Iridium catalysed hydroformylation: a mechanistic study using *para*hydrogen induced polarization.

Dexin Guan,[a,b] Cyril Godard,[b,c] Stacey M. Polas,[d] Robert P. Tooze,[d] Adrian, C. Whitwood[b] and Simon B. Duckett [b*]

[a] *School of Innovation and Entrepreneurship, Zhejiang University of Science and Technology, Hangzhou, Zhejiang Provence, China. 310023.*
[b] *Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK. YO10 5DD.*
[c] *Departament de Química Física i Inorgànica, Universitat Rovira I Virgili, C/Marcel.li Domingo s/n, 43007 Tarragona, Spain.*
[d] *Sasol Technology, St Andrews, Scotland, UK.*

Supporting Information

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1. Experimental Section

General methods and chemicals. All reactions were carried out under nitrogen atmosphere, using glove-box, high vacuum or Schlenk line techniques. PPh_3, P(*p*-tol)$_3$, PPh_2Me, $PPhMe_2$, PMe_3 (Strem Chemicals), hydrogen, CO (99.99 %, BOC) and ^{13}CO (99.9 %, Aldrich), $IrCl_3.3H_2O$ (Metals online) were used without further purification. All NMR solvents (Apollo Scientific) were dried using appropriate methods and degassed prior to use: THF, hexane and toluene were dried over sodium and stilled. Tolune-d_8 was placed over a potassium mirror for 24 hours prior use. ^{13}CO labelling of the iridium complexes was achieved by stirring a toluene solution of the corresponding Vaska's type complex under an atmosphere of ^{13}CO for 48 hours. This procedure was repeated three times to achieve high levels of labelling. *trans*-[Ir(PR_2R')$_2$(CO)Cl] were prepared according to the literature, and confirmed by comparison of key ^{31}P signals. The NMR measurements were made using NMR tubes fitted with Young Teflon valves and solvents added by vacuum transfer on a high vacuum line. For the *para*-hydrogen induced polarization (PHIP) experiments, hydrogen in the para spin state was prepared by cooling H_2 to 18 K over a paramagnetic catalyst (activated charcoal).

Synthesis of precursors. THF (50 ml) solutions of *trans*-[Ir(PR_2R')$_2$(CO)Cl] (1.0 g) were stirred at 273 K for 1 hour in the presence of 10 equivalents of C_3H_5MgBr, which was slowly added via cannula transfer. The solution was then allowed to warm to 295 K slowly and stirred for an additional 15 hours. 50 equivalent of dioxane was then added to quench the excess of C_3H_5MgBr. After filtration, the volume of solution was reduced to ca. 10 ml. The dark orange solution was then filtered and the addition of 50 ml of pentane led to the formation of a pale yellow precipitate. The solid was then washed with hexane (ca. 3 x 20 ml) and dried under vacuum. Yield: **1a**, 73.6%; **1b**, 75.1%; **1c**, 92.6%; **1d**, 94.5%; **1e**, 95.2%.

Instrumentation and preparation of NMR samples. All NMR measurements were recorded on Bruker Avance III series 400 MHz or 500 MHz systems. NMR samples were prepared in 5 mm NMR tubes fitted with Young's valves. Each NMR sample contains 10 mg of precursor and ca. 0.6 ml toluene-d_8. Samples were degassed three times under high vacuum prior to CO and *p*-H_2 (3 bars) addition. The 1D and 2D NMR spectra were recorded using normal sequences to characterize emission signals or modified $\pi/4$ pulse when antiphase signals were expected.

Preparation of NMR samples for line shape analysis. The fluxionality of **1b-e** was studied by line shape analysis. The NMR samples of **1b-e** were prepared by dissolving ca. 50 mg of complex in 0.6 ml toluene-d_8. The ^{31}P NMR spectra of these samples were then recorded, stepwise, from 203 K to

293 K, in temperature intervals of 10 K. Calculated ^{31}P NMR spectra were then obtained by simulation in gNMR and proved to be in good accordance with the experimental spectra.

2. Selected NMR spectra used in this analysis

2.1 Precursor characterisation spectra

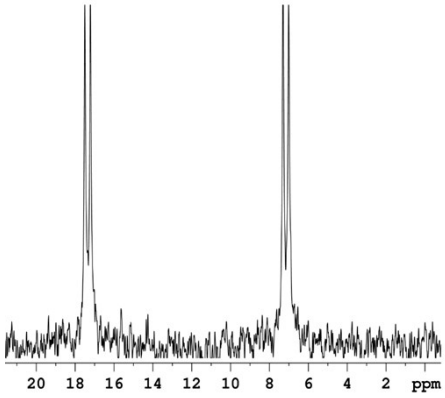


Figure S-1: The 1D ^{31}P NMR spectrum of 1b at 203 K

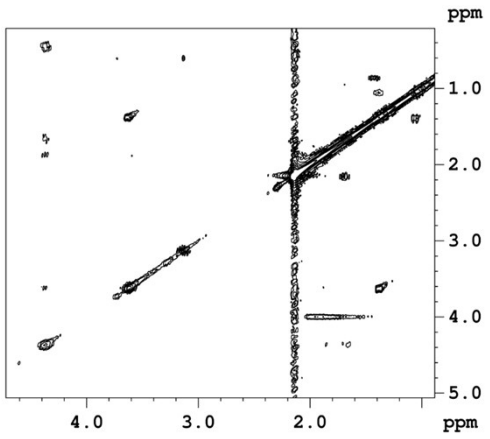


Figure S-2: Expansion of a COSY ^{1}H NMR spectrum showing how all five of the allyl signals for 1b couple at 203 K

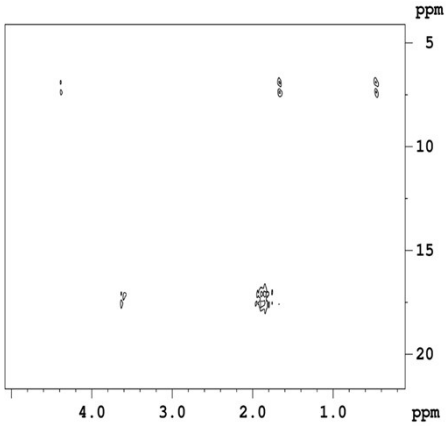


Figure S-3: Expansion of a 2D ^{1}H-^{31}P HMQC NMR spectrum that correlates the allyl proton signals (Figure S-2) to two ^{31}P centres (Figure S-1)

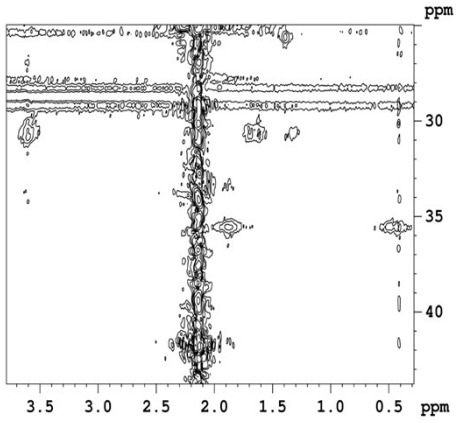


Figure S-4: Expansion of a 2D ^{1}H-^{13}C HMQC NMR spectrum that correlates four CH_2 proton signals to the carbon centres they are attached to in 1b

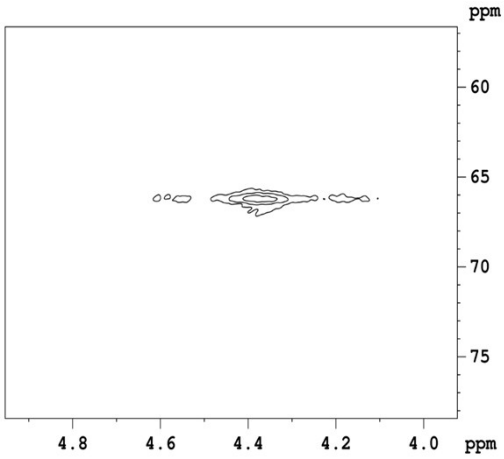


Figure S-5: (left) Expansion of a 2D ^{1}H-^{13}C HMQC NMR spectrum that correlates four CH proton signals to the carbon centres they are attached to in 1b

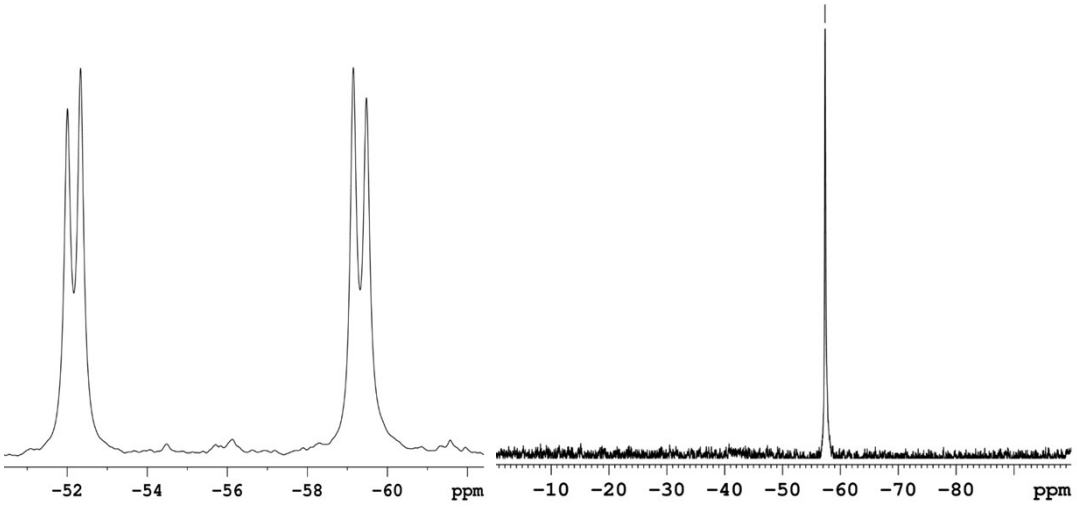


Figure S-6: 1D ^{31}P NMR spectrum of 1e at 203 K (left) and 298 K (right)

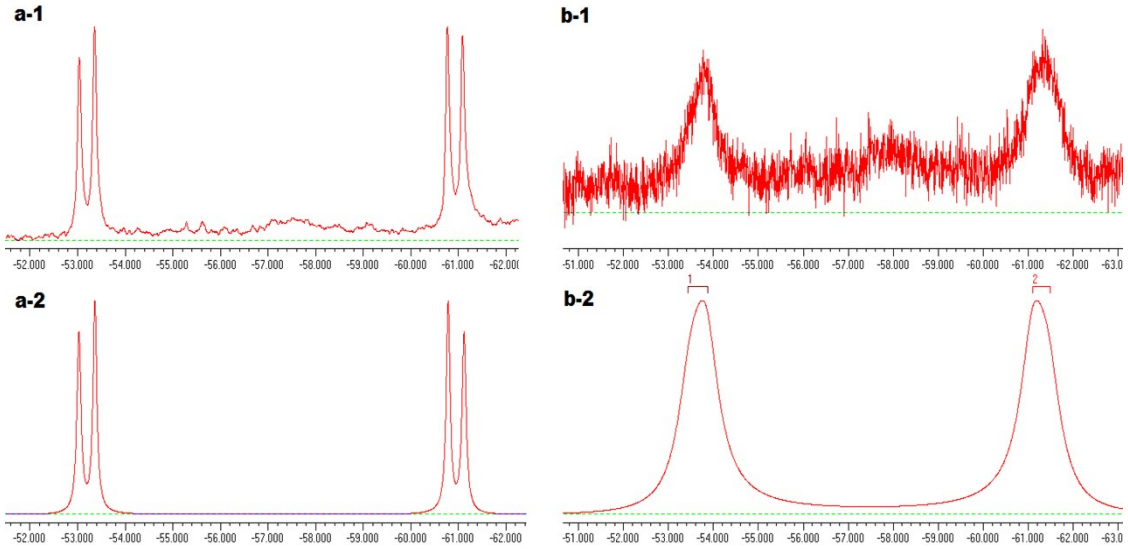


Figure S-7: Comparison of experimental and calculated $^{31}P\{^{1}H\}$ NMR spectra of 1e for line shape analysis. a) 203 K; b) 223 K; label 1: experimental spectra; label 2: calculated spectra

2.2 Typical NMR spectra from reactions with *p*-H_2

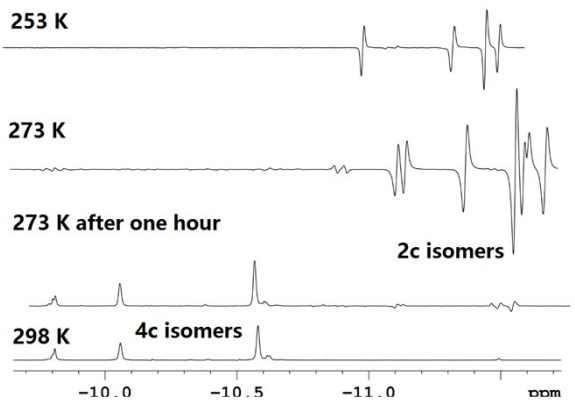


Figure S-8: Series of expansions of 1D $^1H\{^{31}P\}$ NMR spectra when 1c reacts with *p*-H_2 at the indicated temperatures, the formation of $2c_A$, $2c_B$, $3c_M$ and $3c_F$ is revealed

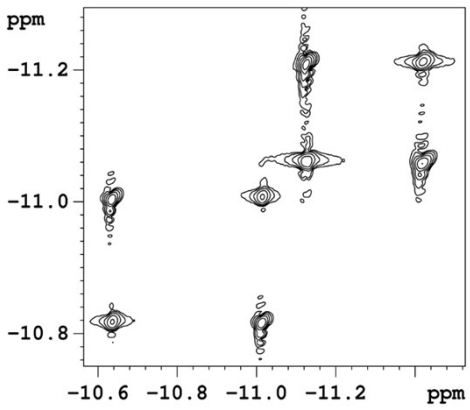


Figure S-9: Selected region of a 2D ^1H-^1H COSY NMR spectrum that links the hydride signals of $2b_A$ and $2b_B$ at 273 K

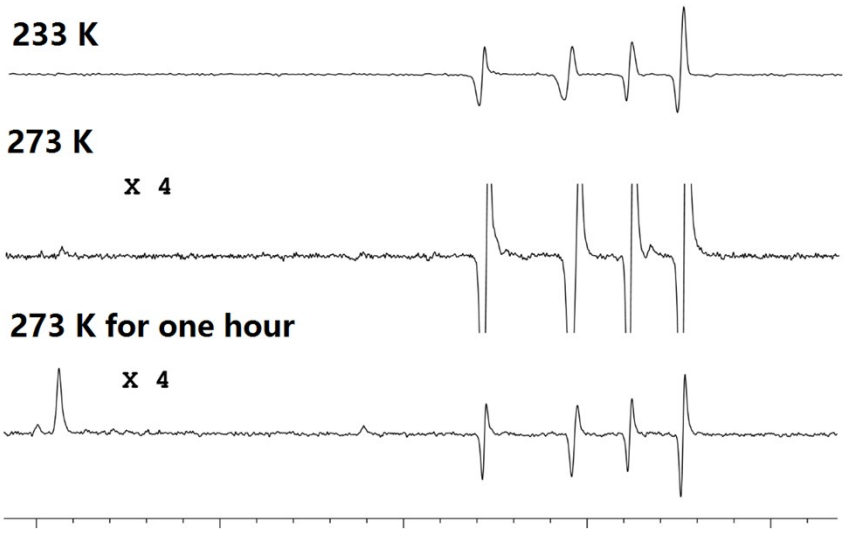


Figure S-10: Series of expansion of 1D $^1H\{^{31}P\}$ NMR spectra shown the different reaction stages that show the formation of $2d_A$, $2d_B$ and $4d_A$ when 1d reacts with *p*-H_2: x 4 indicates vertical expansion level relative to upper spectrum

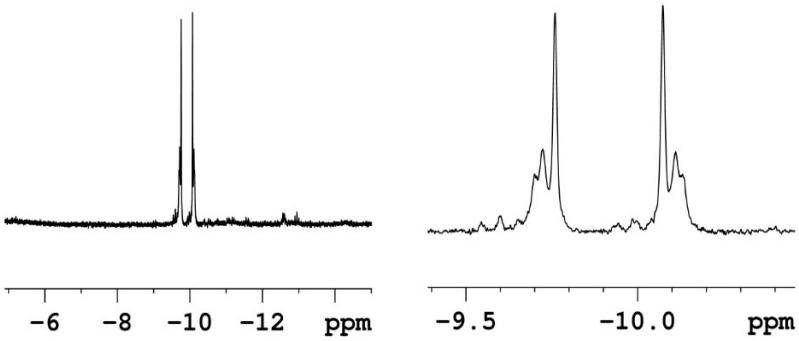


Figure S-11: (left): The hydride region of a ^1H NMR spectrum showing how 4e is the dominant species when 1e reacts with *p*-H_2 and the sample is kept at 333 K for 1 hour. (right): Expansion of the hydride signal for 4e.

