Stable ruthenium indenylidene complexes with a sterically reduced NHC ligand

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General considerations

The catalyst preparation was carried out under Ar in pre-dried glassware using Schlenk techniques. Toluene, *d*-toluene, C_6D_6 (Na) and CH_2Cl_2 (CaH_2) were dried by distillation over the mentioned drying agents and were transferred under argon. Flash column chromatography was performed using silica gel 60 (230–400 mesh). NMR spectra of metathesis products were recorded in $CDCl_3$; chemical shifts (±) are given in ppm relative to TMS, coupling constants are (J) in Hz. IR spectra: wavenumbers are in cm^{-1}. MS (EI, LSIMS) spectra were recorded on AMD 604 Intectra GmbH spectrometer. MS (ESI) spectra were recorded on Mariner Perseptive Biosystems, Inc. GC/MS measurements were done on HP 5890 with HP 5 column.

The measurement of diffraction data was performed on a Kuma KM4CCD -axis diffractometer with graphite-monochromated MoK radiation and equipped with an Oxford Cryosystems nitrogen gas-flow apparatus. The crystal was positioned at 50 mm from the KM4CCD camera. 776 frames were measured at 1˚ intervals with a counting time of 11 sec. The data were corrected for Lorentz and polarization effects. The multi-scan absorption correction was applied. Data reduction and analysis were carried out with the Oxford Diffraction Ltd. suit of programs.[1]

The structure was solved by direct methods[2] and refined using SHELXL.[3] The refinement was based on F2 for all reflections except those with very negative F2 Weighted R factors wR and allgoodness-of-fit S values are based on F^2. Conventional R factors are based on F with F set to zero for negative F^2. The $Fo^2>2(Fo^2)$ criterion was used only for calculating R factors and is not relevant to the choice of reflections for the refinement. The R factors based on F^2 are about twice as large as those based on F. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 in Ref. [4].

Synthesis of [(SI*o*Tol)RuCl$_2$(PCy3)(Ind)] (7)

A flame-dried three-neck round-bottom flask equipped with a stirring bar was charged with 373 mg (2.4 equiv., 1.3 mmol) of 1,3-Di-*o*-tolyl-4,5-dihydro-3*H*-imidazolium chloride (**7**) under an argon atmosphere. Dry toluene (40 mL) was added. In a Schlenk tube, 500 mg (0.542 mmol) of M1 (**5**) were dissolved in dry toluene (30 mL). A solution of potassium hexamethyldisilazide (3.2 equiv., 1.73 mmol) in dry toluene (10 mL) was added dropwise to the suspension of **7**. The mixture was

shortly stirred at rt until it became clear (1-2 min); then, the solution of **5** was added to the now slightly yellow solution via a two-tipped needle with the help of argon pressure. The red-brown solution was stirred for 60 minutes, then concentrated at 30 ºC to a volume of ca. 10 mL. Chromatography was then performed with a 40x50 mm silica column, using a 48:2 (cyclohexane:EtOAc) mixture as the eluent. After evaporation of the eluent of at 30 ºC, the oily crude product was suspended in pentane (5 mL), and the suspension placed into a sonic bath for 5 min. After wards, the brick-red solid was filtered, washed with pentane (2x 5 mL) and dried. Yield: 257 mg (53 %). ^{1}H NMR (400 MHz, $C_6D_5CD_3$): δ 9.20 – 8.60 (m, 3H, 3xH_{Ar}), 7.80 – 7.75 (m, 1H, H_{Ar}), 7.75 – 7.69 (m, 1H, H_{Ar}), 7.64 – 7.48 (m, 1H, H_{Ar}), 7.48 – 7.34 (m, 1H, H_{ar}) 7.34 – 7.25 (m, 1H, H_{ar}) 7.25 – 6.30 (m, 10H, 10xH_{ar}) 3.74 – 3.40 (m, 2H, CH_2-CH_2), 3.15 – 2.83 (m, 2H, CH_2-CH_2), 2.79 – 2.59 (m, 2H,) 2.35 – 2.20 (m, 1H) 2.06 – 1.98 (m, 2H), 1.95 – 0.85 (m, 34H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 140.8, 138.0, 137.7, 136.6, 131.6, 130.9, 129.8, 129.4, 129.0, 128.9, 128.8, 128.4, 128.2, 128.0, 127.9, 127.8, 127.6, 127.4, 127.0, 126.3, 126.3, 125.8, 125.6, 125.2, 120.6, 119.6, 116.5, 116.4, 89.4, 34.6, 34.0, 33.9, 32.8, 29.0, 28.9, 28.8, 27.8, 27.8, 27.7, 27.6, 27.5, 27.4, 26.9, 26.9, 26.9, 26.3, 25.7, 25.2, 24.7, 19.4, 19.0, 18.8, 18.1. ^{31}P NMR (80 MHz, *d*-toluene): δ 21.4, 21.3, 19.1, 15.9. IR (KBr): ν 3436 w, 3052 w, 2923 ss, 2847 s, 1494 s, 1438 s, 1425 s, 1270 s, 755 s, 735 m, 721 m, 697 m. Anal. Calcd for $C_{50}H_{61}N_2Cl_2PRu$: C, 67.25; H, 6.89; N, 3.14; Cl 7.94. Found: C, 67.33; H, 6.90; N, 3.03; Cl, 7.91.

