Supporting Information for *J. Am. Chem. Soc.*

Double C-H Activation During Functionalization of Phenyl(methyl)ketene on Iridium(I) using Alkynes. A Synthesis of 1,4-Dien-3-ones.

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Contents

Preparations and spectroscopic data pages S2-S11

Experimental Section

General Information. Reactions were performed in resealable NMR tubes (J. Young) under dry nitrogen, using a combination of Schlenk line and glovebox techniques. C₆D₆ was distilled from LiAlH₄ prior to use. [(cyclooctene)₂Ir(μ-Cl)]₂ was synthesized according to literature procedure (van der Ent, A.; Onderdelinden, A. L. *Inorg. Synth.* **1973**, *14*, 92; by using (NH₄)₂IrCl₆ instead of hydrated IrCl₃, a higher yield (~89%) could be obtained, see Bennett, M. A.; Latten, J. L. *Inorg. Synth.* **1989**, *26*, 200, footnote 5 therein).

Methylphenylketene was prepared by treating racemic 2-phenylpropionyl chloride with triethylamine in ether, and distilling the product (Baigrie, L. M.; Seiklay, H. R.; Tidwell, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 5391-5396). It was stored as a 0.4 mg per mL solution in benzene and stored at -40 °C in a glovebox. Without dilution in solvent, some samples of the material were seen to polymerize within one month, even at low temperature. Alkyne complexes **2** were prepared as previously reported (Lo, H. C.; Grotjahn, D. B. *J. Am. Chem. Soc.* **1997**, *119*, 2958-2959).

Radial chromatography was carried out on silica gel (SiO₂) plates in a Harrison Research Chromatotron under a N₂ atmosphere. Chromatography solvents were deoxygenated by bubbling nitrogen through them.

Unless otherwise specified, ¹H, ¹³C, COSY, HMQC, HMBC and NOE data were measured at 30 °C on a 500-MHz (499.9 MHz for ¹H and 125.7 MHz for ¹³C) and ³¹P data were measured on a 200-MHz (80 MHz for ³¹P) spectrometer. ¹H and ¹³C NMR chemical shifts are reported in ppm downfield from tetramethylsilane and referenced to solvent resonances (¹H NMR: δ 7.16 for C₆HD₅ and δ 7.27 for CHCl₃; ¹³C NMR: δ 128.39 for C₆D₆ and δ 77.23 for CDCl₃). ¹H NMR chemical shifts are followed (in parentheses) by multiplicity, coupling constants *J* in hertz, and integration. ³¹P{¹H} NMR chemical shifts are referenced to an external 85% H₃PO₄ (aq) capillary placed in C₆D₆. IR spectra at ambient temperatures were obtained on a ThermoNicolet Nexus 670 FT-IR spectrometer. Samples were examined in C₆D₆ solution in NaCl cells. Elemental analyses were performed at NuMega Laboratories in San Diego, CA. Electrospray mass spectra were obtained on a Finnigan LCQ spectrometer.

Preparation of 1. [(cyclooctene)₂Ir(μ-Cl)]₂ (200.0 mg, 0.223 mmol) was weighed into a 20 mL scintillation vial and benzene (*ca.* 5 mL) was added to form an orange suspension. Triisopropylphosphine (170 μL, 0.886 mmol, *d* = 0.839 g/mL) was added, whereupon an immediate increase in solubility was observed, and the reaction was left to stand for 2 h. Methylphenylketene (176 μL stock solution, 0.4 mg/μL, 0.533 mmol) was added slowly to the stirred solution. The resulting clear red solution was allowed to stand for 24 h before extraction with hexanes and concentration of the solution to recrystallize the product **1** (125.8 mg, 83%) as a deep red solid: ¹H NMR (C₆D₆, 500 MHz) δ 7.69 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.34 (dd, *J* = 8.0, 7.5 Hz, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 2.63 (s, 3H), 2.36-2.45 (m, 6H), 1.15-1.26 (m, 36H); ¹³C NMR (C₆D₆, 125.7 MHz) δ 144.95 (t, *J*_{CP} = 4.5 Hz), 137.55, 129.72, 128.72, 125.64, 65.09, 21.92 (vt, *N*_{CP} = 24.9 Hz), 20.32, 19.70.

