

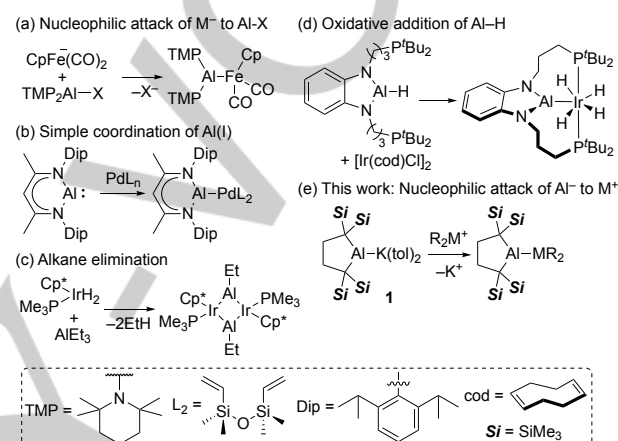
An Alumanyttrium Complex with an Absorption due to a Transition from the Al–Y Bond to an Unoccupied d-Orbital

Kengo Sugita and Makoto Yamashita*

[a] K. Sugita, Prof. Dr. M. Yamashita
Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering
Nagoya University
Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603, Japan
E-mail: makoto@oec.chembio.nagoya-u.ac.jp

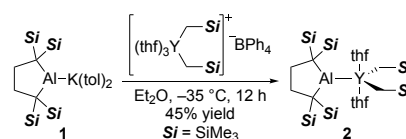
Abstract: The reaction between a dialkyl-substituted alumanyl anion and $[Y(CH_2SiMe_3)_2(thf)_3][BPh_4]$ resulted in the formation of (dialkylalumanyl)yttrium complex **2**, which exhibits the first 2-center-2-electron (2c-2e) Al–Y bond. The 1H and ^{13}C NMR spectra of **2** together with an x-ray crystallographic analysis indicated a C_{2v} symmetrical structure. DFT calculations on **2** revealed that its LUMO consists of overlapping 3p- and 4d-orbitals of the Al and Y atoms, respectively, and that the HOMO–LUMO gap is narrow. The UV-Vis spectrum of **2** exhibited a visible absorption at 432 nm, which suggests that the strong σ -donating and π -accepting character of the three-coordinate dialkylalumanyl ligand generates a colored d^0 -complex that does not contain any π -electrons.

Aluminum contains three valence electrons and is the most electropositive element in the p-block.^[1] Accordingly, aluminum-ligated transition-metal complexes generally exhibit a coordination number of at least four at the aluminum center in order to satisfy the electron deficiency of the aluminum atom. Such Al-containing ligands are typically classified into (i) Z-type Al ligands,^[2] (ii) L-type Al ligands containing Cp*Al ligands^[3] and base-stabilized alumylene ligands,^[4] (iii) X-type Al ligands containing base-stabilized alumanyl ligands^[5] and (iv) bridging forms of (ii) and (iii).^[6] In contrast, examples for the synthesis of transition-metal complexes that possess a three-coordinated aluminum ligand remain limited. Nine reports on such ligands can be ordered according to the following four methods (Scheme 1): (a) A nucleophilic attack of anionic transition-metal complexes to an aluminum electrophile,^[7] (b) the coordination of a base-stabilized Al(I) species to a metal,^[8] (c) an elimination of alkane via a metathesis reaction,^[9] (d) an oxidative addition of an Al–H bond to a metal center in a low oxidation state.^[10] On the other hand, three types of anionic and nucleophilic aluminum species^[11] have been reported recently and used as an Al(I) species in a low oxidation state.^[11b, 12] It should be noted here that the base-stabilized aluminum anion was used for the synthesis of a base-stabilized alumanylgold complex (*cf.* class (iv) complexes; *vide supra*) via a nucleophilic substitution at the gold center.^[5h] Herein, we report the use of dialkyl-substituted Al anion **1** for the synthesis of an alumanyttrium complex (**2**) that exhibits a three-coordinate aluminum atom and the first Al–Y single bond (Scheme 1e).^[13] The properties of **2** were investigated by multinuclear NMR spectroscopy, single-crystal x-ray diffraction analysis, UV-Vis absorption spectroscopy, and DFT calculations. Based on the thus obtained results, the intense yellow color of **2** was assigned to a transition from a high-lying Al–Y σ -bond (HOMO) to the LUMO, which consists of vacant p- and d-orbitals of the Al and Y atoms, respectively.



