Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:

Formal Oxidative Addition of a C-H Bond by a 16e Iridium(I) Complex involves Metal-Ligand Cooperation

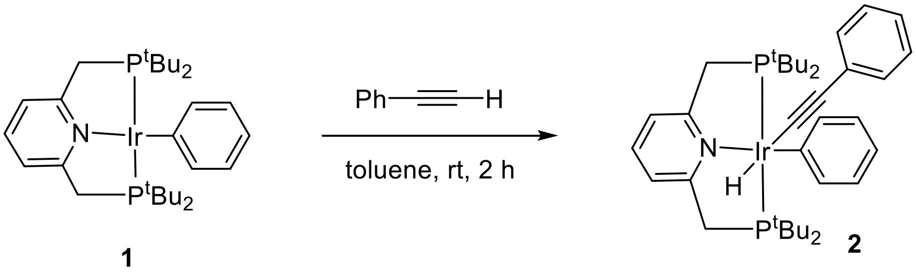
Amit Kumar,[a] Moran Feller,[a] Yehoshoa Ben-David,[a] Yael Diskin-posner[b] and David Milstein[a]

Table of Contents

1. General information

All experiments were carried out in M-BRAUN Unilab 1200/780 glovebox under inert atmosphere of purified nitrogen or using standard Schlenk techniques. Toluene, benzene and *n*-pentane were refluxed over sodium/benzophenone, distilled under argon atmosphere, and stored over 4 Å molecular sieves (MS).[1] Alkynes were purchased from Sigma-Aldrich and used as received. Deuterated solvents were degassed with argon and kept in the glovebox over 4 Å MS. The [(PNP)Ir(phenyl)] (**1**)] was prepared according to the literature procedures described earlier.[2] ^{1}H NMR, ^{13}C{^{1}H} NMR, and ^{31}P{^{1}H} NMR spectra were recorded on Bruker AMX-500 NMR spectrometer and reported in ppm (*δ*). ^{1}H NMR, ^{13}C{^{1}H} NMR, and ^{13}C{^{1}H}-DEPTQ NMR chemical shifts are referenced with respect to tetramethylsilane, while ^{31}P{^{1}H} NMR chemical shifts are reported referenced to an external 85% solution of phosphoric acid in D_2O. NMR spectroscopy abbreviations: b, broad; s, singlet; d, doublet; t, triplet; m, multiplet.

2. Synthesis and characterization of complex 2



A toluene solution (1 mL) of phenylacetylene (8 mg, 0.078 mmol) was added to the [(PNP)Ir(phenyl)] complex (**1**, 50 mg, 0.075 mmol) in a vial. The dark brown solution was stirred at room temperature for 2 h. NMR spectroscopy after 2 h showed complete consumption of the starting complex **1** and formation of a new complex **2**. The toluene solution was evacuated and the resulting brown solid was washed with cold pentane and then dried to obtain the analytically pure complex **2** in 92% yield (52 mg). Single crystals suitable for X-ray diffraction were obtained by cooling the saturated pentane solution of **2** at -25 °C. Identification of ^{1}H and ^{13}C NMR signals are deduced from HSQC and ^{13}CQDEPT NMR spectra.

^{31}P{^{1}H} NMR (121.50 MHz, tol-d_8, 298K): δ 40.1 (s).

^{1}H NMR (500.08 MHz, tol-d_8, 298K): δ –10.85 (t, $^2J_{HP}$ = 18.9 Hz 1H, Ir*H*), 1.15 (t, $^3J_{HP}$ = 5.8 Hz, 18H, $(CH_3)_3CP$), 1.40 (t, $^3J_{HP}$ = 5.8 Hz, 18H, $(CH_3)_3CP$), 3.02 (d, $^2J_{HP}$ = 16.2 Hz, 2H, CH_2P), 3.77 (d, $^2J_{HP}$ = 17.1 Hz, 2H, CH_2P), 6.53 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *Ph*), 6.86-7.05 (m, 4H, *Ph*), 7.13-7.17 (m, 3H, *Ph*), 7.44 (d, $^3J_{HH}$ = 8 Hz, 2H, $CH_{pyri(3,5)}$), 8.23 (bd, $^2J_{HH}$ = 6.2 Hz, 1H, *Ph*), 9.03 (bd, $^2J_{HH}$ = 7.2 Hz, 1H, $CH_{pyri(4)}$).

