Supporting Information for

Synthesis, molecular structure and fluxional behavior of the elusive $[HRu_4(CO)_{12}]^{3-}$ carbonyl anion

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Table S1. Structurally characterized hydridocarbonylates of Fe, Ru and Os.

Nuclearity	Fe	Ref	Ru	Ref	Os	Ref
1	$[HFe(CO)_4]^-$	1				
2	$[HFe_2(CO)_8]^-$	2				
3	$[HFe_3(CO)_{11}]^-$	3	$[HRu_3(CO)_{11}]^-$	7	$[HOs_3(CO)_{11}]^-$	19
					$H_2Os_3(CO)_{11}$	20
					$H_2Os_3(CO)_{10}$	21
4	$[HFe_4(CO)_{13}]^-$	4	$[HRu_4(CO)_{13}]^-$	8	$[HOs_4(CO)_{13}]^-$	22
			$H_2Ru_4(CO)_{13}$	9	$H_2Os_4(CO)_{13}$	19
	$[HFe_4(CO)_{12}]^{3-}$	5	$[HRu_4(CO)_{12}]^{3-}$	This work		
	$[H_2Fe_4(CO)_{12}]^{2-}$	6	$[H_2Ru_4(CO)_{12}]^{2-}$	10	$[H_2Os_4(CO)_{12}]^{2-}$	23
			$[H_3Ru_4(CO)_{12}]^-$	11	$[H_3Os_4(CO)_{12}]^-$	11
			$H_4Ru_4(CO)_{12}$	12	$H_4Os_4(CO)_{12}$	24
5					$H_2Os_5(CO)_{16}$	25
					$[HOs_5(CO)_{15}]^-$	26
	$[HFe_5(CO)_{14}]^{3-}$	6				
6					$H_2Os_6(CO)_{19}$	27
			$[HRu_6(CO)_{18}]^-$	13	$[HOs_6(CO)_{18}]^-$	28
			$H_2Ru_6(CO)_{18}$	14	$H_2Os_6(CO)_{18}$	28
			$H_2Ru_6(CO)_{17}$	15		
7					$H_2Os_7(CO)_{22}$	29
					$H_2Os_7(CO)_{21}$	29
			$[HRu_7(CO)_{20}]^-$	16		
					$H_2Os_7(CO)_{20}$	30
8					$[HOs_8(CO)_{22}]^-$	31
			$[H_2Ru_8(CO)_{21}]^{2-}$	17		
9					$[HOs_9(CO)_{24}]^-$	32
10			$[H_2Ru_{10}(CO)_{25}]^{2-}$	18		
					$[H_4Os_{10}(CO)_{24}]^{2-}$	33
					$[H_5Os_{10}(CO)_{24}]^-$	34
11			$[HRu_{11}(CO)_{27}]^{3-}$	18		

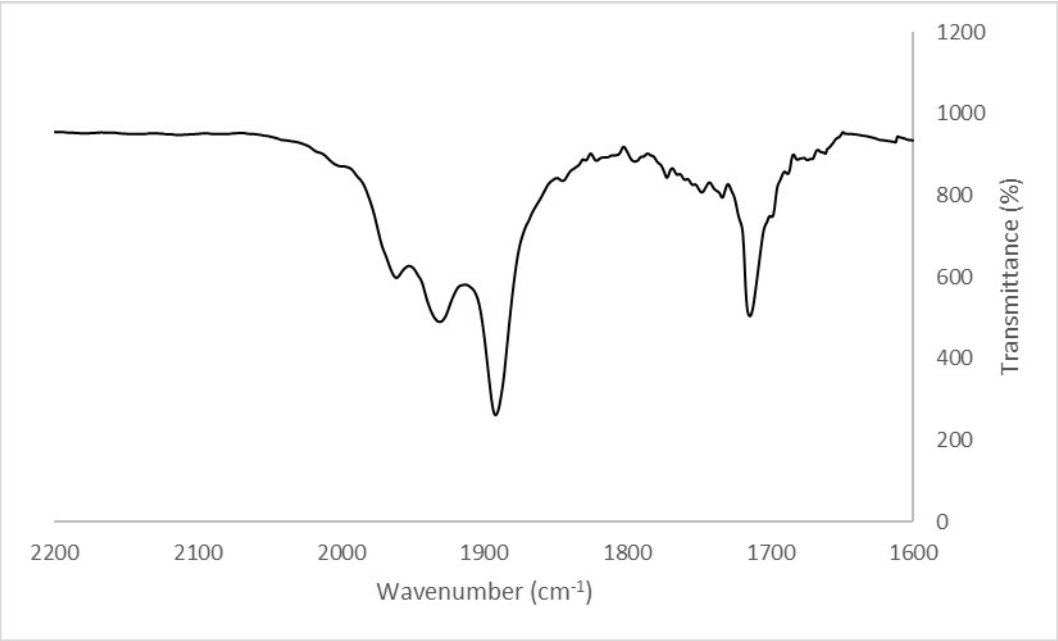

Figure S1. IR spectrum in the ν_{CO} region of $[NEt_4]_3[HRu_4(CO)_{12}]$ in CH_3CN.

