Angewandte
International Edition Chemie

DOI: 10.1002/anie.201310559

Main-Group Ligands

Syntheses and Structures of Terminal Arylalumylene Complexes**

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Dedicated to Professor Renji Okazaki on the occasion of his 77th birthday

Abstract: *Terminal arylalumylene complexes of platinum [Ar-Al-Pt(PCy_3)$_2$] (Ar = 2,6-[$CH(SiMe_3)_2$]$_2C_6H_3$ (Bbp) or 2,6-[$CH(SiMe_3)_2$]$_2$-4-(tBu)C_6H_2 (Tbb)) have been synthesized either by the reaction of a dialumene–benzene adduct with [Pt(PCy_3)$_2$], or by the reduction of 1,2-dibromodialumanes Ar(Br)Al-Al(Br)Ar in the presence of [Pt(PCy_3)$_2$]. X-Ray crystallographic analysis reveals that the Al–Pt bond lengths of these arylalumylene complexes are shorter than the previously reported shortest Al–Pt distance. DFT calculations suggest that the Al–Pt bonds in the arylalumylene complexes have a significantly high electrostatic character.*

Transition-metal complexes of subvalent main-group-element compounds attract considerable attention not only because of their unique electronic structures, but also because of their synthetic potential in organometallic chemistry. In particular, complexes of group 13 metallylenes (:ER, E = B, Al, Ga, In, and Tl) are expected to show particular bonding interactions between the subvalent group 13 elements and transition-metal fragments because these metallylenes possess a lone pair of electrons and two vacant p orbitals, and may act as σ-donor/π-acceptor ligands.[1] The chemistry of borylene complexes has been extensively developed,[2] whereas the examples of the heavier group 13 metallylene complexes, having the formula of [$M(ER)_mL_n$] (R: anionic monodentate ligands), have been limited for the gallium and indium homologues, and have yet to be reported for aluminum.[3] Although Lewis-base-coordinated terminal alumylene complexes (e.g., **A**, **B**, and **C**; Figure 1) have been synthesized as stable compounds,[4–7] there have been no alumylene complexes featuring two-coordinate subvalent aluminum moieties (i.e., **D**). Because the coordination of Lewis bases may mask the intrinsic nature of the alumylene ligands, the development of Lewis base-free alumylene complexes is desirable so as to elucidate the bonding situation between the alumylene and transition-metal moieties. Herein, we report the syntheses and structures of platinum complexes of arylalumylenes, which are the first examples of Lewis-base-free alumylene complexes.

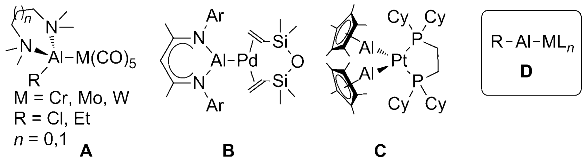
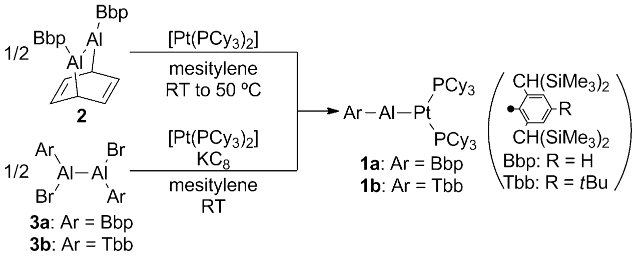


Figure 1. Transition-metal complexes of Lewis-base-coordinated (**A**–**C**) and Lewis-base-free (**D**) alumylenes. Ar = 2,6-(*i*Pr)$_2C_6H_3$.

