Formation of sub-valent carbenoid ligands by metal-mediated dehydrogenation chemistry: coordination and activation of $H_2Ga\{(NDippCMe)_2CH\}$

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Supporting Information (23 pages)

1. General methods and starting materials

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon. Solvents were degassed by sparging with argon and dried by passing through a column of the appropriate drying agent using a commercially available Braun SPS. Fluorobenzene and 1,2-difluorobenzene were dried by refluxing over calcium hydride, distilled, sparged and stored over activated molecular sieves. NMR spectra were recorded in benzene-d_6, dichloromethane-d_2 or bromobenzene-d_5, which were dried over potassium, molecular sieves or calcium hydride respectively, and stored under argon in Teflon valve ampoules. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury-VX-300 or Bruker AVII-500 spectrometers and referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Infrared spectra were measured on a Nicolet 500 FT-IR spectrometer. Elemental analyses were carried out by Stephen Boyer at London Metropolitan University. Starting materials $Mo(CO)_4(COD)$[S1] and $W(CO)_4(COD)$[S1] were prepared by literature procedures. $H_2Ga\{(NDippCMe)_2CH\}$ (**1**) was prepared by a method directly analogous to that reported in the literature,[S2] but employing $Cl_2Ga\{(NDippCMe)_2CH\}$ as a starting material rather than $I_2Ga\{(NDippCMe)_2CH\}$. Photolysis experiments were carried out using a Spectral Energy mercury arc lamp (1 kW) with samples contained either within a quartz Schlenk vessel or a J. Young's NMR tube.

2. Syntheses of new compounds

2a: Cp'Mn(CO)$_3$, (0.1 mL, 0.6 mmol) was added to a quartz Schlenk tube containing a stirred solution of **1** (0.300 g, 0.613 mmol) in toluene (15 mL). The solution was then subjected to UV photolysis at room temperature for 2.5 h. The orange solution was then filtered, concentrated and cooled to -30 ^{o}C, yielding yellow crystals of **2** which were isolated by filtration and dried *in vacuo*. Isolated yield of single crystals: 0.13 g, 31% (*in situ* monitoring of the reaction by ^{1}H NMR in toluene-d$_8$ is consistent with *ca.* 90% conversion of **1** to **2a**; the lower isolated yield reflects – at least in part – the high solubility of **2a** in compatible hydrocarbon solvents and its high sensitivity to air/moisture, resulting in relatively inefficient recrystallization). ^{1}H NMR (300 MHz, benzene-d$_6$, 298 K): δ_H −13.46 (d, $^{2}J_{HH}$ = 19.2 Hz, 2H, MnHGa), 1.15 (d, $^{3}J_{HH}$ = 7.2 Hz, 12H, CH$_3$ of Dipp ^{i}Pr), 1.45 (d, $^{3}J_{HH}$ = 7.2 Hz, 6H, CH$_3$ of Dipp ^{i}Pr), 1.53 (d, $^{3}J_{HH}$ = 7.2 Hz, 6H, CH$_3$ of Dipp ^{i}Pr), 1.55 (s, 3H, CH$_3$ of Cp'), 1.56 (s, 6H, CH$_3$ of β-diketiminato backbone), 3.33 (sept, $^{3}J_{HH}$ = 7.2 Hz, 2H, CH of Dipp ^{i}Pr), 3.46 (sept, $^{3}J_{HH}$ = 7.2 Hz, 2H, CH of Dipp ^{i}Pr), 3.52 (m, 2H, Cp'), 3.62 (m, 2H, Cp'), 4.83 (s, 1H, γ-CH), 7.09−7.13 (overlapping m, 6H, ArH). The terminal GaH resonance is tentatively assigned to a broad signal centred at δ_H ca. 6.9 ppm. ^{13}C NMR (126 MHz, benzene-d$_6$, 298 K): δ_C 13.2 (CH$_3$ of Cp'), 23.9 (CH$_3$ of β-diketiminato backbone), 24.2, 24.6, 24.7, 25.7 (CH$_3$ of Dipp ^{i}Pr), 28.2, 29.4 (CH of Dipp ^{i}Pr), 80.2, 80.5 (CH of Cp'), 94.4 (quaternary-C of Cp'), 95.7 (γ-CH), 124.2, 125.1, 127.2, 142.7, 142.9, 145.0 (ArC), 168.8 (CN), 230.4 (CO). IR (hexanes, ν_{CO}/cm^{-1}): 1886 (s), 1951 (s). EI-MS: m/z 487.2 ([M-Cp'Mn(CO)$_2$H]$^{+}$, 100%), 676.2 ([M-2H]$^{+}$, 1%). Reproducible elemental microanalysis for **2a** proved impossible to obtain due to its very high air/moisture sensitivity. Crystallographic data: $C_{37}H_{50}N_2O_2GaMn$, M_r = 679.41, monoclinic, P2$_1$/*n*, a = 10.1814(2), b = 20.4882(4), c = 16.7346(3) Å, β = 103.1581(11) ^{o}, V = 3399.16(11) Å^3, Z = 4, ρ_c = 1.328 Mg m^{-3}, T = 150(2) K, λ = 0.71073 Å. 7688 independent reflections [R(int) = 0.059], used in all calculations. R_1 = 0.0732, wR_2 = 0.1459 for I > 2σ(I), and R_1= 0.1473, wR_2 = 0.2096 for all unique reflections. Max./min. residual electron densities 1.74 and –2.07 e Å^{-3}. CSD ref.: 944059.

2b: A solution of **2a** (0.240 g, 0.354 mmol) in toluene (20 mL) and subjected to UV photolysis for 2.5 h. The reaction mixture was filtered and the filtrate concentrated to the point of incipient crystallisation. Storage at -30^{o}C produced bright yellow crystals. Isolated yield of single crystals: 0.130 g, 54%. ^{1}H NMR (300 MHz, benzene-d$_6$, 298 K): δ_H 1.06 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, CH$_3$ of Dipp ^{i}Pr), 1.43 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, CH$_3$ of Dipp ^{i}Pr), 1.59 (s, 6H, CH$_3$ of β-diketiminato backbone), 1.73 (s, 3H, CH$_3$ of Cp'), 3.15 (sept, $^{3}J_{HH}$ = 6.9 Hz, 4H, CH of Dipp ^{i}Pr), 3.52 (m, 2H, Cp'), 3.83 (m, 2H, Cp'), 5.10 (s, 1H, γ-CH), 7.12-7.22 (m, 6H, aromatic CH of Dipp). ^{13}C NMR (126 MHz, benzene-d$_6$, 298 K): δ_C 14.3 (CH$_3$ of Cp'), 24.6, 24.6, 24.8 (CH$_3$ of Dipp ^{i}Pr and β-diketiminato backbone), 29.5 (CH of Dipp ^{i}Pr), 76.6, 78.3 (CH of Cp'), 97.2 (quaternary-C of Cp'), 100.3 (γ-C), 125.0, 128.7, 142.5, 143.7 (ArC of Dipp), 167.8 (NC), 233.6 (CO). IR (KBr disc, ν_{CO}/cm^{-1}): 1837 (s), 1903 (s). EI-MS: m/z 676.2 ([M^{+}], 13%), 620.2 ([M-2CO]$^{+}$, 99%), 472 ([M-Cp'Mn(CO)$_2$-Me]$^{+}$, 100%). Elemental microanalysis: calcd. for $C_{37}H_{48}N_2O_2GaMn$: C 65.60% H 7.14% N 4.14%, meas. C 65.30% H 7.16% N 3.97%. Crystallographic data: $C_{37}H_{48}N_2O_2GaMn$, M_r = 677.45, triclinic, P-1, a = 8.8327(1), b = 18.3781(2), c = 20.6752(2) Å, α = 90.008(1), β = 90.007(1), γ = 85.742(1) ^{o}, V = 3346.9(1) Å^3, Z = 4, ρ_c = 1.344 Mg m^{-3}, T = 150(2) K, λ = 0.71073 Å. 15175 independent reflections [R(int) = 0.023], used in all calculations. R_1 = 0.0355, wR_2 = 0.0749 for I > 2σ(I), and R_1= 0.0560, wR_2 = 0.0919 for all unique reflections. Max./min. residual electron densities 0.59 and –0.74 e Å^{-3}. CSD ref.: 952954.

3: Fe(CO)$_5$ (0.083 mL, 0.613 mmol) was added to a quartz schlenk containing a stirred solution of **1** (0.300 g, 0.613 mmol) in toluene (15 mL), The solution was subjected to UV photolysis, whilst stirring, for 50 min, after which time ^{1}H NMR spectroscopy indicated quantitative conversion to **3**. The orange solution was filtered and concentrated, and cooled to -30 ^{o}C overnight to yield very pale yellow crystals of **3**. The crystals were isolated by filtration and dried *in vacuo*. Isolated yield of single crystals: 0.205 g, 51%. ^{1}H and ^{13}C NMR data, together with a single crystal X-ray diffraction study confirmed that the compound is identical to that reported by Power and co-workers.[S3]