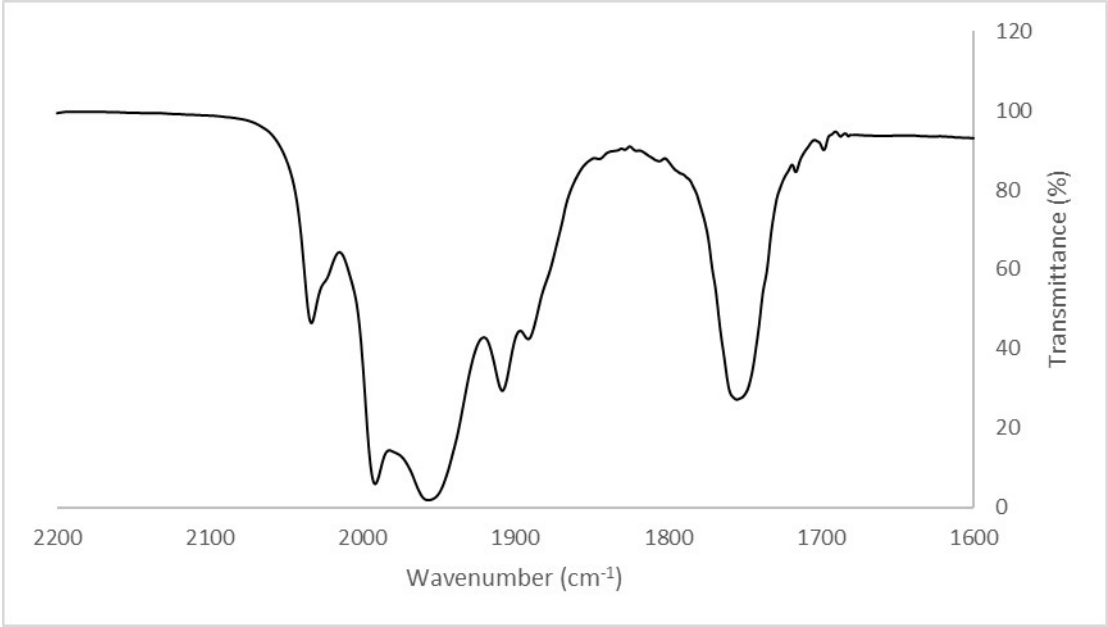

Figure S2. IR spectrum in the ν_{CO} region of $[NEt_4]_2[H_2Ru_4(CO)_{12}]$ in CH_3CN.

