Synthesis and Reactivity Ruthenium Tridentate *bis*-Phosphinite Ligand Complexes

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Supporting Information

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Calculation of H-H Bond Distances Using H-D Coupling

In complexes **18**, **7**+H2 and **20** H-D the coupling constants observed were artificially small, likely a result of the formation of different isotopomers. Only those isotopomers containing H-D should exhibit coupling allowing a more precise H-D coupling constant to be determined. Using these values H-H distances can calculated using the equation previously described by Morris.[1]

Table S1 Calculation of $J_{HDActual}$ and H-H Bond Distances

Complex	J_{HDobs} (Hz).	$J_{HDActual}$ (Hz)	H-H Distance (pm)
18	5.4	21.6	106
7+H_2	7.3	29.2	93
20	7.4	29.6	93

Calculation of H-H Bond Distances Using T_1 Values

As the relaxation of a hydride in rapid exchange with an H_2 ligand is known to affect the observed T_{1min} value of a complex, Morris *et al.* have previously described a means to correct for this effect if the T_1 value for the hydride can be determined after the signal separates from the dihydrogen ligand (equation 1).[2]

$$3/T_{1(obs.)} = 2/T_{1(H2)} + 1/T_{1(H)} \quad \textbf{Equation 1}$$

As T_1 values of the hydride could not be obtained for any of the complexes described, such a correction could not be accurately made. However, metal hydrides are expected to have a $T_{1(H)}$ on the order of half a second,[3] and literature values for the hydride relaxation time in similar compounds have shown $T_{1(H)}$ times around 400 ms (corrected for a 600 MHz spectrometer).[2] Thus, hydride T_1 times of 200 ms, 400 ms and 1s were used so the H-H distance could be estimated to give an indication of where on the hydride-dihydrogen:trihydride continuum the complexes are. Notably, while the values are not exact, due to the nature of the relationship for the $T_{1(H)}$ time in equation 1, as the hydride relaxation time increases its effect is minimized and $T_{1(obs)}$ approaches $T_{1(H2)}$.

Table S2 Calculation of $T_{1(H2)}$ and H-H Bond Distances

Complex	$T_{1(obs.)}$ (ms)	$T_{1(H)}$ (ms)	$T_{1(H2)}$ (ms)	H-H Distance slow spinning H_2 (pm)	H-H Distance fast spinning H_2 (pm)
18	86	200	67	128	101
18	86	400	62	126	100
18	86	1000	59	125	99
7+H_2	39	200	28	110	87
7+H_2	39	400	27	110	87
7+H_2	39	1000	26	109	87
19	44	200	32	113	89
19	44	400	30	112	89
19	44	1000	30	111	88
20	55	200	40	117	93
20	55	400	38	116	92
20	55	1000	37	116	92

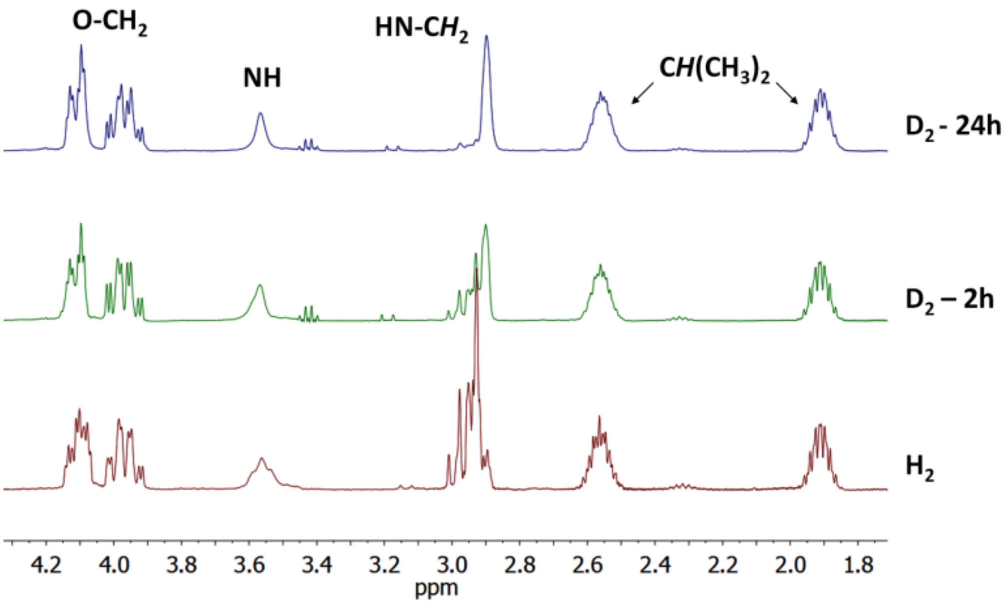
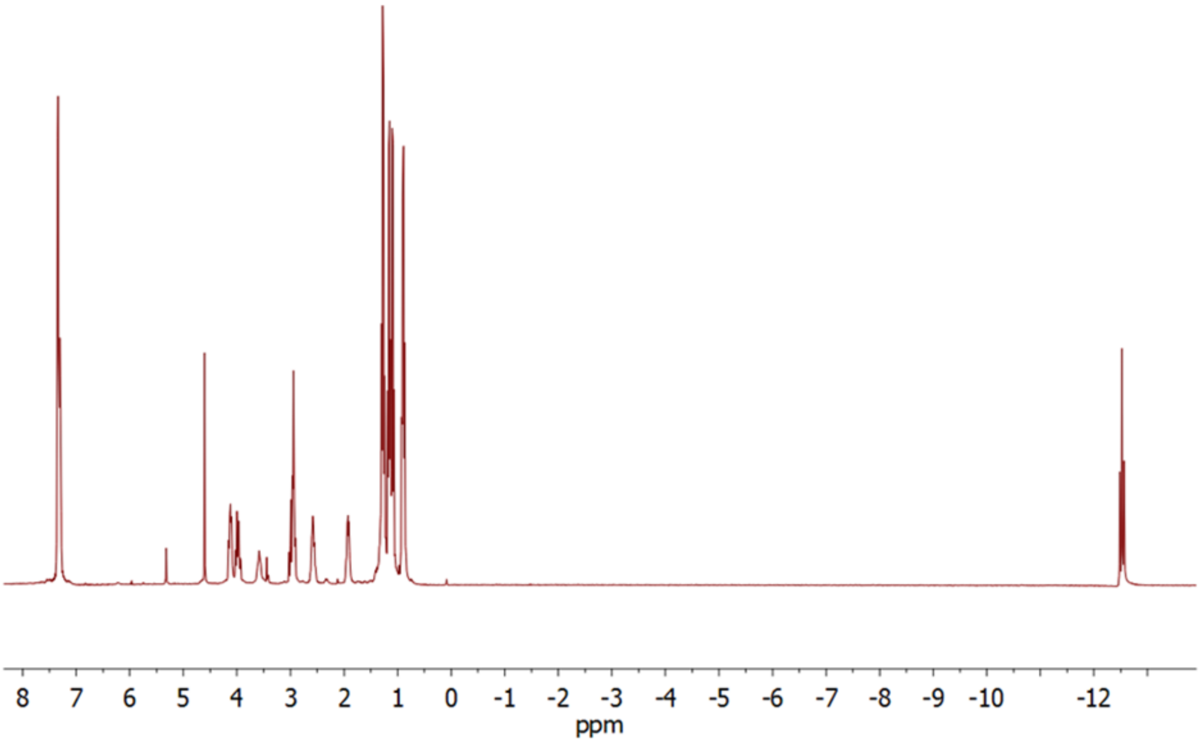


