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SPECIAL ISSUE PAPER

Amido PNP complexes of iridium: Synthesis and catalytic olefin and alkyne hydrogenation

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Abstract

In situ lithiation of HN(*o*-$C_6H_4PPh_2)_2$ (H[**1a**]) or HN(*o*-$C_6H_4PiPr_2)_2$ (H[**1b**]) with *n*BuLi in THF at −35°C followed by addition of $[Ir(\mu\text{-Cl})(COD)]_2$ (COD = 1,5-cyclooctadiene) in toluene at −35°C generates 5-coordinate [**1a**]Ir(η^4-COD) (**2a**) or 4-coordinate [**1b**]Ir(η^2-COD) (**2b**), respectively. Oxidative addition of N-H in H[**1b**] to $[Ir(\mu\text{-Cl})(COD)]_2$ affords square pyramidal [**1b**]Ir(H)(Cl) (**3b**). Metathetical reaction of **3b** with $LiBHEt_3$ in the presence of 1 atm of H_2 in toluene produces [**1b**]$Ir(H)_2$ (**4b**). Both **2a** and **4b** are active for catalytic hydrogenation of olefins and alkynes under extremely mild conditions.

KEYWORDS

amido, hydrogenation, iridium, PNP

1 | INTRODUCTION

Hydrogenation of unsaturated hydrocarbons is one of the most important transition metal-catalyzed reactions in industry.[1] The search for effective catalysts in this regard continues to constitute an active area of exploratory research.[2–8] Wilkinson catalyst, $RhCl(PPh_3)_3$,[9,10] and its cationic variations, $[M(diene)L_2]^+$ (M = Rh, Ir; L = phosphine, phosphite, arsine, pyridine),[11–19] represent pioneering success. Upon hydrogenation of olefins, these group 9 catalyst precursors were proved to transform into dihydride and olefin derivatives in catalytic cycles. We are currently exploring reaction chemistry employing amido PNP complexes.[20–23] We suppose that iridium olefin or dihydride complexes of $[N(o\text{-}C_6H_4PPh_2)_2]^-$ (**1a**) and $[N(o\text{-}C_6H_4PiPr_2)_2]^-$ (**1b**) are potential catalysts for hydrogenation of olefins and alkynes. In this contribution, we aim to synthesize these complexes and demonstrate their catalytic competence. Though iridium complexes similar to those of **1a** and **1b** are known,[24–26] their activities in hydrogenation catalysis have yet to be explored.

2 | RESULTS AND DISCUSSION

The reactions of $[Ir(\mu\text{-Cl})(COD)]_2$ (COD = 1,5-cyclooctadiene) with [**1a**]$Li(THF)_2$ or [**1b**]Li(THF), either isolated or prepared in situ, in toluene at −35°C afford [**1a**]Ir(η^4-COD) (**2a**) or [**1b**]Ir(η^2-COD) (**2b**), respectively (Scheme 1). As indicated by the $^{31}P\{^1H\}$ NMR spectra of reaction aliquots, the generation of **2a** is clean but that of **2b** is not. The isolated yield of the former is therefore nearly quantitative while that of the latter is poor to moderate. Interestingly, **2a** shows a singlet resonance in the $^{31}P\{^1H\}$ NMR spectrum at 14.7 ppm whereas **2b** reveals an AB quartet resonance in the $^{31}P\{^1H\}$ NMR spectrum centered at 28.8 ppm, implicating different coordination geometries for these PNP iridium complexes. A diagnostic difference in solution NMR spectra of these complexes concerns signals ascribable to unbound HC=CH found in the ^1H NMR spectrum of **2b**. The COD ligand in **2a** is therefore bound

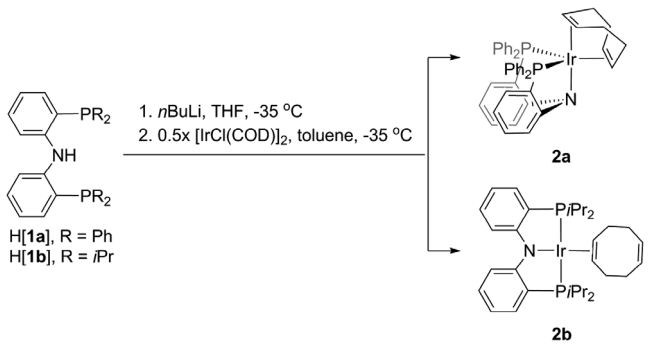
Dedicated to Professor Chien-Hong Cheng on the occasion of his 70th birthday.

to iridium in a η^4 fashion whereas that in **2b** is η^2. Though divergent, these results are consistent with the electronic and steric nature of their corresponding PNP ligands; **1a** is not only less electron-releasing but also less bulky than **1b**,[27–32] making **2a** an 18-electron species while **2b** a 16-electron complex.

