反芳香族炭化水素が配位したニッケル(0)錯体の合成と構造

（京大院工[1]・京大 iCeMS[2]・阪大院工[3]）○今西 勇文[1]・薄葉 純一[2]・安井 孝介[2]・植竹 裕太[3]・深澤 愛子[2]

Synthesis and Structure of Nickel(0) Complex Coordinated with Antiaromatic Hydrocarbon

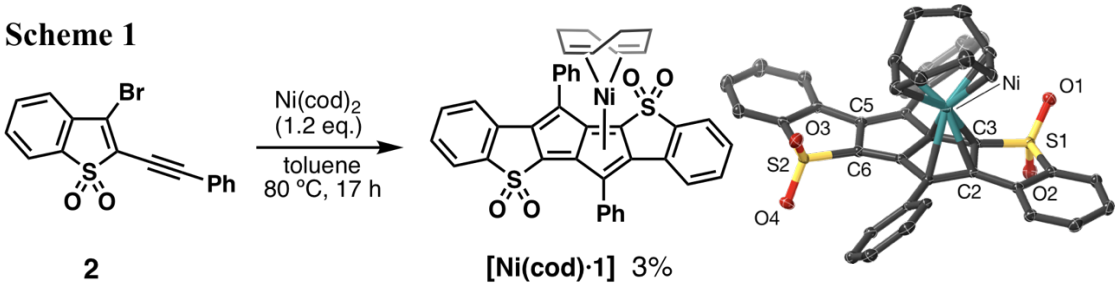
([1]*Graduate School of Engineering, Kyoto University,* [2]*Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University,* [3]*Graduate School of Engineering, Osaka University*)
○Takefumi Imanishi,[1] Junichi Usuba,[2] Kosuke Yasui,[2] Yuta Uetake,[3] Aiko Fukazawa[2]

Antiaromatic hydrocarbons exhibit characteristic electronic structures and structural properties, such as a significantly narrower HOMO-LUMO gap and a larger bond alternation than aromatic hydrocarbons. For this reason, the electronic structure and physical properties of transition-metal complexes bearing an antiaromatic hydrocarbon as a π-coordinating ligand are of interest. However, the transition-metal complexes coordinated by a charge-neutral antiaromatic hydrocarbon have been unexplored. In this work, through an attempt to synthesize benzothiophene-*S,S*-dioxide-fused pentalene **1** by the Ni(cod)$_2$-mediated cyclodimerization of arylacetylene **2**, we coincidentally obtained the Ni complex [Ni(cod)·**1**], albeit in low yield (Scheme 1). The thus obtained [Ni(cod)·**1**] exhibited sufficient stability to be handled under air and moisture without precaution. X-ray crystallography, X-ray absorption spectroscopy, and theoretical calculations revealed that the pentalene coordinates to the nickel center with an η^4-fashion, and the formal oxidation state of nickel is close to zero. In this presentation, the structural characteristics and dynamic behavior of the complex will also be discussed.

Keywords: nickel, antiaromaticity, crystal structure, dynamic behavior, X-ray absorption spectroscopy

反芳香族炭化水素は，芳香族炭化水素と比べて著しく狭い HOMO-LUMO ギャップや大きな結合交替など特徴的な電子構造や構造特性をもつため，遷移金属に π 配位した際の電子状態や物性には興味がもたれる．しかし，電荷中性の反芳香族炭化水素を配位子にもつ遷移金属錯体は僅少である．今回我々は，ベンゾチオフェン-*S,S*-ジオキシドを縮環部位にもつ 8π 電子系ペンタレン **1** の合成を目的に，Ni(cod)$_2$ を用いたアリールアセチレン **2** の環化二量化を行ったところ，ニッケル錯体 [Ni(cod)·**1**] が低収率ながら得られた (Scheme 1)．得られた [Ni(cod)·**1**] は空気中で扱えるほど安定であった．また，X 線結晶構造解析，X 線吸収分光および量子化学計算により，ペンタレンはニッケルに η^4 で配位し，ニッケルの形式酸化数は 0 価に近いことがわかった．本発表では，錯体の構造的特徴や動的挙動についても併せて報告する．

Scheme 1



2 **[Ni(cod)·1]** 3%