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Exploring the Reactivity of C(sp^3)-Cyclometalated Ir^{III} Compounds in Hydrogen Transfer Reactions

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Dedicated to Professor Jochanan Blum on the occasion of his 75th birthday

Abstract: The manuscript describes the synthesis and full characterization of a new PC(sp^3)P-based cyclometalated Ir^{III} complex that manifests an exceptional thermal stability, as well as outstanding reactivity in hydrogen transfer reactions. The described compound represents the first example of a new family of stable C-(sp^3)-metalated compounds.

Keywords: cyclometalation · hydrogenation · iridium · P ligands · pincer complexes

Introduction

After more than 30 years of extensive research, the chemistry and applications of PCP pincer-like complexes are well-documented.[1] These compounds have been widely studied and used as homogeneous catalysts and stoichiometric promoters for challenging chemical transformations,[1a–d] as well as building blocks for the construction of advanced materials.[1e–f] However, research activity in this field has mainly focused on sp^2-carbon- rather than sp^3-carbon-based compounds. This imbalance originates from the greater thermal, conformational and chemical stability of C(sp^2) compared to C(sp^3),[2] which is especially true of complexes bearing all-aliphatic ligands. In these cases, the carbometalated compounds often coexist in equilibrium with isomeric olefinic or carbenic species, as a result of facile α- or β-hydride elimination (Figure 1, left).[2f–h] The reactivity of C(sp^3)- versus C-(sp^2)-based compounds differs significantly, owing to electronic factors, such as a stronger *trans* influence by the metalated carbon and higher nucleophilicity of the metal center.[2a,3]

Herein, we wish to introduce a new class of PC(sp^3)P-based iridium(III) complexes, based on a robust triptycene scaffold, that manifests an exceptional stability and outstanding reactivity in hydrogen transfer reactions (Figure 1, right).

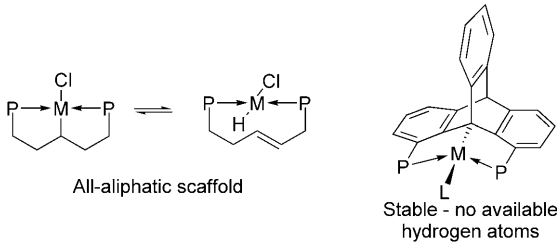

Figure 1. Left: Equilibrium of carbometalated compound bearing all-aliphatic ligands. Right: PC(sp^3)P-based metal complex bearing no available hydrogen atoms.

Results and Discussion

Synthesis and structure: Recently, we studied the coordination preferences of potentially *trans*-chelating ligands based on a triptycene scaffold.[4] Although one of the implied features of these ligands was their chemical inertness toward possible carbometalation (resulting from the low acidity of the methine hydrogen), this process is apparently unavoidable, as *trans*-chelating ligands are structurally related to pincer ligands.[5] Thus, an attempted synthesis of a *trans*-chlorocarbonyl Ir^{I} Vaska-like complex from $IrCl_3(H_2O)_n$ and 1,8-bis(diisopropylphosphino)triptycene (**1**) in boiling DMF led to the isolation of the unusual Ir^{III} PC(sp^3)P-type compound **2** in 71% yield (Scheme 1).

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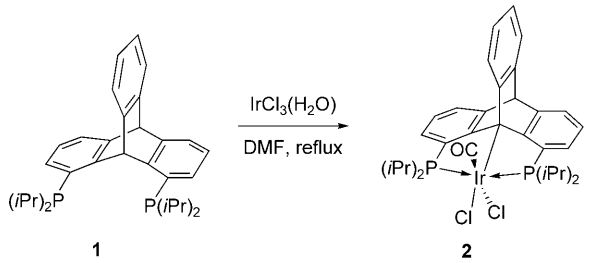


