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Electronic Supplementary Information

for

A stable crystalline N-heterocyclic carbene with a 1,1´-ferrocenediyl backbone

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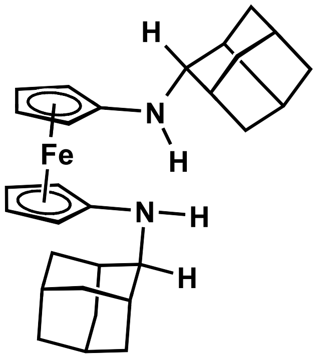
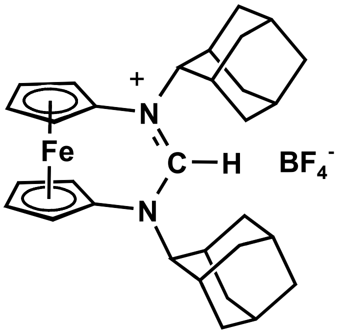
General considerations. All reactions were carried out by applying standard Schlenk techniques. Solvents were appropriately dried and purified prior to use. 1,1'-Diaminoferrocene was prepared according to a literature procedure.[S1] Lithium diisopropylamide was prepared by reaction of *n*-butyllithium with diisopropylamine at room temperature in hexane, isolated by filtration and dried *in vacuo*. Starting materials were procured from standard commercial sources and used as received.
NMR: Varian Unity Inova 500 spectrometer operating at 500.13 MHz for ^{1}H; IR: Bio-Rad FTS-40A; electron spray ionisation (ESI) mass spectra: Finnigan LCQ Deca; high-resolution mass spectra (HRMS): Bruker Daltonics micrOTOF. Elemental analyses were performed by the microanalytical laboratories of the University of Kassel and the Institute of Organic Chemistry, University of Halle.

1,1'-Di(2-adamantylamino)ferrocene



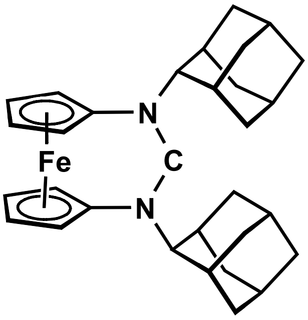
2-Adamantanone (5.03 g, 33.5 mmol) and *p*-toluene sulfonic acid monohydrate (64 mg, 0.34 mmol) were added to a solution of 1,1'-diaminoferrocene (3.62 g, 16.8 mmol) in toluene (225 ml). The flask was equipped with a water separator and a reflux condenser and the mixture refluxed for 48 h. The solvent was subsequently removed *in vacuo*. Lithium aluminium hydride (1.59 g, 41.9 mmol) and THF (100 ml) were added and the mixture was stirred at 50 °C for 1 h. The suspension was cooled in an ice bath and hydrolised by dropwise addition of water (2.9 ml, 161 mmol). The mixture was subsequently filtered through a celite pad, which was subsequently extracted with THF (50 ml). Volatile components were removed *in vacuo*. Recrystallisation of the crude product from toluene afforded an orange, microcrystalline solid. Yield 6.30 g (78%). M.p. 140–141.5 °C. ^{1}H NMR (C_6D_6): δ 3.92 (s, 4H), 3.83 (s, 4H), 3.28 (s, 2H), 2.39 (s, 2H), 2.04–1.96 (m, 8H), 1.84–1.71 (m, 12 H), 1.68 (s, 4H), 1.50–1.43 (m, 4H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 110.4, 63.8, 61.8, 57.6, 37.7, 32.2, 32.0, 28.0. ESI(+)/MS: *m*/*z* (%) = 484.6 (100) $[M]^+$. Anal. calcd for $C_{30}H_{40}N_2Fe$: C, 74.37; H, 8.32; N, 5.78; found C, 73.39; H, 8.28; N, 5.49%.

