Supporting Information for

The [2+2] Cycloaddition of Alkynes at a Ru-P π-Bond

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General experimental

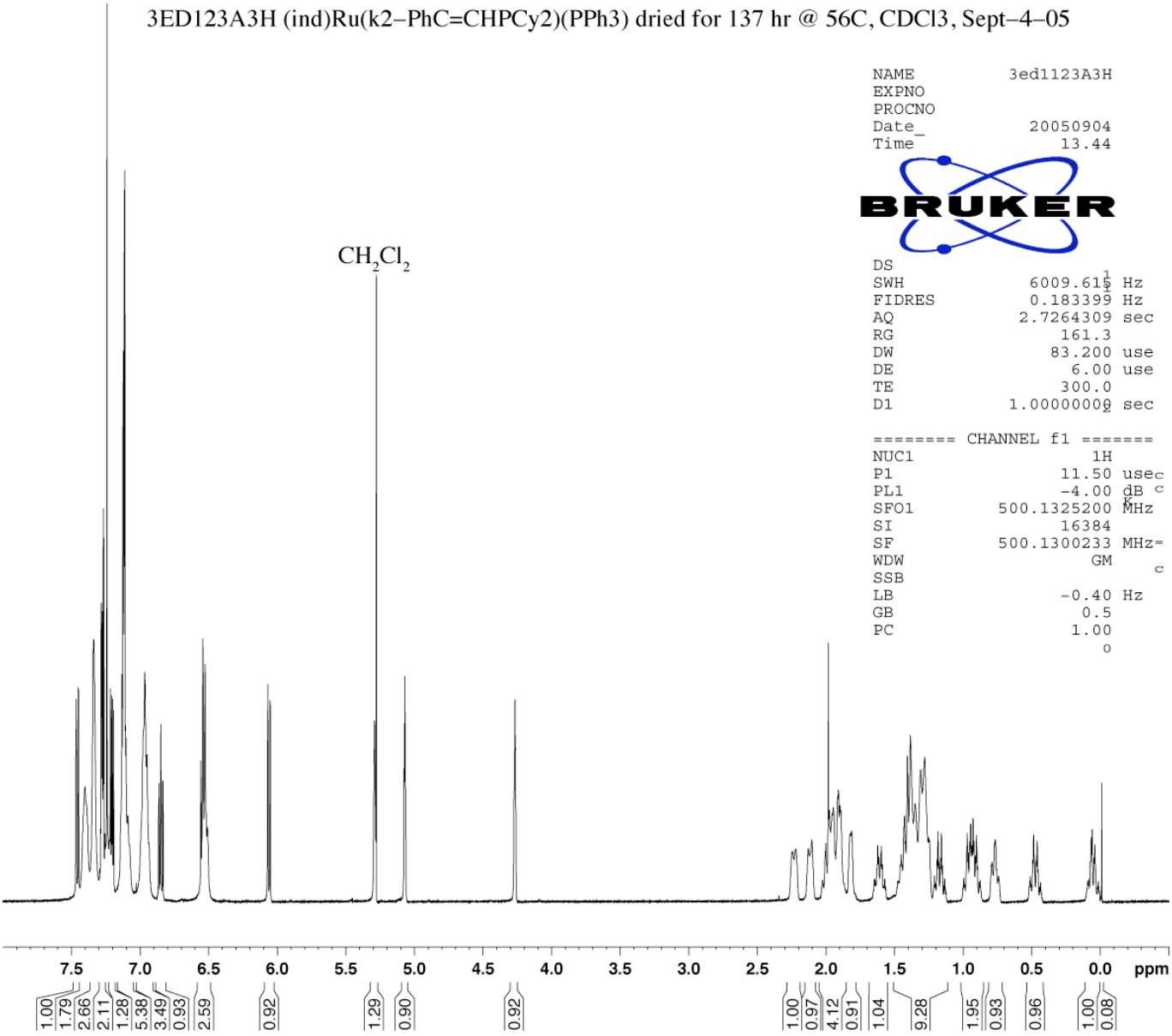
Unless otherwise noted, all reactions and manipulations were performed under an atmosphere of nitrogen in an MBraun Unilab 1200/780 glovebox or using conventional Schlenk line techniques. All solvents were sparged with nitrogen for 25 minutes and dried using an MBraun Solvent Purification System (SPS). Phenylacetylene and 1-hexyne were dried over $MgSO_4$ prior to distillation under nitrogen; all other reagents were used without further purification. Deuterated solvents were purchased from Cambridge Isotope Labs (CIL), freeze-pump-thaw degassed, and vacuum transferred from sodium/benzophenone (d_6-benzene, d_8-toluene) or calcium hydride (*d*-chloroform) before use. All other chemicals were purchased from Sigma-Aldrich® Canada. [Ru(η^5-indenyl)(PCy_2)(PPh_3)] (**1a**)[1], Ru(η^5-indenyl)(PPr^i_2)(PPh_3)$_2$] (**1b**)[1] and [RuCl(η^5-indenyl)(PCy_2H)(PPh_3)][2] were prepared as reported previously. Dicyclohexylphosphine was purchased as a 10% wt solution in hexanes from Strem Chemicals; its 0.6 M concentration was confirmed by quantitative $^{31}P\{^1H\}$ NMR spectroscopy of a known volume with a known mass of triphenylphosphine oxide added as an internal standard. NMR spectra were recorded on a Bruker AVANCE 500 operating at 500.13 MHz for ^1H, 125.77 MHz for ^{13}C, and 202.46 MHz for ^{31}P, or on a Bruker AVANCE 360 operating at 360.13 MHz for ^1H, 55.28 MHz for ^2H, and 145.78 MHz for ^{31}P. Chemical shifts are reported in ppm at ambient temperature unless otherwise noted. ^1H chemical shifts are referenced against residual protonated solvent peaks at 7.16 ppm (C_6D_5H), 2.09 ppm ($PhCD_2H$), and 7.24 ppm ($CHCl_3$). ^{13}C chemical shifts are referenced against d_6-benzene at 128.4 ppm and $CDCl_3$ at 77.5 ppm. All ^1H and ^{13}C chemical shifts are reported relative to tetramethylsilane, while ^{31}P chemical shifts are reported relative to 85% H_3PO_4(aq). Melting/decomposition temperatures were measured using a Gallenkamp apparatus for capillary samples (uncorrected for ambient pressure). Microanalysis was performed by Canadian Microanalytical Service Ltd., Delta, BC, Canada. IR spectra were recorded on a Perkin-Elmer FTIR Spectrum One spectrophotometer using KBr pellets under a nitrogen atmosphere. EI- and FAB-MS was performed by Dr. David McGillivray, Department of Chemistry, University of Victoria. EI-MS was also performed by Dr. Yun Ling, Department of Chemistry, University of British Columbia.

