Facile generation of iridium PC\textsubscript{carbene}P pincer complexes via water elimination from an alcohol proligand

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Experimental

General information
All syntheses were carried out in N₂ atmosphere using a glovebox or with standard Schlenk techniques. All reactions were performed in glassware that was oven-dried for at least 12 h. Ligand 1,¹ 1-H₂,² 1a,³ 1b,³ [IrCl(COD)]₂,⁴ [IrCl(COD)(PPh₃)]₅ and Na[BArF₄]⁶ were prepared according to reported methods. [Ir(COD)₂][BArF₄] was prepared using a similar method for the synthesis of analogous rhodium complexes.⁷ Toluene, DCM, and n-hexane were dried over activated alumina using a LC Technology Solutions Inc. SP-1 solvent purification system and then deoxygenated prior to use. CD₂Cl₂ and C₆D₆ used was stirred over CaH₂ at room temperature under a nitrogen atmosphere overnight prior to distillation under reduced pressure and storage over 4 Å molecular sieves. NMR spectra were recorded using a Bruker AV500 spectrometer. All chemical shifts are quoted in parts per million (ppm) relative to SiMe₄ (¹H, ¹³C) or H₃PO₄ (85%) (³¹P). Coupling constant J values are given in Hz. ¹³C and ³¹P NMR analyses were performed with ¹H decoupling. HRMS (ESI-TOF) spectra were obtained using an Agilent Technologies 6230 TOF LC/MS. Single crystal was measured at low temperature (T = 100K) on a four circles goniometer Kappa geometry Bruker AXS D8 Venture equipped with a Photon 100 CMOS active pixel sensor detector using Copper (λ = 1.54178 Å) or Molybdenum (λ = 0.71073 Å) monochromatized X-Ray radiation sources.
Reaction between complex 7a and Na[BArF₄] that formed [Ir(CO)(PPh₃)₃][BArF₄]

A solution of complex 7a (10.4 mg, 0.01 mmol) in CD₂Cl₂ (0.6 mL) in a screw cap NMR tube was heated to 333 K for 18 h. Analysis by ³¹P{¹H} NMR spectroscopy indicated that no conversion of 7a had occurred. The NMR tube was taken into a glovebox and Na[BArF₄]·2THF (10.3 mg, 0.01 mmol) was then added at room temperature and shaken well to mix. ³¹P{¹H} NMR analyses after 30 min at room temperature revealed the formation of a single species, which was not the desired complex 3 (presumably the corresponding chloride abstracted cationic hydrido Ir complex was present:

δ_H (500 MHz, CD₂Cl₂, 298 K) -19.02 (1H, td, J₁'H-P 18.1, J₂'H-P 15.3, Ir-H), 5.06 (1H, d, J₄'H-P 12.8, 1H, methine C-H), 6.60 – 7.96 (55H, m, Ar-H).

δ_P (202 MHz, CD₂Cl₂, 298 K) -1.6 (1P, t, J₂,'P-P 12.3, PPh₃), 0.7 (2P, d, J₄,'P-P 12.3, POP pincer P's).

When heated the solution was at 323 K overnight, this species was quantitatively converted to [Ir(CO)(PPh₃)₃][BArF₄], with ³¹P{¹H} NMR spectroscopic evidence in agreement with the literature for [Ir(CO)(PPh₃)₃][OTf].

S-3
\[ \delta_H (500 \text{ MHz, CD}_2\text{Cl}_2, 298 \text{ K}) \] 6.93 – 7.10 (12H, m, Ar-H), 7.22 – 7.31 (14H, m, Ar-H), 7.34 – 7.46 (18H, m, Ar-H), 7.56 (4H, s, [BAr\text{F}_4] Ar-H), 7.73 (8H, s, [BAr\text{F}_4] Ar-H).

\[ \delta_p (202 \text{ MHz, CD}_2\text{Cl}_2, 298 \text{ K}) \] 15.4 (2P, d, J_{2, p-p} 29.6, PPh_3), 18.0 (1P, t, J_{2, p-p} 29.6, PPh_3).

