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Iridium PC(sp^3)P Pincer Complexes with Hemilabile Pendant Arms: Synthesis, Characterization, and Catalytic Activity

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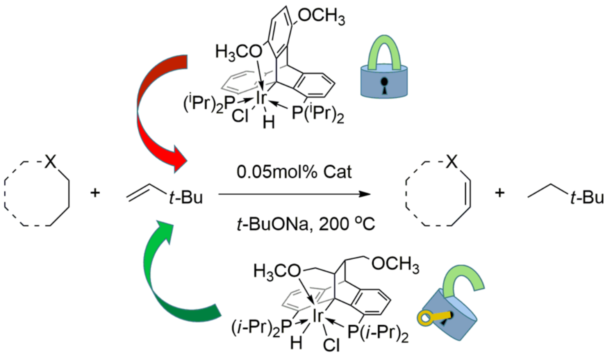
Supporting Information

ABSTRACT: A series of new PC(sp^3)P pincer ligands possessing hemilabile alkoxyl side arms as well as their iridium complexes are reported. All new organometallic compounds were structurally characterized including X-ray analysis. The hemilability of the side arms was probed by reactions with CO, revealing the reversible coordination. The catalytic activity of the new complexes was tested by iridium-catalyzed transfer dehydrogenation of alkanes under mild conditions.



INTRODUCTION

Multifunctional ligands responsible for secondary catalyst−substrate interactions play an increasingly important role in contemporary catalysis. Such ligands can be used to fine-tune the reactivity of the corresponding transition metal catalysts and enhance their performance in terms of efficiency and selectivity.[1]

Some time ago, we introduced a family of dibenzobarrelene-based pincer ligand systems for various applications in homogeneous and heterogeneous catalysis directed toward organic synthesis.[2] This ligand class, prototyped by the simplest triptycene derivative (Figure 1, top left), was initially developed to popularize aliphatic pincer complexes[3] by offering a modular, yet structurally and conformationally stable, platform for the synthesis of robust C(sp^3)-metalated compounds.[4] However, later, we also revealed some interesting properties of complexes bearing pincer ligands crafted with various functional groups (Figure 1, top center and right). Some functional groups exhibited the ability to coordinate the proximate metal center, thus inducing reversible bond activation/bond formation processes (Figure 1, bottom).[5]

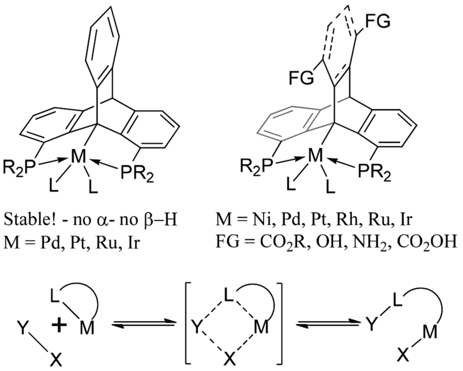


Figure 1. Previously reported and new C(sp^3)-metalated compounds.

In some cases (depending on the nature of the functional group), the additional intramolecular coordination may result in the formation of thermodynamically overly stable (i.e., chemically inert) species, prompting us to investigate ligands possessing more loosely coordinating donors. The presence of a hemilabile coordinating site in a ligand may lead to a marked change in the organometallic behavior and catalytic activity of the corresponding transition metal complex, for example, significantly influencing the reactivity of incoming substrates and the rates of elementary reactions.[1i,6]

Here, we will describe the structural modification of a previously reported ligand, enabling hemilabile coordination with iridium, and its influence on the reactivity of the respective metal complexes.

RESULTS AND DISCUSSION

Synthesis, Structure, and Reactivity. The PC(sp^3)P scaffold was modified using the previously reported hydroxyl-functionalized 1,8-dibromotriptycene (**1**), which can be prepared on a large scale from readily available starting materials in two steps, in >80% yield overall.[7] Three derivatives possessing alkoxyl groups having a different steric bulk (R = methyl, methoxymethylene, and *i*-propyl) were prepared with good yield (**2**−**4**). Subsequently, these precursors were reacted with an *n*-BuLi/TMEDA complex in THF, followed by the addition of *i*-Pr_2PCl, forming the substituted bis(diisopropyl-

