Supplementary Information for

Reactions of Cerium Complexes with Transition Metal Nitrides: Synthesis and Structure of Heterometallic Cerium Complexes Containing Bridging Catecholate Ligands

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Table S1. Crystallographic data and experimental details for **4**, **6** and **9**.

	4	**6**	**9**
Formula	$C_{53}H_{111}CeCl_2Co_3NO_{29}P_9Ru$	$C_{46}H_{78}CeCo_2NO_{22}P_6Ru$	$C_{46}H_{82}CeCo_2O_{26}P_6Re$
Formula weight	1994.03	1541.96	1681.11
Crystal system	Triclinic	monoclinic	Monoclinic
Space group	P-1	C2/c	$P2_1/c$
a, Å	15.0838(5)	22.9360(3)	11.86004(14)
b, Å	17.4193(7)	13.2047(2)	22.5385(3)
c, Å	17.9226(7)	40.2851(7)	24.0165(2)
α, deg	114.874(4)	90	90
β, deg	92.656(3)	93.4905(16)	99.3323(10)
γ, deg	103.838(3)	90	90
V, Å^3	4089.1(3)	12178.2(3)	6334.81(12)
Z	2	8	4
ρ_{calc}, g cm^{-3}	1.620	1.682	1.763
T, K	100.00(10)	100.01(10)	100.15
μ, mm^{-1}	13.236	13.948	15.222
F(000)	2040.0	6264.0	3372.0
Total reflections	23782	33582	35347
Independent reflections	14549	10936	11375
R_{int}	0.0430	0.0611	0.0430
GoF[a]	1.021	1.017	1.0036
R_1,[b] wR_2[c] [$I > 2\sigma(I)$]	0.0394, 0.0886	0.0582, 0.1340	0.0367, 0.0902
R_1, wR_2 (all data)	0.0535, 0.0937	0.0718, 0.1421	0.0450, 0.0943

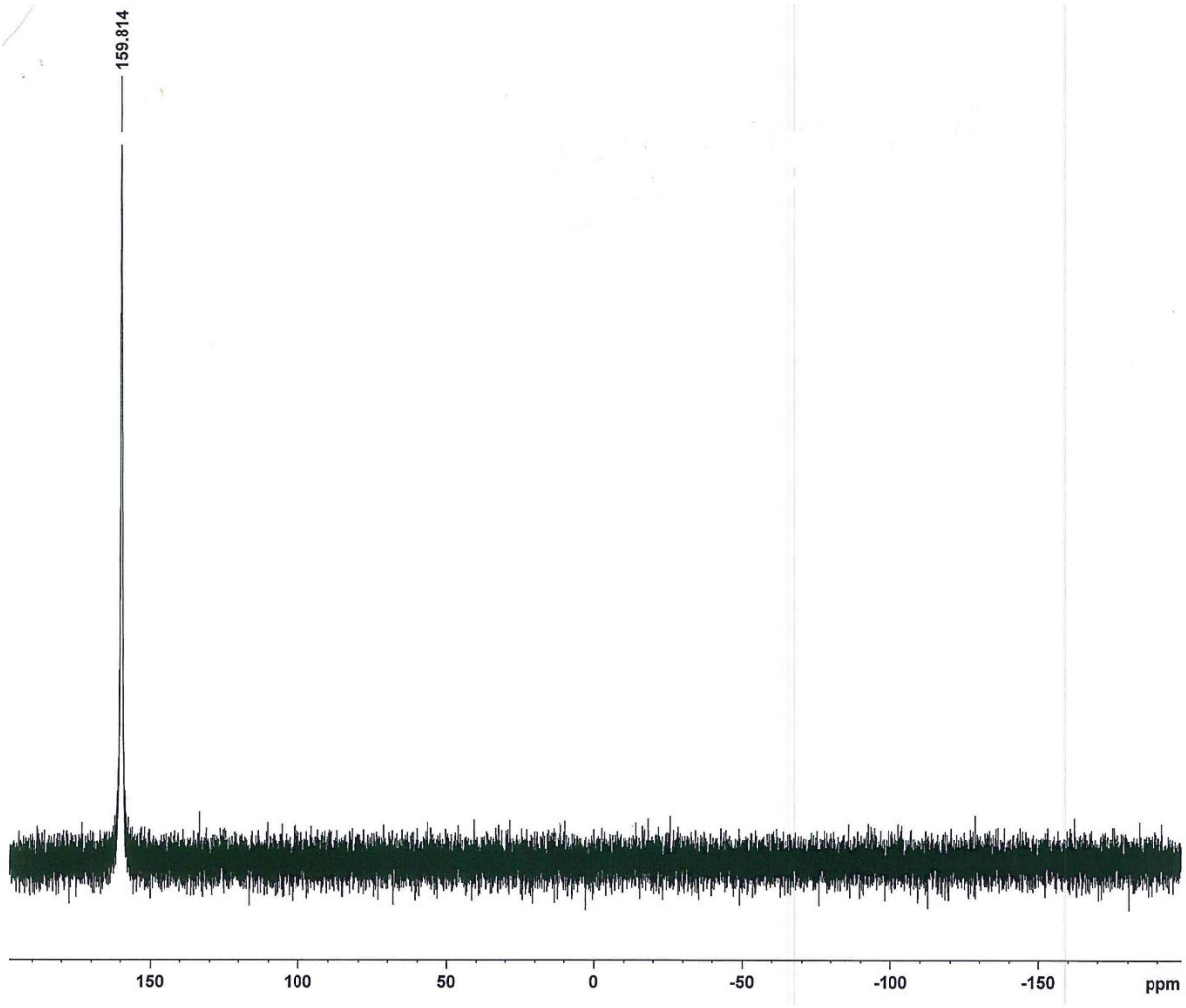

Figure S1. $^{31}P\{^{1}H\}$ NMR (162 MHz, 298 K, CD_3CN) spectrum of $[(L_{OEt})_2(H_2O)Ce^{III}\{\mu\text{-}O,N\text{-}MeC(O)NH\}Ru^{III}(L_{OEt})Cl_2]$ (**4**).