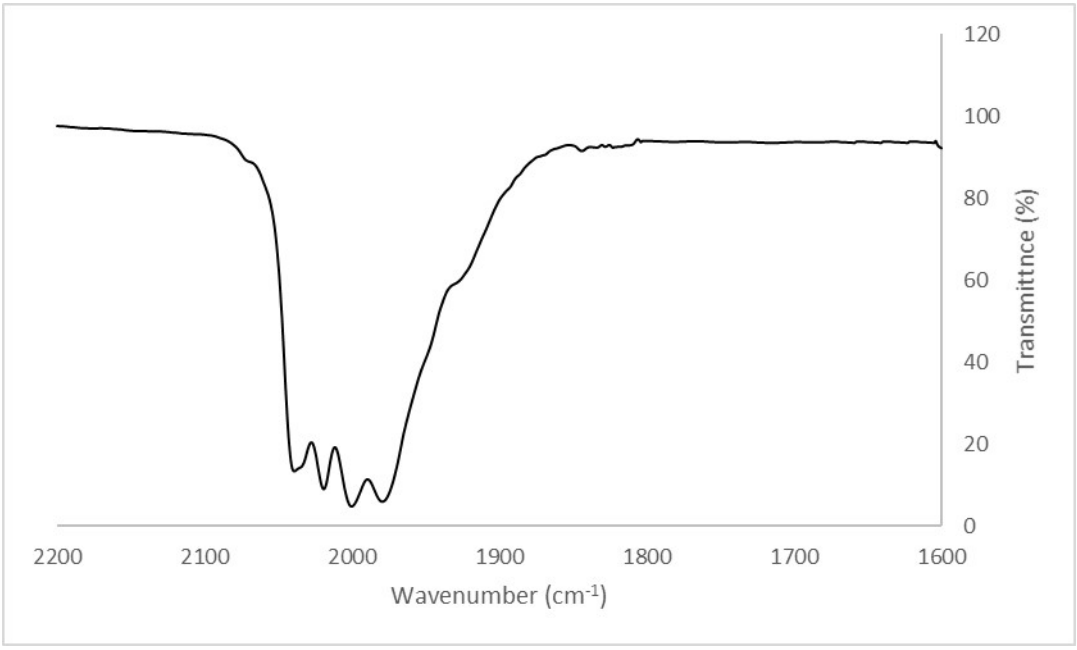

Figure S3. IR spectrum in the ν_{CO} region of $[NEt_4][H_3Ru_4(CO)_{12}]$ in CH_3CN.

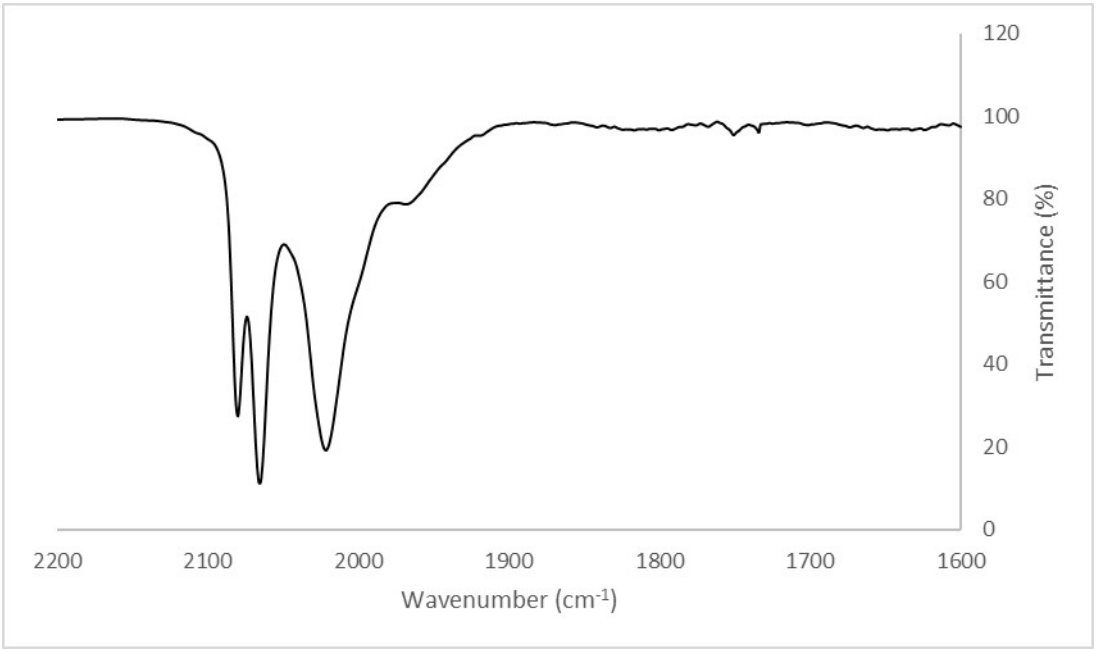

Figure S4. IR spectrum in the ν_{CO} region of $H_4Ru_4(CO)_{12}$ in CH_2Cl_2.