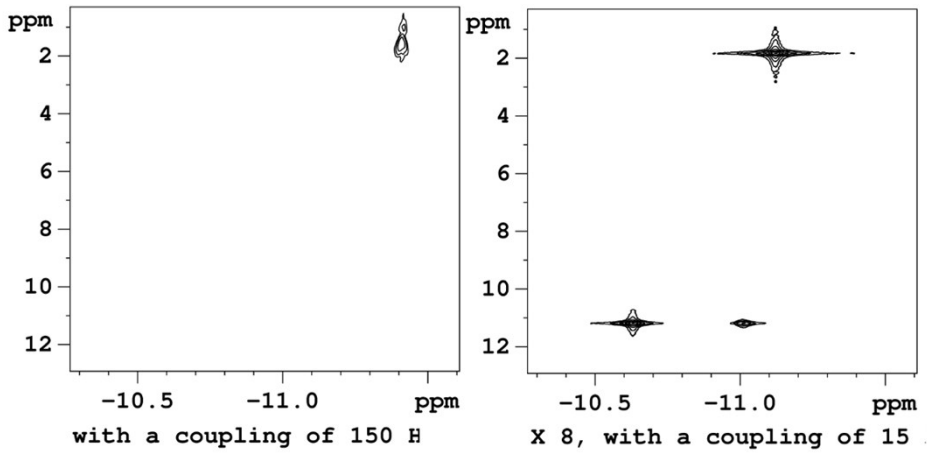


Figure S-12: Expansion of two ^{1}H-^{31}P HMQC NMR spectra which correlate the hydride signals due to $2b_A$ and $2b_B$ to the corresponding ^{31}P centres at 273 K

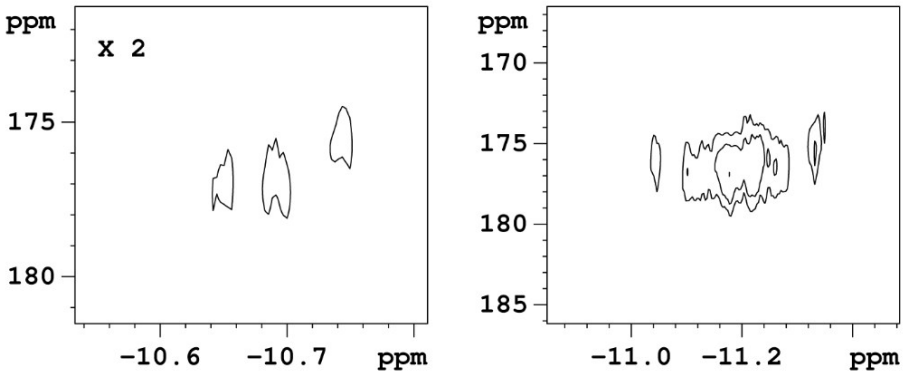


Figure S-13: Expansion of two ^{1}H-^{31}C HMQC NMR spectrum (collected for a coupling constant of 5 Hz) that correlate the hydride signals of $2b_A$ with the corresponding ^{13}C centres at 298 K for a sample employing a mixture of ^{13}CO and H_2

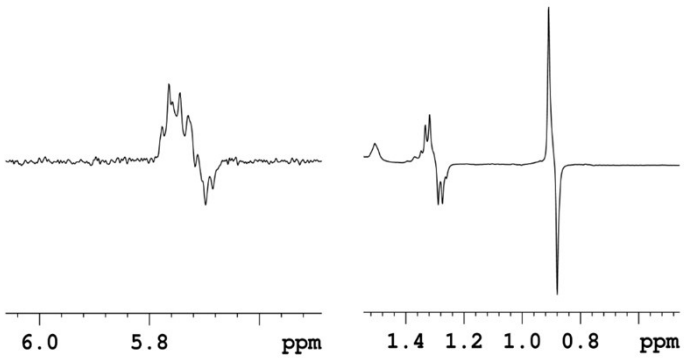


Figure S-14：Expansion of a 1D ^{1}H NMR spectrum showing the enhancement of the hydrogenation products propene (left, alkenic signal) and propane (right, aliphatic signals) from the reaction of 1c with with *p*-H_2 at 273 K

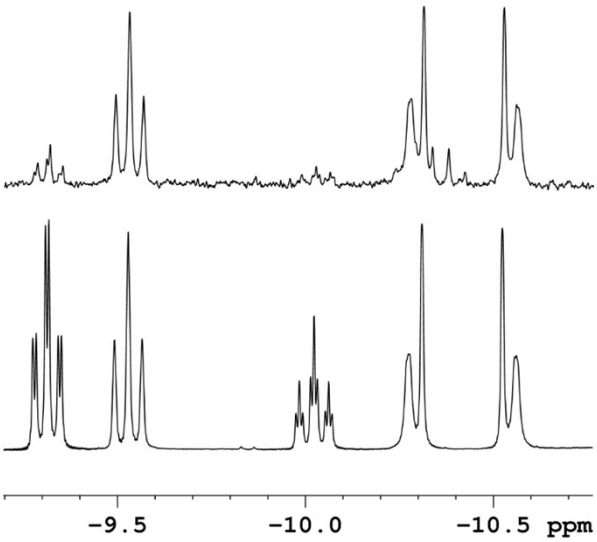


Figure S-15：^{1}H NMR spectra showing evidence for the formation of $3a_F$ during the reaction with H_2 (upper) and the ratio of equilibrated $3a_F$ and $3a_M$ (lower) that is observed after one hour at 373 K (recorded at 298 K).

2.3 Typical NMR spectra from reactions with CO

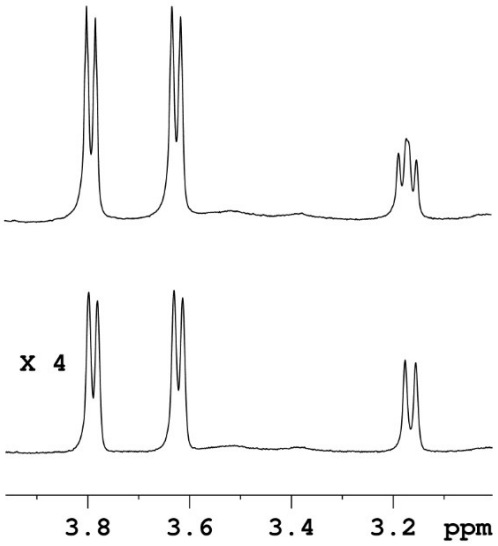


Figure S-16：Expansion of selected regions of 1D ^{1}H (upper) and ^{1}H{^{31}P} (lower) NMR spectra which confirm the formation of 6b, 7b and 8b when 1b is exposed to CO at 298 K

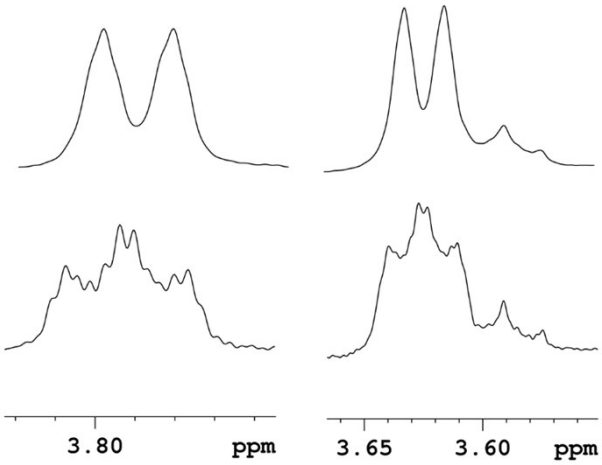


Figure S-17：Expansion of 1D ^{1}H{^{13}C} (upper) and ^{1}H (lower) NMR spectra used to indicate coupling to the ^{13}CO ligand (terminal or acyl carbonyl)

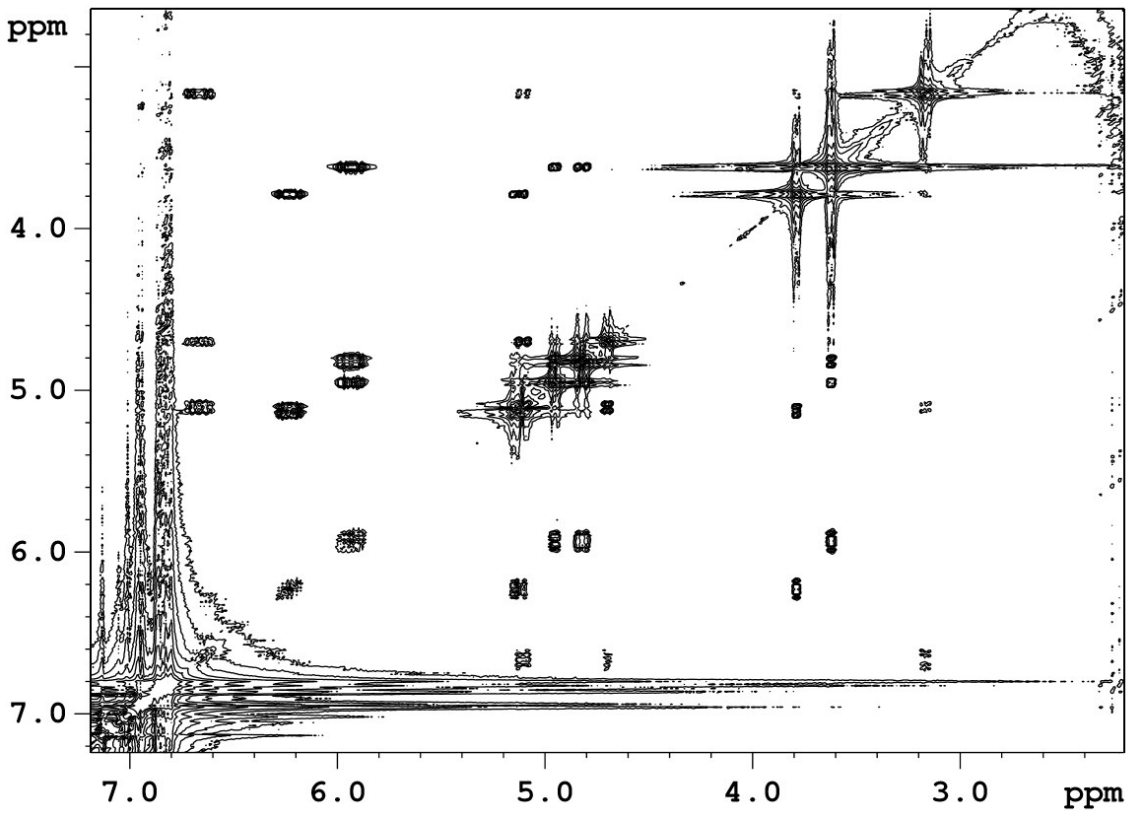


Figure S-18：2D ^{1}H-1H COSY NMR spectrum used to link the proton signals of 6b, 7b and 8b

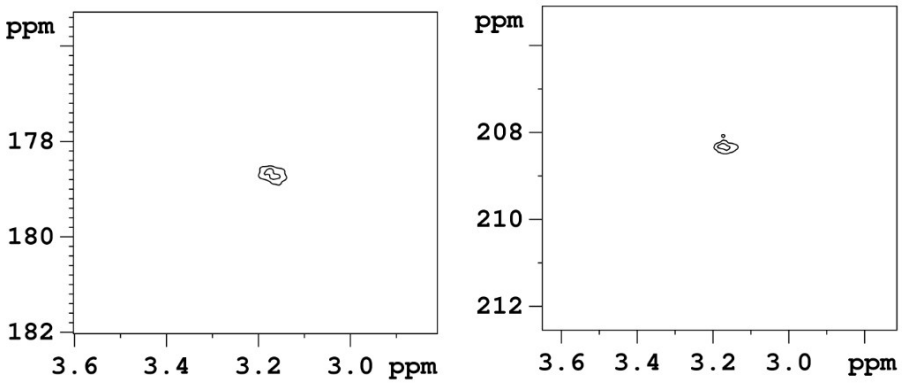


Figure S-19: Expansion of two ^{1}H-^{13}C HMQC NMR spectra used to correlate the proton signal at δ 3.17 for 7b to two ^{13}C centres in a terminal CO ligand (left) and an acyl group (right) respectively as seen when 1b reacts with ^{13}CO

2.4 Typical NMR spectra from the reactions with CO and H_2

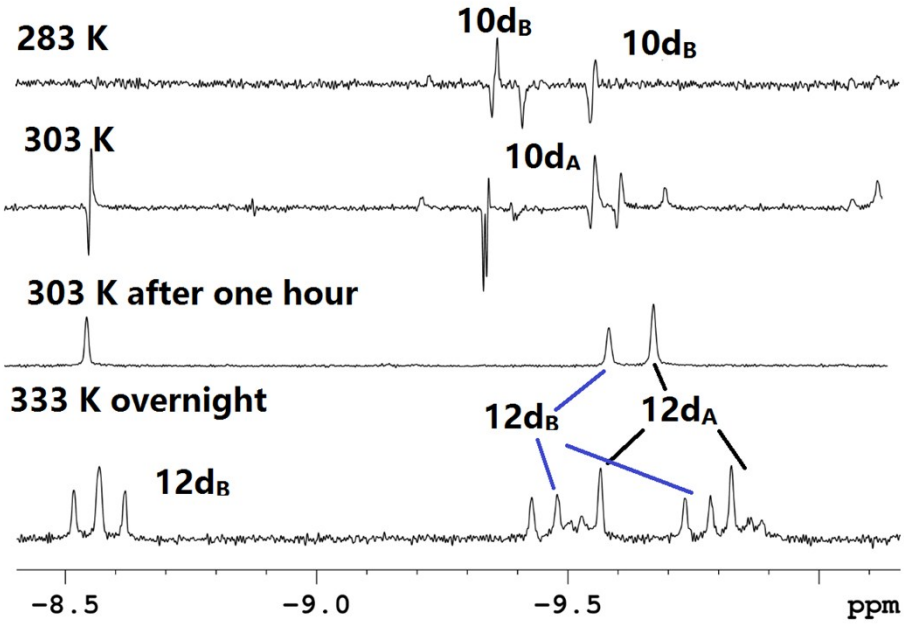


Figure S-20: Series of expansions of four 1D $^{1}H\{^{31}P\}$ and ^{1}H NMR spectra that were recorded when 1d reacts with CO and *p*-H_2 at the indicated temperature. The formation of $10d_A$, $10d_B$, $12d_A$ and $12d_B$ is detailed

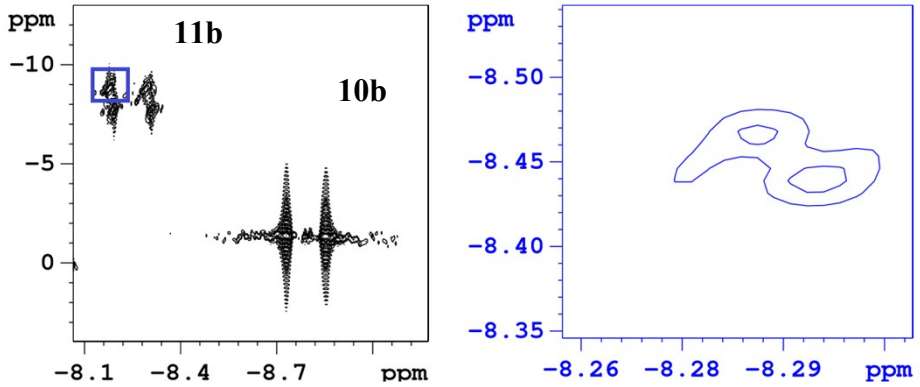


Figure S-21: Left, expansion of a ^{1}H-^{31}P HMQC NMR spectrum which correlates the hydride signals due to 10b and 11b to two ^{31}P centres; right: expansion of part of the cross peak due to 11b as indicated

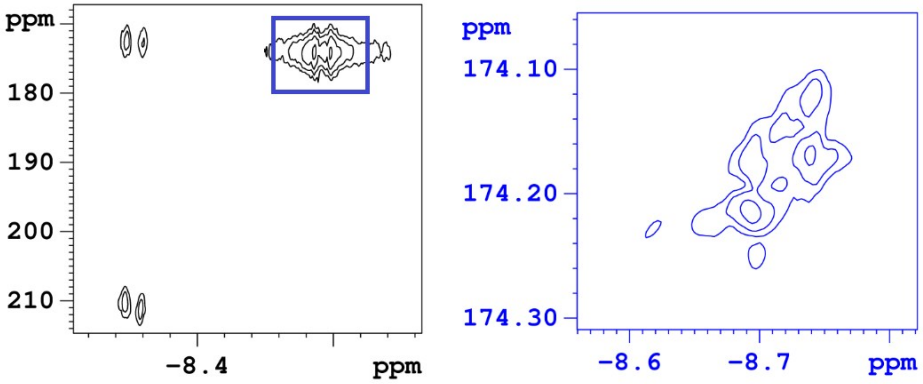


Figure S-22: Left, expansion of a 2D ^{1}H-^{13}C HMQC NMR spectrum to correlate the hydride signals due to 10b and 11b to two ^{13}P centres; right: expansion of part of the cross peak due to 10b

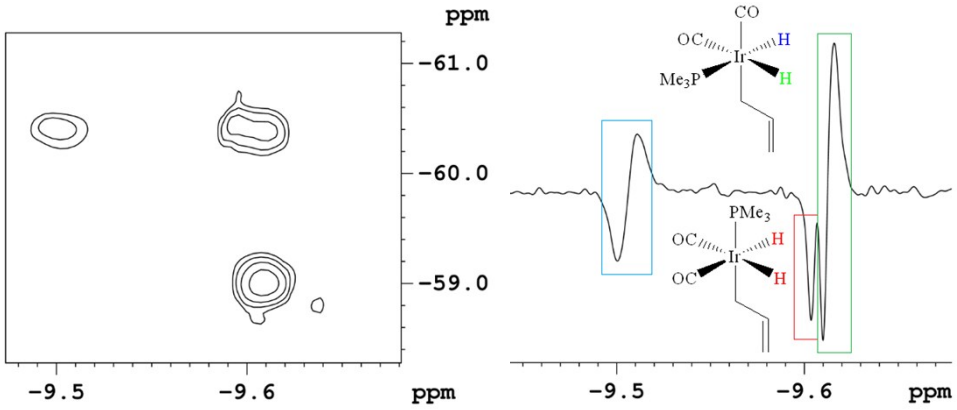


Figure S-23：Left, expansion of a 2D ^{1}H-^{31}P HMQC NMR spectrum used to differentiate the overlapping hydride signals at δ -9.60 due to 10e$_A$ and 10e$_B$ through the second dimension. (right) assignment of hydride signals to 10eA and 10eB.