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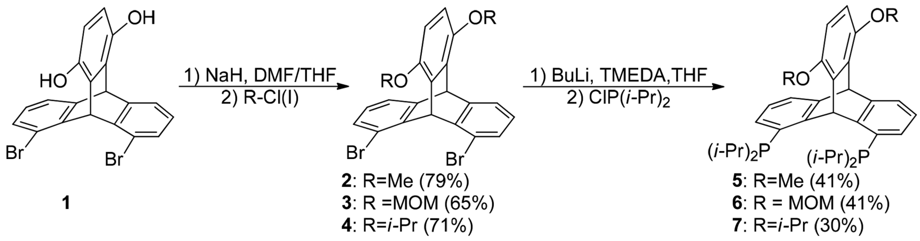
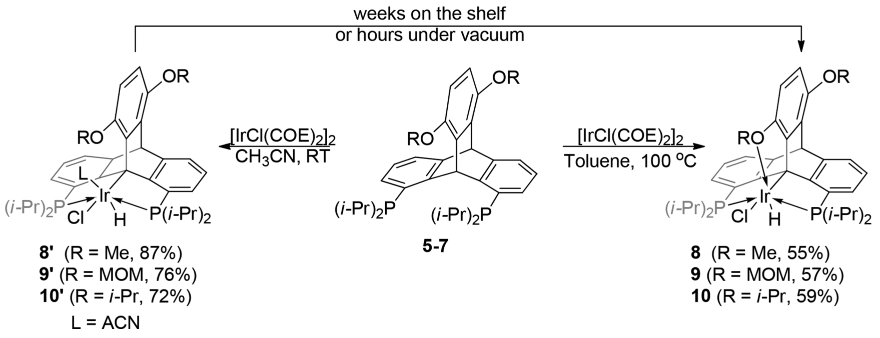
Scheme 1. Synthesis of Ligands 5−7



Scheme 2. Metalation of 5−7 with $[IrCl(COE)_2]_2$ and Coordination



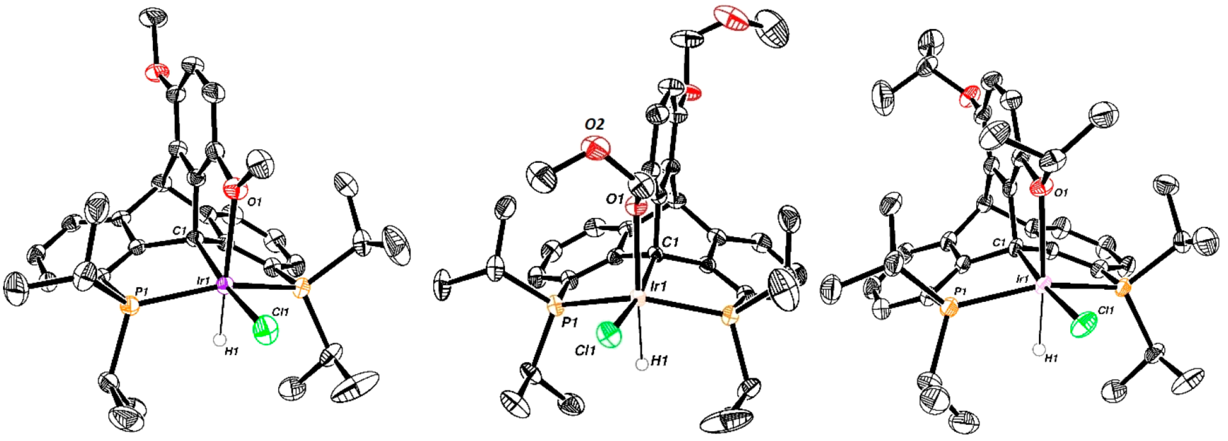


Figure 2. Thermal ellipsoid (50% probability level) representation of **8**−**10**. Most hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg) for **8**: Ir−C(1) 2.044(2), Ir−O(1) 2.3871(17), Ir−P(1) 2.3031(6), Ir−P(2) 2.3022(6), Ir−Cl 2.4603(6), Ir−H(1) 1.56(4); P(1)−Ir−P(2) 152.23(2), C(1)−Ir−Cl 168.63(6), O(1)−Ir−H(1) 172.9(13). For **9**: Ir−C(1) 2.048(4), Ir−O(1) 2.371(3), Ir−O(2) 4.437 (nonbonding), Ir−P(1) 2.3039(12), Ir−P(2) 2.3034(12), Ir−Cl 2.4778(12), Ir−H 1.804 (predicted); P(1)−Ir−P(2) 150.64(4), C(1)−Ir−Cl 167.30(12), O(1)−Ir−H 177.8. For **10**: Ir−C(1) 2.042(4), Ir−O(1) 2.404(3), Ir−P(1) 2.3085(9), Ir−P(2) 2.3121(10), Ir−Cl 2.4639(10), Ir−H 1.73 (predicted); P(1)−Ir−P(2) 153.63(4), C(1)−Ir−Cl 172.72(10), and O(1)−Ir−H(1) 172.7.

phosphino)triptycenes **5**−**7** with a satisfactory yield (Scheme 1).

