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Well-Defined, Versatile and Recyclable Half-Sandwich Nickelacarborane Catalyst for Selective Carbene-Transfer Reactions

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Abstract: Catalytic carbene-transfer reactions constitute a class of highly useful transformations in organic synthesis. Although catalysts based on a range of transition-metals have been reported, the readily accessible nickel(II)-based complexes have been rarely used. Herein, an air-stable nickel(II)-carborane complex is reported as a well-defined, versa-tile and recyclable catalyst for selective carbene transfer re-

Introduction

Carbene transfer reactions, particularly of diazo compounds with electron-withdrawing substituents, have been extensively studied using transition-metal catalysts or Lewis acid catalysts, and successfully applied in preparation of many functional molecules.^[1] Up to now, a number of transition-metals, ranging from the middle (Cr group)^[2] to the late groups (Cu and Zn groups),^[3] have been capable of catalyzing these reactions via metal-carbene intermediates. Among them, rhodium^[4] and copper^[5] are by far the most widely used ones, followed by iridium and ruthenium.^[6] In recent years, iron has received significant attention in this regard and particularly relevant to directed evolution of heme enzymes.^[7] In parallel, cobalt-porphyrin systems have also been employed as reactive and selective

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actions with low catalyst loading under mild conditions. This catalyst is effective for several types of reactions including diastereoselective cyclopropanation, epoxidation, selective X–H insertions (X = C, N, O, S, Si), particularly for the unprotected substrates. This represents a rare example of carborane ligands in base metal catalysis.

catalysts in various carbene transfer reactions.^[8] In view of the broad utility of its all neighbors including palladium and platinum,^[9] therefore, it is surprising that nickel has been rarely used in the carbene transfer catalysis. Sporadic examples involved donor type carbenes that were derived from unstable diazo compounds and using air-sensitive Ni⁰ catalysts.^[10, 11] For example, Hillhouse and co-workers prepared Ni⁰/bis-NHC complex and used it as a catalyst (20 mol%) for cyclopropanation of 1-hexene (Scheme 1a).^[12] Besides, Uyeda's group reported the binuclear Ni⁰ complex and applications in carbene transfer to *t*BuNC or Simmon–Smith-type cyclopropanation.^[13] However, effective transfer reactions of the more synthetically relevant acceptor-containing carbenes using more available Ni^{II}

In most cases, the rate-determining step of a carbene-transfer reaction is denitrogenative formation of the highly electrophilic metal-carbene intermediate (Scheme 1 b).^[15] Although usually the formal valence of the metal center does not change if the carbene is considered as a neutral ligand, this step may well be seen as an oxidative addition step that would lead to higher (formally +2) valence count, particularly with an electron-withdrawing substituent.^[16] Therefore, we reasoned that the poor performance of nickel(II) as catalysts in carbene-transfer reactions was likely due to its lower propensity to be oxidized. Indeed, in comparison with the neighboring elements, high-valence nickel complexes have presented significant challenges in synthetic coordination chemistry.^[17] Consequently, we hypothesized that: 1) introduction of a highly electron-donating ligand should support formation of high-valence nickel species, and 2) an extensive conjugation system might provide an electron sink to be compatible with other steps of the desired catalytic cycle.

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(a) Previous Ni(0)-catalyzed cyclopropanation with donor diazo compounds

$$\bigwedge_{R} + \bigvee_{Ph}^{N_2} \xrightarrow{20 \text{ mol}\%}_{T > 60 \text{ °C}} \xrightarrow{Ph} \bigvee_{Ph}^{Ph}_{R}$$

(b) General mechanism of metal-catalyzed carbene transfer reactions



(c) $nido-C_2B_9H_{11}^{2-}$ ligand and its known Ni(IV) complex



Scheme 1. Half-sandwich nickelacarborane for carbene transfer reaction.

