Electronic Supplementary Material (ESI) for Chemical Communications

Al-H σ-bond coordination: expanded ring carbene adducts of AlH_3 as neutral bi- and tri-functional donor ligands

Joseph A. B. Abdalla, Ian M. Riddlestone, Remi Tirfoin, Nicholas Phillips, Joshua I. Bates and Simon Aldridge*

Supporting Information (17 pages)

1. General methods

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 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, thf-d_8 or pyridine-d_5 which were dried over potassium, sodium, or molecular sieves, 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 ($\delta = 0$ ppm). ^{27}Al NMR spectra were referenced to $[Al(H_2O)_6]^{3+}$. 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 6Mes,[s1] 6Dipp,[s1] $Me_3N{\cdot}AlH_3$,[s2], $Mo(CO)_4(COD)$,[s3] and $Mo(CO)_3(CHT)$[s4] were prepared by literature procedures.

2. Syntheses of novel compounds

Synthesis of 6Mes·AlH$_3$, 2a: To a toluene solution (10 mL) of $Me_3N{\cdot}AlH_3$ (0.61 g, 6.86 mmol) at 0 °C was added dropwise a solution of 6Mes (2.00 g, 6.24 mmol) also in toluene (30 mL), leading to the immediate formation of a colourless precipitate. The reaction mixture was allowed to warm to room temperature and then stirred for 2 h, after which time the reaction appeared complete by ^{1}H NMR. The colourless precipitate was isolated by filtration, washed with diethyl ether (20 mL) and dried *in vacuo* to yield **2a** as a colourless powder. Yield: 1.51 g, 69%. Single crystals suitable for X-ray diffraction were grown from a saturated fluorobenzene solution over 2 weeks at -30 °C. M.p. 163°C. ***Spectroscopic data***: ^{1}H NMR (300 MHz, thf-d$_8$, 298 K): δ 2.24 (s, 6H, Mes *p*-CH$_3$), 2.29 (s, 12H Mes *o*-CH$_3$), 2.31 (quin, 2H, $^3J_{HH}$ = 6.0 Hz, NCH$_2$C*H*$_2$), 3.40 (t, 4H, $^3J_{HH}$ = 6.0 Hz, NC*H*$_2$), 6.84 (s, 4H, Mes *m*-CH) ^{13}C NMR (75 MHz, thf-d$_8$, 298 K): δ 18.3 (Mes *o*-CH$_3$), 21.2 (Mes *p*-CH$_3$), 21.7 (NCH$_2$CH$_2$), 47.4 (NCH$_2$), 130.0 (*m*-Ph), 136.0 (*o*-Ph), 138.4 (*p*-Ph), 142.6 (*ipso*-Ph). ^{27}Al NMR (78 MHz, thf-d$_8$, 298 K): δ 95 (br, s). IR (KBr disc, $\upsilon_{Al\text{-}H\ stretch}$/cm^{-1}) : 1736 (br, s). ***Crystallographic data***: **2a**, $C_{22}H_{31}AlN_2$, M_r = 350.48, orthorhombic, *Pc*21*n* (non-standard setting of *Pna*21), *a* = 8.1095(1), *b* = 15.6301(3), *c* = 16.3634(3) Å, *V* = 2074.1(1) Å^3, *Z* = 4, ρ_c = 1.122 Mg m^{-3}, T = 150(2) K, λ = 0.71073 Å. 2447 independent reflections [R(int) = 0.025], used in all calculations. R_1 = 0.0411, wR_2 = 0.0889 for $I > 2\sigma(I)$, and R_1 = 0.0507, wR_2 = 0.1008 for all unique reflections. Max./min. residual electron densities 0.27 and –0.29 e Å^{-3}. CSD ref.: 931225.

Synthesis of 6Dipp·AlH$_3$, 2b: To a toluene solution (10 mL) of $Me_3N{\cdot}AlH_3$ (0.30 g, 3.34 mmol) at 0 °C was added dropwise a solution of 6Dipp (1.23 g, 3.04 mmol) also in toluene (30 mL). The reaction mixture was allowed to warm to room temperature and then stirred for 2 h, after which time the reaction appeared complete by ^{1}H NMR. The solution was filtered and concentrated *in vacuo* to the point of incipient crystallistation. Storage at -30 °C for 2 d produced large colourless needles of **2b**. Yield: 0.89 g, 67%. M.p. 154°C. ***Spectroscopic data***: ^{1}H NMR (300 MHz, benzene-d$_6$, 298 K): δ 1.16 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH$_3$ of Dipp ^{i}Pr), 1.50 (quin, 2H, $^3J_{HH}$ = 5.7 Hz, NCH$_2$C*H*$_2$), 1.60 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH$_3$ of Dipp ^{i}Pr), 2.89 (t, 4H, $^3J_{HH}$ = 5.7 Hz, NC*H*$_2$), 3.12 (sept, 4H, $^3J_{HH}$ = 6.9 Hz, CH of Dipp ^{i}Pr), 7.08 (d, 4H, $^3J_{HH}$ = 7.5 Hz, Dipp *m*-CH), 7.21 (t, 2H, $^3J_{HH}$ = 7.5 Hz, Dipp *p*-CH). ^{13}C NMR (75 MHz, benzene-d$_6$, 298 K): δ 19.5 (NCH$_2$CH$_2$), 23.8 (CH$_3$ of Dipp ^{i}Pr), 26.0 (CH$_3$ of Dipp ^{i}Pr), 28.9 (CH of Dipp ^{i}Pr), 48.9 (NCH$_2$), 124.6 (*p*-Ph), 129.6 (*m*-Ph), 141.5 (*o*-Ph), 145.5 (*ipso*-Ph). ^{27}Al NMR (78 MHz, benzene-d$_6$, 298 K): δ 116 (br, s). IR (KBr disc, $\upsilon_{Al\text{-}H\ stretch}$/cm^{-1}) : 1740 (s), 1765 (s), 1797 (m). Elemental analysis : calcd. for $C_{28}H_{43}N_2Al$: C 77.38, H 9.97, N 6.45 meas. C 77.14, H 10.21, N 6.57. ***Crystallographic data***: **2b**·C_7H_8, $C_{35}H_{51}AlN_2$, M_r = 526.78, monoclinic, $P2_1/c$, *a* = 10.6568(1), *b* = 19.2990(2), *c* = 16.7649(2) Å, β = 105.360(1)°, *V* = 3324.8(1) Å^3, *Z* = 4, ρ_c = 1.052 Mg m^{-3}, T = 150(2) K, λ = 0.71073 Å. 7562 independent reflections [R(int) = 0.021], used in all calculations. R_1 = 0.0463, wR_2 = 0.1010 for $I > 2\sigma(I)$, and R_1 = 0.0612, wR_2 = 0.1110 for all unique reflections. Max./min. residual electron densities 0.36 and –0.28 e Å^{-3}. CSD ref.: 931226. The asymmetric unit contains one molecule of toluene which was modelled over two positions with a combined occupancy of one. The model was built using restraints on the bond distances (**SAME**: distance between two bonded carbons should be similar over the solvent molecule) and on displacement parameters (**SIMU** and **DELU**: taking into account that atoms which are bound to one another move similarly, both in direction and amount). Overall, 256 least-squares restraints were used in the refinement. In the absence of these restraints no chemically realistic model could be obtained.
Al-H resonances were not observed in the ^{1}H NMR spectrum of either **2a** or **2b**, presumably due to the quadrupolar nature of ^{27}Al (*I* = 5/2).

