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Extremely Electron-Rich, Boron-Functionalized, Icosahedral Carborane-Based Phosphinoboranes

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Abstract

We have prepared the first examples of B9-connected trivalent aryl and alkyl phosphinoborane species via Pd-catalyzed phosphination of 9-iodo-*meta*-carborane. Our studies highlight the unique electronic features of the B9-connected *meta*-carboranyl moiety as compared to its C1-based analogue. This work suggests that the B9-functionalized *meta*-carboranyl substituent in these ligands exhibits more electron-releasing character than any other known carbon-based substituent, ultimately laying the foundation for a new class of phosphine ligands with extremely electron-rich character.

Trisubstituted phosphines (PR₃) represent an important class of ligands in modern chemistry largely due to the ease with which their steric and electronic properties can be rationally tuned using various carbon-rich functional groups (R).^{1,2} Yet, the current pool of substituents provides only a finite window for the modulation of the ligand's electronic character.³ Thus, chemistry faces a fundamental challenge in identifying new and robust substituents which would overcome these limitations.

Three-dimensional aromatic icosahedral dicarba-*closo*-dodecaborane clusters (also referred to as carboranes, general formula - C₂B₁₀H₁₂) have been known to exhibit dramatically different electronic effects on the substituents attached to different vertices (for cluster numbering scheme, see SI).⁴ As a consequence of a non-uniform electron distribution and electronegativity differences between boron and carbon, substituents attached at the carbon vertices usually experience a strong electron-withdrawing effect, whereas the substituents on boron atoms located furthest from the carbons experience a strong electron-donating effect. This fundamental property of carboranes was explored by Hawthorne for tuning the Lewis acidity of Hg(I) in mercurocarborand species,⁵ and later by Teixidor and Viñas, who observed that a methyl substituent attached to several boron vertices in these clusters acts as an electron-withdrawing group.⁶ This effect has been somewhat overlooked in the past, resulting in a number of papers incorrectly generalizing the electronic properties of icosahedral carboranes as “electron-withdrawing”.⁷ A recent report suggested that icosahedral carborane substituents could enable electronic tunability of chalcogen-based ligands that is greater in magnitude than with any known carbon-based functional groups.⁸

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ASSOCIATED CONTENT

Supporting Information. Experimental details, crystallographic data (CIF), NMR and IR spectra, and details for computational experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Specifically, by virtue of vertex differentiation one can access ligands that are sterically invariant, yet either extremely electron-poor or electron-rich.⁸ This begs the question whether such tunability can be translated to other heteroatom-based ligands such as phosphines.

To evaluate this hypothesis, access to both C-P and B-P carboranyl-based species is required. While the chemistry of C-functionalized icosahedral carborane-based phosphines is well established,⁹ its B-functionalized counterparts are largely unknown. The only experimental evidence to support the existence for such a species was provided by Bregadze and Kabachnik in 1992,¹⁰ who reported the syntheses of B9-functionalized *meta*- and *ortho*-carboranyl species (C₂B₁₀H₁₁-PCl₂) in 5 and 10% yields, respectively, upon UV photolysis of mercury carboranyl complexes and phosphorous trichloride. We envisioned that transition metal-catalyzed cross-coupling would provide a suitable route to phosphorous-functionalized B-based phosphinocarborane derivatives. Recent work by Hawthorne, for example, utilized large, electron-rich phosphine ligands capable of supporting active Pd(0)/Pd(II) catalytic species in a facile catalytic amidation of B-iodocarboranes,¹¹ wherein difficulties associated with the oxidative addition of the B-I moiety could be circumvented by judicious choice of the ligand.