4 and **5**: The two compounds were prepared by a similar method, exemplified for **5**. To an ampoule containing **1** (0.300 g, 0.613 mmol) in hexanes (10 mL) was added at room temperature a solution of W(CO)$_4$(COD) (0.143 g, 0.613 mmol) also in hexanes (10 mL) and the resulting pale yellow mixture warmed to 55 ^{o}C, whilst stirring. After 5 d the solvent was removed *in vacuo* and the resulting yellow solid was extracted into fluorobenzene. Layering the fluorobenzene solution with hexanes at -20 ^{o}C yielded yellow crystals, which were isolated by filtration and dried *in vacuo*. Isolated yield of single crystals: 0.020 g, 14%. ^{1}H NMR (500 MHz, dichloromethane-d$_2$, 298 K): δ_H 1.21 (d, 12H, $^{3}J_{HH}$ = 6.5 Hz CH$_3$ of Dipp ^{i}Pr), 1.29 (d, 12H, $^{3}J_{HH}$ = 6.5 Hz CH$_3$ of Dipp ^{i}Pr), 1.905 (s, 6H, CH$_3$ of β-diketiminato backbone), 2.95 (sept, 4H, $^{3}J_{HH}$ = 6.5 Hz CH of Dipp ^{i}Pr), 5.62 (s, 1H, γ-CH), 7.11-7.33 (m, 6H, ArH). ^{13}C NMR (126 MHz, CD_2Cl_2, 298 K): δ_C 23.9 (CH$_3$ of Dipp ^{i}Pr), 24.5 (CH$_3$ of Dipp ^{i}Pr), 24.8 (CH$_3$ of β-diketiminato backbone) 29.6 (γ-CH of Dipp ^{i}Pr), 101.8 (γ-C), 124.8 (Ar-C), 128.4 (Ar-C), 141.0 (Ar-C), 143.1 (Ar-C), 169.1 (CN), 197.9 (CO), 201.0 (CO). IR (CH_2Cl_2, ν_{CO}/cm^{-1}): 1926 (b), 1968 (s), 2058 (s). EI-MS: m/z 726.2 ([M-3CO]$^{+}$, 100%), 810.2 [M]$^{+}$, 10%). Crystallographic data: $C_{34}H_{41}N_2O_5GaW$, M_r = 811.28, orthrhombic, P*bnm*, a = 9.15777(10), b = 35.5896(6), c = 21.050(3) Å, V = 6878.57(17) Å^3, Z = 8, ρ_c = 1.567 Mg m^{-3}, T = 150(2) K, λ = 0.71073 Å. 7351 independent reflections [R(int) = 0.039], used in all calculations. R_1 = 0.0588, wR_2 = 0.1190 for I > 2σ(I), and R_1= 0.0620, wR_2 = 0.1196 for all unique reflections. Max./min. residual electron densities 3.62 and –2.15 e Å^{-3}. CSD ref.: 944061. **4** was prepared in a similar manner, under slightly milder conditions (room temperature, 4 d) and recrystallized from 1,2-difluorobenzene as pale yellow crystals. Isolated yield of single crystals: 0.052 g (40%). ^{1}H NMR (500 MHz, bromobenzene-d$_5$, 298 K): δ_H 1.00 (d, 12H, $^{3}J_{HH}$ = 7.0 Hz CH$_3$ of Dipp ^{i}Pr), 1.24 (d, 12H, $^{3}J_{HH}$ = 7.0 Hz CH$_3$ of Dipp ^{i}Pr), 1.58 (s, 6H, CH$_3$ of β-diketiminato backbone), 2.87 (sept , 4H, $^{3}J_{HH}$ = 7.0 Hz, CH of Dipp ^{i}Pr), 5.22 (s, 1H, γ-CH), 7.16-7.07 (m, 12H, ArH). ^{13}C NMR (126 MHz, bromobenzene-d$_5$, 298 K): δ_C 24.0, 24.6, 24.6 (CH$_3$ of Dipp ^{i}Pr and β-diketiminato backbone), 29.4 (CH of Dipp ^{i}Pr), 101.5 (γ-CH), 124.8 (Ar-C), 128.5 (Ar-C), 140.8 (Ar-C), 142.6 (Ar-C), 168.3 (NC), 208.0 (CO), 212.5 (CO). IR (CH_2Cl_2, ν_{CO}/cm^{-1}): 1932 (b), 1979 (s), 2059 (s). EI-MS: m/z 471 [M-Mo(CO)$_5$(CH$_3$)]$^{+}$, 100%), 724 ([M]$^{+}$, 6%). Elemental microanalysis: calcd. for $C_{34}H_{41}N_2O_5GaMo$: C 56.43% H 5.72% N 3.87% meas. C 55.78% H 5.57% N 3.45%. Crystallographic data: $C_{34}H_{41}N_2O_5GaMo$, M_r = 723.36, tetragonal, P4$_3$2$_1$2, a = 9.08300(10), b = 9.08300(10), c = 41.8928(5) Å, V = 3456.19(7) Å^3, Z = 4, ρ_c = 1.390 Mg m^{-3}, T = 150(2) K, λ = 0.71073 Å. 3933 independent reflections [R(int) = 0.052], used in all calculations. R_1 = 0.0543, wR_2 = 0.1170 for I > 2σ(I), and R_1= 0.0659, wR_2 = 0.1298 for all unique reflections. Max./min. residual electron densities 3.07 and –1.45 e Å^{-3}. CSD ref.: 944060.

7: A stirred solution of **1** (0.300 g, 0.613 mmol) and Mn_2CO_{10} (0.239 g, 0.613 mmol) in toluene (15 mL) was subjected to UV photolysis at room temperature for 6 h, after which time ^{1}H NMR indicated quantitative conversion to **7** and HMn(CO)$_5$. The reaction mixture was filtered and volatiles removed *in vacuo*. The resulting solid was extracted into diethyl ether and cooled to -30 ^{o}C to yield yellow crystals of **7**. The crystals were isolated by filtration and dried *in vacuo*. Isolated yield of single crystals: 0.077 g, 19% (*in situ* monitoring of the reaction by ^{1}H NMR in benzene-d$_6$ is consistent with *ca.* 90% conversion of **1** to **7**; the lower isolated yield reflects – at least in part – the high solubility of **7** in compatible hydrocarbon solvents and its high sensitivity to air/moisture, resulting in relatively inefficient recrystallization). ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ_H – 9.58 (s, 1H, MnH), 1.02 (d, 12H, $^{3}J_{HH}$ = 7.5 Hz CH$_3$ of Dipp ^{i}Pr), 1.40 (d, 12H, $^{3}J_{HH}$ = 7.5 Hz CH$_3$ of Dipp ^{i}Pr), 1.51 (s, 6H, CH$_3$ of Nacnac backbone), 3.00 (sept, 4H, $^{3}J_{HH}$ = 7.5 Hz CH of Dipp ^{i}Pr), 5.06 (s, 1H, γ-CH), 7.08-7.20 (overlapping m, 6H, ArH). ^{13}C NMR (126 MHz, CD_2Cl_2, 298 K): 24.3, 24.6 (CH$_3$ of Dipp ^{i}Pr), 24.3 (CH$_3$ of β-diketiminato backbone), 29.2 (γ-CH of Dipp ^{i}Pr), 101.2 (γ-C), 124.9, 128.6, 140.5, 143.6 (ArC), 169.6 (CN), 220 (br, CO). IR (CH_2Cl_2, ν_{CO}/cm^{-1}): 1922 (b), 1951 (b), 2011 (s), 2043 (s). EI-MS: m/z 542.2 ([M-4(CO)]$^{+}$, 100%), 654.2 ([M]$^{+}$, 12%). Elemental microanalysis: calcd. for $C_{33}H_{42}N_2O_4GaMn$: C 60.46% H 6.46% N 4.28%, meas. C 60.12%

H 6.71% N 4.70%. Crystallographic data: $C_{33}H_{42}N_2O_4GaMn$, M_r = 655.36, monoclinic, $P2_1/m$, a = 8.86000(10), b = 21.5544(2), c = 9.08180(10) Å, β = 108.601(1)°, V = 1643.8(1) Å^3, Z = 2, ρ_c = 1.324 Mg m^{-3}, T = 150(2) K, λ = 0.71073 Å. 3844 indep. reflns [R(int) = 0.025], used in all calcns. R_1 = 0.0293, wR_2 = 0.0653 for I > 2σ(I), and R_1= 0.0435, wR_2 = 0.0787 for all unique reflns. Max./min. residual electron densities 0.62, –0.61 e Å^{-3}. CSD ref.: 944063.

8: A solution of **1** (0.200 g, 0.409 mmol) and $Cl_2Ga\{(NDippCMe)_2CH\}$ (0.228 g, 0.409 mmol) in toluene (20 mL) was heated to 70 °C for 48 h. The solvent was removed *in vacuo* and the resultant colourless solid extracted in diethyl ether. Concentration and cooling the ethereal solution to -30 °C yielded colourless crystals of **8**. Isolated yield of single crystals: 0.259 g, 60%. ^{1}H NMR (300 MHz, benzene-d_6, 298 K): δ_H 1.08 (d, 6H, $^3J_{HH}$ = 6.9 Hz CH_3 of Dipp ^{i}Pr), 1.16 (d, 6H, $^3J_{HH}$ = 6.9 Hz CH_3 of Dipp ^{i}Pr), 1.27 (d, 6H, $^3J_{HH}$ = 7.2 Hz CH_3 of Dipp ^{i}Pr), 1.51 (d, 6H, $^3J_{HH}$ = 7.2 Hz CH_3 of Dipp ^{i}Pr), 1.54 (s, 6H, CH_3 of β-diketiminato backbone), 3.19 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, CH of Dipp ^{i}Pr), 3.64 (sept, 2H, $^3J_{HH}$ = 7.2 Hz, CH of Dipp ^{i}Pr), 4.79 (s, 1H, γ-CH), 5.47 (br s, 1H, GaH), 7.03 – 7.14 (m, 6H, ArH). ^{13}C NMR (126 MHz, benzene-d_6,, 298 K): δ_C 23.3 (CH_3 of β-diketiminato backbone), 24.8 (CH_3 of Dipp ^{i}Pr), 24.8 (CH_3 of Dipp ^{i}Pr), 26.1 (CH_3 of Dipp ^{i}Pr), 28.3 (CH of Dipp ^{i}Pr), 28.8 (CH of Dipp ^{i}Pr), 96.3 (γ-CH), 124.4 (Ar-C), 125.2 (Ar-C), 139.8 (Ar-C), 143.2 (Ar-C), 145.6 (Ar-C), 169.5 (CN). EI-MS : m/z 524.22 ([M]$^+$, 3%); accurate mass : calc. 524.2281, meas. 524.2283. Elemental microanalysis: calcd. for $C_{29}H_{42}ClGaN_2$: C 66.49% H 8.08% N 5.35% meas. C 65.91% H 8.49% N 5.13%.

