Electronic Supplementary Information

M–H–BR₃ and M–Br–BR₃ Interactions in Rhodium and Nickel Complexes of an Ambiphilic Phosphine-Thioether-Borane Ligand

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Table S1. Crystal Data and Structure Refinement for [Rh(μ -H)(CO)(TXPB)] $\cdot$ 2C₆H₁₄.

Identification code	brad31	
Empirical formula	C60 H77 B O P Rh S	
Formula weight	990.96	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.907(2) Å	α = 96.447(4)°.
	b = 13.536(3) Å	β = 93.892(5)°.
	c = 16.766(4) Å	γ = 91.612(6)°.
Volume	2452.3(9) Å ³	
Z	2	
Density (calculated)	1.304 Mg/m ³	
Absorption coefficient	0.464 mm ⁻¹	
F(000)	996	
Crystal size	0.20 x 0.08 x 0.02 mm ³	
Theta range for data collection	1.87 to 25.44°.	
Index ranges	-13<= <i>h</i> <=9, -16<= <i>k</i> <=15, -17<= <i>l</i> <=20	
Reflections collected	26269	
Independent reflections	8972 [R(int) = 0.1320]	
Completeness to theta = 25.44°	98.8 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9908 and 0.9129	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8972 / 0 / 484	
Goodness-of-fit on F ²	0.841	
Final R indices [I>2sigma(I)]	R1 = 0.0608, wR2 = 0.1096	
R indices (all data)	R1 = 0.1268, wR2 = 0.1266	
Largest diff. peak and hole	0.689 and -0.481 e.Å ⁻³	

Table S2. Crystal data and structure refinement for [NiBr(μ -Br)(TXPB)]·toluene.

Identification code	brad13	
Empirical formula	C ₅₄ H ₅₆ B Br ₂ Ni P S	
Formula weight	997.34	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b n 21	
Unit cell dimensions	a = 9.0175(15) Å	$\alpha = 90^\circ$.
	b = 21.625(4) Å	$\beta = 90^\circ$.
	c = 24.361(4) Å	$\gamma = 90^\circ$.
Volume	4750.4(13) Å ³	
Z	4	
Density (calculated)	1.383 Mg/m ³	
Absorption coefficient	2.204 mm ⁻¹	
F(000)	2024	
Crystal size	0.29 x 0.13 x 0.06 mm ³	
Theta range for data collection	1.88 to 26.43°.	
Index ranges	-11 ≤ h ≤ 9, -26 ≤ k ≤ 26, -30 ≤ l ≤ 22	
Reflections collected	41712	
Independent reflections	8162 [R(int) = 0.0867]	
Completeness to theta = 26.43°	99.7 %	
Absorption correction	Numerical	
Max. and min. transmission	0.8791 and 0.5674	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8162 / 1 / 479	
Goodness-of-fit on F ²	0.986	
Final R indices [I > 2sigma(I)]	R1 = 0.0422, wR2 = 0.0882	
R indices (all data)	R1 = 0.0570, wR2 = 0.0924	
Absolute structure parameter	0.035(8)	
Largest diff. peak and hole	0.823 and -0.367 e.Å ⁻³	

Figure S1. ^1H NMR Spectrum of $[\text{RhH}(\text{CO})(\text{TXPB})]$ (600 MHz, CD_2Cl_2 , 298 K).

Figure S2. Expanded Aromatic Region of the ^1H NMR Spectrum of $[\text{RhH}(\text{CO})(\text{TXPB})]$ (600 MHz, CD_2Cl_2 , 298 K).

Figure S3. Expanded Metal–Hydride Region of the ^1H NMR Spectrum of $[\text{RhH}(\text{CO})(\text{TXPB})]$ (600 MHz, CD_2Cl_2 , 298 K).

[illegible]

Figure S5. Expanded Aromatic Region of the ^{13}C NMR Spectrum of $[\text{RhH}(\text{CO})(\text{TXPB})]$ (151 MHz, CD_2Cl_2 , 298 K).