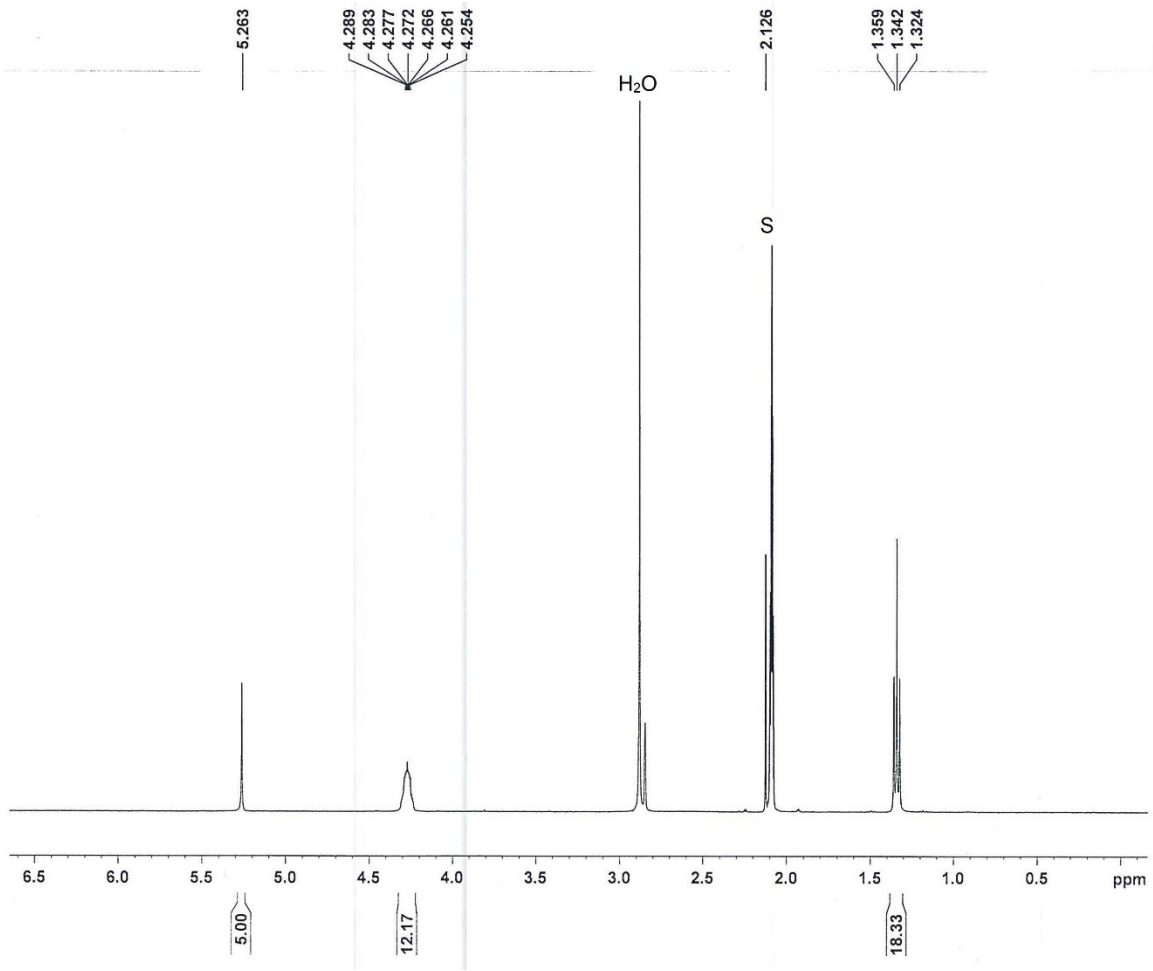

Figure S2. ^{1}H NMR (400 MHz, 298 K, acetone-d_6) spectrum of $[Ce(L_{OEt})_2(H_2O)\{Mn(N)(CN)_4\}]$ (**5**) (S = residual solvent).

