Synthesis and Characterization of Bis(phosphine)carbodicarbene Complexes of Iron, Cobalt, and Nickel

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ABSTRACT: The synthesis and characterization of nickel, cobalt, and iron complexes of the bis(phosphine)carbodicarbene (CDC) ligand 1 is described. The square-planar complexes can be synthesized without the isolation of the deprotonated carbodicarbene ligand, and three different synthetic methods were used to make these first-row transition-metal compounds. The reaction between ligand 1-BPh₄ and Ni(COD)₂ afforded the compound [(CDC)Ni(η⁵-C₈H₁₃)][BPh₄]₂ via the insertion of COD into the Ni–H bond produced by cyclometalation. The complexes [(CDC)MC][BPh₄] for nickel and cobalt were synthesized from the reaction of carbodicarbene ligand 1 with NiCl₂ or CoCl₂ in the presence of triethylamine. For the synthesis of the iron coordination complex of CDC ligand 1, Fe₂Mes₄ was used to produce [(CDC)Fe-Mes][BPh₄](5), an intermediate-spin Fe(II) compound. Complexes 3–7 were characterized by spectroscopic methods and X-ray single-crystal diffraction analysis.

INTRODUCTION

The carbodicarbene (CDC) molecule was predicted in 2007 as a dicoordinated carbon(0) supported by two N-heterocyclic carbene (NHC) units. Since 2007, there have been a number of reports describing the application of carbodicarbones as ligands for transition-metal or main-group compounds. Details from the synthesis and characterization of these compounds have been used to identify characteristics of the CDC ligand, such as redox noninnocence and donor properties.

The CDC ligand framework has been found to have stronger σ-donor properties in comparison to common NHC ligands through IR studies of metal–carbonyl compounds. England, Ye, and co-workers have highlighted the comparison of the electronic structure of the CDC ligand and the NHC ligand by characterizing the CDC ligand’s redox noninnocence. They have shown that the pair of electrons of π symmetry of the carbodicarbene could render the carbon center redox active and allow access to highly charged first-row transition-metal complexes via oxidation.

DEPOTRONTATION TO GIVE THE FREE CARBODICARBENE OR FOR THE SYNTHESIS OF COORDINATIVELY UNSATURATED MOLECULES.
RESULTS AND DISCUSSION

We chose to use a phosphine-substituted 1,4-diazepenium salt, 1, as a ligand precursor toward the synthesis of first-row transition-metal complexes. Meek and co-workers have developed the synthesis of the 1-BF₄ ligand precursor and applied the ligand in rhodium-catalyzed reactions.³,¹⁰−¹² The ligand precursor, 1-BF₄, is ideal because it can be synthesized in two steps from commercial reagents and provides the desired tridentate pincer framework with phosphines as the donor ligands. Additionally, 1-BF₄ has the advantage of being viable for purification by column chromatography. Meek and co-workers have reported that attempts to deprotonate 1-BF₄ to isolate the free CDC molecule were unsuccessful, thus limiting the synthetic approaches toward coordination complexes.³

We began our attempts to synthesize first-row transition-metal coordination complexes of 1-BF₄ with 1 equiv of Ni(COD)₂ to generate a (CDC)NiII product via cyclo-metalation. We followed the reaction between Ni(COD)₂ and 1-BF₄ by ¹H NMR in THF-¿. Immediately after mixing, the ¹H NMR spectrum of the reaction mixture revealed a characteristic triplet resonance of a nickel hydride at −11.5 ppm with a ²JHP value of 65 Hz (Scheme 1). The resonance of the nickel hydride at −11.5 ppm disappears within 20 min at room temperature to give a mixture containing a major product with a ³¹P NMR signal at 80 ppm. From an analysis of the ¹H NMR spectrum of the product of the reaction between 1-BF₄ and Ni(COD)₂, we concluded that a molecule of cyclooctadiene had inserted into the nickel−hydride bond, forming [(CDC)Ni(η⁴-C₈H₁₂)][BF₄] (2-BF₄) (Scheme 1).

