Rapid Markovnikov Addition of HCl to a Pendant Alkyne: Evidence for a Quinoidal Cumulene

Samantha G. Eaves,[a,b] Sam J. Hart,[c] Adrian C Whitwood,[c] Dmitry S. Yufit,[a] Paul J. Low[b] and Jason M. Lynam[c]

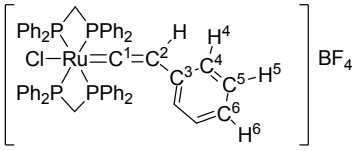
[a] Department of Chemistry, Durham University, South Road, Durham DH1 3LE, UK.
[b] School of Chemistry and Biochemistry, Bayliss Building, The University of Western Australia, 35 Stirling Highway Crawley, Perth Western Australia 6009, e-mail paul.low@uwa.edu.au tel (+61 8) 6488 3045
[c] Department of Chemistry, University of York, Heslington, York, YO10 5DD, e-mail jason.lynam@york.ac.uk tel +44(0)1904322534

S1 General Conditions

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Dichloromethane was dried over CaH_2, all other solvents were standard reagent grade and used as received. No special precautions were taken to exclude air or moisture during workup. *Cis*-$RuCl_2(dppm)_2$[1,2,3] were synthesised by literature methods. All other reagents were commercially available and used as received. NMR spectra were recorded at 25 ºC either on a Jeol 400 (399.78 MHz, ^{13}C 100.53 MHz, ^{19}F 376.17 MHz), Bruker AV500 (500.23 MHz, ^{31}P 202.50 MHz, ^{13}C 125.77 MHz), Bruker Avance 600 (^{1}H, 600.1 MHz; ^{13}C, 150.9 MHz; ^{19}F, 564.6 MHz; ^{31}P, 242.9 MHz) or a Varian Inova 300 (^{1}H, 300.2 MHz; ^{13}C, 75.5 MHz) spectrometer using $CDCl_3$ or CD_2Cl_2 as the solvent. Chemical shifts were determined relative to internal residual solvent signals (^{1}H, ^{13}C),[14] or external 85% H_3PO_4 (^{31}P $\delta = 0.0$ ppm). FT-IR spectra were measured on an Agilent Technologies Cary 660 spectrometer or a Nicolet Avatar 360 spectrometer from solutions in dichloromethane in a thin layer cell fitted with CaF_2 windows. ESI-MS and APCI-MS were recorded on a Waters LCT Premier XE mass spectrometer in positive or negative mode from solutions in methanol. Elemental analyses were performed at the London Metropolitan University.

S2 Synthesis of Ruthenium Complexes

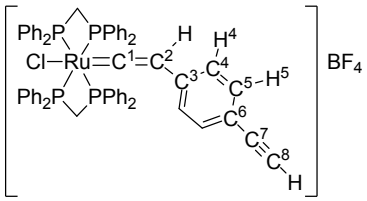
S2.1 Synthesis of *trans*-[RuCl(=C=C(H)C_6H_5)(dppm)$_2$]BF_4



cis-$RuCl_2$(dppm)$_2$ (0.11 g, 0.11 mmol) and $TlBF_4$ (0.038 g, 0.13 mmol) were added to dry degassed CH_2Cl_2 (4 ml) and stirred under N_2 for 30 minutes. The solution colour changed from clear yellow to red with a white precipitate observed (TlCl). The solution was then transferred to a separate dry degassed flask via cannular filtration, phenylacetylene (20 μL, 0.18 mmol) added, and stirred for a further hour under N_2. The solution colour changed from red to orange. The solution is then concentration under high vacuum (to *c.a.* 2 ml) and filtered into vigorously stirred hexane, where the instant precipitation of a pale yellow / brown solid was observed. The solid was then collected by filtration, washed with hexane (2 × 10 ml) and ether (2 × 10 ml) then dried in air (0.072 g, 59 %).

IR (CH_2Cl_2, cm^{-1}): 1605m ν(Ru=C=C). ^{1}H NMR (CD_2Cl_2, 400 MHz) δ / ppm: 3.10 (quin., J = 3 Hz, C=CH, 1H), 5.22 (dm, J = 100 Hz, CH_2, dppm), 5.56 (d, J = 8 Hz, 2H, H^4), 6.79 (t, J = 8 Hz, 2H, H^5), 6.92 (t, J = 8 Hz, 1H, H^6), 7.22 – 7.32 (m, 16H, H_m, dppm), 7.32 – 7.42 (m, 16H, H_o, dppm), 7.48 (t, J = 8 Hz, 8H, H_p, dppm). ^{19}F NMR (CD_2Cl_2, 400 MHz) δ / ppm: - 152.8 (s, BF_4). ^{31}P NMR (CD_2Cl_2, 400 MHz) δ / ppm: - 15.4 (s, dppm). ^{13}C NMR (CD_2Cl_2, 400 MHz) δ / ppm: 46.7 (t, J = 12 Hz, CH_2, dppm), 111.1 (s, C^2), 126.9 (s, C^3), 127.9 (s, C^4), 129.7 (dm, J = 58 Hz, C_m, dppm), 132.14 (s, C^6), 132.4 (s, C^5), 132.4 (d, J = 42 Hz, C_p, dppm), 133.5 (dquin., J = 115, 3 Hz, C_o, dppm), 133.7 (dm, J = 96 Hz, C_i, dppm), 358.2 (s, C^1). ESI (+)-MS (m/z): 1007 [RuCl(=C=C(H)C_6H_5)(dppm)$_2$]$^+$. ESI (-)-MS (m/z): 87 BF_4^-. Anal. Found: C, 63.01; H, 4.55. Calc. for $C_{58}H_{50}BClF_4P_4Ru$: C, 63.67; H, 4.52.

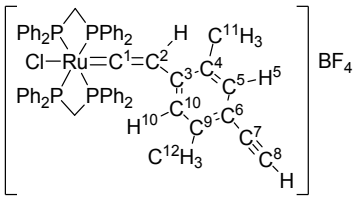
S2.2 Synthesis of *trans*-[RuCl(=C=C(H)C_6H_4-4-C≡CH)$(dppm)_2$]BF_4 [1a]BF_4



cis-$RuCl_2(dppm)_2$ (0.11 g, 0.11 mmol), $TlBF_4$ (0.034 g, 0.12 mmol) and *p*-HC≡CC_6H_4C≡CH (0.085 g, 0.67 mmol) were added to dry degassed CH_2Cl_2 (6 ml) and stirred under N_2 for 80 minutes. The solution colour changed from clear yellow to dark orange with a white precipitate observed (TlCl). The solution was then filtered through a HPLC Teflon filter (-TlCl) and the orange filtrate concentrated to *c.a.* 2 mls. Excess ether (*c.a.* 15 mls) is then added to the filtrate, resulting in the instantaneous precipitation of a pale brown solid. The solid is collected by filtration, washed with ether (3 × 10 ml) and hexane (2 × 10 ml) and dried in air (0.11 g, 87 %).

IR (CH_2Cl_2, cm^{-1}): 1641m ν(Ru=C=C), 2074s (C≡C), 3296s (C≡C-H). ^{1}H NMR ($CDCl_3$, 600 MHz) δ / ppm: 3.04 (s, 1H, C≡CH), 3.07 (quin, J = 3 Hz, 1H, C=CH), 5.38 (dm, J = 82 Hz, CH_2, dppm), 5.46 (d, J = 8 Hz, 2H, H^4), 6.84 (d, J = 8 Hz, 2H, H^5), 7.20 – 7.26 (m, J = 7 Hz, 16H, H_m, dppm), 7.32 – 7.38 (m, 8H, H_p, dppm), 7.39 – 7.46 (m, 16H, H_o, dppm). ^{31}P NMR ($CDCl_3$, 300 MHz) δ / ppm: - 15.3 (s, dppm). ^{19}F NMR ($CDCl_3$, 400 MHz) δ / ppm: - 153.2 (s, BF_4). ^{13}C NMR ($CDCl_3$, 600 MHz) δ / ppm: 46.5 (quin., J = 13 Hz, CH_2, dppm), 83.6 (s, C^7), 110.1 (s, C^8), 112.5 (s, C^2), 119.3 (s, C^3), 127.9 (s, C^5), 126.9 (m, C^4), 128.9 (dm, J = 89 Hz, C_m, dppm), 131.6 (d, J = 43 Hz, C_p, dppm), 130.7 – 131.3 (m, C_i, dppm), 131.9 (s, C^6), 133.0 (dm, J = 145 Hz, C_o, dppm), 356.2 (m, C^1). ESI (+)-MS (m/z): 1031 [RuCl(=C=C(H)C_6H_4C≡CH)$(dppm)_2]^+$, 995 [Ru(=C=C(H)C_6H_4C≡CH)$(dppm)_2]^+$, 906 [RuCl$(dppm)_2$ + H]$^+$. Anal. Found: C, 64.35; H, 4.58. Calc. for $C_{60}H_{50}BClF_4P_4Ru$: C, 64.39; H, 4.51.