Preparation of cycloaddition products 2a-b and deprotonation product 3a

Synthesis of [Ru(η^5-indenyl)(κ^2-PhC=CHPCy$_2$)(PPh$_3$)] (2a)

To a Schlenk flask containing a blue solution of [Ru(η^5-indenyl)(PCy$_2$)(PPh$_3$)] (**1b**, 100 mg, 0.15 mmol) in 5 mL toluene was added phenylacetylene (15 mg, 0.15 mmol). The resulting yellow solution was allowed to stir for 5 min before the solvent was evaporated under vacuum. The resulting orange oil was dissolved in CH_2Cl_2 (10 mL) and filtered. The volume of the solution was reduced to ~1.5 mL under vacuum and 30 mL of acetonitrile was added to give [Ru(η^5-indenyl)(κ^2-PhC=CPhPCy$_2$)(PPh$_3$)] (**2a**, 75 mg, 0.099 mmol, 64% yield) as a dark orange crystalline solid. The product hung onto some CH_2Cl_2 despite multiple washings with pentane and hexanes and extensive drying under vacuum at 56°C. EI-MS; *m/z* (relative intensity): 778 (12%) [M^+], 740 (83%) [M^+– C=C(H)–C–3H], 514 (55%) [M^+–PPh$_3$–2H], 477 (100%) [M^+–PhC=C(H)PCy$_2$–2H], 433 (13%) [M^+–PPh$_3$–Cy], 400 (44%) [M^+– PhC=C(H)PCy$_2$–Ph], 351 (55%) [M^+–PPh$_3$–Cy–C$_6$H$_{10}$], 318 (35%) [M^+–PPh$_3$–PCy$_2$–H], 295 (65%) [M^+–Ru–indenyl–PPh$_3$–C=C(H) – 2H]. FAB-MS (+LSIMS matrix