Photochemical studies of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ and $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Me$: formation of Si-H and C-H bond activation products.

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1. Experimental Materials.

The deuterated NMR solvents (d_6-benzene, d_8-toluene, d_8-THF and d_{12}-cyclohexane) were purchased from Sigma-Aldrich and dried over potassium, and stored under vacuum, in ampoules. Analytical / reagent grade solvents (ethanol, acetone, dibutyl ether) were obtained from Fisher Scientific and used without further purification. Toluene, diethyl ether, THF and cyclohexane were dried over sodium and distilled under nitrogen prior to storage in flame-dried ampoules. Ruthenium trichloride was purchased from Johnson-Matthey. Ethene, carbon monoxide, hydrogen, nitrogen and liquid nitrogen were supplied by BOC gases. All other reagents referred to within this section were purchased from Sigma-Aldrich, and used without further purification

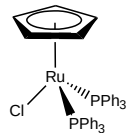
2. NMR Measurements.

NMR data was collected on Bruker DRX 400, DMX 400 (^{1}H 400.13 MHz, ^{13}C 100.62 MHz, ^{31}P 162 MHz, ^{29}Si 79.49 MHz) or AV 700 (^{1}H 700.13 MHz, ^{13}C 176.05 MHz, ^{31}P 283.46 MHz) spectrometers. ^{1}H NMR spectra were referenced relative to the residual proton signals of the deuterated solvents[1] benzene δ 7.15, toluene δ 2.09, THF δ 3.58, cyclohexane δ 1.38, acetone δ 2.05. ^{13}C NMR spectra were referenced relative to the solvent peaks: benzene δ 128.39, toluene δ 20.40, THF δ 25.37, cyclohexane δ 26.43, acetone δ 29.92. ^{31}P resonances were referenced relative to free PPh_3, which was set to δ -6.4, and ^{29}Si signals were referenced to external TMS at δ 0.
Standard pulse sequences were used to obtain 1D ^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H}, ^{29}Si{^{1}H},^{1}H COSY, ^{1}H/^{31}P HMQC, ^{1}H/^{13}C HMQC and ^{1}H/^{29}Si HMQC data.[2] For 1D selective NOE and 2D NOE experiments, the pulse sequences were used as reported in the literature.[3-5]

3. General method of NMR sample preparation.

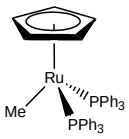
All NMR tubes were charged with 5 mg (unless otherwise stated) of the respective compound under test, and degassed using a high vacuum line prior to transferring to the glovebox (MBRAUN Unilab). Degassed liquid reagents were added to the NMR tube in the glove box, and the sample depth was then made up to 3 cm using the appropriate deuterated solvent. The samples were then brought out of the glovebox and degassed using freeze/thaw methods, to place the sample under vacuum. Prior to lowering the temperature, samples were checked via 1D ^{1}H and ^{31}P{^{1}H} NMR methods at 298 K.

4. Synthesis of $CpRu(PPh_3)_2Cl$ (1).[6] PPh_3 (2.79 g) was dissolved in 200 ml of dry, degassed, ethanol. The solution was heated at reflux (351 K) for 30 minutes under nitrogen. A second solution containing $RuCl_3$ (0.52 g) dissolved in 40 ml of dry and degassed ethanol was then heated at reflux for 30 minutes under a nitrogen atmosphere. The $RuCl_3$ solution was cooled and freshly cracked cyclopentadiene (2 ml) added dropwise. The $RuCl_3$ / cyclopentadienyl solution was then slowly added to the refluxing PPh_3 / ethanol solution with continual stirring. Upon cooling and filtering, a bright orange precipitate of **1** was obtained which proved sufficiently pure as to be used in the subsequent reactions described here.



NMR data for $CpRu(PPh_3)_2Cl$ (**1**): ^{1}H NMR 4.27 (s, 5H, η^5-$C_5\underline{H}_5$), 7.02 (m, *p*-$P(C_6\underline{H}_5)_3$), 7.16 (m, *m*-$P(C_6\underline{H}_5)_3$), 7.74 (m, 12H, $|^3J_{PH}|$ = 8.1 Hz, *o*-$P(C_6\underline{H}_5)_3$). ^{13}C{^{1}H} NMR 81.2 (s, η^5-$\underline{C}_5H_5$), 127.9 (t, $|^3J_{PC}|$ = 9.4 Hz, *m*-$P(\underline{C}_6H_5)_3$), 128.7 (s, *p*-$P(\underline{C}_6H_5)_3$), 133.3 (t, $|^2J_{PC}|$ = 10.9 Hz, *o*-$P(\underline{C}_6H_5)_3$), 141.5 (dd, $|^3J_{PC}|$ = 13.5 Hz, $|^1J_{PC}|$ = 33.6 Hz, *i*-$P(\underline{C}_6H_5)_3$). ^{31}P{^{1}H} NMR 39.6 (s, $\underline{P}(C_6H_5)_3$).

5. Synthesis of $CpRu(PPh_3)_2Me$ (2).[7, 8] To a Schlenk tube charged with, **1** (0.35 g) under nitrogen thoroughly dry and degassed toluene (50 ml) was added. Following continuous stirring at room temperature an ether suspension of methyllithium (6 ml, 1.6 mol) was cautiously added. After 4 hours, any remaining methyllithium was quenched by degassed water and the organic layer recovered and dried over magnesium sulphate. Volatiles were then removed *in vacuo* to yield a light yellow solid, **2**, which showed clean ^{1}H and ^{31}P{^{1}H} NMR spectra.

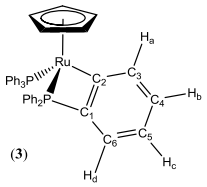


NMR data for $CpRu(PPh_3)_2Me$ (**2**): ^{1}H NMR δ 0.97 (t, 3H, $|^3J_{PH}|$ = 5.7 Hz, Ru-C$\underline{H}_3$), 4.35 (s, 5H, η^5-$C_5\underline{H}_5$), 6.91 (m, *p*-$P(C_6\underline{H}_5)_3$), 6.95 (m, *m*-$P(C_6\underline{H}_5)_3$), 7.34 (m, *o*-$P(C_6\underline{H}_5)_3$). ^{13}C{^{1}H} NMR δ -30.1 (t, $|^2J_{PC}|$ = 10.8 Hz, Ru-$\underline{C}H_3$), 84.2 (s, η^5-$\underline{C}_5H_5$), 126.8 (t, $|^3J_{PC}|$ = 10.3 Hz, *m*-$P(\underline{C}_6H_5)_3$), 127.4 (s, *p*-$P(\underline{C}_6H_5)_3$), 133.7 (t, $|^2J_{PC}|$

= 16.2 Hz, *o*-P(C$_6$H$_5$)$_3$), 141.2 (dd, $|^3J_{PC}|$ = 13.6 Hz, $|^1J_{PC}|$ = 34.9 Hz, *i*-P(C$_6$H$_5$)$_3$). $^{31}P\{^1H\}$ NMR δ 55.3 (s, P(C$_6$H$_5$)$_3$).

6. Synthesis of CpRu(κ^2-2-C$_6$H$_4$PPh$_2$)(PPh$_3$) (3).[9] A flask was charged with CpRu(PPh$_3$)$_2$Me (250 mg) and decalin (300 ml) and placed under N$_2$. The contents of the flask were heated to 368 K with stirring and after 48 hours, the liquid removed *in vacuo*. The remaining solid was then dried overnight before being dissolved in dry cyclohexane and filtered through celite. The cyclohexane was then removed and the product **3** was obtained.

An NMR scale sample of **3** was prepared by UV irradiation of a 5 mg sample of CpRu(PPh$_3$)$_2$Me contained in d$_8$-cyclohexane using a Hg-Xe arc UV lamp for 12 hours. ^{31}P NMR spectroscopy suggested complete conversion was achieved.

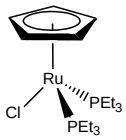


(3)

NMR data for CpRu(κ^2-2-C$_6$H$_4$PPh$_2$)(PPh$_3$) (**3**): ^1H NMR δ 4.27 (s, 5H, η^5-C$_5$H$_5$), 6.72 (m, *p*-P(C$_6$H$_5$)$_3$), 6.82 (m, *m*-P(C$_6$H$_5$)$_3$), 6.98 (m, H$_b$), 7.11 (m, H$_c$), 7.33 (m, H$_d$), 7.33 (m, *o*-P(C$_6$H$_5$)$_3$), 7.53 (m, 1H, H$_a$). $^{13}C\{^1H\}$ NMR δ 80.4 (s, η^5-C$_5$H$_5$), 125.9 (d, C$_3$), 127.3 (s, *m*-P(C$_6$H$_5$)$_3$), 128.7 (s, C$_5$), 129.7 (d, $|^3J_{PC}|$ = 10.3 Hz, *p*-P(C$_6$H$_5$)$_3$), 134.2 (t, C$_4$), 139.8 (d, C$_6$), 142.7 (d, $|^2J_{PC}|$ = 16.2 Hz, *o*-P(C$_6$H$_5$)$_3$), 143.6 (dd, $|^3J_{PC}|$ = 13.6 Hz, $|^1J_{PC}|$ = 34.9 Hz, *i*-P(C$_6$H$_5$)$_3$), 144.5 (d, C$_2$), 155.3 (d, C$_1$). $^{31}P\{^1H\}$ NMR δ -16.9 (d, $|^2J_{PP}|$ = 33.8 Hz, P(Ph)$_2$(κ^2-2-C$_6$H$_4$)), 63.5, (d, $|^2J_{PP}|$ = 33.8 Hz, P(C$_6$H$_5$)$_3$).