In order to access B-functionalized phosphines, we utilized a modified Pd-catalyzed protocol used previously for phosphination of aryl halides.¹²

Upon heating 9-iodo-*meta*-carborane (**2**, Figure 1A, synthesized in a manner analogous to the one reported by the Jones and Hawthorne groups¹³) with diphenylphosphine in toluene at 120 °C in the presence of Pd₂dba₃/DIPPF (6 mol %/12 mol % ratio; dba – dibenzylideneacetone, DIPPF – 1,1'-bis(di-isopropylphosphino)ferrocene) catalyst and Cs₂CO₃, we observed the formation of a new species via *in situ* ³¹P NMR spectroscopy (Figure 1).¹⁴

A broad signal resembling a quartet ($J_{P-B} = 58$ Hz) suggested that a B-P bond was likely formed (see SI). After prolonged heating of this reaction mixture for 36 hours, complete consumption of the phosphine starting material was observed (³¹P NMR). Subsequent work-up and purification of the reaction mixture yielded a crystalline substance, which was subjected to a full NMR spectroscopic analysis. In particular, the ¹¹B NMR spectrum of **3a** exhibits the characteristic pattern of the B9-substituted *meta*-carborane cluster (Figure 1B), where the signal at ca. δ –3 displays no coupling to the proton and integrates 1:9 to the rest of the resonances in the spectrum. A definitive structural confirmation for **3a** was established using single crystal X-ray diffraction. The solid-state structure of **3a** features a trivalent phosphorous center connected to two carbon atoms on the phenyl rings and a B9 atom of the *meta*-carboranyl moiety (Figure 1D). While considering the previously studied phosphinoboranes by Nöth and Power, we found that the B-P bond length in **3a** (1.948 Å) best corresponds to the presence of a purely single bond interaction between the B and P atoms.¹⁴ This interaction is also reminiscent of the diphenylphosphineborabenzene species described by Fu,^{14c} where delocalization of the LUMO orbital on the B atom renders π-donation from the P atom-centered lone electron pair unfavorable. Importantly, **3a** was found to be stable both in solution and as a solid under ambient conditions for several weeks.

Drastic differences between **3a** and **3a'** (C1-based analog of **3a**,¹⁵ see SI and Figure 2) were observed upon reaction with Pt(COD)Cl₂ (COD – 1,4-cyclooctadiene) under similar conditions. Stirring one or two equivalents of **3a** and Pt(COD)Cl₂ in dichloromethane resulted in a mixture of Pt(II) bis-phosphine complexes **4a** and **4b** (Figure 2 and SI).

On the other hand, no coordination of **3a'** was observed to the Pt(II) precursor (Figure 2C). Prolonged reaction times (3 days) or using an excess of **3a'** (3 eq.) resulted in no conversion. Given that ligands **3a** and **3a'** are isosteric, the observed differences in chemical reactivity can most reasonably be attributed to the electronic influences of B9- and C1-functionalized *meta*-carboranyl moieties. Indeed, Natural Bond Orbital (NBO) analysis of the optimized structures of **3a** and **3a'** further corroborate on the drastic differences in partial charges and lone pair energies located on the phosphorous atoms of these ligands, showing that **3a** is significantly more electron-rich and therefore reactive (see SI, Section 3). In total, these observations are consistent with recent work on carborane-based ligands featuring sulfur and selenium atoms on B9 and C1 vertices of the *meta*-carboranyl cluster (*vide supra*).

Using the developed synthetic protocol, we were able to cross-couple **2** with four electron-rich secondary phosphines, thus obtaining alkyl-based phosphinoboranes **3b–3e** (Figure 3A and SI). Attempts to cross-couple ^tBu₂PH using these conditions did not provide any phosphinoborane product. This is likely due to the size of ^tBu₂PH, ultimately rendering the transmetallation step inefficient. Due to difficulties separating the DIPPF ligand from the target phosphinoboranes on silica gel, **3b–3d** mixtures were converted to their BH₃ adducts and purified by recrystallization, yielding pure **5b–5d**. In all cases, a characteristic shift of approximately 25–37 ppm in the ³¹P NMR spectra was observed, consistent with the formation of borane-based adducts (Figure 3B and SI).

