Supporting Information for

One-Pot Atmospheric Pressure Synthesis of $[H_3Ru_4(CO)_{12}]^-$

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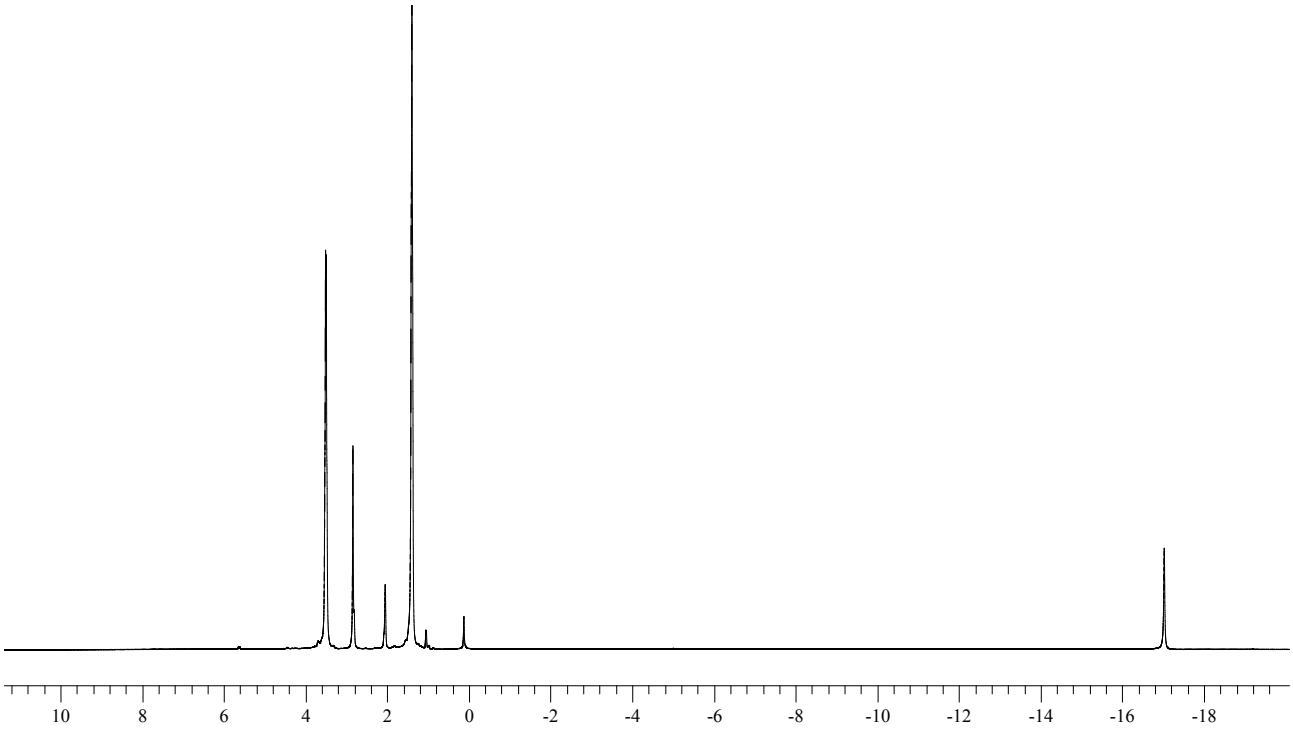

Figure S1. ^{1}H NMR spectrum of $[NEt_4][H_3Ru_4(CO)_{12}]$ (**1**) in acetone-d^6.

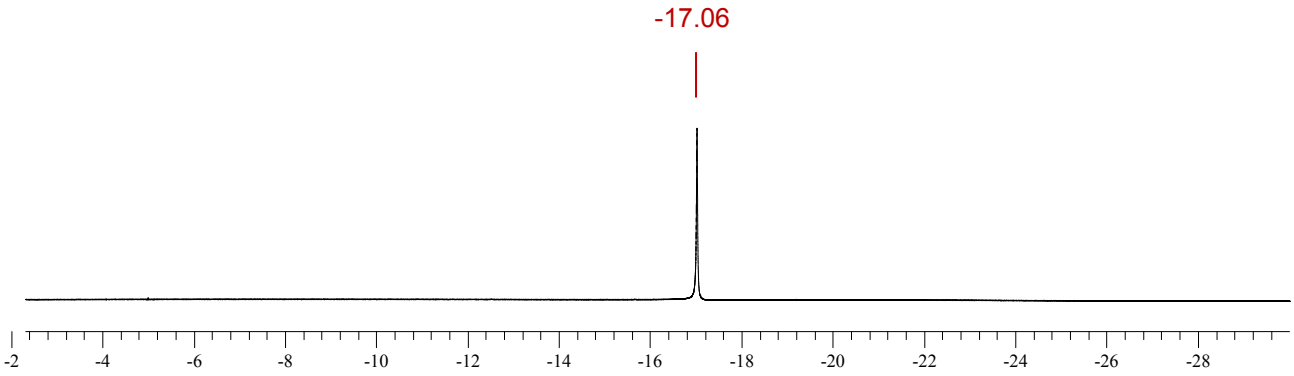

Figure S2. Hydride region of the ^{1}H NMR spectrum of $[NEt_4][H_3Ru_4(CO)_{12}]$ (**1**) in acetone-d^6.