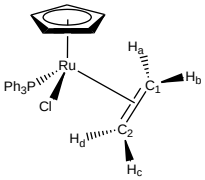
7. NMR data for complexes 4 – 23 as described in the main manuscript

CpRu(PEt$_3$)$_2$Cl (**4**): ^1H NMR δ 0.91 (m, 18H, $|^3J_{PH}|$ = 4.1 Hz, P(CH$_2$-CH$_3$)$_3$), 1.16 & 1.21 (m, 12H, $|^2J_{PH}|$ = 15.9 Hz, P(CH$_2$-CH$_3$)$_3$), 4.17 (s, 5H, η^5-C$_5$H$_5$) $^{13}C\{^1H\}$ NMR δ 9.7 (s, P(CH$_2$-CH$_3$)$_3$), 20.4 (t, $|^1J_{PC}|$ = 12.0 Hz, P(CH$_2$-CH$_3$)$_3$), 79.3 (s, η^5-C$_5$H$_5$) $^{31}P\{^1H\}$ NMR δ 46.8 (s, P(CH$_2$-CH$_3$)$_3$).

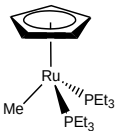


CpRu(PPh$_3$)(PEt$_3$)Cl (**5**): ^1H NMR δ 0.92 (m, 9H, P(CH$_2$-CH$_3$)$_3$), 1.15 & 1.83 (m, 6H, P(CH$_2$-CH$_3$)$_3$), 4.21 (s, 5H, η^5-C$_5$H$_5$), 7.02 (m, *p*-P(C$_6$H$_5$)$_3$), 7.08 (m, *m*-P(C$_6$H$_5$)$_3$), 7.82 (m, 6H, $|^3J_{PH}|$ = 8.4 Hz, *o*-P(C$_6$H$_5$)$_3$). $^{13}C\{^1H\}$ NMR δ 10.1 (t, $|^2J_{PC}|$ = 4.3 Hz, P(CH$_2$-CH$_3$)$_3$), 19.9 (t, $|^1J_{PC}|$ = 15.7 Hz, P(CH$_2$-CH$_3$)$_3$), 79.8 (s, η^5-C$_5$H$_5$), 128.2 (d, $|^3J_{PC}|$ = 9.3 Hz, *m*-P(C$_6$H$_5$)$_3$), 129.1 (s, *p*-P(C$_6$H$_5$)$_3$), 134.4 (d, $|^2J_{PC}|$ = 10.9 Hz, *o*-P(C$_6$H$_5$)$_3$), 140.7 (dd, $|^3J_{PC}|$ = 12.0 Hz, $|^1J_{PC}|$ = 33.2 Hz, *i*-P(C$_6$H$_5$)$_3$). $^{31}P\{1H\}$ NMR δ 27.8 (d, $|^2J_{PC}|$ = 44.0 Hz, P(CH$_2$-CH$_3$)$_3$), 45.5 (d, $|^2J_{PC}|$ = 44.0 Hz, P(C$_6$H$_5$)$_3$).

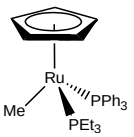
CpRu(PPh$_3$)(η^2-C$_2$H$_4$)Cl (**6**): ^1H NMR δ 0.56 (br, 1H, H$_c$), 1.18 (br, 1H, H$_b$), 2.23 (br, 1H, H$_a$), 2.64 (br, 1H, H$_d$), 4.23 (s, 5H, η^5-C$_5$H$_5$), 7.07 (m, *p*-P(C$_6$H$_5$)$_3$), 7.19 (m, *m*-P(C$_6$H$_5$)$_3$), 7.62 (m, *o*-P(C$_6$H$_5$)$_3$). $^{13}C\{^1H\}$ NMR δ 38.3 (t, $|^2J_{PC}|$ = 8.4 Hz, C$_1$), 41.9 (t, $|^2J_{PC}|$ = 8.4 Hz, C$_2$), 80.6 (s, η^5-C$_5$H$_5$), 127.5 (d, $|^3J_{PC}|$ = 8.9 Hz, *m*-P(C$_6$H$_5$)$_3$), 128.4 (s, *p*-P(C$_6$H$_5$)$_3$), 133.7 (d, $|^2J_{PC}|$ = 10.6 Hz, *o*-P(C$_6$H$_5$)$_3$), 140.3 (d, $|^1J_{PC}|$ = 42.3 Hz, *i*-P(C$_6$H$_5$)$_3$). $^{31}P\{^1H\}$ NMR δ 56.2 (s, P(C$_6$H$_5$)$_3$).



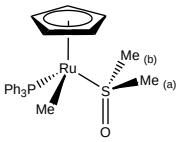
CpRu(PEt$_3$)$_2$Me (**7**): ^1H NMR δ 0.15 (t, 3H, $|^3J_{PH}|$ = 5.8 Hz, Ru-CH$_3$), 0.92 (br, P(CH$_2$-CH$_3$)$_3$), 1.48 & 1.90 (m, P(CH$_2$-CH$_3$)$_3$), 4.54 (s, 5H, η^5-C$_5$H$_5$). $^{13}C\{^1H\}$ NMR δ -25.2 (t, $|^2J_{PC}|$ = 9.7 Hz, Ru-CH$_3$), 28.0 (t, $|^2J_{PC}|$ = 4.2 Hz, P(CH$_2$-CH$_3$)$_3$), 31.8 (t, $|^1J_{PC}|$ = 16.2 Hz, P(CH$_2$-CH$_3$)$_3$), 79.9 (s, η^5-C$_5$H$_5$). $^{31}P\{^1H\}$ NMR δ 40.5 (s, P(CH$_2$-CH$_3$)$_3$).



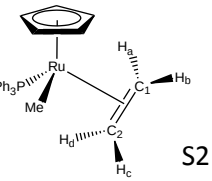
CpRu(PPh$_3$)(PEt$_3$)Me (**8**): ^1H NMR δ 0.39 (t, 3H, $|^3J_{PH}|$ = 5.6 Hz, Ru-CH$_3$), 0.83 (br, 9H, $|^3J_{HH}|$ = 7.5 Hz, P(CH$_2$-CH$_3$)$_3$), 1.39 & 1.50 (m, $|^3J_{HH}|$ = 7.3 Hz, P(CH$_2$-CH$_3$)$_3$), 4.49 (s, 5H, η^5-C$_5$H$_5$), 6.89 (m, *p*-P(C$_6$H$_5$)$_3$), 7.09 (m, *m*-P(C$_6$H$_5$)$_3$), 7.61 (m, *o*-P(C$_6$H$_5$)$_3$). $^{13}C\{^1H\}$ NMR δ -26.7 (t, $|^2J_{PC}|$ = 10.1 Hz, Ru-CH$_3$), 13.5 (t, $|^2J_{PC}|$ = 4.3 Hz, P(CH$_2$-CH$_3$)$_3$), 26.2 (t, $|^1J_{PC}|$ = 16.1 Hz, P(CH$_2$-CH$_3$)$_3$), 81.8 (s, η^5-C$_5$H$_5$), 127.8 (t, $|^3J_{PC}|$ = 10.5 Hz, *m*-P(C$_6$H$_5$)$_3$), 128.5 (s, *p*-P(C$_6$H$_5$)$_3$), 133.4 (t, $|^2J_{PC}|$ = 15.7 Hz, *o*-P(C$_6$H$_5$)$_3$), 141.5 (dd, $|^3J_{PC}|$ = 12.4 Hz, $|^1J_{PC}|$ = 34.7 Hz, *i*-P(C$_6$H$_5$)$_3$). $^{31}P\{^1H\}$ NMR δ 35.2 (d, $|^2J_{PP}|$ = 39.3 Hz, P(CH$_2$-CH$_3$)$_3$), 62.9 (d, $|^2J_{PP}|$ = 39.3 Hz, P(C$_6$H$_5$)$_3$).



CpRu(PPh$_3$)(DMSO)Me (**9**): ^1H NMR δ -0.02 (d, 3H, $|^3J_{PH}|$ = 5.8 Hz, Ru-CH$_3$), 2.37 (s, 3H, S-CH$_3$ (a)), 2.56 (s, 3H, S-CH$_3$ (b)), 4.43 (s, 5H, η^5-C$_5$H$_5$), 7.32 (m, *p*-P(C$_6$H$_5$)$_3$), 7.34 (m, *m*-P(C$_6$H$_5$)$_3$), 7.56 (m, 6H, *o*-P(C$_6$H$_5$)$_3$). $^{13}C\{^1H\}$ NMR δ -27.3 (d, $|^3J_{PC}|$ = 10.2 Hz, Ru-CH$_3$), 46.5 (s, S-CH$_3$ (a)), 48.2 (s, S-CH$_3$ (b)), 83.3 (s, η^5-C$_5$H$_5$), 127.45 (br, *m*-P(C$_6$H$_5$)$_3$), 128.24 (s, *p*-P(C$_6$H$_5$)$_3$), 137.30 (d, $|^2J_{PC}|$ = 16.4 Hz, *o*-P(C$_6$H$_5$)$_3$), 141.0 (d, $|^1J_{PC}|$ = 44.7 Hz, *i*-P(C$_6$H$_5$)$_3$). $^{31}P\{^1H\}$ NMR δ 59.0 (s, P(C$_6$H$_5$)$_3$).