Recently, we reported on the reactivity of the dialumene-benzene adduct **2** as a synthetic equivalent of the diaryldialumene BbpAl=AlBbp.[8,9] During the studies on the reactivity of **2**, the reaction of **2** and [Pt(PCy_3)$_2$] was investigated with the expectation of trapping of the dialumene as a π-dialumene complex of platinum.[10] The reaction progress was monitored by ^{31}P NMR spectroscopy, which showed the formation of a mixture containing a new platinum complex (δ_P = 69.9 ppm). Fractional crystallization of the crude material from *n*-hexane at −35 °C yielded a small amount (3 %) of the arylalumylene complex **1a** as air- and moisture-sensitive dark red crystals (Scheme 1). The formation of **1a** implies that **2** reacts as an arylalumylene source in addition to the diaryldialumene synthon. After screening of the reaction conditions, reduction of the 1,2-dibromodialumanes **3a**[11] and **3b** with KC_8 in the presence of [Pt(PCy_3)$_2$] was found to afford **1a** and **1b**, respectively, as the sole products. After recrystallization from *n*-hexane at −35 °C, the



Scheme 1. Syntheses of the arylalumylene complexes **1a** and **1b**.

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[**] This work was supported by JSPS KAKENHI (Nos. 22350017, 24550048, 24655028, and 24109013), Grants for Excellent Graduate Schools, MEXT (Japan), and the "Molecular Systems Research" project of RIKEN Advanced Science Institute. T.A. thanks the Kyoto Technoscience Center and the Research Institute for Production Development for the financial support. K.N. acknowledges the support from Grants-in-Aid for JSPS Fellows from JSPS (No. 252926). The synchrotron radiation experiments were performed at the BL38B1 beamline of the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI; proposal No. 2013A1183). We are grateful to Dr. K. Miura, Dr. S. Baba, and Dr. N. Mizuno (JASRI) for the X-ray crystallographic analyses at the SPring-8.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201310559.

arylalumylene complexes were obtained in moderate yields (**1a**: 72 %, **1b**: 21 %). The complexes **1a** and **1b** are stable up to 79 and 110 °C, respectively, in the solid state, but they slowly decompose in solution, even at −35 °C, to give complicated mixtures containing [Pt(PCy$_3$)$_2$] and PCy$_3$.

In the ^{31}P NMR spectra, **1a** and **1b** exhibit singlets accompanied by ^{195}Pt satellites at $\delta = 69.9$ ppm ($^1J_{\mathrm{PPt}} = 4015$ Hz) and $\delta = 69.8$ ppm ($^1J_{\mathrm{PPt}} = 4033$ Hz), respectively, which are downfield shifted with respect to those of [Pt(PCy$_3$)$_2$] ($\delta = 62.3$ ppm, $^1J_{\mathrm{PPt}} = 4160$ Hz) and the structurally related carbonyl complex [(Cy$_3$P)$_2$Pt(CO)] ($\delta = 63.7$ ppm, $^1J_{\mathrm{PPt}} = 4101$ Hz).[12] Definite signals could not be observed in the ^{27}Al and ^{195}Pt NMR spectra of **1a** and **1b**, probably because of the signal broadening caused by the high quadrupole moment of the ^{27}Al nuclei.

Molecular structures of **1a** and **1b** were determined by X-ray crystallographic analyses, thereby showing that the aluminum atoms are definitely two-coordinate and are bound to the platinum atoms in a terminal fashion with C1-Al1-Pt1 angles of 179.2(2) (**1a**) and 173.96(14)° (**1b**; Figure 2). The platinum centers adopt distorted trigonal-planar geometries. The Pt1−Al1 bonds of the arylalumylene complexes [**1a**: 2.2857(18) Å, **1b**: 2.2829(13) Å] are slightly shortened compared to the shortest Pt−Al distance previously reported [2.327(2) Å],[6d] most likely reflecting the decreased coordination number of platinum as well as the difference in the aluminum-bound substituents.[13]

