ELECTRONIC SUPPLEMENTARY INFORMATION

Octahedral manganese(I) and ruthenium(II) complexes containing 2-(methylamido)pyridine–borane as a tripod κ^3*N,H,H*-ligand

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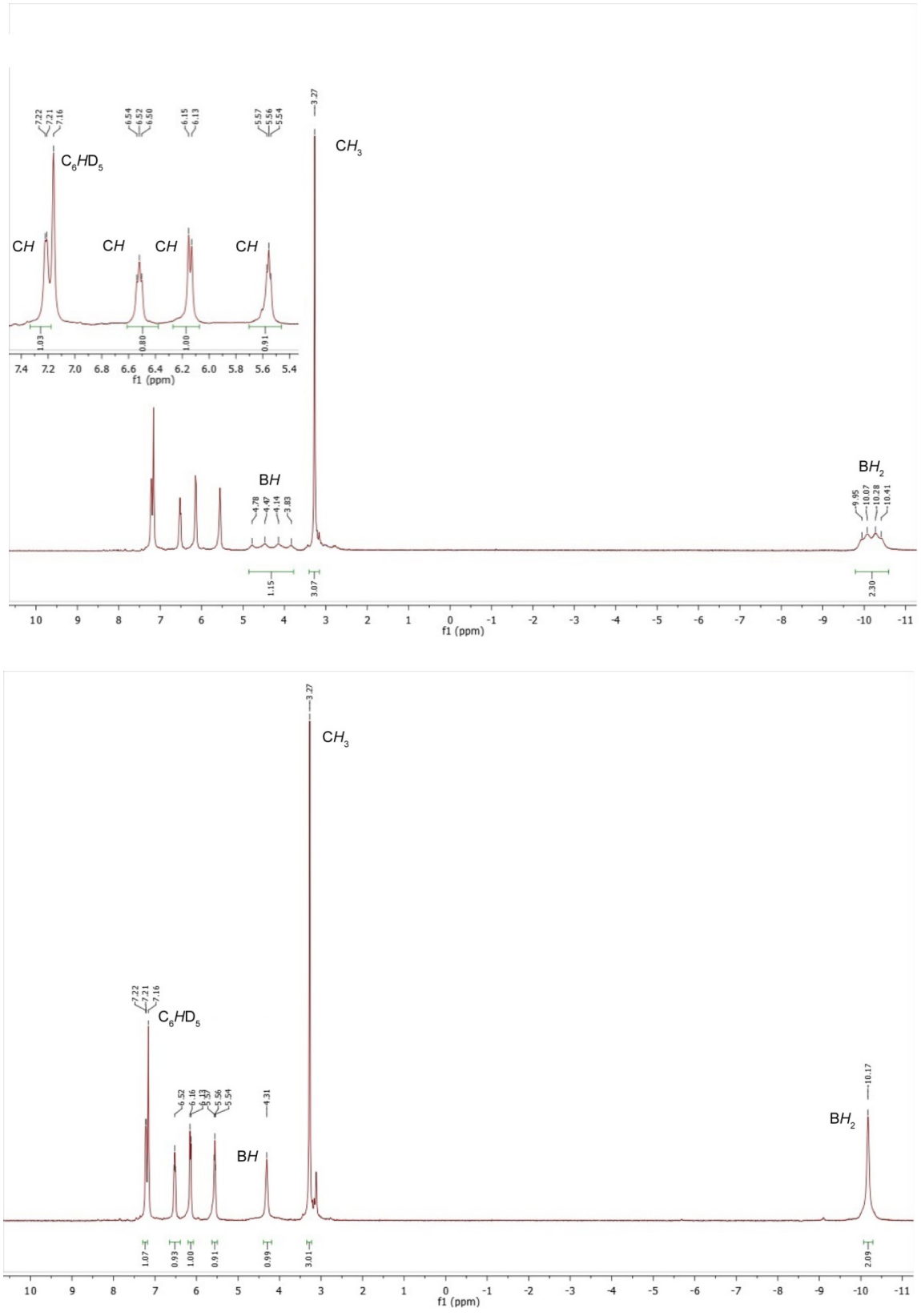

Figure S1. ^{1}H (top) and $^{1}H\{^{11}B\}$ (bottom) NMR spectra ([$^{2}H_6$]-benzene, 298 K, 400.54 MHz) of *fac*-[Mn(κ^3*N*,*H*,*H*-mapyBH$_3$)(CO)$_3$] (**1**).