Representative procedure for the preparation of metallacycles 3a-3d from reaction of ketene complex 1 with alkyne. Reaction of 1 and 2-butyne to form 3a. A J. Young NMR tube was charged with **1** (50.0 mg, 0.0734 mmol) and

tetrakis(trimethylsilyl)methane (TTMS, 1.1 mg), which were dissolved in C₆D₆ (0.7 mL). Inside the glovebox, a pre-cooled syringe was used to transfer 2-butyne (6.3 μ L, 0.0807 mmol) to the solution. The tube was sealed, removed from the glovebox, and placed into a 60 °C oil bath for 18 h, at which time the reaction was complete as determined by ¹H and ³¹P{¹H} NMR spectroscopy. By comparison of integrals before and after the reaction, the yield of **3a** was determined to be 91%. The mixture was purified by radial chromatography (1 mm SiO₂ plate, gradient elution starting with hexane/ethyl acetate = 10:1) to obtain **3a** (41.1 mg, 76%) as a red solid: ¹H NMR (CDCl₃, 500 MHz) δ 10.70 (s, 1H), 7.25 (dd, J = 8.5, 7.4 Hz, 2H), 7.18 (t, J = 7.4 Hz, 1H), 7.00 (d, J = 8.5 Hz, 2H), 5.82 (qq, J = 7.0, 1.4 Hz, 1H), 2.49-2.56 (m, 6H), 1.84 (narrow m, 3H), 1.64 (d, J = 7.0 Hz, 3H), 1.34 (dvt, J = 6.5 Hz, N = 14.9 Hz, 18H), 1.19 (dvt, J = 6.5 Hz, N = 14.9 Hz, 18H), -22.42 (t, J_{HP} = 16.0 Hz, 1H); ¹³C NMR (CDCl₃, 125.7 MHz) δ 203.2, 197.7, 144.9, 143.5, 135.6, 135.5, 128.3, 128.0, 125.7, 24.8 (vt, N_{CP} = 27.1), 19.3, 14.4, 13.8; ³¹P NMR (CDCl₃, 81.0 MHz) δ 22.1; IR (C₆D₆): 2271 (m), 1513 (s), 1456 (m), 1348 (m) cm⁻¹; ESMS calculated 734.31 m/z (EI) 739.1 (32) [M+Li⁺], 688.2 (100) [M-Cl⁻]; Anal. Calcd. for C₃₁H₅₆ClIrOP₂: C, 50.70; H, 7.69. Found C, 50.84; H, 8.09.

Products 3b and 3b' from reaction of 1 with 2-pentyne. From **1** (50.0 mg, 0.0734 mmol) and 2-pentyne (36.1 mg, 0.0734 mmol) in C₆D₆ (0.7 mL) after heating at 60 °C for 31 h was obtained metallacycles **3b** and **3b'** (73% NMR yield combined, 1.96 to 1 ratio of isomers **3b** and **3b'**). Radial chromatography gave a mixture of **3b** and **3b'** as a red solid (30.2 mg, 0.0404 mmol, 55%). For **3b**: ¹H NMR (CDCl₃, 500 MHz) δ 10.88 (s, 1H), 7.23 (m, 1H), 7.22 (m, 2H), 7.13 (m, 2H), 5.77 (t, J = 7.6 Hz, 1H), 2.49-2.56 (m, 6H), 1.98 (s, 1H), 1.93 (dq, J = 7.6, 7.6 Hz, 2H), 1.31 (dvt, J = 6.4 Hz, N = 14.0 Hz, 18H), 1.19 (dvt, J = 6.4 Hz, N = 14.0, 18H), 0.72 (t, J = 7.6 Hz, 3H), -22.48 (t, J_{HP} = 16.0 Hz, 1H); ¹³C NMR (CDCl₃, 125.7 MHz) δ 203.1, 200.1, 144.7, 143.5, 142.1, 133.6, 128.8, 128.5, 128.3, 24.9 (vt, N_{CP} = 25.1 Hz), 19.8, 19.7, 19.6 (from correlation data), 14.1, 13.4; ³¹P NMR (CDCl₃, 81.0 MHz) δ 22.1. For **3b'**: ¹H NMR (CDCl₃, 500 MHz) δ 10.88 (s, 1H), 7.23 (m, 1H), 7.22 (m, 2H), 7.13 (m, 2H), 5.73 (q, J = 6.8 Hz, 1H), 2.58 (q, J = 7.8 Hz, 2H), 2.49-2.56 (m, 6H), 1.48 (d, J = 6.8 Hz, 3H), 1.31 (dvt, J = 6.5 Hz, N = 14.7 Hz, 18H), 1.22 (t, J = 7.6 Hz, 3H), 1.19 (dvt, J = 6.5 Hz, N = 14.7 Hz, 18H), -22.36 (t, J_{HP} = 16.0 Hz); ¹³C NMR (CDCl₃, 125.7 MHz) δ 202.7, 200.5, 144.7, 143.4, 141.3, 136.1, 128.8, 128.5, 128.3, 24.9 (vt, N_{CP} = 25.1 Hz), 19.8, 19.7, 14.3, 14.3; ³¹P NMR (CDCl₃, 81.0 MHz) δ 22.1. Data on the **3b**, **3b'** mixture: IR (C₆D₆): 2270 (m), 1512 (s), 1456 (m), 1349 (m) cm⁻¹; ESMS of the **3b**, **3b'** mixture calculated 748.33 m/z (EI) 753.5 (18) [M+Li⁺], 713.2 (100) [M-Cl⁻].