The ¹¹B NMR spectra of **5b–5d** revealed characteristic ¹¹BH₃ resonances at ca. δ 38–41 (Figure 3C and SI), which integrate to a 1:10 ratio to the corresponding borane regions of the *meta*-carboranyl moieties. Relatively small values for coordination chemical shifts (ccs) observed from ³¹P NMR spectra of these species compared to their free phosphine analogues (+25–37 ppm) is consistent with the ccs values reported for other bulky phosphine-BH₃ adducts.¹⁶ Borane adducts **5b–5d**, were found to be bench stable both in solution and in the solid-state. This observed stability is in contrast to several previously reported phosphineborane-BH₃ species, wherein scrambling of a BH₃ and a boryl moieties *via* hydride transfer occurred, ultimately resulting in the decomposition of the parent species.¹⁷ This further reinforces the notion that the *meta*-carboranyl boryl moiety serves as an innocent substituent and is chemically more stable than many previously studied boryl systems. Upon reacting **5b–5d** with an excess of the weakly nucleophilic base (1,4-diazabicyclo[2.2.2]octane - DABCO) for 18 hours in THF at 70 °C, we observed nearly quantitative conversion of the parent borane species to the free phosphine species **3b–3d** via *in situ* ³¹P NMR. These substances were then purified via flash column chromatography on silica gel, yielding the pure phosphine. Overall, phosphinoborane species **3b–3e** were found to be stable enough to be manipulated at ambient conditions without noticeable oxidation. All other characterization data for **3b–3e** are consistent with the proposed structural formulations (see SI).

Density Functional Theory (DFT) calculations on the geometry-optimized structures of **3b–3e** suggest that these species are more electron-rich than any other known alkyl-based phosphine ligands (*vide supra* and SI). To experimentally determine the electronic properties of **3a–3e**, we synthesized *trans*-Rh(PR₃)₂COCl complexes, bearing the carbonyl (CO) ligand as a spectroscopic handle. The infrared (IR) carbonyl stretching frequency was previously shown to correlate extremely well with the electronic properties of the phosphine ligands in this type of Rh(I) complex.¹⁸ Reacting ligands **3a–3e** with the Rh(I) precursor in CH₂Cl₂ resulted in a quantitative formation of **6a–6e** as observed by *in situ* ³¹P NMR (Figure 4).

Single crystals grown from solutions of **6a** and **6b** further confirmed our structural assignment for these species through X-ray diffraction studies. Notably, for **6b** we observed an extremely short Rh-C bond (1.717 Å) and an elongated Rh-Cl (2.456 Å) interaction (for

comparison, in *trans*-Rh(PCy₃)₂COCl, the Rh-C bond is 1.748 Å and Rh-Cl – 2.388 Å),¹⁸ suggesting that phosphine **3b** is more electron-rich than PCy₃. Finally, the IR spectroscopic data for ν[CO] in complexes **6a–6e** provide strong evidence supporting our computational analyses (Figure 4B). We found that, ν[CO] in species **6b–6e** are consistently lower than in any other known *trans*-Rh(PR₃)₂COCl complexes (the lowest value reported to date is at 1943 cm⁻¹ for PCy₃).¹⁸ Significantly, ν[CO] of 1981 cm⁻¹ in **6a'** indicates that ligand **3a'** is drastically less electron rich than its B9-connected analog - **3a**. Thus crystallographic and IR spectroscopy data obtained for Rh(I) complexes bearing ligands **3b–3e** suggest that these phosphinoborane species are more electron-rich than any known trivalent phosphine species containing only carbon-rich substituents.