Synthesis of [(SI*o*Tol)RuCl$_2$(Py)(Ind)] (24)

In a schlenk tube under an argon atmosphere, 7 (0.112 mmol, 100 mg) was dissolved in dry pyridine (0.9 mL). The red-brown solution was stirred for 1 hour, then pentane (4 mL) was added. The brown suspension was stirred for an additional hour; then, the brown solid was filtered and washed with pentane (2x 4 mL). After drying, the brown solid was dissolved in dichloromethane (3 mL). The solution was topped with pentane (6 mL) and the mixture kept at 4 ºC for 12 hours. After that, the upper solution was decanted, and the brown product washed with pentane and dried. Yield: 59 mg (0.085 mmol, 76 %). ^{1}H NMR (200 MHz, C_6D_6): δ 9.45 – 9.20 (m, 1H, H_{Ar}), 8.60 – 8.42 (m, 2H, 2xH_{Ar}), 8.38 (d, ^{3}J(H, H) 7.0 Hz, 1H, H_{ar}), 7.90 – 7.50 (m, 4H, 4xH_{Ar}), 7.50 – 7.12 (m, 5H, 5xH_{Ar}), 7.12 – 6.30 (m, 8H, 8xH_{Ar}), 6.25 – 6.04 (m, 2H, 2xH_{Ar}), 3.80 – 3.44 (m, 2H, Imid-*H*), 3.19 – 2.96 (m, 1H, Imid-*H*), 2.96 – 2.72 (m, 2H, Imid-*H*), 2.16 (s, 3H, CH_3), 2.00 – 1.76 (m, 3H, CH_3).^{13}C NMR (125 MHz, C_6D_6): 303.3, 211.8, 153.5, 153.3, 150.3, 149.9, 145.6, 142.9, 142.2, 141.4, 141.0, 140.8, 140.6, 138.6, 137.2, 136.9, 135.2, 134.3, 133.0, 131.0, 130.1, 129.4, 129.2, 129.1, 129.0, 128.6, 127.5, 127.2, 126.9, 126.7, 123.5, 123.4, 117.4, 53.4, 52.7, 50.9, 20.2, 19.6, 18.7, 14.3. HR-HR-MS: calculated for $C_{32}H_{28}N_2ClRu$: 577.0984; found 577.0983 (M – pyridine – Cl^-]. Anal. Calcd for $C_{38}H_{35}Cl_4N_3Ru$ (**24**+CH_2Cl_2): C, 58.77; H, 4.54; N, 5.41. Found: C, 58.80; H, 4.55; N, 5,39.

General procedure for activity plot of RCM of diethyl dimethallyl malonate (8)

An NMR tube equipped with a rubber septum was charged with substrate **8** (0.06 mmol, 16.1 mg) and flushed with argon. 0.6 mL of dry C_6D_6 was added to the tube and the sample was equilibrated at 40 ºC in the NMR probe. Then, an aliqout of a catalyst stock solution (0.03 M, 0.1 mL, 0.003 mmol, 5 mol%) was added. The substrate methylene signal at 2.99 ppm was compared to the product signal at 3.14 ppm. Data points were collected over an appropriate period of time using the array function.

