### SUPPORTING INFORMATION FOR

Ring Opening Metathesis Polymerization of an  $\eta^4$ -Benzene Complex: A Direct Synthesis of a Polyacetylene with a Regular Pattern of  $\pi$  Bound Metal Fragments

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All reactions were carried out in inert atmospheres using standard Schlenk and vacuum line techniques. Chemicals were treated as follows: pentane, distilled from Na/benzophenone; ethanol, used as received; other solvents, dried and deoxygenated using a Glass Contour solvent purification system; CDCl<sub>3</sub>, CD<sub>2</sub>Cl<sub>2</sub>, C<sub>6</sub>D<sub>6</sub> (3 × Cambridge Isotope Laboratories), IrCl<sub>3</sub>·*n*H<sub>2</sub>O (Pressure Chemical Company, 52% metal basis), 1,3-cyclohexadiene (Acros, 96%), TlC<sub>5</sub>H<sub>5</sub> (Strem, 95%), Ph<sub>3</sub>C<sup>+</sup> BF<sub>4</sub><sup>-</sup> (Alfa Aesar, 98%), ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co (Alfa Aesar, 98%), Grubbs' catalyst (Aldrich), and ethyl vinyl ether (Alfa Aesar, 99%), used as received. Grubbs' second generation catalyst and Schrock's catalyst were prepared by literature procedures.<sup>\$1,\$2</sup>

NMR spectra were recorded on a Varian NMRS 500 MHz spectrometer at ambient probe temperatures and referenced as follows: <sup>1</sup>H: residual internal CHCl<sub>3</sub> ( $\delta$ , 7.26 ppm), CDHCl<sub>2</sub> ( $\delta$ , 5.32 ppm), or C<sub>6</sub>D<sub>5</sub>H ( $\delta$ , 7.15 ppm); <sup>13</sup>C: internal CDCl<sub>3</sub> ( $\delta$ , 77.2 ppm), CD<sub>2</sub>Cl<sub>2</sub> ( $\delta$ , 54.00 ppm), or C<sub>6</sub>D<sub>6</sub> ( $\delta$ , 128.39 ppm). IR spectra were recorded using a Shimadzu IRAffinity-1 spectrometer with a Pike MIRacle ATR system (diamond/ZnSe crystal). UV-visible spectra were recorded on a Shimadzu UV-1800 spectrometer. Cyclic voltammograms were recorded using a BASi epsilon potentiostat and C-3 cell stand. Interdigitated electrodes were purchased from the Case Western Reserve University Electronics Design Center (item # 102).

 $Ir(\eta^4-1,3-C_6H_8)_2CL^{s3}$  A round bottom flask was charged with  $IrCl_3 \cdot nH_2O$  (4.0013 g, 10.824 mmol), ethanol (60 mL), water (40 mL), and 1,3-cyclohexadiene (9.00 mL, 94.3 mmol). The mixture was refluxed (oil bath, 8 h) and then cooled (ice bath). The precipitate was collected by filtration, washed with ethanol (3 × 5 mL), and dried by oil pump vacuum to afford  $Ir(\eta^4-1,3-C_6H_8)_2Cl$  (3.3843 g, 8.7240 mmol, 81%) as an off white solid.

<sup>1</sup>H NMR (δ, CDCl<sub>3</sub>): 5.12 (m, 4H, CH····CHCH<sub>2</sub>), 4.00 (m, 4H, CH····CHCH<sub>2</sub>), 2.08 and 1.61 (2 m, 2 × 4H, 4CHH' and 4CHH').

 $(\eta^5-C_5H_5)Ir(\eta^4-1,3-C_6H_8).^{s_3,s_4}$  A round bottom flask was charged with TlC<sub>5</sub>H<sub>5</sub> (1.2033 g, 4.4655 mmol),  $Ir(\eta^4-1,3-C_6H_8)_2$ Cl (1.7317 g, 4.4639 mmol), and THF (100 mL) with stirring. After 16 h, the flask was heated to 50 °C. After 2 h, the solvent was removed by oil pump vacuum. The residue was extracted with hexanes (150 mL). The extract was filtered, and the solvent

removed and residue dried by oil pump vacuum to give  $(\eta^5-C_5H_5)Ir(\eta^4-1,3-C_6H_8)$  (1.4471 g, 4.2885 mmol, 96%) as an off white solid.

NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H 4.58 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.55 (m, 2H, CH<sub>2</sub>-CH····CH), 3.23 (m, 2H, CH<sub>2</sub>-CH····CH), 1.30 and 1.10 (2 m, 2 × 2H, 2CHH' and 2CHH'); <sup>13</sup>C{<sup>1</sup>H} 76.4 (C<sub>5</sub>H<sub>5</sub>), 66.3 (CH<sub>2</sub>-CH····CH), <sup>s5</sup> 43.9 (CH<sub>2</sub>-CH····CH), <sup>s5</sup> 28.8 (CH<sub>2</sub>).

 $[(\eta^{5}-C_{5}H_{5})Ir(\eta^{6}-C_{6}H_{6})]^{2+} 2BF_{4}^{-.s^{3}} \text{ A round bottom flask was charged with a solution of } (\eta^{5}-C_{5}H_{5})Ir(\eta^{4}-1,3-C_{6}H_{8}) (0.8482 \text{ g}, 2.514 \text{ mmol}) \text{ in dichloromethane } (10 \text{ mL}) \text{ and a suspension of } Ph_{3}C^{+} BF_{4}^{-} (1.6553 \text{ g}, 5.0604 \text{ mmol}) \text{ in dichloromethane } (10 \text{ mL}) \text{ with stirring. After } 15 \text{ min, ether } (140 \text{ mL}) \text{ was added. The precipitate was collected by filtration, washed with ether } (2 \times 5 \text{ mL}), \text{ and dried by oil pump vacuum to afford } [(\eta^{5}-C_{5}H_{5})Ir(\eta^{4}-C_{6}H_{6})]^{2+} 2BF_{4}^{-} (1.2374 \text{ g}, 2.4309 \text{ mmol}, 97\%) \text{ as an off white solid.}$ 

 $(\eta^5-C_5H_5)Ir(\eta^4-C_6H_6)$  (1).<sup>s3</sup> A round bottom flask was charged with a suspension of  $(\eta^5-C_5H_5)_2Co$  (1.5136 g, 8.0033 mmol) in dichloromethane (20 mL) and a suspension of  $[(\eta^5-C_5H_5)Ir(\eta^6-C_6H_6)]^{2+}$  2BF<sub>4</sub><sup>-</sup> (2.0441 g, 4.0157 mmol) in dichloromethane (20 mL) with stirring. After 10 min, ether (150 mL) was added. The mixture was filtered and the  $(\eta^5-C_5H_5)_2Co^+$  BF<sub>4</sub><sup>-</sup> cake washed with ether (2 × 10 mL). The solvent was removed from the filtrate and the residue dried by oil pump vacuum to give **1** (1.3132 g, 3.9151 mmol, 98%) as a yellow solid.

NMR ( $\delta$ , CDCl<sub>3</sub>): <sup>1</sup>H 6.31 (m, 2H, 2 =C*H*), 5.25 (m, 2H, 2 =CH-CH····C*H*), <sup>s6</sup> 5.16 (s, 5H, C<sub>5</sub>*H*<sub>5</sub>), 3.81 (m, 2H, 2 =CH-CH····CH); <sup>s6</sup> <sup>13</sup>C{<sup>1</sup>H} 132.4 (=*C*H), 76.6 (*C*<sub>5</sub>H<sub>5</sub>), 65.7 (=CH-CH····CH), <sup>s7</sup> 43.9 (=CH-CH····CH). <sup>s7</sup>

NMR ( $\delta$ , CD<sub>2</sub>Cl<sub>2</sub>): <sup>1</sup>H 6.29 (m, 2H, 2 =C*H*), 5.16 (m, 2H, 2 =CH-CH····C*H*), <sup>s6</sup> 5.14 (s, 5H, C<sub>5</sub>*H*<sub>5</sub>), 3.76 (m, 2H, 2 =CH-CH····CH). <sup>s6</sup>

 $(\eta^5-C_5Me_5)Ir(\eta^4-C_6H_6)$  (2). A scintillation vial was charged with  $[(\eta^5-C_5Me_5)Ir(\eta^6-C_6-H_6)]^{2+} 2BF_4^{-}$  (0.3359 g, 0.5800 mmol),<sup>\$8</sup> ( $\eta^5-C_5H_5$ )<sub>2</sub>Co (0.2191 g, 1.159 mmol), and dichloromethane (5 mL) with stirring. After 15 min, the mixture was poured into ether (50 mL) and filtered. The solvent was removed from the filtrate by oil pump vacuum to give **2** (0.2326 g, 0.5735 mmol, 99%) as a yellow-brown solid. Since a satisfactory microanalysis was not obtained, <sup>1</sup>H

and  ${}^{13}C{}^{1}H$  NMR spectra are depicted in Figure s8.

