Ionic composite of palladium(II)/iron bis(dicarbollide) for catalytic oxidative carbonylation in the formation of diphenyl carbonate

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A B S T R A C T

The carborane-based sandwich iron complex, $[n\text{-}Bu_4N]\{Fe(3,3')\text{-}[1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_9H_9]_2\}$, was synthesized in 53.1% yield. A catalyst composite of $PdAc_2/[n\text{-}Bu_4N]\{Fe(3,3')\text{-}[1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_9H_9]_2\}$ was found to be highly active for the oxidative carbonylation of phenol, with the formation of diphenyl carbonate (DPC). A DPC yield of 46% and a turnover number (TON) of 511 were achieved in 4 h using the composite at 110 °C. For comparison, the reaction was also investigated using catalyst composites of $PdAc_2/Mn(acac)_3$, $PdAc_2/Fe(acac)_3$, $PdAc_2/Co(acac)_3$ and $PdAc_2/Ce(acac)_3$ (acac = acetylacetone) under the same conditions of temperature and pressure. The DPC yield was determined by gas chromatography with flame ionization detector (GC-FID). All new products were characterized by elemental analysis, and by ^1H, ^{13}C, ^{11}B and ^{31}P NMR and FT-IR spectroscopy.

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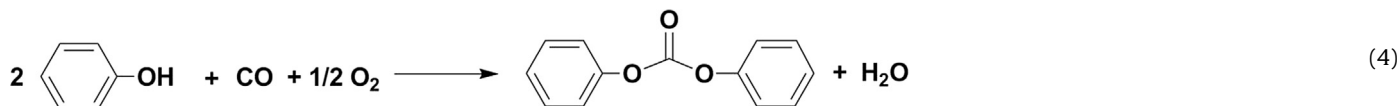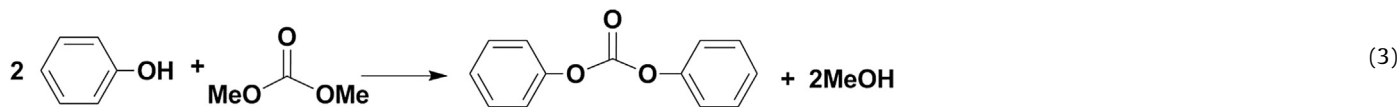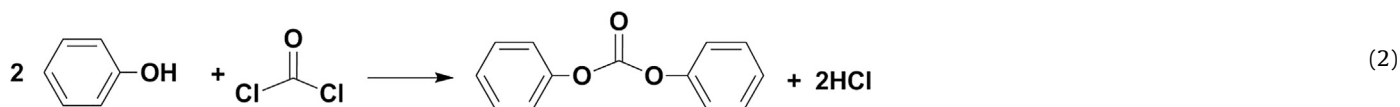
1. Introduction

Diphenylcarbonate (DPC) is an important intermediate for the preparation of polycarbonates (PC), which is one of the major engineering thermoplastics with excellent mechanical, electrical and heat resistance properties [1–3]. PC materials are widely used in our daily life, such as in DVDs and blue-ray discs. Melting DPC with bisphenol (4,4'-(propane-2,2-diyl)diphenol) produces poly-carbonates as shown in Eq (1) [1–3]. Conventionally, DPC is mainly produced by reaction of phenol with phosgene (Eq. (2)) [4]. In this process, the highly toxic and corrosive phosgene is used as raw material. Therefore, the process cannot be considered as green. To avoid using toxic phosgene and to develop environmentally benign processes, transesterification reaction between dimethylcarbonate (DMC) and phenol (Eq. (3)) [5–11], and oxidative carbonylation reaction of phenol to form DPC have been investigated (Eq. (4)) [12–23]. However, it is crucial for transesterification reaction to completely convert DMC to DPC under mild conditions because the reaction is kinetically and thermodynamically unfavorable. At higher temperature, an anisole by-product is formed by the methylation of phenol [5–11]. Whereas polycarbonates produced from DPC, obtained by oxidative carbonylation processes, generally require fewer reaction steps from raw material in the total synthesis procedure, when compared with the current commercialized or phosgene-free processes.