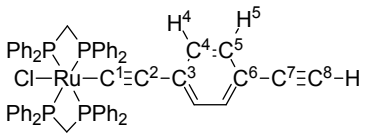
S2.3 Synthesis of *trans*-[RuCl(=C=C(H)C_6H_2-3,5-Me_2-4-C≡CH)$(dppm)_2$]BF_4 [1b]BF_4



cis-$RuCl_2(dppm)_2$ (0.13 g, 0.13 mmol), $TlBF_4$ (0.040 g, 0.13 mmol) and *p*-HC≡CC_6H_2-2,5-Me_2-4-C≡CH (0.17 g, 1.1 mmol) were added to dry degassed CH_2Cl_2 (6 ml) and stirred under N_2 for 80 minutes. The solution colour changed from clear yellow to dark orange with a white precipitate observed (TlCl). The solution was then filtered through a HPLC Teflon filter and the orange filtrate concentrated to *c.a.* 2 mls. Excess ether (*c.a.* 20 mls) is then added to the filtrate, resulting in the instantaneous precipitation of a pale brown solid. The solid is collected by filtration, washed with ether (3 × 10 ml) and hexane (2 × 10 ml) and dried in air (0.10 g, 67 %).

IR (CH_2Cl_2, cm^{-1}): 1636m ν(Ru=C=C), 2099s (C≡C), 3299m (C≡C-H). ^{1}H NMR ($CDCl_3$, 600 MHz) δ / ppm: 1.32 (s, 3H, $C^{11}H_3$), 1.75 (s, 3H, $C^{12}H_3$), 3.18 (s, 1H, C≡CH), 3.46 (quin, J = 3 Hz, 1H, C=CH), 5.26 (dm, J = 94 Hz, CH_2, dppm), 5.46 (s, 1H, H^{10}), 6.97 (s, 1H, H^5), 7.18 – 7.26 (m, 16H, H_m, dppm), 7.35 – 7.44 (m, 8H, H_p, dppm), 7.39 (dm, J = 44 Hz, H_o, dppm). ^{31}P NMR ($CDCl_3$, 300 MHz) δ / ppm: - 14.4 (s, dppm). ^{13}C NMR ($CDCl_3$, 600 MHz) δ / ppm: 17.9 (s, $C^{11}H_3$), 19.3 (s, $C^{12}H_3$), 45.6 – 46.3 (m, CH_2, dppm), 81.5 (s, C^7), 105.0 (s, C^2), 106.5 (s, C^8), 118.6 (s, C^9), 125.0 (s, C^4), 128.2 – 129.6 (m, C_m, dppm), 128.7 (s, C^3), 130.4 – 132.2 (m, C_p, dppm), 130.9 (s, C^{10}), 133.2 (s, C^5), 133.5 (dm, J = 163 Hz, C_o, dppm), 354.7 (s, C^1). APCI (+)-MS (m/z): 1059 [RuCl(=C=C(H)$C_6H_2Me_2$C≡CH)$(dppm)_2]^+$, 1024 [Ru(C≡$CC_6H_2Me_2$C≡CH)$(dppm)_2]^+$, 905 [RuCl$(dppm)_2]^+$. Anal. Found: C, 64.93; H, 4.79. Calc. for $C_{62}H_{54}BClF_4P_4Ru$: C, 64.91; H, 4.75.

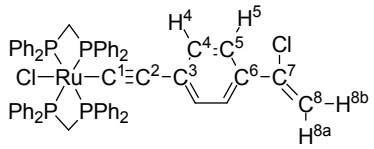
S2.4 Synthesis of *trans*-[RuCl(C≡CC$_6$H$_4$-4-C≡CH)(dppm)$_2$], [5a]



Trans-[RuCl(=C=C(H)C$_6$H$_4$-4-C≡CH)(dppm)$_2$]BF$_4$ (0.070 g, 0.063 mmol) and Proton Sponge (0.050 g, 0.20 mmol) were added to dry degassed CH_2Cl_2 (3 ml) and stirred under N_2 for 2 hrs. The orange solution colour lightened over time. The solution was then concentrated (*c.a.* 0.5 ml), filtered through a very short, basic alumina plug (oven-dried) into vigorously stirred hexane, where a pale orange / brown precipitate formed instantly. The precipitate is collected by filtration and washed with hexane (5 × 10 ml). The solid is then extracted with ether, filtered and filtrate concentrated to dryness yielding a brown solid (0.056 g, 86 %).

IR (CH_2Cl_2, cm^{-1}): 2075m ν(C≡C), 2040s ν(C≡C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ / ppm: 3.05 (s, 1H, C≡CH), 4.91 (quin., J = 4 Hz, 4H, CH_2, dppm), 5.95 (d, J = 8 Hz, 2H, H^4), 7.01 (d, J = 8 Hz, 2H, H^5), 7.11 (dt, J = 32, 8 Hz, 16H, H$_m$, dppm), 7.25 (dt, J = 16, 8 Hz, 8H, H$_p$, dppm), 7.35 – 7.53 (m, 16H, H$_o$, dppm). ^{31}P NMR ($CDCl_3$, 300 MHz) δ / ppm: - 5.4 ppm (s, dppm). ^{13}C NMR ($CDCl_3$, 600 MHz) δ / ppm: 50.5 (quin., J = 10 Hz, CH_2, dppm), 85.2 (s, C^8), 113.1 (s, C^2), 115.0 (s, C^7), 127.7 (s, C$_m$, dppm), 129.4 (d, J = 32 Hz, C$_p$, dppm), 130.1 (s, C^4), 131.0 (s, C^5), 131.4 (s, C^6), 133.7 (d, J = 55 Hz, C$_o$, dppm), 134.7 (dquin., J = 120, 11 Hz, C$_i$, dppm). APCI (+)-MS (m/z): 1031 [RuCl(C≡CC$_6$H$_4$C≡CH)(dppm)$_2$ + H]$^+$, 995 [Ru(C≡CC$_6$H$_4$C≡CH)(dppm)$_2$]$^+$. Anal. Found: C, 69.87; H, 4.86. Calc. for $C_{60}H_{49}ClP_4Ru$: C, 69.90; H, 4.79.

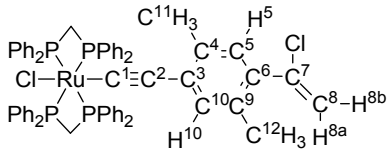
S2.5 Synthesis of *trans*-[RuCl(C≡C-C_6H_4-4-CCl=CH_2)(dppm)$_2$], [6a]



[RuCl(=C=C(H)C_6H_4-4-C≡CH)(dppm)$_2$]BF_4 (0.055 g, 0.049 mmol) and [N^nBu_4]Cl (0.018 g, 0.063 mmol) were added to a dry degassed schlenk containing dry degassed CH_2Cl_2 (4 ml) and the solution stirred under N_2 for 1 hour. The orange solution colour lightened over the reaction period. The solvent is then removed under high vacuum leaving a brown / orange residue. The residue is extracted with minimum CH_2Cl_2 and filtered through a short pad of alumina (basic, oven-dried), eluting with CH_2Cl_2. The first orange band is collected and concentrated to dryness by rotary evaporation, yielding a brown residue. The residue is extracted with ether and filtered, until extracts are colourless. The orange filtrate is concentrated to dryness by rotary evaporation, yielding a red / orange solid, which is then washed with minimum, cold MeOH (2 × 5 ml) and dried under vacuum (0.039 g, 74 %). Single crystals, suitable for X-ray crystallography, may be grown by CH_2Cl_2 / pentane layer diffusion.

IR (CH_2Cl_2, cm^{-1}): 1591s ν(C=C), 2074m ν(C≡C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ / ppm: 4.89 (quin., J = 4 Hz, 4H, CH_2, dppm), 5.33 (d, J = 1.5 Hz, 1H, H^{8a}), 5.60 (d, J = 1.5 Hz, 1H, H^{8b}), 6.01 (d, J = 8 Hz, 2H, H^4), 7.11 (dt, J = 28, 8 Hz, 16H, H_m, dppm), 7.20 (d, J = 8 Hz, 2H, H^5), 7.26 (dt, J = 25, 7 Hz, 8H, H_p, dppm), 7.34 – 7.55 (m, 16H, H_o, dppm). ^{31}P NMR ($CDCl_3$, 300 MHz) δ / ppm: - 5.4 ppm (s, dppm). ^{13}C NMR ($CDCl_3$, 600 MHz) δ / ppm: 50.4 (quin., J = 9 Hz, CH_2, dppm), 110.0 (s, C^8), 112.9 (s, C^2), 125.1 (s, C^5), 127.7 (s, C_m, dppm), 129.4 (d, J = 29 Hz, C_p, dppm), 129.9 (s, C^4), 130.3 (s, C^6), 133.7 (d, J = 57 Hz, C_o, dppm), 134.7 (dm, J = 122 Hz, C_i, dppm), 140.7 (s, C^7). APCI (+)-MS (m/z): 1067 [RuCl(C≡C-C_6H_4CCl=CH_2)(dppm)$_2$ + H]$^+$, 1031 [Ru(C≡C-C_6H_4CCl=CH_2)(dppm)$_2$]$^+$, 905 [RuCl(dppm)$_2$]$^+$. Anal. Found: C, 65.97; H, 4.70. Calc. for $C_{60}H_{50}Cl_2P_4Ru$: C, 67.53; H, 4.73.

