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Synthesis and Reactions of Trifluorovinylferrocene

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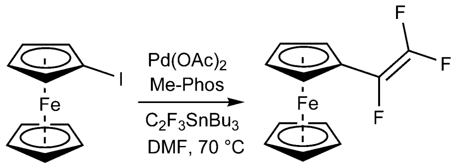
Trifluorovinylferrocene (**1**) is obtained in high yield by a Stille coupling of iodoferrocene with tributyltrifluorovinylstannane. [2+2] Cycloaddition of **1** yields the cyclobutane derivatives **2a** and **2b** under mild conditions. At higher temperature a defluoration reaction takes place yielding the cyclobutane derivative **3** under inert conditions whereas in the presence of air and water the cyclobuta-1,2-dion derivative **4** is formed presumably by an unusual hydrolysis of an aliphatic difluoromethylene group. Nucleophilic attack of the CF_2 group of **1** yields specifically the *trans* isomer of 1,2-Diferrocenyl-1,2-difluoroethene **5**. The crystal and molecular structures of **1**, **2a**, **2b**, **3** and **5** were elucidated by X-ray diffraction.

Introduction

Ferrocene, discovered 1951,[1] as redox-active species remains today one of the most important and extensively studied organometallic compounds. Thousands of ferrocene derivatives with widely varying uses have been created so far.[2] Trifluoromethyl-[3–5], and perfluoropropenylferrocenes[6] are the only ones that contain perfluorinated side chains. Ferrocene derivatives with perfluorinated unsaturated side chains are potentially useful precursors for the synthesis of fluoro-carbon polymers, containing redox-active ferrocenyl units. Furthermore, the trifluorovinyl group can be used as a versatile synthetic functional group for [2+2] cycloaddition reactions[7] or nucleophilic attack at the CF_2 unit.[8]

Results and Discussion

Herein we report on the synthesis and some reactions of trifluorovinylferrocene (**1**), demonstrating its usability as a versatile reagent. The ferrocene derivative **1** was synthesized by Stille coupling[9] of iodoferrocene and tributyltrifluorovinylstannane in dimethylformamide, using palladium(II) acetate and the Buchwald phosphane Me-Phos[10] as catalyst (Scheme 1).



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Scheme 1. Synthesis of trifluorovinylferrocene.

Compound **1** is a red-brown oil with a melting point of 4 °C. Single crystals can be grown directly from the melt by cooling to –35 °C (Figure 1). The trifluorovinyl unit is twisted 17.2° out of the plane of the cyclopentadienyl ring. The two cyclopentadienyl rings are in an almost eclipsed position (5.6°).

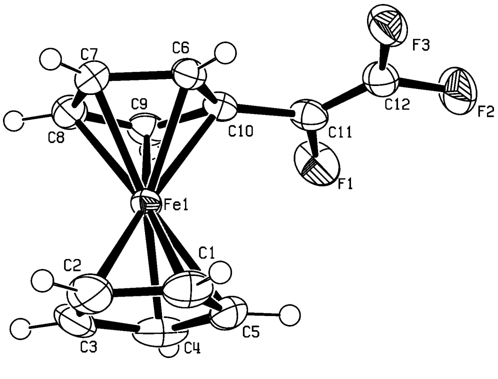

Figure 1. Molecular structure of trifluorovinylferrocene, thermal ellipsoids, probability 50 %.[13]

Like other fluoro alkenes,[11] **1** tends to dimerize on heating without solvent under inert conditions at moderate temperatures (Scheme 2). The *trans*-isomer **2a** and the *cis*-isomer **2b** are formed in equal amounts. The process of dimerization is likely biradical, as recently proven by EPR spectroscopy for the cyclopolymerization of aromatic trifluorovinyl ethers.[12] Both isomers do not show remarkable differences in polarities and solubilities, therefore column chromatographic separation and fractional crystallization are inadequate for obtaining the pure isomers.

