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Highly Ylidic Imidazoline-Based Fulvenes as Suitable Precursors for the Synthesis of Imidazolium-Substituted Metallocenes

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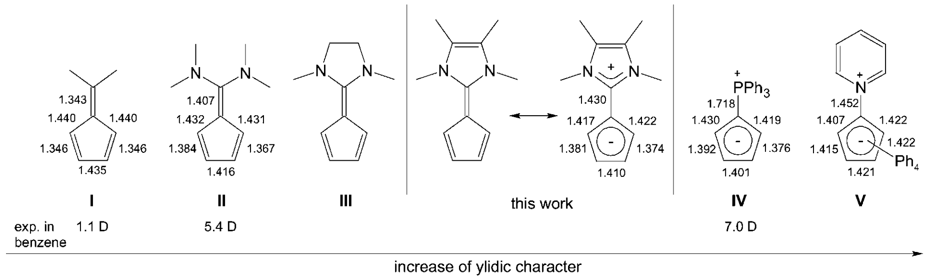

Figure 1. X-ray data and dipole moment (where available) show the increasing ylidic character of fulvenes **I**–**III**[4,5] and cyclopentadienylides **IV** and **V**.[6a,7]

Pentafulvenes are very useful precursors for the synthesis of functionalized metallocenes and half-sandwich complexes.[1] Owing to the electrophilic C6 carbon at the exocyclic double bond they can be easily transformed into the respective cyclopentadienides by reaction with nucleophiles, or alternatively by deprotonation of a C6 substituent (i.e. a methyl group) to receive the reactive cyclopentadienide and subsequent transmetallation to give the η^5-Cp complex. A third possibility is to first prepare a η^6-fulvene metal complex and react it further to the η^5-Cp complex. An ylidic structure is often drawn to describe fulvenes due to their enhanced polarity, even though the ylidic character is rather low.[1a,2] This is displayed by alternating single and double bond lengths that are typically found for fulvenes (Figure 1, type **I**). However, the polarity of fulvenes can be enhanced by electron-donating substituents at C6. Mueller-Westerhoff has shown that 6,6-bis(dimethylamino)-fulvene (**II**) can react with iron(II) chloride in refluxing tetrahydrofuran to give the respective ferrocenylformamidinium salts.[3] This behavior is mainly attributed to the strong dipolar character of 6,6-bis(dimethylamino)fulvene.

We were interested in metallocenes[8] that bear an imidazolium substituent attached via its C2 position to the Cp ring. Metallocenes of this type could exhibit interesting properties for applications in ionic liquids (ILs),[9] as the imidazolium unit is also found in the most common ILs. Reports of imidazolium salts attached to metallocenes at the C2 position are rare and the known examples mainly concern dangling imidazolium groups at an alkyl chain.[10]

We envisaged that attaching the imidazolium salt moiety directly to the Cp ligand would create products whose solubility properties are close to those of imidazolium-based ILs or that the complexes themselves would act as ionic liquids. To the best of our knowledge, apart from imidazolidinoxyl ferrocenes,[11] C2-imidazolium-substituted metallocenes have not been reported so far. For the synthesis of such complexes one could start from 1,1′-diimidazolylmetallocenes[12] with subsequent formation of the imidazolium salt by addition of alkyl halides (Scheme 1). However, this would require to start from 1,1′-metallocenedicarboxaldehydes,[13] compounds that are readily available only for Group 8 metals. In addition, only *N*′-alkylation would be possible starting from imidazolylferrocenes, whereas *N*′-arylation could not be achieved. All these aspects are strongly limiting and therefore we tried to develop a more general and modular approach. Employing the fulvene route developed by Mueller-Westerhoff could fulfil these demands, however the necessary fulvene was not known in literature, even though various other 6,6-diaminofulvenes including imidazolidinfulvene **III**[14] had been synthesized before (Figure 1).