S2.6 Synthesis of *trans*-[RuCl(C≡CC$_6$H$_2$-2,5-Me$_2$-4-CCl=CH$_2$)(dppm)$_2$] [6b]



[RuCl(=C=C(H)C$_6$H$_4$-2,5-Me$_2$-4-C≡CH)(dppm)$_2$]BF$_4$ (0.017 g, 0.015 mmol) and [N^{n}Bu$_4$]Cl (0.005 g, 0.018 mmol) were added to a dry degassed schlenk containing dry degassed CH_2Cl_2 (5 ml) and the solution stirred under N_2 for 1 hour. The orange solution colour lightened over the reaction period. The solvent is then removed under high vacuum leaving an orange residue. The residue is extracted with ether and filtered through a short pad of alumina (basic, oven-dried), until extracts are colourless. The yellow filtrate is concentrated to dryness by rotary evaporation, yielding a yellow solid (0.015 g, 92 %). Single crystals, suitable for X-ray crystallography, may be grown by CH_2Cl_2 / hexane layer diffusion.

IR (CH_2Cl_2, cm^{-1}): 1597s ν(C=C), 2065m ν(C≡C). ^{1}H NMR (CD_2Cl_2, 400 MHz) δ / ppm: 1.24 (s, 3H, C^{11}H$_3$), 2.10 (s, 3H, C^{12}H$_3$), 4.89 – 5.08 (m, 4H, CH_2, dppm), 5.23 (d, J = 1.5 Hz, 1H, H^{8a}), 5.52 (d, J = 1.5 Hz, 1H, H^{8b}), 5.63 (s, 1H, H^{10}), 6.74 (s, 1H, H^5), 7.18 (dt, J = 34, 8 Hz, 16H, H$_m$, dppm), 7.31 (dt, J = 18, 7 Hz, 8H, H$_p$, dppm), 7.56 (dm, J = 28 Hz, 16H, H$_o$, dppm). ^{31}P NMR ($CDCl_3$, 400 MHz) δ / ppm: - 6.0 ppm (s, dppm). ^{13}C NMR (CD_2Cl_2, 400 MHz) δ / ppm: 17.9 (s, C^{12}H$_3$), 18.2 (s, C^{11}H$_3$), 48.6 (t, J = 11 Hz, CH_2, dppm), 111.9 (s, C^2), 114.2 (s, C^8), 126.6 (dquin., J = 20, 2 Hz, C$_m$, dppm), 128.3 (s, C$_p$, dppm), 129.3 (s, C^5), 131.0 (s, C^4), 131.4 (s, C^9), 132.3 (dquin., J = 14, 3 Hz, C$_o$, dppm), 132.7 (s, C^6), 134.2 (dquin., J = 85, 11 Hz, C$_i$, dppm), 134.3 (s, C^{10}), 135.3 (s, C^3), 139.4 (s, C^7), 146.8 (t, J = 19 Hz, C^1). ESI (+)-MS (m/z): 1095 [RuCl(C≡C-C$_6$H$_2$Me$_2$CCl=CH$_2$)(dppm)$_2$ + H]$^+$, 905 [RuCl(dppm)$_2$]$^+$, 871 [Ru(dppm)$_2$ + H$^+$]$^+$. Anal. Found: C, 68.10; H, 4.87. Calc. for $C_{62}H_{54}Cl_2P_4Ru$: C, 68.01; H, 4.94.

S3 NMR Data of [6]

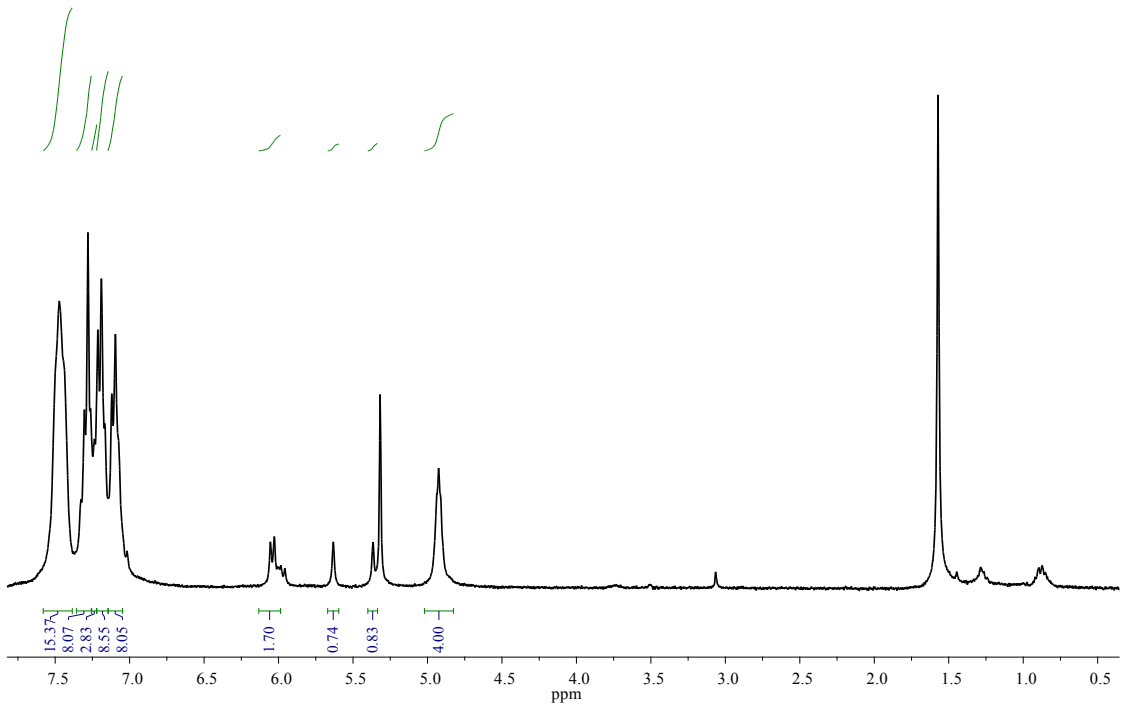


Figure S1: ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of [**6a**].

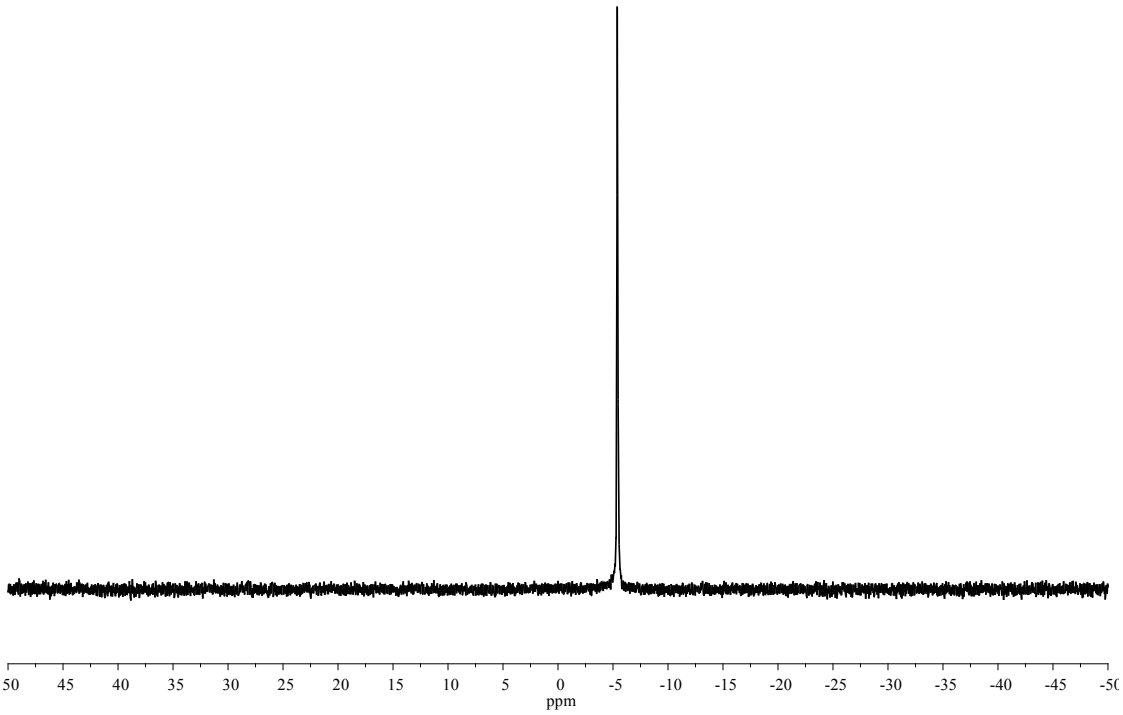


Figure S2: ^{31}P NMR ($CDCl_3$, 300 MHz) spectrum of [**6a**].