Synthesis of Mo(CO)$_4$(κ^2-H$_3$Al·6Mes), 3a: To a suspension of **2a** (0.30 g, 0.85 mmol) in benzene (5 mL) at room temperature was added a solution of Mo(CO)$_4$(COD) (0.25 g, 0.78 mmol) also in benzene (5 mL), and the reaction mixture left to stand for 16 h. The solution turned bright yellow over this period, with accompanying precipitation of a yellow microcrystalline solid. The solid was isolated by filtration, washed with pentane, extracted with fluorobenzene (20 mL) and the resulting solution concentrated *in vacuo*. Storage at -30 °C produced bright yellow crystals of **3a**. Yield: 0.22 g, 51%. ***Spectroscopic data***: ^{1}H NMR (500 MHz, thf-d$_8$, 298 K): δ -7.36 (br s, 2H, Mo-H-Al), 2.29 (s, 6H, Mes *p*-CH$_3$), 2.32 (quin, 2H, $^3J_{HH}$ = 5.5 Hz, NCH$_2$C*H*$_2$), 2.40 (s, 12H, Mes *o*-CH$_3$), 3.52 (t, 4H, $^3J_{HH}$ = 5.5 Hz, NC*H*$_2$), 4.02 (br s, 1H, terminal AlH), 6.99 (s, 4H, Mes *m*-CH), 7.21 (t, 2H, $^3J_{HH}$ = 7.5 Hz, Dipp *p*-CH). ^{13}C NMR (125 MHz, thf-d$_8$, 298 K): δ 18.8 (Mes *o*-CH$_3$), 21.0 (NCH$_2$CH$_2$), 21.2 (Mes *p*-CH$_3$), 47.5 (NCH$_2$), 130.9 (*m*-Ph), 136.9 (*o*-Ph), 139.7 (*p*-Ph), 140.6 (*ipso*-Ph), 211.8 (CO), 220.9 (CO). ^{27}Al NMR shift not observed. IR (CH$_2$Cl$_2$) υ_{CO}/cm^{-1} : 1981 (m), 1938 (s), 1887 (br, m)) $\upsilon_{Al\text{-}H}$/cm^{-1} 1740 (br, s, terminal Al-H) 1668 (br, s, Mo-H-Al). Elemental analysis : calcd. for $C_{26}H_{31}N_2AlMoO_4$: C 55.92, H 5.59, N 5.02 meas. C 56.03, H 5.60, N 4.82. ***Crystallographic data***: **3a**·½C_6H_5F, $C_{58}H_{67}Al_2FMo_2N_4O_8$, M_r = 1213.03, triclinic, *P*-1, *a* = 9.8068(1), *b* = 17.0565(2), *c* = 18.6455(2) Å, α = 75.119(1), β = 88.947(1), γ = 85.738(1)°, *V* = 3005.9(1) Å^3, *Z* = 2, ρ_c = 1.340 Mg m^{-3}, T = 150(2) K, λ = 0.71073 Å. 13693 independent reflections [R(int) = 0.026], used in all calculations. R_1 = 0.0415, wR_2 = 0.0917 for $I > 2\sigma(I)$, and R_1 = 0.0592, wR_2 = 0.1098 for all unique reflections. Max./min. residual electron densities 1.08 and –0.88 e Å^{-3}. CSD ref.: 931227. The asymmetric unit contains one molecule of fluorobenzene which was modelled over two positions with a combined occupancy of one. The model was built using restraints on the bond distances (**SAME**: distance between two bonded carbons should be similar over the solvent molecule) and on displacement parameters (**SIMU** and **DELU**: taking into account that atoms which are bound to one another move similarly, both in direction and amount). Overall, 256 least-squares restraints were used in the refinement. In the absence of these restraints no chemically realistic model could be obtained.

Synthesis of Mo(CO)$_4$(κ^2-H$_3$Al·6Dipp), 3b: To a solution of **2b** (0.12 g, 0.27 mmol) in 1,2-difluorobenzene (4 mL) at room temperature was added a solution of Mo(CO)$_4$(COD) (0.08 g, 0.25 mmol) also in 1,2-difluorobenzene (3 mL), and the reaction mixture left to stand for 3 d, during which time bright yellow crystals suitable for X-ray diffraction were produced. The crystals were washed with pentane and dried *in vacuo* to yield an analytically pure material. Yield: 0.11 g, 68%. **3b** is only sparingly soluble in compatible solvents, and unlike **3a**, decomposes readily in thf-d$_8$. NMR data were therefore obtained for solutions in 1,2-difluorobenzene (using solvent suppression) and referenced to toluene-d$_8$. Here too, the presence in solution of a small amount (<10%) of decomposition product could be detected after several hours. ***Spectroscopic data***: ^{1}H NMR (300 MHz, 1,2-difluorobenzene, 298 K). δ -6.88(br s, 2H, Mo-H-Al), 1.26 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH$_3$ of Dipp ^{i}Pr), 1.63 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH$_3$ of Dipp ^{i}Pr), 2.42 (quin, 2H, $^3J_{HH}$ = 6.3 Hz, NCH$_2$C*H*$_2$), 3.37 (sept, 4H, $^3J_{HH}$ = 6.9 Hz, CH of Dipp ^{i}Pr), 3.73 (t, 4H, $^3J_{HH}$ = 6.3 Hz, NC*H*$_2$) Aromatic signals were not observed due to suppression of the 1,2-difluorobenzene solvent signals. ^{13}C NMR (125 MHz, 1,2-difluorobenzene, 298 K): δ 23.9 (CH$_3$ of Dipp ^{i}Pr), 25.1 (NCH$_2$C*H*$_2$), 27.0 (CH$_3$ of Dipp ^{i}Pr), 29.9 (CH of Dipp ^{i}Pr), 50.3 (NCH$_2$), 211.0 (CO), 220.9 (CO). Aromatic signals were obscured by solvent peaks. ^{27}Al NMR shift not observed. IR (CH$_2$Cl$_2$, υ_{CO}/cm^{-1}) : 1980 (m), 1931 (s), 1893 (br, m) $\upsilon_{Al\text{-}H}$/cm^{-1} 1734 (br, s, terminal Al-H) 1665 (Mo-H-Al). Elemental analysis : calcd. for $C_{32}H_{43}N_2AlMoO_4$: C 59.81, H 6.74, N 4.36 meas. C 59.60, H 6.51, N 4.37. ***Crystallographic data***: **3b**·$C_6H_4F_2$, $C_{38}H_{47}AlF_2MoN_2O_4$, M_r = 756.72, monoclinic, $P2_1/n$, *a* = 15.6606(1), *b* = 10.5232(1), *c* = 23.2731(2) Å, β = 98.838(1) °, *V* = 3789.9(1) Å^3, *Z* = 4, ρ_c = 1.326 Mg m^{-3}, T = 150(2) K, λ = 0.71073 Å. 8607 independent reflections [R(int) = 0.028], used in all calculations. R_1 = 0.0439, wR_2 = 0.0939 for $I > 2\sigma(I)$, and R_1 = 0.0616, wR_2 = 0.1092 for all unique reflections. Max./min. residual electron densities 0.64 and –0.89 e Å^{-3}. CSD ref.: 931228.