We synthesized the desired fulvene **3a** by using a modified version of the route used by Meerwein and Hafner[14a,b] in which we avoided exposure of the reagents and products

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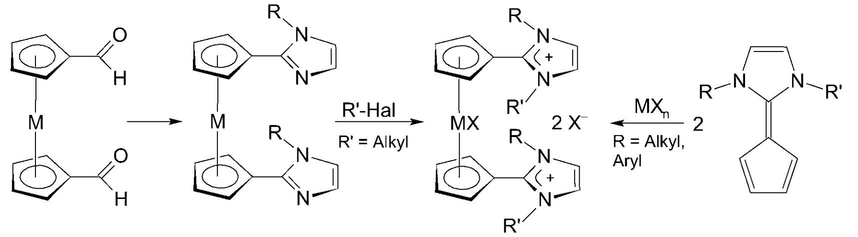
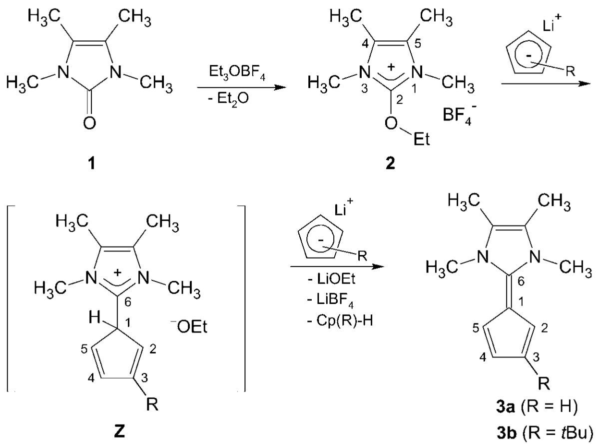


Scheme 1. Strategy for the synthesis of imidazolium salt substituted metallocenes from metallocene dicarbaldehydes and via fulvenes.

to air and moisture not only during the course of reaction but also during workup (Scheme 2): the so far unknown uronium salt **2**, prepared from the imidazolone **1**[15] by addition



Scheme 2. Synthesis of the imidazole-derived, highly dipolar fulvenes **3a** and **3b**.

of triethyloxonium tetrafluoroborate (Meerwein's reagent), was allowed to react with two equivalents of cyclopentadienyllithium (CpLi). According to the literature, nucleophilic attack of CpLi at the C2 of an uronium salt and subsequent elimination of ethanol should lead to the desired fulvene.[14a,b] In our case however, we propose the imidazolium salt **Z** as a rather stable intermediate, owing to the strong aromatic stabilization of the imidazolium moiety. Evidently, this intermediate is concurrently deprotonated by CpLi acting as a base. Therefore a second equivalent of CpLi is necessary to achieve complete conversion of the uronium salt **2** along with formation of one equivalent of cyclopentadiene. Attempts to use one equivalent of lithium diisopropylamide (LDA) and one equivalent of CpLi also resulted in complete conversion of the uronium salt **2**, however, the reaction turned out to be not as clean.

The formation of fulvene **3a** is observed in the ^{1}H NMR spectrum by the presence of two characteristic multiplets for the fulvene protons H2,5 ($\delta = 6.04$–6.06 ppm) and H3,4 ($\delta = 6.19$–6.21 ppm). In the ^{13}C NMR spectrum, the signals for C2,5 and C3,4 are detected at $\delta = 110.4$ and 111.2 ppm and are even more highfield shifted than those of the imidazolidine-derived fulvene **III** ($\delta = 113.4$ and 114.0 ppm).[14d,e] The signals of the quarternary carbon atoms are found at $\delta = 98.0$ (C1) and 148.3 (C6) ppm. According to Neuenschwander et al., the highfield chemical shift of C2,5 and C3,4 correlates with the Hammett σ_p^+ constant.[14e] By slow evaporation of a saturated solution of **3a** in tetrahydrofuran, we were able to obtain pale red single crystals.[16] The molecular structure of compound **3a** confirms the strong single-bond character with a C1–C6 bond length of 1.430(3) Å (Figure 2). To the best of our knowledge this is the longest bond found for an exocyclic C1–C6 bond of a fulvene to date.[17] The other bond lengths in the Cp ring display little alternating single- and double-bond character. This is in contrast to typical fulvenes of type **I** and to a less extent type **II** (Figure 1).[18] Comparing the bond lengths with those available in the literature, it becomes clear that our imidazoline-based fulvene **3a** holds a position that is close to that of the Ramirez ylide **IV**.[6] The fulvene is not planar, but the imidazole and Cp planes are twisted by 32.0°.