$$\text{(1)}$$
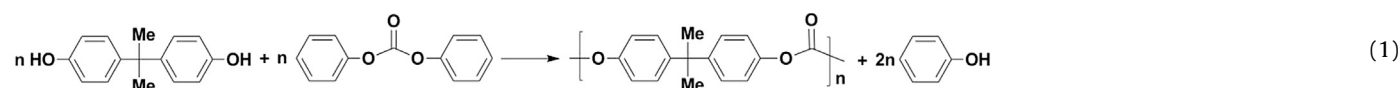
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$$2 \; \text{PhOH} + \text{Cl-CO-Cl} \longrightarrow \text{PhO-CO-OPh} + 2\text{HCl} \tag{2}$$

$$2 \; \text{PhOH} + \text{MeO-CO-OMe} \longrightarrow \text{PhO-CO-OPh} + 2\text{MeOH} \tag{3}$$

$$2 \; \text{PhOH} + \text{CO} + 1/2 \; \text{O}_2 \longrightarrow \text{PhO-CO-OPh} + \text{H}_2\text{O} \tag{4}$$

The production of DPC by the oxidative carbonylation of phenol is well documented [12–23]. In general, a noble metal catalyst such as a palladium complex is used in the process with carbon monoxide (CO), oxygen (O_2), a co-catalyst such as manganese (III) acetylacetonate ($Mn(acac)_3$) and additives such as sodium hydroxide/ tetrabutyl ammonium bromide. The reactions are commonly carried out in acetonitrile (MeCN). A DPC yield of 13.8% has been reported by homogeneous catalyst $PdAc_2$ in the presence of $Mn(acac)_3$ [12]. The reaction was carried out in a Batch model reactor in acetonitrile at 100 °C in the presence of CO and O_2 with a ratio of $V_{CO}/V_{O2} = 11$. The oxidative carbonylation of phenol was also conducted neat at 80 °C [13]. In this process, $Mn(acac)_3$ was also used as co-catalyst and the molten phenol played the role of solvent. The highest yield reported is 10.4% with a selectivity of 100% [13]. It has been well recognized that co-catalyst $Mn(acac)_3$ is crucial to enable the catalytic cycle for the palladium based homogeneous catalysts to operate, as shown in Fig. 1 [12–23]. It is also recognized that other by-products may be formed during DPC synthesis, as shown in Scheme 1. Nevertheless, the existing catalyst systems suffer from low catalytic activity. A high-performance catalyst composite is required for the oxidative carbonylation process.

On the other hand, the iron metal center shows the variable chemical valence of Fe^{II}/Fe^{III} in its bis(dicarbollide) complexes [24,25], therefore it could possibly be used as an *in situ* regenerable co-oxidant, replacing $Mn(acac)_3$. It has been reported that bis(dicarbollide) complexes are efficient co-catalyst for selective oxidation reactions of alcohol to produce the corresponding carbonyl compounds in the presence of palladium-based catalysts [26]. Herein, we report the synthesis of the tetrabutylammonium salt of

iron bis(dicarbollide) and its utility as a co-catalyst in the oxidative carbonylation reaction of phenol to form DPC.

