SUPPLEMENTARY INFORMATION

Never a dull moment with praseodymium metal

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Contents

1. ^{19}F NMR Spectra for complexes

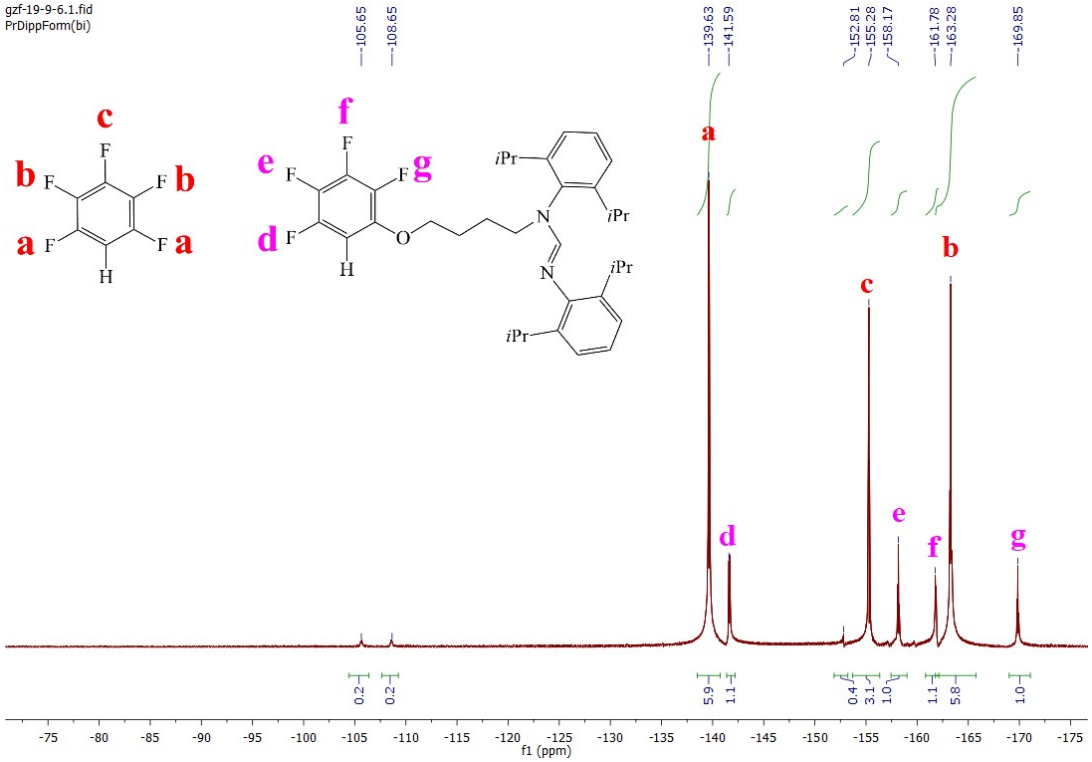
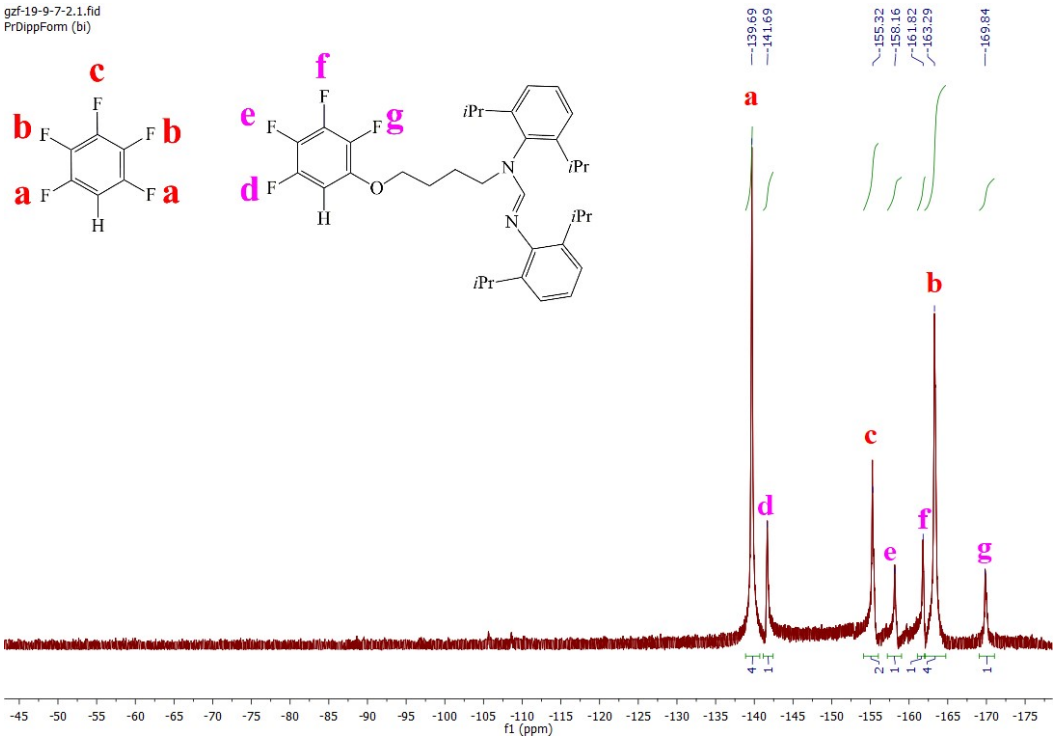