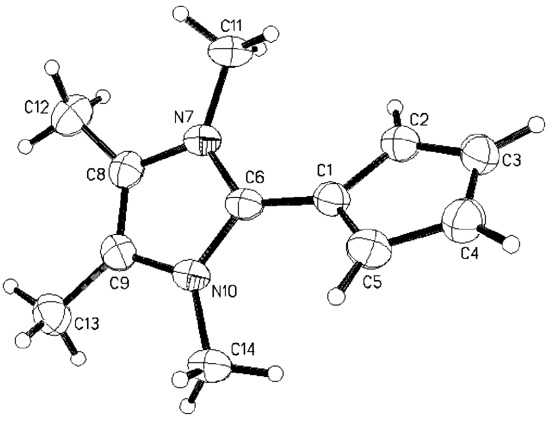
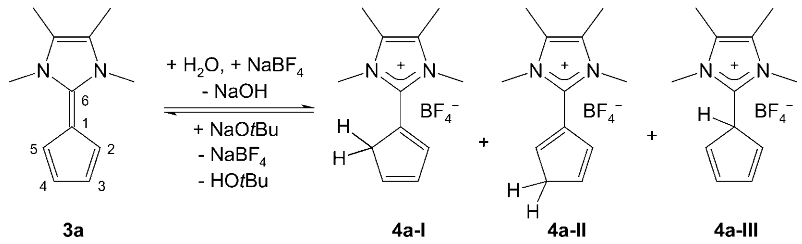


Figure 2. Molecular structure of the imidazole-derived fulvene **3a**. Selected bond lengths [Å] and angles [°]: C1–C2 1.422(3), C2–C3 1.374(3), C3–C4 1.410(3), C4–C5 1.381(3), C1–C5 1.417(3), C1–C6 1.430(3), C6–N7 1.351(2), N7–C8 1.391(3), C8–C9 1.349(3), C9–N10 1.396(3), C6–N10 1.359(2); C5-C1-C2 106.36(18), N7-C6-N10 105.68 (17), ∢ imi-Cp 32.0.

The special electronic structure, as already displayed by the geometric parameters, indicates a special reactivity of fulvene **3a** that is also found for the Ramirez ylide **IV**[6b,19] and pyridinium cyclopentadienides of type **V**.[20] In contrast to other 6,6-disubstituted fulvenes, compounds **3a** and **3b** turned out to be extremely sensitive towards air, but not towards moisture. An excess of 100 equivalents of D_2O in a solution of **3b** in [D$_8$]THF leads to H/D exchange of all fulvenic protons within 30 min.

However, **3a** reacts with water in the presence of salts such as $NaBF_4$ to give the cyclopentadiene-substituted imidazolium salt **4a** in the form of two out of three possible isomeric species in a 1:1 ratio (**4a-I** and **4a-II**; Scheme 3). Crystals of isomer **4a-I** were obtained from a concentrated solution of this mixture in tetrahydrofuran and characterized by X-ray diffraction analysis (Figure 3).[16] The C1–C6 single bond of 1.451(2) Å is only 0.02 Å longer than in fulvene **3a**, which confirms again the strong zwitterionic character of the fulvene. The imidazolium plane and the Cp plane form an angle of 43.8°.



Scheme 3. Facile hydrolysis of fulvene **3a** leading to the imidazolium salt substituted cyclopentadienes **4a-I** and **4a-II**.

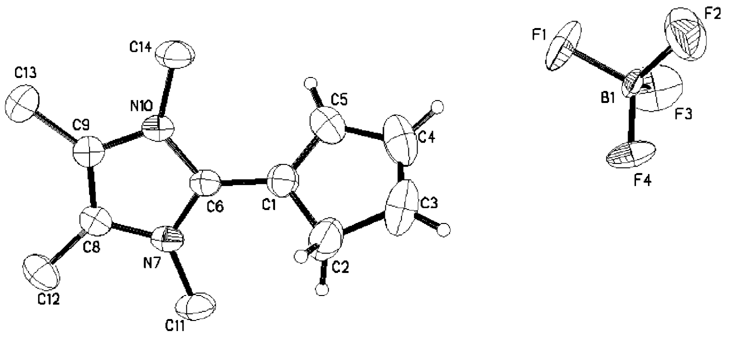


Figure 3. Molecular structure of the imidazolium-substituted cyclopentadiene **4a**. Selected bond lengths [Å] and angles [°]: C1–C2 1.481(2), C2–C3 1.479(3), C3–C4 1.349(4), C4–C5 1.434(3), C1–C5 1.364(2), C1–C6 1.451(2), C6–N7 1.342(2), N7–C8 1.379(2), C8–C9 1.353(2), C9–N10 1.385(2), C6–N10 1.344(2); C5-C1-C2 108.75(15), N7-C6-N10 106.9(11), C5-C1-C6-N10 42.3.