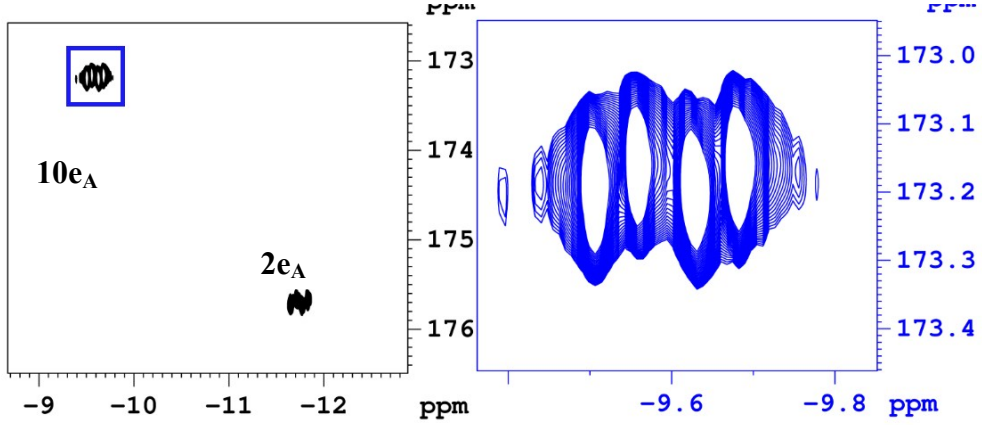
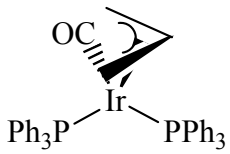


Figure S-24：(left): Expansion of a 2D ^{1}H-^{13}C HMQC NMR spectrum showing how the coupling of the hydride signal in 10e$_A$ and 2e$_A$ to carbonyl groups, when 1e reacts with ^{13}CO and H_2 at 283 K, allows the detection of CO signals; (right) expansion of the cross peak for 10e$_A$ showing extra ^{31}P couplings to the hydride signal in 10e$_A$

3. NMR Characterization data for 1a-1e

3.1 Characterisation of 1a (PPh_3)



NMR spectroscopy (in d_8-toluene at 295 K)

	Chemical shift (ppm)	assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	4.32 (qn)	CH	5.8	J_{HH}
	2.49 (br)	C_3H_5 (*anti*)	-	-
	1.00 (br)	C_3H_5 (*syn*)	-	-
	7-8 (m)	PPh_3	-	-
^{13}C NMR	184.65 (br)	CO	-	-
^{31}P NMR	11.38 (br)	PPh_3		

3. 2 Characterization of 1b (P-tol_3)

	Chemical shift (ppm)	Temperature	Assignment	Coupling constant (Hz)	Assignment
	4.39 (m)	298 K	C<u>H</u>	5.6	J_{HH}
	2.41 (br)	233 K	*syn*-C<u>H</u>$_2$		
	1.12 (br)	233 K	*anti*-C<u>H</u>$_2$		
	4.65 (br)	203 K	C<u>H</u>		
	3.81 (br)	203 K	*syn*-C<u>H</u>$_2$		
	2.21 (br)	203 K	*syn*-C<u>H</u>$_2$'		
^{1}H NMR	1.78 (br)	203 K	*anti*-C<u>H</u>$_2$		
	0.71 (d,d)	203 K	*anti*-C<u>H</u>$_2$'	22	J_{PH}
				5	J_{HH}
	6.97 (m)	203 K	*o*-<u>H</u>-tol	27	J_{PH}
				7.4	J_{HH}
	7.57 (m)	203 K	*m*-<u>H</u>-tol	37	J_{PH}
				7.4	J_{HH}

	2.17 (overlap)	203 K	C<u>H</u>$_3$		
	66.0 (br)	233 K	<u>C</u>H		
	32.7 (br)	233 K	<u>C</u>H$_2$		
	21.2 (overlap)	233 K	<u>Me</u>		
^{13}C NMR	184.7* (br)		<u>C</u>O		
	135.0		*o*-<u>C</u>-tol	44	J_{PC}
	134.1		*m*-<u>C</u>-tol	12.8	J_{PC}
	138.6		*p*-<u>C</u>-tol		
	6.2[a](br)	298 K	<u>P</u>(*p*-tol)$_3$		
^{31}P NMR	8.4[c] (d)	203 K	<u>P</u>(*p*-tol)$_3$		
	17.0[c] (d)	203 K	<u>P</u>(*p*-tol)$_3$	44.5	J_{PP}

3.3 Characterization of 1c (PPh_2Me)

	Chemical shift (ppm)	Temperature	Assignment	Coupling constant (Hz)	Assignment
	4.67 (m)	298 K	C<u>H</u>	5.8	J_{HH}
				1.46	J_{HH}
	4.87 (br)	203 K	C<u>H</u>		
^{1}H NMR	3.33 (br)	203 K	*syn*-C<u>H</u>$_2$		
	1.99 (br)	203 K	*syn*-C<u>H</u>$_2$'		
	1.26(br)	203 K	*anti*-C<u>H</u>$_2$		
	0.58 (br)	203 K	*anti*-C<u>H</u>$_2$'		
	62.6 (s)	233 K	<u>C</u>H		
^{13}C NMR	27.7 (s)	233 K	<u>C</u>H$_2$		
	184.6 (br)		<u>C</u>O		
	-16.6 (br)	298 K	<u>P</u>Ph$_2$Me		
^{31}P NMR	-11.8 (d)	203 K	<u>PPh$_2$Me</u>		
	-18.5 (d)	203 K	<u>PPh$_2$Me</u>	57	J_{PP}

3.4 Characterization of 1d ($PPhMe_2$)

	Chemical shift (ppm)	Temperature	Assignment	Coupling constant (Hz)	Assignment
	4.5 (m)	298 K	C<u>H</u>		
	4.60, m	233 K	C<u>H</u>	5.4	J_{HH}
	2.93 (br)	233 K	*syn*-C<u>H</u>$_2$	-	
	1.04 (br)	233 K	*anti*-C<u>H</u>$_2$	-	
	1.22	233 K	P<u>Me</u>$_2$	-	1.22
	3.02 (br)	203 K	*syn*-C<u>H</u>$_2$	-	
	1.63 (br)	203 K	*anti*-C<u>H</u>$_2$	-	
	1.12 (br)	203 K	*syn*-C<u>H</u>$_2$	-	
	0.56 (br)	203 K	*anti*-C<u>H</u>$_2$	-	
	1.44 (d, t)	203 K	P<u>Me</u>$_2$	5	J_{HH}
				6	J_{PH}
^{1}H NMR	1.24 (d, t)	203 K	P<u>Me</u>	5	J_{HH}
				6	J_{PH}
	1.42 (d, t)	203 K	P<u>Me</u>	5	J_{HH}
				6	J_{PH}
	1.26 (d, t)	203 K	P<u>Me</u>	5	J_{HH}
				6	J_{PH}
	7.27 (m,overlapped)	203 K	*o*-H	12	J_{HH}
	7.07 (overlapped)	203 K	*m*-H		
	7.37 (m, overlapped)	203 K	*o*-H	12	J_{HH}
	7.08 (overlapped)	203 K	*m*-H		
	7.66 (overlapped)	203 K	*p*-H		
	185.9 (d)	203 K	CO	40	J_{PC}
^{13}C NMR	27.7	203 K	Ir-<u>C</u>H$_2$	-	
	60.3	203 K	<u>C</u>H	-	
	-39.9 (br)	298 K	<u>P</u>PhMe$_2$		
^{31}P NMR	-34.0 (d)	203 K	<u>P</u>PhMe$_2$	54.0	J_{PP}
	-43.5 (d)	203 K			

3.5 Characterization of 1e (PMe_3)

	Chemical shift (ppm)	Temperature	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	4.60 (m)	298 K	C<u>H</u>	5.4	J_{HH}
	2.41 (br)	233 K	*syn*-C<u>H</u>$_2$	-	
	1.12 (br)	233 K	*anti*-C<u>H</u>$_2$	-	
	4.83 (br)	203 K	C<u>H</u>	-	
	2.90 (br)	203 K	*syn*-C<u>H</u>$_2$	-	
	1.70 (br)	203 K	*syn*-C<u>H</u>$_2$'	-	
	1.17 (br)	203 K	*anti*-C<u>H</u>$_2$	-	
	0.62(d, br)	203 K	*anti*-C<u>H</u>$_2$'	23.8	J_{PH}
	1.13 (t, overlapped)	203 K	P(C<u>H</u>$_3$)	3.4	virtual coupling
^{3}C NMR	55.6 (br)	203 K	<u>C</u>H	12.8	J_{PC}
				6.5	J_{PC}
	20.8	203 K	<u>C</u>H$_2$		
	24.5	203 K	<u>C</u>H$_2$		
	184.7* (br)		<u>C</u>O		
^{31}P NMR	-57.5 (br)	298 K	<u>P</u>(CH$_3$)		
	-52.1 (d)	203 K	<u>P</u>(CH$_3$)	54.2	J_{PP}
	-59.8 (d)	203 K	<u>P</u>(CH$_3$)		

4. X-ray crystallography:

4.1 Ortep of 1b, Ir(η³-C_3H_5)(CO)(P(*p*-tol)$_3$)$_2$

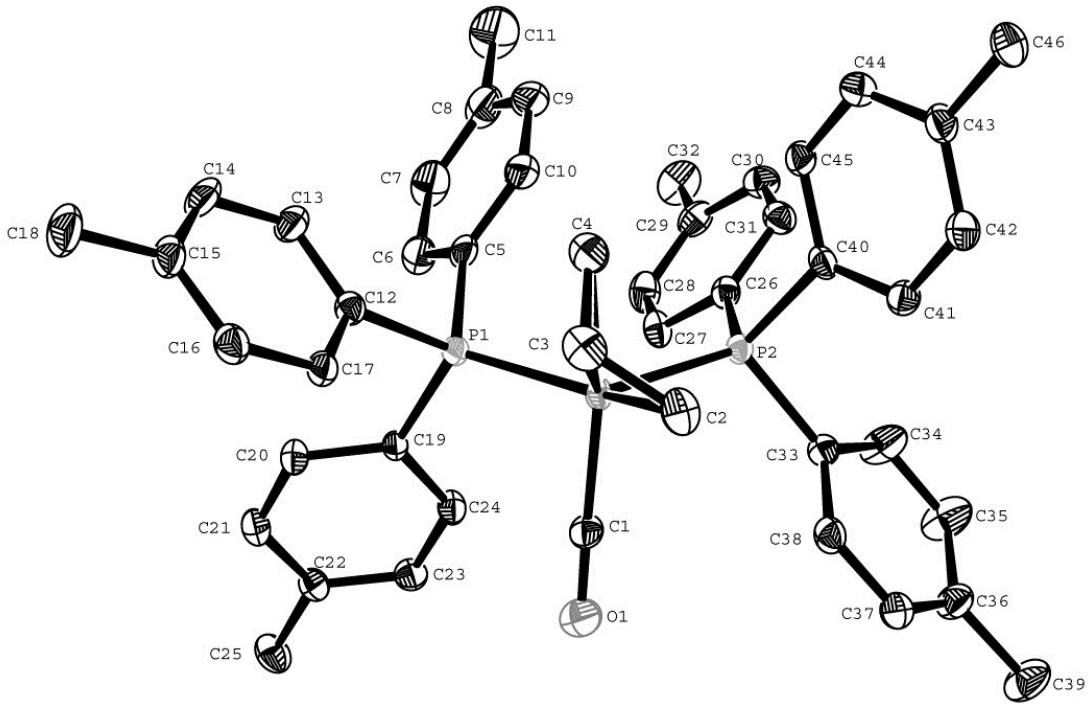


Table S1. Crystal data and structure refinement parameters for Ir(η³-C_3H_5)(CO)(P(*p*-tol)$_3$)$_2$.

Identification code	sbd0409m	
Empirical formula	$C_{46}H_{47}IrOP_2$	
Formula weight	869.98	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.2491(12) Å	α= 67.732(2)°.
	b = 12.2632(12) Å	β= 88.193(2)°.
	c = 16.0048(15) Å	γ = 63.247(2)°.

Volume	1958.4(3) $Å^3$	
Z	2	
Density (calculated)	1.475 Mg/m^3	
Absorption coefficient	3.524 mm^{-1}	
F(000)	876	
Crystal size	0.36 x 0.28 x 0.11 mm^3	
2Theta range for data collection	3.886 to 56.76	
Index ranges	-16<=h<=16, -16<=k<=15, -21<=l<=17	
Reflections collected	14091	
Independent reflections	9580 [R(int) = 0.0295]	
Completeness to theta = 28.38°	97.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.670	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9580 / 0 / 457	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0394, wR2 = 0.1037	
R indices (all data)	R1 = 0.0443, wR2 = 0.1092	
Largest diff. peak and hole	4.07 and -2.43 $e.Å^{-3}$	

Table S2. Fractional Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Ir(η^3-C_3H_5)(CO)(P(*p*-tol)$_3$)$_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir1	5877.4(2)	2033.7(2)	1896.6(2)	16.23(6)
P1	7485.5(9)	-106.8(11)	2384.0(7)	16.6(2)
P2	3945.3(9)	2120.7(11)	1677.4(7)	16.1(2)
O1	6419(3)	3011(4)	-24(2)	32.8(8)
C19	8358(4)	-601(4)	1531(3)	16.3(7)
C12	8740(4)	-449(4)	3202(3)	18.7(8)
C40	2921(4)	2831(5)	2394(3)	18.6(8)
C17	9180(4)	477(5)	2980(3)	22.0(9)
C26	3811(4)	619(4)	1864(3)	18.7(8)
C41	2152(4)	4200(4)	2081(3)	20.6(8)
C5	7153(4)	-1497(5)	2994(3)	21.5(8)
C45	3034(4)	2045(5)	3325(3)	21.1(8)
C1	6219(4)	2595(5)	712(3)	21.3(8)
C44	2379(4)	2614(5)	3904(3)	24.8(9)
C31	2927(4)	317(5)	2311(3)	23.0(9)
C20	9650(4)	-1362(4)	1685(3)	20.6(8)
C42	1519(4)	4768(5)	2664(3)	24.4(9)
C24	7713(4)	-230(5)	680(3)	20.2(8)
C21	10266(4)	-1723(5)	1016(3)	23.8(9)
C16	10192(4)	224(5)	3540(3)	25.1(9)
C23	8335(4)	-604(5)	19(3)	21.9(8)
C3	3022(4)	3268(4)	529(3)	18.4(8)

C23	9619(4)	-1376(5)	177(3)	20.7(8)
C30	2916(4)	-877(5)	2453(3)	25.2(9)
C38	3209(4)	4356(5)	-1(3)	22.6(9)
C15	10786(4)	-954(5)	4328(3)	27.3(10)
C10	6298(4)	-1345(5)	3592(3)	28.0(10)
C43	1616(4)	3991(5)	3580(3)	24.1(9)
C13	9311(4)	-1607(5)	4002(3)	24.4(9)
C27	4654(4)	-283(5)	1537(3)	22.5(9)
C28	4624(4)	-1448(5)	1660(3)	27.8(10)
C37	2478(4)	5270(5)	-850(3)	25.1(9)
C29	3761(5)	-1766(5)	2133(3)	25.7(9)
C14	10327(4)	-1855(5)	4558(3)	28.5(10)
C36	1554(4)	5118(5)	-1201(3)	26.5(10)
C6	7679(4)	-2679(5)	2869(3)	27.7(10)
C7	7366(5)	-3685(6)	3336(4)	38.2(12)
C35	1365(6)	4056(6)	-673(4)	41.6(14)
C34	2085(5)	3142(6)	184(4)	35.3(12)
C9	6005(5)	-2358(6)	4066(4)	37.3(13)
C8	6534(5)	-3542(6)	3945(4)	41.8(14)
C11	6199(7)	-4627(8)	4463(6)	64(2)
C2	5138(4)	3978(5)	1972(3)	26.6(9)
C3	6152(5)	2938(5)	2709(3)	27.3(10)
C4	5888(4)	1887(6)	3306(3)	27.5(10)
C25	10286(5)	-1802(6)	-533(3)	29.3(10)
C46	917(5)	4613(5)	4205(3)	30.3(10)
C32	3753(6)	-3053(6)	2278(4)	38.1(12)
C1	11896(5)	-1212(6)	4909(4)	36.5(12)

8						
C39	736(5)	6154(6)	-2113(4)	39.4(13)		

Table S3 Anisotropic Displacement Parameters ($Å^2×10^3$) for sbd0409m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir1	12.75(8)	18.49(9)	17.94(9)	-8.80(6)	0.96(5)	-6.58(6)
P1	14.0(5)	19.8(5)	15.4(5)	-7.1(4)	1.2(4)	-7.6(4)
P2	13.5(4)	18.0(5)	17.0(5)	-7.8(4)	1.6(4)	-7.0(4)
O1	33.5(19)	31.3(19)	26.8(17)	-8.5(15)	5.0(14)	-12.6(16)
C19	12.7(17)	18.5(19)	16.2(18)	-7.1(15)	2.0(14)	-6.0(15)
C12	16.4(18)	22(2)	18.3(18)	-9.6(16)	2.5(15)	-8.9(17)
C40	13.2(18)	25(2)	20.5(19)	-11.6(17)	4.6(15)	-9.2(16)
C17	16.1(19)	28(2)	18.0(19)	-9.5(17)	1.6(15)	-7.9(18)
C26	17.1(19)	20(2)	18.5(18)	-10.1(16)	0.8(15)	-7.0(16)
C41	20(2)	20(2)	20.2(19)	-8.5(17)	2.4(16)	-7.7(17)
C5	16.0(19)	24(2)	19.9(19)	-3.4(17)	-2.9(15)	-9.6(17)
C45	17.9(19)	21(2)	20(2)	-10.2(17)	2.9(15)	-4.5(17)
C1	21(2)	26(2)	15.3(18)	-9.8(17)	1.3(15)	-8.4(18)
C44	23(2)	29(2)	20(2)	-9.7(18)	5.0(17)	-11.1(19)
C31	22(2)	27(2)	22(2)	-12.7(18)	5.7(16)	-12.0(18)
C20	15.2(19)	20(2)	23(2)	-9.6(17)	1.3(15)	-5.4(16)
C42	22(2)	19(2)	27(2)	-10.3(18)	5.5(17)	-5.2(18)
C24	15.7(18)	24(2)	21(2)	-11.9(17)	2.2(15)	-7.3(17)
C21	15.7(19)	25(2)	29(2)	-11.5(19)	4.1(16)	-8.0(18)
C16	20(2)	34(3)	25(2)	-14(2)	4.0(17)	-14.3(19)
C23	23(2)	27(2)	17.7(19)	-11.5(17)	3.9(16)	-11.7(18)
C33	18.3(19)	20(2)	17.9(18)	-8.5(16)	2.1(15)	-9.0(16)
C22	19(2)	21(2)	24(2)	-11.6(17)	6.3(16)	-9.7(17)
C30	28(2)	28(2)	23(2)	-9.2(19)	4.0(17)	-17(2)
C38	17.1(19)	25(2)	26(2)	-9.9(18)	2.5(16)	-11.0(18)
C15	18(2)	38(3)	23(2)	-16(2)	0.4(17)	-7(2)
C10	23(2)	32(3)	24(2)	-5.8(19)	1.1(17)	-13(2)
C43	18(2)	29(2)	23(2)	-14.5(19)	3.6(16)	-5.9(18)
C13	23(2)	25(2)	20(2)	-5.7(18)	-2.0(16)	-9.8(18)
C27	16.4(19)	27(2)	27(2)	-15.7(19)	3.2(16)	-8.5(17)
C28	23(2)	25(2)	34(2)	-17(2)	0.9(18)	-6.3(19)
C37	21(2)	27(2)	26(2)	-8.6(19)	2.6(17)	-11.2(19)
C29	30(2)	23(2)	23(2)	-8.6(18)	-3.6(18)	-11.6(19)
C14	26(2)	30(3)	19(2)	-5.1(19)	-7.6(17)	-8(2)
C36	27(2)	27(2)	21(2)	-5.0(18)	-2.1(17)	-12(2)
C6	24(2)	23(2)	33(2)	-6.8(19)	1.0(18)	-11.8(19)