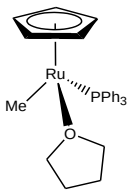


CpRu(PPh$_3$)(η^2-C$_2$H$_4$)Me (**10**): ^1H NMR δ 0.43 (d, 3H, $|^3J_{PH}|$ = 6.7 Hz, Ru-CH$_3$), 0.67 (m, 1H, H$_c$), 1.28 (m, 1H, H$_b$), 2.54 (m, 1H, H$_a$), 2.81 (m, 1H, H$_d$), 4.63 (s, 5H, η^5-C$_5$H$_5$), 7.06 (m, *p*-P(C$_6$H$_5$)$_3$), 7.17 (m, *m*-P(C$_6$H$_5$)$_3$), 7.53 (m, 6H, *o*-P(C$_6$H$_5$)$_3$). $^{13}C\{^1H\}$ NMR δ -28.3 (d, $|^2J_{PC}|$ = 10.2 Hz, Ru-CH$_3$), 37.8 (d, $|^2J_{PC}|$ = 7.6 Hz, C$_1$), 42.5 (d, $|^2J_{PC}|$ = 7.6 Hz, C$_2$), 82.3 (s, η^5-C$_5$H$_5$), 127.3 (d, $|^3J_{PC}|$ =

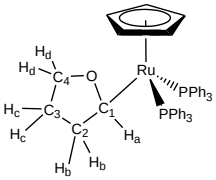


10.5 Hz, *m*-P(C$_6$H$_5$)$_3$), 128.4 (s, *p*-P(C$_6$H$_5$)$_3$), 133.2 (d, $|^2J_{PC}|$ = 16.3 Hz, *o*-P(C$_6$H$_5$)$_3$), 140.2 (d, $|^1J_{PC}|$ = 45.4 Hz, *i*-P(C$_6$H$_5$)$_3$). $^{31}P\{^1H\}$ NMR δ 67.7 (s, P(C$_6$H$_5$)$_3$).

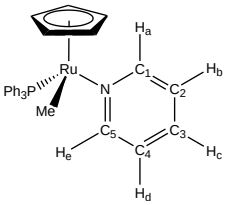
CpRu(PPh$_3$)Me(THF) (**11**): ^1H NMR 0.16 (d, 3H, Ru-CH$_3$), 4.59 (s, 5H, η^5-C$_5$H$_5$), 7.08 (m, *p*-P(C$_6$H$_5$)$_3$), 7.12 (m, *m*-P(C$_6$H$_5$)$_3$), 7.53 (m, $|^3J_{PH}|$ = 5.9 Hz, *o*-P(C$_6$H$_5$)$_3$). $^{13}C\{^1H\}$ NMR -28.7 (d, $|^2J_{PC}|$ = 10.8 Hz, Ru-CH$_3$), 84.4 (s, η^5-C$_5$H$_5$), 126.5 (d, $|^3J_{PC}|$ = 10.4, *m*-P(C$_6$H$_5$)$_3$), 127.6 (s, *p*-P(C$_6$H$_5$)$_3$), 133.8 (d, $|^2J_{PC}|$ = 16.0 Hz, *o*-P(C$_6$H$_5$)$_3$), 141.1 (d, $|^1J_{PC}|$ = 45.3 Hz, *m*-P(C$_6$H$_5$)$_3$). $^{31}P\{^1H\}$ NMR 61.3 (s, P(C$_6$H$_5$)$_3$).



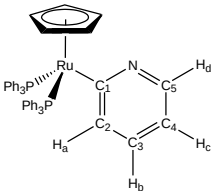
CpRu(PPh$_3$)$_2$(2-C$_4$H$_7$O) (**12**): ^1H NMR 1.75 & 1.94 (t, $|^3J_{HH}|$ = 6.2 Hz, H$_c$), 2.19 & 2.41 (q, 2H, $|^3J_{HH}|$ = 5.4 Hz, H$_b$), 3.70 & 3.86 (q, $|^3J_{HH}|$ = 5.4 Hz, H$_d$), 4.23 (s, 5H, η^5-C$_5$H$_5$), 5.37 (dt, 1H, $|^3J_{HH}|$ = 1.7 $|^3J_{PH}|$ = 16.3 Hz, H$_a$), 7.09 (m, *p*-P(C$_6$H$_5$)$_3$), 7.16 (m, *m*-P(C$_6$H$_5$)$_3$), 7.38 (m, 12, *o*-P(C$_6$H$_5$)$_3$). $^{13}C\{^1H\}$ NMR 50.9 (s, C$_3$), 61.4 (t, $|^3J_{PC}|$ = 3.2 Hz, C$_2$), 82.7 (s, η^5-C$_5$H$_5$), 84.3 (s, C$_4$), 127.3 (t, $|^3J_{PC}|$ = 10.6 Hz, *m*-P(C$_6$H$_5$)$_3$), 128.1 (s, *p*-P(C$_6$H$_5$)$_3$), 133.5 (t, $|^2J_{PC}|$ = 16.5 Hz, *o*-P(C$_6$H$_5$)$_3$), 140.4 (dd, $|^3J_{PC}|$ = 13.3 Hz, $|^1J_{PC}|$ = 35.0 Hz, *i*-P(C$_6$H$_5$)$_3$), 145.7 (t, $|^2J_{PC}|$ = 17.8 Hz, C$_1$). $^{31}P\{^1H\}$ NMR 41.9 (s, P(C$_6$H$_5$)$_3$).



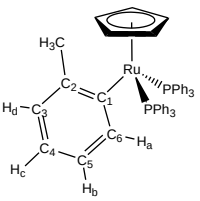
CpRu(PPh$_3$)(NC$_5$H$_5$)Me (**13**): ^1H NMR δ 0.16 (d, 3H, Ru-CH$_3$), 4.59 (s, 5H, η^5-C$_5$H$_5$), 7.08 (m, *p*-P(C$_6$H$_5$)$_3$), 7.12 (m, *m*-P(C$_6$H$_5$)$_3$), 7.53 (m, $|^3J_{PH}|$ = 5.9 Hz, *o*-P(C$_6$H$_5$)$_3$). $^{13}C\{^1H\}$ NMR δ -28.7 (d, $|^2J_{PC}|$ = 10.8 Hz, Ru-CH$_3$), 84.4 (s, η^5-C$_5$H$_5$), 126.5 (d, $|^3J_{PC}|$ = 10.4 Hz, *m*-P(C$_6$H$_5$)$_3$), 127.6 (s, *p*-P(C$_6$H$_5$)$_3$), 133.8 (d, $|^2J_{PC}|$ = 16.0 Hz, *o*-P(C$_6$H$_5$)$_3$), 141.1 (d, $|^1J_{PC}|$ = 45.3 Hz, *m*-P(C$_6$H$_5$)$_3$). $^{31}P\{^1H\}$ NMR δ 61.3 (s, P(C$_6$H$_5$)$_3$).



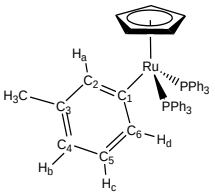
CpRu(PPh$_3$)$_2$(2-C$_5$H$_4$N) (**14**): ^1H NMR δ 1.75 & 1.94 (t, $|^3J_{HH}|$ = 6.2 Hz, H$_c$), 2.19 & 2.41 (q, 2H, $|^3J_{HH}|$ = 5.4 Hz, H$_b$), 3.70 & 3.86 (q, $|^3J_{HH}|$ = 5.4 Hz, H$_d$), 4.23 (s, 5H, η^5-C$_5$H$_5$), 5.37 (dt, 1H, $|^3J_{HH}|$ = 1.7 Hz, $|^3J_{PH}|$ = 16.3 Hz, H$_a$), 7.09 (m, *p*-P(C$_6$H$_5$)$_3$), 7.16 (m, *m*-P(C$_6$H$_5$)$_3$), 7.38 (m, 12H, *o*-P(C$_6$H$_5$)$_3$). $^{13}C\{^1H\}$ NMR δ 50.9 (s, C$_3$), 61.4 (t, $|^3J_{PC}|$ = 3.2 Hz, C$_2$), 82.7 (s, η^5-C$_5$H$_5$), 84.3 (s, C$_4$), 127.3 (t, $|^3J_{PC}|$ = 10.6 Hz, *m*-P(C$_6$H$_5$)$_3$), 128.1 (s, *p*-P(C$_6$H$_5$)$_3$), 133.5 (t, $|^2J_{PC}|$ = 16.5 Hz, *o*-P(C$_6$H$_5$)$_3$), 140.4 (dd, $|^3J_{PC}|$ = 13.3 Hz, $|^1J_{PC}|$ = 35.0 Hz, *i*-P(C$_6$H$_5$)$_3$), 145.7 (t, $|^2J_{PC}|$ = 17.8 Hz, C$_1$). $^{31}P\{^1H\}$ NMR δ 41.9 (s, P(C$_6$H$_5$)$_3$).



