

Synthesis and structural characterization of mixed carbene-carboxylate complexes of palladium(II)

Han Vinh Huynh ^{a,*}, Duc Le Van ^b, F. Ekkehardt Hahn ^{b,*}, T.S. Andy Hor ^a

^a Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

^b Institut für Anorganische und Analytische Chemie der Westfälischen, Wilhelms-Universität Münster, Wilhelm Klemm-Strasse 8, D-48149 Münster, Germany

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Abstract

Mixed carbene-carboxylate complexes of Palladium(II) have been prepared by reacting {1,1'-dimethyl-3,3'-methylenediimidazoline-2,2'-diylidene} palladium(II) diiodide (**1**) [Angew. Chem. 107 (1995) 2602; Angew. Chem. Int. Ed. Engl. 34 (1995) 2371; J. Organomet. Chem. 557 (1998) 93] with AgO₂CR, where R = CF₃, CF₂CF₃ and CF₂CF₂CF₃. In this manner, {1,1'-dimethyl-3,3'-methylenediimidazoline-2,2'-diylidene} palladium(II) bis(trifluoroacetate) (**2**), {1,1'-dimethyl-3,3'-methylenediimidazoline-2,2'-diylidene} palladium(II) bis(pentafluoropropionate) (**3**) and {1,1'-dimethyl-3,3'-methylenediimidazoline-2,2'-diylidene} palladium(II) bis(heptafluorobutyrate) (**4**) were obtained. All three complexes were fully characterized by ¹H-, ¹³C- and ¹⁹F NMR spectroscopy as well as ESI mass spectrometry. X-ray crystal structure analyses of complexes **3** and **4** reveal mononuclear species with a square planar metal center coordinated by a *cis*-chelating dicarbene and two monodentate carboxylate ligands. The results show that the introduction of a *cis*-chelating *N,N*-heterocyclic carbene ligand stabilizes the palladium-carboxylate moiety effectively.

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1. Introduction

Carboxylate ligands have been widely used in coordination chemistry and their complexes are in general known to be stable [1]. However, there are notable exceptions such as Pd(II) phosphine carboxylates, which are believed to decompose through a reductive pathway giving anionic Pd(0) complexes [2,3], black palladium or undergo an autoionization process, especially in polar solvents such as methanol [4]. As catalytically active species in C–C-coupling reactions, such as Heck-type syntheses [5] and CO/olefin copolymerization [4], much effort was put into the study of their reactivities and structures. Hor and co-workers [6] reported the isolation and structural characterization of palladium carboxylate

complexes supported by the chelating and thus stabilizing 1,1'-bis(diphenylphosphino)ferrocene (dppf) ligand. Bianchini et al. [4b] isolated bis(acetate) complexes of palladium stabilized by 1,2-bis-(diphenylphosphino)ethane (dppe) and the more complicated *meso*-2,3-bis(diphenylphosphino)butane (*meso*-2,3-dppb) and *rac*-2,3-bis(diphenylphosphino)butane (*rac*-2,3-dppb) ligands. We attempted to stabilize the palladium-carboxylate moiety further by replacing the diphosphine with a dicarbene ligand. In doing so, we are also a step closer to achieve the objective of making phosphine-free catalysts [7]. Nucleophilic carbene ligands could have similar properties to phosphine ligands (“phosphine mimics”), but they are free of the dissociative problems that many phosphines experience. The use of carbene instead of phosphine as a supporting entity is therefore currently a topic of intense interest [7]. Notable examples are recently found in ruthenium chemistry, in which the second generation Grubbs catalysts for olefin metathesis reactions have been developed. In these, the phosphine ligand of

* Corresponding authors. Tel.: +65-6874-2670; fax: +65-6779-1691 (H.V. Huynh); fax: +49-251-833-3108 (F.E. Hahn).

E-mail addresses: chmhv@nus.edu.sg (H.V. Huynh), fehahn@uni-muenster.de (F. Ekkehardt Hahn).

the original Grubbs-type catalyst is replaced by an *N,N*-heterocyclic “Arduengo carbene” resulting in higher stability as well as catalytic activity. Another interesting example is the substitution of phosphine ligands for *N*-heterocyclic carbenes in palladium complexes for Heck-type reactions [8]. However, mixed carbene carboxylate complexes of palladium(II) have not been studied in depth, yet palladium carboxylates remain the key materials for Heck-syntheses. Herein, we report the synthesis and the first structural characterization of *cis*-dicarbene-bis(carboxylate) complexes of palladium(II).

