Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

Efficient synthesis of carborane azo derivatives and their reactivity

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Table S1 Crystallographic data and structure refinement parameters for **3b**, **4a**, **4b, 5**.

	3b	**4a**	**4b**	**5**
Empirical formula	$C_8H_{15}B_{10}ClN_2$	$C_{19}H_{32}B_{10}ClIrN_2O$	$C_{18}H_{29}B_{10}ClFIrN_2$	$C_{18}H_{29}B_{10}ClFRhN_2$
M_z	282.77	640.21	628.18	538.89
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P 2_1/n	P 2_1/c	P 2_1/n	P 2_1/n
a/Å	7.106(3)	12.581(2)	9.0717(17)	9.089(4)
b/Å	20.835(9)	8.8767(16)	18.623(3)	18.704(8)
c/Å	10.726(5)	23.861(4)	15.039(3)	15.037(6)
α/°	90	90	90	90
β/°	96.190(8)	99.600(3)	105.994	105.323(7)
γ/°	90	90	90	90
V/Ã^3	1578.8(12)	2627.4(8)	2442.4(8)	2465.5(18)
Z	4	4	4	4
D_c/Mgm^{-3}	1.190	1.618	1.708	1.452
μ(Mo-Kα)/mm^{-1}	0.224	5.200	5.594	0.819
F(000)	576	1248	1216	1088
Θ Range/°	1.955-27.969	1.642 -27.452	1.783 - 27.580	2.178 - 27.538
Limiting indices,*hklT*	-9, 9; -26, 27; -14, 12	-16, 16; -11,11; -26, 30	-11, 7; -24, 24, -19, 19	-11, 11; -18, 24; -19, 19
Refections/unique	11764/3755	18172/5979	17061/5627	18003/5645
R(int)	0.0394	0.0448	0.0511	0.0690
Completeness to *Θ*/°(%)	99.4	99.6	99.8	99.4
Data/restraints/parameter	3755 / 0 / 194	5979 / 18 / 317	5627 / 1 / 308	5645 / 1 / 307
Goodness-of-fit on F^2	1.037	1.053	1.076	0.966
Final R indices[I>2σ(I)] [α]	R1 = 0.0566, wR2 = 0.1599	R1 = 0.0321, wR2 = 0.0900	R1 = 0.0415, wR2 = 0.1148	R1 = 0.0378, wR2 = 0.0704
R Indices(all data)	R1 = 0.0977, wR2 = 0.1872	R1 = 0.0429, wR2 = 0.0954	R1 = 0.0452, wR2 = 0.1175	R1 = 0.0797, wR2 = 0.0834
Δρmax,min /e Ã$^{-3}$	0.298, -0.253	1.036, -1.021	3.211, -1.787	0.404, -0.495

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

Table S2 Crystallographic data and structure refinement parameters for **6a**, **6b**, **6c.**

	6a	**6b**	**6c**
Empirical formula	$C_{22}H_{43}B_{20}IrN_2O_3$	$C_{25}H_{37}B_{10}IrN_2OS$	$C_{25}H_{37}B_{10}IrN_2OSe$
M_z	791.98	713.92	760.82
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P -1	P 2_1/n	P 2_1/n
a/Å	10.2100(10)	11.485(3)	11.445(3)
b/Å	13.1239(13)	23.793(6)	23.872(7)
c/Å	14.7976(15)	12.051(3)	12.067(4)
α/°	91.425(2)	90	90
β/°	106.823(2)	111.001(4)	109.743(4)
γ/°	106.644	90	90
V/Ã^3	11805.8(3)	3074.2(14)	3102.9(15)
Z	2	4	4
D_c/Mgm^{-3}	1.457	1.543	1.629
μ(Mo-Kα)/mm^{-1}	3.727	4.434	5.499
F(000)	780	1408	1480
Θ Range/°	2.050 - 26.999	1.712 - 27.532	1.986 to 26.795
Limiting indices,*hklŢ*	-13, 11; -15, 16; -18, 18	-12, 14; -30, 24; -15, 15	-13, 14; -30, 18; -14, 15
Refections/unique	12765/7741	22059/7035	21213/6569
R(int)	0.0456	0.0520	0.0402
Completeness to *Θ*/°(%)	98.2	99.5	99.2
Data/restraints/parameter	7741 / 0 / 439	7035 / 87 / 410	6569 / 87 / 410
Goodness-of-fit on F^2	1.046	1.044	1.039
Final R indices[I>2σ(I)] [α]	R1 = 0.0479, wR2 = 0.1027	R1 = 0.0435, wR2 = 0.1182	R1 = 0.0351, wR2 = 0.1006
R Indices(all data)	R1 = 0.0827, wR2 = 0.1285	R1 = 0.0621, wR2 = 0.1303	R1 = 0.0561, wR2 = 0.1322
Δρmax,min /e Ã$^{-3}$	1.307, -0.678	1.906, -1.860	0.855, -1.000

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