Yellow crystals of **2a** suitable for X-ray diffraction analysis were grown by slow evaporation of a concentrated benzene solution at room temperature while orange crystals of **2b** were grown from a concentrated pentane solution at −35°C. Figures 1 and 2 depict their molecular structures. Selected bond distances and angles are summarized in Table 1.

As illustrated, **2a** is a η^4-COD complex whereas **2b** is a η^2-COD derivative. The coordination geometry of **2a** is best described as trigonal bipyramidal where the **1a** ligand is bound to iridium in a facial coordination mode, contrasting with what has been usually found for PNP as a pincer ligand.[33–38] The dihedral angle between two N-Ir-P planes is 120.21°. The N donor in **1a** and one of the C=C bonds in COD are disposed axially, having the N-Ir-centroid(C37-C38) angle of 173.39°. The iridium center is displaced by 0.266 Å toward the axial olefinic donor from the ideal equatorial plane defined by P1-P2-C41-C42, due likely to the constrained η^4-COD ring that confines the centroid(C37-C38)-Ir-centroid(C41-C42) angle of 85.31°. The displacement of iridium toward olefin instead of amide is consistent with the π-base nature of a monovalent group 9 metal that electronically prefers a π-acid to a π-base. In good agreement with higher s character in orbital hybridization composed of equatorial donors than axial counterparts, the Ir-centroid(C41-C42) distance of 2.014 Å is shorter than the Ir-centroid(C37-C38) distance of 2.069 Å. The C41-C42 bond distance of 1.439(7) Å is therefore longer than the C37-C38 bond distance of 1.417 (7) Å due to better back bonding from Ir(I) to the former.

In contrast to the facial PNP found in **2a**, the **1b** ligand in **2b** is bound typically in a meridional fashion. The dihedral angle between two N-Ir-P planes is 177.84°. The core structure of **2b** is best described as square planar. Its bond distances and angles are not exceptional.



SCHEME 1 Synthesis of iridium COD complexes **2**

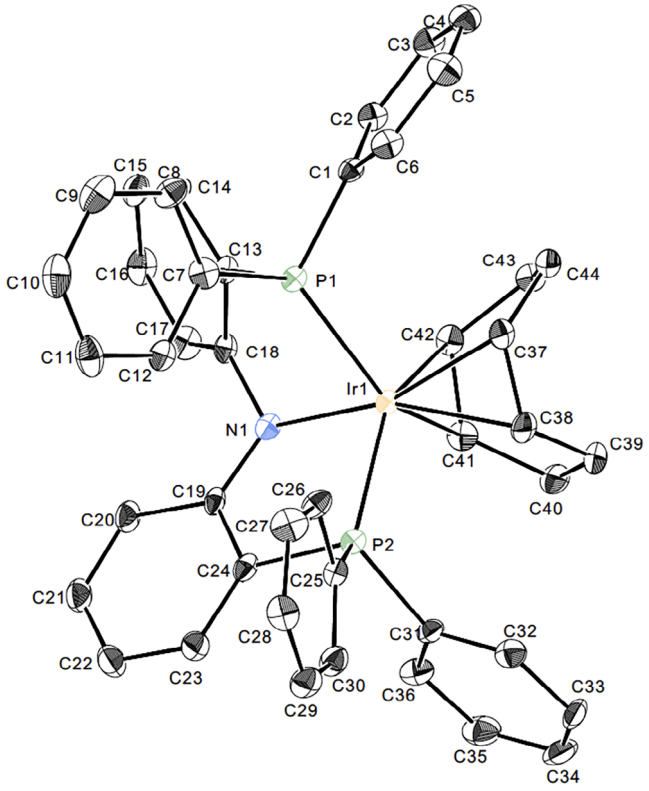


FIGURE 1 Molecular structure of **2a** with thermal ellipsoids drawn at the 35% probability level. All hydrogen atoms are omitted for clarity

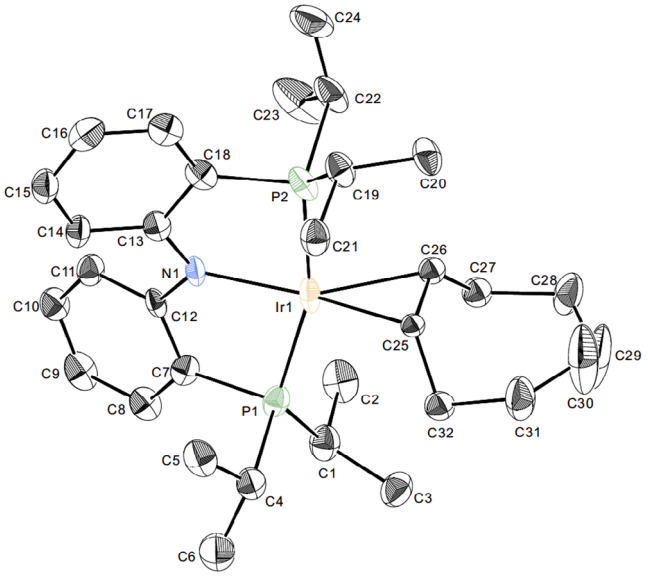
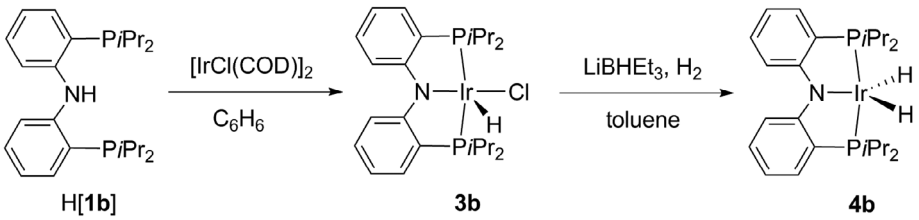


