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Coordinative trapping of the boron β-diketiminato system [B(NMesCMe)$_2$CH] via metal-templated synthesis

Erkan Firinci, Joshua I. Bates, Ian M. Riddlestone, Nicholas Phillips, and Simon Aldridge

Supporting Information (14 pages)

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1. General methods and instrumentation

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with dinitrogen and dried by passing through a column of the appropriate drying agent. Fluorobenzene was dried by refluxing over calcium hydride, distilled, sparged and stored over activated molecular sieve. NMR spectra were recorded in C_6D_6 or CD_2Cl_2 which was dried over potassium (C_6D_6) or molecular sieve (CD_2Cl_2), distilled under reduced pressure and stored under dinitrogen in Teflon valve ampoules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra were recorded on a Varian Mercury-VX-300 spectrometer and referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). ^{11}B and ^{19}F NMR spectra were referenced to $Et_2O{\cdot}BF_3$ and $CFCl_3$, respectively. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Infrared spectra were measured on a Nicolet 500 FT-IR spectrometer. Mass spectra of compound **4** were recorded on a Bruker Microtof mass spectrometer; all other mass spectra were measured by the EPSRC National Mass Spectrometry Service Centre, Swansea University. Elemental analyses were carried out by Stephen Boyer at London Metropolitan University.

Starting materials **1**,[s1] MesN(H)C(Me)CHC(Me)NMes,[s2] Li[(NMesCMe)$_2$CH],[s3] Li[(N^{i}Pr)$_2$CPh],[s4] and Na[BAr$^f_4$] (Ar^f = $C_6H_3(CF_3)_2$-3,5)[s5] were prepared by literature procedures.

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2. Syntheses of new compounds

$Cp^*Fe(CO)_2B(Cl)\{(N^iPr)_2CPh\}$, **2**: A solution **1** prepared in situ from $Na[Cp^*Fe(CO)_2]$ (0.27 g, 1.00 mmol) and BCl_3 (1.0 mL of a 1.0 M solution in heptane, 1.00 mmol) in toluene (10 mL) was transferred onto a suspension of $Li[(N^iPr)_2CPh]$ (1.0 equiv.) also in toluene (10 mL) at -78 °C. After warming to -30 °C and removal of the solvent in vacuo, the resulting brown residue was extracted into hexanes (30 ml). The dark red solution was concentrated to a volume of about 10 mL and stored at -30 °C, affording pale yellow crystals of **2** (isolated yield 0.13 g, 26%). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ_H 1.17 (d, $^3J_{HH}$= 6 Hz, 6H, ^{i}Pr CH_3), 1.58 (d, $^3J_{HH}$ = 6 Hz, 6H, ^{i}Pr CH_3), 1.83 (s, 15H, Cp* CH_3), 3.89 (sept, $^3J_{HH}$= 6 Hz, 2H, ^{i}Pr C*H*), 6.95-7.36 (m, Ph *H*, 5H). ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ_C 10.4 (Cp* *C*H$_3$), 22.5 (^{i}Pr *C*H$_3$), 24.0 (^{i}Pr *C*H$_3$), 46.3 (^{i}Pr *C*H), 95.2 (Cp*), 127.8, 128.2, 128.9, 130.2 (Ph *C*), 163.0 (N*C*N), 221.8 (*C*O). ^{11}B NMR (96 MHz, C_6D_6, 298 K): δ_B 21. IR (CH_2Cl_2, ν_{CO}/cm^{-1}): 1962, 1900. HR-MS (EI): *m/z*: 466.1843, calcd. for $(C_{24}H_{34}BClFeN_2O)^+$= 466.1846 $[(M\text{-}CO)^+]$