Formamidinium tetrafluoroborate 1c



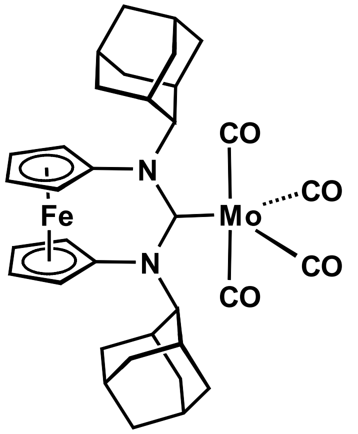
Toluene (50 ml) was added to 1,1'-di(2-adamantylamino)ferrocene (2.50 g, 5.16 mmol), ammonium tetrafluoroborate (0.54 g, 5.16 mmol) and triethyl orthoformiate (0.76 g, 5.16 mmol). The mixture was refluxed for 2.5 h and subsequently allowed to cool to room temperature. Dichloromethane (25 ml) was added and the mixture filtered. The filtrate was concentrated to *ca.* 15 ml. The product was precipitated by slow addition of hexane (25 ml), isolated by filtration and dried *in vacuo*. Yield 1.27 g (42%). Crystals suitable for a single-crystal X-ray-diffraction study were obtained by cooling a solution of **1c** in dichloromethane to –40 °C. ^{1}H NMR ($CDCl_3$): δ 8.03 (s, 1H), 4.61 (s, 4H), 4.38 (s, 4H), 4.08 (s, 2H), 2.38 (s, 4H), 1.97–1.54 (m, 24H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 158.2, 92.7, 72.3, 71.1, 67.8, 36.8, 30.6, 29.7, 26.9, 26.5. ESI(–)/MS *m*/*z* (%) = 668.93 (100%) $[M+BF_4]^-$; ESI(+)/MS *m*/*z* (%) = 495.40 (100%) $[M–BF_4]^+$. Anal. calcd. for $C_{31}H_{39}N_2BF_4Fe$: C, 63.94; H, 6.75; N, 4.81; found C, 63.85; H, 6.74; N, 4.80 %.

N-heterocyclic carbene 2c



Lithium diisopropylamide (17.5 mg, 0.16 mmol) was added to a suspension of **1c** (95 mg, 0.16 mmol) in THF (3 ml). The red solution, which formed immediately, was stirred for 15 minutes. Volatile components were removed *in vacuo*. The yellowish residue was extracted with *n*-hexane (5 ml) and the extract filtered. The filtrate was concentrated and stored at –40 °C to afford **2c** as an orange-brown microcrystalline solid. Yield 32 mg (40%). Crystals suitable for a single-crystal X-ray-diffraction study were obtained by recrystallisation from toluene. ^{1}H NMR (C_6D_6): δ 3.99 (s, 4H), 3.88 (s, 4H), 3.75 (s, 2H), 2.82 (s, 4H), 2.66 (d, *J* = 11.7 Hz, 4H), 1.98 (s, 2H), 1.92–1.81 (m, 6H), 1.79–1.72 (m, 8H), 1.59 (d, *J* = 11.7 Hz, 4H). ^{13}C{^{1}H} NMR (C_6D_6): δ 260.7, 101.8, 72.0, 70.7, 67.7, 39.4, 39.2, 32.5, 32.3, 29.2, 29.1. ESI(+)/MS *m*/*z* (%) = 495.45 (100%) $[M]^+$. HRMS/ESI(+) *m*/*z* = 495.2453 $[M+H]^+$, calcd. for $[C_{31}H_{39}N_2Fe]$ = 495.2458.

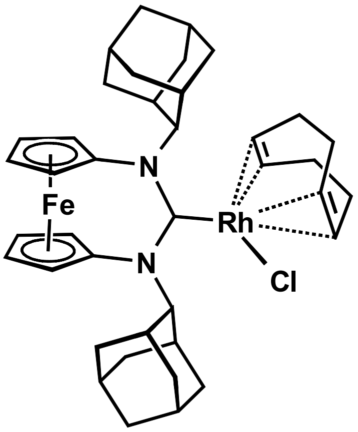
[Mo(2c)(CO)$_4$]



Serendipitous preparation from [Mo(CO)$_6$]:
A solution of molybdenum hexacarbonyl (48 mg, 0.18 mmol) in THF (3 ml) was refluxed for 45 minutes. The yellow solution was subsequently allowed to cool to room temperature. A solution of **2c** (89 mg, 0.18 mmol) in toluene (2 ml) was added dropwise and the mixture stirred for 14 h. NMR spectroscopy revealed the presence of unreacted **2c** and no indication of a complex formation was obvious. Nevertheless, on prolonged standing a few orange crystals formed. One of these was used for a single-crystal X-ray diffraction study, which proved that a small amount of [Mo(**2c**)(CO)$_4$] had formed.