**Attempted conversion of complex 7b to complexes 2 and 3**

A solution of complex 7b (10.4 mg, 0.01 mmol) in C_6D_6 (0.6 mL) in a screw cap NMR tube was heated to 353 K for 5 h. Analysis by \(^1\)H and \(^31\)P\{\(^1\)H\} NMR spectroscopy indicated that no conversion of 7b had occurred. The NMR tube was taken into a glovebox and Na[BAr\text{F}_4]·2THF (10.3 mg, 0.01 mmol) was then added at room temperature and shaken well to mix. NMR analyses after allowing the mixture to react at room temperature and also with heating to 348 K revealed the formation of several unknown species, none of which were the desired product 3.

**NMR spectroscopic analyses of reaction intermediates in the formation of 2**

[\text{IrCl(COD)}]_2 (13.4 mg, 0.020 mmol) and compound 1, 1a, 1b or 1-H_2 (22.1 mg, 0.040 mmol) were added into a J. Young valve NMR tube (see Figure S30 and Figure S28 for the structures of 1a and 1b respectively).
CD$_2$Cl$_2$ (0.6 mL) was vacuum transferred into the NMR tube using a liquid nitrogen bath, and then the NMR tube was filled with a N$_2$ or H$_2$ (≈ 4 atm) atmosphere. The CD$_2$Cl$_2$ solvent was thawed immediately prior to placing the NMR tube into a NMR spectrometer set at the desired temperature for analyses. Intermediates I, II, VI and VII were all characterised by NMR spectroscopy but only VII was isolated.

Intermediate I:

δ$_H$ (500 MHz, CD$_2$Cl$_2$, 263 K) 1.32 – 1.62 (4H, m, COD H), 2.02 (4H, s, COD H), 3.52 (4H, s, COD H), 5.91 (1H, d, $J_{3,HH}$ 3.4, methine C-H), 6.58 (2H, t, $J_{8.0}$, Ar-H), 6.65 (3H, t, $J_{8.1}$, Ar-H), 7.03 (2H, t, $J_{7.4}$, Ar-H), 7.14 – 7.36 (13H, m, Ar-H), 7.44 – 7.48 (5H, m, Ar-H), 7.64 – 7.73 (4H, m, Ar-H), 11.07 (1H, d, $J_{3,HH}$ 3.4, O-H).

δ$_P$ (202 MHz, CD$_2$Cl$_2$, 263 K) -6.1 (2P, s, PCP pincer P).

Intermediate II:

Selected δ$_H$ (500 MHz, CD$_2$Cl$_2$, 268 K) -8.18 (1H, ddd, $J_{2,H-P}$ 93.3, $J_{2,H-P}$ 9.8, $J_{4,HH}$ 2.5 Hz, Ir-H), 0.82 – 0.93 (1H, m, COD H), 2.22 – 2.49 (6H, m, COD H), 3.07 – 3.19 (1H, m, COD H), 4.07 – 4.15 (1H, m, COD H), 4.29 – 4.43 (1H, m, COD H), 5.00 – 5.11 (1H, m, COD H), 6.09 – 6.19 (1H, m, COD H), 6.52 (2H, dd, $J_{10.3}$, $J_{7.7}$, Ar-H), 8.03 (1H, dd, $J_{8.0}$, $J_{2.7}$, Ar-H), 8.28 (1H, dd, $J_{7.9}$, $J_{3.4}$, Ar-H).

δ$_P$ (202 MHz, CD$_2$Cl$_2$, 268 K) 7.5 (1P, d, $J_{2,P-P}$ 17.2, P trans to Ir-H), 19.2 (1P, d, $J_{2,P-P}$ 17.2, P cis to Ir-H).

Intermediate VI:
Selected $\delta_H$ (500 MHz, CD$_2$Cl$_2$, 259 K) -12.57 (2H, t, $J_{2, P}$ 12.3, Ir-H).

Selected $\delta_C$ from HMBC (126 MHz, CD$_2$Cl$_2$, 259 K) 132.1.

$\delta_P$ (202 MHz, CD$_2$Cl$_2$, 259 K) 18.8 (2P, s, PCP pincer $P$).

Complex VII·CH$_2$Cl$_2$:

Within one hour of mixing [IrCl(COD)]$_2$ and compound 1 or 1b in CH$_2$Cl$_2$ or CD$_2$Cl$_2$ respectively, as described above, X-ray quality crystals had precipitated. To isolate, the crystals of VII·CH$_2$Cl$_2$ were filtered, washed with small quantities of DCM (2 x 2 mL) and then dried under vacuum (23 mg, 61% yield when ligand 1 was used). When ligand 1b was used in the reaction, the quantity of crystals appeared to be greater than when ligand 1 was used. This indicated that pathway B may be more favoured than pathway A in the presence of a methine C-D bond in the pincer ligand, which suggests a notable kinetic isotope effect was present for the activation of this bond.