closo-Carboranes, particularly o-carborane, featuring three-dimensional aromaticity, are known as thermally stable sphere boron clusters. A partially deboronated derivative of o-carborane, i.e., *nido*-dicarbollide, could serve as an η^5 , $\pi 6$ 5-ligand for many transition-metals (Scheme 1 c).^[18] Due to the similarity to cyclopentadienyl ligands, good thermal stability and structural tunability, it has long been proposed that nido-dicarbollides might be used as ligands for catalysis.^[19] However, up to date, metallacarboranes have been scarcely employed as catalysts in synthetic organic chemistry.^[20] Relevant to this work, the early reports from Hawthorne had shown that nido-dicarbollide was very strong electron-donor and could support formation of a stable sandwich Ni^{IV} complex.^[21] Therefore, during our recent investigations of boron-based ligands and catalytic cyclopropanation reactions,^[22] we wondered if a suitable nickelacarborane complex could serve as an effective base-metal catalyst for carbene-transfer reactions. Herein we wish to report our results that has led to a well-defined, stable half-sandwich nickelacarborane 1 as robust, generally useful, selective, and recyclable catalyst (Scheme 1 d).

Results and Discussion

Synthesis and characterization of 3,3-(bis(diphenylphosphino)ethane)-3,1,2-*closo*-NiC₂B₉H₁₁ (1)

To test our hypothesis, we first synthesized the half-sandwich nickelacarborane 3,3-dppe-3,1,2-*closo*-NiC₂B₉H₁₁ (1) (dppe = 1,2-bis(diphenylphosphino)ethane) and then explored its usage in catalytic carbene transfer reactions. Compound 1 was prepared by first deboronation of commercial *closo-o*-carborane with ethanolic potassium fluoride to form K⁺[*nido*-7,8-C₂B₉H₁₂]⁻, followed by coordinative metalation with Ni-(dppe)Cl₂ in refluxing benzene. After removal of potassium chloride by simply redissolving the crude product in dichloromethane and filtration, the desired product could be easily isolated as 1:1 co-crystal with one equivalent of dichloromethane, as indicated in ¹H NMR spectrum, in 87% yield over two steps (Scheme 2). The co-crystalized dichloromethane could not be removed under high-vacuum for at least 3 hours.



Crystal structure of 1·CH2CI2

Scheme 2. Synthesis of $1 \cdot CH_2CI_2$ and crystal structure of thermal ellipsoids are drawn at 30% probability level. Deposition Number 1948028 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures. Hydrogen atoms are omitted for clarity.

The diamagnetic nickelacarborane 1 was air-stable at room temperature for at least one month without observable decomposition, as determined by ¹H and ³¹P NMR spectroscopy of its solution structure. The singlet at δ = 64.2 ppm in its ³¹P NMR spectrum indicated a symmetric structure. The solid state structure of 1 was confirmed by X-ray diffraction of a single crystal grown from its solution in dichloromethane/nhexane. The asymmetric unit contains a molecule of 1 and a co-crystallized molecule of dichloromethane. The central Ni atom is surrounded almost "symmetrically" by the dicarbollide ligand (Ni-C 2.124(3) and 2.116(3) Å; Ni-B 2.065(3)-2.171(3) Å) and the dppe ligand (Ni-P 2.173(8) and 2.139(8) Å) in a distorted icosahedral framework. Multiple intermolecular non-classical hydrogen bonds^[23] (C–H···Cl, C–H···π, B–H···π, C–H···H–B, C– H…H–C) and C–Cl… π interaction in crystal were found, as shown in Figures S1-3 and Table S2. The dichloromethane and the adjacent four nickelacarborane molecules are connected by two types of C55-H55A···H4A-B4, C55-H55B···H1-C1 dihydrogen bonds with the corresponding H-H distance being 2.20 Å, 2.34 Å, two kinds of C-H-Cl (H11-Cl1 2.93 Å, H16A…Cl2 2.85 Å) hydrogen bonds, and C--Cl…π interaction (Cl2---Cg2 3.57 Å, Figure S3). In addition, the intermolecular C--

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 $H...\pi$ (H15B...Cg1 2.97 Å, Figure S1), and $B-H...\pi$ interactions (H9...Cg3 3.19 Å, H7A...Cg4 3.57 Å, Figure S2) further link the carborane molecules. These data also reveal the +2-oxidation state of nickel in complex **1**, filled with 18-electron configuration, in agreement with its diamagnetism and thermal stability.