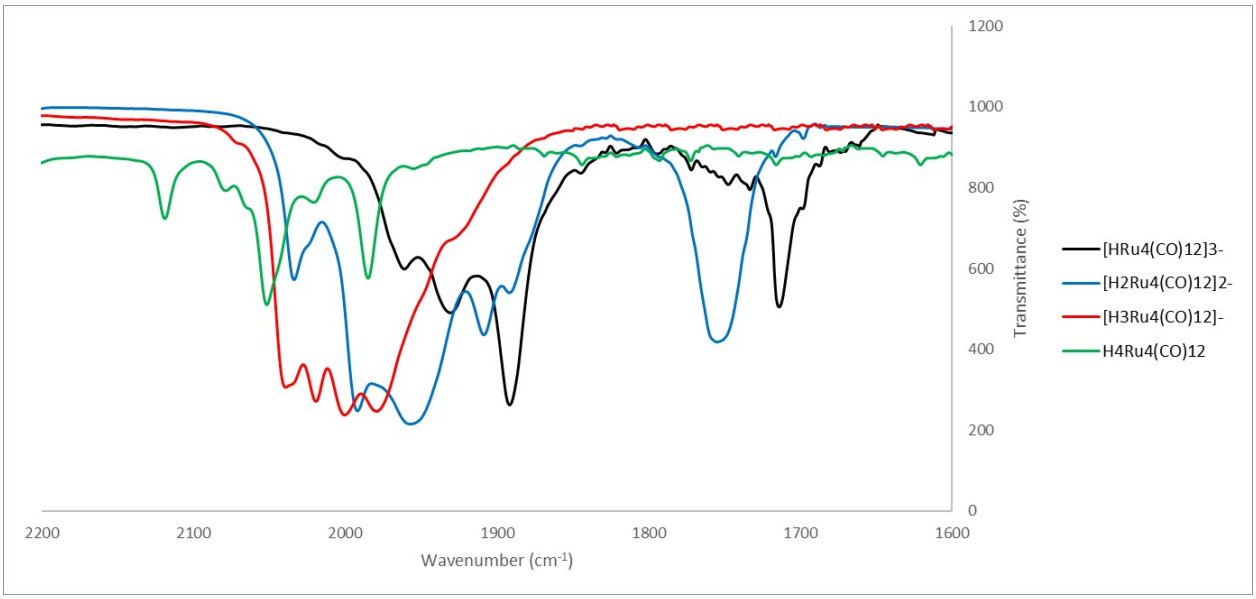

Figure S5. IR spectra in the ν_{CO} region of $[H_{4-n}Ru_4(CO)_{12}]^{n-}$ (n = 0-3) obtained from the stepwise protonation of $[HRu_4(CO)_{12}]^{3-}$ with $HBF_4{\cdot}Et_2O$ in CH_3CN.

