

Organometallic Lewis Acids, Part LXII^[1]. Chiral Carbonyl-Cyclopentadienyl-Triphenylphosphine-Iron and -Ruthenium Complexes with Tertiary Nitriles $[\text{CpM}(\text{CO})(\text{PPh}_3)(\text{N}\equiv\text{C}-\text{CR}^1\text{R}^2\text{R}^3)]^+ \text{BF}_4^-$ ($M = \text{Fe}, \text{Ru}$)

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Dedicated to Professor Gottfried Huttner on the Occasion of his 80th Birthday

Abstract. A series of tertiary nitriles was synthesized by alkylation of acetonitrile, primary and secondary nitriles, using alkylbromides and sodium amide in liquid ammonia. By reaction of the in situ formed organometallic Lewis acids $[\text{CpM}(\text{CO})(\text{PPh}_3)]^+$ ($M =$

Fe, Ru) with the novel tertiary nitriles, the complexes $[\text{CpM}(\text{CO})(\text{PPh}_3)(\text{N}\equiv\text{C}-\text{CR}^1\text{R}^2\text{R}^3)]\text{BF}_4$ were obtained. A di-iron complex was formed with 1,6-dicyanohexane.

Introduction

Chiral complexes of iron and ruthenium with four different ligands $\text{CpM}(\text{CO})(\text{PR}_3)\text{X}$ and $[\text{CpM}(\text{CO})(\text{PR}_3)(\text{L})]^+$ ($M = \text{Fe}, \text{Ru}$)^[2–6] and the Gladysz complexes $[\text{CpRe}(\text{NO})(\text{PPh}_3)(\text{L})]^+[\text{7}] have found high attention as inorganic counter parts of methane derivatives and very many examples have been reported. Brunner was the first to accomplish chiral resolution of organometallic complexes with four different ligands.^[8] Later on, several other researchers also succeeded in separating and isolating the enantiomers, which could be used as optically active auxiliaries in asymmetric organic synthesis^[9,10]$

In the following we report on chiral iron and ruthenium complexes with a series of novel tertiary nitriles $[\text{CpM}(\text{CO})(\text{PPh}_3)(\text{N}\equiv\text{C}-\text{CR}^1\text{R}^2\text{R}^3)]^+$, and with a long chain alkylcyanide. Sterically shielded tertiary nitriles are of interest for special applications because the electrophilic carbon atom of the nitrile group is masked, whereas the nucleophilic nitrogen atom is still well-accessible such as for complexing with Lewis acids. As a consequence, such nitriles are very resistant to alkaline hydrolysis^[11] and more general to the attack of nucleophiles. Moreover, the lack of enolizable hydrogen atoms renders these substances to be robust reagents both under strongly alkaline and acidic media.

Organometallic cyclopentadienyl iron and ruthenium nitrile complexes have found interest as possible materials for non-linear optics,^[12] as compounds with liquid-crystalline properties^[13] and for use in Langmuir-Blodgett films.^[14]

Results and Discussion

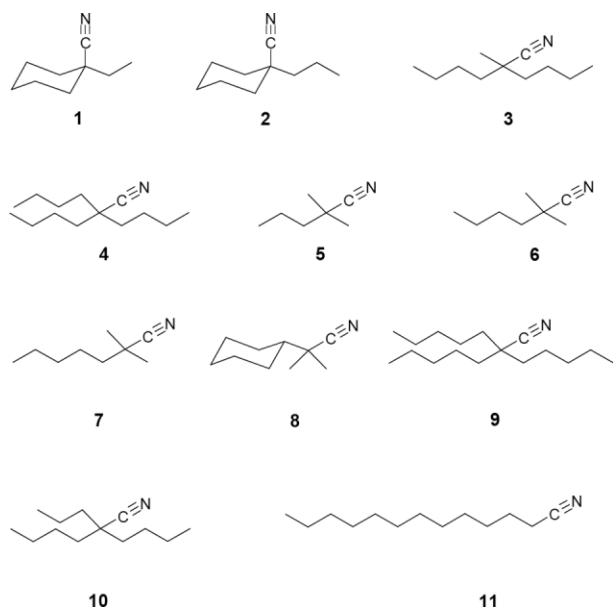
We prepared the tertiary nitriles by alkylation of acetonitrile, primary and secondary nitriles, respectively. Various methods for the alkylation of nitriles were reported such as in the beginning a favored intramolecular ring closure.^[15] The alkylation of nitriles, preferentially activated by phenylsubstituents, by means of an oil suspension of sodium amide in liquid ammonia was reported,^[16] however proved to be comparatively complicated and gave a mixture of alkylation products. The application of potassium amide instead sometimes lead to partial loss of the nitrile group.^[17] A further method for the alkylation by means of a slurry of sodium amide in ether was described^[18] and also gave a mixture of alkylation products. We found the combination of the method of Bergstrom and Agostinho^[16] with the method of Schurch and Huntress^[18] proved to be very satisfying and useful for upscaling. Thus, sodium metal was dissolved in liquid ammonia, converted to sodium amide by means of iron(III) and allowed to react with the corresponding nitrile and alkyl bromide in plenty of anhydrous ethyl ether, while increasing the temperature to ambient. The released gaseous ammonia can be recovered by condensing for cascading batches. Finally, the nitriles were isolated in sufficient purity after aqueous work-up and vacuum distillation. The tertiary nitriles form thermally stable colorless liquids, where three flexible alkyl chains provide both shielding of the nitrile carbon and good solubility; the latter is useful for the preparation of nitrile metal complexes (see Scheme 1).