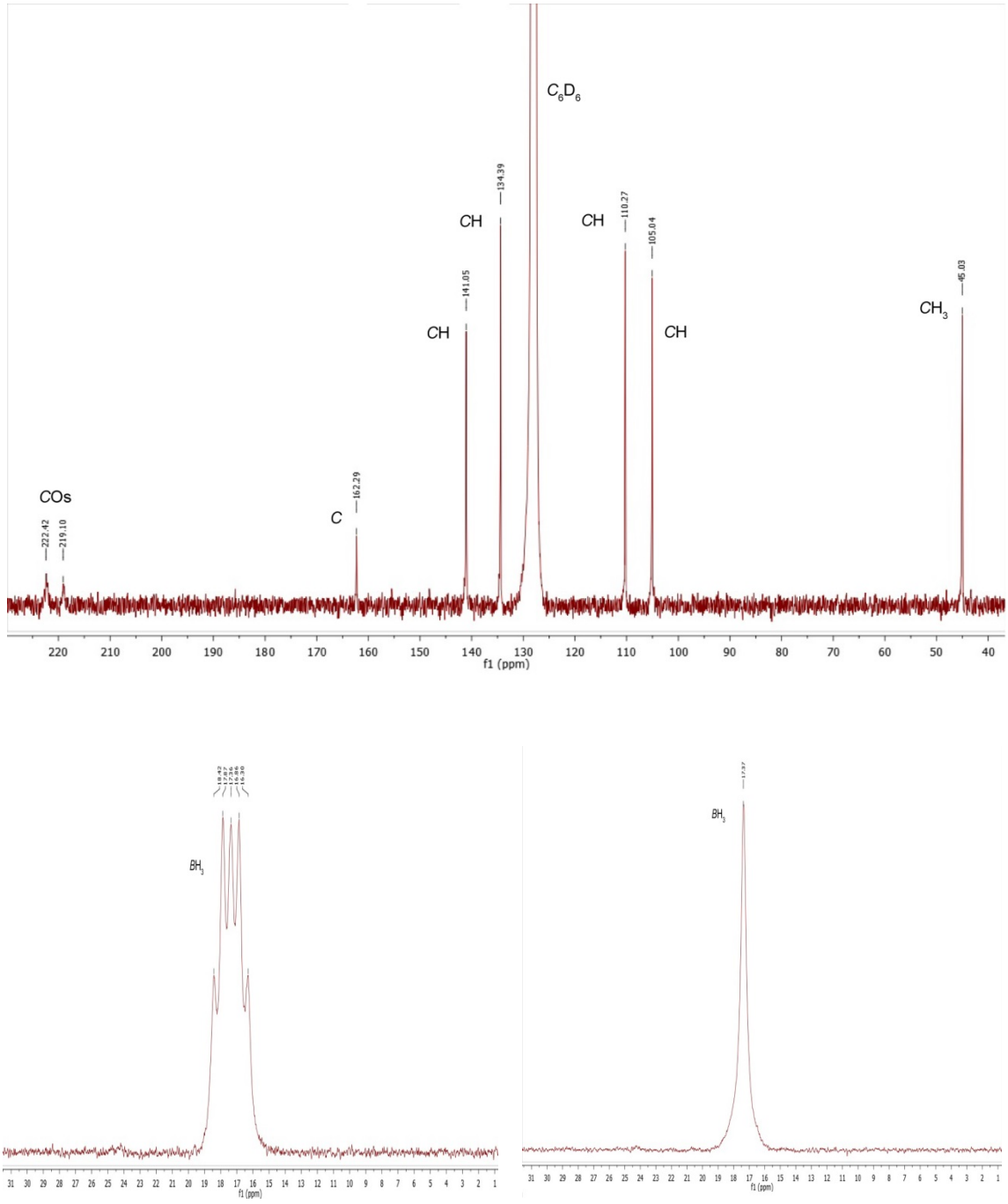

Figure S2. $^{13}C\{^{1}H\}$ (top, 100.62 MHz), ^{11}B (bottom left, 128.51 MHz), and $^{11}B\{^{1}H\}$ (bottom right, 128.51 MHz) NMR spectra ($[^{2}H_6]$-benzene, 298 K) of *fac*-[Mn(κ^3*N*,*H*,*H*-mapyBH$_3$)(CO)$_3$] (**1**).

