Supporting Information

Bimolecular Coupling in Olefin Metathesis: Correlating Structure and Decomposition for Leading and Emerging Ruthenium-Carbene Catalysts

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S1. Experimental Procedures

**General Procedures.** Reactions were carried out under N\textsubscript{2} using glovebox or Schlenk techniques. HPLC-grade CH\textsubscript{2}Cl\textsubscript{2}, n-hexane, C\textsubscript{6}H\textsubscript{6} were dried and degassed using a Glass Contour solvent purification system, toluene by distillation from Na: all were stored under N\textsubscript{2} over 4 Å molecular sieves for at least 18 h prior to use. NMR solvents (CDCl\textsubscript{3}, C\textsubscript{6}D\textsubscript{6} and C\textsubscript{7}D\textsubscript{8}: Cambridge Isotopes) were degassed (freeze/pump/thaw; 5x), and stored as above. CAAC salts\textsuperscript{1} and Feist's ester\textsuperscript{2} were prepared by literature methods. Known Hoveyda-class CAAC complexes,\textsuperscript{3,4} iodide derivative HC\textsubscript{1}\textsuperscript{Ph}(L\textsubscript{2}),\textsuperscript{5} carbide complexes [RuCl\textsubscript{2}(L)PR\textsubscript{3}(≡C:)] and Piers catalysts [RuCl\textsubscript{2}(L)(=CHPR\textsubscript{3})OTf (L = H\textsubscript{2}IMes, R = Cy;\textsuperscript{2,6} L = C\textsubscript{1}\textsuperscript{Me},\textsuperscript{5} or C\textsubscript{1}\textsuperscript{Ph}\textsuperscript{7} R = iPr) were synthesized by literature methods. Ethylene (BOC Gases; Linde, 99.9%), internal standard dimethyl terephthalate (DMT, Aldrich, 99%) and PPr\textsubscript{3} (Alfa, 98%) were used as received. The latter was stored in the glovebox freezer until use.

NMR spectra were recorded on Advance II 500 spectrometers at 23±0.2 °C, unless otherwise specified. Chemical shifts are reported in ppm, referenced to the residual proton or carbon signals of the solvent. MALDI mass spectra were collected on a Bruker UltrafleXtreme MALDI-TOF/TOF mass spectrometer. Solutions of matrix (pyrene) and analyte (20:1) were prepared such that the final concentration of matrix and analyte was ca. 100 mM and 5 mM, respectively. A 1 μL aliquot of the mixed solution was spotted on the MALDI target plate and allowed to evaporate by the dried-droplet method.\textsuperscript{8} Spectra were calibrated internally with pyrene (m/z 202.078).

S1.1. Synthesis of Ru Complexes

**Chart S1.** Overview of complexes synthesized, showing numbering system.
S1.1.1. Synthesis of Carbide Complexes RuX₂(CAAC)(PᵢPr₃)(≡ C:)

Higher yields of the CAAC carbide complexes were obtained, relative to our prior route,⁷ by starting with the known Hoveyda-CAAC complexes rather than the indenylidene CAAC dimer (Scheme S1). Washing the product with n-hexane sufficed to remove the organic side-products, where our original procedure required chromatography to remove a species that gave rise to a broad aromatic signal.

![Scheme S1. Synthesis of Carbide Complexes.](image)

**Representative Procedure for Synthesis of RuCl₂(C₁Ph)(PᵢPr₃)(≡ C:), Carbide-C₁Ph.** To a green solution of HC₁Ph (130 mg, 0.203 mmol) and Feist's ester (55 mg, 0.32 mmol, 1.6 equiv) in 3 mL CH₂Cl₂ was added a solution of PᵢPr₃ (53 mg, 0.33 mmol, 1.6 equiv) in 1 mL CH₂Cl₂. The solution was transferred to an oil bath at 35 °C and stirred for 20 h to give a dark yellow solution in which complete conversion to Carbide-C₁Ph was evident (¹H NMR). The volatiles were removed under vacuum, and the residue was taken up in n-hexane (2 mL). The suspension was stirred vigorously until a fine powder resulted. The suspension was chilled (~35 °C) for 2 h, after which the pale-yellow solid was filtered off, washed with n-hexane (~35 °C, 1 mL), dried, and sublimed at 60 °C under reduced pressure for 2 h. Yield: 117 mg, 82%. The ¹H NMR data in CDCl₃ agree with values reported.⁷ Particularly diagnostic is the most downfield signal: δ 7.73 (d, ³JHH = 6.4 Hz, 2H, m-CH of C₁Ph Ar).

**Synthesis of Carbide-C₂Me.** As in the representative procedure, with HC₂Me (112 mg, 0.194 mmol), Feist's ester (45 mg, 0.27 mmol, 1.4 equiv) and PᵢPr₃ (44 mg, 0.28 mmol, 1.4 equiv). ¹H NMR analysis indicated complete consumption of starting material after 6 h of reaction. Product obtained as a pale-yellow solid. Yield after workup: 84 mg (72%). For NMR spectra (including the assigned ¹H spectrum), see Figure S2 and Figure S3.

¹H NMR (CDCl₃, 500 MHz): δ 7.29 (d, ³JHH = 4.5 Hz, 2H, m-CH of C₂Me Ar), 7.14 (t, ³JHH = 4.6 Hz, 1H, p-CH of C₂Me Ar), 3.05 (sept, ³JHH = 6.5 Hz, 1H, CH of C₂Me tPr), 2.74 (m, 3H, CH of PPr₃), 2.42 (s, 3H, CH₃ of C₂Me), 2.09 (d, ³JHH = 3.3 Hz, 2H, backbone CH₂ of C₂Me), 1.75 (d, ³JHH = 16.9 Hz, 6H CH₃ of C₂Me tPr), 1.47 (s, 3H, CH₃ of C₂Me or CH₃ of PPr₃), 1.41 (s, 3H, CH₃ of C₂Me or CH₃ of PPr₃), 1.34 (m, 21H, CH₃ of PPr₃ and C₂Me, overlapping), 1.17 (d, J = 6.4 Hz, 3H, CH₃ of C₂Me or CH₃ of PPr₃). ¹³C [¹H] NMR (CDCl₃, 125 MHz): δ 474.0, 266.5, 265.9, 147.5, 138.5, 137.1, 129.0, 128.9, 125.1, 80.1, 58.4, 52.3, 31.0, 30.8, 30.5, 28.7, 28.4, 26.5, 24.4, 22.9, 21.7, 19.7, 19.6. MALDI-TOF MS (pyrene matrix), m/z: [Carbide-C₂Me]+ 601.127 (calculated for C₂₈H₄₈Cl₂NPRu: 601.194).

**Synthesis of Carbide-C₃Ph.** As in the representative procedure, with HC₃Ph (148 mg, 0.237 mmol), Feist's ester (52 mg, 0.31 mmol, 1.3 equiv) and PPr₃ (51 mg, 0.32 mmol, 1.4 equiv). ¹H NMR analysis indicated complete consumption of starting material after 2 h. Product obtained as a beige solid.

![Synthesis of Carbide-C₃Ph.](image)
Yield after workup: 130 mg (84%). For NMR spectra (including the assigned $^1$H spectrum), see Figure S4 and Figure S5.

$^1$H NMR (CDCl$_3$, 500 MHz): Note. Signals are broad, causing small deviations in integration. δ 7.82 (s br, 2H, or p-CH of C$_3$Ph), 7.66 (s br, 1H, m-CH of C$_3$Ph Ar or p-CH of C$_3$Ph), 7.42 – 7.17 (m br, 4H, or p-CH of C$_3$Ph and CHCl$_3$, overlapping), 6.93 (s br, 1H, m-CH of C$_3$Ph Ar or p-CH of C$_3$Ph), 6.86 (s br, 1H, m-CH of C$_3$Ph Ar or p-CH of C$_3$Ph), 2.66 (s br, 3H, CH of PPr$_3$), 2.47 (m br, 6H, CH$_3$ of C$_3$Ph), 2.39 (s br, 4H, CH$_3$ and backbone CH$_2$ of C$_3$Ph), 2.26 (s br, 4H, CH$_3$ of C$_3$Ph), 1.58 (s br, 1H, backbone CH$_2$ of C$_3$Ph), 1.46 (s br, 3H, CH$_3$ of C$_3$Ph), 1.28 (s br, 2H, CH$_3$ of C$_3$Ph), 1.13 (m br, 20H, CH$_3$ of PPr$_3$).

Synthesis of Carbide-C$_1$Ph(I$_2$). As in the representative procedure, with minor modifications: HCl$_1$Ph(I$_2$) (193 mg, 0.235 mmol), Feist's ester (61 mg, 0.36 mmol, 1.5 equiv), PPr$_3$ (57 mg, 0.36 mmol, 1.5 equiv). Toluene was used as solvent. No starting material remained after 22 h at 80 °C. Yield of brown product after workup: 176 mg (88%). For NMR spectra (including the assigned $^1$H NMR spectrum), see Figure S6 and Figure S7.

$^1$H NMR (CD$_2$Cl$_2$, 500 MHz): δ 7.79 (d, $^3$J$_{HH}$ = 7.5 Hz, 2H, CH of C$_1$Ph Ar or Ph), 7.34 (t, $^3$J$_{HH}$ = 7.9 Hz, 2H, CH of C$_1$Ph Ar or Ph), 7.18 (s, 2H, CH of C$_1$Ph Ar or Ph), 7.13 (d, $^3$J$_{HH}$ = 8.1 Hz, 1H, CH of C$_1$Ph Ar or Ph), 7.05 (t, $^3$J$_{HH}$ = 7.6 Hz, 1H, p-CH of C$_1$Ph Ar or Ph), 3.64 (dq, $^3$J$_{HH}$ = 15.0, 7.4 Hz, 1H, CH$_2$ of C$_1$Ph Ar), 3.45 (dq, $^3$J$_{HH}$ = 14.6, 7.3 Hz, 1H, CH$_2$ of C$_1$Ph Ar), 3.08 (m, 3H, CH$_3$ of PPr$_3$), 2.88 (d, $^3$J$_{HH}$ = 12.3 Hz, 1H, backbone CH$_2$ of C$_1$Ph), 2.73 (dq, $^3$J$_{HH}$ = 14.7, 7.3 Hz, 2H, CH$_2$ of C$_1$Ph Ar), 2.42 (s, 3H, backbone CH$_3$ of C$_1$Ph), 1.69 (d, $^3$J$_{HH}$ = 12.3 Hz, 1H, backbone CH$_2$ of C$_1$Ph), 1.39 (t, $^3$J$_{HH}$ = 7.4 Hz, 3H, CH$_3$ of C$_1$Ph Ar), 1.34 (t, $^3$J$_{HH}$ = 7.4 Hz, 3H, CH$_3$ of C$_1$Ph Ar), 1.28 (dd, $^3$J$_{HH}$ = 13.4, 7.3 Hz, 6H, CH$_3$ of PPr$_3$ and backbone CH$_3$ of C$_1$Ph, overlapping), 1.18 – 1.11 (m, 15H, CH$_3$ of PPr$_3$).