The chiral cationic nitrile complexes of the type $[\text{CpM}(\text{CO})(\text{PR}_3)(\text{NCR}')^+]$ ($M = \text{Fe}, \text{Ru}$; “Cp” = substituted or unsubstituted cyclopentadienyl) were prepared before, usually by halide abstraction from the corresponding halide complexes $[\text{CpM}(\text{CO})(\text{PR}_3)(\text{X})]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) by means of Ag^+ salts in the presence of the corresponding nitriles (see Scheme 2). Using a chiral neomenthyl substituent on the cyclopentadienyl

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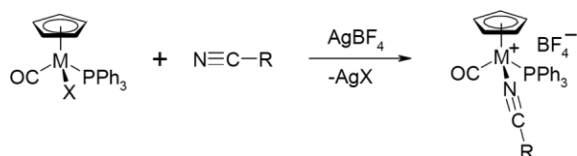
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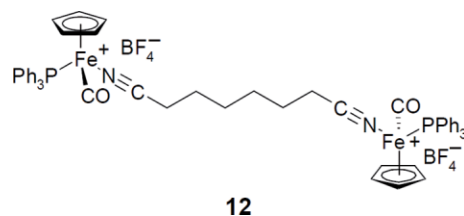
Scheme 1. The alkylnitriles **1** to **11** applied as ligands.

ring allowed the separation of the chiral-at-metal MeCN complexes.^[21] Nitriles used in these reactions include MeCN, olefinic and aromatic nitriles as well as cyanoacetic methyl ester.^[5,22,23] Quite interesting, it was not successful to obtain the corresponding Ru complex with the long chain nitrile C₁₈H₃₇CN by this method, whereas the reaction of the more electron rich [CpRu(PR₃)₂Cl] proceeded without difficulty.^[14] A rather unusual synthesis of [CpFe(CO)(PPh₃)(MeCN)]⁺ used the reaction of the vinylidene complex [CpFe(CO)(PPh₃)(=C=CH₂)]⁺ with hydrazine derivatives.^[19] In our laboratory the “organometallic Lewis acids” [CpM(CO)(PPh₃)]⁺ (*M* = Fe, Ru) and [Re(CO)₅]⁺ were added to the nitrile groups of CpFe-(CH₂)_{*n*}C≡N (*n* = 1,2) to give cationic dinuclear complexes.^[24]



Scheme 2. Synthesis of nitrile complexes: (i) *M* = Fe; **1a**, **3a** – **11a**; *X* = I. (ii) *M* = Ru; **2b** – **6b**, **11b**; *X* = Cl.

The in situ – from CpM(CO)(PPh₃)X (*M* = Fe, Ru; *X* = Cl, I) and AgBF₄ – formed “organometallic Lewis acids” [CpM(CO)(PPh₃)]⁺ react with the novel tertiary nitriles to afford the iron complexes **1a**, **3a**–**10a** and the ruthenium compounds **2b**–**6b** (see Scheme 2). With CH₃(CH₂)₁₁CN the complexes **11a** and **11b** are formed and with 1,6-dicyanohexane the dinuclear iron complex **12** could be obtained (see Scheme 3). The iron complexes are isolated as deep red, the ruthenium complexes as yellow compounds.



Scheme 3. The dinuclear complex **12** (one stereoisomer is shown).

The reactions were performed in dichloromethane. However, in contrast to reactions of the isosteric rhenium Lewis acid [CpRe(CO)(PPh₃)]⁺, where the dichloromethane complex [CpRe(CO)(PPh₃)(ClCH₂Cl)]⁺ is formed,^[25,26] “no evidence for a dichloromethane adduct” was observed with the iron and ruthenium compounds.^[20] This observation can be certainly attributed to the stronger rhenium Lewis acidity – due to the stronger acceptor ability of the NO ligand – in comparison to the iron and ruthenium CO analogues. However, it should be noted that isolation of the methyl iodide complex [CpRu(CO)(PPh₃)(I Me)]⁺ is possible; addition of MeCN to this compound leads to substitution of MeI by the nitrile.^[20]

The complexes **1**–**12** are characterized by their CN and CO IR absorptions at 2295–2242 cm^{−1} and 1970–1980 cm^{−1}, respectively, and a broad BF₄ absorption at 1055 cm^{−1}. In many cases the diastereotopic groups can be detected in the ¹H and ¹³C NMR spectra (see Experimental Section).

Molecular Structure of **4b**

Compound **4b** crystallizes in the centrosymmetric monoclinic space group *P*2₁/*c*; therefore, both enantiomers of the chiral pseudo-tetrahedral cation can be found in the unit cell (Figure 1). The bond lengths and angles are similar to the ones found in the three crystallographically characterized [CpRu(CO)(PR₃)(NCMe)]⁺ complexes (Ru–N: 2.049–2.074 Å; Ru–C: 1.855–1.870 Å; Ru–P: 2.324–2.351 Å; Ru–Cp: 1.868–

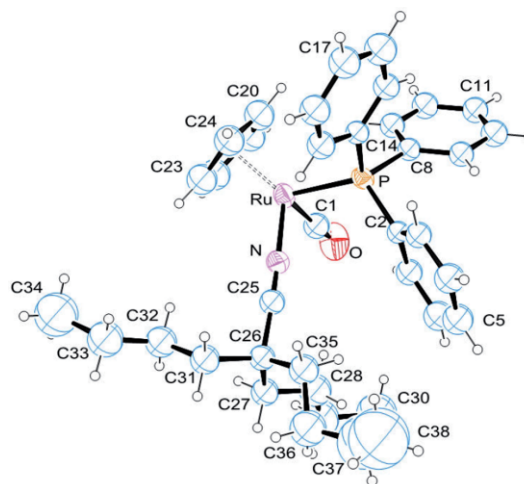


Figure 1. ORTEP3 view (30% probability ellipsoids) of the cation of complex **4b**. Selected bond lengths /Å and angles /°: Ru–P: 2.319(5); Ru–N: 1.990(17); Ru–C1: 1.86(2); Ru–Cp: 1.858(10); N–C25: 1.13(2); C25–N–Ru: 174.4(17); N–C25–C26: 177(2).

1.883 Å; C–N–Ru: 173.1–178.5°; and N–C–C: 176.4–178.8°).^[21,27,28] The longer Ru–N bond reflects the steric demands of the tertiary alkyl group. As is observed quite often with similar compounds, the three butyl groups exhibit severe disorder in the two “terminal” carbon atoms, and the BF₄ anion is also heavily disordered. The crystal structure contains approximately 3.7% solvent accessible voids, which are probably filled by the CH₂Cl₂ crystallization solvent, which is most likely severely disordered and could not be localized. Due to these disorders, and the relative weak reflections at larger 2 θ angles, only some atoms could be refined anisotropically and thus, rather poor R values could be obtained in the refinement.