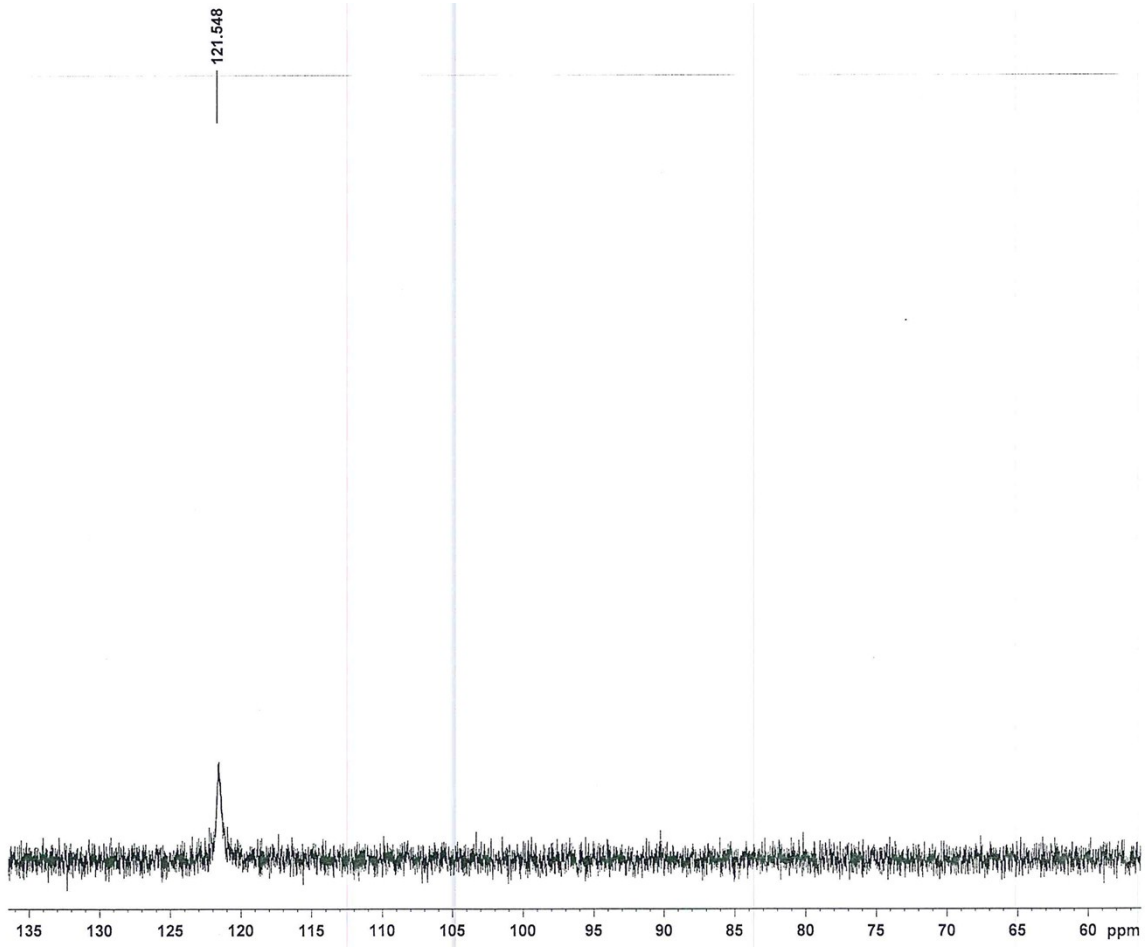

Figure S3. $^{31}P\{^{1}H\}$ NMR (162 MHz, 298 K, acetone-d_6) spectrum of $[Ce(L_{OEt})_2(H_2O)\{Mn(N)(CN)_4\}]$ (**5**).