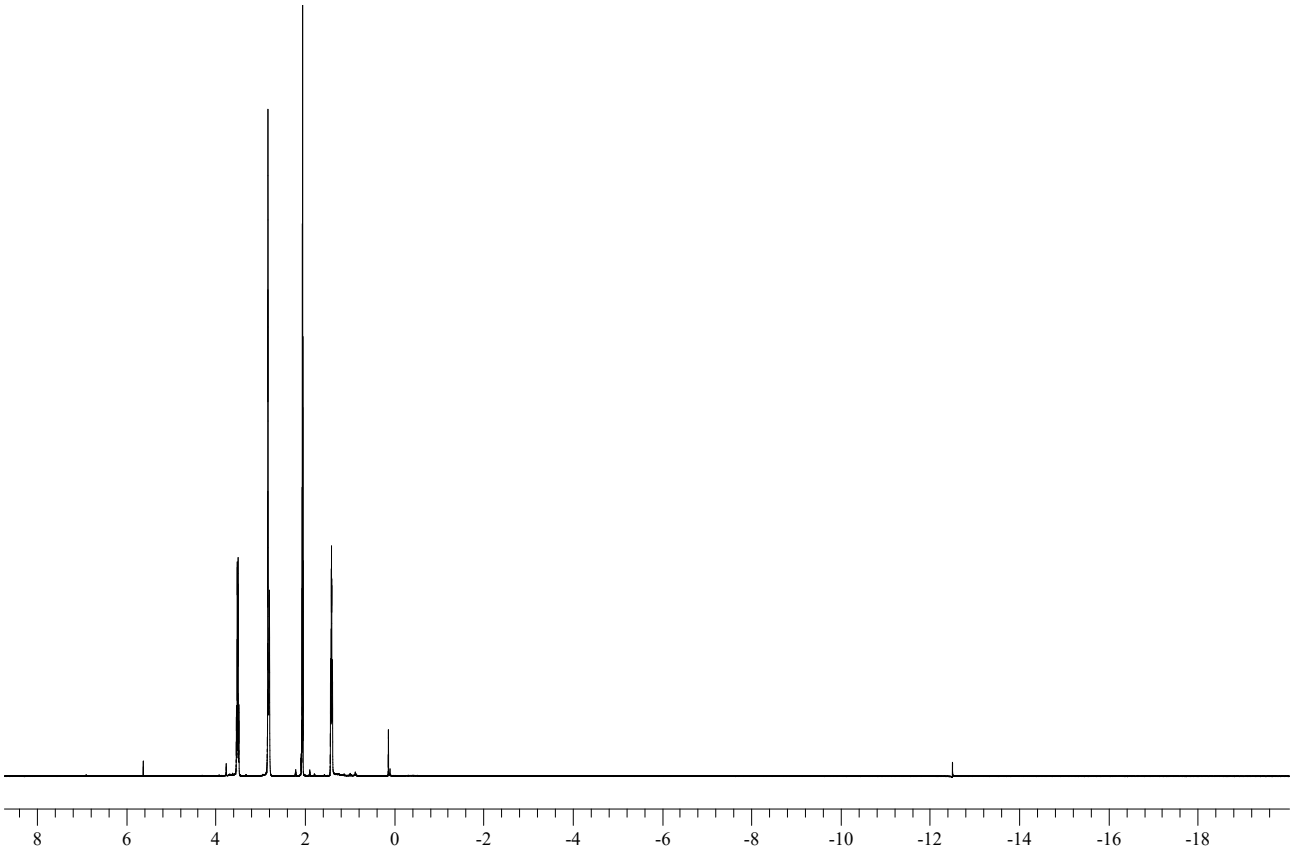

Figure S6. ^{1}H NMR spectrum of $[NEt_4][HRu_3(CO)_{11}]$ in acetone-d^6 at 298 K.

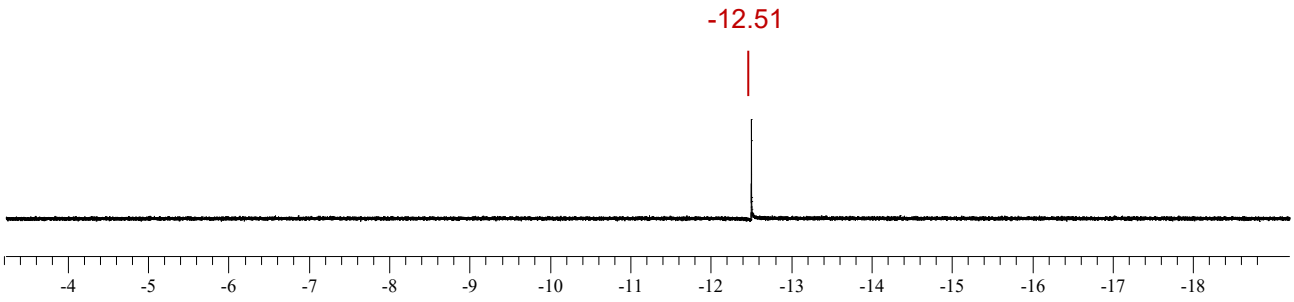

Figure S7. Hydride region of the ^{1}H NMR spectrum of $[NEt_4][HRu_3(CO)_{11}]$ in acetone-d^6 at 298 K.