2. Results and discussion

Closo-1,2-Bis-(diphenylphosphino)-1,2-carborane (**2**) was prepared from *closo*-1,2-carborane (**1**) following literature procedures, as shown in Scheme 2 [27]. The functional *closo*-carborane was decapitated by reacting with potassium hydroxide in ethanol to form an intermediate carboranyl mono anion, *nido*-7,8-bis-(diphenylphosphino)-7,8-$C_2B_9H_{10}$ (**3**) in 64.1% yield. Further deprotonation of compound **3** was accomplished by refluxing with sodium hydride (NaH) in THF, that generated *in situ* the dianionic intermediate, [*nido*-7,8-bis-(diphenylphosphino)-7,8-$C_2B_9H_9$]^2. Ferrous chloride was then reacted with the dianion in THF followed by treating with an aqueous solution of tetrabutylammonium bromide, which led to the formation of the tetrabubutylammonium salt of iron bis(dicarbollide) (**4**) in 53.1% yield. Compound **3** showed the typical absorptions of phenyl and methyl functional groups, as well as the B-H bonds in *nido*-carborane cage in the ^{1}H-NMR spectra (DMSO-d_6). The ^{13}C-NMR spectra exhibited the peaks for phenyl and methyl groups and for carbons of the cage. In ^{11}B-NMR spectra, **3** showed a splitting pattern of 2:3:2:1:1. Compound **4** was analyzed by elemental analysis and FT-IR as described in the experimental section. In FT-IR spectra, strong absorption at 2518 cm^{-1} was observed for both of **3** and **4**, which are attributed to B-H stretching mode of vibrations (ν_{BH}). Polarographic measurements in acetone-water (v/v = 1/:1) were conducted with a 0.1 N $LiClO_4$ supporting electrolyte with use of a dropping mercury electrode. A single-wave reduction polarogram was obtained at $E_{1/}$
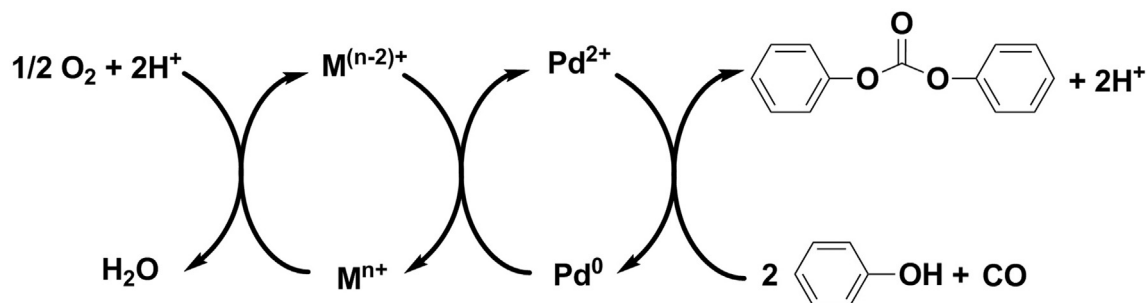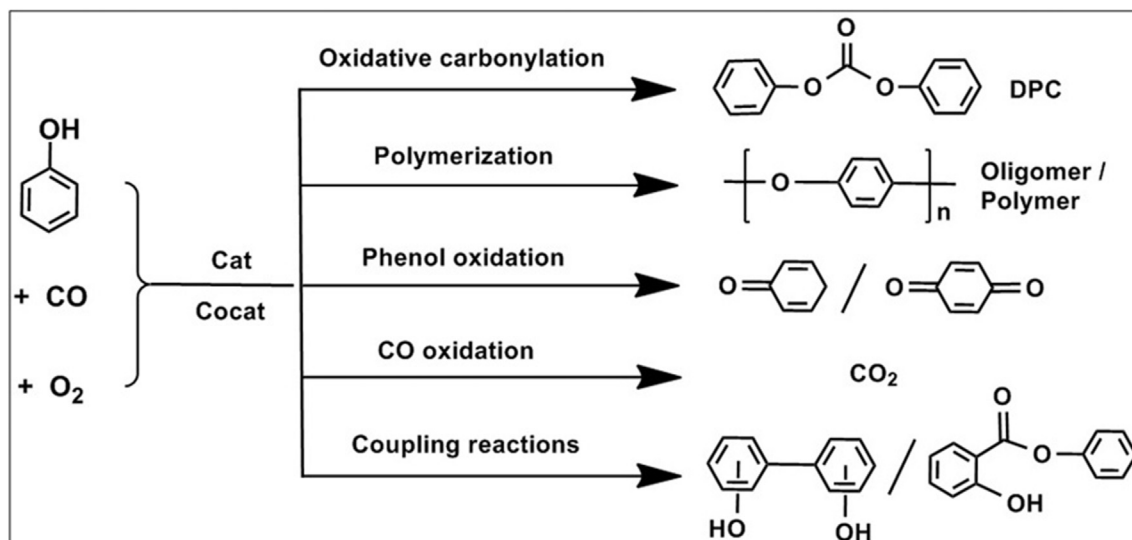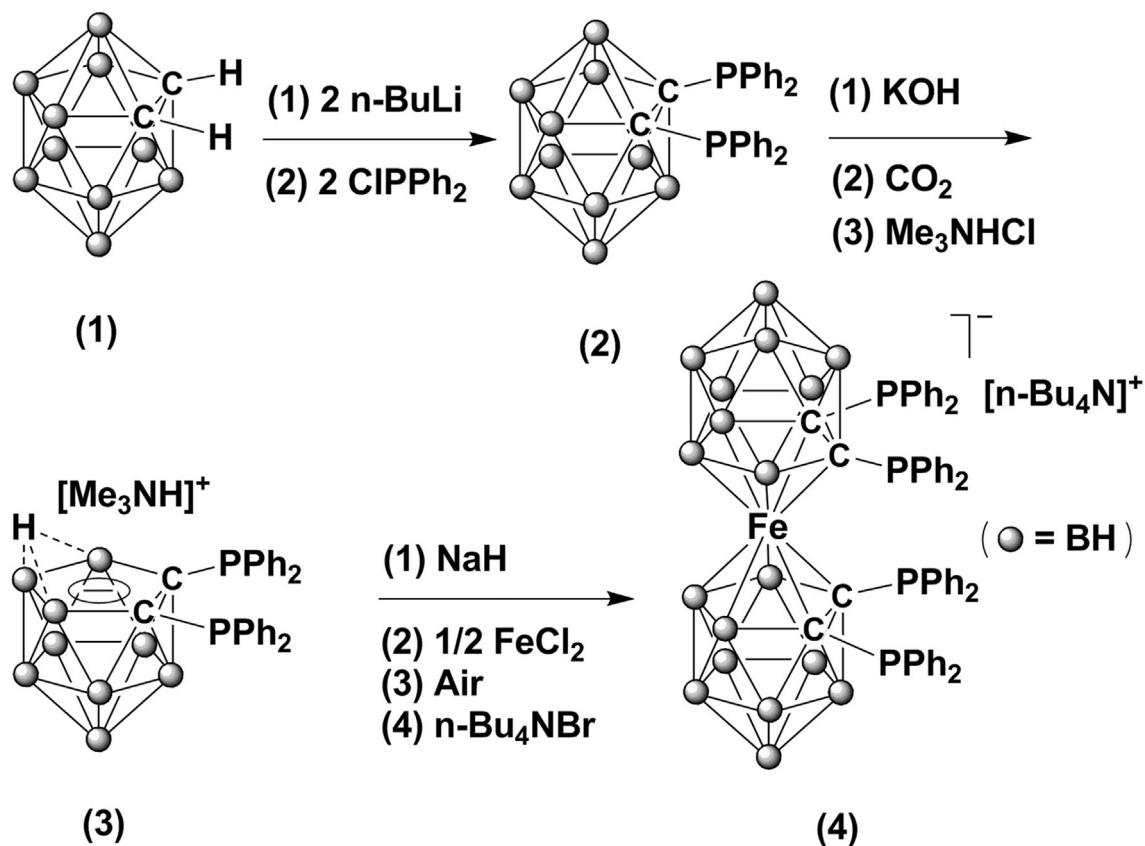