The cyclooctenyl ligand of 2-BF₄ is evident from the multiplet resonance of the two olefinic protons at 5.36 ppm and the aliphatic proton signals of the remaining 11 protons between 0 and 2 ppm (Figure S4). A related complex of a monoanionic amido diphosphine (PNP) pincer ligand has been reported and characterized by single-crystal X-ray crystallography by Liang and co-workers.¹³ The PNP nickel hydride complexes from the reactions between Ni(COD)₂ and the PNP amine ligand precursors were only found to undergo insertion of COD when phenyl substituents of the phosphines in the PNP ligand were used. Similarly, Fryzuk and co-workers reported the synthesis of an o-phenylene-bridged diphosphine-NHC (PCP) pincer nickel hydride complex, (PCP)Ni-H, from the reaction with Ni(COD)₂.¹⁴ The (PCP)Ni-H complex reported by Fryzuk was not found to insert COD into the nickel−hydride bond, which may be attributed to the more sterically bulky and electron rich isopropyl-substituted phosphines of the PCP ligand used.

From our studies of the coordination of the pincer ligand derived from 1, we found the use of a tetraphenylborate (BPh₄⁻) counteranion to be useful in the purification and isolation of several compounds. When 1-BPh₄ was used for the synthesis of the compound 2-BPh₄, the nickel cyclooctenyl molecule was more readily isolated with a yield of 74%. Attempts to crystallize compounds 2-BPh₄ and 1-BF₄ for single-crystal X-ray crystallography studies have been unsuccessful.

To test if compound 2-BPh₄ could serve as a masked nickel hydride, we added excess 1,5-COD to compound 2-BPh₄ in C₆D₆. After 3 days at room temperature, no isomerization of 1,5-COD to 1,3-COD was observed. Additionally, we did not observe any reaction between excess styrene and compound 2-BPh₄.

One attempt at the crystallization of the cyclooctenyl compound 2-BF₄ in dichloromethane resulted in the formation of [(CDC)Ni-Cl][BF₄] (3-BF₄). Compound 3-BF₄ could be synthesized directly from the protonation of the cyclooctenyl ligand of 2-BF₄ with 1 M HCl in diethyl ether. Alternatively, 3-BF₄ may be isolated in 70% yield from the addition of triethylamine to a mixture of 1-BF₄ and NiCl₂ (Scheme 2). Crystals of compound 3-BF₄ were grown as large orange needles from the diffusion of hexanes into a DCM solution of 3-BF₄ (Figure 2). Compound 3-BF₄ has a square-planar geometry at nickel with τ₄ = 0.08.¹⁶ The planar geometry of the central CDC carbon and the CDC C−Ni (C1−Ni1) distance of 1.911(3) Å both support the structural assignment of 3-BF₄.

Scheme 1. Synthesis of Compound 2-BF₄ with the ¹H NMR Signal of the Ni Hydride Intermediate Complex

![Scheme 1](image1)

Scheme 2. Synthesis of Compounds 3-BF₄, 4, and 5

![Scheme 2](image2)
In an attempt to synthesize the proposed nickel hydride intermediate formed during the reaction between Ni(COD)$_2$Cl and the ligand 1-BPh$_4$, we added 1 equiv of LiEt$_3$BH to compound 3-BPh$_4$. We followed the reaction by $^1$H and $^{31}$P NMR in THF-d$_8$. We did not observe any characteristic resonance for the nickel hydride in the $^1$H NMR spectrum of the reaction mixture. In the $^{31}$P NMR spectrum (Figure S24) there were multiple signals in low concentration between 0 and 115 ppm. We believe that the nickel hydride compound may have decomposed to an intractable mixture in the absence of coordinating solvents such as acetonitrile to give the dicationic compound $^+$.