Nickelacarborane 1-catalyzed diastereoselective cyclopropanation and epoxidation

We began our investigation in nickelacarborane 1-catalyzed cyclopropanation and the diastereoselectivity using styrene (0.6 mmol) as the substrate and methyl 2-diazo-2-phenylacetate (0.2 mmol) as a donor-acceptor carbene precursor (Table 1). After screening various reaction parameters, we found that a combination of 1·CH₂Cl₂ co-crystal as the catalyst and NaPF₆ as the additive under argon atmosphere at $35\,^\circ\text{C}$ provided the best results (Tables S3-5). NMR analysis of the crude product indicated formation of the expected cyclopropane in 88% yield, 90% conversion and its d.r. ratio was beyond 20:1 (Entry 1). After purification by flash column chromatography, the cyclopropane (4a) was obtained in 85% yield. Under the same condition, we tested the different classes of nickel catalysts and found that NiCl₂, Ni(dppe)Cl₂ with chelating diphosphine ligand, Ni(dtbpy)Cl₂ with bipyridine ligand gave only trace amount of the expected product while no reaction occurred in the presence of $Ni(PPh_3)_2Cl_2$ (Entries 2–5). Interestingly, with a different nickelacarborane complex 3,3-(PPh₃)₂-3,1,2-closo-NiC₂B₉H₁₁ as the catalyst,^[24] the cyclopropanation gave 21% yield and over 20:1 d.r. (Entry 6). While only trace amount of product was produced in the absence of the catalyst (Entry 7). Remarkably, these results revealed the key effects

Table 1. Variationsofthenickelacarborane1-catalyzedcyclo-propanation.[a]								
	N ₂	[Ni] 1.7 mol%, NaPF ₆ 18 mol%	∧,,CO ₂ Me					
Pn 🥆	Ph CO ₂ Me	CDCl _{3,} Ar, 12 h	Ph					
2a	3		4a					
	[Ni 1]:	2 Ph ₃ P v [Ni 2]:	PPh ₃					
Entry	Catalyst	Viold (04)[b]	d r ^[b]					
Entry	Catalyst	field (%)**	u. i.					
1	[Ni 1]·CH ₂ Cl ₂	88 (85 ^[c])	>20:1					
1 2	[Ni 1]·CH ₂ Cl ₂ NiCl ₂	88 (85 ^[c]) 10	>20:1					
1 2 3	[Ni 1]·CH ₂ Cl ₂ NiCl ₂ Ni(dppe)Cl ₂	88 (85 ^[c]) 10 8	>20:1					
1 2 3 4	[Ni 1]-CH ₂ Cl ₂ NiCl ₂ Ni(dppe)Cl ₂ Ni(dtbpy)Cl ₂	88 (85 ^[c]) 10 8 3	>20:1					
1 2 3 4 5	[Ni 1]-CH ₂ Cl ₂ NiCl ₂ Ni(dppe)Cl ₂ Ni(dtbpy)Cl ₂ Ni(dtbpy)Cl ₂ Ni(PPh ₃) ₂ Cl ₂	88 (85 ^[c]) 10 8 3 -	>20:1					
1 2 3 4 5 6	[Ni 1]-CH ₂ Cl ₂ NiCl ₂ Ni(dppe)Cl ₂ Ni(dtbpy)Cl ₂ Ni(PPh ₃) ₂ Cl ₂ [Ni 2]	88 (85 ^[c]) 10 8 3 - 21	>20:1 - - - - >20:1					
1 2 3 4 5 6 7	[Ni 1]-CH ₂ Cl ₂ NiCl ₂ Ni(dppe)Cl ₂ Ni(dtbpy)Cl ₂ Ni(PPh ₃) ₂ Cl ₂ [Ni 2]	88 (85 ^[c]) 10 8 3 - 21 5	> 20:1 - - - - > 20:1					
1 2 3 4 5 6 7 8 ^[d]	[Ni 1]-CH ₂ Cl ₂ NiCl ₂ Ni(dppe)Cl ₂ Ni(dtbpy)Cl ₂ Ni(PPh ₃) ₂ Cl ₂ [Ni 2] – [Ni 1]-CH ₂ Cl ₂	88 (85 ^(c)) 10 8 3 - 21 5 60	> 20:1 - - - > 20:1 - - > 20:1 - > 20:1					