Fig. S1. ^{19}F{^{1}H} NMR spectra of the reaction mixture of Pr + $Bi(C_6F_5)_3$ + DippFormH in



C_6D_6 (reaction time 3 days)

Fig. S2. $^{19}F\{^{1}H\}$ NMR spectra of the reaction mixture Pr + $Bi(C_6F_5)_3$ + DippFormH in C_6D_6 (reaction time one week)

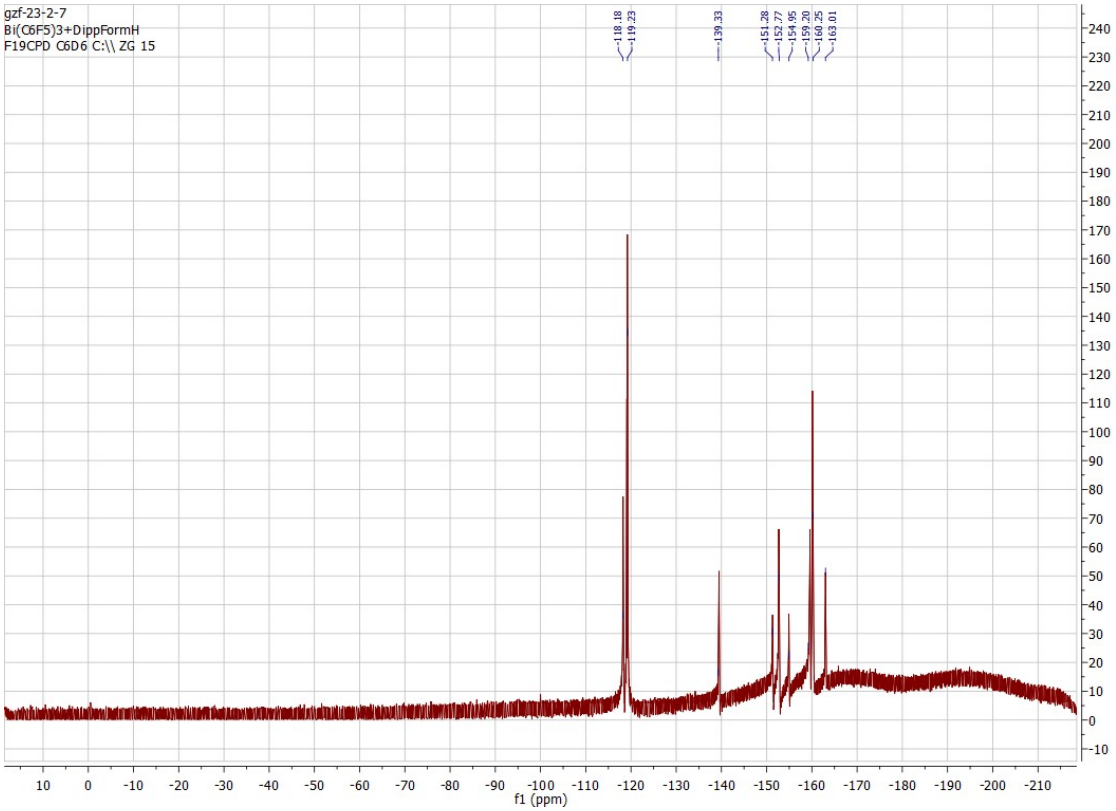


Fig. S3. $^{19}F\{^{1}H\}$ NMR spectra of the reaction mixture $Bi(C_6F_5)_3$ + DippFormH in C_6D_6