^{13}C{^{1}H} NMR (125.76 MHz, C_6D_6, 298K): δ 29.0 (s, $(CH_3)_3CP$), 29.9 (s, $(CH_3)_3CP$), 35.7 (d,$^1J_{PC}$ = 11.6 Hz, $(CH_3)_3CP$), 35.7 (d,$^1J_{PC}$ = 11.6 Hz, $(CH_3)_3CP$), 38.1 (d,$^1J_{PC}$ = 9.9 Hz, $(CH_3)_3CP$), 38.1 (d,$^1J_{PC}$ = 9.9 Hz, $(CH_3)_3CP$), 40.8 (d,$^1J_{PC}$ = 12.1 Hz, CH_2P), 40.8 (d,$^1J_{PC}$ = 12.1 Hz, CH_2P), 109.1 (brs, C_{ipso}), 118.4 (m, *Ph*), 120.1 (s, *Ph*) 123.3 (s, *Ph*), 125.8 (s, *Ph*), 126.4 (s, *Ph*), 126.6 (t, $^2J_{PC}$ = 9.2 Hz, C_{ipso}, CC*Ph*), 130.6 (s, *Ph*), 131.7 (s, C_{ipso}, *Ph*) 134.8 (s, *Ph*), 144.9 (s, *Py*), 147.8 (s, *Py*), 162.6 (s, C_{ipso},*Py*).

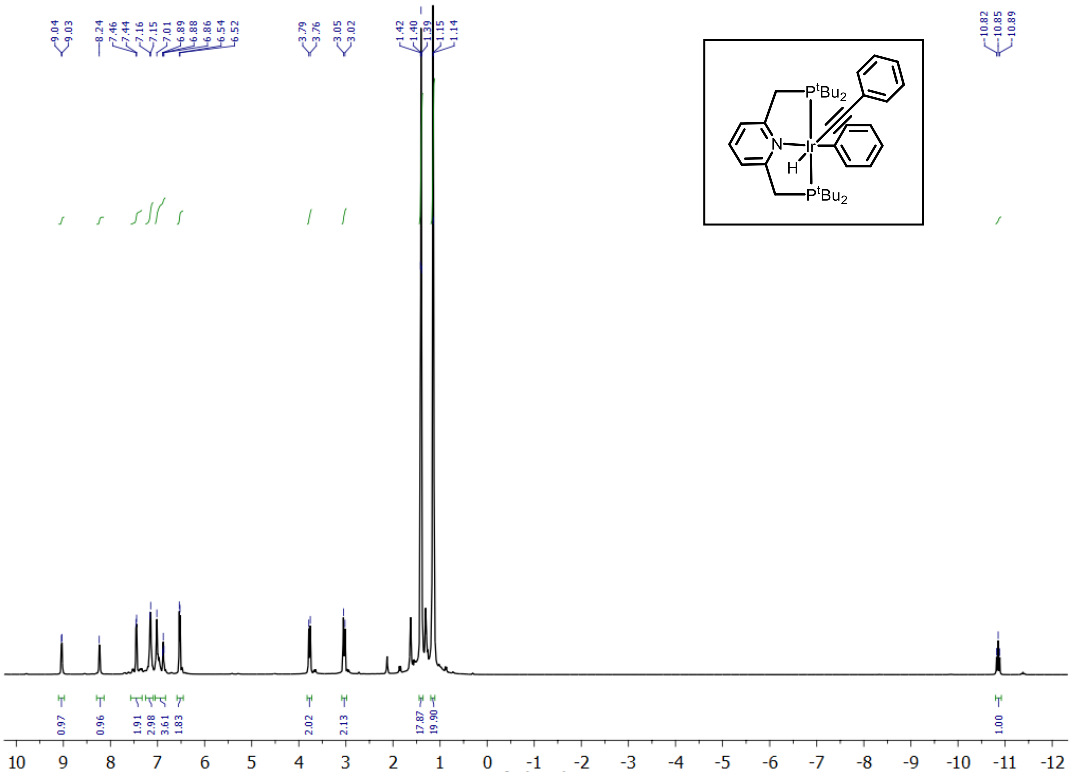


Figure S1. ^{1}H NMR (500.08 MHz, tol-d8, 298K) spectrum of complex **2**.

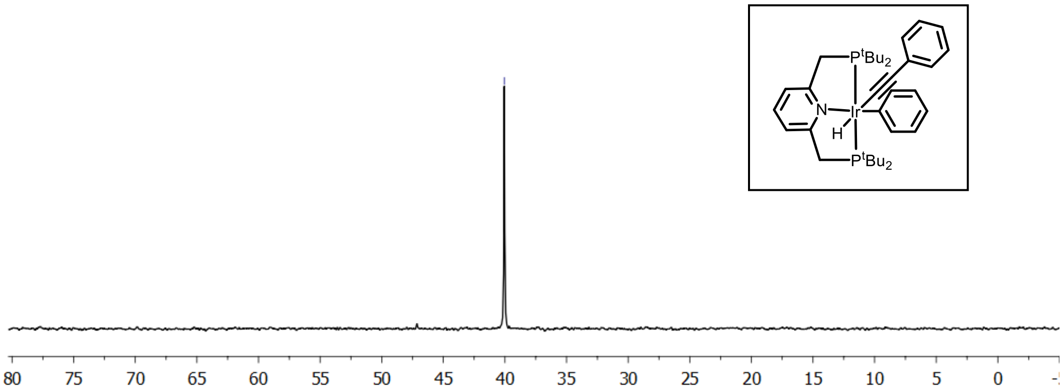


Figure S2. ^{31}P{^{1}H} NMR (121.50 MHz, tol-d8, 298K) spectrum of complex **2**.