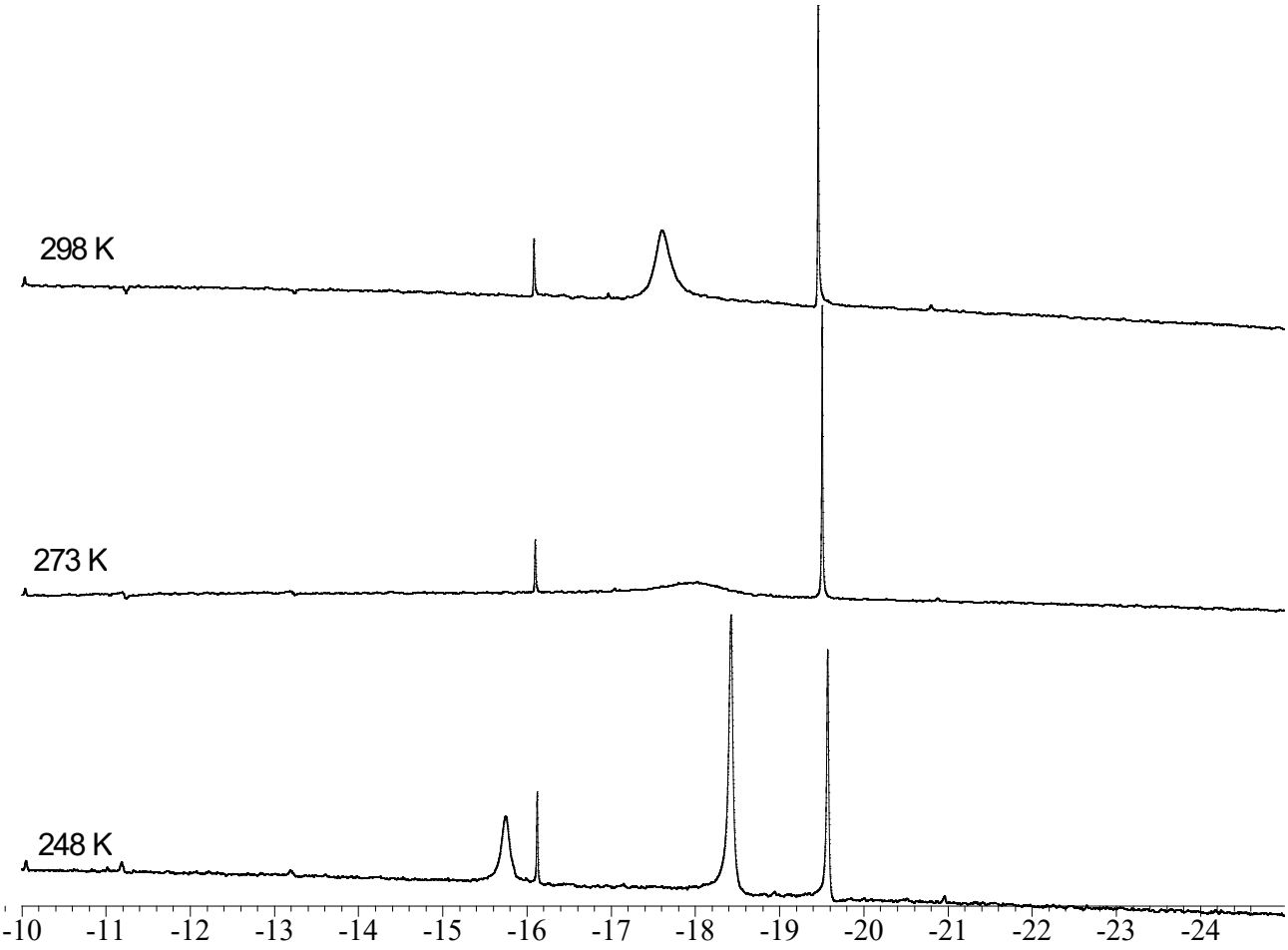

Figure S8. Hydride region of the VT ^{1}H NMR spectra of $[NEt_4]_3[HRu_4(CO)_{12}]$ in CD_3CN.

