Syntheses, Structural Characterizations and Reactivity Studies of Half-Sandwich Cobalt, Rhodium and Iridium Metallatricarbadecaboranyl Complexes

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Supporting Information

Table S1. Crystallographic data.

	4: 1,1-dppe-2-Ph-*closo*-1,2,3,4-$CoC_3B_7H_9$	**5**: 1,1-dppe-2-Ph-*closo*-1,2,3,4-$RhC_3B_7H_9$	**6**: 8-CO-8,8-dppe-9-Ph-*nido*-8,7,9,10-$IrC_3B_7H_9$
empirical formula	$C_{35}B_7H_{38}P_2Co$	$C_{35}B_7H_{38}P_2Rh$	$C_{73}B_{14}H_{78}P_4O_2Cl_2Ir_2$
formula weight	655.19	699.17	1717.87
crystal class	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
Z	4	4	1
a, Å	11.5192(6)	11.6572(9)	9.7645(7)
b, Å	17.6108(8)	18.1448(13)	9.7920(7)
c, Å	16.6383(10)	15.8603(12)	18.9940(15)
α, deg			101.746(4)
β, deg	102.849(3)	92.054(4)	93.362(5)
γ, deg			96.229(3)
V, Å^3	3290.8(3)	3352.6(4)	1761.5(2)
D_{calc}, g/cm^3	1.322	1.385	1.619
μ, mm^{-1}	0.645	0.630	3.988
λ, Å (Mo–K_α)	0.71073	0.71073	0.71073
crystal size, mm	0.35x0.15x0.02	0.32x0.14x0.02	0.22x0.18x0.04
F(000)	1360	1432	850

2θ angle, deg	3.42–55.04	3.42–55.2	4.22–55.04
temperature, K	143(1)	143(1)	143(1)
hkl collected	$-14 \le h \le 14$ $-22 \le k \le 22$ $-21 \le l \le 21$	$-15 \le h \le 15$ $-23 \le k \le 23$ $-20 \le l \le 20$	$-12 \le h \le 12$ $-12 \le k \le 12$ $-24 \le l \le 24$
no. meas reflns	56996	85331	34960
no. of unique reflns	7513 [R_{int} = 0.0566]	7755 [R_{int} = 0.0259]	8005 [R_{int} = 0.0506]
no. parameters	443	437	479
R^a indices (F>2σ)	R_1 = 0.0346, wR_2 = 0.0719	R_1 = 0.0291, wR_2 = 0.0661	R_1 = 0.0542, wR_2 = 0.1489
R^a indices (all data)	R_1 = 0.0580, wR_2 = 0.0801	R_1 = 0.0365, wR_2 = 0.0722	R_1 = 0.0587, wR_2 = 0.1527
GOF[b]	1.012	1.077	1.200
final difference peaks, e/Å^3	0.343, –0.268	0.619, –0.519	5.069, –2.907

Table S1 (cont). Crystallographic data.

	7: 1,1-COD-2-Ph-*closo*-1,2,3,4-$RhC_3B_7H_9$	**8**: 1,1-COD-2-Ph-*closo*-1,2,3,4-$IrC_3B_7H_9$	**9**: 8,8,8-$(CN^tBu)_3$-9-Ph-*nido*-8,7,9,10-$CoC_3B_7H_{9\ 9}$
empirical formula	$C_{17}B_7H_{26}Rh$	$C_{17}B_7H_{26}Ir$	$C_{24}B_7H_{41}N_3Co$
formula weight	408.96	498.25	506.20
crystal class	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	Cc
Z	8	2	4
a, Å	16.5192(19)	6.6522(10)	10.1503(3)
b, Å	12.4153(15)	12.267(2)	17.9661(5)
c, Å	19.305(2)	13.771(2)	16.5896(5)
α, deg		115.260(6)	
β, deg	111.525(6)	93.055(7)	102.937(2)
γ, deg		93.212(7)	
V, Å^3	3683.1(7)	1011.0(3)	2948.51(15)
D_{calc}, g/cm^3	1.475	1.637	1.140
μ, mm^{-1}	0.923	6.599	0.599
λ, Å (Mo–K_α)	0.71073	0.71073	0.71073
crystal size, mm	0.22x0.10x0.04	0.28x0.20x0.18	0.40x0.07x0.03
F(000)	1664	480	1072
2θ angle, deg	2.78–55.10	3.68–55.24	4.54–55.02
temperature, K	143(1)	143(1)	100(1)

hkl collected	$-21 \le h \le 19$ $0 \le k \le 16$ $0 \le l \le 25$	$-8 \le h \le 8$ $-15 \le k \le 15$ $-17 \le l \le 17$	$-13 \le h \le 13$ $-23 \le k \le 23$ $-21 \le l \le 21$
no. meas reflns	191449	32785	48878
no. of unique reflns	8465 [$R_{int} = 0.0565$]	4640 [$R_{int} = 0.0214$]	6688 [$R_{int} = 0.0319$]
no. parameters	660	331	481
R^a indices ($F>2\sigma$)	$R_1 = 0.0291$, $wR_2 = 0.0692$	$R_1 = 0.0158$, $wR_2 = 0.0386$	$R_1 = 0.0244$, $wR_2 = 0.0538$
R^a indices (all data)	$R_1 = 0.0380$, $wR_2 = 0.0725$	$R_1 = 0.0165$, $wR_2 = 0.0392$	$R_1 = 0.0286$, $wR_2 = 0.0559$
GOF[b]	0.999	1.246	0.907
final difference peaks, e/Å^3	0.719, –0.370	1.176, –1.478	0.338, –0.153

Table S1 (cont). Crystallographic data.

	10: 8,8,8-(CN^tBu)$_3$-9-Ph-*nido*-8,7,9,10-$IrC_3B_7H_9$	**11**: 8,8-COD-8-CN^tBu-9-Ph-*nido*-8,7,9,10-$IrC_3B_7H_9$	**13**: 1-(η^4-C_4Me_4)-2-Ph-*closo*-1,2,3,4-$CoC_3B_7H_9$
empirical formula	$C_{24}B_7H_{41}N_3Ir$	$C_{22}B_7H_{35}NIr$	$C_{17}B_7H_{26}Co$
formula weight	639.47	581.38	364.98
crystal class	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1$/c
Z	4	4	4
a, Å	10.8239(2)	10.5125(5)	7.0025(8)
b, Å	19.4299(4)	20.7768(9)	33.184(4)
c, Å	14.8809(3)	10.5997(5)	8.5261(9)
α, deg			
β, deg	92.9850(10)	90.414(2)	107.089(5)
γ, deg			
V, Å^3	3125.32(11)	2315.08(18)	1893.7(4)
D_{calc}, g/cm^3	1.359	1.668	1.280
μ, mm^{-1}	4.288	5.778	0.901
λ, Å (Mo–K_α)	0.71073	0.71073	0.71073
crystal size, mm	0.38x0.38x0.10	0.48x0.15x0.04	0.25x0.18x0.10
F(000)	1272	1144	760
2θ angle, deg	4.20–55.06	3.84–55.12	4.92-55.16
temperature, K	100(1)	100(1)	143(1)