General procedure for Table 1, Entries 2, 3 and Table 2

A schlenk tube was under argon charged with substrate (0.5 mmol), solvent (0.1 M; dichloromethane for reactions at rt, toluene for reactions at 60 °C) and, in the case of CM, methyl acrylate (2. equiv. 1 mmol). The mixture was heated up to the indicated temperature and the respective amount of catalyst was added. The mixture was stirred at the indicated temperature, then concentrated and submitted to column chromatography (ethyl acetate and cyclohexane as eluents).

3,4-Dimethyl-1-[(4-methylphenyl)sulfonyl]-2,5-dihydro-1H-pyrrole (**12**)[5]
^{1}H NMR (200 MHz, $CDCl_3$): δ 7.72 (d, J = 8.6 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 3.97 (s, 4H), 2.21 (s, 3H), 1.54 (s, 6H).

4,5-Dimethyl-1-tosyl-1,2,3,6-tetrahydropyridine (**14**)[6]
^{1}H NMR (200 MHz, $CDCl_3$): δ 7.62 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 3.36 – 3.27 (m, 2H), 3.07 (t, J = 5.8 Hz, 2H), 2.38 (s, 3H), 2.12 – 1.99 (m, 2H), 157 – 1.47 (m, 6H).

5-Methyl-1-[(4-methylphenyl)sulfonyl]-1,2,3,6-tetrahydropyridine (**16**)[7]
^{1}H NMR (200 MHz, $CDCl_3$): δ 7.66 (d, J = 6.6 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 5.48 – 5.38 (m, 1H), 4.98 – 4.94 (m, 2H), 3.38 (s, 2H), 3.08 (t, J = 5.6 Hz, 2H), 2.40 (s, 3H), 2.21 – 2.08 (m, 2H), 1.60 (s, 3H).

2,2-Diphenyl-3-vinyl-2,5-dihydrofuran (**18**)[8]
^{1}H NMR (200 MHz, $CDCl_3$): 7.10 – 7.40 (m, 10H), 6.20 – 6.27 (m, 1H), 6.16–6.18 (m, 1H), 5.31 (dd, J = 17.4 Hz 1.4 Hz, 1H), 5.10 (dd, J = 10.6, 1.2 Hz, 1H), 4.11 (q, J = 1.0 Hz, 1H).

Methyl (*E*)-6-(tert-butyldimethylsilyloxy)hex-2-enoate (**20**)[9]

^{1}H NMR (200 MHz, $CDCl_3$): δ 6.99 (dt, J = 7.0 Hz 15.8 Hz, 1H), 5.82 (d, J = 15.8, 1H), 3.72 (s, 3H), 3.62 (t, J = 6.4, 2H), 2.27 (ddd, J = 1.2 Hz 6.6 Hz 7.4 Hz, 2H), 1.78 – 1.58 (m, 2H), 0.88 (s, 9H), 0.04 (s, 6H).

General procedure for stability experiments

The corresponding catalyst (0.0177 mmol) was weighed into an NMR tube. The tube was evacuated and refilled with argon. A stock solution of durene (0.0887 mmol, 11.9 mg) in dry *d*-toluene (1 mL) was prepared under argon. An aliquot of this solution (0.1 mL) was injected into the NMR tube with the catalyst, followed by 0.6 mL of dry *d*-toluene.

Grubbs SI*o*Tol catalyst (**3**) was taken from a freshly opened bottle (Aldrich).

In the case of precatalyst **8**, the integral under the multiplet at 8.5 – 9.2 ppm in the ^{1}H NMR spectrum was compared to the integral under the signal at 6.80 ppm of durene. In the case of precatalyst **3**, the intergral under the signal at 19.58 ppm was compared to the integral under the signal at 6.80 ppm of durene.

