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研究課題名(和文) 反芳香族B,N-カルベン 配位子の開発と常磁性/アニオン性金錯体の合成と物性解明

研究課題名(英文) Isolatable paramagnetic and anionic transition metal complexes stabilized by main group heterocyclic carbenes for redox and photoredox active functional materials

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研究成果の概要(和文)：本研究では、新規に開発する反芳香族ヘテロ環状カルベン 配位子BNCを利用することで、特異な電子状態を有する遷移金属錯体の安定化と構造解析、さらには酸化還元挙動、構造-物性相関を解明することを目的としました。遷移金属錯体の酸化還元特性に及ぼす反芳香族 配位子の影響を調べるために、1)単離可能な常磁性およびアニオン性有機金属錯体の設計原理と合理的合成ルートの確立と、2)選択的化学変換のための化学的特性の解明を目指しました。反芳香族性カルベン 配位子BNCの有する高い 酸性と強い ドナー性の両立は、金属中心の特異な酸化状態やラジカル挙動を安定化に寄与し、電子状態をチューニングするのに理想的である。

研究成果の学術的意義や社会的意義

The successful isolation of thermally stable, previously inaccessible complexes means we have developed an effective design strategy to access molecules with unusual photophysical properties, providing a powerful tool for further studies towards understanding of photoredox behaviors of metal complexes.

研究成果の概要(英文)：This project established synthetic route to a highly π -accepting anti-aromatic 4-*B*, *N*-heterocyclic Carbene (BNC), which allowed the isolation of an anionic gold(I) complex. This demonstrates that an interplay of electronegative elements such as boron and the numbers of π electrons in a planar conjugated ligand is crucial in tuning electronic properties of metal complexes. By using the same strategy, a CCC-type pincer based on a dipyrrolic-annulated *N*-heterocyclic carbene was developed, which allowed complexation to a Ir(I) precursor to form a homoleptic octahedral Ir(III) bispincer metallacycle. This dark purple complex underwent a step-wise 4e oxidation to yield a chiral Ir(III) complex with a triplet ground state. Together these findings present an effective design strategy for tuning electronic properties and/or accessing higher spin states of transition metal complexes.

研究分野：無機・錯体化学関連

キーワード：photoredox redox active ligand

様式 C - 19、F - 19 - 1、Z - 19 (共通)

1. 研究開始当初の背景

In the accelerating development of TM photocatalysts in organic synthesis, aromatic heterocyclic structures have been widely applied in the design of ligands as a strategy for stabilization. However, the effect of antiaromatic ligands on the photoredox behavior of TM complexes remains poorly understood due to a lack of synthetic procedures to readily access isolable radical organometallic complexes. The highly electron-deficient nature of antiaromatic ligand lowers the energy of the lowest unoccupied molecular orbitals (LUMO), resulting in super acidity (highly π -accepting). The inclusion of electron-positive elements such as boron rises the energy of the highest occupied molecular orbital (HOMO), leading to super σ -basicity (highly σ -donating). These design features are proposed in this project to stabilize highly electron-rich metal centers and modulate their chemical and photophysical properties in reactions, and thus provide access to distinct bond-activation modes to those traditionally used in the field of catalysis and enable reaction development through entirely new mechanistic paradigms.

2. 研究の目的

To examine the effect of electron-positive ligand on the photoredox and redox properties of transition metal complexes, this project aims to 1) establish a general design and synthetic route for isolable radical organometallic complexes bearing antiaromatic ligand and 2) study their chemical and photophysical properties for selective chemical transformations.

3. 研究の方法

This can be achieved by targeting a highly π -withdrawing 4-antiaromatic B, N-containing heterocyclic Carbene (BNC) that can delocalize the electron density at electron-rich gold center through its conjugated π -orbitals (Fig. 2). Furthermore, at oxidation state of 0 and I-, the Au 6s electrons shield the 5d electrons effectively, raising their energy for backdonation to the π -acidic BNC ligand. This enables an effective π -conjugation between metal and ligand, electronically stabilizes electron-rich radical and anionic gold complexes (T1, T2) for investigation of their chemical and photophysical properties.