Scheme 1. Synthesis of Ir^{III} PC(sp^3)P complex **2.**

The existence of the C(sp^3)–Ir bond in **2** was initially indicated by NMR spectroscopic analysis. ^{1}H NMR spectra of all nonmetalated complexes bearing triptycene-based ligands show a very characteristic low-field resonance (9-10 ppm) for the central methine hydrogen.[4] This signal does not appear in the ^{1}H NMR spectrum of **2**.[6] X-ray crystallographic analysis unequivocally proved the structural arrangement of **2** (Figure 2).[7] The iridium center adopted a slightly distorted octahedral coordination environment, with two nonequivalent chlorine atoms located in *trans* and *cis* positions with respect to the metalated carbon and to the carbon monoxide ligand. Comparison of the iridium–chlorine bond lengths, *cis* and *trans* to C1 confirmed a strong *trans*-influence exerted by the sp^3 carbon, indicating a possible lability of the *trans* chlorine. However, the most interesting structural feature of the new compound is an abnormal distortion of the metalated carbon C1 from its natural tetrahedral geometry. For example, the C15-C1-Ir angle was found to be 127° (compared to 109°, as is normal for sp^3 carbon). However, the C1–Ir bond length was within the usual range.[8]

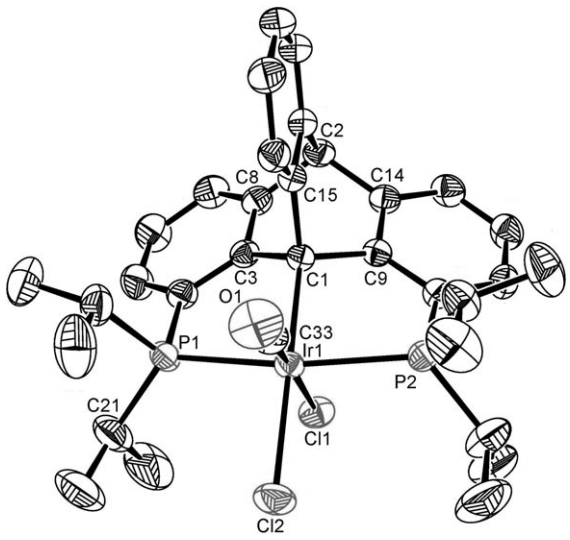
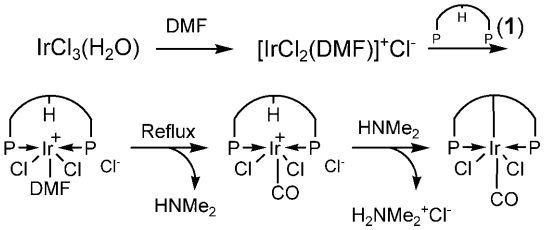


Figure 2. ORTEP representation of **2**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms have been removed for clarity. Selected bond lengths [Å] and angles [°]: Ir–C1 = 2.154, Ir–Cl1 = 2.389, Ir–Cl2 = 2.463, Ir–C33 = 1.839, Ir–P1 = 2.365, Ir–P2 = 2.364; P1-Ir-P2 = 164.74, C1-Ir-Cl2 = 173.64, C33-Ir-Cl1 = 173.36, C15-C1-Ir = 127.38.

In principle, this extreme distortion may indicate "hemilability" of the C(sp^3)–Ir bond. However, the rigidity and chemical inertness of the polycyclic backbone, in combination with the absence of easily abstractable β-hydrogens, apparently compensates for this "weak" bond. Indeed, we found that **2** decomposes above 260 °C, and no structural mutations were observed after a prolonged heating in DMSO near to its boiling point. It is also worth noting that, although the synthesis of carbonylated transition-metal complexes by DMF decarbonylation is very common, the formation of Ir^{III} carbonyl species, such as **2**, is less typical. However, it can be rationalized as depicted in Scheme 2.