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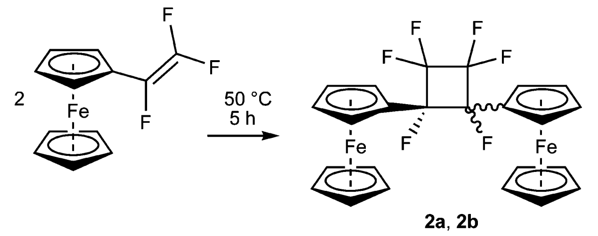


Scheme 2. Formation of trifluorovinylferrocene dimers (*cis*- and *trans*-isomer) by [2+2] cycloaddition.

As the *cis*-isomer crystallizes in form of orange plates (Figure 2), whereas the *trans*-isomer (Figure 3) crystallizes as orange needles, the two isomers can be separated mechanically under a microscope. The 3,4-diferrocenyl-1,1,2,2,3,4-hexafluorocyclobutane rings are puckered in both cases (torsion angle for **2a**: 15.1°). Deviations from the eclipsed position of the cyclopentadienyl ligands are 1.1°/0.8° and angles of the centers of the cp-ligands with the iron atoms are 178.6/177.9 for **2a**.

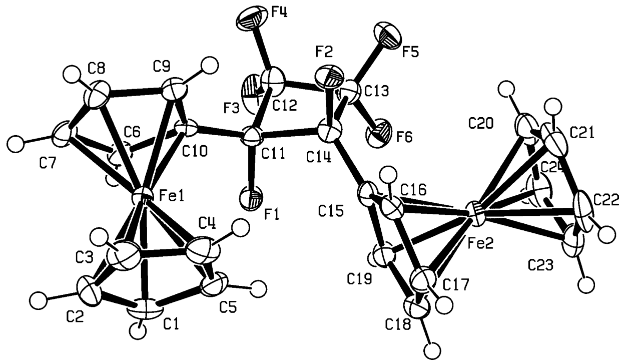


Figure 2. Molecular structure of the *trans*-isomer (**2a**), thermal ellipsoids, probability 50 %.[13]

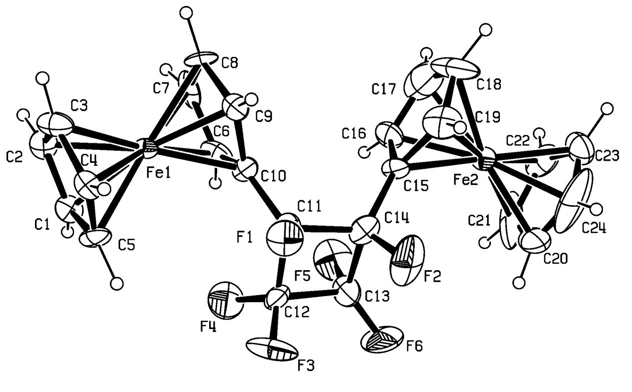
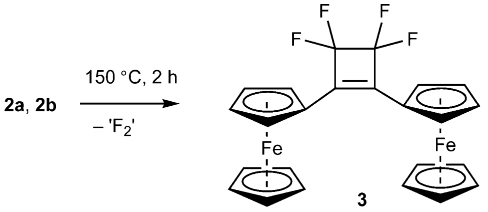


Figure 3. Molecular structure of the *cis*-isomer **2b** (thermal ellipsoids, probability 30 %).[13]

The carbon–fluorine bonds C11–F1 and C14–F2 are strikingly long with 1.397(8) Å/1.397(7) Å (for **2a**). On heating of **2a**/**2b** at 150 °C under inert atmosphere a reaction takes place. Both isomers suffer a *formal* elimination of fluorine which leads to the cyclobutene derivative **3** (Scheme 3). Comparable defluoration reactions of perfluorinated alkanes were reported to take place only in the presence of auxiliary substances.[14–16]



Scheme 3. Formation of the cyclobutene derivative **3**.