mNBA); *m/z* (relative intensity): 779.1 (100%) [M^+]. HR-MS (+LSIMS matrix mNBA): exact mass (monoisotopic) calcd for $C_{47}H_{50}P_2Ru$, 778.2431; found, 779.2514 ± 0.0010 (average of 3 trials); Anal. Calcd for $C_{47}H_{50}P_2Ru$: C, 72.57; H, 6.48. Found: C, 70.15; H, 6.25; Anal. Calcd for $C_{47}H_{50}P_2Ru$•0.4CH_2Cl_2: C, 70.12; H, 6.31 (See ^{1}H NMR below). Mp: 161 – 162 °C (dec).

^{1}H NMR spectrum of **2a** showing purity:



Synthesis of [Ru(η^5-indenyl)(κ^2-PhC=CHPPr$^i_2$)(PPh$_3$)] (2b)

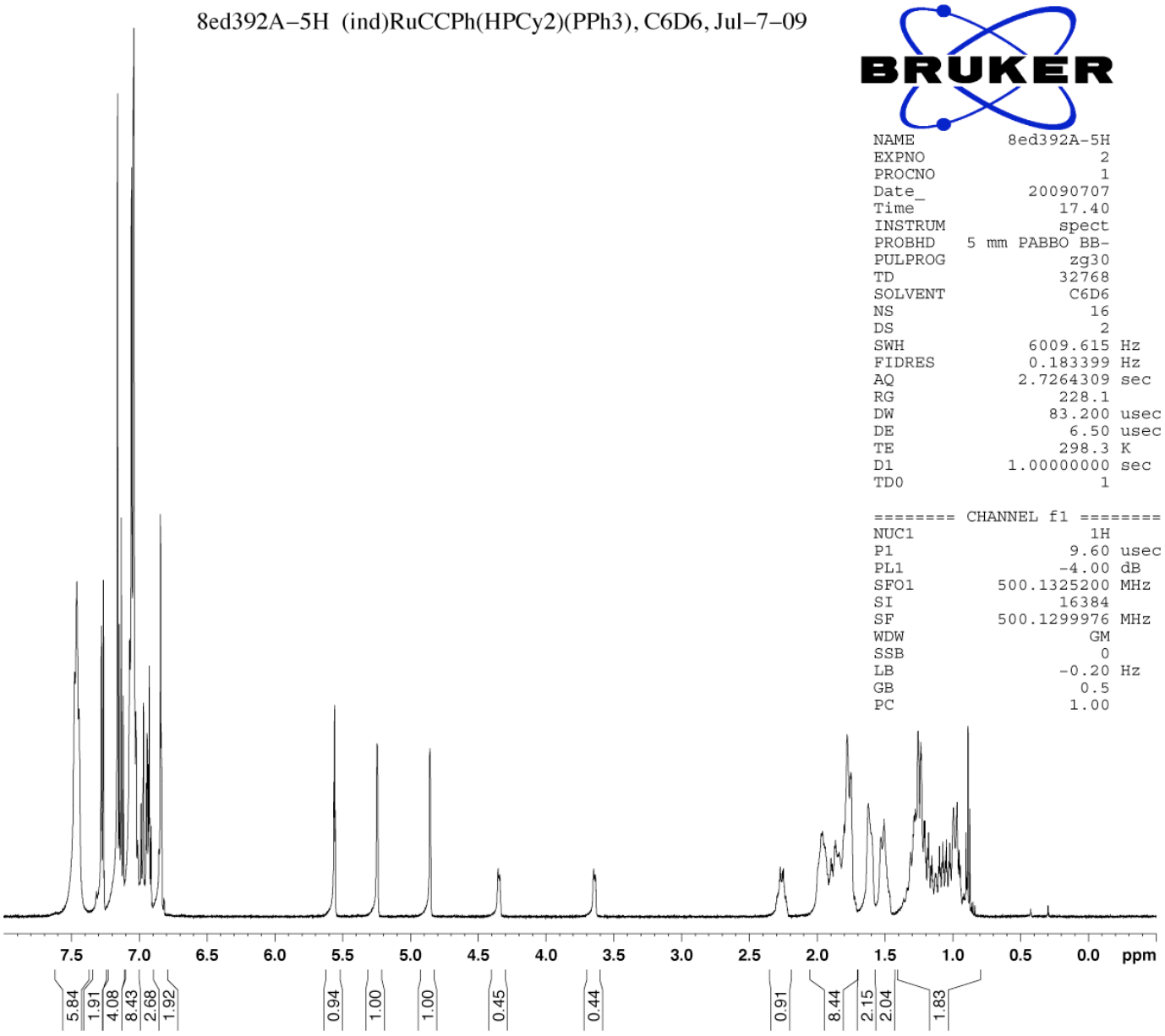
To a Schlenk flask containing a blue solution of [Ru(η^5-indenyl)(PPr$^i_2$)(PPh$_3$)] (**1b**, 77 mg, 0.13 mmol) in 5 mL toluene was added ~0.1 mL phenylacetylene (0.9 mmol). The resulting yellow solution was allowed to stir for 30 min before the solvent was evaporated under vacuum. Hexanes (10 mL) were added to the yellow powder and the resulting suspension was stirred for 1 h. The suspension was filtered and the resulting powder was washed with hexanes (3 × 10 mL) to give analytically pure [Ru(η^5-indenyl)(κ^2-PhC=CPhPPr$^i_2$)(PPh$_3$)] (**2b**, 64 mg, 0.092 mmol, 71% yield) as a yellow powder. EI-MS; *m/z* (relative intensity): 698 (50%) [M$^+$], 436