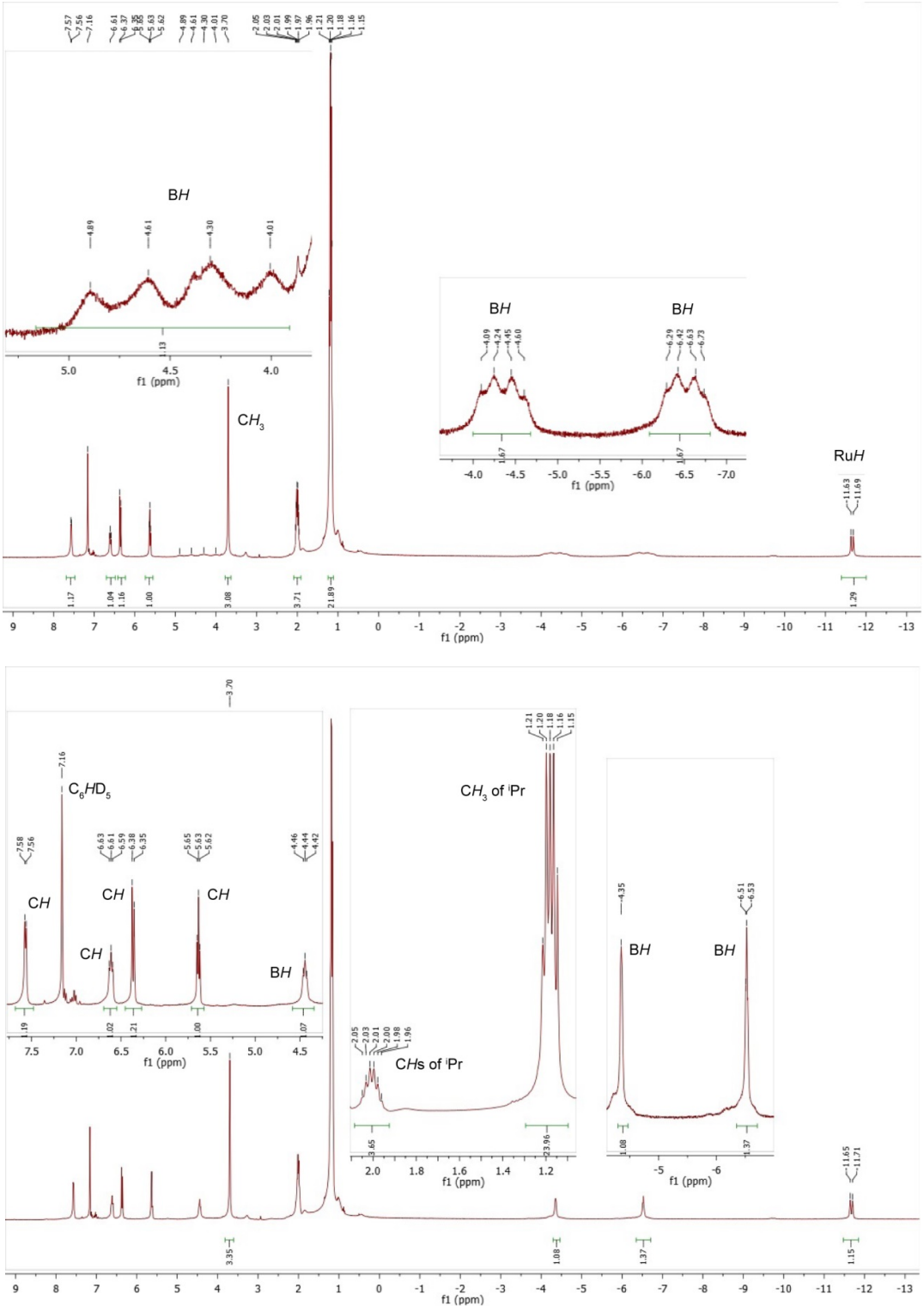

Figure S3. ^{1}H (top) and $^{1}H\{^{11}B\}$ (bottom) NMR spectra ([$^{2}H_6$]-benzene, 298 K, 400.54 MHz) of *fac*-[RuH(κ^3*N*,*H*,*H*-mapyBH$_3$)(CO)(P*i*Pr$_3$)] (**2**).