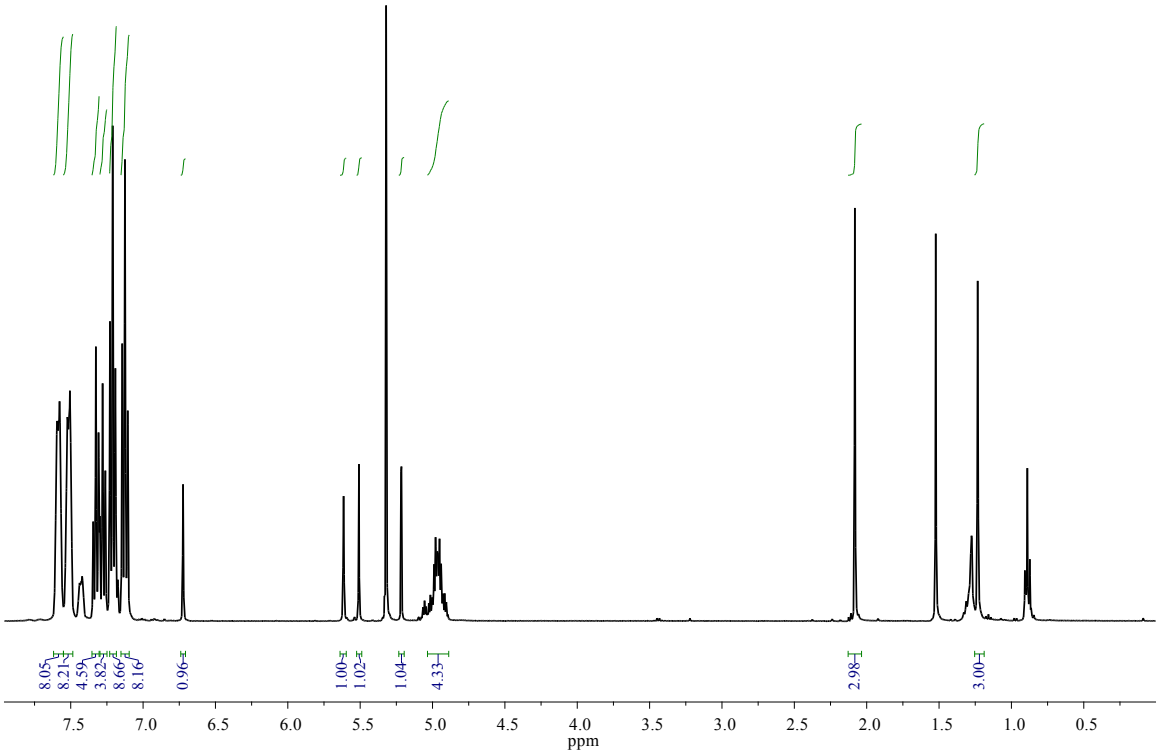


Figure S3: ^{1}H NMR (CD_2Cl_2, 400 MHz) spectrum of [**6b**].

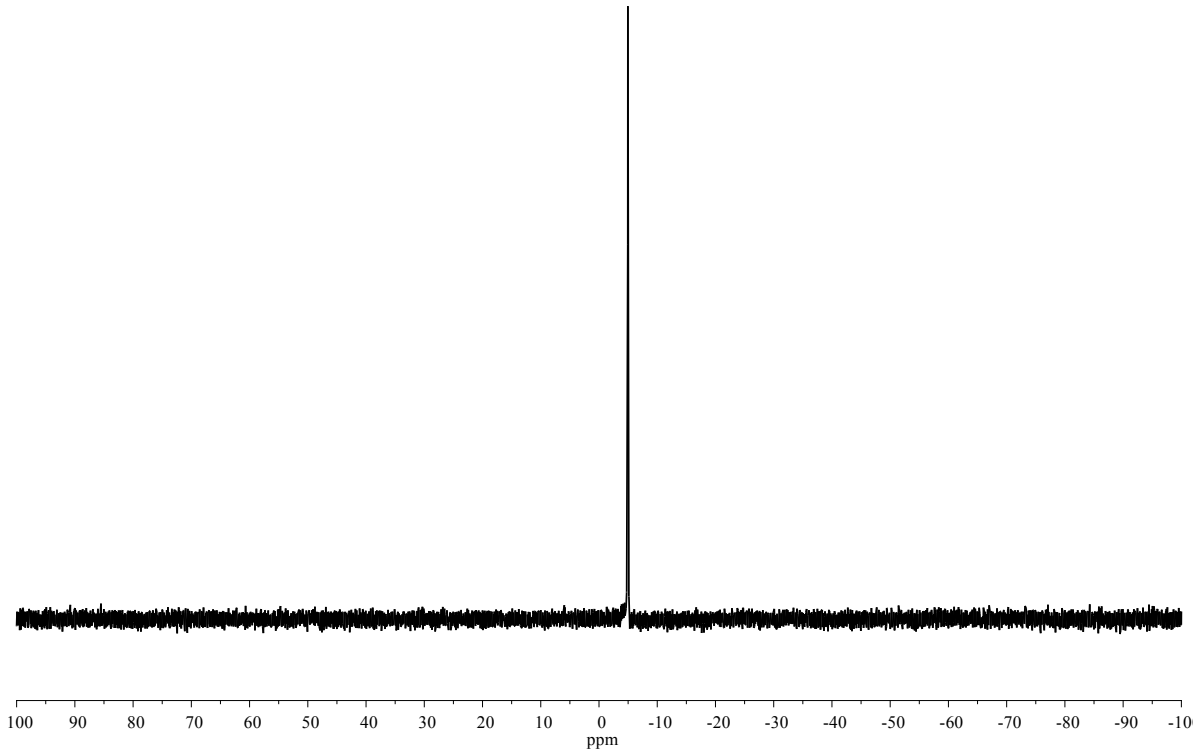


Figure S4: ^{31}P NMR (CD_2Cl_2, 400 MHz) spectrum of [**6b**].

S4 NMR Monitoring Reactions

Reaction 1: $[RuCl(C{=}CHPh)(dppm)_2]BF_4$ and $[N^nBu_4]Cl$

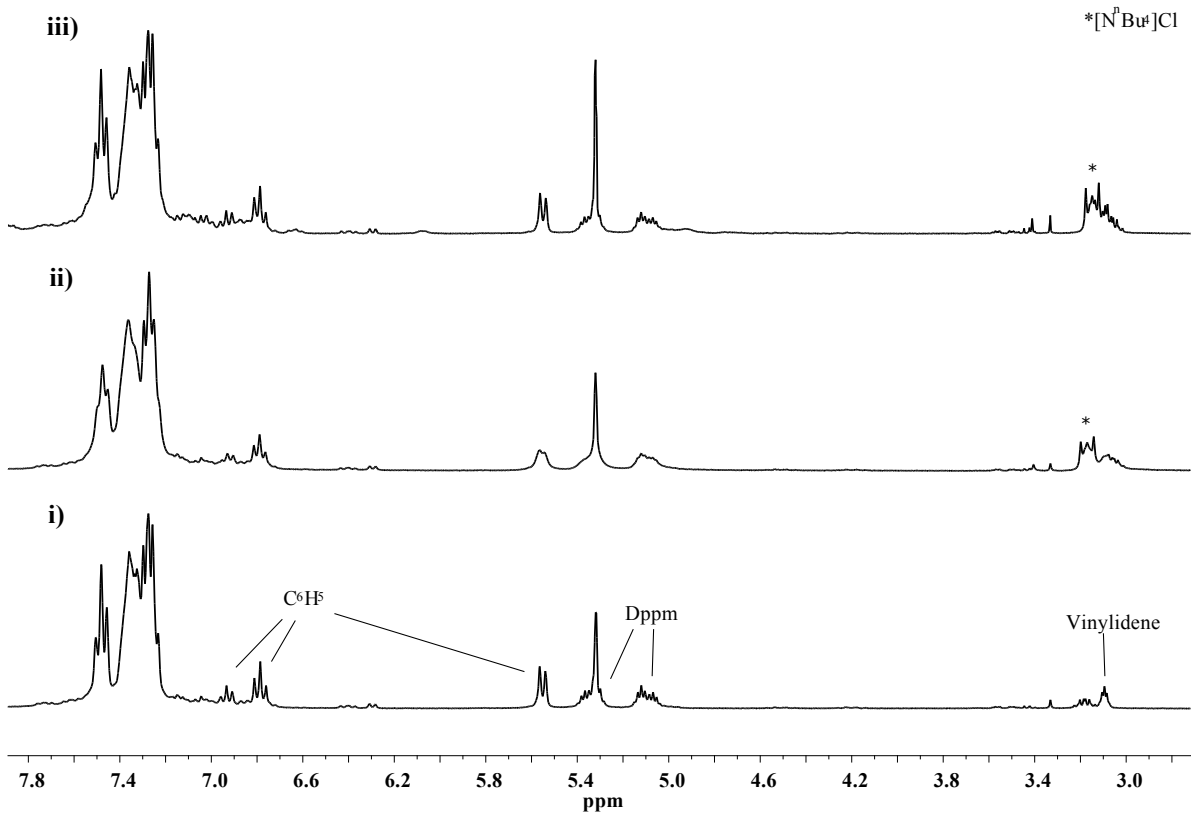


Figure S5: Reaction monitoring using ^1H NMR spectroscopy (300 MHz, CD_2Cl_2) where i) $[RuCl(C{=}CHPh)(dppm)_2]BF_4$ ii) + $[N^nBu_4]Cl$, 15m and iii) 15hrs.