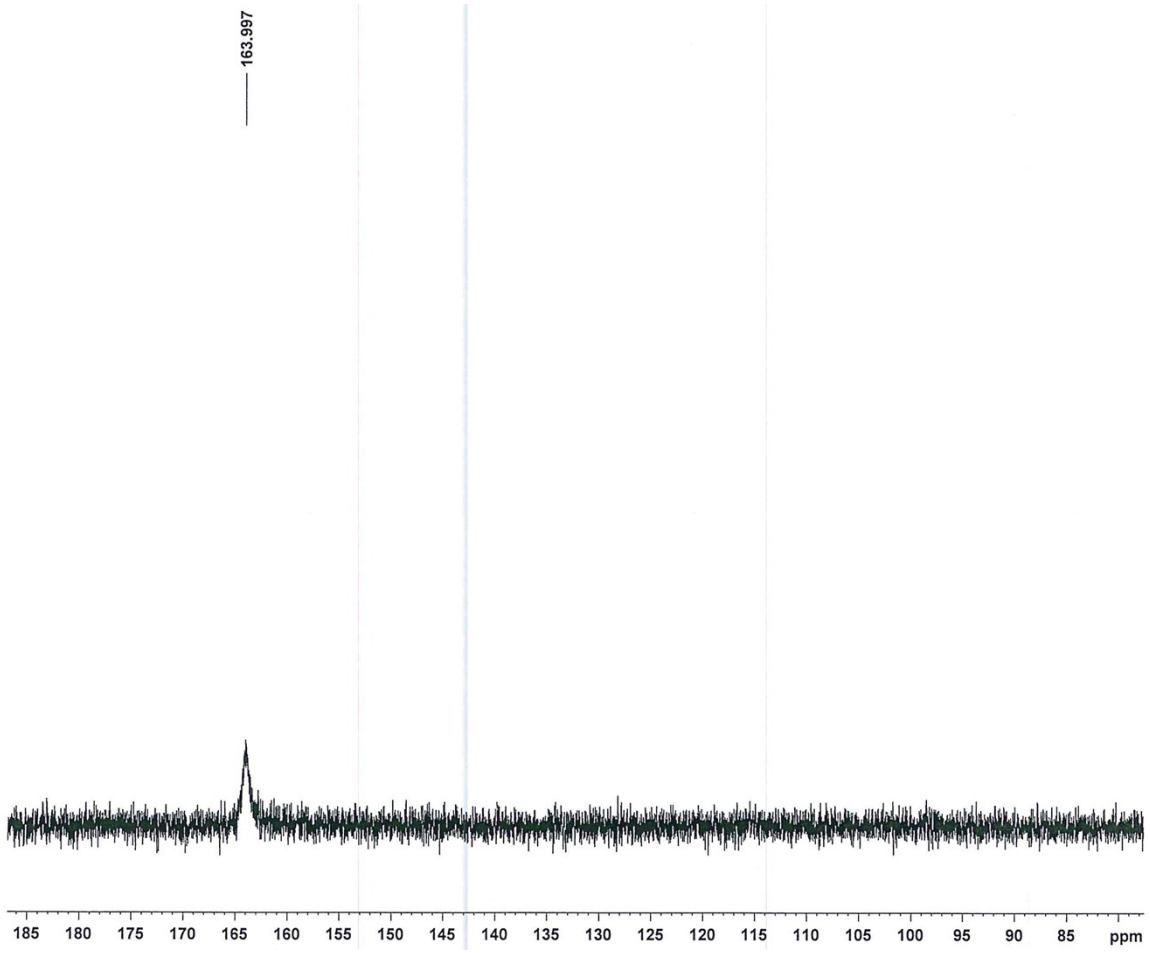

Figure S4. $^{31}P\{^{1}H\}$ NMR (162 MHz, 298 K, acetone-d_6) spectrum of $[(L_{OEt})_2Ce^{III}\{(\mu\text{-cat})_2Ru^{VI}(N)\}]$ (**6**).

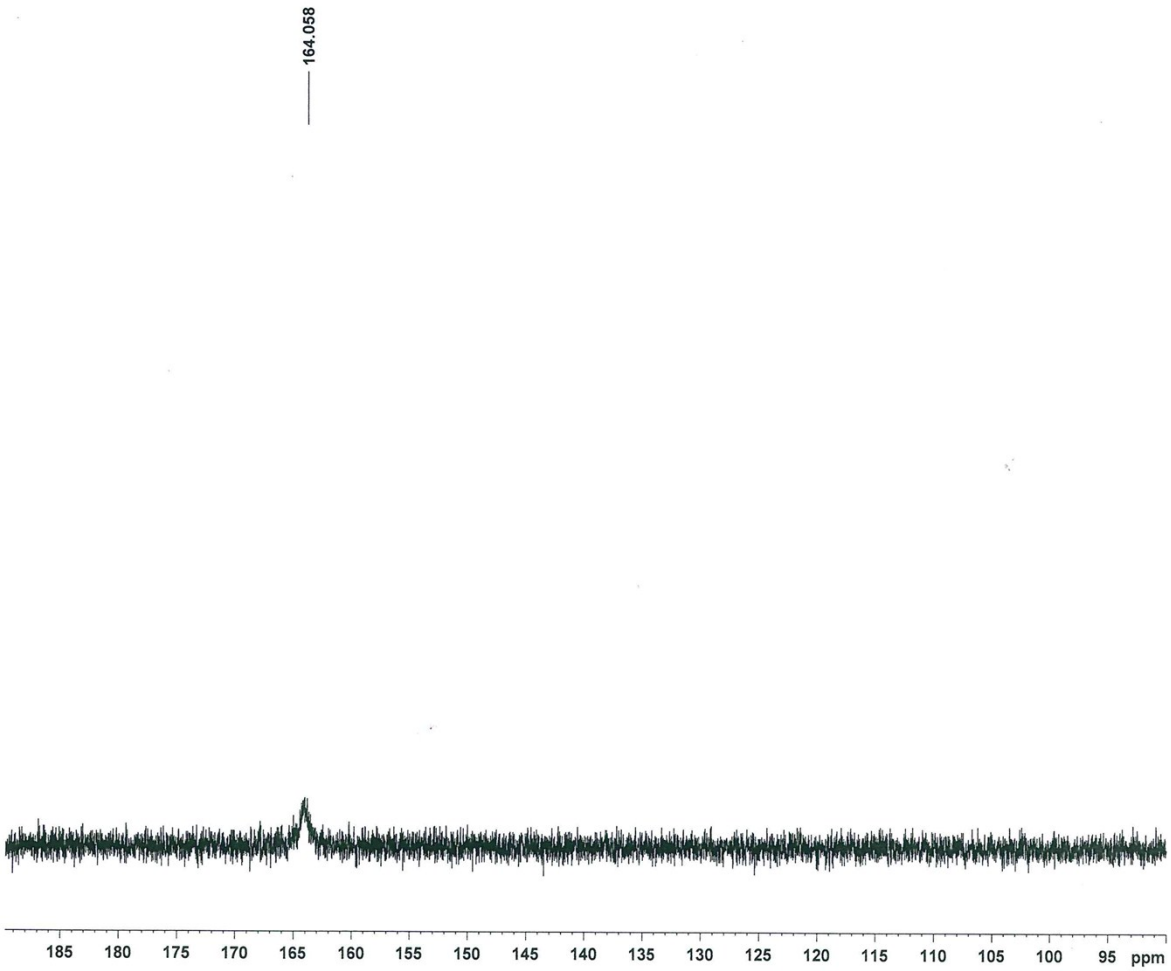

Figure S5. $^{31}P\{^{1}H\}$ NMR (162 MHz, 298 K, acetone-d_6) spectrum of $[(L_{OEt})_2Ce^{III}\{(\mu\text{-cat})_2Os^{VI}(N)\}]$ (**7**).

