Synthesis and Coordination Behavior of Hexakispyrazolylethane with High Stability

([1]*Graduate School of Engineering, The University of Tokyo*) ○Yuta Takemasa,[1] Kyoko Nozaki[1]

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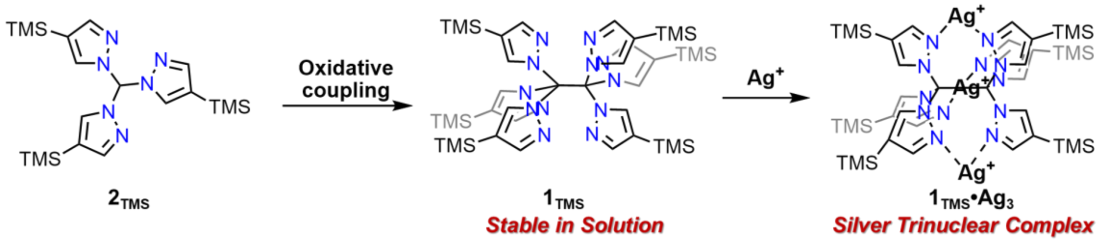
Hexaphenylethane (**HPE**) is one of the most attractive compounds with riddles many researchers have tried to solve for a long time.[1] It is known that there is an equilibrium between hexaphenylethane (α,α-dimer) and trityl radical, which dimerizes to form another isomer, thermally stable quinoidal dimer (α,*p*-dimer). To isolate the labile hexaphenylethane structure, there have been reported two strategies. As one approach, the introduction of sterically bulky substituents was successfully applied to stabilization of the α,α-dimer structure by London dispersion interactions.[2,3] Another strategy is bridging: Phenyl groups of each triarylmethyl unit were covalently connected. We envisaged a novel approach to isolate non-bridged hexaarylethane by introducing heterocycles. Herein, we report the synthesis and isolation of hexakis(4-trimethylsilylpyrazol-1-yl)ethane ($\mathbf{1}_{\mathbf{TMS}}$) which shows much higher stability compared with other non-bridged hexaarylethanes.

$\mathbf{1}_{\mathbf{TMS}}$ was synthesized by the oxidative dimerization of tris(4-trimethylsilylpyrazol-1-yl)methane ($\mathbf{2}_{\mathbf{TMS}}$). Single-crystal X-ray structural analysis of 1_{TMS} showed that the ethane C–C bond (1.623(4) Å) is shorter than that in hexaphenylethane (1.67(3) Å).[3] In solution, 1_{TMS} existed as a single species, contrastive that conventional hexaphenylethanes can keep the central C–C bond only by the aid of additional bridges between the two triarylmethyl units. Theoretical calculations indicated that the stabilization of the central carbon radical is much less significant in case of pyrazolyl compared to phenyl, due to lack of delocalization. Furthermore, introduction of pyrazole groups allowed additional bridging between the two triarylmethyl moieties through metal coordination to the adjacent N atoms: 1_{TMS} exhibited unique coordination to three Ag atoms affording a hexaarylethane analog bearing three N–Ag–N bridges ($\mathbf{1}_{\mathbf{TMS}}\bullet\mathbf{Ag}_{\mathbf{3}}$). In the crystal structure of $\mathbf{1}_{\mathbf{TMS}}\bullet\mathbf{Ag}_{\mathbf{3}}$, the ethane C–C bond (1.73(2) Å) was elongated from 1_{TMS} by coordination.



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