In conclusion, we have discovered a new class of stable and extremely electron-rich phosphinoboranes featuring the B9-functionalized *meta*-carboranyl substituent. Consistent with the recent study on carboranyl thioether and selenol ligands,⁸ we observe that the B9-based *meta*-carboranyl moiety exhibits more electron-releasing character than any carbon-based substituent and thus can potentially provide chemists with a new approach to overcome the fundamental electronic property limitations associated with carbon-based substituents pertaining to ligand design. The phosphinoboranes reported herein can also be potentially interesting molecules to explore in the context of transition metal-based¹ and – free¹⁹ catalysis.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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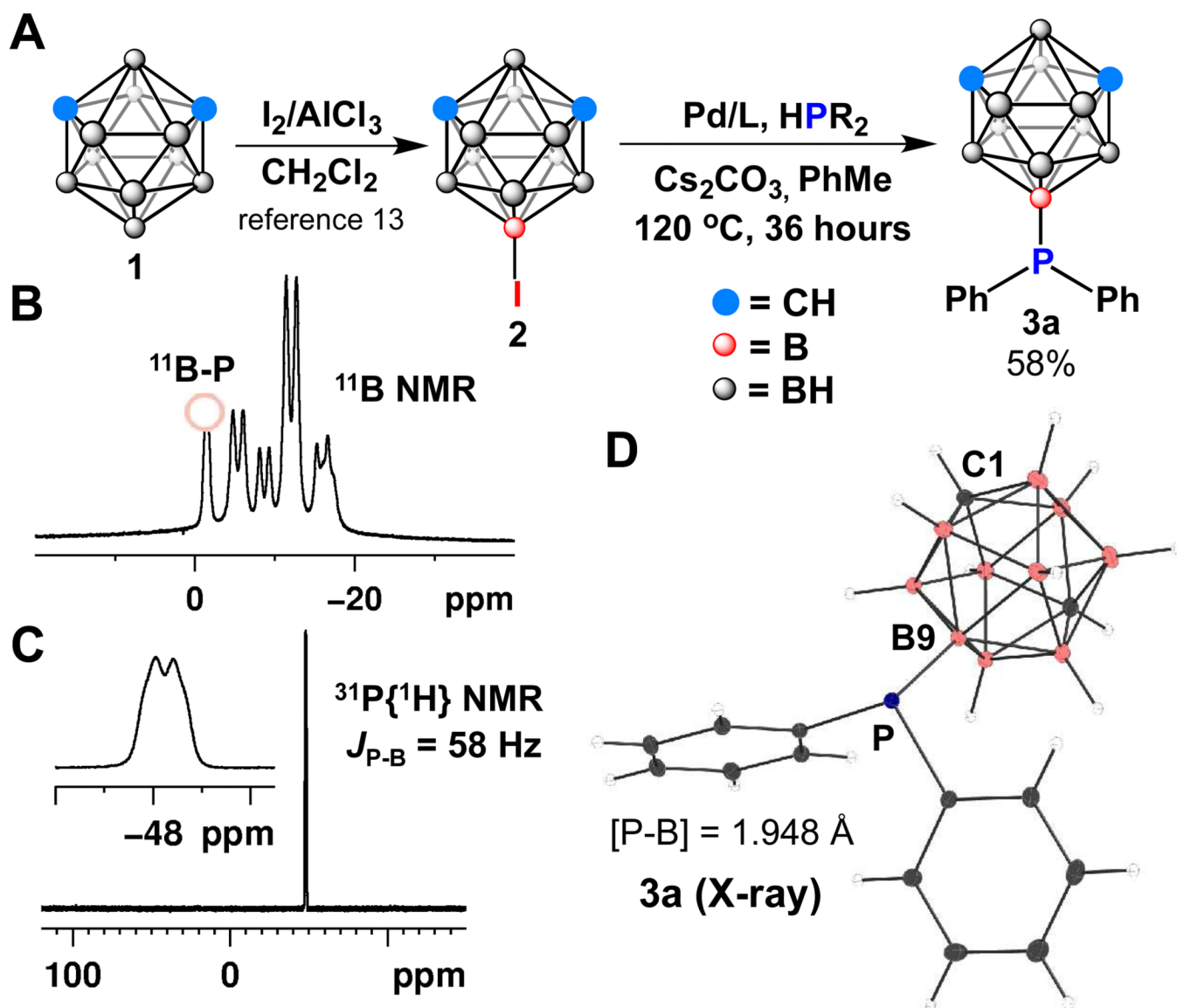


Figure 1. (A) Synthesis and (B, C) selected spectroscopic data for B9-functionalized 9-*meta*-carboranyl phosphine species **3a** (R=Ph). (D) Crystallographically derived molecular structure of **3a** depicted with 50% thermal ellipsoid probabilities.