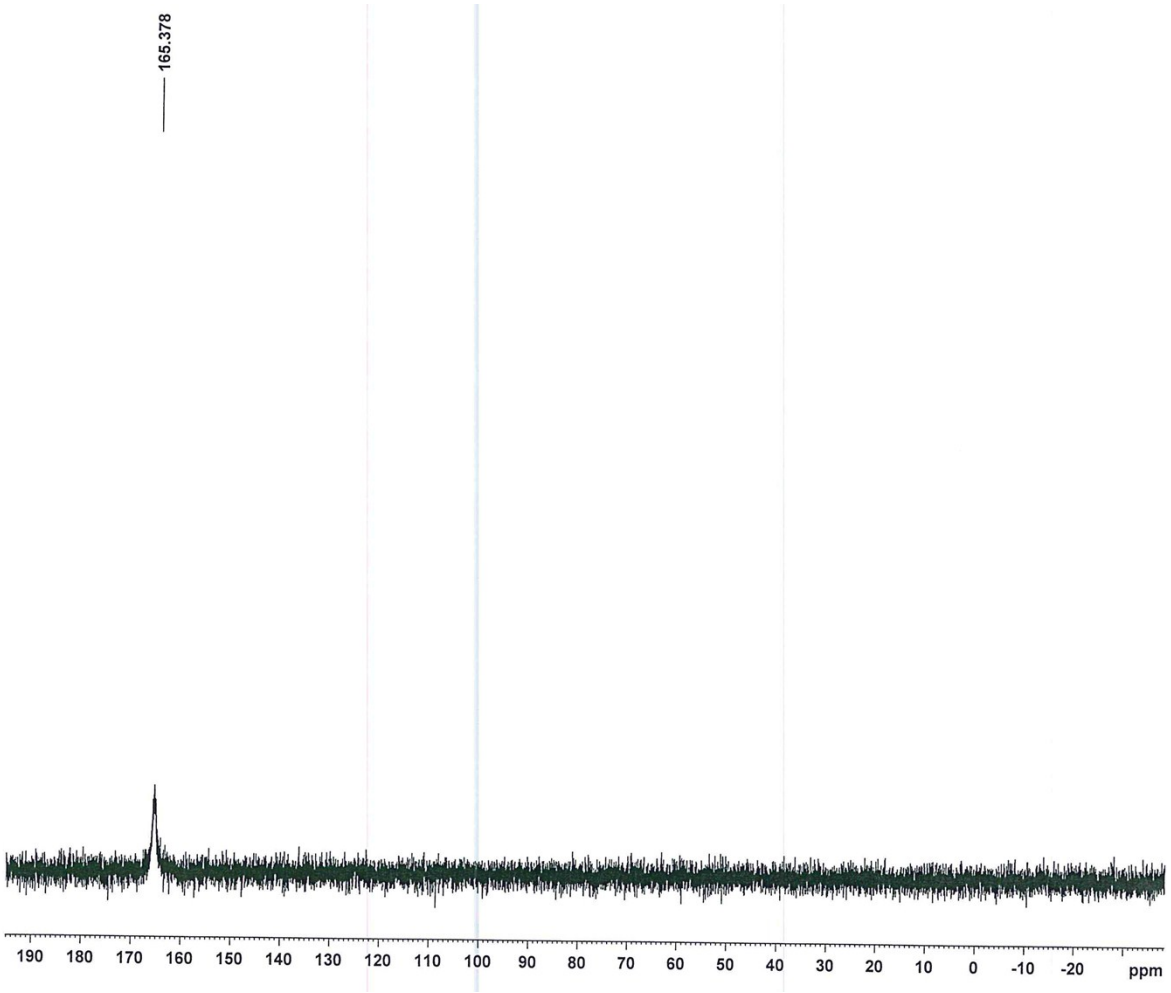

Figure S6. $^{31}P\{^{1}H\}$ NMR (162 MHz, 298 K, $CDCl_3$) spectrum of $[(L_{OEt})_2Ce^{III}\{(\mu\text{-cat})_2Re^{V}(O)\}]$ (**8**).