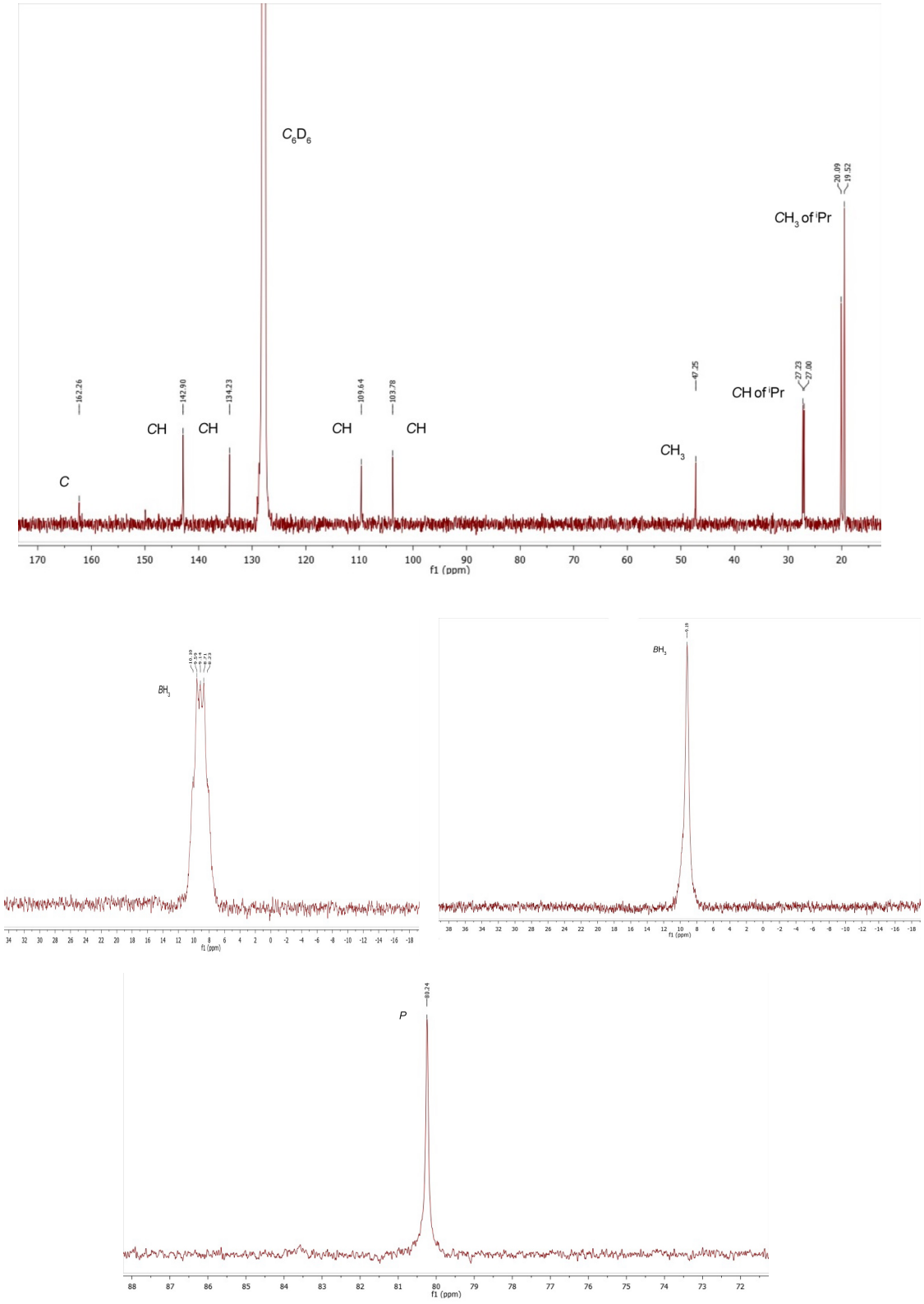

Figure S4. $^{13}C\{^{1}H\}$ (top, 100.72 MHz), ^{11}B (middle left, 128.51 MHz), $^{11}B\{^{1}H\}$ (middle right, 128.51 MHz), and $^{31}P\{^{1}H\}$ NMR spectra (bottom, 162.14 MHz) NMR spectra ([$^{2}H_6$]-benzene, 298 K) of *fac*-[RuH(κ^3*N*,*H*,*H*-mapyBH$_3$)(CO)(P*i*Pr$_3$)] (**2**).