Reaction 2: *i) trans*-[Ru(C≡C-C_6H_4-4-C≡CH)Cl(dppm)$_2$] [**5a**] and [N^nBu_4]Cl followed by the addition of HBF_4

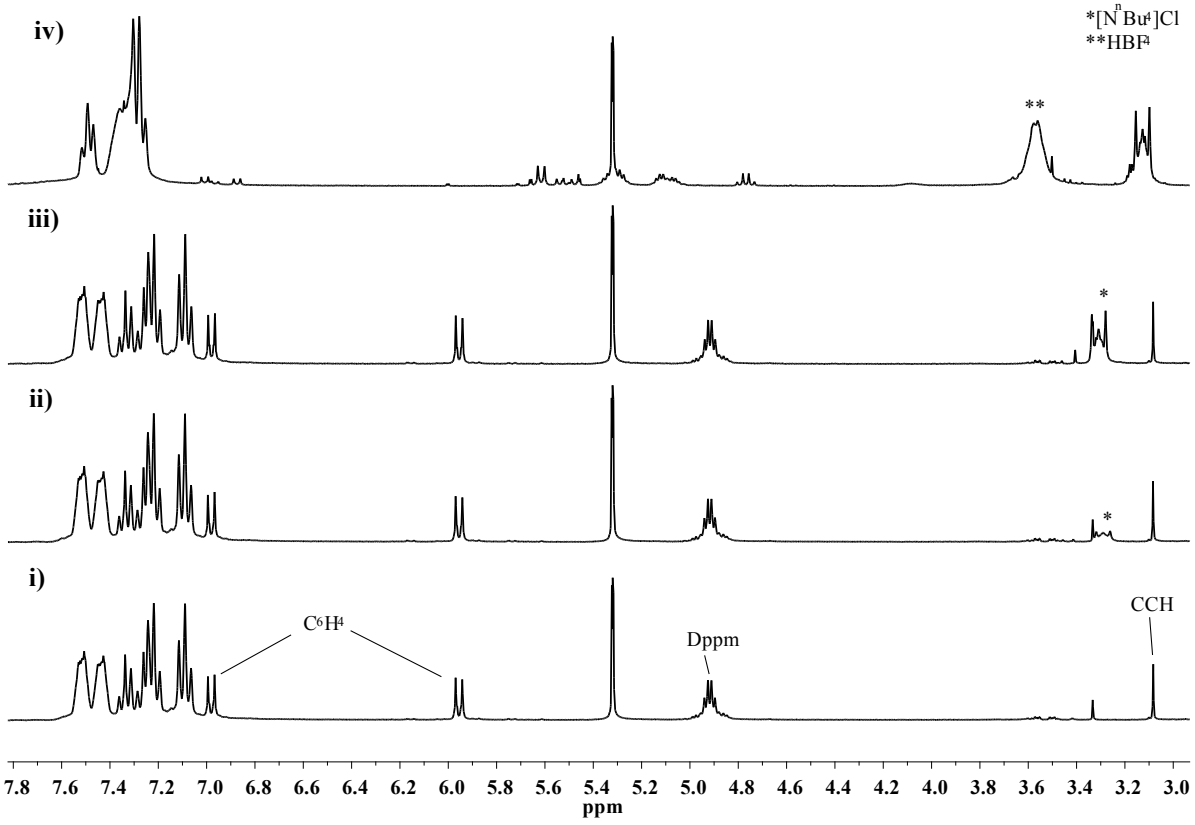


Figure S6: Reaction monitoring using ^{1}H NMR spectroscopy (300 MHz, CD_2Cl_2) where i) *trans*-[Ru(C≡C-C_6H_4-4-C≡CH)Cl(dppm)$_2$]; ii) + [N^nBu_4]Cl, 5m; iii) 3 hr 45m and iv) + HBF_4, 5m.

S5 Crystal Structure Analysis

S5.1 Structure of [6a]

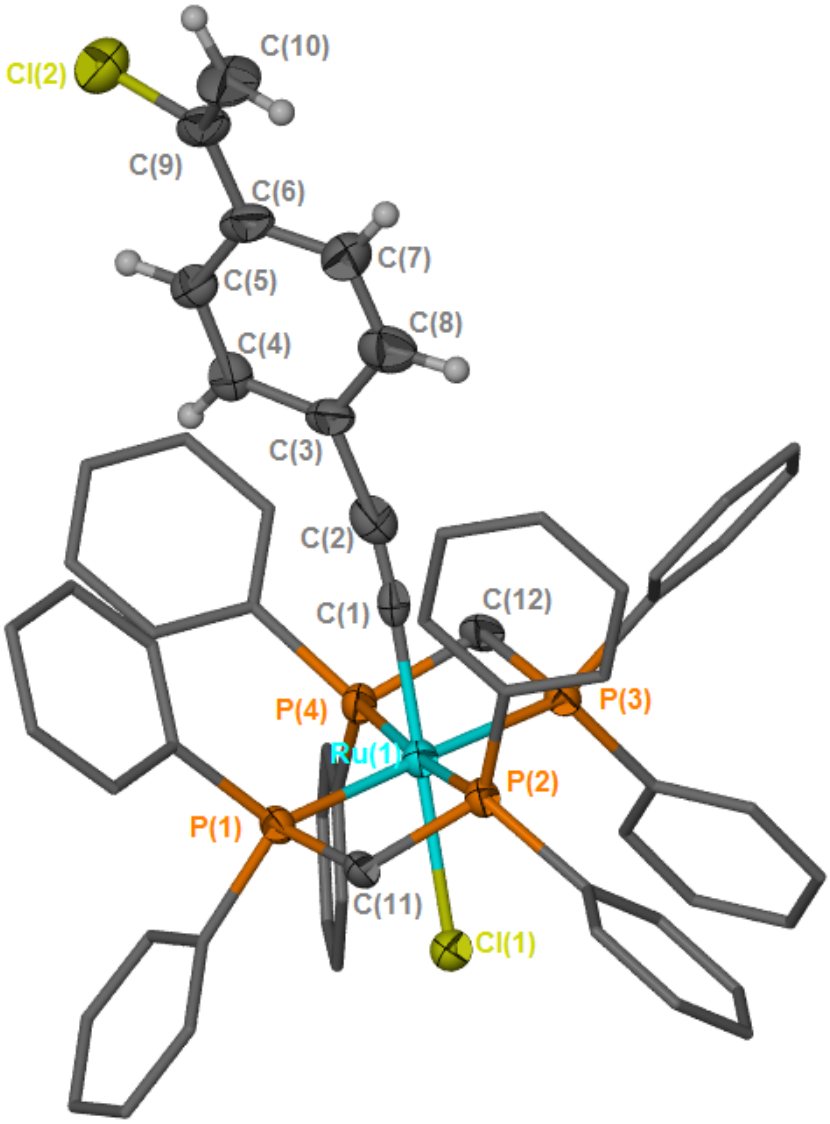


Figure S7 Solid state structure of [**6a**], solvent of crystallisation and selected hydrogen atoms removed for clarity. Anisotropic displacement parameters (where shown) are at the 50 % probability level.

The X-ray single crystal data for **[6a]** have been collected at 120.0 K on an Agilent XCalibur S-Ultra diffractometer (graphite monochromator, λMoKα, λ =0.71073 Å) equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostat. The structures was solved by direct method and refined by full-matrix least squares on F^2 for all data using Olex2[5] and SHELXTL[6] software. All non-disordered non-hydrogen atoms were refined anisotropically, hydrogen atoms were placed in the calculated positions and refined in riding mode. the phenyl rings of the *dppm* ligands have been refined as regular hexagons, the dichloromethane was disordered and modelled isotropically in four positions with equal occupancy..