2. Results and discussion

2.1. Synthesis and characterization

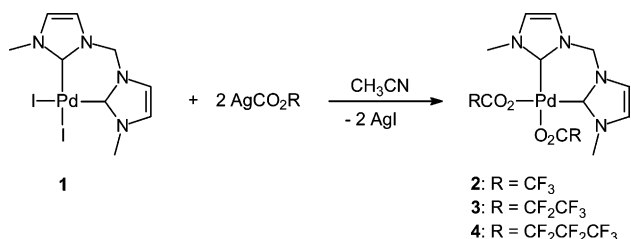
The mixed carbene-carboxylate complexes **2**, **3** and **4** were synthesized by reacting [$\{1,1'$ -dimethyl-3,3'-methyleneimidazoline-2,2'-diylidene}palladium(II) diiodide] (**1**) [8] with appropriate silver fluorocarboxylates under elimination of AgI as depicted in Scheme 1. A similar approach has already been used by Herrmann et al. [9] to generate the corresponding Pd(II) bis(acetate) complex. We prefer to work with fluorocarboxylates owing to their higher degree of coordination mobility [6a], which is a key element in the catalyst design. The complexes **2–4** are air-stable in the solid state and show an excellent solubility in polar solvents such as acetonitrile, acetone, DMF and DMSO. As expected, the solubility increases with the chain length of the fluorocarboxylates. While the pentafluoropropionate derivative **3** is only sparingly soluble in dichloromethane, chloroform and THF, the bis(septafluorobutyrate) derivative **4** readily dissolves in these solvents. The stability in solution is also influenced by the carboxylate chain length. The tendency to decompose to black palladium, which is related to the basicity of the carboxylate ligand, increases in the order $\text{CO}_2\text{CF}_3 < \text{CO}_2\text{CF}_2\text{CF}_3 < \text{CO}_2\text{CF}_2\text{CF}_2\text{CF}_3$. However, decomposition occurs very slowly and even DMSO solutions of **3** and **4** can be kept for at least a week, while **2** is stable in solution for months without any sign of decomposition. Complex **3** crystallizes as colorless prisms and complex **4** can be

obtained as crystalline and colorless plates, both suitable for X-ray structure determination.

The coordination of the carboxylate ligands to the carbene complex fragment results only in minor changes of the ^1H resonances of the *cis*-chelating dicarbene ligand in **2–4** compared to the precursor **1** [8a,8b]. These resonances are also not strongly influenced by the length of the carboxylate chains and have almost identical values for complexes **2–4**. Furthermore, all three complexes showed only a singlet for the methylene bridge between the carbene moieties at $\delta = 6.34\text{--}6.36$ ppm indicating fluxional behavior of the boat conformation of the six-membered chelate rings at room temperature [9,10]. ^{13}C NMR spectroscopy has been carried out for further characterization. Fig. 1 depicts the ^{13}C NMR spectrum of complex **4** as a representative. Upon coordination of carboxylate ligands, a significant upfield shift for the carbene carbon resonance is observed as compared to the precursor **1** [8a,8b]. Values for **1** ($\delta = 185.5$ ppm) and the corresponding bis(acetate) complex ($\delta = 154.8$ ppm) [9] have been reported. For the fluorocarboxylate complexes **2–4**, values of $\delta = 148.9$, 149.3 and 149.1 ppm were found, respectively, demonstrating an increased shielding effect due to the fluoro substituents. However, only substituents at the α -carbon atom of the carboxylate are involved and an increase of the fluorocarboxylate chain again shows no influence on the chemical shift of the carbene carbon resonance. The resonances for the fluorocarboxylates ligands were more difficult to assign due to the relative low intensities and the complicated pattern resulting from C–F coupling, especially for complex **4** with three inequivalent C–F groups (Fig. 1). The CF coupling constants fall in the range of $^1J(\text{C},\text{F}) = 263\text{--}295$ Hz and $^2J(\text{C},\text{F}) = 23\text{--}37$ Hz. Although both the carbene and carboxylate ligand can coordinate in a bridging mode, there is no evidence for such coordination in the NMR spectra.