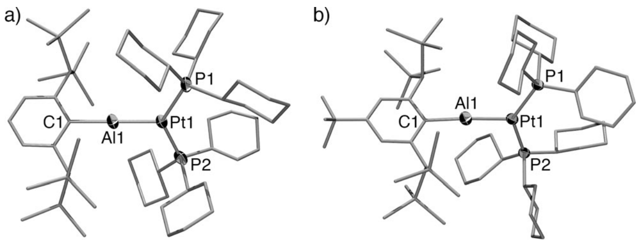

Figure 2. Molecular structures of a) **1a** and b) **1b**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted, and the Bbp, Tbb, and Cy groups are shown in wireframe format for clarity. Three Cy and two Me groups in **1a** were disordered over two positions (see the Supporting Information for details). Selected bond lengths [Å] and angles [°]: **1a**: Al1–Pt1 2.2857(18), C1–Al1 2.001(6), Pt1–P1 2.2828(17), Pt1–P2 2.2903(16); C1-Al1-Pt1 179.2(2), Al1-Pt1-P1 114.86(6), Al1-Pt1-P2 117.85(6), P1-Pt1-P2 127.29(6). **1b**: Al1–Pt1 2.2829(13), C1–Al1 1.986(4), Pt1–P1 2.3071(9), Pt1–P2 2.2673(10); C1-Al1-Pt1 173.96(14), Al1-Pt1-P1 119.14(4), Al1-Pt1-P2 109.20(4), P1-Pt1-P2 131.56(4).

To gain further information on the bonding situation in **1a** and **1b**, density functional theory (DFT) calculations at the M062X[14]/SDD[Pt]:6-311G(2df)[Al,P]:6-31G(d)[Si,C,H] level of theory were performed on a real molecule of **1a**. The comparison of the optimized and experimental bond lengths and angles of **1a** shows that the DFT-optimized structure is well-matched to that found in the single crystals. The natural bond orbital (NBO) analysis[15] on the optimized geometry of **1a** showed that the Al-Pt bond has a small Wiberg bond index (0.59), thus indicating that the Al-Pt bond is highly ionic and that the contribution of the covalent interaction is less important.[6d,16] The calculated NBO corresponding to the Al−Pt bond is predominantly formed from the overlap of the 3s(Al) and 6s(Pt) orbitals [$\sigma(\text{Al-Pt}) = 0.87(3s3p^{0.03})\text{Al} + 0.50(6s6p^{0.03}6d^{0.02})\text{Pt}$]. Meanwhile, the Pt→Al π-back donation interactions were identified as donor/acceptor interactions, and the stabilization energies from the two 5d(Pt)→3p(Al) π-back donations were estimated to be 19.86 and 4.54 kcal mol^{-1} by using a second-order perturbation theory analysis. The nature of the Al−Pt bond in **1a** was further investigated in terms of the energy decomposition analysis,[17,18] thus showing that the Al-Pt bonding interaction is mainly electrostatic. The electrostatic interaction contributes 74.0 % of the total attractive interactions between the BbpAl and [Pt(PCy$_3$)$_2$] moieties. The breakdown of the Al-Pt orbital-interaction energy into σ and π components indicates that the Pt→Al π-back donation significantly contributes to the covalent bonding (σ: 55.8 %, π: 44.2 %).

In summary, the first Lewis-base-free terminal arylalumylene complexes were obtained by two different routes: the treatment of a dialumene–benzene adduct (**2**) with [Pt(PCy$_3$)$_2$] and the reduction of the 1,2-dibromodialumanes **3** in the presence of [Pt(PCy$_3$)$_2$]. The Al−Pt bonds in the arylalumylene complexes were shortened compared to the previously reported Al−Pt distances, thus indicating the stronger bonding interactions between the alumylene and platinum moieties. The DFT calculations suggested that the Al−Pt bonds in the arylalumylene complexes possess significantly high electrostatic character and that the contribution of the Pt→Al π-back donation to the covalent interactions is comparable to that of the Al→Pt σ-donation.

Experimental Section

All the manipulations were performed under a dry argon atmosphere by using the Schlenk techniques and glove boxes. Solvents were purified by the Ultimate Solvent System, Glass Contour Company[19] (*n*-hexane) or by the bulb-to-bulb distillation from a potassium mirror (C$_6$D$_6$ and mesitylene). [Pt(PCy$_3$)$_2$] was prepared according to a literature.[20]

Reaction of **2** with [Pt(PCy$_3$)$_2$]: A solution of **2** (13.4 mg, 0.0124 mmol) and [Pt(PCy$_3$)$_2$] (17.4 mg, 0.0230 mmol) in mesitylene (2 mL) was stirred at room temperature for 2.5 h and then at 50 °C for 2 h, thus affording a mixture containing **1a** and [Pt(PCy$_3$)$_2$] in a ratio of ca. 1.0:1.5. Small amounts of pure **1a** (1.0 mg, 0.00085 mmol, 3 %) were obtained by fractional crystallization from *n*-hexane at −35 °C.