Figure S1 ^{1}H NMR spectra of **18** under D_2 showing H/D exchange at one of the site in the CH_2 fragment α to NH.

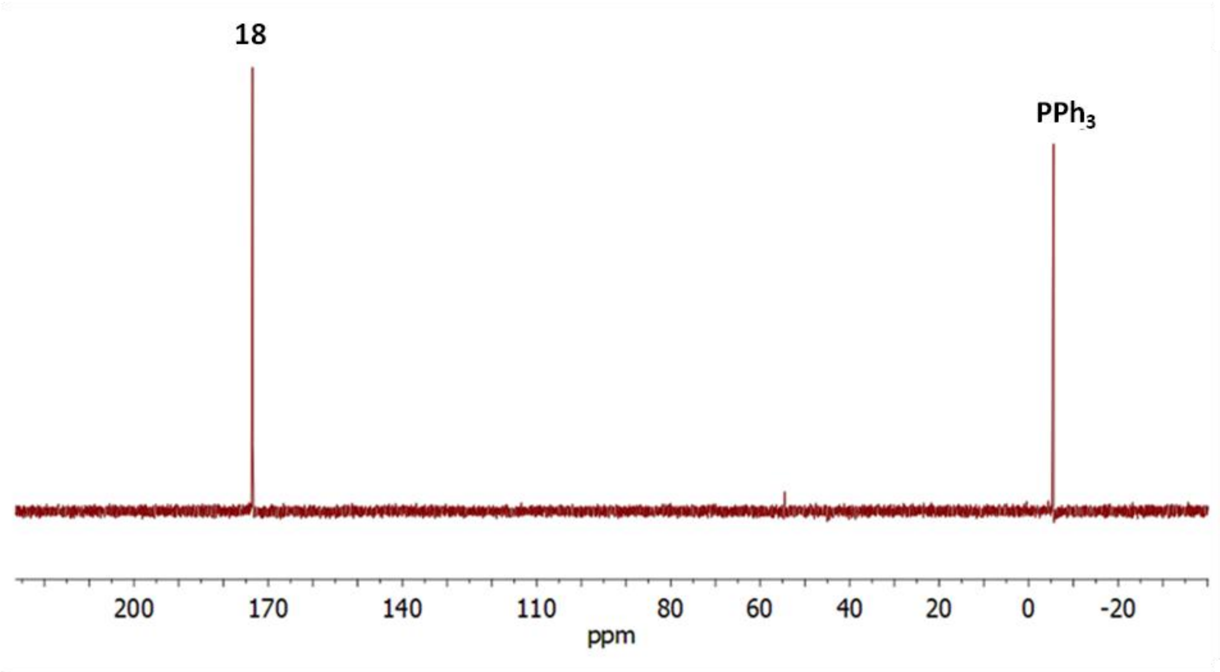
(18)

^{1}H NMR (CD_2Cl_2)