$^{13}$C {$^1$H} NMR (CD$_2$Cl$_2$, 125 MHz): δ 269.6, 269.0, 147.7, 144.1, 142.1, 139.5, 129.4, 129.2, 127.0, 126.8, 126.6, 79.0, 67.4, 67.4, 36.2, 28.0, 27.0, 25.8, 25.5, 25.4, 20.4, 20.3, 15.8, 15.0. MALDI-TOF MS (pyrene matrix), $m/z$: [Carbide-C$_3$Ph–C$_1$Ph/Pr$_3]$+ 517.109 (calc’d for C$_{29}$H$_{41}$ClNPrRu: 517.171).

S1.1.2. Synthesis of Piers Complexes [RuX$_2$(CAAC)(=CHP(Pr)$_3$)]OTf

Representative Procedure for Synthesis of [RuCl$_2$(C$_1$Ph)(=CHP(Pr)$_3$)]OTf, PC$_1$Ph. The Piers complexes were prepared according to the method reported for C$_1$Ph (Scheme S2; reproduced here for convenience). To a stirred yellow solution of Carbide-C$_1$Ph (117 mg, 0.166 mmol) in 4 mL CH$_2$Cl$_2$ was added a solution of HOTf (27 mg, 0.18 mmol, 1.1 equiv) in 1.5 mL CH$_2$Cl$_2$. The solution immediately turned dark-green. The mixture was stirred for 45 min at RT, after which the solvent was removed under vacuum. A fine green precipitate was obtained by adding n-hexane (2 mL) and stirring vigorously. This material was filtered off, washed with n-hexane (2 mL) and dried. Yield: 127 mg (89%). The $^1$H NMR data in CDCl$_3$ agree with values reported. Key alkylidene signal: δ 18.67 (d, $^2$J$_{HP}$ = 35.3 Hz, 1H, Ru=CH).
Scheme S2. Synthesis of Piers Complexes.

**Synthesis of PC2Me.** As above, with Carbide-C2Me (70 mg, 0.116 mmol) and HOTf (18 mg, 0.12 mmol, 1 equiv). Product obtained as a light-green solid. Yield after workup: 75 mg (80%). For NMR spectra (including the assigned 1H spectrum), see Figure S8 and Figure S9.

1H NMR (CDCl3, 500 MHz): δ 18.12 (d, 2JHH = 41.9 Hz, 1H, Ru=C(H)), 7.60 – 7.49 (m, 2H, m-CH of C2Me Ar), 7.34 (d, 3JHH = 7.3 Hz, 1H, p-CH of C2Me Ar), 3.20 – 3.11 (m, 3H, CH of Ph), 3.10–3.05 (m, 1H, CH of C2Me iPr), 2.30 (d, 2JHH = 1.6 Hz, 2H, backbone CH2 of C2Me), 2.25 (s, 3H, CH3 of C2Me), 1.84 (s, 3H, CH3 of C2Me), 1.46 (s, 3H, CH3 of C2Me), 1.39 – 1.34 (m, 6H, CH3 of C2Me and CH3 of Ph, overlapping), 1.30 (m, 5H, CH3 of Ph), 1.22 (m, 6H, CH3 of Ph), 0.87 (d, 3JHH = 6.6 Hz, 3H, CH3 of Ph). 

13C(1H) NMR (CDCl3, 125 MHz): δ 254.6, 232.6, 148.4, 136.9, 130.3, 130.2, 126.6, 81.1, 51.9, 29.6, 29.3, 29.0, 28.7, 26.6, 24.3, 23.9, 23.0, 18.3, 18.2, 14.3. MALDI-TOF MS (pyrene matrix), m/z: [PC2Me–Cl,H]+ 715.171 (calc’d for C29H48Cl3NO3PRuS: 715.178).

**Synthesis of PC3Ph.** As above, with Carbide-C3Ph (70 mg, 0.116 mmol) and HOTf (18 mg, 0.12 mmol, 1 equiv). Product obtained as a green solid. Yield after workup: 113 mg (82%). For NMR spectra (including the assigned 1H spectrum), see Figure S10 and Figure S11.

1H NMR (CDCl3, 500 MHz): δ 18.74 (d, 2JHH = 34.0 Hz, 1H, Ru=C(H)), 7.79 (s, 1H, m-CH of C3Ph Mes), 7.53 (t, 3JHH = 7.7 Hz, 2H, m-CH of C3Ph Ph), 7.38 (t, 3JHH = 7.5 Hz, 1H, p-CH of C3Ph Ph), 7.26 (s, 1H, m-CH of C3Ph Mes), 7.12 (d, 3JHH = 10.0 Hz, 2H, o-CH of C3Ph Ph). 2.94 (m, 3H, CH of Ph), 2.77 (s, 1H, backbone CH2 of C3Ph), 2.49 (d, 2JHH = 13.3 Hz, 1H, backbone CH2 of C3Ph), 2.38 (m, 9H, CH3 of C3Ph), 2.03 (s, 3H, CH3 of C3Ph), 1.50 (s, 3H, CH3 of C3Ph), 1.39 (s, 3H, CH3 of C3Ph), 1.11 (m, 18H, CH3 of Ph). 13C(1H) NMR (CDCl3, 125 MHz): δ 241.9, 140.5, 137.9, 136.5, 134.7, 131.4, 131.2, 130.6, 128.6, 126.3, 81.2, 64.0, 31.7, 30.5, 29.6, 28.1, 22.8, 22.1, 21.8, 21.1, 17.9, 17.8, 17.7, 14.3. MALDI-TOF MS (pyrene matrix), m/z: [PC3Ph–Cl, OTf]+ 615.201 (calc’d for C32H49ClNPRu: 615.233).

**Synthesis of PC1Ph(I2).** As above, with minor modifications: Carbide-C1Ph(I2) (174 mg, 0.205 mmol) and HOTf (34 mg, 0.23 mmol, 1.1 equiv). CaH6 was chosen as the solvent to avoid possible halide exchange during reaction, which was stirred for 2.5 h at RT. Product obtained as an olive-green solid. Yield after workup: 179 mg (87%). To limit the possibility of halide exchange, NMR analysis was carried out in CD2Cl2. For NMR spectra (including the assigned 1H spectrum), see Figure S12 and Figure S13.

1H NMR (CD2Cl2, 500 MHz): δ 16.66 (d, 2JHH = 30.1 Hz, 1H, Ru=C(H)), 8.71 (s br, 2H, CH of C1Ph Ar or Ph), 8.10 (m br, 3H, CH of C1Ph Ar or Ph), 8.03 – 7.88 (m br, 3H, CH of C1Ph Ar or Ph), 3.70 (s br, 1H, backbone CH of C1Ph), 3.44 (m, 3H, CH of Ph), 3.31 – 3.23 (s br, 1H, backbone CH of C1Ph), 3.17 (m br, 1H, CH2 of C1Ph Ar), 3.07 (m br, 1H, CH2 of C1Ph Ar), 2.95 (m, 2H, CH2 of C1Ph Ar), 2.09
(d br, $^{3}J_{HH} = 5.7$ Hz 3H, CH$_3$ of C$_{1}^{\text{Ph}}$ Ar), 1.92 (m, 7H, CH$_3$ of C$_{1}^{\text{Ph}}$ Ar and backbone, overlapping), 1.75 (m, 6H, CH$_3$ of C$_{1}^{\text{Ph}}$ backbone), 1.63 (m, 19H, CH$_3$ of P$_3$iPr$_3$)$_{3}$. $^{13}$C{[H]} NMR (CD$_2$Cl$_2$, 125 MHz): $\delta$ 248.9, 146.6, 142.8, 142.1, 137.6, 132.7, 131.5, 130.6, 128.4, 124.3, 81.1, 63.4, 33.3, 32.1, 31.4, 28.4, 28.0, 25.5, 21.9, 21.6, 19.9, 19.6, 19.0, 18.8, 18.2, 17.2, 17.0, 14.3, 14.1. MALDI-TOF MS (pyrene matrix), m/z: [PC$_{1}^{\text{Ph}}$(I)]$^{+}$ 721.130 (calc’d for C$_{33}$H$_{51}$INPRu: 721.184).

S1.1.3. Synthesis of Pyridine Adducts RuX$_2$(L)(py)$_n$(=CH$_2$)$_1$

The pyridine adducts were prepared by minor modification of the method reported for 1-C$_{1}^{\text{Ph}}$ and 1-H$_{2}$IMes (Scheme S3).$^{7,9}$ A representative procedure is provided for 1-C$_{1}^{\text{Ph}}$.

Scheme S3. Synthesis of Pyridine Adducts.

Representative Procedure for Synthesis of RuCl$_2$(C$_{1}^{\text{Ph}}$)(py)(=CH$_2$)$_1$, 1-C$_{1}^{\text{Ph}}$. In a 10 mL Schlenk flask, a dark-green solution of the PC$_{1}^{\text{Ph}}$ (100 mg, 0.117 mmol) in 2 mL CH$_2$Cl$_2$ was frozen in N$_2$(l). The sample was freeze-pump-thaw degassed 3x, and thawed under 1 atm ethylene at $-45^\circ$C (MeCN–dry ice bath). The resulting dark red solution was stirred for 15 min, briefly exposed to vacuum to remove ethylene, then stirred under N$_2$. A solution of pyridine (18.7 $\mu$L, 0.231 mmol, 2 equiv) in 500 $\mu$L n-hexane, chilled in an EtOH-N$_2$(l) cold bath ($-110$ to $-80$ °C), was then added via syringe as a slow dribble down the flask wall (ca. 10 sec). The solution rapidly turned dark green, then brown-yellow. The mixture was stirred for a further 10 min. Cold n-hexane (4 mL; $-110$ to $-80$ °C) was then added using a cannula chilled with dry ice. The mixture was stirred for 10 min to precipitate the brown phosphonium salt [H$_2$C=CHP$_3$iPr$_3$]OTf, filtered cold, and the orange filtrate was immediately stripped to dryness at $-45$ °C to afford yellow 1-C$_{1}^{\text{Ph}}$. The flask containing solid 1-C$_{1}^{\text{Ph}}$ was transferred to a $-35$ °C freezer inside a glovebox until use. Product masses were not measured, given their high static charge, and the high relative error inherent in weighing small amounts of material in even a small Schlenk flask on a balance in the glovebox. Instead, Ru concentrations for the decomposition experiments were quantified based on known concentrations of injected internal standard: see next section.

NMR data for 1-C$_{1}^{\text{Ph}}$ and 1-H$_{2}$IMes agree with values reported.$^{7}$ For NMR spectra, see Figure S14, Figure S15, Figure S16, Figure S17, and Figure S18. Key [Ru]=CH$_2$ signals: $^1$H NMR (CDCl$_3$, 500 MHz, $-40$ °C): 1-C$_{1}^{\text{Ph}}$, $\delta$ 18.35 ppm; 1-H$_{2}$IMes, $\delta$ 18.76 ppm; 1-C$_{1}^{\text{Me}}$, $\delta$ 17.98 ppm; 1-C$_{3}^{\text{Ph}}$, $\delta$ 18.31 ppm; 1-C$_{1}^{\text{Ph}}$(I)$_2$, $\delta$ 16.73 ppm; 1-C$_{2}^{\text{Me}}$, 18.22 ppm (not isolated, generated in situ).