The new ligands **5**−**7** exhibit a phosphine-coupled triplet signal (at 7.84, 7.79, and 7.63 ppm, respectively, with coupling constants J_{HP} of ca. 4.5 Hz) in their ^{1}H NMR spectra corresponding to the methine proton spanned by phosphine groups, along with a singlet assigned to the back methine hydrogen (at 5.86, 5.87, and 5.81 ppm, respectively). The through-space H−P splitting[8] implies that static phosphine groups converged at the front methine hydrogen.[9] The three-dimensional shape of the molecule results in perfectly resolved anisochronous *i*-propyl methyl and methine groups within each of the *iso*-propylphosphine substituents (please see the Supporting Information). Singlet signals at −8.95, −9.08, and −8.24 ppm, correspondingly, in the ^{31}P[^{1}H] NMR spectrum were assigned to the two identical phosphine environments.

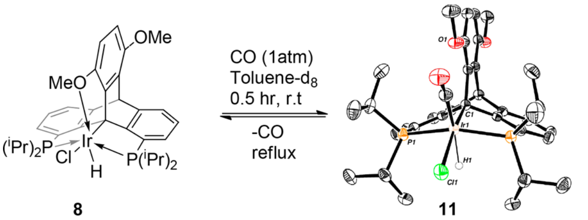
Reacting **5** with a 1/2 equiv of $[Ir(COE)_2Cl]_2$ (COE = cyclooctene) at room temperature for 12 h in acetonitrile led to the formation of carbometalated species **8′** bearing an acetonitrile ligand (Scheme 2). It can be concluded, using ^{1}H NMR, that carbometalation occurred because of the disappearance of the characteristic triplet signal assigned to the methine proton spanned by the phosphine groups and the appearance of the typical Ir-hydride triplet around −19.5 ppm split with a P−H coupling constant of 12 Hz. The ^{31}P[^{1}H] NMR spectrum also displays an expected low-field shift of the signal up to 31.6 ppm. The same transformation in toluene results in an acetonitrile-free product, **8**, characterized by only slightly different ^{1}H and ^{31}P[^{1}H] NMR patterns but with a stronger low-field shift of the phosphine signal (up to 52.78 ppm) and a stronger high-field hydride triplet (up to −31.69 ppm, $J_{H\text{-}P}$ = 18 Hz).

Single crystals of **8** were grown by diffusing *n*-hexane into a saturated benzene solution (Figure 2, left). The solid-state molecular structure displays an almost perfect octahedral geometry around the iridium center with a P(1)−Ir−P(2) angle of 152.23(2)°, an O(1)−Ir−H(1) angle of 172.9(13), and a C(1)−Ir−Cl angle of 168.63(6)°. The Ir−O(1) distance of 2.387(17) Å is somewhat longer than expected but still indicates coordination of the anisole oxygen.[10] The remaining distances (i.e., Ir−P(1) = 2.3031(6) Å, Ir−P(2) = 2.3022(6) Å, and Ir−Cl = 2.4603(6) Å) are within the usual range for iridium PC(sp^3)P pincer complexes of this type, which were characterized by us in the past.[5d,7,11] The hydride ligand was identified in the electron difference map. Here again, the Ir−H bond of 1.56(4) Å is not surprising. Mutual disposition of the chloride and hydride ligands around the metal center is consistent with the σ donor strengths of the ligands occupying positions *trans* with respect to them (H is located *trans* with respect to OMe, whereas Cl is located *trans* with respect to the metalated C(sp^3)). Notably, the metalated methine carbon remains nearly tetrahedral, with angles ranging from 101.34(3)° to 115.94(3)°, in contrast with some previously characterized triptycene-based PC(sp^3)P complexes that were found highly distorted from tetrahedral shapes with larger angles up to 129°.[5a,12]

Coordination studies of ligands **6** and **7** bearing larger chelating groups (MOM and *i*-Pr, respectively) revealed a similar behavior and spectral patterns (Scheme 2). Single-crystal analysis of the corresponding complexes **9** and **10** (ORTEPs are shown in Figure 2, center and right) also show similar structural parameters except for a slightly longer Ir−O(1) bond in **10** bearing a more structurally demanding alkoxyl group (2.404(3) Å for **10** versus 2.371(3) Å in **9**). The Ir−O(2) distance in the MOM-containing **9** is too long to be considered even as a weak interaction (4.437 Å) .