Scheme 1. Synthesis of transition-metal complexes that contain a three-coordinate aluminum ligand.

The reaction of alumanylpotassium **1** with the cationic complex $[Y(CH_2SiMe_3)_2(thf)_3][BPh_4]$ ^[14] in diethyl ether at -35 °C furnished the corresponding alumanyttrium complex (**2**) as a bright yellow crystalline solid (Scheme 2). The 1H NMR spectrum of **2** in C_6D_{12} exhibited two singlets for the trimethylsilyl groups in 1:2 integral ratio and a singlet for the methylene groups in the five-membered ring, indicating a C_{2v} -symmetrical structure in solution. Additionally, a characteristic doublet ($^2J_{YH} = 2.6$ Hz) was found for the yttrium-bonded CH_2 groups at $\delta_H = -0.65$ ppm, whose protons are coupled to the ^{89}Y nuclei (100% abundance; $I = 1/2$).^[15] In the ^{13}C NMR spectrum of **2**, the two tetrasubstituted carbon atoms at the α position relative to the Al atom were also coupled to the Y atom ($^2J_{YC} = 6$ Hz).^[16] This value is smaller than that for the directly bonded CH_2 groups to the Y atom ($^1J_{YC} = 36$ Hz). This result clearly indicates that in solution, the Al atom is directly bonded to the Y atom.



Scheme 2. Synthesis of tetraalkylalumanyttrium complex **2**.

The molecular structure of **2** was unambiguously determined by a single-crystal x-ray diffraction analysis (Figure 1). In the

COMMUNICATION

crystalline state, the Al and Y atoms adopt a trigonal planar and trigonal bipyramidal coordination geometry, respectively. The Al–Y bond is the first example of a 2-center-2-electron (2c-2e) bond between Al and Y atoms. The Al–Y bond lengths [3.1870(8), 3.1942(8) Å] of the two crystallographically independent molecules of **2** per asymmetric unit are longer than the sum of the covalent radii (2.87 Å) of the Al and Y atoms.^[17] A structural comparison of **2** with the previously reported **1** and its precursor **3** is summarized in Table 1. The Al–C bond lengths [2.028(3), 2.038(3), 2.033(3), 2.041(3) Å] in **2** are shorter than those in **1** and longer than those in **3**. Simultaneously, the C–Al–C angles in **2** [93.81(11)°, 93.66(11)°] are wider and narrower than those of **1** and **3**, respectively. These results indicate that the Al atom in **2** is sp²-hybridized, similar to that in **3** rather than to the s-rich Al–K bond in **1**, which was supported by a natural bond orbital (NBO) analysis (35.35% s-orbital character and 64.45% p-orbital character on the Al atom for the Al–Y bond). The Y–O and Y–C bonds in **2** are similar to those of previously reported five-coordinated Y complexes (*cf.* Si),^[18] which indicates that the structural factors around Al atom do not perturb the electronic structure of the Y atom. The C–Al–Y–C torsion angles of **2** [7.4(1)°, 8.0(2)°] are close to zero, and stand thus in stark contrast to a previously reported (boryl)Y(CH₂SiMe₃)₂(thf)₂ complex (**4**),^[18d, 18e] which exhibits an almost orthogonal torsion angle between the boron plane and the equatorial plane around the Y atom [–73.4(3)°].