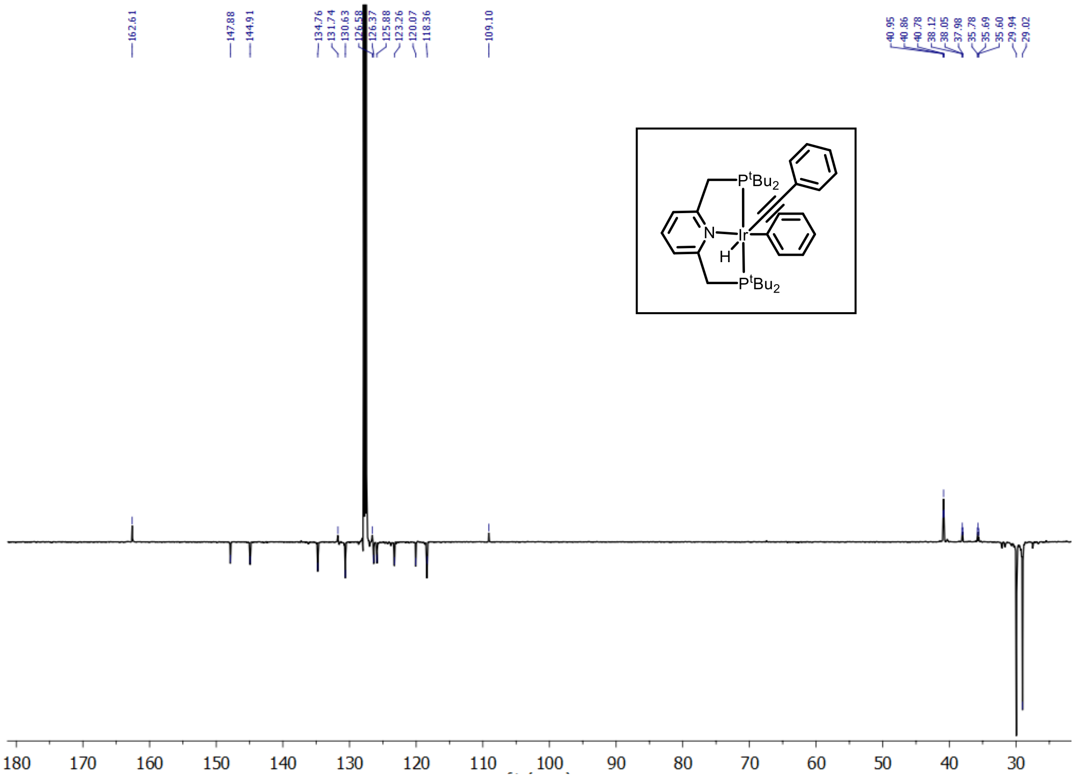


Figure S3. $^{13}C\{^1H\}$ NMR (125.76 MHz, tol-d8, 298K) spectrum of complex **2**.

Crystallographic details

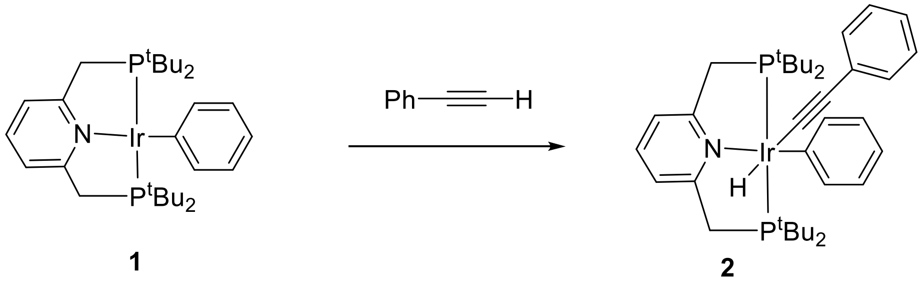
The diffraction data of complex **2** was collected on a Rigaku XtaLAB^{PRO} dual source diffractometer and processed with CrysAlis^{PRO}. Data collection was performed under LN at 100 K from very small crystals. The structure was solved by direct methods using SHELXT. All non-hydrogen atoms were further refined by SHELXL with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients, and their coordinates were allowed to ride on their respective carbons. Hydride atom was located in the electron density map. Crystallographic data and refinement parameters are summarized in Table S1.

Table S1. Crystallographic data.