C7	34(3)	25(3)	50(3)	-6(2)	-2(2)	-17(2)
C35	46(3)	46(3)	33(3)	-3(2)	-13(2)	-32(3)
C34	41(3)	33(3)	32(3)	1(2)	-8(2)	-29(2)
C9	27(3)	44(3)	30(2)	1(2)	2(2)	-21(2)
C8	29(3)	39(3)	43(3)	5(3)	-6(2)	-22(2)
C11	55(4)	46(4)	75(5)	6(4)	4(4)	-36(4)
C2	25(2)	25(2)	36(2)	-19(2)	6.4(19)	-11.7(19)
C3	31(2)	36(3)	30(2)	-22(2)	6.4(19)	-20(2)
C4	24(2)	41(3)	24(2)	-16(2)	2.9(17)	-18(2)
C25	26(2)	37(3)	32(2)	-22(2)	13.4(19)	-14(2)
C46	28(2)	24(2)	32(2)	-17(2)	10(2)	-3(2)
C32	48(3)	26(3)	44(3)	-16(2)	1(2)	-19(2)
C18	22(2)	49(3)	33(3)	-18(2)	-6(2)	-11(2)
C39	38(3)	41(3)	29(3)	0(2)	-12(2)	-21(3)

Table S4 Bond Lengths for sbd0409m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ir1	P1	2.2954(11)	C42	C43	1.385(6)
Ir1	P2	2.3519(10)	C24	C23	1.382(6)
Ir1	C1	1.862(4)	C21	C22	1.393(6)
Ir1	C2	2.188(5)	C16	C15	1.392(7)
Ir1	C3	2.119(4)	C23	C22	1.392(6)
Ir1	C4	2.193(5)	C33	C38	1.399(6)
P1	C19	1.823(4)	C33	C34	1.383(6)
P1	C12	1.840(4)	C22	C25	1.496(6)
P1	C5	1.835(5)	C30	C29	1.375(7)
P2	C40	1.825(4)	C38	C37	1.388(6)
P2	C26	1.833(5)	C15	C14	1.382(7)
P2	C33	1.837(4)	C15	C18	1.511(6)
O1	C1	1.161(5)	C10	C9	1.386(7)
C19	C20	1.398(6)	C43	C46	1.501(6)
C19	C24	1.402(5)	C13	C14	1.400(6)
C12	C17	1.392(6)	C27	C28	1.384(7)
C12	C13	1.389(6)	C28	C29	1.393(7)
C40	C41	1.387(6)	C37	C36	1.393(6)
C40	C45	1.405(6)	C29	C32	1.511(7)
C17	C16	1.396(6)	C36	C35	1.374(7)
C26	C31	1.391(6)	C36	C39	1.513(7)
C26	C27	1.392(6)	C6	C7	1.392(7)
C41	C42	1.386(6)	C7	C8	1.387(9)
C5	C10	1.394(6)	C35	C34	1.391(7)
C5	C6	1.388(7)	C9	C8	1.387(9)
C45	C44	1.388(6)	C8	C11	1.504(8)
C44	C43	1.394(7)	C2	C3	1.445(7)

C31	C30	1.401(7)	C3	C4	1.449(7)
C20	C21	1.386(6)			

Table S5 Bond Angles for sbd0409m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Ir1	P2	112.02(4)	C26	C31	C30	120.8(4)
C1	Ir1	P1	94.89(14)	C21	C20	C19	121.1(4)
C1	Ir1	P2	103.18(13)	C43	C42	C41	121.4(4)
C1	Ir1	C2	96.0(2)	C23	C24	C19	121.0(4)
C1	Ir1	C3	115.7(2)	C20	C21	C22	121.2(4)
C1	Ir1	C4	154.25(19)	C15	C16	C17	121.1(5)
C2	Ir1	P1	146.62(13)	C24	C23	C22	121.5(4)
C2	Ir1	P2	96.02(13)	C38	C33	P2	119.8(3)
C2	Ir1	C4	66.9(2)	C34	C33	P2	122.1(3)
C3	Ir1	P1	108.27(15)	C34	C33	C38	118.0(4)
C3	Ir1	P2	120.02(14)	C21	C22	C25	121.1(4)
C3	Ir1	C2	39.15(19)	C23	C22	C21	117.7(4)
C3	Ir1	C4	39.21(19)	C23	C22	C25	121.3(4)
C4	Ir1	P1	90.84(14)	C29	C30	C31	120.9(4)
C4	Ir1	P2	97.83(12)	C37	C38	C33	120.6(4)
C19	P1	Ir1	117.79(14)	C16	C15	C18	119.8(5)
C19	P1	C12	100.59(18)	C14	C15	C16	118.3(4)
C19	P1	C5	102.7(2)	C14	C15	C18	121.9(5)
C12	P1	Ir1	113.06(15)	C9	C10	C5	120.9(5)
C5	P1	Ir1	118.04(15)	C44	C43	C46	120.9(4)
C5	P1	C12	102.09(19)	C42	C43	C44	118.1(4)
C40	P2	Ir1	110.90(13)	C42	C43	C46	121.0(4)
C40	P2	C26	103.8(2)	C12	C13	C14	120.7(4)
C40	P2	C33	101.42(19)	C28	C27	C26	121.3(4)
C26	P2	Ir1	121.89(14)	C27	C28	C29	120.8(4)
C26	P2	C33	101.63(19)	C38	C37	C36	120.9(4)
C33	P2	Ir1	114.72(14)	C30	C29	C28	118.5(4)
C20	C19	P1	123.5(3)	C30	C29	C32	121.2(5)
C20	C19	C24	117.5(4)	C28	C29	C32	120.2(5)
C24	C19	P1	119.0(3)	C15	C14	C13	121.0(4)
C17	C12	P1	117.8(3)	C37	C36	C39	120.1(4)
C13	C12	P1	123.6(3)	C35	C36	C37	118.2(4)
C13	C12	C17	118.5(4)	C35	C36	C39	121.6(4)
C41	C40	P2	121.0(3)	C5	C6	C7	120.6(5)
C41	C40	C45	117.4(4)	C8	C7	C6	121.1(6)
C45	C40	P2	120.8(3)	C36	C35	C34	121.3(5)
C12	C17	C16	120.4(4)	C33	C34	C35	120.9(5)
C31	C26	P2	124.5(3)	C10	C9	C8	121.0(5)
C31	C26	C27	117.7(4)	C7	C8	C11	121.7(7)

C27	C26	P2	117.8(3)	C9	C8	C7	118.2(5)
C42	C41	C40	121.2(4)	C9	C8	C11	120.1(6)
C10	C5	P1	118.4(4)	C3	C2	Ir1	67.8(3)
C6	C5	P1	123.4(4)	C2	C3	Ir1	73.0(3)
C6	C5	C10	118.2(4)	C2	C3	C4	113.1(4)
C44	C45	C40	121.2(4)	C4	C3	Ir1	73.2(3)
O1	C1	Ir1	176.3(4)	C3	C4	Ir1	67.6(2)
C45	C44	C43	120.7(4)				

Table S6 Torsion Angles for sbd0409m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Ir1	P1	C19	C20	138.3(3)	C26	P2	C33	C34	25.3(5)
Ir1	P1	C19	C24	-43.1(4)	C26	C31	C30	C29	-1.6(7)
Ir1	P1	C12	C17	-48.3(4)	C26	C27	C28	C29	-1.4(7)
Ir1	P1	C12	C13	135.1(4)	C41	C40	C45	C44	1.4(6)
Ir1	P1	C5	C10	-37.0(4)	C41	C42	C43	C44	0.5(7)
Ir1	P1	C5	C6	140.8(3)	C41	C42	C43	C46	-179.3(4)
Ir1	P2	C40	C41	89.0(3)	C5	P1	C19	C20	-90.1(4)
Ir1	P2	C40	C45	-80.3(4)	C5	P1	C19	C24	88.5(4)
Ir1	P2	C26	C31	137.0(3)	C5	P1	C12	C17	-176.2(3)
Ir1	P2	C26	C27	-42.9(4)	C5	P1	C12	C13	7.3(4)
Ir1	P2	C33	C38	-25.2(4)	C5	C10	C9	C8	-1.3(8)
Ir1	P2	C33	C34	158.8(4)	C5	C6	C7	C8	-0.7(8)
Ir1	C2	C3	C4	-62.6(3)	C45	C40	C41	C42	-0.1(6)
P1	C19	C20	C21	179.2(4)	C45	C44	C43	C42	0.8(7)
P1	C19	C24	C23	-178.8(4)	C45	C44	C43	C46	-179.4(4)
P1	C12	C17	C16	-175.2(4)	C31	C26	C27	C28	-0.6(6)
P1	C12	C13	C14	174.8(4)	C31	C30	C29	C28	-0.4(7)
P1	C5	C10	C9	179.6(4)	C31	C30	C29	C32	-179.7(4)

P1	C5	C6	C7	-178.5(4)	C20	C19	C24	C23	-0.1(7)
P2	C40	C41	C42	-169.7(3)	C20	C21	C22	C23	2.6(7)
P2	C40	C45	C44	171.1(3)	C20	C21	C22	C25	-178.2(4)
P2	C26	C31	C30	-177.8(3)	C24	C19	C20	C21	0.6(7)
P2	C26	C27	C28	179.3(3)	C24	C23	C22	C21	-2.1(7)
P2	C33	C38	C37	-176.8(4)	C24	C23	C22	C25	178.7(4)
P2	C33	C34	C35	177.3(5)	C16	C15	C14	C13	1.5(7)
C19	P1	C12	C17	78.2(4)	C33	P2	C40	C41	-33.2(4)
C19	P1	C12	C13	-98.4(4)	C33	P2	C40	C45	157.4(3)
C19	P1	C5	C10	-168.5(3)	C33	P2	C26	C31	-93.9(4)
C19	P1	C5	C6	9.4(4)	C33	P2	C26	C27	86.3(4)
C19	C20	C21	C22	-1.9(7)	C33	C38	C37	C36	-0.9(7)
C19	C24	C23	C22	0.9(7)	C38	C33	C34	C35	1.2(9)
C12	P1	C19	C20	15.0(4)	C38	C37	C36	C35	1.7(8)
C12	P1	C19	C24	-166.4(4)	C38	C37	C36	C39	177.7(5)
C12	P1	C5	C10	87.6(4)	C10	C5	C6	C7	-0.6(7)
C12	P1	C5	C6	-94.6(4)	C10	C9	C8	C7	0.0(8)
C12	C17	C16	C15	0.2(7)	C10	C9	C8	C11	-179.7(5)
C12	C13	C14	C15	0.2(8)	C13	C12	C17	C16	1.6(7)
C40	P2	C26	C31	11.1(4)	C27	C26	C31	C30	2.1(6)
C40	P2	C26	C27	-168.7(3)	C27	C28	C29	C30	1.9(7)
C40	P2	C33	C38	94.4(4)	C27	C28	C29	C32	-178.8(4)
C40	P2	C33	C34	-81.6(5)	C37	C36	C35	C34	-1.0(9)
C40	C41	C42	C43	-0.9(7)	C36	C35	C34	C33	-0.4(10)

C40	C45	C44	C43	-1.8(7)	C6	C5	C10	C9	1.6(7)
C17	C12	C13	C14	-1.8(7)	C6	C7	C8	C9	1.0(8)
C17	C16	C15	C14	-1.7(7)	C6	C7	C8	C11	-179.3(6)
C17	C16	C15	C18	178.7(5)	C34	C33	C38	C37	-0.6(7)
C26	P2	C40	C41	-138.4(3)	C2	C3	C4	Ir1	62.6(3)
C26	P2	C40	C45	52.3(4)	C18	C15	C14	C13	-178.9(5)
C26	P2	C33	C38	-158.7(4)	C39	C36	C35	C34	-177.0(6)

Table S7 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for sbd0409m.

Atom	*x*	*y*	*z*	U(eq)
H17	8789.3	1285.23	2443.89	26
H41	2057.43	4758.37	1454.32	25
H45	3568.12	1106.75	3562.54	25
H44	2452.61	2058.17	4526.85	30
H31	2322.12	928.49	2523.11	28
H20	10112.69	-1635.87	2257.95	25
H42	1008.55	5710.42	2432.13	29
H24	6834.47	285.62	554.45	24
H21	11145.61	-2217.11	1130.99	29
H16	10480.17	866.33	3379.78	30
H23	7875.56	-328.61	-555.77	26
H30	2318.19	-1076.65	2773.32	30
H38	3841.38	4470.63	223.59	27
H10	5911.17	-534.59	3675.8	34
H13	9007.69	-2237.82	4173.35	29
H27	5262.65	-95.13	1224.35	27
H28	5197.74	-2036.73	1418.93	33
H37	2608.84	6010.75	-1197.71	30
H14	10707.66	-2654.1	5101.01	34
H6	8257.22	-2802.3	2459.94	33
H7	7727.84	-4483.32	3237.24	46
H35	730.05	3944.74	-896.84	50
H34	1929.8	2420.82	536.27	42
H9	5433.14	-2240.84	4480.2	45
H11A	6406.01	-5234.45	4155.97	96
H11	5307.81	-4225.9	4482.84	96

B				
H11C	6664.68	-5129.45	5089.37	96
H2A	4395.04	3924.69	1919.01	32
H2B	5214.08	4716.03	1541.07	32
H3	6913.66	2941.82	2794.24	33
H4A	5109.86	1931.8	3189.59	33
H4B	6493.6	1152.77	3813	33
H25A	11038.72	-1703.82	-559.64	44
H25B	9744.18	-1240.45	-1131.46	44
H25C	10510.59	-2739.55	-373.15	44
H46A	687.52	5565.27	3943.67	45
H46B	1440.84	4165.51	4805.77	45
H46C	164.44	4513.02	4273.38	45
H32A	3152.45	-3163.49	2676.84	57
H32B	4581.23	-3808.86	2565.68	57
H32C	3518.76	-3021.28	1686.31	57
H18A	11713.9	-408.96	5006.35	55
H18B	12614.19	-1433.5	4595.22	55
H18C	12078.92	-1960.3	5501.17	55
H39A	387.31	5751.32	-2374.69	59
H39B	1229.52	6477.32	-2531.67	59
H39C	61.23	6905.49	-2022.78	59

Table S8 Crystal data and structure refinement for sbd0306.

Identification code	sbd0306
Empirical formula	$C_{62}H_{54}IrOP_3$
Formula weight	1100.16
Temperature/K	115
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	13.22571(13)
b/Å	18.46616(17)
c/Å	20.7044(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	5056.61(8)
Z	4
ρ_{calc}g/cm^3	1.445
μ/mm^{-1}	2.777
F(000)	2224.0
Crystal size/mm^3	0.34 × 0.26 × 0.26
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.654 to 60.068
Index ranges	-17 ≤ h ≤ 18, -25 ≤ k ≤ 25, -21 ≤ l ≤ 28
Reflections collected	40071
Independent reflections	14716 [R_{int} = 0.0124, R_{sigma} = 0.0130]
Data/restraints/parameters	14716/0/608
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0152, wR_2 = 0.0367
Final R indexes [all data]	R_1 = 0.0155, wR_2 = 0.0368
Largest diff. peak/hole / e Å^{-3}	0.71/-0.35
Flack parameter	-0.0196(12)

Data collected solved and refined by Adrian C Whitwood

Refinement Special Details

The toluene of crystallisation was disordered and modelled in two positions with refined occupancies of 0.618:0.384(6). The phenyl rings were constrained to be regular hexagons with a C-C bond length of 1.39 angstroms. The ADP of several pairs of carbons were constrained to be equal as follows: C56A & C59A, C57A & C60A, C58A & C61A, C56B & C59B, C57B & C60B, C58B & C61B and C62A & C62B.