9: A solution of **8** (0.100 g, 0.191 mmol) in toluene (10 ml) was added to a solution of $Co_2(CO)_8$ (0.065 g, 0.191mmol), also in toluene (10 mL). Immediate gas evolution was observed and the solution was stirred for 2 h at room temperature. Volatiles were removed *in vacuo* and the resultant solid extracted into hexanes. Storage of the hexane solution at -30 °C yielded pale yellow crystals of **9.** Isolated yield of single crystals: 0.020g, 15% (*in situ* monitoring of the reaction by ^{1}H NMR in benzene-d_6 is consistent with *ca*. 90% conversion of **8** to **9**; the lower isolated yield reflects – at least in part – the high solubility of **9** in compatible hydrocarbon solvents and its high sensitivity to air/moisture, resulting in relatively inefficient recrystallization). ^{1}H NMR (300 MHz, benzene-d_6, 298 K): δ_H 1.10 (d, 6H, $^3J_{HH}$ = 6.9 Hz CH_3 of Dipp ^{i}Pr), 1.40 (d, 6H, $^3J_{HH}$ = 6.9 Hz CH_3 of Dipp ^{i}Pr), 1.54 (d, 6H, $^3J_{HH}$ = 6.9 Hz CH_3 of Dipp ^{i}Pr), 1.62 (s, 6H, CH_3 of β-diketiminato backbone), 3.29 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, CH of Dipp ^{i}Pr), 3.73 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, CH of Dipp ^{i}Pr), 4.91 (s, 1H, γ-CH), 7.07- 7.17(m, 6H, ArH). ^{13}C NMR (126 MHz, benzene-d_6, 298 K): 24.5 (CH_3 of β-diketiminato backbone), 24.8 (CH_3 of Dipp ^{i}Pr), 24.9 (CH_3 of Dipp ^{i}Pr), 25.4 (CH_3 of Dipp ^{i}Pr), 25.6 (CH_3 of Dipp ^{i}Pr), 28.5 (CH of Dipp ^{i}Pr), 29.2 (CH of Dipp ^{i}Pr), 98.0 (γ-CH), 124.7 (Ar-C), 125.2 (ArC), 140.3 (Ar-C), 144.3 (Ar-C), 145.8 (Ar-C), 170.5 (CN), 199.3 (CO), 201.3 (CO).). IR (CH_2Cl_2, ν_{CO}/cm^{-1}): 1968 (s), 2000 (s), 2015 (s), 2083 (s). EI-MS : m/z 471 ([M-Co(CO)$_4$-Cl-Me]$^+$, 55%), 506 ([M-Co(CO)$_4$-CH_3]$^+$, 28%), 558 ([M-3CO-Cl-CH_3], 12%). Contamination even of crystalline samples with small quantities of $Co_4(CO)_{12}$ meant that C/H elemental microanalyses for **9** were reproducibly low. Crystallographic data: $C_{33}H_{41}N_2O_4ClGaCo$, M_r = 693.80, monoclinic, C2/c, a = 21.42720(10), b = 16.89020(10), c = 21.5723(2) Å, β = 108.7295(4) °, V = 7393.79(9) Å^3, Z = 8, ρ_c = 1.246 Mg m^{-3}, T = 150(2) K, λ = 0.71073 Å. 8414 independent reflections [R(int) = 0.024], used in all calculations. R_1 = 0.0333, wR_2 = 0.0816 for I > 2σ(I), and R_1= 0.0480, wR_2 = 0.0992 for all unique reflections. Max./min. residual electron densities 0.56 and –0.61 e Å-3. CSD ref.: 944065.

[(OC)$_4$CoGa{(NDippCMe)$_2$CH}][BAr$^f_4$]: A solution of **8** (0.100 g, 0.191 mmol) in toluene (10 mL) was added to a solution of $Co_2(CO)_8$ (0.065 g, 0.191 mmol) in toluene (10 mL) and the reaction mixture stirred at room temperature for 30 min, after which time ^{1}H NMR spectroscopy revealed quantitative conversion to compound **9**. Volatiles were removed *in vacuo* and the resulting solid extracted into dichoromethane (5 mL). This solution was added to a suspension of Na[BAr$^f_4$] (0.169 g, 0.191 mmol) in dichloromethane (5 mL), and a colourless precipitate was formed immediately. The reaction mixture was stirred at room temperature for 30 min, after which time it was filtered and volatiles removed *in vacuo*. The resulting solid was washed with hexane (3 x 5 mL) and dried *in vacuo* to yield a spectroscopically pure, pale yellow powder (0.256 g, 88% yield). This solid was extracted into fluorobenzene and layered with hexane. Storage at room temperature yielded pale yellow crystals suitable for X-ray diffraction. Isolated yield of single crystals: 0.207 g, 71%. ^{1}H NMR (300 MHz, dichloromethane-d_2, 298 K): δ_H 1.24 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH_3 of Dipp ^{i}Pr), 1.26 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH_3 of Dipp ^{i}Pr), 2.14 (s, 6H, CH_3 of β-diketiminato backbone), 2.74 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, CH of Dipp ^{i}Pr), 6.07 (s, 1H, γ-CH), 7.36 (d, $^3J_{HH}$ = 7.5 Hz, 4H, *m*-CH of Dipp), 7.48 (t, $^3J_{HH}$ = 7.5 Hz, 2H, *p*-CH of Dipp), 7.56 (s, 4H, *p*-CH of [BAr$^f_4$]$^-$), 7.72 (s, 8H, *o*-CH of [BAr$^f_4$]$^-$). ^{13}C NMR (75 MHz, dichloromethane-d_2, 298 K): δ_C 24.6, 25.1, 25.2 (CH_3 of Dipp ^{i}Pr and β-diketiminato backbone), 29.6 (CH of Dipp ^{i}Pr), 104.9 (γ-C), 118.0 (*p*-CH of [BAr$^f_4$]$^-$), 125.2 (q, $^1J_{CF}$ = 271 Hz, CF_3 of [BAr$^f_4$]$^-$), 126.4, 131.2, 136.8, 143.5 (ArC of Dipp) 129.5 (q, $^2J_{CF}$ = 34.3 Hz, *m*-C of [BAr$^f_4$]$^-$), 135.4 (*o*-CH of [BAr$^f_4$]$^-$), 162.3 (q, $^1J_{CB}$ = 49.2 Hz, *ipso*-C of [BAr$^f_4$]$^-$), 175.3 (NC), 192.6 (br s, CO). ^{11}B NMR (96 MHz, dichloromethane-d_2, 298 K): δ_B -6.8. ^{19}F NMR (282 MHz, dichloromethane-d_2, 298 K): δ_F -62.8. IR (KBr disc, ν_{CO}/cm^{-1}): 2025 (s), 2047 (s), 2072 (s), 2121 (s). ESI-MS (cation) : 657 ([M]+, 18%); accurate mass: calc. 657.1649, meas. 657.1635. Elemental microanalysis: calc. (for $C_{65}H_{53}N_2O_4F_{24}GaCoB$) C 51.31% H 3.51% N 1.84%; meas. C 51.45% H 3.50% N 1.87%. Crystallographic data: $C_{65}H_{53}N_2O_4CoF_{24}GaMn$, M_r = 1521.56, triclinic, P-1, a = 12.5663(2), b = 13.2686(3), c = 20.7262(4) Å, α = 78.486(2), β = 83.945(2), γ = 83.491(2) °, V = 3352.3(1) Å^3, Z = 4, ρ_c = 1.507 Mg m^{-3}, T = 150(2) K, λ = 1.54180 Å. 13907 independent reflections [R(int) = 0.023], used in all calculations. R_1 = 0.0489, wR_2 = 0.1201 for I > 2σ(I), and R_1= 0.0521, wR_2 = 0.1228 for all unique reflections. Max./min. residual electron densities 1.74 and –1.09 e Å^{-3}. CSD ref.: 952955.

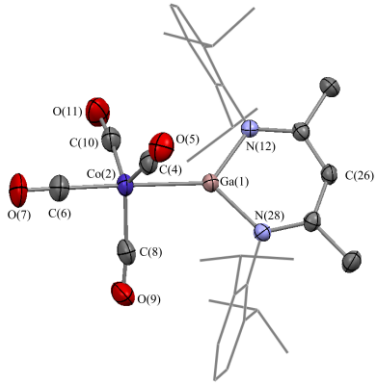


Figure S1: Molecular structure of the cationic component of $[(OC)_4CoGa\{(NDippCMe)_2CH\}][BAr^f_4]$. H atoms and counter-anion omitted, and Dipp groups shown in wireframe format for clarity. Thermal ellipsoids set at the 50% probability level.

3. Details of DFT calculations

The DFT calculations were performed using the Amsterdam Density Functional (ADF) Package Software 2012 and 2013.[S4] Calculations were performed using the Vosko-Wilk-Nusair local density approximation with exchange from Becke,[S5] and correlation corrections from Perdew (BP).[S6] Slater-type orbitals (STOs)[S7] 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. General numerical integration was 6.
Thermodynamic data was obtained from frequency calculations conducted on the optimised geometries of the species, calculated as detailed above. Analysis of the bonding in complex **5** was conducted using the ETS-NOCV approach,[S8] and the relevant run file is listed below. Run files for the frequency calculations are found below and complete output files provided upon request.