Species	**Complex 2**
CCDC No.	1827435
Formula	$C_{37}H_{54}IrNP_2$
Formula weight	766.95
Crystal system	Triclinic
Space group	$P\bar{1}$
Crystal size (mm)	0.157×0.027×0.013
Crystal color and shape	Colorless plate
Temperature (K)	100
Wavelength (Å)	0.71073
a (Å)	9.1192(4)
b (Å)	10.6683(5)
c (Å)	17.8231(5)
α (°)	93.180(3)
β (°)	92.823(3)
γ (°)	95.767(4)
Volume ($Å^3$)	1719.89(12)
Z	2
ρ_{calcd},(g cm^{-1})	1.481
μ (mm^{-1})	4.000
No. of reflection (unique)	32278 (7852)
R_{int}	0.0614
Completeness to θ (%)	99.7
Data / restraints / parameters	7852 / 0 / 383
Goodness-of-fit on F^2	1.035
Final R_1 and wR_2 indices [$I > 2\sigma(I)$]	0.0306, 0.0667
R_1 and wR_2 indices (all data)	0.0384, 0.0692

3. Kinetic experiments

I. Initial rate experiments for the order of reaction:



A stock solution of PhCCH was prepared by dissolving 10 mg of PhCCH in 2.5 mL tol-d8 to obtain a stock solution concentration of 4 x10^{-2} M. 0.5 – 2 mg of complex **1** was weighed in a vial to which the appropriate amount of PhCCH stock solution was added and the resulting mixture was further diluted by the appropriate amount of tol-d8. For example, for entry 2, 1 mg of complex **1** was mixed with 0.25 mL of the stock solution of PhCCH and the resulting solution was further diluted to 0.5 mL total volume of tol-d8. Then, 0.05 mmol (6 mg) of mesitylene was added and the resulting solution was transferred to a Young's NMR tube. Reaction progress was monitored by the ^{1}H NMR spectroscopy by analyzing the benzylic C*H$_2$* signals in complexes **1** and **2**. For initial rate studies, data corresponding to first 30 min accounting for ~10% conversion of complex **1** were considered.

Table S2. Initial rates of oxidative addition of alkynes by complex **1**.

Entry	Conc of PhCCH (M x 10^{-2})	Conc of complex 1 (M x 10^{-2})	Rate (Ms^{-1})
1	4	0.3	4.15x10^{-7} ± 5.2x10^{-9}
2	2	0.3	2.05x10^{-7} ± 9.5x10^{-9}
3	1	0.3	1.02x10^{-7} ± 9.8x10^{-9}
4	0.5	0.3	0.6x10^{-7} ± 1.2x10^{-8}
5	2	1.2	8.0x10^{-7} ± 7.2x10^{-9}
6	2	0.6	4.21x10^{-7} ± 9.2x10^{-9}
7	2	0.15	1. 1x10^{-7} ± 4x10^{-9}

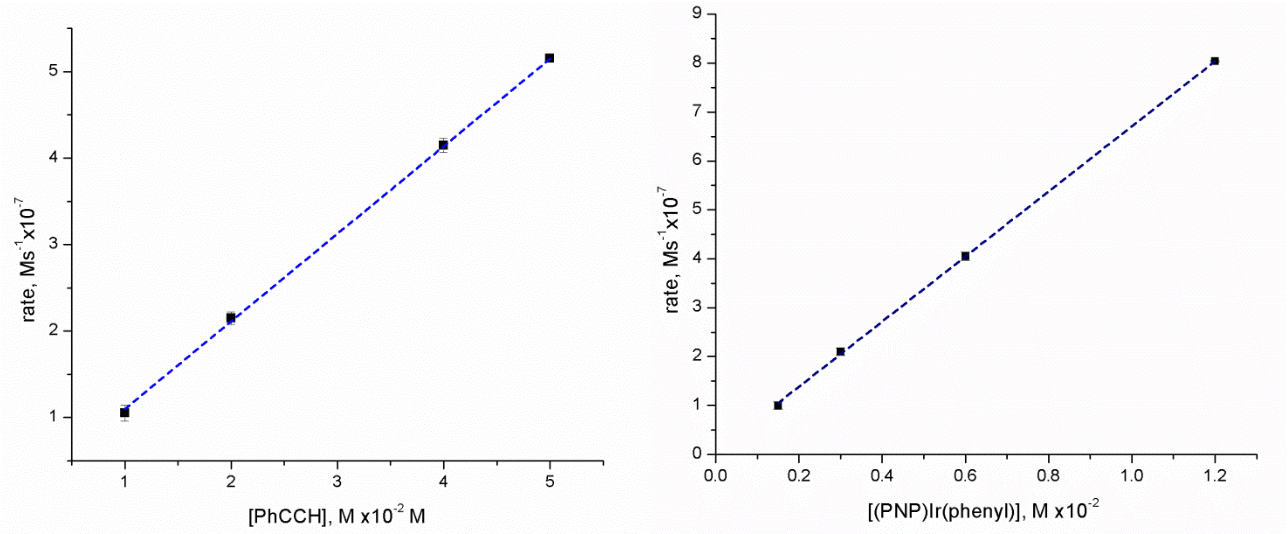
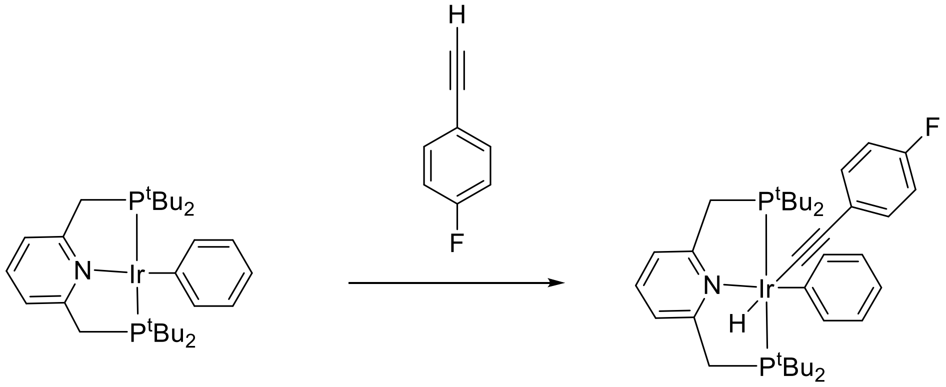