$Cp^*Fe(CO)_2B(Cl)[\kappa^1\text{-}\{(NMesCMe)_2CH\}]$, **3**: A solution of **1** prepared in situ from $Na[Cp^*Fe(CO)_2]$ (0.27 g, 1.00 mmol) and BCl_3 (1.0 mL of a 1.0 M solution in heptane, 1.00 mmol) in toluene (10 mL) was transferred onto a solution of $Li[(NMesCMe)_2CH]$ (1.0 equiv.) also in toluene (10 mL) at -78 °C, and the reaction mixture warmed to room temperature. The resulting mixture was slowly warmed to room temperature and stirred for 12 h. Removal of volatiles in vacuo gave a brown residue, which was extracted with pentane (50 ml), concentrated (to ca. 20 ml) and cooled to -30 °C, affording colourless crystals of **3** (isolated yield 0.15 g, 24%). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ_H 1.67 (s, 15H, Cp* CH_3), 1.69 (s, 3H, Mes *p*-CH_3), 2.09 (s, 6H, Mes *o*-CH_3), 2.12 (s, 3H, CCH_3), 2.24 (s, 3H, CCH_3), 2.34 (s, 3H, Mes *p*-CH_3), 2.44 (s, 6H, Mes *o*-CH_3), 6.19 (s, 1H, CC*H*C), 6.82 (s, 2H, Ar-*H*), 6.87 (s, 2H, Ar-*H*). ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ_C 10.2 (Cp* *C*H$_3$), 18.5 (*C*H$_3$), 19.6 (*C*H$_3$), 19.8 (*C*H$_3$), 20.8 (*C*H$_3$), 21.0 (*C*H$_3$), 21.6 (*C*H$_3$), 96.6 (Cp*), 125.3 (C*C*HC), 129.1, 129.9, 130.1, 131.5, 135.8, 136.1, 143.1, 147.8 ,(Ar*C*), 151.4 (C*C*N), 164.4 (C*C*=N), 216.9 (*C*O). ^{11}B NMR (96 MHz, C_6D_6, 298 K): δ_B 73 (br). IR (CH_2Cl_2, ν_{CO}/cm^{-1}): 1986, 1930. HR-MS (EI): *m/z*: 596.2626, calcd. for $(C_{34}H_{44}BClFeN_2O)^+$= 596.2627 $[(M\text{-}CO)^+]$

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3. Crystallographic details

2: $C_{25}H_{34}N_2BClFeO_2$, M_r = 496.67, monoclinic, $P2_1/n$, a = 12.3060(1), b = 15.6594(2), c = 13.3532(2) Å, β = 92.941(1)°, V = 2569.8(1) Å^3, Z = 4, ρ_c = 1.284 Mg m^{-3}, T = 150(2) K, λ = 0.71073 Å. 5857 independent reflections [R(int) = 0.027], used in all calculations. R_1 = 0.0358, wR_2 = 0.0810 for $F^2 > 2\sigma(F^2)$, and R_1 = 0.0577, wR_2 = 0.1039 for all unique reflections. Max./min. residual electron densities 0.56 and –0.48 e Å^{-3}. CSD ref.: 908735.

3: $C_{35}H_{44}N_2BClFeO_2$, M_r = 626.86, monoclinic, $P2_1/n$, a = 13.9947(2), b = 16.4994(2), c = 14.7643(2) Å, β = 95.885(1)°, V = 3391.2(1) Å^3, Z = 4, ρ_c = 1.228 Mg m^{-3}, T = 150(2) K, λ = 0.71073 Å. 7705 independent reflections [R(int) = 0.044], used in all calculations. R_1 = 0.0470, wR_2 = 0.0955 for $F^2 > 2\sigma(F^2)$, and R_1 = 0.0860, wR_2 = 0.1316 for all unique reflections. Max./min. residual electron densities 0.63 and –0.66 e Å^{-3}. CSD ref.: 908736.

4. Details of DFT calculations

The DFT calculations were performed using the Amsterdam Density Functional (ADF) Package Software 2012.[s6] Calculations were performed using the Vosko-Wilk-Nusair local density approximation with exchange from Becke[s7] and correlation corrections from Perdew[s8] (BP). Slater-type orbitals (STOs)[s9] were used for the triple zeta basis set with an additional set of polarization functions (TZP). The large frozen core basis set approximation was applied with no molecular symmetry. The general numerical integration was 6. Frequency calculations were performed for the cationic metal complexes and no significant imaginary frequencies were observed. Estimates of binding energies were obtained following the strategy outlined by Baerends[s10] using the counterpoise method.[s11] Calculations of ^{11}B NMR chemical shifts were performed using the NMR program contained in the ADF Package.[s12] Chemical shifts are referenced to $Et_2O.BF_3$ (δ = 0 ppm) as the experimental standard. For optimized coordinate of the calculated complexes, see the frequency calculation run files (below).