Rational synthesis from [Mo(CO)$_4$(nbd)]:
Lithium diisopropylamide (18.4 mg, 0.17 mmol) was added to a stirred suspension of **1c** (100 mg, 0.17 mmol) in THF (3 ml). A red solution of **2c** formed immediately, which was allowed to stir for 15 minutes. The solvent was removed *in vacuo*. The residue was extracted with *n*-hexane (5 ml) and the extract filtered. A solution of [Mo(CO)$_4$(nbd)] (51 mg, 0.17 mmol) in *n*-hexane (2 ml) was added dropwise to the filtrate. The solution was stirred for 15 hours, during which time a dark orange precipitate formed, which was collected by filtration. The solid was dried *in vacuo*. Yield 30 mg (25%). ^{1}H NMR (CD$_2$Cl$_2$): δ 4.48 (s, 4H), 4.39 (s, 4H), 3.86 (s, 2H), 2.23 (s, 4H), 1.95–1.86 (m, 8H), 1.84–1.71 (m, 12H), 1.65–1.59 (m, 4H). ^{13}C NMR (CD$_2$Cl$_2$): δ 205.8, 201.6, 92.7, 72.8, 72.4, 69.1, 37.4, 37.1, 31.0, 27.4, 27.2. The intensity ratio of the two carbonyl C signals at low field was unity, indicating the presence of two sets of chemically inequivalent carbonyl groups with equal numbers of CO ligands. A downfield signal for the carbene C atom could not be detected despite a prolonged acquisition time. IR(ATR): ν(CO) = 2025 m, 1905 s, 1876 s, 1828 s cm^{-1}. Four carbonyl bands are expected for a trigonal bipyramidal C_{2v} symmetric tetracarbonyl complex.[S2] Anal. calcd. for $C_{35}H_{38}N_2FeMoO_4$: C, 59.84; H, 5.45; N, 3.99; found C, 60.08; H, 5.82; N, 4.03 %.

[RhCl(2c)(cod)]



Toluene (3 ml) was added to **2c** (84 mg, 0.17 mmol) and [{RhCl(cod)}$_2$] (42 mg, 0.085 mmol). A yellow precipitate formed almost immediately from the stirred solution. The mixture was stirred for 14 h, filtered and dried *in vacuo* to obtain a yellow, crystalline solid. Yield 63 mg (50 %). Crystals suitable for a single-crystal X-ray-diffraction study were obtained by slow evaporation of a dichloromethane solution of the product. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.58 (s, 2H), 4.84 (s, 2H), 4.31 (s, 2H), 4.22 (s, 4H), 3.87 (s, 2H), 3.15 (s, 2H), 2.62 (s, 2H), 2.53–2.45 (m, 4H), 2.44–2.36 (m, 4H), 2.31–2.24 (m, 2H), 2.21 (s, 2H), 2.03–1.95 (m, 4H), 1.88–1.78 (m, 6H), 1.73–1.62 (m, 6H), 1.56–1.50 (m, 2H), 1.27–1.16 (m, 4H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ .129.2, 97.0, 93.6 (d, J_{RhC} = 7.2 Hz), 71.7, 71.0, 70.55 (d, J_{RhC} = 14.5 Hz), 70.5, 70.3, 69.9, 41.4, 40.4, 38.8, 34.9, 34.0, 32.8, 32.1, 31.4, 29.3, 28.7, 27.4; a downfield signal for the carbene C atom could not be detected despite a prolonged acquisition time. ESI(+)/MS *m*/*z* (%) = 740.25 (100%) [M]$^+$. Anal. calcd. for $C_{39}H_{50}N_2ClFeRh$: C, 63.21; H, 6.80; N, 3.78; found C, 62.96; H, 6.77; N, 3.60%.

X-ray crystallography

For each data collection a single crystal was mounted on a glass fibre and all geometric and intensity data were taken from this sample. Data collection using MoKα radiation (λ = 0.71073 Å) was made on a Stoe IPDS2 diffractometer equipped with a 2-circle goniometer and an area detector. Absorption correction was done by integration using X-red, except for **1c**.[S3] The data sets were corrected for Lorentz and polarisation effects. The structures were solved by direct methods (SHELXS97) and refined using alternating cycles of least squares refinements against F^2 (SHELXL97).[S4] H atoms were placed in constrained positions according to the riding model with the 1.2 fold isotropic displacement parameters. All non H atoms were found in difference Fourier maps and were refined with anisotropic displacement parameters. Exceptions occur with some of the carbon atoms of **2c** and [Mo(**2c**)(CO)$_4$]. In the case of **2c**, the carbon atoms of the solvent molecule had to be refined isotropically without H atoms. The weak scattering behaviour of the present crystal of **2c** is a result of (*i*) lack in size and (*ii*) partial occupation of void space by solvent molecules (toluene) and (*iii*) the disorder of one adamantyl group. Nevertheless, the result of the crystal structure analysis proves the identity of the compound, since the quality of the data obtained allows establishing all connectivities unambiguously. The crystal structure analysis of [Mo(**2c**)(CO)$_4$] suffers from the low completeness of the data (93 %). Unfortunately, the measurement stopped prior to the sufficient number of scans as a consequence of icing and no other single crystal has been available. The small number of independent reflections observed for [Mo(**2c**)(CO)$_4$] leads to the isotropic refinement of C9, which is located close to an electron-rich heavy atom bonding partner (Mo). The displacement ellipsoid of C9 of [RhCl(**2c**)(cod)] is notably elongated orthogonally to its C–C bond axes, which might indicate a minor disorder problem. Graphical representations were made using ORTEP-3 win.[S5]

References to Supplementary Information

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