Electronic Supplementary Material (ESI) for Dalton Transactions.

Acetate Ion Addition to and Exchange in (1,5-cyclooctadiene)rhodium(I) Acetate: Relevance for the Coagulation of Carboxylic Acid-Functionalized Shells of Core-crosslinked Micelle Latexes

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Supporting Information

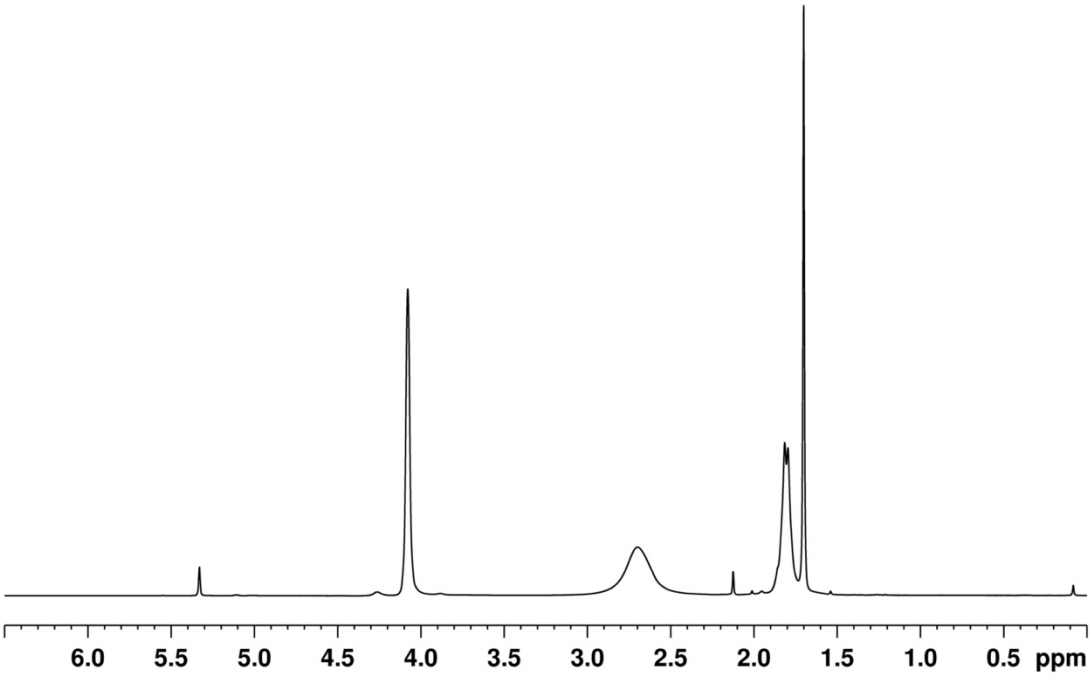


Figure S1. ^{1}H NMR spectrum of $[Rh(COD)(\mu\text{-}OAc)]_2$ (CD_2Cl_2, 400 MHz, 293 K).

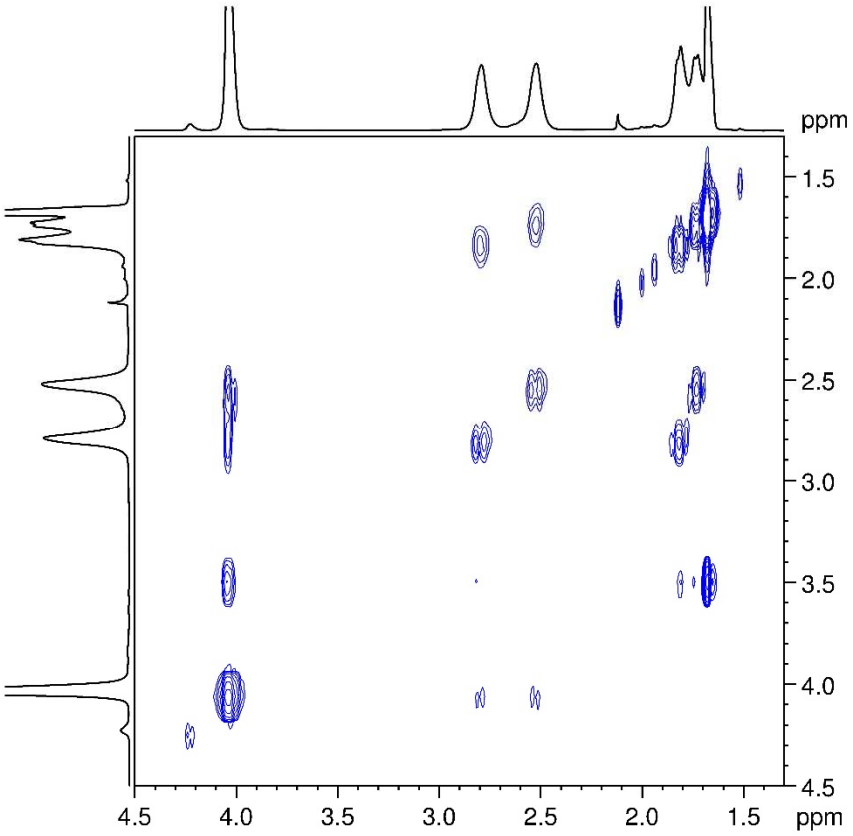


Figure S2. ^{1}H COSY spectrum of $[Rh(COD)(\mu\text{-}OAc)]_2$ (CD_2Cl_2, 400 MHz, 253 K).