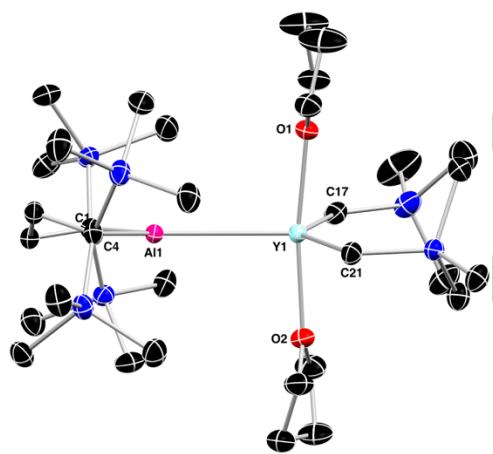
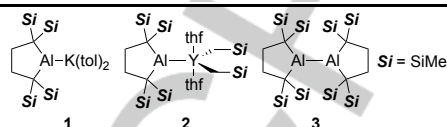


Figure 1. Molecular structure of **2** (thermal ellipsoids set at 50% probability; one of the two crystallographically independent molecules and hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Al–Y 3.1870(8), 3.1942(8); Al–C 2.028(3), 2.038(3), 2.033(3), 2.041(3); Y–C 2.398(3), 2.401(3), 2.390(3), 2.405(3); Y–O 2.3651(18), 2.3651(18), 2.3637(19), 2.365(2); C–Al–C 93.81(11), 93.66(11); C–Y–C 129.70(9), 129.64(10); O–Y–O 171.64(7), 171.40(7).

Table 1. A structural comparison of the aluminum-containing five-membered rings in **1–3**.

Compound	1	2	3
C–Al (Å)	2.0846(9)	2.028(3), 2.038(3) 2.033(3), 2.041(3)	2.005(3), 2.011(3)
C–Al–C (°)	90.40(5)	93.81(11), 93.66(11)	97.78(12)



The electronic structure of **2** was examined by DFT calculations. The theoretically optimized structure of **2** was in good agreement with the experimentally obtained structure (e.g., calculated Al–Y bond: 3.281 Å; experimental: 3.187(8) Å). The HOMO and LUMO are illustrated in Figure 2. The HOMO represents the 2c-2e bond between the Al and Y atoms, which exhibits Al[–] and Y⁺ character with reflection of their electronegativity [Pauling, Al: 1.61, Y: 1.22; Allen, Al: 1.613, Y: 1.12].^[11] On the other hand, the LUMO consists of significantly overlapping vacant 3p- and 4d-orbitals of the Al and Y atoms, respectively, due to the strong electron affinity of the Al atom. The HOMO level of **2** (–4.62 eV) is higher than that of **4**^[18d, 18e] (–5.02 eV), when calculated at the same level of theory (Figure 3; for details, see the SI) due to the stronger σ -donor ability of the Al atom relative to that of the B atom, which is based on the difference in electronegativity of these atoms.^[11] The LUMO level (–1.176 eV) of **2** is lower than that of **4** (–0.461 eV) due to the effective overlapping of the vacant orbitals between the Al and Y atoms in **2** and π -bonding interaction between the N and B atoms in **4** (Figure S4). An atoms-in-molecule (AIM) analysis^[19] of **2** afforded insight into the properties of this unprecedented Al–Y bond (for details, see the SI). The $\nabla\rho(r)$ values (0.028237 e/a_0^3) at the bond critical point (BCP) between the Al and Y atoms in **2** indicate that the Al–Y bond is stronger than the previously reported Al[–]–K⁺ bond in **1** [$\nabla\rho(r) = 0.01173 e/a_0^3$]. Considering the $\nabla^2\rho(r)$ value (0.009537 e/a_0^5) at the BCP for Al–Y bond in **2** is smaller than that for the Al[–]–K⁺ bond in **1** [$\nabla^2\rho(r) = 0.020826 e/a_0^5$], the Al–Y bond in **2** should be less polarized than that in **1**, but is apparently ionic because the value is positive.