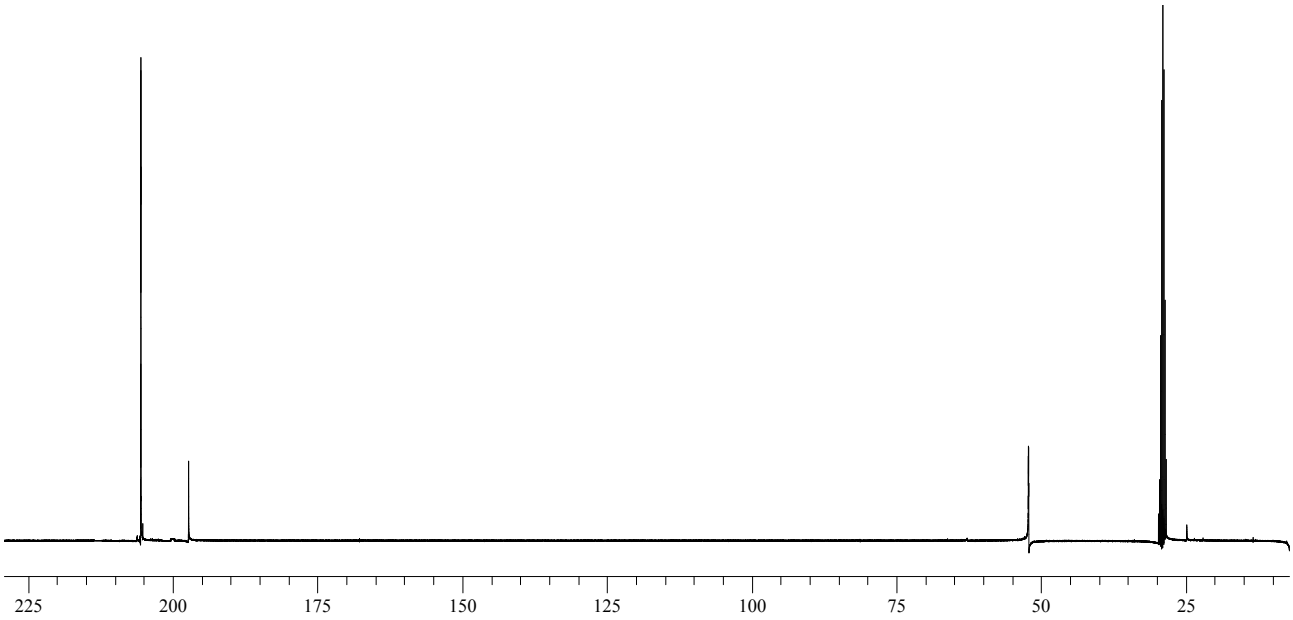

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of $[NEt_4][H_3Ru_4(CO)_{12}]$ (**1**) in acetone-d^6.

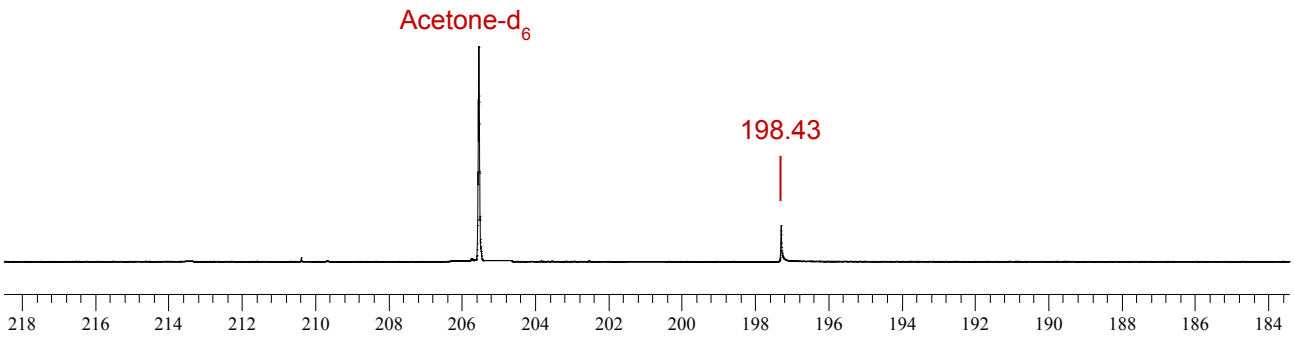

Figure S4. Carbonyl region of the $^{13}C\{^{1}H\}$ NMR spectrum of $[NEt_4][H_3Ru_4(CO)_{12}]$ (**1**) in acetone-d^6.