As expected, the presence of a hemilabile moiety influences the basic organometallic behavior of the complexes. For example, we demonstrated that **8** binds even to strongly coordinating ligands in a reversible manner. For example, exposing **8** (in toluene-d_8) to the atmospheric carbon monooxide results in an immediate color change from orange to yellow, accompanied by a high-field $^{31}P[^1H]$ NMR shift of the phosphine signal, indicating the formation of carbonyl complex **11** (which was isolated and structurally characterized;[13] ORTEP is shown in eq 1, Scheme 3). Heating the same NMR sample for 5 min after releasing CO regenerates **8** (eq 1). This reversible coordination of CO by **8** is in sharp contrast to the prototypical iridium triptycene-based PC(sp^3)P complexes possessing no hemilabile side arm, which are known to coordinate carbon monoxide irreversibly (Scheme 3).[2b,5d]

Scheme 3. Reversible Coordination of CO to Complex 8



(1)

The presence of the hemilabile side arm was also found to accelerate reductive elimination from the present complexes. For example, when **8′** was treated with *t*-BuONa under atmospheric H_2 in toluene-d_8 at 50 °C for 30 min, dihydride complex **12** was formed (which can only occur after successive reductive elimination of HCl from **8′** and oxidative addition of H_2 to the apparent Ir(I) intermediate (Scheme 4)). Although we were unable to crystallize **12** with X-ray quality, its ^1H NMR spectrum exhibited a very characteristic doublet of triplets at −20.5 ($^2J_{HP}$ = 16.1 Hz, $^2J_{HH}$ = 6.6 Hz) and −29.4 ppm ($^2J_{HP}$ = 10.6 Hz, $^2J_{HH}$ = 6.6 Hz) assigned to the hydride signals. The upfield resonance at −29.4 ppm can most likely be attributed to the hydride ligand located *trans* to the methoxy oxygen, since the moderately π-donating ligands shift signals upfield. The symmetrical phosphines appear as a virtual H-coupled multiplet located at 47.9 ppm in the corresponding ^{31}P NMR spectrum.

The analogous complexes **9′** and **10′** exhibited a similar reactivity, whereas, here again, the prototypical iridium triptycene-based PC(sp^3)P complexes, possessing no hemilabile side arm, require much longer reaction times to achieve reductive elimination of HCl.[14]

Taking into account the relatively facile reductive elimination of HCl from **8′**−**10′** and the apparent formation of intramolecularly stabilized Ir(I) species, we decided to investigate the transfer dehydrogenation of alkanes using the newly synthesized iridium complexes in order to benchmark their reactivity.[15]

The complexes **8′**−**10′** and **12** were tested as catalysts for transfer dehydrogenation of cyclooctane (COA) with *tert*-butylethylene (TBE) as the hydrogen acceptor. The results are summarized in Table 1. Coordinatively unsaturated catalysts were generated through the dehydrohalogenation of **8′**−**10′** using a 2.5-fold excess of NaO*t*Bu in the presence of an acceptor and TBE (15 mmol). Overall, a system containing a mixture of 1.3 mM (50 μmol, 0.5 mol %) of iridium catalyst (**8′**−**10′** or **13**), COA (15 mmol), and TBE (15 mmol) was heated at 200 °C under argon or nitrogen in a sealed tube.

Unfortunately, the modified systems displayed very low activity for this transformation in comparison with the prototypical (unsubstituted) triptycene-based and other PC(sp^3)P iridium catalysts.[14a,b] On the one hand, the reactions took place under both argon or nitrogen, apparently because an additional hemilabile coordination makes the Ir(I) species less sensitive to the coordination of dinitrogen, which is known to inhibit the reactivity of pincer catalysts of this type. On the other hand, disappointing TONs are most likely caused by lack of dissociation of the alkoxyl groups, which was slower than initially hypothesized. This is necessary for the alkane insertion to take place; however, it might limit the reactivity of the system in the oxidative addition step (the representative results are shown in Table 1).

In order to facilitate complexation of substrates to the metal center during the catalytic cycle, a ligand possessing a more flexible side arm was synthesized. The Diels−Alder adduct **13** formed from 1,8-dibromoanthracene and diethylfumatate, which was successfully converted to the air- and moisture-stable complex **16** via a series of trivial chemical steps according to Scheme 5.