S1.1.4. Bimolecular Coupling of Methylidene Complex 1

The procedure for the coupling reaction is summarized in Scheme S4. In our original study, the objective was quantitation of ethylene evolved from 1-C$_{1}^{\text{Ph}}$, and considerations of purity were minor.$^{7}$ The solid methylidene complex 1-C$_{1}^{\text{Ph}}$ was thus not purified to remove the phosphonium salt [H$_2$C=CHP$_3$iPr$_3$]OTf. In the present kinetics study, removal of phosphonium salt as described above yielded a powder with a high static charge, which could not be weighed: moreover, the CAAC
complexes were obtained in low yields owing to their much faster decomposition. Samples were therefore made up by adding a known volume of cold CDCl₃ to the Schlenk flask to dissolve the complex, and transferring the solution to an NMR tube containing a known volume of a stock solution of DMT. To protect against warming, the IS stock solution, NMR tubes, pipettes, CDCl₃ and sand-bath were kept in the glovebox freezer (−35 °C) for at least 12 h prior to use. To improve accuracy in NMR integrations, the recycle delay (d1) was raised to 0.1 sec from 0.01 sec.

\[
\begin{align*}
\text{Scheme S4.} & \quad \text{Methylidene Coupling.} \\
\end{align*}
\]

**Representative Procedure for Bimolecular Coupling of 1-C1\text{Ph}:** The Schlenk flask containing solid 1-C1\text{Ph} was removed from the glovebox freezer and bedded in a cold sand-bath (chilled to −35 °C by storing in the freezer overnight). To a J-Young NMR tube also bedded in the sand-bath was added cold DMT (20.0 μL of a stock solution of 10 mg DMT in 1 mL CDCl₃; 1.03 μmol); NMR integration standard (IS). Solid 1-C1\text{Ph} was dissolved in cold CDCl₃ (0.6 mL) and transferred to the NMR tube via a chilled pipette. The NMR tube was sealed, transported to the NMR facility in a dry ice-MeCN bath (−45 °C), then quickly shaken and inserted into an NMR probe precooled to −40 °C. The initial integration ratio of 1-C1\text{Ph} vs IS was measured, after which the NMR probe was warmed to −10 °C to effect liberation of four-coordinate 2-C1\text{Ph}. After an initial 15 min period for thermal equilibration, loss of the [Ru]=CH₂ NMR signal was measured over time: see Figure 1 in the main text.

The same procedure was carried out for 1-C1\text{Me}, 1-C3\text{Ph} and 1-C1\text{Ph}(I₂). For H₂IMEs complex 1-H₂IMEs, a higher volume of 1.2 mL CDCl₃ was used to reduce the headspace, to ensure that any propenes formed via β-H elimination could be detected (none were observed).

**Sample calculation: initial Ru concentration of 2-C1\text{Ph}, based on known concentration of DMT.**

\[
\text{Concentration}_{\text{DMT}} = \frac{0.010 \,(g)}{0.001 \,(L)} \cdot \frac{1}{194.18} \,(mol) \,(g) = 0.0515 \,(M) \\
\text{Equation S1}
\]

For a volume of 20 μL injected into the NMR tube:

\[
n_{\text{DMT}} = 0.0515 \,(mol) \,(L) \cdot \frac{1}{10^6} \,(μL) \cdot 20 \,(μL) = 1.03 \cdot 10^{-6} \,(mol) \\
\text{Equation S2}
\]

Ratio of Ru=CH₂ protons : DMT methyl protons = 2 H : 6 H

Integration of Ru=CH₂ signal : DMT methyl protons = 1.21 : 98.79

\[
\frac{n_{\text{Ru}}}{n_{\text{DMT}}} = \frac{\text{Integration}_{\text{Ru}}}{\text{Integration}_{\text{DMT}}} \cdot H \text{ ratio} \\
\text{Equation S3}
\]

\[
n_{\text{Ru}} = \frac{1.21}{98.79} \cdot 1.03 \cdot 10^{-6} \,(mol) \cdot 3 = 3.78 \cdot 10^{-8} \,(mol) \\
\text{Equation S4}
\]

\[
\text{Initial Ru concentration} = \frac{n_{\text{Ru}}}{V_{\text{total}}} = \frac{3.78 \cdot 10^{-8} \,(mol)}{0.00062 \,(L)} = 6.10 \cdot 10^{-5} \,(M) \\
\text{Equation S5}
\]
Figure S1. Second-order rate data for BMC reactions at –10 °C. (a) Rate plots with equations and R² for each run. (b) Tabulated numeric values for k_{obs} obtained in replicate experiments. The k_{rel} value shown is the average between the two trials. The trend in k_{rel} is consistent, but the absolute values of k_{obs} should be treated with caution, as the relative errors range from 5% (1-C1Ph) to 24% (1-C1Me).
S2. NMR Spectra

S2.1. Carbide Complexes

Figure S2. $^1$H NMR spectrum (CDCl$_3$, 500 MHz) of Carbide-C$^2$Me.

Figure S3. $^{13}$C($^1$H) NMR spectrum (CDCl$_3$, 125 MHz) of Carbide-C$^2$Me. Inset shows the carbide carbon.
Figure S4. $^1$H NMR spectrum (CDCl$_3$, 500 MHz) of Carbide-C$_3^{\text{Ph}}$.

Figure S5. $^{13}$C($^1$H) NMR spectrum (CDCl$_3$, 125 MHz) of Carbide-C$_3^{\text{Ph}}$. Inset shows carbide carbon.
Figure S6. $^1$H NMR spectrum (C₆D₆, 500 MHz) of Carbide-C1$^{Ph}$I$_2$.

Figure S7. $^{13}$C[¹H] NMR spectrum (C₆D₆, 125 MHz) of Carbide-C1$^{Ph}$I$_2$. Carbide signal not observed.
S2.2. Piers Catalysts

Figure S8. $^1$H NMR spectrum (CDCl$_3$, 500 MHz) of PC$_2$Me. The small downfield signals in the alkylidene region are assigned to a rotamer, as seen for other CAAC complexes.$^{10}$

Figure S9. $^{13}$C-$^1$H NMR spectrum (CDCl$_3$, 125 MHz) of PC$_2$Me.
Figure S10. $^1$H NMR spectrum (CDCl$_3$, 500 MHz) of PC$^3_{\text{Ph}}$.

Figure S11. $^{13}$C{$^1$H} NMR spectrum (CDCl$_3$, 125 MHz) of PC$^3_{\text{Ph}}$. 
Figure S12. $^1\text{H}$ NMR spectrum (CD$_2$Cl$_2$, 500 MHz) of PC$_1$Ph(I$_2$).

Figure S13. $^{13}\text{C}(^1\text{H})$ NMR spectrum (CD$_2$Cl$_2$, 125 MHz) of PC$_1$Ph(I$_2$).
S2.3. Pyridine-stabilized methyldiene complexes

Figure S14. $^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 1-C$^1$Me at –40 °C. The downfield signal in the alkylidene region is assigned to a rotamer, as seen for other CAAC complexes. The instability of the complex over 7 h at –40 °C hindered acquisition of a $^{13}$C{$^1$H} NMR spectrum.

Figure S15. $^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 1-C$^3$Ph at –40 °C. The instability of the complex over 7 h at –40 °C hindered acquisition of a $^{13}$C{$^1$H} NMR spectrum.
Figure S16. $^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 1-C1$^{\text{Ph}}$(I$_2$) at $-40 \, ^\circ$C.

Figure S17. $^{13}$C($^1$H) NMR spectrum (CDCl$_3$, 125 MHz) of 1-C1$^{\text{Ph}}$(I$_2$) at $-40 \, ^\circ$C.
Figure S18. $^1$H NMR spectrum (CDCl$_3$, 500 MHz) showing in situ generation of \( \text{1-C}_2^\text{Me} \) at –40 °C.
S3. Computational Results and Discussion

S3.1. Mechanism of Bimolecular Coupling of Ru Methylidene

In our prior communication, we briefly outlined key inferences from a computational analysis of the mechanism for bimolecular coupling: that is, interaction of two Ru-methylidene species to form a bond between the methylidene carbons, ultimately releasing ethylene. Here we present fuller details of this pathway (Figure S19, Figure S21, and Figure S22). In the discussion of the computational results, the py-stabilized methylidene species 1-H$_2$IMes is represented by model structure M1. The latter is the reference point against which relative free energies are calculated at 263 K (the temperature at which bimolecular decomposition was explored experimentally). M1 is presumed to release pyridine to form methylidene species M2. These 14-electron species may increase their electronic saturation by reacting with each other to form chloride-bridged ruthenium dimers, the nature of which is discussed below.

Figure S19. Molecular models related to formation and dimerization of M2. Free energies (kcal/mol, at 1 mM standard-state concentration) are reported relative to M1.

Whereas the methylidene unit is largely coplanar with RuCl$_2$ in M1, it is essentially orthogonal to this plane in the most stable conformer of 14-electron M2. Assuming a mechanism that is dissociative in py, this conformer may dimerize with minimal conformational and geometrical changes to form M3. We
refer to dimers with this M2-like methyldiene conformation as dimer1 (see Scheme 3 in the main text). Although numerous possible mechanisms exist for dimerization, including pathways with involvement of solvent, the minimal geometrical adaption required to form dimer1 suggests that this reaction requires negligible enthalpic activation, if any. Rather than screening a vast number of possibilities, if any (see Computational Methods) to attempts to instead single and M3

In addition to corresponding explorations of the potential energy surface between M3 and M8, the transition state for rotation of one Ru=CH2 unit. Following the intrinsic reaction coordinate of M8 along either direction led to the same basin of M7. In conclusion, all these explorations of the potential energy surface between M6 and M7 suggest that no minimum exists that corresponds to a structure with a single methyldiene twisted relative to its geometry in M3.

Whereas M3 exhibits the syn-methyldiene disposition of the H2C=Ru—Ru=CH2 moieties required for C–C coupling, bond formation also requires rotation of both methyldiene units by ca. 90°, to become essentially coplanar with their respective RuCl2 planes, as in M1.9 We refer to this structure as dimer2 below and in the main text. Within the H2IMes system, M7 is a model for dimer2 and already has a C–C bond distance (3.39 Å) more than 1 Å shorter than that of M3 (4.54 Å). M7 is readily accessed from M3 via transition state M6. The imaginary mode of M6 is dominated by rotation of a single Ru=CH2 bond, whereas the second Ru=CH2 bond twists later along the minimum-energy pathway connecting M6 and M7. On the latter pathway, the potential energy surface surrounding the geometry in which only a single Ru=CH2 twist has occurred is quite flat. All attempts to locate a minimum in this flat region instead converged to M7. Similarly, rotating the Ru=CH2 bond in M7 to move backwards toward M6 led to M8, the transition state for rotation of one Ru=CH2 unit. Following the intrinsic reaction coordinate of M8 along either direction led to the same basin of M7. In conclusion, all these explorations of the potential energy surface between M6 and M7 suggest that no minimum exists that corresponds to a structure with a single methyldiene twisted relative to its geometry in M3.