from both the carborane ligand and the chelating diphosphine ligand on the catalytic activity of cyclopropanation. Lastly, the reaction at 25 °C was inferior, leading to lower yields but the diastereoselectivity could be maintained (Entry 8).

Stimulated by the above results, we briefly tested Darzenstype epoxidation with diazo compounds catalyzed by nickelacarborane **1** using benzaldehyde as the substrate. Pleasingly, the reaction afforded the *trans*-epoxide product in 79% isolated yield as a single diastereomer (Scheme 3).



Scheme 3. Nickelacarborane 1-catalyzed epoxidation.

Nickelacarborane 1-catalyzed X–H (X = C, N, O, S, Si) insertion and their regio- or chemoselectivity

Encouraged by these results, we further examined the scope of nickelacarborane 1 as a catalyst for other types of carbene transfer reactions, such as (hetero)aromatic C-H functionalization or X–H insertion reactions (X = C, N, O, S, Si) (Scheme 4). Whenever possible, the results were compared with literaturereported results using other metal-based catalytic systems. First, directly using the Ni catalytic system analogous to the above cyclopropanation (1.7 mol% of 1, CDCl₃ as the solvent at 35-45 °C), various electron-rich arenes, such as N, N-dimethylaniline, phenylpyrrolidine, 1,3,5-trimethoxybenzene gave C-H insertion products in good yields (6a 74%, 6b 65%, 6c 75%) and azine as the only byproduct. The catalytic activity was comparable to the known catalytic systems.^[25-30] Furthermore, we found that both substituted and unprotected indoles, pyrroles were well tolerated and high regioselectivity, chemoselectivity and yields were realized (6d-6h). Generally, unprotected indoles and pyrroles have been problematic due to regioselectivity between C-2 and C-3 C-H insertion and chemoselectivity among cyclopropanation, C-H insertion and N-H insertion. $^{\left[31\right] }$ Pleasingly, in our conditions, the reaction could selectively afford C-H insertion products 6e, 6f and 6h in high yields. Thus, the Ni catalyst showed better regioselectivity and chemoselectivity than the previously reported ones based on Ru,^[34] Rh,^[35] Cu^[33,35] or Pd.^[36] Different from indoles, benzofuran smoothly underwent cyclopropanation instead of C-H insertion, affording the product **6i** in 62% yield and comparing favorably with previous Rh-based system.[37] In contrast, when 2-ethylfuran was used as the substrate, carbene transfer/ring opening product 6j was isolated in 73% yield.

Next, we investigated that if the Ni catalyst could be also used in N–H or O–H insertion reactions. We particularly focused on the chemoselectivity in cases where multiple sites were potentially reactive. First, anilines were found as competent substrates and the desired N–H insertion products (**6k**, **61–6n**, crystal structure of **61** Figure S4) could be isolated in good yields. The yield from simple aniline was comparable with reported systems using Rh, Cu, etc.^[39,40] Remarkably, ani-

