Short Note

2,6-Bis[bis(1,1-dimethylethyl)phosphinito-κ*P*]phenyl-κ*C*]-*trans*-chlorohydro(phenylphosphine)iridium(III)

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Abstract: The molecular structure of an iridium complex featuring a phenylphosphine ligand is described. Reaction of (POCOP)IrHCl (**1**, POCOP = 2,6-(^{t}Bu$_2$PO)$_2$C$_6$H$_3$$^-$) with phenylphosphine gives (POCOP)IrHCl(PH$_2$Ph) (**2**) under mild conditions. Structural features are consistent with a classic pseudo-octahedral iridium compound with three neutral phosphine donors. Compound **1** is unreactive at elevated temperature and unreactive toward excess phenylphosphine under conditions sampled.

Keywords: iridium; phosphine; dehydrocoupling; pincer

1. Introduction

Pincer compounds of iridium have exhibited remarkable popularity, with a strong focus on C–H bond activation in alkane dehydrogenation catalysis.[1] Among these, (POCOP)IrHCl (**1**, POCOP = 2,6-(^{t}Bu$_2$PO)$_2$C$_6$H$_3$$^-$) demonstrated good reactivity when initially described independently by each Brookhart and Jensen.[2-4] There have been countless studies with these and related systems, but our interest in such compounds focuses on main group bond formation. Indeed, Si–H bond activation and dehydrocoupling has been observed with **1**,[5] studies inspired by the successful polymerization of amine boranes led by Manners among other amine-borane dehydrogenation catalysis with **1**.[6-8] Likewise, highly related (POCOP)Ir(H)$_2$ has been a successful phosphine borane dehydropolymerization catalyst as reported by Braunschweig.[9] Our on-going interest in catalysis involving P–H bond activation,[10] including phosphine dehydrocoupling,[11-12] made an exploration of **1** in such catalysis a logical choice. However, extension of iridium studies to catalysis that leverages P–H bond activation such as dehydrocoupling or hydrophosphination did not give similar reactivity, and the isolation of a stable, formally 18-electron compound gives good indication that competitive substrate coordination is the origin of the inertness of **1** with respect to P–H bond activation in our hands. Nevertheless, this new pseudo-octahedral iridium compound has been isolated and structurally characterized in the course of these studies.

2. Results

Treatment of **1** with 1 equiv. of phenylphosphine in toluene solution at ambient temperature results in a gradual color change to pale pink (Eq 1).

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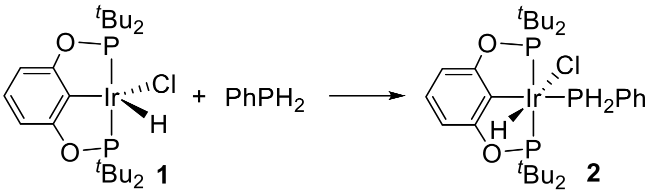

(1)

Removing solvent volume under reduced pressure afforded a nearly colorless precipitate in approximately quantitative yield. NMR spectra of reaction mixtures indicated qualitative conversion as well. The product, (POCOP)IrHCl(PPH_2Ph) (**2**), can be recrystallized from cooled, highly concentrated toluene solution to afford analytically pure, X-ray quality crystals. Molecular structure was determined by a single crystal diffraction study, and a pseudo-octahedral iridium compound was obtained. The quality of the data was adequately high to locate the hydrido ligand, which is suggested by the dispositions of the ligands cis to the hydrido position as well as the iridium–chlorine bond length (Ir–Cl(1) = 2.4956(5) Å). All phosphine ligands have similar Ir–P bond lengths, consistent with tertiary phosphine ligands, and the two hydrogen atoms on the phenylphosphine phosphorus were also located from the Fourier difference map. Coordination of the phenylphosphine ligand trans to the phenyl carbon atom of the POCOP ligand appears to best satisfy steric constraints at iridium, but it can also be anticipated from trans effect arguments. Selected bond lengths and angles are summarized in Table 1 with a perspective view of **2** in Figure 1.

Table 1. Selected bond lengths (Å) and angles (°) for compound **2**.

Atom–Atom	Length [Å]	Atom–Atom–Atom	Angle [°]
Ir–C(7)	2.0562(18)	P(3)–Ir–P(1)	101.272(18)
Ir–P(3)	2.3246(5)	P(3)–Ir–P(2)	103.980(19)
Ir–P(1)	2.3246(5)	P(3)–Ir–Cl(1)	86.923(19)
Ir–P(2)	2.3344(5)	P(1)–Ir–P(2)	152.967(17)
Ir–Cl(1)	2.4956(5)	C(7)–Ir–Cl(1)	87.57(5)
Ir–H1	1.41(2)[1]	P(1)–Ir–Cl(1)	97.438(18)
		P(2)–Ir–Cl(1)	93.415(18)
		C(7)–Ir–P(3)	174.40(5)
		C(7)–Ir–P(1)	78.47(5)
		C(7)–Ir–P(2)	77.34(5)

[1] H(1) located from the Fourier difference map.

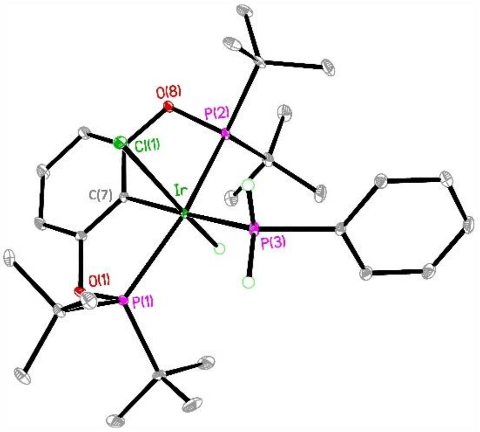

Figure 1. Molecular structure of (POCOP)IrHCl(PPH_2Ph) (**2**) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms, except those located on P(3) and Ir, are omitted for clarity.