Table S9 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for sbd0306. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ}

tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	2613.2(17)	4818.6(13)	6747.1(11)	18.8(4)
C2	542.5(15)	4932.6(13)	5320.3(10)	16.2(4)
C3	713(2)	4194.3(13)	5330.0(14)	24.3(5)
C4	-47(2)	3708.3(15)	5163.3(16)	31.5(6)
C5	-994(2)	3960.0(16)	4987.4(14)	28.4(6)
C6	-1180.6(19)	4698.6(16)	4987.6(13)	25.2(5)
C7	-422.8(18)	5182.4(14)	5154.4(11)	21.0(5)
C8	842.7(17)	6179.9(12)	6038.4(11)	16.1(4)
C9	512.1(19)	5910.4(14)	6636.2(12)	22.3(5)
C10	-45(2)	6344.7(17)	7051.2(14)	27.7(6)
C11	-271(2)	7051.3(16)	6884.4(15)	30.0(6)
C12	45(2)	7322.0(15)	6298.6(15)	29.3(6)
C13	595.3(18)	6890.1(13)	5870.2(14)	22.5(5)
C14	1760.0(17)	6058.3(12)	4774.8(11)	17.1(4)
C15	2401(2)	6660.1(14)	4787.2(13)	23.3(5)
C16	2665(2)	7010.1(16)	4220.0(15)	33.9(7)
C17	2309(3)	6758(2)	3632.5(16)	41.7(8)
C18	1678(2)	6163.6(19)	3612.7(14)	35.7(7)
C19	1391.1(19)	5815.6(15)	4180.1(12)	23.9(5)
C20	3820.6(18)	6866.2(13)	6390.4(11)	16.9(4)
C21	2906.5(19)	6989.4(14)	6710.6(13)	23.1(5)
C22	2543(2)	7688.3(15)	6799.6(15)	27.9(6)
C23	3074(2)	8272.6(13)	6553.6(13)	29.0(5)
C24	3975(2)	8159.5(14)	6229.4(14)	26.2(5)
C25	4359(2)	7460.8(13)	6153.7(12)	20.7(5)
C26	5419.7(17)	6048.8(11)	5852.5(12)	16.6(4)
C27	6368.0(19)	6020.9(14)	6147.9(13)	21.9(5)
C28	7246(2)	6119.1(15)	5794.9(15)	28.5(6)
C29	7193(2)	6267.9(15)	5137.8(14)	27.3(5)
C30	6259(2)	6299.3(14)	4834.1(13)	23.4(5)
C31	5375.3(19)	6187.8(13)	5186.5(12)	20.1(4)
C32	4710.6(18)	5717.1(13)	7109.3(11)	18.2(4)
C33	4867(2)	6236.0(16)	7586.2(13)	28.6(6)
C34	5283(3)	6037(2)	8179.1(14)	39.4(7)
C35	5554(3)	5326(2)	8293.5(14)	38.6(7)
C36	5408(2)	4807.7(18)	7822.3(14)	32.2(6)
C37	4980.1(18)	5000.2(14)	7233.9(11)	23.4(5)
C38	4893.0(18)	3675.1(12)	5745.8(11)	17.0(4)
C39	5658(2)	4185.8(13)	5693.7(13)	22.5(5)
C40	6655.4(19)	4010.3(15)	5836.5(15)	27.9(6)
C41	6898(2)	3313.0(15)	6036.8(13)	29.3(5)
C42	6150(2)	2793.5(15)	6081.2(14)	29.3(6)

C43	5153.0(19)	2973.5(13)	5937.8(15)	24.1(5)
C44	2891.4(16)	3186.2(11)	5896.0(12)	17.3(4)
C45	2938(2)	3055.0(13)	6563.3(12)	24.1(5)
C46	2431(3)	2465.2(15)	6830.9(15)	31.3(6)
C47	1855(3)	2010.2(14)	6439.7(14)	32.5(6)
C48	1800(2)	2138.9(13)	5785.7(14)	26.6(5)
C49	2320.3(19)	2719.5(13)	5512.8(13)	20.4(4)
C50	3513.2(18)	3796.4(13)	4697.6(11)	17.2(4)
C51	4073(2)	3239.6(15)	4408.8(13)	24.7(5)
C52	3980(2)	3096.6(17)	3752.7(14)	29.8(6)
C53	3333(2)	3507.1(17)	3375.8(13)	29.9(6)
C54	2777(2)	4059.1(17)	3655.3(13)	30.2(6)
C55	2874(2)	4204.6(14)	4311.7(12)	22.8(5)
Ir01	3078.8(2)	5092.9(2)	5918.0(2)	12.34(2)
O1	2356.0(16)	4661.2(12)	7260.3(9)	31.2(4)
P1	1577.3(4)	5557.7(3)	5526.7(3)	13.64(10)
P2	4233.7(4)	5922.0(3)	6299.4(3)	13.91(10)
P3	3586.4(4)	3967.0(3)	5571.3(3)	14.22(10)
C56B	5653(6)	5215(4)	3220(3)	56(2)
C57B	6554(5)	5101(4)	2890(4)	49(2)
C58B	6693(4)	5402(4)	2281(3)	46.2(19)
C59B	5932(5)	5817(4)	2002(3)	56(2)
C60B	5031(4)	5930(4)	2333(3)	49(2)
C61B	4891(4)	5629(4)	2942(3)	46.2(19)
C58A	4976(4)	5219(3)	3645(2)	70(2)
C59A	5903(5)	4873(3)	3711(2)	65(2)
C60A	6627(3)	4931(3)	3227(3)	71.8(19)
C61A	6423(4)	5335(3)	2676(2)	70(2)
C56A	5495(5)	5682(2)	2609(2)	65(2)
C57A	4772(3)	5624(3)	3094(3)	71.8(19)
C62A	5382(10)	6118(5)	1994(4)	92(3)
C62B	5485(17)	4867(10)	3861(8)	92(3)

Table S10 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for sbd0306. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	15.5(9)	20.1(11)	20.8(10)	-0.3(8)	-0.2(8)	0.5(8)
C2	15.0(9)	18.3(10)	15.2(9)	-0.7(8)	1.4(7)	-1.3(8)
C3	18.5(11)	18.8(11)	35.6(14)	-1.9(10)	-1.3(10)	0.1(9)
C4	24.3(13)	21.0(12)	49.1(18)	-5.3(12)	1.9(12)	-5.6(10)
C5	20.3(12)	31.3(14)	33.5(14)	-9.1(11)	2.8(10)	-8.4(10)
C6	16.7(11)	34.7(14)	24.0(12)	-2.7(10)	-0.3(9)	-1.9(10)
C7	17.5(10)	22.9(12)	22.6(11)	1.1(9)	-0.4(8)	-0.2(9)
C8	14.3(10)	16.2(9)	17.7(11)	-2.1(8)	-0.3(8)	-0.8(8)
C9	21.9(12)	23.4(12)	21.8(11)	-0.3(9)	3.0(9)	2.3(9)
C10	21.7(12)	38.8(15)	22.8(12)	-5.7(11)	6.1(10)	0.4(11)
C11	20.7(12)	32.6(14)	36.5(15)	-13.5(12)	6.6(11)	3.7(10)
C12	24.2(13)	19.9(12)	43.8(16)	-5.5(11)	4.9(11)	6.5(10)
C13	21.1(11)	19.4(10)	27.1(12)	-0.1(10)	2.9(10)	3.8(8)
C14	16.0(11)	16.4(10)	19.0(10)	4.4(8)	2.5(8)	3.1(8)
C15	23.0(12)	18.8(11)	28.1(13)	4.3(9)	4.4(10)	-0.1(9)
C16	34.1(14)	26.5(13)	41.2(17)	13.0(11)	13.6(12)	0.9(11)
C17	49(2)	46.6(19)	29.1(15)	19.4(14)	13.9(14)	4.7(15)
C18	39.8(18)	49.3(18)	18.0(12)	6.7(12)	2.2(11)	5.3(13)
C19	22.0(12)	30.6(12)	19.1(12)	3.0(9)	0.1(9)	3.9(9)
C20	17.0(11)	15.7(10)	18.0(10)	-3.0(8)	-2.8(8)	-0.4(8)
C21	19.8(13)	20.7(11)	28.8(12)	-6.6(9)	2.1(10)	-1.8(9)
C22	19.8(12)	26.2(13)	37.8(15)	-14.2(11)	0.1(10)	3.7(10)
C23	29.7(13)	18.9(11)	38.4(14)	-9.5(9)	-10.9(13)	6.0(12)
C24	32.1(14)	14.6(11)	31.9(14)	-1.8(9)	-4.3(11)	-0.7(9)
C25	22.0(12)	16.8(10)	23.2(11)	-1.5(8)	0.7(9)	-0.6(9)
C26	17.5(10)	12.3(9)	20.0(11)	-0.2(8)	2.4(9)	-0.3(7)
C27	17.8(11)	22.7(12)	25.2(11)	2.3(9)	0.5(9)	-0.5(9)
C28	16.9(11)	29.3(13)	39.3(16)	5.0(11)	0.2(10)	0.1(9)
C29	20.6(12)	25.5(12)	35.9(14)	4.3(10)	11.1(10)	0.7(9)
C30	24.2(12)	22.0(12)	24.1(12)	2.2(9)	6.8(10)	0.5(9)
C31	21.0(11)	19.1(11)	20.2(11)	1.4(8)	2.9(9)	-0.6(9)
C32	16.7(10)	22.3(11)	15.7(10)	-0.1(8)	0.1(8)	-2.9(8)
C33	33.0(14)	30.3(14)	22.4(12)	-5.1(10)	-6.2(10)	0.5(11)
C34	48.0(19)	48.2(19)	21.8(13)	-6.8(13)	-10.6(13)	-0.4(15)
C35	39.3(17)	57(2)	20.0(12)	8.3(12)	-9.1(11)	-1.9(14)
C36	32.2(13)	33.4(15)	31.2(14)	12.1(12)	-6.8(11)	-1.3(12)
C37	25.1(11)	24.6(13)	20.4(10)	3.3(9)	-2.1(8)	-0.5(9)
C38	17.0(10)	15.0(10)	19.1(10)	-1.0(7)	0.8(8)	2.2(8)
C39	19.5(12)	17.1(11)	30.9(12)	-1.3(9)	4.9(9)	2.5(9)
C40	16.6(11)	26.4(12)	40.8(16)	-5.4(11)	4.3(10)	0.7(8)
C41	17.9(11)	33.4(13)	36.7(14)	-2.6(10)	-1.8(11)	5.7(11)

C42	26.2(13)	24.5(12)	37.4(16)	4.0(10)	-2.0(11)	9.3(10)
C43	22.0(11)	18.7(10)	31.7(12)	2.9(11)	-0.7(11)	1.6(8)
C44	18.7(10)	13.3(8)	20.0(10)	0.1(8)	2.7(9)	1.6(7)
C45	31.9(15)	19.7(11)	20.8(11)	-1.1(8)	4.0(10)	-2.9(10)
C46	47.0(18)	21.8(12)	25.0(13)	2.2(10)	11.2(12)	-3.4(12)
C47	37.2(16)	20.4(11)	40.0(15)	0.2(10)	18.4(14)	-6.8(12)
C48	23.6(13)	18.1(10)	38.1(15)	-5.5(9)	4.2(11)	-5.2(9)
C49	19.9(11)	15.7(10)	25.6(12)	-2.2(9)	0.1(9)	0.7(8)
C50	18.2(10)	17.3(10)	16.0(10)	-3.0(8)	2.2(8)	-1.0(8)
C51	26.7(13)	24.0(12)	23.4(12)	-4.7(10)	0.4(10)	5.3(10)
C52	33.2(15)	32.2(14)	24.1(13)	-10.7(11)	4.6(11)	3.1(11)
C53	34.8(16)	38.7(15)	16.4(11)	-6.4(10)	2.6(10)	-5.0(11)
C54	36.3(15)	34.8(15)	19.6(12)	-0.4(10)	-5.4(10)	2.3(11)
C55	27.4(14)	22.4(11)	18.6(10)	-2.6(8)	0.5(9)	4.5(9)
Ir01	12.41(3)	11.25(3)	13.35(3)	-0.47(3)	0.61(3)	0.15(3)
O1	32.2(10)	41.1(11)	20.3(9)	7.5(8)	6.6(8)	-1.4(9)
P1	13.2(2)	12.3(2)	15.4(2)	0.25(19)	0.34(19)	0.61(18)
P2	14.4(2)	12.6(2)	14.7(2)	-0.79(18)	0.5(2)	-0.82(19)
P3	15.4(3)	12.1(2)	15.2(3)	-0.90(19)	0.7(2)	0.98(19)
C56B	64(5)	50(5)	54(4)	-10(4)	8(4)	-26(4)
C57B	39(4)	55(4)	52(5)	-7(4)	0(3)	-20(3)
C58B	24(3)	48(4)	67(5)	-9(3)	10(3)	-15(3)
C59B	64(5)	50(5)	54(4)	-10(4)	8(4)	-26(4)
C60B	39(4)	55(4)	52(5)	-7(4)	0(3)	-20(3)
C61B	24(3)	48(4)	67(5)	-9(3)	10(3)	-15(3)
C58A	91(4)	56(3)	64(3)	-27(3)	27(3)	-45(3)
C59A	114(5)	30(2)	52(3)	-3(2)	-39(3)	-19(3)
C60A	63(3)	39(3)	114(5)	-27(3)	-35(4)	-4(2)
C61A	91(4)	56(3)	64(3)	-27(3)	27(3)	-45(3)
C56A	114(5)	30(2)	52(3)	-3(2)	-39(3)	-19(3)
C57A	63(3)	39(3)	114(5)	-27(3)	-35(4)	-4(2)
C62A	154(10)	58(5)	64(5)	-5(4)	9(6)	-34(6)
C62B	154(10)	58(5)	64(5)	-5(4)	9(6)	-34(6)

Table S11 Bond Lengths for sbd0306.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	Ir01	1.893(2)	C34	C35	1.381(5)
C1	O1	1.153(3)	C35	C36	1.380(5)
C2	C3	1.382(3)	C36	C37	1.390(3)
C2	C7	1.400(3)	C38	C39	1.387(3)
C2	P1	1.841(2)	C38	C43	1.398(3)
C3	C4	1.391(4)	C38	P3	1.846(2)
C4	C5	1.385(4)	C39	C40	1.390(4)
C5	C6	1.386(4)	C40	C41	1.390(4)
C6	C7	1.386(4)	C41	C42	1.382(4)
C8	C9	1.404(3)	C42	C43	1.391(4)
C8	C13	1.396(3)	C44	C45	1.404(3)
C8	P1	1.840(2)	C44	C49	1.394(3)
C9	C10	1.387(4)	C44	P3	1.837(2)
C10	C11	1.383(4)	C45	C46	1.394(4)
C11	C12	1.377(4)	C46	C47	1.393(4)
C12	C13	1.397(4)	C47	C48	1.377(4)
C14	C15	1.398(3)	C48	C49	1.394(3)
C14	C19	1.398(3)	C50	C51	1.401(3)
C14	P1	1.827(2)	C50	C55	1.386(3)
C15	C16	1.385(4)	C50	P3	1.839(2)
C16	C17	1.385(5)	C51	C52	1.389(4)
C17	C18	1.379(5)	C52	C53	1.384(4)
C18	C19	1.392(4)	C53	C54	1.384(4)
C20	C21	1.397(3)	C54	C55	1.391(4)
C20	C25	1.398(3)	Ir01	P1	2.3102(6)
C20	P2	1.837(2)	Ir01	P2	2.3023(6)
C21	C22	1.389(4)	Ir01	P3	2.2996(6)
C22	C23	1.384(4)	C56B	C57B	1.3900
C23	C24	1.385(4)	C56B	C61B	1.3900
C24	C25	1.395(3)	C56B	C62B	1.490(16)
C26	C27	1.396(3)	C57B	C58B	1.3900
C26	C31	1.404(3)	C58B	C59B	1.3900
C26	P2	1.836(2)	C59B	C60B	1.3900
C27	C28	1.384(4)	C60B	C61B	1.3900
C28	C29	1.390(4)	C58	C59	1.3900

			A	A	
C29	C30	1.387(4)	C58 A	C57 A	1.3900
C30	C31	1.393(3)	C59 A	C60 A	1.3900
C32	C33	1.391(3)	C60 A	C61 A	1.3900
C32	C37	1.395(3)	C61 A	C56 A	1.3900
C32	P2	1.831(2)	C56 A	C57 A	1.3900
C33	C34	1.395(4)	C56 A	C62 A	1.516(10)

Table S12 Bond Angles for sbd0306.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	C1	Ir01	177.9(2)	C45	C44	P3	118.28(18)
C3	C2	C7	118.5(2)	C49	C44	C45	118.5(2)
C3	C2	P1	119.59(18)	C49	C44	P3	123.2(2)
C7	C2	P1	121.89(19)	C46	C45	C44	120.3(2)
C2	C3	C4	121.0(2)	C47	C46	C45	120.2(3)
C5	C4	C3	120.2(3)	C48	C47	C46	119.8(2)
C4	C5	C6	119.4(2)	C47	C48	C49	120.3(2)
C5	C6	C7	120.4(2)	C44	C49	C48	120.8(2)
C6	C7	C2	120.5(2)	C51	C50	P3	121.20(19)
C9	C8	P1	116.78(18)	C55	C50	C51	118.4(2)
C13	C8	C9	118.7(2)	C55	C50	P3	120.40(18)
C13	C8	P1	124.52(18)	C52	C51	C50	120.7(3)
C10	C9	C8	120.4(2)	C53	C52	C51	120.1(3)
C11	C10	C9	120.4(3)	C54	C53	C52	119.8(2)
C12	C11	C10	119.8(2)	C53	C54	C55	120.1(3)
C11	C12	C13	120.7(3)	C50	C55	C54	121.0(2)
C8	C13	C12	120.0(3)	C1	Ir01	P1	97.92(7)
C15	C14	C19	118.9(2)	C1	Ir01	P2	94.75(7)
C15	C14	P1	117.83(19)	C1	Ir01	P3	97.83(7)
C19	C14	P1	122.84(18)	P2	Ir01	P1	116.33(2)
C16	C15	C14	120.6(3)	P3	Ir01	P1	118.51(2)
C17	C16	C15	120.1(3)	P3	Ir01	P2	120.97(2)
C18	C17	C16	119.9(3)	C2	P1	Ir01	119.18(8)
C17	C18	C19	120.5(3)	C8	P1	C2	97.62(10)
C18	C19	C14	120.0(3)	C8	P1	Ir01	118.94(7)
C21	C20	C25	118.7(2)	C14	P1	C2	102.58(10)
C21	C20	P2	117.42(19)	C14	P1	C8	104.15(10)
C25	C20	P2	123.92(19)	C14	P1	Ir01	111.92(8)
C22	C21	C20	120.9(3)	C20	P2	Ir01	117.98(8)

C23	C22	C21	120.0(3)	C26	P2	C20	100.64(10)
C22	C23	C24	119.8(2)	C26	P2	Ir01	118.60(8)
C23	C24	C25	120.5(3)	C32	P2	C20	101.81(11)
C24	C25	C20	120.1(2)	C32	P2	C26	101.16(11)
C27	C26	C31	118.3(2)	C32	P2	Ir01	113.90(8)
C27	C26	P2	122.82(19)	C38	P3	Ir01	118.44(8)
C31	C26	P2	118.85(18)	C44	P3	C38	99.64(10)
C28	C27	C26	121.2(2)	C44	P3	C50	101.49(11)
C27	C28	C29	120.0(3)	C44	P3	Ir01	116.69(7)
C30	C29	C28	119.8(2)	C50	P3	C38	101.06(11)
C29	C30	C31	120.2(2)	C50	P3	Ir01	116.53(8)
C30	C31	C26	120.4(2)	C57B	C56B	C61B	120.0
C33	C32	C37	119.0(2)	C57B	C56B	C62B	120.1(10)
C33	C32	P2	124.0(2)	C61B	C56B	C62B	119.9(10)
C37	C32	P2	116.96(18)	C56B	C57B	C58B	120.0
C32	C33	C34	120.1(3)	C59B	C58B	C57B	120.0
C35	C34	C33	120.3(3)	C58B	C59B	C60B	120.0
C36	C35	C34	120.1(3)	C61B	C60B	C59B	120.0
C35	C36	C37	120.0(3)	C60B	C61B	C56B	120.0
C36	C37	C32	120.6(2)	C59A	C58A	C57A	120.0
C39	C38	C43	118.2(2)	C60A	C59A	C58A	120.0
C39	C38	P3	117.96(18)	C59A	C60A	C61A	120.0
C43	C38	P3	123.82(19)	C56A	C61A	C60A	120.0
C38	C39	C40	121.1(2)	C61A	C56A	C62A	114.5(7)
C39	C40	C41	119.9(3)	C57A	C56A	C61A	120.0
C42	C41	C40	119.8(3)	C57A	C56A	C62A	125.5(7)
C41	C42	C43	119.9(2)	C56A	C57A	C58A	120.0
C42	C43	C38	121.0(2)				

Table S13 Torsion Angles for sbd0306.