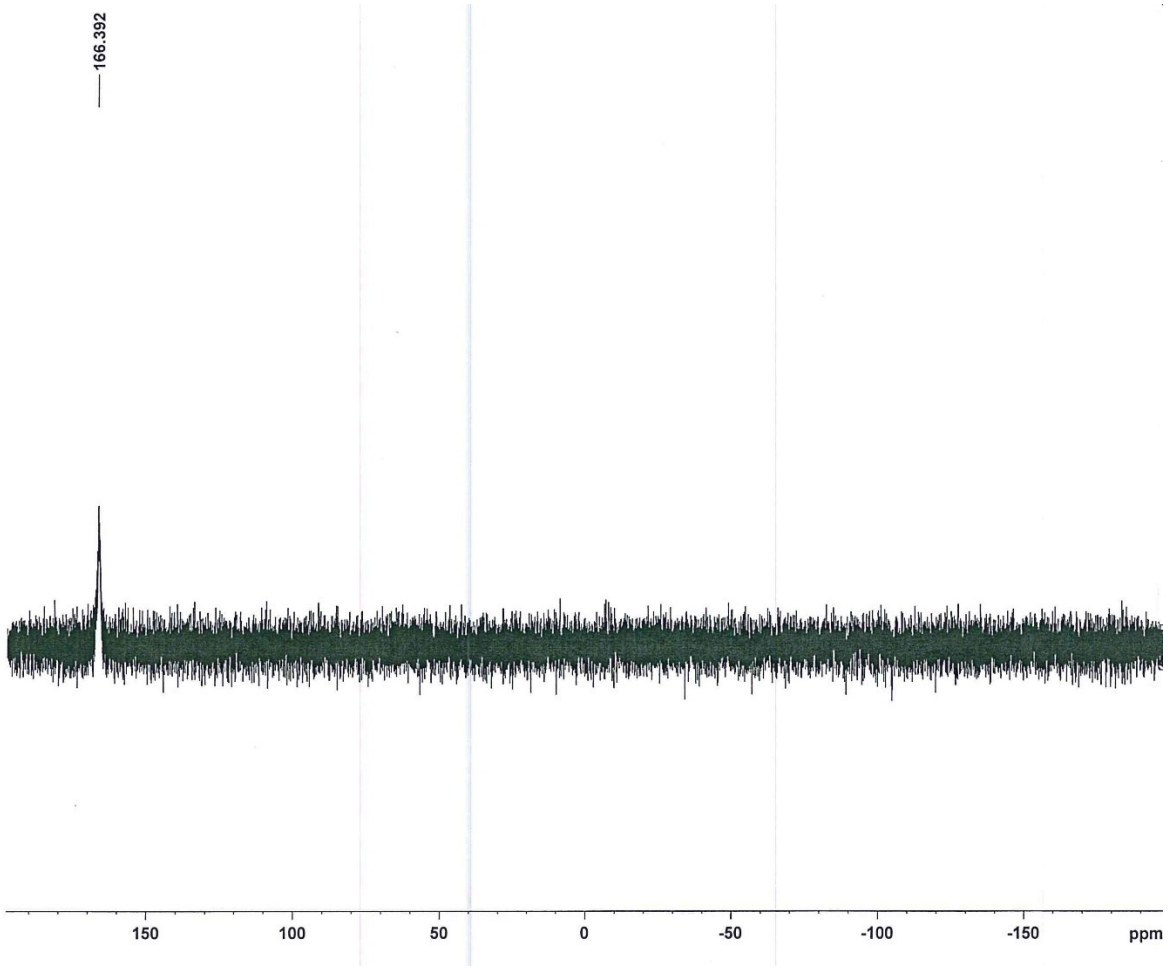

Figure S7. $^{31}P\{^{1}H\}$ NMR (162 MHz, 298 K, $CDCl_3$) spectrum of $[Ce^{III}(L_{OEt})_2(H_2O)_2][cis\text{-}\{Re^{VII}(O)_2(cat)_2\}]$ (**9**).

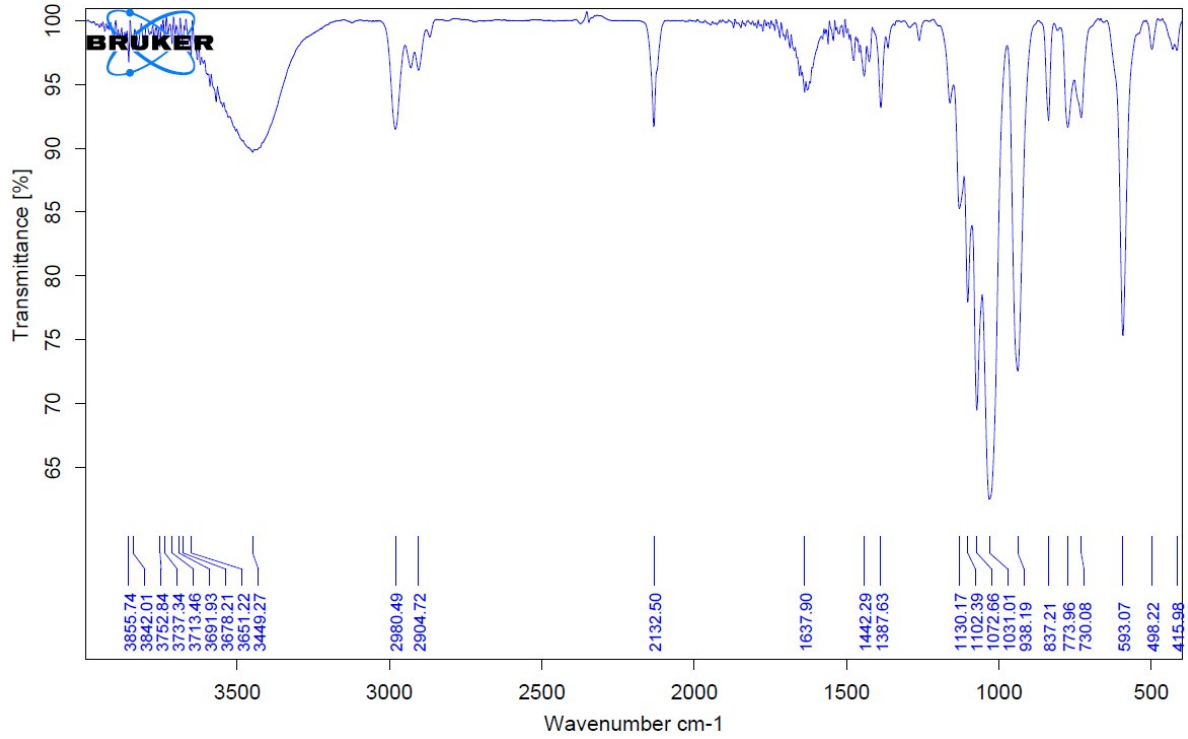

Figure S8. FT-IR spectrum of $[Ce(L_{OEt})_2(H_2O)\{Mn(N)(CN)_4\}]$ (**5**).