FIGURE 2 Molecular structure of **2b** with thermal ellipsoids drawn at the 35% probability level. All hydrogen atoms are omitted for clarity

TABLE 1 Selected bond distances (Å) and angles (deg) of **2a**, **2b**, **3b**, and **4b**[a]

Compound	2a	2b[b]	3b	4b
Ir-N	2.104(4)	2.065(5)	2.035(9)	2.060(6)
Ir-P	2.2965(11)	2.292(2)	2.290(3)	2.270(2)
	2.3607(11)	2.306(2)	2.297(3)	2.275(2)
Ir-X	2.069	2.034	2.349(4)	
	2.014			
C═C	1.417(7)	1.436(15)		
	1.439(7)			
P-Ir-P	117.55(4)	162.28(7)	164.54(12)	167.69(7)
N-Ir-P	78.42(10)	81.41(17)	83.1(3)	84.17(17)
	82.47(11)	81.01(17)	82.3(3)	83.52(17)
P-Ir-X	105.79	85.47	96.55(14)	
	116.17	112.03	98.48(14)	
	99.67			
	122.02			
N-Ir-X	88.25	166.72	174.5(3)	
	173.39			
X-Ir-X	85.31			

[a]X represents Cl or the centroid of a bound C═C bond.
[b]Data refer to the major conformation due to a disordered COD.



H[**1b**] **3b** **4b**

SCHEME 2 Synthesis of iridium hydride complexes of **1b**

The rather unsatisfactory synthesis of **2b** implicates the necessity of a second approach to iridium complexes of **1b**. Oxidative addition of H[**1b**] to $[Ir(\mu\text{-}Cl)(COD)]_2$ in benzene at room temperature generates forest green [**1b**]Ir(H)(Cl) (**3b**) in nearly quantitative yield (Scheme 2). The ^1H NMR spectrum of **3b** shows a diagnostic triplet resonance for its hydride ligand at −45.2 ppm with $^2J_{HP}$ of 14 Hz. Subsequent metathetical reaction of **3b** with $LiBHEt_3$ in the presence of 1 atm of H_2 in toluene at room temperature produces red crystalline [**1b**]$Ir(H)_2$ (**4b**). Its hydride ligands resonate in the ^1H NMR spectrum at −25.5 ppm.

Crystals of **3b** suitable for X-ray diffraction analysis were grown by layering pentane on top of a concentrated diethyl ether solution at −35°C while those of **4b** were grown from a concentrated diethyl ether solution at −35°C. Figures 3 and 4 depict their molecular structures. Similar to **2b**, the **1b** ligand in **3b** and **4b** is also bound in a meridional manner. The coordination geometry of **3b** is best described as square pyramidal with its hydride ligand at the apical position whereas that of **4b** is trigonal bipyramidal. Bond distances and angles of these complexes are not atypical.

The reactivity of complexes **2a** and **4b** was assessed with respect to catalytic hydrogenation of unsaturated hydrocarbons. As summarized in Table 2, these complexes are active catalyst precursors to hydrogenate olefins and alkynes under extremely mild conditions.

Styrene is successfully hydrogenated to give ethylbenzene with turnover numbers (TONs) up to 800 (entries 1–6) under the conditions examined. Carrying an ester functional group, *n*-butyl acrylate is quantitatively converted to *n*-butyl propanoate (entries 7–8). In contrast to these terminal olefins, internal alkenes are much less reactive due to their steric hindrance. The conversions of cyclohex-2-en-1-one, *cis*-cyclooctene (COE), and COD are poor to moderate (entries 9–14) though these reactions proceed cleanly.