2.2. Molecular structure of complexes **3** and **4**

Single crystals suitable for X-ray diffraction studies of complexes **3** and **4** were obtained by slow evaporation of the solvents at ambient temperature from a concentrated acetonitrile/toluene solution. The molecular structure of **3** and **4** are depicted in Fig. 2. As found by NMR spectroscopy in solution, both compounds crystallize as mononuclear complexes. In both cases the palladium atom is coordinated in a nearly perfect square-planar geometry (sum of angles around Pd 359.96° for **3** and 359.98° for **4**) by two monodentate carboxylates and a *cis*-chelating dicarbene ligand. The resulting six-membered $\text{C}_3\text{N}_2\text{Pd}$ ring is fixed in the boat conformation typically found for such compounds. The pendant oxygen atoms of the carboxylates in both complexes are in a *syn*-conformation and *exo*-orientated to the methylene



Scheme 1. Preparation of complexes **2–4** from **1**.

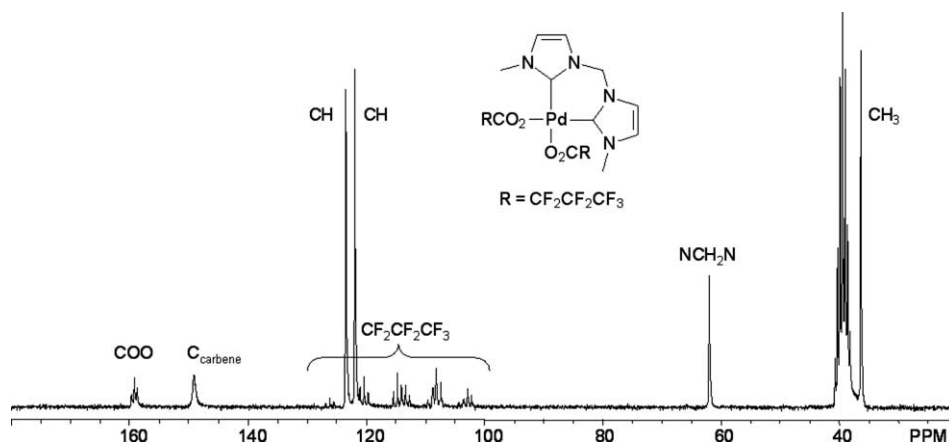


Fig. 1. ^{13}C NMR spectrum of complex 4.

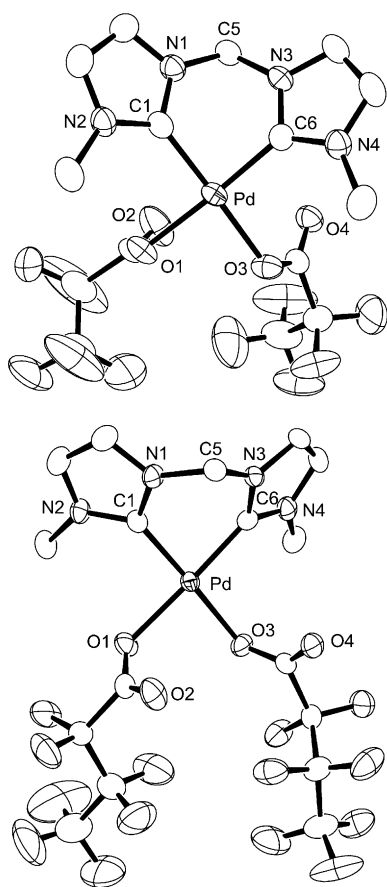


Fig. 2. Molecular structure of complexes **3** (top) and **4** (bottom). Selected bond lengths (Å) and bond angles ($^\circ$) for **3** [**4**]: Pd–O1 2.085(2) [2.080(3)], Pd–O3 2.071(3) [2.083(3)], Pd–C1 1.948(3) [1.955(4)], Pd–C6 1.949(3) [1.958(4)], N1–C1 1.343(4) [1.360(5)], N1–C5 1.444(4) [1.456(6)], N2–C1 1.338(4) [1.349(5)], N3–C5 1.449(4) [1.447(6)], N3–C6 1.345(4) [1.353(6)], N4–C6 1.339(4) [1.349(6)]; O1–Pd–O3 84.88(11) [84.39(12)], O1–Pd–C1 92.99(12) [93.76(15)], O1–Pd–C6 177.18(12) [176.83(15)], O3–Pd–C1 177.48(11) [178.12(15)], O3–Pd–C6 97.53(12) [97.0(2)], C1–Pd–C6 84.56(13) [84.8(2)], Pd–C1–N1 123.3(2) [124.3(3)], Pd–C1–N2 130.9(3) [130.9(3)], N1–C1–N2 105.7(3) [104.8(4)], Pd–C6–N3 123.3(2) [123.9(3)], Pd–C6–N4 131.6(3) [130.9(3)], N3–C6–N4 105.0(3) [105.2(4)], N1–C5–N3 109.3(3) [108.8(4)].

bridge of the dicarbene ligand. Since the molecular structure of both complexes are very similar, only that of complex **3** is discussed in detail herein.