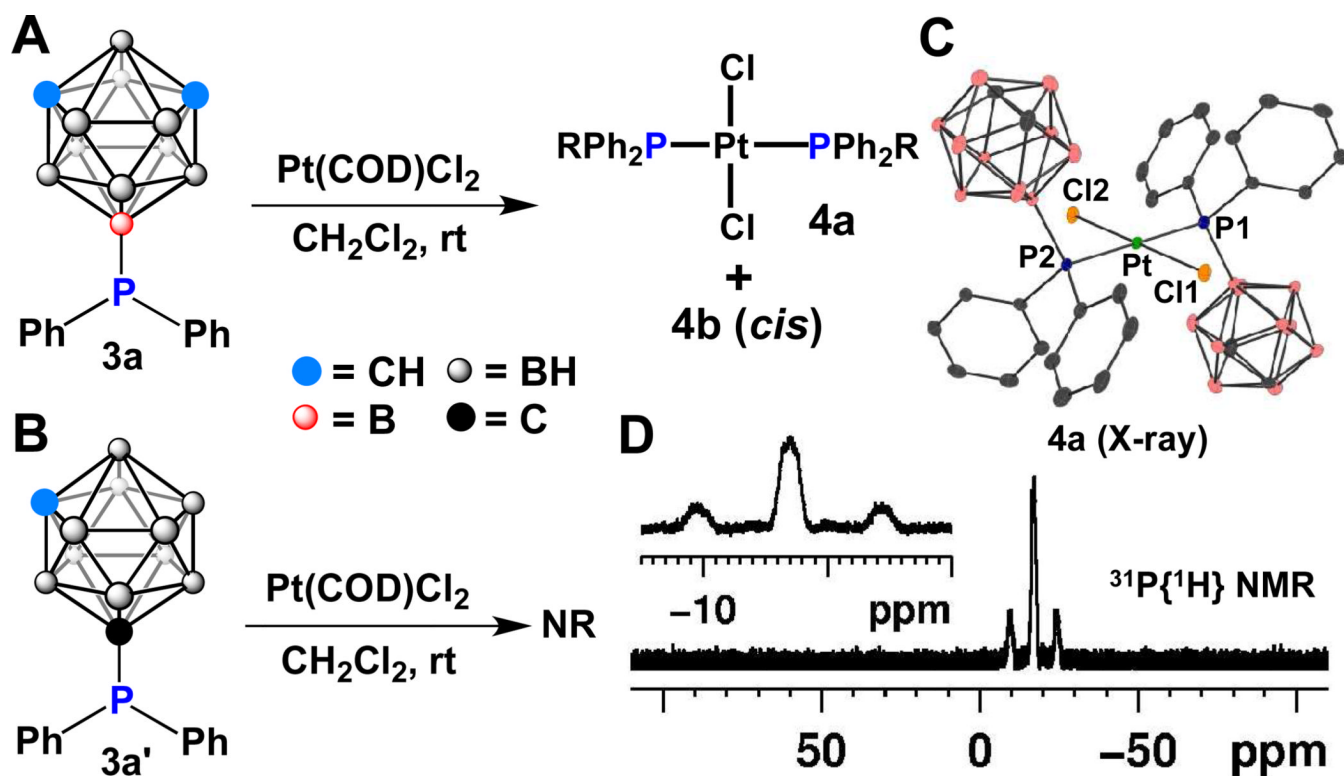


Figure 2. (A, B) Comparison of the reactivity of ligands **3a** and **3a'** with $\text{Pt}(\text{COD})\text{Cl}_2$. (C) Crystallographically derived molecular structure of **4a** depicted with 50% thermal ellipsoid probabilities (H atoms omitted for clarity). (D) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4a**.