Alternative (PCP)Ni-Cl compounds have been reported previously and have been applied as catalysts in a variety of transformations. As a related class of carbon(0) compounds, likely the most relevant (PCP)Ni-Cl compounds previously reported are the carbodiphosphorane-based nickel pincer complexes. In comparison to square-planar nickel complexes derived from pincer ligands, the number of structurally characterized square-planar cobalt complexes is quite limited. When we employed the same synthetic strategy used to synthesize 3-BF$_4$, from NiCl$_2$ with CoCl$_2$, an orange precipitate could be isolated after heating for 20 min (Scheme 2). The $^1$H NMR spectrum of this molecule was consistent with it being $^+$ square-planar Co(II). The CDC C-Co (C1-Co1) distance in 4 is slightly longer than the C–Ni distance of 3-BF$_4$ at 1.927(3) Å. The solution magnetic moment of complex 4 determined using the Evans method ($\mu_{eff} = 1.82$ B.M) is consistent with it being $^+$ = 1/2 square-planar Fe(II). The intermediate-spin state (S = 1) of compound 5 has been observed in other square-planar Fe(II) complexes having aryl ligands.

The cobalt and iron complexes 4 and 5 are rare example of carbodiphosphorane pincer ligand used in the synthesis of a Co(II) carbene complex. However, carbodiphosphorane ligands have been used for the synthesis and characterization of low-coordinate Fe(II) complexes.

Given the rich redox chemistry of the reported six-coordinate complexes of chromium, iron, and cobalt with the bis(pyridine)carbodiphosphine ligand (Figure 1), we probed the redox properties of the nickel compound 3-BF$_4$ using cyclic voltammetry (Figure 3). We observed a reversible redox couple at 0.4 V and an irreversible wave at $-2$ V. We assign the reversible redox couple at 0.4 V to a one-electron oxidation of compound 3-BF$_4$. Currently, we are unable to conclude whether this oxidation is ligand- or nickel-centered. We assigned the irreversible wave at $-2$ V as a Ni(II)/Ni(I) redox pair.

With the isolation of the Fe, Co, and Ni square-planar coordination complexes of the carbodiphosphine pincer ligand, we set out to explore the lability and reactivity of the chloride ligand of the nickel complexes 3-BF$_4$ and 3-BPh$_4$. First, the chloride ligand of 3-BF$_4$ may be abstracted by AgBF$_4$ in coordinating solvents such as acetoniitrile to give the dicaticonic compound 6 (Scheme 3). Single-crystal X-ray diffraction
studies of compound 6 revealed the expected square-planar, four-coordinate geometry with acetonitrile coordination. The 31P NMR resonance of the ligand phosphines is a single peak shifted downfield relative to compound 3-BF4 at 80 ppm. The CDC–Ni (C1–Ni1) distance of 1.914(3) Å is similar to that of the monocationic complex 3-BF4 (Figure 4).

The chloride ligand may also be substituted with nucleophiles. For example, [CDC-Ni-Ph][BPh4] (7) can be synthesized from 3-BPh4 and phenylmagnesium bromide. If 3-BF4 is used instead of 3-BPh4, there is no observable nickel phenyl complex formed, likely due to the reaction of the tetrafluoroborate anion with the Grignard reagent. The structural parameters of compound 7 are similar to those of compounds 3-BF4 and 6 (Figure 5). Compound 7 remains square planar with a CDC–Ni (C1–Ni1) distance of 1.9373(12) Å.

Compounds 6 and 7 can be synthesized in moderate isolated yields of about 80% and 70%, respectively. Recent reports have discussed the synthesis of related PNP pincer ligated nickel phenyl complexes and their relevance to nickel-catalyzed Kumada or Suzuki−Miyaura coupling reactions.35,36 Given the relevance of the nickel phenyl complex 7 to the above cross-coupling reactions, we explored the coupling of compound 7 with bromobenzene. After 24 h of heating compound 7 with excess bromobenzene at 80 °C in C6D6, no biphenyl formation was observed and compound 7 remained intact.

■ CONCLUSIONS

In conclusion, we have synthesized and characterized iron, cobalt, and nickel coordination complexes of the bis(phosphine)carbodi carbene pincer 1. The synthesis from Ni(COD)2 was found to result in a square-planar compound having a cyclooctenyl ligand from the insertion of a molecule of COD into an intermediate nickel hydride. The
syntheses of square-planar structures of the CDC ligand with Ni, Co, and Fe were developed. The spin states of the cobalt and iron complexes were determined from Evans method experiments. In particular, the four-coordinate iron complex 5 is a rare example of an Fe(II) compound of intermediate spin. The chloride ligand of the nickel complex 3 is a rare example of an Fe(II) compound of intermediate spin.