Found: C, 59.4; H, 4.5. Calc. for C$_{105}$H$_{70}$BF$_{24}$IrP$_4$·CH$_2$Cl$_2$: C, 59.0; H, 4.6%.

$\delta_H$ (500 MHz, CDCl$_3$, 298 K) 1.54 – 1.82 (6H, m, COD $H$), 2.31 – 2.47 (2H, m, COD $H$), 2.78 (2H, s (br), COD $H$), 3.13 – 3.31 (2H, m, COD $H$), 5.21 (1H, s, methine C-$H$), 5.30 (2H, s, CH$_2$Cl$_2$ solvate), 6.49 – 6.57 (2H, m, Ar-$H$), 6.83 – 6.92 (6H, m, Ar-$H$), 7.03 – 7.08 (2H, m, Ar-$H$), 7.10 – 7.24 (8H, m, Ar-$H$), 7.32 – 7.39 (6H, m, Ar-$H$), 7.57 – 7.66 (4H, m, Ar-$H$).

$\delta_P$ (202 MHz, CD$_2$Cl$_2$, 298 K) -11.1 (2P, s, PCP pincer $P$).

$\delta_C$ (126 MHz, CD$_2$Cl$_2$, 298 K) 30.3 (s, COD $C$), 35.7 (s, COD $C$), 53.5 (s, CH$_2$Cl$_2$ solvate), 61.6 (d, $J_{12.5, C-P}$ 5.7, methine $C$), 125.8 (t, $J_{2.7, Ar-C}$), 127.6 (t, $J_{4.5, Ar-C}$), 128.6
(t, J 5.8, Ar-C), 129.1 (s, Ar-C), 129.9 (t, J 4.1, Ar-C), 132.9 (t, J 5.3, Ar-C), 133.4 (t, J 5.9, Ar-C), 133.4 (s), 152.5 (d, J 6.2, Ar-C).

HRMS (ESI-TOF) m/z: [M]+ Calcd for C_{48}H_{41}IrOP$_2$ 852.2259; Found 852.2263.

**Addition of HCl to complex VII·CH$_2$Cl$_2$**

Complex VII·CH$_2$Cl$_2$ (8.5 mg, 0.009 mmol) and CD$_2$Cl$_2$ (0.6 mL) were added into a NMR tube, sealed with a septum and opentop screw cap and brought outside the glovebox. HCl in Et$_2$O (5 µL, 0.010 mmol, 2 M) was added through the septum at room temperature, the NMR tube was shaken vigorously and then immediately analysed by $^1$H and $^{31}$P{H} NMR spectroscopy.
NMR Spectra of complex 2

Figure S1 $^1$H NMR of complex 2 in CD$_2$Cl$_2$ at 298 K.

Figure S2 $^{31}$P($^1$H) NMR of complex 2 in CD$_2$Cl$_2$ at 298 K.
Figure S3 $^{13}$C(H) NMR of complex 2 in CD$_2$Cl$_2$ at 298 K. Inset shows zoomed in spectrum of the Ir=C resonance.
NMR Spectra of complex 3

Figure S4 $^1$H NMR of complex 3 in CD$_2$Cl$_2$ at 298 K. n-Hexane and silicone grease contaminants present.

Figure S5 $^{31}$P($^1$H) NMR of complex 3 in CD$_2$Cl$_2$ at 298 K. Inset shows zoomed in spectrum.
Figure S6 $^{13}$C($^1$H) NMR of complex 3 in CD$_2$Cl$_2$ at 298 K. Inset shows zoomed in spectrum of the Ir=C resonance.
NMR Spectra of complex 4

Figure S7 $^1$H NMR of complex 4 in CD$_2$Cl$_2$ at 298 K. Silicone grease contaminant present.

Figure S8 $^{31}$P($^1$H) NMR of complex 4 in CD$_2$Cl$_2$ at 298 K. Inset shows zoomed in spectrum.
Figure S9 $^{13}$C($^1$H) NMR of complex 4 in CD$_2$Cl$_2$ at 298 K. n-Hexane contaminant present. Inset shows zoomed in spectrum of the Ir=C resonance.
NMR Spectra of complex 5

Figure S10 \(^1\)H NMR of complex 5 in CD\(_2\)Cl\(_2\) at 298 K. \(n\)-Hexane and silicone grease contaminants present.