Fig. 1. Proposed mechanism of DPC synthesis.

Scheme 1. By-reactions of oxidative carbonylation.

Scheme 2. Synthesis of the tetrabubutylammonium salt of iron bis(dicarbollide) (4).

$_2 = -0.49$ V and the reduced species being the formal iron (II) derivatives as indicated. The result is consistent with literature observations [25].

Oxidative carboranylation of phenol to produce DPC was carried out in a Parr reactor using acetonitrile as solvent at 110 °C with a volume rate of CO to O_2 of 25/1 in which the CO concentration is below the CO explosion limit [28] in the reaction processes. As per previous results, co-catalyst plays the second important role in the

reaction after the catalyst [12–23]. Therefore, commonly used co-catalysts were investigated and the results are listed in Table 1. The phenol conversion, along with DPC yield and DPC selectivity, were also calculated as following. A typical GC-FID spectrum of the product mixture was shown in Fig. 2. Peaks arising from by-products were observed near the DPC peak and they are labeled. To investigate the by-products of the oxidative carbonylation of PhOH, the product mixture was analyzed by GC-MS (gas

Table 1
Catalyst performance in the semi-continuous model.[a,b]

$$2 \; C_6H_5\text{-OH} + CO + 1/2 \; O_2 \xrightarrow{\text{Cat}} C_6H_5\text{-O-C(=O)-O-}C_6H_5 + H_2O$$

Entry	Catalyst	Co-catalyst	Phenol Conv.(%)	DPC Yield (%)	DPC Sel. (%)	TON
1	PdAc$_2$	Mn(acac)$_3$	24	4	18	175
2	PdAc$_2$	Fe(acac)$_3$	29	2	6	98
3	PdAc$_2$	Co(acac)$_3$	20	3	12	157
4	PdAc$_2$	Ce(acac)$_3$	30	2	6	71
5	–	Mn(acac)$_3$	3	0	0	0
6	PdAc$_2$	4	51	46	89	511
7	PdCl$_2$	4	47	23	49	242
8	PdCl$_2$(MeCN)$_2$	4	44	26	61	357
9	Pd/AC	4	45	9	19	195