Experimental Section

Preparation of the Tertiary Nitriles

1-Ethylcyclohexanecarbonitrile (1): Sodium metal (18.0 g, 785 mmol) was dissolved in liquid ammonia (250 mL), treated with the amount of a micro spatulum of iron(III)nitrate, allowed to stand for 1 h, treated drop wise with stirring within 1 h with a solution of cyclohexanecarbonitrile (46 g, 421 mmol) and 1-bromoethane (59.6 g, 547 mmol) in anhydrous ether (150 mL), stirred for 1 h, allowed to warm to room temperature while evaporating the ammonia (5 h), treated with anhydrous ether (250 mL), stirred for 1 d, treated drop wise with anhydrous ethanol (50 mL) for the degradation of residual sodium amide, hydrolyzed with distilled water, acidified with 2 N sulfuric acid separated from the aqueous phase with extraction of the latter (3 \times 50 mL), dried with magnesium sulfate, evaporated, and distilled. Yield 25.2 g (44%), b.p. 105–107 °C/24 mbar, n_D^{20} = 1.4518. **IR** (film): $\tilde{\nu}$ = 2970 (s), 2930 (s), 2860 (s), 2230 (m, CN), 1455 (s), 1390 (m), 1075 (w), 1000 (m), 945 (m), 905 (m), 850 (w), 780 (w) cm⁻¹. **¹H NMR** (CDCl₃, 20 °C, 400 MHz): δ = 0.95–2.05 (m) ppm. **¹³C NMR** (CDCl₃, 20 °C, 101 MHz): δ = 8.76, 23.12, 25.54, 33.41, 35.32, 39.62 (s), 123.58 (s, CN) ppm.

1-Propylcyclohexanecarbonitrile (2): Sodium metal (18.0 g, 785 mmol) was dissolved in liquid ammonia (250 mL), treated with the amount of a micro spatulum of iron(III)nitrate, allowed to stand for 1 h, treated drop wise with stirring within 1 h with a solution of cyclohexanecarbonitrile (46 g, 421 mmol) and 1-bromopropane (67.3 g, 547 mmol) in anhydrous ether (150 mL), stirred for 1 h, allowed to warm to room temperature while evaporating the ammonia (5 h), treated with anhydrous ether (250 mL), stirred for 1 d, treated drop wise with anhydrous ethanol (50 mL) for the degradation of residual sodium amide, hydrolyzed with distilled water, acidified with 2 N sulfuric acid separated from the aqueous phase with extraction of the latter (3 \times 50 mL), dried with magnesium sulfate, evaporated and distilled. Yield 43.5 g (68%), b.p. 94–96 °C/24 mbar, n_D^{20} = 1.4541. **IR** (film): $\tilde{\nu}$ = 2960 (s), 2940 (s), 2860 (s), 2230 (m, CN), 1470 (m), 1455 (s), 1385 (w), 1115 (w), 975 (w), 940 (w), 850 (w), 745 (w) cm⁻¹. **¹H NMR** (CDCl₃, 20 °C, 400 MHz): δ = 0.88–2.05 (m) ppm. **¹³C NMR** (CDCl₃, 20 °C, 101 MHz): δ = 14.09, 17.63, 22.99, 25.42, 35.66, 38.93 (s), 42.71, 123.68 (s, CN) ppm.

2-Butyl-2-methylhexanenitrile (3): Sodium metal (18.0 g, 785 mmol) was dissolved in liquid ammonia (250 mL), treated with the amount of a micro spatulum of iron(III)nitrate, allowed to stand for 1 h, treated drop wise with stirring within 1 h with a solution of propionitrile (9.6 g, 174 mmol) and 1-bromobutane (95.0 g, 695 mmol) in anhydrous ether (150 mL), stirred for 1 h, allowed to warm to room temperature while evaporating the ammonia (5 h), treated with anhydrous

ether (250 mL), stirred for 1 d, treated drop wise with anhydrous ethanol (50 mL) for the degradation of residual sodium amide, hydrolyzed with distilled water, acidified with 2 N sulfuric acid separated from the aqueous phase with extraction of the latter (3 \times 50 mL), dried with magnesium sulfate, evaporated and distilled. Yield 20.8 g (71%), b.p. 101–102 °C/24 mbar, n_D^{20} = 1.4294. **IR** (film): $\tilde{\nu}$ = 2960 (s), 2940 (s), 2860 (s), 2230 (m, CN), 1725 (w), 1470 (s), 1380 (m), 1345 (w), 1295 (w), 735 (w) cm⁻¹. **¹³C NMR** (CDCl₃, 20 °C, 101 MHz): δ = 13.79, 22.75, 23.93, 26.90, 36.59 (s), 39.14, 124.55 (s, CN) ppm. C₁₁H₂₁N (167.3): calcd. C 78.97, H 12.65, N 8.37%; found C 78.28, H 12.91, N 8.61%.

2,2-Dibutylhexanenitrile (4): Sodium metal (30.0 g, 1.3 mol) was dissolved in liquid ammonia (250 mL), treated with the amount of a micro spatulum of iron(III)nitrate, allowed to stand for 1 h, treated drop wise with stirring within 1 h with a solution of acetonitrile (12.25 g, 300 mmol) and 1-bromobutane (163 g, 1.19 mol) in anhydrous ether (150 mL), stirred for 1 h, allowed to warm to room temperature while evaporating the ammonia (5 h), treated with anhydrous ether (250 mL), stirred for 1 d, treated drop wise with anhydrous ethanol (50 mL) for the degradation of residual sodium amide, hydrolyzed with distilled water, acidified with 2 N sulfuric acid separated from the aqueous phase with extraction of the latter (3 \times 50 mL), dried with magnesium sulfate, evaporated and distilled. Yield 40.14 g (64%), b.p. 105–106 °C/1.3 mbar, n_D^{20} = 1.4404. **IR** (film): $\tilde{\nu}$ = 2980 (s), 2940 (s), 2870 (s), 2230 (m, CN), 1465 (s), 1380 (m), 1345 (w), 1265 (w), 1105 (w), 900 (w), 735 (w) cm⁻¹. **¹H NMR** (CDCl₃, 20 °C, 400 MHz): δ = 0.94 (m, 9 H), 1.43 (m, 18 H) ppm.