3a. The model system $Fe(CO)_4$ + $H_2Ga\{(NMeCMe)_2CH\}$

```
#! /bin/sh

# ==============================
# Fe(CO)4
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 C       0.935647735200       4.145000000000      15.941447960000
2 C       3.319089802000       5.745592402000      17.336860370000
3 C       1.635012872000       4.145000000000      18.388866260000
4 O       1.046728286000       4.145000000000      19.390355660000
5 O       3.772238038000       1.537793833000      17.689650720000
6 Fe       2.518334654000       4.145000000000      16.886484090000
7 C       3.319089802000       2.544407598000      17.336860370000
8 O      -0.092075079320       4.145000000000      15.405742340000
9 O       3.772238038000       6.752206167000      17.689650720000
END
```

```
GUIBONDS
1 1 8 2.0
2 1 6 2.0
3 2 9 2.0
4 2 6 2.0
5 3 4 2.0
6 3 6 1.5
7 6 7 1.5
8 7 5 2.0
END

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

# ==============================
# MeNacNacGaH2
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 H        2.201593941000       4.153201807000      14.898703330000
2 H        4.982015829000       0.658967441000      13.352769630000
3 H        3.203737040000       0.716005908600      13.238016520000
4 C        4.065213720000       7.019526069000      13.665684010000
5 H        4.021853543000       1.252044094000      14.718993140000
6 H        5.521027491000       1.103108638000      11.214619320000
7 C        4.090935367000       1.246954116000      13.624274460000
8 N        4.161376711000       2.622851252000      13.137438730000
9 H        4.774351821000       2.021570906000       9.888387022000
10 H        3.776182867000       0.992412219300      10.944579920000
11 C        4.418313325000       2.861026886000      11.851711870000
12 H        4.735543109000       4.138022804000      10.201434960000
13 H        3.759953230000       7.254096292000      10.839789130000
14 C        4.414050508000       5.431886668000      11.841980900000
15 C        4.520406720000       4.143262144000      11.267967810000
16 C        4.638584040000       6.594205329000      10.885517460000
17 H        5.498353447000       7.207190555000      11.193553680000
18 H        4.820473620000       7.151772391000      14.458009530000
19 H        3.076907869000       7.183012781000      14.126009470000
20 H        4.221723925000       7.802390253000      12.914985230000
21 N        4.143363510000       5.668748065000      13.122775300000
22 Ga        3.775406039000        4.145705287000       14.533880030000
23 H        4.964908114000       4.149463321000      15.627862970000
24 H        4.834794738000       6.221181744000       9.875354747000
25 C        4.632644111000       1.682271048000      10.919508710000
END
```

```
GUIBONDS
1 21 22 1.0
2 5 7 1.0
3 2 7 1.0
4 18 4 1.0
5 3 7 1.0
6 19 4 1.0
7 22 8 1.0
8 20 4 1.0
9 4 21 1.0
10 23 22 1.0
11 1 22 1.0
12 14 21 1.0
13 25 9 1.0
14 25 10 1.0
15 14 15 1.5
16 14 16 1.0
17 15 12 1.0
18 15 11 1.5
19 16 24 1.0
20 16 13 1.0
21 16 17 1.0
22 25 6 1.0
23 11 8 1.0
24 11 25 1.0
25 7 8 1.0
END

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

# ==============================
# Fe gallyl (anti)
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 C       1.202891619000       4.987041302000      16.568402730000
2 C       3.955180072000       5.329359404000      16.236910260000
3 C       2.982220027000       4.140490749000      18.516439590000
4 C       2.197272049000       6.504767971000      12.978485590000
5 O       1.803070513000       1.242310474000      16.532878890000
6 H       7.069192143000       2.042863687000      13.590756700000
7 C       4.479263560000       1.268285500000      13.765294590000
8 N       4.395866624000       2.695304839000      13.455180370000
9 H       7.517277029000       3.205765302000      12.317288360000
10 H       6.556846468000       1.764932089000      11.920006330000
11 C       5.448162400000       3.329942668000      12.933066470000
12 H       6.416489307000       5.049389204000      12.179163870000
13 H       4.163059140000       7.231703586000      11.116567440000
14 C       4.434708114000       5.656985400000      12.583157270000
15 C       5.466055605000       4.694339352000      12.572200350000
16 C       4.771863622000       7.017915684000      12.008061600000
17 H       4.570070326000       7.816268528000      12.737123870000
18 O       0.214272084200       5.586965873000      16.481880210000
19 O       4.768283925000       6.121063523000      15.998117150000
20 O       3.135153819000       4.193281892000      19.662999470000
21 N       3.200065518000       5.442228625000      13.044573740000
22 Ga       2.688590363000       3.710945893000      14.088488970000
23 Fe       2.769262900000       4.044369340000      16.712805730000
24 H       5.826528127000       7.067993222000      11.719706160000
25 C       6.720968725000       2.546644684000      12.677217640000
26 C       2.136806646000       2.354019477000      16.583453490000
27 H       5.117717670000       1.073234486000      14.643446200000
28 H       4.873549732000       0.684795968200      12.920197340000
29 H       3.476810611000       0.886946984400      13.991225640000
30 H       2.420312223000       7.329750192000      13.675816690000
31 H       1.216857939000       6.094345663000      13.247500940000
32 H       2.112570569000       6.928437729000      11.966532880000
33 H       4.078408872000       3.242105729000      16.629979690000
34 H       1.342424288000       3.063554918000      13.470077700000
END
```

```
GUIBONDS
1 1 18 2.0
2 1 23 2.0
3 2 19 2.0
4 2 23 2.0
5 3 20 2.0
6 3 23 1.5
7 22 8 1.0
8 22 23 3
9 4 21 1.0
10 23 26 1.5
11 26 5 2.0
12 14 21 1.0
13 25 9 1.0
14 25 10 1.0
15 14 15 1.5
16 14 16 1.0
17 15 12 1.0
18 15 11 1.5
19 16 24 1.0
20 16 13 1.0
21 16 17 1.0
22 25 6 1.0
23 11 8 1.0
24 11 25 1.0
25 7 8 1.0
26 21 22 1.0
27 27 7 1.0
28 28 7 1.0
29 29 7 1.0
30 30 4 1.0
31 31 4 1.0
32 32 4 1.0
33 23 33 1.0
34 34 22 1.0
END

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

# ==============================
# Fe transition state gallyl (anti) to gallyl (syn)
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 C       1.673701995000       5.425383597000      16.458100730000
2 C       4.344673878000       4.691543205000      16.329011650000
3 C       2.861878523000       4.020290889000      18.531106890000
4 C       1.658685563000       6.012751996000      12.824304650000
5 O       0.729783364400       1.769771571000      16.526291160000
6 H       7.486820890000       2.979460853000      13.701743110000
7 C       5.157906950000       1.565829842000      13.962473130000
8 N       4.725689710000       2.902449735000      13.556193810000
9 H       7.617318333000       4.058673353000      12.291212200000
10 H       7.045541672000       2.386809800000      12.093913430000
11 C       5.589664555000       3.734849479000      12.970412730000
12 H       6.108901661000       5.578596856000      12.080893360000
13 H       3.391739153000       7.056339934000      10.905694720000
14 C       4.040210086000       5.716900803000      12.482956760000
15 C       5.274076972000       5.033109192000      12.516161080000
16 C       4.034530727000       7.069745784000      11.798921780000
17 H       3.641613919000       7.851023289000      12.466045660000
18 O       1.008107685000       6.364568343000      16.316211090000
19 O       5.412917513000       5.107403310000      16.156569690000
20 O       2.959787576000       4.049505215000      19.684262150000
21 N       2.895522054000       5.248013476000      12.986294880000
22 Ga       2.803786641000       3.492491104000      14.116837730000
23 Fe       2.733598007000       3.954472780000      16.717783630000
24 H       5.044730587000       7.353178925000      11.487198060000
25 C       7.015060396000       3.268881348000      12.751046290000
26 C       1.481742179000       2.651315320000      16.577581480000
27 H       5.914909158000       1.599295671000      14.763507320000
28 H       5.578037128000       0.995171066400      13.119733720000
29 H       4.295470792000       1.006486191000      14.343695530000
30 H       1.675324413000       6.959096946000      13.388597880000
31 H       0.814907043200       5.419592166000      13.195775570000
32 H       1.458134850000       6.247680670000      11.767429770000
33 H       3.627866238000       2.700236994000      16.729559020000
34 H       1.691609375000       2.494313477000      13.498477020000
END
```

```
GUIBONDS
1 1 18 2.0
2 1 23 2.0
3 2 19 2.0
4 2 23 2.0
5 3 20 2.0
6 3 23 1.5
7 22 8 1.0
8 22 23 3
9 4 21 1.0
10 23 26 1.5
11 26 5 2.0
12 14 21 1.0
13 25 9 1.0
14 25 10 1.0
15 14 15 1.5
16 14 16 1.0
17 15 12 1.0
18 15 11 1.5
19 16 24 1.0
20 16 13 1.0
21 16 17 1.0
22 25 6 1.0
23 11 8 1.0
24 11 25 1.0
```

```
25 7 8 1.0
26 21 22 1.0
27 27 7 1.0
28 28 7 1.0
29 29 7 1.0
30 30 4 1.0
31 31 4 1.0
32 32 4 1.0
33 23 33 1.0
34 34 22 1.0
END

BASIS
type TZP
core Large
createoutput None
END

XC
GGA Becke Perdew
END



SCANFREQ -1000 0
```

```
AnalyticalFreq
END

SAVE  TAPE21 TAPE13

SCF
diis
END

#! /bin/sh

# ==============================
# Fe gallyl (syn)
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 C       4.634025752000       3.767838961000      16.769181450000
2 C       2.227975992000       2.365976476000      16.680617970000
3 C       2.543177835000       4.459069749000      18.448159440000
4 C       1.583428203000       5.918195784000      12.640781830000
5 O       2.805368436000       6.878680168000      15.717383840000
6 H       7.446459243000       3.017062519000      13.803623500000
7 C       5.132016847000       1.575773492000      13.788706200000
8 N       4.708930659000       2.947067412000      13.506181160000
9 H       7.649727903000       4.259495120000      12.541480960000
10 H       7.120798226000       2.619407131000      12.109699170000
11 C       5.588502069000       3.837214727000      13.040583930000
12 H       6.108161617000       5.761559295000      12.334289340000
13 H       3.430529607000       7.124806336000      10.927797170000
14 C       4.002871571000       5.778800196000      12.527846110000
15 C       5.263866261000       5.158868313000      12.663156250000
16 C       3.982898061000       7.147772928000      11.879379800000
17 H       3.482572745000       7.883262744000      12.526275460000
18 O       5.774471395000       3.572556609000      16.836204870000
19 O       1.776187406000       1.296888840000      16.702824180000
20 O       2.344612353000       4.709380365000      19.560955080000
21 N       2.845815098000       5.228925257000      12.905043080000
22 Ga       2.791486570000       3.521431658000      14.099885600000
23 Fe       2.828261027000       4.076122928000      16.694097420000
24 H       4.999787995000       7.496628973000      11.673373240000
25 C       7.033185436000       3.414937193000      12.865343430000
26 C       2.862593162000       5.771415421000      16.061659880000
27 H       5.826596763000       1.522564692000      14.643267090000
28 H       5.624039305000       1.110984073000      12.920563460000
29 H       4.251616395000       0.969314155900      14.031860070000
30 H       1.483804689000       6.842781166000      13.232310430000
31 H       0.750264335600       5.256754393000      12.907064910000
32 H       1.473264384000       6.177866135000      11.576752450000
33 H       1.328880552000       4.308120375000      16.430662860000
34 H       1.664897596000       2.501456015000      13.553649850000
END


GUIBONDS
1 1 18 2.0
2 1 23 2.0
3 2 19 2.0
4 2 23 2.0
5 3 20 2.0
6 3 23 1.5
7 22 8 1.0
8 22 23 3
9 4 21 1.0
10 23 26 1.5
11 26 5 2.0
12 14 21 1.0
13 25 9 1.0
14 25 10 1.0
15 14 15 1.5
16 14 16 1.0
17 15 12 1.0
18 15 11 1.5
19 16 24 1.0
20 16 13 1.0
21 16 17 1.0
22 25 6 1.0
23 11 8 1.0
24 11 25 1.0
25 7 8 1.0
26 21 22 1.0
27 27 7 1.0
28 28 7 1.0
29 29 7 1.0
30 30 4 1.0
31 31 4 1.0
32 32 4 1.0
33 23 33 1.0
34 34 22 1.0
END

BASIS
type TZP
core Large
createoutput None
END

XC
FULLSCF
INTEGRATION 6

NoBeckeGrid
NOPRINT LOGFILE

eor
```

```
GGA Becke Perdew
END



SCANFREQ -1000 0

AnalyticalFreq
END
```

```
SAVE  TAPE21 TAPE13

FULLSCF
INTEGRATION 6.0

NOPRINT LOGFILE

eor
```

```
#! /bin/sh

# ==============================
# Fe transition state H2 loss
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 C       4.484560000000       4.739900000000      17.353300000000
2 C       3.126510000000       2.315260000000      16.727200000000
3 C       2.033470000000       3.979920000000      18.471800000000
4 C       2.404140000000       6.618730000000      12.972400000000
5 O       1.320190000000       6.572850000000      16.168100000000
6 H       6.795820000000       1.621790000000      12.529400000000
7 C       4.314360000000       1.227270000000      13.516100000000
8 N       4.360050000000       2.660530000000      13.218900000000
9 H       7.001030000000       2.729490000000      11.146900000000
10 H       5.771430000000       1.449910000000      11.096200000000
11 C       5.253570000000       3.140350000000      12.347800000000
12 H       6.128850000000       4.700830000000      11.226500000000
13 H       3.830330000000       6.929150000000      10.543400000000
14 C       4.402460000000       5.541170000000      12.105200000000
15 C       5.309830000000       4.479300000000      11.907400000000
16 C       4.633520000000       6.793090000000      11.283500000000
17 H       4.645660000000       7.691340000000      11.917000000000
18 O       5.540680000000       5.142580000000      17.613700000000
19 O       3.249320000000       1.155930000000      16.715400000000
20 O       1.484400000000       3.887280000000      19.489600000000
21 N       3.352400000000       5.503440000000      12.931800000000
22 Ga       3.135560000000       3.948520000000      14.283200000000
23 Fe       2.833830000000       4.101280000000      16.851100000000
24 H       5.583260000000       6.730560000000      10.743000000000
25 C       6.266030000000       2.185620000000      11.748500000000
26 C       1.950310000000       5.618100000000      16.393300000000
27 H       5.155710000000       0.913380000000      14.154400000000
28 H       4.330820000000       0.623450000000      12.597600000000
29 H       3.387700000000       0.996641000000      14.050500000000
30 H       2.824270000000       7.496060000000      13.489600000000
31 H       1.505210000000       6.311640000000      13.515600000000
32 H       2.097160000000       6.925030000000      11.962100000000
33 H       1.654850000000       3.567180000000      15.714000000000
34 H       1.497710000000       3.395280000000      14.567600000000
END
```

```
GUIBONDS
1 1 18 2.0
2 1 23 2.0
3 2 19 2.0
4 2 23 2.0
5 3 20 2.0
6 3 23 1.5
7 22 8 1.0
8 22 23 3.0
9 4 21 1.0
10 23 26 1.5
11 26 5 2.0
12 14 21 1.0
13 25 9 1.0
14 25 10 1.0
15 14 15 1.5
16 14 16 1.0
17 15 12 1.0
18 15 11 1.5
19 16 24 1.0
20 16 13 1.0
```

```
21 16 17 1.0
22 25 6 1.0
23 11 8 1.0
24 11 25 1.0
25 7 8 1.0
26 21 22 1.0
27 27 7 1.0
28 28 7 1.0
29 29 7 1.0
30 30 4 1.0
31 31 4 1.0
32 32 4 1.0
33 23 33 1.0
34 34 22 1.0
END

BASIS
type TZP
core Large
createoutput None
END
```

```
XC
GGA Becke Perdew
END



SCANFREQ -1000 0

AnalyticalFreq
END
```

```
RESTART
$SCM_RESULTDIR/SP_43_LT_gallyl_to_dihydrogen
_a6_v7_fine.t21

SAVE  TAPE21 TAPE13

FULLSCF
INTEGRATION 6.0

NOPRINT LOGFILE

eor
```