Figure S11 \(^{31}\)P\(^1\)H) NMR of complex 5 in CD\(_2\)Cl\(_2\) at 298 K. Inset shows zoomed in spectrum.
Figure S12 $^{13}$C[$^1$H] NMR of complex 5 in CD$_2$Cl$_2$ at 298 K.

Figure S13 Comparison of $^1$H and $^1$H[$^{31}$P] NMR spectra of the hydride resonance of complex 5 in CD$_2$Cl$_2$ at 298 K.
Figure S14 $^1$H-$^{13}$C HMBC NMR spectrum of complex 5 in CD$_2$Cl$_2$ at 298 K. Highlights the correlation between the Ir-H resonance at $\delta_{H}$ -9.61 ppm and Ir-C(sp$^3$) resonance at $\delta_{C}$ 55.11 ppm.
NMR Spectra of complex 6

Figure S15 \(^1\)H NMR of complex 6 in CD\(_2\)Cl\(_2\) at 298 K. n-Hexane and silicone grease contaminants present.

Figure S16 \(^{31}\)P\(^{(1)}\)H NMR of complex 6 in CD\(_2\)Cl\(_2\) at 298 K. Inset shows zoomed in spectrum.
Figure S17 $^{13}$C($^1$H) NMR of complex 6 in CD$_2$Cl$_2$ at 298 K. $n$-Hexane contaminant present.
NMR Spectra of complex 7a

Figure S18 $^1$H NMR of complex 7a in CD$_2$Cl$_2$ at 298 K. Toluene and silicone grease contaminants present.

Figure S19 $^{31}$P($^1$H) NMR of complex 7a in CD$_2$Cl$_2$ at 298 K. Inset shows zoomed in spectrum.
Figure S20 $^{13}$C-$^1$H NMR of complex 7a in CD$_2$Cl$_2$ at 298 K.

Figure S21 $^1$H-$^{13}$C HMQC NMR spectrum of complex 7a in CD$_2$Cl$_2$ at 298 K that shows correlation at $\delta_H$ 5.05 and $\delta_C$ 78.6 – 78.8 ppm confirming the presence of a methine C-H.
Figure S22 Comparison of $^1$H and $^1$H(31P) NMR spectra of complex 7a in C$_6$D$_6$ at 298 K showing methine C-H and Ir-H resonances at $\delta$H 5.05 and -18.34 ppm respectively. Highlights the long range $^4$J$_{HP}$ coupling between the PPh$_3$ ligand ($\delta$P -0.08 ppm) and methane C-H, and coupling between the pincer phosphines ($\delta$P -8.18 ppm) and PPh$_3$ with the Ir-H.
NMR Spectra of complex 7b

Figure S23 $^1$H NMR of complex 7b in C$_6$D$_6$ at 298 K. Toluene, n-hexane contaminants present. * Minor quantity of 7a is also present.

Figure S24 $^{31}$P($^1$H) NMR of complex 7b in C$_6$D$_6$ at 298 K. Inset shows zoomed in spectrum.
Figure S25: $^{13}$C[¹H] NMR of complex 7b in C₆D₆ at 298 K.
Reaction between complex 7a and Na[BAr₄⁺] that formed [Ir(CO)(PPh₃)₃][BArF₄]$_2$

Figure S26 $^1$H NMR spectra in CD$_2$Cl$_2$ taken at 298 K showing the species formed on addition of Na[BArF₄⁻]·2THF to complex 7a at room temperature and after heating at 323 K.

Figure S27 $^{31}$P($^1$H) NMR spectra in CD$_2$Cl$_2$ taken at 298 K showing the species formed on addition of Na[BArF₄⁻]·2THF to complex 7a at room temperature and after heating at 323 K.
NMR Spectra of intermediate I

Figure S28 ¹H NMR spectrum showing major intermediate I-b made using C-D labelled ligand 1b in CD₂Cl₂ at 263 K. Methine resonance at 5.91 ppm not present. Minor quantity of Intermediate II-b also present. * in the reaction scheme denotes κ¹-COD coordination.
Figure S29 Comparison of $^1$H NMR spectra in CD$_2$Cl$_2$ at 263 K highlighting the presence and absence of the methine resonance in intermediate I and I-b when ligand 1 (top) or C-D labelled ligand 1b (bottom) were used respectively. Intermediate II or II-b also present in both spectra. * indicates resonance from intermediate I and I-b.