2,2-Dimethylpentanenitrile (5): Sodium metal (18.0 g, 785 mmol) was dissolved in liquid ammonia (250 mL), treated with the amount of a micro spatulum of iron(III)nitrate, allowed to stand for 1 h, treated drop wise with stirring within 1 h with a solution of isobutyronitrile (34.5 g, 500 mmol) and 1-bromopropane (80 g, 650 mmol) in anhydrous ether (150 mL), stirred for 1 h, allowed to warm to room temperature while evaporating the ammonia (5 h), treated with anhydrous ether (250 mL), stirred for 1 d, treated drop wise with anhydrous ethanol (50 mL) for the degradation of residual sodium amide, hydrolyzed with distilled water, acidified with 2 N sulfuric acid separated from the aqueous phase with extraction of the latter (3 \times 50 mL), dried with magnesium sulfate, evaporated and distilled. Yield 35.1 g (63%), b.p. 41–43 °C/24 mbar, n_D^{20} = 1.4033. **IR** (film): $\tilde{\nu}$ = 2970 (s), 2940 (s), 2880 (s), 2240 (m, CN), 1470 (m), 1460 (m), 1395 (w), 1375 (w), 1270 (w), 1220 (w), 1205 (w), 750 (w) cm⁻¹. **¹H NMR** (CDCl₃, 20 °C, 400 MHz): δ = 0.96 (m, 3 H), 1.31 (s, 6 H), 1.49 (m, 4 H) ppm. **¹³C NMR** (CDCl₃, 20 °C, 101 MHz): δ = 13.97, 18.48, 26.59, 32.29 (s), 43.19, 125.09 (s, CN) ppm. C₇H₁₃N (111.2): calcd. C 75.61, H 11.79, N 12.60%; found C 75.83, H 11.60, N 12.63%.

2,2-Dimethylhexanenitrile (6): Sodium metal (18.0 g, 785 mmol) was dissolved in liquid ammonia (250 mL), treated with the amount of a micro spatulum of iron(III)nitrate, allowed to stand for 1 h, treated drop wise with stirring within 1 h with a solution of isobutyronitrile (34.5 g, 500 mmol) and 1-bromobutane (89 g, 650 mmol) in anhydrous ether (150 mL), stirred for 1 h, allowed to warm to room temperature while evaporating the ammonia (5 h), treated with anhydrous ether (250 mL), stirred for 1 d, treated drop wise with anhydrous ethanol (50 mL) for the degradation of residual sodium amide, hydrolyzed with distilled water, acidified with 2 N sulfuric acid separated from the aqueous phase with extraction of the latter (3 \times 50 mL), dried with magnesium sulfate, evaporated and distilled. Yield 39.5 g (63%), b.p. 65–66 °C/27 mbar, n_D^{20} = 1.4109. **IR** (film): $\tilde{\nu}$ = 2980 (s), 2960 (s), 2870 (s), 2235 (m, CN), 1470 (s), 1460 (s), 1395 (m), 1375 (m), 1250 (w), 1210 (w), 1100 (w), 735 (w) cm⁻¹. **¹H NMR** (CDCl₃, 20 °C,

400 MHz): δ = 0.94 (m, 3 H), 1.35 (s, 6 H), 1.50 (m, 6 H) ppm. ^{13}C NMR (CDCl_3 , 20 °C, 101 MHz): δ = 13.76, 22.60, 26.57, 27.29, 32.26 (s), 40.71, 125.07 (s, CN) ppm.

2,2-Dimethylheptanenitrile (7): Sodium metal (18.0 g, 785 mmol) was dissolved in liquid ammonia (250 mL), treated with the amount of a micro spatulum of iron(III)nitrate, allowed to stand for 1 h, treated drop wise with stirring within 1 h with a solution of isobutyronitrile (34.5 g, 500 mmol) and 1-bromopentane (98.2 g, 650 mmol) in anhydrous ether (150 mL), stirred for 1 h, allowed to warm to room temperature while evaporating the ammonia (5 h), treated with anhydrous ether (250 mL), stirred for 1 d, treated drop wise with anhydrous ethanol (50 mL) for the degradation of residual sodium amide, hydrolyzed with distilled water, acidified with 2 N sulfuric acid separated from the aqueous phase with extraction of the latter (3×50 mL), dried with magnesium sulfate, evaporated and distilled. Yield 36.4 g (52 %), b.p. 72–74 °C/24 mbar, n_D^{20} = 1.4167. **IR** (film): $\tilde{\nu}$ = 2970 (s), 2940 (s), 2870 (s), 2240 (m, CN), 1470 (s), 1395 (m), 1375 (m), 1240 (w), 1215 (w), 735 (w) cm^{-1} . **^1H NMR** (CDCl_3 , 20 °C, 400 MHz): δ = 0.90 (m, 3 H), 1.33 (s, 6 H), 1.49 (m, 8 H) ppm. ^{13}C NMR (CDCl_3 , 20 °C, 101 MHz): δ = 13.76, 22.27, 24.75, 26.51, 31.63, 32.23 (s), 40.93, 124.98 (s, CN) ppm.

2-Cyclohexyl-2-methylpropionitrile (8): Sodium metal (18.0 g, 785 mmol) was dissolved in liquid ammonia (250 mL), treated with the amount of a micro spatulum of iron(III)nitrate, allowed to stand for 1 h, treated drop wise with stirring within 1 h with a solution of isobutyronitrile (34.5 g, 500 mmol) and 1-bromocyclohexane (106 g, 650 mmol) in anhydrous ether (150 mL), stirred for 1 h, allowed to warm to room temperature while evaporating the ammonia (5 h), treated with anhydrous ether (250 mL), stirred for 1 d, treated drop wise with anhydrous ethanol (50 mL) for the degradation of residual sodium amide, hydrolyzed with distilled water, acidified with 2 N sulfuric acid separated from the aqueous phase with extraction of the latter (3×50 mL), dried with magnesium sulfate, evaporated and distilled. Yield 34.5 g (46 %), b.p. 165–166 °C/27 mbar, n_D^{20} = 1.4577. **IR** (film): $\tilde{\nu}$ = 2980 (s), 2930 (s), 2850 (s), 2230 (m, CN), 1450 (s), 1390 (m), 1370 (m) 1255 (m), 1220 (w), 1200 (m), 1030 (w), 900 (m), 850 (w), 690 (w) cm^{-1} . **^1H NMR** (CDCl_3 , 20 °C, 400 MHz): δ = 1.19 (m, 1 H), 1.33 (s, 6 H), 1.83 (m, 10 H) ppm. ^{13}C NMR (CDCl_3 , 20 °C, 101 MHz): δ = 27.42, 25.96, 26.29, 27.90, 36.26 (s), 45.83, 124.95 (s, CN) ppm.

