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Synthesis of a Hybrid *m*-Terphenyl/*o*-Carborane Building Block: Applications in Phosphine Ligand Design

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Supporting Information

ABSTRACT: A hybrid terphenyl/*o*-carborane ligand building block is synthesized by the reaction of *m*-terphenylalkyne with $B_{10}H_{14}$. This sterically demanding substituent can be installed into ligands, as demonstrated by the preparation of carboranylphosphine. The bulky phosphine reacts with $[ClRh(CO)_2]_2$ to produce monophosphine complex $ClRhL(CO)_2$, which subsequently extrudes CO under vacuum to afford the dimeric species $[ClRhL(CO)]_2$. The latter complex does not react with excess phosphine and is resistant toward cyclometalation, which is in contrast to related *o*-carborane phosphine complexes. Data from a single-crystal X-ray diffraction study are utilized to quantify the steric impact of the ligand via the percent buried volume approach.

Bulky hydrocarbon substituents are key components in ligand design. Sterically demanding groups both favor the formation of low-coordinate species and kinetically protect reactive metal centers. Low-coordinate transition-metal complexes are of practical importance because of their prominent role in catalysis and the formation of M−M multiply bonded species. One of the bulkiest ligand substituent families is derivatives of the *m*-terphenyl **1** (Figure 1, top left). The coordinating atom or group is typically attached at position A[1] or B[2] on the central terphenyl aromatic ring. Alternatively, as exemplified by the elegant work of Power and co-workers,[3] the terphenyl itself can be used as a massive X-type ligand when coordinated directly to a metal center at position B.

Interesting alternatives to bulky hydrocarbon groups are the carborane and boron cluster compounds.[4] Because of their unusual electronic structure and distinct polyhedral geometries, these ligand substituents produce unique coordination environments.[4a,b] Particular progress has been made in the design of carboranylphosphine ligands[5] and, more recently, N-heterocyclic carbenes (NHCs).[6] Most investigations have focused on the utilization of icosahedral dicarbaborane clusters (C_2B_{10}) or anionic nido derivatives ($C_2B_9^{-1}$) as hydrocarbon surrogates.[4a,b] Because of their accessibility,[7] derivatives of the *o*-carborane **2** are most often implemented in ligand design (Figure 1, top right). *o*-Carborane clusters can be assembled by the reaction of functionalized alkynes with decaborane ($B_{10}H_{14}$).[7] We envisioned utilizing this reaction methodology to couple a substituted *m*-terphenyl **1** with an *o*-carborane motif **2** to create a superbulky ligand building block (Figure 1). Here we report the synthesis of such a hybrid *m*-terphenyl/*o*-carborane architecture, its derivatization to a phosphine ligand, and subsequent coordination chemistry with rhodium(I).

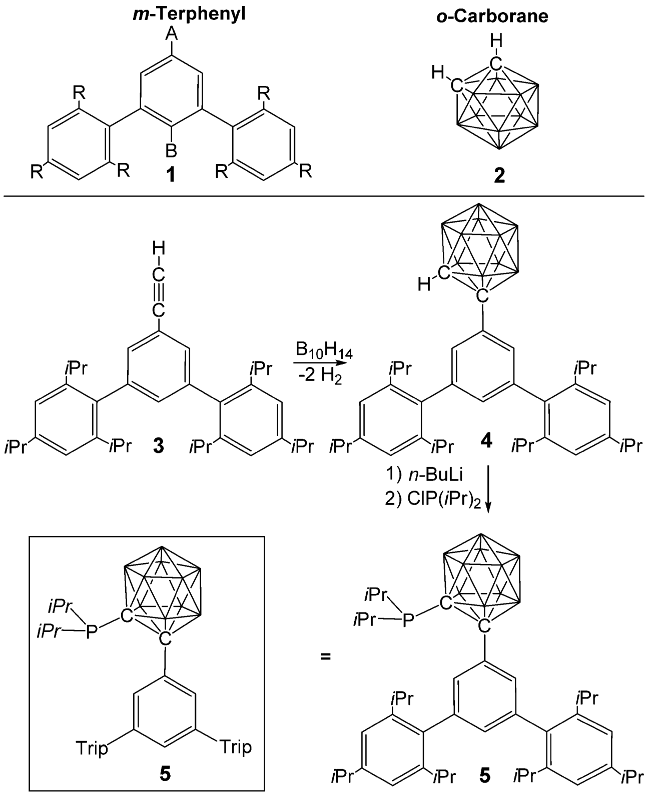

Figure 1. Representations of *m*-terphenyl **1** and *o*-carborane **2** (top). Synthesis of the hybrid *m*-terphenyl/*o*-carborane building block **4** and its derivatization to a phosphine ligand **5** (bottom). Unlabeled carborane vertices = B−H.