CCDC Code	1029206
Empirical formula	$C_{62}H_{54}Cl_6P_4Ru$
Formula weight	1236.70
Temperature/K	120
Crystal system	Triclinic
Space group	P-1
a/Å	12.3129(7)
b/Å	14.9215(8),
c/Å	18.0053(11)
α/°	67.588(5)
β/°	85.054(5)
γ/°	78.028(5)
Volume/Å^3	2991.6(3)
Z	2
ρ_{calc} mg/mm^3	1.373
μ /mm^{-1}	0.675
F(000)	1264
Crystal size/mm^3	0.1711× 0.1442 × 0.0487
Radiation	Mo Kα (λ = 0.7107)
2Θ range for data collection/°	2.66-26.00
Index ranges	$-15 \leq h \leq 15$, $-18 \leq k \leq 18$, $-22 \leq l \leq 22$
Reflections collected	37868
Independent reflections	11752 unique (R_{int} =0.1584)
Data/restraints/parameters	11752/12/579
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0999 wR_2 = 0.2459
Final R indexes [all data]	R_1 = 0.1876 wR_2 0.3129
Largest diff. peak/hole / e Å^{-3}	1.856/-0.784

S5.2 Structure of [6b]

Single crystals of $C_{63.5}H_{57}Cl_5P_4Ru$ [**6b**] were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the complex.. A suitable crystal was selected and mounted in mineral oil on a cryoloop. Data were collected on an Oxford SuperNova Eos diffractometer using Mo-Kα radiation. The crystal was kept at 110.05(10) K during data collection. Using Olex2,[5] the structure was solved with the Superflip [7] structure solution program using Charge Flipping and refined with the ShelXL [6] refinement package using Least Squares minimisation. One of the dichloromethane molecules was disordered over a special position, and has been modelled in two positions with equal occupancy. One of the chlorines in this molecule was restrained to be approximately isotropic.

CCDC Code	1029207
Empirical formula	$C_{63.5}H_{57}Cl_5P_4Ru$
Formula weight	1222.29
Temperature/K	110.05(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.3506(3)
b/Å	12.3819(3)
c/Å	21.4222(5)
α/°	80.7264(18)
β/°	74.684(2)
γ/°	83.7147(19)
Volume/Å^3	2858.75(11)
Z	2
ρ_{calc}mg/mm^3	1.420
μ/mm^{-1}	0.660
F(000)	1254.0
Crystal size/mm^3	0.2714 × 0.2050 × 0.1432
Radiation	Mo Kα (λ = 0.7107)
2Θ range for data collection/°	5.72 to 64.36
Index ranges	$-16 \le h \le 17$, $-17 \le k \le 18$, $-32 \le l \le 31$
Reflections collected	52246
Independent reflections	18443[R(int) = 0.0257]
Data/restraints/parameters	18443/6/678
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0384, wR_2 = 0.0944
Final R indexes [all data]	R_1 = 0.0479, wR_2 = 0.1011
Largest diff. peak/hole / e Å^{-3}	1.26/-1.21

S6 DFT Calculations

Initial optimisations were performed at the (RI-)BP86/SV(P) level, followed by frequency calculations at the same level. Transition states were located by initially performing a constrained minimisation (by freezing internal coordinates that change most during the reaction) of a structure close to the anticipated transition state. This was followed by a frequency calculation to identify the transition vector to follow during a subsequent transition state optimisation. A final frequency calculation was then performed on the optimised transition-state structure. All minima were confirmed as such by the absence of imaginary frequencies and all transition states were identified by the presence of only one imaginary frequency. Energies, coordinates and first 50 vibrational modes are given for complexes [**1a**]$^+$, [**2a**]$^+$ **6a** and **7a** and sample parts of the linear transit scan for the addition of Cl^- to [**1a**]$^+$ and [**2a**]$^+$ with a C-Cl distance of 2.5 Å.

Single-point calculations on the (RI-)BP86/SV(P) optimised geometries were performed using the hybrid PBE0 functional and the flexible def2-TZVPP basis set. The (RI-)PBE0/def2-TZVPP SCF energies were corrected for their zero point energies, thermal energies and entropies (obtained from the (RI-)BP86/SV(P)-level frequency calculations). In all calculations, a 28 electron quasi-relativistic ECP replaced the core electrons of Ru and Rh. No symmetry constraints were applied during optimisations. Solent corrections were applied with the COSMO dielectric continuum model[8] and dispersion effects modelled with Grimme's D3 method.[9] All calculations were performed using the TURBOMOLE V6.4 package using the resolution of identity (RI) approximation.[10]

S6.1 Complex $[1a]^+$

SCF Energy (au) (RI)BP86/SV(P) -4234.9795961170
SCF Energy (au) PBE0/def2-TZVPP -4234.309748570
SCF Energy (au) PBE0/def2-TZVPP -4234.3657658168 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.8897230
Chemical potential (kJ mol^{-1}) 2056.13
Dispersion correction (au) PBE0/def2-TZVPP -0.22488237

xyz coordinates
116

C	-0.23448	-1.19117	0.11721
C	-1.38355	1.08798	-2.98984
C	1.57731	1.07965	-3.54802
C	0.17765	-1.43714	-3.19837
C	1.25965	0.70500	2.67121
C	-1.09356	2.48886	2.99935
C	-1.50192	-0.35132	3.17775
C	3.44496	-0.14888	0.79877
P	-2.24174	0.86701	-1.34326
Cl	-0.12217	3.07503	-0.62272
P	2.00132	0.97652	0.96950
P	0.25259	0.28033	-2.53417
P	-0.55645	0.91093	2.21302
Ru	-0.13033	0.62363	-0.15411
C	-0.46488	-2.50175	0.26338
H	-1.52554	-2.76700	0.06505
C	0.40730	-3.62406	0.62209
C	-3.37046	-0.58342	-1.47925
C	-3.43154	2.26341	-1.11530
C	2.78422	2.64495	1.02044
H	-1.15963	2.16851	-3.10364
H	-1.91041	0.73145	-3.89915
H	1.63500	1.37228	3.47620
H	1.44345	-0.35146	2.96200
C	-3.05997	-2.26230	4.56248
C	-1.75031	-2.57501	4.16149
C	-0.97682	-1.63021	3.46570
C	-2.82375	-0.04565	3.57913
C	-3.59581	-0.99688	4.26590
H	-3.66255	-3.00411	5.11165
H	-1.32040	-3.56420	4.38757
H	0.04019	-1.91323	3.15256
H	-3.24995	0.94932	3.37127
H	-4.61978	-0.73990	4.58323
C	-1.98803	4.84229	4.26601
C	-1.23969	3.89570	4.99096
C	-0.79796	2.72115	4.36402
C	-1.84623	3.43805	2.27729
C	-2.29202	4.61019	2.91515
H	-2.33560	5.76414	4.76071
H	-1.00450	4.07000	6.05366
H	-0.23242	1.97705	4.95024

H	-2.06264	3.27497	1.21150
H	-2.87639	5.34859	2.34305
C	5.73008	-1.76591	0.46437
C	4.97413	-1.37804	-0.65522
C	3.83208	-0.57583	-0.48993
C	4.21562	-0.52984	1.91955
C	5.34943	-1.34180	1.75035
H	6.62253	-2.39961	0.33502
H	5.27175	-1.70369	-1.66509
H	3.24365	-0.27024	-1.37090
H	3.94160	-0.18894	2.93168
H	5.94417	-1.63829	2.62971
C	3.99958	5.19232	1.08805
C	4.59487	4.14665	0.36311
C	3.99284	2.87793	0.32713
C	2.18142	3.70436	1.73485
C	2.79361	4.96676	1.77318
H	4.47707	6.18525	1.12047
H	5.54383	4.31243	-0.17262
H	4.48272	2.06611	-0.23300
H	1.22791	3.55839	2.26505
H	2.31648	5.78211	2.34056
C	0.24791	-4.06372	-4.24383
C	1.11258	-3.69766	-3.19777
C	1.07530	-2.39529	-2.67617
C	-0.68593	-1.81373	-4.24987
C	-0.65124	-3.12030	-4.76740
H	0.27361	-5.08794	-4.65035
H	1.81517	-4.43297	-2.77404
H	1.75001	-2.12878	-1.84729
H	-1.39070	-1.09092	-4.68900
H	-1.33164	-3.39849	-5.58874
C	3.58974	2.33416	-5.07821
C	3.15239	2.91502	-3.87519
C	2.15471	2.29300	-3.10660
C	2.02427	0.49462	-4.75568
C	3.02509	1.12351	-5.51479
H	4.37445	2.82484	-5.67727
H	3.59083	3.86414	-3.52600
H	1.80379	2.75966	-2.17106
H	1.59519	-0.45649	-5.10797
H	3.36484	0.66025	-6.45563
C	-5.23753	-2.69972	-1.56110
C	-4.58622	-2.38324	-0.35717
C	-3.65266	-1.33266	-0.31569
C	-4.04321	-0.89521	-2.68078
C	-4.96485	-1.95383	-2.72134
H	-5.96535	-3.52673	-1.59549
H	-4.80250	-2.95687	0.55878
H	-3.14457	-1.09022	0.63304
H	-3.86662	-0.30414	-3.59404
H	-5.48069	-2.19182	-3.66588
C	-5.29673	4.34637	-0.69986
C	-4.19015	4.54529	-1.54229
C	-3.25609	3.51560	-1.74533
C	-4.54684	2.07029	-0.26724

