

Cationic, 'semi-cationic' and neutral bismuth pentamethylbenzene π complexes

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Extending former investigations^[1] we recently synthesized the compounds ((CH₃)₅C₆HBiCl₃) (**1**), [((CH₃)₅C₆H)(1,2,3,5-(CH₃)₄C₆H₂)Bi₂Cl₅][AlCl₄]·1,2,4,5-(CH₃)₄C₆H₂ (**2**) and [(CH₃)₅C₆HBiCl₂][AlCl₄] (**3**), establishing a unique series of neutral, "semi-cationic" and cationic organometallic complexes exhibiting the bismuth pentamethylbenzene π -interaction.

1 was prepared by dissolving BiCl₃ in a solution of (CH₃)₅C₆H in 1,2,3,5-(CH₃)₄C₆H₂ and subsequent crystallization (110 °C, 20 min). **2** and **3** were prepared by reaction of stoichiometric amounts of BiCl₃ and AlCl₃ in a solution of (CH₃)₅C₆H/1,2,4,5-(CH₃)₄C₆H₂ in 1,2,3,5-(CH₃)₄C₆H₂ (110 °C, 25 min) and a solution of (CH₃)₅C₆H in toluene (80 °C, 10 min), respectively.

The characterisation of **1-3** by single crystal X-ray crystallography shows that the coordination geometry at the bismuth atoms is very similar in all cases and best described as distorted octahedral with five chlorine ligands and one arene ligand. The similarity allows a detailed experimental study of the influence of metal acidity on the strength of bismuth arene π -interaction.

As shown in Table 1 the bismuth ring-centroid distance and the valence sum of the Bi-Cl bonds^[2] decrease from **1** to **3**. This indicates the increasing strength of the bismuth-arene interaction with rising charge of the bismuth atom quantitatively.

Table 1: Selected aspects of bismuth pentamethylbenzene π -interaction

	COR ^a [Å]	$\sum s(\text{Bi-Cl})^b$	s(Bi-Arene) ^c
1	2,898(3)	2,708	0,272
2	2,811(6)	2,508	0,492
3	2,666(5)	2,318	0,682

^a COR: bismuth-arene centroid distance; ^b $\sum s(\text{Bi-Cl})$: bond valence sum Bi-Cl calculated from $s = \exp[(r-r_0)/B]$, $r_0 = 2,432 \text{ \AA}^{[3]}$, $B = 0,37$; ^c s(Bi-Arene): $3 - \sum s(\text{Bi-Cl})$

Literatur:

[1] W. Frank, J. Weber, E. Fuchs, *Angew. Chem. Int. Ed.* **1985**, *24*, 893. [2] I.D. Brown, *Chem. Rev.* **2009**, *109*, 6858. [3] J. Sanderson, C.A. Bayse, *Tetrahedron* **2008**, *64*, 7685. [4] H. Schmidbaur, A. Schier, *Organometallics* **2008**, *27*, 2361.