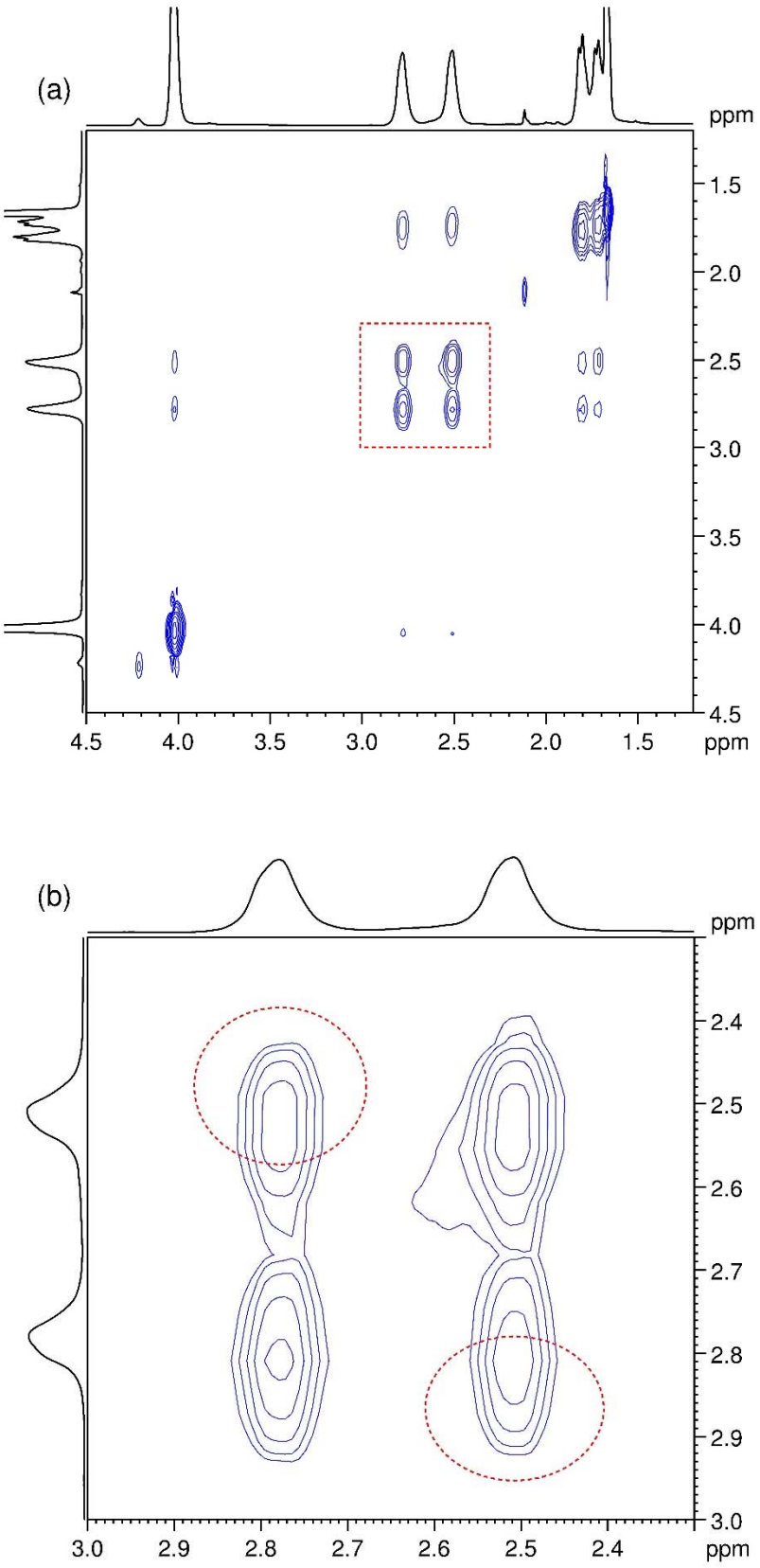


Figure S3. (a)Portion of the ^{1}H EXSY spectrum $[Rh(COD)(\mu\text{-}OAc)]_2$ (CD_2Cl_2, 400 MHz, 233 K). (b)Expansions of selected areas.