Fulvene **3a** can be reobtained from the protonated species **4a** by deprotonation with LDA. Leaving a sample of fulvene **3a** under nitrogen at room temperature leads to decomposition after several weeks. Therefore we tried to shield the bonds of the Cp ring sterically by introducing a *tert*-butyl substituent. Following the route shown in Scheme 2 we prepared fulvene **3b** that indeed shows a higher stability and can be purified by filtration under nitrogen over a short column of neutral alumoxane to give the product as pale yellow crystalline plates with a pearly shine in 59% yield. The spectroscopic data is similar to that of fulvene **3a**, with characteristic shifts for the C1 and C6 signals at $\delta = 96.1$ and 149.8 ppm. Single crystals suitable for structure analysis were obtained from a concentrated solution of fulvene **3b** in tetrahydrofuran, and the molecular structure is shown in Figure 4; however, the quality of the structure data is reduced due to disorder in the *tert*-butyl substituent. The C1–C6 "double" bond for fulvene **3b** is exceptionally long (1.436(7) Å). This underlines again the highly dipolar structure of the imidazoline-based fulvene. The imidazole and Cp planes are twisted by 23.8°.

Reacting the fulvenes **3a** and **3b** with one equivalent of iron(II) chloride[3] leads to the formation of the imidazolium-substituted 1,1′-ferrocenes **5a** and **5b** with $[FeCl_4]^{2-}$ as the counterion (Scheme 4). In contrast to the procedure employed by Mueller-Westerhoff using 6,6-bis(dimethylamino)fulvene **II**, our reaction already proceeds at room temperature, which again displays the enhanced ylidic character of the fulvenes **3a** and **3b**. The paramagnetic dianion $[FeCl_4]^{2-}$ can be exchanged upon addition of two equivalents of sodium tetrafluoroborate or lithium tetrakis(pentafluorophenyl)borate. We find that formation of tetrachloroferrate can be avoided completely if sodium tetrafluoroborate is added already at the beginning of the reaction. In contrast to ferrocene, the imidazolium-substituted ferrocenes **5a** and **5b** are air-sensitive. The ^{1}H NMR spectrum ([D$_6$]acetone) of complex **5a** shows the formation of the ferrocene with characteristic Cp signals at $\delta = 5.03$ and 5.21 ppm as broad singlets. The electron-withdrawing imidazolium unit leads to a lowfield shift of about 1 ppm in comparison to ferrocene ($\delta = 4.14$ ([D$_6$]acetone), 4.17 ppm ($CDCl_3$)) and 0.3 to 0.4 ppm lowfield shifted compared to 1,1′-ferrocenedicarboxaldehyde ($\delta = 4.65$ and 4.9 ppm, $CDCl_3$).[13] Reaction of the prochiral fulvene **3b** leads to the two diastereomeric complexes *rac*-**5b** and *meso*-**5b**. The compound is dissolved readily in the IL [BMIM][BF$_4$][21] or

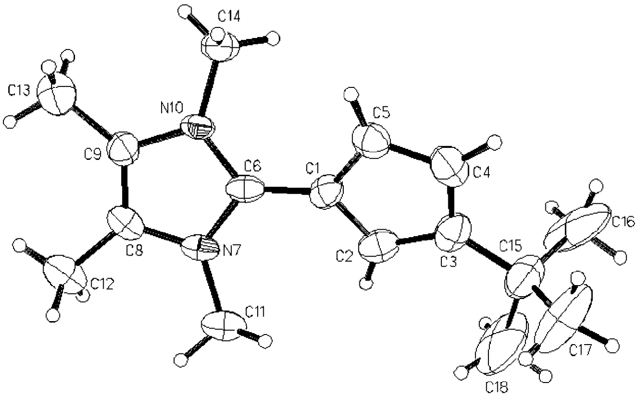
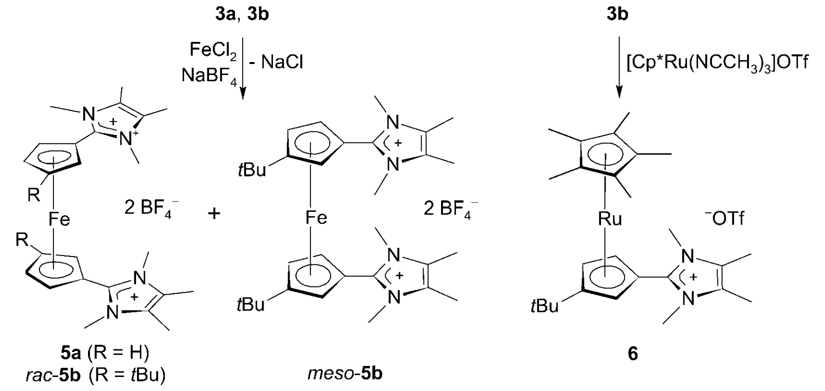