Synthesis of [Mo(CO)$_3$(6Mes·AlH$_3$)]$_2$, 4a: To a solution of **2a** (0.30 g, 0.86 mmol) in 1,2-difluorobenzene (15 mL) at room temperature was added a solution of Mo(CO)$_3$(CHT) (0.21 g, 0.78 mmol) also in 1,2-difluorobenzene (10 mL), and the reaction mixture left to stand for 3 d. The solution turned dark brown with concomitant formation of bright yellow crystals suitable for X-ray diffraction. The crystals were isolated by filtration, washed with toluene (10 mL) and fluorobenzene (5 mL) and dried *in vacuo*. Yield: 0.21 g, 46%. **4a** is extremely poorly soluble in hydrocarbon, oxygen donor and chlorocarbon solvents, and characterizing data in solution could only be obtained by dissolution in pyridine-d$_5$. ***Spectroscopic data***: ^{1}H NMR (300 MHz, pyridine-d$_5$, 298 K): δ -6.97 (br s, Mo-H-Al), -6.79 (br s, Mo-H-Al), 2.10 (qn, 4H, $^3J_{HH}$ = 5.7 Hz, NCH$_2$C*H*$_2$), 2.22 (s, 12H, Mes *p*-CH$_3$), 2.36 (s. 24H,

Mes *o*-CH_3), 3.10 (t, 8H, $^3J_{HH}$ = 5.7 Hz, NCH_2), 5.21 (br s, Al-H), 6.91 (s, 8H, Mes *m*-CH). The aluminium hydride resonances did not prove amenable to precise integration relative to other signals due to their very broad nature. ^{27}Al NMR signal not observed. ^{13}C NMR (75 MHz, pyridine-d_5, 298 K): δ 18.5 (Mes *o*-CH_3), 21.3 (Mes *p*-CH_3), 22.6 (NCH_2CH_2), 42.8 (NCH2), 126.2 (*m*-Ph), 129.1 (*o*-Ph), 137.2 (*p*-Ph), 146.0 (*ipso*-Ph), 229.0 (CO). IR (KBr disc, υ_{CO}/cm^{-1}) : 1965 (m), 1937 (s), 1872 (s), 1837 (s). $\upsilon_{Al\text{-}H}$/cm^{-1} 1750 (br, m, terminal Al-H) 1602 (br, s, Mo-H-Al). Elemental analysis : calcd. for $C_{100}H_{124}N_8Al_4Mo_4O_{12}$: C 56.61, H 5.89, N 5.28 meas. C 55.40, H 6.32, N 5.38. ***Crystallographic data***: **4a**·$2C_6H_4F_2$, $C_{112}H_{132}Al_4F_4Mo_4N_8O_{12}$, M_r = 2350.00, monoclinic, *C* 2/c, *a* = 29.5361(2), *b* = 19.9130(2), *c* = 26.0448(2) Å, β = 124.330(1) °, *V* = 12649.9(2) Å^3, *Z* = 4, ρ_c = 1.234 Mg m^{-3}, T = 150(2) K, λ = 0.71073 Å. 14393 independent reflections [R(int) = 0.047], used in all calculations. R_1 = 0.0567, wR_2 = 0.1360 for $I > 2\sigma(I)$, and R_1 = 0.0951, wR_2 = 0.1759 for all unique reflections. Max./min. residual electron densities 2.53 and –1.16 e Å^{-3}. CSD ref.: 931229. The SQUEEZE program was used to remove contributions from disordered fluorobenzene in the crystal structure of **4a**.[s5]

3. 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 (BP).[s8] 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. General numerical integration was 6. Run files for the geometry calculations are found below and complete output files provided upon request.

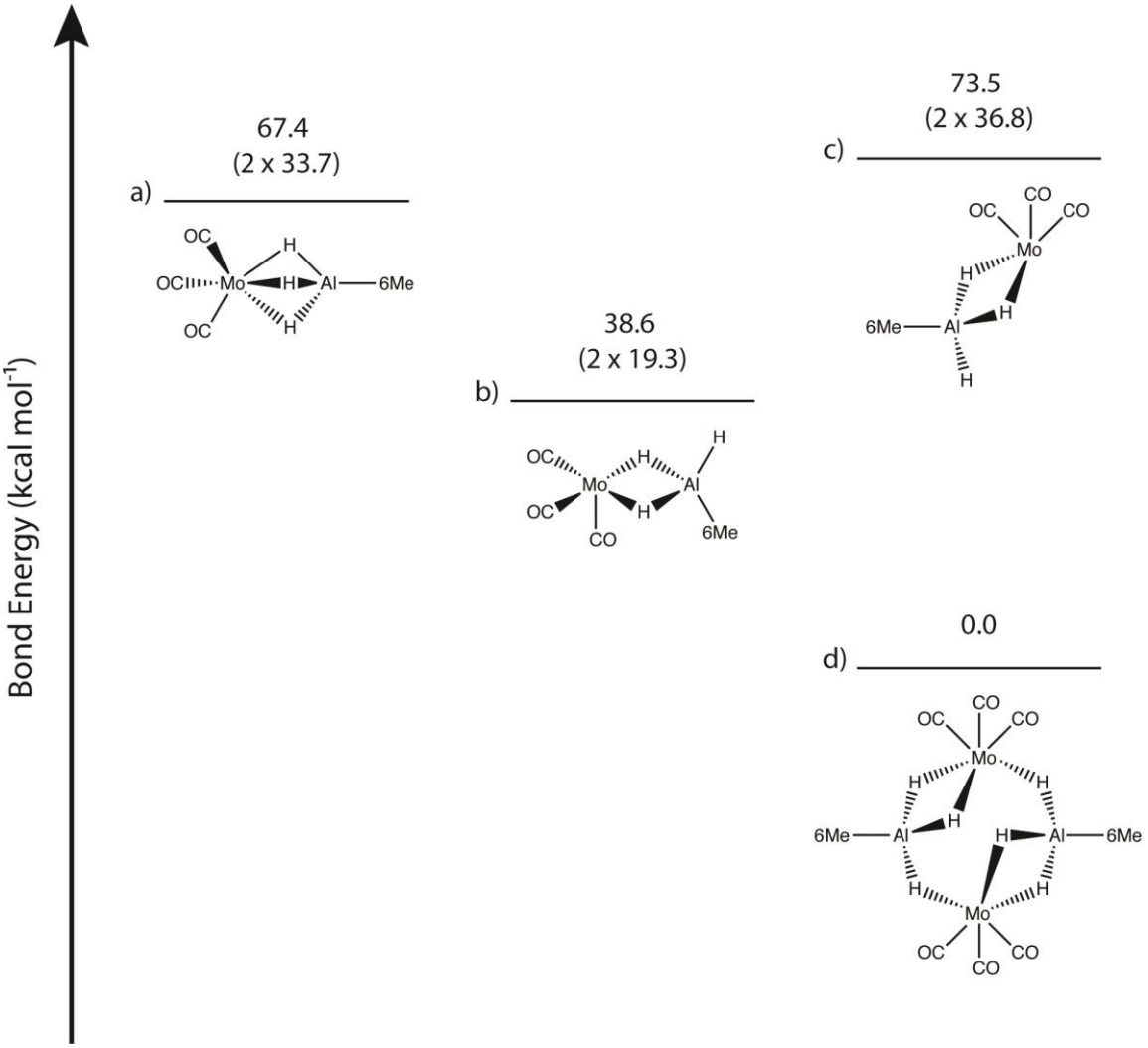

Figure s1: Relative bond energies for model $Mo(CO)_3$/alane systems: (a) optimized κ^3-binding $(OC)_3Mo(\kappa^3\text{-}H_3Al{\cdot}6Me)$; (b) optimized κ^2-binding $(OC)_3Mo(\kappa^2\text{-}H_3Al{\cdot}6Me)$; (c) κ^2-bound fragment '$(OC)_3Mo(\kappa^2\text{-}H_3Al{\cdot}6Me)$' fetauring the geometry as found in the $[(OC)_3Mo(\mu{:}\kappa^2,\kappa^1\text{-}H_3Al{\cdot}6Me)]_2$ symmetrical dimer; (d) optimized symmetrical dimer $[(OC)_3Mo(\mu{:}\kappa^2,\kappa^1\text{-}H_3Al{\cdot}6Me)]_2$.