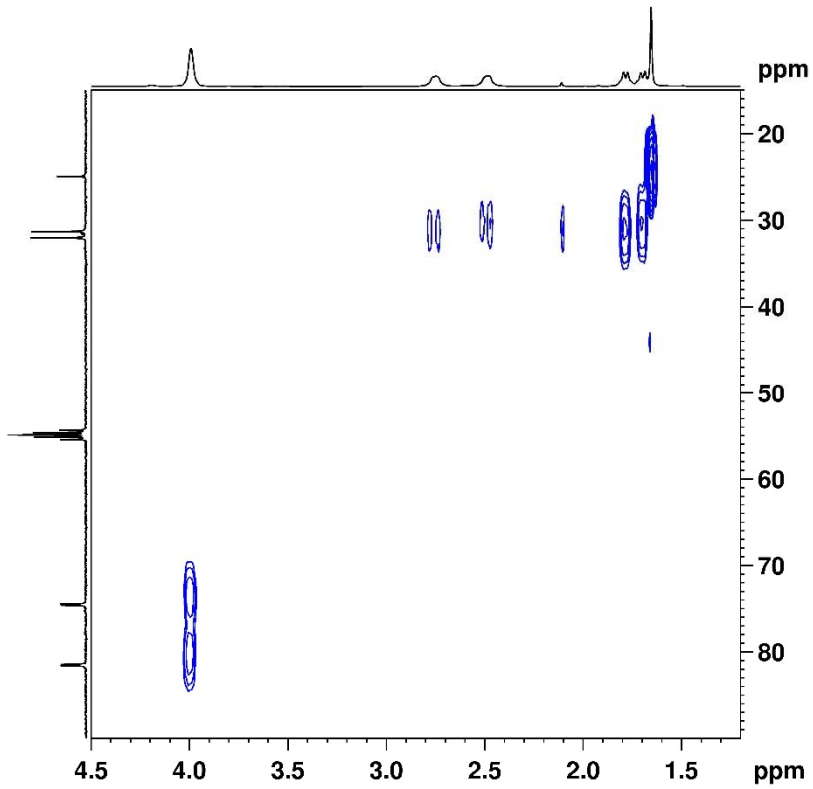
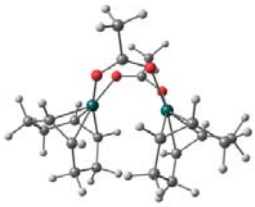


Figure S4. ^{1}H-^{13}C HMQC spectrum of $[Rh(COD)(\mu\text{-}OAc)]_2$ (CD_2Cl_2, 223 K).

Table S1. Comparison of observed and DFT calculated structure for the most relevant bond distances and angles.



Parameter	Observed [a]	Calculated	Parameter	Observed [a]	Calculated
Distances (Å)			Angles (°)		
Rh···Rh	3.344	3.378	O-Rh-O	91.35(8), 90.99(8)	90.175, 90.201
Rh-O	2.100(2), 2.096(2) 2.095(2), 2.089(2)	2.115, 2.122 2.115, 2.121	X-Rh-O_{cis} [b]	89.049, 90.311 89.016, 90.464	89.988, 90.310 90.020, 90.267
Rh-C	2.107(3), 2.081(3) 2.097(3), 2.087(2) 2.085(2), 2.096(3) 2.080(3), 2.106(3)	2.113, 2.137 2.115, 2.137 2.113, 2.137 2.115, 2.137	X-Rh-O_{trans} [b]	168.329, 174.831 170.069, 174.085	169.158, 175.561 169.170, 175.616
			X-Rh-X	88.341, 88.527	88.696, 88.698

[a] X-ray structure from C. M. Filloux and T. Rovis, , 2015, 137, 508-517 (CCDC 936197). [b] X = center of the COD C=C bond.