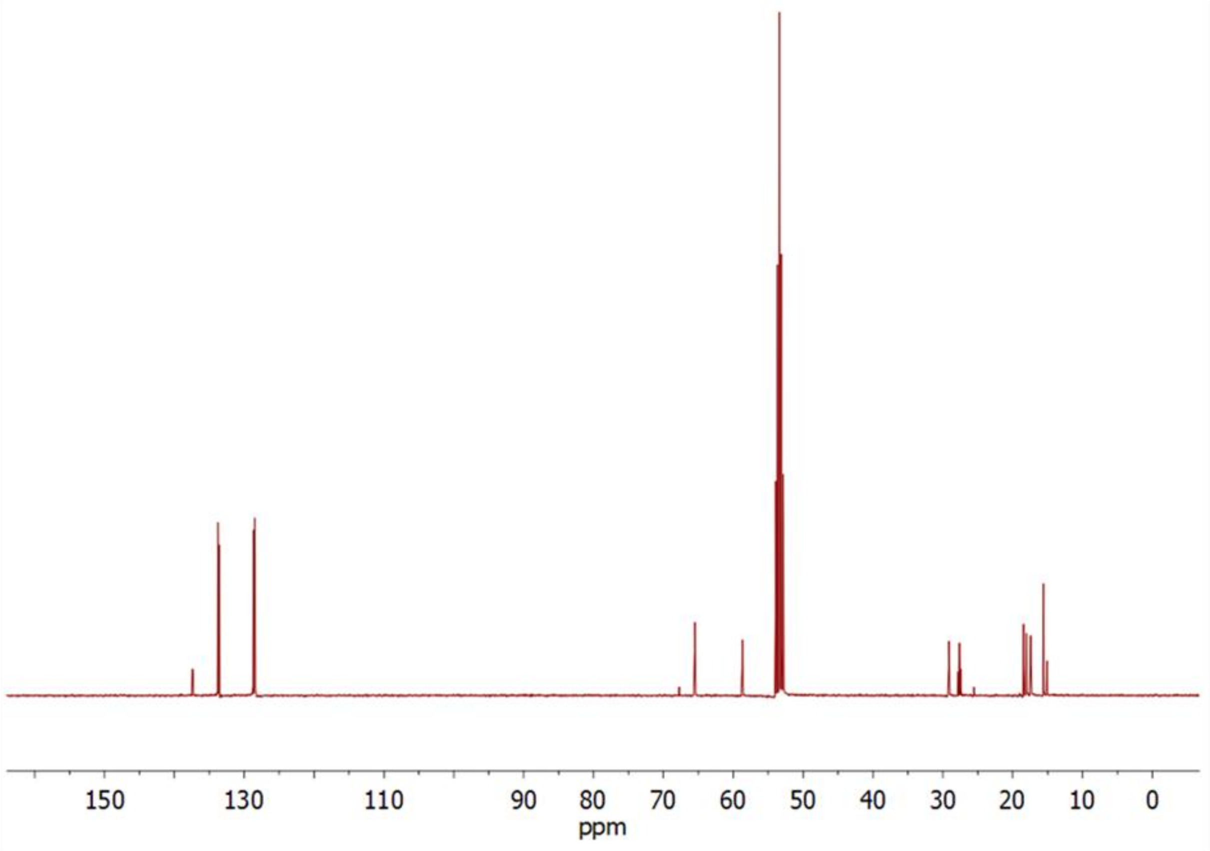
(18)

$^{31}P\{^1H\}$ NMR (CD_2Cl_2)



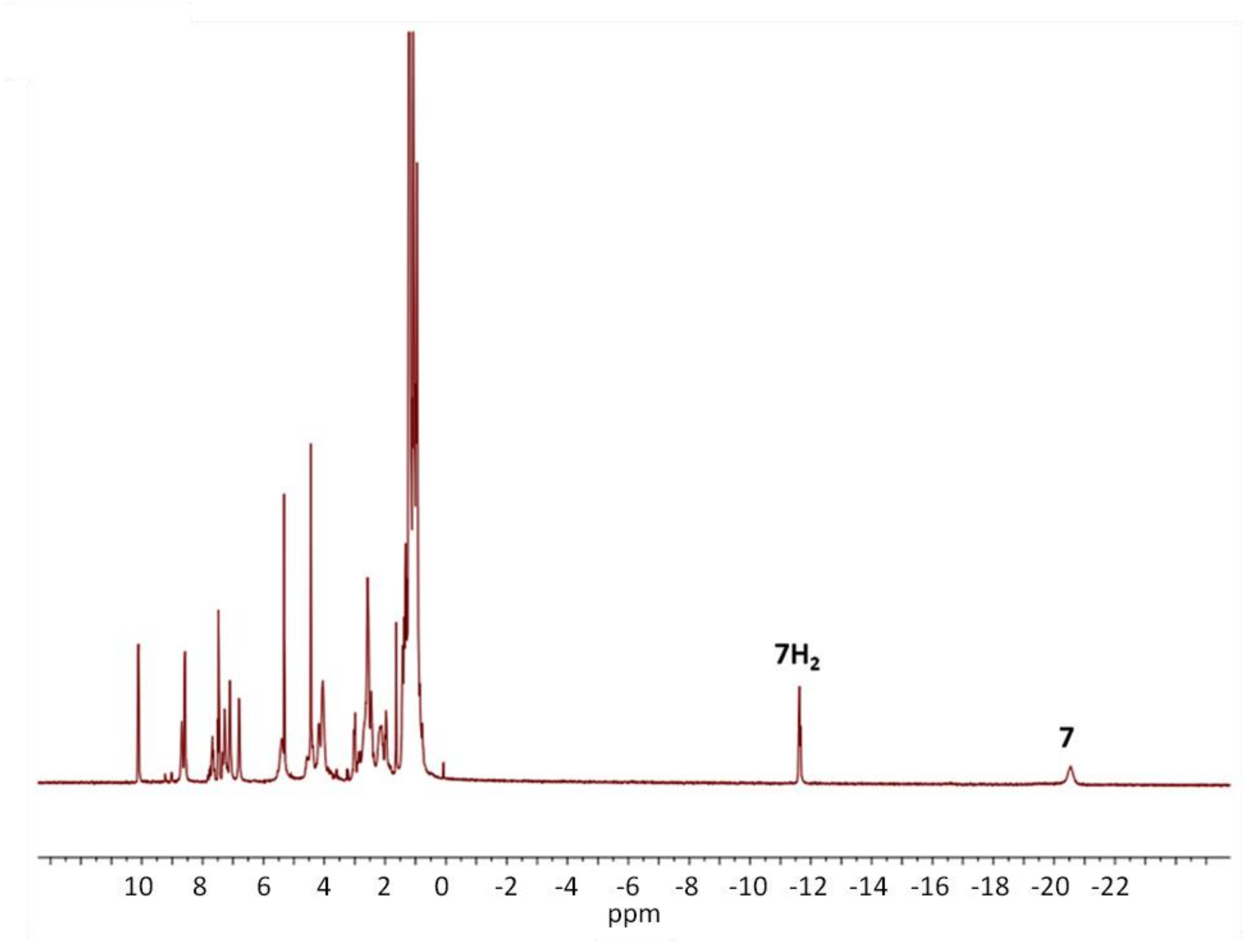
(**18**)

