Syntheses and Structures of Terminal Arylalumylene Complexes

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

Abstract: Terminal arylalumylene complexes of platinum [Ar–Al–Pt(PCy3)2] (Ar=Bbp or Tbb, Bbp=2,6-[CH(SiMe3)2]2C6H3, Tbb=2,6-[CH(SiMe3)2]2-4-(t-Bu)C6H2) have been synthesized by the reaction of a dialumene–benzene adduct with [Pt(PCy3)2] or by the reduction of 1,2-dibromodialumanes Ar(Br)Al–Al(Br)Ar in the presence of [Pt(PCy3)2]. X-Ray crystallographic analysis revealed that the Al–Pt bond lengths of these arylalumylene complexes are shorter than the previously reported shortest Al–Pt distance. DFT calculations suggested that the Al–Pt bonds in the arylalumylene complexes have significantly high electrostatic character rather than covalent character.

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 metalloynes (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, since these metalloynes possess a lone pair and two vacant p orbitals and may act as aluminum.[3] Although Lewis base-coordinated terminal alumylene organometallic chemistry. Especially, complexes of group 13 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 metalloynes (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, since these metalloynes possess a lone pair and two vacant p orbitals and may act as aluminum.[3] Although Lewis base-coordinated terminal alumylene organometallic chemistry.

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 reaction progress was monitored by 31P NMR spectroscopy, showing the formation of a mixture containing a new platinum complex (δ(C)=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 synthons. After screening of the reaction conditions, finally, reduction of 1,2-dibromodialumanes 3a,[11] and 3b with KCs in the presence of [Pt(PCy3)2] was found to afford 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.

FIGURE 1. Transition metal complexes of Lewis base-coordinated (I-III) and Lewis base-free (IV) arylalumylene. Ar = 2,6-(i-Pr)2C6H4.

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, $J_{PPt} = 1610$ Hz) and the structurally related carbonyl complex [(Cy$_2$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.

Figure 2. Molecular structures of (a) 1a and (b) 1b. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted, and Bbp, Tbb, and Cy group are shown in wireframe format for clarity. Three Cy and two Me groups in complex 1a were disordered over two positions (see the Supporting Information for detail). Selected bond lengths [Å] and angles [°]: (for 1a) Al1–Pt1 2.2857(18), Al1–Pt1–C1 127.92(2), C1–Al1–Pt1 119.86(6), Al1–Pt1–P1 117.85(6), P1–Pt1–P2 127.29(6); (for 1b) Al1–Pt1 2.2829(13), Al1–C1 1.986(4), P1–Pt1 2.307(9), P1–Pt1–C1 2.2673(10), C1–Al1–P1 173.96(14), Al1–P1–C1 119.14(4), Al1–P1–P1 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 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 covalent. 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 BbpAl and [Pt(PCy$_3$)$_2$] moieties. The breakdown of the Al–Pt orbital interaction energy into σ- and π-components indicates that the Al–Pt interaction 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 arylalumylene complexes were shortened compared to the previously reported Al–Pt distances, indicating the stronger bonding interactions between the aluminylene 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 (CD$_3$D and mesitylene). [Pt(PCy$_3$)$_2$] was prepared according to a literature.[20]

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Crystal data for 1b: monoclinic, space group P21/c, -173 °C, a=13.152(5) Å, b=19.5941(4) Å, 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), 2.080°<θ<25.50°, Rint=0.0845, Completeness to 98.9%, 760 parameters refined, R (I=2σ(F))=0.0456, wR2 (all data)=0.1110, GOE=1.018, largest diff. peak and hole 1.253 e Å⁻³. CCDC-948098 (1a) and 948113 (1b)hexane can 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.

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A terminal arylalumylene complex of platinum was obtained by the reaction of a dialumene–benzene adduct and \([\text{Pt(PCy}_3\text{)}_2]\). Reduction of 1,2-dibromodialumanes in the presence of \([\text{Pt(PCy}_3\text{)}_2]\) 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.