**Experimental Section**

**General Considerations.** Unless otherwise stated, all manipulations were performed under a nitrogen atmosphere using Schlenk techniques or in a Vigor glovebox maintained at or below 1 ppm of O2.

**Experimental Methods.** Elemental analyses were performed at the Elemental Analysis Facility at the Shanghai Institute of Organic Chemistry (Chinese Academy of Sciences). Glassware was dried at 150 °C overnight. Celite and molecular sieves were dried at 200 °C overnight. The chloride ligand of the nickel complex is a rare example of an Fe(II) compound of intermediate spin.

**Preparation of 1-BPh 4.** A 20 mL vial was charged with compound 1-BPh 4 (86.7 mg, 0.10 mmol 1.0 equiv), THF (3 mL), and a stir bar. Ni(COD) 2 (27.5 mg, 0.10 mmol, 1.0 equiv) was dissolved in 5 mL of THF and added to the solution of compound 1-BPh 4. The reaction mixture changed from yellow to red-orange immediately. After the mixture was stirred for 30 min, the volatiles were removed by vacuum. The remaining solid was washed with diethyl ether (10 mL × 3). The solid was extracted with toluene (6 mL), and the volatiles were removed to provide a yellow powder of 1-BPh 4 (75.8 mg, 74%).

**Preparation of 1-BF 4.** A 20 mL vial was charged with compound 1-BPh 4 (86.7 mg, 0.10 mmol 1.0 equiv), THF (3 mL), and a stir bar. Ni(COD) 2 (27.5 mg, 0.10 mmol, 1.0 equiv) was dissolved in 5 mL of THF and added to the solution of compound 1-BPh 4. The reaction mixture changed from yellow to red-orange immediately. After the mixture was stirred for 30 min, the volatiles were removed by vacuum. The remaining solid was washed with diethyl ether (10 mL × 3). The solid was extracted with toluene (6 mL), and the volatiles were removed to provide a yellow powder of 1-BPh 4 (75.8 mg, 74%).

**Preparation of 2-BPh 4.** A 20 mL vial was charged with compound 1-BPh 4 (86.7 mg, 0.10 mmol 1.0 equiv), THF (3 mL), and a stir bar. Ni(COD) 2 (27.5 mg, 0.10 mmol, 1.0 equiv) was dissolved in 5 mL of THF and added to the solution of compound 1-BPh 4. The reaction mixture changed from yellow to red-orange immediately. After the mixture was stirred for 30 min, the volatiles were removed by vacuum. The remaining solid was washed with diethyl ether (10 mL × 3). The solid was extracted with toluene (6 mL), and the volatiles were removed to provide a yellow powder of 1-BPh 4 (75.8 mg, 74%).