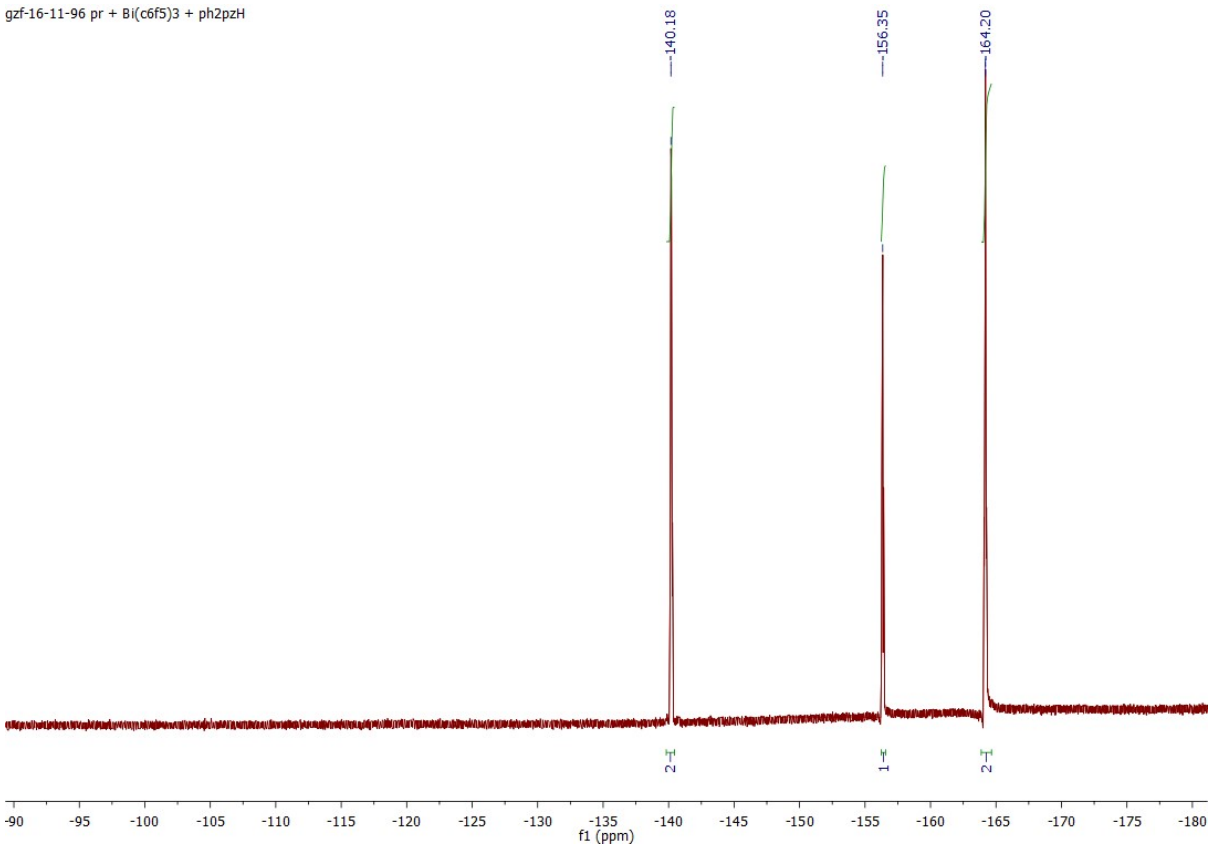


Fig. S4. Typical $^{19}F\{^{1}H\}$ NMR spectra of the reaction mixture of **8** in C_6D_6

2. Experimental

The compounds described here are highly air- and moisture sensitive, hence were prepared and were handled using vacuum-nitrogen line techniques and a dry box under an atmosphere of purified nitrogen. DippFormH was prepared by literature methods.[1] Praseodymium metal was from Santoku. Large chunks were filed in the drybox before use. All other reagents were purchased from Sigma and used without purification. Solvents (thf, toluene, 1,4-dioxane, diethyl ether, C_6D_6) were pre-dried by distillation over sodium or sodium benzophenone ketyl before being stored under an atmosphere of nitrogen. Proton decoupled ^{19}F NMR spectra were recorded with a Bruker 400MHz instrument. Crystals were immersed in crystallography oil and were examined on a Rigaku SynergyS diffractometer or the MX1 beamlines at the Australian Synchrotron. Crystal data and refinement details are given in **Table S1**. CCDC 2243049-2243053 for compound **1-5** and CCDC 2243054 for compound **7**, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Tris(pentafluorophenyl)bismuth(III) as the 1,4-dioxane solvate was synthesized by the reported method.[2]

Complexes 1-6