4. 研究成果

The interplay of aromaticity and antiaromaticity of conjugated systems is a crucial design strategy for tuning light-initiated electron-transfer properties in designing functional molecules. For transition metal (TM) photocatalysts, while heterocyclic aromatic ligands are widely used for modulation of their (photo)redox behaviors, the effect of antiaromatic ligands remains poorly understood due to a lack of synthetic methodologies. This project proposed a design and synthesis to isolate radical and anionic gold complexes bearing a 4- π -withdrawing B, N-heterocyclic Carbene (BNC). The expected antiaromaticity and the inclusion of boron atoms in BNC results in its super π -accepting and σ -donating abilities which are ideal to stabilize and tune unusual oxidation states and radical behaviors of the metal.

BNC system (4): The synthesis of several derivatives of BNC Au(I) complexes were established. The anionic (BNC^{Cl}) at Au(I) can be converted to a neutral 4-BNC ligand by halide abstraction. However, without any coordination from halides or triflate at the heterocyclic ligand, the 4-BNC-gold(I) complex is thermally unstable. A 2e⁻ reduction of the (BNC^{Cl})AuL complex by lithium metal allowed isolation and full structural characterization of a bright orange lithium aurate complex Li[(BNC)AuL]. Computational analysis indicated that, despite of the 4 electron counting, the

neutral BNC ligand on Au(I) is mostly non-aromatic in character, owing to the localized electrons between boron and nitrogen atoms. After reduction, the gold center remained +I in oxidation state, whereas the BNC moiety became a 6 π aromatic system. In particular, the occupied p orbital at the ligating carbon center was shown to interact strongly with the Au(I) 6p orbital with an interaction energy between 15.5 to 42.5 kcal/mol (depending on the lithium coordination). This multiple Au-C bond character was also reflected from the shortened Au-C distance after reaction. It has been well-known that it is difficult to invoke multiple bonding at Au(I). This result showed that the gold(I) can form multiple bonds with ligand through its empty 6p orbital ligands instead of occupied 5d orbitals.

BNP system (6): As a direct contrast to the π -withdrawing NBC ligand, the synthesis (BNP)Au(L) complexes have been achieved. The ligand precursor, a cyclic (amino)(boryl)(chloro)phosphine, was synthesized by an overall cycloaddition reaction between azadiboriridine and (chloro)iminophosphine. A 2e⁻ reduction by lithium or lithium naphthalide lead to clean generation of a lithium phosphide, which then reacts with (Cl)AuL to form the targeted (BNP)AuL complexes. The phosphorus adopts a trigonal pyramidal geometry. However, bonding parameters from its solid-state structure showed a slight increase in the B-P double bond character after complexation. The redox behaviour of this new class of complexes is being investigated. Complexation on 5d metals will be also attempted for a metal-phosphenium type bonding which has stronger π interactions between metal and ligand.

CCC-pincer (26): Metallation to Ir(I) via facile deprotonation/C-H activation led to a homoleptic octahedral Ir(III) bispincer metallocycle with an overall anionic charge. While most of Ir(III) complexes are lightly coloured (yellow to pale orange), this Ir(III) is dark purple in colour, suggesting unusual electronic properties. It was easily oxidized: a 2e⁻ oxidation led to a clean generation of a racemic mixture of chiral spiro complex. This is likely formed from an oxidative coupling between two adjacent aryl moieties at the iridium center, forming a figure of 8 cationic structure. This new purple cationic complex, taking on two nitrile as ligand, adopts a pseudo-octahedral geometry around the Ir(III) center, which can be further oxidized. A 2e⁻ oxidation allowed formation of a tricationic iridium complex, which was isolated as a black solid and structurally characterized. While the monocationic and tricationic iridium complexes are isostructural, their solid-state structures showed distinct bonding parameters. A comparison of the NBO analysis on both complexes revealed that the oxidation mostly occurred at the ligand, and the metal oxidation state remained around +III after oxidation. In addition, computational analysis suggested that the tricationic Ir(III) complex had a triplet ground state, with small singlet-triplet energy gap of ca. 1.3 kcal/mol.² This was confirmed by experimental VT EPR measurements as well as and SQUID measurements. This discovery confirms our hypothesis that by designing cyclic ligands that allow π -conjugation with the metal center and ligands, we can modulate the electronic properties or state through redox chemistry.

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〔図書〕 計0件

〔産業財産権〕

〔その他〕

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6. 研究組織

	氏名 (ローマ字氏名) (研究者番号)	所属研究機関・部局・職 (機関番号)	備考
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7. 科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

8. 本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関
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