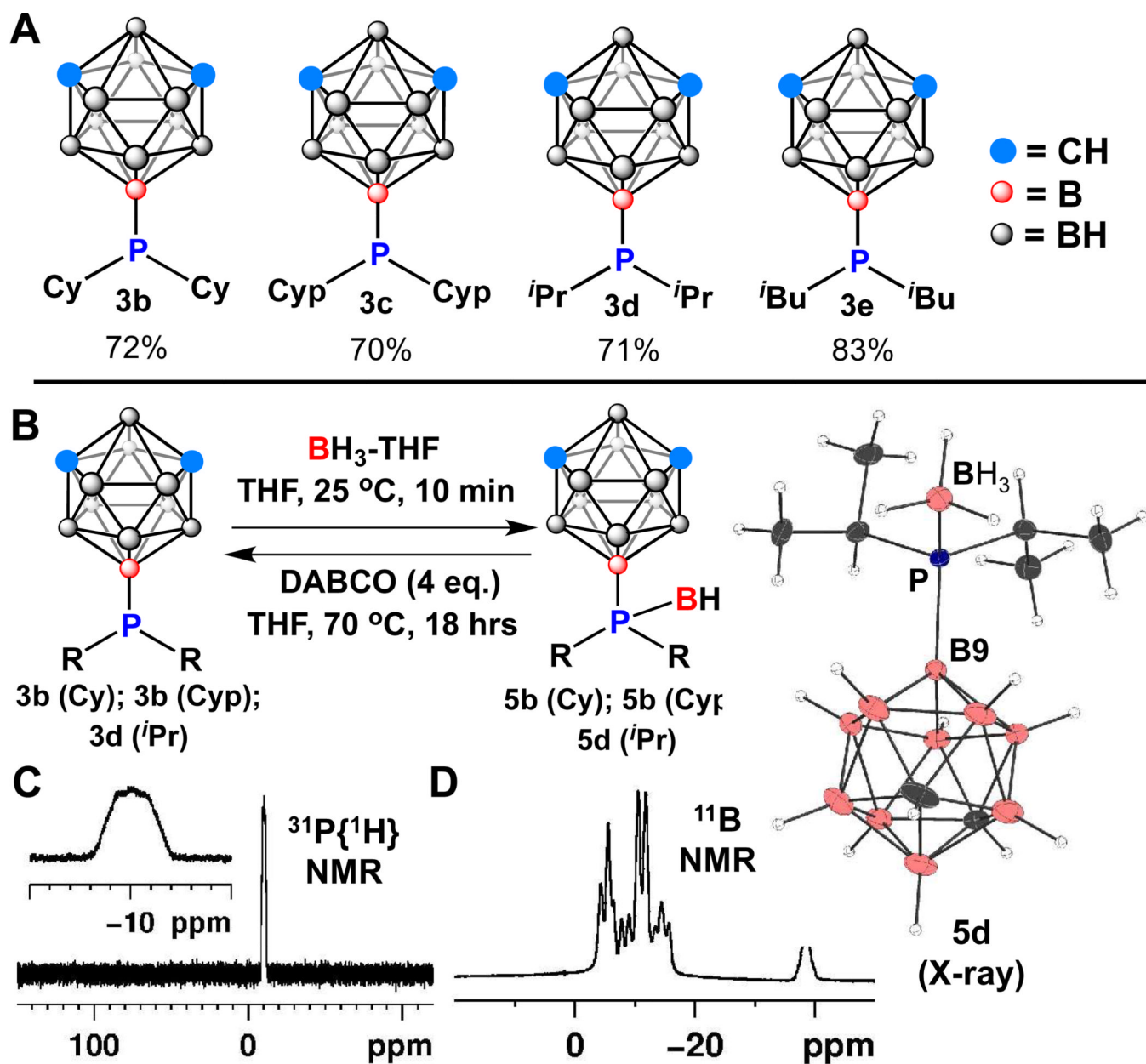


Figure 3. (A) Synthesized alkyl-based phosphinoboranes (**3b–3e**). For all compounds (except for **3e**), the yield is calculated based the combination of protection/deprotection steps. (B) Syntheses of *m*-carborane-based phosphinoborane-BH₃ adducts and their subsequent deprotection. (C–D) Selected NMR spectroscopic data for **5d**. (E) Crystallographically derived molecular structure of **5d** depicted with 50% thermal ellipsoid probabilities.