**Preparation of 2-BF 4.** A 20 mL vial was charged with compound 1-BPh 4 (86.7 mg, 0.10 mmol 1.0 equiv), THF (3 mL), and a stir bar. Ni(COD) 2 (27.5 mg, 0.10 mmol, 1.0 equiv) was dissolved in 5 mL of THF and added to the solution of compound 1-BPh 4. The reaction mixture changed from yellow to red-orange immediately. After the mixture was stirred for 30 min, the volatiles were removed by vacuum. The remaining solid was washed with diethyl ether (10 mL × 3). The solid was extracted with toluene (6 mL), and the volatiles were removed to provide a yellow powder of 1-BPh 4 (75.8 mg, 74%).
Preparation of 4. A 20 mL Schlenk flask was charged with 1-BF₄ (593 mg, 0.935 mmol, 1.0 equiv), CoCl₂ (121.4 mg, 0.935 mmol, 1.0 equiv), THF (15 mL), TEA (2.0 mL), and a stir bar. The reaction mixture immediately turned blue. The reaction mixture was heated to 70 °C. After it was stirred for 20 min, the solution turned dark green with an orange precipitate. The reaction mixture was filtered. The orange solid was washed with THF to provide compound 4 (270 mg, 40%). X-ray quality crystals were grown by diffusion of diethyl ether into a dichloromethane solution of 4. ¹H NMR (400 MHz, CDCl₃): δ 4.48, 22.02, 18.11, 11.70, 9.57, 8.59. UV–vis (THF, λ (nm) (ε (M⁻¹ cm⁻¹))): 357 (1901), 444 (9040), 474 (7724). IR-ATR (cm⁻¹): 2875 (vw), 1568 (vw), 1558 (s), 1468 (vw), 1434 (s), 1366 (vw), 1347 (s). ¹³C NMR (126 MHz, CDCl₃): δ 36.90, 35.21, 134.14, 133.13 (t, J = 21.9 Hz), 122.28, 122.22 ( dd, J = 5.4, 2.7 Hz), 122.15 ( d, J = 3.7 Hz). ¹³P NMR (126 MHz, CDCl₃): δ 69.50. UV–vis (THF, λ (nm) (ε (M⁻¹ cm⁻¹))): 362 (3880), 424 (360), 548 (77). IR-ATR (cm⁻¹): 3054 (vw), 1571 (s), 1357 (s), 1467 (s), 1450 (s), 1423 (w), 1373 (w), 1288 (w), 1186 (w), 1103 (s), 991 (w), 848 (w), 744 (w), 732 (s), 690 (w), 611 (w), 532 (s). Anal. Calcd for C₆₃H₅₇BClN₄NiP₂: C, 75.17; H, 5.74; N, 5.59. Found: C, 76.23; H, 5.66; N, 5.66.

Preparation of 5. A 20 mL vial was charged with 1-BF₄ (68.4 mg, 0.079 mmol, 1.0 equiv), Fe₃Mes₂Et₃O (26.1 mg 0.039 mmol, 0.5 equiv), THF (15 mL), and a stir bar. The solution immediately turned light yellow. After 5 min, the solution was transferred to a 100 mL Schlenk tube, removed from the glovebox, and heated to 70 °C for 1 h. The volatile materials were removed under vacuum. The orange-red crystals were crushed and were grown over 2 days from the diethyl ether solution into a benzene solution. UV (THF, λ = 331 (8980)). IR-ATR (cm⁻¹): 362 (3880), 424 (360), 548 (77). IR-ATR (cm⁻¹): 3054 (vw), 1571 (s), 1357 (s), 1467 (s), 1450 (s), 1423 (w), 1373 (w), 1288 (w), 1186 (w), 1103 (s), 991 (w), 848 (w), 744 (w), 732 (s), 690 (w), 611 (w), 532 (s). Anal. Calcd for C₆₃H₅₇BClN₄NiP₂: C, 75.17; H, 5.74; N, 5.59. Found: C, 76.23; H, 5.62; N, 5.66.

Preparation of 7. A 20 mL vial was charged with 3-BPBF₄ (61.4 mg, 0.064 mmol, 1.0 equiv), THF (10 mL), and a stir bar. The 3-BPBF₄ solution was cooled to −30 °C, and bromophenylmagnesium (64 µL, 1M) was slowly added. The reaction mixture was warmed to room temperature and stirred for 1 h. After the reaction mixture turned yellow. The volatile materials were removed under vacuum. The solid was washed with pentane (2 mL) and diethyl ether (2 mL × 2). The solid was dried under vacuum, resulting in a yellow powder (46.5 mg, 73%). X-ray-quality crystals were grown by diffusion of pentane into a benzene solution. UV (THF, λ = 331 (8980)). IR-ATR (cm⁻¹): 3054 (vw), 1571 (s), 1357 (s), 1467 (s), 1450 (s), 1423 (w), 1373 (w), 1288 (w), 1186 (w), 1103 (s), 991 (w), 848 (w), 744 (w), 732 (s), 690 (w), 611 (w), 532 (s). Anal. Calcd for C₆₃H₅₇BClN₄NiP₂: C, 75.17; H, 5.74; N, 5.59. Found: C, 76.23; H, 5.62; N, 5.66.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.1c00241.

NMR spectra, FTIR spectra, UV–vis spectra, electrochemistry data, and X-ray crystallography procedures (PDF)

Accession Codes

CCDC 2077808–2077812 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes
The authors declare no competing financial interest.

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