(12%) [M^+– PPh_3]. Anal. Calcd for $C_{41}H_{42}P_2Ru$: C, 70.57; H, 6.07. Found: C, 70.53; H, 6.10. Mp: 184 – 187 °C (dec).

Synthesis of [Ru(CCPh)(η^5-indenyl)(PCy_2H)(PPh_3)] (3a)

In a Schlenk flask equipped with a condenser, a mixture of [RuCl(η^5-indenyl)(PCy_2H)(PPh_3)] (54 mg, 0.076 mmol) and phenylacetylene (77 mg, 0.76 mmol) in methanol (15 mL) was heated to reflux for 15 minutes. To the resulting clear, orange solution was added 0.5 mL of KOH in methanol (0.01 M, 0.09 mmol). There was no immediate colour change. As the mixture cooled to RT, an orange precipitate formed, which lightened to yellow in colour as the mixture stood for 24h. The mixture was filtered and the resulting yellow powder was washed with hexanes (3 × 10 mL) and dried under vacuum, to give [Ru(CCPh)(η^5-indenyl)(PCy_2H)(PPh_3)] (**3a**, 40 mg, 0.051 mmol, 68% yield). EI-MS; *m/z* (relative intensity): 778 (24%) [M^+], 677 (5%) [M^+–CCPh], 580 (4%) [M^+–$HPCy_2$], 516 (4%) [M^+–PPh_3], 262 (100%) [PPh_3^+]; HR-MS (EI): exact mass (monoisotopic) calcd for $C_{47}H_{50}P_2Ru$, 778.24313; found, 778.24233 (1ppm error); Anal. Calcd for $C_{47}H_{50}P_2Ru$: C, 72.57; H, 6.48. Found: C, 71.98; H, 6.58.; mp: 167 – 169 °C (dec). IR: 2347 cm^{-1} (w. $\nu_{P\text{-}H}$), 2071 cm^{-1} (s, ν_{CC}).