hkl collected	$-14 \le h \le 14$ $-25 \le k \le 25$ $-19 \le l \le 19$	$-13 \le h \le 13$ $-27 \le k \le 27$ $-13 \le l \le 13$	$-9 \le h \le 9$ $-43 \le k \le 43$ $-11 \le l \le 11$
no. meas reflns	47509	72534	41040
no. of unique reflns	7183 [$R_{int} = 0.0243$]	5345 [$R_{int} = 0.0384$]	4374 [$R_{int} = 0.0273$]
no. parameters	481	285	331
R^a indices ($F>2\sigma$)	$R_1 = 0.0174$, $wR_2 = 0.0414$	$R_1 = 0.0453$, $wR_2 = 0.0970$	$R_1 = 0.0402$ $wR_2 = 0.0900$
R^a indices (all data)	$R_1 = 0.0192$, $wR_2 = 0.0423$	$R_1 = 0.0461$, $wR_2 = 0.0974$	$R_1 = 0.0417$ $wR_2 = 0.0906$
GOF[b]	1.119	1.128	1.332
final difference peaks, e/Å^3	0.923, –0.832	6.432, –1.806	0.057, –0.592

Table S1 (cont). Crystallographic data.

	14: 2,2-COD-10-Ph-*closo*-2,1,6,10-$IrC_3B_6H_8$	**15**: 8,8-COD-8-CN^{t}Bu-9-Ph-11-I-*nido*-8,7,9,10-$IrC_3B_7H_8$
empirical formula	$C_{17}B_6H_{25}Ir$	$C_{22}B_7H_{34}NIIr$
formula weight	486.43	707.27
crystal class	triclinic	monoclinic
space group	$P\bar{1}$	*Pn*
Z	8	4
a, Å	9.9269(7)	9.7484(5)
b, Å	14.9468(11)	17.0714(9)
c, Å	25.482(2)	15.9074(8)
α, deg	107.029(4)	
β, deg	95.462(6)	104.075(2)
γ, deg	91.425(4)	
V, Å^3	3593.2(5)	2567.8(2)
D_{calc}, g/cm^3	1.798	1.829
μ, mm^{-1}	7.425	6.413
λ, Å (Mo–K_α)	0.71073	0.71073
crystal size, mm	0.35x0.05x0.02	0.40x0.25x0.04
F(000)	1872	1352
2θ angle, deg	2.86–55.12	3.56–55.20
temperature, K	143(1)	100(1)

hkl collected	$-12 \le h \le 12$ $-19 \le k \le 19$ $-33 \le l \le 33$	$-12 \le h \le 12$ $-22 \le k \le 22$ $-20 \le l \le 20$
no. meas reflns	82455	62161
no. of unique reflns	16204 [$R_{int} = 0.0466$]	10581 [$R_{int} = 0.0325$]
no. parameters	901	585
R^a indices ($F>2\sigma$)	$R_1 = 0.0560$, $wR_2 = 0.1114$	$R_1 = 0.0238$, $wR_2 = 0.0622$
R^a indices (all data)	$R_1 = 0.0749$, $wR_2 = 0.1203$	$R_1 = 0.0245$, $wR_2 = 0.0629$
GOF[b]	1.052	1.048
final difference peaks, e/Å^3	7.438, –6.040	2.574, –1.037

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$

[b] GOF = $\{\Sigma w(F_o^2 - F_c^2)^2/(n-p)\}^{1/2}$ where n = no. of reflns; p = no. of params refined

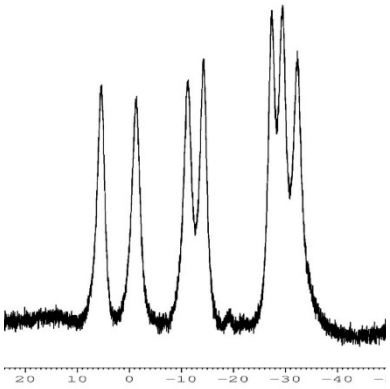

Figure S1. $^{11}B\{^{1}H\}$ NMR spectrum of 1,1-$(CO)_2$-2-Ph-*closo*-1,2,3,4-$CoC_3B_7H_9$ (**1**).

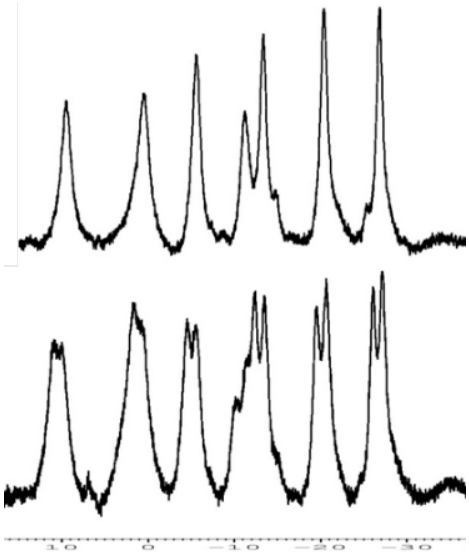

Figure S2. $^{11}B\{^{1}H\}$ (top) and ^{11}B (bottom) NMR spectra of 1,1-$(CO)_2$-2-Ph-*closo*-1,2,3,4-$RhC_3B_7H_9$ (**2**).

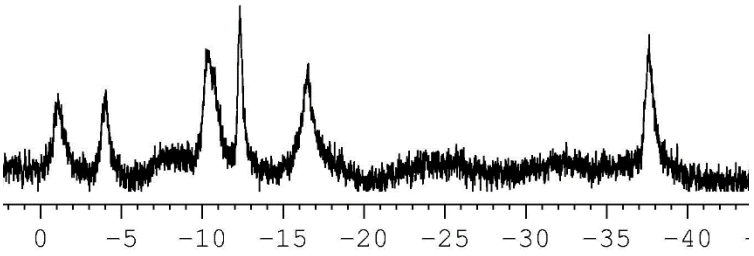

Figure S3. $^{11}B\{^{1}H\}$ NMR spectrum of 8,8,8-$(CO)_3$-9-Ph-*nido*-8,7,9,10-$IrC_3B_7H_9$ (**3**).