Product 3c from reaction of 1 with 3-hexyne. From **1** (50.0 mg, 0.0734 mmol) and 3-hexyne (6.6 mg, 0.0919 mmol) in C₆D₆ (0.7 mL) after heating at 60 °C for 12 h was obtained **3c** (71% NMR yield). Radial chromatography gave **3c** as a red solid (32.5 mg, 0.0425 mmol, 58%). ¹H NMR (CDCl₃, 500 MHz) δ 10.72 (s, 1H), 7.26 (m, 2H), 7.08 (t, J = 8.4 Hz, 1H), 7.02 (d, J = 8.4 Hz, 2H), 5.42 (t, J = 7.6 Hz, 1H), 2.45-2.53 (m, 6H), 2.10-2.18 (m, 2H), 1.98 (q, J = 7.6 Hz, 2H), 1.31 (dvt, J = 6.4 Hz, N = 14.1 Hz, 18H), 1.21 (dvt, J = 6.4 Hz, N = 14.1 Hz, 18H), 1.21 (t, J = 7.6 Hz, 3H), 0.70 (t, J = 7.6 Hz, 3H), -22.58 (t, J_{HP} = 15.9 Hz, 1H); ¹³C NMR (CDCl₃, 125.7 MHz) δ 204.0, 196.9, 146.2, 144.2, 143.9, 143.0, 128.2, 128.0, 127.0, 24.5, 24.5 (vt, N = 27.0 Hz), 19.5, 19.4, 16.6,

15.4, 13.1; ^{31}P NMR (CDCl_3 , 81.0 MHz) δ 22.0; IR (C_6D_6): 2271 (m), 1509 (s), 1453 (m), 1344 (m) cm^{-1} ; ESMS calculated 762.34 m/z (EI) 767.5 (22) $[\text{M}+\text{Li}^+]$, 727.1 (100) $[\text{M}-\text{Cl}]$.

Products $3\text{d}'$ and $3\text{d}''$ from reaction of **1 with 1-phenyl-1-propyne.** From **1** (50.0 mg, 0.0734 mmol) and 1-phenyl-1-propyne (9.38 mg, 0.0807 mmol) in C_6D_6 (0.7 mL) after heating at 60 $^\circ\text{C}$ for 48 h were obtained metallacycles **$3\text{d}'$** and **$3\text{d}''$** (68% NMR yield combined, 1 to 1.10 ratio of isomers **$3\text{d}'$** and **$3\text{d}''$**). Radial chromatography gave a mixture of **$3\text{d}'$** and **$3\text{d}''$** as a red solid (32.1 mg, 0.0528 mmol, 55%). For **$3\text{d}'$** : ^1H NMR (CDCl_3 , 500 MHz) δ 10.90 (s, 1H), 7.30 (m, 2H), 7.28 (m, 2H), 7.24 (m, 1H), 7.22 (m, 1H), 7.11 (m, 2H), 7.09 (m, 2H), 6.69 (m, 1H), 2.51-2.59 (m, 6H), 2.13 (d, $J = 1.1$ Hz, 3H), 1.37 (dvt, $J = 6.4$ Hz, $N = 13.4$ Hz, 18H), 1.21 (dvt, $J = 6.4$ Hz, $N = 13.4$ Hz, 18H), -22.50 (t, $J = 16.0$ Hz, 1H); ^{13}C NMR (CDCl_3 , 125.7 MHz) δ 203.1, 199.5, 144.8, 142.1, 137.4, 136.6, 135.4, 129.5, 128.5, 128.3, 128.3, 128.1, 125.7, 24.3 (vt, $N_{\text{CP}} = 27.1$ Hz), 19.3, 19.1, 15.6; ^{31}P NMR (CDCl_3 , 81.0 MHz) δ 23.1. For **$3\text{d}''$** : ^1H NMR (CDCl_3 , 500 MHz) δ 10.96 (s, 1H), 7.24 (m, 1H), 7.00 (m, 2H), 6.99 (m, 1H), 6.92 (m, 2H), 6.72 (m, 2H), 6.67 (m, 2H), 6.50 (s, 1H), 2.43-2.53 (m, 6H), 2.32 (s, 3H), 1.29 (dvt, $J = 6.6$ Hz, $N = 13.6$ Hz, 18H), 1.18 (dvt, $J = 6.6$ Hz, $N = 13.6$ Hz, 18H), -22.31 (t, $J_{\text{HP}} = 16.0$ Hz, 1H); ^{13}C NMR (CDCl_3 , 125.7 MHz) δ 201.7, 199.9, 145.2, 141.0, 140.8, 135.6, 132.5, 128.3, 127.6, 127.6, 126.9, 127.1, 124.8, 24.5, 22.8 (vt, $N_{\text{CP}} = 27.1$), 19.8, 19.6; ^{31}P NMR (CDCl_3 , 81.0 MHz) δ 28.8. Data on the mixture of **$3\text{d}'$** and **$3\text{d}''$** : IR (C_6D_6): 2271 (m), 1505 (s), 1455 (m), 1340 (m) cm^{-1} ; ESMS calculated 796.32 m/z (EI) 799.7 (10) $[\text{M}+3]$, 761.2 (100) $[\text{M}-\text{Cl}]$.

