Supplementary Materials: Isomerization of Internal Alkynes to Iridium(III) Allene Complexes via C–H Bond Activation: Expanded Substrate Scope, and Progress towards a Catalytic Methodology

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**General Remarks.** Chemicals and solvents were purchased from commercial suppliers and were used as received except as follows: TBE and 1-Phenyl-1-butyne were degassed. Reactions were carried out under argon gas in a J-Young nmr tube. Chemical shifts are given in ppm. Unless otherwise noted, the NMR spectra were recorded in C₆D₆. Coupling constants (J) are given in Hertz (Hz). The terms m, s, d, t, q, quint., sext., vt, represent multiplet, singlet, doublet, triplet, quartet, quintet, sextet, virtual triplet respectively. The term br means that the signal is broad. X-ray diffraction experiments were performed at the Chemistry Department X-ray Diffraction Facility of the Texas Tech University.

**Typical Procedure for Preparation of η²-allene Complexes (1b–4b):** In a J-Young NMR tube, (POCOP)IrH₂ (12 mg, 20 µmol) was dissolved in C₆D₆ and ca. 1.5 eq. tert-butylethylene added via microsyringe. The removal of H₂ with concomitant formation of 1 eq. of tert-butylethane is easily monitored using both ¹H and ³¹P [¹H] NMR spectroscopy. Addition of 1 eq. of alkyne affords exclusively the η²-adducts of alkynes 1a–5a. The solutions of η²-alkyne complexes, prepared as above, were warmed to ca. 75 °C for 5–10 h to reach full conversion to the allene complex. Definitive assignment of diastereomers is hampered by closely overlapping peaks in the ¹H NMR spectra and tentative assignments are made on the basis of previously reported NMR data of related allene complexes and 2-D NMR experiments.

**Spectroscopic Characterization of 1b:**

**Trans-(POCOP)Ir(η²-(Ph)(C(H)=C(H)=C(H)(CH₃))) and Cis-(POCOP)Ir(η²-(Ph)(C(H)=C(H)=C(H)(CH₃))) (1b & 1b’):** ¹H NMR (500 MHz, C₆D₆): δ 7.46–6.83 (m, 8H, Ar), 6.51 (br d, 1H, Ph-H=C=C), 4.15 (br t, 1H, ²Jₖₖ = 6.0 Hz, C=C=CH–CH₃), 1.96 (d, 3H, ²Jₖₖ = 6.0 Hz, C=C=CH–CH₃), 1.36–1.05 (m, 36H, C(CH₃)₃). ³¹P [¹H] (162 MHz, C₆D₆): δ 182.36 (AB, ²Jₖₖ = 351.13 Hz), 171.70 (AB, ²Jₖₖ = 351.13 Hz).

¹H-NMR (500 MHz, C₆D₆): δ 7.46–6.83 (m, 8H, Ar), 5.36 (br d, 1H, Ph-H=C=C), 4.15 (br t, 1H, ²Jₖₖ = 6.0 Hz, C=C=CH–CH₃), 1.36–1.05 (m, 36H, C(CH₃)₃), 0.79 (d, 3H, ²Jₖₖ = 14 Hz, C=C=CH–CH₃). ³¹P [¹H] (162 MHz, C₆D₆): δ 177.58 (AB, ²Jₖₖ = 353.29 Hz), 167.6327 (AB, ²Jₖₖ = 353.29 Hz).
Spectroscopic Characterization of 1b–d5:

**Trans-(POCOP)Ir(η²-Ph)(C(D)=C=C(D)(CD₃)) and Cis-(POCOP)Ir(η²-Ph)(C(D)=C=C(D)(CD₃))**

(1b–d₅ & 1b–d₅’):

$^{31}$P {$^1$H} (162 MHz, C₆D₆): δ 181.72 (AB, $J_{A-B} = 348.96$ Hz), 171.70 (AB, $J_{A-B} = 348.96$ Hz).