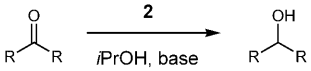


Scheme 2. Formation of carbonylated Ir^{III} complex **2** by DMF decarbonylation

We believe that cationic $[IrCl_2(DMF)_n]^+$, formed upon dissolution of the iridium precursor in DMF,[9] coordinates to the bidentate ligand **1** to produce an ideal environment for abstraction of the only available proximal methine hydrogen. Conversely, steric congestion around the metal center suppresses further reduction processes under the given conditions.

Catalysis: With compound **2** in hand, we investigated its catalytic activity in hydrogen-transfer reactions. Although the transformation is well-studied and many efficient (mainly ruthenium-based) catalysts are available,[10] there is still much room for improvement in developing better catalytic systems. In addition, the reactivity of iridium PCP compounds in transfer hydrogenation of ketones is underexplored and, even more importantly, can be extrapolated onto other related transformations.[11]

Our initial experiments indicated that **2** is a highly efficient precatalyst for transfer hydrogenation of ketones using isopropanol as the hydrogen source [Eq. (1)]. The injection



of 2′-chloroacetophenone into a preheated solution of **2** (0.05 mol%) and NaO*t*Bu (5 mol%) in isopropanol results in its rapid (< 30 sec) and essentially quantitative (> 99%) conversion into the corresponding alcohol under air. The turnover frequency (TOF) calculated for this run at 50% conversion corresponds to $3.6 \times 10^6\ h^{-1}$ and is among the highest such values reported.[12]

The catalyst was also active at lower catalyst/substrate (C/S) ratios. For example, with the reduction in the concentration of **2** to 0.01 mol%, complete conversion was detected after 5 min with halogenated acetophenone substrates (Table 1, runs 9-11). However, the reduction of simple acetophenone proceeded rather slowly and complete conversion was achieved after 12 h.[13] On the other hand, despite a lower TOF, the catalyst remains active and the reaction goes to completion even under low catalyst loading conditions at 15 g scale (C/S = 1:100000) (Table 1, runs 12–13).

Table 1. Caption: Transfer hydrogenation of representative ketones catalyzed by 2.

Run	Ketone	S/C	Time	TOF[e]	Conv. [%][f]	Yield [%][g]
1[a]	2′-chloroacetophenone	2000:1	5 sec	3.6×10^6	99	98
2[a]	2′-bromoaceto-phenone	2000:1	5 sec	3.6×10^6	99	98
3[a]	4′-bromoaceto-phenone	2000:1	5 sec	3.6×10^6	96	95
4[a]	3′-bromoaceto-phenone	2000:1	30 min	1.2×10^4	99	98
5[a]	acetophenone	2000:1	30 min	1.2×10^4	94	93
6[a]	2-acetonaphthone	2000:1	30 min	1.2×10^4	95	94
7[a]	4,4′-dichlorobenzo-phenone	2000:1	30 min	1.2×10^4	97	96
8[a]	4-methylbenzo-phenone	2000:1	30 min	1.2×10^4	98	98
9[b]	2′-chloroacetophenone	10000:1	5 min	9×10^5	99	99
10[b]	2′-bromoaceto-phenone	10000:1	5 min	9×10^5	99	99
11[b]	4′-bromoaceto-phenone	10000:1	5 min	9×10^5	96	95
12[b]	acetophenone	10000:1	12 h	N/D	96	95
13[c]	acetophenone	100000:1	48 h	N/D	94	93
14[d]	acetophenone	100:1	12 h	N/D	45	N/D

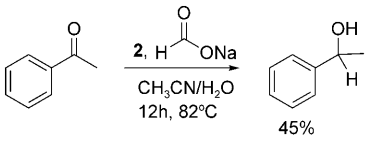
[a] Ratio of catalyst/substrate/base (C/S/B) = 1:2000:100, *i*PrOH (1 M) at 82 °C under air. [b] C/S/B = 1:10000:500, *i*PrOH (4 M) at 8 °C under air. [c] C/S/B = 1:100000:5000, *i*PrOH (4 M) at 8 °C under air. [d] C/S/HCO_2Na = 1:100:500, CH_3CN/H_2O (2:1) at 82 °C. [e] Determined at approximately 50% conversion. [f] Conversion determined by GC analysis. [g] Isolated yields of at least 95% pure compound (average of two runs).