In addition to M3 and M7, we considered the singly-Cl bridged intermediate M4. This intermediate could in principle enable formation of a doubly-bridged dimer. However, its high energy excludes its involvement in the dimerization. Similarly, although known M5 is the most stable methyldiene dimer, the methyldiene carbon atoms are too far apart to engage in C–C bond formation. Moreover, its Ru=C bond conformations correspond to those in M1, and are thus incompatible with a dimerization pathway that requires minimal geometric adaptation by monomeric M2. M7, although more stable than M3, 

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**Figure S20.** Selected geometrical parameters of the optimized geometries of M2, M3 (dimer1), and M7 (dimer2). Bond lengths are in Å and bond angle in degrees. Color coding: Ru (pink), Cl (green), C (grey), N (blue), H (white).
would also require considerable conformational adaption to form directly from M2. All these computational results, and the experimentally-observed evolution of ethylene (which implies an M3–M5 equilibrium if M5 is the primarily formed dimer), suggest that M3, formed by dimerization of M2, rearranges to M7, which undergoes C–C bond formation as described below.

From dimer M7, C–C bond formation commences with geometric distortion (via transition state M9) to bring the π orbital of one methylidene into the metal coordination sphere of the other Ru=CH2 entity. In the resulting shallow minimum M10, one methylidene serves as an unusual dative ligand for the other Ru center. Close in energy is transition state M11, in which the bonding interaction between the two methylidene carbons first emerges. We previously described the orbital interaction involved.9 Here we point out that the barrier to C–C bond formation from M7 via M11 is lower than that for sequential rotation of the Ru=CH2 bonds to transform M7 into M3 (ca. 9 vs 12 kcal/mol, respectively), and considerably lower than the 19 kcal/mol overall barrier from pyridine adduct M1 to M7 via M3 (that is, the variational transition state for dimerization of M2). We conclude that the rate-determining step in this pathway is dimerization, rather than formation of the C–C bond between the two methylidene units.

The first intermediate following C–C bond formation is M12, in which the carbon atoms are singly-bonded, as judged from the 1.55 Å C–C distance and the C-C-H bond angles (107°, 112°, 113°, 113°). The geometry suggests interaction of one CH2 moiety with both Ru centers, while the other CH2 moiety is bonded to only one Ru atom. The Ru atoms are only 2.5 Å apart, suggesting a metal–metal bond. Whereas electronic rearrangements leading to a spin-triplet pathway are treated below, the spin-singlet reaction pathway involves facile sliding of the C2Me4H4 fragment to form M14 via transition state M13. M14 is best interpreted as containing an ethylene ligand (C–C 1.42 Å) η2-coordinated to one Ru center and with a C–H agostic interaction to the second Ru atom. Breaking this agostic interaction is unexpectedly demanding, with a barrier of ca. 10 kcal/mol from M14 via M15, but is facilitated by η2-coordination of a H2IMes mesityl ring trans to the agostic site. Mesityl binding, although transient, contributes to a rather substantial change in configuration at one Ru center, accounting for the significant energy barrier associated with M15. In the resulting structure M16, a conventional η2-bound ethylene ligand (C–C 1.40 Å) is coordinated to a single Ru atom. Alternative structures bearing an ethylene ligand bound to a single Ru center (see M18, and M19) are higher in energy than M16, although not prohibitively so.

Finally, we modelled hypothetical spin-singlet species resulting from dissociation of ethylene. The pair of electron-deficient Ru(II) centers is likely to coordinate any electron-donating ligand, in particular the pyridine released earlier from the starting material. Moreover, especially when pyridine is not present in sufficient amounts, the Ru(II) species are expected to engage in aggregation to form Ru nanoparticles.13
Figure S21. Reaction pathway for formation of ethylene from methylidenes along the spin-singlet surface. Free energy (kcal/mol, at 1 mM standard-state concentration) relative to M1.

As indicated above, M12 may undergo electronic rearrangement to reach its spin-triplet counterpart \(^3\text{M23}\) (the superscript indicates spin multiplicity) via the minimum energy crossing point (MECP) M22. In \(^3\text{M23}\), the two Ru centers are bridged by an ethylene moiety, in which the former methylidene carbon atoms again form a single C–C bond (1.51 Å). This structure is the lowest-energy species in the present reaction network and is thus an important and well-populated intermediate in the bimolecular decomposition pathway. Moreover, the estimated energy barrier via MECP M22 is comparable to, or lower than, the corresponding barrier (10.4 kcal/mol, via M15) on the spin-singlet surface.
Figure S22. Reaction pathway for formation of ethylene along the spin-triplet surface. Free energy (kcal/mol, at 1 mM standard-state concentration) relative to M1. Superscript prefixes indicate spin multiplicities higher than unity.

Given the stability of $^3$M23, we evaluated possible reactions on the spin-triplet surface starting from this intermediate. The high-spin analogue of transition state M11, in which C–C bond formation starts, was ruled out on the basis of the prohibitively high energy for the relevant transition state $^3$M24. The least energetically demanding step from $^3$M23 led to a C–H agostic interaction via transition state $^3$M25. No further energetically viable steps could be identified for evolution of the resulting species $^3$M26. Instead, we found, with $^3$M27, a step analogous to the C$_2$H$_4$ sliding observed at M13 on the spin-singlet surface. However, in contrast to the spin-singlet surface, the minimum following $^3$M27, i.e., $^3$M28, does not involve C–H agostic interaction. Thus, $^3$M28 can be viewed as the spin-triplet analogue of M16. Although we cannot exclude the existence of a MECP between M16 and $^3$M28, the only related MECP
that could be found (i.e., M31) connects M18 and 3M30. The latter intermediates are conformers of M16 and 3M28, respectively, which differ by rotation about the Ru–ethylene bond. Notably, this ethylene twist permits access to the most stable ethylene-bound species on the spin-triplet surface, i.e., 3M33, without crossing any substantial energy barrier.

Finally, as with the spin-singlet surface, we considered the relative energy of ethylene-free intermediates of high spin. However, the energies of both the triplet 3M34 and quintet 5M35 are significantly higher than M20, their simplest counterpart on the spin-singlet surface. Ethylene dissociation may thus occur either completely on the singlet surface, or may terminate on the spin-singlet surface after undergoing spin inversion during ethylene dissociation.

The most significant barrier along the spin-triplet path is associated with rupture of the Ru–CH2CH2–Ru bridge in 3M23 via 3M27 (16 kcal/mol). The ensuing release of ethylene may occur from the resulting 3M28 or by rearrangement via 3M29 to give isomer 3M33 (barrier ca. 17 kcal/mol from 3M23). Either barrier is lower than the variational estimate for dimerization of M2 (19 kcal/mol vs M1). Similarly, the most demanding step after formation of the C–C bond on the spin-singlet surface is rearrangement of M14 to yield M16 (<12 kcal/mol from M14), which could already release ethylene. Overall, the barriers along both the spin-singlet and spin-triplet pathways of C–C bond formation are lower than the barrier estimated for dimerization of M2. Thus, irrespective of whether the ethylene-generating part of the bimolecular decomposition involves spin-singlet or spin-triplet species, the initial dimerization is predicted to be rate limiting.

S3.2. H2IMes vs C3Ph

To limit the computational demand arising from the asymmetry of C3Ph, which also involves a chiral center, we assumed that the general mechanistic features established for the H2IMes catalyst would remain valid also for C3Ph. Therefore, only the stationary points and elementary steps found to influence the decomposition rate of the H2IMes-coordinated catalyst were investigated for the C3Ph-coordinated catalyst (Figure S23 and Table S1).

First, the calculations predicted that the two rotamers of the catalyst precursor (M36 and M37, in which the CAAC N-Ar moiety is syn or anti relative to the methylidene ligand, respectively) have similar solution stability. M36 is marginally more stable, by 0.4 kcal/mol. Each rotamer exists as a racemic mixture.

Dissociation of pyridine from M36 and M37 leads to the 14-electron methylidene complexes (M39 and M38, respectively). These are 6.2 kcal/mol and 5.7 kcal/mol less stable than M36, the most stable precursor rotamer. Loss of py is thus less costly with C3Ph as ligand (6.2 or 5.7 kcal/mol) than with H2IMes (7.4 kcal/mol). Opposite orders of stability are found for the rotamers of the 14-electron methylidene complex with respect to the catalyst precursor: The most stable rotamer for the precursor, M36, leads to the least stable 14-electron rotamer M39. The rotational barrier (via M40) between M38 and M39 is 15.9 kcal/mol vs M36, uphill from M39 by only 9.7 kcal/mol. Given the very low concentration of the 14-electron species, equilibration of the rotamers M38 and M39 is likely to precede dimerization. The less stable C3Ph rotamer in the precursor is thus probably the most abundant in the dimer, meaning that both rotamers are important for bimolecular decomposition.

For the H2IMes complex, pyridine dissociation is accompanied by methylidene rotation. Whereas the methylidene unit is largely coplanar with RuCl2 in M36 and M37, it is essentially orthogonal to the RuCl2 plane in the four 14-electron species M38 (R’ and S’) and M39 (R and S); see Figure S23 for labelling). As seen above for the H2IMes catalyst (Figure S19), coupling of 14-electron methylidene
species may lead to a number of different dimers. For $\text{C3}\text{Ph}^\text{H}$, we investigated only those dimers, labeled $\text{M3 (dimer1)}$ and $\text{M7 (dimer2)}$ for the $\text{H}_2\text{IMes}$ catalyst, that are located along the C–C coupling pathway (Figure S23). The methyldiene orientation of the 14-electron monomer is retained in $\text{dimer1}$, and dimerization is associated with minimal geometrical adaption. Assuming (as for the $\text{H}_2\text{IMes}$ catalyst) that formation of this dimer is limited only by monomer diffusion in the solvent (see Section S4.4.1 The Barrier of Diffusion-Controlled Reactions), the barrier to dimerization is estimated to be 2–3 kcal/mol lower for the $\text{C3}\text{Ph}^\text{H}$ species than its $\text{H}_2\text{IMes}$ analogue.

![Diagram of dimerization](image)

Labeling rule for dimeric species: $\text{L}_\text{left}\text{L}_\text{right}\text{L}_\text{Ru-left}\text{L}_\text{Ru-right}$ where $\text{L}_\text{left}$ is the label defining the left-hand side monomer, $\text{L}_\text{right}$ is the label defining the right-hand side monomer, $\text{L}_\text{Ru-left}$ is the configuration of the Ru atom on the left-hand side, and $\text{L}_\text{Ru-right}$ is the configuration of the Ru atom on the right-hand side. $\text{L}_\text{Ru-left}$ and $\text{L}_\text{Ru-right}$ are defined in Figure S24. (e.g., RS’AA is the dimer resulting from having monomer R on the left-hand side, S’ on the right-hand side, and both Ru atoms with configuration corresponding to chiral symbol A)

**Figure S23.** Stationary points and variational transition states along the bimolecular decomposition pathway of $\text{RuCl}_2(\text{C3}\text{Ph})(\text{py})(=\text{CH}_2)$. Free energy (kcal/mol, at 1 mM standard-state concentration) relative to $\text{M36}$. 