Ruby-red single crystals of **3** were grown from a solution in pentane/dichloromethane (Figure 4). Compound **3** exhibits an almost planar cyclobutene ring with a torsion angle of 0.8°. Again, the cyclopentadienyl ligands are in an almost eclipsed position (2.2°/3.9°).

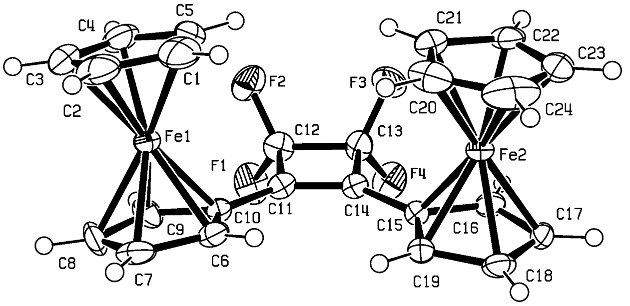
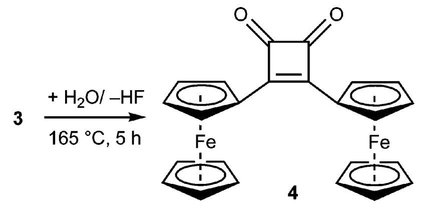


Figure 4. Molecular structure of the cyclobutene **3**, thermal ellipsoids, probability 50 %.[13]

Heating of **1**, **2a**/**2b** and **3** *without* inert conditions to 165 °C results in a quantitative conversion to 3,4-diferrocenylcyclobut-3-ene-1,2-dione (**4**) (Scheme 4). The latter is formed presumably through hydrolysis of an aliphatic difluoromethylene group and elimination of HF, a very unusual reaction.[17] Zora and co-workers synthesized **4** previously from squaric dichloride and ferrocene, using either a Friedel–Crafts alkylation or a palladium-catalyzed coupling reaction with yields of 15 % and 19 %,[18] compared to 76 % from **3**.



Scheme 4. Hydrolysis: formation of **4**.

Compound **1** exhibits an excellent reactivity towards nucleophiles. Treatment of **1** with lithioferrocene gives *trans*-1,2-diferrocenyl-1,2-difluoroethene in good yields. Ruby-red single crystals of **5** were obtained from dichloromethane (Figure 5). Presumably, the reaction proceeds via an addition-elimination mechanism (Scheme 5).

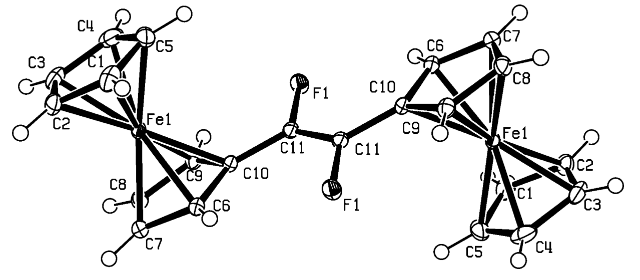
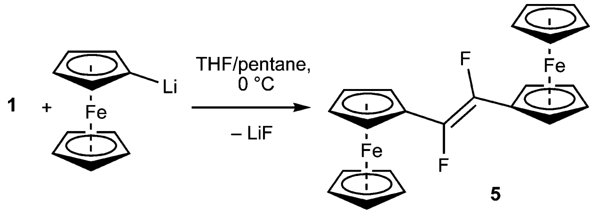


Figure 5. Molecular structure of **5**, thermal ellipsoids, probability 50%.[13]



Scheme 5. Nucleophilic attack on the CF_2-unit: formation of **5**.

Electrochemical studies involving cyclic voltammetry are exhibiting a good reversibility for the redox processes of the iron centers (Fe^{2+}/Fe^{3+}) for **1** and **5**. Potentials of +65 mV for the one process in **1** (Fe^{2+}/Fe^{3+}) and +59 mV ($Fe^{2+},Fe^{2+}/Fe^{2+},Fe^{3+}$) and +263 mV ($Fe^{2+},Fe^{3+}/Fe^{3+},Fe^{3+}$) for the two processes of **5** were estimated (vs. ferrocene/ferrocenium).