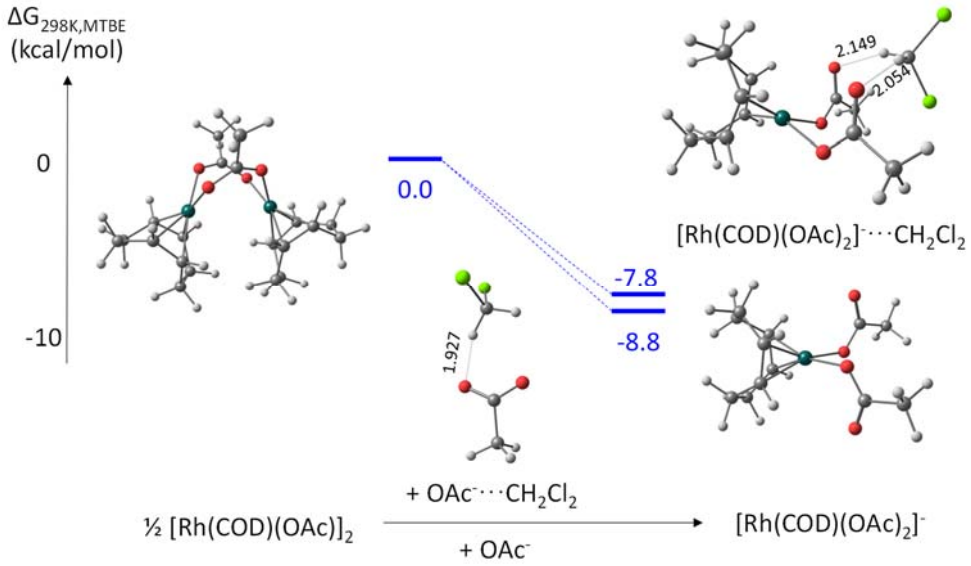


Figure S5. Gibbs energy profile for the acetate coordination to [Rh(COD)(OAc)] in the presence of one explicitly included dichloromethane molecule.

(a) 

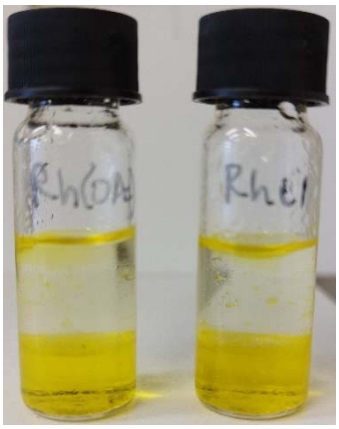
(b) 

Figure S6. (a) Solutions of $[Rh(COD)(\mu\text{-}Cl)]_2$ (left) and $[Rh(COD)(\mu\text{-}OAc)]_2$ (right) in dichloromethane, in contact with neat water, after extensive shaking followed by decantation. (b) Solutions of $[Rh(COD)(\mu\text{-}OAc)]_2$ (left) and $[Rh(COD)(\mu\text{-}Cl)]_2$ (right) in dichloromethane, in contact with a water solution of NaOAc (Rh:OAc 1:5), after extensive shaking followed by decantation.

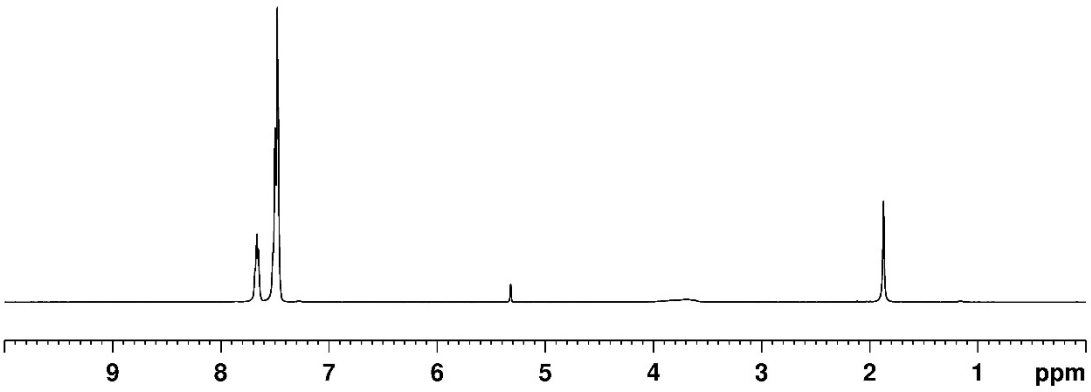


Figure S7. ^{1}H NMR spectrum of $[PPN]^{+}OAc^{-}$ (CD_2Cl_2, 400 MHz, 298 K).