Time [h]	**Intact Precatalyst 7 [%]**	**Intact Precatalyst 2 [%]**
50	96	78
330	21	0

Solution-State Structure of 7 via ^{31}P NMR Analysis

In the publication *J. Am. Chem. Soc.*, **2009**, *131* 1931–1938., Grubbs observed two atropoisomers of a Hoveyda-type complex with an *o*-tolyl-NHC ligand. In the solid state, the complex formed a disordered crystal composed of a mixture of atropoisomers (91% syn and 9% anti). In a CD_2Cl_2 solution at -48 °C, the autors observed two signals from the benzylidene proton with intensity ratio 6.1:1, which coalesced at room temperature. These signals were assigned by Grubbs to atropoisomers, which was additionally confirmed using a 2D-NOESY experiment.

In the ^{31}P NMR spectrum of our catalyst **7**, there are four signals with chemical shifts δ 21.4, 21.3, 19.1, 15.9 and intensity ratios 8.3:3.7:1.4:1. Basing on the aforementioned work by Grubbs, and fact that the indenylidene substituent is symmetry-breaking, we assumed the existence of four atropoisomers of **7** (two *syn* and two *anti*) in solution (Fig. 1).

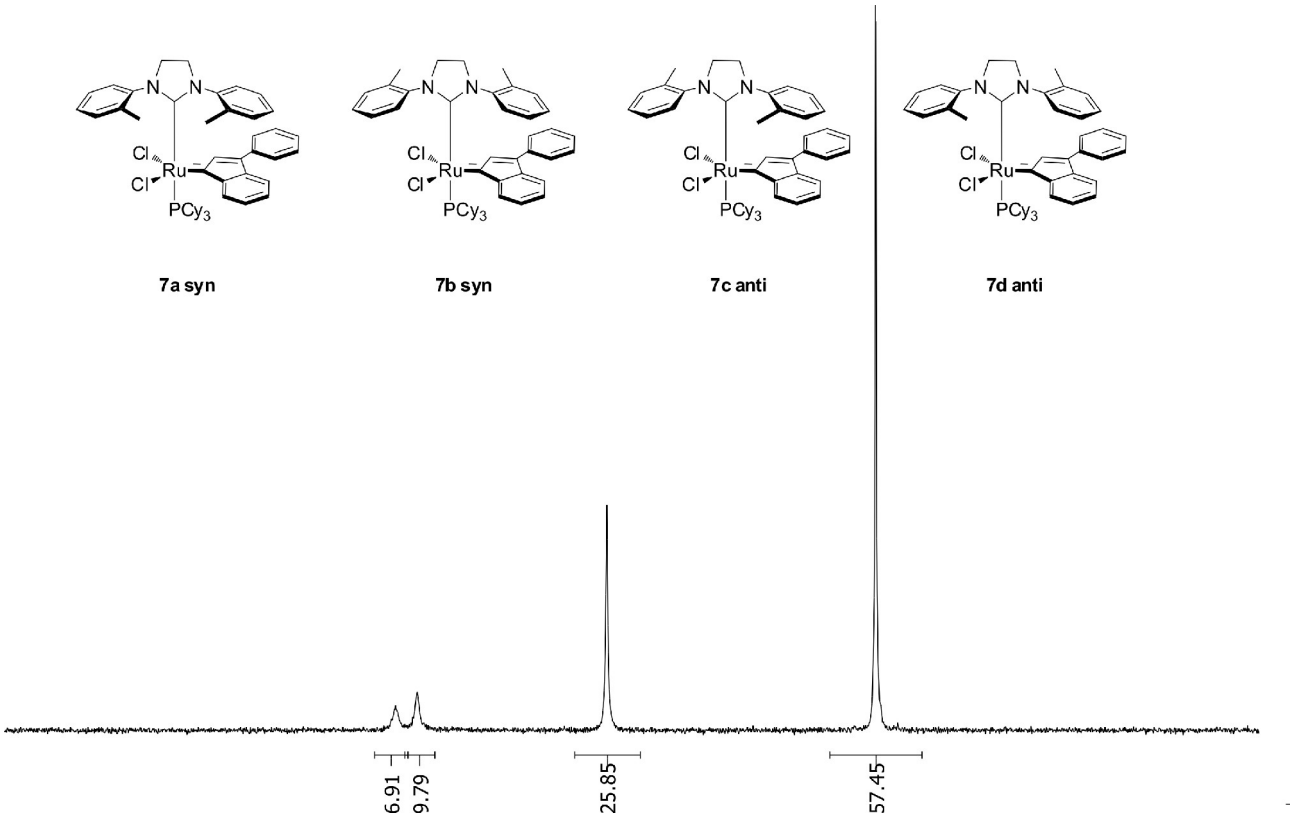


Fig. 1

In order to confirm the existence of an equilibrium mixture of atropoisomers in solution, we recorded the ^{31}P NMR spectrum at several different temperatures (Fig. 2).