Conclusions

In summary, the trifluorovinyl group of **1** functionalizes ferrocene in a special manner, opening the door to a versatile ferrocene based building block chemistry.

Experimental Section

1: 1000 mg (3.2 mmol) of iodoferrocene, 1300 mg (3.5 mmol) of tributyltrifluorovinylstannane, 11 mg (0.048 mmol) of palladium(II) acetate and 88 mg (0.240 mmol) of Me-Phos (2-di-*tert*-butylphosphanyl-2′-methylbiphenyl) were dissolved in 50 mL of dimethylformamide and heated in a Schlenk tube under inert conditions for 12 h to 70 °C. Dichloromethane and brine were added to the black mixture. Extraction for several times and drying of the organic phase over anhydrous magnesium sulfate led to a dark brown oil as crude product. Column chromatographic purification on silica gel with pentane as eluent afforded 540 mg (2.0 mmol, 63%) of a red-brown oil in the first fraction; m.p. 4 °C. ^1H NMR (399.65 MHz, $CDCl_3$, TMS): δ = 4.20 (s, 5 H, cp), 4.29, 4.42 (AA′BB′, 4 H, subst. cp) ppm. $^{13}C\{^1H, ^{19}F\}$ NMR NMR (100.40 MHz, $CDCl_3$, TMS): δ = 65.7 (s, 2 C, subst. cp), 69.0 (s, 2 C, subst. cp), 69.5 (s, 5 C, unsubst. cp), 72.2 (s, 1 C, *ipso*-C), 128.3 (s, 1 C, C_2F_3), 151.6 (s, 1 C, C_2F_3) ppm. ^{19}F NMR (376.00 MHz, $CDCl_3$, $CFCl_3$): δ = –172.5 [dd, ^2J(F-F) = 30, ^3J(F-F) = 111 Hz], –118.5 [dd, ^3J(F-F) = 80, ^3J(F-F) = 111 Hz], –101.0 [dd, ^2J(F-F) = 30, ^3J(F-F) = 80 Hz] ppm. IR: $\tilde{\nu}$ = 544 (w), 568 (w), 662 (w), 734 (w), 814 (s), 871 (s), 922 (m), 1028 (m), 1064 (s), 1107 (w), 1145 (s), 1219 (w), 1278 (s), 1311 (w), 1384 (w), 1412 (w), 1480 (w), 1771 (s), 2855 (w), 2926 (w), 2959 (w), 3098 (w) cm^{-1}. Raman: $\tilde{\nu}$ = 307 (s), 362 (m), 400 (m), 646 (w), 661 (m), 873 (w), 922, 1065 (m), 1107 (s), 1149 (w), 1282 (w), 1384 (w), 1412 (w), 1480 (m), 1772 (m), 3112 (s) cm^{-1}. MS (80 eV/EI): *m*/*z* (%) = 266 (100) [M^+]. MS (high resolution): calculated: 266.00076; found 266.00058.

2a, 2b: 200 mg (0.75 mmol) of **1** was heated under inert conditions for 5 h at 50 °C. The resulting product mixture was dissolved in dichloromethane and filtered through silica gel. Evaporation of the solvent afforded 164 mg (0.62 mmol) of an equimolar mixture of the *cis*- and the *trans*-isomer. Orange crystals were obtained via recrystallization from pentane at 4 °C. Both isomers were mechanically separated by using a microscope (combined yield 164 mg, 82%). $C_{24}H_{18}F_6Fe_2$ (532.09): calcd. C 54.18, H 3.41; found C 53.93, H 3.25.