Further experimentation showed that a number of alkyl, aryl, or diaryl ketones can be converted, in high yields, into the corresponding alcohols within minutes at 82 °C and with a base/catalyst/substrate ratio of 100:1:2000 or higher (Table 1, runs 1-10). It is worth noting that the turnover frequencies calculated at ≈50% conversion vary in the range of 1.2×10^4–$3.6\times10^6\ h^{-1}$ depending on the stereoelectronic parameters of substrates.

For each run, essentially identical reactivity was detected under air and under air-free conditions, indicating the robustness of **2**. Similarly, there was no difference in reactivity between experiments conducted in anhydrous and commercial *i*PrOH.

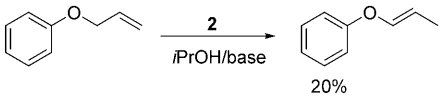
Notably, most known transfer-hydrogenation catalysts require relatively high-dilution reaction conditions and open reactors, in order to remove by-product acetone from the reaction mixture and consequently shift the substrate/product equilibrium, representing a potential scale-up obstacle in designing industrially relevant processes.[14] Unlike the aforementioned transfer-hydrogenation catalysts, the reactivity of **2** is essentially insensitive to the presence of acetone and the hydrogenation can be carried out in a closed flask in concentrated solutions (up to 4 M).

Clearly, compound **2** is not a true catalyst, but is in fact a precatalyst. As postulated for transition-metal-catalyzed transfer-hydrogenation chemistry, the mechanism of the ketone reduction mainly follows either "mono- or dihydridic" routes.[15] However, the direct MPV (Meerwein-Ponndorf-Verley)-type hydride transfer pathway cannot be completely ruled out. Higher reduction rates were detected for reactions involving halogenated ketones (Table 1), which may be consistent with a classical MPV case, in which a $-I$ effect facilitates ketone reduction.[16] However, other results suggest a hydride-involving mechanism: 1) In accord with the general trends of the "hydridic" route, essentially no conversion was detected under base-free conditions.[17] 2) The conditions obviate the need for acetone-removal over the course of the reaction to achieve complete conversion, even with a C/S ratio of 1:100000. This fact explains why the forward reaction (reduction) is much faster than the reverse (oxidation), which is not typical MPV behavior.[18] 3) An attempted hydrogenation of acetophenone, with sodium formate as the hydride source in acetonitrile/water medium, led to the, admittedly less efficient, formation of hydrogenated product [Table 1, run 14 and Eq. (2)].



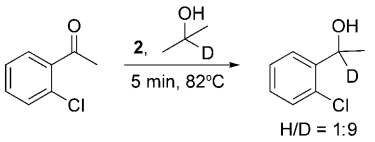
(2)

This result is inconsistent with the direct MPV-type mechanism; 4) An attempted hydrogenation of allyl phenyl ether with **2** under the described reaction conditions yielded partially isomerized product (although no hydrogenation occurred, [Eq. (3)]). This process is also unlikely to proceed



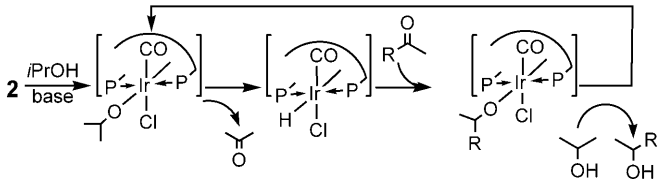
(3)

under hydride-free conditions. 5) Finally, the experiment conducted in deuterium-labeled *i*PrOH led to the formation of approximately 90% monodeuterated product in 5 min (in accord with the accepted monohydride mechanism).[15] Even more prolonged reaction times (1 h) did not change the degree of deuteration [Eq. (4)]. This result rules out the possibility of the dihydridic route,[19] indicating that the catalytic cycle is similar to the previously suggested monohydride route.[15] Such steps as ketone insertion into the Ir–H