Figure 4. Molecular structure of the imidazole–derived fulvene **3b**. Selected bond lengths [Å] and angles [°]: C1–C2 1.425(7), C2–C3 1.390(7), C3–C4 1.432(8), C4–C5 1.381(8), C1–C5 1.432(7), C1–C6 1.436(7), C6–N7 1.377(6), N7–C8 1.393(7), C8–C9 1.342(7), C9–N10 1.398(6), C6–N10 1.358(6); C5-C1-C2 106.3(5), N7-C6-N10 105.9 (5), $\sphericalangle$ imi-Cp 23.8.



Scheme 4. Synthesis of the imidazolium-substituted metallocene complexes **5a**, **5b**, and **6**.

acetone. The ^{1}H NMR spectrum ([D$_6$]acetone) shows two sets of signals with a 2:1 ratio. Cp-H signals are found as broad singlets at $\delta = 4.86$, 5.25, and 5.43 ppm for the major isomer and $\delta = 5.05$, 5.09 and 5.13 ppm for the minor isomer. In the ^{13}C NMR spectrum, the signals of the Cp-CH carbon atoms are found at $\delta = 69.3$, 73.1, and 73.4 ppm for the major and at $\delta = 69.4$, 72.5, and 72.8 for the minor isomer.

Figure 5 shows the molecular structure of complex **5b**-$(R,S)_p$ that was obtained from red single crystals in the case of [FeCl$_4$]$^{2-}$ as a counter ion.[16] Both cyclopentadienyl rings are uniformly η^5-coordinated to the iron center with Fe–C bond lengths in a typically relatively narrow range of 2.047(4)–2.074(5) Å. The C–C bonds of the five-membered rings of the Cp units are all very similar in length 1.406(7)–1.432(6) Å [1.406(6)–1.436(6) Å]. The imidazolium plane is distorted from the Cp plane by 33.7° [30.3°]. The bond between the two rings is 1.465(7) Å [1.443(6) Å] and thus only 0.01–0.03 Å longer than that of fulvene **3a**, demonstrating again the strong zwitterionic character of imidazole-derived fulvenes. The Cp rings are oriented *gauche* with an angle of 87° between the two imidazolium substituents. α-Metallocenylcarbenium ions are usually stabilized by iron d-orbitals which leads mainly to a displacement of the carbenium ion out of the Cp plane towards the iron center, resulting in an angle α and a shift Δx of the iron–Cp bond out of the Cp-gravity point towards the carbenium substituent (see Figure 4).[22]

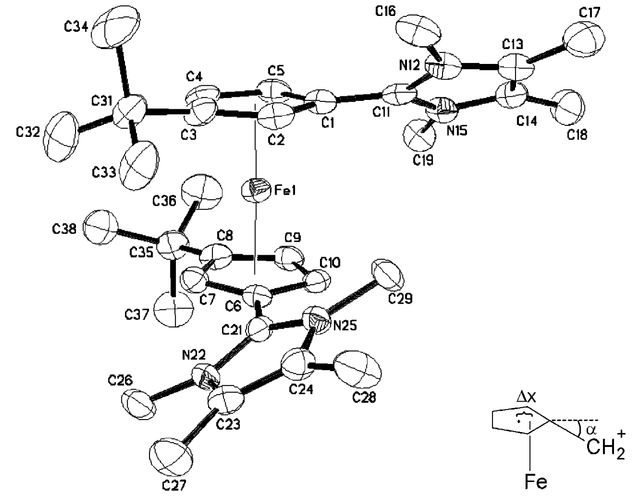


Figure 5. Left: Molecular structure of the imidazolium-substituted ferrocene *meso*-**5b**. The [FeCl$_4$]$^{2-}$ counterion is omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–C2 1.432(6), C2–C3 1.406(7), C3–C4 1.430(6), C4–C5 1.414(7), C1–C5 1.425(6), C1–C11 1.465(7), C11–N12 1.342(6), N12–C13 1.379(6), C13–C14 1.350(6), C14–N15 1.381(6), C11–N15 1.351(6), Fe–C1 2.070(5), Fe–C2 2.058(5), Fe–C3 2.074(5), Fe–C4 2.049(4), Fe–C5 2.047(4), Fe–Cp$_{\text{centroid}}$ 1.668; N12-C11-N15 106.8(4). Right: Definition of the angle α and the distance Δx to describe the geometric properties of α-ferrocenylmethylium ions.