2a: M.p. 136 °C. ^1H NMR (399.65 MHz, $CDCl_3$, TMS): δ = 4.19 (s, 10 H, cp), 4.24, 4.26, 4.32, 4.46 (ABCD, 8 H, subst. cp) ppm. ^{19}F NMR (376.00 MHz, $CDCl_3$, $CFCl_3$): δ = –164.52 (s, 2 F), –129.58 (d, J = 227 Hz, 2 F), –125.67 (d, J = 227 Hz, 2 F) ppm. IR: $\tilde{\nu}$ = 538 (w), 546 (w), 565 (m), 577 (m), 591 (w), 619 (w), 648 (m), 783 (s), 810 (s), 821 (s), 837 (m), 848 (m), 856 (w), 870 (m), 891 (w), 897 (w), 912 (m), 999 (m), 1019 (s), 1026 (m), 1032 (m), 1039 (m), 1054 (w), 1076 (m), 1106 (m), 1128 (m), 1158 (m), 1174 (s), 1204 (w), 1224 (w), 1242 (w), 1261 (m), 1283 (w), 1301 (w), 1339 (w), 1357 (w), 1367 (m), 1379 (w), 1393 (w), 1409 (w), 1471 (w), 1650 (w), 1680 (w), 1714 (w), 1744 (w), 1768 (w), 1788 (w), 2254 (w), 2462 (w), 2928 (w), 3093 (w), 3103 (w), 3126 (w), 3138 (w), 3935 (w) cm^{-1}. MS (80 eV/EI): *m*/*z* (%) = 532 (100) [M^+], 392 (42) [$M^+ – C_5H_5FFe$], 266 (85) [$M^+ – C_{12}H_9F_3Fe$]. MS (high resolution): calculated: 532.00116; found 531.99960.

2b: M.p. 206 °C. ^1H NMR (399.65 MHz, $CDCl_3$, TMS): δ = 3.89, 4.04, 4.05, 4.13 (ABCD, 8 H, subst. cp); 4.14 (s, 10 H, cp) ppm. ^{19}F NMR (376.00 MHz, $CDCl_3$, $CFCl_3$): δ = –167.23 (s, 2 F), –129.72 (d, J = 228 Hz, 2 F), –125.38 (d, J = 227 Hz, 2 F) ppm. IR: $\tilde{\nu}$ = 529 (w), 551 (w), 564 (w), 571 (w), 578 (w), 591 (w), 608 (w), 619 (w), 649 (w), 785 (m), 796 (s), 814 (s), 824 (w), 848 (w), 866 (w), 902 (w), 909 (w), 949 (w), 1002 (m), 1014 (m), 1020 (m), 1037 (w), 1071 (w), 1086 (w), 1106 (w), 1140 (w), 1168 (m), 1183 (m), 1229 (w), 1264 (w), 1303 (w), 1332 (w), 1356 (w), 1367 (w), 1384 (w), 1395 (w), 1411 (w), 1465 (w), 1479 (w), 1646 (w), 1779 (w), 3094 (w), 3935 (w) cm^{-1}. MS (80 eV/EI): *m*/*z* (%) = 532 (100) [M^+], 392 (42) [$M^+ – C_5H_5FFe$], 266 (85) [$M^+ – C_{12}H_9F_3Fe$]. MS (high resolution): calculated: 532.00116; found 531.99960.