The UV-Vis absorption and emission spectra of **2** were measured in cyclohexane (Figure 4). The UV-Vis spectrum exhibited two absorption maxima at 351 ($\epsilon = 3700$) and 432 nm ($\epsilon = 2400$), while the emission spectrum ($\lambda_{\text{ex}} = 440$ nm) showed an emission maximum at 536 nm. The fluorescent quantum yield of the latter was low ($\phi = 0.0016$), probably due to the high degree of freedom for all the aliphatic substituents. It should be noted that the emission became weaker upon repetitive measurements, probably due to the decomposition of **2** to an unidentified non-emissive product. Based on TD-DFT calculations (for details, see the SI), the absorption at 432 nm was assigned to the HOMO-LUMO transition (421 nm; $f = 0.0316$). To reveal the substituent effect of the dialkylaluminum ligand in **2**, the UV-Vis spectrum of independently synthesized Y(CH₂SiMe₃)₃(thf)₃^[20] was measured in cyclohexane, albeit that an absorption beyond 300 nm was not observed. Additionally, the HOMO-LUMO transition of the previously reported "pale yellow microcrystalline powder" of **4**^[18d] was estimated to be at 304 nm based on TD-DFT calculations (Figure S6, Table S4). Thus, the introduction of the dialkylaluminum ligand to the yttrium atom narrows the HOMO-

LUMO gap of the d^0 -complex without π -electrons and results in a visible absorption.

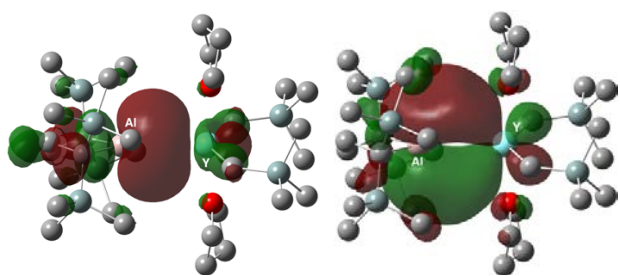


Figure 2. HOMO (left) and LUMO (right) of **2** calculated at the B3LYP level of theory using LANL2DZ (for Y) and 6-31+g(d) (all other atoms) basis sets.

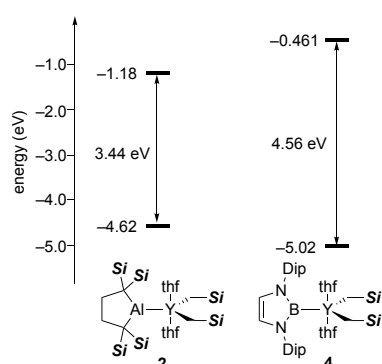


Figure 3. Energy diagram for the frontier orbitals of **2** and borylyttrium complex **4**.

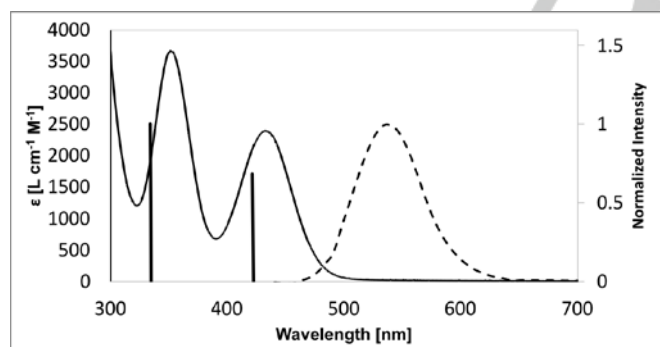


Figure 4. The UV-Vis absorption (solid line; $\lambda_{\text{max}} = 351, 432 \text{ nm}$, $\epsilon = 3700, 2400$) and emission (dashed line; $\lambda_{\text{em}} = 536 \text{ nm}$, $\lambda_{\text{ex}} = 440 \text{ nm}$) spectra of **2** in cyclohexane. Two vertical lines describe simulated absorptions by TD-DFT calculations (relative intensities are normalized to 1 at 334 nm, See Table S3 for details).

In conclusion, the reaction between dialkylaluminumpotassium **1** with a cationic dialkylttrium complex furnished the first example of an aluminylttrium complex (**2**). A spectral and structural analysis of **2** in combination with DFT calculations revealed its electronic properties. The UV-Vis spectrum of **2** showed an absorption in the visible region due to a narrow HOMO-LUMO gap, which stems from the strong σ -donor ability of the dialkylaluminum substituent and the overlapping vacant 3p- and 4d-orbitals of the Al and Y atoms, respectively.