NMR (δ, CDCl<sub>3</sub>): <sup>1</sup>H 5.73 (m, 2H, 2 =C*H*), 5.09 (m, 2H, 2 =CH-CH····C*H*), <sup>s6</sup> 3.03 (m, 2H, 2 =CH-C*H*····CH), <sup>s6</sup> 1.95 (s, 15H, 5 CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} 130.6 (=*C*H), 89.7 (*C*CH<sub>3</sub>), 66.3 (=CH-CH····CH), <sup>s7</sup> 48.4 (=CH-CH···CH), <sup>s7</sup> 10.7 (*C*H<sub>3</sub>).

**Polymerizations. A.** A J. Young NMR tube was charged with **1** (0.0320 g, 0.0954 mmol), Grubbs' catalyst (0.0076 g, 0.0092 mmol), and  $CD_2Cl_2$  (1 mL). The ROMP was monitored by <sup>1</sup>H NMR at room temperature. Analogous experiments were conducted with Grubbs' second generation catalyst and Schrock's catalyst (10 mol%) at room temperature and 40 °C. **B**. A tube was charged with **1** (0.2347 g, 0.6997 mmol), Grubbs' catalyst (0.1150 g, 0.1397 mmol), and dichloromethane (10 mL) and sealed with a threaded stopper. The closed system was heated to 40 °C with stirring. After 3 d, the mixture was cooled and ethyl vinyl ether (0.750 mL) was added. After 10 min, the volatiles were removed by oil pump vacuum to give poly-**1**' (0.3402 g) as a red-brown solid.

<sup>13</sup>C{<sup>1</sup>H} NMR, Figure s1 ( $\delta$ , CD<sub>2</sub>Cl<sub>2</sub>):

0.33 h, **1** at 132.4 (=CH), 76.9 (C<sub>5</sub>H<sub>5</sub>), 65.8 (=CH-CH····CH), 44.2 (=CH-CH····CH); poly-**1** at 128.8 (=CH), 77.8 (C<sub>5</sub>H<sub>5</sub>), 47.2 (=CH-CH····CH), 26.1 (=CH-CH····CH); Grubbs' catalyst<sup>§9</sup> at 131.3, 129.4, 32.5, 30.1, 28.4, 27.1.

2.17 h, **1** at 132.4 (=*C*H), 76.9 (*C*<sub>5</sub>H<sub>5</sub>), 65.8 (=*C*H-*C*H···*C*H), 44.2 (=*C*H-*C*H···*C*H); poly-**1** at 128.8 (=*C*H), 77.8 (*C*<sub>5</sub>H<sub>5</sub>), 47.2 (=*C*H-*C*H···*C*H), 26.1 (=*C*H-*C*H···*C*H); Grubbs' catalyst<sup>\$9</sup> at 129.4, 32.5, 31.8, 30.1, 28.4, 27.1.

9.0 h, **1** at 132.4 (=*C*H), 76.9 (*C*<sub>5</sub>H<sub>5</sub>), 65.8 (=*C*H-*C*H···*C*H), 44.2 (=*C*H-*C*H···*C*H); poly-**1** at 128.8 (=*C*H), 77.8 (*C*<sub>5</sub>H<sub>5</sub>), 47.2 (=*C*H-*C*H···*C*H), 26.1 (=*C*H-*C*H···*C*H); Grubbs' catalyst<sup>s9</sup> at 31.8, 30.1, 28.3.

24.0 h, **1** at 132.4 (=*C*H), 76.9 ( $C_5H_5$ ), 65.8 (=*C*H-*C*H····*C*H), 44.2 (=*C*H-*C*H····*C*H); poly-**1** at 128.8 (=*C*H), 77.8 ( $C_5H_5$ ), 47.2 (=*C*H-*C*H····*C*H), 26.1 (=*C*H-*C*H····*C*H); Grubbs' catalyst<sup>s9</sup> at 30.3, 28.2.