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Figure S24. Definition of stereochemical descriptors of Ru atom in dimer1, dimer2 and TScc according to IUPAC recommendations.\textsuperscript{14} (a) Determination of chiral symbols for the square pyramidal Ru centers of dimer1 and dimer2. The square pyramid is observed from the apical position toward the Ru atom, and Cahn-Ingold-Prelog priority rules (integers 1–4 represent priority 1 > 2 > 3 > 4) are applied to the substituents in the plane to determine whether the clockwise (C) or anticlockwise (A) order has highest priority. (b) Set of possible stereoisomers at the Ru centers for dimer1 and dimer2. With achiral L, (A,C) and (C,A) are symmetric. (c) Determination of chiral symbols for the Ru centers in TScc. While one center is treated as a square pyramidal center (see above), the other center is approximately octahedral. The chiral symbol is defined by observing the complex along the axis involving the ligand with priority 1 (i.e., a bridging Cl) and the trans ligand with lowest priority (\(=\text{CH}_2\)). Clockwise (C) or anticlockwise (A) sequence of the ligands in the perpendicular plane is considered according to Cahn-Ingold-Prelog priority rules. (d) Enantiomeric core structures for TScc.

Dimerization of any pair of the four monomers R, R’, S, and S’ (nomenclature of monomers defined in Figure S23) into any of the four possible alternative stereochemistries AA, AC, CA, CC (configuration of Ru atoms in dimeric species defined in Figure S24) gives rise to 64 possible combinations. In 32 of
these combinations (involving AC and CA), the Ru=CH₂ moieties are mutually anti, as in M₅, and these structures are not suitable for direct C–C bond formation. The remaining 32 consist of 16 pairs of enantiomers, six of which are redundant due to the symmetry of the dimer, leaving 10 diastereoisomeric dimers to model (see Table S1). Whereas two of these combinations (S’S’AA and RSAA, each with its degenerate stereoisomers (see Table S1) converge directly to dimer2, two (SS’AA and R’SAA) lead to a dimer with features intermediate between dimer1 and dimer2 (see Table S1 for details). The free energies of the six minima clearly corresponding to dimer1 span over 5.8 kcal/mol (from 7.1 to 12.7 kcal/mol vs M₃₆), with four being more stable than dimer1 of the H₂IMes catalyst (M₃, at 12.2 kcal/mol vs M₁). Thus, with C₃Ph as ligand, some of the dimer1 isomers form more rapidly, and are thermodynamically more stable, than those of H₂IMes.

**Figure S25.** Selected geometrical parameters of the optimized geometries of M₃₈, M₃₉, and the corresponding dimerization products dimer1 and dimer2. Bond lengths in Å, bond angles in degrees. Color coding: Ru (pink), Cl (green), C (grey), N (blue), H (white).
Nevertheless, dimer1 is not the most stable dimer and, as for the H₂IMes catalyst, relaxation of dimer1 leads to the more stable dimer2 in which both methylidene ligands are essentially coplanar with RuCl₂. Except for the high-energy, symmetric combinations of R and S monomers (RR and SS), relaxation to dimer2 leads to significant shortening of the distance between the two methylidene units. The energies of the dimer2 complexes span 6.3 kcal/mol (from −1.9 to 4.4 kcal/mol, Table S1). With the exception of M49 (enantiomers RRAA and SSAC), all are higher in energy relative to M36 than the corresponding H₂IMes dimer M7, relative to M1 (0.2 kcal/mol). Still, in all cases dimer2 is more stable than dimer1 and has the appropriate methylidene conformation for C–C coupling via transition state TScc.

In TScc the two methylidene ligands have very different chemical environments, with one methylidene being weakly coordinated to the second ruthenium center (Figure S23). Therefore, whereas some stereochemical combinations were symmetrically redundant for dimer1 and dimer2 (e.g., RR’AA = R’RAA and RSAA = SRAA), these combinations become independent stereoisomers in TScc (e.g., RR’AA ≠ R’RAA and RSAA ≠ SRAA). In total, 16 diastereoisomeric alternatives exist for TScc (Table S1), spanning 8.6 kcal/mol in free energy (from 7.5 to 16.1 kcal/mol vs M36). For most of these isomers, C–C coupling is thus more costly than for the H₂IMes catalyst (with M11 at 9.4 kcal/mol vs M1). However, by grouping all the alternatives for each symmetrically equivalent pair of monomers we identify six groups (I–VI in Table S1).

To illustrate, we consider the equivalence between the combination of two monomers R and that of two monomers S. Model M59 represents TScc with stereochemistry RRAA and its mirror image SSAC. Instead, M63 represents TScc with stereochemistry SSAA and its mirror image RRCC. Group I includes M59 and M63 because these identify two alternative pathways for a pair of either R or S monomers. Within this group, M59 identifies the lowest-energy pathway. Therefore, the coupling of a pair of either R or S monomers occurs via M59 and not via M63.

The lowest energy values for TScc of each group (values underlined in Table S1) span the range 7.5–9.8 kcal/mol vs M36. Thus, in all cases the barrier to C–C bond formation is lower than that of the initial dimerization (TSVAR at 16–17 kcal/mol vs M36). The dimerization step is thus rate-determining for C3Ph, as it is for H₂IMes. Moreover, with TSVAR at 16–17 kcal/mol vs M36, the dimerization step is clearly easier with C3Ph than with H₂IMes as ligand (TSVAR at 19 kcal/mol vs M1), accounting for the more rapid bimolecular decomposition observed for the C3Ph catalyst.

The above results are obtained for a standard-state concentration for all the species equal to 1 mM. However, in the kinetic experiments, the initial concentration of 1 varies: it is 1.4 mM for 1-H₂IMes and 0.027 mM for 1-C3Ph. The concentration affects the relative energies. Table S2 displays the values for the lowest energy TScc calculated for a standard-state concentration corresponding to the initial experimental concentration of 1. (See Section S5, Computational Data, for the complete list of concentration-corrected energies). For H₂IMes, the change is small, and the barrier to dimerization (ΔG †₂ = 19.5 kcal/mol, see Table 1 of main text) remains clearly higher than that to CC coupling (M11, ΔG[^1.4 mM] = 9.1 kcal/mol vs M7). For C3Ph, the change is greater, due to the larger numerical difference between 1 mM and the experimental value of 0.027 mM. Thus, nearly all the dimer2 species become more stable than the precursor M36 (Table S2). Nevertheless, the energy demands of C–C coupling remain substantially lower than the barrier to dimerization (ΔG †₂ = 12.1 kcal/mol; see Table 1 in the main text). The latter therefore remains the rate determining step when a standard-state concentration of 0.027 mM is used for all species in the decomposition of 1-C3Ph.
Table S1. Relative Free Energies (kcal/mol) of Representative Intermediates and Transition States for C–C Bond Formation Calculated for 1-C3Ph at 1 mM Standard-State Concentration.

| Stereochemical Labels | Model ID | $\Delta G^{1 \text{mm}}$ [kcal/mol]$^b$ | Stereochemical Labels | Model ID | $\Delta G^{1 \text{mm}}$ [kcal/mol]$^b$ | Stereochemical Labels | Group$^c$ | Model ID | $\Delta G^{1 \text{mm}}$ [kcal/mol]$^b$ |
|-----------------------|----------|----------------------------------------|-----------------------|----------|----------------------------------------|-----------------------|----------|----------|----------------------------------------|
| RRAA, SSCC            | M41      | 12.7                                   | RRAA, SSCC            | M49      | -1.9                                   | RRAA, SSCC            | I        | M59      | 7.5                                   |
| RR'AA, SS'CC, R'RRAA, S'SCC | M42 | 10.3                                   | RR'AA, SS'CC, R'RRAA, S'SCC | M50 | 1.5                                    | RR'AA, SS'CC, R'RRAA, S'SCC | II | M60 | 8.3 |
| RR'AA, SS'CC, R'RRAA, S'SCC | M43 | 8.6                                    | R'R'AA, S'S'CC        | M51 | 0.7                                    | R'R'AA, S'S'CC        | III | M62 | 9.8 |
| SSAA, RRCC            | M44      | 12.4                                   | SSAA, RRCC            | M52      | 2.2                                    | SSAA, RRCC            | I        | M63 | 14.2 |
| SS'AA, RR'CC, S'SAA, R'RCC | M45 | 3.7                                    | SS'AA, RR'CC, S'SAA, R'RCC | M53 | 2.3                                    | SS'AA, RR'CC, S'SAA, R'RCC | II | M64 | 15.4 |
| S'S'AA, R'R'CC        | M54      | 4.4                                    | S'S'AA, R'R'CC        | M54      | 4.4                                    | S'S'AA, R'R'CC        | III | M66 | 11.8 |
| RSAA, SRCC, SRAA, RSCC | M46 | 10.4                                   | RSAA, SRCC, SRAA, RSCC | M55 | 0.3                                    | RSAA, SRCC, SRAA, RSCC | IV | M67 | 8.2 |
| RS'AA, SR'CC, S'RRAA, R'SCC | M47 | 4.0                                    | RS'AA, SR'CC, S'RRAA, R'SCC | M56 | 1.7                                    | RS'AA, SR'CC, S'RRAA, R'SCC | V | M69 | 9.0 |
| R'SAA, SR'CC, S'RRAA, R'SCC | M48 | 7.1                                    | R'S'AA, SR'CC, S'RRAA, R'SSCC | M57 | 2.2                                    | R'S'AA, SR'CC, S'RRAA, R'SSCC | V | M70 | 8.6 |
| R'S'AA, SR'SCC, S'R'AA, R'S'CC | M49 | 2.0                                    | R'S'AA, SR'SCC, S'R'AA, R'S'CC | M58 | 2.0                                    | R'S'AA, SR'SCC, S'R'AA, R'S'CC | VI | M73 | 12.9 |
| S'R'AA, R'S'CC        | M50      | 11.7                                   | S'R'AA, R'S'CC        | M51      | 11.7                                   | S'R'AA, R'S'CC        | VI | M74 | 9.6 |

$^a$Labeling rules defined in Figure S23. $^b$Energies calculated relative to M36. The most favorable pathways within each group are rendered in bold face. $^c$Attempts to optimize the geometry of dimer1 gave a dimer with features intermediate between dimer1 and dimer2, in which the monomer S’ or R’ retains the methylidene conformation present in dimer1, but the methylidene ligand in monomer S is rotated by ca. 90° as in dimer2. $^d$Attempts to optimize the geometry of dimer1 resulted in dimer2. $^e$Despite several attempts, this stationary point could not be located. $^f$Grouping based on the combination of symmetrically equivalent pairs of monomers.
### Table S2. Relative Free Energies (kcal/mol) of Representative Intermediates and Transition States for C–C Bond Formation Calculated for 1-H$_2$IMes (1.4 mM) and 1-C$_3$Ph (27 μM).