C	-5.47044	3.10698	-0.06011
H	-6.02786	5.15671	-0.54556
H	-4.04617	5.51306	-2.04970
H	-2.38908	3.70504	-2.39389
H	-4.71184	1.09864	0.22527
H	-6.33835	2.93861	0.59812
C	2.02086	-5.88145	1.33528
C	2.56175	-4.56787	1.32149
C	1.77361	-3.46775	0.97343
C	-0.12969	-4.93841	0.63828
C	0.65436	-6.04201	0.98476
C	2.82795	-7.00563	1.69284
H	3.61918	-4.42101	1.59116
H	2.22636	-2.46366	0.97056
H	-1.18810	-5.09075	0.36870
H	0.21446	-7.05173	0.98869
C	3.52033	-7.97028	1.99958
H	4.12884	-8.82392	2.27035

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules	
#		cm**(-1)	km/mol	IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	12.81	0.12928	YES	YES
8	a	14.28	0.07389	YES	YES
9	a	18.24	0.05144	YES	YES
10	a	21.47	0.03011	YES	YES
11	a	22.96	0.10528	YES	YES
12	a	25.09	0.15693	YES	YES
13	a	26.67	0.06942	YES	YES
14	a	29.37	0.11987	YES	YES
15	a	32.70	0.02625	YES	YES
16	a	32.94	0.12237	YES	YES
17	a	34.79	0.02693	YES	YES
18	a	35.70	0.08040	YES	YES
19	a	38.99	0.01829	YES	YES
20	a	41.87	0.05463	YES	YES
21	a	43.87	0.10197	YES	YES
22	a	45.79	0.05129	YES	YES
23	a	48.73	0.28380	YES	YES
24	a	49.78	0.02616	YES	YES
25	a	51.51	0.03242	YES	YES
26	a	57.39	0.31904	YES	YES
27	a	59.07	0.29112	YES	YES
28	a	60.08	0.08508	YES	YES
29	a	61.89	0.02549	YES	YES
30	a	71.31	0.10038	YES	YES
31	a	71.98	0.08567	YES	YES
32	a	76.83	0.79346	YES	YES
33	a	81.43	0.12633	YES	YES

34	a	88.12	0.48646	YES	YES
35	a	100.23	0.11266	YES	YES
36	a	106.78	0.04008	YES	YES
37	a	114.03	3.84046	YES	YES
38	a	119.37	1.75504	YES	YES
39	a	130.43	4.55262	YES	YES
40	a	141.54	2.48114	YES	YES
41	a	145.26	0.46869	YES	YES
42	a	148.16	2.58487	YES	YES
43	a	151.46	3.39655	YES	YES
44	a	154.61	0.40068	YES	YES
45	a	161.08	1.04541	YES	YES
46	a	165.66	0.23462	YES	YES
47	a	181.78	3.48363	YES	YES
48	a	189.31	0.77701	YES	YES
49	a	198.26	1.05578	YES	YES
50	a	200.55	2.86424	YES	YES

S6.2 Complex $[2a]^+$

SCF Energy (au) (RI)BP86/SV(P) -4234.9758845480
SCF Energy (au) PBE0/def2-TZVPP -4234.297480281
SCF Energy (au) PBE0/def2-TZVPP -4234.3513354867 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.8891168
Chemical potential (kJ mol^{-1}) 2051.94
Dispersion correction (au) PBE0/def2-TZVPP -0.22208344

xyz coordinates
116

C	0.09033	-1.06223	0.19112
C	-1.41386	0.83583	-3.01331
C	1.41190	1.59215	-3.58602
C	0.73858	-1.19225	-3.24855
C	1.29732	1.02824	2.67063
C	-0.98936	2.92274	2.75794
C	-1.52810	0.12489	3.15710
C	3.36720	-0.26908	0.98159
P	-2.15432	0.71585	-1.29252
Cl	-0.03001	3.18044	-0.84243
P	2.08227	1.05132	0.95710
P	0.37565	0.47956	-2.55026
P	-0.48761	1.26261	2.13369
Ru	-0.01686	0.80246	-0.18551
C	0.22953	-2.30543	0.42565
C	0.38934	-3.64949	0.70506
C	-3.17247	-0.82452	-1.28060
C	-3.44895	2.02980	-1.14683
C	3.06607	2.61010	0.89622
H	-1.46909	1.88442	-3.37256
H	-1.85483	0.16478	-3.78040
H	1.68433	1.78631	3.38415
H	1.43552	0.01668	3.10837
C	-3.19708	-1.61772	4.63292
C	-1.92103	-2.04055	4.22211
C	-1.09354	-1.17947	3.48201
C	-2.81540	0.54101	3.56839
C	-3.64279	-0.32721	4.29982
H	-3.84329	-2.29344	5.21688
H	-1.56200	-3.05030	4.48000
H	-0.10576	-1.53841	3.15341
H	-3.17187	1.55519	3.32800
H	-4.64038	0.01453	4.62088
C	-1.86003	5.40140	3.78210
C	-1.08122	4.54548	4.58275
C	-0.65105	3.30960	4.07630
C	-1.77298	3.78232	1.96003
C	-2.20625	5.01697	2.47672
H	-2.19813	6.37202	4.18069
H	-0.81176	4.83895	5.61048
H	-0.06037	2.63969	4.72411
H	-2.02533	3.49892	0.92803

H	-2.81447	5.68421	1.84493
C	5.37824	-2.24622	0.98171
C	4.50536	-2.13007	-0.11263
C	3.49951	-1.14752	-0.11281
C	4.25043	-0.38796	2.07917
C	5.24854	-1.37530	2.07907
H	6.16603	-3.01756	0.98100
H	4.60066	-2.81166	-0.97352
H	2.80753	-1.07105	-0.96725
H	4.17075	0.30169	2.93687
H	5.93490	-1.45944	2.93779
C	4.53720	5.01593	0.73984
C	5.09667	3.81686	0.26729
C	4.36656	2.61837	0.34258
C	2.50214	3.82264	1.35387
C	3.24039	5.01459	1.28208
H	5.11297	5.95434	0.68596
H	6.11518	3.80772	-0.15449
H	4.82278	1.68307	-0.01940
H	1.48132	3.84816	1.76585
H	2.79179	5.95234	1.64824
C	1.33363	-3.75683	-4.28131
C	2.30555	-2.74273	-4.30831
C	2.01147	-1.46674	-3.79847
C	-0.22664	-2.22284	-3.20515
C	0.06845	-3.49228	-3.72939
H	1.56009	-4.75256	-4.69633
H	3.29842	-2.93784	-4.74606
H	2.77464	-0.67346	-3.85172
H	-1.22118	-2.04201	-2.76557
H	-0.70214	-4.28055	-3.71120
C	3.02499	3.23954	-5.20469
C	3.27663	3.14292	-3.82613
C	2.46983	2.32666	-3.01501
C	1.16304	1.68829	-4.97417
C	1.96574	2.51273	-5.77802
H	3.65423	3.88709	-5.83718
H	4.09864	3.71758	-3.36966
H	2.65238	2.28071	-1.93074
H	0.34366	1.11280	-5.43719
H	1.76425	2.58565	-6.85934
C	-4.82522	-3.11129	-1.18509
C	-4.01782	-2.77902	-0.08461
C	-3.18957	-1.64265	-0.13144
C	-3.99900	-1.15624	-2.37909
C	-4.81452	-2.29794	-2.33334
H	-5.47249	-4.00299	-1.14759
H	-4.02832	-3.40599	0.82161
H	-2.55478	-1.38962	0.73192
H	-4.02418	-0.51407	-3.27549
H	-5.45426	-2.54796	-3.19558
C	-5.43216	4.01798	-0.81707
C	-4.28889	4.28074	-1.59058
C	-3.29691	3.29853	-1.75130
C	-4.59889	1.77437	-0.36381
C	-5.58174	2.76388	-0.20063

