(27) 335 pm).

EXPERIMENTAL

All experiments described were conducted with careful exclusion of air and moisture. Solvents were dried using standard procedures. *Cis*-dichloro(η^4-cyclooctadiene-1,5)platinum(II) [(cod)PtCl$_2$] [7] and chlorodifluorophosphine [8] were prepared by literature methods. The NMR spectra were recorded on BRUKER AC-200 and BRUKER AC-400 spectrometers, employing the following standards and conditions: ^{1}H (200.1 MHz, CDCl$_3$, TMS internal), ^{19}F (188.3 MHz, CDCl$_3$, CFCl$_3$ external), ^{31}P (81.0 MHz, CDCl$_3$, H$_3$PO$_4$ external). Low field shifts were allocated positive signs. The mass spectra were recorded on a FINNIGAN MAT 8430 instrument under EI conditions.

Preparation of bis[2,4-bis(trifluoromethyl)phenyl]fluorophosphine, 1, and 2,4-bis(trifluoromethyl)phenyl-[2,6-bis(trifluoromethyl)phenyl]fluorophosphine, 2

This preparation was conducted by analogy to the literature method [1]. A solution of 1,3-bis(trifluoromethyl)benzene (40 g; 0.187 mol) in 100 ml ether was treated with *n*-butyllithium (12.0 g; 0.187 mol as a 1.6 molar solution in hexane) in a 500 ml heavy-wall glass tube, fitted with a TEFLON® stopcock. The mixture was held at 60°C for 20 h and PF$_2$Cl (21.0 g; 0.201 mol) was then condensed onto the mixture at −196°C. The tube was resealed, and its contents were allowed to warm up to 23°C over 15 min. Lithium chloride and fluoride were removed by filtration and the residue was distilled *in vacuo* (98-101°C/0.6 mm). Double distillation at 98-99°C/0.2 mm yielded 17.1 g (38%) of 1 and 2 as a *ca.* 1 : 1 mixture.

$C_{16}H_6F_{13}P$	(476.2)	found:	C 41.0	H 1.7	P 6.6
		calc.:	C 40.4	H 1.3	P 6.5

^{1}H-NMR spectrum: δH 8.11 ppm (d, J 8 Hz; 2H); 8.03 ppm (s; 3H); 7.88 ppm (m; 3H); 7.67 ppm (m; 3H); 7.14 ppm (d, J 8 Hz; 1H).

^{19}F-NMR spectrum: 1: δF(*para*-CF$_3$) −63.8 ppm (s; 6F); δF(*ortho*-CF$_3$) −57.5 ppm (dd, ^{4}J(PF) 64 Hz, ^{5}J(FF) ~ 6 Hz; 6F); δF(PF) −190.0 ppm (d of septets, ^{1}J(PF) ~930 Hz, ^{5}J(FF) ~6Hz;

1F); 2: δF(*para*-CF_3) -63.4 ppm (s; 3F); δF(*ortho*-CF_3) -56.0 ppm (broad; 6F); -59.2 ppm (dd, $^4J(PF)$ ~44 Hz, $^5J(FF)$ ~ 7 Hz; 3F); δF(PF) -191.7 ppm (dm, $^1J(PF)$ ~990 Hz, $^5J(FF)$ ≈ 6 Hz (approximately a quartet) and 21 Hz (approximately a septet); 1F). All signals were broad. Mass spectrum (30°C): $M^{\rceil +}$ 476 (98%); $M\text{-}F^{\rceil +}$ 457 (30); $M\text{-}CF_3^{\rceil +}$ 407 (base peak); $M\text{-}F\text{-}2CF_3^{\rceil +}$ 319 (64%). No other peak above 20% relative intensity was observed.

Preparation of *cis*-dichloro-bis[bis(2,4-bis(trifluoromethyl)phenyl)fluorophosphino]platinum(II), 3

A solution of (cod)$PtCl_2$ (1.0 g; 2.76 mmol) in 50 ml dichloromethane was mixed with a solution of 1 and 2 (2.55 g; 5.53 mmol) in 10 ml dichloromethane. After standing for 4 h, half the solvent was removed *in vacuo* and 10 ml of ether were added. The white precipitate formed was filtered. Five weeks later a second batch of crystals was isolated from the mother liquor. Yield: 1.73 g (53%).

In a second preparation ether vapour was allowed to diffuse into a mixture of (cod)$PtCl_2$ (0.5 g; 1.34 mmol) and 1 and 2 (2.5 g; 5.25 mmol) in 70 ml dichloromethane for six weeks. A few crystals were obtained, one of which was used for the X-ray crystal structure determination. The main batch was obtained by concentrating the solution to 10 ml and adding 60 ml of ether. This mixture was stirred overnight. Yield: 0.87 g (53 %); Fp. >280°C (dec.).

$C_{32}H_{12}Cl_2F_{26}P_2Pt$ (1218.34) found: C 32.2 H 1.2 P 5.3

calc.: C 31.5 H 1.0 P 5.1

^{1}H-NMR spectrum: δH 8.14 ppm (broad; 2H); 7.98 ppm (very broad, 1H).

^{19}F-NMR spectrum: δF(*ortho*-CF_3) -58.5 ppm (broad,d, $^4J(PF)$ ≈ 20 Hz; 12F); δF(*para*-CF_3) -64.2 ppm (s; 12F); δF(PF) -130.5 ppm (broad,d, $^{|1+3|}J(PF)$ ≈ 957 Hz, $^2J(PtF)$ ≈ 410 Hz).