Partial NMR data for **3d** from a chromatographically enriched mixture of **3d** , **$3\text{d}'$** and **$3\text{d}''$** : ^1H NMR (CDCl_3 , 500 MHz) δ 10.91 (s, 1H), 5.88 (q, 1H, $J = 7.5$ Hz), 2.44-2.53 (m, 6H), 1.42 (d, $J = 7.5$ Hz, 3H), 1.29 (dvt, $J = 6.6$ Hz, $N = 13.6$ Hz, 18H), 1.18 (dvt, $J = 6.6$ Hz, $N = 13.6$ Hz, 18H), -23.29 (t, $J_{\text{HP}} = 16.0$ Hz, 1H); ^{31}P NMR (CDCl_3 , 81.0 MHz) δ 23.7.

nOe data on an **3d** -enriched mixture of **3d** , **$3\text{d}'$** and **$3\text{d}''$** (12:39:49): a cycle nOe experiment was employed to ensure complete and selective saturation of the target resonances, see Neuhaus, D.; Williamson, M. P. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*. **2000**, 240-43. Complete saturation was verified for each irradiated resonance. The most obvious piece of evidence supporting the assignment of the regiochemistry shown in **3d** is the 7.5-Hz coupling between vinyl and methyl protons, which is absent in the other two isomers, **$3\text{d}'$** and **$3\text{d}''$** .

Proton chemical shifts (δ) and enhancements (%)

Structure **3d**: Irradiation of the signal at δ 5.58 led to 9.00 % enhancement of the signal at δ 7.58. Enhancement of δ 1.34 could not be observed within the subtraction artifacts due to the isopropylphosphine ligands. Irradiation of the signal at δ 1.34 led to 1.69 % enhancement of the signal at δ 5.58 and 0.82 % enhancement of the signal at δ 7.28.

Structure **3d'**: Irradiation of the signal at δ 2.12 led to 2.68 % enhancement of the signal at δ 7.11 and no enhancement of δ 6.69. Attempts to irradiate at 6.69 were inconclusive, efficient selectivity could not be obtained.

Structure **3d''**: Irradiation of the signal at δ 6.50 led to 2.26 % enhancement of the signal at δ 6.67 and a 7.13 % enhancement of the signal at δ 2.32. Irradiation of the signal at δ 2.32 led to 1.36 % enhancement of the signal at δ 6.72 and 4.99 % enhancement of the signal at δ 6.50.

Representative procedure for the preparation 3a-d from reaction of η^2 -alkyne complexes 2 with methylphenylketene. Preparation of 3a. A 5 mL benzene solution of 2-butyne complex **2a** (33.6 mg, 0.0558 mmol) was prepared in a 20 mL scintillation vial inside the glovebox. Methylphenylketene (46 μL stock solution, 0.4 mg/ μL , 0.140 mmol) was added and left to react for 18 h at room temperature. The reaction was monitored with ^1H and ^{31}P NMR (94% **3a** by NMR). All volatiles were removed by vacuum and **3a** was extracted from the residue with *ca.* 20 mL hexane. The resulting orange solution was purified with radial chromatography (1 mm SiO_2 plate, gradient elution starting with hexane/ethyl acetate = 10:1) to obtain **3a** (41.1 mg, 78%) as a red solid.