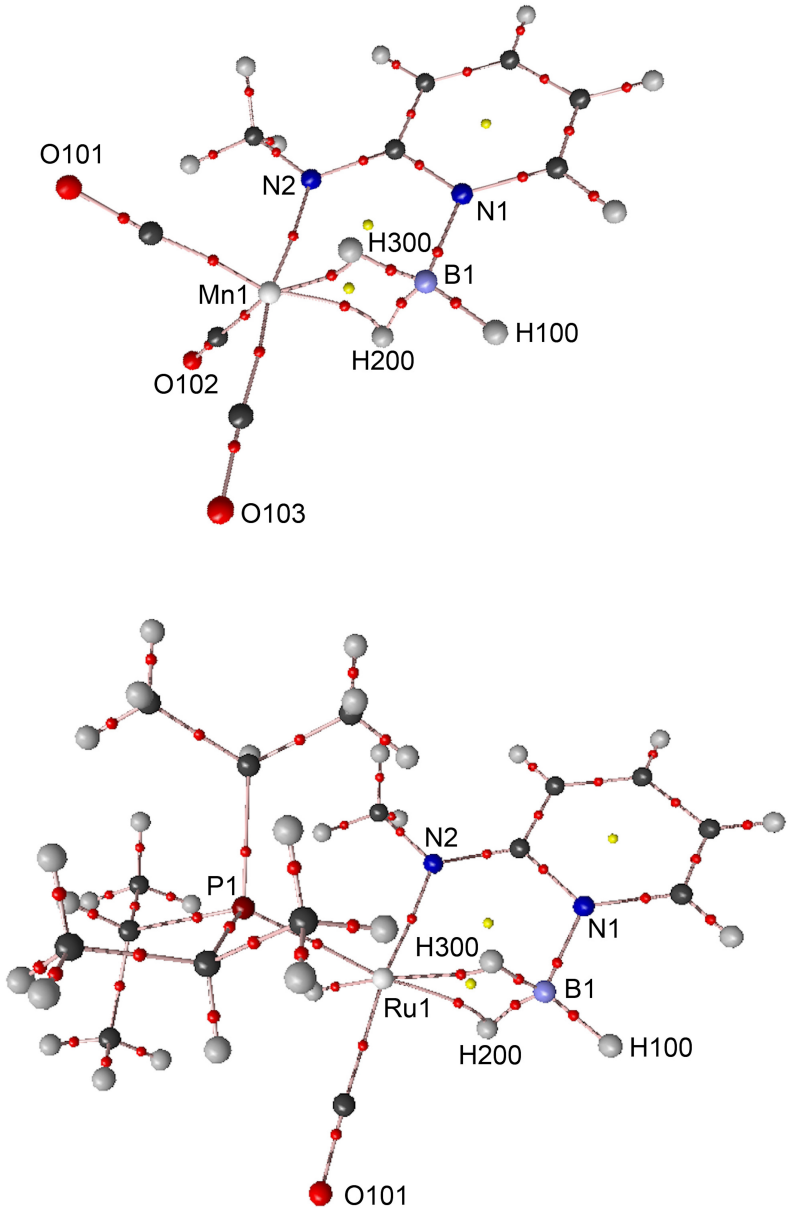

Figure S5. Perspective QTAIM images of *fac*-[Mn(κ^3*N,H,H*-mapyBH$_3$)(CO)$_3$] (**1**; top) and *fac*-[RuH(κ^3*N,H,H*-mapyBH$_3$)(CO)(P*i*Pr$_3$)] (**2**; bottom), showing the atoms (large circles), bond paths (beige lines), bond critical points (small red circles), and ring critical points (small yellow circles).

