

Rh (I) complexes with anionic aluminum ligand: Theoretical study of geometry and bonding nature.

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[Introduction] Newly synthesized Rh(I) complexes **1a**, **1b** and **1c** (Figure 1) with anionic aluminium ligand possess interesting geometry and bonding interaction.¹ In **1a** and **1b**, for instance, norbornadiene coordinates at an unusual position above the Rh-Al molecular plane which deviates very much from the normal square planar geometry of Rh(I) complexes. The characteristic features of aluminum ligand are the presence of a lone pair and a vacant π -orbitals at the Al center which in turn leads to its bifunctional nature of nucleophilicity and electrophilicity. The NBO and molecular orbital analyses clearly show that Al is positively charged but has a lone pair orbital at high energy, indicating this is strongly σ -donating. This suggests also that the Rh-Al bond is covalent rather than usual coordinate bond.

We investigated the geometry and bonding nature of the anionic aluminium ligand with Rh centre using the DFT and CAS-CI methods.

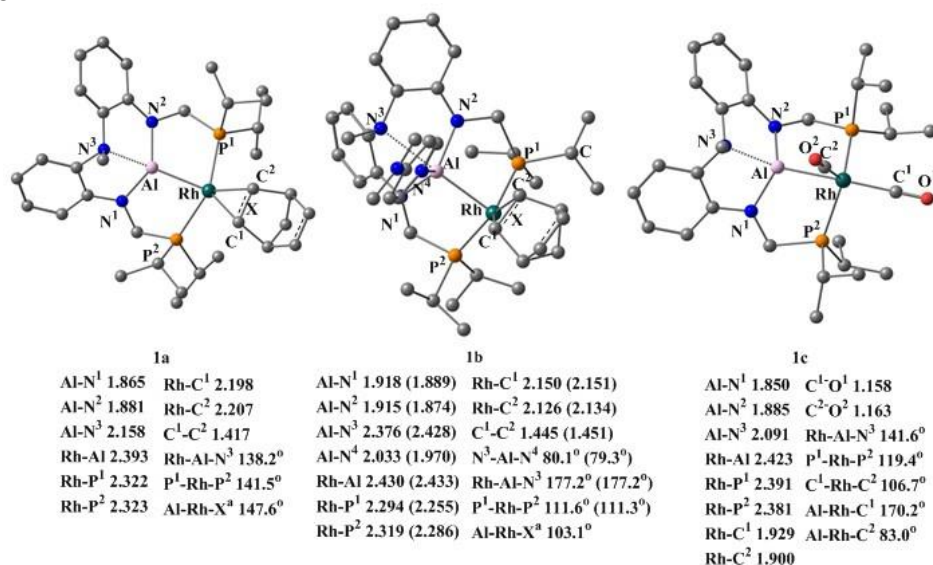


Figure 1. The optimized geometry of rhodium complexes **1a**, **1b** and **1c** with selected bond lengths (Å) and bond angles (°); the experimental values are given inside the parenthesis; H atoms have been omitted for clarity..

[Computations] Geometry optimization was carried out by the DFT method with the B3LYP functional. The LANL2DZ basis set was used for Rh atom. In evaluation of energy, the functional wB97XD was employed, where the 6-311G(d) basis sets were used for all nonmetal elements, 6-311+G(2d) basis set was used for Al atom, and the SDD (Stuttgart-Dresden-Bonn) basis set was

employed for the Rh atom. The CAS-CI calculation was performed with localized MOs (LMO) after CAS-SCF calculation with a (2e, 2o) active space. This active space was taken here to make valence bond type analysis.

[Results and Discussion] As shown in Figure 1, **1a** and **1b** have a similar trigonal pyramidal structure to each other and **1c** has a five-coordinated trigonal bipyramidal structure. The analysis of the frontier orbitals of a model anionic aluminum ligand suggests this Al ligand (abbreviated as PAIP) is understood with a canonical form of diamido–Al⁺. The Kohn-Sham orbitals of the Rh-complexes show significantly large bonding overlap between the Rh d and the Al lone pair orbitals [Figure 2(a-c)]. Because the d orbital (-8.5 eV) of a neutral [Rh(nbd)] is at considerably lower energy than the Al valence orbital (-4.7 eV) of PAIP, the Rh-Al bond is polarized as Rh^{δ-} and Al^{δ+}. Because the d orbital (-8.5 eV) of a neutral [Rh(nbd)] is at considerably lower energy than the Al valence orbital (-4.7 eV) of PAIP, the Rh-Al bond is polarized as Rh^{δ-} and Al^{δ+}. These results suggest that a large covalent bonding interaction is formed between the Rh and Al atoms in these complexes. The CAS-CI analysis indicates that the covalency is about 60%, which clearly shows that the Rh-Al bond is considerably different from the usual coordinate bond.

In **1a** and **1b**, the position of the C=C double bond of norbornadiene is above the molecular plane. This position can be understood as a result of the geometrical constraint by the Al-N(Ph)-CH₂-P chain structure which allows the PiPr₂ moieties taking positions below the molecular plane with the PRhP angle of 141.5° and 111.6° (Figure 1). The two phosphines groups destabilizes d orbital which expands to the opposite direction from the phosphines. Because of the strong π-back donation, the C=C double bond takes the position trans to these two phosphines, which in turn lead to the strong overlap with the d orbital. The presence of the empty Al 3p orbitals allow the Rh-complexes to coordinates with DMAP very easily. This coordination increases the constraint on the Al-N(Ph)-CH₂-P chain to decrease the P-Rh-P angle. This in turn leads a further change in position of PiPr moieties more downward from the molecular plane and the C=C double bond moves more upward. Therefore, in **1b** the C=C double bond occupies almost perpendicular position to the Rh-Al bond. In **1c**, smaller steric repulsion by CO molecule causes the coordination of two CO molecules with the Rh centre. The Rh-C¹ at the position trans to the PAIP is moderately longer than the Rh-C² by 0.03 Å, suggesting that the trans-influence of PAIP is strong. In the presence of the CH₃ ligand, the Rh-C¹ distance is moderately shorter than in **1c**. This result indicates that the trans-influence of PAIP is as strong as that of CH₃. From these features, it is concluded that this new PAIP ligand has unique natures and its Rh(I) complex **1a** is reactive for the heterolytic σ-bond activation because the empty 3p of Al can interact a nucleophilic moiety of reactant and the doubly occupied 4d of Rh can interact with an electrophilic moiety.

Reference

- 1) T. Saito, N. Kuriakose, S. Sakaki, Y. Nakao, *to be published*.

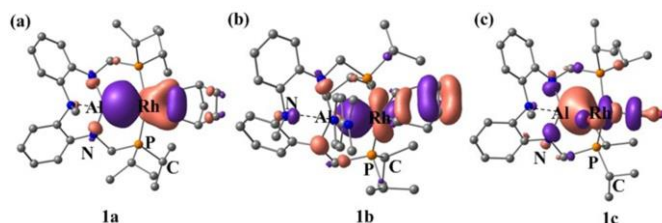


Figure 2. Kohn-Sham MOs of **1a**, **1b**, and **1c**