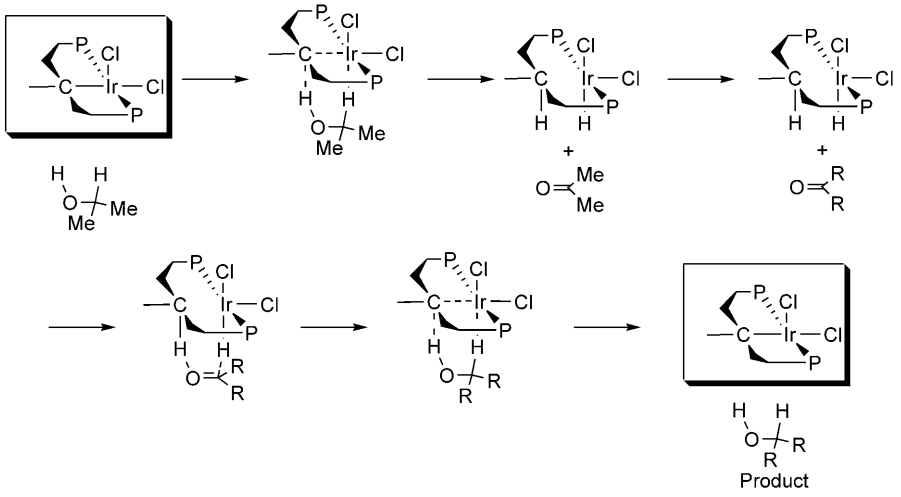
(4)

bond, and displacement of the product from Ir by the isopropoxide ligand might be greatly facilitated by a strong *trans*-influence imposed by the C(sp³) ligand (Scheme 3).[20]



Scheme 3. Proposed catalytic cycle for **2.**

Another interesting point to be addressed in our future studies is the possible "hemilability" of the PC(sp³)P ligand. At this point, we can only speculate about the reasons for the high catalytic activity of **2**, but if the ligand is indeed "hemilabile", an alternative mechanism involving a dissociation–association sequence could play a role in the catalytic cycle (Scheme 4). Indeed, hemilabile PNP pincer-type catalysts were recently reported.[21]



Scheme 4. An alternative catalytic cycle for **2.**

Conclusions

To conclude, we reported the synthesis of a robust Ir^III PC(sp³)P compound, based on a 1,8-bis(diisopropylphosphino)triptycene scaffold, that demonstrated fascinating coordination chemistry, a robust nature and exceptional catalytic activity in hydrogen transfer reactions, even under non-inert atmospheres. Although the active catalytic species are still unknown, the reactivity of the C(sp³)-metalated **2** is exciting and different from well-studied C(sp²)-metalated compounds. Currently, mechanistic studies and the syntheses of more sophisticated complexes, as well as enantiopure chiral compounds of this type, are in progress.

Experimental Section

General considerations: Iridium chloride hydrate (98%), *i*PrOH (HPLC grade), and all starting ketones were purchased from Aldrich. All reagents were used without further purification. 1,8-bis(diisopropylphosphino)triptycene was synthesized according to the published procedure.[5] All reagents were weighed and handled in air. Flash column chromatography was performed with Merck ultra pure silica gel (230–400 mesh) purchased from Fluka. All reactions were carried out under air in single-use screw-capped tubes. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz instrument with chemical shifts reported in ppm relative to the residual deuterated solvent or the internal standard tetramethylsilane. IR spectra were recorded using Bruker Vector 22 instrument. Gas chromatography analyses were performed on a Hewlett Packard 5890 instrument with a FID detector and a Hewlett Packard 25 m × 0.2 mm internal diameter Supelcowax–10 capillary column. Yields refer to isolated compounds of greater than 95% purity, as determined by ^{1}H NMR analysis. Yields reported in Table 1 are an average of two runs.