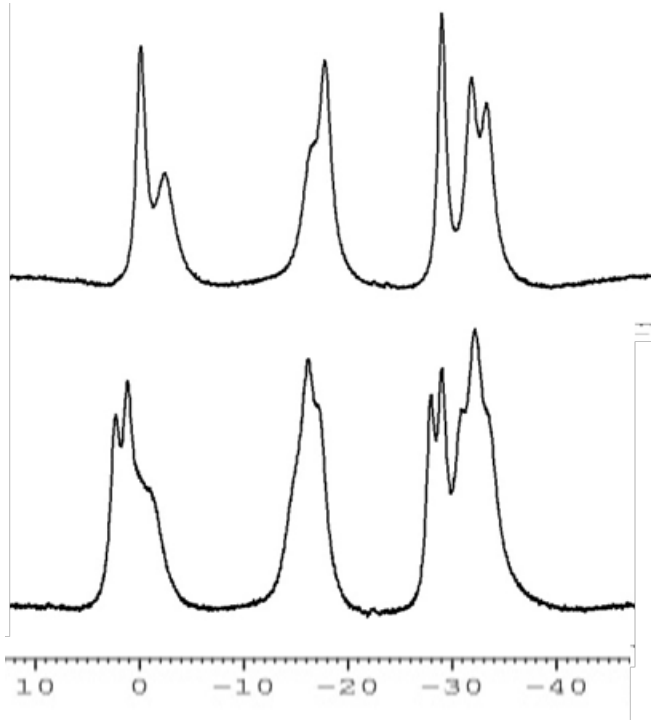

Figure S4. $^{11}B\{^{1}H\}$ (top) and ^{11}B (bottom) NMR spectra of 1,1-dppe-2-Ph-*closo*-1,2,3,4-$CoC_3B_7H_9$ (**4**).

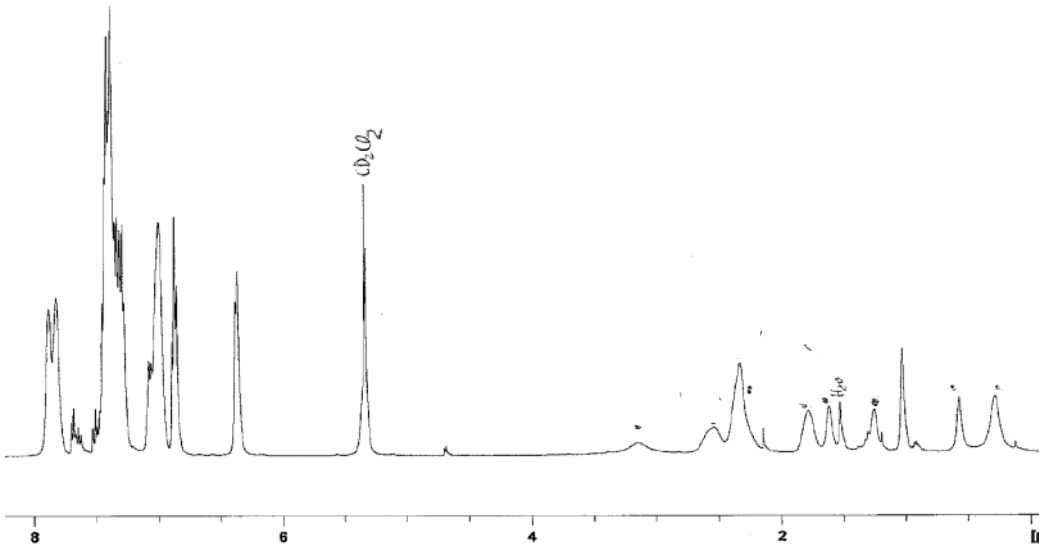

Figure S5. $^{1}H\{^{11}B\}$ NMR spectrum of 1,1-dppe-2-Ph-*closo*-1,2,3,4-$CoC_3B_7H_9$ (**4**).

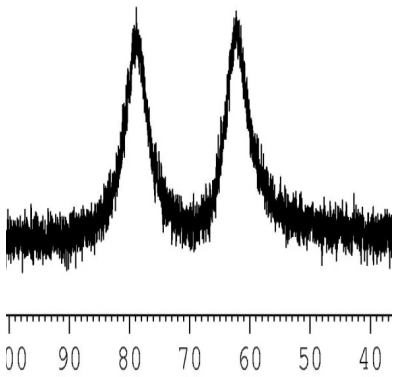

Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of 1,1-dppe-2-Ph-*closo*-1,2,3,4-$CoC_3B_7H_9$ (**4**).

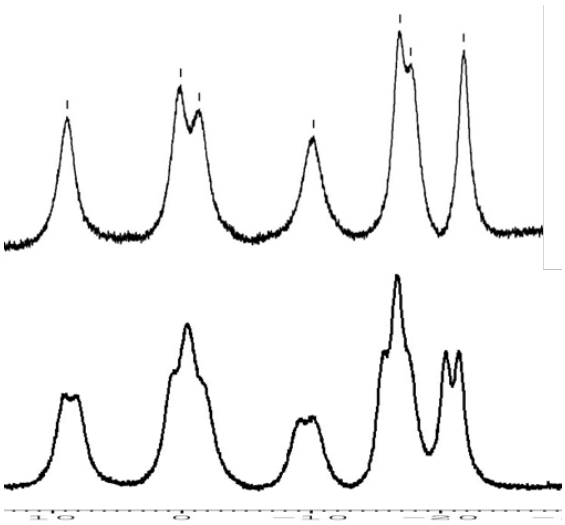

Figure S7. $^{11}B\{^{1}H\}$ (top) and ^{11}B (bottom) NMR spectra of 1,1-dppe-2-Ph-*closo*-1,2,3,4-$RhC_3B_7H_9$ (**5**).