[a] Reaction conditions: catalyst loading amounts: [Pd]/[co-catalyst]/[PhOH] = 1:5:1610; PhOH 10.0 g, weight ratio of PhOH/MeCN = 1/4; 4 Å MS: 2.0 g, NaOH: 20 mg, ^{n}Bu$_4$NBr: 170 mg; P_{CO+O_2} = 60 bar (at room temperature), V_{CO}/V_{O_2} = 25:1; reaction temperature 110 °C; reaction time = 4 h.
[b] Yield (%) is determined by GC-FID.
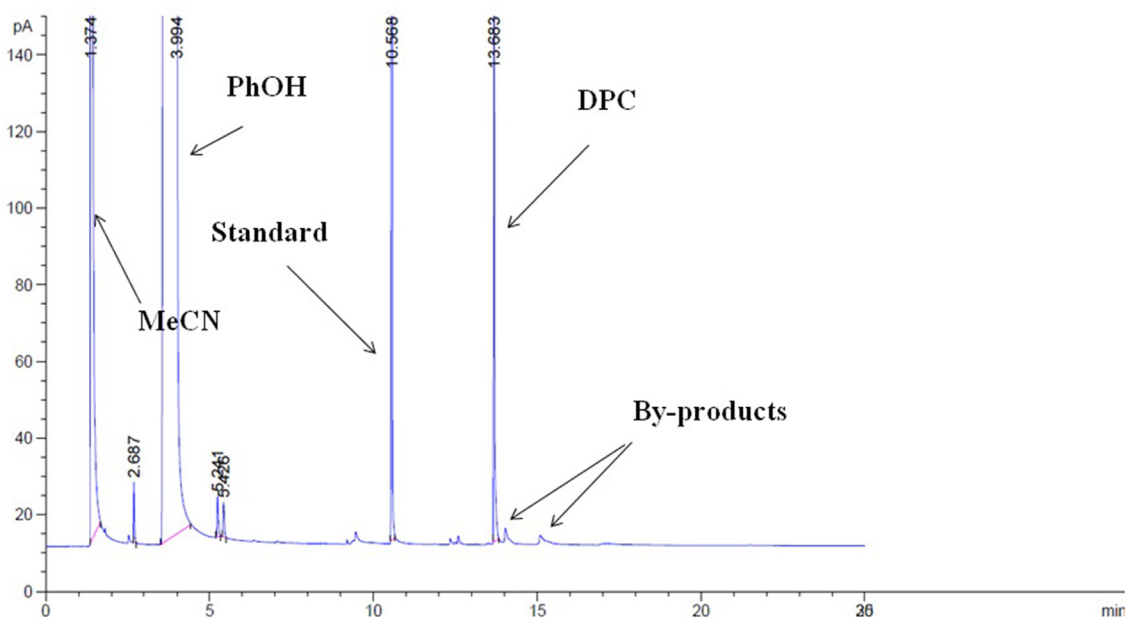
Fig. 2. GC–FID of the product mixture from the oxidative carbonylation reaction.

chromatography-mass spectrometry) and GPC (gel permeation chromatography). The GC-MS and GPC spectra of the reaction mixture are presented in Figs. S-1 and S-2. Based on GC-MS results, compounds formed by O-C and C-C coupling reaction between PhOH are the main by-products. In addition, high molecular weight products (around 966) are observed. They could be generated by multiple cross-coupling reactions within the PhOH substrate.

Phenol conversion = (total amount of phenol consumed) x 100% / (total amount of phenol added)

DPC selectivity = (amount of phenol reacted to produce DPC) x 100% / (total amount of phenol consumed)

DPC yield = phenol conversion x DPC selectivity

TON = moles of DPC / moles of palladium

The co-catalyst, tetrabubutylammonium salt of iron

bis(dicarbollide) is found to be significantly effective for the oxidative carbonylation of phenol to form DPC in comparison with other compounds examined. A fairly high DPC yield of 46% was reached with 89% selectivity. The results further demonstrate that co-catalysts are essential for the reaction under same conditions of temperature and pressure. It is also demonstrated that a PdAc$_2$ catalyst is more active than PdCl$_2$, PdCl$_2$(MeCN)$_2$ and heterogeneous catalyst Pd/C. The real mechanism is not known at this stage. However, considering the homogeneous catalyst, PdAc$_2$ has been well explored in the oxidative carbonylation reaction of phenol, a similar proposed mechanism in Fig. 1 could be applicable for the catalyst composite of PdAc$_2$/[n-Bu$_4$N]{Fe(3,3′)-[1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_9$H$_9$]$_2$}. A study of its mechanism is currently underway in our laboratory.