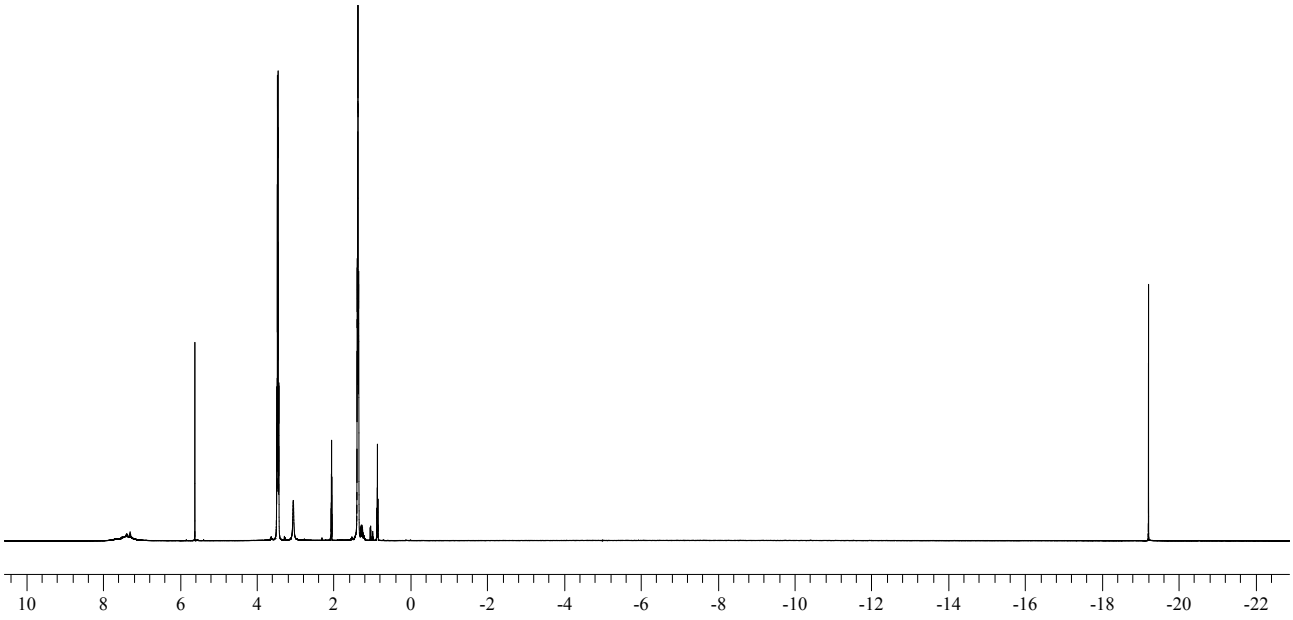

Figure S5. ^{1}H NMR spectrum of $[NEt_4]_2[H_2Ru_4(CO)_{12}]$ in acetone-d^6.

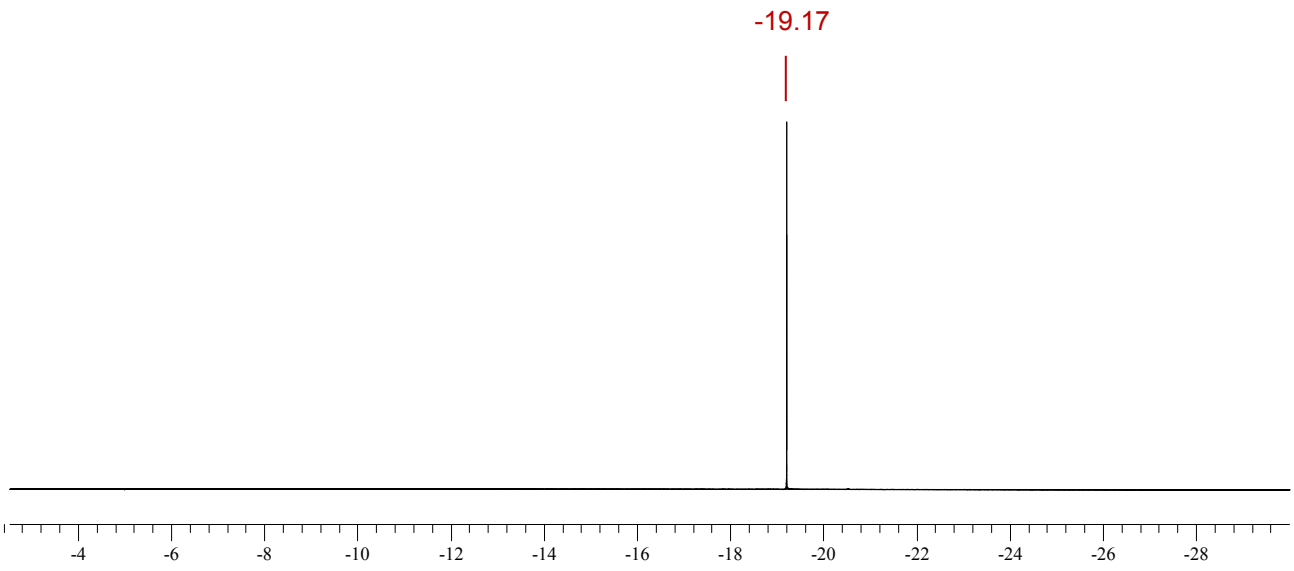

Figure S6. Hydride region of the ^{1}H NMR spectrum of $[NEt_4]_2[H_2Ru_4(CO)_{12}]$ in acetone-d^6.