Figure S4. Plot of initial rates against concentration of alkynes (left) or concentration of complex **1** (right).

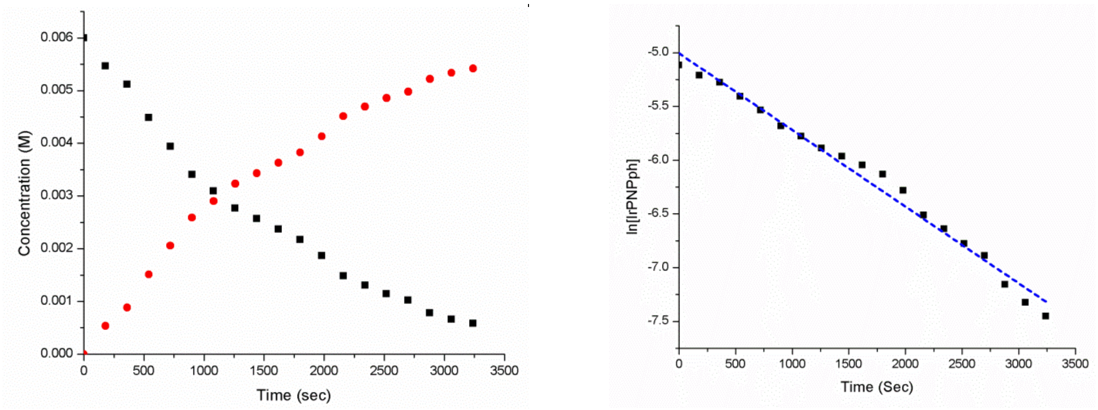
II. Kinetics for the oxidative addition of various alkynes

1 mg (1.5 x 10^{-3} mmol) of complex **1** was mixed with 0.25 mL of the stock solution of alkyne (as described above in Section 3.1) and the resulting solution was further diluted to 0.5 mL of total volume of tol-d8. Then, 0.05 mmol (6 mg) of mesitylene was added and the resulting solution was transferred to a Young's NMR tube. Reaction progress was monitored by the ^{1}H NMR spectroscopy by analyzing the benzylic C*H*$_2$ signals in complexes **1** and the corresponding oxidative addition products **2** or **2**$_\mathbf{F}$ or **2**$_\mathbf{OMe}$.