$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2)



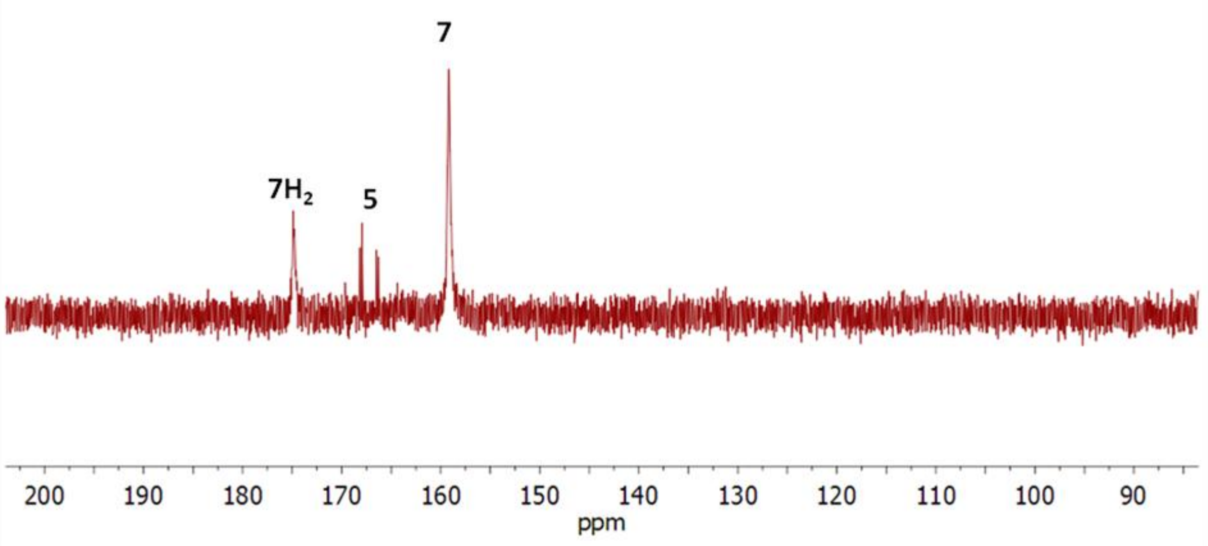
(**7**) + H_2

^1H NMR (CD_2Cl_2)



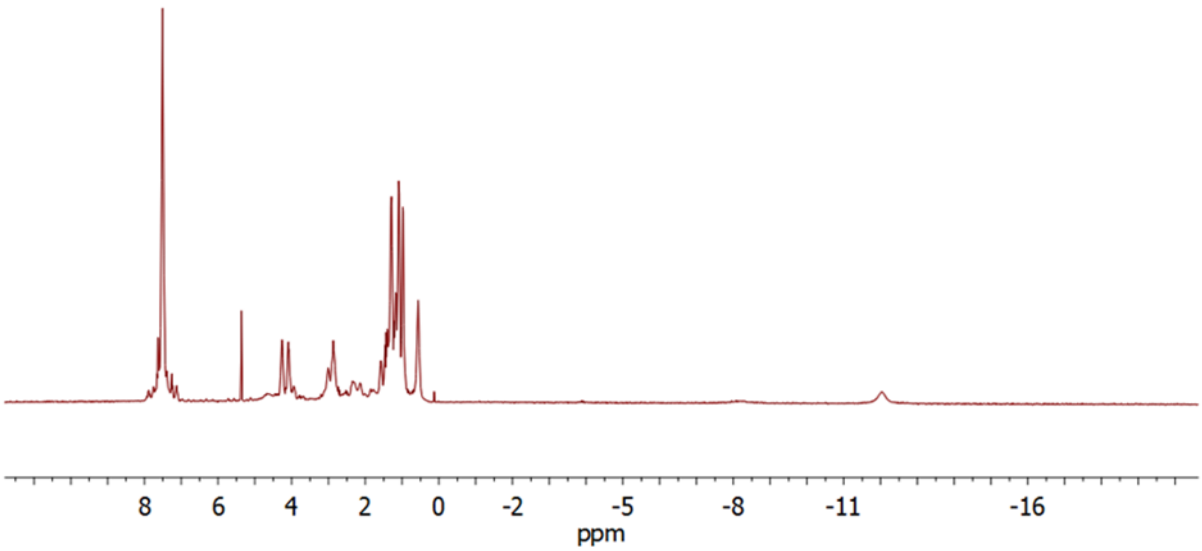
(**7**) + H_2

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2)



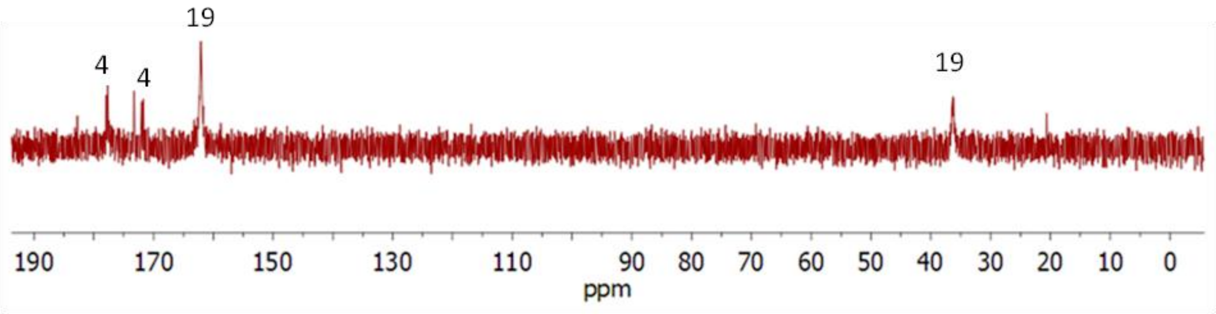
(19)