The Pd–C bond lengths in **3** (1.948(3) and 1.949(3) Å) are almost identical. They are shorter than those reported for **1** (1.988(7), 1.989(8) Å) [8c] and its bis(benzimidazolin-2-ylidene) homologue (1.990(8), 1.991(7) Å) [11], presumably a reflection of the higher electron donation of the carbene centers to palladium as a consequence of higher Lewis acidity of the metal center induced by the fluorocarboxylates. The Pd–O distances of 2.085(2) and 2.071(3) Å are consistent with those in [(dppf)Pd(O₂CCF₂CF₃)₂] (2.076(3), 2.065(3) Å) [6a] and [(dppf)Pd(O₂CCF₂CF₂CF₃)₂] (2.096(4), 2.105(4) Å) [6b]. Due to the short methylene bridge between the carbenes, the C–Pd–C bite angle is reduced from the ideal value for a square planar complex to 84.6(1) $^\circ$. It has been demonstrated, that lengthening of the bridge between two *cis*-coordinated *N*-heterocyclic carbenes increases this angle [12].

The two monodentate carboxylate ligands are relatively flexible and free from distortion, apart from the interligand van der Waals repulsion. However, the O–Pd–O angle is also short of ideal (84.88(11) $^\circ$), which gives rise to an almost linear C–Pd–O arrangement with angles of 177.48(11) $^\circ$ and 177.18(12) $^\circ$, respectively. The monodentate coordination mode of the carboxylate ligands is also reflected in the CO_{coord} bond lengths of 1.245(5) and 1.259(4) Å as compared to the significantly shorter C–O_{pendant} distances of 1.195(5) and 1.213(4) Å. Further structural parameters for complex **3** are unexceptional and do not require further comment.

We have demonstrated that stable carbene-fluorocarboxylate complexes of palladium(II) can be conveniently synthesized and isolated. Current directions in our laboratories involve their use as precursors for mixed-metal carbene-carboxylates, which are not common in the literature, and their application in catalytic transformations in an environment that demands the exclusion of phosphines.

3. Experimental

3.1. General procedures

All manipulations were performed in an atmosphere of dry nitrogen by standard Schlenk techniques. All solvents were used as received and degassed prior to use. 1,1'-dimethyl-3,3'-methylenediimidazolium diiodide and [1,1'-dimethyl-3,3'-methylenediimidazoline-2,2'-diylidene}palladium(II) diiodide] (**1**) were prepared according to the literature procedures [8]. Pd(OAc)₂ was purchased from Avocado[®], silver carboxylates from Sigma–Aldrich[®] and used as received. ¹H-, ¹³C- and ¹⁹F NMR spectra were recorded on Bruker AC 200 or Bruker ACF 300 spectrometers using Me₄Si as internal and CCl₃F as an external standard. ESI mass spectra were obtained using a Finnigan MAT LCQ spectrometer. Elemental analyses were performed on a Perkin–Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