Acknowledgements

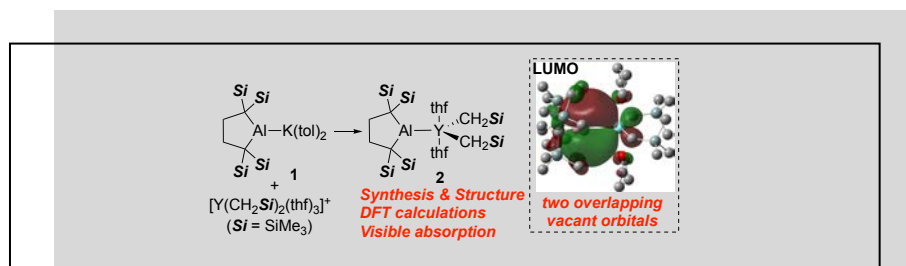
This research was supported by a Grant-in-Aid for Scientific Research (A) (JSPS KAKENHI grant 17H01191) and by a JST CREST grant (14529307). Theoretical calculations were carried out using resources at the Research Center for Computational Science (Okazaki, Japan). We thank Prof. Hiroshi Shinokubo, Dr. Norihito Fukui, and Mr. Keita Tajima for measuring the quantum fluorescence yield.

Keywords: aluminyl complex • X-type ligand • LMCT • yttrium • absorption spectrum