2,2-Dipentyl-heptanenitrile (9): Sodium metal (30.0 g, 1.3 mol) was dissolved in liquid ammonia (250 mL), treated with the amount of a micro spatulum of iron (III)nitrate, allowed to stand for 1 h, treated drop wise with stirring within 1 h with a solution of acetonitrile (12.25 g, 300 mmol) and 1-bromopentane (179.7 g, 1.19 mol) in anhydrous ether (150 mL), stirred for 1 h, allowed to warm to room temperature while evaporating the ammonia (5 h), treated with anhydrous ether (250 mL), stirred for 1 d, treated drop wise with anhydrous ethanol (50 mL) for the degradation of residual sodium amide, hydrolyzed with distilled water, acidified with 2 N sulfuric acid separated from the aqueous phase with extraction of the latter (3×50 mL), dried with magnesium sulfate, evaporated and distilled. Yield 56.2 g (75 %), b.p. 108–110 °C/0.53 mbar, n_D^{20} = 1.4448. **IR** (film): $\tilde{\nu}$ = 2980 (s), 2940 (s), 2870 (s), 2230 (m, CN), 1465 (s), 1385 (m), 1160 (w), 1115 (w), 730 (w) cm^{-1} . **^1H NMR** (CDCl_3 , 20 °C, 400 MHz): δ = 0.90 (m, 9 H), 1.30 (m, 24 H) ppm. ^{13}C NMR (CDCl_3 , 20 °C, 101 MHz): δ = 13.94, 22.42, 23.93, 31.90, 36.11, 40.62 (s), 124.34 (s, CN) ppm.

2-Butyl-2-propylhexanenitrile (10): Sodium metal (18.0 g, 785 mmol) was dissolved in liquid ammonia (250 mL), treated with the amount of a micro spatulum of iron(III)nitrate, allowed to stand

for 1 h, treated drop wise with stirring within 1 h with a solution of valeronitrile (14.2 g, 174 mmol) and 1-bromobutane (95.0 g, 695 mmol) in anhydrous ether (150 mL), stirred for 1 h, allowed to warm to room temperature while evaporating the ammonia (5 h), treated with anhydrous ether (250 mL), stirred for 1 d, treated drop wise with anhydrous ethanol (50 mL) for the degradation of residual sodium amide, hydrolyzed with distilled water, acidified with 2 N sulfuric acid separated from the aqueous phase with extraction of the latter (3×50 mL), dried with magnesium sulfate, evaporated and distilled. Yield 15.3 g (46 %), b.p. 117–119 °C/24 mbar, n_D^{20} = 1.4381. **IR** (film): $\tilde{\nu}$ = 2960 (s), 2930 (s), 2860 (s), 2225 (m, CN), 1470 (s), 1380 (m), 1345 (w), 1105 (w), 935 (w), 900 (w), 790 (w), 735 (m) cm^{-1} . ^{13}C NMR (CDCl_3 , 20 °C, 101 MHz): δ = 13.88, 14.21, 17.66, 22.87, 26.45, 35.93, 38.44, 40.62 (s), 124.37 (s, CN) ppm.

Preparation of the Nitrile Complexes

The starting complexes $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{I}^{[29]}$ and $\text{CpRu}(\text{CO})(\text{PPh}_3)\text{Cl}^{[30]}$ were prepared as described.

General Method for the Preparation of the Iron Complexes 1a, 3a–11a, and 12: To a suspension of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{I}$ (118 mg, 0.22 mmol) and AgBF_4 (44 mg, 0.22 mmol) in dichloromethane (5 mL) the corresponding nitrile (0.22 mmol) was added. The mixture was stirred under exclusion of light at room temperature for 20 min, whereby the dark green suspension quickly turned to dark red. AgI was separated by centrifugation and the solvent was removed in vacuo from the solution. The residue was washed with ethyl ether, then with *n*-pentane. All the iron complexes are brick colored and stable on air.

(Carbonyl)(cyclopentadienyl)(1-ethylcyclohexanecarbonitrile)(triphenylphosphine)iron-tetrafluoroborate (1a): Yield 127 mg (88 %). M.p. 135 °C (dec.). **IR** (KBr): $\tilde{\nu}$ = 2261 w (CN), 1980s (CO), 1055 vs, br (BF_4) cm^{-1} . **^1H NMR** ($[\text{D}_6]\text{acetone}$, 270 MHz): δ = 0.79 (t, J = 7.5 Hz, 3 H, CH_3), 1.00–1.71 (m, 24 H, CH_2), 1.41 (q, J = 7.5 Hz, 2 H, CH_2CH_3), 5.09 (d, J = 1.5 Hz, 5 H, Cp), 7.43–7.67 (m, 15 H, PPh_3) ppm. **^{31}P NMR** ($[\text{D}_6]\text{acetone}$, 109.4 MHz): δ = 66.84 (s) ppm. $\text{C}_{33}\text{H}_{35}\text{BF}_4\text{FeNOP} \cdot 0.25\text{CH}_2\text{Cl}_2$ (656.5): calcd. C 60.83, H 5.45, N 2.13 %; found C 60.35, H 5.88, N 2.35 %.