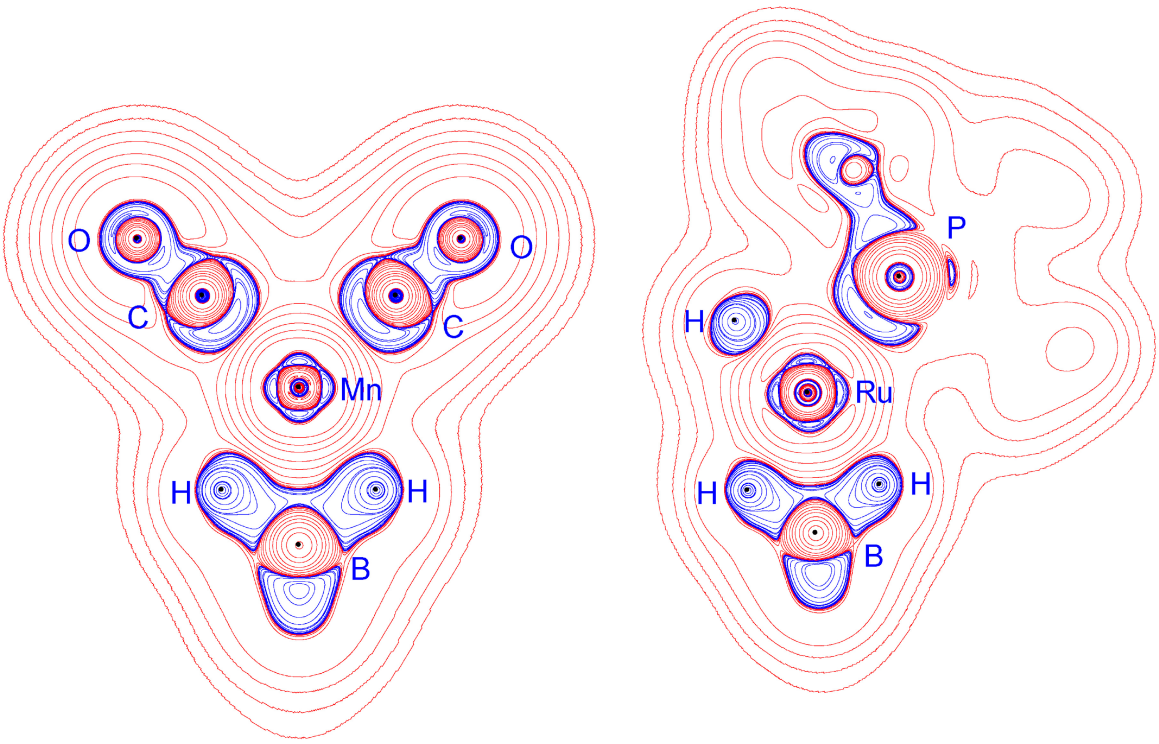

Figure S6. Laplacian of the electron density in the MH_2B planes of *fac*-[Mn(κ^3*N,H,H*-mapyBH_3)$(CO)_3$] (**1**; M = Mn; left) and *fac*-[RuH(κ^3*N,H,H*-mapyBH_3)(CO)(P*i*Pr_3)] (**2**; M = Ru; right). Contour levels at 0.0 and ± (1,2,4,8) x 10^n e Å^{-5}, with *n* ranging from +3 to –3). Blue and red lines represent negative and positive values, respectively.

Table S1. Crystal, Measurement, and Refinement Data for the Compounds Studied by X-Ray Diffraction

	1	**2**
formula	$C_9H_{10}BMnN_2O_3$	$C_{16}H_{32}BN_2OPRu$
fw	259.94	411.28
cryst syst	monoclinic	monoclinic
space group	*C*2/c	$P2_1/n$
a, Å	13.2584(3)	7.4628(2)
b, Å	12.7142(3)	15.8516(3)
c, Å	13.3824(3)	16.3342(3)
α, deg	90	90
β, deg	98.196(2)	92.340(2)
γ, deg	90	90
V, Å^3	2232.83(9)	1930.68(7)
Z	8	4
F(000)	1056	856
D_{calcd}, g cm^{-3}	1.547	1.415
μ, mm^{-1} (Cu Kα)	9.572	7.361
cryst size, mm	0.37 x 0.12 x 0.07	0.16 x 0.12 x 0.09
T, K	145(2)	151(2)
θ range, deg	4.84 to 69.73	3.89 to 69.54
min./max. *h*, *k*, *l*	–16/8, –15/11, –16/15	–7/9, –18/18, –14/19
no. collected reflns	4899	8817
no. unique reflns	2059	3556
no. reflns with $I > 2\sigma(I)$	1950	3401
no. params/restraints	158/0	222/0
GOF (on F^2)	1.077	1.041
R_1 (on *F*, $I > 2\sigma(I)$)	0.027	0.023
wR_2 (on F^2, all data)	0.077	0.056
min./max. $\Delta\rho$, e Å^{-3}	–0.393/0.257	–0.656/0.833
CCDC dep. no.	1524082	1524083

Table S2. QTAIM topological parameters of selected bonds of complexes **1** and **2**.

Bond[a]	Comp.[a]	d (Å)[b]	ρ_b (e Å^{-3})[c]	$\nabla^2\rho_b$ (e Å^{-5})[d]	H_b/ρ_b (h e^{-1})[e]	G_b/ρ_b (h e^{-1})[f]	ε_b[g]	δ(A–B)[h]
M1–H200	**1**	1.890	0.550	5.176	–0.296	0.956	1.267	0.408
	2	2.183	0.543	4.613	–0.270	0.864	8.889	0.437
M1–H300	**1**	1.880	0.551	5.275	–0.296	0.967	1.245	0.411
	2	2.040	0.557	4.962	–0.272	0.896	2.518	0.466
M1–H400	**2**	2.033	0.657	3.796	–0.365	0.770	0.088	0.946
M1–P1	**2**	2.322	0.598	8.861	–0.243	1.280	0.043	0.554
M1–N2	**1**	2.033	0.598	8.861	–0.243	1.280	0.043	0.554
	2	2.158	0.558	8.813	–0.172	1.277	0.065	0.570
M1–C[i]	**1**	1.811	0.980	13.917	–0.434	1.428	0.047	1.125
	2	1.856	1.116	14.107	–0.493	1.377	0.063	1.413
B1–H100	**1**	1.198	1.236	–9.271	–1.125	0.600	0.008	0.557
	2	1.202	1.217	–8.753	–1.119	0.616	0.023	0.553
B1–H200	**1**	1.315	0.920	–3.743	–0.952	0.668	0.252	0.389
	2	1.315	0.929	–4.444	–0.954	0.618	0.250	0.407
B1–H300	**1**	1.316	0.919	–3.728	–0.952	0.667	0.253	0.388
	2	1.329	0.898	–4.012	–0.938	0.624	0.293	0.395
B1–N1	**1**	1.508	1.125	7.594	-0.957	1.430	0.032	0.423
	2	1.527	1.072	7.459	-0.933	1.420	0.039	0.419