^{1}H NMR spectrum of **3a** showing purity:



NMR scale reactions of 1a-b

Stock solutions (38 mM) of the appropriate reagents were prepared by dissolving 0.19 mmol of each reagent (phenylacetylene (21 μL), 1-hexyne (21 μL), or diphenylacetylene (34 mg)) in d_8-toluene in a 5 mL volumetric flask. In the glovebox solid [Ru(η^5-indenyl)(PR_2)(PPh_3)] (**1a**: 20 mg, 0.030 mmol; **1b**: 18 mg, 0.030 mmol) was placed in a sealable NMR tube. The stock solution (0.8 mL, 0.03 mmol, 1 equiv) was added to the tube, which was then capped with a Teflon needle valve adaptor, removed from the glovebox and connected to

a Schlenk line. Each sample was degassed using three freeze-pump-thaw cycles, and flame-sealed. The thawed solution was shaken to mix the reagents before the tube was placed in the NMR spectrometer.

Addition of phenylacetylene to 1a-b

The mixed reagents gave a dark yellow/orange solution, indicative of the formation of [Ru(η^5-indenyl)(κ^2-Ph<u>C</u>=CH<u>P</u>R$_2$)(PPh$_3$)] (**2a-b**), prior to the tube being placed in the NMR spectrometer. For **1a**: ^{31}P{^{1}H} NMR spectrum shows **2a** as the major product (94%), alkynyl complex **3a** (6%) as the minor product. For **1b**: ^{31}P{^{1}H} NMR spectrum shows **2b** as the major product (92%), alkynyl complex **3b** (7%) as the minor product and one unidentified product (1%).

Addition of 1-hexyne to 1a-b

The mixed reagents gave a dark yellow/orange solution, indicative of the formation of [Ru(η^5-indenyl)(κ^2-Bu^n<u>C</u>=CH<u>P</u>R$_2$)(PPh$_3$)] (**4a-b**), prior to the tube being placed in the NMR spectrometer. For **1a**: ^{31}P{^{1}H} NMR spectrum shows **4a** as the major product (96%), alkynyl complex **5a** (2%) as the minor product and two unidentified products (2%). For **1b**: ^{31}P{^{1}H} NMR spectrum shows **4b** as the major product (95%), alkynyl complex **5b** (3%) as the minor product and two unidentified products (2%).

Addition of diphenylacetylene to 1a-b

The mixed reagents maintained the dark blue colour of **1a-b** prior to the tube being placed in the NMR spectrometer. The progress of the reaction was monitored by ^{31}P{^{1}H} spectroscopy periodically for 10 (**1a**) or 17 (**1b**) days at which point the solution was dark black-yellow and contained mostly [Ru(η^5-indenyl)(κ^2-Ph<u>C</u>=CPh<u>P</u>R$_2$)(PPh$_3$)] (**6a-b**). For **1a**: ^{31}P{^{1}H} NMR spectrum recorded after 10 days shows **6a** as the major product (59%), along with 6-7 unidentified products (7%), free PPh$_3$ (1%), unreacted **1a** (22%), and the orthometallation product derived from **1a**, complex **7a** (11%)[1]. For **1b**: ^{31}P{^{1}H} NMR spectrum recorded after 17 days shows **6b** as the major product (64%), along with 7-8 unidentified products (11%), free PPh$_3$ (1%), unreacted **1b** (7%), and the the orthometallation product derived from **1b**, complex **7b** (17%)[1].

Preliminary NMR scale reactions relevant to catalytic hydrophosphination

In the glovebox, reagents and solvents in the specified amounts were added to sealable NMR tubes, which were then capped with Teflon needle valve adaptors, removed from the glovebox and connected to a Schlenk line. Each sample was degassed using three freeze-pump-thaw cycles, and flame-sealed.