Figure S30 $^1$H NMR spectrum showing intermediate I-a made using O-D labelled ligand 1a (72% deuteration) in CD$_2$Cl$_2$ at 268 K highlighting the reduced integration for the O-H resonance at $\delta$ 11.10 ppm. Intermediate II-a also present. * in the reaction scheme denotes $\kappa^1$-COD coordination.
Figure S31 $^1$H-$^1$H COSY NMR spectrum of intermediate I in CD$_2$Cl$_2$ at 253 K showing the correlation between the O-H and C-H resonances at $\delta_H$ 11.10 and 5.91 ppm respectively.

Figure S32 $^{31}$P{$^1$H} NMR spectrum of intermediate I in CD$_2$Cl$_2$ at 263 K.
NMR Spectra of intermediate II

Figure S33 $^1$H NMR spectrum highlighting the identified resonances of intermediate II in CD$_2$Cl$_2$ at 263 K. Intermediate I also present.

Figure S34 $^1$H NMR spectrum showing intermediate II-b made using C-D labelled ligand 1b (99% deuterated) in CD$_2$Cl$_2$ at 278 K highlighting the reduced integration for the Ir-H resonance at $\delta$H -8.18 ppm relative to in II. Intermediate I-b also present. Given that the C-D group in ligand 1b used was 99% deuterated, the slightly higher than expected integration
for the Ir-H resonance (0.36 observed vs. 0.01 expected) indicates that a H-D exchange process had occurred. The mechanism for the H-D exchange likely involved intermediate VI and may be analogous to that described by Piers et al for a similar Ir complex.9

Figure S35 Comparison of $^1$H and $^1$H($^{31}$P) NMR spectra of intermediate II in CD$_2$Cl$_2$ at 273 K showing the Ir-H resonance at δ$_H$ -8.18 ppm. Confirms the hydride ligand is trans and cis disposed to the two phosphine groups of a facially coordinated PCP pincer ligand.

Figure S36 $^{31}$P($^1$H) NMR spectrum of intermediate II in CD$_2$Cl$_2$ at 268 K. Unknown species at δ$_P$ 9.9 ppm.
NMR Spectra of intermediate VI

Figure S37 $^1$H NMR spectrum at 259 K from the reaction between [IrCl(COD)]$_2$ and ligand 1 in CD$_2$Cl$_2$ highlighting intermediate VI.

Figure S38 $^1$H-$^{13}$C HMBC NMR spectrum of intermediate VI in CD$_2$Cl$_2$ at 259 K showing the correlation between the Ir-H resonance and a $^{13}$C signal at 132.1 ppm, typical of a bound $\eta^2$-carbonyl with the same pincer ligand.$^{10}$
Figure S39 Comparison of $^1$H and $^1$H($^{31}$P) NMR spectra of intermediate VI formed by reaction between intermediate VII and HCl in CD$_2$Cl$_2$ at 298 K, showing the Ir-H resonance at $\delta^H$ -12.64 ppm.

Figure S40 $^{31}$P($^1$H) NMR spectra of intermediate VI in CD$_2$Cl$_2$ at 298 K formed by reaction between intermediate VII and HCl.
NMR Spectra of complex VII

Figure S41 $^1$H NMR spectrum of isolated complex VII·CH$_2$Cl$_2$ in CD$_2$Cl$_2$ at 298 K.

Figure S42 Comparison of $^1$H NMR spectra in CD$_2$Cl$_2$ at 298 K highlighting the absence and presence of the methine resonance in VII-b and VII when ligands 1b (top) or 1 (bottom) were used respectively.
Figure S43 $^1$H NMR spectrum of isolated complex $\text{VII-CH}_2\text{Cl}_2$ in CDCl$_3$ at 298 K showing the one solvate molecule of CH$_2$Cl$_2$ at $\delta_H$ 5.30 ppm.

Figure S44 $^{31}$P($^1$H) NMR spectrum of complex $\text{VII-CH}_2\text{Cl}_2$ in CD$_2$Cl$_2$ at 298 K.
Figure S45 $^{13}$C($^1$H) NMR spectrum of complex VII·CH$_2$Cl$_2$ in CDCl$_3$ at 298 K.
Addition of HCl to complex VII

Figure S46 $^1$H NMR spectrum at 298 K taken 1 min after reacting complex VII-CH$_2$Cl$_2$ with HCl in CD$_2$Cl$_2$, highlighting the formation of intermediates I, II, and VI.

