Supporting Information to

Adaptive Behavior of Redox-Active Gallium Carbenoid in Complexes with Molybdenum^{†‡}

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15 General remarks: All manipulations were carried out under vacuum using glass ampoules. The solvents THF, benzene and toluene were dried over sodium/benzophenone. Benzene-d₆ (Aldrich) was dried over sodium/benzophenone at ambient temperature and, just prior to use, condensed under vacuum into the NMR tubes already containing the respective compound. The IR spectra were recorded on a FSM-1201 spectrometer in a Nujol, the ¹H NMR spectra – on a Bruker DPX-200 (200 MHz) NMR spectrometer. The EPR spectrum of

- 20 compound **2** was obtained using a Bruker EMX spectrometer (9.75 GHz), the signal was referred to the signal of diphenylpicrylhydrazyl (g = 2.0037). Melting points were measured in sealed capillaries. The dpp-bian was prepared by the condensation of acenaphthenequinone with 2,6-diisopropylaniline (both from Aldrich) in acetonitrile under reflux according to the literature procedure [1]. Starting compound **1** has been prepared by reflux of dpp-bian (0.5 g, 1.0 mmol) with an excess of gallium metal in toluene (50 mL) as described earlier [2].
- 25 The separation of toluene solution from gallium metal, evaporation of the solvent and dissolution of the crude 1 in THF (30 mL) gave a clear blue solution, which was used in the reactions with molybdenum carbonyls. The yields of the products were calculated from the amount of the dpp-bian used (0.5 g, 1.0 mmol) in the syntheses. [1] A. A. Paulovicova, U. El Ayaan, K. Shibayama, T. Morita, Y. Fukuda, Eur. J. Inorg. Chem., 2001, 2641.

[2] I. L. Fedushkin, A. N. Lukoyanov, A. N. Tishkina, G. K. Fukin, K. A. Lyssenko, M. Hummert, Chem.–Eur. 30 J., 2010, 16, 7563.

Synthesis of (dpp-bian)Ga–Mo(CO)₅ (2). Molybdenum hexacarbonyl (0.39 g, 1.5 mmol) was added to a solution of compound 1 (in situ from 0.5 g, 1.0 mmol of dpp-bian) in THF (30 mL) in a glass ampoule (70 mL). The ampoule was sealed off under vacuum, placed behind a plexiglass protecting wall and heated to 100 °C. 35 After 15 hours the reaction mixture was cooled to ambient temperature and opened under vacuum. Removal of

the volatiles under vacuum and sublimation of an excess of Mo(CO)₆ left the crude product, which was dissolved in benzene (25 mL). The resulting green solution was concentrated by evaporation of the solvent to a volume of 10 mL. Crystallisation at 10 °C gave deep green, almost black, crystals of compound **2**. Yield 0.76 g (95 %). M.p. > 230 °C (dec.). IR (Nujol, v/cm⁻¹): 2056 s, 1925 vs, 1628 m, 1601 s, 1579 m, 1540 m, 1507 w, 5 1413 w, 1358 w, 1308 s, 1250 w, 1233 w, 1184 m, 1146 m, 1126 m, 1062 w, 933 m, 891 w, 861 w, 847 w, 825 w, 789 m, 767 w, 717 s, 684 w, 640 m, 604 m, 582 s, 494 w, 460 w.

Synthesis of (dpp-bian)Ga–Mo(CO)₃Cp (3). [CpMo(CO)₃]₂ (0.25 g, 0.52 mmol) was added to a solution of compound 1 (in situ from 0.5 g, 1.0 mmol of dpp-bian) in THF (30 mL) in a glass ampoule (70 mL). The 10 ampoule was sealed off under vacuum, placed behind a plexiglass protecting wall and heated to 80 °C. After 1 hour the reaction mixture was cooled to ambient tempearture and opened under vacuum. The residual solid left after evaporation of the solvent was dissolved in 1,2-dimethoxyethane (25 mL). The brown solution formed was concentrated to 10 mL under reduced pressure. Storing of the solution at 10 °C for 24 hours resulted in deep brown, almost black crystals of compound 3 (0.76 g, 93 %). M.p. > 200 °C (dec.). ¹H NMR (200 MHz, C₆D₆, 15 298 K, δ, ppm, J/Hz): 7.40-7.06 (m, 12H, arom.), 6.88 (t, 2H, *J* = 8.2, arom.), 6.43 (d, 2H, *J* = 6.7, arom.), 4.40 (s, 5H, Cp ring), 3.83 (sept, 4H, *J* = 6.8, CH(CH₃)₂), 1.34 (d, 12H, *J* = 6.8, CH(CH₃)₂), 1.15 (d, 12H, *J* = 6.8, CH(CH₃)₂). IR (Nujol, v/cm⁻¹): 2007 vs, 1944 s, 1900 vs, 1612 m, 1595 m, 1539 w, 1505 m, 1443 vs, 1354 s, 1321 m, 1211 w, 1195 w, 1179 w, 1140 w, 1106 w, 1057 w, 1032 w, 1013 w, 1001 w, 928 s, 908 m, 840 w, 820

s, 811 s, 804 s, 762 vs, 723 m, 670 w, 651 w, 618 w, 586 s, 565 vs, 505 s, 462 s.





Figure S1. ¹H NMR spectrum of compound **3** in C_6D_6 . The signals between 3.0 and 3.5 ppm correspond to 1,2-dimetoxyethane admixture.

Synthesis of [{(dpp-bian)Ga-Mo(CO)₅}{Na(THF)₂}]₂ (4). Sodium metal (0.05 g, 2.1 mg-atom) was added to a solution of compound 1 (in situ from 0.5 g, 1.0 mmol of dpp-bian) in THF (30 mL). The mixture was stirred till the sodium dissolved completely. In the course of the reaction the mixture turned from deep blue to green brown. To the solution formed molybdenum hexacarbonyl (0.26 g, 1.0 mmol) was added. The resulting mixture 5 was stirred at ambient temperature for 1 h. Removal of THF under vacuum and dissolution of the product in

benzene (30 mL) gave a green solution, which was then concentrated to 10 mL. Crystallization at 10 °C afforded dark green crystals of compound 4. Yield 0.94 g (97 %). M.p. > 200 °C (dec.). ¹H NMR (200 MHz, C₆D₆, 298 K, δ, ppm, J/Hz): 7.31 (s, 6H, C₆H₆), 7.20-7.00 (m, 7H, arom.), 6.81 (d, 2H, *J* = 8.0, arom.), 6.68 (spt, 2H, *J* = 8.0, arom.), 5.77 (d, 2H, *J* = 6.7, arom.), 3.83 (spt, 4H, *J* = 6.8, CH(CH₃)₂), 3.65 (m, 8H, THF), 1.78 (m, 10 8H, THF), 1.35 (d, 12H, *J* = 6.8, CH(CH₃)₂), 1.08 (d, 12H, *J* = 6.8, CH(CH₃)₂). IR (Nujol, v/cm⁻¹): 2058 w, 2041 s, 1986 s, 1465 m, 1965 vs, 1934 vs, 1872 vs, 1613 w, 1591 s, 1541 w, 1512 m, 1434 m, 1353 s, 1323 s, 1258 m, 1212 w, 1193 w, 1181 w, 1140 w, 1107 w, 1047 s, 1000 w, 928 m, 901 m, 834 w, 809 s, 787 w, 765 m,

684 s, 675 m, 649 w, 613 vs, 589 vs, 518 m.



Figure S2. ¹H NMR spectrum of compound 4 in C_6D_6 .

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