Reaction of 2-pentyne complex 2b with methylphenylketene to give 3b and 3b'. From **2b** (34.39 mg, 0.0558 mmol) and a stock solution of methylphenylketene (55 μL stock solution, 0.4 mg/ μL , 0.167 mmol) in benzene (5 mL) after 24 h at ambient temperature were obtained metallacycles **3b** and **3b'** (89% NMR yield combined, 1.24 to 1 ratio of isomers **3b** and **3b'**). Radial chromatography gave a mixture of **3b** and **3b'** as a red solid (29.6 mg, 0.0396 mmol, 71%).

Reaction of 3-hexyne complex 2c with methylphenylketene to give 3c. From **2c** (35.17 mg, 0.0558 mmol) and a stock solution of methylphenylketene (46 μL stock solution, 0.4 mg/ μL , 0.140 mmol) in benzene (5 mL) after 18 h at ambient temperature **3c** was obtained (96% NMR yield). Radial chromatography gave **3c** as a red solid (34.46 mg, 0.0452 mmol, 81%).

Reaction of 1-phenylpropyne complex 2d with methylphenylketene to give 3d' and 3d''. From **2d** (37.07 mg, 0.0558 mmol) and a stock solution of methylphenylketene (64 μ L stock solution, 0.4 mg/ μ L, 0.195 mmol) in benzene (5 mL) after 48 h at ambient temperature were obtained metallacycles **3d'** and **3d''** (86% NMR yield combined, 1 to 1.09 ratio of isomers **3d'** and **3d''**). Radial chromatography gave a mixture of **3d'** and **3d''** as a red solid (31.99 mg, 0.0402 mmol, 72%).

Representative demetallation of a metallacycle (3a) with CO to give a dienone (5a, 1,4-(E)-4-methyl-2-phenylhexa-1,4-diene-3-one). Complex **3a** (23.5 mg, 0.0320 mmol) was transferred to a J. Young tube by dissolving it in portions of C₆D₆ in the glovebox. The volume was adjusted to 0.7 mL by vacuum and 0.9 mg TTMS was added. The N₂ was displaced with CO via syringe. The sealed tube was placed in an 80 °C oil bath and monitored by ¹H and ³¹P{¹H} for completion of the reaction. After heating for 72 h, **3a** had been consumed to generate **5a** in 92% yield as determined by comparison of integrals with those of internal standard (TTMS). The resulting yellow solution was purified using radial chromatography (1 mm SiO₂ plate, gradient elution starting with hexane/ethyl acetate = 1:1) to yield **5a** (5.0 mg, 78% yield) as a pale yellow oil: ¹H NMR (C₆D₆, 500 MHz) δ 7.37 (d, J = 6.9 Hz, 2H), 7.10 (m, 1H), 7.08 (m, 2H), 6.51 (qq, J = 7.0, 1.1 Hz, 1H), 5.54 (s, 1H), 5.15 (s, 1H), 1.84 (q, J = 1.1 Hz, 3H), 1.31 (q, J = 7.0 Hz, 3H); ¹³C NMR (C₆D₆, 125.7 MHz) δ 198.6, 141.8, 138.3, 138.3, 138.6, 128.8, 128.4, 126.8, 116.7, 14.4, 11.2; IR (C₆D₆): 1657 (s), 1641 (m), 1617 (w) cm⁻¹; ESMS calculated 186.10 m/z (EI); observed 187.1 (M+H).

Dienones 5b and 5b' from demetallation of 3b and 3b'. From **3b** and **3b'** (25.2 mg, 0.0337 mmol, 1.22 to 1 mixture) dissolved in C₆D₆ (0.7 mL) and containing TTMS (0.9 mg) was obtained a mixture of **4** and **5b** + **5b'** (1.23 to 1 ratio, 87% NMR yield). Radial chromatography gave **5b** and **5b'** (1.15 to 1 ratio, 5.0 mg, 66%) as a pale yellow oil. **5b**: ¹H NMR (C₆D₆, 500 MHz) δ 7.40 (m, 1H), 7.31 (m, 2H), 7.08 (m, 2H), 6.42 (t, J = 7.6 Hz, 1H), 5.53 (s, 1H), 5.23 (s, 1H), 1.87 (s, 3H), 1.82 (dq, J = 7.6, 7.6 Hz, 2H), 0.67 (t, J = 7.6, 3H); ¹³C NMR (C₆D₆, 125.7 MHz) δ 198.4, 149.5, 148.3, 143.5, 138.5, 128.9, 128.8, 127.3, 116.9, 22.7, 22.4, 13.6; IR (C₆D₆): 1656 (s), 1638 (m), 1615 (w) cm⁻¹; ESMS calculated 200.12 m/z (EI) 187.1 (M+H). **5b'**: ¹H NMR (C₆D₆, 500 MHz) δ 7.40 (m, 1H), 7.31 (m, 2H), 7.08 (m, 2H), 6.52 (q, J = 7.1 Hz, 1H), 5.55 (s, 1H), 5.18 (s, 1H), 2.44 (q, J = 7.6 Hz, 2H), 1.37 (d, J = 7.1 Hz, 3H), 1.05 (t, J = 7.6, 3H); ¹³C NMR (C₆D₆, 125.7 MHz) δ 198.4, 149.0, 142.8, 142.4, 138.5, 128.9, 128.8, 127.3, 117.5, 19.7, 14.6, 14.2.