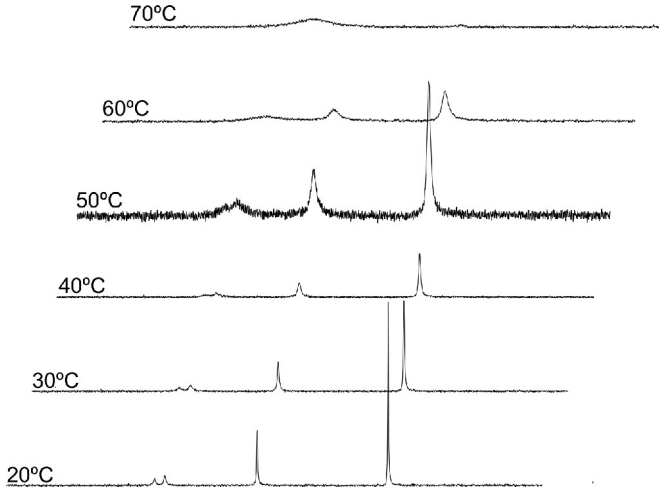
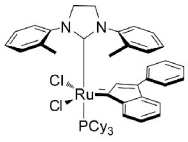


Fig. 2

As the temperature increases, the signals become broader and closer to each other. However, at 70 °C we observed coalescence of the signals, disappearance of key signals was observed further cooling of the sample to rt. The behavior suggests existence of four atropoisomers, which transform into each other increasingly quickly. However, due to the limited stability of the complex at 70 °C we were unable to deliver final proof of the process.

^{1}H, ^{31}P and ^{13}C NMR spectral data



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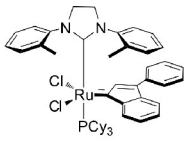

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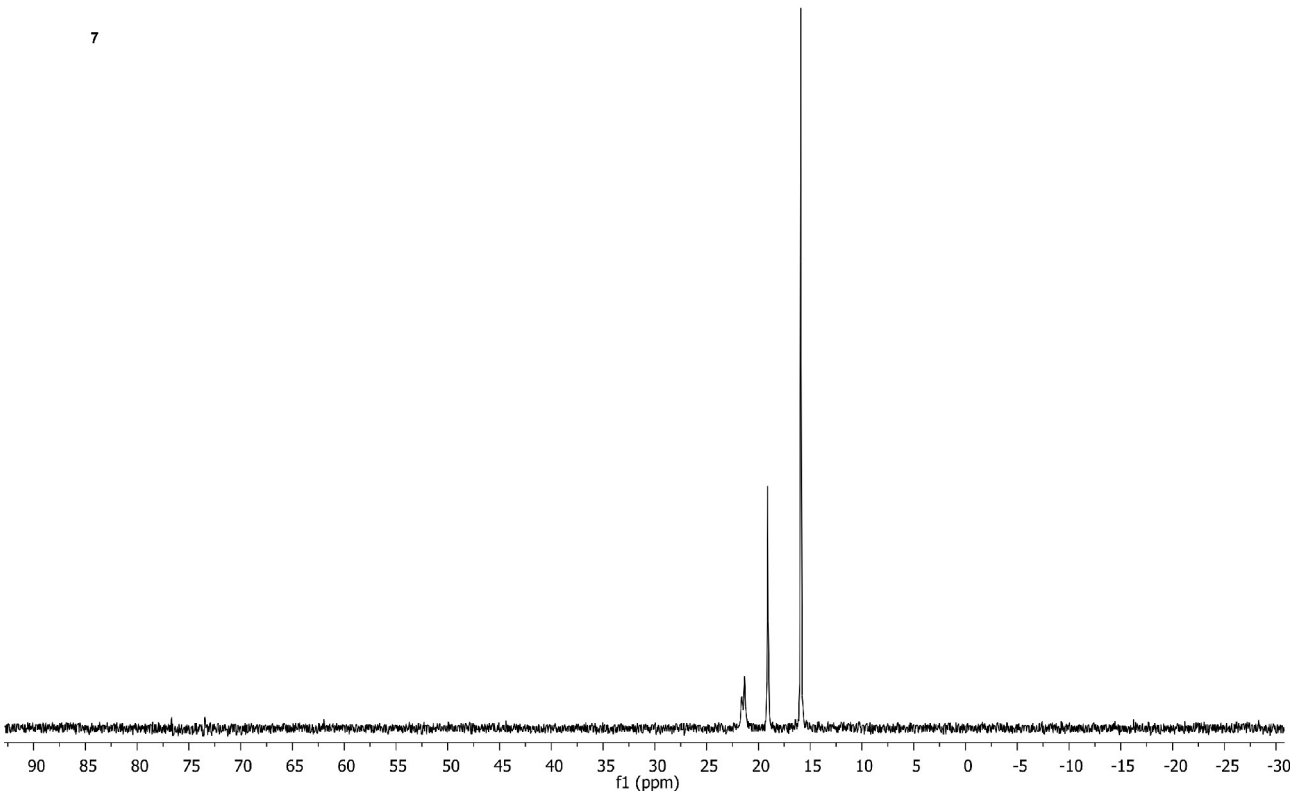