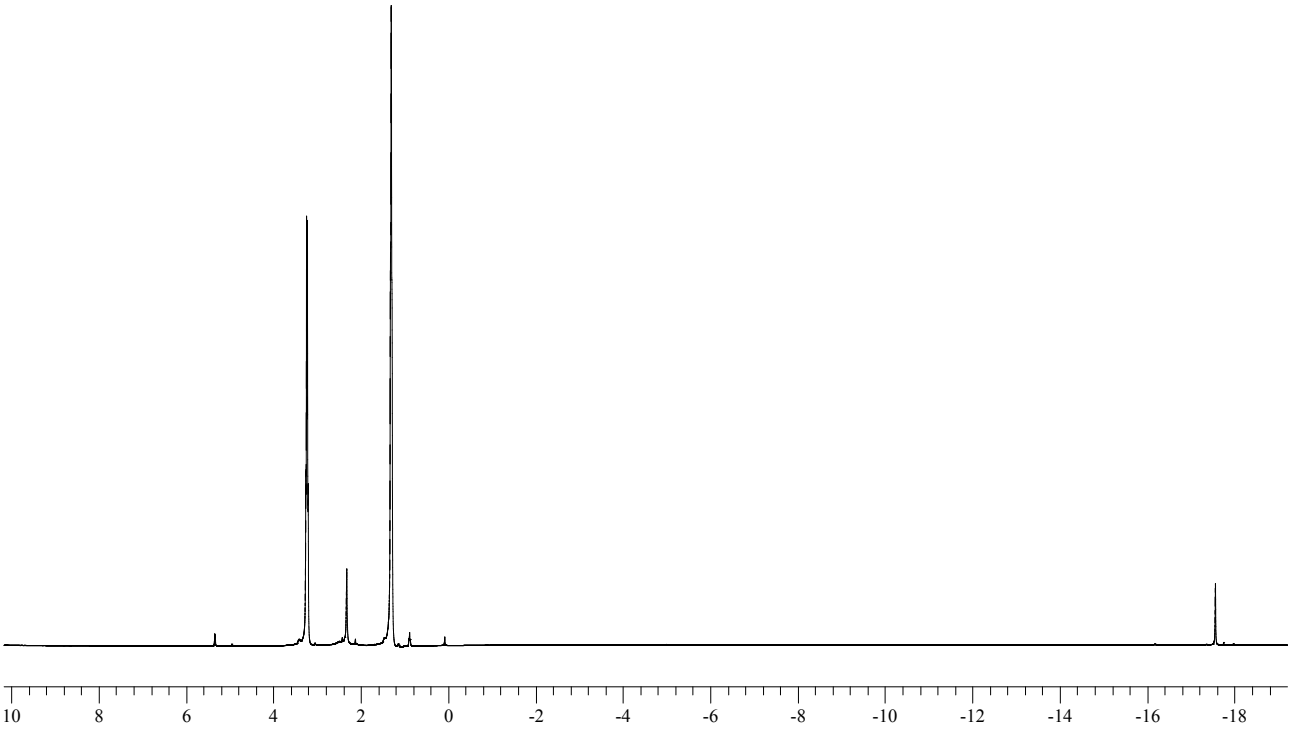

Figure S7. ^{1}H NMR spectrum of $[H_3Ru_4(CO)_{12}(CuCH_3CN)]$ in CD_2Cl_2.

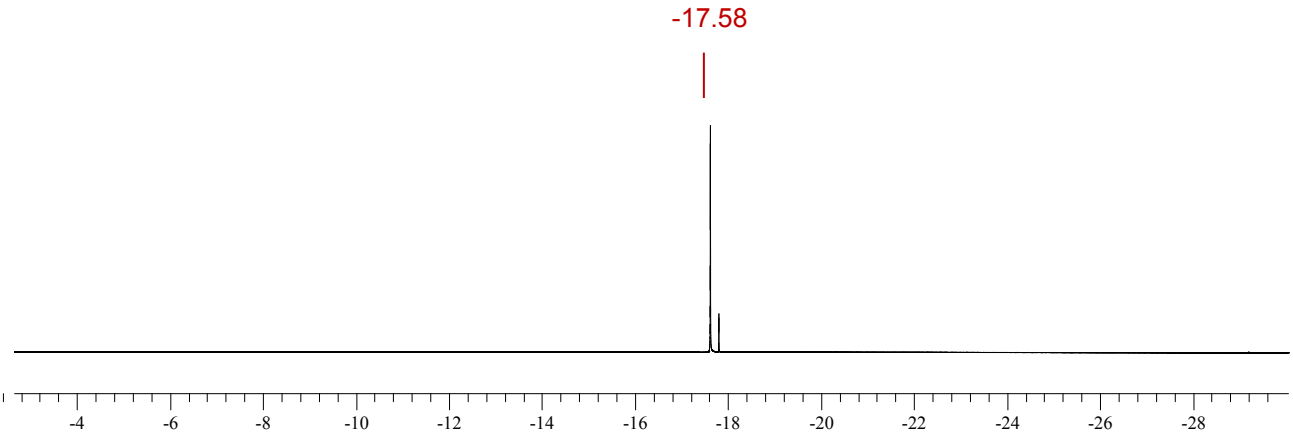

Figure S8. Hydride region of ^{1}H NMR spectrum of $[H_3Ru_4(CO)_{12}(CuCH_3CN)]$ in CD_2Cl_2.