Praseodymium powder (2.00 mmol), trispentafluorophenylbismuth $[Bi(C_6F_5)_3]\cdot 0.5$diox (0.50 mmol) and DippFormH (1.50 mmol) were ultrasonicated in dry thf (10 ml) under nitrogen for 3 days. After filtration of the reaction mixture, a small (0.3ml) aliquot was monitored by ^{19}F NMR, ^{19}F NMR (C_6D_6, ppm): δ= -105.65, -108.65, -139.63 (m, 6F, C_6F_5H F-2, 6), -141.59 (m, 1F,-*o*-$HC_6F_4O(CH_2)_4$DippForm), -152.81, -155.28 (m, 3F, C_6F_5H F-4), -158.17(m, 1F,-*o*-$HC_6F_4O(CH_2)_4$DippForm), -161.78(m, 1F,-*o*-$HC_6F_4O(CH_2)_4$DippForm), -163.28 (m, 6F, C_6F_5H F-3, 5), -169.85 (m, 1F,-*o*-$HC_6F_4O(CH_2)_4$DippForm), which confirmed the consumption of $Bi(C_6F_5)_3$ on completion and formation of C_6F_5H, *o*-$HC_6F_4O(CH_2)_4$DippForm, *p*-HC_6F_4DippForm and other minor products, and the ratio of C_6F_5H and *o*-$HC_6F_4O(CH_2)_4$DippForm is 3:1. After filtration of the reaction mixture, the filtrates were evaporated to half volume under vacuum. Different kinds of crystals were obtained at -20 °C overnight. Orange crystals of **1** and **2**, green-yellow crystals of **3**, and colourless crystals of **5** were handpicked and identified by X-ray structures. Because compounds **3** and **4** are in the similar colour, and we could not successfully distinguish them under a microscope, the filtrates were dried under vacuum and recrystallized from toluene, and green crystals of **4** was obtained. **6** was identified by ^{19}F NMR only.