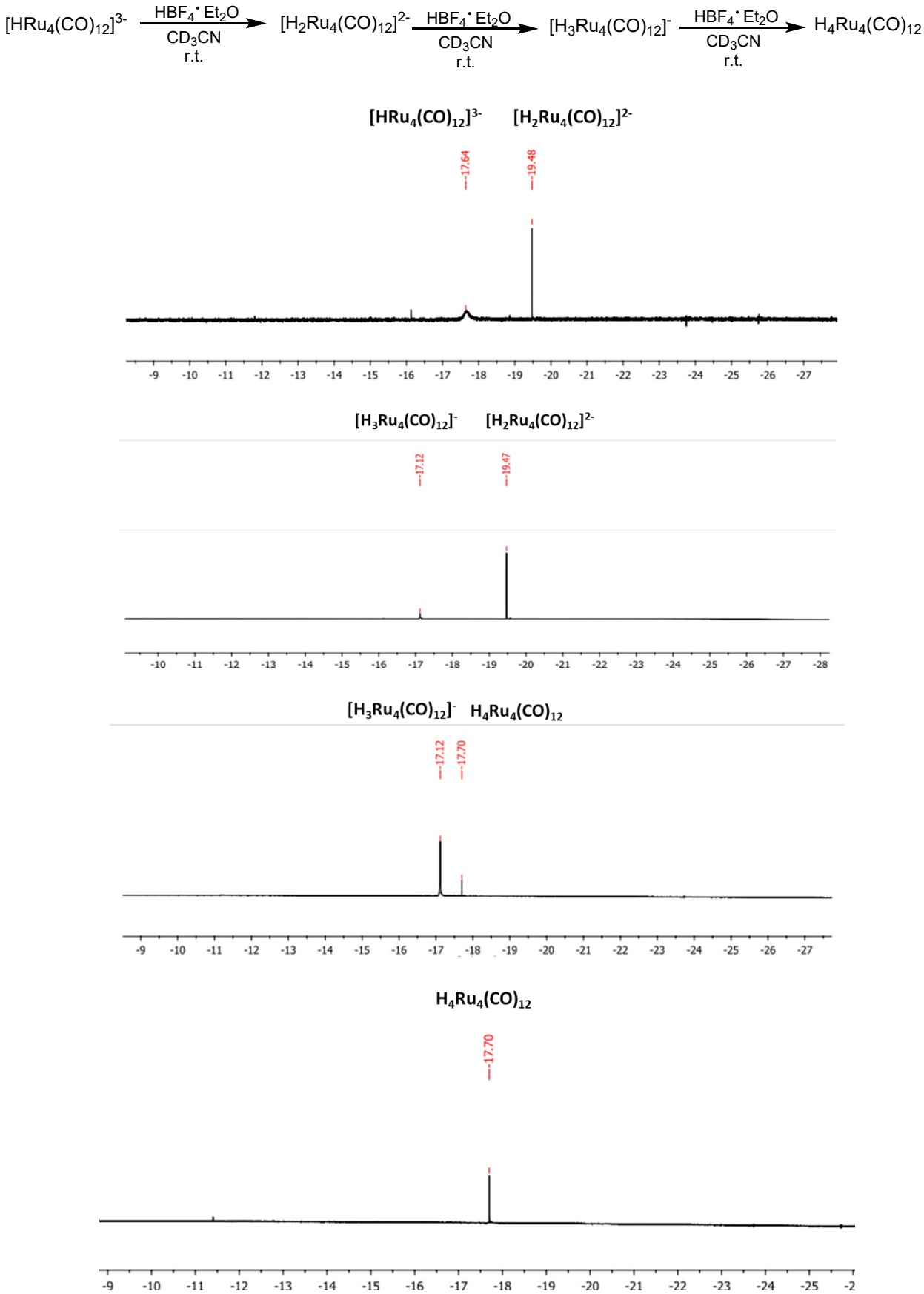

Figure S9. Hydride region of the ^{1}H NMR spectra of $[H_{4-n}Ru_4(CO)_{12}]^{n-}$ (n = 0-3) obtained from the stepwise protonation of $[HRu_4(CO)_{12}]^{3-}$ with $HBF_4{\cdot}Et_2O$ in CD_3CN at 298 K.

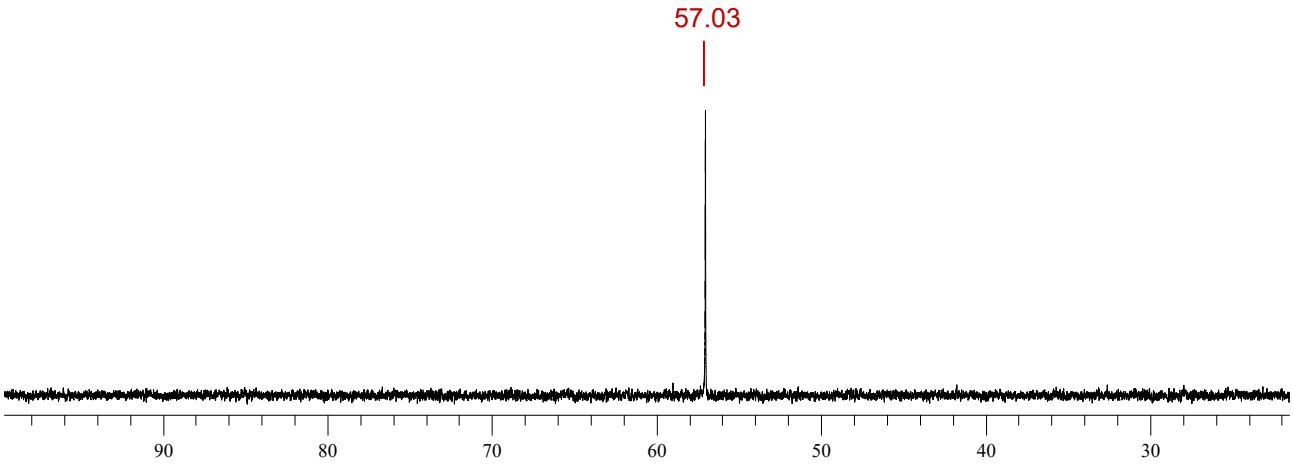

Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of $[NEt_4][Ru_3(CO)_9(NPPh_3)]$ in CD_2Cl_2 at 298 K.

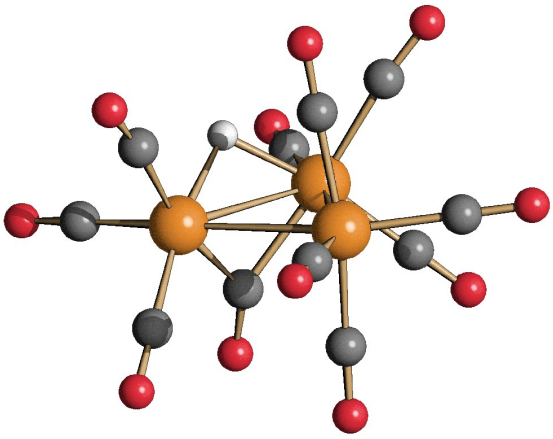

Figure S11. Molecular structure of $[HRu_3(CO)_{11}]^-$ (orange Ru; red O; grey C; white H).