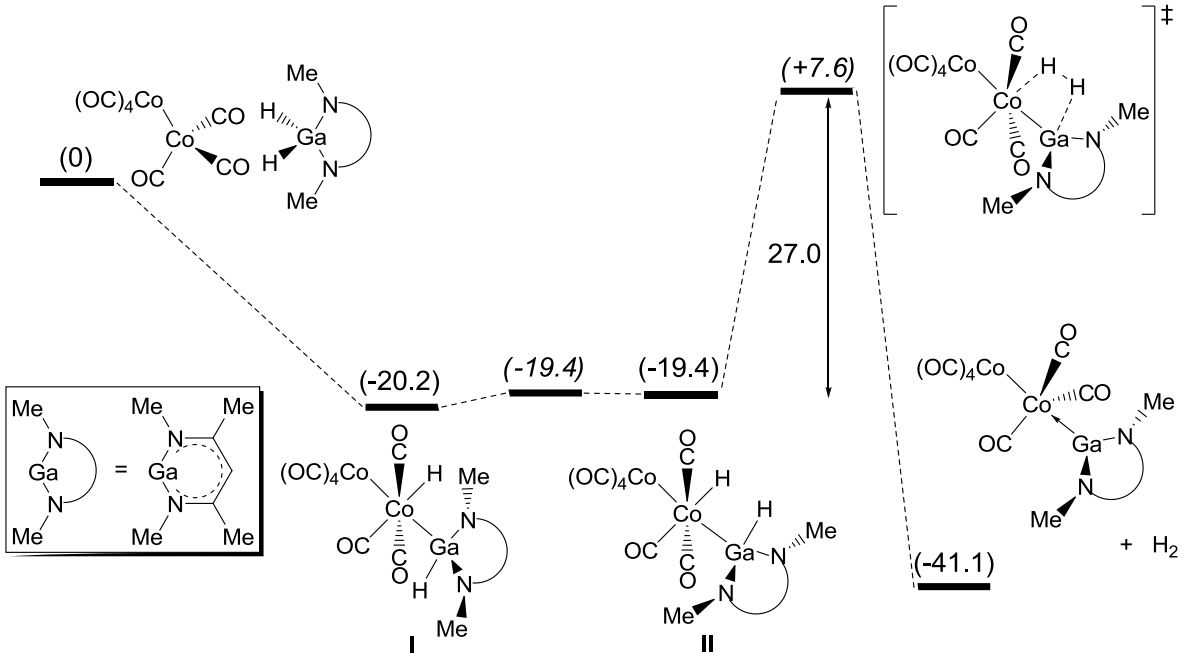
```
#! /bin/sh

# ==============================
# Fe(CO)4(Me_NacNacGa)
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 C       1.129819222000       4.626029794000      15.738429210000
2 C       3.912304080000       5.431643887000      16.884633090000
3 C       1.965288571000       4.274998139000      18.188813500000
4 C       3.208760435000       6.866759191000      13.377586990000
5 O       3.316408484000       1.270265761000      17.021751450000
6 H       6.470820395000       1.459596352000      11.548329650000
7 C       4.684020610000       1.297040901000      13.625176740000
8 N       4.507472173000       2.661442979000      13.111013900000
9 H       5.870518492000       2.232866279000      10.062331560000
10 H       4.886994217000       1.011597166000      10.903590800000
11 C       4.930976380000       2.952751187000      11.869963720000
12 H       5.218439073000       4.271260320000      10.250368040000
13 H       3.307726616000       6.992455363000      10.625134670000
14 C       4.280833871000       5.419209495000      11.753336900000
15 C       4.821743942000       4.215280844000      11.262035070000
16 C       4.321191441000       6.614565457000      10.825156010000
17 H       4.889119040000       7.442875154000      11.273685100000
18 O       0.108527189800       4.945662070000      15.271323580000
19 O       4.679691080000       6.269518432000      17.153560110000
20 O       1.502164043000       4.360677680000      19.250660950000
21 N       3.743402498000       5.562514736000      12.970960070000
22 Ga       3.605724859000       4.033015432000      14.370266760000
23 Fe       2.679301505000       4.144401361000      16.548686910000
24 H       4.787380120000       6.352461713000       9.870124355000
25 C       5.575980359000       1.856901543000      11.047076320000
26 C       3.083841120000       2.393177099000      16.797721590000
27 H       5.746406832000       1.011536442000      13.658635790000
28 H       4.148366883000       0.559654044800      13.008158440000
29 H       4.287081761000       1.236374111000      14.642313020000
30 H       3.989133894000       7.642773041000      13.375372970000
31 H       2.811335072000       6.787919925000      14.395670340000
32 H       2.391567169000       7.193337979000      12.716825830000
END
```

```
GUIBONDS
1 1 18 2.0
2 1 23 2.0
3 2 19 2.0
4 2 23 2.0
5 3 20 2.0
6 3 23 1.5
7 22 8 1.0
8 22 23 3
9 4 21 1.0
10 23 26 1.5
11 26 5 2.0
12 14 21 1.0
13 25 9 1.0
14 25 10 1.0
15 14 15 1.5
16 14 16 1.0
17 15 12 1.0
18 15 11 1.5
19 16 24 1.0
20 16 13 1.0
21 16 17 1.0
22 25 6 1.0
23 11 8 1.0
24 11 25 1.0
25 7 8 1.0
26 21 22 1.0
27 27 7 1.0
28 28 7 1.0
29 29 7 1.0
30 30 4 1.0
31 31 4 1.0
32 32 4 1.0
END

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
```