$^{31}$P {$^1$H} (162 MHz, C₆D₆): δ 177.48 (AB, $J_{A-B} = 353.29$ Hz), 167.60 (AB, $J_{A-B} = 353.29$ Hz).

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Spectroscopic Characterization of 2b:

**Trans-(POCOP)Ir(η²-(p-MeO-Ph)(C(D)=C=C(D)(CD₃)) and Cis-(POCOP)Ir(η²-(p-MeO-Ph)(C(D)=C=C(D)(CD₃))**

(2b & 2b’):

$^{31}$P {$^1$H} (162 MHz, C₆D₆): δ 181.55 (AB, $J_{A-B} = 351.13$ Hz), 171.56 (AB, $J_{A-B} = 351.13$ Hz).

$^{31}$P {$^1$H} (162 MHz, C₆D₆): δ 178.38 (AB, $J_{A-B} = 355.46$ Hz), 167.77 (AB, $J_{A-B} = 355.46$ Hz).
Spectroscopic Characterization of 3b:

**Trans-(POCOP)Ir(η²-(Ph)C(D)=C(C(D)(CD₃))) and Cis-(POCOP)Ir(η²-(Ph)C(D)=C(C(D)(CD₃)))** (3b & 3b')

**31P {1H} (162 MHz, C₆D₆):**
- δ 182.97 (AB, Jₐ₋ₐ = 348.96 Hz)
- δ 171.61 (AB, Jₐ₋ₐ = 348.96 Hz)

**31P {1H} (162 MHz, C₆D₆):**
- δ 172.70 (AB, Jₐ₋ₐ = 351.13 Hz)
- δ 167.72 (AB, Jₐ₋ₐ = 351.13 Hz)
Spectroscopic Characterization of 4b:

Trans-(POCOP)Ir(η²-(Ph)C(D)=C=CD(CD₃)) and Cis-(POCOP)Ir(η²-(Ph)C(D)=C=CD(CD₃)) (4b & 4b')

$^{31}$P $\{^{1}$H$\}$ (162 MHz, C₆D₆): $\delta$ 182.09 (AB, $J_{A-B} = 346.79$ Hz), 171.86 (AB, $J_{A-B} = 346.79$ Hz). $^{31}$P $\{^{1}$H$\}$ (162 MHz, C₆D₆): $\delta$ 177.56 (AB, $J_{A-B} = 353.29$ Hz), 167.62 (AB, $J_{A-B} = 353.29$ Hz).
Crossover Experiment

Figure S1. 2D NMR of crossover labeling experiment of the mixture of 1b and 1b–d5 allene.
Figure S2. Stacked plot of product 1b and mixture of 1b and 1b-d5.

Liberation of Allene Using CO
Figure S3. GC-MS of the isolated 2b product from the CO experiment.

Figure S4. The ¹H NMR of isolated allene from 2b after CO treatment (mixture of allene and Ir-CO complex).
\(^{1}\)H NMR: Mixture of isolated allene 2b and the Ir-CO complex

![Diagram of molecules]

Isolated allene 2b \(^{1}\)H NMR: 7.22-7.19 (m, 2Ha), 6.77–6.75 (m, 2Hb), 6.13–6.10 (m, Hc), 5.35 (m, Hd), 3.26 (s, –OCH\(_3\)), 1.57-1.55 (m, –CH\(_3\)).

Ir-CO complex \(^{1}\)H NMR: 6.83 (m, Ar, 3H),1.30 (vt, 36H, 2 x P(tBu)). \(^{31}\)P NMR: 198.9

Figure S5. Stacked \(^{1}\)H NMR of 2b and isolated allene from 2b after CO treatment.