Reaction of a 1:1 mixture of phenylacetylene and dicyclohexylphosphine with catalytic amounts of [RuCl(η^5-indenyl)(PCy_2H)(PPh_3)] and $KOBu^t$

The sealed sample contained an orange d_8-toluene solution of the Ru complex (0.010 mg, 0.014 mmol), $KOBu^t$ (3 mg, 0.03 mmol), $HPCy_2$ (0.2 mL of a 0.6 M solution in hexanes, 0.1 mmol), and phenylacetylene (14 mg, 0.14 mmol). Initial $^{31}P\{^1H\}$ NMR spectra showed unreacted starting materials as well as a small amount of [Ru(η^5-indenyl)(κ^2-Ph<u>C</u>=CH<u>P</u>Cy_2)(PPh_3)] (**2a**) and traces of PPh_3 and unidentified Ru-containing complexes. After the sample was heated at 65°C in an oil bath for ~21h, the solution remained red-orange. Aside from unreacted $HPCy_2$ and a small amount of unreacted starting Ru complex, the major products observed by $^{31}P\{^1H$ NMR) were complex **2a**, a second, unidentified Ru complex showing signals at 75.8 ppm (br s, $\omega_{1/2}$~100 Hz) and –29.4 (d, J_{PP}~31 Hz), free PPh_3 at –5.1 ppm, and a product giving a singlet at 65.2 ppm of comparable intensity to the PPh_3 signal.

Addition of phenylacetylene to 2a

The sealed sample contained a golden d_8-toluene solution of **2a** (0.010 mg, 0.013 mmol) and phenyacetylene (25 mg, 0.14 mmol). The mixture was monitored periodically by $^{31}P\{^1H\}$ and ^1H NMR over 24h at RT. No new products were observed.

Addition of dicyclohexylphosphine to 2a

The sealed sample contained a golden d_8-toluene solution of **2a** (0.010 mg, 0.013 mmol) and $HPCy_2$ (0.2 mL of a 0.6 M solution in hexanes, 0.1 mmol). The mixture was monitored periodically by $^{31}P\{^1H\}$ and ^1H NMR over 24h at RT. No new products were observed.

NMR data

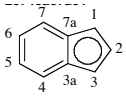
Table S1. $^{31}P\{^{1}H\}$ NMR data for new compounds at 300 K: δ in ppm (multiplicity in Hz).[a]

Complex	Number	Ru-PR_2-	Ru-PPh_3
[Ru(η^5-indenyl)(κ^2-PhC=CHPCy$_2$)(PPh$_3$)]	**2a**[b]	–36.9 (d, 28)	58.0 (d)
[Ru(η^5-indenyl)(κ^2-PhC=CHPPr$^i_2$)(PPh$_3$)]	**2b**[c]	–26.5 (d, 26)	57.9 (d)
[Ru(-C≡CPh)(η^5-indenyl)(PCy$_2$H)(PPh$_3$)]	**3a**	64.7 (d, 34)	58.1 (d)
[Ru(-C≡CPh)(η^5-indenyl)(PPr$^i_2$H)(PPh$_3$)]	**3b**	73.3 (d, 35)	57.1(d)
[Ru(η^5-indenyl)(κ^2-Bu^{n}C=CHPCy$_2$)(PPh$_3$)]	**4a**	–35.8 (d, 26)	55.9 (d)
[Ru(η^5-indenyl)(κ^2-Bu^{n}C=CHPPr$^i_2$)(PPh$_3$)]	**4b**	–24.8 (d, 26)	54.2 (d)
[Ru(-C≡CPBu^n)(η^5-indenyl)(PPr$^i_2$H)(PPh$_3$)]	**5a**	66.9 (d, 36)	58.2 (d)
[Ru(-C≡CBu^n)(η^5-indenyl)(PPr$^i_2$H)(PPh$_3$)]	**5b**	75.4 (d, 35)	58.0 (d)
[Ru(η^5-indenyl)(κ^2-PhC=CPhPCy$_2$)(PPh$_3$)]	**6a**	–18.6 (d, 29)	50.7 (d)
[Ru(η^5-indenyl)(κ^2-PhC=CPhPPr$^i_2$)(PPh$_3$)]	**6b**	–7.8 (d, 29)	50.3 (d)

[a] 145.8 MHz, sample in d_8-toluene, unless otherwise noted. [b]202.5 MHz, sample in d_1-chloroform. [c]202.5 MHz, sample in d_6-benzene.

