Gallyl Lanthanide Complexes Containing Unsupported Ln-Ga (Ln = Sm, Eu, Yb or Tm) Bonds

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SUPPLEMENTARY INFORMATION

Experimental Section

General considerations. All manipulations were carried out using standard Schlenk and glove box techniques under atmospheres of high purity argon or dinitrogen. Toluene, hexane and tmeda were distilled over molten potassium metal, while diethylether was distilled over Na/K alloy. Melting points were determined in sealed glass capillaries under argon and are uncorrected. Mass spectra were recorded at the EPSRC National Mass Spectrometric Service at Swansea University. The microanalysis on **6** was obtained from Campbell Microanalytical, Ottago. In general, however, the highly air and moisture sensitive nature of the compounds in this study led to irreproducible microanalyses. IR spectra were recorded using a Nicolet 510 FT-IR spectrometer as Nujol mulls between NaCl plates. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian DPX 300 spectrometer. Solution state magnetic moments were determined in C_6D_6 at 298 K using the Evan's method.[1] [K(tmeda)][:Ga{(ArNCH)$_2$}],[2] [TmI$_2$(THF)$_5$][3] and THF solutions of LnI$_2$(THF)$_n$ (Ln = Sm, Eu or Yb)[4] were prepared by literature procedures. All other reagents were purchased commercially and used as received.

Synthesis of [Sm{Ga[(ArNCH)$_2$]}$_2$(tmeda)$_2$] 5. To a solution of SmI$_2$ (0.25 mmol) in THF (10 cm^3) at 25 °C was added tmeda (2.2 cm^3, 14.7 mmol) and all volatiles subsequently removed from the resultant dark green solution *in vacuo*. The residue was suspended in a toluene (40 cm^3) / tmeda (1.5 cm^3) mixture and cooled to -80 °C. To this, a solution of [K(tmeda)][:Ga{(ArNCH)$_2$}] (0.30 g, 0.50 mmol) in toluene (20 cm ^{3}) was added over 5 mins. The mixture was warmed to room temperature overnight and all volatiles removed *in vacuo*. The residue was extracted into diethylether (20 cm^3), the extract filtered and stored at –30 °C overnight to yield dark green crystals of **5**. Yield: 0.18g (56 %). M.p. 164-166 °C; μ_{eff} = 3.3 B.M.; IR ν/cm^{-1} (Nujol): 1651w, 1586w, 1377s, 1355s, 1319m, 1258s, 1103m, 754m; MS (EI/70 eV), *m*/*z* (%): 445.2 ([Ga{(ArNCH)$_2$}]$^+$, 3), 333.3 ((ArNCH)$_2$-Pr^{i+}, 100).

Synthesis of [Eu{Ga[(ArNCH)$_2$]}$_2$(tmeda)$_2$] 6. An equivalent procedure to that used to prepare **5** was used for the synthesis of orange **6**. Yield: 23 %. M.p. 185-187 °C (decomp); μ_{eff} = 7.3 B.M.; IR ν/cm^{-1} (Nujol): 1651w, 1586w, 1378s, 1356s, 1319s, 1258s, 1103s, 754s; MS (EI/70 eV), *m*/*z* (%): 445.2 ([Ga{(ArNCH)$_2$}]$^+$, 5), 378 ((ArNCH)$_2$H$^+$, 72), 333.3 ((ArNCH)$_2$-Pr^{i+}, 100); $C_{64}H_{104}Ga_2N_8Eu$ requires C 60.19, H 8.22, N 8.77 %; found C 59.35, H 8.14, N 8.62 %.