[a]M = Mn (**1**), Ru (**2**). [b]Bond path length. [c]Electron density at the bcp. [d]Laplacian of the electron density at the bcp. [e]Total energy density ratio at the bcp. [f]Kinetic energy density ratio at the bcp. [g]Ellipticity at the bcp. [h]Delocalization index. [i]Axial carbonyl ligand.

Table S3. Delocalization indexes, δ(A···B), of selected non-bonding A···B interactions in **1** and **2**.

Interaction[a]	M1···B1	M1···N1	B1···N2
1	0.160	0.060	0.024
2	0.191	0.059	0.018

[a]M = Mn (**1**), Ru (**2**).

Table S4. QTAIM (ZORA-B1PW91/QZ4P**)** atomic charges, *Q*(A) (*e*), for selected atoms of complexes **1** and **2**.

Complex	M[a]	H100	H200	H300[c]	B1	N1	N2
1	1.056	–0.586	–0.504	–0.500	1.823	–1.436	–1.173
2	0.603	–0.587	–0.514	–0.491	1.787	–1.404	–1.121

[a]M = Mn (**1**), Ru (**2**).

Table S5. Cartesian coordinates (B3P86/6-31G(d,p)) for complex **1**.

Atom	x	y	z
Mn	3.654038	0.653552	1.886013
N	0.833907	1.565806	1.562547
N	1.948132	-0.403110	1.935604
O	4.919795	-1.274728	0.072378
C	0.782847	0.200808	1.767344
O	5.940758	2.499999	1.753884
O	4.640773	-0.624289	4.336136
C	-1.631956	0.340226	1.588224
H	-2.606266	-0.138942	1.597592
B	2.213405	2.176435	1.559608
C	-0.508132	-0.415610	1.776937
H	-0.581505	-1.482919	1.934877
C	4.281499	-0.130492	3.356243
C	1.901326	-1.841475	2.151863
H	1.334995	-2.102528	3.055394
H	2.912889	-2.223498	2.276273
H	1.449663	-2.369863	1.302126
C	4.448267	-0.519331	0.807320
C	-1.537818	1.735940	1.381564
H	-2.415841	2.350336	1.230486
C	5.051164	1.767298	1.807487
C	-0.294694	2.298836	1.376999
H	-0.125221	3.358364	1.226523
H	2.224042	3.358178	1.380113
H	2.785090	1.895507	2.684008
H	2.917940	1.585600	0.651557

Table S6. Cartesian coordinates (B3P86/6-31G(d,p)/LanL2DZ) for complex **2**.

Atom	x	y	z
Ru	0.205856	-0.963623	-0.408343
P	-1.663510	0.335299	0.076222
N	1.637039	0.583172	-0.803527
O	-1.440873	-3.483106	-0.251448
N	3.157431	-0.669663	0.399552
C	-1.251020	2.106604	0.542683
H	-0.806192	2.474436	-0.388385
C	4.390391	-0.866291	0.924143
H	4.503279	-1.795742	1.468493
C	-2.688557	-0.441451	1.452650
H	-2.788013	-1.470623	1.088286
C	-0.832872	-2.496160	-0.279384
C	2.864323	0.469691	-0.326504
C	-0.166886	2.208225	1.616805
H	0.210772	3.235243	1.658828
H	0.671447	1.542793	1.405542
H	-0.556529	1.964069	2.607449
C	5.155152	1.200786	0.037388
H	5.939926	1.936999	-0.103302
C	1.391670	1.714455	-1.676463
H	1.463651	2.676131	-1.147458
H	0.393219	1.628101	-2.097185
H	2.097683	1.742322	-2.516658
C	-3.463532	-0.812729	-1.749082
H	-4.235742	-0.666078	-2.510931
H	-3.906438	-1.398662	-0.939987
H	-2.659397	-1.405785	-2.192319
C	-2.934690	0.542884	-1.283323
H	-3.765806	1.109679	-0.848258
B	2.057895	-1.715065	0.556168
C	3.920898	1.419499	-0.506841
H	3.725658	2.320987	-1.070443
C	-2.429896	3.019237	0.878629
H	-2.848238	2.786556	1.860843
H	-3.236711	2.966761	0.143733
H	-2.085962	4.058393	0.914031
C	5.412453	0.028080	0.778057
H	6.380215	-0.172353	1.217498
C	-1.929640	-0.515474	2.778135
H	-1.916592	0.453692	3.284132
H	-0.898030	-0.848454	2.641725
H	-2.426845	-1.225023	3.446758
C	-2.394177	1.329050	-2.474047
H	-1.546882	0.805760	-2.927098
H	-2.077030	2.340407	-2.205768
H	-3.173211	1.423600	-3.237290
C	-4.101458	0.098898	1.672684
H	-4.614292	-0.533938	2.404686
H	-4.705336	0.093982	0.762742
H	-4.096979	1.115500	2.070840
H	1.079997	-1.214476	1.238546
H	-0.313057	-0.817072	-1.903272
H	1.655138	-2.036969	-0.654837
H	2.454524	-2.706533	1.098199