^{1}H NMR (CD_2Cl_2)



(19)

^{13}C{^{1}H} NMR (CD_2Cl_2)



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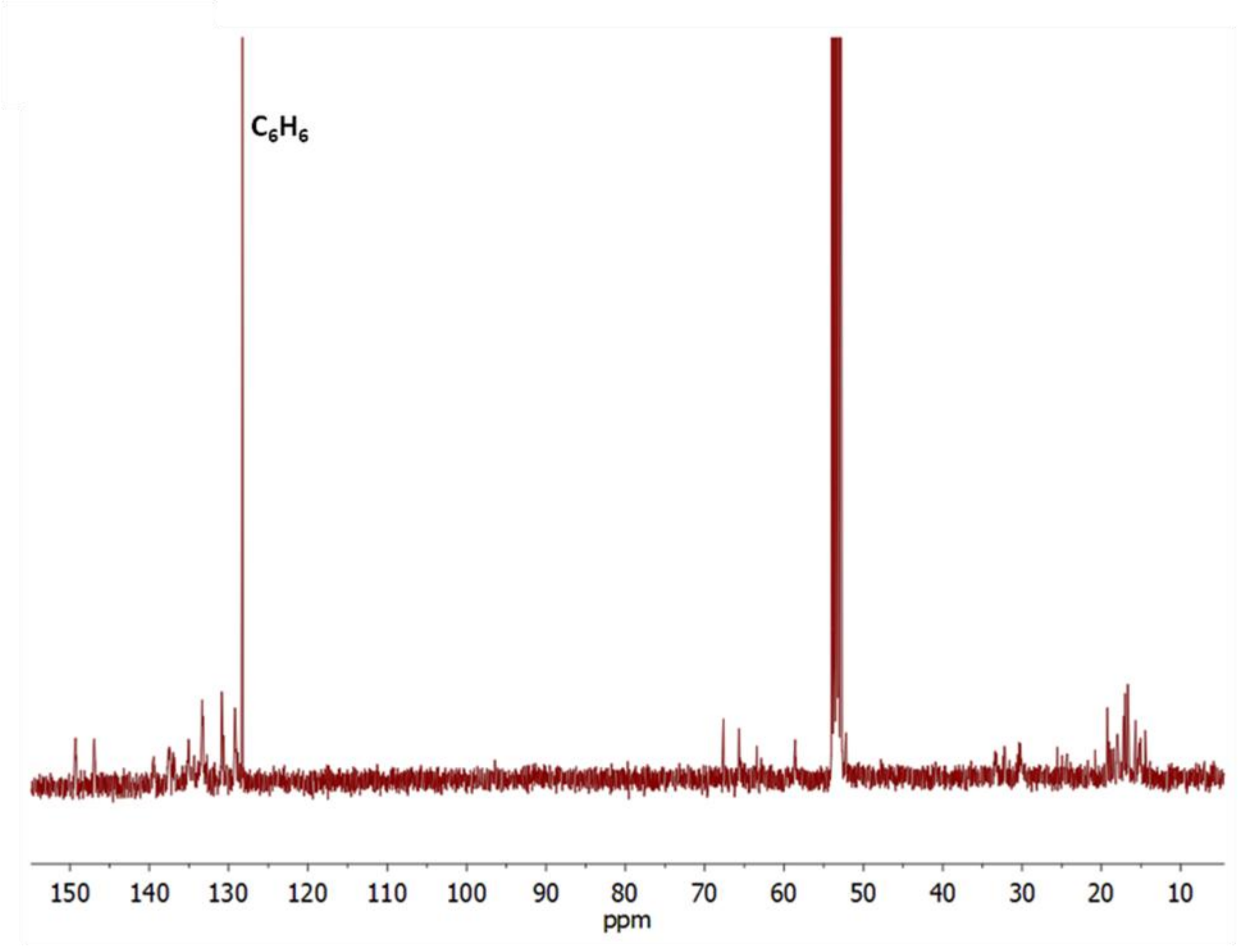
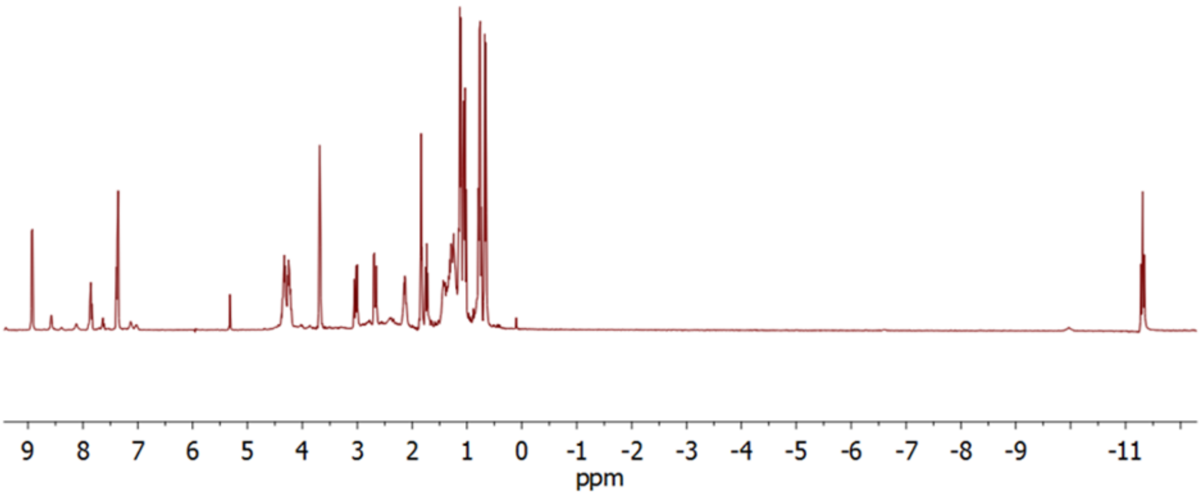
$^{13}C\{^1H\}$ NMR (CD_2Cl_2)