Synthesis of [Yb{Ga[(ArNCH)$_2$]}$_2$(tmeda)$_2$] 7. An equivalent procedure to that used to prepare **5** was used for the synthesis of red-orange **7**. Yield: 11 %. M.p. 170-174 °C (decomp); ^{1}H NMR (300 MHz, C_6D_6, 298 K): major isomer δ 1.26 (d, 24 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.45 (d, 24 H, CH(C*H*$_3$)$_2$), 1.90 (br., 32 H, tmeda), 3.55 (sept., 8 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$) 6.57 (s, 4 H, NC*H*), 7.02-7.34 (m, 12 H, Ar-*H*); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): 23.8 (CH(*C*H$_3$)$_2$), 24.2 (CH(*C*H$_3$)$_2$), 28.4 (*C*H(CH$_3$)$_2$), 46.7 (N(*C*H$_3$)$_2$), 62.1 (N*C*H$_2$), 122.7 (N*C*H), 124.6, 125.2, 145.8 (Ar-*C*) *ipso*-C not observed . IR ν/cm^{-1} (Nujol): 1652w, 1584w, 1377s, 1356s, 1319s, 1257s, 1103m, 756m; MS (EI/70 eV), *m*/*z* (%): 445.2 ([Ga{(ArNCH)$_2$}]$^+$, 52), 378 ((ArNCH)$_2$H$^+$, 40), 333.3 ((ArNCH)$_2$-Pr^{i+}, 100).

Synthesis of [Tm{Ga[(ArNCH)$_2$]}{(ArNCH)$_2$}(tmeda)] 8. TMEDA (1.5 cm^3) was added to a solution of [TmI$_2$(THF)$_5$] (0.38 mmol) in toluene (10 cm^3) at room temperature. The resultant green solution was cooled to -80 ^{o}C and a solution of [K(tmeda)][:Ga{(ArNCH)$_2$}] (0.45 g, 0.75 mmol) in

10 cm^3 added to it over 5 mins. The mixture was warmed to room temperature overnight and all volatiles removed *in vacuo*. The residue was washed with hexane (10 cm^3), then extracted into diethylether (25 cm^3) and filtered. The filtrate was concentrated to *ca.* 10 cm^3 and stored at –30 °C to give dark red crystals of **8**. Yield: 0.04g (10 %). M.p. 208-210 ^{o}C; μ_{eff} = 7.0 B.M.; IR ν/cm^{-1} (Nujol): 1624w, 1587w, 1378s, 1356s, 1260s, 1100s, 1022s, 799s, 759m; MS (EI/70eV), *m*/*z* (%): 445.2 ([Ga{(ArNCH)$_2$}]$^+$, 15), 378 ((ArNCH)$_2$H$^+$, 42), 333.3 ((ArNCH)$_2$-Pr^{i+}, 100).

N.B. An attempt to prepare a tris(gallyl) cerium(III) complex from the reaction of three equivalents of [K(tmeda)][:Ga{(ArNCH)$_2$}] with [CeI$_3$(THF)$_4$] in a toluene/tmeda solution led, instead to a very low isolated yield (< 1%) of [{Ce[(ArNCH)$_2$](tmeda)(μ-I)}$_2$] as pale yellow crystals (M.p. 280-282 ^{o}C). No other compounds could be isolated or identified from the reaction mixture. No spectroscopic data could be obtained on the compound because of its low yield. Its X-ray crystal structure is, however, included below.

X-Ray Crystallography

Crystals of all compounds suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using either an Nonius Kappa CCD or Bruker X8 CCD diffractometer. The structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97[5]) using all unique data. Two crystallographically independent molecules were refined in the asymmetric unit of **8**. There are no significant geometric differences between them.

Crystal data for [{Ce[(ArNCH)$_2$](tmeda)(μ-I)}$_2$].(hexane)$_3$: $C_{82}H_{146}Ce_2I_2N_8$, *M* = 1778.11, monoclinic, space group *C*2/*c*, *a* = 37.609(8) Å, *b* = 8.9281(18) Å, *c* = 27.205(5) Å, β = 110.41(3)°, *V* = 8561(3) Å^3, *Z* = 4, D_C = 1.380 gcm^{-3}, *F*(000) = 3664, μ(Mo-Kα) = 1.815 mm^{-1}, 123(2) K, 9280 unique reflections [*R*(*int*) 0.0327], *R* (on *F*) 0.0373, *wR* (on F^2) 0.0847 ($I > 2\sigma I$).