$^{31}P[^1H]$ NMR of **15** shows an expected set of doublets around −9.8 and −11.6 ppm owing to the presence of two different phosphine groups ($J_{P\text{-}P}$ = 9 Hz). As mentioned previously, the central methine proton situated between the phosphine groups is through-space phosphine-coupled and appears as a poorly resolved multiplet signal in the lower field region of the ^1H NMR spectrum (δ = 6.18 ppm), whereas the

Scheme 4. Formation of the Dihydride Iridium Complex 12

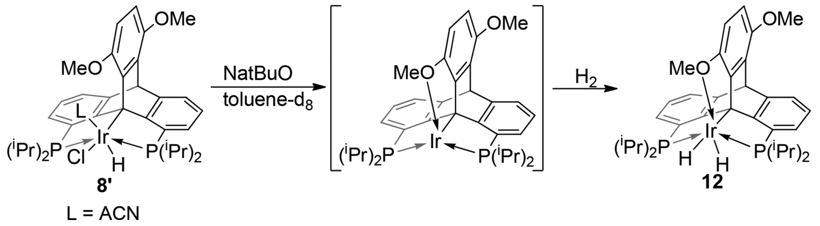
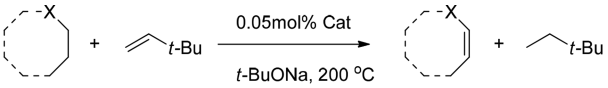


Table 1. Transfer Dehydrogenation of Cyclooctane Catalyzed by 8′−10′, 12, and 16



entry	cat.	conditions	TON (TOF, min^{-1})
1	**8′**	COA, 0.5 mol %, TBE, NaO*t*-Bu, Ar, 200 °C	1.2 (N/A)
2	**8′**	COA, 0.5 mol %, TBE, NaO*t*-Bu, N_2, 200 °C	1.3 (N/A)
3	**9′**	COA, 0.5 mol %, TBE, NaO*t*-Bu, Ar, 200 °C	0 (N/A)
4	**10′**	COA, 0.5 mol %, TBE, NaO*t*-Bu, Ar, 200 °C	0 (N/A)
5	**12**	COA, 0.5 mol %, TBE, Ar, 200 °C	0 (N/A)
6	**16**	COA, 0.5 mol %, TBE, NaO*t*-Bu, N_2, 200 °C	47 (171)
7	**16**	COA, 0.5 mol %, TBE, NaO*t*-Bu, Ar, 200 °C	46 (169)
8	**16**	THF, 0.5 mol %, TBE, NaO*t*-Bu, N_2, 120 °C	18 (150)
9	**16**	chromane, 0.5 mol %, TBE, NaO*t*-Bu, N_2, 120 °C	15 (134)

corresponding back methine hydrogen appears as a sharp singlet at 4.4 ppm.

A stoichiometric reaction of the resulting phosphine **15** with $[IrCl(COE)_2]_2$ in benzene leads to oxidative cleavage of the methine C−H bond toward the formation of metalated **16**. Metalation of sp^3-hybridized carbon can be easily verified by ^{1}H NMR from the clean transformation of a very characteristic multiplet signal at 6.18 ppm to a perfectly resolved doublet of doublets at −10.21 ppm ($J_{\text{P1-H}}$ = 151.8 Hz, $J_{\text{P2-H}}$ = 7.4 Hz) assigned to the hydride ligand. Surprisingly, the ^{31}P[^{1}H] NMR signals of **16** were transformed into a couple of virtual singlets shifted to a low-field region (δ = 33.28 and 32.15 ppm). The remarkably large difference between the $J_{\text{P1-H}}$ and $J_{\text{P2-H}}$ coupling constants, together with the absence of through-metal coupling of two different phosphine groups, suggests a very atypical for the traditional PCP complex *cisoid* arrangement of phosphine ligands around the octahedral metal center, where the phosphines and the hydride ligands are mutually adjacent in such a way that P1 is located *trans* to the hydride.[16]

X-ray analysis of the product (ORTEP is shown in the Figure 3) supports the NMR assignment, whereby an almost octahedral environment appears around the iridium center, and where P1 and P2 are located 107.77(4)° with respect to each other, and are, consequently, *trans* and *cis* to the hydride with P1−Ir−H and P2−Ir−H angles of 174.6(12)° and 73.3(12)°, correspondingly. The oxygen atom of the hemilabile