Both terminal and internal alkynes are satisfactorily hydrogenated, having quantitative conversions to afford their corresponding products composed of alkenes and

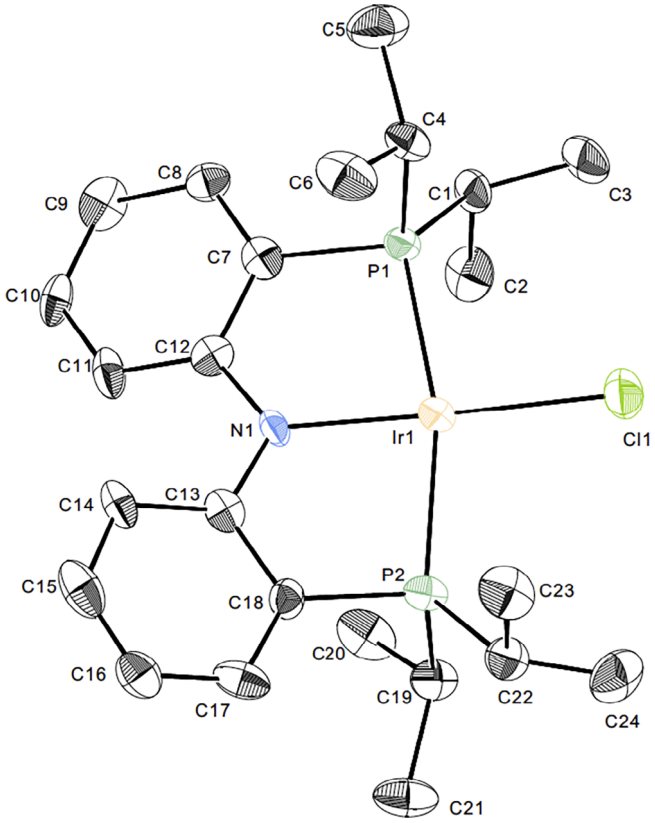


FIGURE 3 Molecular structure of **3b** with thermal ellipsoids drawn at the 35% probability level. All hydrogen atoms are omitted for clarity

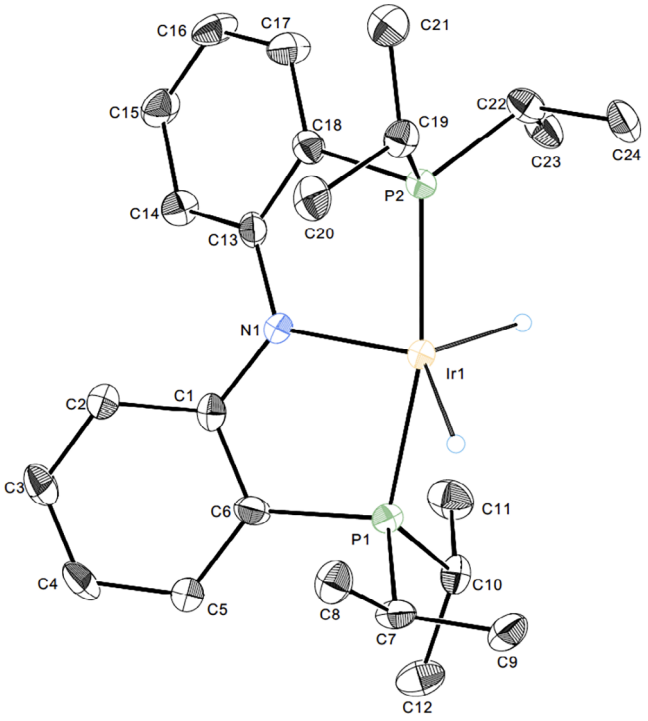


FIGURE 4 Molecular structure of **4b** with thermal ellipsoids drawn at the 35% probability level. All hydrogen atoms except hydrides are omitted for clarity

alkanes (entries 15–18). The consequence that alkynes and *n*-butyl acrylate are more reactive than other unsaturated substrates examined in this study is ascribable to higher π acidity of the former. Interestingly, stilbene, though an internal olefin that is produced from hydrogenation of diphenylacetylene (entries 17–18), is more reactive than styrene (entries 15–16). Attempts to hydrogenate nitriles,[39–46] however, were not successful (entries 19–22). Collectively, the catalytic activity of **2a** is comparable to that of **4b**. Unsaturated substrates bearing aryl, ester, and ketone functional groups are compatible but nitriles are not.