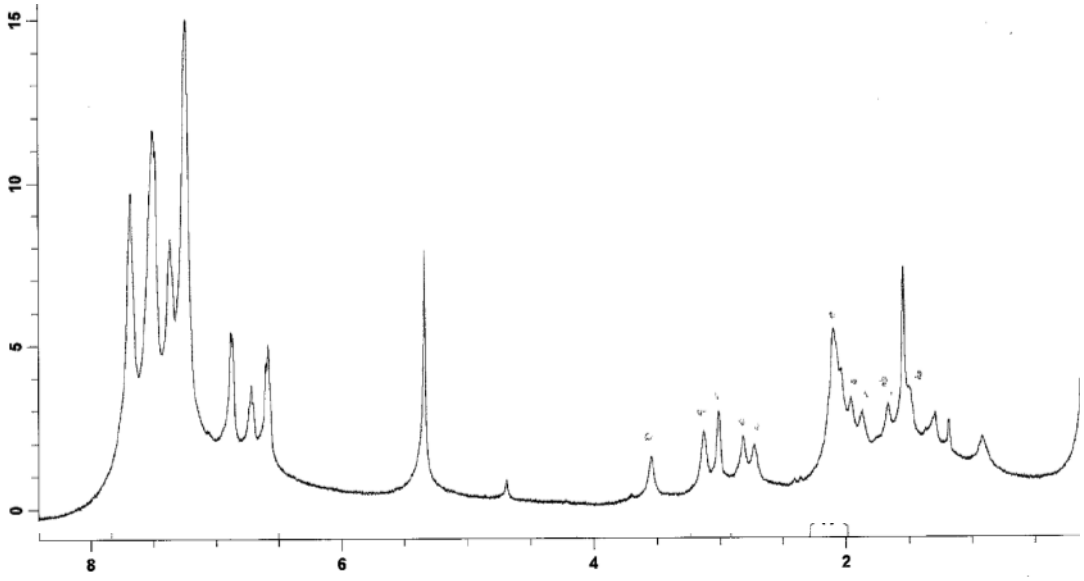

Figure S8. $^{1}H\{^{11}B\}$ NMR spectrum of 1,1-dppe-2-Ph-*closo*-1,2,3,4-$RhC_3B_7H_9$ (**5**).

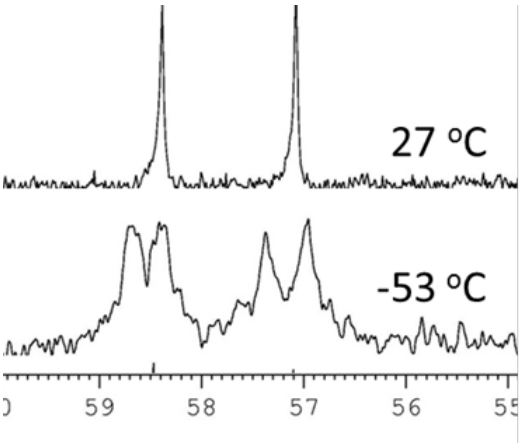

Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of 1,1-dppe-2-Ph-*closo*-1,2,3,4-$RhC_3B_7H_9$ (**5**) at 27 °C (top, $J_{Rh\text{-}P}$ = 165 Hz), at –53 °C (bottom, $J_{Rh\text{-}P}$ = ~160 Hz and $J_{Rh\text{-}P}$ = ~174 Hz).

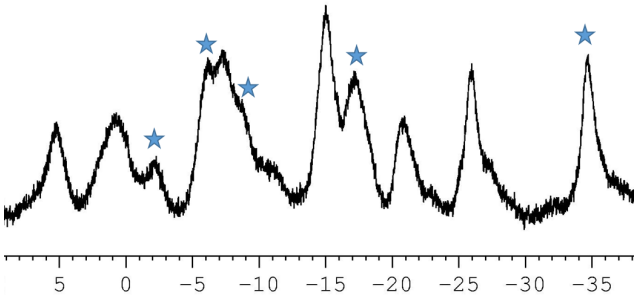

Figure S10. $^{11}B\{^{1}H\}$ NMR spectrum of reaction mixure durring 1,1-dppe-2-Ph-*closo*-1,2,3,4-$RhC_3B_7H_9$ (**5**) synthesis. Starred peaks not present in isolated product $^{11}B\{^{1}H\}$ NMR spectrum.

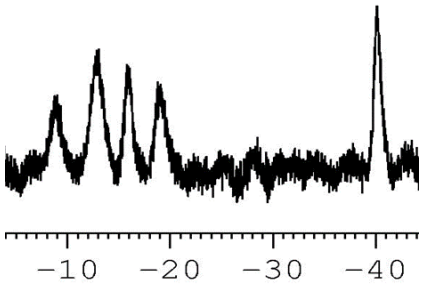

Figure S11. $^{11}B\{^{1}H\}$ NMR spectrum of 8-CO-8,8-dppe-9-Ph-*nido*-8,7,9,10-$IrC_3B_7H_9$ (**6**).

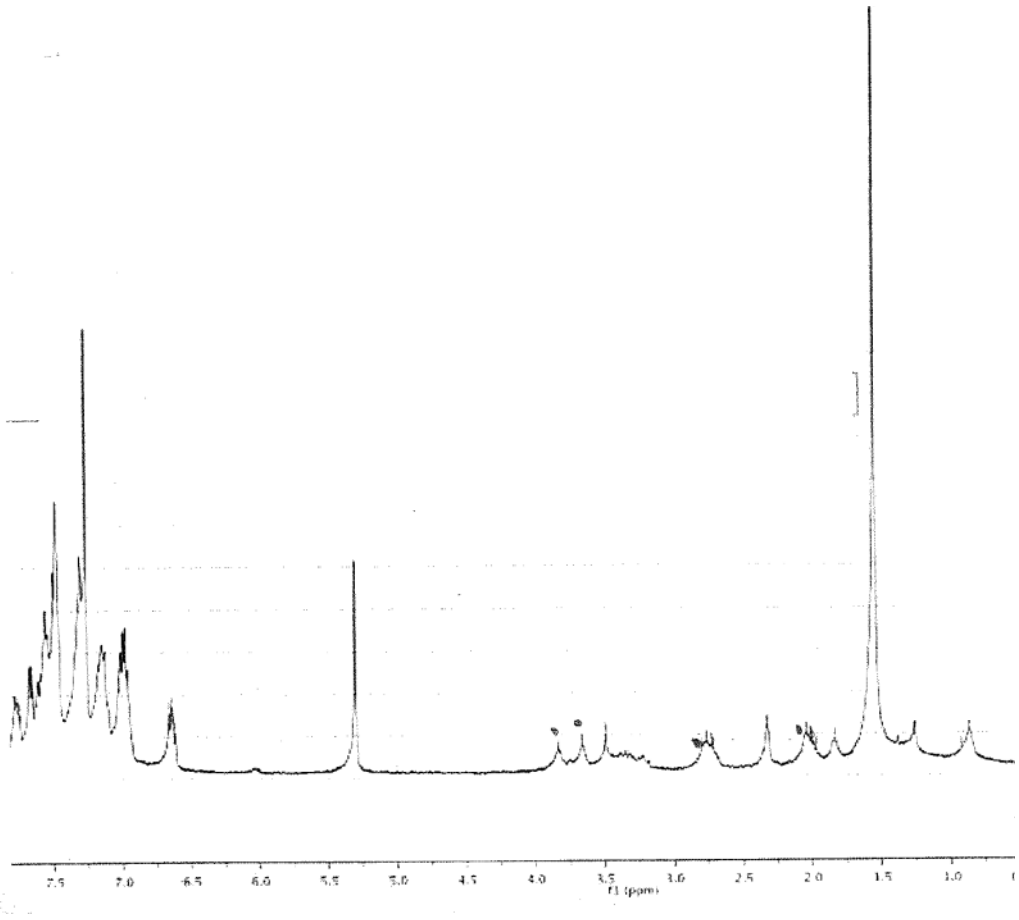

Figure S12. $^{1}H\{^{11}B\}$ NMR spectrum of 8-CO-8,8-dppe-9-Ph-*nido*-8,7,9,10-$IrC_3B_7H_9$ (**6**).