(Carbonyl)(2-butyl-2-methylhexanenitrile)(cyclopentadienyl)(triphenylphosphine)iron-tetrafluoroborate (3a): Yield 130 mg (89 %). M.p. 124 °C (dec.). **IR** (KBr): $\tilde{\nu}$ = 2264 w (CN), 1979s (CO), 1054 vs, br (BF_4) cm^{-1} . **^1H NMR** ($[\text{D}_6]\text{acetone}$, 270 MHz): δ = 0.85, 0.92 (t, J = 7.1 Hz, 6 H, CH_3), 1.08, 1.10 (s, 3 H, CCH_3), 1.13–1.34 (m, 12 H, CH_2), 5.07 (s, 5 H, Cp), 7.35–7.64 (m, 25 H, PPh_3) ppm. ^{13}C NMR- ($\text{acetone-}d_6$, 100.5 MHz): δ = 9.90, 18.91 (CH_3), 18.99, 19.19, 23.36, 23.41, (CH_2), 23.50 (CCH_2), 34.58 (CCH_3), 34.94, 36.56 (CCH_2), 81.78 (Cp), 126.07 (d, J = 10.0 Hz, *m*) 128.27 (s, *p*), 129.22 (d, J = 46.4 Hz, *I*), 129.99 (d, J = 10.5 Hz, *o*), 140.41 (CN) ppm. **^{31}P NMR** ($[\text{D}_6]\text{acetone}$, 109.4 MHz): δ = 67.16 (s) ppm. $\text{C}_{35}\text{H}_{41}\text{BF}_4\text{FeNOP} \cdot 0.25\text{CH}_2\text{Cl}_2$ (686.6): calcd. C 61.67, H 6.09, N 2.04 %; found C 61.90, H 5.83, N 2.65 %.

(Carbonyl)(cyclopentadienyl)(2,2-dibutylhexanenitrile)(triphenylphosphine)iron-tetrafluoroborate (4a): Yield 153 mg (87 %). M.p. 141 °C (dec.). **IR** (KBr): $\tilde{\nu}$ = 2267 vw (CN), 1976s (CO), 1052 vs, br (BF_4) cm^{-1} . **^1H NMR** ($[\text{D}_6]\text{acetone}$, 270 MHz): δ = 0.84 (m, 9 H, CH_2CH_3), 1.14–1.44 (m, 18 H, CH_2), 5.07 (d, J = 1.4 Hz, 5 H), 7.21–7.69 (m, 15 H) ppm. **^{31}P NMR** ($[\text{D}_6]\text{acetone}$, 109.4 MHz): δ = 66.92 ppm. $\text{C}_{38}\text{H}_{47}\text{BF}_4\text{FeNOP} \cdot \text{CH}_2\text{Cl}_2$ (792.4): Calcd. C 59.12, H 6.23, N 1.77; found C 59.92, H 6.25, N 1.55.

(Carbonyl)(cyclopentadienyl)(2,2-dimethylpentanenitrile)(triphenylphosphine)iron-tetrafluoroborate (5a): Yield 130 mg (90 %). M.p. 138 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2265 vw (CN), 1974s (CO), 1055vs,br (BF₄) cm⁻¹. ¹H NMR ([D₆]acetone, 270 MHz): δ = 0.84 (t, *J* = 7.1 Hz, 3 H, CH₂CH₃), 1.08, 1.10 (s, 6 H, CCH₃), 1.29–1.39 (m, 4 H, CH₂), 5.07 (d, *J* = 1.4 Hz, 5 H), 7.43–7.67 (m, 15 H) ppm. ¹³C NMR (acetone-D₆, 67.8 MHz): δ = 13.36 (CH₂CH₃), 18.34 (CH₂CH₃), 24.80, 25.40 (C(CH₃)₂), 35.49 (C(CH₃)₂), 41.94 (CCH₂) ppm. ³¹P NMR ([D₆]acetone, 109.4 MHz): δ = 67.52 (s) ppm. C₃₁H₃₃BF₄FeNOP•0.5 CH₂Cl₂ (651.7): calcd. C 58.06, H 5.26, N 2.15; found C 58.68, H 5.09, N 1.75.

(Carbonyl)(cyclopentadienyl)(2,2-dimethylhexanenitrile)(triphenylphosphine)iron-tetrafluoroborate (6a): Yield 140 mg (95 %). M.p. 133 °C. IR (KBr): $\tilde{\nu}$ = 2264 vw (CN), 1978s (CO), 1055vs. (BF₄) cm⁻¹. ¹H NMR ([D₆]acetone, 270 MHz): δ = 0.86 (t, *J* = 6.2 Hz, 3 H, CH₂CH₃), 1.10 (s, 6 H, CCH₃), 1.22–1.35 (m, 6 H, CH₂), 5.09 (s, 5 H), 7.21–7.88 (m, 15 H) ppm. ³¹P NMR ([D₆]acetone, 109.4 MHz): δ = 67.53 (s) ppm. C₃₂H₃₅BF₄FeNOP•0.5 CH₂Cl₂ (665.7): calcd. C 58.64, H 5.45, N 2.10%; found C 58.81, H 5.25, N 1.74%.

(Carbonyl)(cyclopentadienyl)(2,2-dimethylheptanenitrile)(triphenylphosphine)iron-tetrafluoroborate (7a): Yield 131 mg (88 %). M.p. 119 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2266 vw (CN), 1977s (CO), 1056vs,br (BF₄) cm⁻¹. ¹H NMR ([D₆]acetone, 270 MHz): δ = 0.87 (t, *J* = 7.1 Hz, 3 H, CH₂CH₃), 1.09, 1.11 (s, 6 H, CCH₃), 1.16–1.34 (m, 10 H, CH₂), 5.07 (d, *J* = 1.4 Hz, 5 H), 7.25–7.88 (m, 15 H) ppm. ³¹P NMR ([D₆]acetone, 109.4 MHz): δ = 67.49 (s) ppm. C₃₄H₃₉BF₄FeNOP•0.25CH₂Cl₂ (672.6): calcd. C 61.17, H 5.92, N 2.08%; found C 60.81, H 6.09, N 2.09%.

(Carbonyl)(cyclopentadienyl)(2-cyclohexyl-2-methylpropionitrile)(triphenylphosphine)iron-tetrafluoroborate (8a): Yield 125 mg (87 %). M.p. 113 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2269 vw (CN), 1983s (CO), 1057s,br (BF₄) cm⁻¹. ¹H NMR ([D₆]acetone, 270 MHz): δ = 1.06, 1.08 (s, 6 H, CCH₃), 1.16–1.88 (m, 11 H, CH₂ and CH), 5.06 (d, *J* = 1.3 Hz, 5 H), 7.41–7.68 (m, 15 H) ppm. ³¹P NMR ([D₆]acetone, 109.4 MHz): δ = 67.13 (s) ppm. C₃₄H₃₇BF₄FeNOP•1.5CH₂Cl₂ (776.7): calcd. C 54.90, H 5.19, N 1.80%; found C 54.79, H 5.09, N 2.04%.