The same reaction was carried out under the same condition, except the reaction time was one week, after filtration of the reaction mixture, a small (0.3ml) aliquot was monitored by ^{19}F NMR, ^{19}F NMR (C_6D_6, ppm): δ= -139.69 (m, 4F, C_6F_5H F-2, 6), -141.69 (m, 1F,-*o*-$HC_6F_4O(CH_2)_4$DippForm), -155.32 (m, 2F, C_6F_5H F-4), -158.16(m, 1F, -*o*-$HC_6F_4O(CH_2)_4$DippForm), -161.82(m, 1F,-*o*-$HC_6F_4O(CH_2)_4$DippForm), -163.29 (m, 4F, C_6F_5H F-3, 5), -169.84 (m, 1F,-*o*-$HC_6F_4O(CH_2)_4$DippForm), which confirmed the consumption of $Bi(C_6F_5)_3$ on completion and formation of C_6F_5H and *o*-$HC_6F_4O(CH_2)_4$DippForm, and the ratio of C_6F_5H and *o*-$HC_6F_4O(CH_2)_4$DippForm is 2:1.

$[Bi_2(Ph_2pz)_4]\cdot$dioxane 7

$Bi(C_6F_5)_3$ (0.355 g, 0.50 mmol), Ph_2pzH (0.330 g, 1.50 mmol) and praseodymium powder (0.282 g, 2 mmol) were treated in THF (10 ml) for 3 days. The green solution was filtered. ^{19}F NMR (THF, ext. $CFCl_3$, ppm): δ= -140.18 (m, 2F, C_6F_5H F-2, 6), -156.35 (m, 1F, C_6F_5H F-4), -164.20 (m, 2F, C_6F_5H F-3, 5). Orange crystals (0.128 g, 37.0 %, M.p.238-240 °C) were obtained at -20 °C. IR (Nujol): 1605s, 1538m, 1263s, 1222m, 1178m, 1157m, 1065vs, 1027s, 981s, 960s, 910s, 874w, 842w, 806s, 759vs, 722m, 694s, 667m cm^{-1}. Unit cell: *a*=9.730(2) Å,

b=12.096(2) Å, *c*=12.680(3) Å, α=117.21(3)°, β=90.85(3) °, γ=101.57(3) °, *V*=1290.5(6) Å^3, different from the reported unsolvated [$Bi_2(Ph_2pz)_4$], Unit cell: *a*=10.095 Å, *b*=10.808 Å, *c*=12.034 Å, α=84.30°, β=88.64°, γ=74.43°, *V*=1258.498 Å^3.[3]

[Bi_2(*t*Bu_2pz)$_4$] 8

$Bi(C_6F_5)_3$ (0.355 g, 0.50 mmol), $^tBu_2$pzH (0.270 g, 1.50 mmol), praseodymium powder (0.282 g, 2 mmol) and dry THF (10 ml) were placed in a Schlenk flask in a nitrogen- filled dry box. The mixture was ultrasonicated for 3 days. The solution was filtered. Orange crystals (0.235 g, 83 %, M.p.182-184 °C) were obtained at -20 °C. IR (Nujol): 1563m, 1510s, 1361s, 1304m, 1261s, 1222w, 1206w, 1155m, 1075s, 1021s, 1006m, 967m, 803m, 778w, 722s cm^{-1}. Elemental analysis calcd (%) for $Bi_2C_{44}H_{76}N_8$: C, 46.56; H, 6.75; N, 9.87. Found: C, 46.35; H, 6.86; N, 9.84. Unit cell: *a*=11.241(2) Å, *b*=22.535(5) Å, *c*=28.756(6) Å, α=83.29(3)°, β=84.04(3) °, γ=89.82(3) °, *V*=7195(3) Å^3, similar to the reported unit cell: *a*=11.369 Å, *b*=23.075 Å, *c*=28.850 Å, α=83.92°, β=83.96 °, γ=89.82 °, *V*=7501.592 Å^3.[3]