Dienone 5c from demetallation of 3c. From **3c** (48.3 mg, 0.0634 mmol) in C₆D₆ (0.7 mL) containing TTMS (0.9 mg) and CO was obtained after heating 80 °C for 72 h dienone **5c** (93% NMR yield). After purification by radial chromatography, **5c** (8.5 mg, 82%) was obtained as a pale yellow oil. ¹H NMR (C₆D₆, 500 MHz) δ 7.39 (d, J = 7.6 Hz, 2H), 7.08 (m, 2H), 7.04 (m, 1H), 6.43 (t, J = 7.5 Hz, 1H), 5.56 (s, 1H), 5.23 (s, 1H), 2.44 (q, J = 7.3 Hz, 2H), 1.84 (dq, J = 7.6, 7.5, 2H), 1.04 (t, J = 7.5 Hz, 3H), 0.68 (t, J = 7.5 Hz, 3H); ¹³C NMR (C₆D₆, 125.7 MHz) δ 198.8, 149.1, 148.3, 143.4, 138.4, 129.2, 128.6, 127.9, 117.7, 22.4, 19.5, 14.5, 13.5; IR (C₆D₆): 1653 (s), 1634 (m), 1612 (w) cm⁻¹; ESMS calculated 214.14 m/z (EI) 215.1 (M+H).

Dienones 5d' and 5d'' from demetallation of 3d' and 3d''. From **3d'** and **3d''** (50.0 mg, 0.0628 mmol, 1 to 2.76 mixture) containing TTMS (1.0 mg) was obtained a

mixture of **4** and **5d'** + **5d''** (1 to 2.74 ratio, 81% NMR yield). After radial chromatography, a mixture of **5d'** and **5d''** (11.5 mg, 60% total) was obtained as a yellow oil. NMR integration shows a 1 to 2.50 ratio of the minor (**5d'**) and major (**5d''**) isomers. In the proton NMR spectra, the region 6.62 to 7.15 ppm showed several multiplets overlapping with each other and the signal for C₆HD₅ in the solvent, precluding full assignments.

For **5d''**: partial ¹H NMR (C₆D₆, 500 MHz) δ 6.38 (m, 1H), 5.45 (s, 1H), 5.31 (s, 1H), 1.94 (d, *J* = 1.3 Hz, 3H); partial ¹³C NMR (C₆D₆, 125.7 MHz) δ 201.8, 147.8, 138.3, 137.0, 130.8, 128.6, 128.3, 22.2 (using gHMBC and gHMQC, only the ipso carbons of the phenyls could be assigned); IR (C₆D₆): 1642 (s), 1632 (m), 1610 (w) cm⁻¹; ESMS calculated 248.12 *m/z* (EI) 249.0 (M+H). For **5d'**: partial ¹H NMR (C₆D₆, 500 MHz) δ 7.50 (s, 1H), 5.84 (s, 1H), 5.60 (s, 1H), 2.15 (s, 3H); partial ¹³C NMR (C₆D₆, 125.7 MHz) δ 199.8, 147.9, 143.4, 138.0, 137.6, 128.2, 117.7, 13.4 (using gHMBC and gHMQC, only the ipso carbons of the phenyls could be assigned).

Thermolysis of 1: A J. Young tube was prepared with **1** (11.8 mg, 0.0173 mmol), C₆D₆ (0.7 mL) and TTMS (0.9 mg). The tube was placed in an 85 °C oil bath and monitored by ¹H and ³¹P{¹H}. Complete reaction of **1** to *trans*-(P(*i*-Pr)₃)₂Ir(CO)(Cl) (**4**) and styrene (each in ≥ 98% yield) occurred after 6 d.

Thermal stability of 3d' and 3d'': A J. Young tube containing a chromatographically enriched sample of isomers **3d**, **3d'** and **3d''** (9.8 mg, 0.0123 mmol; 7 : 68 : 21 ratio) and TTMS (0.8 mg) in C₆D₆ (0.7 mL) was subjected to a 70 °C oil bath in the absence of light. After 6 d at 70 °C, as observed by ¹H and ³¹P NMR, the ratio of **3d**, **3d'** and **3d''** was 7 : 40 : 49, showing slow conversion of **3d'** to **3d''**.