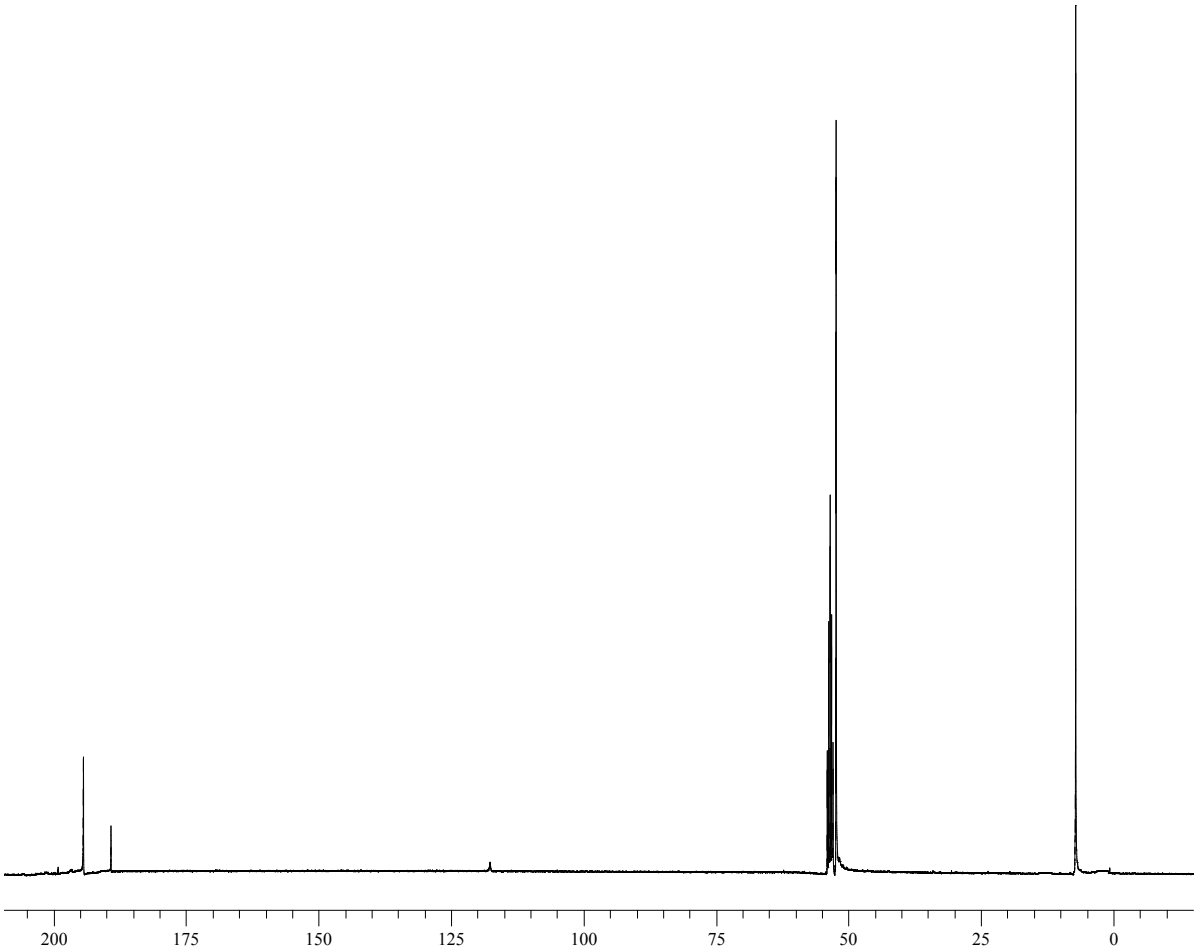

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of $[H_3Ru_4(CO)_{12}(CuCH_3CN)]$ in CD_2Cl_2.

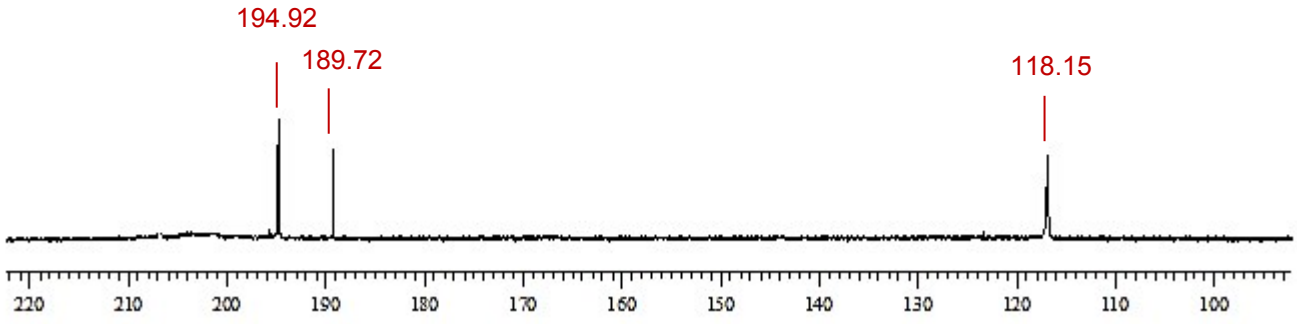

Figure S10. Carbonyl region of $^{13}C\{^{1}H\}$ NMR spectrum of $[H_3Ru_4(CO)_{12}(CuCH_3CN)]$ in CD_2Cl_2.

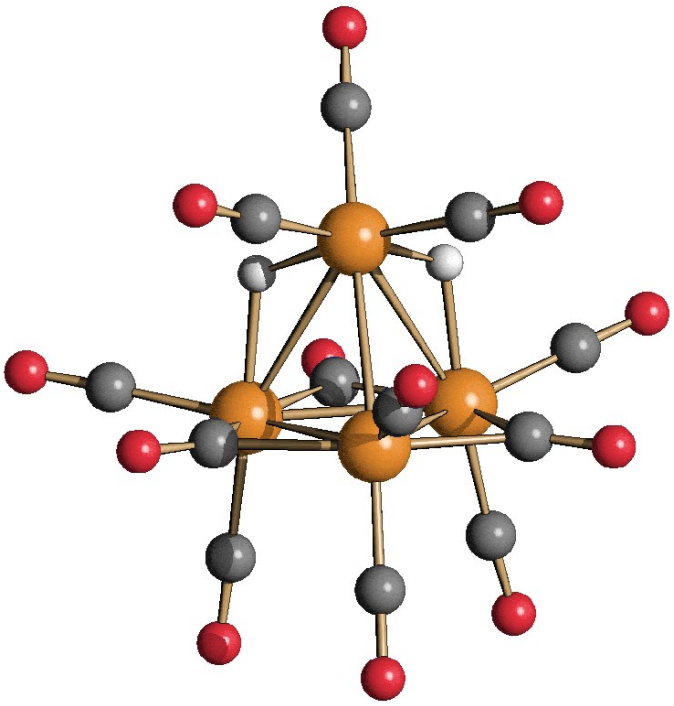

Figure S11. Molecular structure of $[H_2Ru_4(CO)_{12}]^{2-}$ (orange Ru; red O; grey C; white H).