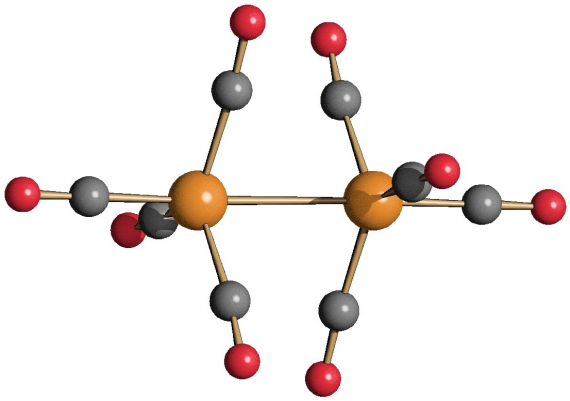

Figure S12. Molecular structure of $[Ru_2(CO)_8]^{2-}$ (orange Ru; red O; grey C).

Computational analysis of $[HRu_3(CO)_9(NPPh_3)]$ (9)

DFT calculations afforded a stationary point closely comparable to the structure determined by SC-XRD. AIM and Mayer analyses were carried out on the P-N and Ru-N bonds of the compound and on the DFT-optimized $[HRu_3(CO)_9(NPPh_3)]$ hydride with the same CO stereochemistry.[35] Electron density (ρ) and potential energy density (V) average values at selected b.c.p. are summarized in Figure S13. The computed data suggest that the P-N bond is stronger in **9** with respect to $[HRu_3(CO)_9(NPPh_3)]$. Such a result is supported by the Mayer bond order analysis, with values for the P-N bonds of 1.525 and 1.403 for **9** and $[HRu_3(CO)_9(NPPh_3)]$, respectively. The different P-N bond strengths can be explained on the basis of lower N→Ru σ-donation in the case of the more electron rich anionic cluster. Such hypothesis is confirmed by the Ru-N b.c.p. data in Figure S13, indicating slightly weaker Ru-N bonds in $[Ru_3(CO)_9(NPPh_3)]^-$, and by the Mayer analysis, with average Ru-N bond orders of 0.370 for **9** and 0.402 for $[HRu_3(CO)_9(NPPh_3)]$.

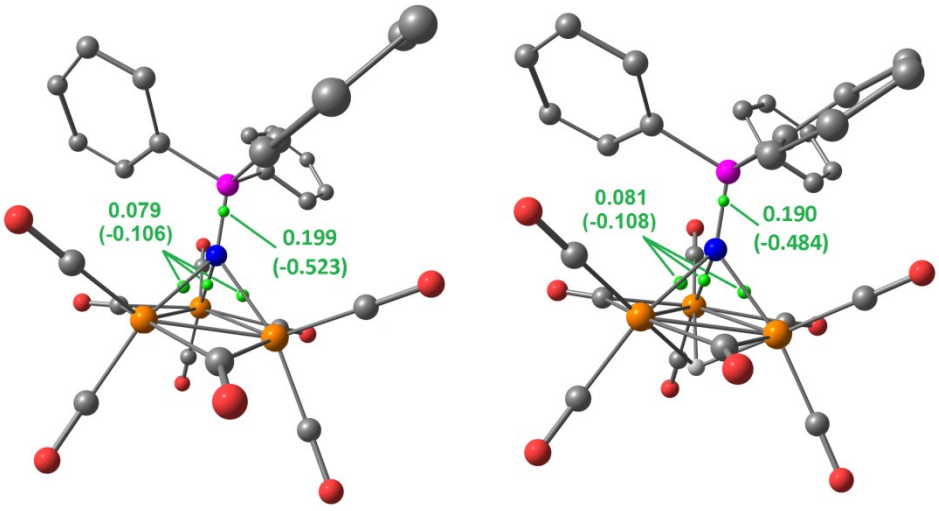

Fig. S13 DFT-optimized structures of $[Ru_3(CO)_9(NPPh_3)]^-$ (**9**) and $[HRu_3(CO)_9(NPPh_3)]$ (orange Ru; purple P; blue N; red O; grey C; white H) and selected (3,-1) b.c.p. (green) with density values at b.c.p. (potential energy density values in parenthesis). Data in a.u.

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