3 | EXPERIMENTAL

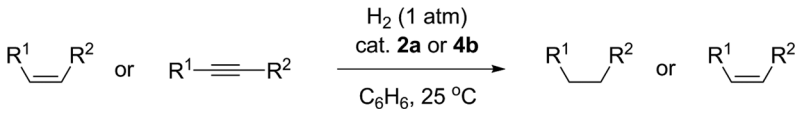
3.1 | General procedures

Unless otherwise specified, all experiments were performed under nitrogen using standard Schlenk or glovebox techniques. All solvents were reagent grade or better and purified by standard methods. Compounds H[**1a**],[20,28] H[**1b**],[28] [**1a**]Li(THF)$_2$,[20,28] [**1b**]Li(THF),[28] and [Ir(μ-Cl)(COD)]$_2$[47] were prepared following reported procedures. All other chemicals were obtained from commercial vendors and used as received. Unless otherwise noted, all NMR spectra were recorded at room temperature in specified solvents on Varian Unity or **Bruker AV** instruments. Chemical shifts (δ) are listed as parts per million downfield from tetramethylsilane. Coupling constants (*J*) and peak widths at half-height ($\Delta\nu_{1/2}$) are listed in hertz. ^{1}H NMR spectra are referenced using the residual solvent peak at δ 7.16 for C_6D_6. ^{13}C NMR spectra are referenced using the internal solvent peak at δ 128.39 for C_6D_6. The assignment of the carbon atoms for all new compounds is based on the DEPT ^{13}C NMR spectroscopy. ^{31}P NMR spectra are referenced externally using 85% H_3PO_4 at δ 0. Routine coupling constants are not listed. Elemental analysis was performed on a Heraeus CHN-O Rapid analyzer. The hydrogenation reactions were analyzed by GC on a Varian chrompack CP-3800 instrument equipped with a CP-Sil 5 CB chrompack capillary column. Conversions and yields were calculated versus decane as the internal standard. The identity of the hydrogenated products was confirmed by comparison with authentic samples.

3.2 | X-ray crystallography

Data were collected on a diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å).

TABLE 2 Catalytic hydrogenation of olefins and alkynes by **2a** or **4b**[a]



Entry	Substrate	Cat. (mol%)	Time (hr)	Conv. (%)	Product(s)	Yield (%)	TON[b]
1	Styrene	**2a** (0.5)	1	19	Ethylbenzene	19	38
2	Styrene	**4b** (0.5)	1	7	Ethylbenzene	7	14
3	Styrene	**2a** (0.5)	24	95	Ethylbenzene	95	190
4	Styrene	**4b** (0.5)	24	91	Ethylbenzene	91	182
5	Styrene	**2a** (0.05)	72	30	Ethylbenzene	30	600
6	Styrene	**4b** (0.05)	72	40	Ethylbenzene	40	800
7	*n*-Butyl acrylate	**2a** (0.5)	24	100	*n*-Butyl propanoate	100	200
8	*n*-Butyl acrylate	**4b** (0.5)	24	100	*n*-Butyl propanoate	100	200
9	Cyclohex-2-en-1-one	**2a** (0.5)	24	45	Cyclohexanone	45	90
10	Cyclohex-2-en-1-one	**4b** (0.5)	24	5	Cyclohexanone	5	10
11	*cis*-Cyclooctene	**2a** (0.5)	24	11	Cyclooctane	11	22
12	*cis*-Cyclooctene	**4b** (0.5)	24	10	Cyclooctane	10	20
13	1,5-Cyclooctadiene	**2a** (0.5)	24	29	*cis*-Cyclooctene	9	98
					Cyclooctane	20	
14	1,5-Cyclooctadiene	**4b** (0.5)	24	16	*cis*-Cyclooctene	14	36
					Cyclooctane	2	
15	Phenylacetylene	**2a** (0.5)	24	100	Styrene	60	280
					Ethylbenzene	40	
16	Phenylacetylene	**4b** (0.5)	24	100	Styrene	55	290
					Ethylbenzene	45	
17	Diphenylacetylene	**2a** (0.5)	24	100	Stilbene	12	376
					Dibenzyl	88	
18	Diphenylacetylene	**4b** (0.5)	24	100	Stilbene	2	396
					Dibenzyl	98	
19	Benzonitrile	**2a** (0.5)	24	0	NA	0	0
20	Benzonitrile	**4b** (0.5)	24	0	NA	0	0
21	Benzyl cyanide	**2a** (0.5)	24	0	NA	0	0
22	Benzyl cyanide	**4b** (0.5)	24	0	NA	0	0

[a]Conversions, product identity, and yields were characterized by GC with decane as the internal standard, average of two runs. Reaction time was not optimized.
[b]Sum of reduced bond order from olefins or alkynes per catalyst precursor.

Structures were solved by direct methods and refined by full matrix least squares procedures against F^2 using SHELXL-97[48] or SHELXL-2014.[49] All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. The COD ligand in **2b** is disordered in a ratio of 60:40 over two conformations. CCDC 1961799–1961802 contain 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.

3.3 | Synthesis of [1a]Ir(η⁴-COD) (2a)

Solid [**1a**]Li(THF)$_2$ (102 mg, 0.148 mmol) was dissolved in toluene (4 ml) and cooled to −35°C. To this was added solid [Ir(μ-Cl)(COD)]$_2$ (50 mg, 0.074 mmol, 0.5 equiv).