(Carbonyl)(cyclopentadienyl)(2,2-dipentylheptanenitrile)(triphenylphosphine)iron-tetrafluoroborate (9a): IR (KBr): $\tilde{\nu}$ = 2261 vw (CN), 1979 s (CO), 1055vs,br (BF₄) cm⁻¹. ¹H NMR ([D₆]acetone, 270 MHz): δ = 0.84 (m, 9 H, CH₂CH₃), 0.94–1.40 (m, 24 H, CH₂), 5.07 (s, 5 H), 7.27–7.78 (m, 15 H) ppm. ³¹P NMR ([D₆]acetone, 109.4 MHz): δ = 66.88 (s) ppm.

Carbonyl(cyclopentadienyl)(2-butyl-2-propylhexanenitrile)(triphenylphosphine)iron-tetrafluoroborate (10a): Yield 151 mg (93 %). M.p. 114 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2241 vw (CN), 1980 s (CO), 1054 vs,br (BF₄) cm⁻¹. ¹H NMR ([D₆]acetone, 270 MHz): δ = 0.87, 0.89, 0.92, (t, *J* = 7.3 Hz, 9 H, CH₂CH₃), 1.12–1.62 (m, 16 H, CH₂), 5.08 (d, *J* = 1.4 Hz, 5 H), 7.43–7.68 (m, 15 H) ppm. ³¹P NMR ([D₆]acetone, 109.4 MHz): δ = 66.93 (s) ppm. C₃₇H₄₅BF₄FeNOP•0.5CH₂Cl₂ (735.9): calcd. C 61.21, H 6.30, N 1.90%; found C 60.56, H 6.78, N 1.90%.

(Carbonyl)(cyclopentadienyl)(tridecanenitrile)(triphenylphosphine)iron-tetrafluoroborate (11a): Yield 151 mg (90 %). M.p. 131 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2282 vw (CN), 1980 s (CO), 1055 vs,br (BF₄) cm⁻¹. ¹H NMR ([D₆]acetone, 270 MHz): δ = 0.86 (t, *J* = 7.1 Hz, 3 H, CH₂CH₃), 2.58 (t, *J* = 7.1 Hz, 2 H, NCCH₂), 1.14–1.58 (m, 18 H, CH₂), 5.05 (d, *J* = 1.4 Hz, 5 H), 7.49–7.65 (m, 15 H) ppm.

³¹P NMR ([D₆]acetone, 109.4 MHz): δ = 67.47 (s) ppm. C₃₆H₄₃BF₄FeNOP•CH₂Cl₂ (764.3): calcd. C 58.15, H 5.93, N 1.83%; found C 59.45, H 5.57, N 1.33%.

1,6-Dicyanohexane-bis[(carbonyl)(cyclopentadienyl)(triphenylphosphine)iron]-bis(tetrafluoroborate) (12): Yield 233 mg (84 %). M.p. 107 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2282 vw (CN), 1982 s (CO), 1054 vs, br (BF₄) cm⁻¹. ¹H NMR ([D₆]acetone, 270 MHz): δ = 0.91–1.27 (m, 8 H, (CH₂)₄), 2.51 (m, 4 H, NCCH₂ and CH₂CN), 5.03 (d, *J* = 1.4 Hz, 10 H), 7.46–7.59 (m, 30 H) ppm. ³¹P NMR ([D₆]acetone, 109.4 MHz): δ = 67.49 (s) ppm. C₅₆H₅₂B₂F₈Fe₂N₂O₂P₂•1.5CH₂Cl₂ (1259.7): calcd. C 54.83, H 4.40, N 2.22%; found C 54.93, H 4.68, N 2.27%.

General Method for the Preparation of the Ruthenium Complexes 2b–6b and 11b: To a suspension of CpRu(CO)(PPh₃)Cl (108 mg, 0.22 mmol) and AgBF₄ (45 mg, 0.23 mmol) in dichloromethane (5 mL) the corresponding nitrile (0.22 mol) was added. The mixture was stirred under exclusion of light for 45 min, whereby the yellow color of the mixture became more intensive. AgCl was separated by centrifugation and the solvent was removed in vacuo. The residue was washed with ethyl ether and with *n*-pentane. The yellow complex was dried in vacuo. It turned gradually brown, when exposed under argon to light.

(Carbonyl)(cyclopentadienyl)(1-propylcyclohexanecarbonitrile)(triphenylphosphine)ruthenium-tetrafluoroborate (2b): Yellow complex, which turns brown on light. Yield 137 mg (90 %). M.p. 153 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2266 w (CN), 1972 s (CO), 1054 br (BF₄) cm⁻¹. ¹H NMR ([D₆]acetone, 270 MHz): δ = 0.84 (t, *J* = 7 Hz), 3 H, CH₃), 0.92–1.73 (m, 14 H, CH₂), 5.45 (s, 5 H, Cp), 7.45–7.79 (m, 15 H, Cp) ppm. ³¹P NMR ([D₆]acetone, 109.4 MHz): δ = 49.58 (s) ppm. C₃₄H₃₇BF₄NOPRu: calcd. C 58.80, H 5.37, N 2.02%; found C 58.83, H 5.12, N 1.88%.

(Carbonyl)(2-butyl-2-methylhexanenitrile)(cyclopentadienyl)(triphenylphosphine)ruthenium-tetrafluoroborate (3b): Yield 147 mg (88 %). M.p. 98 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2267 vw (CN), 1981 s (CO), 1053 vs,br (BF₄) cm⁻¹. ¹H NMR ([D₆]acetone, 270 MHz): δ = 0.85, 0.86 (t, *J* = 7.2 Hz, 6 H, CH₂CH₃), 1.13 (s, 3 H, CCH₃), 1.14–1.30 (m, 12 H, CH₂), 5.42 (d, *J* = 0.3 Hz, 5 H), 7.38–7.65 (m, 15 H) ppm. ³¹P NMR ([D₆]acetone, 109.4 MHz): δ = 49.76 (s) ppm. C₃₅H₄₁BF₄NOPRu•0.5 CH₂Cl₂ (753.0): calcd. C 56.62, H 5.62, N 1.86%; found C 56.73, H 5.80, N 2.26%.