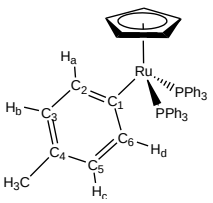
CpRu(PPh$_3$)$_2$(*o*-tolyl) (**15a**): ^1H NMR δ 2.31 (s, CH$_3$), 4.37 (s, η^5-C$_5$H$_5$), 6.97 (br, H$_d$), 7.01 (m, *p*-P(C$_6$H$_5$)$_3$), 7.10 (m, *m*-P(C$_6$H$_5$)$_3$), 7.13 (br, H$_c$), 7.37 (m, *o*-P(C$_6$H$_5$)$_3$), 7.41 (br, 1, H$_b$), 7.54 (br, 1, H$_a$). $^{13}C\{^1H\}$ NMR δ 21.7 (s, CH$_3$), 85.9 (s, η^5-C$_5$H$_5$), 112.1 (t, $|^4J_{PC}|$ = 3.3 Hz, C$_5$), 121.3 (t, $|^3J_{PC}|$ = 17.8 Hz, C$_6$), 127.4 (s, C$_4$), 127.5 (d, $|^3J_{PC}|$ = 10.3 Hz, *m*-P(C$_6$H$_5$)$_3$), 128.1 (s, *p*-P(C$_6$H$_5$)$_3$), 133.4 (d, $|^2J_{PC}|$ = 16.4 Hz, *o*-P(C$_6$H$_5$)$_3$), 136.5 (d, $|^4J_{PC}|$ = 4.7 Hz, C$_3$), 140.8 (dd, $|^3J_{PC}|$ = 14.3 Hz, $|^1J_{PC}|$ = 34.7 Hz, *i*-P(C$_6$H$_5$)$_3$), 142.8 (t, $|^3J_{PC}|$ = 14.6 Hz, C$_2$), 149.7 (t, $|^2J_{PC}|$ = 21.2 Hz, C$_1$). $^{31}P\{^1H\}$ NMR δ 50.2 (s, P(C$_6$H$_5$)$_3$).



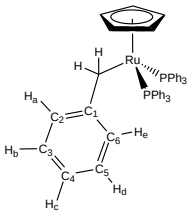
CpRu(PPh$_3$)$_2$(*m*-tolyl) (**15b**): ^1H NMR δ 2.36 (s, CH$_3$), 4.34 (s, η^5-C$_5$H$_5$), 6.94 (br, H$_c$), 7.01 (m, *p*-P(C$_6$H$_5$)$_3$), 7.07 (br, H$_b$), 7.10 (m, *m*-P(C$_6$H$_5$)$_3$), 7.12 (br, H$_a$), 7.15 (br, H$_d$), 7.35 (m, *o*-P(C$_6$H$_5$)$_3$). $^{13}C\{^1H\}$ NMR δ 21.2 (s, CH$_3$), 85.6 (s, η^5-C$_5$H$_5$), 112.5 (d, $|^4J_{PC}|$ = 2.7 Hz, C$_5$), 119.2 (s, C$_4$), 127.4 (d, $|^3J_{PC}|$ = 10.3 Hz, *m*-P(C$_6$H$_5$)$_3$), 128.1 (s, *p*-P(C$_6$H$_5$)$_3$), 133.2 (t, $|^2J_{PC}|$ = 16.4 Hz, *o*-P(C$_6$H$_5$)$_3$), 133.9 (t, $|^4J_{PC}|$ = 4.4 Hz, C$_3$), 140.6 (dd, $|^3J_{PC}|$ = 14.3 Hz, $|^1J_{PC}|$ = 37.7 Hz, *i*-P(C$_6$H$_5$)$_3$), 141.3 (t, $|^3J_{PC}|$ = 19.6 Hz, C$_6$), 146.4 (t, $|^3J_{PC}|$ = 14.3 Hz, C$_2$), 151.6 (t, $|^2J_{PC}|$ = 21.6 Hz, C$_1$). $^{31}P\{^1H\}$ NMR δ 52.3 (s, P(C$_6$H$_5$)$_3$)



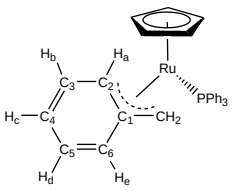
CpRu(PPh$_3$)$_2$(*p*-tolyl) (**15c**): ^1H NMR δ 2.38 (s, CH$_3$), 4.30 (s, η^5-C$_5$H$_5$), 6.94 (m, H$_a$ & H$_d$), 7.01 (m, *p*-P(C$_6$H$_5$)$_3$), 7.11 (m, *m*-P(C$_6$H$_5$)$_3$), 7.21 (m, H$_b$ & H$_c$), 7.34 (m, *o*-P(C$_6$H$_5$)$_3$). $^{13}C\{^1H\}$ NMR δ20.6 (s, CH$_3$), 85.2 (s, η^5-C$_5$H$_5$), 112.3 (s, C$_4$), 124.8 (t, $|^4J_{PC}|$ = 4.5 Hz, C$_3$ & C$_5$), 127.4 (d, $|^3J_{PC}|$ = 10.3 Hz, *m*-P(C$_6$H$_5$)$_3$), 128.1 (s, *p*-P(C$_6$H$_5$)$_3$), 133.7 (t, $|^2J_{PC}|$ = 16.4 Hz, *o*-P(C$_6$H$_5$)$_3$), 140.5 (dd, $|^3J_{PC}|$ = 14.2 Hz, $|^1J_{PC}|$ = 37.7 Hz, *i*-P(C$_6$H$_5$)$_3$), 144.7 (t, $|^3J_{PC}|$ = 14.3 Hz, C$_2$ & C$_6$), 149.8 (t, $|^2J_{PC}|$ = 21.6 Hz, C$_1$). $^{31}P\{^1H\}$ NMR δ 52.6 (s, P(C$_6$H$_5$)$_3$).



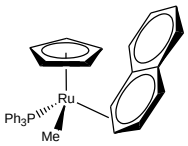
CpRu(PPh$_3$)$_2$(CH$_2$C$_6$H$_5$) (**16**): ^{1}H NMR δ 3.07 (t, $|^3J_{PH}|$ = 7.3 Hz, C$\underline{H}_2$-Ph), 4.19 (s, η^5-C$_5\underline{H}_5$), 6.98 (m, *p*-P(C$_6\underline{H}_5$)$_3$), 7.07 (m, $\underline{H}_c$), 7.07 (m, *m*-P(C$_6\underline{H}_5$)$_3$), 7.28 (m, *o*-P(C$_6\underline{H}_5$)$_3$), 46 (m, $\underline{H}_b$ & $\underline{H}_d$), 7.53 (m, $\underline{H}_a$ & $\underline{H}_e$). ^{13}C{^{1}H} NMR δ 3.01 (t, $|^2J_{PC}|$ = 5.5 Hz, $\underline{C}$H$_2$-Ph), 84.7 (s, η^5-$\underline{C}_5$H$_5$), 120.6 (s, $\underline{C}_3$ & $\underline{C}_5$), 120.6 (s, $\underline{C}_4$), 127.4 (d, $|^3J_{PC}|$ = 10.4 Hz, *m*-P(C$_6\underline{H}_5$)$_3$), 128.7 (s, *p*-P(C$_6\underline{H}_5$)$_3$), 133.5 (t, $|^2J_{PC}|$ = 12.7 Hz, *o*-P(C$_6\underline{H}_5$)$_3$), 138.2 (s, $\underline{C}_2$ & $\underline{C}_6$), 141.4 (dd, $|^3J_{PC}|$ = 14.8 Hz, $|^1J_{PC}|$ = 37.2 Hz, *i*-P(C$_6\underline{H}_5$)$_3$), 145.0 (s, $\underline{C}_1$). ^{31}P{^{1}H} NMR δ 51.6 (s, P(C$_6\underline{H}_5$)$_3$).



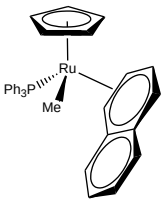
CpRu(PPh$_3$)(η^3-CH$_2$C$_6$H$_5$) (**17**): ^{1}H NMR δ 2.67 (m, $|^3J_{PH}|$ = 7.2 Hz, $\underline{H}_a$), 4.02 (m, $|^3J_{PH}|$ = 7.2 Hz, C$\underline{H}_2$-Ph), 4.21 (s, η^5-C$_5\underline{H}_5$), 6.24 (m, $\underline{H}_b$), 6.62 (m, $\underline{H}_c$), 6.97 (m, *p*-P(C$_6\underline{H}_5$)$_3$), 7.03 (m, $\underline{H}_d$), 7.05 (m, *m*-P(C$_6\underline{H}_5$)$_3$), 7.14 (m, $\underline{H}_e$), 7.52 (m, *o*-P(C$_6\underline{H}_5$)$_3$). ^{13}C{^{1}H} NMR δ 3.3 (d, $|^2J_{PC}|$ = 5.0 Hz, $\underline{C}$H$_2$-Ph), 81.1 (s, η^5-$\underline{C}_5$H$_5$), 98.8 (br, $\underline{C}_2$), 120.4 (br, $\underline{C}_3$), 127.4 (d, $|^3J_{PC}|$ = 10.2 Hz, *m*-P(C$_6\underline{H}_5$)$_3$), 127.6 (s, $\underline{C}_5$), 128.4 (s, $\underline{C}_4$), 128.6 (s, *p*-P(C$_6\underline{H}_5$)$_3$), 132.5 (br, $\underline{C}_6$), 134.1 (d, $|^2J_{PC}|$ = 11.6 Hz, *o*-P(C$_6\underline{H}_5$)$_3$), 142.1 (d, $|^2J_{PC}|$ = 6.4 Hz, $\underline{C}_1$), 142.7 (d, $|^1J_{PC}|$ = 42.9 Hz, *i*-P(C$_6\underline{H}_5$)$_3$). ^{31}P{^{1}H} NMR δ 60.3 (s, P(C$_6\underline{H}_5$)$_3$).