The reaction mixture was stirred at room temperature for 1 hr and evaporated to dryness under reduced pressure. The solid residue was extracted with benzene (5 ml), filtered through a pad of Celite, and evaporated to dryness. The solid thus obtained was washed with pentane (1 ml × 2) and dried in vacuo, affording the product as a yellowish-orange solid; yield 122 mg (98%). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.75 (m, 4, Ar), 7.49 (t, 2, Ar), 7.46 (m, 2, Ar), 7.37 (t, 4, Ar), 7.10 (m, 6, Ar), 6.88 (t, 2, Ar), 6.82 (t, 2, Ar), 6.75 (t, 4, Ar), 6.60 (t, 2, Ar), 3.77 (m, 2, CH=C*H*CH$_2$), 3.17 (m, 2, CH=C*H*CH$_2$), 2.01 (m, 2, CH=CHC*H*$_2$), 1.58 (m, 2, CH=CHC*H*$_2$), 1.21 (m, 2, CH=CHC*H*$_2$), 1.11 (m, 2, CH=CHC*H*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ 14.65 ($\Delta\nu_{1/2}$ = 4.54). ^{13}C{^{1}H} NMR (C_6D_6, 125.70 MHz) δ 164.42 (d, J_{CP} = 27.48, C), 139.32 (dd, J_{CP} = 43.87 and 5.41, C), 137.79 (d, J_{CP} = 29.24, C), 133.92 (vt, J_{CP} = 7.28, CH), 133.47 (s, CH), 133.09 (vt, J_{CP} = 5.40, CH), 130.02 (d, J_{CP} = 53.97, C), 130.21 (s, CH), 129.42 (s, CH), 129.13 (s, CH), 128.50 (vt, J_{CP} = 11.04, CH), 128.45 (vt, J_{CP} = 7.28, CH), 120.02 (d, J_{CP} = 8.16, CH), 118.53 (d, J_{CP} = 2.76, CH), 65.80 (s, CH=*C*HCH$_2$), 61.01 (dd, J_{CP} = 28.41 and 5.41, CH=*C*HCH$_2$), 32.73 (s, CH=CH*C*H$_2$), 32.25 (s, CH=CH*C*H$_2$). Anal. Calcd. for $C_{44}H_{40}IrNP_2$: C, 63.14; H, 4.82; N, 1.67. Found: C, 63.25; H, 4.88; N, 1.76.

3.4 | Synthesis of [1b]Ir(η^2-COD) (2b)

Procedures were similar to those of **2a** with the employment of [**1b**]Li(THF) in the place of [**1a**]Li(THF)$_2$, affording the product as an orange solid; yield 40%. ^{1}H NMR (C_6D_6, 200 MHz) δ 7.74 (d, 2, Ar), 6.99 (m, 4, Ar), 6.56 (t, 2, Ar), 6.06 (m, 1, unbound HC=CH), 5.82 (m, 1, unbound HC=CH), 3.35 (m, 2, bound HC=CH), 2.91 (m, 1, C*H*Me$_2$), 2.65 (m, 1, C*H*Me$_2$), 2.51 (m, 2, C*H*Me$_2$), 2.30 (br s, 8, CH$_2$ and CH*Me*$_2$), 1.72 (m, 4, CH$_2$), 1.33 (br s, 12, CH*Me*$_2$), 1.01 (br s, 8, CH$_2$ and CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 80.95 MHz) δ 28.77 (AB quartet). Anal. Calcd. for $C_{32}H_{48}IrNP_2$: C, 54.84; H, 6.90; N, 2.00. Found: C, 55.13; H, 7.12; N, 1.95.

3.5 | Synthesis of [1b]Ir(H)(Cl) (3b)

Solid H[**1b**] (300 mg, 0.747 mmol) was dissolved in benzene (10 ml). To this was added solid [Ir(μ-Cl)(COD)]$_2$ (251 mg, 0.373 mmol, 0.5 equiv) at room temperature. The reaction mixture was stirred at room temperature for 1 h and evaporated to dryness under reduced pressure. The solid residue was dissolved in a mixture of pentane (8 ml) and diethyl ether (4 ml). The solution was concentrated under reduced pressure to ca. 0.5 ml. The solid thus precipitated was collected and dried in vacuo to afford the product as a forest green solid; yield 445 mg (95%). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.87 (d, 2, Ar), 7.04 (m, 2, Ar), 6.87 (t, 2, Ar), 6.52 (t, 2, Ar), 2.90 (m, 2, C*H*Me$_2$), 2.44 (m, 2, C*H*Me$_2$), 1.35 (dt, 6, CH*Me*$_2$), 1.18 (dt, 6, CH*Me*$_2$), 1.05 (dt, 6, CH*Me*$_2$), 0.94 (dt, 6, CH*Me*$_2$), −45.18 (t, 1, $^{2}J_{HP}$ = 14, Ir*H*). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ 44.17 ($\Delta\nu_{1/2}$ = 30.3). ^{13}C{^{1}H} NMR (C_6D_6, 125.70 MHz) δ 165.71 (t, J_{CP} = 6.4, C), 133.14 (s, CH), 130.87 (s, CH), 122.42 (t, J_{CP} = 21.08, C), 118.15 (s, CH), 117.57 (s, CH), 27.38 (t, J_{CP} = 13.68, *C*HMe$_2$), 25.11 (t, J_{CP} = 15.56, *C*HMe$_2$), 18.86 (s, CH*Me*$_2$), 18.49 (s, CH*Me*$_2$). Anal. Calcd. for $C_{24}H_{37}ClIrNP_2$: C, 45.82; H, 5.93; N, 2.23. Found: C, 45.94; H, 6.12; N, 1.95.