Figure S47 $^{31}$P($^1$H) NMR spectrum at 298 K taken 2 min after reacting complex VII-CH$_2$Cl$_2$ with HCl in CD$_2$Cl$_2$, highlighting the formation of intermediates I, VI, and product 2. Intermediate II is not clearly visible, likely due to fluxionality in solution.
Reaction between 1-H₂ and [IrCl(COD)]₂ under a H₂ atmosphere

Figure S48 ³¹P{¹H} NMR spectra at 298 K after reacting 1-H₂ and [IrCl(COD)]₂ under a H₂ atmosphere in CD₂Cl₂, highlighting the formation of intermediates VI, VII-CH₂Cl₂ and product 2. The absence of the peak for 2 after 21 h 15 min indicates that 2 is unstable over long periods in these conditions.
HRMS (ESI-TOF) Spectra

Mass spectrum of complex 2

Figure S49 Positive mode HRMS (ESI-TOF) spectrum of [M+H]^+ ion of 2. Inset shows expected isotope pattern.
Mass spectrum of complex 3

Figure S50 Positive mode HRMS (ESI-TOF) spectrum of [M]⁺ ion of 3. Inset shows expected isotope pattern.

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Mass spectrum of complex 4

Figure S51 Positive mode HRMS (ESI-TOF) spectrum of [M]+ ion of 4. Inset shows expected isotope pattern.
Mass spectrum of complex 5

Figure S52 Positive mode HRMS (ESI-TOF) spectrum of [M]⁺ ion of 5. Inset shows expected isotope pattern.
Figure S53 Positive mode HRMS (ESI-TOF) spectrum of [M]+ ion of 6. Inset shows expected isotope pattern.
Mass spectrum of complex 7a

Figure S54 Positive mode HRMS (ESI-TOF) spectrum of [M-Cl]+ ion of 7a. Inset shows expected isotope pattern.
Figure S55 Positive mode HRMS (ESI-TOF) spectrum of [M]+ ion of VII. Inset shows expected isotope pattern.
## X-Ray Crystallography Data

### Crystallographic data table

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<td>3588.61(14)</td>
<td>4699.6(3)</td>
<td>1897.2(2)</td>
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<td>1.757</td>
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<td>3.781</td>
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<td><strong>θ max / °</strong></td>
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<td><strong>GoF (S)</strong></td>
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<td>1.00</td>
<td>1.03</td>
<td>1.02</td>
<td>1.04</td>
<td>1.01</td>
<td>1.09</td>
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<tr>
<td><strong>R factor (I &gt; 2σ)</strong></td>
<td>0.025 (2816)</td>
<td>0.075 (13694)</td>
<td>0.068 (21251)</td>
<td>0.039 (16063)</td>
<td>0.040 (12972)</td>
<td>0.062 (12255)</td>
<td>0.033 (7867)</td>
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</table>

Table S1 Crystal Data, Data Collection and Refinement Parameters for the structures of 2 – 6, 7b and VII.
X-ray crystal structures

Figure S56 Molecular structure of 2 (50% probability thermal ellipsoids). Hydrogen atoms omitted for clarity.

Figure S57 Molecular structure of 3 (50% probability thermal ellipsoids). Hydrogen atoms omitted for clarity.
Figure S58 Molecular structure of 4 (50% probability thermal ellipsoids). Hydrogen atoms omitted for clarity.

Figure S59 Molecular structure of 5·CH2Cl2 (50% probability thermal ellipsoids). Hydrogen atoms except for H1 omitted for clarity.
Figure S60 Molecular structure of $6 \cdot C_{6}H_{14}$ (50% probability thermal ellipsoids). Hydrogen atoms except for H11, H441, H451, and H451 omitted for clarity.

Figure S61 Molecular structure of $7b$ (50% probability thermal ellipsoids). Hydrogen atoms except for H1 and H12 omitted for clarity.
Figure S62 Molecular structure of VII·CH₂Cl₂ (50% probability thermal ellipsoids). Hydrogen atoms except for H1 omitted for clarity.
References


(10) A similar $^{13}$C NMR chemical shift for a bound η²-carbonyl carbon ligand was observed for a previously described rhodium complex in Reference 3.