**NMR Kinetics of Allene Complex Formation:** The rate of conversion of 1a to 1b was determined by monitoring the disappearance of the singlet of 1a in the \(^{31}\)P \(^{1}\)H NMR spectrum. The disappearance of 1b (10 µmol) in a C\(_6\)D\(_6\) solution (0.6 mL) was measured at 348, 338 and 328 K over at least 3 half-lives to allow accurate determination of rate constants. A plot of \(\ln [1a]/[1b]\) vs time was essentially linear, the average \((k_{obs} = 4.173 \times 10^{-4} \text{ (348 K)}; 1.169 \times 10^{-4} \text{ (338 K); 3.718 \times 10^{-5} (328 K)})\). By plotting the change in reaction rate \(v.s.\) temperature an Eyring Plot could be constructed \((\ln(k/T) \text{ vs. } 1/T)\). The rates of isomerization, and activation parameters, for 1a–d5, 2a and 4a are qualitatively similar to those of 1a. Representative plots are given below; in addition the corresponding thermodynamic parameters are calculated.
Kinetic Plots:
Plot of rate of consumption of 1a at 328 K, 338 K, and 348 K

1a $\rightarrow$ 1b 328K Trial 1

\[ y = -0.00004176x \]
\[ R^2 = 0.99092049 \]

1a $\rightarrow$ 1b 328K Trial 2

\[ y = -0.00003259x \]
\[ R^2 = 0.99002951 \]
1a -> 1b 338K Trial 1

\[ y = -0.00012206x \]

\[ R^2 = 0.98765238 \]

1a -> 1b 338K Trial 2

\[ y = -0.00011179x \]

\[ R^2 = 0.99055421 \]
1a -> 1b 348K Trial 1

\[ y = -0.00049790x \]
\[ R^2 = 0.99437542 \]

1a -> 1b 348K Trial 2

\[ y = -0.0003763x \]
\[ R^2 = 0.99931754 \]
Plot of rate of consumption of 1a–d5 at 328 K, 338 K, and 348 K
1a-d5 -> 1b-d5 338K Trial 2

\[ y = -0.00003166x \]

\[ R^2 = 0.99286386 \]

\[ \ln(C/Co) \]

1a-d5 -> 1b-d5 348K Trial 1

\[ y = -0.00010852x \]

\[ R^2 = 0.99844714 \]
1a-d5 -> 1b-d5 348K Trial 2

\[
y = -0.00011434x \\
R^2 = 0.99493868
\]

1a-d5 Isomerization Eyring Plot

\[
y = -13,235.7803x + 23.0371 \\
R^2 = 0.9962
\]

| \(T (K)\) | \(k_D (s^{-1})\) Trial 1 | \(k_D (s^{-1})\) Trial 2 | \(k_D (s^{-1})\) Average | \(\Delta G^\ddagger (\text{kcal/mol})\) Average |
|---|---|---|---|---|
| 328.0 | 1.053 \times 10^{-5} | 1.008 \times 10^{-5} | 1.031 \times 10^{-5} | 27.07 |
| 338.0 | 3.034 \times 10^{-5} | 3.166 \times 10^{-5} | 3.100 \times 10^{-5} | 27.17 |
| 348.0 | 1.0852 \times 10^{-4} | 1.1434 \times 10^{-4} | 1.1143 \times 10^{-4} | 27.09 |

\(\Delta H^\ddagger = 26.62 \text{ kcal/mol}^{-1} ; \Delta S^\ddagger = -1.43 \text{ e.u.}\)
Kinetic Isotope Effect:

| Average $k_H/k_D$ | $T$ (K) |
|------------------|---------|
| 3.61             | 328.0   |
| 3.77             | 338.0   |
| 3.75             | 348.0   |

Plot of rate of consumption of 2a at 328, 338, 348 K respectively.
2a -> 2b 338K Trial 1

\[ y = -0.00011263x \]

\[ R^2 = 0.99886535 \]

2a -> 2b 338K Trial 2

\[ y = -0.00011496x \]

\[ R^2 = 0.99885450 \]
\[ y = -0.00039470x \]
\[ R^2 = 0.99660234 \]

\[ y = -0.00041450x \]
\[ R^2 = 0.99845603 \]
| T (K) | Trial 1      | Trial 2      | Average    | Average    |
|-------|--------------|--------------|------------|------------|
| 328.0 | $3.288 \times 10^{-5}$ | $3.69 \times 10^{-5}$ | $3.489 \times 10^{-5}$ | 26.27      |
| 338.0 | $1.1263 \times 10^{-4}$ | $1.1496 \times 10^{-4}$ | $1.1379 \times 10^{-4}$ | 26.28      |
| 348.0 | $3.947 \times 10^{-4}$ | $4.145 \times 10^{-4}$ | $4.046 \times 10^{-4}$ | 26.19      |