- [1] (a) L. Pauling, *J. Am. Chem. Soc.* **1932**, *54*, 3570-3582; (b) L. Pauling, *The Nature of The Chemical Bond*, 3 ed., Cornell University Press, Ithaca, **1960**; (c) L. C. Allen, *J. Am. Chem. Soc.* **1989**, *111*, 9003-9014; (d) J. B. Mann, T. L. Meek, L. C. Allen, *J. Am. Chem. Soc.* **2000**, *122*, 2780-2783; (e) J. B. Mann, T. L. Meek, E. T. Knight, J. F. Capitani, L. C. Allen, *J. Am. Chem. Soc.* **2000**, *122*, 5132-5137.
- [2] (a) J. M. Burlitch, M. E. Leonowicz, R. B. Petersen, R. E. Hughes, *Inorg. Chem.* **1979**, *18*, 1097-1105; (b) J. M. Mayer, J. C. Calabrese, *Organometallics* **1984**, *3*, 1292-1298; (c) B. Buchin, C. Gemel, A. Kempter, T. Cadenbach, R. A. Fischer, *Inorg. Chim. Acta* **2006**, *359*, 4833-4839; (d) H. Braunschweig, K. Gruss, K. Radacki, *Angew. Chem. Int. Ed.* **2007**, *46*, 7782-7784; (e) J. Bauer, H. Braunschweig, P. Brenner, K. Kraft, K. Radacki, K. Schwab, *Chem. Eur. J.* **2010**, *16*, 11985-11992; (f) P. A. Rudd, S. Liu, L. Gagliardi, V. G. Young, C. C. Lu, *J. Am. Chem. Soc.* **2011**, *133*, 20724-20727; (g) J. Bauer, R. Bertermann, H. Braunschweig, K. Gruss, F. Hupp, T. Kramer, *Inorg. Chem.* **2012**, *51*, 5617-5626; (h) J. Bauer, H. Braunschweig, K. Radacki, *Chem. Commun.* **2012**, *48*, 10407-10409; (i) P. A. Rudd, N. Planas, E. Bill, L. Gagliardi, C. C. Lu, *Eur. J. Inorg. Chem.* **2013**, *2013*, 3898-3906; (j) M. Oishi, M. Oshima, H. Suzuki, *Inorg. Chem.* **2014**, *53*, 6634-6654; (k) M. Devillard, E. Nicolas, A. W. Ehlers, J. Backs, S. Mallet - Ladeira, G. Bouhadir, J. C. Sootweg, W. Uhl, D. Bourissou *Chem. Eur. J.* **2015**, *21*, 74-79; (l) B. E. Cowie, F. A. Tsao, D. J. H. Emslie, *Angew. Chem. Int. Ed.* **2015**, *54*, 2165-2169; (m) M. Devillard, R. Declercq, E. Nicolas, A. W. Ehlers, J. Backs, N. Saffon-Merceron, G. Bouhadir, J. C. Sootweg, W. Uhl, D. Bourissou, *J. Am. Chem. Soc.* **2016**, *138*, 4917-4926; (n) A. B. Thompson, D. R. Pahls, V. Bernales, L. C. Gallington, C. D. Malonzo, T. Webber, S. J. Tereniak, T. C. Wang, S. P. Desai, Z. Li, I. S. Kim, L. Gagliardi, R. L. Penn, K. W. Chapman, A. Stein, O. K. Farha, J. T. Hupp, A. B. F. Martinson, C. C. Lu, *Chem. Mater.* **2016**, *28*, 6753-6762; (o) T. Saito, N. Hara, Y. Nakao, *Chem. Lett.* **2017**, *46*, 1247-1249; (p) J. T. Moore, N. E. Smith, C. C. Lu, *Dalton Trans.* **2017**, *46*, 5689-5701; (q) N. Hara, T. Saito, K. Semba, N. Kuriakose, H. Zheng, S. Sakaki, Y. Nakao, *J. Am. Chem. Soc.* **2018**, *140*, 7070-7073; (r) A. Hofmann, A. Lamprecht, J. O. C. Jiménez - Halla, T. Tröster, R. D. Dewhurst, C. Lenczyk, H. Braunschweig, *Chem. Eur. J.* **2018**, *24*, 11795-11802.
- [3] (a) Q. Yu, A. Purath, A. Donchev, H. Schnöckel, *J. Organomet. Chem.* **1999**, *584*, 94-97; (b) D. Weiss, T. Steinke, M. Winter, R. A. Fischer, N. Fröhlich, J. Uddin, G. Frenking, *Organometallics* **2000**, *19*, 4583-4588; (c) T. Steinke, C. Gemel, M. Cokoja, M. Winter, R. A. Fischer, *Angew. Chem. Int. Ed.* **2004**, *43*, 2299-2302; (d) T. Steinke, C. Gemel, M. Winter, R. A. Fischer, *Chem. Eur. J.* **2005**, *11*, 1636-1646; (e) T. Steinke, M. Cokoja, C. Gemel, A. Kempter, A. Krapp, G. Frenking, U. Zenneck, R. A. Fischer, *Angew. Chem. Int. Ed.* **2005**, *44*, 2943-2946; (f) B. Buchin, T. Steinke, C. Gemel, T. Cadenbach, R. A. Fischer, *Z. Anorg. Allg. Chem.* **2005**, *631*, 2756-2762; (g) M. T. Gamer, P. W. Roesky, S. N. Konchenko, P. Nava, R. Ahlrichs, *Angew. Chem. Int. Ed.* **2006**, *45*, 4447-4451; (h) T. Cadenbach, C. Gemel, T. Bollermann, R. A. Fischer, *Inorg. Chem.* **2009**, *48*, 5021-5026; (i) M. Molon, T. Bollermann, C. Gemel, J. Schaumann, R. A. Fischer, *Dalton Trans.* **2011**, *40*, 10769-10774; (j) M. Molon, C. Gemel, R. A. Fischer, *J. Organomet. Chem.* **2014**, *751*, 573-578; (k) J. Weßing, C. Göbel, B. Weber, C. Gemel, R. A. Fischer, *Inorg. Chem.* **2017**, *56*, 3517-3525; (l) J. Hornung, J. Weßing, P. Jerabek, C. Gemel,