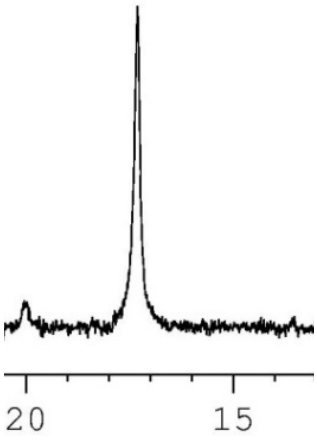

Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of 8-CO-8,8-dppe-9-Ph-*nido*-8,7,9,10-$IrC_3B_7H_9$ (**6**).

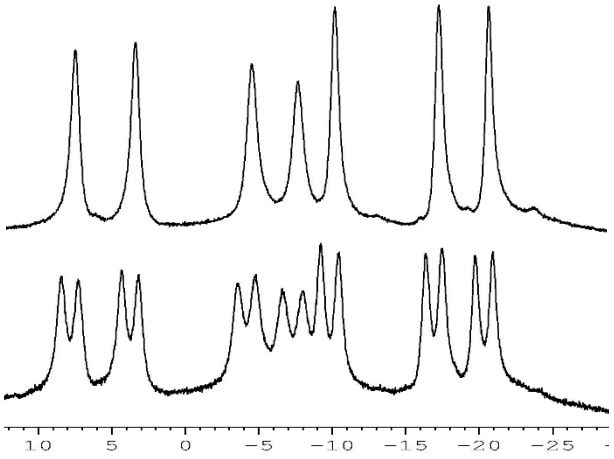

Figure S14. $^{11}B\{^{1}H\}$ (top) and ^{11}B (bottom) NMR spectra of 1,1-COD-2-Ph-*closo*-1,2,3,4-$RhC_3B_7H_9$ (**7**).

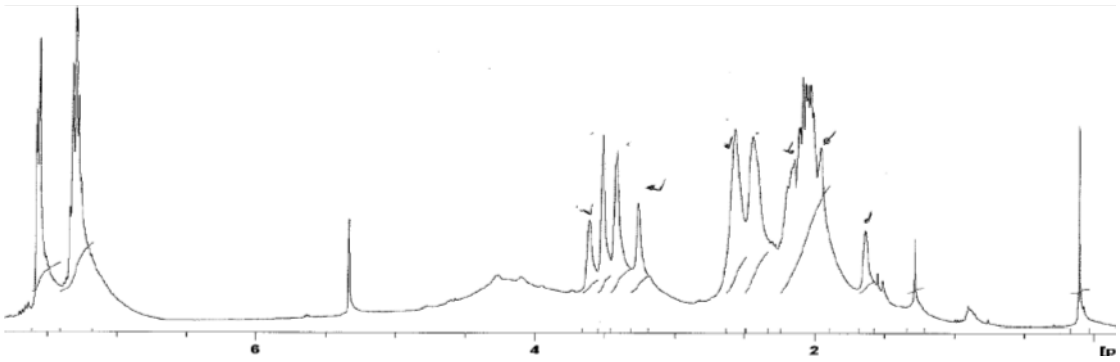

Figure S15. $^{1}H\{^{11}B\}$ NMR spectrum of 1,1-COD-2-Ph-*closo*-1,2,3,4-$RhC_3B_7H_9$ (**7**).

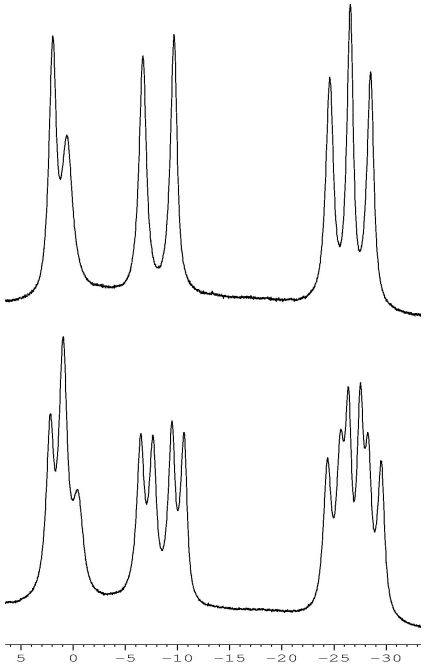

Figure S16. $^{11}B\{^{1}H\}$ (top) and ^{11}B (bottom) NMR spectra of 1,1-COD-2-Ph-*closo*-1,2,3,4-$IrC_3B_7H_9$ (**8**).

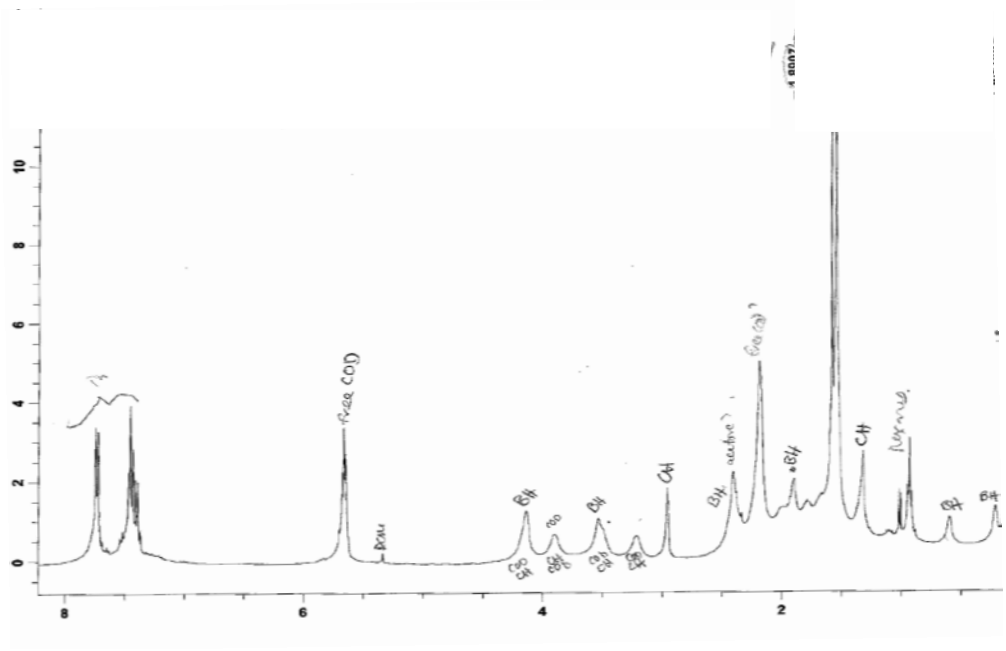

Figure S17. $^{1}H\{^{11}B\}$ NMR spectra of 1,1-COD-2-Ph-*closo*-1,2,3,4-$IrC_3B_7H_9$ (**8**).