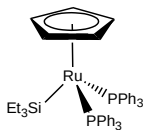
CpRu(PPh$_3$)(η^2-C$_{10}$H$_8$)Me (**18a**), major isomer: ^{1}H NMR δ 0.95 (d, 3H, $|^2J_{PH}|$ = 6.7 Hz, Ru-C$\underline{H}_3$), 3.72 (br, $\underline{H}_b$), 4.13 (br, $\underline{H}_a$), 4.55 (s, 5H, C$_5\underline{H}_5$), 6.61 (br, $\underline{H}_d$), 6.74 (br, $\underline{H}_c$), 7.05 (m, *p*-P(C$_6\underline{H}_5$)$_3$), 7.15 (m, *m*-P(C$_6\underline{H}_5$)$_3$), 7.49 (m, 6, *o*-P(C$_6\underline{H}_5$)$_3$). ^{13}C{^{1}H} NMR δ -27.3 (d, $|^2J_{PC}|$ = 9.9 Hz, Ru-$\underline{C}$H$_3$), 82.4 (s, $\underline{C}_5$H$_5$), 124.8 (m, $\underline{C}_4$), 127.5 (d, $|^3J_{PC}|$ = 10.3 Hz, *m*-P(C$_6\underline{H}_5$)$_3$), 128.8 (s, *p*-P(C$_6\underline{H}_5$)$_3$), 130.3 (m, $\underline{C}_3$), 134.2 (d, $|^2J_{PC}|$ = 16.2 Hz, *o*-P(C$_6\underline{H}_5$)$_3$), 142.5 (d, $|^1J_{PC}|$ = 44.8 Hz, *i*-P(C$_6\underline{H}_5$)$_3$), 156.4 (m, $\underline{C}_1$), 158.1 (m $\underline{C}_2$). ^{31}P{^{1}H} NMR δ 63.2 (s, P(C$_6\underline{H}_5$)$_3$).



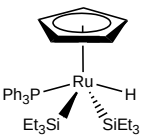
CpRu(PPh$_3$)(η^2-C$_{10}$H$_8$)Me (**18b**), minor isomer: ^{1}H NMR δ 0.89 (d, 3H, $|^2J_{PH}|$ = 6.6 Hz, Ru-C$\underline{H}_3$), 3.67 (br, $\underline{H}_b$), 4.06 (br, $\underline{H}_a$), 4.51 (s, 5H, C$_5\underline{H}_5$). ^{13}C{^{1}H} NMR δ -26.5 (d, $|^2J_{PC}|$ = 10.0, Ru-$\underline{C}$H$_3$), 81.9 (s, $\underline{C}_5$H$_5$). ^{31}P{^{1}H} NMR δ 62.8 (s, P(C$_6\underline{H}_5$)$_3$).



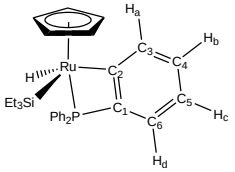
CpRu(PPh$_3$)$_2$SiEt$_3$ (**19**): ^{1}H NMR δ 1.19 (br, 9H, Si-CH$_2$C$\underline{H}_3$), 1.31 (br, 6H, Si-C$\underline{H}_2$CH$_3$), 4.53 (s, 5H, η^5-C$_5\underline{H}_5$), 6.88 (m, *p*-P(C$_6\underline{H}_5$)$_3$), 6.97 (m, *m*-P(C$_6\underline{H}_5$)$_3$), 7.26 (m, *o*-P(C$_6\underline{H}_5$)$_3$). ^{13}C{^{1}H} NMR δ 12.6 (s, Si-CH$_2\underline{C}$H$_3$), 14.4 (t, Si-$\underline{C}$H$_2$CH$_3$), 83.1 (s, η^5-$\underline{C}_5$H$_5$), 127.0 (t, $|^3J_{PC}|$ = 10.5 Hz, *m*-P(C$_6\underline{H}_5$)$_3$), 128.1 (s, *p*-P(C$_6\underline{H}_5$)$_3$), 133.7 (t, $|^2J_{PC}|$ = 16.4 Hz, *o*-P(C$_6\underline{H}_5$)$_3$), 140.3 (dd, $|^3J_{PC}|$ = 14.3 Hz, $|^1J_{PC}|$ = 35.8 Hz, *i*-P(C$_6\underline{H}_5$)$_3$). ^{31}P{^{1}H} NMR δ 54.4 (s, P(C$_6\underline{H}_5$)$_3$). ^{29}Si{^{1}H} NMR δ 16.0 (t, $|^2J_{PSi}|$ = 25.6 Hz).



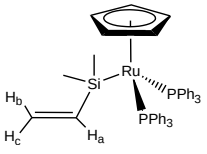
CpRu(PPh$_3$)(SiEt$_3$)$_2$H (**20**): ^{1}H NMR δ -11.89 (d, 1H, $|^3J_{PH}|$ = 9.7 Hz, Ru-$\underline{H}$), 0.97 (br, 18H, Si-CH$_2$C$\underline{H}_3$), 1.15 (br, 12H, Si-C$\underline{H}_2$CH$_3$), 4.76 (s, 5H, η^5-C$_5\underline{H}_5$), 6.98 (m, *p*-P(C$_6\underline{H}_5$)$_3$), 7.06 (m, *m*-P(C$_6\underline{H}_5$)$_3$), 7.41 (m, *o*-P(C$_6\underline{H}_5$)$_3$). ^{13}C{^{1}H} NMR δ 12.8 (s, Si-CH$_2\underline{C}$H$_3$), 14.2 (d, $|^3J_{PC}|$ = 6.8 Hz, Si-$\underline{C}$H$_2$CH$_3$), 85.1 (s, η^5-$\underline{C}_5$H$_5$), 127.2 (d, $|^3J_{PC}|$ = 10.2 Hz, *m*-P(C$_6\underline{H}_5$)$_3$), 128.6 (s, *p*-P(C$_6\underline{H}_5$)$_3$), 133.6 (d, $|^3J_{PC}|$ = 16.6 Hz, *o*-P(C$_6\underline{H}_5$)$_3$), 140.4 (dd, $|^3J_{PC}|$ = 13.4 Hz, $|^1J_{PC}|$ = 45.1 Hz, *i*-P(C$_6\underline{H}_5$)$_3$). ^{31}P{^{1}H} NMR δ 58.0 (s, P(C$_6\underline{H}_5$)$_3$). ^{29}Si{^{1}H} NMR δ 24.3 (d, $|^2J_{PSi}|$ = 14.4 Hz).



CpRu(κ^2-2-C$_6$H$_4$PPh$_2$)(SiEt$_3$)H (**21**): ^{1}H NMR δ -9.13 (d, 1H, $|^3J_{PH}|$ = 23.0 Hz, Ru-$\underline{H}$), 0.38 & 0.54 (br, Si-CH$_2$C$\underline{H}_3$), 0.81 (br, Si-C$\underline{H}_2$CH$_3$), 4.78 (s, 5H, η^5-C$_5\underline{H}_5$), 7.01 (m, *p*-P(C$_6\underline{H}_5$)$_3$), 7.07 (m, *m*-P(C$_6\underline{H}_5$)$_3$), 7.18 (m, $\underline{H}_c$), 7.37 (m, *o*-P(C$_6\underline{H}_5$)$_3$), 7.55 (m, $\underline{H}_b$), 7.62 (m, $\underline{H}_d$), 7.74 (m, $\underline{H}_a$). ^{13}C{^{1}H} NMR δ 9.0 (s, Si-CH$_2\underline{C}$H$_3$), 13.8 (d, $|^2J_{PC}|$ = 6.2, Si-$\underline{C}$H$_2$CH$_3$), 83.9 (s, η^5-$\underline{C}_5$H$_5$), 127.7 (d, $|^3J_{PC}|$ = 10.1 Hz, *m*-P(C$_6\underline{H}_5$)$_3$), 128.4 (*p*-P(C$_6\underline{H}_5$)$_3$), 128.6 ($\underline{C}_5$), 130.6 (d, $|^4J_{PC}|$ = 4.3 Hz, $\underline{C}_4$), 133.8 (d, *o*-P(C$_6\underline{H}_5$)$_3$), 135.4 (d, $\underline{C}_6$), 141.2 (d, $|^3J_{PC}|$ = 44.7 Hz, *i*-P(C$_6\underline{H}_5$)$_3$), 141.6 (d, $|^2J_{PC}|$ = 16.3 Hz, $\underline{C}_2$), 144.8 (d, $|^3J_{PC}|$ = 11.4 Hz, $\underline{C}_3$), 153.5 (d, $|^1J_{PC}|$ = 43.2 Hz, $\underline{C}_1$). ^{31}P{^{1}H} NMR δ -16.9 (s, P(Ph)$_2$(κ^2-2-C$_6$H$_4$)). ^{29}Si{^{1}H} NMR δ 25.6 (d, $|^2J_{PSi}|$ = 15.8 Hz).