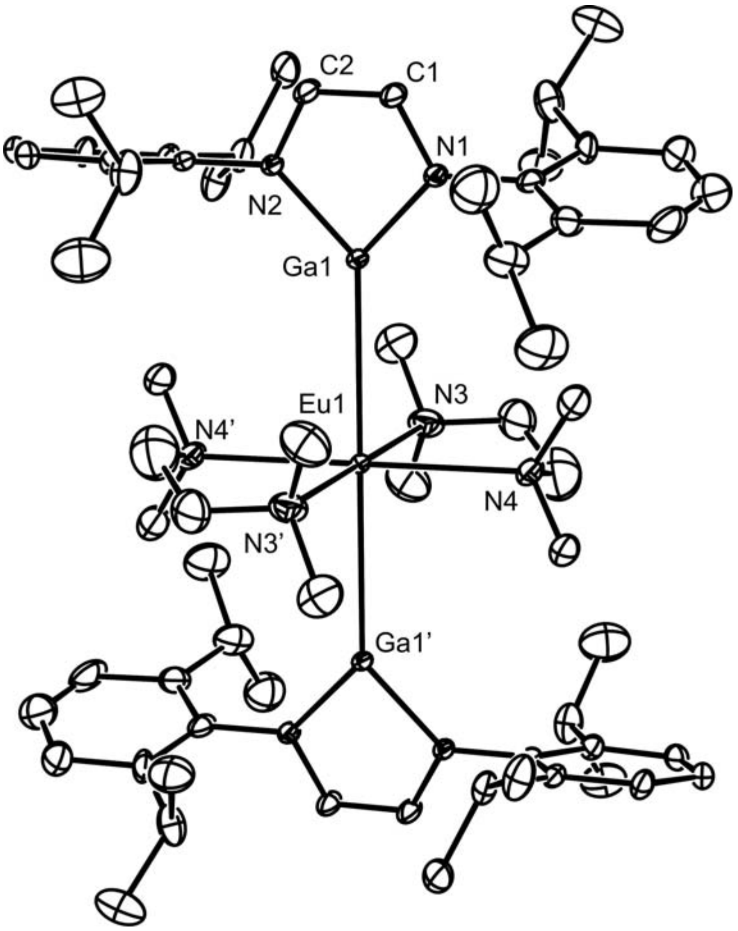

Fig. S1. Molecular structure of **6** (20% thermal ellipsoids; hydrogen atoms omitted). Symmetry operation: ' -x, -y, -z.