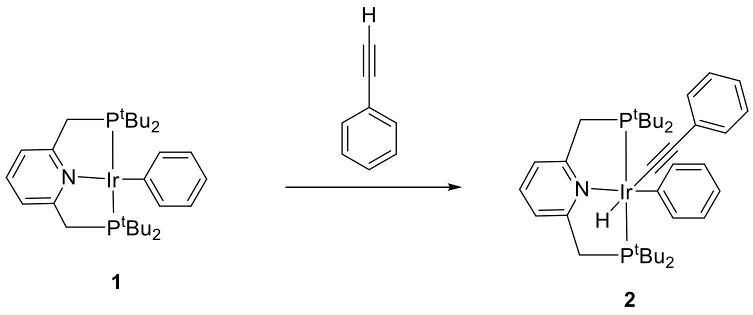
1

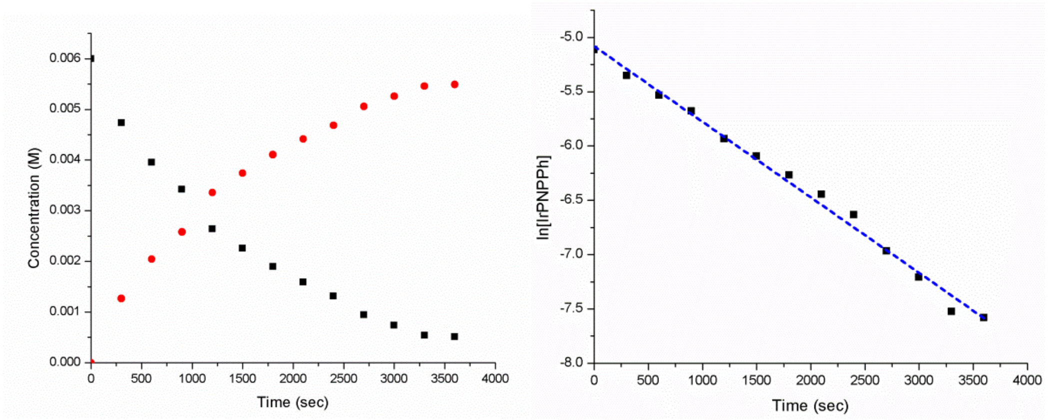
2$_\mathrm{F}$



$$K = 6.5x10^{-4} \pm 2.0x10^{-5}\ s^{-1}$$

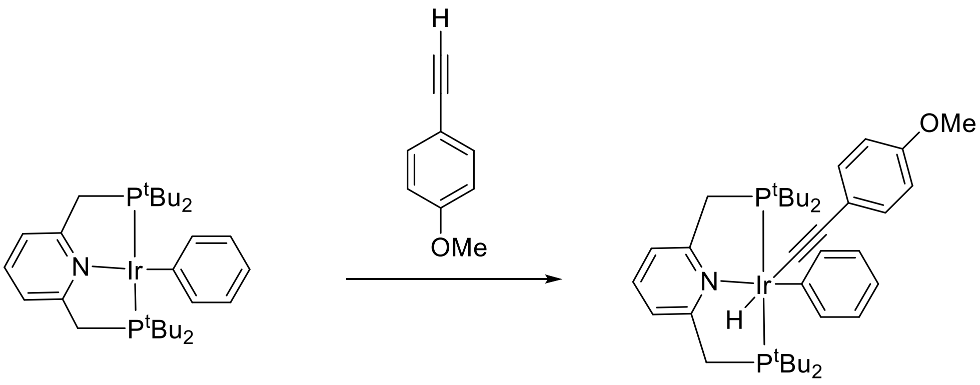
Figure S5. Left: Plot of concentration vs time, ▪ represents the concentration of complex **1** and ● represents the concentration of the corresponding oxidative addition iridium (III) complex **2**F. Right: Plot of ln[**1**] vs time exhibiting a first order plot relative to the complex **1**.





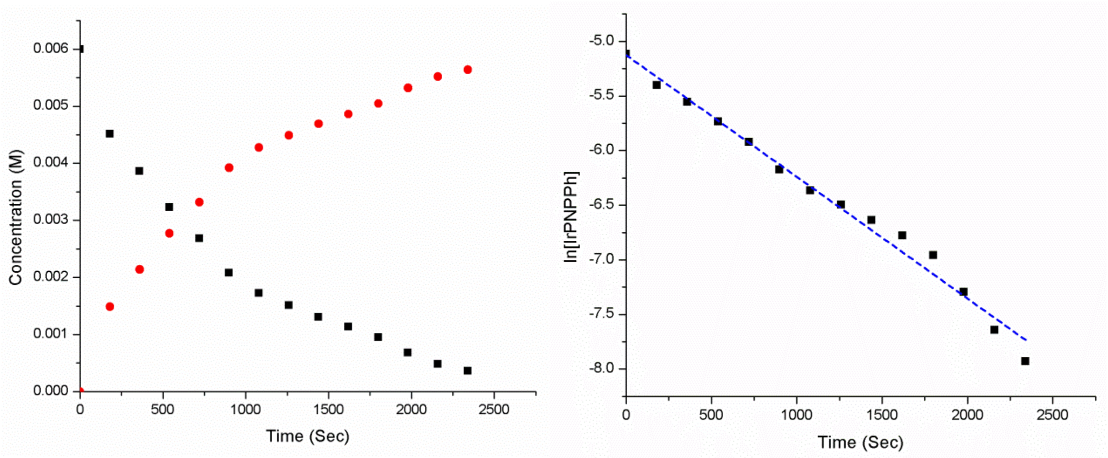
$$K = 7.2x10^{-4} \pm 1.1x10^{-5}\ s^{-1}$$

Figure S6. Left: Plot of concentration vs time, ▪ represents the concentration of complex **1** and ● represents the concentration of the corresponding oxidative addition iridium (III) complex **2**. Right: Plot of ln[**1**] vs time exhibiting a first order plot relative to the complex **1**.



1

$\mathbf{2}_{OMe}$

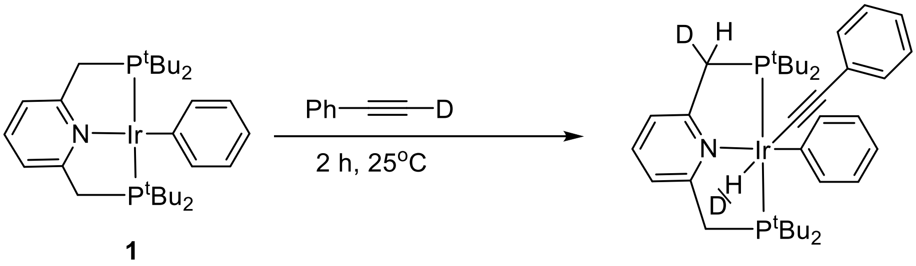


$K = 11.1\times10^{-4} \pm 3.7\times10^{-5}\ s^{-1}$

Figure S7. Left: Plot of concentration vs time, ▪ represents the concentration of complex **1** and ● represents the concentration of the corresponding oxidative addition iridium (III) complex $\mathbf{2}_{\mathbf{OMe}}$. Right: Plot of ln[**1**] vs time exhibiting a first order plot relative to the complex **1**.

