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<th>Syntheses and structures of terminal arylalumylene complexes.</th>
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Transition metal complexes of subvalent main group element compounds attract considerable attention, because of not only their unique electronic structures but also their synthetic potentials in organometallic chemistry. Especially, complexes of group 13 metallylenes (E= B, Al, Ga, In, and Tl) are expected to show particular bonding interactions between the subvalent group 13 elements and transition metal fragments, since these metallylenes possess a lone pair and two vacant p orbitals and may act as σ-donor/π-acceptor ligands.[1] Recently, the chemistry of borylone complexes has been extensively developed,[2] while the examples of heavier group 13 metallylene complexes with the formula of [M(ER)mLn] (R: anionic monodentate ligands) have been limited for the gallium and indium homologues and are yet to be reported for aluminum.[3] Although Lewis base-coordinated terminal alumylene compounds attract considerable attention, because of not only their unique electronic structures but also their synthetic potentials in organometallic chemistry. Especially, complexes of group 13 metallylene derivatives are expected to show shortester bond lengths of these arylalumylene complexes are shorter than the previously reported shortest Al-Pt distance. DFT calculations suggested that the Al-Pt bond distances in the arylalumylene complexes are significantly high (Fig. 1) due to their high electrostatic character rather than covalent character.

Recently, we have communicated a reactivity of dialumene-benzene adduct 2 as a synthetic equivalent of diaryldialumene BbpAl=AlBbp.[8,9] During the research on the reactivities of 2, the reaction of 2 and [Pt(PCy3)2] was investigated with the expectation of trapping of the dialumene as a π-dialumene complex of platinum,[10] the formation of the π-dialumene complex of platinum (δ(Δ)=69.9 ppm). Fractional crystallization of the crude material from n-hexane at −35 °C yielded a small amount (3%) of arylalumylene complex 1a as air- and moisture-sensitive dark red crystals (Scheme 1). The formation of 1a implies that compound 2 has reactivities as an arylalumylene source in addition to the diaryldialumene synthon. After screening of the reaction conditions, finally, reduction of 1,2-dibromodialumene Ar(Br)Al–Al(Br)Ar was found to afford complex 1a and 1b, respectively, as sole products. After recrystallization from n-hexane at −35 °C, the arylalumylene complexes were obtained in moderate yields (1a: 72%, 1b: 21%). Complexes 1a and 1b are stable up to 79 and 110 °C in the solid state, respectively, though they slowly decompose in solution even at −35 °C to give complicated mixtures containing [Pt(PCy3)2] and PCy3.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

**Scheme 1.** Syntheses of arylalumylene complexes 1a and 1b.
In the $^{31}$P NMR spectra, complexes 1a and 1b exhibit singlet signals accompanied by $^{195}$Pt satellites at $\delta=69.9$ ppm ($J_{PPt}=4015$ Hz) and at $\delta=69.8$ ppm ($J_{PPt}=4033$ Hz), respectively, which are downfield shifted with respect to those of [Pt(PCy$_3$)$_2$] ($\delta=62.3$ ppm, $J_{PPt}=1660$ Hz) and the structurally related carbonyl complex ([Cy$_3$P]$_2$Pt(CO)) ($\delta=63.7$ ppm, $J_{PPt}=4101$ Hz).[12] Definite signals could not be observed in the $^{27}$Al and $^{195}$Pt NMR spectra of complexes 1a and 1b, probably because of the signal broadening caused by the high quadrupole moment of the $^{27}$Al nuclei.