Compound 2: A solution of $IrCl_3 \cdot H_2O$ (0.2 g, 0.67 mmol) and 1,8-bis(diisopropylphosphino)triptycene (**1**, 0.65 g, 1.34 mmol) in *N,N*-dimethylformamide (DMF, 10 mL) was heated at reflux for 48 h under nitrogen. DMF was removed from the reaction mixture by distillation under reduced pressure, and the off-white residue was recrystallized three times from methanol, affording **2** (0.37 g, 0.48 mmol, 71%). ^{1}H NMR (400 MHz, CDCl3): $\delta = 1.02$ (6H, dd, $J = 7.0$ Hz, $J = 8.0$ Hz), 1.29 (6H, dd, $J = 7.0$ Hz, $J = 8.0$ Hz), 1.71 (12H, m), 2.52 (H, m), 3.85 (2H, m), 5.35 (1H, s), 6.81 (1H, t, $J = 6.5$ Hz), 6.88 (1H, t, $J = 7.3$), 7.08 (2H, t, $J = 8.6$ Hz), 7.17 (1H, d, $J = 6.5$ Hz), 7.28 (2H, d), 7.30 (2H, t, $J = 7.3$ Hz), 7.40 ppm (1H, t, $J = 7.3$ Hz); ^{13}C NMR, (400 MHz, $CDCl_3$): $\delta = 0.0$ (d, $J = 30.8$ Hz), 20.80, 21.86, 26.63 (t, $J = 14.7$ Hz), 28.29 (t, $J = 14.7$ Hz), 34.81, 52.03, 54.66, 123.03, 124.3 (d, $J = 24.1$ Hz), 125.03, 125.6 (d, $J = 16.1$ Hz), 128.53, 130.70 (t, $J = 26.2$ Hz), 144.39 (t, $J = 7.0$ Hz), 149.02, 151.70, 164.3 (t, $J = 12.1$ Hz), 167.27 ppm; ^{31}P NMR (100 MHz, $CDCl_3$): $\delta = 34.38$ ppm. IR (neat): $\tilde{\nu} = 2020\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{33}H_{39}Cl_2IrOP_2$: C 51.03, H 5.06; found: C 50.71, H 5.23.

General procedure for catalytic transfer hydrogenation of ketones: In a typical catalytic transfer-hydrogenation procedure, in a single-use screw-capped reaction tube, as solution of the catalyst and NaO*t*Bu in *i*PrOH (0.5 mL) was preheated to 82°C. A solution of the substrate in 4 M *i*PrOH was then injected into the reaction mixture. After equilibrium was attained, the solvent was removed by evaporation under reduced pressure. Products were isolated after a standard workup and purified, if needed, by flash chromatography.

1-Phenylethanol (CAS Registry No.: 98-85-1): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.5$ (3H, d, $J = 6.5$ Hz), 2.02 (1H, s), 4.89 (1H, q, $J = 6.5$ Hz),

7.29–7.38 ppm(5H, m); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 25.1, 70.3, 125.4, 127.4, 128.4, 145.9 ppm.

1-(2-Naphthyl)ethanol (CAS Registry No.: 7228-47-9): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.61 (3H, d, J = 6.5 Hz), 1.97 (1H, br), 5.10 (1H, q, J = 6.5 Hz), 7.49–7.55 (3H, m), 7.84–7.87 ppm (3H, m); ^{13}C NMR (400 MHz, CDCl3): δ = 70.5, 123.8, 125.8, 126.1, 127.6, 127.9, 128.3, 133.0, 133.3, 143.1 ppm.