This is also found for a cyclopropenium substituent in which the positive charge is stabilized by the aromatic character.[23] In contrast to this observation the opposite geometric behavior is found for the imidazolium-substituted ferrocene **5b**: the carbenium ion is bent away from the iron center and the Cp plane with a negative angle α of −4.5° (Cp1) and −3.0° (Cp2). The Fe–Cp bond is shifted by $\Delta x = -0.023$ Å (Cp1) and −0.052 Å (Cp2) from the gravity point. The negative values indicate that the shift is in the opposite direction to that observed for α-ferrocenylmethylium ions. The reasons for this unusual behavior might be the already strong stabilization of the carbenium ion in the imidazolium ring together with steric reasons.

An experiment on the NMR scale shows the formation of the ruthenocene complex **6** upon reaction of [Cp*Ru(NCCH$_3$)$_3$]OTf with fulvene **3b** (Scheme 4). Characteristic signals of the Cp protons are observed as broad singlets at $\delta = 4.50$, 4.81, and 4.83 ppm ([D$_8$]THF), and the Cp* signal is shifted lowfield to $\delta = 1.84$ ppm in comparison to that in the starting material ($\delta = 1.59$ ppm).

Our results show that aromatic stabilisation of imidazolium salts leads to the most pronounced zwitterionic structure of 6,6-diaminofulvenes in fulvene **3** so far. This is displayed by the easy hydrolysis to cyclopentadiene **4a**, a typical reaction of cyclopentadienyl anions. We demonstrated that these fulvenes are suitable precursors for imidazolium-substituted Group 8 metallocenes. Modifications of the ferrocenyl complexes to obtain ionic liquids and the synthesis of imidazolium metallocenes of other transition metals are currently under investigation in our laboratory.

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Keywords: cyclopentadienyl ligands • iron • metallocenes • nitrogen heterocycles • ylides