| Label$^a$ | Model ID | $\Delta G{[^M]}$ [kcal/mol]$^b$ | Label$^a$ | Model ID | $\Delta G{[^M]}$ [kcal/mol]$^b$ | Label$^a$ | Model ID | $\Delta G{[^M]}$ [kcal/mol]$^b$ |
|-----------|----------|-------------------------------|-----------|----------|-------------------------------|-----------|----------|-------------------------------|
| -         | M3       | 12.4                          | -         | M7       | 0.4                           | -         | M11      | 9.5                           |
| RRAA, SS'CC | M41     | 10.8                          | RRAA, SS'CC | M49   | -3.8                          | RRAA, SS'CC | M59      | 5.6                           |
| RR'AA, SS'CC | M42     | 8.4                           | RR'AA, SS'CC | M50   | -0.4                          | RR'AA, SS'CC | M60      | 6.4                           |
| R'R'AA, S'S'CC | M43    | 6.7                           | R'R'AA, S'S'CC | M51  | -1.2                          | R'R'AA, S'S'CC | M62      | 7.9                           |
| RSAA, SRCC | _d      | _d                            | RSAA, SRCC | M55   | -1.6                          | RSAA, SRCC | M67      | 6.3                           |
| S'R'AA, R'S'CC | M46  | 8.5                           | S'R'AA, R'S'CC | M56  | -0.2                          | S'R'AA, R'S'CC | M70      | 6.8                           |
| S'R'AA, R'S'CC | M48  | 5.2                           | S'R'AA, R'S'CC | M58  | 0.2                           | S'R'AA, R'S'CC | M74      | 7.7                           |

$^a$Labeling rules defined in Figure S23. $^b$Energies calculated relative to M36. $^c$Attempts to optimize the geometry of dimer1 gave a dimer with features intermediate between dimer1 and dimer2, in which the monomer S’ or R’ retains the methylidene conformation present in dimer1, but the methylidene ligand in monomer S is rotated by ca. 90° as in dimer2. $^d$Attempts to optimize the geometry of dimer1 resulted in dimer2. $^e$Despite several attempts, this stationary point could not be located.

### S3.3. Computational Models for Catalysts Bearing Carbenes C1$^\text{Ph}$, C2$^\text{Me}$, and C1$^\text{Me}$

The data above for 1-H$_2$IMes and 1-C$_3$Ph suggests that dissociation of pyridine from 1 and the ensuing dimerization of 2 are the key factors governing the rate of bimolecular decomposition. We therefore extended our computational investigation to include the pyridine-bound catalysts 1 and the 14-electron complexes 2 for the other CAAC catalysts, i.e., 1-C1$^\text{Ph}$ (Figure S26), 1-C1$^\text{Ph}$(I2) (Figure S27), 1-C2$^\text{Me}$ (Figure S28), and 1-C1$^\text{Me}$ (Figure S29).
Figure S26. Computational investigation of pyridine dissociation from 1 to give 2 for 1-C1Ph. Free energies (kcal/mol, at 1 mM standard-state concentration) calculated relative to M75.

Figure S27. Computational investigation of pyridine dissociation from 1 to give 2 for 1-C1Ph(I2). Free energies (kcal/mol, at 1 mM standard-state concentration) calculated relative to M87.
Figure S28. Computational investigation of pyridine dissociation from 1 to give 2 for 1-C2Me. Free energies (kcal/mol, at 1 mM standard-state concentration) calculated relative to M79.

Figure S29. Computational investigation of pyridine dissociation from 1 to give 2 for 1-C1Me. Free energies (kcal/mol, at 1 mM standard-state concentration) calculated relative to M83.
Table S3. Selected Interaction Energies $E(2)$ from Second-Order Perturbation Theory Analysis of the Fock Matrix in NBO Basis.\textsuperscript{a}

| Complex     | Donor NBO           | Acceptor NBO        | $E(2)$ (kcal/mol) |
|-------------|---------------------|---------------------|-------------------|
| 1-H\textsubscript{2}Mes | BD (2) C 17- C 18 | BD* (2) N 56- C 59 | 0.38              |
| 1-C\textsubscript{1}Ph     | BD (2) C 39- C 43 | BD* (2) N 50- C 53 | 0.70              |
| 1-C\textsubscript{1}Ph(I\textsubscript{2}) | BD (2) C 47- C 51 | BD* (1) C 60- H 64 | 0.45              |
| 1-C\textsubscript{3}Ph     | BD (2) C 40- C 44 | BD* (2) N 51- C 54 | 0.75              |

\textsuperscript{a} Interaction energies $<0.3$ kcal/mol not shown.
S4. Computational Methods

Construction, analysis, and visualization of molecular structures were carried out using the following software packages: ChemAxon’s Marvin (version 6.2.1),15 UCSF Chimera (version 1.14),16 and Molden (version 5.0).17 Conformational searches and preliminary strain relaxations of molecular models were performed in Spartan18 using the Merck force field (MMFF94)18 and the semi-empirical PM6 methods19. As such empirical and semi-empirical methods are generally less accurate for transition-metal chemistry than for organic chemistry, internal coordinates, such as metal-ligand bond distances and angles, describing the immediate metal coordination environment, were frozen in these preliminary calculations. All density functional theory (DFT) calculations were performed with the Gaussian suite of programs, versions 09 D.0120 and 16 C.01.21

S4.1. Location of Stationary Points and Minimum Energy Crossing Points (MECPs)

Molecular geometries were optimized using Head-Gordon’s long-range- and dispersion-corrected hybrid density functional oB97XD functional.22 This functional produces geometries in good agreement with those from X-ray diffraction for ruthenium catalysts for olefin metathesis and other homogeneous catalysts.23 All elements except ruthenium were described with Dunning’s correlation-consistent valence double-ζ plus polarization basis sets (cc-pVDZ)24,25 as obtained from the EMSL basis set exchange database.26,27 Ruthenium atoms were described by combining the Stuttgart 28-electron relativistic effective core potential (termed ECP28MDF28 at the Stuttgart/Cologne Group website)29 with the correlation-consistent valence double-ζ plus polarization basis set (cc-pVDZ-PP)28 obtained from the EMSL basis set exchange database.26,27 Numerical integration was performed using Gaussian’s “ultrafine” grid. Wavefunctions were converged using the default convergence criteria for self-consistent field (SCF) procedures (RMS change in density matrix < 1.0·10⁻⁸, max. change in density matrix = 1.0·10⁻⁶), which correspond to the SCF option conver=8. All SCF solutions were checked for internal instability before optimizing geometry. Unstable solutions were re-optimized to a real, spin-restricted or unrestricted solution for spin-singlet or higher multiplets, respectively.

Next, geometries were optimized without symmetry constraints using tight convergence criteria (i.e., opt=tight, corresponding to max. force 1.5·10⁻⁵, RMS force 1.0·10⁻⁵, max. displacement 6.0·10⁻², RMS displacement 4.0·10⁻⁵). In a few cases, the SCF convergence criteria were tightened tenfold compared to the above-described default (i.e., conver=9 was used instead of conver=8) to speed up geometry optimization. In all these cases, the resulting geometry was re-optimized with the default SCF convergence criteria. All reported geometries have thus been obtained with the default SCF convergence criteria (conver=8).

Minimum energy crossing points (MECPs) between spin-singlet and spin-triplet surfaces were located using Gaussian 09.d01 in conjunction with via the seam-of-crossing optimizer developed by Harvey (version: November-2009).30 The DFT model, basis sets, and options of these calculations were identical to those of the regular geometry optimizations described above. To convergence criteria for the seam-of-crossing optimizations were as follows: The maximum allowed electronic energy gradient was 1.0·10⁻⁴ a.u., and the maximum allowed energy difference between the two spin-states was 0.00050 a.u. The curvature along the seam was confirmed by the eigenvalues of state-averaged Hessian matrix obtained using the Glowfreq program (version November-2015).31

The input files of the geometry optimizations and Hessian calculations are available in the ioChem-BD repository,32,33 at https://doi.org/10.19061/iochem-bd-6-79.
S4.2. Hessian Calculations and Thermochemical Corrections

All located stationary points were subjected to analytical calculation of the second derivatives, i.e., the Hessian matrix. Except for the integration grid being reduced from “ultrafine” to “finegrid” in these coupled perturbed Hartree-Fock (CPHF) calculations, the basis sets and options of these Hessian calculations were identical to those of the geometry optimizations. The eigenvalues of the analytically calculated Hessian matrices were used to characterize each stationary point as either a minimum (positive eigenvalues only) or a transition state (a single negative eigenvalue) on the potential energy surface. The translational, rotational, and vibrational components of the thermal corrections to enthalpies and Gibbs free energies were calculated within the ideal-gas, rigid-rotor, and harmonic oscillator approximations (temperature = 263 K), except that all frequencies below 100 cm$^{-1}$ were shifted to 100 cm$^{-1}$ when calculating the vibrational component of entropy (i.e., quasi-harmonic oscillator approximation).

S4.3. Single-Point Energy Calculations

The energy of all stationary points and MECPs was calculated with the PBE functional developed by Perdew, Burke and Ernzerho$^{36,37}$ in combination with Grimme’s D3 empirical dispersion term with Becke-Johnson damping (GD3BJ).$^{38}$ When corrected for basis set superposition errors (BSSE), this combination of functional and empirical dispersion was found to be the most accurate in a validation study of density functionals for ruthenium-catalyzed olefin metathesis, reproducing mass-spectrometry-determined relative energies of olefin metathesis reaction steps in the gas phase with absolute errors close to 2 kcal/mol.$^{39}$ The PBE-D3BJ combination is expected to perform well also in the present study of ruthenium-mediated reactions related to olefin metathesis, and the large single-point (SP) basis sets (see below) should eliminate the need for BSSE corrections and contribute to accurate relative energies, with errors expected to remain within 2–5 kcal/mol. The BJ damping parameters used were those of Smith and co-workers, which were shown to increase the accuracy substantially compared to the original parameters.$^{40}$ Electrostatic and non-electrostatic solvation effects in CHCl$_3$ were accounted for using the polarizable continuum model (PCM) in combination with the “Dis”, “Rep”, and “Cav” keywords.$^{41-43}$ The solvent (CHCl$_3$) was characterized by the built-in value for the dielectric constant, and the solute cavity was constructed using the united atom topological model with atomic radii optimized for Hartree-Fock (keyword “UAHF”). Ruthenium was described by the ECP28MDF relativistic effective core potential$^{28}$ accompanied by a correlation-consistent valence quadruple-$\zeta$ plus polarization basis set (ECp28MDF_VQZ),$^{28}$ both obtained from the Stuttgart/Cologne Group website.$^{29}$ Carbon and hydrogen atoms were described by valence quadruple-$\zeta$ plus polarization (cc-pVQZ)$^{24,25}$ as obtained from the EMSL basis set exchange database.$^{26,27}$ For all other atoms, augmented valence quadruple-$\zeta$ plus polarization (aug-cc-pVQZ)$^{24,25,44}$ basis sets were taken from the EMSL repository.$^{26,27}$

Finally, numerical integrations were performed with the “ultrafine” grid of Gaussian 16. The density-based SCF convergence criteria were 1.0·10$^{-5}$ (RMS change) and 1.0·10$^{-3}$ (maximum change), respectively, corresponding to the SCF option conver=5.