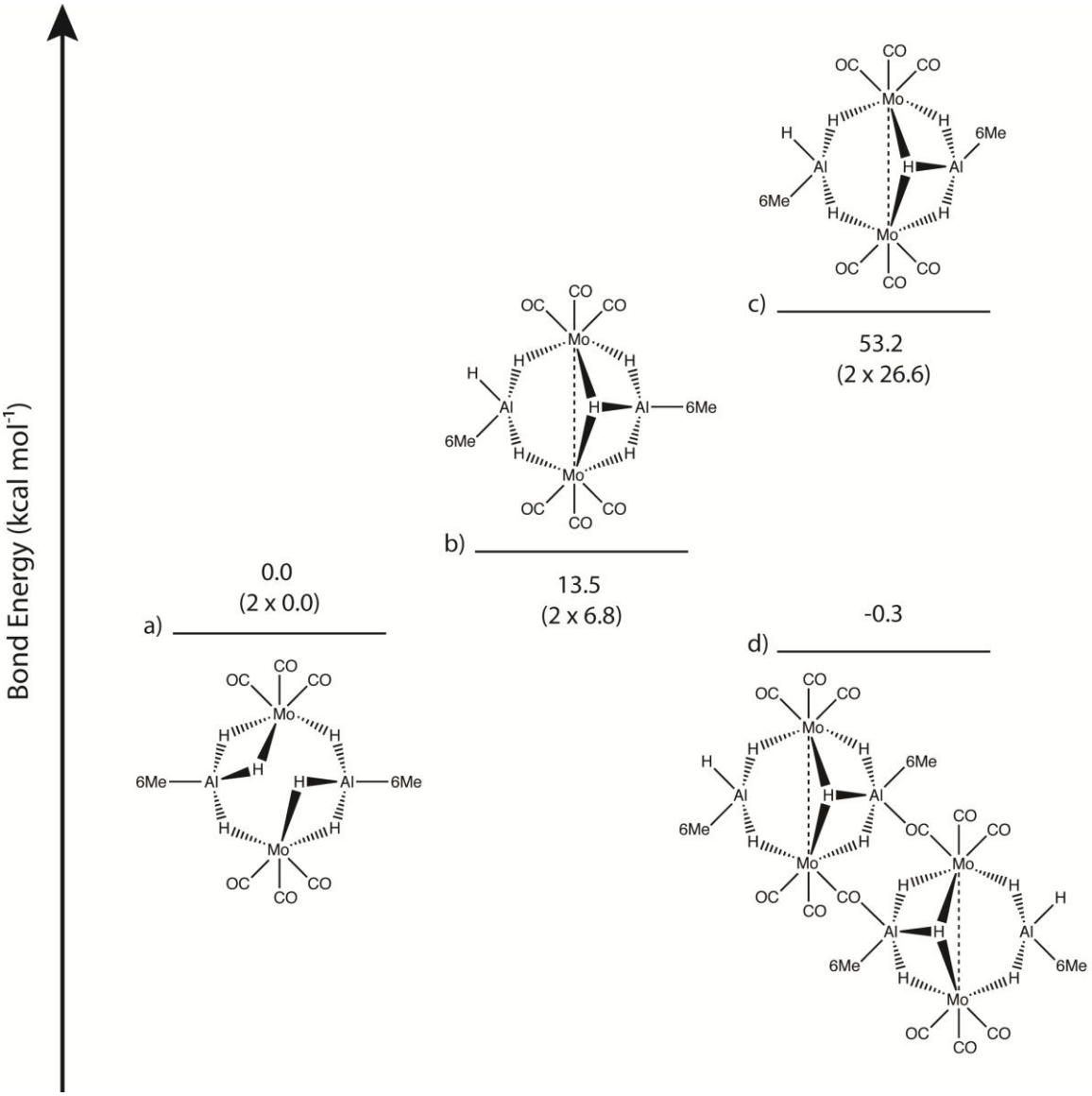

Figure s2: Relative bond energies for model dimeric systems: (a) optimized symmetrical dimer $[(OC)_3Mo(\mu{:}\kappa^2,\kappa^1\text{-}H_3Al{\cdot}6Me)]_2$; (b) optimized unsymmetrical "dimer" $[\{(OC)_3Mo\}_2(\mu{:}\kappa^2,\kappa^2\text{-}H_3Al{\cdot}6Me)(\mu{:}\kappa^1,\kappa^1\text{-}H_3Al{\cdot}6Me)]$; (c) unsymmetrical "dimer" fragment $[\{(OC)_3Mo\}_2(\mu{:}\kappa^2,\kappa^2\text{-}H_3Al{\cdot}6Me)(\mu{:}\kappa^1,\kappa^1\text{-}H_3Al{\cdot}6Me)]$' as found in the "dimer of dimers" $[(\{\mu{:}OC\}\{OC\}_2Mo)(\{OC\}_3Mo)(\mu{:}\kappa^2,\kappa^2\text{-}H_3Al{\cdot}6Me)(\mu{:}\kappa^1,\kappa^1\text{-}H_3Al{\cdot}6Me)]_2$; (d) optimized "dimer of dimers" $[(\{\mu{:}OC\}\{OC\}_2Mo)(\{OC\}_3Mo)(\mu{:}\kappa^2,\kappa^2\text{-}H_3Al{\cdot}6Me)(\mu{:}\kappa^1,\kappa^1\text{-}H_3Al{\cdot}6Me)]_2$.

Run Files:

```
# ==============================
# 6Me-AlH3
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 H      7.463936509000    14.751187550000    10.608037030000
2 Al     7.465378396000    14.247643510000     5.610813683000
3 C      7.890707357000    14.010712130000     7.696197309000
4 N      9.162526630000    13.725875900000     8.047115820000
5 C      9.602448000000    13.378837000000     9.411317267000
6 C      8.439599247000    12.842281130000    10.232054290000
7 C      7.259476462000    13.793470030000    10.097140440000
8 N      6.962424061000    14.047930760000     8.676466120000
9 H      5.368705579000    15.402044390000     8.963656211000
10 H     6.356623930000    13.365426330000    10.556010180000
11 C     5.584104358000    14.468117770000     8.420659000000
12 C    10.235759620000    13.711394950000     7.050758492000
13 H    11.121886070000    14.204269990000     7.476629305000
14 H    10.498131070000    12.680589900000     6.769550406000
15 H     5.880700039000    14.535397050000     5.447743288000
16 H     5.441692773000    14.628046920000     7.345386397000
17 H     4.885807994000    13.691961540000     8.768986419000
18 H     9.927684549000    14.266107460000     6.157259435000
19 H     7.967067427000    12.820469320000     5.026455914000
20 H    10.046253130000    14.270408560000     9.888310346000
21 H    10.398597290000    12.624853160000     9.324402085000
22 H     8.731298637000    12.741317980000    11.286257180000
23 H     8.415842947000    15.495816790000     5.189973886000
24 H     8.153201401000    11.845352000000     9.864615741000
END
```

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

```
BASIS
type TZP
core Large
createoutput None
END

XC
GGA Becke Perdew
END


GEOMETRY
   optim Delocalized
END

SAVE  TAPE21 TAPE13

FULLSCF
INTEGRATION 6.0

NOPRINT LOGFILE

eor
```

```
# ==============================
# K3-(CO)3Mo-H3Al-6Me
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 Mo      7.230135229000     14.635274050000      3.243217506000
2 Al      7.464889311000     14.280085540000      5.706288420000
3 C       7.898953412000     13.980794210000      7.697106731000
4 N       9.168762304000     13.692848550000      8.028155001000
5 C       9.607263095000     13.405831130000      9.407986839000
6 C       8.446899939000     12.876134690000     10.238688900000
7 C       7.250203538000     13.804651420000     10.085076790000
8 N       6.960849589000     14.043244820000      8.657926763000
9 H       5.330436849000     15.356442900000      8.918752054000
10 O      5.500263994000     12.928945760000      1.241378089000
11 C      6.595527382000     16.269920850000      2.342395687000
12 O      6.218977110000     17.251131240000      1.815776545000
13 C      8.716275298000     14.558091650000      1.963236612000
14 O      9.615113593000     14.507357120000      1.205503524000
15 H      5.930599958000     14.598826320000      5.184597877000
16 H      5.440570842000     14.611285340000      7.298470953000
17 H      4.890347989000     13.637413090000      8.690913194000
18 H      9.891417905000     14.028023660000      6.057268078000
19 H      7.890498196000     13.047143070000      4.676767740000
20 H     10.028062890000     14.325986920000      9.847188867000
21 H     10.418873940000     12.667351790000      9.350333499000
22 H      8.739070821000     12.809017320000     11.294787900000
23 H      8.294036933000     15.527624410000      4.980543396000
24 H      8.177750309000     11.864486680000      9.900663673000
25 H      7.428961003000     14.773248340000     10.582033340000
26 H      6.350159322000     13.364653850000     10.536046880000
27 C      6.147484518000     13.571033040000      1.983219187000
28 C     10.241404120000     13.656028720000      7.027651806000
29 H     11.068792230000     14.298785020000      7.359920356000
30 H     10.610729530000     12.628253810000      6.902313384000
31 C      5.577067063000     14.434355160000      8.372472836000
END

GUIBONDS
```

```
1 16 31 1.0
```