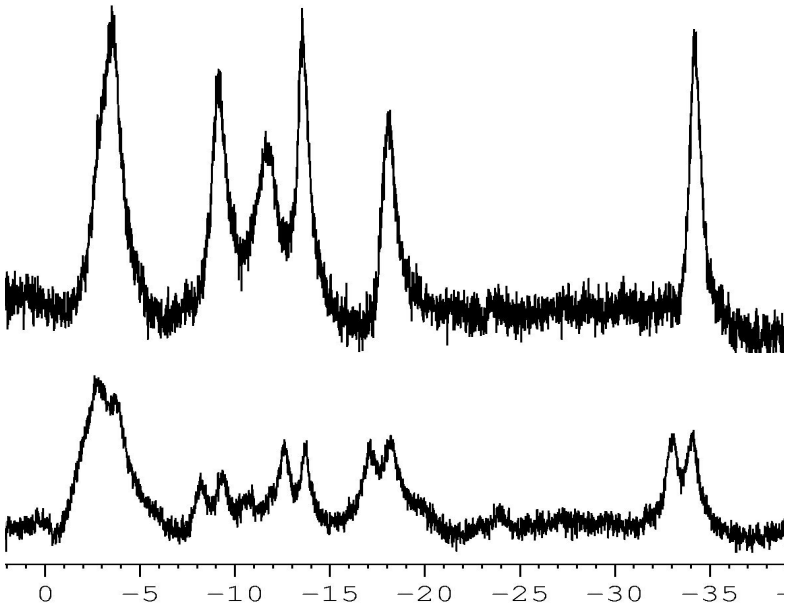

Figure S18. $^{11}B\{^{1}H\}$ (top) and ^{11}B (bottom) NMR spectra of 8,8,8-$(CN^{t}Bu)_3$-9-Ph-*nido*-8,7,9,10-$CoC_3B_7H_9$ (**9**).

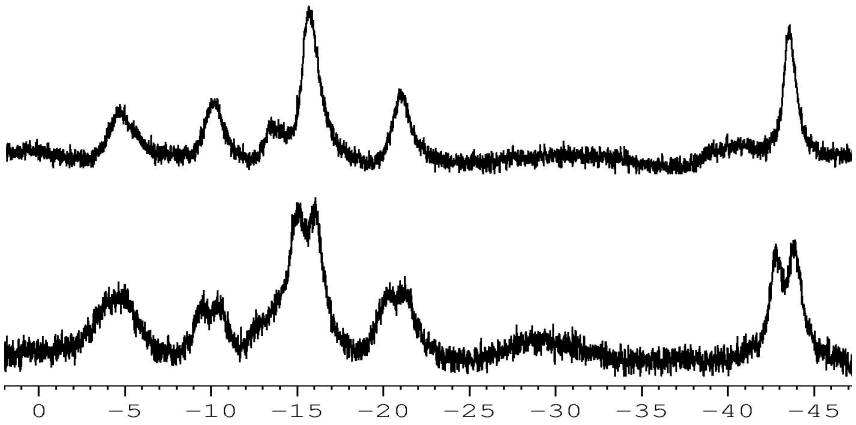

Figure S19. $^{11}B\{^{1}H\}$ (top) and ^{11}B (bottom) NMR spectra of 8,8,8-(CN^{t}Bu)$_3$-9-Ph-*nido*-8,7,9,10-IrC$_3$B$_7$H$_9$ (**10**).

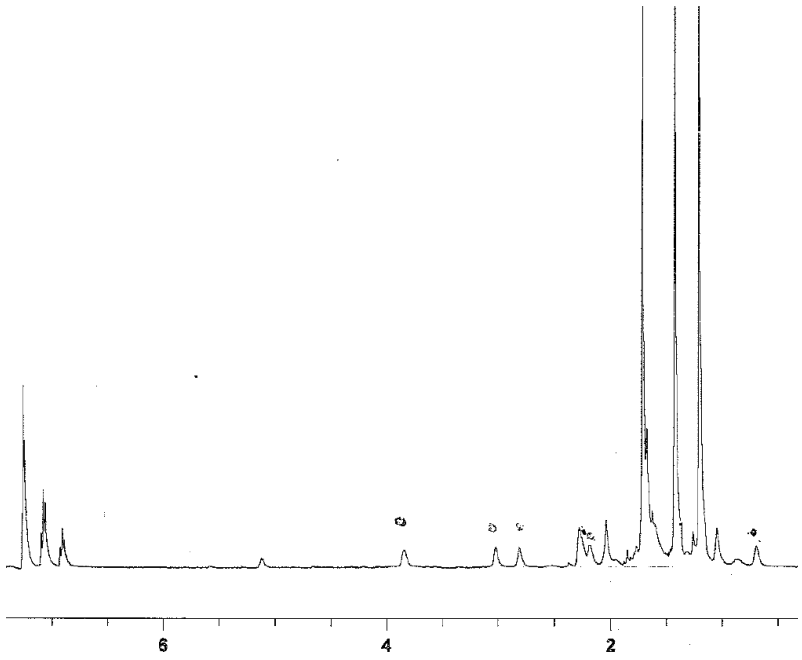

Figure S20. $^{1}H\{^{11}B\}$ NMR spectrum of 8,8,8-(CN^{t}Bu)$_3$-9-Ph-*nido*-8,7,9,10-IrC$_3$B$_7$H$_9$ (**10**).