Table S2. 500 MHz ^{1}H NMR data for isolated complexes at 300 K: δ in ppm (multiplicity, RI, J_{avg} or $\omega_{1/2}$ in Hz).[a]

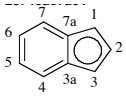
	η^5-C_9H_7				PPh_3	Others
	H_7, H_4	H_6, H_5	H_2	H_3, H_1		
2a[b]	7.46 (d, 1H, 9) 6.06 (d, 1H, 9)	6.85 (t, 1H, 7) 6.54 (t, 1H, 7)	5.07 (s, 1H)	5.29 (s, 1H) 4.27 (s, 1H)	H_m, H_p 7.34 (br s, 3H, 21), 7.14-7.09 (om, 3H) H_p 7.25-7.22 (m, 1H) H_m, H_o 7.00-6.94 (br m, 4H) H_o 7.40 (br, 2H, 19), 6.56-6.51(br, 2H, overlaps with H_5)	CH=CPh: 7.29-7.26 (m, 2H, H_o), 7.20 (dd, 1H, 7, 4, CH), 7.12-7.11 (m, 3H, H_m, H_p, overlaps with $H_{m,p}$ of PPh_3). Cy (PCy_2): 2.25-2.22 (m), 2.13-2.10 (m), 2.03-1.82 (m), 1.65-1.56 (m), 1.48-1.15 (m),1.00-0.88 (m), 0.79-0.74 (m), 0.51-0.44 (m), 0.09-0.01 (m)
2b[c]	7.55 (d, 1H, 8) 6.43 (d, 1H, 8)	6.93 (t, 1H, 8) 6.72 (t, 1H, 7)	5.20 – 5.19 (m, 1H)	5.36 (s, 1H) 4.59 (s, 1H)	H_m, H_p ~7.15-7.01 (br om, ~6H), 6.86 (br, ~3H, ~50) H_o 7.76 (br, 2H, 35), ~7.22 (br, 2H), ~6.73 (br, 2H, overlaps with H_5)	CH=CPh: 7.59-7.56 (m, 2H, H_o), 7.36 (dd, 1H, 7, 4, CH), 7.20-7.16 (m, 2H, H_m, overlaps with H_o of PPh_3), 7.13-7.10 (m, 1H, H_p) Pr^i (PPr^i_2): 2.20 (d sept, 1H, 10, 7, CH), 1.41 (dd, 3H, 15, 7, CH_3), 1.33 (dd, 3H, 15, 7, CH_3), 1.11 (d sept, 1H, 5, 7, CH), 0.68 (dd, 3H, 11, 7, CH_3), 0.62 (dd, 3H, 14, 7, CH_3)
3a[c]	6.99-6.82 (om, overlaps with Ru-CC-Ph H_p, 4H)		5.56 (t, 1H, 3)	5.25 (s, 1H) 4.86 (s, 1H)	H_o 7.53-7.42 (m, 6H) H_m, H_p 7.09-7.02 (m, 9H)	Ru-CC-Ph: 7.29-7.26 (dm, 2H, H_o), 7.15-7.12 (m, 2H, H_m), 6.99-6.82 (m, overlaps with indenyl H_{4-7}, 1H, H_p) H-PCy_2: 4.00 (d m, 1H, 315[d]) Cy (H-PCy_2): 2.34-2.22 (m, 1H), 2.05-1.71 (om, 7H), 1.69-1.57 (m, 2H), 1.57-1.44 (om, 3H), 1.38-0.86 (om, 9H)

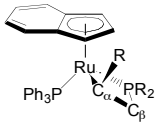
[a]Numbering scheme: 

, [b]Sample in $CDCl_3$, [c]Sample in C_6D_6, [d]From ^{31}P NMR spectrum.