Reduction of **3a** in the presence of [Pt(PCy$_3$)$_2$]: To a mesitylene (5 mL) solution of **3a** (13.2 mg, 0.013 mmol) and [Pt(PCy$_3$)$_2$] (19.0 mg, 0.025 mmol) was added KC$_8$ (3.8 mg, 0.028 mmol). The mixture was stirred at room temperature for 4.5 h. After removal of the solvents, the residue was extracted with *n*-hexane and filtered. The filtrate was concentrated and stored at −35 °C to give **1a** as dark red crystals (22.2 mg, 0.019 mmol, 72 %). m.p. 79 °C (dec.); ^{1}H NMR (600 MHz, C$_6$D$_6$): $\delta = 0.29$ (s, 36 H, Si(C*H*$_3$)$_3$), 1.22–1.43 (m, 24 H, *Cy*), 1.65–1.73 (m, 18 H, *Cy*), 1.90–1.92 (m, 12 H, *Cy*), 2.20–2.22 (m, 12 H, *Cy*), 2.75 (s, 2 H, C*H*(SiMe$_3$)$_2$), 6.78 (d, $^3J = 7.7$ Hz, 2 H, *m*-Ar*H*), 7.08 ppm (t, $^3J = 7.7$ Hz, 1 H, *p*-Ar*H*); ^{13}C{^{1}H} NMR (151 MHz, C$_6$D$_6$): $\delta = 1.28$ (s, Si*Me*$_3$), 27.1 (s, *C*^{4}(Cy)), 28.3 (virtual triplet, $J_{\mathrm{CP}} = 4.5$ Hz, *C*^{2,6}(Cy),), 31.2 (s, *C*H(SiMe$_3$)$_2$), 31.3 (s, $^4J_{\mathrm{CPt}} = 24.1$ Hz, *C*^{3,5}(Cy)), 41.3 (virtual triplet, $J_{\mathrm{CP}} = 9.1$ Hz, $^2J_{\mathrm{CPt}} = 36.2$ Hz, *C*^{1}(Cy)), 123.9 (s, $^4J_{\mathrm{CPt}} = 22.7$ Hz, *m*-*C*(Ar)), 129.22 (s, *p*-*C*(Ar)), 149.4 (s, *o*-*C*(Ar)), 160.0 ppm (t, $^3J_{\mathrm{CP}} = 25.7$ Hz, *ipso*-*C*(Ar)); ^{31}P NMR (120 MHz, C$_6$D$_6$): $\delta = 69.9$ ppm (s, $^1J_{\mathrm{PPt}} = 4015$ Hz); UV/vis (hexane): $\lambda = 447$ (ε 1600), 488 (ε 1800) nm; UV/Vis (THF): $\lambda = 446$ (ε 1400), 489 (ε 1500) nm; HRMS (DART-TOF, positive mode) m/z calcd. for $[C_{56}H_{107}AlP_2Si_4{}^{195}Pt]^+$: 1175.6388; found: 1175.6412.

