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A Heterobimetallic Gallyl Complex Containing an Unsupported Ga−Y Bond

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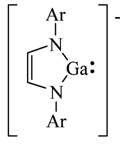
The synthesis and characterization of the first unsupported Ga−Y bond in $[Y\{Ga(NArCH)_2\}\{C(PPh_2NSiMe_3)_2\}(THF)_2]$ (Ar = 2,6-diisopropylphenyl) is described; structural and computational analyses are consistent with a highly polarized covalent Ga−Y bond.

Although metal−metal bonding is ubiquitous in transition-metal chemistry and important from fundamental and applications standpoints,[1] it is still relatively undeveloped where the lanthanide (Ln) elements are concerned.[2] In recent years, a limited number of unsupported, donor−acceptor Ln group 13 bonds have been reported, including $[(Cp^*)_2Ln\{Al(Cp^*)\}]$ (Ln = Eu, Yb; $Cp^* = C_5Me_5$)[3] and $[(Cp^*)_2Eu\{Ga(Cp^*)\}_2]$ and $[(Cp^*)_2Yb\{Ga(Cp^*)\}(THF)]$ (THF = tetrahydrofuran).[4] For the area to develop at any pace, it seemed to us that systems containing polarized covalent bonds would give more amenable complexes than donor−acceptor systems.



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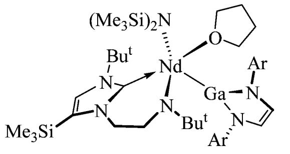

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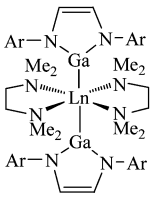
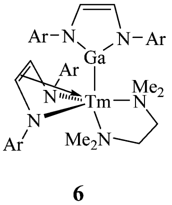


Ln = Sm (**3**), Eu (**4**) Yb (**5**)



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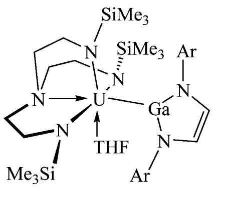

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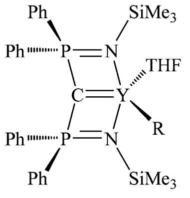

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Thus, in a collaborative project we have set out to employ the gallium(I) heterocycle $[:Ga\{(NArCH)_2\}]^-$ (**1**) developed by the Jones group,[5] which is valence isoelectronic to N-heterocyclic carbenes (NHCs), in f-element chemistry. Despite its reducing nature, **1** is suited to forming Ga−Ln bonds, as exemplified by **2**,[6] isostructural **3**−**5**, and **6**.[7] The efficacy and utility of **1** is underscored by our recent report of the first polarized covalent Ga^I-U^{IV} bond in **7**,[8] which complements the first donor−acceptor Al^I-U^{III} bond in $[(C_5H_4SiMe_3)_3U\{Al(Cp^*)\}]$.[9]

Recently, we in the Liddle group have been exploring the chemistry of Ln complexes supported by the bis(iminophosphorano)methandiide ligand, $\{C(PPh_2NSiMe_3)_2\}^{2-}$ (BIPM), because it gives novel lanthanide−carbene complexes.[10] Complex **8**[11] ($R = CH_2SiMe_3$) was prepared from the reaction between H_2-BIPM[12] and $[Y(CH_2SiMe_3)_3(THF)_2]$,[13] but we recognized that the alkyl group may limit its synthetic utility. We have therefore prepared an analogous iodide precursor (**10**, see below) with which to expand the range of Ga−Ln bonds, focusing on yttrium because only one unsupported yttrium−metal bond has been reported, namely, $[Cp_2YReCp_2]$.[14] Herein, we report our preliminary result in this area, namely, the synthesis and characterization of the

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‡ Monash University.