Table S3. 125 MHz $^{13}C\{^1H\}$ NMR data for isolated complexes at 300 K: δ in ppm (multiplicity, J_{PC} or $\omega_{1/2}$ in Hz).[a]

	η^5-C_9H_7						PPh_3	Others
	C_6, C_5	C_7, C_4	C_{3a},C_{7a}	$\Delta\delta(C_{3a,7a})^b$	C_2	C_3, C_1		
2a[c,e]	123.9 (s) 121.2 (s)	124.6 (s) 120.8 (s)	111.1 (s) 105.6 (s)	–22.4 (av)	94.3 (s)	69.7 (d, 10) 66.2 (d, 11)	C_i 143.6 (d, 36), 136.0 (d, 44), ~134.7 (overlaps with C_o) C_o 135.7 (d, 13, 134.6 (d, 8), 132.7 (d, 10) C_m 127.4 (d, 10), 127.2 (d, 8, ~126.9 (overlaps with H_m of CH=CPh C_p 129.0 (br, 8), 128.4 (br, 11), 128.2 (br, 8)	CH=CPh: 180.3 (dd, 25, 15, C_α), 147.2 (d, 21 C_i), 127.3 (s, C_m), 127.0 (d, 1, C_o), 126.4 (s, C_p), 121.2 (dd, 45, 3, C_β) P*C*H: 40.2 (d, 20), 38.6 (d, 9) Other PCy_2: 32.4 (s), 30.0 (s), 29.1 (d, 8), 28.9 (s), 28.1 (d, 10), 27.9 (d, 11), 27.3 (d, 11), 27.1 (s), 27.0 (s), 26.4 (s)
2b[d,e]	124.7 (s) 121.8 (s)	125.3 (s) 121.7 (s)	112.4 (s) 106.8 (s)	–21.1 (av)	95.5 (s)	70.8 (d, 10) 66.2 (d, 11)	C_i 144.3 (br in baseline) C_o 136.4 (br, 56), 135.4, (br, 28), 133.3 (br, 42) C_m ~127.4 (br, overlaps with solvent peak) C_p 128.9 (d, 4)	CH=CPh: 182.2 (dd, 26, 14, C_α), 148.1 (d, 22, C_i), 128.0 (s, C_m), 127.8 (d, 2, C_o), 127.2 (s, C_p), 122.9 (dd, 44, 2, C_β) P*C*H: 28.0 (d, 9), 27.0 (d, 20) PCH(CH_3)$_2$: 22.7 (d, 2), 21.1 (d, 1), 19.0 (d, 7), 18.5 (s)
3a[d]	125.0 (os)	124.8 (s) 123.5 (s)	109.4 (d, 2) 109.0 (d, 2)	–21.5 (av)	91.7 (s)	70.6 (d, 3) 69.5 (s)	C_i 137.6 (d, 40) C_o 134.9 (d, 8) C_m 127.9 (d, 9) C_p 129.5 (s)	Ru-$C_\alpha C_\beta$-Ph: 131.8 (s, C_i), 131.4 (s, C_o), 123.7 (s, C_p), 114.5 (t, 25, C_α), 113.3 (s, C_β) P*C*H: 40.9 (d, 22), 37.7 (dd, 27, 2) Other $HPCy_2$: 34.0 (d, 5), 33.2(s), 32.7 (d, 3), 29.5 (s), 28.4 (s), 28.3 (d, 4), 28.2 (d, 4), 28.1 (s), 26.8 (2 x s)

[a]Numbering scheme: 

, [b]$\Delta\delta(C_{3a,7a}) = \delta(C_{3a,7a}(\eta\text{-indenyl complex})) - \delta(C_{3a,7a}(\eta\text{-sodium indenyl}))$. $\delta(C_{3a,7a})$ for sodium indenyl = 130.7 ppm.[3, 4] [c]Sample in $CDCl_3$, [d]Sample in C_6D_6, [e]General numbering scheme for metallacycle carbons: 

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