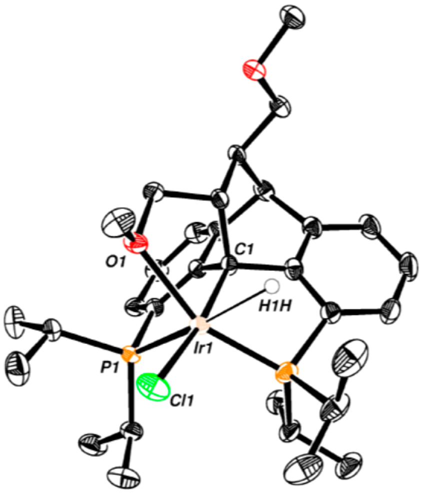
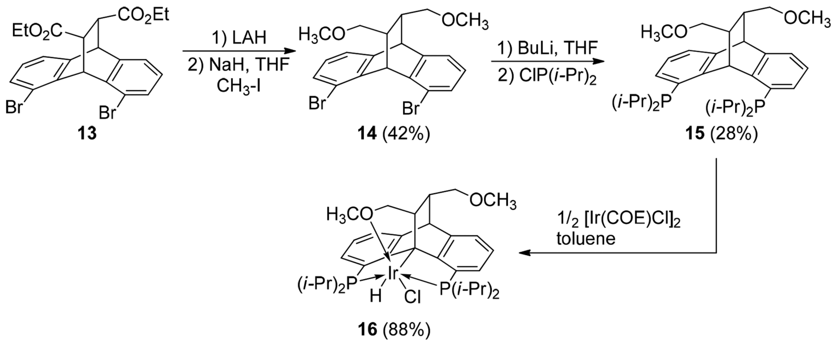


Figure 3. Thermal ellipsoid (50% probability level) representation of **16**. Most hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ir−C(1) 2.049(4), Ir−O(1) 2.272(3), Ir−P(2) 2.2031(12), Ir−P(1) 2.3724(12), Ir−Cl 2.4744(11), Ir−H(1) 2.23(5); P(1)−Ir−P(2) 107.77(4), C(1)−Ir−Cl 169.46(12), P(2)−Ir−O(1) 156.96(8), H(1)−Ir−Cl(1) 86.4(12), H(1)−Ir−P(1) 174.6(12), H(1)−Ir−O(1) 89.8(12).

Scheme 5. Formation of the Coordinatively Flexible Iridium Complex 16



group is *trans* to the P_2 atom. The Ir1−P1 bond length is significantly longer than the corresponding Ir1−P2 [2.3724(12) versus 2.2031(12) Å] owing to the *trans* influence of hydride, which is greater than that of oxygen,[17] whereas other distances are within the normal range.

The newly prepared complex was employed as a precatalyst in the dehydrogenation of COA in the presence of TBE, as an acceptor under the described reaction conditions under both N_2 and Ar. As we expected, the reactivity of the complex possessing a more flexible side arm was higher and a TON of 47 was achieved (Table 1, entries 6 and 7). With success in the dehydrogenation of COA, we employed the same catalyst in the dehydrogenation of polar substrates such as tetrahydrofuran (THF) and chromane in the presence of TBE as an acceptor at only 120 °C. The results, in Table 1 (entries 8 and 9), show that the more flexible complex **16** is also capable of catalyzing the dehydrogenation of polar substrates.

CONCLUSIONS

We synthesized and characterized a series of new PC(sp^3)P pincer ligands bearing potentially hemilabile functional groups. Their coordination chemistry and the properties of the corresponding iridium complexes were studied. The new compounds exhibited remarkably different coordination behavior in comparison with the prototypical complexes possessing no additional functional groups. Transfer dehydrogenation of cyclooctane was probed through a coordinatively unsaturated species obtained by the dehydrohalogenation of **8′**−**10′** with a strong base or by the dehydrogenation of **12** with an acceptor. Unfortunately, the catalytic tests produced results that are significantly less satisfactory in comparison to the state-of-the-art complexes, apparently owing to the slower than desired dissociation of the alkoxyl groups from the metal center. We also demonstrated that the reactivity might be improved by designing a more flexible version of the ligand. The activity of the new compound is still slower than that of the state-of-the-art catalysts; however, the modularity of our ligand holds promise to develop more active catalytic substances for this and other transformations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00105.

Spectroscopic data for compounds (PDF)

Accession Codes

CCDC 1589709−1589712 and 1815198 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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