As a starting *m*-terphenylalkyne, we chose the triisopropylphenyl-substituted derivative **3**, whose isopropyl resonances provide a convenient NMR signature (Figure 1, bottom). Installation of the alkyne moiety at position A on the *m*-terphenyl was strategically chosen to project the massive aromatic ring system in the coordination sphere of subsequent transition-metal complexes, vide infra. The novel alkyne **3** is readily prepared from the corresponding bromo-*m*-terphenyl[1a] via Sonogashira coupling (see the Supporting Information for details). The

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subsequent reaction of **3** with $B_{10}H_{14}$ in acetonitrile affords the corresponding hybrid *m*-terphenyl/*o*-carborane **4** in 75% yield. Deprotonation of the C−H vertex of **4** with *n*-butyllithium, followed by the reaction with $ClP(iPr)_2$ affords the corresponding air-stable phosphine **5**.

We next turned our attention to the coordinative ability of ligand **5** with rhodium(I). The carbonyl complex $[ClRh(CO)_2]_2$ was chosen as a starting material because IR analysis of the CO stretching frequencies of the ensuing complex would provide insight into the donor ability of the ligand. The reaction of ligand **5** with $[ClRh(CO)_2]_2$ at 60 °C very slowly (6 days) produces the corresponding *cis*-dicarbonyl complex **6** (Figure 2), as confirmed by multinuclear NMR (^{31}P, $\delta = 88.4$ ppm, d, $^{1}J_{Rh,P} = 190.5$ Hz) and IR [$\nu(CO) = 2089$ and $2022\ cm^{-1}$] analysis. Complex **6** is stable in solution but extrudes CO under vacuum to produce the monocarbonyl chloro-bridged dimer **7**, as indicated by multinuclear NMR (^{31}P, $\delta = 96.7$ ppm, d, $^{1}J_{Rh,P} = 194.3$ Hz) and IR [$\nu(CO) = 1987\ cm^{-1}$] analysis. Bubbling CO through a solution of **7** reforms **6**, which indicates that the process is reversible. Comparison of the CO stretching frequencies of **6** with reported analogous $ClRhL(CO)_2$ species supported by $P(tBu)_3$ [$\nu(CO) = 1960\ cm^{-1}$][8] and PPh_3 [$\nu(CO) = 1979\ cm^{-1}$][9] shows that ligand **5** is a relatively poor electron donor. This observation is in agreement with Röhrscheid and Holm's[5b] and Teixidor et al.'s[5m,n] reports, which demonstrate that *o*-carborane acts as a strong electron-withdrawing group when bound to phosphines by the carbon vertex.

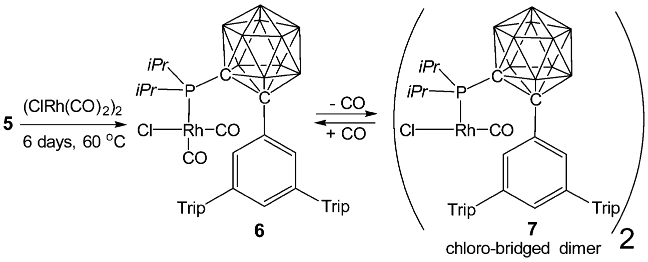

Figure 2. Synthesis of complexes **6** and **7**. Unlabeled carborane vertices = B−H.

Many classical phosphines behave similarly to **5** to produce analogous dimeric $[ClRhL(CO)]_2$ species.[9] Such complexes readily react with an additional phosphine ligand to produce $ClRhL_2(CO)$ species. What is unusual in this case is that the addition of excess (5 equiv, 60 °C, 24 h) phosphine ligand **5** to **7** does not result in the formation of a diphosphine adduct, as indicated by ^{31}P NMR and IR spectroscopy. Additionally, in contrast to related $[ClRhL(CO)]_2$ complexes containing *o*-carborane phosphines that feature an unsubstituted C−H vertex,[5i] **7** is indefinitely stable in solution and does not undergo decomposition by B−H cyclometalation. The resistance of **7** toward additional phosphine coordination and cyclometalation is likely due to the steric influence of the *m*-terphenyl substituent.