A	B	C	D	Angle/°	A	B	C	D	Angle/°

C2	C3	C4	C5	-0.4(5)	C37	C32	P2	Ir01	44.4(2)
C3	C2	C7	C6	-1.7(3)	C38	C39	C40	C41	-0.2(4)
C3	C2	P1	C8	-136.8(2)	C39	C38	C43	C42	0.8(4)
C3	C2	P1	C14	116.8(2)	C39	C38	P3	C44	-166.9(2)
C3	C2	P1	Ir01	-7.5(2)	C39	C38	P3	C50	89.2(2)
C3	C4	C5	C6	-0.9(5)	C39	C38	P3	Ir01	-39.3(2)
C4	C5	C6	C7	0.8(4)	C39	C40	C41	C42	1.2(4)
C5	C6	C7	C2	0.5(4)	C40	C41	C42	C43	-1.3(4)
C7	C2	C3	C4	1.6(4)	C41	C42	C43	C38	0.2(4)
C7	C2	P1	C8	43.0(2)	C43	C38	C39	C40	-0.9(4)
C7	C2	P1	C14	-63.5(2)	C43	C38	P3	C44	11.9(2)
C7	C2	P1	Ir01	172.29(15)	C43	C38	P3	C50	-91.9(2)
C8	C9	C10	C11	-0.7(4)	C43	C38	P3	Ir01	139.5(2)
C9	C8	C13	C12	1.2(4)	C44	C45	C46	C47	-1.4(5)
C9	C8	P1	C2	69.6(2)	C45	C44	C49	C48	0.5(4)
C9	C8	P1	C14	174.65(19)	C45	C44	P3	C38	65.3(2)
C9	C8	P1	Ir01	-59.9(2)	C45	C44	P3	C50	168.76(19)
C9	C10	C11	C12	1.0(4)	C45	C44	P3	Ir01	-63.5(2)
C10	C11	C12	C13	-0.1(4)	C45	C46	C47	C48	0.9(5)
C11	C12	C13	C8	-1.0(4)	C46	C47	C48	C49	0.4(4)
C13	C8	C9	C10	-0.3(4)	C47	C48	C49	C44	-1.1(4)
C13	C8	P1	C2	-110.2(2)	C49	C44	C45	C46	0.7(4)
C13	C8	P1	C14	-5.1(2)	C49	C44	P3	C38	-114.8(2)
C13	C8	P1	Ir01	120.32(19)	C49	C44	P3	C50	-11.4(2)
C14	C15	C16	C17	-1.1(4)	C49	C44	P3	Ir01	116.40(18)
C15	C14	C19	C18	1.2(4)	C50	C51	C52	C53	0.3(5)
C15	C14	P1	C2	170.76(19)	C51	C50	C55	C54	1.0(4)
C15	C14	P1	C8	69.4(2)	C51	C50	P3	C38	30.3(2)

C15	C14	P1	Ir01	-60.3(2)	C51	C50	P3	C44	-72.0(2)
C15	C16	C17	C18	0.9(5)	C51	C50	P3	Ir01	160.11(19)
C16	C17	C18	C19	0.4(5)	C51	C52	C53	C54	-0.2(5)
C17	C18	C19	C14	-1.4(5)	C52	C53	C54	C55	0.6(5)
C19	C14	C15	C16	0.0(4)	C53	C54	C55	C50	-1.0(4)
C19	C14	P1	C2	-17.3(2)	C55	C50	C51	C52	-0.7(4)
C19	C14	P1	C8	-118.6(2)	C55	C50	P3	C38	-151.7(2)
C19	C14	P1	Ir01	111.63(19)	C55	C50	P3	C44	105.9(2)
C20	C21	C22	C23	1.9(4)	C55	C50	P3	Ir01	-21.9(2)
C21	C20	C25	C24	-1.1(4)	P1	C2	C3	C4	-178.6(2)
C21	C20	P2	C26	179.20(19)	P1	C2	C7	C6	178.59(18)
C21	C20	P2	C32	-76.9(2)	P1	C8	C9	C10	179.9(2)
C21	C20	P2	Ir01	48.6(2)	P1	C8	C13	C12	-179.1(2)
C21	C22	C23	C24	-1.2(4)	P1	C14	C15	C16	172.3(2)
C22	C23	C24	C25	-0.6(4)	P1	C14	C19	C18	-170.7(2)
C23	C24	C25	C20	1.7(4)	P2	C20	C21	C22	179.9(2)
C25	C20	C21	C22	-0.7(4)	P2	C20	C25	C24	178.3(2)
C25	C20	P2	C26	-0.1(2)	P2	C26	C27	C28	180.0(2)
C25	C20	P2	C32	103.8(2)	P2	C26	C31	C30	178.89(19)
C25	C20	P2	Ir01	-130.78(19)	P2	C32	C33	C34	-176.6(2)
C26	C27	C28	C29	1.8(4)	P2	C32	C37	C36	175.9(2)
C27	C26	C31	C30	-0.4(4)	P3	C38	C39	C40	178.1(2)
C27	C26	P2	C20	101.0(2)	P3	C38	C43	C42	-178.0(2)
C27	C26	P2	C32	-3.5(2)	P3	C44	C45	C46	-179.4(2)

C27	C26	P2	Ir01	−128.77(18)	P3	C44	C49	C48	−179.37(19)
C27	C28	C29	C30	-1.6(4)	P3	C50	C51	C52	177.3(2)
C28	C29	C30	C31	0.5(4)	P3	C50	C55	C54	-177.0(2)
C29	C30	C31	C26	0.5(4)	C56B	C57B	C58B	C59B	0.0
C31	C26	C27	C28	-0.7(4)	C57B	C56B	C61B	C60B	0.0
C31	C26	P2	C20	-78.31(19)	C57B	C58B	C59B	C60B	0.0
C31	C26	P2	C32	177.25(18)	C58B	C59B	C60B	C61B	0.0
C31	C26	P2	Ir01	51.9(2)	C59B	C60B	C61B	C56B	0.0
C32	C33	C34	C35	0.9(5)	C61B	C56B	C57B	C58B	0.0
C33	C32	C37	C36	-0.7(4)	C58A	C59A	C60A	C61A	0.0
C33	C32	P2	C20	-11.1(3)	C59A	C58A	C57A	C56A	0.0
C33	C32	P2	C26	92.4(2)	C59A	C60A	C61A	C56A	0.0
C33	C32	P2	Ir01	-139.2(2)	C60A	C61A	C56A	C57A	0.0
C33	C34	C35	C36	-0.5(5)	C60A	C61A	C56A	C62A	178.6(5)
C34	C35	C36	C37	-0.5(5)	C61A	C56A	C57A	C58A	0.0
C35	C36	C37	C32	1.1(4)	C57A	C58A	C59A	C60A	0.0
C37	C32	C33	C34	-0.3(4)	C62A	C56A	C57A	C58A	-178.5(6)
C37	C32	P2	C20	172.51(19)	C62B	C56B	C57B	C58B	177.4(10)
C37	C32	P2	C26	-84.0(2)	C62B	C56B	C61B	C60B	-177.4(10)

Table S14 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for sbd0306.

Atom	*x*	*y*	*z*	U(eq)
H3	1359.27	4016.12	5452.37	29
H4	84.48	3202.54	5170.2	38
H5	-1511.37	3629.33	4867.61	34
H6	-1831.41	4874.22	4872.79	30

H7	-559.51	5687.47	5156.16	25
H9	670.66	5427.31	6757.28	27
H10	-271.74	6155.59	7452.46	33
H11	-643.34	7349.21	7173.08	36
H12	-112.54	7807.36	6184.47	35
H13	800.92	7079.79	5464.38	27
H15	2656.7	6830.56	5188.04	28
H16	3091.74	7423.65	4234.05	41
H17	2498.3	6994.69	3243.41	50
H18	1437.7	5990.39	3208.86	43
H19	944.56	5413.1	4163.28	29
H21	2528.44	6589.93	6869.63	28
H22	1930.97	7765.2	7029.41	34
H23	2819.38	8750.01	6606.95	35
H24	4335.62	8560.53	6057.18	31
H25	4987.97	7389.2	5941.04	25
H27	6411.28	5932.86	6599.1	26
H28	7885.25	6084.83	6001.86	34
H29	7794.38	6347.81	4897.32	33
H30	6222.14	6397.12	4384.29	28
H31	4738.59	6206.01	4974.8	24
H33	4690.97	6726.87	7507.79	34
H34	5380.29	6391.18	8505.76	47
H35	5841.97	5193.62	8697.04	46
H36	5600.67	4319.77	7900.15	39
H37	4869.72	4640.34	6913.63	28
H39	5497.3	4663.59	5558.1	27
H40	7170.28	4366.28	5797.24	34
H41	7576.97	3194.1	6142.95	35
H42	6315.01	2314	6209.39	35
H43	4641.47	2614.3	5970.83	29
H45	3316.22	3369.86	6833.86	29
H46	2477.48	2373.16	7281.35	38
H47	1502.72	1612.37	6623.7	39
H48	1404.48	1830.4	5519.04	32
H49	2285.44	2798.17	5059.94	25
H51	4520.36	2956.98	4664.15	30
H52	4360.91	2716.29	3562.36	36
H53	3270.95	3410.34	2926.86	36
H54	2327.42	4339.02	3398.65	36
H55	2497.22	4589.41	4498.14	27
H	3500(30)	5310(20)	5275(17)	40(10)
H57 B	7074.37	4818.26	3079.91	58
H58	7308.86	5324.73	2054.8	55

B				
H59 B	6026.78	6022.28	1586.25	67
H60 B	4510.18	6213.37	2142.81	58
H61 B	4275.67	5706.9	3167.91	55
H58 A	4482.03	5179.32	3975.8	84
H59 A	6042.89	4596	4087.77	78
H60 A	7260.31	4693.85	3272.34	86
H61 A	6916.88	5375.02	2344.92	84
H57 A	4138.6	5860.51	3048.37	86
H62 D	5570.38	6623.28	2076.55	138
H62 E	4678.64	6097.24	1846.67	138
H62F	5825.25	5917.04	1659.21	138
H62 A	5268.25	4364.7	3797.48	138
H62 B	4961.31	5132.94	4096.68	138
H62 C	6116.34	4875.01	4108.59	138

Table S15 Atomic Occupancy for sbd0306.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
C56 B	0.382(6)	C57 B	0.382(6)	H57 B	0.382(6)
C58 B	0.382(6)	H58 B	0.382(6)	C59 B	0.382(6)
H59 B	0.382(6)	C60 B	0.382(6)	H60 B	0.382(6)
C61 B	0.382(6)	H61 B	0.382(6)	C58 A	0.618(6)
H58 A	0.618(6)	C59 A	0.618(6)	H59 A	0.618(6)
C60 A	0.618(6)	H60 A	0.618(6)	C61 A	0.618(6)
H61 A	0.618(6)	C56 A	0.618(6)	C57 A	0.618(6)
H57 A	0.618(6)	C62 A	0.618(6)	H62 D	0.618(6)

H62E	0.618(6)	H62F	0.618(6)	C62B	0.382(6)
H62A	0.382(6)	H62B	0.382(6)	H62C	0.382(6)

sbd0306

Table S16 Crystal data and structure refinement for sbd0306.

Identification code	sbd0306
Empirical formula	$C_{62}H_{54}IrOP_3$
Formula weight	1100.16
Temperature/K	115
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	13.22571(13)
b/Å	18.46616(17)
c/Å	20.7044(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	5056.61(8)
Z	4
ρ_{calc}g/cm^3	1.445
μ/mm^{-1}	2.777
F(000)	2224.0
Crystal size/mm^3	0.34 × 0.26 × 0.26
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.654 to 60.068
Index ranges	-17 ≤ h ≤ 18, -25 ≤ k ≤ 25, -21 ≤ l ≤ 28
Reflections collected	40071
Independent reflections	14716 [R_{int} = 0.0124, R_{sigma} = 0.0130]
Data/restraints/parameters	14716/0/608
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0152, wR_2 = 0.0367
Final R indexes [all data]	R_1 = 0.0155, wR_2 = 0.0368
Largest diff. peak/hole / e Å^{-3}	0.71/-0.35
Flack parameter	-0.0196(12)

5. Kinetic studies

5.1 Table S17 Estimated rate constants for allyl rotation in 1b-1e (s^{-1})

T/K	1b	1c	1d	1e
205	20	12	30	40
215	60	35	55	100
225	100	100	120	350
235	160	300	250	800
245	280	600	600	1800
255	800	2000	1600	4900
265	1400	3200	3600	8000
275	2800	9000	5000	18000
285	4600	12000	6400	35000

Figure S25: Eyring plot for 1b

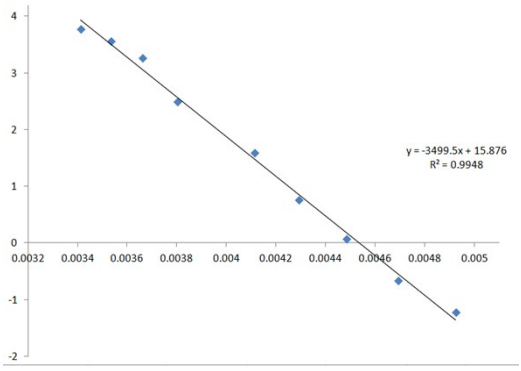


Figure S26: Eyring plot for 1c

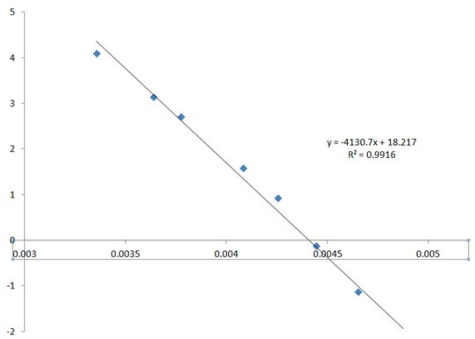


Figure S27: Eyring plot for 1d

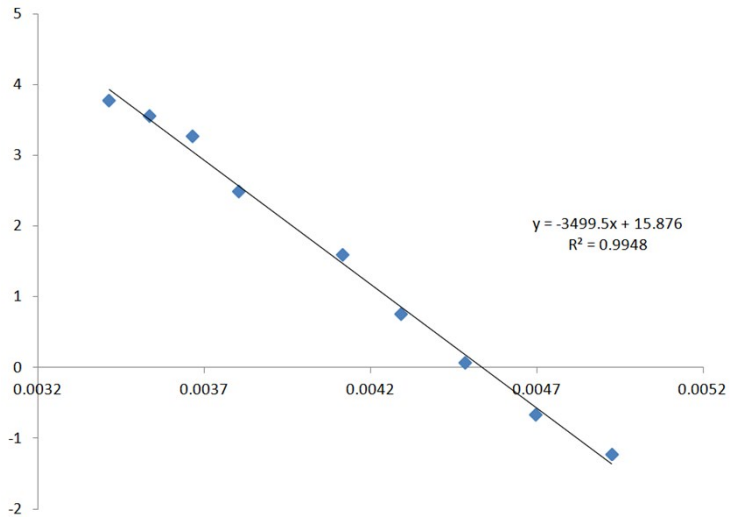
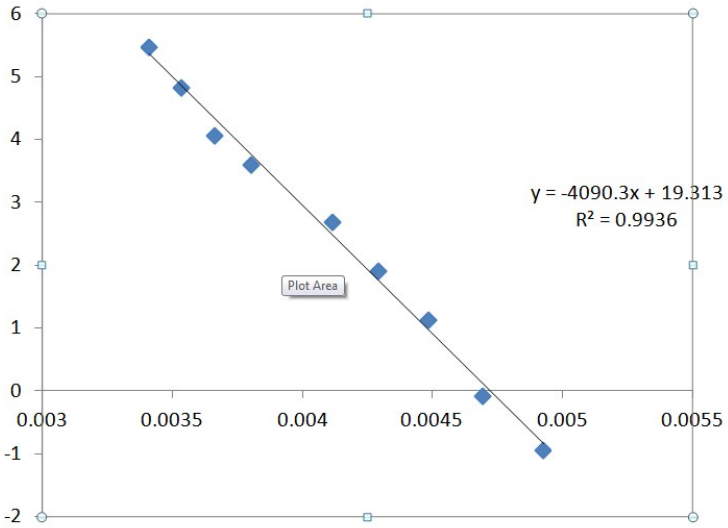


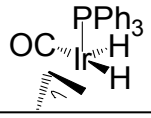
Figure S28: Eyring plot for 1e



5. NMR data for reaction intermediates

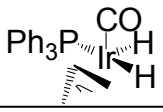
5. 1 NMR data for products derived from 1a

NMR data for $2a_A$ (d_8-toluene, 273 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-10.80 (dd)	Ir-$\underline{H}_a$	4.7	J_{HH}
			15.1	J_{PH}
	-11.20 (dd)	Ir-$\underline{H}_b$	4.7	J_{HH}
			24.7	J_{PH}
^{13}C NMR*	174.7 (d)	$\underline{C}$O		
^{31}P NMR	14.00 (s)	$\underline{P}Ph_3$		

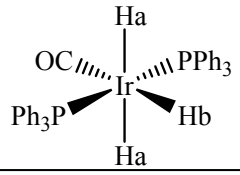
NMR data for $2a_B$ (d_8-toluene, 273 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	- 11.25 (dd)	Ir-$\underline{H}_a$	4.6	J_{HH}
			15.6	J_{PH}
	- 11.55 (dd)	Ir-$\underline{H}_b$	4.9	J_{HH}
			150.8	J_{PH}
^{13}C NMR*	175.5 (d)	$\underline{C}$O		
^{31}P NMR	3.77 (s)	$\underline{P}Ph_3$		