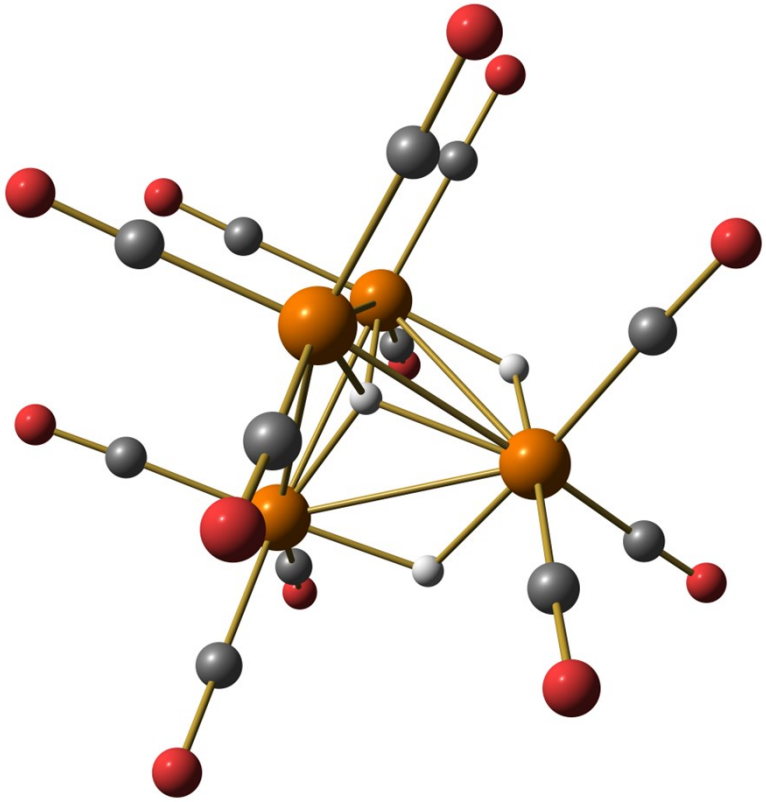

Fig. S12. DFT-optimized structure of the most stable $[H_3Ru_4(CO)_{12}]^{-}$ isomer with one μ_4-H (orange Ru; red O; grey C; white H).

Table S1

Crystal data and experimental details for $[NEt_4][H_3Ru_4(CO)_{12}]$, $K_2[NEt_4]_2[Ru_8(CO)_{16}(Br)_4(CO_3)_4]\cdot 5CH_3COCH_3$, $K_2[NEt_4]_3[Ru_8(CO)_{16}(Br)_4(CO_3)_4][Br]\cdot 4CH_3COCH_3$, $[NEt_4]_4[Ru_8(CO)_{16}(Br)_4(CO_3)_4]\cdot 2CH_3COCH_3$, $K_2[NBu_4]_2[Ru_8(CO)_{16}(Br)_4(CO_3)_4]\cdot 4CH_3COCH_3$, $K_2[NEt_4]_2[Ru_8(CO)_{16}(Cl)_4(CO_3)_4]\cdot 6CH_3CN\cdot$solv, $[NEt_4]_4[Ru_8(CO)_{16}(I)_4(CO_3)_4]\cdot 4CH_3COCH_3$, $K[NEt_4]_3\{[Ru_{10}(CO)_{20}(Br)_4(CO_3)_4]_2\}$, $[NEt_4]_2[H_2Ru_4(CO)_{12}]$, $[Ag(IPr)_2][H_3Ru_4(CO)_{12}]\cdot$solv, $[NEt_4]_2[Ru_6C(CO)_{16}]\cdot CH_2Cl_2$, $[Cu(IMes)_2]_2[\{Ru_6C(CO)_{16}\}_2Cu_4Cl_2]\cdot CH_2Cl_2\cdot$solv, $[H_3Ru_4(CO)_{12}(CuCH_3CN)]$, $[NEt_4]_2[H_2Ru_4(CO)_{12}(CuBr)_2]\cdot CH_2Cl_2$, and $[NEt_4]_2[H_2Ru_{12}(CO)_{34}Cu_6Br_2]\cdot$solv.

	$[NEt_4][H_3Ru_4(CO)_{12}]$	**$K_2[NEt_4]_2[Ru_8(CO)_{16}(Br)_4(CO_3)_4]\cdot 5CH_3COCH_3$**	**$K_2[NEt_4]_3[Ru_8(CO)_{16}(Br)_4(CO_3)_4][Br]\cdot 4CH_3COCH_3$**
Formula	$C_{20}H_{23}NO_{12}Ru_4$	$C_{51}H_{70}Br_4K_2N_2O_{33}Ru_8$	$C_{56}H_{84}Br_5K_2N_3O_{32}Ru_8$
Fw	873.67	2445.49	2597.57
T, K	100(2)	100(2)	100(2)
λ, Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a, Å	16.1592(7)	19.1095(8)	17.210(3)
b, Å	11.8097(5)	17.8113(7)	24.421(4)
c, Å	29.3937(13)	22.7190(9)	19.758(4)
α, °	90	90	90
β, °	100.7560(10)	93.1740(10)	90.980(6)
γ, °	90	90	90
Cell Volume, Å^3	5510.8(4)	7720.9(5)	8303(3)
Z	8	4	4
D_c, g cm^{-3}	2.106	2.104	2.078
μ, mm^{-1}	2.209	3.780	4.000
F(000)	3376	4736	5048
Crystal size, mm	0.19×0.16×0.14	0.21×0.18×0.16	0.18×0.16×0.11
θ limits, °	1.575–25.998	1.454–25.999	1.556–25.000
Index ranges	-19≤ h ≤19 -14 ≤ k ≤14 -36≤ l ≤36	-23 ≤ h ≤ 23 -21 ≤ k ≤ 21 -28 ≤ l ≤28	-20 ≤ h ≤ 20 -29 ≤ k ≤ 29 -23 ≤ l ≤23
Reflections collected	105608	142356	59265
Independent reflections	10814 [R_{int} = 0.0724]	15106 [R_{int} = 0.1080]	14377 [R_{int} = 0.1250]
Completeness to	99.9%	99.8%	98.3%