3b. The model system $Co_2(CO)_7$ + $H_2Ga\{(NMeCMe)_2CH\}$



Scheme S1: Model for potential gallane dehydrogenation pathway at thermally generated $[Co_2(CO)_7]$, via (hydrido)cobalt gallyl intermediates **I** and **II** (relative energies in kcal mol^{-1}). Calculations performed using the Vosko-Wilk-Nusair local density approximation with BP86 exchange-correlation corrections. A triple zeta basis set with an additional set of polarization functions (TZP) was employed.

```
#! /bin/sh

# ==============================
# Co2(CO)7
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 O       1.326889999000      15.052190410000       6.210589118000
2 Co       3.419049043000       14.539626480000       4.131161212000
3 Co       5.324854453000       14.700287760000       5.950576165000
4 C       4.707976954000      16.418382580000       6.228814901000
5 O       4.374818685000      17.499035790000       6.455233018000
6 C       6.488563430000      14.358053560000       4.556368455000
7 O       7.269385160000      14.145773950000       3.734809945000
8 C       6.621555340000      14.818257380000       7.190442525000
9 O       7.453238744000      14.895562080000       7.985686463000
10 C       4.470307502000       13.280140900000       6.767948579000
11 O       3.990111500000       12.393300730000       7.327041004000
12 C       4.172612368000       15.940587190000       3.215079223000
13 O       4.622036344000       16.822657560000       2.614060365000
14 C       3.923003984000       12.815678910000       3.752153344000
15 O       4.213051739000       11.725649270000       3.489584437000
16 C       2.151245471000       14.855155730000       5.421446237000
END

GUIBONDS
1 14 15 2.0
2 16 1 2.0
3 12 13 2.0
4 2 16 2.0
5 2 14 2.0
6 2 12 1.5
7 2 3 1.5
8 3 8 2.0
9 3 4 2.0
10 3 10 2.0
11 3 6 2.0
12 4 5 2.0
13 6 7 2.0
14 8 9 2.0
15 10 11 2.0
END

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

# ==============================
# Co gallyl (anti)
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 Ga       2.213272256000      14.638443450000       1.561151997000
2 Co       3.583941411000      14.609454020000       3.759065918000
3 Co       5.006811178000      14.508115620000       6.147355072000
4 C       4.268439541000      16.148831720000       6.468703117000
5 O       3.854540287000      17.193956690000       6.759063342000
6 C       6.463359212000      14.478879310000       5.044152664000
7 O       7.449917988000      14.463175110000       4.432816968000
8 C       5.888419865000      14.334567320000       7.707645165000
9 O       6.452415961000      14.223800250000       8.713039410000
10 C       3.978602877000       13.012551050000       6.317483014000
11 O       3.377674149000       12.040821200000       6.530556839000
12 C       4.405923114000       16.170940260000       3.266395870000
13 O       4.904490883000       17.154942260000       2.923467100000
14 C       4.576408033000       13.369237130000       2.926732569000
15 O       5.149843815000       12.509991040000       2.404032685000
16 C       2.092527939000       15.184399900000       4.580039430000
```

```
17 O       1.114367569000      15.476750290000       5.123121916000
18 N       0.824941375200      13.102926670000       1.656696463000
19 H       0.646472676700      11.162807230000       0.788593413700
20 H      -2.393883390000      16.698341100000       2.605549586000
21 C      -0.481833898600      15.876432190000       2.022800949000
22 N       0.769130174900      16.124547560000       1.620004855000
23 H       0.527180793500      18.015300950000       0.664987965200
24 H      -2.037516849000      14.573102890000       2.603090898000
25 H      -1.008458835000      17.761391560000       2.955825298000
26 H      -2.310878311000      12.437409790000       2.672635533000
27 H      -1.591748620000      17.589769440000       1.293783797000
28 H      -0.886342334500      11.430482540000       3.032906080000
29 H      -1.487830222000      11.547567610000       1.373049394000
30 C      -1.424028205000      17.043111720000       2.233921913000
31 C      -0.433359204300      13.314245790000       2.056470427000
32 C      -1.332093598000      12.119294810000       2.300343172000
33 C      -1.006715464000      14.588000170000       2.255392267000
34 C       1.198682922000      17.501490460000       1.368836552000
35 H       1.244604285000      18.097934890000       2.294638763000
36 H       2.200294017000      17.493162240000       0.923765454100
37 C       1.309468160000      11.736376420000       1.452994869000
38 H       2.299626040000      11.768276700000       0.984249711700
39 H       1.403062424000      11.184563470000       2.402736505000
40 H       2.866747710000      13.336581840000       4.091215914000
41 H       3.068811952000      14.659170680000       0.195718578400
END
```

```
GUIBONDS
1 1 18 1.0
2 1 22 1.0
3 1 2 3
4 2 16 2.0
5 2 14 2.0
6 2 12 1.5
7 2 3 1.5
8 3 8 2.0
9 3 4 2.0
10 3 10 2.0
11 3 6 2.0
12 4 5 2.0
13 6 7 2.0
14 8 9 2.0
15 10 11 2.0
16 12 13 2.0
17 14 15 2.0
18 16 17 2.0
19 18 31 1.0
20 19 37 1.0
21 30 25 1.0
22 33 21 1.5
23 21 22 1.0
24 21 30 1.0
25 23 34 1.0
26 31 33 1.5
27 30 27 1.0
28 30 20 1.0
29 31 32 1.0
30 32 28 1.0
31 32 26 1.0
32 32 29 1.0
33 33 24 1.0
34 35 34 1.0
35 36 34 1.0
36 34 22 1.0
37 38 37 1.0
38 39 37 1.0
39 37 18 1.0
40 40 2 1.0
41 41 1 1.0
END

BASIS
type TZP
core Large
createoutput None
END

XC
GGA Becke Perdew
END



SCANFREQ -1000 0

AnalyticalFreq
END

SAVE  TAPE21 TAPE13

SCF
diis
END

FULLSCF
INTEGRATION 6

NoBeckeGrid
NOPRINT LOGFILE

eor
```

```
#! /bin/sh

# ==============================
# Co transition state gallyl (anti) to gallyl (syn)
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 Ga       2.109204759000      13.996950960000       1.659104465000
2 Co       3.517460996000      14.318379250000       3.818027188000
3 Co       5.056203514000      14.543461390000       6.124558936000
```

```
4 C       3.625455909000      15.436171970000       6.833872946000
5 O       2.775191549000      16.016279320000       7.369557951000
6 C       6.165074053000      15.533260240000       5.061301025000
7 O       6.927731525000      16.180275280000       4.471905845000
8 C       6.087541697000      14.540890530000       7.600201569000
9 O       6.748719205000      14.540243310000       8.550898227000
10 C       4.973971002000      12.733551530000       5.929470738000
11 O       4.992304650000      11.572083100000       5.912821370000
12 C       3.356511492000      16.141009050000       3.732563752000
13 O       3.246536929000      17.288789220000       3.659351401000
14 C       4.919771263000      13.999644110000       2.742320681000
15 O       5.797572694000      13.711580120000       2.046766309000
16 C       2.055297207000      13.872040880000       4.755454176000
17 O       1.137590357000      13.500287340000       5.354156604000
18 N       0.162411725500      13.476137050000       2.143117338000
19 H      -1.039057521000      11.732514020000       1.899962140000
20 H      -0.760740549400      18.257102310000       1.473049699000
21 C       0.413762425600      16.445707770000       1.367636572000
22 N       1.548027658000      15.866917810000       0.959352911300
23 H       2.048521538000      17.045260290000      -0.744740731300
24 H      -1.452485635000      16.408287570000       2.358109375000
25 H       0.998633038100      18.532558230000       1.407979641000
26 H      -2.729572021000      14.857177130000       3.160072420000
27 H       0.124110692900      18.054639750000      -0.054592669490
28 H      -1.946760744000      13.445908270000       3.916336346000
29 H      -2.631771631000      13.311222260000       2.289800405000
30 C       0.177478734300      17.903623950000       1.034144571000
31 C      -0.766258325400      14.409787430000       2.375183964000
32 C      -2.092761341000      13.987489180000       2.970422718000
33 C      -0.610086354400      15.780190370000       2.075536554000
34 C       2.512358107000      16.625471160000       0.160674333100
35 H       2.963319305000      17.454294100000       0.729721479800
36 H       3.319610427000      15.957395890000      -0.161400685200
37 C      -0.127552795100      12.067846410000       2.417208710000
38 H       0.703936073200      11.451563450000       2.055583359000
39 H      -0.252165510900      11.872322220000       3.494374793000
40 H       3.580060954000      12.818931150000       3.799515344000
41 H       2.737698852000      13.044555020000       0.521412547900
END
```

```
GUIBONDS
1 1 18 1.0
2 1 22 1.0
3 1 2 3
4 2 16 2.0
5 2 14 2.0
6 2 12 1.5
7 2 3 1.5
8 3 8 2.0
9 3 4 2.0
10 3 10 2.0
11 3 6 2.0
12 4 5 2.0
13 6 7 2.0
14 8 9 2.0
15 10 11 2.0
16 12 13 2.0
17 14 15 2.0
18 16 17 2.0
19 18 31 1.0
20 19 37 1.0
21 30 25 1.0
22 33 21 1.5
23 21 22 1.0
24 21 30 1.0
25 23 34 1.0
26 31 33 1.5
27 30 27 1.0
28 30 20 1.0
29 31 32 1.0
30 32 28 1.0
31 32 26 1.0
32 32 29 1.0
33 33 24 1.0
34 35 34 1.0
35 36 34 1.0
36 34 22 1.0
37 38 37 1.0
38 39 37 1.0
39 37 18 1.0
40 40 2 1.0
41 41 1 1.0
END

BASIS
type TZP
core Large
createoutput None
END

XC
GGA Becke Perdew
END



SCANFREQ -1000 0

AnalyticalFreq
END

SAVE  TAPE21 TAPE13

SCF
diis
END

FULLSCF
INTEGRATION 6

NoBeckeGrid
NOPRINT LOGFILE

eor
```

```
#! /bin/sh

# ==============================
# Co gallyl (syn)
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 Ga       2.170339723000      14.947901880000       1.585582609000
2 Co       3.519987705000      14.737668100000       3.801712664000
3 Co       5.055842462000      14.498660500000       6.108017490000
4 C        3.718829086000      13.407061130000       6.713292415000
5 O        2.923886363000      12.707238350000       7.187623805000
6 C        4.758901491000      16.295514140000       6.248584960000
7 O        4.620434483000      17.433619870000       6.430782714000
8 C        6.152207950000      14.333771800000       7.526399702000
9 O        6.854887159000      14.226819770000       8.440578355000
10 C       6.226792653000      13.862407430000       4.863185955000