$\Delta H^\ddagger = 27.43 \text{ kcal/mol}; \Delta S^\ddagger = 3.47 \text{ e.u.}$

Plot of rate of consumption of 4a at 328 K, 338 K, 348 K
4a -> 4b 328K Trial 2

\[ y = -0.00003238x \]
\[ R^2 = 0.99492932 \]

4a -> 4b 338K Trial 1

\[ y = -0.00011400x \]
\[ R^2 = 0.98267573 \]
\[ y = -0.00038293x \]
\[ R^2 = 0.99285105 \]

\[ y = -13,548.4275x + 25,1865 \]
\[ R^2 = 0.9998 \]

| \( T \) (K) | \( k \) (s\(^{-1}\)) Trial 1 | \( k \) (s\(^{-1}\)) Trial 2 | Average | \( \Delta G^\ddagger \) (kcal/mol) Average |
|---|---|---|---|---|
| 328.0 | \( 3.372 \times 10^{-5} \) | \( 3.238 \times 10^{-5} \) | \( 3.305 \times 10^{-5} \) | 26.30 |
| 338.0 | \( 1.14 \times 10^{-4} \) | \( 1.108 \times 10^{-4} \) | \( 1.124 \times 10^{-4} \) | 26.30 |
| 348.0 | \( 3.7065 \times 10^{-4} \) | \( 3.8293 \times 10^{-4} \) | \( 3.7679 \times 10^{-4} \) | 26.24 |

\( \Delta H^\ddagger = 27.25 \text{ kcal/mol} \); \( \Delta S^\ddagger = 2.84 \text{ e.u.} \)
**Eyring Calculation:**

\[ \text{Gradient} = -\Delta H^\ddagger / R; \text{Intercept} = \ln(k' / h) + \Delta S^\ddagger / R \]

**General Data Collection**

Data was collected on a Bruker PLATFORM three circle diffractometer equipped with an APEX II CCD detector and operated at 1500 W (50 kV, 30 mA) to generate (graphite monochromated) Mo Kα radiation (\( \lambda = 0.71073 \) Å). Crystals were transferred from the vial and placed on a glass slide in Paratone® N oil. Two microscopes, a Motic SMZ-140 and an AmScope XY-PRT polarizing microscope, were used to identify a suitable specimen for X-ray diffraction from a representative sample of the material. The crystal and a small amount of the oil were collected on a MiTiGen cryoloop and transferred to the instrument where it was placed under a cold nitrogen stream (Oxford) maintained at 100 K throughout the duration of the experiment. The sample was optically centered with the aid of a video camera to insure that no translations were observed as the crystal was rotated through all positions.

A unit cell collection was then carried out. After it was determined that the unit cell was not present in the CCDC database a sphere of data was collected. Omega scans were carried out with a 20 s/frame exposure time and a rotation of 0.33° per frame. After data collection, the crystal was measured for size, morphology, and color.

**Refinement Details**

After data collection, the unit cell was re-determined using a subset of the full data collection. Intensity data were corrected for Lorentz, polarization, and background effects using the Bruker program APEX II. A semi-empirical correction for adsorption was applied using the program SADABS. The SHELXL-2014, series of programs was used for the solution and refinement of the crystal structure.

**X-ray Characterization Data**

![Figure S6. ORTEP diagram of 2b with 40% probability thermal ellipsoids. Key bond lengths (Å) and bond angles (deg): C1–C2 = 1.324 (7), C2–C3 = 1.398 (7), Ir–C2 = 2.052 (5), Ir–C3 = 2.218 (4), C1–C2–C3 = 145.0 (5), P1-Ir-P2 = 157.01 (4).](image_url)