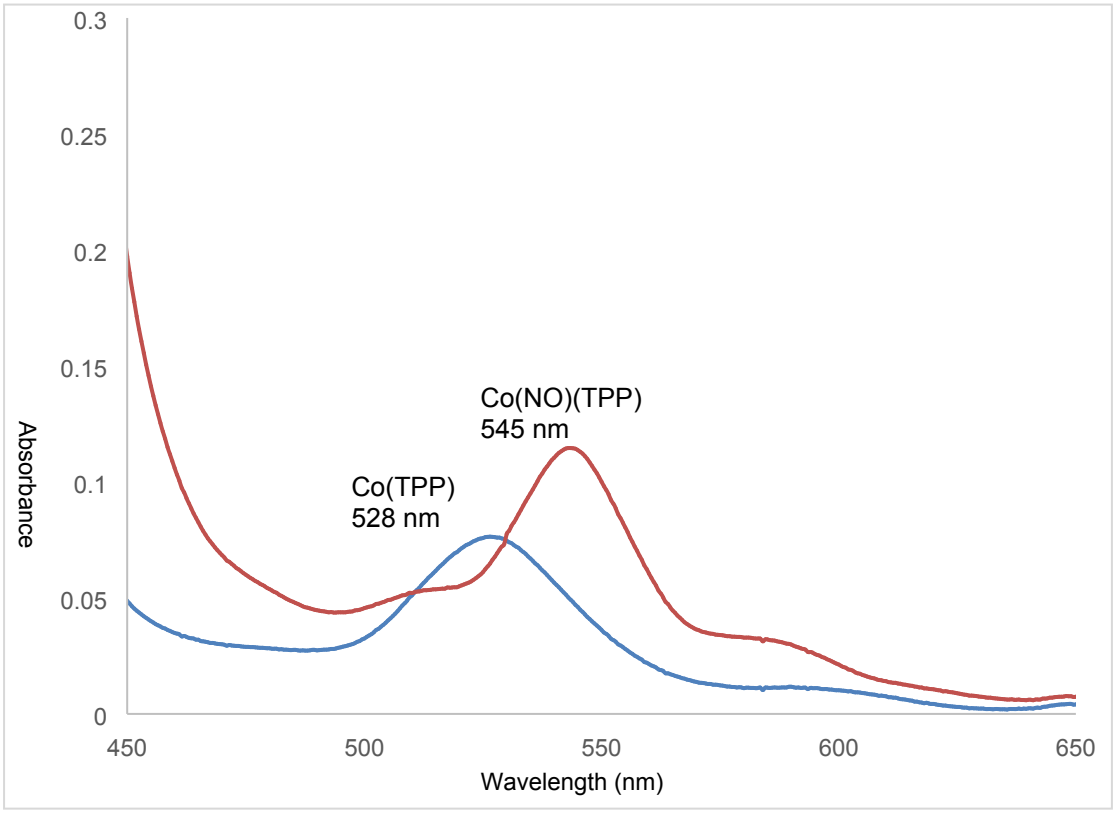

Fig. S9. UV-visible spectra (450-700 nm region) of [Co(TPP)] (0.059 mM in THF, blue) and [Co(NO)(TPP)] species that was generated upon reacting [Co(TPP)] with NO released from the reaction of **1** (10 mg, 0.076 mmol) with **2** (5.5 mg, 0.076 mmol) in tetrahydrofuran at room temperature.