CpRu(PPh$_3$)(η^3-Si(Me$_2$)CH=CH$_2$) (**22**): ^{1}H NMR δ -0.33 (s, 3H, Si(C$\underline{H}_3$) ↓), 0.73 (s, 3H, Si(C$\underline{H}_3$) ↑), 1.98 (m, $|^2J_{PH}|$ = 11.2 Hz, $\underline{H}_a$), 2.14 (m, $|^2J_{PH}|$ = 11.2 Hz, $\underline{H}_b$), 3.53 (m, $|^2J_{PH}|$ = 11.2 Hz, $\underline{H}_c$), 4.29 (s, η^5-C$_5\underline{H}_5$), 6.97 (m, *p*-P(C$_6\underline{H}_5$)$_3$), 7.01 (m, *m*-P(C$_6\underline{H}_5$)$_3$), 7.68 (m, $|^3J_{PH}|$ = 8.1 Hz, *o*-P(C$_6\underline{H}_5$)$_3$). ^{13}C{^{1}H} NMR δ -3.1 (s, Si($\underline{C}$H$_3$) ↑), -3.5 (s, Si($\underline{C}$H$_3$) ↓), 31.0 (d, $|^3J_{PC}|$ = 6.4 Hz, Si-CH$\underline{C}$H$_2$), 38.4 (d, $|^3J_{PC}|$ = 6.4 Hz, Si-$\underline{C}$HCH$_2$), 81.6 (s, η^5-$\underline{C}_5$H$_5$), 127.6 (d, $|^3J_{PC}|$ = 10.3 Hz, *m*-P(C$_6\underline{H}_5$)$_3$), 128.5 (s, *p*-P(C$_6\underline{H}_5$)$_3$), 133.6 (d, $|^2J_{PC}|$ = 12.0 Hz, *o*-P(C$_6\underline{H}_5$)$_3$), 141.1 (d, $|^1J_{PC}|$ = 42.3 Hz, *i*-P(C$_6\underline{H}_5$)$_3$). ^{31}P{^{1}H} NMR δ 66.5 (s, P(C$_6\underline{H}_5$)$_3$). ^{29}Si{^{1}H} NMR δ 35.9 (d, $|^2J_{PSi}|$ = 22 Hz).



$CpRu(PPh_3)_2(Si(Me_2)CH=CH_2)$ (**23**): ^1H NMR δ 0.23 (s, $Si(C\underline{H}_3)$), 4.39 (s, η^5-$C_5\underline{H}_5$), 5.39 (m, $|^3J_{HH}|$ = 6.8, $\underline{H}_c$), 5.52 (m, $|^3J_{HH}|$ = 11.3 Hz, $\underline{H}_b$), 6.31 (m, $|^3J_{HH}|$ = 6.8 Hz, $|^3J_{HH}|$ = 11.3 Hz, $\underline{H}_a$), 7.02 (m, *p*-$P(C_6\underline{H}_5)_3$), 7.18 (m, *m*-$P(C_6\underline{H}_5)_3$), 7.49 (m, $|^3J_{PH}|$ = 7.8 Hz, *o*-$P(C_6\underline{H}_5)_3$). $^{13}C\{^1H\}$ NMR δ -2.9 (s, $Si(\underline{C}H_3)$), 34.4 (s, Si-$CHC\underline{H}_2$), 37.5 (s, Si-$C\underline{H}CH_2$), 82.3 (s, η^5-$\underline{C}_5H_5$), 127.9 (t, $|^3J_{PC}|$ = 10.9 Hz, *m*-$P(\underline{C}_6H_5)_3$), 128.4 (s, *p*-$P(\underline{C}_6H_5)_3$), 133.7 (t, $|^2J_{PC}|$ = 13.5 Hz, *o*-$P(\underline{C}_6H_5)_3$), 142.1 (dd, $|^3J_{PC}|$ = 14.3, $|^1J_{PC}|$ = 37.4 Hz, *i*-$P(\underline{C}_6H_5)_3$). $^{31}P\{^1H\}$ NMR δ 51.8 (s, $P(C_6H_5)_3$). $^{29}Si\{^1H\}$ NMR δ 17.2 (t, $|^2J_{PSi}|$ = 26.8 Hz).

8. C**haracterisation of $CpRu(PPh_3)_2(\sigma$-$CH_2C_6H_5)$ (16):**
The 1D $^{31}P\{^1H\}$ NMR spectrum of the complex displays a peak at δ 51.6, which is typical of a ^{31}P resonance for a triphenylphosphine ligand bound to a ruthenium centre. A $^1H/^{31}P$ HMQC NMR spectrum connected this signal to proton signals at δ 4.19, 7.28, 7.07 and 6.98 which are characteristic of the proton resonances of a cyclopentadienyl ring, and the *ortho*, *meta* and *para* positions of the phenyl rings of a triphenylphosphine ligand. An additional proton resonance was found at δ 3.07 (triplet) in this spectrum for the protons of the CH_2 group which links the phenyl moiety to the ruthenium centre. These signals show a triplet splitting due to coupling to the two phosphorus centres of the triphenylphosphine ligands.

9. Characterisation of $CpRu(PPh_3)(\eta^3$-$CH_2C_6H_5)$ (17):
17 produces a ^{31}P signal at δ 60.3. In the corresponding $^1H/^{31}P$ HMQC experiment, this signal couples to five ^1H-NMR signals at δ 4.02, 4.21, 7.52, 7.05 and 6.97. The latter three of these signals are typical for those of the *ortho*, *meta* and *para* protons of a phenyl ring of triphenylphosphine while the former arises from a cyclopentadienyl ring. The remaining 2-proton resonance at δ 4.02 connects to a ^{13}C signal at δ 3.3 which signal appears as a simple ^{31}P coupled doublet of 5.0 Hz. This demonstrates that there is only a single phosphine ligand in 17. NOe connections from the δ 4.02 signal to ^1H signals at δ 2.67 and 7.14 were also evident. These two signals mutually coupled according to ^1H COSY methods but belonged to a 5-proton-set where three further signals at δ 6.24, 6.62 and 7.03 were evident. These five signals correspond to the protons of a phenyl group which is coordinate to the ruthenium centre via an η^3-based coordination mode as shown when complex 17 is illustrated in the experimental. Confirmation of this structure was found by observation of the doublet splitting (6.4 Hz) to a carbon resonance at δ 98.8, which couples to the ^1H resonance at δ 2.67 in the $^1H/^{13}C$ HMQC spectrum. The identity of this complex is therefore $CpRu(PPh_3)(\eta^3$-$CH_2C_6H_5)$ (**17**) and there are spectral similarities between it and that of the recently reported Cp^* derivative [10]

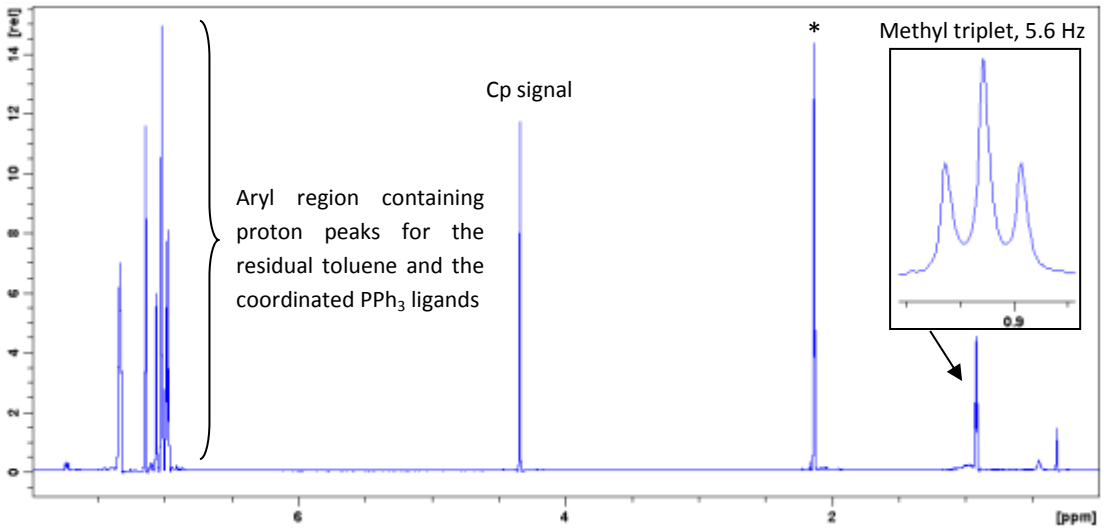
10. $CpRu(PPh_3)_2H$. The hydride resonance of $CpRu(PPh_3)_2H$ [11] appears as a triplet at δ -11.59 (J_{PH} = 33.8 Hz) due to coupling to a ^{31}P nucleus that appears at δ 68.3. This ^{31}P resonance was then shown to couple to signals at δ 4.49 and 7.52, which are diagnostic of the cyclopentadienyl ring and the *ortho*-phenyl protons of a triphenylphosphine ligand.

11. $CpRu(PPh_3)(\eta^3$-$Si(Me)_2$-$CH=CH_2)$ (22). For **22,** ^1H resonances were readily observed at δ -0.33, 0.73, 1.98, 2.14, 3.53 and 7.68. The demonstrated nOe interaction found between the signals at δ -0.33 and δ 0.73 suggested that they must arise from two methyl groups bound to silicon in agreement with their connection to a ^{29}Si resonance at δ 35.98. The δ 0.73 signal also showed a strong interaction with a signal at δ 4.29 due to the Cp resonance of **22**, which suggests that the associated methyl group points toward the Cp ring. Evidence for the vinyl ligand in **22**, which provides the ^1H signals at δ 1.98, 2.14 and 3.53, binding directly to the ruthenium centre was provided by the observation of a doublet splitting of 6.4 Hz on both the corresponding vinyl carbon signals at δ 31.0 and δ 38.3 due to a single phosphorus atom. This splitting is typical of a $^2|J_{CP}|$ coupling and suggests η^2-coordination.