Effect of acid on conversion of 3d' to 3d'': 2-phenylpropionic acid (0.010 mL of a prepared solution containing 3.3 mg/mL of C₆D₆, 0.665 μmol) was injected in a J. Young tube containing a chromatographically enriched sample of isomers **3d'** and **3d''** (7.9 mg, 0.0112 mmol; 58 : 42 ratio) and TTMS (0.9 mg) in C₆D₆ (0.7 mL). The NMR tube was heated in a 70 °C oil bath in the absence of light. After 24 h at 70 °C, as observed by ¹H and ³¹P NMR, the ratio of **3d'** and **3d''** was 51 : 49, also showing slow conversion of **3d'** to **3d''**.

Table S1. ¹H NMR data for metallacycles in CDCl₃. Multiplicities and coupling *J*(Hz) or *N* in parentheses.

Complex	H ^a 1H	H ^b 6H	H ^c 18H; 18H	H ^d 1H	R ²	R ¹	H ^e 1H	H ^f 2H	H ^g 2H	H ^h 1H
3a	-22.42 (t, 16.0)	2.49-2.56 (m)	1.34, 1.19 (2 d, 6.5, vt, 14.9)	5.82 (q, 7.0; q, 1.4)	1.60 (d, 7.0)	1.84 (narrow m)	10.70 (s)	7.00 (d, 8.5)	7.25 (dd, 8.5, 7.4)	7.18 (t, 7.4)
3b	-23.09 (t, 16.0)	2.49- 2.56 (m)	1.19, 1.31 (2 d, 6.4, vt, 14.0)	5.77 (t, 7.6)	1.93 (d,q; 7.6) 0.72 (t, 7.6)	1.98 (s)	10.88 (s)	7.13 (m)	7.22 (m)	7.23 (m)
3b'	-23.12 (t, 16.0)	2.49- 2.56 (m)	1.19, 1.31 (2 d, vt, 6.5 14.7)	5.73 (q, 6.8)	1.48 (d, 6.8)	2.58 (q, 7.6) 1.22 t, 7.6	10.88 (s)	7.13 (m)	7.22 (m)	7.23 (m)
3c	-22.58 (t, 15.9)	2.45-2.53 (m)	1.31, 1.21 (2 d, 6.4, vt, 14.1)	5.42 (t, 7.6)	2.10-2.18 (m) 1.21 (t, 7.6)	1.98 (q, 7.6) 0.70 (t, 7.6)	10.72 (s)	7.02 (d, 8.4)	7.26 (m)	7.08 (t, 8.4)
3d	-23.29 (t, 16.0)	2.44-2.53 (m)	1.18, 1.29 (2 d, 6.6, vt, 13.6)	5.58 (q, 7.5)	1.42 (d, 7.5)	7.58 (2 H)	10.91 (s)	7.28 (m)	***	***
3d'	-23.50 (t, 16.0)	2.51-2.59 (m)	1.21, 1.37 (2 d, 6.4, vt, 13.4)	6.69 (m)	**	2.13 (d, 1.1)	10.90 (s)	7.09 (m)	7.28 (m)	7.24 (m)
3d''	-22.31 (t, 16.0)	2.43-2.51 (m)	1.18, 1.29 (2 d, 6.6, vt, 13.6)	6.50 (s)	*	2.32 (s)	10.96 (s)	6.72 (m)	7.00 (m)	7.24 (m)

* Hortho = 6.67, Hmeta = 6.92, Hpara = 6.99. Coupling is not possible to resolve due to overlapping peaks.

** Hortho = 7.11, Hmeta = 7.30, Hpara = 7.22. Coupling is not possible to resolve due to overlapping peaks.

*** Overlapping peaks made these impossible to identify.

Table S2. $^{13}\text{C}\{^1\text{H}\}$ Data for metallacycles in CDCl_3 . Coupling $J(\text{Hz})$ or N