θ max			
Data / restraints / parameters	10814 / 0 / 693	15106 /12 / 919	14377 / 571 / 955
Goodness on fit on F^2	1.237	1.043	1.199
R_1 ($I > 2\sigma(I)$)	0.0320	0.0286	0.1514
wR_2 (all data)	0.0672	0.0656	0.3675
Largest diff. peak and hole, e Å^{-3}	0.759 / –0.714	1.059 / –1.376	4.955 / –2.562

	$[NEt_4]_4[Ru_8(CO)_{16}(Br)_4(CO_3)_4]\cdot 2CH_3COCH_3$	**$K_2[NBu_4]_2[Ru_8(CO)_{16}(Br)_4(CO_3)_4]\cdot 4CH_3COCH_3$**	**$K_2[NEt_4]_2[Ru_8(CO)_{16}(Cl)_4(CO_3)_4]\cdot 6CH_3CN\cdot solv$**
Formula	$C_{58}H_{92}Br_4N_4O_{30}Ru_8$	$C_{64}H_{96}Br_4K_2N_2O_{32}Ru_8$	$C_{48}H_{58}Cl_4K_2N_8O_{28}Ru_8$
Fw	2453.55	2611.82	2223.58
T, K	100(2)	100(2)	100(2)
λ, Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Tetragonal
Space Group	*C*2/*c*	$P\bar{1}$	$P4_2/nmc$
a, Å	20.2618(8)	14.0395(9)	18.2867(6)
b, Å	19.7427(8)	16.7852(11)	18.2867(6)
c, Å	21.4241(8)	21.5954(14)	22.1854(8)
α, °	90	74.768(2)	90
β, °	109.0000(10)	72.962(2)	90
γ, °	90	67.148(2)	90
Cell Volume, Å^3	8103.2(6)	4419.3(5)	7418.9(6)
Z	4	2	4
D_c, g cm^{-3}	2.011	1.963	1.991
μ, mm^{-1}	3.500	3.308	1.919
F(000)	4800	2560	4336
Crystal size, mm	0.16×0.11×0.10	0.24×0.21×0.14	0.18×0.16×0.12
θ limits, °	1.481–25.099	1.528–27.037	2.147–27.000
Index ranges	-24 ≤ h ≤ 24 -23 ≤ k ≤ 23 -25 ≤ l ≤ 25	-16 ≤ h ≤ 17 -20 ≤ k ≤ 21 -26 ≤ l ≤ 27	-23 ≤ h ≤ 23 -23 ≤ k ≤ 23 -28 ≤ l ≤ 28
Reflections	71584	89032	150870

collected			
Independent reflections	7213 [R_{int} = 0.0772]	19223 [R_{int} = 0.0835]	4320 [R_{int} = 0.0642]
Completeness to θ max	99.9%	99.9%	99.9%
Data / restraints / parameters	7213 / 157 / 462	19223 / 60 /1010	4320 / 0 / 248
Goodness on fit on F^2	1.093	1.063	1.259
R_1 ($I > 2\sigma(I)$)	0.0683	0.0696	0.0290
wR_2 (all data)	0.1712	0.1918	0.0518
Largest diff. peak and hole, e Å^{-3}	3.434 / –2.847	2.510 / –3.628	0.491 / –0.748

	$[NEt_4]_4[Ru_8(CO)_{16}(I)_4(CO_3)_4]\cdot 4CH_3COCH_3$	**$K[NEt_4]_3[Ru_{10}(CO)_{20}(Br)_4(CO_3)_4]_2\}\cdot CH_3COCH_3$**	**$[NEt_4]_2[H_2Ru_4(CO)_{12}]$**
Formula	$C_{64}H_{104}I_4N_4O_{32}Ru_8$	$C_{39}H_{36}Br_4K_{0.5}N_{1.5}O_{33}Ru_{10}$	$C_{28}H_{42}N_2O_{12}Ru_4$
Fw	2757.67	2403.58	1002.91
T, K	100(2)	100(2)	100(2)
λ, Å	0.71073	0.71073	0.71073
Crystal system	Tetragonal	Monoclinic	Monoclinic
Space Group	$I4_1/a$	$C2/c$	$P2_1/c$
a, Å	14.6311(5)	31.7547(15)	13.3251(5)
b, Å	14.6311(5)	13.3024(6)	20.1945(7)
c, Å	42.7670(16)	32.2056(15)	13.4433(5)
α, °	90	90	90
β, °	90	99.623(2)	94.4270(10)
γ, °	90	90	90
Cell Volume, Å^3	9155.1(7)	13412.7(11)	3603.7(2)
Z	4	8	4
D_c, g cm^{-3}	2.001	2.381	1.847
μ, mm^{-1}	2.707	4.682	1.701
F(000)	5344	9072	1984
Crystal size, mm	0.21×0.16×0.12	0.15×0.13×0.06	0.19×0.16×0.15
θ limits, °	1.905–26.998	1.663–25.998	1.533–26.000
Index ranges	-18≤ h ≤ 18 -18≤ k ≤ 18	-39 ≤ h ≤ 39 -16 ≤ k ≤ 16	-16≤ h ≤ 16 -24≤ k ≤ 24

	-54≤ l ≤54	-39 ≤ l ≤39	-16≤ l ≤16
Reflections collected	92507	86381	69738
Independent reflections	5001 [R_{int} = 0.0911]	13176 [R_{int} = 0.0602]	7091 [R_{int} = 0.0783]
Completeness to θ max	100.0%	99.9%	100.0%
Data / restraints / parameters	5001 / 366 / 363	13176 / 121 / 831	7091 / 0 / 429
Goodness on fit on F^2	1.375	1.156	1.199
R_1 ($I > 2\sigma(I)$)	0.1081	0.0529	0.0324
wR_2 (all data)	0.2152	0.1128	0.0585
Largest diff. peak and hole, e Å^{-3}	1.841 / –2.988	1.310 / –1.581	0.990 / –0.644