11 O       7.054443909000      13.441154150000       4.165652455000
12 C       2.120946030000      15.381841610000       4.795015116000
13 O       1.232138650000      15.796388490000       5.405237626000
14 C       4.321631770000      16.238418570000       3.228022288000
15 O       4.883434237000      17.155143540000       2.800664343000
16 C       3.160736914000      12.982233950000       3.751538341000
17 O       3.004632064000      11.837676540000       3.675456381000
18 N       1.238756054000      13.156212010000       1.122115551000
19 H       1.429276629000      11.727280020000      -0.447175298600
20 H      -2.682713187000      15.215141070000       3.251896856000
21 C      -0.702212671400      15.183578140000       2.387580291000
22 N       0.375929081000      15.888268170000       2.027930566000
23 H      -0.483072823600      17.792494750000       1.603288094000
24 H      -1.752355028000      13.365333820000       2.626035757000
25 H      -1.618191095000      16.525203600000       3.822579886000
26 H      -1.456896233000      11.328550120000       1.957313596000
27 H      -2.327504653000      16.604501900000       2.202764330000
28 H       0.213967419700      10.713063280000       1.878790655000
29 H      -0.623085276000      11.190873780000       0.394433464400
30 C      -1.900503835000      15.918505530000       2.949852596000
31 C       0.031906820420      12.857007870000       1.614407965000
32 C      -0.490412129400      11.444737040000       1.457022629000
33 C      -0.818736501100      13.783168790000       2.254935421000
34 C       0.368967682000      17.347951200000       2.139189623000
35 H       0.326250063100      17.684526460000       3.187774794000
36 H       1.285986523000      17.748852240000       1.692036997000
37 C       2.005219400000      12.144627120000       0.392588694400
38 H       2.908296705000      12.606956370000      -0.022848776270
39 H       2.318380189000      11.312439970000       1.042804319000
40 H       4.627257834000      14.212638390000       2.936772016000
41 H       2.947398175000      15.584308090000       0.325844736500
END


GUIBONDS
1 1 18 1.0
2 1 22 1.0
3 1 2 3
4 2 16 2.0
5 2 14 2.0
6 2 12 1.5
7 2 3 1.5
8 3 8 2.0
9 3 4 2.0
10 3 10 2.0
11 3 6 2.0
12 4 5 2.0
13 6 7 2.0
14 8 9 2.0
15 10 11 2.0
16 12 13 2.0
17 14 15 2.0
18 16 17 2.0
19 18 31 1.0
20 19 37 1.0
21 30 25 1.0
22 33 21 1.5
23 21 22 1.0
24 21 30 1.0
25 23 34 1.0
26 31 33 1.5
27 30 27 1.0
28 30 20 1.0
29 31 32 1.0
30 32 28 1.0
31 32 26 1.0
32 32 29 1.0
33 33 24 1.0
34 35 34 1.0
35 36 34 1.0
36 34 22 1.0
37 38 37 1.0
38 39 37 1.0
39 37 18 1.0
40 40 2 1.0
41 41 1 1.0
END

BASIS
type TZP
```

```
core Large
createoutput None
END

XC
GGA Becke Perdew
END



SCANFREQ -1000 0

AnalyticalFreq
END

SAVE  TAPE21 TAPE13

SCF
diis
END

FULLSCF
INTEGRATION 6

NoBeckeGrid
NOPRINT LOGFILE

eor
```

```
#! /bin/sh

# ==============================
# Co transition state H2 loss
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 Ga       1.688673902000      14.532372470000       2.326387815000
2 Co       3.422045229000      14.570524730000       4.058615711000
3 Co       5.334361600000      14.617991570000       6.066891991000
4 C        4.496336787000      13.111086780000       6.686439597000
5 O        4.027669336000      12.156966710000       7.148747663000
6 C        4.567041016000      16.211341220000       6.545778476000
7 O        4.143284091000      17.223767140000       6.918805162000
8 C        6.679623387000      14.641520720000       7.260994734000
9 O        7.548265277000      14.656462000000       8.026233831000
10 C       6.393845374000      14.526427270000       4.581380994000
11 O       7.149686436000      14.469291170000       3.703378572000
12 C       2.109898261000      14.658221410000       5.325359139000
13 O       1.217610457000      14.712172370000       6.064335247000
14 C       4.025593286000      16.206168110000       3.560039406000
15 O       4.412576587000      17.244121320000       3.208927871000
16 C       3.948212269000      12.870188890000       3.711893127000
17 O       4.285988251000      11.787814820000       3.457344677000
18 N       0.447053339900      13.004342390000       1.760471476000
19 H       1.138323836000      11.038873090000       1.309122513000
20 H      -2.136609035000      16.626741110000      -0.355724901900
21 C      -0.550728661000      15.803022360000       0.857574753500
22 N       0.519413706300      16.059082470000       1.620174955000
23 H       1.300703409000      17.940629890000       0.992403580600
24 H      -1.909196868000      14.506245700000      -0.097858821870
25 H      -1.743259544000      17.597949450000       1.080635021000
26 H      -2.238614022000      12.384401300000      -0.158891554100
27 H      -0.659240704300      17.621657210000      -0.317057313900
28 H      -1.885443240000      11.529943790000       1.359748160000
29 H      -0.808902334400      11.329322980000      -0.029492829380
30 C      -1.317220358000      16.974291480000       0.280770907300
31 C      -0.611519133400      13.239734860000       0.975410813800
32 C      -1.433885827000      12.058094560000       0.506893459800
33 C      -1.034832796000      14.515258970000       0.549290831500
34 C       0.918834966500      17.441837130000       1.897177662000
35 H       0.082827940820      18.035000840000       2.294781588000
36 H       1.717264752000      17.445416320000       2.645303603000
37 C       0.781609434700      11.635459500000       2.163566931000
38 H       1.580098094000      11.662794440000       2.911152745000
39 H      -0.080671346470      11.120836060000       2.611270469000
40 H       3.667734594000      14.485881160000       2.332557352000
41 H       3.162697999000      14.446633410000       1.217527322000
END

GUIBONDS
1 1 18 1.0
2 1 22 1.0
3 1 2 3
4 2 16 2.0
5 2 14 2.0
6 2 12 1.5
7 2 3 1.5
8 3 8 2.0
9 3 4 2.0
10 3 10 2.0
11 3 6 2.0
12 4 5 2.0
13 6 7 2.0
14 8 9 2.0
15 10 11 2.0
16 12 13 2.0
17 14 15 2.0
18 16 17 2.0
19 18 31 1.0
20 19 37 1.0
21 30 25 1.0
```

```
22 33 21 1.5
23 21 22 1.0
24 21 30 1.0
25 23 34 1.0
26 31 33 1.5
27 30 27 1.0
28 30 20 1.0
29 31 32 1.0
30 32 28 1.0
31 32 26 1.0
32 32 29 1.0
33 33 24 1.0
34 35 34 1.0
35 36 34 1.0
36 34 22 1.0
37 38 37 1.0
38 39 37 1.0
39 37 18 1.0
40 40 2 1.0
41 41 1 1.0
END

BASIS
type TZP
core Large
createoutput None
END

XC
GGA Becke Perdew
END


SCANFREQ -1000 0

AnalyticalFreq
END

SAVE  TAPE21 TAPE13

SCF
diis
END

FULLSCF
INTEGRATION 6

NoBeckeGrid
NOPRINT LOGFILE

eor


#! /bin/sh

# ==============================
# Co2(CO)7(MeNacNacGa)
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 Ga       1.695301557000      14.504386480000       2.545211471000
2 Co       3.408294431000      14.535545130000       4.122955032000
3 Co       5.356890509000      14.700446180000       5.981433548000
4 C        4.693517110000      16.391857000000       6.199289532000
5 O        4.332175514000      17.475873100000       6.394937621000
6 C        6.452777513000      14.366061020000       4.551529656000
7 O        7.212546172000      14.163208340000       3.700909408000
8 C        6.651965556000      14.817672690000       7.223270015000
9 O        7.485262945000      14.894222710000       8.023027870000
10 C       4.454986436000      13.295817850000       6.736679638000
11 O       3.943148473000      12.408096070000       7.277073531000
12 C       4.163948960000      15.922104130000       3.227559760000
13 O       4.631200677000      16.810072440000       2.637823314000
14 C       3.914730643000      12.832678250000       3.750899712000
15 O       4.229299964000      11.739702640000       3.499975500000
16 C       2.172049450000      14.856606830000       5.412800659000
17 O       1.360961523000      15.060043210000       6.222474268000
18 N       0.869576466300      13.212257190000       1.170334215000
19 H       1.856273328000      11.679543940000       0.059996708790
20 H      -2.200359193000      16.914430670000       0.120015440200
21 C      -0.570323828900      15.941611680000       1.153734866000
22 N       0.390907663000      16.040745450000       2.081209505000
23 H       0.793976351100      18.134086370000       2.160361690000
24 H      -1.633893087000      14.877718080000      -0.325678936300
25 H      -2.005416141000      17.422961470000       1.814954463000
26 H      -1.529495690000      12.902467260000      -1.170440158000
27 H      -0.876830065000      18.009619260000       0.587508195300
28 H      -1.024684643000      11.600177950000      -0.067574713340
29 H       0.097526014770      12.192915680000      -1.298288464000
30 C      -1.465709952000      17.135070070000       0.900760700400
31 C      -0.165958657400      13.540304450000       0.379003510300
32 C      -0.688057323300      12.505035630000      -0.594488324000
33 C      -0.812858487700      14.788152490000       0.382661914900
34 C       0.556220326300      17.292975970000       2.828710870000
35 H      -0.349745206500      17.546312250000       3.399230639000
36 H       1.383302721000      17.179744570000       3.538222766000
37 C       1.458724015000      11.870356910000       1.068137474000
38 H       2.285570414000      11.780798530000       1.778469699000
39 H       0.723003153400      11.086901110000       1.304029219000
END
```

```
GUIBONDS
1 1 18 1.0
2 1 22 1.0
3 1 2 3
4 2 16 2.0
5 2 14 2.0
6 2 12 1.5
7 2 3 1.5
8 3 8 2.0
9 3 4 2.0
10 3 10 2.0
11 3 6 2.0
12 4 5 2.0
13 6 7 2.0
14 8 9 2.0
15 10 11 2.0
16 12 13 2.0
17 14 15 2.0
18 16 17 2.0
19 18 31 1.0
20 19 37 1.0
21 30 25 1.0
22 33 21 1.5
23 21 22 1.0
24 21 30 1.0
25 23 34 1.0
26 31 33 1.5
27 30 27 1.0
28 30 20 1.0
29 31 32 1.0
30 32 28 1.0
31 32 26 1.0
32 32 29 1.0
33 33 24 1.0
34 35 34 1.0
35 36 34 1.0
36 34 22 1.0
37 38 37 1.0
38 39 37 1.0
39 37 18 1.0
END

BASIS
type TZP
core Large
createoutput None
END

XC
GGA Becke Perdew
END



SCANFREQ -1000 0

AnalyticalFreq
END

SAVE  TAPE21 TAPE13

SCF
diis
END

FULLSCF
INTEGRATION 6

NoBeckeGrid
NOPRINT LOGFILE

eor
```