[Eu(*t*Bu_2pz)$_3$(thf)$_2$] 9

[Bi_2(*t*Bu_2pz)$_4$] (0.114 g, 0.1 mmol), and europium powder (0.075g, 0.5 mmol) and dry THF (10 ml) were placed in a Schlenk flask in a nitrogen- filled dry box. The mixture was ultrasonic for 3 days. The solution was filtered. Colourless crystals (0.09 g, 75%, M.p.140-142 °C) were obtained at -20 °C. IR (Nujol): 1566m, 1503m, 1313m, 1260s, 1205m, 1096s, 1018s, 995m, 920m, 873m, 791s, 724s cm^{-1}. Unit cell: *a*=11.74 Å, *b*=19.79 Å, *c*=39.11 Å, β=98.14°, corresponds to the reported one *a*=11.723(2) Å, *b*=19.673(4)Å, *c*=38.943(8) Å, β=98.21(3)°.[4]

3. Supplementary Structural Discussion

The structure of the complex [Bi^{II}_2(DippForm)$_2$(C_6F_5)$_2$] 2

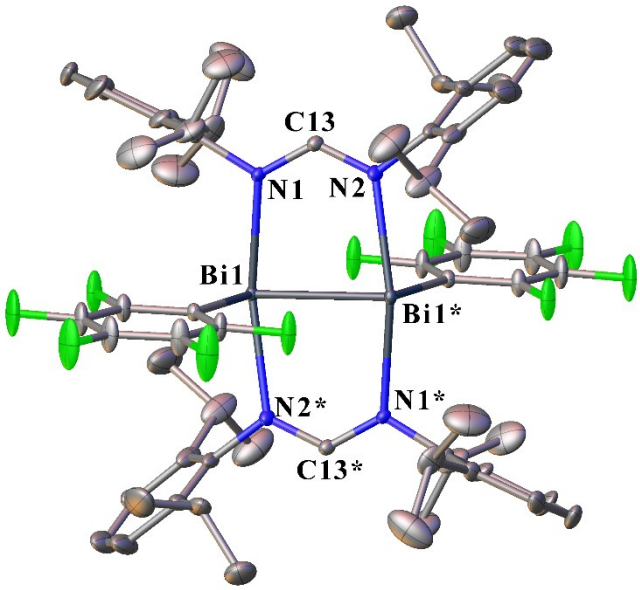


Fig. S5. Molecular diagrams of $[Bi^{II}_2(DippForm)_2(C_6F_5)_2]$ (**2**) represented by 50% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

The structure of the complex $[Bi_2(Ph_2pz)_4]$·dioxane 7

$[Bi_2(Ph_2pz)_4]$·dioxane (**7**) crystallized in the triclinic space group P-1. The inversion centre is at the midpoint of the Bi–Bi bond, indicating that the overall ligand arrangement around the Bi_2 core is found to be an almost perfect paddlewheel structure. Each bismuth atom is coordinated with four η^1-Ph_2Pz ligands. The average Bi–N and Bi-Bi* bond length are 2.473 and 2.8722(7) Å, which is similar to those of the reported $[Bi_2(Ph_2pz)_4]$.[3] The planes of **7** are almost perpendicular to each other, with an average dihedral angle close to 90° (N(1)-Bi(1)-N(3) 84.17(18)).