3.2. Synthesis of {1,1'-dimethyl-3,3'-methylenediimidazoline-2,2'-diylidene}palladium(II) bis(trifluoroacetate) (**2**)

A mixture of **1** (300 mg, 0.68 mmol) and AgO₂CCF₃ (301 mg, 1.36 mmol) was suspended in acetonitrile (40 ml) and stirred at 70 °C for 12 hours shielded from light. The resulting brownish suspension was filtered from the precipitated AgI over celite and the acetonitrile was removed in vacuo to give the crude product as an off-white solid. Recrystallization from acetone/hexane gave the product as an analytically pure white solid (249 mg, 0.49 mmol, 72%). Anal. Calc. for C₁₃H₁₂F₆N₄O₄Pd: C, 30.70; H, 2.38; N, 11.01. Found: C, 30.79; H, 2.69; N, 11.04%. ¹H NMR (300 MHz, DMSO-d₆): δ 7.67 (d, ³J(H,H) = 2.2 Hz, 2H, CH), 7.40 (d, ³J(H,H) = 2.2 Hz, 2H, CH), 6.34 (s, 2H, CH₂), 3.76 (s, 6H, NCH₃). ¹³C{¹H} NMR (75.48 MHz, DMSO-d₆): δ 159.8 (q, ²J(C,F) = 28.4 Hz, COO), 148.9 (s, N–C–N), 123.8 (s, CH), 122.2 (s, CH), 116.5 (q, ¹J(C,F) = 295.0 Hz, CF₃), 62.2 (s, CH₂), 36.7 (s, CH₃). ¹⁹F NMR (282.38 MHz, DMSO-d₆): δ –101.31 (s, CF₃). MS (ESI, positive ions): *m/z*: 904 [2M–O₂CCF₃]⁺, 395 [M–O₂CCF₃]⁺.

3.3. Synthesis of {1,1'-dimethyl-3,3'-methylenediimidazoline-2,2'-diylidene}palladium(II) bis(pentafluoropropionate) (**3**)

Complex **3** was prepared in analogy to **2** from **1** (300 mg, 0.68 mmol) and AgO₂CCF₂CF₃ (370 mg, 1.37 mmol). Yield: 393 mg (0.65 mmol, 95%). Slow evaporation at ambient temperature of a concentrated acetonitrile/toluene solution yielded transparent prisms suitable for X-ray diffraction studies. Anal. Calc. for C₁₅H₁₂F₁₀N₄O₄Pd: C, 29.60; H, 1.99; N, 9.20. Found:

C, 30.02; H, 2.09; N, 9.04%. ¹H NMR (300 MHz, DMSO-d₆): δ 7.67 (d, ³J(H,H) = 1.5 Hz, 2H, CH), 7.40 (d, ³J(H,H) = 1.5 Hz, 2H, CH), 6.36 (s, 2H, CH₂), 3.75 (s, 6H, NCH₃). ¹³C{¹H} NMR (75.48 MHz, DMSO-d₆): δ 159.7 (t, ²J(C,F) = 24.7 Hz, COO), 149.3 (s, N–C–N), 123.8 (s, CH), 122.2 (s, CH), 119.0 (qt, ¹J(C,F) = 285.7 Hz, ²J(C,F) = 36.0 Hz, CF₃), 116.8 (tq, ¹J(C,F) = 263.5 Hz, ²J(C,F) = 37.0 Hz, CF₂), 62.2 (s, CH₂), 36.7 (s, CH₃). ¹⁹F NMR (282.38 MHz, DMSO-d₆): δ –77.07 (s, CF₃), –113.58 (s, CF₂). MS (ESI, positive ions): *m/z*: 1054 [2M–O₂CCF₂CF₃]⁺, 395 [M–O₂CCF₂CF₃]⁺.

3.4. Synthesis of {1,1'-dimethyl-3,3'-methylenediimidazoline-2,2'-diylidene}palladium(II) bis(heptafluorobutyrate) (**4**)

Complex **4** was prepared like **2** and **3** from **1** (300 mg, 0.68 mmol) and AgO₂CCF₂CF₂CF₃ (301 mg, 1.36 mmol). The off white crude product was brought into a Soxhlet-thimble and extracted with dichloromethane (50 ml). Evaporation of the solvent afforded a white powder (400 mg, 83%). Slow evaporation at ambient temperature of a concentrated acetonitrile/toluene solution afforded transparent plates suitable for X-ray diffraction studies. Anal. Calc. for C₁₇H₁₂F₁₄N₄O₄Pd: C, 28.81; H, 1.71; N, 7.91. Found: C, 29.19; H, 1.93; N, 7.90%. ¹H NMR (200 MHz, DMSO-d₆): δ 7.67 (d, ³J(H,H) = 1.8 Hz, 2H, CH), 7.40 (d, ³J(H,H) = 1.8 Hz, 2H, CH), 6.36 (s, 2H, CH₂), 3.75 (s, 6H, NCH₃). ¹³C{¹H} NMR (50.33 MHz, DMSO-d₆): δ 159.2 (t, ²J(C,F) = 23.7 Hz, COO), 149.1 (s, N–C–N), 123.5 (s, CH), 122.0 (s, CH), 117.6 (qt, ¹J(C,F) = 287.8 Hz, ²J(C,F) = 34.7 Hz, CF₃), 108.7 (m, ¹J(C,F) = 263.0 Hz, CF₂CF₃), 108.1 (tt, ¹J(C,F) = 264.7 Hz, ²J(C,F) = 30.8 Hz, CF₂COO), 62.0 (s, CH₂), 36.4 (s, CH₃). ¹⁹F NMR (188.29 MHz, DMSO-d₆): δ –75.30 (t, ³J(F,F) = 8.3 Hz, 3 F, CF₃), 110.87 (q, ³J(F,F) = 8.3 Hz, 2 F, CF₂), –121.31 (br, 2 F, CF₂–COO). MS (ESI, positive ions): *m/z*: 1202 [2M–O₂CCF₂CF₂CF₃]⁺, 495 [M–O₂CCF₂CF₂CF₃]⁺.