Complex	C ^a 6C	C ^b , C ^c 9C; 9C	C ^d 1C	C ^e 1C	C ^f 1C	C ^g 1C	C ^h 1C	C ⁱ 1C	C ^j 1C	C ^k 1C	C ^l 2C	C ^m 2C	C ⁿ 1C	C ^o 1C	C ^p 1C
3a	24.8 (vt, 27.1)	19.3, 19.5	197.7	144.9	203.2	135.6	135.5	14.4	13.8	143.5	128.0	128.3	125.7	NA	NA
3b	24.9 (vt, 25.1)	19.7, 19.8	200.1	144.7	203.1	142.1	133.6	19.6 ^a	14.1	143.4	128.3	128.8	128.5	13.4	NA
3b'	24.9 (vt, 25.1)	19.7, 19.8	200.5	144.7	202.7	141.3	136.1	14.3	25.0	143.4	128.3	128.8	128.5	NA	14.3
3c	24.5 (vt, 27.0)	19.4, 19.5	196.9	144.2	204.0	143.9	143.0	24.5	15.4	146.2	128.0	128.2	127.0	16.6	13.1
3d'	24.3 (vt, 27.1)	19.1, 19.3	199.5	144.8	203.1	135.4	137.4	*	15.6	142.1	128.1	128.5	128.3	NA	NA
3d''	22.8 (vt, 27.1)	19.6, 19.8	199.9	145.2	201.7	135.6	132.5	**	24.5	140.8	126.9	127.6	127.1	NA	NA

^a = 19.6 is tentative, it looks like there are correlations, but resonance is obscured by the resonances for C^{b} and C^{c} .

* = Ph in place of C^{b} ; C1 = 136.6, C2 = 129.5, C3 = 128.3, C4 = 125.7.

** = Ph in place of C^{b} ; C1 = 141.0, C2 = 128.3, C3 = 127.6, C4 = 124.8.

Table S3. ¹H Data for dienones **5 in C₆D₆.** Spectra referenced to benzene at 7.16 ppm, multiplicities and coupling *J* in Hz in parentheses.

Dienone	H ^a 1H	H ^b 1H	H ^c 1H	H ^d 0-3H	H ^e 0-3H	H ^f 0-3H	H ^g 0-3H	H ^h 1H	H ⁱ 2H	H ^j 1H
5a	5.14 (s)	5.54 (s)	6.51 (q, q; 1.1, 7.0)	1.31 (q, 7.0)	1.84 (q, 1.1)	NA	NA	7.37 (d, 6.9)	7.08 (m)	7.10 (m)
5b	5.23 (s)	5.53 (s)	6.42 (t, 7.6)	1.82 (dq, 7.6, 7.6)	1.87 (s)	0.67 (t, 7.6)	NA	7.31 (m)	7.08 (m)	7.40
5b'	5.18 (s)	5.55 (s)	6.52 (q, 7.1)	1.37 (d, 7.1)	2.44 (q, 7.6)	NA	1.05 (t, 7.6)	*	*	*
5c	5.23 (s)	5.56 (s)	6.43 (t, 7.5)	1.84 (d, q; 7.5)	2.44 (q, 7.3)	0.68 (t, 7.5)	1.04 (t, 7.5)	7.39 (d, 7.6)	7.08 (m)	7.04 (m)
5d'	5.84 (s)	5.60 (s)	7.50 (s)	**	2.15 (s)	NA	NA	*	*	*
5d''	5.45 (s)	5.31 (s)	6.38 (m)	**	1.94 (d, 1.3)	NA	NA	*	*	*

* = not assignable. Overlapping resonances.

* = Ph in place of H^d; peaks not assignable because of overlapping resonances.

Table S4. ¹³C{¹H} data for dienones in C₆D₆. Spectra referenced to solvent resonance at 128.39 ppm.

Dienone	C ^a 1C	C ^b 1C	C ^c 1C	C ^d 1C	C ^e 1C	C ^f 1C	C ^g 1C	C ^h 1C	C ⁱ 1C	C ^j 1C	C ^k 2C	C ^l 2C	C ^m 1C
5a	116.7	138.3	198.6	138.6	141.8	14.4	11.2	NA	NA	138.3	126.8	128.4	128.8
5b	116.9	149.5	198.4	143.5	148.3	22.4	22.7	13.6	NA	138.5	128.8	128.9	127.3
5b'	117.5	149.0	198.4	142.8	142.4	14.6	19.7	NA	14.2	138.5	128.8	128.9	127.3
5c	117.7	149.1	198.8	143.4	148.3	22.4	19.5	13.5	14.5	138.4	127.9	128.6	129.2
5d'	117.7	138.0	199.8	147.9	137.6	*	13.4	NA	NA	128.2	***	***	***
5d''	128.3	147.8	201.8	130.8	138.3	**	22.2	NA	NA	137.0	***	***	***

* = Ph in place of C^f; C1 = 143.3, other resonances unassignable because of many overlapping peaks.

** = Ph in place of C^f; C1 = 128.6, other resonances unassignable because of many overlapping peaks.

*** Resonances unassignable because of many overlapping peaks.