3.6 | Synthesis of [1b]Ir(H)$_2$ (4b)

To a toluene solution (2 ml) of **3b** (59 mg, 0.093 mmol) was added LiBHEt$_3$ (0.1 ml, 1.0 M in THF, 0.1 mmol) at room temperature. The reaction solution was degassed with three times of freeze-pump-thaw cycles and charged with H_2 (1 atm) at room temperature. After being stirred at room temperature overnight, the reaction solution was evaporated to dryness under reduced pressure. The product was extracted with diethyl ether (10 ml). The ether extract was filtered through a pad of Celite and evaporated to dryness to afford the product as a red solid; yield 51 mg (92%). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.88 (d, 2, Ar), 7.07 (m, 4, Ar), 6.60 (t, 2, Ar), 2.11 (m, 4, C*H*Me$_2$), 1.18 (dd, 12, CH*Me*$_2$), 0.96 (dd, 12, CH*Me*$_2$), −25.51 (t, 2, $^{2}J_{HP}$ = 11.5, IrH$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz) δ 58.71 ($\Delta\nu_{1/2}$ = 33.9). ^{13}C{^{1}H} NMR (C_6D_6, 125.70 MHz) δ 166.76 (t, J_{CP} = 10.98, C), 133.93 (s, CH), 131.40 (s, CH), 126.90 (t, J_{CP} = 19.70, C), 118.68 (s, CH), 115.94 (t, J_{CP} = 5.02, CH), 25.73 (t, $^{1}J_{CP}$ = 15.31, *C*HMe$_2$), 20.46 (t, J_{CP} = 3.20, CH*Me*$_2$), 18.88 (s, CH*Me*$_2$). Anal. Calcd. for $C_{24}H_{38}IrNP_2$: C, 48.47; H, 6.44; N, 2.36. Found: C, 48.59; H, 6.56; N, 2.16.

3.7 | General procedures for catalytic hydrogenation of olefins and alkynes

A Schlenk flask was charged with a benzene solution (2 ml) of **2a** or **4b** (0.6 mM), olefin or alkyne, decane, and a magnetic stir bar (Table 2). The reaction solution was degassed with three times of freeze-pump-thaw cycles and charged with H_2 (1 atm) at room temperature. The reaction solution was stirred at room temperature for a prescribed period of time and an aliquot was taken for GC analysis.

4 | CONCLUSIONS

We have prepared amido PNP complexes of iridium by oxidative addition and metathetical reactions. The facial

coordination mode of PNP found in 5-coordinate **2a** is unusual. Consistent with the electronic and steric nature of these PNP ligands, COD in **2a** is bound in a η^4 fashion whereas that in **2b** is η^2. Not only were formally monovalent **2a** and **2b** prepared, but trivalent **3b** and **4b** were also characterized. Both **2a** and **4b** are active in catalytic hydrogenation of olefins and alkynes under extremely mild conditions.