3.5. Selected crystallographic details for **3**

Colorless crystals of **3** were obtained from a concentrated acetonitrile/toluene solution by evaporation of the solvent. Selected crystallographic details for **3**: size of data crystal 0.21 × 0.17 × 0.11 mm, formula C₁₅H₁₂F₁₀N₄O₄Pd, *M* = 608.69 amu, triclinic, space group *P*1̄ (No. 2), *a* = 8.6909(13) Å, *b* = 10.1922(15) Å, *c* = 11.676(2) Å, α = 90.023(3)°, β = 97.936(3)°, γ = 95.599(3)°, *V* = 1019.4(3) Å³, *Z* = 2, ρ_{calc} = 1.983 g cm^{–3}, Mo Kα radiation, μ(Mo Kα) = 1.033 mm^{–1}. 4665 symmetry independent diffraction data were measured at 203(2) K in the 2θ-range 3–55°. Structure solution with Patterson and refinement with Fourier methods, refinement (on *F*²) of positional parameters of all

non-hydrogen atoms with anisotropic thermal parameters. $R = 0.040$, $wR_2 = 0.104$ for 4133 structure factors $I \geq 2\sigma(I)$ and 309 refined parameters, maximum residual electron density $0.87 (-0.55) \text{ e } \text{Å}^{-3}$ hydrogen atoms reside on calculated positions and were refined as riding atoms. All calculations were carried out with the SHELX program package [13,14].

3.6. Selected crystallographic details for 4

Colorless crystals of **4** were obtained from a concentrated acetonitrile/toluene solution by evaporation of the solvent. Selected crystallographic details for **4**: size of data crystal $0.23 \times 0.11 \times 0.04 \text{ mm}$, formula $\text{C}_{17}\text{H}_{12}\text{F}_{14}\text{N}_4\text{O}_4\text{Pd}$, $M = 708.71 \text{ amu}$, triclinic, space group $P\bar{1}$ (No. 2), $a = 8.504(2) \text{ Å}$, $b = 10.245(3) \text{ Å}$, $c = 12.634(3) \text{ Å}$, $\alpha = 99.891(4)^\circ$, $\beta = 91.770(5)^\circ$, $\gamma = 95.223(5)^\circ$, $V = 1183.9(5) \text{ Å}^3$, $Z = 2$, $\rho_{\text{calc}} = 1.988 \text{ g cm}^{-3}$, Mo $K\alpha$ radiation, $\mu(\text{Mo } K\alpha) = 0.928 \text{ mm}^{-1}$. 4146 symmetry independent diffraction data were measured at $123(2) \text{ K}$ in the 2θ -range $3\text{--}50^\circ$. Structure solution with Patterson and refinement with Fourier methods, refinement (on F^2) of positional parameters of all non-hydrogen atoms with anisotropic thermal parameters. Hydrogen positions were identified and refined with isotropic thermal parameters. $R = 0.040$, $wR_2 = 0.104$ for 3569 structure factors $I \geq 2\sigma(I)$ and 409 refined parameters, maximum residual electron density $1.22 (-0.52) \text{ e } \text{Å}^{-3}$. All calculations were carried out with the SHELX program package [13,14].

4. Supplementary material

Further details of the crystal structure investigations (excluding structure factors) may be obtained free of charge from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1ZE, UK (e-mail: deposit@ccdc.cam.ac.uk) on quoting the depository numbers CCDC 223475 for **3** and CCDC 223476 for **4**.

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