Rate of C-H oxidative addition: $FC_6H_5CCH < C_6H_5CCH < MeOC_6H_5CCH$

4. Reaction of complex 1 with PhCCD



Complex **1** (10 mg, 0.015 mmol) was mixed with PhCCD (~8 mg, 0.075 mmol) to which benzene or toluene solvent was added and the reaction mixture was transferred to a Young's NMR tube. The NMR tube was left at room temperature for 2 hours. ^{1}H NMR spectrum of the reaction mixture after 2 hours showed the formation of a hydride signal at δ –10.85 (t, $^2J_{HP} = 18.9$ Hz) suggestive of the Ir*H* signal. ^{2}H NMR spectroscopy showed a signal at δ 3.70 (br) corresponding to the CH*D* signal at the arm suggestive of the deuterium incorporation in the arm. Additionally, a signal at δ –10.85 (br) was observed corresponding to the Ir*D* moiety (Figure S11). In order to quantify the IrH/IrD signal, we carried two separate reactions of complex **1** (10 mg, 0.015 mmol) with PhCCD (~8 mg, 0.075 mmol) in Young's NMR tubes as below:

(I) In the first one, C_6D_6 (0.5 mL) solvent was used. Additionally, a sealed capillary containing the mixture of CH_2Cl_2 (5 μL) and C_6D_6 (~0.05 mL) was added to the NMR tube as an internal standard in order to quantify the Ir*H* signal. The ^{1}H NMR spectrum is shown in Figure S12.

(II) In the second one, C_6H_6 (0.5 mL) solvent was used. Additionally, a sealed capillary containing the mixture of CD_2Cl_2 (5 μL) and C_6H_6 (~0.05 mL) was added to the NMR tube as an internal standard in order to quantify the Ir*D* signal. The ^{2}H NMR spectrum is shown in Figure S13.

Figures S9 and S10 show that the ratio of IrH/IrD signal is 30:1.

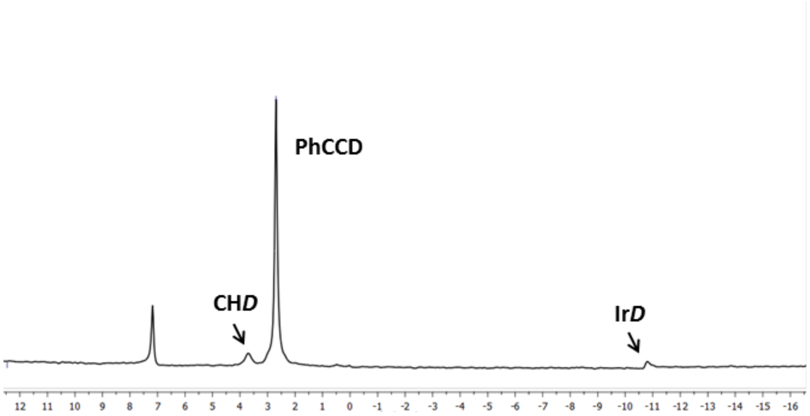


Figure S8. ^{2}H NMR (76.77 MHz, 298 K) spectrum of the reaction of complex **1** with PhCCD without using any internal standard.