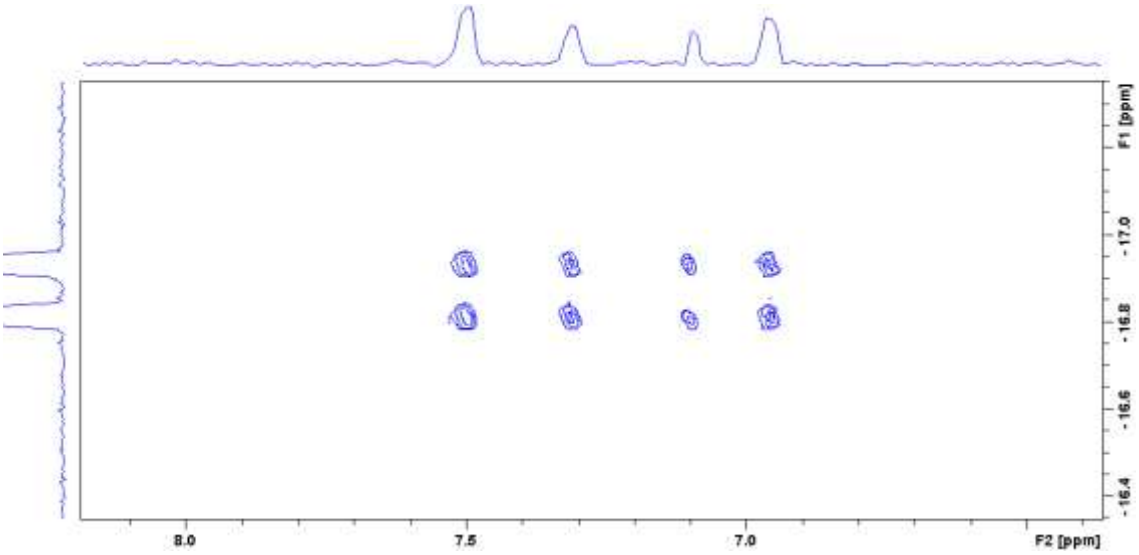
12. $CpRu(PPh_3)_2(Si(Me)_2$-$CH=CH_2)$ (23). The corresponding *bis*-phosphine product **23** yields notable ^1H resonances for the now equivalent $SiMe_2$ group at δ 0.23 and the free vinyl at δ 5.39, 5.52 and 6.31. Attempts to separate these complexes proved impractical owing to their high air sensitivity.

13 Typical NMR Spectra:

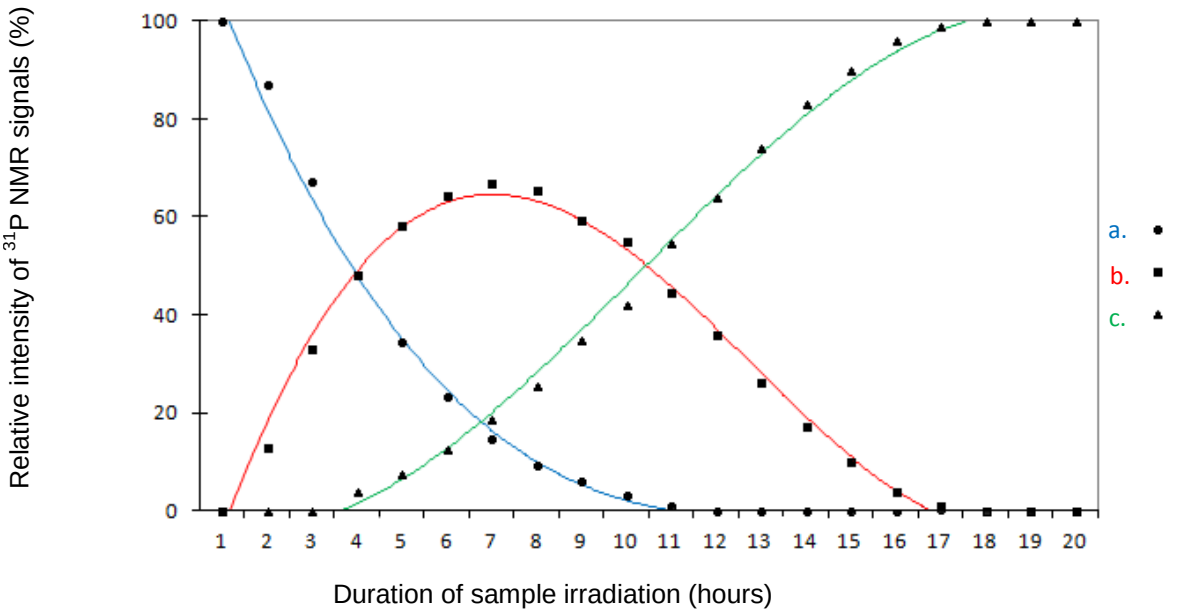
(a) ^1H NMR spectrum of $CpRu(PPh_3)_2Me$ with Cp and Me resonances indicated. (* = the residual CHD_2 resonances of the $C_6D_5CD_3$ solvent).



(b) A $^{1}H/^{31}P$ HMQC NMR spectrum showing the coupling between the ^{31}P signal at δ -16.9 and the corresponding phenyl protons of **3.**

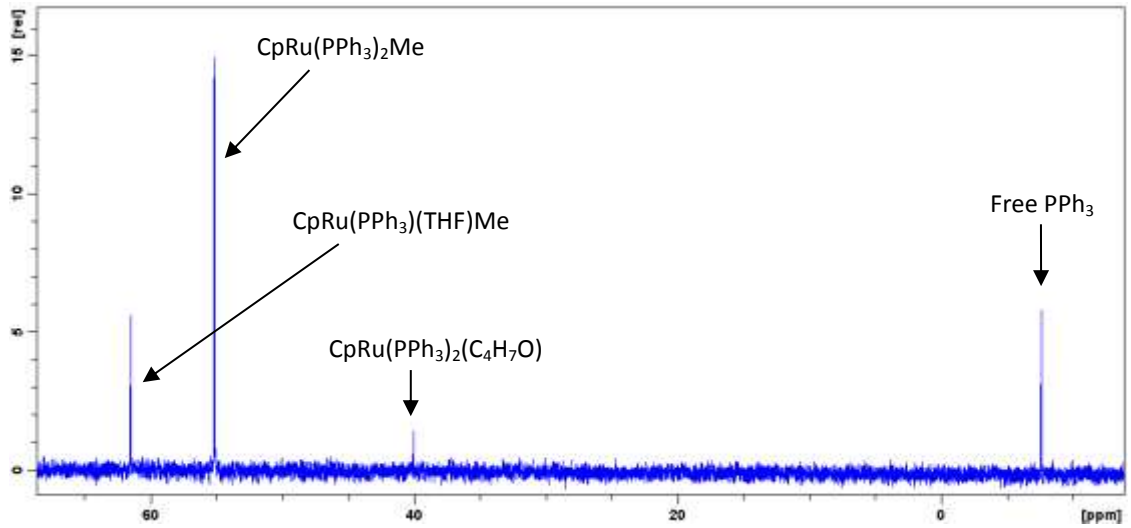


(c) A plot of the relative ^{31}P resonances over time, for the photochemically formed products of the reaction between $CpRu(PPh_3)_2Me$ and PEt_3, at 298 K (original illustration appears in colour).

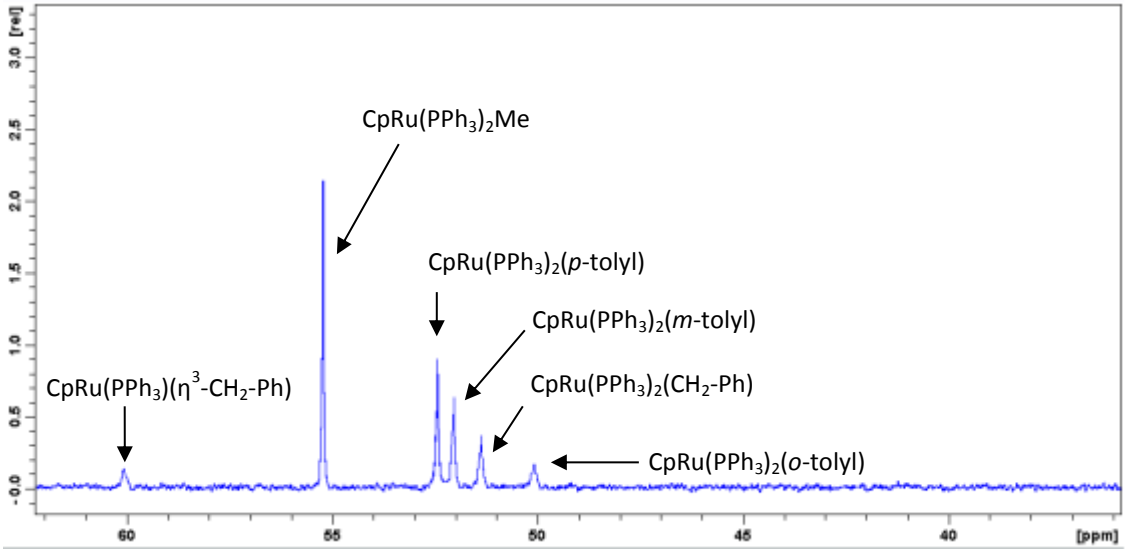


a. $CpRu(PPh_3)_2Me$ b. $CpRu(PPh_3)(PEt_3)Me$ c. $CpRu(PEt_3)_2Me$

(d) $^{31}P\ \{^1H\}$ NMR spectrum showing the ^{31}P signals corresponding to $CpRu(PPh_3)(THF)Me$ and $CpRu(PPh_3)_2(C_4H_7O)$, following 5 hours of photolysis.