31.0 h, **1** at 132.4 (=*C*H), 76.9 (*C*<sub>5</sub>H<sub>5</sub>), 65.8 (=*C*H-*C*H···*C*H), 44.2 (=*C*H-*C*H···*C*H);

poly-**1** at 128.8 (=*C*H), 77.8 (*C*<sub>5</sub>H<sub>5</sub>), 47.2 (=*C*H-*C*H···*C*H), 26.1 (=*C*H-*C*H···*C*H); Grubbs' catalyst<sup>s9</sup> at 30.3, 27.5.

49.0 h, **1** at 132.4 (=CH), 76.9 ( $C_5H_5$ ), 65.8 (=CH-CH····CH), 44.2 (=CH-CH····CH); poly-**1** at 128.8 (=CH), 77.8 ( $C_5H_5$ ), 47.2 (=CH-CH····CH), 26.1 (=CH-CH····CH); Grubbs' catalyst<sup>§9</sup> at 30.3, 28.0, 27.5, 26.9.

<sup>1</sup>H NMR, Figure s2 ( $\delta$ , CD<sub>2</sub>Cl<sub>2</sub>; for full integral data, see Figure s3):

bottom (before ethyl vinyl ether addition, peaks  $\geq 2.5\%$  of the cyclopentadienyl signal intensity), 6.11, 5.76, 5.63, 5.43, 5.21 (s, C<sub>5</sub>H<sub>5</sub>), 5.17, 5.13, 4.32, 3.96;

top (after ethyl vinyl ether addition, vinyl peaks and those  $\geq 2.5\%$  of the cyclopentadienyl signal intensity), 6.65 (apparent d,  ${}^{2}J_{\text{HH}} = 8.3 \text{ Hz}$ , =CH<sub>2</sub>), 6.57 (apparent t,  ${}^{2}J_{\text{HH}} = 7.2 \text{ Hz}$ , 1H, CH=CH<sub>2</sub>), 6.11, 5.90, 5.79, 5.75, 5.62, 5.54, 5.53, 5.47, 5.37, 5.25, 5.21 (s, 38H vs. CH=, C<sub>5</sub>H<sub>5</sub>), 5.17, 4.31, 3.96, 3.59 (m), 3.44 (m), 3.33 (m).

**Conductivity.** A 0.025 mL aliquot of a solution of poly-1' (0.0100 g) in dichloromethane (0.0679 mL) was dropped onto an interdigitated electrode in an argon glove box. The sample was dried first under ambient glove box conditions (1 h) and then under vacuum (14 h). The electrode and one crystal of  $I_2$  were sealed in a vial under static vacuum (24 h). The remaining  $I_2$  was removed and the electrode kept under dynamic vacuum (24 h). A potentiostat from a cyclic voltammetry instrument was used to apply a potential across the film, and the current was measured. A two electrode connection was made by combining the red (auxiliary) and white (reference) leads together as one electrode and the black (working) lead as the other electrode.

**Crystallography.** A saturated pentane solution of **2** was allowed to slowly evaporate. After one day, the yellow plates were taken to an APEXII BRUKER X-ray diffractometer for data collection as outlined in Table s1. Cell parameters were obtained from 36 frames using a 5° scan and refined with 16005 reflections. A suitable cell was found and refined by nonlinear least squares and Bravais lattice procedures. No super-cell or erroneous reflections were observed. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2.<sup>\$10</sup> Lorentz, polarization, and absorption corrections<sup>\$11</sup> were applied.

The space group, P–1, was determined from systematic reflection conditions and statistical tests. The structure was solved by direct methods using SHELXTL (SHELXS).<sup>s12</sup> All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in idealized positions. The parameters were refined by weighted least squares refinement on  $F^2$  to convergence.<sup>s12</sup> Two independent molecules were found in the unit cell.

#### References

(s1) Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T. L.; Ding, S.; Day, M. W.; Grubbs, R. H. J. Am. Chem. Soc. 2003, 125, 2546-2558.

(s2) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A.H. J. Am. Chem. Soc. 1988, 110, 1423-1435.

(s3) Müller, J.; Gaede, P. E.; Qiao, K. J. Organomet. Chem. **1994**, 480, 213-220. Since this paper is in German, English language procedures for the complexes used in this study are provided.

(s4) Johnson, B. F. G.; Lewis, J.; Yarrow, D. J. J. Chem. Soc., Dalton Trans. 1972, 2084-2089.