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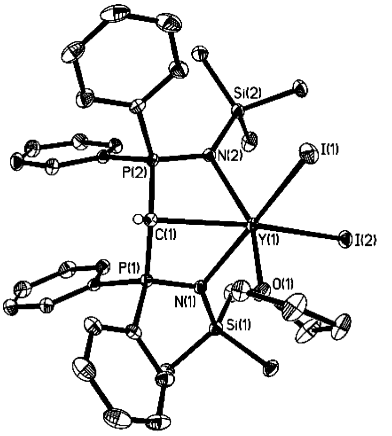

Figure 1. Molecular structure of **9**. Minor components of THF disorder and all nonmethanide H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Y(1)−I(1) 3.0234(5), Y(1)−I(2) 2.9888(5), Y(1)−N(1) 2.3858(18), Y(1)−N(2) 2.3466(18), Y(1)−C(1) 2.599(2), Y(1)−O(1) 2.3429(16), C(1)−P(1) 1.761(2), C(1)−P(2) 1.750(2); P(1)−C(1)−P(2) 122.93(12), N(1)−Y(1)−N(2) 93.99(6).

first Ga−Y bond, which adds to the range of carbene−metal−gallyls.[6,15]

Accordingly, treatment of $[YI_3(THF)_{3.5}]$[16] with [K(H-BIPM)(THF)$_2$][17] affords [YI$_2$(H-BIPM)(THF)] (**9**) in 64% crystalline yield.[18] Surprisingly, formation of **9** at room temperature is sluggish, and the reaction must be refluxed for 4 h to optimize the yield; longer reflux times result in the formation of significant quantities of H$_2$-BIPM. We note that reflux conditions were employed in the preparation of the chloro congener of **9**,[19] but in contrast to this, salt elimination chemistry proceeds easily with the less sterically demanding N-Mes variant of BIPM (Mes = 2,4,6-$Me_3C_6H_2$).[20] The $^{31}P\{^1H\}$ NMR spectrum of **9** exhibits a doublet at 18.7 ppm ($J_{YP} = 6.48$ Hz) and the central carbon of BIPM resonates as a triplet of doublets at 15.8 ppm ($J_{CP} = 133$ Hz and $J_{CY} = 7.40$ Hz) in the $^{13}C\{^1H\}$ NMR spectrum of **9**; both values compare well with those of the chloro congener.[19]

Colorless crystals of **9** were obtained by slow cooling of a warm, saturated solution in THF. The molecular structure is illustrated in Figure 1 with selected bond lengths and angles. The yttrium center adopts a distorted octahedral geometry, where C(1) and I(2) can be considered to be occupying axial sites. The monomeric nature of **9** contrasts with the chloride congener, which is dimeric in the solid state.[19] The BIPM bite angle in **9** [93.99(6)°] is much more acute than that observed in **8** (125.4°), which reflects the monodeprotonated versus doubly deprotonated nature of **9** and **8**, respectively.[11]

The Y(1)−C(1) bond distance of 2.599(2) Å is unsurprisingly longer than that in **8** but significantly shorter than the corresponding distance of 2.642(4) Å in the chloride congener.[19] In contrast, the Y−N bond lengths in **9** are longer than those in the chloro analogue,[19] which may reflect the fact that all of the halide ligands in **9** are terminal.

To minimize the possibility of side reactions, we reduced the number of available iodide ligands in **9** by treating it with 1 equiv of benzylpotassium to give toluene, KI, and [Y(BIPM)(I)(THF)$_2$] (**10**). The reaction is easily monitored by ^{31}P NMR spectroscopy, and full details of this compound and other lanthanide congeners will be reported elsewhere. The addition of 1 equiv of **1** to an in situ prepared solution of **10** in THF afforded the anticipated KI precipitate. Filtration of the red solution and removal of volatiles afforded a deep-yellow solid in quantitative yield, which was recrystallized from toluene to afford [Y{Ga(NArCH)$_2$}(BIPM)(THF)$_2$] (**11**) as yellow crystals in 26% yield.[21] The spectroscopic and analytical data for **11** support the formulation. Of note, the $^{13}C\{^1H\}$ NMR spectrum exhibits a characteristic triplet of doublets at 61.5 ppm ($^1J_{PC} = 203.27$ Hz; $^1J_{YC} = 5.03$ Hz) for the carbene, and the $^{31}P\{^1H\}$ NMR spectrum exhibits a doublet at 4.1 ppm ($^2J_{YP} = 14.58$ Hz).[11] The phenyl *ipso*-carbons and silyl silicons resonate as virtual triplets in the $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra, respectively, due to chemical equivalence but magnetic inequivalence. The FTIR spectrum exhibits an absorption at 1585 cm^{-1}, which is characteristic of **1**.[5]

The X-ray crystal structure of **11** is illustrated in Figure 2 with selected bond lengths and angles. The yttrium center is six-coordinate, is distorted from octahedral geometry by the bite angle of the BIPM ligand [N(1)−Y(1)−N(2) = 134.34(8)°], and is coordinated by the N and C atoms of the BIPM ligand, the O atoms of two molecules of THF, and the gallium center of the gallyl heterocycle that resides trans to the carbene center.