Input files are available in the ioChem-BD repository.$^{32,33}$ at https://doi.org/10.19061/iochem-bd-6-79.
S4.4. Calculation of Gibbs Free Energies

Gibbs free energies were calculated at 263 K according to Equation S6:

\[ G^{[M]} = E_{CHCl_3} + \Delta G_{WB97XD,qh}^{T=263 K} + \Delta G_{atm-\{M\}}^{T=263 K}, \]

Equation S6

where \( E_{CHCl_3} \) is the energy resulting from single-point calculation, including solvent effects (from the implicit solvation model) and the dispersion correction, \( \Delta G_{WB97XD,qh}^{T=263 K} \) is the thermal correction to the Gibbs free energy calculated at the geometry optimization level using the quasi-harmonic approximation, and \( \Delta G_{atm-\{M\}}^{T=263 K} \) is the standard-state correction corresponding to a solution (but exhibiting infinite-dilution, ideal-gas-like behavior) with a given concentration ([M]). The concentration is set to either 1 mM for general-purpose data that need to be comparable across different species, or to the experimental concentration used in the kinetic experiments, namely, 1.4 mM for computational data referring to experiments with 1-H2IMes, 61 μM for 1-C1Ph, 586 μM for 1-C1Ph(I2), 10 μM for 1-C2Me, 10 μM for 1-C1Me, and 27 μM for 1-C3Ph. Free energy values calculated with one or the other concentration are clearly identified by table/figure captions and footnotes.

All values are collected in Table S4, Table S6, Table S7, Table S8, Table S9, and Table S10 of the Computational Data section.

S4.4.1. The Barrier of Diffusion-Controlled Reactions

Dissociative elementary reaction steps that require small or no geometrical strain sometimes do not involve enthalpic barriers on the potential energy surface. In such cases, attempts to explore the dissociation of the two fragments typically lead to minimum energy pathways with monotonically increasing potential energy, with the barrier corresponding to complete separation of the two fragments. However, even without a maximum on the potential energy surface, the corresponding free energy surface in solution may still be associated with a maximum corresponding to a variational transition state. The free energy of the latter can be estimated by reversing the Eyring equation using a typical rate constant \( (4 \times 10^9 \text{ s}^{-1}) \) in common organic solvents) for diffusion-controlled reactions in usual conditions.\(^{45}\) The associated free-energy barrier (4.4 kcal/mol) is calculated by reversing the Eyring equation (using 298 K to account for the fact that the above typical value of the reaction rate refers to usual conditions, thus room temperature rather than \(-10^\circ\text{C})\(^{46}\) Finally, the estimated free energy for the variational transition state (labeled TS\(_{VAR} \)) of dimerization is obtained by adding the above correction to the energy of the two isolated monomers.

S4.4.2. The Barrier Associated with Spin Inversion

The free energy of MECPs was calculated as follows: i) The single-point energy was taken to be the average of the single-point energies obtained for the two spin multiplicities at the MECP geometry, ii) the thermochemical corrections were taken to be the average obtained for the minima on either side of the MECP on the seam of crossing, and, iii) an additional penalty (\( \Delta G_{pXover} \)), suggested by Schneider and co-workers to be in the range 1–5 kcal/mol,\(^{47}\) was added to account for a lower-than-unity spin-crossing probability.\(^{48}\)

\[ G^{[M]} = E_{CHCl_3} + \Delta G_{WB97XD,qh}^{T=263 K} + \Delta G_{pXover} + \Delta G_{atm-\{M\}}^{T=263 K}, \]

Equation S7

where
\[ E^{CHCl_3} = \frac{E(S=0)^{CHCl_3} + E(S=1)^{CHCl_3}}{2} \]

and where \( E(S = 0)^{CHCl_3} \) and \( E(S = 1)^{CHCl_3} \) are the single-point energies calculated for the MECP geometry with spin-singlet and triplet-state multiplicity, respectively, and

\[ \Delta G(T=263 K)_{W97XD,qh} = \frac{\Delta G(\text{opt}, S = 0)^{T=263 K}_{W97XD,qh} + \Delta G(\text{opt}, S = 1)^{T=263 K}_{W97XD,qh}}{2} \]

where \( \Delta G(\text{opt}, S = 0)^{T=263 K}_{W97XD,qh} \) and \( \Delta G(\text{opt}, S = 1)^{T=263 K}_{W97XD,qh} \) are the thermal corrections to the Gibbs free energy calculated at the geometry-optimization level with the quasi-harmonic approximation for the neighboring minima on the spin-singlet and spin-triplet surface, respectively. The resulting values are collected in Table S5.

**S4.5. Natural Bond Order and Partial Charge Analysis**

The natural bond orbital analyses were performed with the NBO7 software, using the electron density of the single-point energy calculations as input. To obtain a comparable set of orbitals among the complexes, Lewis structures were explicitly given via the $CHOOSE input section.

**S4.6. Calculations of Buried Volume**

Buried volumes (the percentage of a sphere that is occupied, \( \%V_{\text{bur}} \)) for the DFT-optimized pyridine-free, 14-electron active complexes 2, including hydrogen atoms, were obtained using the SambVca 2.1 web application developed by Cavallo and co-workers. A sphere of radius 3.5 Å centered on ruthenium was used, and the van der Waals radii were those of Bondi, scaled by 1.17. The mesh spacing for numerical integration was 0.10 Å.
S5. Computational Data

A data set collection of computational results is available in the ioChem-BD repository\textsuperscript{32} and can be accessed via https://doi.org/10.19061/iochem-bd-6-79.

Table S4. Free Energies (a.u.) and Relative Free Energies (kcal/mol) of Minima and Transition States of Complexes Bearing an H₂JMes Ligand.

| Model ID | Spin multiplicity | $\Delta G_{T=298 K}$ [kcal/mol] | $G_{1\rightarrow m}$ [a.u.] | $\Delta G_{1\rightarrow m}$ [kcal/mol]$^a$ | $G_{1\rightarrow 4\rightarrow m}$ [a.u.] | $\Delta G_{1\rightarrow 4\rightarrow m}$ [kcal/mol]$^a$ |
|----------|-------------------|-------------------------------|-----------------------------|---------------------------------|---------------------------------|---------------------------------|
| pyridine | 1                 | 0.065840                      | -248.030422                 | -                               | -                               | -                               |
| ethylene | 1                 | 0.032032                      | -78.479204                  | -                               | -                               | -                               |
| M1       | 1                 | 0.495474                      | -2226.414704                | 0.0                             | -2226.414424                   | 0.0                             |
| M2       | 1                 | 0.406017                      | -1978.372526                | 7.4                             | -1978.372246                   | 7.6                             |
| 2 x M2   | 1                 | 0.406017                      | -1978.372526                | 14.8                            | -1978.372246                  | 15.1                            |
| M3       | 1                 | 0.840285                      | -3956.749092                | 12.2                            | -3956.748812                   | 12.4                            |
| M4       | 1                 | 0.837806                      | -3956.727056                | 26.0                            | -3956.726776                   | 26.2                            |
| M5       | 1                 | 0.840847                      | -3956.774398                | -3.7                            | -3956.774118                   | -3.5                            |
| M6       | 1                 | 0.839666                      | -3956.749031                | 12.3                            | -3956.748751                   | 12.4                            |
| M7       | 1                 | 0.841639                      | -3956.768223                | 0.2                             | -3956.767942                   | 0.4                             |
| M8       | 1                 | 0.840809                      | -3956.756514                | 7.6                             | -3956.756234                   | 7.7                             |
| M9       | 1                 | 0.842329                      | -3956.750866                | 11.1                            | -3956.750586                   | 11.3                            |
| M10      | 1                 | 0.841393                      | -3956.756531                | 7.6                             | -3956.756251                   | 7.7                             |
| M11      | 1                 | 0.843175                      | -3956.753657                | 9.4                             | -3956.753377                   | 9.5                             |
| M12      | 1                 | 0.845729                      | -3956.761010                | 4.7                             | -3956.760730                   | 4.9                             |
| M13      | 1                 | 0.844168                      | -3956.759646                | 5.6                             | -3956.759365                   | 5.8                             |
| M14      | 1                 | 0.844976                      | -3956.769100                | -0.3                            | -3956.768820                   | -0.2                            |
| M15      | 1                 | 0.847407                      | -3956.751975                | 10.4                            | -3956.751695                   | 10.6                            |
| M16      | 1                 | 0.846193                      | -3956.778221                | -6.1                            | -3956.779414                   | -5.9                            |
| M17      | 1                 | 0.847272                      | -3956.764240                | 2.7                             | -3956.763960                   | 2.9                             |
| M18      | 1                 | 0.846072                      | -3956.769584                | -0.6                            | -3956.769304                   | -0.5                            |
| M19      | 1                 | 0.845289                      | -3956.766949                | 1.0                             | -3956.766669                   | 1.2                             |
| M20      | 1                 | 0.794186                      | -3878.281330                | 5.0                             | -3878.281050                   | 5.4                             |
| M21      | 1                 | 0.791629                      | -3878.274401                | 9.4                             | -3878.274121                   | 9.7                             |
| M22      | 3                 | 0.842978                      | -3956.785285                | -10.5                           | -3956.785005                   | -10.3                           |
| M24      | 3                 | 0.838258                      | -3956.691330                | 48.5                            | -3956.691050                   | 48.6                            |
| M25      | 3                 | 0.841034                      | -3956.766485                | 1.3                             | -3956.766204                   | 1.5                             |
| M26      | 3                 | 0.843467                      | -3956.766672                | 1.2                             | -3956.766392                   | 1.4                             |
| M27      | 3                 | 0.842811                      | -3956.759736                | 5.5                             | -3956.759456                   | 5.7                             |
| M28      | 3                 | 0.844677                      | -3956.768176                | 0.2                             | -3956.767896                   | 0.4                             |
| M29      | 3                 | 0.844269                      | -3956.757819                | 6.7                             | -3956.757539                   | 6.9                             |
| M30      | 3                 | 0.844182                      | -3956.765891                | 1.7                             | -3956.765611                   | 1.9                             |
| M32      | 3                 | 0.844526                      | -3956.767132                | 0.9                             | -3956.766852                   | 1.1                             |
| M33      | 3                 | 0.844063                      | -3956.769939                | -0.9                            | -3956.769659                   | -0.7                            |
| M34      | 3                 | 0.788207                      | -3878.265508                | 15.0                            | -3878.265228                   | 15.3                            |
| M35      | 5                 | 0.788922                      | -3878.266684                | 14.2                            | -3878.266404                   | 14.6                            |

$^a$ Relative energies are calculated with respect to M1.
**Table S5.** Estimated Free Energy Components (a.u.) and Relative Free Energies (kcal/mol) of Minimum Energy Crossing Points (MECPs) of Complexes Bearing an H$_2$Mes Ligand.

| Model ID | $\Delta G_{\text{W997D,4b}}$ [a.u.] | $G_{\text{1.mM}}$ [a.u.] | $\Delta G_{\text{1.mM}}$ [kcal/mol] | $\Delta G_{\text{1.4 mM}}$ [kcal/mol] | $G_{\text{1.4 mM}}$ [a.u.] | $\Delta G_{\text{1.4 mM}}$ [kcal/mol] | $\Delta G_{\text{1.4 mM}}$ [kcal/mol] |
|----------|-----------------------------------|--------------------------|------------------------------------|------------------------------------|--------------------------|------------------------------------|------------------------------------|
| M22      | 0.844353648                       | -3956.759179             | 6.9                                | 10.9                               | -3956.758899            | 7.1                                | 11.1                               |
| M31      | 0.845126959                       | -3956.759363             | 6.8                                | 10.8                               | -3956.759083            | 6.9                                | 10.9                               |

*a* Relative energies are calculated with respect to M1. *b*: Calculated using $\Delta G_{\text{pXover}} = 1$. *c*: Calculated using $\Delta G_{\text{pXover}} = 5$.