To gain insight into the steric parameters of ligand **5**, we carried out a single-crystal X-ray diffraction study of complex **7** (Figure 3). In the solid state, the *m*-terphenyl substituents are projected above and below each of the square-planar rhodium centers (Figure 3, top). The geometric parameters of each half of the dimer are essentially identical; thus, a simplifed view of **7** is provided for further discussion (Figure 3, bottom). The Rh−P−C1−C2 dihedral angle is 47.7(5)°, which skews the *m*-terphenyl group to the side of the square plane containing the carbonyl substituent. This observation reveals that the P−C1 bond can rotate to some extent even with the presence of two gearing P−*i*Pr groups that direct the *m*-terphenyl substituent toward the metal center. While the unusual shape of the ligand renders the cone angle description of the steric parameter uninstructive, the percent buried volume (% V_{bur}) approach[10] provides a better gauge of the steric impact of this ligand. In the observed conformation, % V_{bur} of ligand **5** in complex **7** is 45.7%. Comparatively, % V_{bur} for uncoordinated $P(iPr)_3$ is 37.6%.[10] This means that replacement of a single *i*Pr substituent of $P(iPr)_3$ with the *m*-terphenyl/*o*-carborane substituent leads to an increase in % V_{bur} of at least 8.1%. When % V_{bur} of ligand **5** in complex **7** is calculated with the Rh−P−C1−C2 torsional angle set to 0°, which rotates the central benzene ring of the *m*-terphenyl group directly underneath the square-planar rhodium atom, a significant increase in steric impact is observed (% $V_{bur} = 52.1$). On the basis of the symmetry of the ^{1}H NMR spectra of **7**, this is a likely conformation in solution because the *m*-terphenyl substituent swings back and forth underneath the rhodium square plane (via partial P−C1 rotation). Therefore, the actual steric effect resulting from *i*Pr substitution by the *m*-terphenyl/*o*-carborane substituent is an increase of +8.1−14.5% V_{bur}, depending on the conformation adopted in solution.

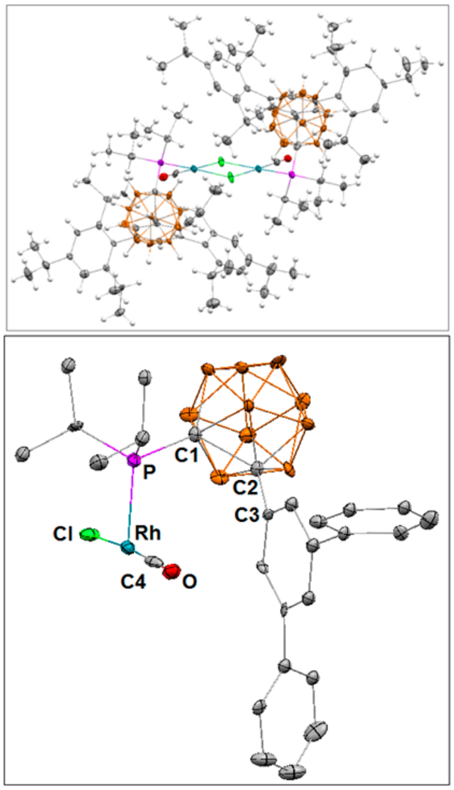

Figure 3. Full molecular structure of complex **7** (top). Simplified view of half of dimer **7** (bottom; hydrogen atoms and Trip isopropyl groups are omitted for clarity). Thermal ellipsoids drawn at the 50% probability level. Color code: C, gray; B, brown; O, red; H, white; P, violet; Rh, blue; Cl, green. Selected bond lengths (Å; average from both halves of the dimer): P−Rh = 2.2297(19), P−C1 = 1.895(9), C1−C2 = 1.775(10), C2−C3 = 1.513(10), Rh−C4 = 1.785(8), C4−O = 1.156(8).

■ CONCLUSION

The results described above demonstrate the facile and efficient synthesis of a hybrid *m*-terphenyl/*o*-carborane ligand building block. Its utility as a sterically demanding ligand substituent is demonstrated by the preparation of phosphine **5** and subsequent reaction with $[ClRh(CO)_2]_2$. The carborane substituent bestows unusual stability to the ensuing chloro-bridged dimer **7**, as shown by its unreactivity with additional phosphine and resistance to B−H cyclometalation. Because the synthesis of ligand **5** is modular, it should be possible to further increase its steric profile by installing bulkier alkyl or aryl substituents at phosphorus or perhaps appending phosphorus with two *m*-terphenyl/*o*-carborane substituents. We are currently investigating this possibility as well as designing nitrogen- and carbon-based ligands for applications in catalysis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, spectroscopic data, and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. These authors contributed equally.

Notes

The authors declare no competing financial interest.

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