(s5) These <sup>13</sup>C NMR assignments follow from those of complexes of the formula ( $\eta^5$ -C<sub>6</sub>-R<sub>6</sub>)M( $\eta^4$ -1,3-C<sub>6</sub>H<sub>8</sub>): Bennett, M. A.; McMahon, I. J.; Pelling, S.; Brookhart, M.; Lincoln, D. M. *Organometallics* **1992**, *11*, 127-138.

(s6) These <sup>1</sup>H NMR assignments were established for 1 in reference s3.

(s7) These <sup>13</sup>C NMR signals were assigned by a gHMQC spectrum of **1** (CD<sub>2</sub>Cl<sub>2</sub>). The assignments are analogous to those of  $(\eta^5-C_5H_5)Ir(\eta^4-1,3-C_6H_8)$ , and  $\eta^4-1,3$ -butadiene and  $\eta^4-1,3,5$ -hexatriene complexes reported by Bianchini, C.; Caulton, K. G.; Johnson, T. J.; Heli, A.; Peruzzini, M.; Vizza, F. *Organometallics* **1995**, *14*, 933-943.

(s8) Grundy, S. L.; Maitlis, P. M. J. Organomet. Chem. 1984, 272, 265-282.

(s9) Schwab, P.; Grubbs, R. H.; Ziller, J. W. J. Am. Chem. Soc. 1996, 118, 100-110.

(s10) APEX2 "Program for Data Collection on Area Detectors" BRUKER AXS Inc.,5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.

(s11) SADABS, Sheldrick, G. M. "Program for Absorption Correction of Area Detector Frames", BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.
(s12) Sheldrick, G. M. Acta Cryst. 2008, A64, 112-122.

Empirical formula	C <sub>16</sub> H <sub>21</sub> Ir
Formula weight	405.53
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 8.371(3)  Å
	b = 11.414(4)  Å
	c = 14.760(5)  Å
	$\alpha = 87.652(4)^{\circ}$
	$\beta = 88.522(4)^{\circ}$
	$\gamma = 79.837(4)^{\circ}$
Volume	1386.8(8) Å <sup>3</sup>
Z	4
Density (calculated)	1.942 Mg/m <sup>3</sup>
Absorption coefficient	$9.604 \text{ mm}^{-1}$
F (000)	776
Crystal size	$0.42 \times 0.34 \times 0.09 \text{ mm}^3$
Theta range for data collection	1.81 to 27.97°
Index range (h, k, l)	-11, 10; -14, 15; -19, 19
Reflections collected	16005
Independent reflections	6511 [R(int) = 0.0476]
Completeness to theta = $27.97^{\circ}$	97.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4786 and 0.1073
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	6511 / 0 / 317
Goodness-of-fit on F <sup>2</sup>	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0342, wR2 = 0.0855
R indices (all data)	R1 = 0.0445, wR2 = 0.0981
Largest diff. peak and hole	2.679 and -2.643 eÅ <sup>-3</sup>

#### Table s1. Summary of crystal and refinement data for 2.

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Figure s1. ROMP of 1 monitored by <sup>13</sup>C NMR in  $CD_2Cl_2$  (\* = 1, † = poly-1, § = Grubbs' catalyst, ‡ = solvent)



Figure s2. <sup>1</sup>H NMR spectra ( $CD_2Cl_2$ ) of poly-1 (bottom, before quenching with ethyl vinyl ether) and poly-1' (top, quenched material), and expanded views of the vinyl and cyclopentadienyl region (insets, \* = vinyl group,  $\dagger = cyclopentadienyl signal$ , # = impurity).



Figure s3. Integral data for the spectra in Figure s2.

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Figure s4. UV-visible spectrum of 1 (0.662 mM or 0.222 g/L in  $CH_2Cl_2$ ) and poly-1' (0.205 g/L in  $CH_2Cl_2$ ).

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![](_page_12_Figure_1.jpeg)

![](_page_12_Figure_2.jpeg)

![](_page_13_Figure_1.jpeg)

Figure s6. Current/potential response for an interdigitated electrode coated with iodine doped poly-1'.

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![](_page_14_Figure_1.jpeg)

 $\label{eq:Figure s7. Cyclic voltammograms} (THF, 50 \text{ mM } Bu_4 \text{N}^+ \text{ BF}_4^-, 0.10 \text{ V/s}) \text{ of } \textbf{1} (top, 1.0 \text{ mM}) \text{ and poly-1'} (bottom, 1.0 \text{ mM}).$ 

![](_page_15_Figure_0.jpeg)