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

BASIS
type TZP
core Large
createoutput None
END

XC
GGA Becke Perdew
END


GEOMETRY
   optim Delocalized
END

SAVE  TAPE21 TAPE13

FULLSCF
INTEGRATION 6.0

NOPRINT LOGFILE

eor
```

```
# ==============================
# K2-(CO)3Mo-H3Al-6Me
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 C     -1.528336707000     10.301639780000      3.338970774000
2 H     -2.692271857000      9.984302018000     -1.746127750000
3 H     -4.473571219000     11.141427950000     -0.039037904710
4 C     -2.658627483000     11.192534120000      2.841823150000
5 C     -3.121223737000      9.357737477000      1.223467003000
6 N     -3.219320493000     10.650624150000      1.589298326000
7 C     -3.833558716000     11.638055380000      0.700948547500
8 O      0.850100706000     10.665770970000     -3.264140475000
9 C     -0.002452049648      7.078872260000     -2.383903694000
10 H     -1.203514796000     10.624283740000      4.336964072000
11 H     -5.127960342000      8.890288689000     -0.979257361600
12 C      0.086248787910      9.897876483000     -2.818227437000
13 H     -4.471798092000     12.308134340000      1.294038297000
14 H     -3.100769804000      6.816114753000      0.878894835500
15 C     -0.267458953600      8.834539389000     -0.358132823500
16 O      0.343486303100      8.951843786000      0.651556340000
17 C     -2.007309624000      8.857159009000      3.384902345000
18 N     -2.607501737000      8.474243414000      2.092081156000
19 C     -2.527217423000      7.047077118000      1.781294500000
20 Mo     -1.229377087000      8.618155819000     -2.015671697000
21 H     -0.669879211700     10.372622220000      2.655852934000
22 H     -1.482116761000      6.750388346000      1.612708172000
23 H     -2.756896156000      7.488344558000     -1.324401269000
24 H     -2.747757332000      8.701293281000      4.188499338000
25 H     -2.940709068000      6.468793735000      2.620264239000
26 Al     -3.542142281000      8.886669952000     -0.755044142000
27 H     -1.164083659000      8.177090493000      3.568738664000
28 O      0.709693231700      6.167980501000     -2.571743218000
29 H     -3.463605081000     11.278901540000      3.592292986000
30 H     -2.292112631000     12.207361450000      2.630230943000
31 H     -3.070895846000     12.234356260000      0.178540973800
END
```

```
GUIBONDS
1 5 18 1.0
2 12 8 2.0
3 2 26 1.0
4 9 28 2.0
5 5 6 1.0
6 6 7 1.0
7 4 29 1.0
8 4 30 1.0
9 6 4 1.0
10 17 18 1.0
11 18 19 1.0
12 26 11 1.0
13 25 19 1.0
14 22 19 1.0
15 17 27 1.0
16 31 7 1.0
17 14 19 1.0
18 20 26 1.5
19 26 23 1.0
20 17 24 1.0
21 26 5 2.0
22 1 17 1.0
23 4 1 1.0
24 13 7 1.0
25 3 7 1.0
26 15 16 1.0
27 15 20 3.0
28 20 23 1.0
29 20 9 1.5
30 20 12 1.5
31 1 21 1.0
32 1 10 1.0
END

BASIS
type TZP
core Large
createoutput None
END

XC
GGA Becke Perdew
END


GEOMETRY
   optim Delocalized
END

SAVE  TAPE21 TAPE13

FULLSCF
INTEGRATION 6.0

NOPRINT LOGFILE

eor
```

```
# ==============================
# Symmetric K1,K2-dimer
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 C     -1.660080544000     10.162021390000      3.218823983000
2 H     -3.419468769000     11.151085070000     -1.701230708000
3 H     -4.785433700000     11.377718700000      0.124207567800
4 C     -2.983237233000     10.873711160000      2.969452285000
5 C     -3.068167444000      9.608296822000      0.835504315600
6 N     -3.422269374000     10.669786630000      1.576688710000
7 C     -4.333420087000     11.697822710000      1.068908242000
8 O     -2.898275269000     13.220172580000     -4.946650417000
9 C     -0.827095958400     10.100066780000     -4.487319332000
10 H     -1.401130160000     10.205663080000      4.285102518000
11 H     -4.361782553000      7.966990114000     -1.355348713000
12 C     -2.658215487000     12.271316240000     -4.289530080000
13 H     -5.144680684000     11.848032940000      1.794611440000
14 H     -2.580985030000      7.322065895000     -0.235383400600
15 C     -0.919970258800     11.787797390000     -2.115920535000
16 O     -0.136833882000     12.442771170000     -1.546850797000
17 C     -1.776837713000      8.712833090000      2.765888880000
18 N     -2.311259173000      8.644902660000      1.393240331000
19 C     -1.959090546000      7.427756101000      0.659605392500
20 Mo     -2.266555377000     10.666900900000     -3.160386047000
21 H     -0.858018390200     10.663261890000      2.656405346000
22 H     -0.900097907500      7.440366464000      0.362718710700
23 H     -2.073940574000      9.088526389000     -1.952444307000
24 H     -2.433652137000      8.135295714000      3.439215411000
25 H     -2.144564726000      6.554735841000      1.301598083000
26 Al     -3.555320450000      9.483595138000     -1.176462859000
27 H     -0.792297208100      8.222648359000      2.763915620000
28 O      0.027993513260      9.781590524000     -5.216771699000
29 H     -3.769758505000     10.508214490000      3.651893078000
```

30 H	-2.882215706000	11.956647400000	3.130133263000
31 H	-3.797259525000	12.645297320000	0.910891836400
32 C	-7.643683321000	11.527584330000	-7.369155835000
33 H	-5.888664650000	10.400506600000	-2.475679523000
34 H	-5.422302880000	12.401214540000	-3.479573607000
35 C	-7.058228931000	12.599242510000	-6.459278639000
36 C	-5.731615410000	10.767810500000	-5.434699460000
37 N	-6.301447859000	11.980252970000	-5.355581129000
38 C	-6.166432894000	12.821624150000	-4.164197212000
39 O	-6.822195469000	9.388988880000	1.158945268000
40 C	-6.466296132000	6.647820777000	-1.397754622000
41 H	-8.092270606000	11.989468430000	-8.258752189000
42 H	-3.236931532000	9.496005632000	-4.299834538000
43 C	-6.549854152000	9.091572806000	0.051337724430
44 H	-5.817959425000	13.818571370000	-4.467405744000
45 H	-4.434305696000	8.608736361000	-5.948249073000
46 C	-8.033285185000	8.913747373000	-2.349057266000
47 O	-9.159639925000	9.071091122000	-2.617281748000
48 C	-6.541205408000	10.560446480000	-7.779307184000
49 N	-5.807294139000	10.083989430000	-6.592169532000
50 C	-5.139996457000	8.792706716000	-6.765023221000
51 Mo	-6.083260588000	8.602373782000	-1.831048907000
52 H	-8.437154498000	10.982035320000	-6.836590663000
53 H	-5.873470656000	7.973715224000	-6.797271697000
54 H	-5.504694806000	8.298745488000	-3.720503473000
55 H	-5.831061097000	11.036919830000	-8.477098418000
56 H	-4.569261124000	8.804292261000	-7.704740179000
57 Al	-4.840057570000	9.881544352000	-3.784541250000
58 H	-6.961634395000	9.679514444000	-8.286009504000
59 O	-6.715281900000	5.528632946000	-1.174275556000
60 H	-6.390267661000	13.277881860000	-7.017062829000
61 H	-7.854357849000	13.211794490000	-6.012449883000
62 H	-7.130685643000	12.909122230000	-3.641972349000

END

GUIBONDS
1 5 18 1.0
2 12 8 2.0
3 2 26 1.0
4 9 28 2.0
5 5 6 1.0
6 6 7 1.0
7 4 29 1.0
8 4 30 1.0
9 6 4 1.0
10 17 18 1.0
11 18 19 1.0
12 26 11 1.0
13 25 19 1.0
14 22 19 1.0
15 17 27 1.0
16 31 7 1.0
17 14 19 1.0
18 20 26 1.5
19 26 23 1.0
20 17 24 1.0
21 26 5 2.0
22 1 17 1.0
23 4 1 1.0
24 13 7 1.0
25 3 7 1.0
26 15 16 1.0
27 15 20 3.0
28 20 23 1.0
29 20 9 1.5
30 20 12 1.5
31 1 21 1.0
32 1 10 1.0
33 36 49 1.0
34 43 39 2.0
35 33 57 1.0
36 40 59 2.0
37 36 37 1.0
38 37 38 1.0
39 35 60 1.0
40 35 61 1.0
41 37 35 1.0
42 48 49 1.0
43 49 50 1.0
44 57 42 1.0
45 56 50 1.0
46 53 50 1.0
47 48 58 1.0
48 62 38 1.0
49 45 50 1.0
50 51 57 1.5
51 57 54 1.0
52 48 55 1.0
53 57 36 2.0
54 32 48 1.0
55 35 32 1.0
56 44 38 1.0
57 34 38 1.0
58 46 47 1.0
59 46 51 3.0
60 51 54 1.0
61 51 40 1.5
62 51 43 1.5
63 32 52 1.0
64 32 41 1.0
65 42 20 1.0