Figure S6. Expanded Aromatic Region of the ^{13}C NMR Spectrum of $[\text{RhH}(\text{CO})(\text{TXPB})]$ (151 MHz, CD_2Cl_2 , 298 K).

Figure S7. Expanded Aromatic Region of the ^{13}C NMR Spectrum of $[\text{RhH}(\text{CO})(\text{TXPB})]$ (151 MHz, CD_2Cl_2 , 298 K).

Figure S8. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of $[\text{RhH}(\text{CO})(\text{TXPB})]$ (203 MHz, CD_2Cl_2 , 298 K).

Figure S9. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of $[\text{RhH}(\text{CO})(\text{TXPB})]$ (203 MHz, CD_2Cl_2 , 298 K).

Figure S10. ^1H NMR Spectrum of $[\text{NiBr}(\mu\text{-Br})(\text{TXPB})]$ (500 MHz, CD_2Cl_2 , 298 K).

Figure S11. Expanded Aromatic Region of the ^1H NMR Spectrum of $[\text{NiBr}(\mu\text{-Br})(\text{TXPB})]$ (500 MHz, CD_2Cl_2 , 298 K).

Figure S12. ^{13}C NMR Spectrum of $[\text{NiBr}(\mu\text{-Br})(\text{TXPB})]$ (126 MHz, CD_2Cl_2 , 298 K).

Figure S13. Expanded Aromatic Region of the ^{13}C NMR Spectrum of $[\text{NiBr}(\mu\text{-Br})(\text{TXPB})]$ (126 MHz, CD_2Cl_2 , 298 K).

Figure S14. Expanded Aliphatic Region of the ^{13}C NMR Spectrum of $[\text{NiBr}(\mu\text{-Br})(\text{TXPB})]$ (126 MHz, CD_2Cl_2 , 298 K).

Figure S15. Variable Temperature $^{31}\text{P}\{^1\text{H}\}$ NMR Spectra of $[\text{NiBr}(\mu\text{-Br})(\text{TXPB})]$ (203 MHz, CD_2Cl_2 , 298–206 K).

Figure S16. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of $[\text{NiBr}(\mu\text{-Br})(\text{TXPB})]$ (203 MHz, CD_2Cl_2 , 206 K).

Figure S17. ^{11}B NMR Spectrum of $[\text{NiBr}(\mu\text{-Br})(\text{TXPB})]$ (161 MHz, CD_2Cl_2 , 298 K).

Figure S18. Superimposed X-ray (red) and Calculated (blue) Structures of $[(\text{TXPB})\text{Rh}(\mu\text{-H})(\text{CO})]$ (**2**); 2 views.

Table S3. Coordinates for the DFT (ADF, PBE, D3BJ, TZ2P, all-electron, ZORA) Calculated Structure of [(TXPB)Rh(μ -H)(CO)] (2).