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(18) Synthesis of **9**: A mixture of [K(BIPM)(THF)$_2$] (11.12 g, 15.00 mmol) and $YI_3(THF)_{3.5}$ (10.83 g, 15.00 mmol) in THF (40 mL) was refluxed for 4 h at 80 °C. The mixture was cooled to room temperature and filtered, and volatiles were removed in vacuo to afford the crude solid, which was washed with hexane (3 × 10 mL) and dried in vacuo. Recrystallization from hot THF (15 mL) yielded colorless crystals of **9**. Yield: 8.66 g, 64%. Anal. Calcd for $C_{39}H_{55}I_2N_2O_2P_2Si_2Y$: C, 44.84; H, 5.31; N, 2.68. Found: C, 44.80; H, 5.28; N, 2.66. ^1H NMR (C_6D_6, 300 K): δ 0.33 (m, 18H, CH_3), 1.52 (m, br, 4H, CH_2-THF), 1.97 (d, $^2J_{HP} = 2.75$ Hz, 1H, C*H*, $^2J_{YH}$ not resolved), 3.64 (m, br, 4H, OCH_2-THF), 7.22 (m, 12H, *o*/*p*-Ar−*H*), 8.11 (m, 8H, *m*-Ar−*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 300 K): δ 4.49 (*C*H$_3$), 15.80 (dt, $J_{CP} = 133$ Hz, $J_{CY} = 7.40$ Hz, *C*H), 24.50 (*C*H$_2$-THF), 66.65 (O*C*H$_2$-THF), 127.51 (*m-C*−Ar), 128.66 (*p-C*−Ar), 131.34 (*o-C*−Ar), 143.96 (br, *ipso-C*−Ar). $^{31}P\{^1H\}$ NMR (C_6D_6, 300 K): δ 18.68 (d, $J_{YP} = 6.48$ Hz). IR υ/cm^{-1} (Nujol): 1437 (m), 1261 (s), 1245 (m), 1153 (s), 1113 (s), 840 (s), 694 (s), 661 (m).

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(21) Synthesis of **11**: **1** (0.50 g, 0.83 mmol) was added to a cold (−78 °C) solution of **10** (0.82 g, 0.08 mmol) prepared in situ from **9** and 1 equiv of benzylpotassium. The mixture was allowed to slowly warm to room temperature with stirring over 18 h and filtered. Volatiles were removed in vacuo, and the resulting deep-yellow solid was recrystallized from toluene (10 mL) to afford **11** as yellow crystals. Yield: 0.25 g, 26%. Anal. Calcd for $C_{65}H_{90}GaN_4O_2P_2Si_2Y$: C, 61.15; H, 7.34; N, 4.53. Found: C, 63.08; H, 7.24; N, 4.51. Carbon analysis was typically low, which we attribute to carbide formation. ^1H NMR (benzene-*d*$_6$, 298 K): δ 0.33 (s, 18H, NSi(CH_3)$_3$), 1.37 (m, 8H, OCH$_2$CH_2), 1.54 (dd, $^3J_{HH} = 6.80$ Hz, 24H, CH(CH_3)$_3$), 4.07 (m, 8H, OCH_2CH$_2$), 4.20 (sept, $^3J_{HH} = 6.80$ Hz, 4H, C*H*(CH$_3$)$_3$), 6.53 (s, 2H, C*H*N), 7.09 (virtual t, $^3J_{HH} = 7.20$ Hz, 8H, *m*-Ar−C*H*), 7.15 (d, $^3J_{HH} = 7.20$ Hz, 4H, *m*-Ar−C*H* Dipp), 7.28 (m, 2H, *p*-Ar−C*H* Dipp), 7.36 (d, $^3J_{HH} = 7.20$ Hz, 4H, *p*-Ar−C*H*), 7.57 (dd, $^3J_{PH} = 1.20$ Hz, $^3J_{HH} = 7.20$ Hz, 8H, *o*-Ar−C*H*). $^{13}C\{^1H\}$ NMR (benzene-*d*$_6$, 298 K): δ 3.86 (NSi(*C*H$_3$)$_3$), 23.65 (CH(C*H*$_3$)$_2$), 24.06 (OCH$_2$*C*H$_2$), 25.60 (CH(C*H*$_3$)$_2$), 27.55 (C*H*(CH$_3$)$_2$), 61.53 (td, $^1J_{PC} = 203.27$ Hz, $^1J_{YC} = 5.03$ Hz, Y*C*P$_2$), 71.90 (O*C*H$_2$CH$_2$), 121.52 (*C*HN), 121.90 (Ar−*C*), 122.88 (Ar−*C*), 126.36 (Ar−*C*), 128.38 (Ar−*C*), 130.34 (t, $^2J_{PC} = 6.04$ Hz, *o*-Ar−*C*), 140.80 (t, $^1J_{PC} = 47.30$ Hz, *ipso*-Ar−*C*), 145.27 (Ar−*C*), 150.72 (Ar−*C*). $^{31}P\{^1H\}$ NMR (benzene-*d*$_6$, 298 K): δ 4.06 (d, $^2J_{YP} = 14.58$ Hz, N*P*C). $^{29}Si\{^1H\}$ NMR (benzene-*d*$_6$, 298 K): δ −9.51 (virtual t, $^2J_{PSi} = 3.42$ Hz, N*Si*(CH$_3$)$_3$). IR υ/cm^{-1} (Nujol): 1585 (w), 1247 (m), 1103 (m), 1077 (s), 891 (m), 801 (m), 763 (m), 745 (m), 720 (m), 604 (m).