**Table S6.** Free Energies (a.u.) and Relative Free Energies (kcal/mol) of Species Bearing Ligand C1$^{\text{Ph}}$.

| Model ID | Spin multiplicity | $\Delta G_{\text{W997D,4b}}$ [a.u.] | $G_{\text{1.mM}}$ [a.u.] | $\Delta G_{\text{1.mM}}$ [kcal/mol] | $G_{\text{1.61 }\mu\text{M}}$ [a.u.] | $\Delta G_{\text{1.61 }\mu\text{M}}$ [kcal/mol] |
|----------|-------------------|------------------------------------|--------------------------|------------------------------------|--------------------------|------------------------------------|
| M75      | 1                 | 0.541081                           | -2249.575410             | 0.0                                | -2249.577739            | 0.0                                |
| M76      | 1                 | 0.540887                           | -2249.572938             | 1.6                                | -2249.575267            | 1.6                                |
| M77      | 1                 | 0.452479                           | -2001.536374             | 5.4                                | -2001.538703            | 3.9                                |
| M78      | 1                 | 0.452422                           | -2001.535894             | 5.7                                | -2001.538223            | 4.2                                |

*a* Relative energies are calculated with respect to M75.

**Table S7.** Free Energies (a.u.) and Relative Free Energies (kcal/mol) of Species Bearing Ligand C1$^{\text{Ph}(I_2)}$.

| Model ID | Spin multiplicity | $\Delta G_{\text{W997D,4b}}$ [a.u.] | $G_{\text{1.mM}}$ [a.u.] | $\Delta G_{\text{1.mM}}$ [kcal/mol] | $G_{\text{1.50 }\mu\text{M}}$ [a.u.] | $\Delta G_{\text{1.50 }\mu\text{M}}$ [kcal/mol] |
|----------|-------------------|------------------------------------|--------------------------|------------------------------------|--------------------------|------------------------------------|
| M87      | 1                 | 0.538352                           | -1920.928934             | 0.0                                | -1920.929379            | 0.0                                |
| M88      | 1                 | 0.539464                           | -1920.923557             | 3.4                                | -1920.924003            | 3.4                                |
| M89      | 1                 | 0.449530                           | -1672.891054             | 4.7                                | -1672.891499            | 4.4                                |
| M90      | 1                 | 0.449227                           | -1672.887831             | 6.7                                | -1672.888276            | 6.4                                |

*a* Relative energies are calculated with respect to M87.
Table S8. Free Energies (a.u.) and Relative Free Energies (kcal/mol) of Species Bearing Ligand C2Me.

| Model ID | Spin multiplicity | $\Delta G_{W=298 K}^\text{298 K}^\text{M79}$ [a.u.] | $G_{1 \text{ mol}}^\text{1 mol}$ [a.u.] | $\Delta G_{1 \text{ mol}}^\text{M79}$ [kcal/mol] | $G_{10 \text{ μM}}^\text{10 μM}$ [a.u.] | $\Delta G_{10 \text{ μM}}^\text{M79}$ [kcal/mol] |
|----------|------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| M79      | 1                | 0.488464                        | -2058.039357                    | 0.0                             | -2058.043193                    | 0.0                             |
| M80      | 1                | 0.488460                        | -2058.036992                    | 1.5                             | -2058.040827                    | 1.5                             |
| M81      | 1                | 0.399787                        | -1810.008293                    | 0.4                             | -1810.012129                    | -2.0                            |
| M82      | 1                | 0.400387                        | -1810.002984                    | 3.7                             | -1810.006819                    | 1.3                             |

* Relative energies are calculated with respect to M79.

Table S9. Free Energies (a.u.) and Relative Free Energies (kcal/mol) of Species Bearing Ligand C1Me.

| Model ID | Spin multiplicity | $\Delta G_{W=298 K}^\text{298 K}^\text{M83}$ [a.u.] | $G_{1 \text{ mol}}^\text{1 mol}$ [a.u.] | $\Delta G_{1 \text{ mol}}^\text{M83}$ [kcal/mol] | $G_{10 \text{ μM}}^\text{10 μM}$ [a.u.] | $\Delta G_{10 \text{ μM}}^\text{M83}$ [kcal/mol] |
|----------|------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| M83      | 1                | 0.488604                        | -2058.042235                    | 0.0                             | -2058.046071                    | 0.0                             |
| M84      | 1                | 0.488743                        | -2058.039066                    | 2.0                             | -2058.042901                    | 2.0                             |
| M85      | 1                | 0.400675                        | -1810.007392                    | 2.8                             | -1810.011228                    | 0.4                             |
| M86      | 1                | 0.400887                        | -1810.000609                    | 7.0                             | -1810.004445                    | 4.6                             |

* Relative energies are calculated with respect to M83.
**Table S10.** Free Energies (a.u.) and Relative Free Energies (kcal/mol) of Species Bearing Ligand C3Ph.

| Model ID | Spin multiplicity | $\Delta G_{\text{rel}}^{27^\circ C}$ (a.u.) | $G_{\text{f} [\text{m}M]}$ [a.u.] | $\Delta G_{\text{f} [\text{mol}]}$ [kcal/mol] | $G_{\text{f} [\text{mol}]}$ [a.u.] | $\Delta G_{\text{f} [\text{mol}]}$ [kcal/mol] |
|----------|--------------------|--------------------------------------------|---------------------------------|----------------------------------|---------------------------------|----------------------------------|
| M36      | 1                  | 0.511926                                   | -2210.336449                   | 0.0                              | -2210.339457                   | 0.0                              |
| M37      | 1                  | 0.511858                                   | -2210.335789                   | 0.4                              | -2210.338797                   | 0.4                              |
| M38      | 1                  | 0.423786                                   | -1962.296917                   | 5.7                              | -1962.299925                   | 3.8                              |
| 2 x M38  | 1                  | 0.423786                                   | -1962.296917                   | 11.4                             | -1962.299925                   | 7.7                              |
| M39      | 1                  | 0.421810                                   | -1962.296105                   | 6.2                              | -1962.299113                   | 4.3                              |
| 2 x M39  | 1                  | 0.421810                                   | -1962.296105                   | 12.5                             | -1962.299113                   | 8.7                              |
| M40      | 1                  | 0.422686                                   | -1962.280632                   | 15.9                             | -1962.283640                   | 14.0                             |
| M41      | 1                  | 0.871500                                   | -3924.591816                   | 12.7                             | -3924.594824                   | 10.8                             |
| M42      | 1                  | 0.872383                                   | -3924.595678                   | 10.3                             | -3924.598686                   | 8.4                              |
| M43      | 1                  | 0.874039                                   | -3924.598378                   | 8.6                              | -3924.601386                   | 6.7                              |
| M44      | 1                  | 0.871334                                   | -3924.592334                   | 12.4                             | -3924.595343                   | 10.5                             |
| M45      | 1                  | 0.873821                                   | -3924.606152                   | 3.7                              | -3924.609160                   | 1.8                              |
| M46      | 1                  | 0.871764                                   | -3924.595446                   | 10.4                             | -3924.598454                   | 8.5                              |
| M47      | 1                  | 0.873641                                   | -3924.605618                   | 4.0                              | -3924.608626                   | 2.2                              |
| M48      | 1                  | 0.873897                                   | -3924.600710                   | 7.1                              | -3924.603718                   | 5.2                              |
| M49      | 1                  | 0.872348                                   | -3924.615050                   | -1.9                             | -3924.618058                   | -3.8                             |
| M50      | 1                  | 0.873504                                   | -3924.609674                   | 1.5                              | -3924.612682                   | -0.4                             |
| M51      | 1                  | 0.873502                                   | -3924.610984                   | 0.7                              | -3924.613992                   | -1.2                             |
| M52      | 1                  | 0.872516                                   | -3924.608541                   | 2.2                              | -3924.611549                   | 0.3                              |
| M53      | 1                  | 0.872762                                   | -3924.608402                   | 2.3                              | -3924.611410                   | 0.4                              |
| M54      | 1                  | 0.874516                                   | -3924.605013                   | 4.4                              | -3924.608021                   | 2.5                              |
| M55      | 1                  | 0.872099                                   | -3924.611565                   | 0.3                              | -3924.614573                   | -1.6                             |
| M56      | 1                  | 0.872536                                   | -3924.609323                   | 1.7                              | -3924.612332                   | -0.2                             |
| M57      | 1                  | 0.872809                                   | -3924.608495                   | 2.2                              | -3924.611503                   | 0.3                              |
| M58      | 1                  | 0.872302                                   | -3924.608797                   | 2.0                              | -3924.611805                   | 0.2                              |
| M59      | 1                  | 0.875099                                   | -3924.600101                   | 7.5                              | -3924.603109                   | 5.6                              |
| M60      | 1                  | 0.874598                                   | -3924.598879                   | 8.3                              | -3924.601887                   | 6.4                              |
| M61      | 1                  | 0.875409                                   | -3924.593438                   | 11.7                             | -3924.596446                   | 9.8                              |
| M62      | 1                  | 0.874884                                   | -3924.596384                   | 9.8                              | -3924.599393                   | 7.9                              |
| M63      | 1                  | 0.875529                                   | -3924.589374                   | 14.2                             | -3924.592382                   | 12.3                             |
| M64      | 1                  | 0.874382                                   | -3924.587563                   | 15.4                             | -3924.590571                   | 13.5                             |
| M65      | 1                  | 0.875408                                   | -3924.593816                   | 11.4                             | -3924.596824                   | 9.6                              |
| M66      | 1                  | 0.874597                                   | -3924.593204                   | 11.8                             | -3924.596212                   | 9.9                              |
| M67      | 1                  | 0.874562                                   | -3924.598954                   | 8.2                              | -3924.601962                   | 6.3                              |
| M68      | 1                  | 0.875946                                   | -3924.586420                   | 16.1                             | -3924.589428                   | 14.2                             |
| M69      | 1                  | 0.874905                                   | -3924.597655                   | 9.0                              | -3924.600663                   | 7.1                              |
| M70      | 1                  | 0.875046                                   | -3924.598285                   | 8.6                              | -3924.601293                   | 6.8                              |
| M72      | 1                  | 0.875422                                   | -3924.588378                   | 14.9                             | -3924.591386                   | 13.0                             |
| M73      | 1                  | 0.874609                                   | -3924.591562                   | 12.9                             | -3924.594570                   | 11.0                             |
| M74      | 1                  | 0.874750                                   | -3924.596715                   | 9.6                              | -3924.599723                   | 7.7                              |

* Relative energies are calculated with respect to M36.
S6. References

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