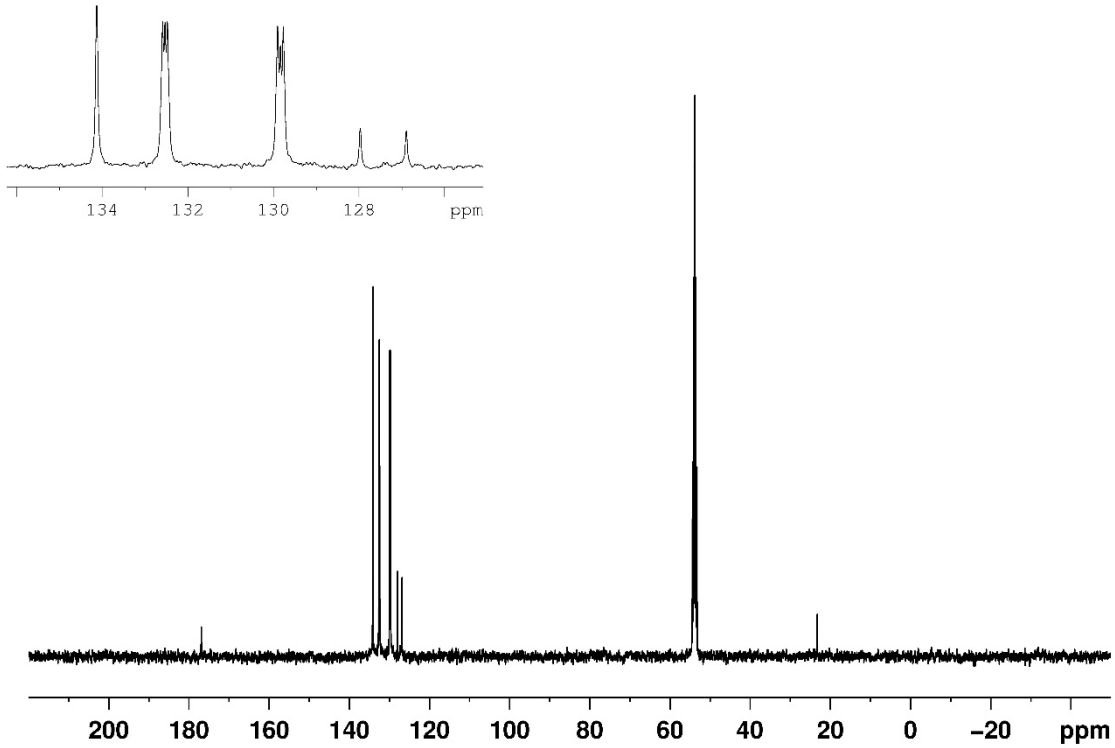


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of $[PPN]^{+}OAc^{-}$ (CD_2Cl_2, 100 MHz, 298 K).

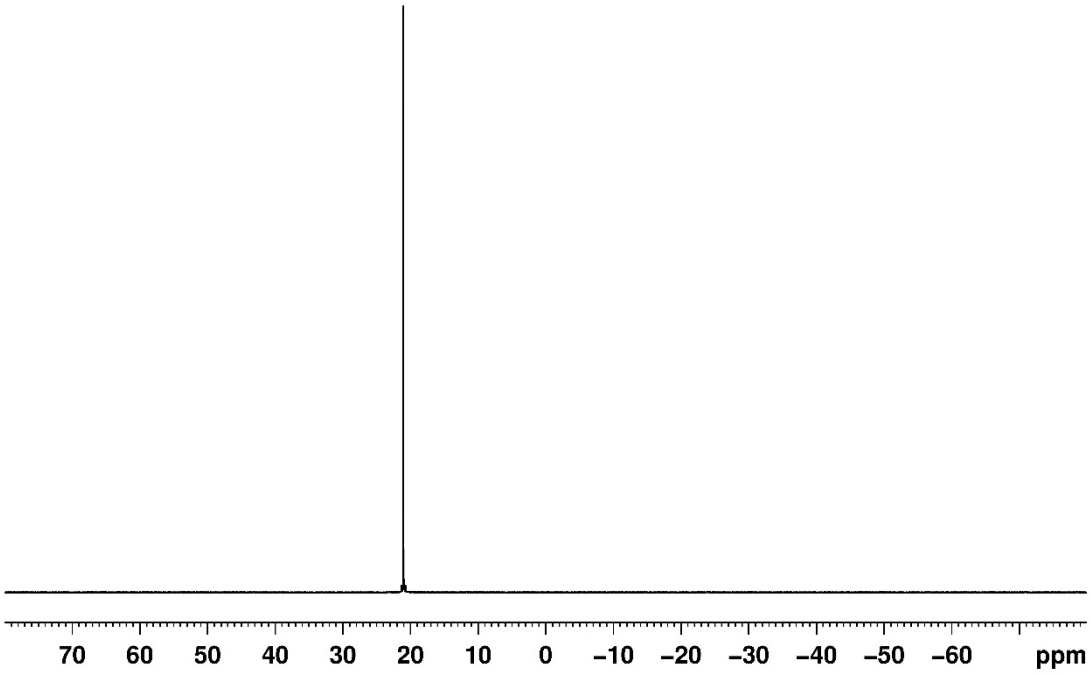


Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of $[PPN]^{+}OAc^{-}$ (CD_2Cl_2, 162 MHz, 298 K).