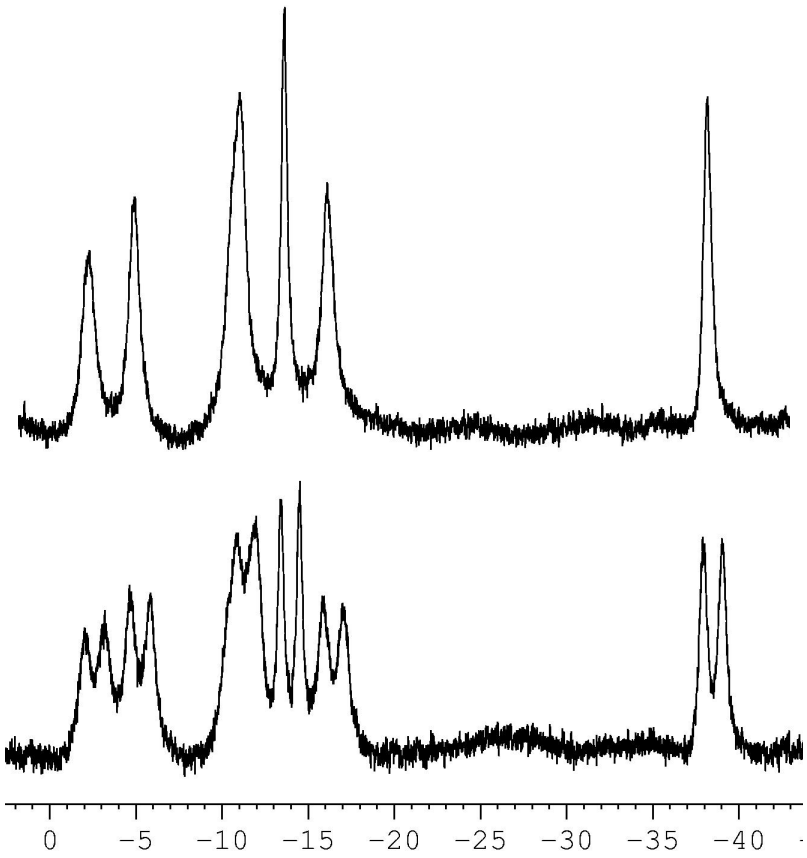

Figure S21. $^{11}B\{^{1}H\}$ (top) and ^{11}B (bottom) NMR spectra of 8,8-COD-8-CN^{t}Bu-9-Ph-*nido*-8,7,9,10-$IrC_3B_7H_9$ (**11**).

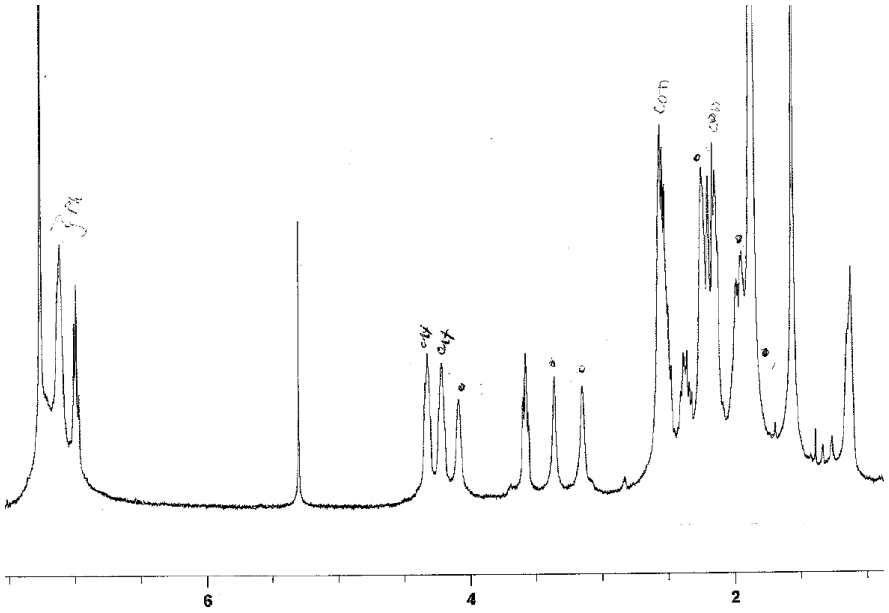

Figure S22. $^{1}H\{^{11}B\}$ NMR spectrum of 8,8-COD-8-CN^{t}Bu-9-Ph-*nido*-8,7,9,10-$IrC_3B_7H_9$ (**11**).

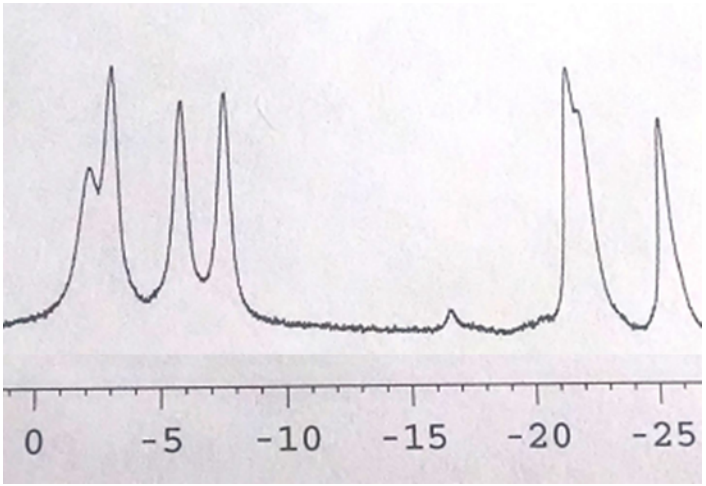

Figure S23. $^{11}B\{^{1}H\}$ NMR spectrum of 1-(η^4-$C_4(CH_3)_4$)-2-Ph-*closo*-1,2,3,4-$CoC_3B_7H_9$ (**13**).

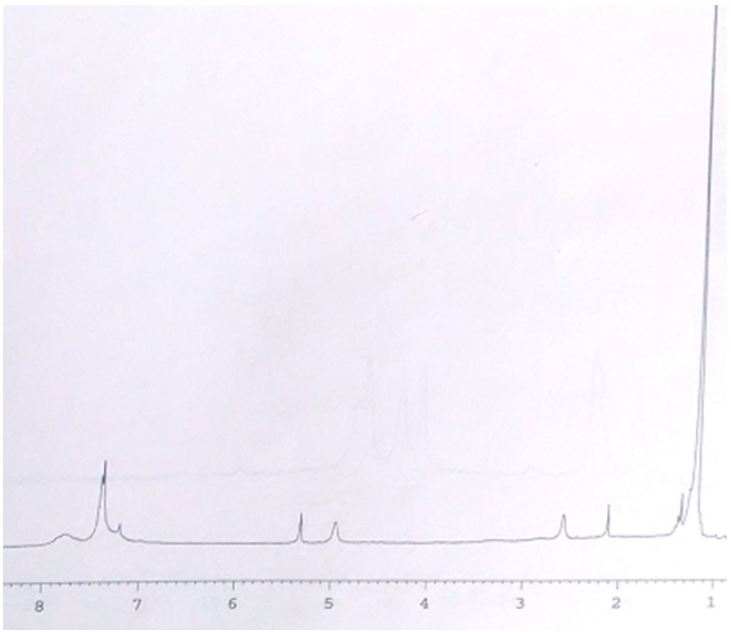

Figure S24. $^{1}H\{^{11}B\}$ NMR spectrum of 1-(η^4-C_4Me_4)-2-Ph-*closo*-1,2,3,4-$CoC_3B_7H_9$ (**13**).