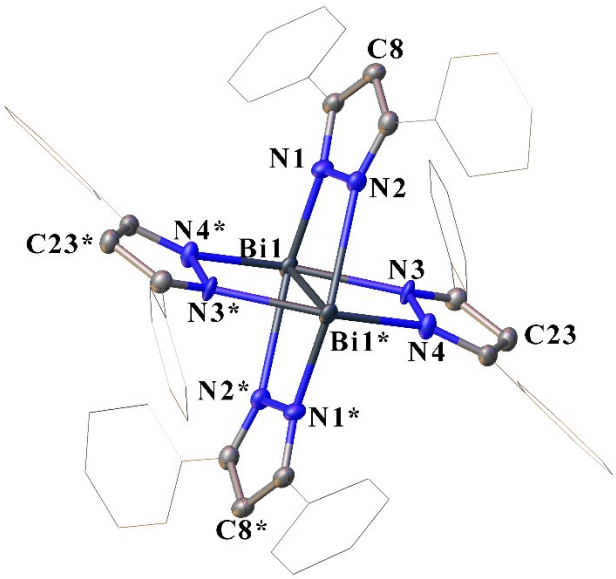
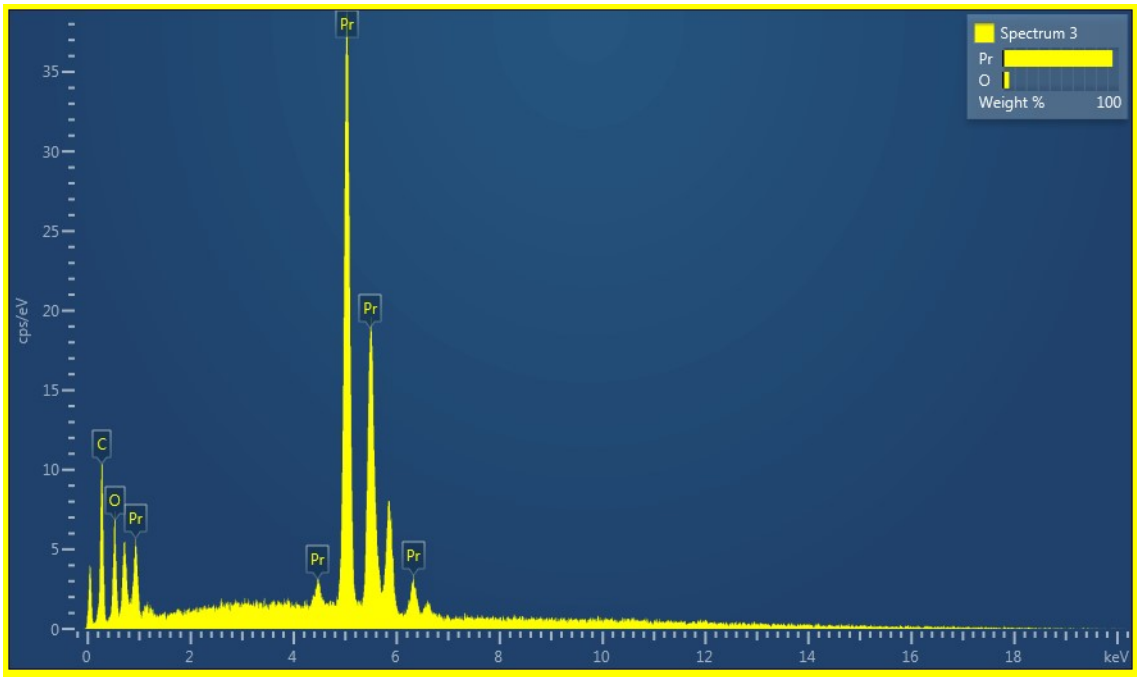


Fig. S6. Molecular diagrams of $[Bi_2(Ph_2pz)_4]$·dioxane (**7**) represented by 50% thermal ellipsoids. The lattice dioxane molecules and hydrogen atoms have been omitted for clarity. Selected bond angles (°) and lengths (Å) Bi-N1 2.296(5), Bi-N2* 2.696(5), Bi-N3 2.400(5), Bi-N4* 2.501(5), Bi-Bi* 2.8722(7).