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Scheme 4. Substrate scope and selectivity of nickelacarborane 1-catalyzed carbene transfer reaction.^[a] [a] Conditions: 5 (0.6 mmol), 3 (0.2 mmol), [Ni 1] (0.0034 mmol), NaPF₆ (0.036 mmol) in 1 mL of CDCl₃, 35–45 °C, 5–24 h and yield of isolated product. [b] NaBAr^F₄ (0.006 mmol) was used, instead of NaPF₆. [c] 45 °C, 24 h. [d] Adding 50 equiv 4 Å MS. [e] No sodium additives were added. [f] Reaction solvent: acetonitrile. [g] 10 mmol scale, salicyclic acid (1.5 equiv), 2.6 g **6x** was prepared.

line N–H group could be selectively reacted in the presence of unprotected hydroxyl even sulfhydryl groups, and the electron-rich multiple arene C–H sites. Carbazole, a relatively hindered secondary aniline, still preferred N–H insertion and generated **60** in 75% yield. The reaction of benzamide also formed N–H insertion product **6p** albeit in lower yield.

This catalytic system worked also well for O-H insertion reactions of alcohols, phenols and carboxylic acids. Thus, using 1.7 mol% of nickelacarborane 1 as the catalyst, reaction of diazoester 3 with primary alcohols such as n-butanol and ethanol gave the desired products **6g** and **6r** in excellent yield. Secondary and tertiary alcohols were also viable substrates although the yields were somehow lower (6s and 6t). Using phenol and 2-hydroxypyridine as the reaction partner also generated the desired O-H insertion products in high yields (6u and 6v). Insertion to acetic acid was also possible, forming the product in 82% yield (6w). When salicyclic acid (for 6x, see Figure S5) or osalmid (for 6z) was used as the substrate, O-H insertion selectively took place at the carboxylic acid site and the phenolic hydroxyl group remained intact. When 3-butenol was reacted with 3, selective O-H insertion product 6aa was isolated in 82% yield; no cyclopropanation was observed. In addition, S–H insertion reaction of *p*-methoxythiophenol was tested and the desired product **6ab** could also be isolated in 47% yield.

Furthermore, Si–H insertion product **6ac** was smoothly formed in high yield using simple triethylsilane as the coupling partner. Besides the representative push–pull diazoester **3**, simple and commercially available ethyl diazoacetate could also be successfully used. For example, using catalyst **1**, reaction of ethyl diazoacetate with salicyclic acid cleanly formed the O–H insertion product **6y** in 99% yield. Finally, to exemplify the scalability, 2.6 g of **6x** was prepared with the catalytic system in 10 mmol scale in 91% yield.

The stability and recycling of catalyst 1

Most organometallic catalysts are susceptible to decomposition when, if possible, isolated from the reaction mixture. In this work, however, we found that the nickelacarborane catalyst 1 was stable enough that after completion of the catalytic reactions it could be readily recovered in high yield by usual silica gel flash chromatography. NMR spectra indicated its structural homogeneity. Therefore, we attempted to reuse the

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recovered catalyst for further transformations. Pleasingly, we found that when salicylic acid was used as the substrate, at least for continuous 5 runs, catalyst 1 could be recovered with little loss (>87%) and showed nearly constant catalytic activity (>93% yield) (Figures 1, S18, Table S14 for detail). That a homogeneous catalyst exhibits both high activity and recyclability is remarkable considering that most catalysts need in situ activation and are not amenable to recycling.^[54] We attribute the robustness of catalyst 1 to its neutrality, stable valence, and coordinative saturation of nickel, and its unique three dimensional aromaticity.



Figure 1. Recycling experiments of 1 in O-H insertion.