1b: As described for the reduction of **3a**, a mesitylene (5 mL) solution of **3b** (21.5 mg, 0.0193 mmol) and $[Pt(PCy_3)_2]$ (29.1 mg, 0.0386 mmol) was treated with KC_8 (5.3 mg, 0.039 mmol). After workup and recrystallization, **1b** was obtained as dark red crystals (10.0 mg. 0.0082 mmol, 21 %). m.p. 110 °C (dec.); ^{1}H NMR (600 MHz, C_6D_6): $\delta = 0.32$ (s, 36 H, Si(C*H*$_3$)$_3$), 1.20–1.44 (m, 24 H, *Cy*), 1.35 (s, 9 H, C(C*H*$_3$)$_3$), 1.68–1.72 (m, 18 H, *Cy*), 1.90–1.92 (m, 12 H, *Cy*), 2.21–2.23 (m, 12 H, *Cy*), 2.72 (s, 2 H, C*H*(SiMe$_3$)$_2$), 6.81 ppm (s, 2 H, *m*-Ar*H*); $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): $\delta = 1.30$ (s, Si*Me*$_3$), 27.1 (s, C^4(Cy)), 28.3 (virtual triplet, $J_{CP} = 4.6$ Hz, $C^{2,6}$(Cy)), 31.0 (s, *C*H-(SiMe$_3$)$_2$), 31.2 (s, $C^{3,5}$(Cy)), 31.4 (s, C*Me*$_3$), 34.5 (s, *C*Me$_3$), 41.4 (virtual triplet, $J_{CP} = 8.3$ Hz, C^1(Cy)), 121.3 (s, $^4J_{CPt} = 22.7$ Hz, *m*-*C*(Ar)), 149.0 (s, *p*-*C*(Ar)), 151.1 (s, *o*-*C*(Ar)), 157.0 ppm (t, $^3J_{CP} = 27.2$ Hz, *ipso*-*C*(Ar)); ^{31}P NMR (243 MHz, C_6D_6): $\delta = 69.8$ ppm (s, $^1J_{PPt} = 4033$ Hz); UV/vis (hexane): $\lambda = 447$ (ε 1700), 483 (ε 1900) nm; UV/Vis (THF): $\lambda = 447$ (ε 1500), 483 (ε 1600) nm; HRMS (DART-TOF, positive mode) m/z calcd. for $[C_{60}H_{115}AlP_2Si_4{}^{195}Pt]^+$: 1231.7021; found: 1231.7026.

Single crystals of **1a** and **1b**·hexane were obtained by cooling their saturated solutions in *n*-hexane to −35 °C. The crystal data of **1a** was collected on a Rigaku Saturn 70 CCD diffractometer with a VariMax Mo Optic System using a $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å), while that of **1b**·hexane was collected at the BL38B1 beamline of the SPring-8 using an ADSC Quantum 315 CCD detector and Si(111)-monochromated X-ray radiation ($\lambda = 0.85000$ Å). The structures were solved with the Shelx program package.[21] Crystal data for **1a**: monoclinic, space group $P2_1/c$, −173 °C, $a = 13.1525(3)$, $b = 19.5941(4)$, $c = 24.5674(5)$ Å, $\beta = 96.2678(15)$, $V = 6293.5(2)$ Å^3, $Z = 4$, $\mu = 2.402$ mm^{-1} ($\lambda = 0.71070$ Å), $2.08° < \theta < 25.50°$, $R_{int} = 0.0845$, completeness to θ_{max} 99.9 %, 760 parameters refined, R_1 ($I > 2\sigma(I)$) = 0.0456, wR_2 (all data) = 0.1110, GOF = 1.018, largest diff. peak and hole 1.917 and −1.714 e Å^{-3}. Crystal data for **1b**·hexane: triclinic, space group *P*-1, −170 °C, $a = 12.5246(1)$, $b = 13.9973(2)$, $c = 21.9295(3)$ Å, $\alpha = 89.9651(6)$, $\beta = 83.0595(5)$, $\gamma = 73.3812(6)°$, $V = 3654.56(8)$ Å^3, $Z = 2$, $\mu = 0.243$ mm^{-1} ($\lambda = 0.85000$ Å), $2.05° < \theta < 31.00°$, $R_{int} = 0.0507$, completeness to θ_{max} 99.0 %, 683 parameters refined, R_1 ($I > 2\sigma(I)$) = 0.0423, wR_2 (all data) = 0.1172, GOF = 1.086, largest diff. peak and hole 1.253 and −2.204 e Å^{-3}. CCDC-948098 (**1a**) and 948113 (**1b**·hexane) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: December 5, 2013
Revised: January 17, 2014

Keywords: aluminum · density functional calculations · metal–metal interactions · platinum · structure elucidation

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