4. SEM/EDS



Element	Wt%	Wt% Sigma	Atomic %
O	5.37	0.24	33.31
Pr	94.63	0.24	66.69
Total:	100.00		100.00

Fig. S7. SEM-EDS of Pr metal

5. X-ray crystallography

Single crystals coated with viscous hydrocarbon oil were mounted on glass fibres or loops. Complexes **2** and **4** were measured on a Rigaku SynergyS diffractometer. The SynergyS operated using microsource Mo-Kα radiation (λ = 0.71073 Å) at 123 K. Data processing was conducted using CrysAlisPro.55 software suite.[5] Complexes (**1**, **3**, **5**, and **7**) were measured at the Australian Synchrotron on the MX1 beamline, data integration was completed using Blue-ice [6] and XDS [7] software programs. Structural solutions were obtained by either direct methods [8] or charge flipping [9] methods and refined using full-matrix least-squares methods against F^2 using SHELX2018,[10] in conjunction with the Olex2 [11] graphical user interface. All hydrogen atoms were placed in calculated positions using the riding model. Crystal data and refinement details are given in Table S1.

Table S1 Crystal data and structural refinement for complexes **1-7**

	1	**2**	**3**
	$[Bi_2(DippForm)_2]$	$[Bi_2(DippForm)_2(C_6F_5)_2]$	$[Bi(DippForm)_2(C_6F_5)]$
Formula	$C_{50}H_{70}Bi_2N_4$	$C_{62}H_{70}Bi_2F_{10}N_4$	$C_{56}H_{70}BiF_5N_4$
M_r	1145.06	1479.18	1103.14
Space group	*P*nnm	*P*-1	*P*-1
a (Å)	18.348(4)	11.32528(13)	10.980(2)
b (Å)	19.217(4)	12.25378(12)	12.580(3)
c (Å)	10.939(2)	12.54848(12)	21.130(4)
α (°)	90	105.9880(9)	73.17(3)
β (°)	90	106.5627(10)	77.93(3)
γ (°)	90	102.5770(9)	70.19(3)
V (Å^3)	3857.0(14)	1519.42(3)	2608.3(11)
Z	2	1	2
ρ_{calc}, g cm^{-3}	0.986	1.617	1.405
μ, mm^{-1}	4.579	5.854	3.437
N_τ	45171	49963	45146
N (R_{int})	3524(0.0931)	10875(0.0399)	9171(0.0317)
$R_1(I > 2\sigma(I))$	0.0839	0.0242	0.0214
wR_2 (all data)	0.2102	0.0570	0.0520
GOF	1.121	1.086	1.042

	4	**5**	**7**
	$[Pr(DippForm)_2F(thf)]\cdot PhMe$	$[p\text{-}HC_6F_4(DippForm)]\cdot 0.5thf$	$[Bi_2(Ph_2pz)_4]\cdot dioxane$
Formula	$C_{61}H_{86}FN_4OPr$	$C_{33}H_{40}F_4N_2O_{0.5}$	$C_{64}H_{52}Bi_2N_8O_2$
M_r	1051.24	548.67	1383.09
Space group	$P2_1/c$	$P2_1/n$	*P*-1
a (Å)	12.0787(2)	11.020(2)	9.7300(19)
b (Å)	13.8725(2)	19.180(4)	12.096(2)
c (Å)	33.8375(5)	14.340(3)	12.680(3)
α (°)	90	90	117.21(3)

β (°)	92.9560(10)	97.09(3)	90.85(3)
γ (°)	90	90	101.57(3)
V (Å^3)	5662.33(15)	3007.8(11)	1290.5(6)
Z	4	4	1
ρ_{calc}, g cm^{-3}	1.233	1.212	1.780
μ, mm^{-1}	0.905	0.089	6.865
N_τ	95583	69721	23882
N (R_{int})	19825(0.0458)	5111(0.0308)	4548(0.0771)
$R_1(I > 2\sigma(I))$	0.0328	0.0456	0.0346
wR_2 (all data)	0.0772	0.1285	0.0909
GOF	1.047	1.023	1.080

6. References

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