NMR spectra, which are slightly contaminated with ambient solvents from the glovebox atmosphere, confirm the solid-state structure. Two resonances for the phosphorus nuclei are observed in the $^{31}P\{^{1}H\}$ NMR spectrum with the POCOP ligand resonating at $\delta = 160.5$ and the phenylphosphine ligand at $\delta = -84.4$, as assigned by relative integration. Anticipated couplings to phosphorus and the hydrido ligand were not resolved. Both peaks were broad featuring width-at-half-height of >25 Hz. It is reasonable that typical J_{PP} and J_{PH} values would not be resolved with peaks of such breadth. Several diagnostic resonances appear in the ^{1}H NMR spectrum. The hydrido resonance is observed as a non-first order multiplet at $\delta = -20.7$ with coupling to the phosphorus nuclei of POCOP ($|J_{PH}|$ = 14.2 Hz) and phenylphosphine ($|J_{PH}|$ = 11.6 Hz) obtained by simulation. The phenylphosphine hydrogen atoms resonate at $\delta = 5.9$ as a doublet of triplets ($|J|$ = 348.9, 5.91 Hz) where the magnitude of the P-H scalar coupling is consistent with a metal-coordinated primary phosphine ligand.

Excess phenylphosphine failed to react with **1** to provide any new products beside compound **2**. Extended reaction times were also unproductive. Benzene-d_6 solutions of phenylphosphine with 5 mol % of **2** failed to react at ambient temperature as well as under extended heating at 80 °C, where trace conversions of 1,2-diphenyldiphosphine were observed. Only upon grossly extended reaction times at elevated temperature were reagents driven to decomposition, but no additional amounts of productive products were identified in those decomposition reactions. It is, of course, not unexpected that a formally 18-electron, pseudo-octahedral compound, particularly with this stereochemistry, would be unreactive.

3. Materials and Methods

3.1. General considerations

Manipulations were performed under a purified nitrogen atmosphere with dried, deoxygenated solvents in an M. Braun glovebox. Toluene was dried over alumina. Benzene-d_6 was degassed and dried over an activated mixture of 3 Å and 4 Å molecular sieves. Phenylphosphine was used as received. Compound **1** was prepared by the literature protocol.[2] NMR spectra were recorded with a Bruker AXR 500 MHz spectrometer. All ^{31}P NMR spectra were ^{1}H decoupled and referenced to external 85% H_3PO_4. Resonances in ^{1}H NMR spectra are referenced to the residual solvent resonance ($C_6D_6 = \delta\ 7.16$). Spectral data for 1,2-diphenyldiphopshine is consistent with literature reports.[13] Crystals for X-ray analysis were handled and mounted under Paratone-N oil. The X-ray data was collected on a Bruker AXS single crystal X-ray diffractometer using MoKα radiation and a SMART APEX CCD detector and analyzed with Bruker software.

3.2. Synthesis of Compound **2**

In a nitrogen-filled glove box, a 25 mL round-bottom flask was charged with 82.4 mg (0.132 mmol) of (POCOP)IrHCl (**1**) and 14.5 mg (0.132 mmol) of phenylphosphine followed by approximately 7 mL of toluene at ambient temperature. All components dissolved quickly upon stirring, and the resultant solution gradually lightened from a dark blood-red color to a dark shade of pink. After stirring for approximately 1 h, the solution was subjected to reduced pressure to increase concentration. At approximately 2 mL, substantial precipitation had occurred, and the nearly colorless solids were collected by decanting and dried. The crude product was then recrystallized by cooling a concentrated toluene solution to –20 °C. An initial crop of 65 mg (67%) was collected with additional crops forming thereafter. X-ray quality crystals were obtained at this step. An optimized yield was not sought. ^{1}H NMR (500 MHz, 25 °C, C_6D_6): δ 7.60 (m, 2 H, *Ar*); 7.15 (m, 2 H, *Ar*); 7.02 (m, 2 H, *Ar*); 6.91 (m, 1 H, *Ar*); 6.82 (m, 2 H, *Ar*); 5.90 (dt, *J* = 348.9, 5.91 Hz, 2 H, PH_2); 1.55 (t, *J* = 6.5 Hz, 18 H, CH_3) 1.06 (t, *J* = 6.5 Hz, 18 H, CH_3), –20.7 (m, *J* = 14.2, 11.6 Hz 1 H Ir–*H*). ^{31}P NMR (202.5 MHz): δ 160.6 (br m, 2 P, P^tBu_2); –84.4 (br m, 1 P, PH_2Ph). Anal. Calcd. for $C_{28}H_{47}ClIrO_2P_3$: C, 45.68; H, 6.43. Found: C, 45.93; H, 6.55.

4. Conclusions

Pseudo-octahedral compound **2**, (POCOP)IrHCl(PH_2Ph), was readily prepared by reaction of the well-studied five coordinate POCOP compound **1** with phenylphosphine and structurally characterized. The relative inertness of the precursor **1** and compound **2** toward P–H bonds as compared to prior observations of Si–H bond activation and amine- and phosphine-borane polymerization highlight the challenges associated with the phosphorus lone pair in catalysis seeking to active P–H bonds.

Supplementary Materials: The following are available online: NMR spectra of **2** and the catalytic dehydrocoupling experiments, fully labeled molecular structure, crystallographic information file (CIF) and CheckCIF report for compound **2**.

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Data Availability Statement: CCDC-2173986 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk. All other data in this study can be found in **Supplementary Materials** and original data files at https://www.uvm.edu/~waterman/pubs.html.

Conflicts of Interest: The authors declare no conflict of interest.

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