論文審査の要旨

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論文題目

Development of multi-centered reactivity among metal and
main-group Lewis acids and bases
（金属および典型元素 Lewis ペアを用いた多活性中心反応の究明）

論文審査担当者

委員長（Committee chair）	助　教	SHANG RONG
	教　授	灰野　岳晴
	教　授	水田　勉
	特任教授	山本　陽介（学術・社会連携室）
	教　授	吉田　拡人
	准教授	中本　真晃

〔論文審査の要旨(Summary of Dissertation Review)〕

Chapter 1, General Introduction: The reactivity and properties of transition metal complexes are dictated by the ligand bound to the metal center. Metal cations are typically stabilized by electronegative main-group organic elements of Group 14-17, with formally 1-electron donating (X-type, e.g. halides) or 2-electron donating (L-type, e.g. phosphines) functionalities. Since the 1960s, the reversed dative bond between Lewis basic (electron-rich) metal centers and Lewis acidic boranes has attracted fundamental interest, in which borane is serving as a σ 2-electron acceptor, also known as a Z-type ligand (M→Z, Z = borane). Despite of ample number of attempts, it was not until 1999, the first structurally confirmed metal complex featuring a borane Z-type ligand was reported by using an ambiphilic ligand which contained both L-type and Z-type functionalities in a single multidentate scaffold. Since then, the M→Z type bonding in metal complexes has been shown to heterolytically active bond through metal-ligand (M-L) cooperativity. It has also been shown to stabilize electron-rich anionic metal systems. However, to date these reactivity patterns have found limited applications in catalytic systems. Aiming to provide new strategies for utilizing the M→Z type bonding in chemical transformations, this thesis proposed and examined two main approaches to harness metal-ligand cooperativity.

The first approach of this thesis (**Chapter 2**) proposed that, an intermolecular metal base/borane Lewis pair can also be used to access M→Z type metal-ligand cooperativity. By using readily available low-valent electron-rich metal complexes and boranes, one can avoid the costly design and synthesis of ambiphilic ligand and its complexation to metal, which should increase the accessibility to metal-borane Lewis pairs and allow rapid screening of their catalytic reactivity. The commercially available compounds $\mathrm{Pt(P}t\mathrm{Bu_3)_2}$(**1**) and $\mathrm{B(C_6F_5)_3}$(**2**) were used as the highly reactive Lewis pair to investigate the hydrogen activation reaction initially. Theoretical calculations suggested that the platinum(0) center and borane can cooperatively cleave the H-H bond heterolytically to form $[(t\mathrm{Bu_3P})_2\mathrm{Pt\text{-}H}]^+[\mathrm{H\text{-}B(C_6F_5)_3}]^-$ (**3**) reversibly. Experimentally, hydrogen activation and its reverse reaction by **1** and **2** was confirmed. Followed by this, catalytic hydrogenation of styrene and ammonia borane (AB) dehydrogenation using **1**/**2** as catalysts were also confirmed.[1] Although theoretical calculation results are mostly consistent to the experimental results, there are noticeable discrepancies in both hydrogen activation and AB dehydrogenation reactions. This clearly indicates that reaction mechanisms other than theoretically proposed are at work. Overall, it can be concluded that the intermolecular system by using unsupported metal base/Lewis acid pair is indeed useful for catalytic reactions. Theoretical investigations on the reactions provided useful insight into the mechanism of the reactions, though owing to the nature of the "free" (unlinked) Lewis pair, it is very difficult to model the entire reaction system.

The second part of this thesis investigated three-centered bond activation by using a new ligand design that contains two Lewis acidic centers and one Lewis base. Currently, almost all bond activation reported by Lewis pairs are based on two-activation centers (namely one Lewis acid and base each), which allow heterolytic bond cleavage. An additional Lewis acid is expected to activate a second functional group or substrate, which may result in unprecedented reaction paradigm or chemo-selectivity. This thesis proposed a bisborane-substituted phosphine design (BPB) as an ambiphilic ligand. **Chapter 3** describes the synthesis, isolation and characterization of BPB-Bpin and BPB-9BBN derivatives. The BPB-9BBN derivative has been found to form Lewis adduct with isocyanides tBuNC and be able to activate aldehyde as well as CO reversibly. In addition, it also reacted with water to produce dihydrogen and phosphine oxide via a phosphonium intermediate, confirmed by ^{31}P NMR measurements at –80℃. Although highly reduced form of main-group element-hydride species have been known to produce H_2 in presence of H_2O, this reaction is the first example where protic H^+ could be reduced to hydridic H^- at a non-metal center.[2] This provides an unprecedented working paradigm for main-group chemistry to mimic metal-centered reactivity, which confirms our hypothesis that a 3-reaction center has potential to show completely unexpected reactivity.

After successful synthesis of the BPB ligands, **Chapter 4** describes their complexation chemistry to iridium, platinum, and gold centers (Group 9-11). The complexation chemistry of BPB-9BBN with platinum(0/II) precursors did not allow successful isolation of Pt(PBP) complexes. However, reactions with gold(I) and Ir(I) precursors produced gold(I)-(BPB) and Ir(I)-(BPB) complexes respectively. Solid-state structures of these complexes suggested attractive interaction between metal and highly Lewis acidic 9-BBN center. Currently, small molecule activation by these metal complexes is being investigated.

Finally, it is agreed from the above results that the author of the present thesis has enough credentials to be awarded the doctoral degree (Science).

公表論文:

1. Zhang, L.; Oishi, T.; Gao, L.; Hu, S.; Yang, L.; Li, W.; Wu, S.; Shang, R.; Yamamoto, Y.; Li, S.; Wang, W.; Zeng, G., Catalytic Dehydrogenation of Ammonia Borane Mediated by a Pt(0)/Borane Frustrated Lewis Pair: Theoretical Design. *ChemPhysChem* **2020,** *21* (23), 2573-2578.
2. Oishi, T.; Lugo-Fuentes, L. I.; Jing, Y.; Jimenez-Halla, J. O. C.; Barroso-Flores, J.; Nakamoto, M.; Yamamoto, Y.; Tsunoji, N.; Shang, R., Proton to hydride umpolung at a phosphonium center via electron relay: a new strategy for main-group based water reduction. *Chem. Sci.* **2021**, 15603-15608.