```
66 11 51 1.0
END

BASIS
type TZP
core Large
createoutput None
END

XC
GGA Becke Perdew
END

GEOMETRY
   optim Delocalized
END

SAVE  TAPE21 TAPE13

FULLSCF
INTEGRATION 6.0

NOPRINT LOGFILE

eor
```

```
# ==============================
# Asymmetric "dimer" k2,k2 + k1,k1
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 Mo     -3.128953859000     11.426607080000     -2.636028854000
2 H      -1.613452350000     10.375303170000     -1.843881515000
3 Al     -2.374956517000      9.554115600000     -4.803731487000
4 H      -0.873209457400      8.230089327000     -6.323021772000
5 H      -5.059907344000     10.154775070000     -5.319729610000
6 H      -6.494388782000      9.104004965000     -5.456282610000
7 C      -3.462461476000      8.344268584000     -6.206303929000
8 N      -2.745224176000      7.382812082000     -6.823534985000
9 C      -3.314423620000      6.339708704000     -7.699696282000
10 H     -2.795146724000     10.399644370000      4.941629638000
11 H     -4.305766959000     10.088299430000     -1.741169544000
12 C      0.557139803300      9.242074380000     -3.451118198000
13 C     -1.859590824000     12.644741020000     -3.641529629000
14 N     -4.782869695000      8.416767838000     -6.478438243000
15 C     -5.626287223000      9.510232398000     -5.995542225000
16 H     -3.648849756000     10.492967780000     -4.224329227000
17 C     -2.459750761000      8.871212017000      3.450347339000
18 N     -2.533596444000      8.714140729000      1.984714381000
19 C     -1.856215164000      7.506307233000      1.503913340000
20 H     -5.502189419000      7.937232771000     -8.409770343000
21 H     -1.896902167000     10.953561520000      3.511867096000
22 O     -1.130680901000     13.364399160000     -4.198053802000
23 H     -2.674240167000      7.923494647000     -1.464973459000
24 H     -3.183990184000      8.185121278000      3.923766791000
25 C     -1.294781657000      7.268759169000     -6.636138148000
26 H     -1.325017973000     10.256473770000     -5.783922353000
27 H     -1.454258920000      8.551970401000      3.759392721000
28 H     -2.044870558000      8.109759562000     -3.962073685000
29 H     -4.893569876000     10.255905870000      3.651472075000
30 H     -4.173177848000     11.845685650000      3.322777587000
31 C     -2.801866855000     12.629531520000     -1.063906440000
32 O     -2.630455501000     13.385856420000     -0.178460753400
33 C     -4.714918238000     12.580782310000     -3.078883191000
34 O     -5.650009577000     13.251920170000     -3.301909565000
35 C     -3.249275894000      9.527707366000      1.180586778000
36 N     -4.003401345000     10.490787320000      1.749824948000
37 C     -4.978765065000     11.292721130000      1.005319667000
38 O      1.493902608000      9.628102866000     -4.031560862000
39 C     -0.395313619100      6.647312844000     -2.626671318000
40 C     -4.793233036000      6.138957857000     -7.409248067000
41 H     -1.978022751000      7.394980034000      0.423938076900
42 C      0.176812203300      8.690652695000     -0.800594147100
43 O      0.929447764500      8.740441302000      0.101558147500
44 Mo    -1.024964384000      8.543240408000     -2.408286603000
45 C     -5.478616349000      7.496639014000     -7.397118736000
46 H     -2.291007150000      6.630232765000      2.008755187000
```

```
47 Al    -2.948698382000     9.498988757000    -0.903124199000
48 O     -0.032274679960     5.537219126000    -2.733319762000
49 H     -2.751237808000     5.412554252000    -7.519512091000
50 H     -3.151020262000     6.624727826000    -8.753740473000
51 H     -5.246018216000     5.488345275000    -8.169514604000
52 H     -4.919382314000     5.652188086000    -6.430346989000
53 H     -5.982632200000    11.100064030000     1.413355244000
54 H     -0.784151653800     7.560132216000     1.730696430000
55 H     -4.743632914000    12.359376670000     1.109496356000
56 H     -6.519592726000     7.409830079000    -7.054057303000
57 H     -4.965016273000    11.036483800000    -0.056183351660
58 C     -4.023015738000    10.763698080000     3.200229891000
59 C     -2.725333243000    10.312994820000     3.849224511000
60 H     -5.989211430000    10.107584990000    -6.846160724000
61 H     -0.839369467400     6.998525171000    -7.599019529000
62 H     -1.048670101000     6.499734996000    -5.890543359000
END

GUIBONDS
1 35 18 1.0
2 12 38 2.0
3 2 47 1.0
4 39 48 2.0
5 35 36 1.0
6 36 37 1.0
7 58 29 1.0
8 58 30 1.0
9 36 58 1.0
10 17 18 1.0
11 18 19 1.0
12 47 11 1.0
13 46 19 1.0
14 54 19 1.0
15 6 15 1.0
16 60 15 1.0
17 61 25 1.0
18 62 25 1.0
19 47 23 1.0
20 1 16 1.0
21 47 35 2.0
22 47 1 2.0
23 4 25 1.0
24 53 37 1.0
25 57 37 1.0
26 42 43 1.0
27 42 44 3.0
28 44 23 1.0
29 44 39 1.5
30 44 12 1.5
31 1 11 1.0
32 1 13 1.5
33 5 15 1.0
34 55 37 1.0
35 41 19 1.0
36 44 47 1.5
37 44 3 1.5
38 59 17 1.0
39 58 59 1.0
40 59 21 1.0
41 59 10 1.0
42 1 33 1.5
43 1 31 1.5
44 1 3 1.5
45 3 16 1.0
46 3 26 1.0
47 3 28 1.0
48 3 7 2.0
49 7 14 1.0
50 7 8 1.0
51 8 25 1.0
52 8 9 1.0
53 17 24 1.0
54 17 27 1.0
55 9 50 1.0
56 9 49 1.0
57 9 40 1.0
58 40 52 1.0
59 40 51 1.0
60 40 45 1.0
61 45 20 1.0
62 45 56 1.0
63 45 14 1.0
64 14 15 1.0
65 13 22 2.0
66 31 32 2.0
67 33 34 2.0
END