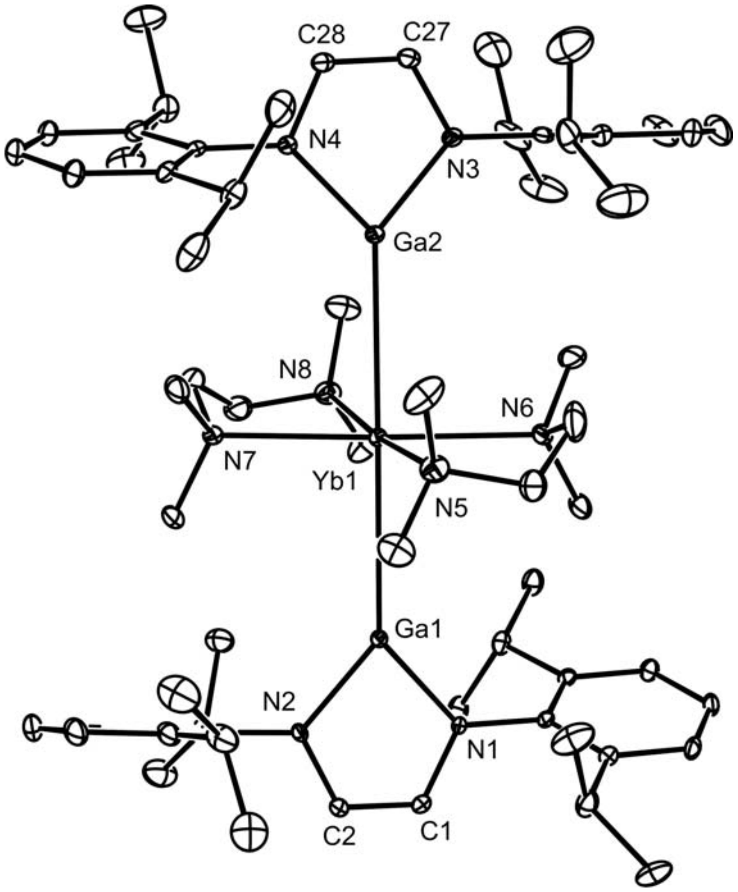

Fig. S2. Molecular structure of **7** (20% thermal ellipsoids; hydrogen atoms omitted).

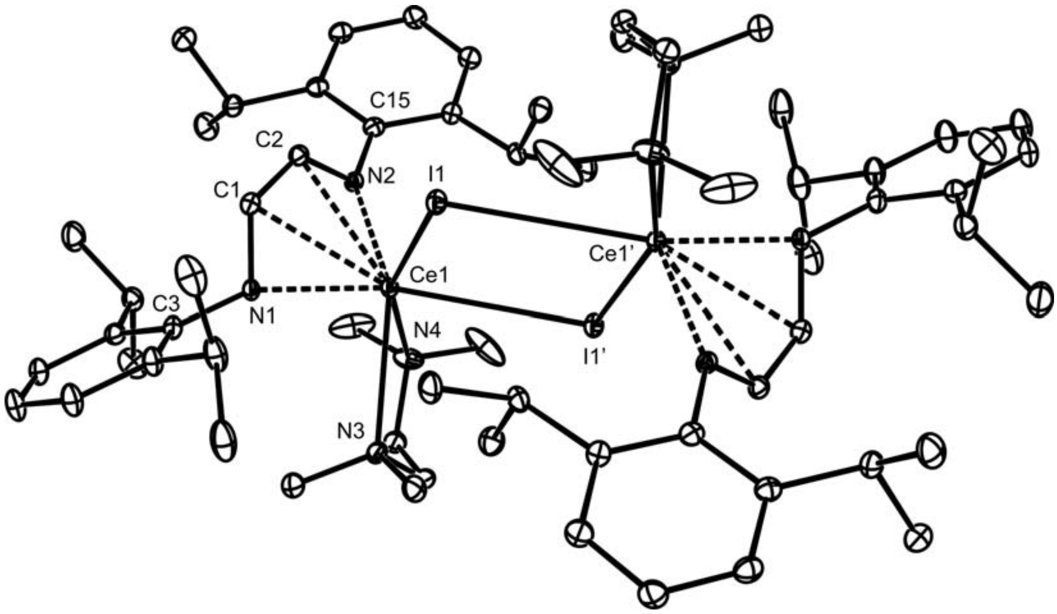

Fig. S3 Molecular structure of [{Ce[(ArNCH)$_2$](tmeda)(μ-I)}$_2$] (20% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Ce(1)-N(1) 2.280(3), Ce(1)-N(2) 2.333(3), Ce(1)-C(1) 2.679(4), Ce(1)-C(2) 2.691(4), Ce(1)-N(3) 2.717(4), Ce(1)-N(4) 2.808(4), Ce(1)-I(1) 3.3795(6), Ce(1)-I(1)' 3.4438(14), N(1)-C(1) 1.408(5), C(1)-C(2) 1.361(5), N(2)-C(2) 1.396(5), N(1)-Ce(1)-N(2) 80.60(11), N(3)-Ce(1)-N(4) 66.26(11), I(1)-Ce(1)-I(1)' 71.759(18), Ce(1)-I(1)-Ce(1)' 108.241(18). Symmetry operation: ' -x, -y, -z.

References

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