3. Conclusions

The tetrabubutylammonium salt of iron bis(dicarbollide) has

been synthesized and shown to be an efficient co-catalyst for the oxidative carbonylation of phenol to produce diphenyl carbonate. A good yield of 46% was reached in the presence of a palladium acetate catalyst. Considering the high performance of the co-catalyst, we expect our prototype co-catalyst to find broader applications both in academia and in the fine chemical industry, especially for oxidative reactions.

4. Experimental

All synthetic procedures and operations were carried out in an argon atmosphere using standard Schlenk techniques or a glove box. Organic solvents such as tetrahydrofuran (THF) and hexane were dried using standard procedures and distilled under argon before use [29]. The 1,2-Bis-(diphenylphosphino)-carborane and the trimethylammonium salt of [7,8-bis-(diphenylphosphino)-7,8-dicarba-nido-$C_2B_9H_{10}$]$^-$ were prepared as per the literature procedures [24–27]. *Closo*-1,2-carborane, trimethylammonium chloride, n-butyllithium solution (1.6 M in hexane), diphenylphosphrous chloride, tetrabutylammonium bromide and other chemicals were purchased from Sigma-Aldrich Pte Ltd. ^{1}H, ^{13}C and ^{11}B NMR were recorded on a Bruker Fourier-Transform multinuclear NMR spectrometer at 400, 100.6 and 128.4 MHz, relative to external Me$_4$Si (TMS) and BF$_3$·OEt$_2$ standards. Infrared (IR) spectra were measured using a BIO-RAD spectrophotometer with KBr pellets technique and presented in the sequence of signal strength as strong (s), medium (m) and weak (w), and peak pattern as single (s), multiple (m) and broad (br). Elemental analyses were carried out on a CHNSO Elemental Analyzer. ICP analysis was determined using a VISTA-MPX, CCD Simultaneous ICP-OES analyzer. Product mixtures were analyzed in an Agilent GC (GC-FID).

4.1. Synthesis of complex [Me$_3$NH][nido-7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$] (3)

The literature method was used to prepare the trimethyl-lammonium salt of dicarbadodecahydroundecaborate anion [24–27]. A solution of 0.70 g (12 mmol) of KOH in 25 mL of anhydrous ethanol was added in a 100-mL two-necked round bottom flask equipped with a magnetic stirring bar and a reflux condenser. After the KOH dissolving completely, *closo*-1,2-bis-(diphenylphosphino)-carborane (2.56 g, 5 mmol) was added and resulting mixture was heated to reflux for 10 h until hydrogen evolution ceased. The solution was cooled to room temperature and CO$_2$ gas was bubbled to the solution with continually stirring to precipitate the excess KOH. After filtration to remove the resulting solid and washed with 10 mL of ethanol, the combined filtrate was evaporated under reduced pressure. The crude potassium salt was dissolved in 20 mL of de-ionized water, and treated with an aqueous solution of 0.76 g (8 mmol) Me$_3$HNCl in 10 mL of de-ionized water. The precipitated trimethylammonium salt was isolated by filtration, washed with 5 mL cold water and dried *in vacuo*. The crude product was further purified by re-crystallization from water to obtain pure product [Me$_3$NH] [7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$] 1.80 g in 64.1% yield. Elemental analysis for C$_{29}$H$_{40}$B$_9$NP$_2$: Calculated (%) C 61.99, H 7.18, B 17.32, N 2.49; Found (%) C 62.23, H 7.00, B 17.04, N 2.15 (B was analyzed by ICP analysis). ^{1}H NMR (DMSO-d_6, ppm), δ = 8.91 (s, 1H, N$\underline{H}$), 7.75–7.32(m, br, 20H, 4C$_6$$\underline{H}$$_5$), 2.72 (s, 9H, 3 C$\underline{H}$$_3$), 1.79–1.19 (m, br, 9H, 9B$\underline{H}$), −1.92- -2.31 (br, 1H, bridge B-$\underline{H}$). ^{13}C NMR (DMSO-d_6, ppm), δ = 133.01, 132.98, 130.76, 130.60, 129.55, 129.39 ($\underline{C}$$_6H_5$), 57.16 ($\underline{C}$$_{cage}$), 44.48 ($\underline{C}H_3$-N). ^{11}B NMR (DMSO-$d_6$, ppm), δ = −13.68 (2B, ^{1}J$_{BH}$ = 119 Hz), −16.94 (3B, ^{1}J$_{BH}$ = 163 Hz), −22.21 (2B, ^{1}J$_{BH}$ = 146 Hz), −33.24 (1B, ^{1}J$_{BH}$ = 134 Hz), −37.75 (1B, ^{1}J$_{BH}$ = 142 Hz). ^{31}P NMR (DMSO-d_6, ppm), δ = 20.97. IR (KBr pellet, cm^{-1}), 3384 (w, s), 3055 (m, s), 3021