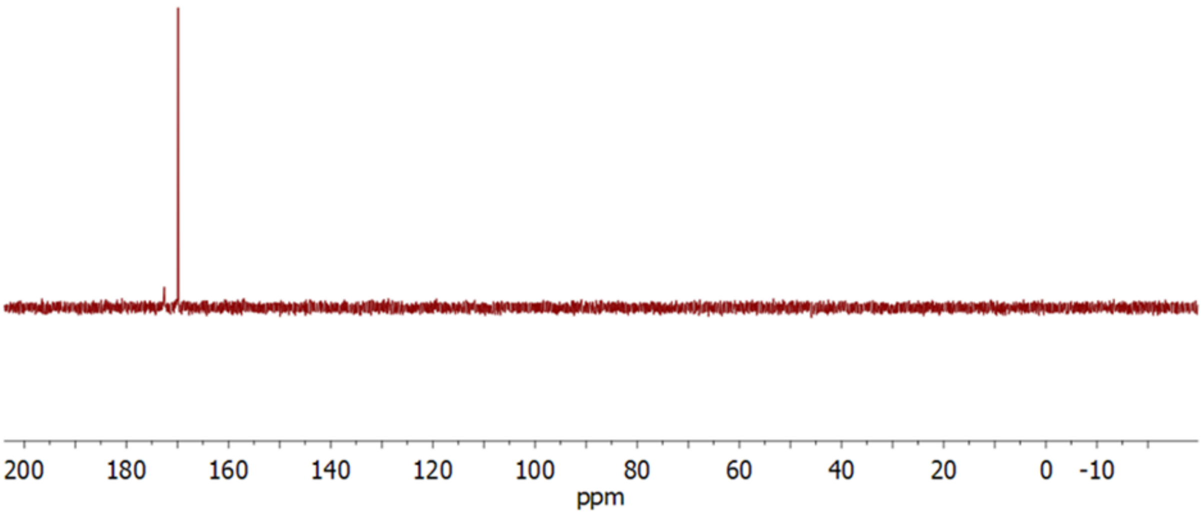
(**20**)

^{1}H NMR (CD_2Cl_2)



(**20**)

^{31}P{^{1}H} NMR (CD_2Cl_2)



(**20**)

$^{13}C\{^1H\}$ NMR (CD_2Cl_2)