Table s1: Binding Energy Summary {$\Delta E_{(Binding)} = \Delta E_{(Complex)} - \Delta E_{(Free\ Fragments)}$}[a]

	From Closed Shell Fragments (kcal mol^{-1})	From Open Shell Fragments (kcal mol^{-1})
$[Cp^*Fe(CO)_2\{B(N^iPr)_2CPh\}]^+$	-103.65	-84.57
$[Cp^*Fe(CO)_2\{B(NMesCMe)_2CH\}]^+$ (**4**)	-82.76	-44.22
$[CpFe(CO)_2\{IMes\}]^+$	-81.05	-73.89

[a] For a given complex, a more negative binding energy reflects less stable fragments

Table s2: Calculated spectroscopic properties

	Calculated ^{11}B NMR Shift (ppm)	Calculated CO Stretching Frequencies (cm^{-1})
$[Cp^*Fe(CO)_2\{B(N^iPr)_2CPh\}]^+$	91.3	1981, 1940
$[Cp^*Fe(CO)_2\{B(NMesCMe)_2CH\}]^+$ (**4**)	66.3	1959, 1912

Run Files

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# [Cp*Fe(CO)2{B(NiPr)2CPh}]+
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6 C        9.148856393000      13.744079130000      12.101858960000
7 C        8.561137189000      15.030828120000      12.601393370000
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9 C       11.917910880000      11.683384200000      10.547991530000
10 C       9.715604379000      10.009491680000      12.152458610000
11 C       7.677184072000      12.084104440000      13.489308840000
12 C       8.265540439000      13.962482870000       9.280814121000
13 O       7.994909813000      14.874587680000       8.610845200000
14 C       9.027228456000      11.458247220000       8.988610564000
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47 38 59 1.0
48 38 61 1.0
49 39 62 1.0
50 39 64 1.0
51 39 63 1.0
52 40 67 1.0
53 40 65 1.0
54 40 66 1.0
55 41 68 1.0
56 41 70 1.0
57 41 69 1.0
58 1 2 1.0
59 1 5 1.0
60 1 10 1.0
61 2 3 1.0
62 2 9 1.0
63 3 4 1.0
64 3 8 1.0
65 4 5 1.0
66 4 7 1.0
67 5 6 1.0
68 6 16 1.0
69 6 17 1.0
70 6 15 1.0
71 7 18 1.0
72 7 19 1.0
73 7 20 1.0
74 8 22 1.0
75 8 21 1.0
76 8 23 1.0
77 9 25 1.0
78 9 26 1.0
79 9 24 1.0
80 10 28 1.0
81 10 29 1.0
82 10 27 1.0
83 11 12 2.0
84 13 14 2.0
85 30 11 1.0
86 30 13 1.0
87 30 71 3
88 30 4 1.0
89 30 1 1.0
90 30 5 1.0
91 30 3 1.0
92 30 2 1.0
END
```