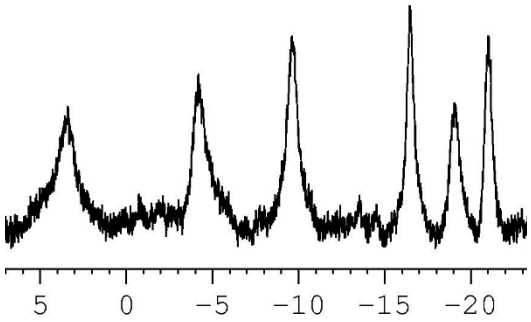

Figure S25. $^{11}B\{^{1}H\}$ NMR spectrum of 2,2-COD-10-Ph-*closo*-2,1,6,10-$IrC_3B_6H_8$ (**14**).

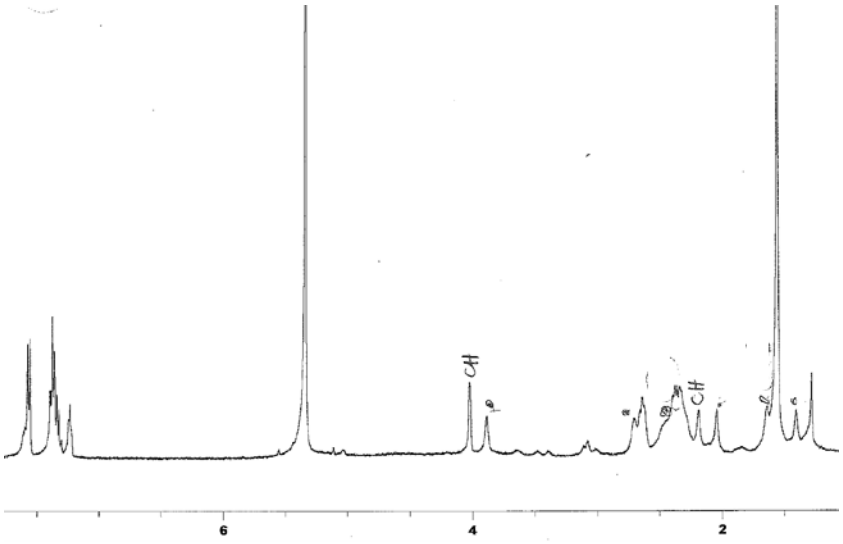

Figure S26. $^{1}H\{^{11}B\}$ NMR spectrum of 2,2-COD-10-Ph-*closo*-2,1,6,10-$IrC_3B_6H_8$ (**14**).

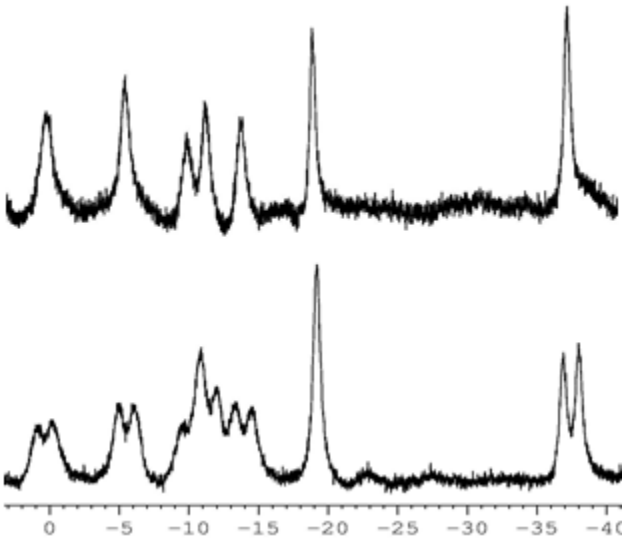

Figure S27. $^{11}B\{^{1}H\}$ (top) and ^{11}B (bottom) NMR spectra of 8,8-COD-8-CN^{t}Bu-9-Ph-11-I-*nido*-8,7,9,10-$IrC_3B_7H_8$ (**15**).

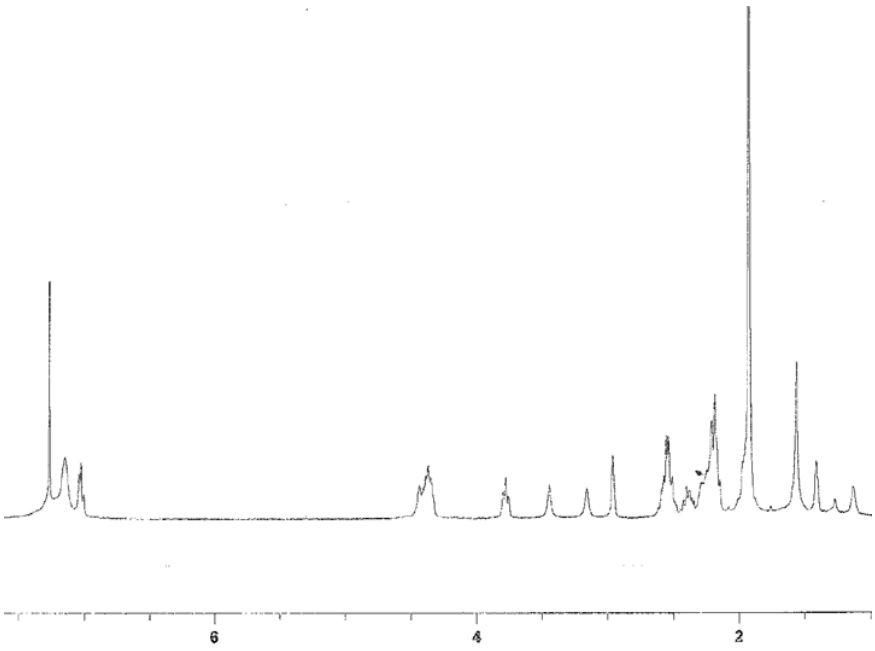

Figure S28. $^{1}H\{^{11}B\}$ NMR spectrum of 8,8-COD-8-CN^{t}Bu-9-Ph-11-I-*nido*-8,7,9,10-$IrC_3B_7H_8$ (**15**).