- A. Pöthig, G. Frenking, R. A. Fischer, *Inorg. Chem.* **2018**, *57*, 12657-12664.
- [4] (a) R. A. Fischer, M. M. Schulte, J. Weiss, L. Zsolnai, A. Jacobi, G. Huttner, G. Frenking, C. Boehme, S. F. Vyboishchikov, *J. Am. Chem. Soc.* **1998**, *120*, 1237-1248; (b) H. Fölsing, O. Segnitz, U. Bossek, K. Merz, M. Winter, R. A. Fischer, *J. Organomet. Chem.* **2000**, *606*, 132-140; (c) G. Tan, T. Szilvási, S. Inoue, B. Blom, M. Driess, *J. Am. Chem. Soc.* **2014**, *136*, 9732-9742; (d) D. Dange, C. P. Sindlinger, S. Aldridge, C. Jones, *Chem. Commun.* **2017**, *53*, 149-152.
- [5] (a) M. D. Fryzuk, N. T. McManus, S. J. Rettig, G. S. White, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 73-75; (b) R. A. Fischer, T. Priemeier, *Organometallics* **1994**, *13*, 4306-4314; (c) H. Braunschweig, J. Müller, B. Ganter, *Inorg. Chem.* **1996**, *35*, 7443-7444; (d) C. Jones, S. Aldridge, T. Gans-Eichler, A. Stasch, *Dalton Trans.* **2006**, 5357-5361; (e) I. M. Riddlestone, J. Urbano, N. Phillips, M. J. Kelly, D. Vidovic, J. I. Bates, R. Taylor, S. Aldridge, *Dalton Trans.* **2013**, *42*, 249-258; (f) J. Takaya, N. Iwasawa, *J. Am. Chem. Soc.* **2017**, *139*, 6074-6077; (g) D. W. Agnew, C. E. Moore, A. L. Rheingold, J. S. Figueroa, *Dalton Trans.* **2017**, *46*, 6700-6707; (h) J. Hicks, A. Mansikkamäki, P. Vasko, J. M. Goicoechea, S. Aldridge, *Nat. Chem.* **2019**, *11*, 237-241; (i) K. Semba, I. Fujii, Y. Nakao, *Inorganics* **2019**, *7*, 140-147.
- [6] (a) C. Üffing, A. Ecker, R. Köppe, H. Schnöckel, *Organometallics* **1998**, *17*, 2373-2375; (b) A. Kempter, C. Gemel, R. A. Fischer, *Chem. Commun.* **2006**, 1551-1553; (c) A. Noor, G. Glatz, R. Müller, M. Kaupp, S. Demeshko, R. Kempe, *Nat. Chem.* **2009**, *1*, 322-325; (d) C. Dohmeier, H. Krautscheid, H. Schnöckel, *Angew. Chem. Int. Ed. Engl.* **1995**, *33*, 2482-2483.
- [7] (a) B. N. Anand, I. Krossing, H. Nöth, *Inorg. Chem.* **1997**, *36*, 1979-1981; (b) T. Agou, T. Yanagisawa, T. Sasamori, N. Tokitoh, *Bull. Chem. Soc. Jpn.* **2016**, *89*, 1184-1186; (c) T. Yanagisawa, Y. Mizuhata, N. Tokitoh, *Heteroat. Chem.* **2018**, *29*, e21465.
- [8] (a) A. Kempter, C. Gemel, R. A. Fischer, *Chem. Eur. J.* **2007**, *13*, 2990-3000; (b) K. Nagata, T. Agou, N. Tokitoh, *Angew. Chem. Int. Ed.* **2014**, *53*, 3881-3884; (c) T. N. Hooper, M. Garcon, A. J. P. White, M. R. Crimmin, *Chem. Sci.* **2018**, *9*, 5435-5440.
- [9] (a) J. J. Schneider, C. Krüger, M. Nolte, I. Abraham, T. S. Ertel, H. Bertagnolli, *Angew. Chem. Int. Ed. Engl.* **1995**, *33*, 2435-2437; (b) J. T. Golden, T. H. Peterson, P. L. Holland, R. G. Bergman, R. A. Andersen, *J. Am. Chem. Soc.* **1998**, *120*, 223-224.
- [10] S. Morisako, S. Watanabe, S. Ikemoto, S. Muratsugu, M. Tada, M. Yamashita, *Angew. Chem. Int. Ed.* **2019**, *58*, 15031-15035.
- [11] (a) J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *Nature* **2018**, *557*, 92-95; (b) R. J. Schwamm, M. D. Anker, M. Lein, M. P. Coles, *Angew. Chem. Int. Ed.* **2019**, *58*, 1489-1493; (c) S. Kurumada, S. Takamori, M. Yamashita, *Nat. Chem.* **2020**, *12*, 36-39; (d) M. S. Hill, R. Schwamm, M. Coles, M. Mahon, C. McMullin, N. Rajabi, A. Wilson, *Angew. Chem. Int. Ed.* **2020**, *59*, doi: 10.1002/anie.201914986.