BASIS
type TZP
core Large
createoutput None
END

XC
GGA Becke Perdew
END


GEOMETRY
   optim Delocalized
END

SAVE  TAPE21 TAPE13

FULLSCF
INTEGRATION 6.0

NOPRINT LOGFILE

eor

# ============================
```

```
# Dimer of asymmetric dimer - xtal
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 C     -0.516507651600     10.908615680000      1.280038315000
2 O     -1.418631128000     10.867387180000      0.458872637500
3 Mo     0.880411340100     11.153373510000      2.591250469000
4 Al     2.599235553000     10.033002680000      0.696061585200
5 Mo     3.163810647000      8.450425942000      2.796920585000
6 Al     2.825107804000     10.553160020000      4.824341729000
7 C      4.121055840000     12.031098800000      5.683826069000
8 N      3.512820586000     13.100003420000      6.239079098000
9 C      4.208276222000     14.315810760000      6.705601628000
10 C     5.562337952000     14.455348980000      6.028484142000
11 C     6.305697107000     13.133279390000      6.142953225000
12 N     5.469840355000     12.027291510000      5.639797226000
13 C     6.238343207000     10.858994190000      5.208975631000
14 N    -5.469840358000      7.885708497000     -5.639797233000
15 C    -6.238343210000      9.054005819000     -5.208975638000
16 H    -3.966610858000     10.380516600000     -4.146310028000
17 C    -3.534864149000      7.944666904000      3.220307455000
18 N    -3.036491933000      8.318728241000      1.877979741000
19 C    -1.799816714000      7.611322922000      1.522984543000
20 H    -6.592622286000      6.983120921000     -7.190016499000
21 H    -3.688864861000      9.891716161000      4.122991991000
22 C     2.055120289000     13.164407250000      6.384145607000
23 H    -2.219184677000      8.313627894000     -1.271137721000
24 H    -4.124741020000      7.015958923000      3.131000126000
25 C    -2.055120292000      6.748592753000     -6.384145614000
26 H    -2.004268446000      9.853474818000     -6.106238528000
27 H    -2.657059192000      7.723464908000      3.842547513000
28 H    -2.205139777000      8.128271123000     -3.850863648000
29 H    -6.141404268000      8.779127834000      2.622620536000
30 H    -5.885936015000     10.450714250000      3.164564155000
31 C     2.179878435000      7.318275024000      4.161981334000
32 O     1.577766936000      6.652652727000      4.912845681000
33 C     2.684880546000      7.010358850000      1.472576946000
34 O     2.460724934000      6.103174437000      0.764109756700
35 C     4.887475322000      7.449001663000      3.056062063000
36 O     5.900630236000      6.865682328000      3.166404772000
37 C     3.577932029000     10.634274030000     -1.103058949000
38 N     4.704191509000     10.027626650000     -1.538452671000
39 C     5.338549087000      8.914612602000     -0.828983384000
40 C    -5.562337955000      5.457651027000     -6.028484149000
41 H    -1.573792598000      7.729155443000      0.461258663300
42 C     0.516507648500      9.004384323000     -1.280038322000
43 O     1.418631124000      9.045612825000     -0.458872644700
44 Mo   -0.880411343300      8.759626494000     -2.591250476000
45 C    -6.305697110000      6.779720613000     -6.142953233000
46 H    -1.931166493000      6.539510803000      1.726508250000
47 Al   -2.599235556000      9.879997330000     -0.696061592300
48 C     5.370586926000     10.366290870000     -2.812416954000
49 C     4.354278313000     10.847211050000     -3.834731162000
50 C     3.534864146000     11.968333100000     -3.220307462000
51 N     3.036491930000     11.594271770000     -1.877979748000
52 C     1.799816710000     12.301677080000     -1.522984550000
53 H    -6.406401582000     10.779563590000      0.679964111200
54 H    -0.959040514400      7.988378818000      2.122767520000
55 H    -5.247247727000     11.921059240000      1.421405918000
56 H     2.205139774000     11.784728880000      3.850863641000
57 H    -4.878098142000     11.153426490000     -0.149633220000
58 H     2.004268443000     10.059525190000      6.106238521000
59 H     4.012804818000      9.708527178000      1.625469882000
60 H     3.966610854000      9.532483411000      4.146310021000
61 C    -0.429191878300     10.606049670000      4.032748443000
62 O    -1.220434468000     10.286877280000      4.838121846000
63 C     0.302720364800     13.081850440000      2.757981676000
```

64 O	-0.021181867040	14.201514950000	2.860969356000
65 H	3.563811801000	15.175625850000	6.471471467000
66 H	4.314481164000	14.273254790000	7.803742613000
67 H	6.141506875000	15.262395460000	6.497062690000
68 H	5.424591909000	14.711550950000	4.967170980000
69 H	7.229790811000	13.147653760000	5.547496672000
70 H	6.592622283000	12.929879090000	7.190016492000
71 H	-4.860917406000	8.709498827000	4.741966135000
72 H	-4.012804821000	10.204472830000	-1.625469889000
73 C	0.429191875100	9.306950335000	-4.032748450000
74 C	-2.179878439000	12.594724980000	-4.161981341000
75 O	-1.577766939000	13.260347280000	-4.912845688000
76 C	-2.684880550000	12.902641160000	-1.472576953000
77 O	-2.460724937000	13.809825570000	-0.764109763900
78 C	-4.887475325000	12.463998340000	-3.056062070000
79 O	-5.900630239000	13.047317680000	-3.166404780000
80 C	-3.577932033000	9.278725972000	1.103058942000
81 N	-4.704191512000	9.885373360000	1.538452664000
82 C	-5.338549090000	10.998387400000	0.828983376800
83 O	1.220434465000	9.626122732000	-4.838121853000
84 C	-0.302720368000	6.831149568000	-2.757981684000
85 O	0.021181863890	5.711485061000	-2.860969363000
86 H	-3.563811804000	4.737374155000	-6.471471474000
87 H	-4.314481167000	5.639745218000	-7.803742620000
88 H	-6.141506879000	4.650604551000	-6.497062698000
89 H	-5.424591913000	5.201449054000	-4.967170987000
90 H	-7.229790814000	6.765346246000	-5.547496679000
91 C	-5.370586929000	9.546709139000	2.812416946000
92 C	-4.354278316000	9.065788955000	3.834731155000
93 H	2.219184674000	11.599372110000	1.271137714000
94 H	-1.821007309000	6.301039491000	-7.360415619000
95 H	-1.603572003000	6.137894334000	-5.589762708000
96 Mo	-3.163810650000	11.462574060000	-2.796920592000
97 Al	-2.825107807000	9.359839988000	-4.824341736000
98 H	-1.624922889000	7.755419190000	-6.360808861000
99 H	-5.568796846000	9.832986789000	-4.837654608000
100 H	-6.931071555000	8.770412171000	-4.403498282000
101 C	-4.121055843000	7.881901202000	-5.683826076000
102 N	-3.512820589000	6.812996585000	-6.239079105000
103 C	-4.208276225000	5.597189250000	-6.705601635000
104 H	6.141404265000	11.133872170000	-2.622620543000
105 H	5.885936012000	9.462285752000	-3.164564162000
106 H	4.860917402000	11.203501180000	-4.741966142000
107 H	3.688864857000	10.021283850000	-4.122991998000
108 H	4.124741017000	12.897041080000	-3.131000133000
109 H	2.657059188000	12.189535100000	-3.842547520000
110 H	-6.823563557000	9.449250680000	-6.053554034000
111 H	6.931071552000	11.142587840000	4.403498275000
112 H	5.568796842000	10.080013220000	4.837654601000
113 H	6.823563554000	10.463749330000	6.053554027000
114 H	1.603572000000	13.775105670000	5.589762701000
115 H	1.821007305000	13.611960520000	7.360415612000
116 H	1.624922886000	12.157580820000	6.360808854000
117 H	1.931166490000	13.373489200000	-1.726508257000
118 H	1.573792595000	12.183844560000	-0.461258670400
119 H	0.959040511200	11.924621190000	-2.122767527000
120 H	6.406401578000	9.133436413000	-0.679964118300
121 H	5.247247724000	7.991940769000	-1.421405926000
122 H	4.878098139000	8.759573512000	0.149633212900
123 H	1.530271904000	9.330835881000	2.158111649000
124 H	-1.530271907000	10.582164130000	-2.158111656000

END

GUIBONDS
1 1 2 1.0
2 1 3 3.0
3 2 47 1.0
4 3 93 1.0
5 3 63 1.5
6 3 61 1.5
7 3 4 1.5
8 3 6 1.5
9 4 59 1.0

10 4 93 1.0
11 4 43 1.0
12 4 37 2.0
13 4 5 2.0
14 5 60 1.0
15 5 59 1.0
16 5 31 1.5
17 5 35 1.5
18 5 33 1.5
19 5 6 1.5
20 6 60 1.0
21 6 58 1.0
22 6 56 1.0
23 6 7 2.0
24 7 12 1.0
25 7 8 1.0
26 8 22 1.0
27 8 9 1.0
28 9 66 1.0
29 9 65 1.0
30 9 10 1.0
31 10 68 1.0
32 10 67 1.0
33 10 11 1.0
34 11 70 1.0
35 11 69 1.0
36 11 12 1.0
37 12 13 1.0
38 92 17 1.0
39 91 92 1.0
40 92 21 1.0
41 92 71 1.0
42 96 78 1.5
43 96 76 1.5
44 96 97 1.5
45 97 16 1.0
46 97 26 1.0
47 97 28 1.0
48 97 101 2.0
49 101 14 1.0
50 101 102 1.0
51 102 25 1.0
52 102 103 1.0
53 17 24 1.0
54 17 27 1.0
55 103 87 1.0
56 103 86 1.0
57 103 40 1.0
58 40 89 1.0
59 40 88 1.0
60 40 45 1.0
61 45 20 1.0
62 45 90 1.0
63 45 14 1.0
64 14 15 1.0
65 74 75 2.0
66 76 77 2.0
67 78 79 2.0
68 80 18 1.0
69 73 83 2.0
70 84 85 2.0
71 80 81 1.0
72 81 82 1.0
73 91 29 1.0
74 91 30 1.0
75 81 91 1.0
76 17 18 1.0
77 18 19 1.0
78 31 32 2.0
79 33 34 2.0
80 35 36 2.0
81 37 51 1.0
82 37 38 1.0
83 38 39 1.0
84 38 48 1.0
85 47 23 1.0
86 96 16 1.0
87 47 80 2.0
88 47 96 2.0
89 111 13 1.0
90 112 13 1.0
91 113 13 1.0
92 42 43 1.0
93 42 44 3.0
94 44 23 1.0
95 44 84 1.5
96 44 73 1.5
97 96 72 1.0
98 96 74 1.5
99 114 22 1.0
100 115 22 1.0
101 116 22 1.0
102 44 47 1.5
103 44 97 1.5
104 47 72 1.0
105 48 104 1.0
106 48 105 1.0
107 48 49 1.0
108 49 107 1.0
109 49 106 1.0
110 49 50 1.0
111 50 108 1.0
112 50 109 1.0
113 50 51 1.0
114 51 52 1.0
115 55 82 1.0
116 41 19 1.0
117 46 19 1.0
118 54 19 1.0
119 61 62 2.0
120 63 64 2.0
121 94 25 1.0
122 95 25 1.0
123 98 25 1.0
124 53 82 1.0
125 57 82 1.0
126 99 15 1.0
127 100 15 1.0
128 110 15 1.0
129 117 52 1.0
130 118 52 1.0
131 119 52 1.0
132 120 39 1.0
133 121 39 1.0
134 122 39 1.0
135 123 4 1.0
136 124 47 1.0
END

BASIS
type TZP
core Large
createoutput None
END

XC