```
CHARGE 1.0

BASIS
type TZP
core Large
createoutput None
END

XC
GGA Becke Perdew
END
```

```
SCANFREQ -1000 0

AnalyticalFreq
END

SAVE  TAPE21 TAPE13

FULLSCF
INTEGRATION 6.0

NOPRINT LOGFILE

eor
```

```
#! /bin/sh

# ==============================
# [CpFe(CO)2{IMes}]+
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 C        0.499168718900      14.154882160000       5.993025605000
2 C        1.743267875000      14.829888240000       6.160393845000
3 C        1.646215034000      16.122872840000       5.568272824000
4 C        0.315496976200      16.257195240000       5.040187444000
5 C       -0.388335033300      15.049606460000       5.299880337000
6 H       -1.418691472000      14.840256910000       5.025135484000
7 H       -0.083961876780      17.130674200000       4.531701510000
8 H        2.426036151000      16.877385520000       5.529022463000
9 H        2.625415329000      14.424383630000       6.645179197000
10 H       0.251032030900      13.154591900000       6.335518228000
11 C       1.515169342000      15.687986640000       2.610540972000
12 O       1.498861513000      16.407691190000       1.703924756000
13 C       0.274647150300      13.510401060000       3.087733306000
14 O      -0.499766795600      12.909911570000       2.471603925000
15 C       3.018289420000      13.606201860000       3.786780869000
16 N       3.222517548000      12.247069480000       3.861570161000
17 H       3.811720288000      11.388075090000       6.376110023000
18 N       4.274841488000      14.117112880000       3.547607168000
19 C       4.565888205000      11.931762160000       3.672327134000
20 Fe      1.302375012000      14.627763020000       4.034808405000
21 C       5.223503649000      13.100883590000       3.475767047000
22 H       6.279458603000      15.595229780000       6.078051245000
23 H       4.917214084000      10.907157630000       3.693062831000
24 H       6.269941574000      13.311667650000       3.291376126000
25 C       4.658164498000      15.501226550000       3.328013078000
26 C       4.707940813000      15.978875090000       2.001435636000
27 C       5.129037882000      17.296302850000       1.799655793000
28 C       5.521624817000      18.126718020000       2.859523340000
29 C       5.505572280000      17.594790020000       4.152480043000
30 C       5.096263373000      16.278507010000       4.414080157000
31 H       5.258663194000      14.498069900000       0.529564032300
32 H       5.161787169000      17.681601290000       0.777681810700
33 H       6.762887463000      19.575206190000       1.842370844000
34 H       5.845073804000      18.212338350000       4.987913881000
35 C       2.244053636000      11.190309190000       4.056122459000
36 C       1.668015143000      10.591177560000       2.921929643000
37 C       0.778990080800       9.526784122000       3.127487244000
38 C       0.487152407900       9.034350857000       4.402718565000
39 C       1.129004579000       9.626069379000       5.501215379000
40 C       2.019518409000      10.694760390000       5.357078195000
41 H       1.200970505000      10.763567480000       0.824787791800
42 H       0.313828898600       9.061381646000       2.255584996000
43 H      -0.024768045820       7.098552984000       5.220760326000
44 H       0.951010319900       9.227033545000       6.502971314000
45 C       2.740381784000      11.238884620000       6.568331506000
```

```
46 H       2.333082239000      12.206183050000       6.892138455000
47 H       2.643107357000      10.545080180000       7.411396555000
48 C       2.014669778000      11.015017550000       1.515031251000
49 H       2.213153650000      12.090607860000       1.434322857000
50 H       2.917415110000      10.490590670000       1.164327127000
51 C      -0.471945612400       7.886175423000       4.598391570000
52 H      -1.386924623000       8.221512685000       5.109118794000
53 H      -0.765963547400       7.440343346000       3.640915177000
54 C       5.219197762000      15.735867630000       5.819132254000
55 H       4.805917791000      16.436890270000       6.556585367000
56 H       4.724901559000      14.766726330000       5.939833220000
57 C       4.383630207000      15.102759880000       0.815213739200
58 H       3.561441153000      14.405305630000       1.016634072000
59 H       4.109398760000      15.714013720000      -0.052339063500
60 C       5.967324051000      19.544673390000       2.600046379000
61 H       5.135218776000      20.154304880000       2.217975658000
62 H       6.345761496000      20.021921940000       3.511721658000
END
```

```
GUIBONDS
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2 15 18 1.0
3 16 19 1.0
4 17 45 1.0
5 20 1 1.0
6 20 15 3
7 20 11 1.0
8 20 13 1.0
9 6 5 1.0
10 19 21 2.0
11 23 19 1.0
12 24 21 1.0
13 1 2 1.0
14 1 5 1.0
15 9 2 1.0
16 10 1 1.0
17 20 4 1.0
18 20 5 1.0
19 11 12 2.0
20 2 3 1.0
21 20 2 1.0
22 3 4 1.0
23 13 14 2.0
24 4 5 1.0
25 22 54 1.0
26 7 4 1.0
27 8 3 1.0
28 20 3 1.0
29 21 18 1.0
30 25 26 1.5
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36 31 57 1.0
37 32 27 1.0
38 33 60 1.0
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40 25 18 1.0
41 35 36 1.5
42 36 37 1.5
43 37 38 1.5
44 38 39 1.5
45 39 40 1.5
46 40 35 1.5
47 41 48 1.0
48 42 37 1.0
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51 35 16 1.0
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56 50 48 1.0
57 48 36 1.0
58 52 51 1.0
59 53 51 1.0
60 51 38 1.0
61 55 54 1.0
62 56 54 1.0
63 54 30 1.0
64 58 57 1.0
65 59 57 1.0
66 57 26 1.0
67 61 60 1.0
68 62 60 1.0
69 60 28 1.0
END

CHARGE 1.0

BASIS
type TZP
core Large
createoutput None
END

XC
GGA Becke Perdew
END



SCANFREQ -1000 0

AnalyticalFreq
END

SAVE  TAPE21 TAPE13

FULLSCF
INTEGRATION 6.0

NOPRINT LOGFILE
```

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eor

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