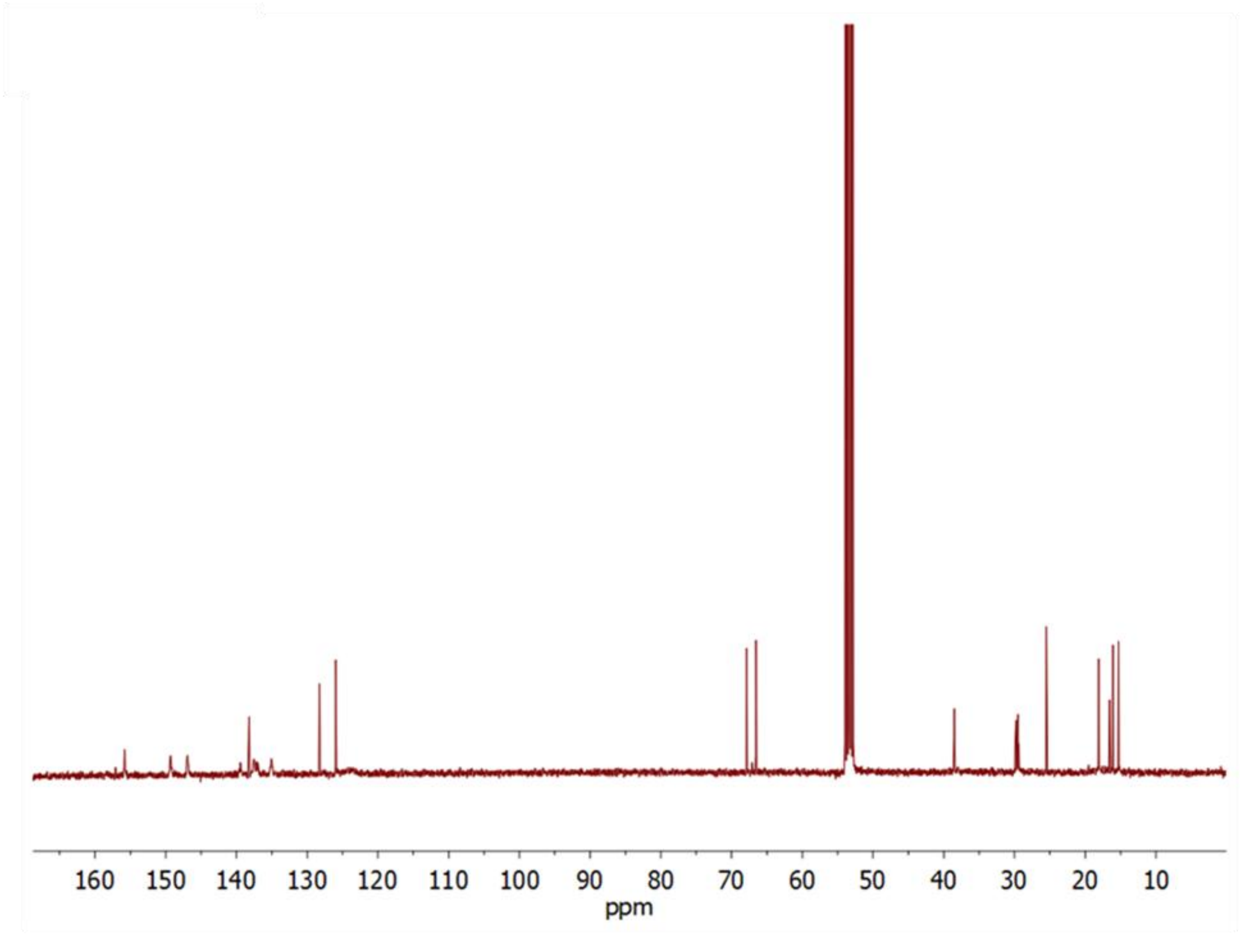


Table S3 Data for the Dehydrogenation of HMe_2NBH_3 to $[Me_2NBH_2]_2$

Catalyst	Time (h)*	Loading (mol % Ru)	Conversion (%)	TON
4	24	5	12.7	3
5	24	5	8.5	2
6	24	5	100	20
7	24	5	100	20
8	24	5	100	20
9	24	5	19	4
10	24	5	100	20
12	24	5	100	20
15	24	5	10.4	2
16	24	5	8.2	2
6	24	2.5	100	40
7	24	2.5	100	40
8	24	2.5	100	40
10	24	2.5	100	40
12	24	2.5	36	14
6	24	1	57	57
7	24	1	100	100
8	24	1	49	49
10	24	1	67	67
12	24	1	18	18

Conditions: Reactions completed in a 2 dram push top vial equipped with a magnetic stir bar at 25^{o}C.
*Most reactions were complete prior to 24 h but all reactions were left to ensure maximum TON were achieved

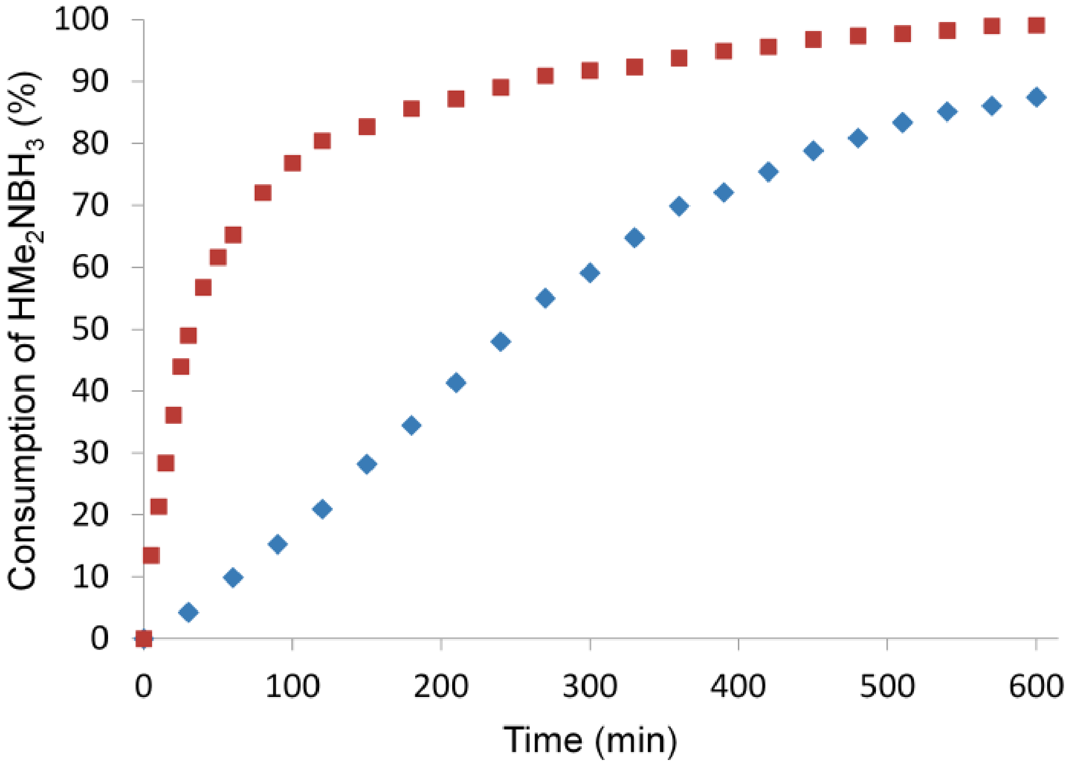


Fig. S2 Plot of the consumption of HMe_2NBH_3 as a function of time using 2.5 mol % **8** and **12**. Key: **8** (diamonds), **10** (squares).