```
GGA Becke Perdew
END


GEOMETRY
   optim Delocalized
END
```

```
SAVE  TAPE21 TAPE13

FULLSCF
INTEGRATION 6.0

NOPRINT LOGFILE

eor
```

4. References for Supporting Information

References

s1. M. Iglesias, D.J. Beetstra, J.C. Knight, L.-L. Ooi, A. Stasch, S. Coles, L. Male, M.B. Hursthouse, K.J. Cavell, A. Dervisi and I.A. Fallis, *Organometallics*, 2008, **27**, 3279.

s2. K. Ruff and M.F. Hawthorne, *J. Am. Chem. Soc.*, 1960, **82**, 2141.

s3. A. Tekkaya, C. Ceyhan and S. Özkar, *Inorg. Chem.*, 1994, **33**, 2439.

s4. E.W. Abel, M.A. Bennett, R. Burton and G. Wilkinson, *J. Chem. Soc.*, 1958, 4559.

s5. A.L. Spek, *Acta Cryst.*, 2009, **A64**, 112.

s6. (a) G. te Velde, F. M. Bickelhaupt, S. J. A. van Gisbergen, C. Fonseca Guerra, E. J. Baerends, J. G. Snijders and T. Ziegler, J. Comput. Chem., 2001, 22, 931-967. (b) C. Fonseca Guerra, J. G. Snijders, G. te Velde and E. J. Baerends, Theor. Chem. Acc., 1998, 99, 391-403. (c) E.J. Baerends, T. Ziegler, J. Autschbach, D. Bashford, A. Bérces, F.M. Bickelhaupt, C. Bo, P.M. Boerrigter, L. Cavallo, D.P. Chong, L. Deng, R.M. Dickson, D.E. Ellis, M. van Faassen, L. Fan, T.H. Fischer, C. Fonseca Guerra, A. Ghysels, A. Giammona, S.J.A. van Gisbergen, A.W. Götz, J.A. Groeneveld, O.V. Gritsenko, M. Grüning, S. Gusarov, F.E. Harris, P. van den Hoek, C.R. Jacob, H. Jacobsen, L. Jensen, J.W. Kaminski, G. van Kessel, F. Kootstra, A. Kovalenko, M.V. Krykunov, E. van Lenthe, D.A. McCormack, A. Michalak, M. Mitoraj, J. Neugebauer, V.P. Nicu, L. Noodleman, V.P. Osinga, S. Patchkovskii, P.H.T. Philipsen, D. Post, C.C. Pye, W. Ravenek, J.I. Rodríguez, P. Ros, P.R.T. Schipper, G. Schreckenbach, J.S. Seldenthuis, M. Seth, J.G. Snijders, M. Solà, M. Swart, D. Swerhone, G. te Velde, P. Vernooijs, L. Versluis, L. Visscher, O. Visser, F. Wang, T.A. Wesolowski, E.M. van Wezenbeek, G. Wiesenekker, S.K. Wolff, T.K. Woo and A.L. Yakovlev, ADF2012, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam. The Netherlands. http://www.scm.com.

s7. A. D. Becke, Phys. Rev. A, 1988, 38, 3098-3100.

s8. J. P. Perdew, Phys. Rev. B, 1986, 33, 8822-8824.

s9. J. G. Snijders, P. Vernooijs and E. J. Baerends, At. Data Nucl. Data Tables, 1982, 26, 483-509.