1-(4-Bromophenyl)ethanol (CAS Registry No.: 5391-88-8): ^{1}H NMR (400 MHz,$CDCl_3$): δ = 1.46 (3H, d, J = 6.5 Hz), 1.78 (1H, br), 4.86 (1H, q, J = 6.5 Hz), 7.23–7.26 (2H, m),7.44–7.46 pm(2H, m); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 25.2, 69.7, 121.1, 127.1, 131.5, 144.8 ppm.

1-(2-Chlorophenyl)ethanol (CAS Registry No.: 13524-04-4): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.49 (3H, d, J = 6.5 Hz), 1.94 (1H, br), 5.29 (1H, q, J = 6.5 Hz), 7.19 (1H, td, ^2J = 1.5, ^3J = 7.5 Hz), 7.27–7.33 (2H, m), 7.19 ppm(1H, dd, ^2J = 1.7, ^3J = 7.8 Hz); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 23.5, 66.8, 126.4, 127.2, 128.3, 129.3, 131.6, 143.1 ppm.

1-(2-Bromophenyl)ethanol (CAS Registry No.: 5411-56-3): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.51 (3H, d, J = 6.5 Hz), 2.00 (1H, br), 5.26 (1H, q, J = 6.5 Hz), 7.15 (1H, t, J = 8 Hz), 7.38 (1H, t, J = 8 Hz), 7.54 (1H, t, J = 8 Hz), 7.62 ppm(1H, t, J = 8 Hz); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 23.5, 69.1, 121.7, 126.7, 127.8, 128.7, 132.6, 144.7 ppm.

1-(3-Bromophenyl)ethanol (CAS Registry No.: 52780-14-0): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.51 (3H, d, J = 6.5 Hz), 1.81 (1H, br), 4.9 (1H, q, J = 6.5 Hz), 7.24 (1H, t, J = 7.0 Hz), 7.31 (1H, d, J = 7.0 Hz), 7.42 (1H, t, J = 7 Hz), 7.56 pm(1H, s). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 25.2, 69.6, 122.5, 124.0, 128.5, 130.1, 130.4, 148.1 ppm

Bis(4-chlorophenyl)methanol (CAS Registry No.: 90-97-1): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.08 (1H, s), 5.81 (1H, s), 7.29–7.34 ppm(8H,m); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 74.9, 127.8, 128.5, 133.5, 141.8 ppm.

2-Methylbenzhydrol (CAS Registry No.: 5472-13-9): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.35 (3H, s), 5.84 (1H, s), 7.16–7.37 (9H, m); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 21.1, 75.9, 126.5, 126.6, 127.4, 128.4, 129.2, 137.2, 141.0, 144.0 ppm.

Acknowledgements

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[6] Other spectral data is in agreement with the proposed structure: The ^{31}P NMR spectrum shows a single resonance frequency at δ = 34.4 ppm. The splitting of the phosphorus-coupled carbon signals into 1:2:1 triplets was observed in the ^{13}C NMR spectrum of **2** (see supporting information). Similar triplets have been observed in spectra for numerous compounds, forming AXX' spin systems where the two phosphorus nuclei couple to each other with a large coupling constant, characteristic of *trans*-coordinated compounds (for example, see ref. [5]).

[7] CCDC-683153 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[20] Unfortunately, our attempts to convert **2** into an unambiguously identifiable catalytic species are yet to succeed. When **2** was allowed to react with *i*PrOH in the NMR tube, with or without stoichiometric base, hydrogen, or metal hydrides, we observed in the 1H NMR spectrum a pair of triple doublets (−12.00 ppm, J_{H-P} = 19.8 Hz, J_{H-H} = 4.4 Hz and −13.3 ppm, J_{H-P} = 14.3 Hz, J_{H-H} = 4.4 Hz), that can be assigned to the expected hydridic ligands. However, we were unable to isolate it for more detailed characterization.

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