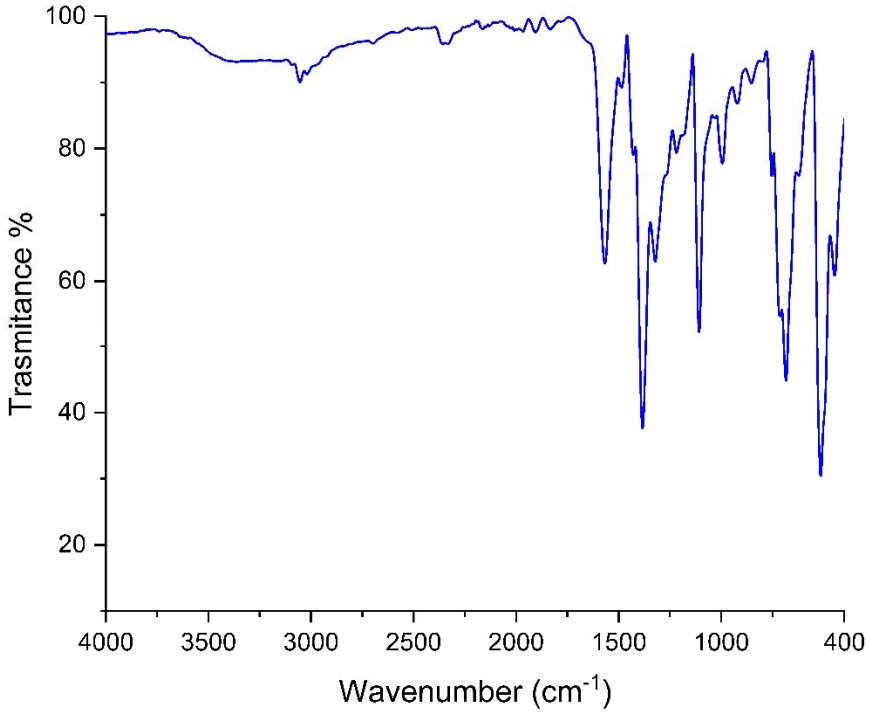


Figure S10. FT-IR spectrum of $[PPN]^{+}OAc^{-}$ (ATR).

Table S2. Cartesian coordinates (Å) and energies (hartrees) of all optimized geometries.

Acetate (CH_3COO^-)

E = -228.592082687
$G_{298,1M}$ = -228.567326

8	1.159740000	0.700257000	0.000000000
8	-1.104603000	0.811139000	0.000000000
6	0.000000000	0.206297000	0.000000000
6	-0.052061000	-1.351045000	0.000000000
1	0.474548000	-1.743940000	0.879417000
1	-1.077821000	-1.734802000	0.000000000
1	0.474548000	-1.743940000	-0.879417000

Dichloromethane (CH_2Cl_2)

E = -959.701555006
$G_{298,1M}$ = -959.696078

1	0.000129000	1.385794000	-0.902433000
6	0.000799000	0.778975000	-0.000071000
1	-0.000041000	1.386367000	0.902375000
17	-1.498840000	-0.218904000	0.000011000
17	1.498553000	-0.219097000	0.000017000

$CH_3COO^-\cdots CH_2Cl_2$

E = -1188.30747933
$G_{298,1M}$ = -1188.262681

8	1.623836000	-0.295636000	1.055545000
8	1.803407000	0.233825000	-1.140815000
6	2.269927000	-0.037301000	-0.003821000
6	3.813022000	-0.091071000	0.107514000
1	4.181714000	-0.999657000	-0.386181000
1	4.265465000	0.760038000	-0.413593000
1	4.148679000	-0.104605000	1.149029000
1	-0.200228000	-0.159155000	0.449836000
6	-1.060295000	-0.029734000	-0.225335000
1	-0.724074000	0.002084000	-1.257437000
17	-2.197381000	-1.432247000	-0.037087000
17	-1.874703000	1.546624000	0.147108000

$[Rh(COD)(O_2CCH_3)]_2$

E = -1302.5379287
$G_{298,1M}$ = -1302.121260

6	-1.879559000	-1.039739000	-1.526891000
1	-1.184384000	-0.678704000	-2.285896000
6	-3.089551000	-0.333063000	-1.373978000
1	-3.237198000	0.543514000	-2.003492000
6	-4.356173000	-0.942370000	-0.777449000
1	-4.380872000	-2.016843000	-0.984515000
1	-5.231840000	-0.514191000	-1.275726000
6	-4.454512000	-0.679705000	0.743220000
1	-4.950200000	0.283792000	0.906556000
1	-5.085465000	-1.440056000	1.227440000
6	-3.095526000	-0.606208000	1.419430000
1	-3.075215000	0.001414000	2.324201000
6	-2.029479000	-1.510206000	1.235249000
1	-1.267804000	-1.535460000	2.013458000
6	-2.122630000	-2.754369000	0.352955000
1	-3.152437000	-3.124815000	0.354792000
1	-1.512761000	-3.553422000	0.786545000
6	-1.647593000	-2.476972000	-1.092626000
1	-0.573435000	-2.664446000	-1.153256000
1	-2.125728000	-3.174036000	-1.796858000
6	-0.073001000	2.050378000	-1.855711000
6	-0.079829000	3.192842000	-2.849202000
1	-1.075140000	3.628162000	-2.949308000
1	0.273179000	2.839161000	-3.822188000
1	0.619649000	3.963293000	-2.506485000
6	0.076376000	2.049155000	1.853859000
6	0.098849000	3.167014000	2.874827000
1	-0.727905000	3.856576000	2.677788000
1	1.045406000	3.708700000	2.851529000
1	-0.057003000	2.745395000	3.873202000
6	2.026413000	-1.516119000	-1.234594000
1	1.264662000	-1.542816000	-2.012675000
6	2.118698000	-2.758114000	-0.349102000
1	3.148153000	-3.129541000	-0.350424000
1	1.507885000	-3.557679000	-0.780410000
6	1.644538000	-2.476634000	1.096050000
1	0.570272000	-2.663226000	1.157733000
1	2.122565000	-3.172221000	1.801815000
6	1.877725000	-1.038449000	1.526398000
1	1.183250000	-0.675056000	2.284965000
6	3.088221000	-0.333085000	1.371119000
1	3.236771000	0.545045000	1.998271000
6	4.354192000	-0.944935000	0.775815000
1	4.378072000	-2.018906000	0.985575000
1	5.230336000	-0.516212000	1.272786000
6	4.452243000	-0.686153000	-0.745515000
1	4.948646000	0.276532000	-0.911442000
1	5.082372000	-1.448243000	-1.228063000
6	3.093064000	-0.613335000	-1.421358000
1	3.072846000	-0.008035000	-2.327683000
8	-0.989059000	1.357652000	1.796859000
8	1.113634000	1.875334000	1.149976000
8	-1.113041000	1.874841000	-1.156560000
8	0.989050000	1.353239000	-1.802083000
45	1.683956000	0.274679000	-0.120569000
45	-1.685426000	0.277636000	0.116819000