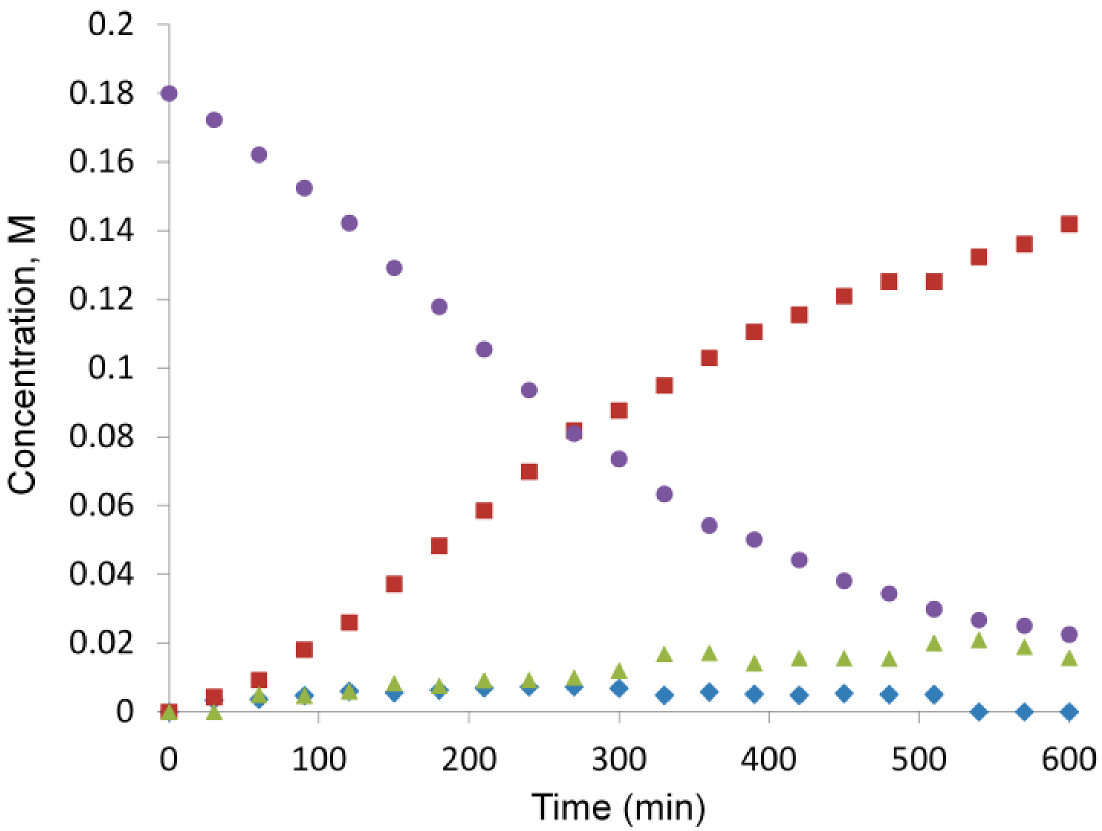


Figure S3 Concentration-time Plots for B-containing products of dehydrogenation using 2.5 mol % **8** and 0.18 M HMe_2NBH_3. Key: HMe_2NBH_3 (circles) Me_2NBH_2 (diamonds) $[Me_2NBH_2]_2$ (squares) $HMe_2NBH_2NMe_2BH_3$ (triangles).

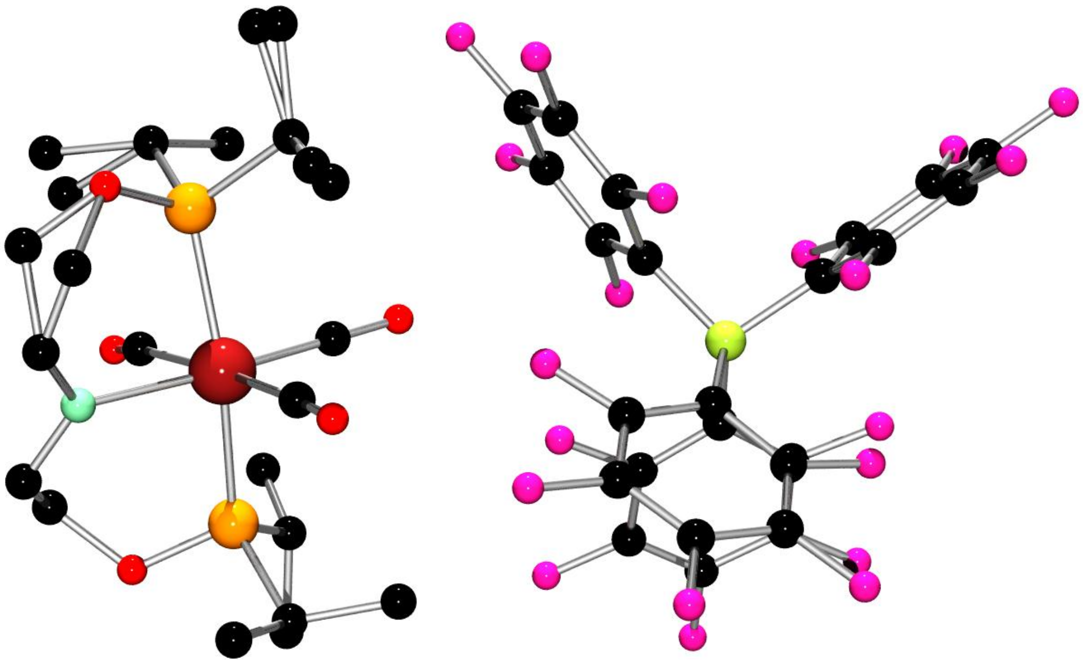


Figure S4 POV-Ray depiction of the molecular structure of **13** showing the CO-hydride disorder at the metal center and ligand disorder. C: black, O: red, P: orange, N: aquamarine, F: deep pink, B: yellow green, Ru: scarlet; Hydrogen atoms omitted for clarity.

References

1. R. H. Morris, *Coord. Chem. Rev.*, 2008, **252**, 2381-2394.
2. M. T. Bautista, K. A. Earl, P. A. Maltby, R. H. Morris, C. T. Schweitzer and A. Sella, *J. Am. Chem. Soc.*, 1988, **110**, 7031-7036.
3. R. H. Crabtree, in The Organometallic Chemistry of the Transition Metals, Wiley, 5th edn., 2009, pp. 263-295.