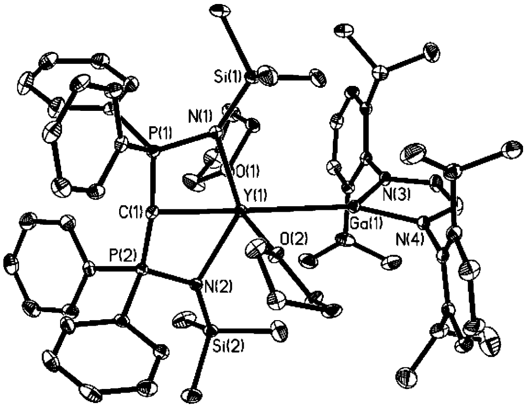

Figure 2. Molecular structure of **11**. Selected bond lengths (Å) and angles (deg): Ga(1)−Y(1) 3.1757(4), Ga(1)−N(3) 1.936(2), Ga(1)−N(4) 1.925(2), Y(1)−N(1) 2.377(2), Y(1)−N(2) 2.369(2), Y(1)−C(1) 2.348(3), Y(1)−O(1) 2.331(2), Y(1)−O(2) 2.3468(19), C(1)−P(1) 1.637(3), C(1)−P(2) 1.643(3), P(1)−N(1) 1.629(2), P(2)−N(2) 1.630(2); P(1)−C(1)−P(2) 171.2(2), N(1)−Y(1)−N(2) 134.34(8), Ga(1)−Y(1)−C(1) 178.92(7).

Whereas the Ga(1)−Y(1)−C(1) angle is essentially linear [178.92(7)°], the O(1)−Y(1)−O(2) angle [166.78(7)°] is distorted away from the bulky BIPM ligand and toward the gallyl heterocycle. Interestingly, the carbene center adopts a planar T-shaped geometry [$\Sigma \angle = 358.3°$]. The Ga−Y bond length of 3.1757(4) Å is without precedent, but it is only slightly longer than the sum of the covalent radii of gallium and yttrium (3.12 Å),[22] which is perhaps not surprising considering the sterically crowded environment at yttrium. The Ga−Y bond length is only 0.04 Å shorter than the Ga−Nd bond length of 3.2199(3) Å observed in **2**[6] (Nd is 0.11 Å larger than Y[22]) although the neodymium center in **2** is only five-coordinate. The Y(1)−C(1), Y(1)−N(1), and Y(1)−N(2) bond lengths of 2.348(3), 2.377(2), and 2.369(2) Å, respectively, are similar to the analogous bond lengths in **8**.