$[Rh(COD)(O_2CCH_3)]$

E = -651.24241077
$G_{298,1M}$ = -651.044226

6	2.792034000	-0.000354000	0.008237000
6	4.292339000	0.005529000	-0.008919000
1	4.662818000	-1.022467000	0.046800000
1	4.689378000	0.592069000	0.820805000
1	4.638220000	0.429886000	-0.957512000
6	-1.216123000	-0.387552000	-1.473870000

1	-0.681243000	-0.440777000	-2.422457000
6	-2.367468000	0.614284000	-1.424271000
1	-3.270316000	0.119106000	-1.055060000
1	-2.595864000	0.951060000	-2.440326000
6	-2.021585000	1.838341000	-0.544418000
1	-1.514914000	2.589754000	-1.159865000
1	-2.938284000	2.313475000	-0.165341000
6	-1.087744000	1.491226000	0.601803000
1	-0.479232000	2.326461000	0.953959000
6	-1.225144000	0.389486000	1.470261000
1	-0.697486000	0.440298000	2.423017000
6	-2.381364000	-0.606184000	1.412018000
1	-3.278893000	-0.106353000	1.036124000
1	-2.619185000	-0.941899000	2.426254000
6	-2.035281000	-1.832077000	0.534743000
1	-1.536971000	-2.585976000	1.153938000
1	-2.951563000	-2.302476000	0.148818000
6	-1.091189000	-1.490003000	-0.604548000
1	-0.484043000	-2.328200000	-0.951931000
8	2.142938000	-0.710579000	-0.837047000
8	2.140589000	0.704706000	0.854373000
45	0.285301000	-0.002737000	0.003954000

$[Rh(COD)(O_2CCH_3)_2]^-$

E = -879.879101441

$G_{298,1M}$ = -879.641914

6	1.985917000	-2.093990000	-0.027643000
6	3.144644000	-2.838624000	0.637797000
1	3.538599000	-3.616795000	-0.020119000
1	2.821675000	-3.284217000	1.584096000
1	3.946461000	-2.128553000	0.870853000
6	1.985861000	2.093981000	0.027641000
6	3.144281000	2.839021000	-0.637869000
1	3.537840000	3.617462000	0.019962000
1	2.821167000	3.284332000	-1.584251000
1	3.946450000	2.129290000	-0.870757000
6	-1.604280000	-1.523353000	0.140871000
1	-1.081320000	-2.473986000	0.045944000
6	-2.759217000	-1.305451000	-0.834962000
1	-3.662580000	-1.022314000	-0.284055000
1	-2.994131000	-2.249563000	-1.338135000
6	-2.415230000	-0.233514000	-1.896017000
1	-1.907011000	-0.720670000	-2.736113000
1	-3.333729000	0.214734000	-2.306013000
6	-1.474749000	0.839021000	-1.367933000
1	-0.869069000	1.319876000	-2.137243000
6	-1.604218000	1.523352000	-0.140881000
1	-1.081267000	2.473991000	-0.045951000
6	-2.759185000	1.305476000	0.834930000
1	-3.662538000	1.022357000	0.283998000
1	-2.994091000	2.249595000	1.338092000
6	-2.415258000	0.233531000	1.895998000
1	-1.907032000	0.720672000	2.736099000
1	-3.333780000	-0.214678000	2.305983000
6	-1.474808000	-0.839035000	1.367930000
1	-0.869125000	-1.319897000	2.137232000
8	1.720569000	2.295456000	1.223554000
8	1.375292000	1.276330000	-0.767030000
8	1.720626000	-2.295487000	-1.223544000
8	1.375113000	-1.276573000	0.767114000
45	-0.110486000	-0.000043000	0.000010000