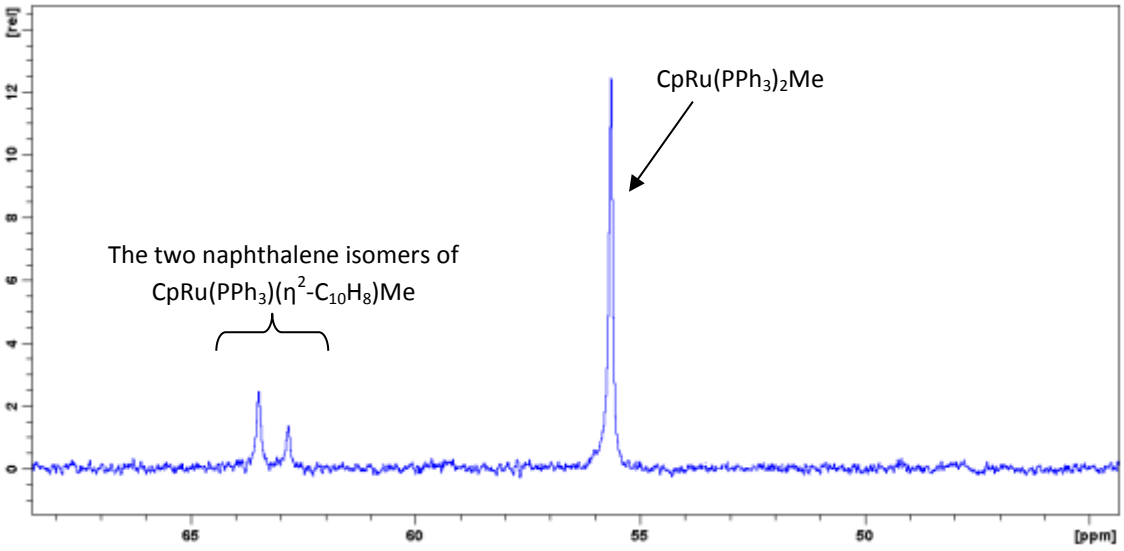


(e) $^{31}P\{^{1}H\}$ NMR spectrum showing the ^{31}P signals of the activated toluene products.

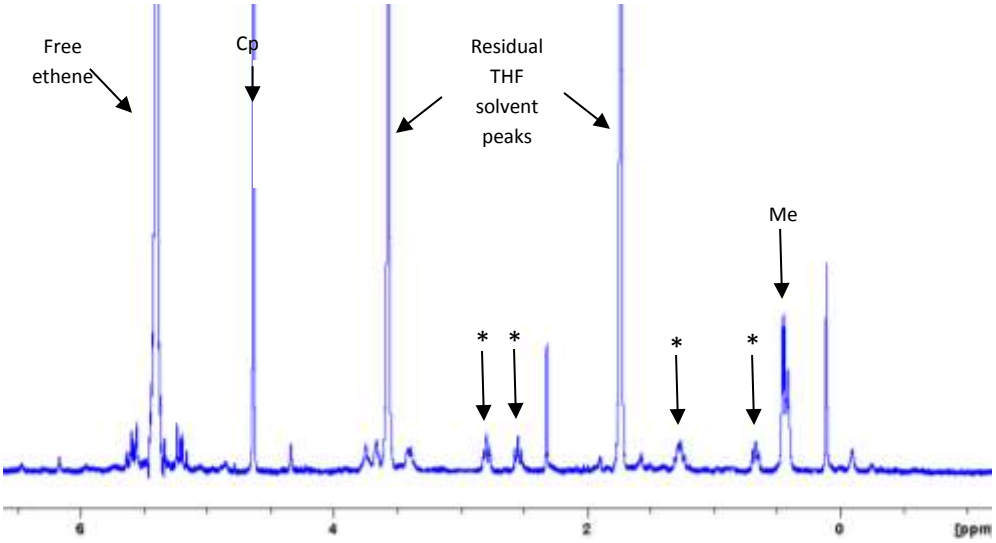


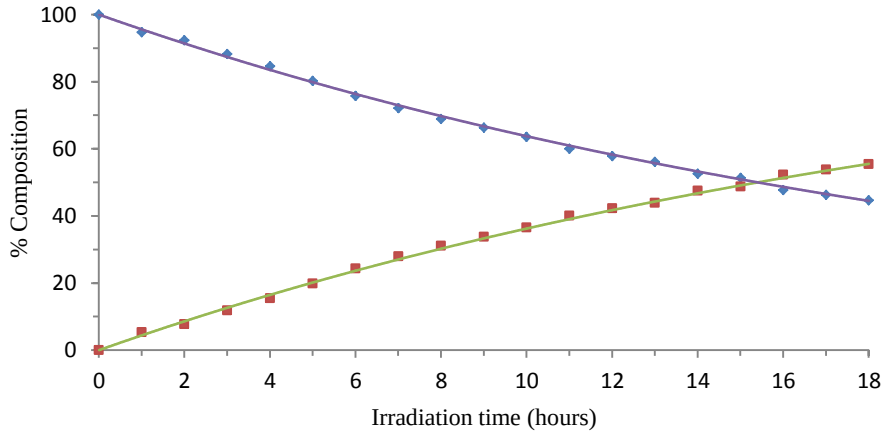
Previously the thermal reactivity of $CpRu(PPh_3)_2Me$ with toluene has been explored by Lehmkuhl *et al.*[12] He observed a series of tolyl C-H activation products: *meta*, *para* and benzyl, which have been described here, the *ortho* and η^3 products were not observed.

(f) $^{31}P\ \{^{1}H\}$ NMR spectrum showing the conversion of $CpRu(PPh_3)_2Me$ into two isomers of $CpRu(PPh_3)(\eta^2\text{-}C_{10}H_8)Me$.

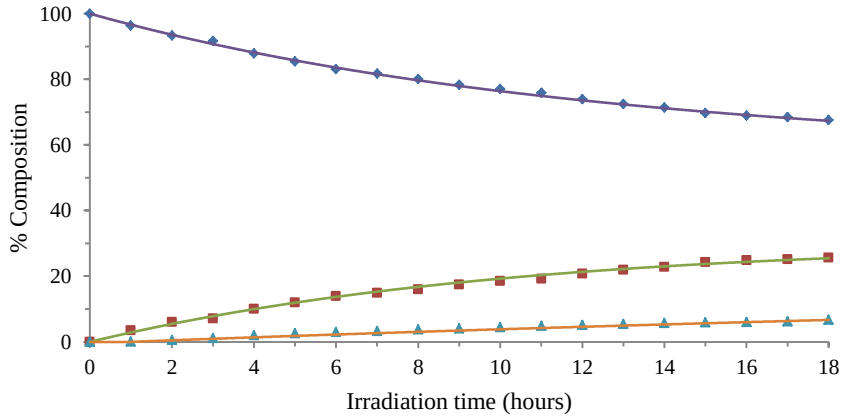


(g) ^{1}H NMR spectrum of $CpRu(PPh_3)(C_2H_4)Me$ (**10**)

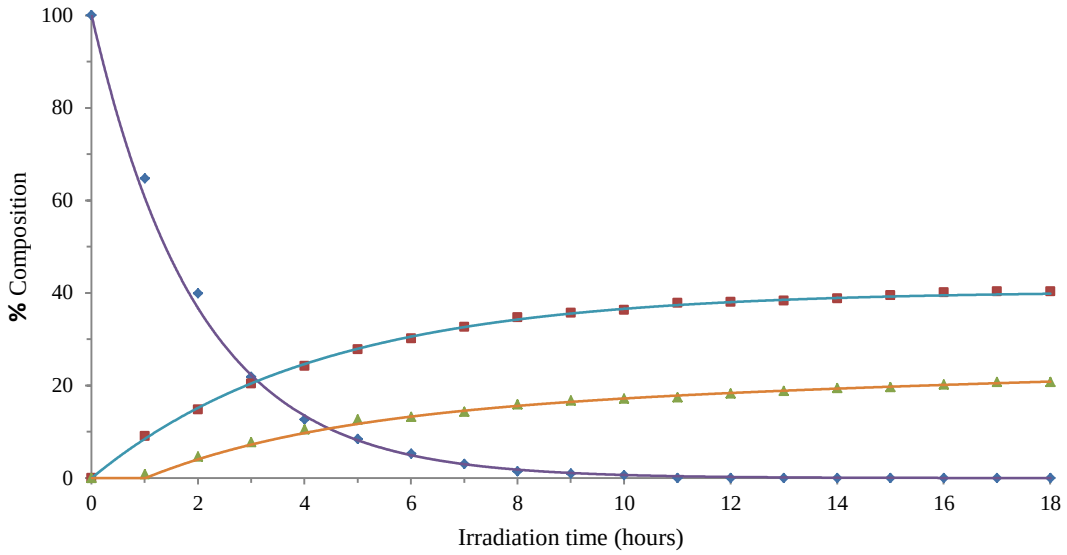




sFigure 1. Plot of the observed relative ^{31}P NMR resonance intensities at δ 55.3 and δ 59.0 as seen during the reaction between **2** and DMSO at 198 K as a function of irradiation time; these signals are attributed to **2** (♦) and **9** (■)



sFigure 2. Plot of the observed ^{31}P resonance intensities as a function of irradiation time for the conversion of **2** (♦) into **11** (▲) and **12** (■) at 198 K.



sFigure 3. Change in relative ^{31}P resonance intensity as a function of the UV irradiation time for the reaction of **2** and $HSi(Me)_2CH=CH_2$ at 198 K in d_8-THF; ♦ is **2** , ■ is **22** and ▲ is **23**.

14. References.

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