	[Ag(IPr)$_2$] [$H_3Ru_4(CO)_{12}$]·solv	**[NEt_4]$_2$[$Ru_6C(CO)_{16}$]·CH_2Cl_2**	**[Cu(IMes)$_2$]$_2$[{$Ru_6C(CO)_{16}$}$_2$$Cu_4Cl_2$]· CH_2Cl_2·solv**
Formula	$C_{66}H_{72}AgN_4O_{12}Ru_4$	$C_{34}H_{42}Cl_2N_2O_{16}Ru_6$	$C_{119}H_{98}Cl_4Cu_6N_8O_{32}Ru_{12}$
Fw	1625.42	1412.01	3887.93
T, K	100(2)	100(2)	100(2)
λ, Å	0.71073	0.71073	0.71073
Crystal system	Tetragonal	Monoclinic	Triclinic
Space Group	*P*4/*nnc*	$P2_1/c$	$P\bar{1}$
a, Å	18.1524(9)	12.3521(4)	15.5683(11)
b, Å	18.1524(9)	25.1854(8)	17.3394(13)
c, Å	21.1288(13)	43.6498(15)	29.112(2)
α, °	90	90	88.836(3)
β, °	90	91.6680(10)	82.133(3)
γ, °	90	90	66.550(2)
Cell Volume, Å^3	69621.1(8)	13573.4(8)	7136.7(9)
Z	4	12	2
D_c, g cm^{-3}	1.551	2.073	1.809
μ, mm^{-1}	1.183	2.137	2.245
F(000)	3260	8232	3788
Crystal size, mm	0.16×0.13×0.12	0.19×0.16×0.12	0.21×0.18×0.15
θ limits, °	1.479–25.997	1.617–25.000	1.589–25.100
Index ranges	-22≤ h ≤22 -22≤ k ≤22	-14≤ h ≤ 14 -29≤ k ≤ 29	-18≤ h ≤18 -20≤ k ≤20

	-26≤ l ≤26	-51≤ l ≤51	-34≤ l ≤34
Reflections collected	69729	179585	127331
Independent reflections	3442 [R_{int} = 0.1026]	23904 [R_{int} = 0.0817]	25412 [R_{int} = 0.0909]
Completeness to θ max	100.0%	100.0%	99.9%
Data / restraints / parameters	3442 / 372 / 267	23904 / 209 / 1611	25412 / 1309 / 2003
Goodness on fit on F^2	1.237	1.142	1.037
R_1 ($I > 2\sigma(I)$)	0.1013	0.0599	0.0366
wR_2 (all data)	0.1954	0.1214	0.0848
Largest diff. peak and hole, e Å^{-3}	1.418 / –1.806	3.052 / –1.815	0.908 / –0.738

	$[H_3Ru_4(CO)_{12}(CuCH_3CN)]$	**$[NEt_4]_2[H_2Ru_4(CO)_{12}(CuBr)_2]\cdot CH_2Cl_2$**	**$[NEt_4]_2[H_2Ru_{12}(CO)_{34}Cu_6Br_2]\cdot$ solv**
Formula	$C_{14}H_6CuNO_{12}Ru_4$	$C_{29}H_{44}Br_2Cl_2Cu_2N_2O_{12}Ru_4$	$C_{50}H_{42}Br_2Cu_6N_2O_{34}Ru_{12}$
Fw	848.02	1374.74	2968.75
T, K	100(2)	100(2)	293(2)
λ, Å	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space Group	$P\bar{1}$	*I*2/*a*	*P*2/*m*
a, Å	8.5369(3)	22.849(6)	13.7124(12)
b, Å	10.0317(4)	12.166(3)	19.7578(17)
c, Å	13.1229(5)	31.936(10)	17.3324(15)
α, °	86.3950(10)	90	90
β, °	71.6300(10)	99.819(5)	111.328(4)
γ, °	85.3670(10)	90	90
Cell Volume, Å^3	1062.25(7)	8748(4)	4374.2(7)
Z	2	8	2
D_c, g cm^{-3}	2.651	2.088	2.254
μ, mm^{-1}	3.825	4.304	4.412
F(000)	796	5328	2800
Crystal size, mm	0.21×0.18×0.14	0.16×0.12×0.10	0.18×0.16×0.12
θ limits, °	1.636–27.000	1.160–24.999	1.629–25.048

Index ranges	-10≤ h ≤ 10 -12≤ k ≤ 12 -16≤ l ≤16	-27 ≤ h ≤ 26 -14 ≤ k ≤ 14 -37 ≤ l ≤ 37	-16 ≤ h ≤ 16 -23 ≤ k ≤ 23 -20 ≤ l ≤ 20
Reflections collected	20903	33801	50323
Independent reflections	4626 [R_{int} = 0.0428]	7716 [R_{int} = 0.1227]	8024 [R_{int} = 0.0956]
Completeness to θ max	99.9%	100.0%	99.9%
Data / restraints / parameters	4626 / 0 / 299	7716 / 215/ 470	8024 / 270/ 516
Goodness on fit on F^2	1.179	1.172	1.082
R_1 ($I > 2\sigma(I)$)	0.0170	0.1706	0.0643
wR_2 (all data)	0.0399	0.4055	0.1727
Largest diff. peak and hole, e $Å^{-3}$	1.082 / –0.501	3.404 / –5.407	1.746 / –1.094