3: 200 mg (0.75 mmol) of **1** was heated under inert conditions for two hours at 150 °C. The resulting product mixture was dissolved in dichloromethane and purified by column chromatography on silica gel, using pentane as eluent. **3** exhibits a dramatically lower R_f value than remaining **1** and **2a**/**2b**, therefore the separation is fast and efficient. Recrystallization from a mixture of pentane and dichloromethane (4:1) afforded 117 mg (0.47 mmol, 63%) of the title compound as ruby-red crystals. $C_{24}H_{18}F_4Fe_2$ (494.09): calcd. C 58.34, H 3.67; found C 58.24, H 4.62; m.p. 148 °C. ^1H NMR (399.65 MHz, $CDCl_3$, TMS): δ = 4.19 (s, 10 H, cp), 4.45, 4.67 (AA′BB′, 8 H, subst. cp) ppm. $^{13}C\{^1H, ^{19}F\}$ NMR (100.40 MHz, $CDCl_3$, TMS): δ = 60.4 (s), 68.6 (s), 69.7 (s), 70.2 (s), 70.9 (s) ppm. ^{19}F NMR (376.00 MHz, $CDCl_3$, $CFCl_3$): δ = –114.30 (s, 4 F) ppm. IR: $\tilde{\nu}$ = 532 (w), 546 (w), 573 (w), 588 (w), 616 (w), 659 (w), 701 (w), 729 (m), 756 (m), 791 (s), 813 (s), 827 (m), 861 (w), 868 (w), 892 (w), 902 (w), 915 (w), 1002 (m), 1017 (m), 1028 (m), 1043 (m), 1053 (m), 1074 (s), 1106 (m), 1149 (m), 1191 (m), 1243 (m), 1260 (m), 1292 (m), 1304 (m), 1338 (m), 1346 (w), 1355 (w), 1410 (w), 1432 (w), 1465 (w), 1496 (m), 1504 (m), 1654 (w), 2852 (w), 2922 (w), 2958 (w), 3089 (w) cm^{-1}. MS (80 eV/EI): *m*/*z* (%) = 494 (100)

$[M^+]$. MS (high resolution): calculated: 494.00433; found 494.00108.

4: 55 mg (0.11 mmol) of **3** was heated in an open Schlenk tube to 165 °C for 5 h. The black product mixture was dissolved in dichloromethane and filtered through silica gel. Compound **4** exhibits a dramatically low R_f value, in contrast to remaining **3**. Recrystallization afforded 38 mg (0.08 mmol, 76%) of small black-violet crystals. ^{1}H NMR (399.65 MHz, $CDCl_3$, TMS): δ = 4.17 (s, 10 H, cp), 4.67, 5.09 (AA′BB′, 8 H, subst. cp) ppm. MS (80 eV/EI): m/z = 450 $[M^+]$, 394 $[M^+ - 2\ CO]$. IR: $\tilde{\nu}$ = 1752 (s), 1771 (s) cm^{-1}.

5: 350 mg (1.9 mmol) of ferrocene was dissolved in 40 mL of THF/pentane (1:1). Then 2.5 mL (3.8 mmol) of tertiary butyllithium (1.5 M in hexane) was added with rapid stirring slowly over one hour at 0 °C. Stirring was continued for an additional hour, then 500 mg (1.9 mmol) of **1** was added slowly over aperiod of 20 min. Hydrolysis was performed with the addition of 5 mL of aqueous sodium hydroxide solution (1 M). The solution was extracted with brine and ether, the organic layer was dried with magnesium sulfate. Column chromatographic purification on silica gel with pentane as eluent afforded **5** as third fraction. Red single crystals (623 mg, 76%) were obtained by crystallization from dichloromethane at 4 °C. $C_{22}H_{18}F_2Fe_2$ (432.08): calcd. C 61.16%, H 4.20%; found C 61.24%, H 4.16. ^{1}H NMR (399.65 MHz, $CDCl_3$, TMS): δ = 4.13 (s, 5 H, cp); 4.27, 4.57 (AA′BB′, 8 H, subst. cp) ppm. ^{19}F NMR (376.00 MHz, $CDCl_3$, $CFCl_3$): δ = –153.00 (s, 2 F) ppm. IR: $\tilde{\nu}$ = 590 (w), 647 (w), 687 (w), 731 (m), 791 (m), 810 (s), 820 (s), 834 (m), 860 (m), 873 (w), 886 (w), 889 (w), 934 (w), 972 (w), 1001 (m), 1028 (s), 1045 (m), 1065 (w), 1106 (m), 1126 (s), 1146 (w), 1222 (w), 1260 (m), 1274 (s), 1311 (w), 1334 (w), 1353 (w), 1367 (w), 1379 (m), 1390 (w), 1410 (m), 1466 (w), 1484 (w), 1588 (w), 1659 (w), 1732 (w), 1772 (w), 2856 (m), 2925 (s), 2956 (s), 3101 (m) cm^{-1}. MS (80 eV/EI): m/z (%) = 432 (100) $[M^+]$. MS (high resolution): calculated: 432.00754; found 432.00678.