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REFERENCES

[1] H.-U. Blaser, F. Spindler, M. Thommen, in *The handbook of homogeneous hydrogenation* (Eds: J. G. de Vries, C. J. Elsevier), Wiley-VCH, Weinheim, Germany **2008**, p. 1279.
[2] T. Zell, D. Milstein, *Acc. Chem. Res.* **2015**, *48*, 1979.
[3] P. J. Chirik, *Acc. Chem. Res.* **2015**, *48*, 1687.
[4] R. H. Morris, *Acc. Chem. Res.* **2015**, *48*, 1494.
[5] S. Chakraborty, P. Bhattacharya, H. G. Dai, H. R. Guan, *Acc. Chem. Res.* **2015**, *48*, 1995.
[6] S. Kaufhold, L. Petermann, R. Staehle, S. Rau, *Coord. Chem. Rev.* **2015**, *304*, 73.
[7] R. Noyori, S. Hashiguchi, *Acc. Chem. Res.* **1997**, *30*, 97.
[8] C. Pettinari, F. Marchetti, D. Martini, in *Comprehensive coordination chemistry II* (Eds: J. A. McCleverty, T. J. Meyer), Pergamon, Turkey, Oxford **2003**, p. 75.
[9] J. A. Osborn, F. H. Jardine, J. F. Young, G. Wilkinson, *J. Chem. Soc. A* **1966**, 1711.
[10] J. A. Osborn, G. Wilkinson, J. J. Mrowca, *Inorg. Synth.* **1967**, *10*, 67.
[11] J. R. Shapley, R. R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.* **1969**, *91*, 2816.
[12] R. R. Schrock, J. A. Osborn, *J. Chem. Soc. D* **1970**, 567.
[13] R. R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.* **1971**, *93*, 2397.
[14] R. R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.* **1971**, *93*, 3089.
[15] R. R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.* **1976**, *98*, 2134.
[16] R. R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.* **1976**, *98*, 2143.
[17] R. R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.* **1976**, *98*, 4450.
[18] R. Crabtree, *Acc. Chem. Res.* **1979**, *12*, 331.
[19] R. H. Crabtree, S. M. Morehouse, J. M. Quirk, *Inorg. Synth.* **1986**, *24*, 173.
[20] L.-C. Liang, J.-M. Lin, C.-H. Hung, *Organometallics* **2003**, *22*, 3007.
[21] L.-C. Liang, *Coord. Chem. Rev.* **2006**, *250*, 1152.
[22] X.-R. Zou, S.-M. Liao, K.-W. Huang, L.-C. Liang, *Chem. Lett.* **2019**, *48*, 811.
[23] C. Yao, P. Chakraborty, E. Aresu, H. Li, C. Guan, C. Zhou, L.-C. Liang, K.-W. Huang, *Dalton Trans.* **2018**, *47*, 16057.
[24] E. Calimano, T. D. Tilley, *Dalton Trans.* **2010**, *39*, 9250.
[25] O. V. Ozerov, C. Y. Guo, V. A. Papkov, B. M. Foxman, *J. Am. Chem. Soc.* **2004**, *126*, 4792.
[26] L. Fan, S. Parkin, O. V. Ozerov, *J. Am. Chem. Soc.* **2005**, *127*, 16772.
[27] L.-C. Liang, P.-S. Chien, Y.-L. Huang, *J. Am. Chem. Soc.* **2006**, *128*, 15562.
[28] L.-C. Liang, P.-S. Chien, J.-M. Lin, M.-H. Huang, Y.-L. Huang, J.-H. Liao, *Organometallics* **2006**, *25*, 1399.
[29] L.-C. Liang, P.-S. Chien, P.-Y. Lee, *Organometallics* **2008**, *27*, 3082.
[30] L.-C. Liang, Y.-T. Hung, Y.-L. Huang, P.-S. Chien, P.-Y. Lee, W.-C. Chen, *Organometallics* **2012**, *31*, 700.
[31] Y.-T. Hung, M.-T. Chen, M.-H. Huang, T.-Y. Kao, Y.-S. Liu, L.-C. Liang, *Inorg. Chem. Front.* **2014**, *1*, 405.
[32] L.-C. Liang, P.-S. Chien, L.-H. Song, *J. Organomet. Chem.* **2016**, *804*, 30.
[33] M.-H. Huang, L.-C. Liang, *Organometallics* **2004**, *23*, 2813.
[34] L.-C. Liang, J.-M. Lin, W.-Y. Lee, *Chem. Commun.* **2005**, 2462.
[35] L.-C. Liang, P.-S. Chien, P.-Y. Lee, J.-M. Lin, Y.-L. Huang, *Dalton Trans.* **2008**, 3320.
[36] P.-Y. Lee, L.-C. Liang, *Inorg. Chem.* **2009**, *48*, 5480.
[37] L.-C. Liang, C.-W. Li, P.-Y. Lee, C.-H. Chang, H. Man Lee, *Dalton Trans.* **2011**, *40*, 9004.
[38] L.-C. Liang, P.-S. Chien, Y.-C. Hsiao, C.-W. Li, C.-H. Chang, *J. Organomet. Chem.* **2011**, *696*, 3961.
[39] H. Li, A. Al-Dakhil, D. Lupp, S. S. Gholap, Z. Lai, L.-C. Liang, K.-W. Huang, *Org. Lett.* **2018**, *20*, 6430.
[40] D. B. Bagal, B. M. Bhanage, *Adv. Synth. Catal.* **2015**, *357*, 883.
[41] S. Chakraborty, D. Milstein, *ACS Catal.* **2017**, *7*, 3968.
[42] S. Chakraborty, G. Leitus, D. Milstein, *Chem. Commun.* **2016**, *52*, 1812.
[43] S. Elangovan, C. Topf, S. Fischer, H. J. Jiao, A. Spannenberg, W. Baumann, R. Ludwig, K. Junge, M. Beller, *J. Am. Chem. Soc.* **2016**, *138*, 8809.
[44] A. Mukherjee, D. Srimani, S. Chakraborty, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2015**, *137*, 8888.
[45] C. Bornschein, S. Werkmeister, B. Wendt, H. J. Jiao, E. Alberico, W. Baumann, H. Junge, K. Junge, M. Beller, *Nat. Commun.* **2014**, *5*, 4111.
[46] S. Chakraborty, H. Berke, *ACS Catal.* **2014**, *4*, 2191.
[47] J. L. Herde, J. C. Lambert, C. V. Senoff, M. A. Cushing, *Inorg. Synth.* **1974**, *15*, 18.
[48] G. Sheldrick, *Acta Cryst. A* **2008**, *64*, 112.
[49] G. M. Sheldrick, *Acta Cryst. C* **2015**, *71*, 3.

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