(m, s), 2959 (w, s), 2518 (vs, s, ν_{BH}), 2340 (m, s), 1975 (w, s), 1922 (w, s), 1824 (w, s), 1590 (m, s), 1482 (s, s), 1438 (vs, s), 1308 (w, s), 1182 (vs, s), 1127 (vs, s), 1069 (w, s), 1024 (w, s), 948 (m, s), 919 (w, s), 744 (m, s), 720 (m, s), 695 (s, s), 553 (m, s), 523 (w, s), 486 (m, s).

4.2. Synthesis of complex [n-Bu$_4$N]{Fe(3,3′)-[1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_9$H$_9$]$_2$} (4)

Compound (4) was synthesized by a modified literature procedure [24–26]. [Me$_3$NH] [nido-7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$] (1.69 g, 3 mmol) was added slowly added to a solution of NaH (0.17 g, 7 mmol) in 30 mL of anhydrous THF. The mixture was heated to reflux for 4 h with continuous stirring. The resulting trimethyl-amine was removed by passing a stream of argon. After reaction, the unreacted NaH was filtered off and the filtrate was added to a stirring suspension of ferrous chloride (0.76 g, 6 mmol) in 16 mL anhydrous THF. The resulting mixture was stirred at room temperature for 1.5 h in argon followed by 1.5 h in air. The solvent was removed in vacuum, and the residue was dissolved in 20 mL of de-ionized water and treated with aqueous tetrabutylammonium chloride (1.45 g, 4.5 mmol). The precipitating red solid was collected and purified by recrystallizing from a mixed solvent of acetone and water (v/v = 2.5:1) to produce 2.07 g (4) in 53.1% yield. Elemental analysis for C$_{68}$H$_{94}$B$_{18}$NP$_4$Fe: Calculated (%) C 62.83, H 7.29, B 14.97, N 1.08, Fe 4.30; Found: C 62.54, H 7.06, B 14.55, N 1.14, Fe 4.10 (B and Fe were analyzed by ICP analysis). IR (KBr pellet, cm^{-1}), 3415 (m, br), 2963 (s, s), 2924 (vs, s), 2854 (s, s), 2518 (s, s, ν_{BH}), 1734 (m, s), 1654 (w, s), 1459 (m, s), 1438 (m, s), 1378 (m, s), 1261 (w, s), 1129 (m, s), 1024 (m, s), 726 (m, s), 695 (m, s), 459 (w, s).

4.3. Procedures of catalytic oxidative carbonylation of phenol

Before conducting a reaction, the reactor was checked for leakage using helium gas. Palladium catalyst (~1mol%), co-catalyst (Mn(acac)$_3$ or Co(acac)$_3$ or Ce(acac)$_3$ or 4), and molecular sieves (2 g) were charged to an autoclave of internal volume 160 mL. Under a He atmosphere, a solution of phenol (5.0 g in 40 g acetonitrile) was charged by syringe. The vessel was then fed with ~57.7 bar of carbon monoxide followed by ~2.3 bar of oxygen. The vessel was heated to 110 °C with constant stirring followed by the work up the reaction after the desired number of hours. The resulting mixtures were analyzed by GC-FID chromatography. The experimental results are summarized in Table 1.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2017.05.040.

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