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[13] Crystal structure determination (SMART-CCD, Bruker, structure solution: SHELXS-97,[18] direct methods, and least-squares refinement SHELXL-97,[19] molecular graphics: (ORTEP-3 for Windows®[20]): **1**: monoclinic, $P2_1/c$, a = 5.931(1) Å, b = 7.438(1) Å, c = 23.172(3) Å, β = 93.424(2)°, V = 1020.4(3) Å^3, Z = 4, ρ_{calcd} = 1.730 gcm^{-1}, T = 173(2) K, 12244 observed, 3118 independent (R_{int} = 0.027) and 2656 reflections with $I > 2\sigma(I)$, Mo$_{K\alpha}$, λ = 0.71069 Å, θ_{max} = 30.52°, R_1 = 0.035, wR_2 = 0.0626, 145 parameters, anisotropic thermal parameters, H atoms isotropic. **2a**: monoclinic, $P2_1/n$, a = 15.552(5) Å, b = 5.860(2) Å, c = 22.169(7) Å, β = 103.238(6)°, V = 1966.6(10) Å^3, Z = 4, ρ_{calcd} = 1.785 gcm^{-1}, T = 173(2) K, 16889 observed, 3475 independent (R_{int} = 0.052) and 2257 reflections with $I > 2\sigma(I)$, Mo$_{K\alpha}$, λ = 0.71073 Å, θ_{max} = 25.11°, R_1 = 0.089, wR_2 = 0.119, 289 parameters, anisotropic thermal parameters, H atoms isotropic. **2b**: triclinic, $P\bar{1}$, a = 11.257(5) Å, b = 11.259(5) Å, c = 16.139(8) Å, α = 101.294(11)°, β = 101.213(9)°, γ = 93.373(10)°, V = 1958(2) Å^3, Z = 4, ρ_{calcd} = 1.805 gcm^{-1}, T = 173(2) K, 17443 observed, 17433 independent (R_{int} = 0.096) and 10644 reflections with $I > 2\sigma(I)$, Mo$_{K\alpha}$, λ = 0.71073 Å, θ_{max} = 25.18°, R_1 = 0.151, wR_2 = 0.233, 578 parameters, anisotropic thermal parameters, H atoms isotropic. **3**: orthorhombic, $Pbca$, a = 15.605(4) Å, b = 12.151(3) Å, c = 20.273(6) Å, V = 3844.3(2) Å^3, Z = 8, ρ_{calcd} = 1.710 gcm^{-1}, T = 173(2) K, 44334 observed, 5859 independent (R_{int} = 0.066) and 3915 reflections with $I > 2\sigma(I)$, Mo$_{K\alpha}$, λ = 0.71073 Å, θ_{max} = 30.50°, R_1 = 0.036, wR_2 = 0.083, 271 parameters, anisotropic thermal parameters, H atoms isotropic. **5**: tetragonal, $P4_2/n$, a = b = 16.977(2) Å, c = 5.864(2) Å, V = 1690.0 (5) Å^3, Z = 4, ρ_{calcd} = 1.698 gcm^{-1}, T = 173(2) K, 38211 observed, 3180 independent (R_{int} = 0.024) and 2903 reflections with $I > 2\sigma(I)$, Mo$_{K\alpha}$, λ = 0.71073 Å, θ_{max} = 33.35°, R_1 = 0.027, wR_2 = 0.062, 118 parameters, anisotropic thermal parameters, H atoms isotropic. CCDC-695348 (for **1**), -695349 (for **2a**), -695350 (for **2b**), -695351 (for **3**), and -695352 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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