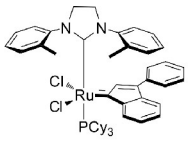

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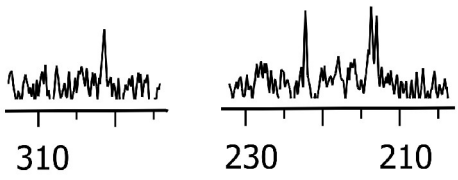

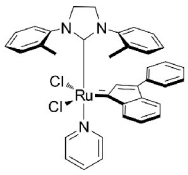

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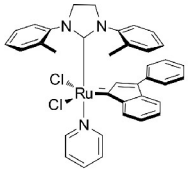

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Table 1. Crystal data and structure refinement for structure **7** and **24**.

	7 CCDC 906001	24 CCDC 906002
Crystal data		
Chemical formula	C50H61Cl2N2PRu	C37H33Cl2N3Ru·CH2Cl2
Mr	892.95	776.56
Crystal system, space group	Monoclinic, P21/c	Monoclinic, P21/n
Temperature (K)	100	100
a, b, c (Å)	13.7210 (3), 19.7109 (4), 16.1632 (3)	10.7214 (3), 29.0839 (9), 10.8935 (3)
β (°)	92.489 (2)	96.311 (3)
V (Å3)	4367.27 (15)	3376.23 (17)
Z	4	4
Radiation type	MoKα, λ = 0.71073 Å	MoKα, λ = 0.71073 Å
μ (mm-1)	0.56	0.81
Crystal size (mm)	0.30 × 0.30 × 0.05	0.30 × 0.20 × 0.10
Crystal data		
Diffractometer	KUMA4 CCD diffractometer	KUMA4 CCD diffractometer
Absorption correction	Multi-scan CrysAlis PRO, Agilent Technologies, Version 1.171.35.15 SCALE3 ABSPACK scaling algorithm.	Multi-scan CrysAlis PRO, Agilent Technologies, Version 1.171.35.15 SCALE3 ABSPACK scaling algorithm.
Tmin, Tmax	0.851, 0.973	0.792, 0.923
No. of measured, independent and observed [I > 2σ(I)] reflections	101262, 8291, 6456	60014, 6636, 5554
Rint	0.065	0.073
(sin θ/λ)max (Å-1)	0.610	0.617
Refinement		
R[F2 > 2σ(F2)], wR(F2), S	0.046, 0.149, 1.26	0.049, 0.114, 1.12
No. of reflections	8291	6636
No. of parameters	507	411
No. of restraints	1	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
Δ<max, Δ>min (e Å-3)	1.12, -0.94	2.06, -0.87

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