$[Rh(COD)(O_2CCH_3)_2]^-\cdots CH_2Cl_2$

E = -1839.59660324

$G_{298,1M}$ = -1839.335797

6	-0.849597000	2.178517000	-0.663475000
6	-1.617629000	3.154014000	-1.552830000
1	-2.492803000	3.546376000	-1.030817000
1	-1.932467000	2.657463000	-2.475935000
1	-0.964424000	3.987059000	-1.836748000
6	-0.885887000	-2.101768000	-0.613393000
6	-1.641244000	-3.081551000	-1.509957000
1	-2.538011000	-3.449746000	-1.006582000
1	-0.989811000	-3.936889000	-1.728097000
1	-1.911157000	-2.618628000	-2.462611000
6	2.943475000	1.319028000	-0.172525000
1	2.823869000	2.077064000	-0.946412000
6	4.261647000	0.546281000	-0.209873000
1	4.732643000	0.569018000	0.778137000
1	4.958328000	1.049449000	-0.889247000
6	4.056126000	-0.913746000	-0.676634000
1	4.101704000	-0.944774000	-1.771457000
1	4.874958000	-1.554569000	-0.314271000
6	2.703295000	-1.475741000	-0.268675000
1	2.334809000	-2.272601000	-0.915046000
6	2.116880000	-1.367700000	1.008031000
1	1.310837000	-2.058318000	1.245854000
6	2.792613000	-0.699684000	2.203886000
1	3.879550000	-0.806266000	2.125064000
1	2.502171000	-1.223593000	3.121063000
6	2.401307000	0.792432000	2.323545000
1	1.473592000	0.867354000	2.902234000
1	3.165816000	1.348680000	2.888015000
6	2.135340000	1.444188000	0.975970000
1	1.451179000	2.290697000	1.015853000
8	-1.072242000	-2.125752000	0.618754000
8	-0.072413000	-1.327026000	-1.245800000
8	-1.180253000	2.030893000	0.528956000
8	0.127752000	1.583289000	-1.256630000
45	1.234072000	0.049157000	-0.328655000
6	-3.419699000	-0.030310000	0.753639000
1	-2.843644000	0.883770000	0.895452000
1	-2.825554000	-0.924843000	0.937829000
17	-3.939145000	-0.068334000	-0.975413000
17	-4.828345000	-0.024241000	1.887690000

$[Rh(COD)(O_2CCH_3)_3]^{2-}$

E = -1108.46216541

$G_{298,1M}$ = -1108.177332

6	0.973570000	2.029430000	-1.609426000
6	0.637764000	3.477426000	-1.992235000
1	-0.001625000	3.510239000	-2.878063000
1	1.557883000	4.040093000	-2.184076000
1	0.126208000	3.971400000	-1.158657000
6	-0.628358000	-0.582281000	1.408642000
6	-1.833724000	-0.216099000	2.303979000
1	-2.295304000	0.709665000	1.940219000
1	-1.502849000	-0.024754000	3.330937000
1	-2.588777000	-1.007991000	2.305971000

6	2.629787000	-1.017051000	-1.193662000
1	1.824592000	-0.780998000	-1.884782000
6	2.756693000	-2.494967000	-0.807406000
1	3.753408000	-2.874978000	-1.066871000
1	2.048865000	-3.089078000	-1.397503000
6	2.461188000	-2.709051000	0.696503000
1	1.380912000	-2.831090000	0.814599000
1	2.948405000	-3.624823000	1.070965000
6	2.841547000	-1.500010000	1.538731000
1	2.264551000	-1.385187000	2.455770000
6	4.060978000	-0.799820000	1.448294000
1	4.325690000	-0.159316000	2.286211000
6	5.223152000	-1.223068000	0.548928000
1	5.199116000	-2.307857000	0.398394000
1	6.170257000	-1.009472000	1.058149000
6	5.171189000	-0.486420000	-0.805148000
1	5.755563000	0.439141000	-0.735045000
1	5.647071000	-1.087836000	-1.597769000
6	3.743044000	-0.103974000	-1.172446000
1	3.685174000	0.735558000	-1.868607000
8	-0.721214000	-1.617311000	0.709110000
8	0.339645000	0.244242000	1.479252000
8	0.468202000	1.094675000	-2.250395000
8	1.781458000	1.956427000	-0.606754000
45	2.501798000	0.277882000	0.442857000
6	3.549971000	2.700886000	2.275899000
6	4.412939000	3.023545000	1.045915000
1	4.968407000	3.954468000	1.193954000
1	3.783864000	3.092156000	0.154739000
1	5.123878000	2.205410000	0.877808000
8	3.670315000	3.411376000	3.293962000
8	2.757012000	1.695488000	2.176663000