Mechanistic investigation

In order to gain more insights into the mechanism, we chose the O-H insertion as a model reaction that was relatively less studied compared to the well-established concerted processes for C-H insertion.^[55] First, we did kinetic experiments on O-H insertion of salicylic acid and measured the initial rates of the reaction by in situ ¹H NMR spectroscopy (Figures S7–S13, Tables S10-12, for details). The reaction appeared to have a nearly first-order dependence of nickel catalyst (1) and diazo compound (3) while a zeroth-order dependence on salicylic acid. To investigate the electronic nature of the rate-determining step, a Hammett plot with a series of para-substituted aryl methyl diazoesters (Figures S14-S17, Table S13) and a designed competition experiment were performed (Scheme 5). Thus, using salicyclic acid as the substrate, simultaneously adding 1.0 equivalent of electron rich 3' and 1.0 equivalent of electron poor 3", after full conversion, led to corresponding O-H products 6x' and 6x" in 97:3 ratio, and adding 3 and 3" led to 6x and 6x" in 91:9 ratio. Similarly, adding 3' and 3 led to 6x' and 6x in 60:40 ratio. The fact that more electron rich diazoester showed higher reaction rate and a Hammett plot of log $(k_{\rm X}/k_{\rm H})$ as a function of the characteristic σ_{para^+} value for each substituent affords a better linear correlation ($\rho = -0.98$, $R^2 =$ 0.98) than $\sigma_{\rm para}$ or $\sigma_{\rm para}{}^-$, suggesting incoming positive charge on the carbenoid carbon in the transition state.

(a) Competition experiments: electronic effects of para-substituents



Scheme 5. Mechanistic study of nickelacarborane 1-catalyzed O-H insertion.

Next, to examine whether the O–H insertion occurred in a concerted or stepwise manner, we conducted an aldol-type experiment using 4-nitrobenzaldehyde **8** to trap the possible enolate intermediate that would form during stepwise process (Scheme 6a).^[56] Thus, the nickelacarborane **1**-catalyzed reaction of (4-methoxyphenyl)methanol **7**, methyl 2-diazo-2-(4-methoxyphenyl)acetate **3'** and 4-nitrobenzaldehyde **8** generated a mixture of mainly three products. Together with the O–H insertion product **9**, two diastereomeric three-component ad-



Scheme 6. Evidence of stepwise process in O-H insertion.

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ducts **10** and **11** were formed. Besides, controlling experiments indicated that the formation of **10/11** was neither from a ring opening reaction of the potential epoxide **12** with benzyl alcohol **7** (Scheme 6b) nor from the O–H insertion product (**9**) with aldehyde **8** (Scheme 6c). These results provided evidence for a stepwise mechanism involving oxonium ylide and/or enolate-like intermediates.

On the above basis, we proposed possible catalytic cycles for nickelacarborane 1-catalyzed carbene transfer reactions as shown in Figure 2. Thus, unlike many other in situ-activated catalyst,^[57] 1 serves as the genuine catalyst and slowly reacts with a diazoester to generate nickel-carbene complex Int-1. The electrophilic Int-1 then reacts with a hydroxyl group donor ROH to form an oxonium ylide Int-2. With or without nickel dissociation, Int-2 may behave as an ester enolate and be trapped by an aldehyde through aldol reaction. A formal 1,2-proton shift of Int-2 then affords the O–H insertion product and regenerate catalyst 1. Reactions including cyclopropanation, epoxidation, C–H and X–H insertion reactions might take place from Int-1 via processes analogous to previously reported other transition metal-carbene intermediates.^[58]



Figure 2. Mechanism of nickelacarborane 1-catalyzed carbene transfer reactions.

Conclusions

In summary, we have demonstrated that the readily accessible yet previously incapable base metal nickel(II) species could be enabled with a dicarbollide ligand for carbene transfer reactions. In particular, the stable nickelacarborane complex 1 acted as a well-defined, highly active and recyclable catalyst for a broad range of carbene transfer reactions under operationally simple conditions. In most cases, high chemoselectivity and diastereoselectivity if applicable were achieved. With catalyst 1, chemoselective or site-selective X–H insertion (X = C, N, O, S, Si) reactions of unprotected substrates are possible. Considering the structural modularity of 1 and the unique electronic property of dicarbollide ligand, this new mode of cata-

lyst system might be extended to other relevant catalytic transformations such as nitrene-involved reactions and to their chiral versions.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: carbenes · carboranes · homogeneous catalysis · nickel · selectivity

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