- [12] (a) M. D. Anker, M. P. Coles, *Angew. Chem. Int. Ed.* **2019**, *58*, 13452-13455; (b) M. D. Anker, M. P. Coles, *Angew. Chem. Int. Ed.* **2019**, *58*, 18261-18265; (c) J. Hicks, A. Heilmann, P. Vasko, J. M. Goicoechea, S. Aldridge, *Angew. Chem. Int. Ed.* **2019**, *58*, 17265-17268; (d) J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *J. Am. Chem. Soc.* **2019**, *141*, 11000-11003; (e) K. Sugita, R. Nakano, M. Yamashita, *Chem. Eur. J.* **2020**, *25*, doi: 10.1002/chem.201905830.
- [13] It should be noted that two compounds possessing an Cp*Al-1anthanide bond have been reported, in which Cp*Al unit behaves as a L-type ligand. See ref 3g.
- [14] B. R. Elvidge, S. Arndt, P. M. Zeimentz, T. P. Spaniol, J. Okuda, *Inorg. Chem.* **2005**, *44*, 6777-6788.
- [15] A similar value of $^2J_{\text{YH}} = 2.4$ Hz was reported for $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$. S. Bambirra, E. Otten, D. v. Leusen, A. Meetsma, B. Hessen, *Z. Anorg. Allg. Chem.* **2006**, *632*, 1950-1952.
- [16] A similar value of $^2J_{\text{YC}} = 5$ Hz was reported for $[\text{Cp}^*\text{Y}(\text{THF})_2(\mu\text{-OCH}_2\text{CH}_2\text{O})]$. B.-J. Deelman, M. Booi, A. Meetsma, J. H. Teuben, H. Kooijman, A. L. Spek, *Organometallics* **1995**, *14*, 2306-2317.
- [17] J. Emsley, *The Elements*, 3rd ed., Oxford University Press, New York, **1998**.
- [18] (a) L. T. J. Evans, M. P. Coles, F. G. N. Cloke, P. B. Hitchcock, *Inorg. Chim. Acta* **2010**, *363*, 1114-1125; (b) A. G. Trambitas, T. K. Panda, J. Jenter, P. W. Roesky, C. Daniliuc, C. G. Hrib, P. G. Jones, M. Tamm, *Inorg. Chem.* **2010**, *49*, 2435-2446; (c) W. J. Evans, R. N. R. Broomhall-Dillard, J. W. Ziller, *Organometallics* **1996**, *15*, 1351-1355; (d) L. M. A. Saleh, K. H. Birjumar, A. V. Protchenko, A. D. Schwarz, S. Aldridge, C. Jones, N. Kaltsoyannis, P. Mountford, *J. Am. Chem. Soc.* **2011**, *133*, 3836-3839; (e) S. Li, J. Cheng, Y. Chen, M. Nishiura, Z. Hou, *Angew. Chem. Int. Ed.* **2011**, *50*, 6360-6363.
- [19] (a) R. F. W. Bader, *Atoms In Molecules - A Quantum Theory*, Oxford University Press, New York, **1990**; (b) R. F. W. Bader, *Chem. Rev.* **1991**, *91*, 893-928.
- [20] (a) W. J. Evans, J. C. Brady, J. W. Ziller, *J. Am. Chem. Soc.* **2001**, *123*, 7711-7712; (b) M. F. Lappert, R. Pearce, *J. Chem. Soc., Chem. Commun.* **1973**, 126-126; (c) K. C. Hultsch, P. Voth, K. Beckerle, T. P. Spaniol, J. Okuda, *Organometallics* **2000**, *19*, 228-243.

Entry for the Table of Contents



The many)yttrium complex **2**, possessing the unprecedented 2c-2e Al–Y bond as characterized by the NMR spectra and x-ray analysis. DFT calculations on **2** revealed its overlapping 3p- and 4d-orbitals of the Al and Y atoms to be LUMO. A visible absorption of **2** at 432 nm was assigned to a transition from Al–Y bond to LUMO without any π -electrons.

Institute and/or researcher Twitter usernames: makoto_B (Makoto Yamashita)