In order to assess the nature of the Ga−Y bond in **11**, we carried out density functional theory calculations with the *ADF2007.01* code on the model **11a**, where the isopropyl groups were replaced by methyls for computational efficacy.[23] The principal features of the X-ray structure are reproduced well by the calculation. The calculation typically overestimates bond lengths by ca. 0.05 Å; conversely, the Ga−Y bond length is underestimated by 0.04 Å, which may be a consequence of the reduction of the steric bulk of the aryl groups. Calculated bond angles are reproduced well; for example, the P(1)−C(1)−P(2) and Ga(1)−Y(1)−C(1) bond angles are calculated to be 171.1 and 178.9°, respectively. Thus, we conclude that **11a** gives a qualitative description of the electronic structure of **11**.

The Kohn−Sham orbital representations of the HOMO (35% N 2p, 35% C 2p, 11% Ga 4p, 2% Y 4d$_{z^2}$), HOMO−1 (52% C 2p, 7% Ga 4p, 2% Y 4d$_{yz}$), HOMO−2 (34% C 2p, 16% Ga 4s, 12% Ga 4p), and HOMO−4 (25% C 2p, 9% Y 5s and 4d$_{xz}$) are illustrated in Figure 3, which correspond to the π combinations on the gallium (HOMO) and carbene (HOMO−1) units and the gallium (HOMO−2) and carbene (HOMO−3) σ-donor combinations, respectively. The calculated natural bond order (NBO) charges (Y +1.86, P$_{av}$ +1.58, N$_{BIPM\text{-}av}$ −1.56, N$_{Ga\text{-}av}$ −0.89, Ga +0.71, and C −1.58) and NBO Wiberg bond orders (Ga−Y 0.51, Ga−N$_{av}$ 0.32, Y−N$_{av}$ 0.20, Y−C 0.29, C−P$_{av}$ 1.19, P−N$_{av}$ 0.99, and Y−O$_{av}$ 0.10) are consistent with (i) an electron-deficient yttrium center, (ii) charge accumulation at the carbene center, (iii) domination of the dipolar N$^-$−P$^+$−C^{2-}−P$^+$−N$^-$ resonance form of BIPM, which has now emerged as the most accurate description of the bonding in BIPM,[11,24] (iv) minimal C → P negative hyperconjugation (the total percent of P character in orbitals 178, 177, and 175 is ca. 9%), and (v) a highly polarized covalent Ga−Y bond. Interestingly, the calculated Ga−Y bond order in **11a** is significantly smaller than the calculated Ga−Nd bond order in **2** (+0.83),[6] which indicates that Ga−Ln bonds can be substantially perturbed by ancillary ligands. The 2% contribution of yttrium to the Ga−Y bond contrasts strongly with the 20% uranium contribution to the π bond in the Ga−U bond in **7**.[8] This highlights the differences between group 3/lanthanide[2] and actinide bonding and is in agreement with calculations on **2**[6] and Ln NHCs,[25] which do not reveal π-donor phenomena.[26]

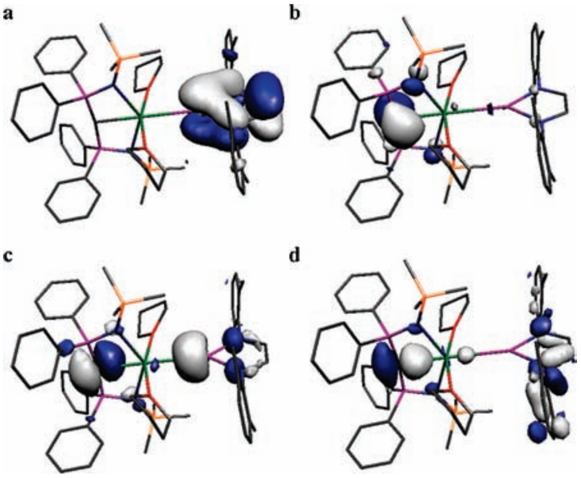

Figure 3. Kohn−Sham orbital representations of (a) HOMO (179), −2.874 eV; (b) HOMO−1 (178), −4.482 eV; (c) HOMO−2 (177), −4.499 eV; (d) HOMO−4 (175), −5.119 eV in **11a**.

To conclude, the first Ga−Y bond has been structurally authenticated, and calculations support a highly polarized covalent bond description. Six Ga−Ln bonds are now available: Ga−Y, Ga−Nd, Ga−Yb, Ga−Tm, Ga−Eu, or Ga−Sm. Synthetic and reactivity studies of these, and related systems, are ongoing and will be reported in due course.

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Supporting Information Available: Crystallographic details for **9** and **11** and computational details for **11a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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