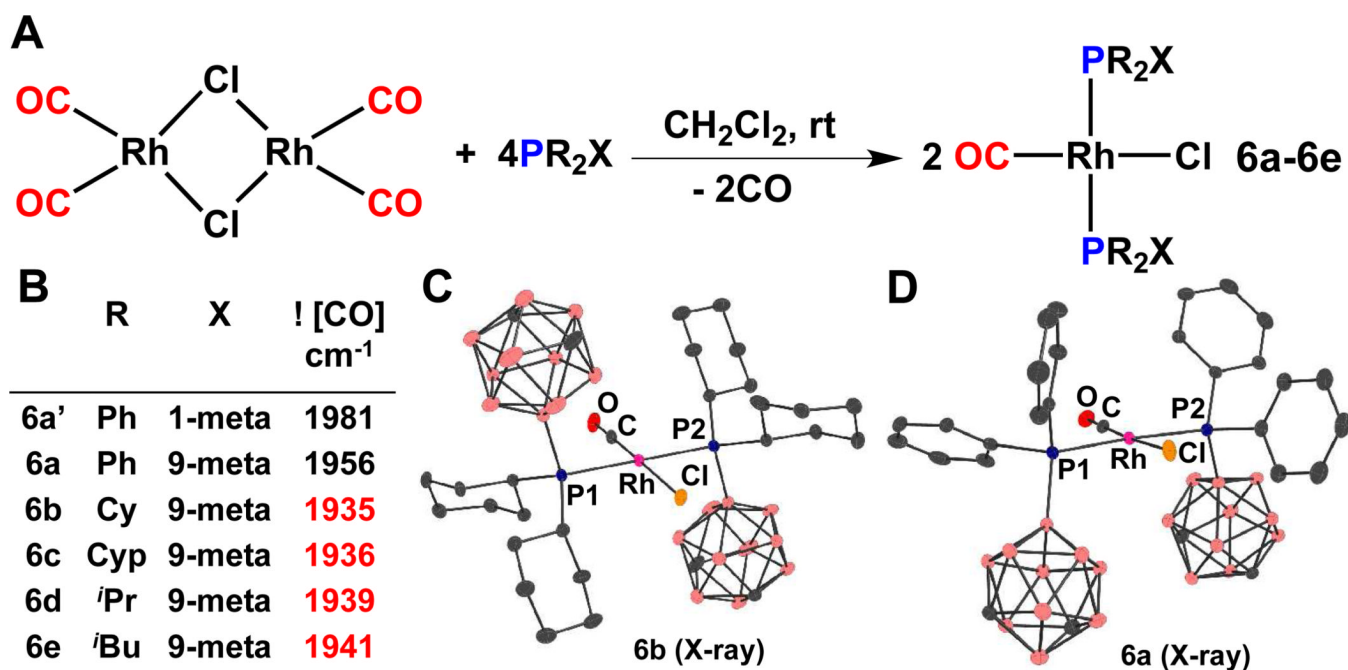


Figure 4. (A) Syntheses of Rh(I) complexes bearing *m*-carborane-based phosphinoborane ligands. (B) IR spectroscopic data for carbonyl stretches $\nu[\text{CO}]$ in **6a–6e**. (C, D) Crystallographically derived molecular structures of **6b** and **6a** depicted with 50% thermal ellipsoid probabilities (H atoms are omitted for clarity).