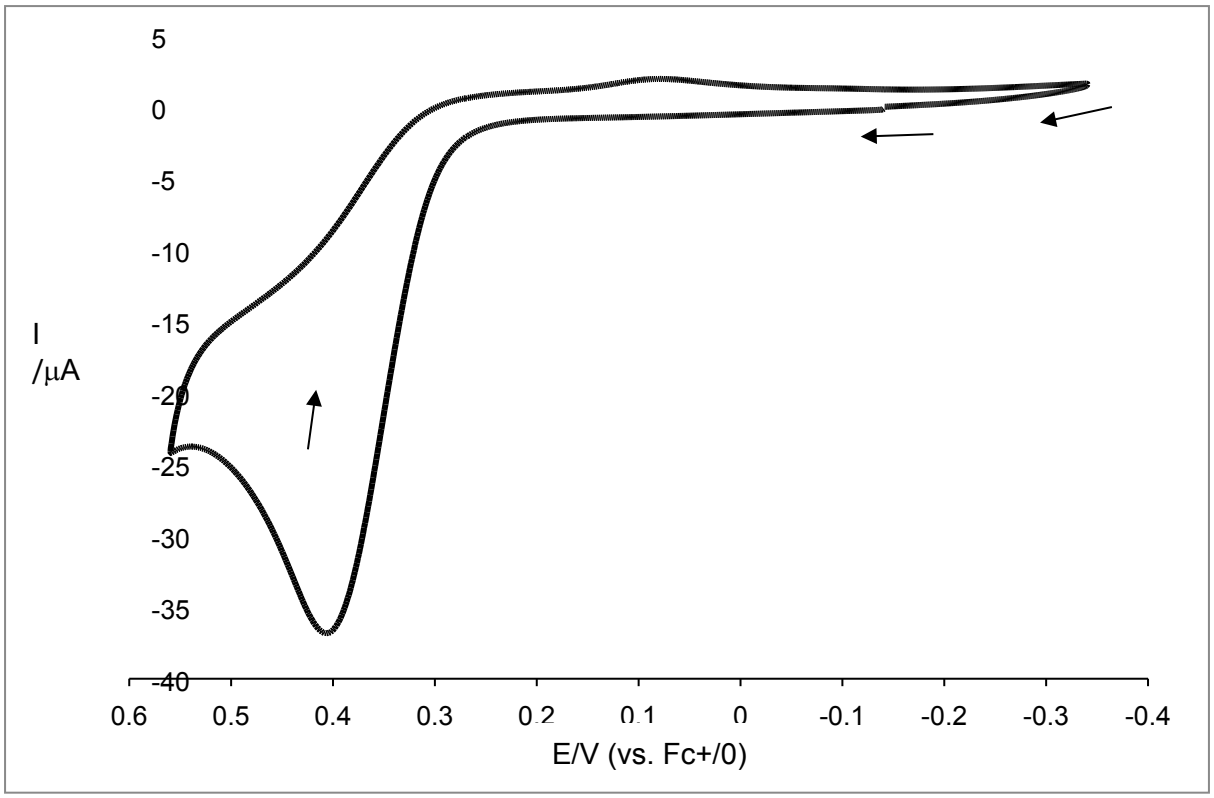

Figure S10. CV of [$^{n}Bu_4N$][Ru(N)(cat)$_2$]; measured at a glassy carbon electrode in CH_2Cl_2, supporting electrolyte: 0.2 M of [$^{n}Bu_4N$][PF_6], scan rate = 100 mVs^{-1}.

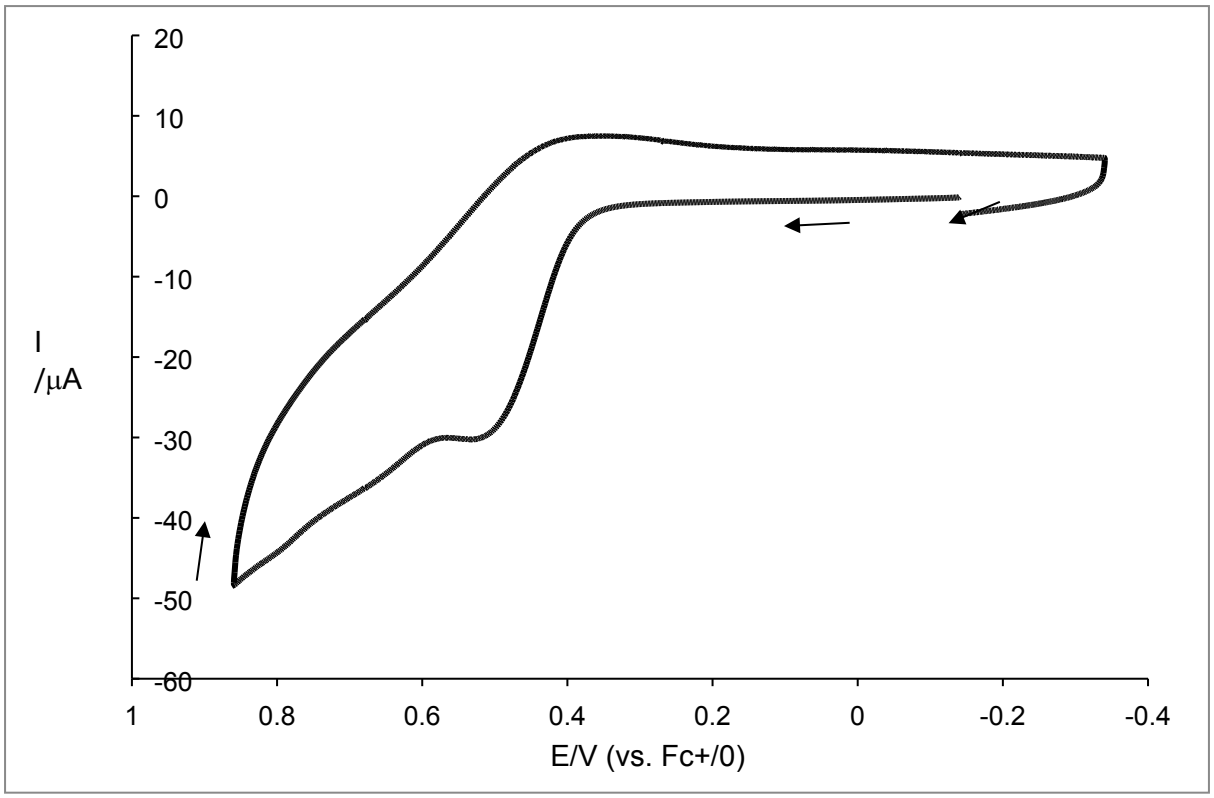

Figure S11. CV of $[^{n}Bu_4N][Os(N)(cat)_2]$; measured at a glassy carbon electrode in CH_2Cl_2, supporting electrolyte: 0.2 M of $[^{n}Bu_4N][PF_6]$, scan rate = 100 mVs^{-1}.