Table S7. Cartesian coordinates (PW91-ZORA/QZ4P) for complex **1**.

Atom	x	y	z
Mn	3.647743	0.633927	1.880699
N	0.819768	1.571792	1.558802
N	1.921318	-0.413386	1.962035
O	4.945756	-1.289856	0.054986
C	0.755527	0.201206	1.787946
O	5.980357	2.453952	1.725533
O	4.758100	-0.611509	4.317999
C	-1.665939	0.351943	1.611542
H	-2.647070	-0.122153	1.632071
B	2.201484	2.176663	1.546433
C	-0.541198	-0.407426	1.814277
H	-0.620595	-1.475249	1.994394
C	4.323527	-0.135356	3.348137
C	1.875174	-1.853311	2.210379
H	1.308322	-2.087997	3.123354
H	2.890508	-2.229096	2.340171
H	1.417580	-2.395327	1.369147
C	4.443500	-0.540788	0.791758
C	-1.561089	1.744861	1.374275
H	-2.438025	2.363851	1.209424
C	5.063554	1.739719	1.783600
C	-0.312728	2.306964	1.358430
H	-0.139663	3.365691	1.188331
H	2.217924	3.358668	1.353605
H	2.785068	1.895829	2.677975
H	2.909247	1.565728	0.637301

Table S8. Cartesian coordinates (PW91-ZORA/QZ4P) for complex **2**.

Atom	x	y	z
Ru	3.319653	2.410399	1.988133
P	3.837549	3.430393	-0.031109
N	1.202798	2.803827	2.041685
O	6.245739	1.852569	2.523309
N	0.923671	0.577299	2.637527
C	2.314047	3.669797	-1.133355
H	1.650680	4.217967	-0.448433
C	0.138039	-0.499335	2.920436
H	0.688394	-1.409970	3.140134
C	5.166807	2.448227	-0.959099
H	6.002813	2.529257	-0.245669
C	5.116245	2.062927	2.277891
C	0.359394	1.813157	2.330117
C	1.615147	2.343052	-1.467047
H	0.612776	2.545750	-1.872190
H	1.501751	1.707190	-0.582163
H	2.166490	1.779959	-2.231067
C	-1.843041	0.803657	2.638964
H	-2.929771	0.890007	2.635866
C	0.601784	4.125516	1.887992
H	-0.078848	4.181259	1.021459
H	1.394687	4.860063	1.753639
H	0.025754	4.414834	2.781512
C	5.910380	5.170238	0.808614
H	6.313362	6.192400	0.836662
H	6.676362	4.525238	0.361709
H	5.746937	4.841486	1.842336
C	4.591848	5.157155	0.022979
H	4.799881	5.430085	-1.022457
B	2.446780	0.475028	2.654226
C	-1.073319	1.905867	2.358025
H	-1.543663	2.858378	2.133749
C	2.482067	4.532957	-2.393080
H	3.091613	4.034888	-3.156420
H	2.929723	5.512485	-2.185940
H	1.491127	4.714419	-2.836786
C	-1.231881	-0.440449	2.927652
H	-1.814328	-1.328355	3.154694
C	4.841921	0.952657	-1.085249
H	4.069456	0.766492	-1.842346
H	4.498508	0.532469	-0.134344
H	5.745461	0.407759	-1.394767
C	3.616945	6.185340	0.611943
H	3.385801	5.933650	1.656356
H	2.675223	6.250875	0.052623
H	4.077363	7.183260	0.601718
C	5.639499	3.017314	-2.303995
H	6.543378	2.480080	-2.625892
H	5.892852	4.083672	-2.257074
H	4.885724	2.877415	-3.089477
H	2.899071	0.684342	1.447687
H	3.560840	3.879476	2.600322
H	2.908558	1.399181	3.471894
H	2.824856	-0.600523	3.033700