Atom	X	Y	Z (Angstrom)				
1.Rh	8.122147	8.551729	11.834925	52.H	11.123465	14.161168	11.982920
2.S	6.033791	9.384793	11.379392	53.C	6.697215	5.037031	7.184766
3.P	7.088229	6.551662	11.538617	54.H	6.604626	4.686698	6.156306
4.O	10.874971	7.653266	10.944326	55.C	8.592870	2.926605	13.975555
5.B	8.248556	10.539157	13.235014	56.H	8.970327	2.088084	14.561770
6.C	4.344057	10.909108	12.915538	57.C	2.257968	3.931709	12.958136
7.C	3.209242	10.044264	12.334749	58.H	1.766879	4.189927	12.009221
8.C	9.881514	12.474853	12.509659	59.H	1.648418	3.172159	13.469630
9.H	9.514438	12.349331	11.488240	60.H	3.230427	3.477341	12.726582
10.C	7.625531	5.078714	12.468810	61.C	11.253071	13.694405	14.088146
11.C	2.834982	7.568975	13.019213	62.H	11.954919	14.499669	14.309802
12.H	1.864074	7.849608	13.417443	63.C	6.031323	4.904694	9.506315
13.C	5.189512	12.666112	14.401765	64.H	5.421065	4.451927	10.288494
14.C	6.497057	12.287567	14.086805	65.C	7.695774	6.523693	8.810268
15.H	7.337755	12.779420	14.572713	66.H	8.366305	7.345402	9.065689
16.C	4.895079	8.166805	11.988761	67.C	7.431878	5.046211	13.857839
17.C	9.420889	11.603807	13.512151	68.H	6.922531	5.871911	14.353744
18.C	2.410538	5.175686	13.854409	69.C	8.322006	4.036631	11.840298
19.C	9.461968	8.634484	14.620088	70.H	8.487442	4.060091	10.763288
20.H	10.386073	8.956787	14.139777	71.C	10.811960	12.843480	15.103080
21.C	5.354740	6.847604	12.085094	72.H	11.166239	12.981511	16.126013
22.C	6.785761	11.227853	13.208803	73.C	7.907676	3.970158	14.604237
23.C	8.348179	7.285324	16.292558	74.H	7.753896	3.956084	15.683645
24.H	8.391804	6.544697	17.092513	75.C	5.916780	4.458981	8.191542
25.C	6.924856	5.939428	9.822228	76.H	5.214230	3.661260	7.949867
26.C	3.251922	6.236179	13.136204	77.C	7.586641	6.066637	7.494936
27.C	5.683211	10.633691	12.594618	78.H	8.192779	6.522095	6.712046
28.C	4.882841	13.822751	15.363132	79.C	3.137674	4.777129	15.156774
29.C	7.128595	7.854388	15.922518	80.H	3.257814	5.648220	15.817239
30.H	6.208620	7.563137	16.432327	81.H	4.136941	4.370520	14.947407
31.C	4.127895	11.940526	13.829978	82.H	2.560274	4.010078	15.694925
32.H	3.108242	12.187598	14.118014	83.C	1.010276	5.691010	14.213357
33.C	2.978016	10.410104	10.846197	84.H	1.053764	6.534305	14.916598
34.H	2.687846	11.467608	10.774293	85.H	0.436020	4.887807	14.695733
35.H	2.172043	9.789475	10.429358	86.H	0.456391	6.012040	13.319813
36.H	3.877266	10.261724	10.236112	87.C	4.272380	14.987137	14.556131
37.C	1.887050	10.295164	13.068256	88.H	4.036904	15.830645	15.223643
38.H	1.580936	11.340653	12.942138	89.H	3.345492	14.678162	14.052070
39.H	1.960521	10.083605	14.143164	90.H	4.976055	15.338520	13.788224
40.H	1.090640	9.674020	12.639164	91.C	3.874264	13.375468	16.439842
41.C	9.913380	11.813136	14.813027	92.H	4.262536	12.519601	17.009879
42.H	9.574514	11.161235	15.620559	93.H	2.908197	13.085551	16.004631
43.C	7.078265	8.808190	14.903529	94.H	3.686136	14.202324	17.141180
44.H	6.114792	9.254561	14.653749	95.C	6.145322	14.329803	16.075312
45.C	3.632995	8.565497	12.437562	96.H	6.627224	13.531288	16.656412
46.C	8.242184	9.245210	14.224000	97.H	5.874204	15.139510	16.768102
47.C	9.515895	7.673294	15.625862	98.H	6.883085	14.728318	15.366516
48.H	10.473333	7.229537	15.900122	99.C	8.802052	2.964943	12.595099
49.C	4.517799	5.885273	12.643718	100.H	9.342113	2.158106	12.099775
50.H	4.886090	4.866581	12.758096	101.C	9.836544	7.993587	11.338718
51.C	10.785488	13.502719	12.784615	102.H	8.605983	10.198539	11.925