(Carbonyl)(cyclopentadienyl)(2,2-dibutylhexanenitrile)(triphenylphosphine)ruthenium-tetrafluoroborate (4b): Yield 164 mg (89 %). M.p. 148 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2264 vw (CN), 1979 s (CO), 1054 vs,br (BF₄) cm⁻¹. ¹H NMR ([D₆]acetone, 270 MHz): δ = 0.85 (t, *J* = 6.8 Hz, 9 H, CH₃), 1.18–1.46 (m, 18 H, CH₂), 5.41 (s, 5 H), 7.38–7.67 (m, 15 H) ppm. ³¹P NMR ([D₆]acetone, 109.4 MHz): δ = 49.68 (s) ppm. C₃₈H₄₇BF₄NOPRu•CH₂Cl₂ (837.6): calcd. C 55.93, H 5.90, N 1.67%; found C 56.16, H 6.23, N 1.71%.

(Carbonyl)(cyclopentadienyl)(2,2-dimethylpentanenitrile)(triphenylphosphine)ruthenium-tetrafluoroborate (5b): Yield 132 mg (86 %). M.p. 115 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2281 vw (CN), 1975 s (CO), 1053 vs,br (BF₄) cm⁻¹. ¹H NMR ([D₆]acetone, 270 MHz): δ = 0.84 (t, *J* = 7.1 Hz, 3 H, CH₃), 1.12, 1.13 (s, 6 H, CCH₃), 1.07–1.32 (m, 4 H, CH₂), 5.42 (s, 5 H), 7.38–7.65 (m, 15 H) ppm. ¹³C NMR ([D₆]acetone, 100.5 MHz): δ = 13.84 (CH₂CH₃), 18.87 (CH₂CH₃), 25.39 (C(CH₃)₂), 35.69 (C(CH₃)₂), 42.49 (CCH₂), 87.65 (Cp), 129.87 (d, *J* = 10.7 Hz, *m*), 132.13 (s, *p*), 133.91 (s, *o*), 134.03 (s, *i*), 133.61 (CN) ppm. ³¹P NMR ([D₆]acetone, 109.4 MHz): δ = 49.88 (s) ppm.

$C_{31}H_{33}BF_4NOPRu \cdot 0.5CH_2Cl_2$ (696.9): calcd. C 54.29, H 4.92 N 2.01%; found C 54.04, H 5.15, N 2.06%.

(Carbonyl)(cyclopentadienyl)(2,2-dimethylhexanenitrile)(triphenylphosphine)ruthenium-tetrafluoroborate (6b): Yield 139 mg (88%). M.p. 125 °C (dec.). IR (KBr): $\tilde{\nu}$ = 22.84 vw (CN), 1983 s (CO), 1055 vs,br (BF₄) cm⁻¹. ¹H NMR ([D₆]acetone, 270 MHz): δ = 0.84 (t, *J* = 7.1 Hz, 3 H, CH₃), 1.13, 1.14 (s, 6 H, CCH₃), 1.06–1.27 (m, 6 H, CH₂), 5.41 (s, 5 H), 7.38–7.77 (m, 15 H) ppm. ³¹P NMR ([D₆]acetone, 109.4 MHz): δ = 49.97 (s) ppm. $C_{32}H_{35}BF_4NOPRu \cdot 0.5CH_2Cl_2$ (711.0): calcd. 54.91, H 5.10, N 1.97%; found C 54.75, H 5.18, N 2.17%.

(Carbonyl)(cyclopentadienyl)(tridecanenitrile)(triphenylphosphine)ruthenium-tetrafluoroborate (11b): Oily product. IR (KBr): $\tilde{\nu}$ = 2293 vw (CN), 1982 s (CO), 1056 vs,br (BF₄) cm⁻¹. ¹H NMR ([D₆]acetone, 270 MHz): δ = 0.84 (t, *J* = 7.1 Hz, 3 H, CH₃), 1.14–1.23 (m, 16 H, CH₂), 2.61 (m, 2 H, NCCH₂), 5.35 (s, 5 H), 7.46–7.59 (m, 15 H) ppm. ¹³C NMR ([D₆]acetone, 100.5 MHz): δ = 14.20 (CH₃), 19.22 (NCCH₂), 23.11, 25.10, 32.40 (CH₂), 87.66 (Cp), 129.83 (d, *J* = 10.7 Hz, *m*), 132.01 (d, *J* = 2, *p*), 133.43 (d, *J* = 49.0 Hz, *i*), 134.05 (d, *J* = 12.1 Hz, *o*), 133.86 (CN), 201.71 (d, *J* = 0.2 Hz, CO) ppm. ³¹P NMR ([D₆]acetone, 109.4 MHz): δ = 50.14 (s) ppm.

Crystal Structure Determination of Complex 4b: A yellowish-orange platelet (dimensions: 0.78 × 0.38 × 0.15 mm³) was mounted on top of a glass fibre, using epoxy glue, and transferred to a SYNTeX R3 diffractometer. Data collection was performed in omega-scan mode, using Mo-*K*_α radiation with a graphite monochromator. Data collection and data processing was done with the XDISK program routine of the diffractometer. The structure was solved with SHELXS-86^[31a] and refined with SHELXL Version 2014/7.^[31b] Further details relating to the data collection and refinement are collected in Table 1

Table 1. Experimental details for the structure determination of 4b.

	4b
Empirical formula	C ₃₈ H ₄₇ BF ₄ NOPRu
Formula weight	752.61
Temperature /K	293(2)
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	10.062(4)
<i>b</i> /Å	18.740(9)
<i>c</i> /Å	22.136(10)
β	98.94(3)°
Volume /Å ³	4123(3)
<i>Z</i>	4
ρ_{calc} /g·cm ⁻³	1.212
μ /mm ⁻¹	0.464
θ range for data collection /°	2.049 to 20.045
Reflections measured	4248
<i>R</i> _{int}	0.0747
Observed reflections	3872
Absorption correction	Empirical (SHELXA)
Max. and min. transmission	0.8191 and 0.3171
Parameters/restraints	284/21
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.1020, <i>wR</i> ₂ = 0.2613
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1727, <i>wR</i> ₂ = 0.3130
<i>S</i>	1.018
Max electron density /e·Å ⁻³	1.127
Min electron density /e·Å ⁻³	−0.556
CCDC	no 1574068

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