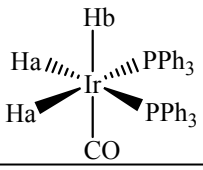
* Data obtained with ^{13}CO labelling

NMR data for $3a_M$ (d_8-toluene, 298 K)



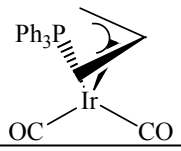
	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-9.53	Ir-H (Ha)	-4.4	J_{HH}
			18	J_{PH}
	-10.02	Ir-H (Hb)	-4.5	J_{HH}
			19.5	J_{PH}
^{31}P NMR	-7.8	PMe_3	-	

NMR data for $3a_F$ (d_8-toluene, 298 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-10.83	Ir-H (Ha)	-4.4	J_{HH}
			107	$\lvert J_{PH(cis)}+J_{PH(trans)}\rvert$
	-9.32	Ir-H (Hb)	-4.4	J_{HH}
			18	J_{PH}
^{31}P NMR	7.8			

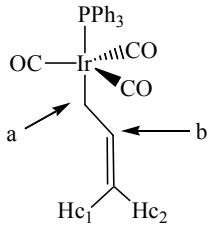
NMR data for 5a (d_8-toluene, 298 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	4.73 (qn)	CH	6.5	J_{HH}
	2.59 (br)	CH_2 (*syn*)	-	-
	0.55 (br)	CH_2 (*anti*)	-	-
^{13}C NMR	67.7 (d)	CH	3	J_{PC}
	31.15 (s)	CH_2	-	-
	179.85 (d)	CO	7.25	J_{PC}
^{31}P NMR	9.40 (br)	PPh_3	6.8*	J_{PC}*

* Data obtained with ^{13}CO labelling

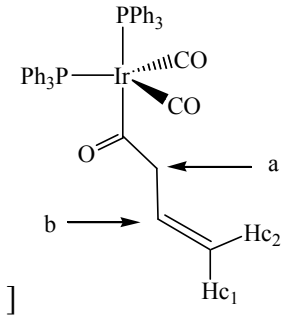
NMR data for 6a (d_8-toluene, 298 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	3.12 (dd)	C<u>H</u>$_2$ (a)	6	J_{PH}
			8	J_{HH}
	4.67 (dt)	C<u>H</u> (b)	9.8	J_{HH} (*cis*)
			2.5	J_{HH} (*gem*)
	5.08 (m)	C<u>H</u>$_2$ (c_1)	17.5	J_{HH} (*trans*)
			2	J_{HH}
	6.62 (m)	C<u>H</u>$_2$ (c_2)	-	-
^{13}C NMR	178.75 (d)	<u>C</u>O	7.6	J_{PC}
	148.5 (d)	<u>C</u>H$_2$ (a)	4.5	J_{PC}
	107.4 (d)	<u>C</u>H (b)	6.1	J_{PC}
	116.96 (s)	=<u>C</u>H$_2$ (c)	-	-
^{31}P NMR	1.5 (q*)	<u>P</u>Ph$_3$	10*	J_{PC}*

* Data obtained with ^{13}CO labelling

NMR data for 7a (d_8-toluene, 298 K)

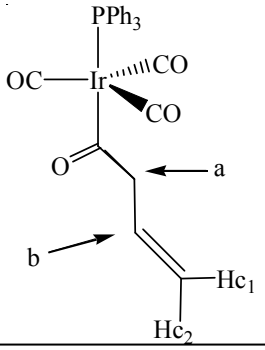


]

	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	3.63 (dt)	C<u>H</u>$_2$ (a)	6.9	J_{HH}
			1	J_{HH}
	4.94 (d)	C<u>H</u> (b)	10.3	J_{HH} (*cis*)
	4.87	=C<u>H</u>$_2$ (c_2)	17.2	J_{HH} (*trans*)

	5.85 (ddt)	=C<u>H</u>$_2$ (c_1)	6.87	J_{HH}
			10.22	J_{HH} (*cis*)
			17.2	J_{HH} (*trans*)
^{13}C NMR	211.7 (t)	<u>C</u>O$_{acyl}$	26	J_{PC}
	185.1 (t)	<u>C</u>O$_{terminal}$	13.4	J_{PC}
	72.13 (t)	<u>C</u>H$_2$ (a)	11	J_{PC}
	135.0 (d)	<u>C</u>H (b)	3.5	J_{PC}
	115.3 (s)	=<u>C</u>H$_2$ (c)	-	-
^{31}P NMR	0.34 (s)	<u>P</u>Ph$_3$	-	-

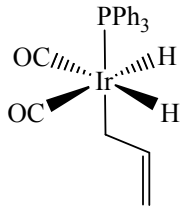
NMR data for 8a (d_8-toluene, 298 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	3.74 (dt)	C<u>H</u>$_2$ (a)	7	J_{HH}
			1.4	J_{HH}
	5.07 (m)	C<u>H</u> (b)	16.8	J_{HH} (*trans*)
	5.12 (m)	=C<u>H</u>$_2$ (c_2)	9	J_{HH} (*cis*)
	6.19 (ddt)	=C<u>H</u>$_2$ (c_1)	6.9	J_{HH}
			10.0	J_{HH}
			17.2	J_{HH} (*trans*)
^{13}C NMR	202.9 (dt)	<u>C</u>O$_{acyl}$	62.5	J_{PC}
			4*	J_{CC}*
	178.0 (dd)	<u>C</u>O$_{terminal}$	11	J_{PC}
			3.1*	J_{CC}*
	73.8 (d)	<u>C</u>H$_2$ (a)	25.3	J_{PC}
	133.6 (s)	<u>C</u>H (b)	-	-
	116.95 (s)	=<u>C</u>H$_2$ (c)	-	-
^{31}P NMR	- 6.3 (s)	<u>P</u>Ph$_3$	-	-

* Data obtained with ^{13}CO labelling

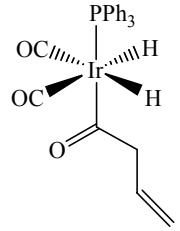
NMR data for $10a_A$ (d_8-toluene, 298 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-8.91 (2nd order)	Ir-H	49.8	$J_{H\text{-}CO(cis)+(trans)}$
			18.4	J_{PH}
			4	J_{HH}
	3.05	CH_2	2.4	$J_{HHydride}$
			8	J_{HH}
			8	J_{PH}
			5*	$J_{H\text{-}CO}$*
^{13}C NMR	173.7 (d)	CO	6.3	J_{PC}
^{31}P NMR	2.54 (“t”)	PPh_3	-	-

* Data obtained with ^{13}CO labelling

NMR data for $11a_L$ (d_8-toluene, 298 K)

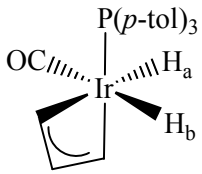


	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-8.4 (2nd order)	Ir-<u>H</u>	47.4*	$J\|_{H\text{-}CO(cis)+(trans)\|}$*
			18.8	J_{PH}
			4.1	J_{HH}
^{13}C NMR	171.6 (d)	<u>C</u>$O_{terminal}$	4.7	J_{PC}
	209.5 (dd)	<u>C</u>O_{acyl}	75.7	J_{PC}
			21.6*	J_{CC}*
^{31}P NMR	- 8.4 (m)	<u>P</u>Ph_3	75.6	J_{PC}

* Data obtained with ^{13}CO labelling

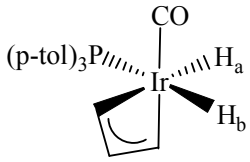
5.2 NMR data for products derived from 1b

NMR data for $2b_A$ (d_8-toluene, 273 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
	-11.0 (m)	Ir-$\underline{H}_a$	4.5	J_{HH}
			22.7	J_{PH}
^{1}H NMR	-10.61 (m)	Ir-$\underline{H}_b$	4	J_{HH}
			15	J_{PH}
			47*	J_{CO-H}
^{13}C NMR	176.4* (d)	$\underline{C}$O	5	J_{PC}
^{31}P NMR	11.2 (s)	$\underline{P}(p\text{-tol})_3$		

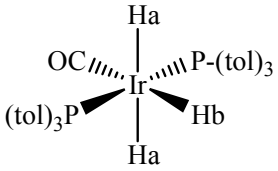
NMR data for $2b_B$ (d_8-toluene, 273 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
	-11.10 (dd)	Ir-$\underline{H}_a$	4.5	J_{HH}
			15	J_{PH}
^{1}H NMR	-11.40 (dd)	Ir-$\underline{H}_b$	4.9	J_{HH}
			149	J_{PH}
^{31}P NMR	1.9 (s)	$\underline{P}(p\text{-tol})_3$		

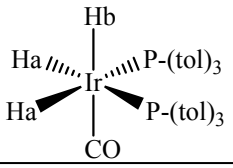
* Data obtained with ^{13}CO labelling

NMR data for $3b_M$ (d_8-toluene, 298 K)



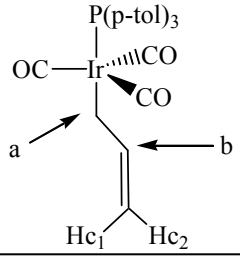
	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-9.89	Ir-H (Ha)	-4.5	J_{HH}
			20	J_{PH}
	-9.25	Ir-H (Hb)	-4.5	J_{HH}
			16.7	J_{PH}
^{31}P NMR	13.8	PMe_3	-	

NMR data for $3b_F$ (d_8-toluene, 298 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-10.43	Ir-H (Ha)	-4.4	J_{HH}
			106	$\lvert J_{PH(cis)}+J_{PH(trans)}\rvert$
	-9.43	Ir-H (Hb)	-4.4	J_{HH}
			18.8	J_{PH}

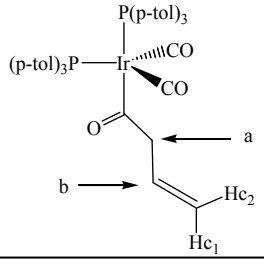
NMR data for 6b (d_8-toluene, 298 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	3.17 (br)	C<u>H</u>$_2$ (a)	5.7	J_{PH}
			8	J_{HH}
	6.67 (m)	C<u>H</u> (b)		
	5.12 (overlap)	=C<u>H</u>$_2$ (c_1)		
	4.71 (overlap)	=C<u>H</u>$_2$ (c_2)	9	J_{HH}
^{13}C NMR	178.8 (d)	<u>C</u>O	9*	J_{PC}*
	106.8 (s)	<u>C</u>$_c$		
^{31}P NMR	-2.35 (s)	<u>P</u>(*p*-tol)$_3$		

* Data obtained with ^{13}CO labelling

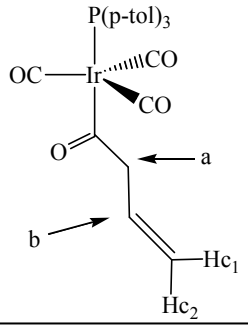
NMR data for 7b (d_8-toluene, 298 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	3.63	C<u>H</u>$_2$ (a)		
	5.92 (overlap)	C<u>H</u> (b)		
	4.95 (overlap)	=C<u>H</u>$_2$ (c_1)		
	4.82 (overlap)	=C<u>H</u>$_2$ (c_2)		
^{13}C NMR	211.6 (t)	<u>C</u>O$_{acyl}$	32*	J_{PC}*
	179.9	<u>C</u>O$_{terminal}$		
	71.4 (t)	<u>C</u>$_a$		
	114.6 (s)	<u>C</u>$_c$		
^{31}P NMR	5.6 (s)	<u>P</u>(*p*-tol)$_3$		

* Data obtained with ^{13}CO labelling

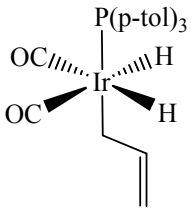
NMR data for 8b (d_8-toluene, 298 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	3.75	C<u>H</u>$_2$ (a)		
	6.24	C<u>H</u> (b)		
	5.13 (overlap)	=C<u>H</u>$_2$ (c_1)		
	5.15 (overlap)	=C<u>H</u>$_2$ (c_2)		
^{13}C NMR	203.25 (d)	<u>C</u>O$_{acyl}$	65*	J_{PC}*
	73.4	<u>C</u>$_a$	38*	J_{PC}*
	116.3(s)	<u>C</u>$_c$		

* Data obtained with ^{13}CO labelling

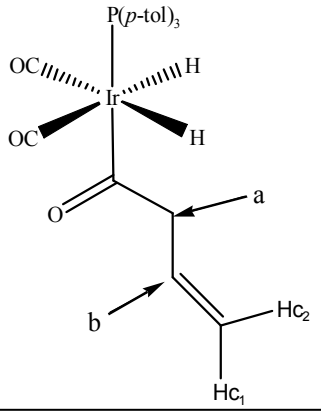
NMR data for 10b$_A$ (d_8-toluene, 298 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-8.78 (2nd order)	Ir-<u>H</u>	45*	$J_{\|H\text{-}CO\ (trans+cis)\|}$
			19	J_{PH}
			5.5	J_{HH}
	3.08	Ir-C<u>H</u>$_2$	4	$J_{HHydride}$
			8	J_{HH}
			8	J_{PH}
^{13}C NMR	174 (d)	CO	3	J_{PC}
^{31}P NMR	- 8.22 (s)	P(*p*-tol)$_3$	-	-

* Data obtained with ^{13}CO labelling

NMR data for $11b_L$ (d_8-toluene, 298 K)



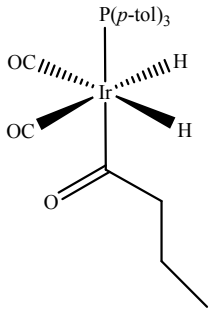
	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-8.23 (2n^d order)	Ir-H	42*	$J_{H\text{-}CO}$*
			18.8	J_{PH}
			5	J_{HH}
^{13}C NMR	171.9 (d)	$CO_{terminal}$	4	J_{PC}
	210.3 (d)	CO_{acyl}	78	J_{PC}
^{31}P NMR	-1.3 (s)	P(*p*-tol)$_3$	-	-

* Data obtained with ^{13}CO labelling

NMR data for $11b_B$ (d_8-toluene, 298 K)

	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	–8.00 (2n^d order)	Ir-H	50.8*	$J_{H\text{-}CO}$*
			17.4	J_{PH}
			4.8	J_{HH}
^{13}C NMR	172.5 (d)	$CO_{terminal}$		
	208.7 (d)	CO_{acyl}		
^{31}P NMR	-0.3 (s)	P(*p*-tol)$_3$	-	-

NMR data for 13b (d_8-toluene, 298 K)

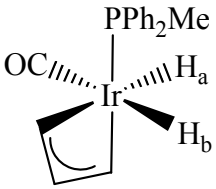


	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	–9.80 (2nd order)	Ir-H	39.7*	$J_{H\text{-}CO}$*
			17.0	J_{PH}
			3.1	J_{HH}
^{13}C NMR	172.3 (d)	$CO_{terminal}$		
	198.5 (d)	CO_{acyl}		
^{31}P NMR	-0.03 (s)	P(*p*-tol)$_3$	-	-

* Data obtained with ^{13}CO labelling

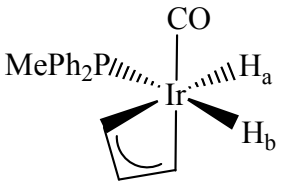
5.3 NMR data for product derived from 1c

NMR data for $2c_A$ (d_8-toluene, 253 K)



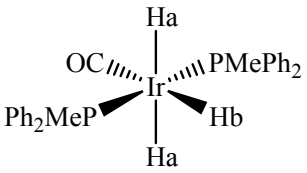
	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-10.96	Ir-H_a	4.7	J_{HH}
			15.7	J_{PH}
	-11.48	Ir-H_b	4.6	J_{HH}
			24	J_{PH}
^{31}P NMR	-11.3 (s)	PPh_2Me		

NMR data for $2c_B$ (d_8-toluene, 253 K)



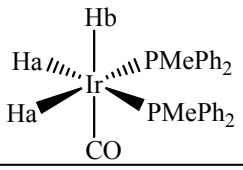
	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-11.45 (dd)	Ir-$\underline{H}_a$	4.2	J_{HH}
			17	J_{PH}
	-11.3 (dd)	Ir-$\underline{H}_b$	5	J_{HH}
			150	J_{PH}
^{31}P NMR	-15.7 (s)	$\underline{P}Ph_2Me$		

NMR data for $3c_M$ (d_8-toluene, 298 K)



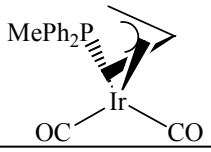
	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-9.8	Ir-$\underline{H}$ (Ha)	-4.6	J_{HH}
			16.8	J_{PH}
	-10.61	Ir-$\underline{H}$ (Hb)	-4.6	J_{HH}
			20.8	J_{PH}
^{31}P NMR	-18.3	PMe_3	-	

NMR data for $3c_F$ (d_8-toluene, 298 K)



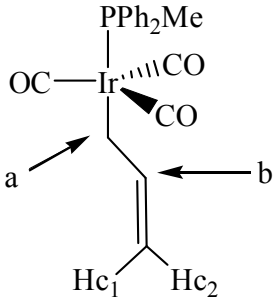
	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-10.05	Ir-$\underline{H}$ (Ha)	-3.3	J_{HH}
			107	$\lvert J_{PH(cis)}+J_{PH(trans)}\rvert$
	-10.57	Ir-$\underline{H}$ (Hb)	-3.1	J_{HH}
			21	J_{PH}

NMR data for 5c (d_8-toluene, 298 K)



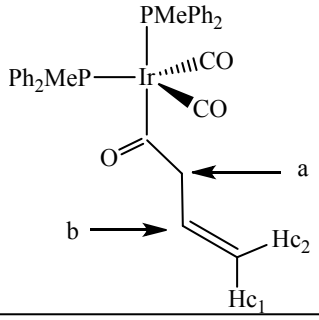
	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	4.80 (m)	C<u>H</u>	-	-
	Too broad	C<u>H</u>$_2$ (*anti*)	-	-
	Too broad	C<u>H</u>$_2$ (*syn*)	-	-
	7-8 (m)	P<u>Ph</u>$_2$Me	-	-
	1.79 (d)	PPh$_2$<u>Me</u>	8	J_{PH}
^{13}C NMR	66.65 (s)	<u>C</u>H	-	-
	29.7 (s)	<u>C</u>H$_2$	-	-
	179.8 (d)	<u>C</u>O	10	J_{PC}
^{31}P NMR	-18.98 (s)	<u>P</u>Ph$_2$Me	-	-