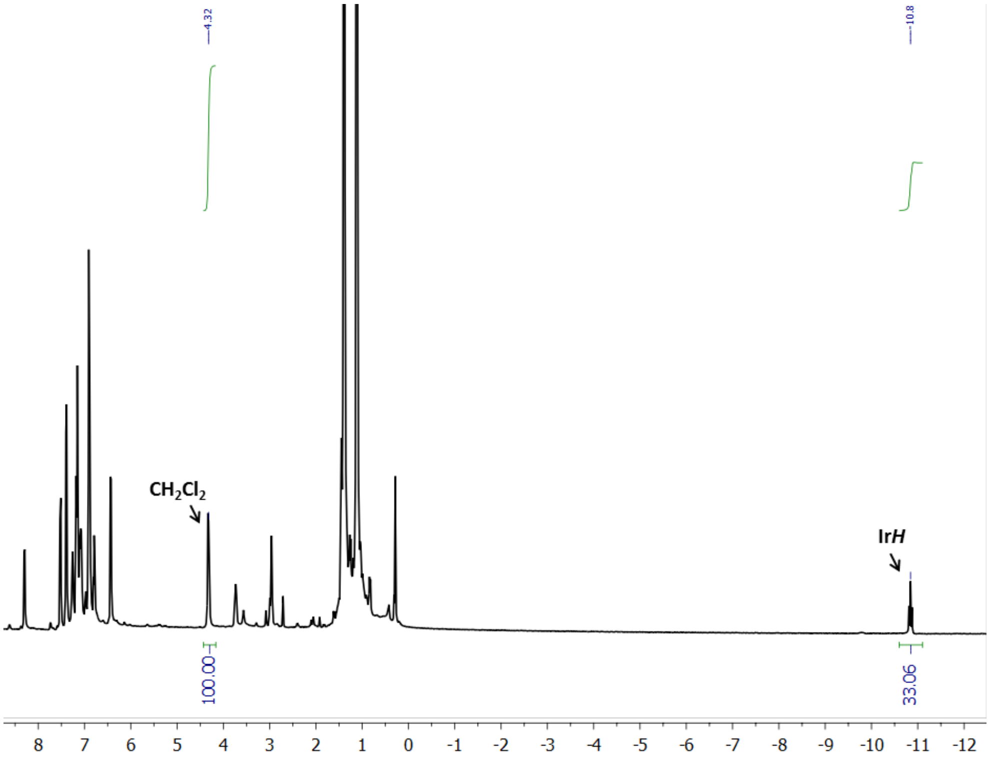


Figure S9. ^{1}H NMR (500.08 MHz, 298 K) spectrum of the reaction of complex **1** with PhCCD. A sealed capillary containing CH_2Cl_2 in C_6D_6 was inserted in the NMR tube for the quantification of Ir*H* signal.

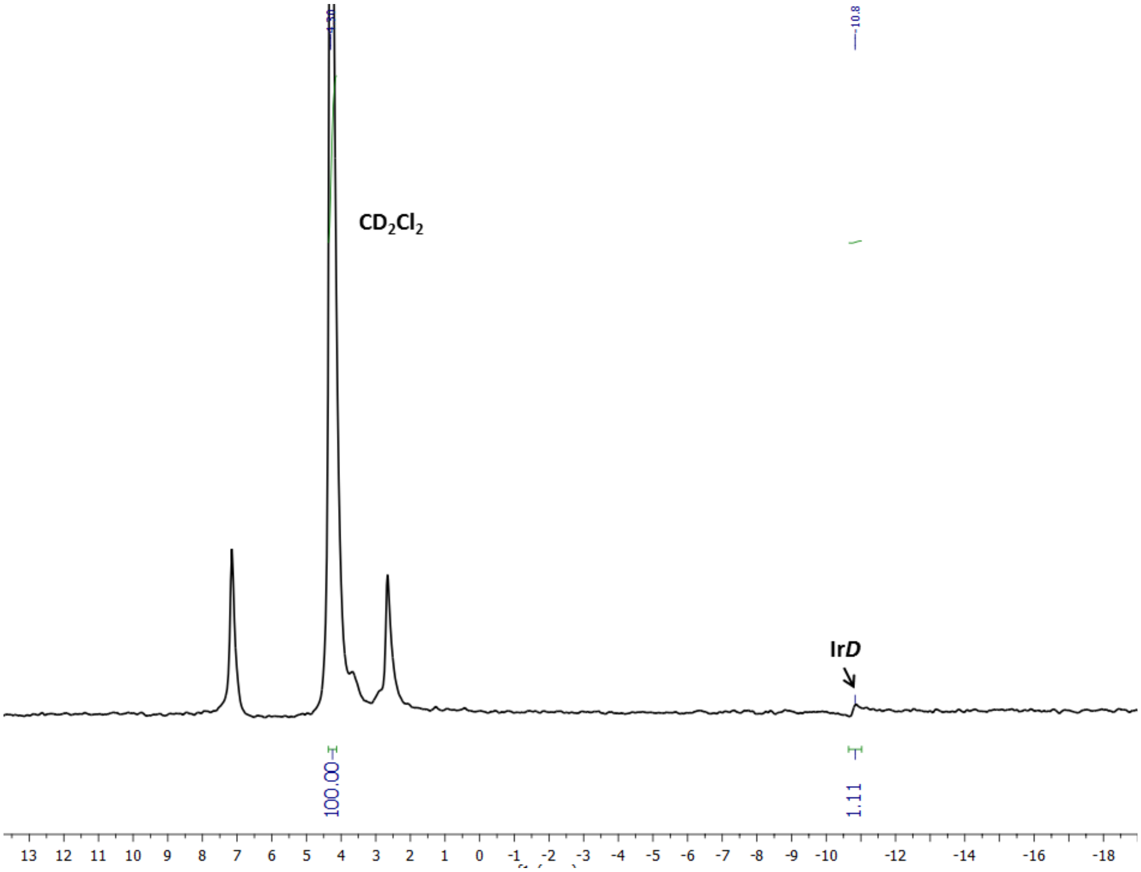


Figure S10. ^{2}H NMR (76.77 MHz, 298 K) spectrum of the reaction of complex **1** with PhCCD. A sealed capillary containing CD_2Cl_2 in C_6H_6 was inserted in the NMR tube for the quantification of Ir*D* signal.

5. References

1. W. L. F. Armarego, D. D. Perrin, *Purification of Laboratory Chemicals*, 4th Edition, Butterworth-Heinemann: Oxford, *2000.*
2. E. Ben-Ari, G. Leitus, L. J. W. Shimon and D. Milstein, *J. Am. Chem. Soc.*, 2006, **128**, 15390-15391.