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[16] **2**: colorless crystal (polyhedron), dimensions $0.36\times0.22\times0.16$ mm^3, crystal system monoclinic, space group $P2_1/c$, $Z=4$, $a=10.7219(14)$, $b=9.0659(11)$, $c=13.7840(17)$ Å, $\beta=110.594(2)°$, $V=1254.2(3)$ Å^3, $\rho=1.356$ g cm^{-3}, $T=200(2)$ K, $\theta_{max}=28.30°$, radiation Mo$_{K\alpha}$, $\lambda=0.71073$ Å, 0.3° ω scans with CCD area detector, covering a whole sphere in reciprocal space, 12804 reflections measured, 3107 unique (R(int)=0.0264), 2712 observed ($I>2\sigma(I)$), $\mu=0.13$ mm^{-1}, $T_{min}=0.96$, $T_{max}=0.98$, 159 parameters refined, hydrogen atoms were treated by using appropriate riding models, goodness of fit 1.14 for observed reflections, final residual values $R1(F)=0.062$, $wR(F^2)=0.146$ for observed reflections, residual electron density −0.22 to 0.24 e Å^{-3}. **3a**: pale red crystal (polyhedron), dimensions $0.16\times0.10\times0.09$ mm^3, crystal system triclinic, space group $P\bar{1}$, $Z=2$, $a=6.9870(5)$, $b=7.8068(5)$, $c=9.9378(7)$ Å, $\alpha=76.546(2)°$, $\beta=81.302(2)°$, $\gamma=84.540(2)°$, $V=520.11(6)$ Å^3, $\rho=1.202$ g cm^{-3}, $T=200(2)$ K, $\theta_{max}=24.71°$, radiation Mo$_{K\alpha}$, $\lambda=0.71073$ Å, 0.3° ω scans with CCD area detector, covering a whole sphere in reciprocal space, 4335 reflections measured, 1765 unique (R(int)=0.0536), 1160 observed ($I>2\sigma(I)$), $\mu=0.07$ mm^{-1}, $T_{min}=0.99$, $T_{max}=0.99$, 132 parameters refined, hydrogen atoms were treated by using appropriate riding models, goodness of fit 1.01 for observed reflections, final residual values $R1(F)=0.049$, $wR(F^2)=0.101$ for observed reflections, residual electron density −0.16 to 0.21 e Å^{-3}. **3b**: colorless crystal (polyhedron), dimensions $0.28\times0.24\times0.02$ mm^3, crystal system triclinic, space group $P\bar{1}$, $Z=2$, $a=7.155(4)$, $b=8.378(5)$, $c=13.205(7)$ Å, $\alpha=82.064(12)°$, $\beta=88.896(11)°$, $\gamma=85.005(13)°$, $V=780.9(7)$ Å^3, $\rho=1.039$ g cm^{-3}, $T=200(2)$ K, $\theta_{max}=22.03°$, radiation Mo$_{K\alpha}$, $\lambda=0.71073$ Å, 0.3° ω scans with CCD area detector, covering a whole sphere in reciprocal space, 4566 reflections measured, 1915 unique (R(int)=0.0509), 1465 observed ($I>2\sigma(I)$), $\mu=0.06$ mm^{-1}, $T_{min}=0.98$, $T_{max}=1.00$, 180 parameters refined, hydrogen atoms were treated by using appropriate riding models, goodness of fit 1.29 for observed reflections, final residual values $R1(F)=0.110$, $wR(F^2)=0.195$ for observed reflections, residual electron density −0.21 to 0.20 e Å^{-3}. **4a**: brownish crystal (polyhedron), dimensions $0.35\times0.28\times0.26$ mm^3, crystal system triclinic, space group $P\bar{1}$, $Z=2$, $a=8.2144(11)$, $b=8.4614(11)$, $c=10.9017(14)$ Å, $\alpha=77.246(2)°$, $\beta=87.425(2)°$, $\gamma=64.806(2)°$, $V=667.69(15)$ Å^3, $\rho=1.373$ g cm^{-3}, $T=200(2)$ K, $\theta_{max}=28.31°$, radiation Mo$_{K\alpha}$, $\lambda=0.71073$ Å, 0.3° ω scans with CCD area detector, covering a whole sphere in reciprocal space, 6870 reflections measured, 3253 unique (R(int)=0.0215), 2837 observed ($I>2\sigma(I)$), $\mu=0.12$ mm^{-1}, $T_{min}=0.96$, $T_{max}=0.97$, 289 parameters refined, hydrogen atoms at the methyl groups were treated by using appropriate riding models, the rest of the hydrogen atoms was refined isotropically, goodness of fit 1.09 for observed reflections, final residual values $R1(F)=0.049$, $wR(F^2)=0.148$ for observed reflections, residual electron density −0.22 to 0.31 e Å^{-3}. *meso*-**5b**: red crystal (polyhedron), dimensions $0.31\times0.07\times0.05$ mm^3, crystal system triclinic, space group $P\bar{1}$, $Z=2$, $a=11.2519(8)$, $b=13.6632(10)$, $c=15.4593(11)$ Å, $\alpha=109.148(2)°$, $\beta=90.117(2)°$, $\gamma=108.188(2)°$, $V=2118.5(3)$ Å^3, $\rho=1.346$ g cm^{-3}, $T=200(2)$ K, $\theta_{max}=25.38°$, radiation Mo$_{K\alpha}$, $\lambda=0.71073$ Å, 0.3° ω scans with CCD area detector, covering a whole sphere in reciprocal space, 17979 reflections measured, 7755 unique (R(int)=0.0619), 5496 observed ($I>2\sigma(I)$), $\mu=0.97$ mm^{-1}, $T_{min}=0.75$, $T_{max}=0.95$, 469 parameters refined, hydrogen atoms were treated by using appropriate riding models, goodness of fit 1.13 for observed reflections, final residual values $R1(F)=0.075$, $wR(F^2)=0.125$ for observed reflections, residual electron density −0.36 to 0.47 e Å^{-3}. For all structures the intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied by using SADABS[24] based on the Laue symmetry of the reciprocal space. All structure were solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL-PLUS software package.[25] CCDC-691612 (**2**), CCDC-691613 (**3a**), CCDC-703208 (**3b**), CCDC-691614 (**4a**), and CCDC-691615 (**5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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