NMR data for 6c (d_8-toluene, 298 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	2.54 (d)	CH$_2$ (a)	8	J_{HH}
	6.72 (m)	CH (b)	-	-
	5.00 (d)	CH$_2$ (c_1)	14	J_{HH} (*trans*)
	4.68 (d)	CH$_2$ (c_2)	11	J_{HH} (*cis)*
	7-8 (m)	P<u>Ph</u>$_2$Me		
	1.62 (d)	PPh$_2$<u>Me</u>	7	J_{PH}
^{13}C NMR	188.2 (d)	CO	11	J_{PC}
	104.6 (m)	C_c	-	-
	18.49 (m)	PPh$_2$<u>Me</u>	-	-
^{31}P NMR	-19.73 (s)	PPh$_2$Me	-	-

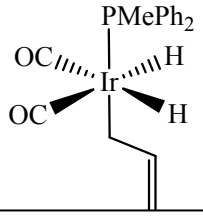
NMR data for 7c (d_8-toluene, 298 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	3.74 (dt)	C<u>H</u>$_2$ (a)	7	J_{HH}
			2	J_{HH}
	6.12 (m)	C<u>H</u> (b)	-	-
	4.91 (d)	=C<u>H</u>$_2$ (c_1)	17	J_{HH} (*trans*)
	5.01 (d)	=C<u>H</u>$_2$ (c_2)	8	J_{HH} (*cis*)
^{13}C NMR	213.3 (d)*	<u>C</u>O$_{acyl}$	61	J_{PC}
	187.75 (d) *	<u>C</u>O$_{terminal}$	10	J_{PC}
	72.86 (s)	<u>C</u>H$_2$ (a)	-	-
	135.3 (s)	<u>C</u>H (b)	-	-
	114.9 (s)	=<u>C</u>H$_2$ (c)		-

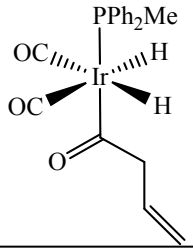
* broad signals at RT, coupling values obtained at 253 K

NMR data for 10c$_A$ (d_8-toluene, 298 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	- 9.22 (2nd order)	Ir-<u>H</u>	49	$J_{H\text{-}CO}$
			20	J_{PH}
	2.97 (ddd)	C<u>H</u>$_2$	3	$J_{H\text{-}Hydride}$
			10	J_{HH}
			10	J_{PH}
^{13}C NMR	173.05 (d)	<u>C</u>O	5	J_{PC}
^{31}P NMR	-23.4 (s)	<u>P</u>Ph$_2$Me	-	-

NMR data for $11c_L$ (d_8-toluene, 298 K)

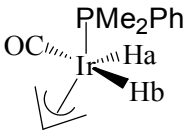


	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	- 8.68 (2nd order)	Ir-H	47	J_{H-CO}*
			20	J_{PH}
^{13}C NMR	170.9 (d)	$CO_{terminal}$	3	J_{PC}
	210.3 (d)	CO_{acyl}	77	J_{PC}
^{31}P NMR	-30.65 (s)	PPh_2Me	-	J_{PC}

* Data obtained with ^{13}CO labelling

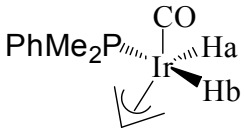
5.4 NMR data for products derived from 1d

NMR data for $2d_A$ (d_8-toluene, 233 K)



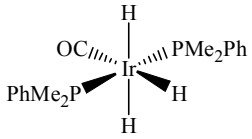
	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-11.2	Ir-H (a)	-5	J_{HH}
			12	J_{PH}
	-11.6	Ir-H (b)	-5	J_{HH}
			17	J_{PH}
^{31}P NMR	-32.83	PMe_2Ph	-	

NMR data for $2d_B$ (d_8-toluene, 233 K)



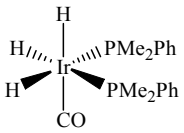
	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-11.43	Ir-H (a)	-7	J_{HH}
			18	J_{PH}
	-11.74	Ir-H (b)	-7	J_{HH}
^{31}P NMR	-39.5	PMe_2Ph	-	

NMR data for $3d_M$ (d_8-toluene, 298 K)



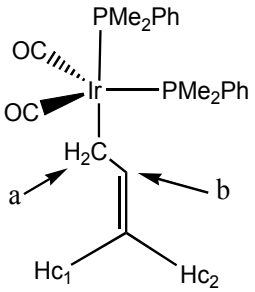
	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-10.19	Ir-H	-5	J_{HH}
			17	J_{PH}
	-10.74	Ir-H	-5	J_{HH}
			21.4	J_{PH}
^{31}P NMR	-30.2	PMe_2Ph	-	

NMR data for $3d_F$ (d_8-toluene, 298 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-10.27	Ir-H	-2	J_{HH}
			21	J_{PH}
	-10.97	Ir-H	-2	J_{HH}
			124	$\lvert J_{PH(cis)}+J_{PH(trans)}\rvert$
^{31}P NMR	-41.3	PMe_2Ph	-	

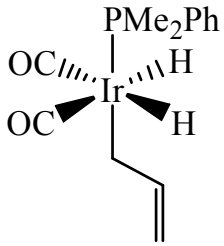
NMR data for 9d (d_8-toluene, 298 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	5.27 (d)	=C<u>H</u>$_2$ (c_1)	16.6	J_{HH} (*trans*)
	4.87(d)	=C<u>H</u>$_2$ (c_2)	9.2	J_{HH} (*cis*)
	7.13 (m)	C<u>H</u>		
	2.78 (m)	Ir-C<u>H</u>$_2$		
	1.07	*a*-P<u>Me</u>	-	-
	1.33	*e*-P*Me*	-	-
^{31}P NMR	-39.9 (d)	<u>P</u>Me$_2$Ph	15	J_{PP}
			31*	J_{PC}
	-45.42 (d)	<u>P</u>Me$_2$Ph	15	J_{PP}
			11*	J_{PC}
^{13}C NMR	190.0* (d,d)	<u>C</u>O	31*	J_{PC}
			11*	J_{PC}

* Data obtained with ^{13}CO labelling

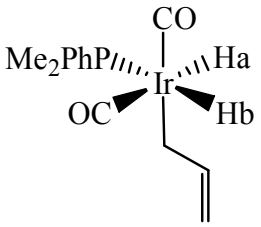
NMR data for $10d_A$ (d_8-toluene, 298 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-9.41 (m)	Ir-<u>H</u>	22	J_{PH}
			2.8	J_{HH}
			40	$\lvert J_{C(trans)H}+J_{C(cis)H}\rvert$
	2.88 (t, d, d)	Ir-C<u>H</u>$_2$	8	J_{PH}
			8.8	J_{HH}
			-2.8	$J_{HH(hydride)}$
^{31}P NMR	-44.1	<u>P</u>Me$_2$Ph		
^{13}C NMR	172.9*	<u>C</u>O		

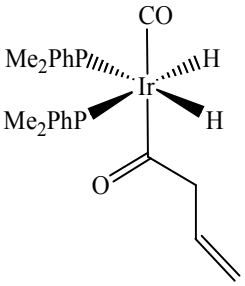
* Data obtained with ^{13}CO labelling

NMR data for $10d_B$ (d_8-toluene, 298 K)



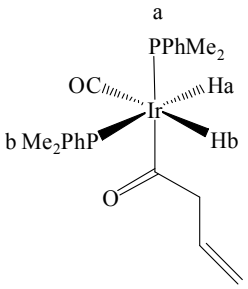
	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-9.36	Ir-H (a)	-4	J_{HH}
			160	J_{PH}
	-9.56	Ir-H (b)	-4	J_{HH}
			20	J_{PH}

NMR data for $12d_A$ (d_8-toluene, 298 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-9.70 (2nd order)	Ir-H	120	$\lvert J_{C(trans)H}+J_{C(cis)H}\rvert$
	3.87 (m)	CO-CH_2	6.9	J_{HH}
	6.49	CH=		
	5.17 (overlap)	=CH_2		
	5.20 (overlap)	=CH_2		
	1.40	PMe		
	1.55	PMe		
	7.05	*o*-H		
	7.23	*m*-H		
^{31}P NMR	-44.6	PMe_2Ph		
^{13}C NMR	77.4	CH_2-CO		
	114.3	CH=CH_2		

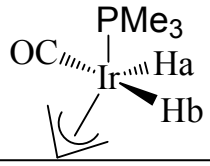
NMR data for 12d$_B$ (d$_8$-toluene, 298 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-9.65	Ir-H$_a$	122	$J_{PH(trans)}$
			20	$J_{PH(cis)}$
	-8.56	Ir-H$_b$	40	$J_{CH(cis)}$
	3.74 (m)	CO-C$\underline{H}_2$	7.4	J_{HH}
	6.42 (m)	C$\underline{H}$=		
	5.14	=C$\underline{H}_2$		
	5.18	=C$\underline{H}_2$		
	1.53	P$\underline{Me}_a$		
	1.57	P$\underline{Me}_a$		
	1.29	P$\underline{Me}_b$		
	1.32	P$\underline{Me}_b$		
	7.12	*o*-H, P$_a\underline{Ph}$		
	6.94	*m*-H, P$_a\underline{Ph}$		
^{31}P NMR	–42.3 (d)	PMe$_2$Ph (b)	20	J_{PP}
	–52.5 (d)	PMe$_2$Ph (a)		
^{13}C NMR	-177.68	$\underline{CO}_{terminal}$		
	77.5	CO-$\underline{C}H_2$		
	114.3	CH=$\underline{C}H_2$		

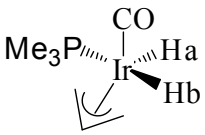
5.5 NMR data for products derived from 1e

NMR data for $2e_A$ (d_8-toluene, 233 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-11.44	Ir-H (a)	-8	J_{HH}
			17	J_{PH}
	-11.77	Ir-H (b)	-8	J_{HH}
			24	J_{PH}
			45*	J_{CH}
^{13}C NMR	175.7 (d)	CO	6*	J_{PC}
^{31}P NMR	-47.47	PMe_3	-	

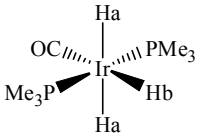
NMR data for $2e_B$ (d_8-toluene, 233 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-12.03	Ir-H (a)	-9.5	J_{HH}
			18	J_{PH}
	-11.60	Ir-H (b)	-9.5	J_{HH}
			14	J_{PH}
^{31}P NMR	-57.0	PMe_3	-	

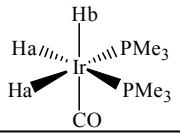
* Data obtained with ^{13}CO labelling

NMR data for $3e_M$ (d_8-toluene, 298 K)



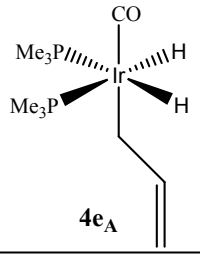
	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-10.61	Ir-H (Ha)	-4.7	J_{HH}
			18.1	J_{PH}
	-10.82	Ir-H (Hb)	-4.7	J_{HH}
			21.4	J_{PH}
^{31}P NMR	-49.6	PMe_3	-	

NMR data for $3e_F$ (d_8-toluene, 298 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-11.16	Ir-H (Ha)	-2.4	J_{HH}
			128	$\lvert J_{PH(cis)}+J_{PH(trans)}\rvert$
	-10.71	Ir-H (Hb)	-2.4	J_{HH}
			22	J_{PH}
	1.32	PMe_3		
^{31}P NMR	-59.3	PMe_3	-	
^{13}C NMR	175.8	CO		

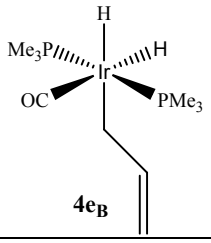
NMR data for4e$_A$ (d_8-toluene, 263K)



4e$_A$

	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-10.02, 2nd order -10.12* 2nd order	Ir-H	145.5	$\lvert J_{P(trans)H}+J_{P(cis)H}\rvert$
	1.16	PMe_3		
	1.95	Ir-CH_2 (a)	6.6	J_{PH}
			7	J_{HH}
	6.94	CH= (b)	10	J_{HH}
			17	J_{HH}
			7	J_{HH}
	4.60	=CH_2 (c_1)	17	J_{HH}
	4.76	=CH_2 (c_2)	10	J_{HH}
^{31}P NMR	-59.0	PMe_3	-	

NMR data for4e$_B$ (d_8-toluene, 263 K)

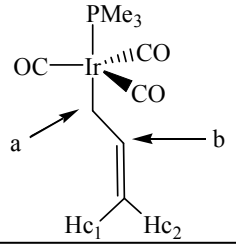


4e$_B$

	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-12.67	Ir-H	18.7	J_{PH}
			7.1	J_{HH}
	-10.06	Ir-H	20.7	J_{PH}
			7.1	J_{HH}
^{31}P NMR	-47.2			

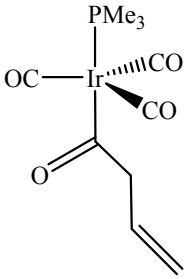
* Data obtained at 283K

NMR data for 6e ((d$_8$-toluene, 203 K)



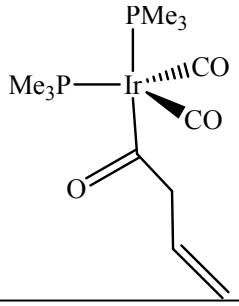
	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	5.28 (d)	=C<u>H</u>$_2$ (Hc$_1$)	17.2	J_{HH}
	4.89(d)	=C<u>H</u>$_2$ (Hc$_2$)	9.6	J_{HH}
			3	J_{HH}
	6.80 (m, overlap)	C<u>H</u> (Hb)		
	3.16 (m)	Ir-C<u>H</u>$_2$ (Ha)		
	0.74	P<u>Me</u>$_3$		
^{31}P NMR	-60.6	<u>P</u>Me$_3$		

NMR data for 7e ((d$_8$-toluene, 203 K)



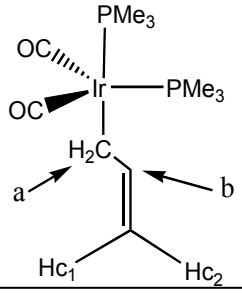
	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	5.26(overlap)	=C<u>H</u>$_2$ (Hc)		
	6.61 (m, overlap)	C<u>H</u> (Hb)		
	4.09 (m)	Ir-C<u>H</u>$_2$ (Ha)	6.5	J_{HH}
	0.86	P<u>Me</u>$_3$		
^{13}C NMR	115.5	<u>C</u>c		

NMR data for 8e (d_8-toluene, 203 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	5.15 (overlap)	=C<u>H</u>$_2$ (Hc$_1$)		
	5.24 (overlap)	=C<u>H</u>$_2$ (Hc$_2$)		
	6.38 (m, overlap)	C<u>H</u> (Hb)		
	3.84 (m)	Ir-C<u>H</u>$_2$ (Ha)	6.5	
	0.86	P<u>Me</u>$_3$	8	J_{PH}
^{31}P NMR	-62.4.	<u>P</u>Me$_3$		

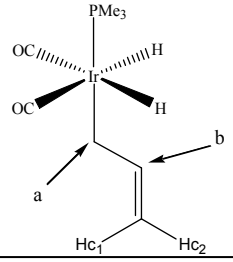
NMR data for 9e$_B$ (d_8-toluene, 203 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	5.43 (d)	=CH$_2$ (c$_1$)	16.6	J_{HH}
	4.87(d)	=CH$_2$ (c$_2$)	9.2	J_{HH}
	7.10 (m, overlap)	CH (b)		
	2.72 (m)	Ir-CH$_2$ (a)		
	0.86	*a*-P<u>Me</u>$_3$		
	1.06	*e*-P<u>*Me*</u>$_3$		
^{31}P NMR	-63.3 (d)	<u>P</u>Me$_3$	21	J_{PP}
			32*	J_{PC}
	-53.9 (d)	<u>P</u>Me$_3$	15	J_{PP}
			11*	J_{PC}
^{13}C NMR	190.5 (d,d)	<u>C</u>O	32*	J_{PC}
			11*	J_{PC}
	104.5	=<u>C</u>H$_2$ (c)		
	109.6	=<u>C</u>H (b)		

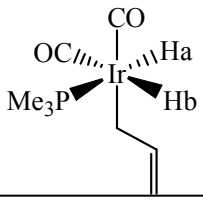
* Data obtained with ^{13}CO labelling

NMR data for $10e_A$ (d_8-toluene, 283 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-9.61 (m)	Ir-H	22.8	J_{PH}
			2.2	J_{HH}
			48*	$\lvert J_{C(trans)H}+J_{C(cis)H}\rvert$
	2.82 (m)	Ir-CH_2 (Ha)	8	J_{PH}
			8.7	J_{HH}
			2.2	J_{HH}
	6.66 (m)	=CH (Hb)		
	5.0-5.1	=CH_2 (Hc)		
	1.09	PMe_3		
^{31}P NMR	-58.9 (d)	PMe_3	4.7*	J_{Pc}
^{13}C NMR	173.2	CO		

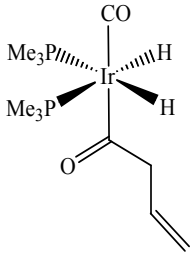
NMR data for $10e_B$ (d_8-toluene, 283 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-9.50 (m)	Ir-H (a)	135.5	J_{PH}
			4*	J_{CH}
			-5	J_{HH}
	-9.60 (m)	Ir-H (b)	25.3	J_{PH}
			-5	J_{HH}
^{31}P NMR	-60.4	PMe_3		

* Data obtained with ^{13}CO labelling

NMR data for $13e_A$(d_8-toluene, 298 K)



	Chemical shift (ppm)	Assignment	Coupling constant (Hz)	Assignment
^{1}H NMR	-9.68 (2nd order)	Ir-H	104	$\lvert J_{P(trans)H}+J_{P(cis)H}\rvert$
	3.88 (d)	CO-CH_2 (Ha)	5.0	J_{HH}
			1.4	J_{HH} (hydride)
	6.36 (m)	CH= (Hb)		
	5.1-5.2 (br)	=CH_2 (Hc)		
	1.25	PMe_3		
^{13}C NMR	178.0* (t)	$CO_{terminal}$	5	J_{PC}
	114.1	=CH_2 (Cc)		
^{31}P NMR	-53.4	PMe_3	-	

* Data obtained with ^{13}CO labelling