2c. ETS-NOCV calculation on $(OC)_5W(Ga\{(NMeCMe)_2CH\})$

```
#! /bin/sh

# ==============================
# W(CO)5(MeNacNacGa)
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 W       6.555255167000      17.306178090000      15.830581080000  f=Metal b=Metal
2 Ga       4.584797417000       15.487383540000       15.824942020000  f=Ligand b=Ligand
3 N       3.023831362000      15.011966260000      14.506215440000  f=Ligand b=Ligand
4 H       3.057203333000      15.215093740000      12.379948150000  f=Ligand b=Ligand
5 H       2.421376289000      12.564967460000      18.973349180000  f=Ligand b=Ligand
6 C       2.937792892000      13.152582140000      16.950230310000  f=Ligand b=Ligand
7 C       2.623575996000      12.102156550000      17.996051800000  f=Ligand b=Ligand
8 H       1.748426287000      11.511694280000      17.706557620000  f=Ligand b=Ligand
9 H       3.472875905000      11.417063360000      18.135929240000  f=Ligand b=Ligand
10 O       5.845918008000       17.982866140000       18.939388080000  f=Metal b=Metal
11 H       1.290575899000       12.460176930000       15.826325040000  f=Ligand b=Ligand
12 H       0.382511168200       12.997237910000       13.947446510000  f=Ligand b=Ligand
13 H       0.438065150600       14.722162930000       13.513132380000  f=Ligand b=Ligand
14 H       1.490302730000       13.572469460000       12.679050600000  f=Ligand b=Ligand
15 N       3.981247219000       13.970635320000       17.143736270000  f=Ligand b=Ligand
16 C       2.120557982000       14.041409750000       14.700690180000  f=Ligand b=Ligand
17 C       2.092417733000       13.195983180000       15.825688440000  f=Ligand b=Ligand
18 C       1.046725621000       13.816961250000       13.655619330000  f=Ligand b=Ligand
19 C       8.063481727000       18.704102900000       15.836044670000  f=Metal b=Metal
20 O       8.915642305000       19.494656190000       15.839575020000  f=Metal b=Metal
21 C       6.963045306000       16.818759000000       13.830368530000  f=Metal b=Metal
22 O       7.188850211000       16.555038630000       12.722335200000  f=Metal b=Metal
23 C       7.884544902000       15.812339300000       16.466847050000  f=Metal b=Metal
24 O       8.622610060000       14.989682470000       16.823167660000  f=Metal b=Metal
25 C       5.172786979000       18.749627910000       15.191483900000  f=Metal b=Metal
```

```
26 O       4.412192774000      19.550427490000      14.832775640000  f=Metal b=Metal
27 H       5.589743650000      14.571975380000      18.348292680000  f=Ligand b=Ligand
28 C       6.094247006000      17.742179630000      17.830922720000  f=Metal b=Metal
29 C       2.947352920000      15.825996870000      13.289170280000  f=Ligand b=Ligand
30 H       1.995260793000      16.374580930000      13.222039110000  f=Ligand b=Ligand
31 H       3.759158763000      16.562135460000      13.299513970000  f=Ligand b=Ligand
32 C       4.786838721000      13.826145140000      18.360228880000  f=Ligand b=Ligand
33 H       4.188557836000      13.988851870000      19.269946300000  f=Ligand b=Ligand
34 H       5.252041275000      12.830662550000      18.427954090000  f=Ligand b=Ligand
END
```

```
GUIBONDS
1 1 25 1.5
2 1 19 1.5
3 1 23 1.5
4 1 21 1.5
5 1 28 1.0
6 1 2 3
7 2 3 1.0
8 2 15 1.0
9 3 16 1.0
10 4 29 1.0
11 19 20 2.0
12 21 22 2.0
13 23 24 2.0
14 25 26 2.0
15 15 6 1.0
16 27 32 1.0
17 7 5 1.0
18 7 8 1.0
19 6 7 1.0
20 7 9 1.0
21 28 10 2.0
22 16 17 1.5
23 16 18 1.0
24 17 11 1.0
25 17 6 1.5
26 18 14 1.0
27 18 13 1.0
28 18 12 1.0
29 30 29 1.0
30 31 29 1.0
31 29 3 1.0
32 33 32 1.0
33 34 32 1.0
34 32 15 1.0
END

SYMMETRY NOSYM

BASIS
type TZP
core Large
createoutput None
END

XC
GGA Becke Perdew
END



Fragments
    Ligand Frag_W(CO)5_Me_Ga_d6.Ligand.t21
    Metal Frag_W(CO)5_Me_Ga_d6.Metal.t21
end
ETSNOCV
PRINT ETSLOWDIN
SAVE  TAPE21 TAPE13

SCF
diis
END

FULLSCF
INTEGRATION 6
```

```
NoBeckeGrid
NOPRINT LOGFILE

eor
```

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