^{31}P-NMR spectrum: δP 130.0 ppm (broad, d, $^{|1+3|}J(PF)$ ≈ 954 Hz, $^1J(PtP)$ 4468 Hz) (width at half height ≈ 40 Hz).

Mass spectrum (120°C): $M^{\rceil +}$ 1218 (12%); $M\text{-}F^{\rceil +}$ 1199 (4%); $M\text{-}HCl^{\rceil +}$ 1182 (14%);

M-2HCl$^{\rceil+}$ 1146 (24%); M-2HCl-L$^{\rceil+}$ 670 (17%); M-2HCl-CF$_4$-L$^{\rceil+}$ 582 (20%); L+Cl$^{\rceil+}$ 511 (42%); L$^{\rceil+}$ 476 (36%); L-CF$_3$$^{\rceil+}$ 407 (70); L-2CF$_3$-H$^{\rceil+}$ 337 (42%); L-2CF$_3$-F$^{\rceil+}$ 319 (base peak); $C_7H_3F_3P^{\rceil+}$ 175 (66%). No other peak above 30% relative intensity was observed.

Crystal Structure Analysis of 3

Crystal Data : $C_{32}H_{12}Cl_2F_{26}P_2Pt$, M = 1218.4. Monoclinic, space group $C2/c$, a = 1331.8(3), b = 2392.5(4), c = 1263.1(2) pm, β = 93.75(2)°, V = 4.016 nm^3, Z = 4, D_x = 2.01 Mg m^{-3}, $F(000)$ = 2728, λ(Mo $K\alpha$) = 71.069 pm, μ = 4.3 mm^{-1}.

Data Collection and Reduction : A colourless prism *ca.* 0.4 x 0.3 x 0.25 mm was mounted parallel to $01\bar{1}$ in a glass capillary. 6440 profile-fitted intensities [10] were measured on a Stoe-Siemens four-circle diffractometer using monochromated Mo $K\alpha$ radiation ($2\theta_{max}$ 55°). Averaging equivalents gave 4598 independent reflections (R_{int} 0.011), of which 4165 with $F > 4\sigma(F)$ were used for all calculations (program system SHELX-76, modified by its author Prof. G.M.Sheldrick). An absorption correction based on ψ-scans gave transmission factors 0.72-0.86. Cell constants were refined from 2θ values of 32 reflections in the range 20-22°.

Structure Solution and Refinement : The structure was solved with the heavy-atom method and refined anisotropically to R 0.027, R_w 0.026. H-atoms were included using a riding model. Weighting scheme $w^{-1} = \sigma^2(F) + 0.0001 F^2$; 285 parameters; S 1.7; max. Δ/σ 0.025; max $\Delta\rho$ 0.4 x 10^{-6} e pm^{-3}.

Final atomic coordinates are given in Table 3; selected bond lengths and angles are given in the caption to Fig. 2. Further crystallographic details (complete bond lengths and angles, H atom coordinates, temperature factors, structure factors) have been deposited at the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, Fed. Rep. of Germany; they may be ordered on quoting a full literature citation and the reference number CSD 53693.

TABLE 3

Atomic Coordinates (x 10^4) and Equivalent Isotropic Thermal Parameters ($pm^2 x10^{-1}$)*

	x	y	z	U(eq)
Pt	5000	5573.4(1)	7500	42(1)
P	5631.3(5)	6211.8(4)	6458.6(6)	45(1)
Cl	4287.4(7)	4877.2(4)	8495.0(7)	63(1)
F(1)	5996(1)	6744(1)	7086(1)	60(1)
C(11)	6693(2)	6015(1)	5704(2)	50(1)
C(12)	7706(2)	5998(2)	6084(3)	56(1)
C(13)	8425(3)	5817(2)	5424(3)	72(1)
C(14)	8153(3)	5640(2)	4401(3)	76(1)
C(15)	7168(3)	5641(2)	4033(3)	72(1)
C(16)	6447(2)	5829(2)	4679(3)	61(1)
C(17)	8059(3)	6176(2)	7173(3)	78(2)
F(2)	7468(2)	6005(1)	7909(2)	99(1)
F(3)	8981(2)	6006(2)	7455(2)	118(1)
F(4)	8086(2)	6737(2)	7264(2)	116(1)
C(18)	8955(4)	5439(3)	3713(5)	116(3)
F(5)	9743(3)	5757(3)	3780(4)	219(3)
F(6)	9281(3)	4935(2)	4021(3)	180(2)
F(7)	8635(3)	5371(2)	2716(3)	152(2)
C(21)	4689(2)	6479(1)	5483(2)	47(1)
C(22)	4709(3)	6995(2)	4930(3)	64(1)
C(23)	3917(3)	7119(2)	4215(3)	78(2)
C(24)	3108(3)	6758(2)	4030(3)	69(1)
C(25)	3091(2)	6258(2)	4542(3)	59(1)
C(26)	3875(2)	6125(1)	5274(2)	50(1)
C(27)	5533(4)	7414(2)	5092(5)	98(2)
F(8)	5516(3)	7787(2)	4333(3)	172(2)
F(9)	5443(3)	7707(1)	6003(3)	132(2)
F(10)	6441(2)	7198(1)	5191(2)	104(1)
C(28)	2270(4)	6923(3)	3236(5)	107(2)
F(11)	1519(3)	6584(2)	3223(4)	215(3)
F(12)	2558(3)	6952(2)	2283(3)	189(3)
F(13)	1918(3)	7424(2)	3431(3)	136(2)

* equivalent isotropic U calculated as a third of the trace of the orthogonal U_{ij} tensor.

ACKNOWLEDGEMENTS

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