Molecular structures of complexes 1a and 1b were determined by X-ray crystallographic analyses, showing that the aluminum atoms are definitely two-coordinated and are bound to the platinum atoms in terminal fashions with the C–Al–Pt angles of 179.2(2)° (1a) and 173.96(14)° (1b) (Figure 2). The platinum centers adopt distorted trigonal planar geometries. The Pt–Al1 bond of the aryllumylene complexes (1a: 2.2857(18) Å, 1b: 2.2829(13) Å) are slightly shortened compared with the shortest Pt–Al distance previously reported (2.327(2) Å),[6e] most likely due to the decreased covalent bonding (for 1a: Al1–Pt1 2.2829(13), C1–Al1 1.986(4), Pt1–P1 2.2567(10), 1b: Al1–Pt1 2.2857(18), C1–Al1 1.987(4), Pt1–P1 2.2567(10), 119.14(4), Al1–Pt1–P1 114.86(6), Al1–Pt1–P2 117.85(6), P1–Pt1–P2 127.20(6); for 1b) Al1–Pt1 2.2829(13), C1–Al1 1.986(4), P1–Pt1 2.307(9), P1–Pt1 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/6-311G(2df)[Al,P]-6-31G(d)[Si,C,H] level 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 well reproduces that found in the single crystals. The natural bond orbital (NBO) analysis[13] on the optimized geometry of 1a showed that the Al–Pt bond has a small Wiberg bond index (0.59), indicating that the Al–Pt bond is highly ionic and that the contribution of the covalent interaction is less important.[6c,16] The calculated NBO corresponding to the Al–Pt bond is predominantly formed from the overlap of the 3s(Al) and 6s(Pt) orbitals (σ(Al–Pt)=0.87(3s3p$^{1/2}$)Al+0.50(6s6p$^{1/2}$)Pt). Meanwhile, the Pt–Al π-back donation interactions were identified as donor/acceptor interactions, and the stabilization energies by the two 5d(Pt)→3p(Al) π-back donations were estimated to be 19.86 and 4.54 kcal mol$^{-1}$ by the 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] showing that the Al–Pt bonding interaction is mainly electrostatic. The electrostatic interaction contributes 74.0% of the total attractive interactions between the BbPtAl and [Pt(PCy$_3$)$_2$] moieties. The breakdown of the Al–Pt orbital interaction energy into σ- and π-components indicates that the Al π$\rightarrow$Pt 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 the dialumene–benzene adduct with [Pt(PCy$_3$)$_2$] and the reduction of the 1,2-dibromodialumenes in the presence of [Pt(PCy$_3$)$_2$]. The Al–Pt bonds in the aryllumylene complexes were shortened compared to the previously reported Al–Pt distances, indicating the stronger bonding interactions between the alulylene and platinum moieties. The DFT calculations suggested that the Al–Pt bonds in the aryllumylene 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 π$\rightarrow$Pt 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 (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, affording a mixture containing 1a and [Pt(PCy$_3$)$_2$] in a ratio of ca. 1:0.15. Small amount of pure 1a (1.0 mg, 0.00085 mmol, 3%) was 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$_3$ (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%). 

$\text{[C}_6\text{H}_{103}\text{AlP}_2\text{Si}_4\text{Pt}]^+$: $m/z$ ca. 1175.64, $\text{HRMS (DART-TOF, positive mode)}$ $m/z$ 1175.6388; found: 1175.6412. 

$\text{[C}_6\text{H}_{115}\text{AlP}_2\text{Si}_4\text{Pt}]^+$: $m/z$ 1231.7021; found: 1231.7026. 

To 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$_3$ (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.); $\text{[C}_6\text{H}_{103}\text{AlP}_2\text{Si}_4\text{Pt}]^+$: $m/z$ ca. 1175.64, $\text{HRMS (DART-TOF, positive mode)}$ $m/z$ 1175.6388; found: 1175.6412. 

$\text{[C}_6\text{H}_{115}\text{AlP}_2\text{Si}_4\text{Pt}]^+$: $m/z$ 1231.7026; found: 1231.7026.

Single crystals of 1a and 1bhexane 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 Max Optic System using a Mo Kα 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 (λ=0.8500 Å). The structures were solved with the Sheldx program package.\textsuperscript{[21]} Crystal data for 1a: monoclinic, space group P2₁/c, -173 °C, a=13.1525(4), b=19.5941(4), c=24.5674(5) Å, β=96.2678(5), V=6293.5(2) Å³, Z=4, μ=2.402 mm⁻¹ (λ=0.7107 Å). 2.08°<θ<25.50°, Rwp=0.0845, Completeness to θmax 99.99%, 760 parameters refined, R1 (I/2σ(I))=0.0456, wR2 (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 P1, -170 °C, a=12.5246(1), b=13.9737(2), c=21.9205(3) Å, α=89.6516(6), β=85.0395(5), γ=73.3812(6)°, V=3654.568(3) Å³, Z=2, μ=0.243 mm⁻¹ (λ=0.8500 Å), 2.05°<θ<31.00°, Rwp=0.0507, Completeness to θmax 99.0%, 683 parameters refined, R1 (I/2σ(I))=0.0423, wR2 (all data)=0.1127, GOF=1.086, largest diff. peak and hole 1.253 and -2.204 e Å⁻³. CCDC-946098 (1a) and 948113 (1b•hexane) contain the supplementary crystallographic data for this paper. These date can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Syntheses and Structures of Terminal Arylalumylene Complexes

A terminal arylalumylene complex of platinum was obtained by the reaction of a di alumene–benzene adduct and [Pt(PCy₃)₂]. Reduction of 1,2-dibromodialumanes in the presence of [Pt(PCy₃)₂] also afforded the terminal arylalumylene complexes. DFT calculations suggested that the Al–Pt bonds in the arylalumylene complexes have significantly high electrostatic character rather than covalent character.