H	-6.20976	4.79013	-0.69700
H	-4.16231	5.26180	-2.07709
H	-2.39517	3.53830	-2.33370
H	-4.73891	0.79134	0.11356
H	-6.47666	2.54681	0.40535
C	0.71344	-6.45166	1.31344
C	1.45539	-5.42943	2.04191
C	1.29487	-4.09885	1.74803
C	-0.34081	-4.67104	-0.02295
C	-0.19485	-6.00477	0.26383
C	0.86454	-7.76670	1.59985
H	2.15322	-5.75104	2.83117
H	1.87332	-3.33809	2.29563
H	-1.03129	-4.34540	-0.81563
H	-0.76298	-6.76577	-0.29424
C	1.01113	-9.03769	1.87608
H	1.77527	-9.66103	1.36695
H	0.37783	-9.54802	2.63116

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules	
#		cm**(-1)	km/mol	IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	11.16	0.15361	YES	YES
8	a	12.66	0.08797	YES	YES
9	a	15.74	0.16218	YES	YES
10	a	17.29	0.03157	YES	YES
11	a	21.96	0.08026	YES	YES
12	a	24.33	0.09478	YES	YES
13	a	30.32	0.09821	YES	YES
14	a	31.03	0.18645	YES	YES
15	a	32.97	0.07815	YES	YES
16	a	33.58	0.12737	YES	YES
17	a	37.43	0.07348	YES	YES
18	a	38.91	0.21470	YES	YES
19	a	40.11	0.00786	YES	YES
20	a	43.48	0.06781	YES	YES
21	a	46.63	0.00671	YES	YES
22	a	47.52	0.20387	YES	YES
23	a	49.37	0.06790	YES	YES
24	a	52.38	0.26943	YES	YES
25	a	53.67	0.19952	YES	YES
26	a	54.97	0.69018	YES	YES
27	a	55.90	0.03483	YES	YES
28	a	57.40	0.21227	YES	YES
29	a	59.48	0.02338	YES	YES
30	a	63.29	0.25800	YES	YES
31	a	68.78	0.09977	YES	YES
32	a	71.95	0.06341	YES	YES
33	a	79.31	0.18096	YES	YES

34	a	86.07	0.06981	YES	YES
35	a	95.99	0.00523	YES	YES
36	a	102.01	0.37222	YES	YES
37	a	104.96	1.23874	YES	YES
38	a	113.91	2.51210	YES	YES
39	a	127.20	4.40553	YES	YES
40	a	132.93	1.37501	YES	YES
41	a	144.32	0.58978	YES	YES
42	a	148.93	0.29900	YES	YES
43	a	149.84	1.80162	YES	YES
44	a	150.21	0.10308	YES	YES
45	a	161.15	0.89438	YES	YES
46	a	168.45	0.30204	YES	YES
47	a	177.21	2.12046	YES	YES
48	a	184.89	1.77470	YES	YES
49	a	188.98	4.50497	YES	YES
50	a	194.24	1.47915	YES	YES

S6.3 Complex [6a]

SCF Energy (au) (RI)BP86/SV(P) -4695.3128936920
SCF Energy (au) PBE0/def2-TZVPP -4694.606198521
SCF Energy (au) PBE0/def2-TZVPP -4694.6350623670 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.8910708
Chemical potential (kJ mol^{-1}) 2046.62
Dispersion correction (au) PBE0/def2-TZVPP -0.22675811

xyz coordinates
117

C	0.07077	-1.00692	0.15120
C	-1.42531	0.90973	-3.07328
C	1.38405	1.69759	-3.64557
C	0.75371	-1.09187	-3.27660
C	1.27134	0.95340	2.58473
C	-0.95264	2.88779	2.80950
C	-1.58884	0.10928	3.01606
C	3.35010	-0.21612	0.81720
P	-2.15494	0.81391	-1.34041
Cl	-0.04878	3.34317	-0.93862
P	2.04166	1.08679	0.86525
P	0.36824	0.58050	-2.58208
P	-0.50623	1.25963	2.04440
Ru	-0.03818	0.92797	-0.25768
C	0.20870	-2.22244	0.41719
C	0.36916	-3.59506	0.74637
C	-3.19708	-0.71654	-1.34198
C	-3.46334	2.12722	-1.22505
C	3.02630	2.65390	0.89954
H	-1.49229	1.95003	-3.45457
H	-1.85672	0.21124	-3.82188
H	1.66950	1.64390	3.35903
H	1.38983	-0.09650	2.92807
C	-3.35487	-1.65345	4.35348
C	-2.05990	-2.07599	4.00845
C	-1.18331	-1.20485	3.33839
C	-2.89657	0.52412	3.36091
C	-3.77164	-0.35160	4.02430
H	-4.04041	-2.33919	4.87878
H	-1.72324	-3.09647	4.25409
H	-0.18574	-1.56918	3.05116
H	-3.23406	1.54388	3.11503
H	-4.78574	-0.00982	4.29060
C	-1.69974	5.33362	4.00198
C	-1.10493	4.32387	4.78219
C	-0.73744	3.10584	4.19084
C	-1.54749	3.90252	2.03150
C	-1.91981	5.12016	2.63204
H	-1.99066	6.29031	4.46756
H	-0.93222	4.48454	5.85956
H	-0.29168	2.31315	4.81614
H	-1.67482	3.75183	0.94740

H	-2.38044	5.90893	2.01463
C	5.35251	-2.20086	0.72010
C	4.42312	-2.08549	-0.32655
C	3.42173	-1.09974	-0.27778
C	4.28796	-0.33602	1.86786
C	5.28302	-1.32566	1.81955
H	6.13258	-2.97962	0.68341
H	4.46315	-2.77584	-1.18479
H	2.67637	-1.03130	-1.08558
H	4.24868	0.35316	2.72897
H	6.01027	-1.41245	2.64424
C	4.46296	5.09075	0.84750
C	5.03715	3.92223	0.31966
C	4.32423	2.71090	0.34380
C	2.44786	3.83842	1.40852
C	3.16748	5.04375	1.39076
H	5.02412	6.03994	0.83325
H	6.05343	3.94690	-0.10807
H	4.79094	1.79981	-0.06396
H	1.42627	3.82928	1.81881
H	2.70292	5.95723	1.79732
C	1.37233	-3.68637	-4.22030
C	2.27542	-2.62926	-4.41987
C	1.96988	-1.33917	-3.95223
C	-0.13959	-2.16543	-3.06165
C	0.16530	-3.44963	-3.54035
H	1.61043	-4.69744	-4.59007
H	3.22565	-2.80395	-4.95193
H	2.68286	-0.51740	-4.12568
H	-1.07855	-2.00634	-2.50800
H	-0.54416	-4.27532	-3.36825
C	2.97548	3.36496	-5.27171
C	3.23427	3.26737	-3.89431
C	2.43812	2.44251	-3.08121
C	1.12855	1.79736	-5.03140
C	1.91918	2.63008	-5.83983
H	3.59607	4.01956	-5.90632
H	4.05287	3.84914	-3.43983
H	2.62213	2.39468	-1.99711
H	0.31040	1.21537	-5.48885
H	1.71045	2.70327	-6.92027
C	-4.85437	-3.00182	-1.27186
C	-4.01495	-2.70594	-0.18562
C	-3.18362	-1.57051	-0.21963
C	-4.05277	-1.01455	-2.42762
C	-4.87168	-2.15392	-2.39525
H	-5.49991	-3.89563	-1.24525
H	-3.99471	-3.36442	0.69783
H	-2.50773	-1.35501	0.62185
H	-4.09408	-0.34599	-3.30432
H	-5.53280	-2.37820	-3.24899
C	-5.44897	4.12305	-0.92311
C	-4.28924	4.38440	-1.67213
C	-3.29728	3.39960	-1.81782
C	-4.62942	1.87508	-0.46596
C	-5.61298	2.86649	-0.31580

```
H         -6.22521        4.89855       -0.81181
H         -4.14710        5.36934       -2.14742
H         -2.37655        3.63891       -2.37020
H         -4.77874        0.89092        0.00650
H         -6.51840        2.64932        0.27523
C          0.69503       -6.37645        1.44638
C          1.55973       -5.37676        1.96631
C          1.40411       -4.03186        1.62969
C         -0.48460       -4.60759        0.21697
C         -0.32121       -5.95350        0.55353
C          0.85534       -7.78667        1.85104
H          2.39230       -5.66683        2.62768
H          2.10681       -3.28437        2.03167
H         -1.29319       -4.31106       -0.46994
H         -0.99911       -6.70785        0.12448
C          1.47671       -8.25022        2.96148
H          1.88758       -7.54827        3.70542
H          1.57274       -9.32969        3.15549
Cl         0.15016       -8.99076        0.75351
$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection
rules
#                         cm**(-1)        km/mol          IR
RAMAN
     1                        0.00         0.00000        -       -
     2                        0.00         0.00000        -       -
     3                        0.00         0.00000        -       -
     4                        0.00         0.00000        -       -
     5                        0.00         0.00000        -       -
     6                        0.00         0.00000        -       -
     7        a               2.31         0.31999       YES     YES
     8        a               9.87         0.21520       YES     YES
     9        a              12.24         0.06591       YES     YES
    10        a              14.39         0.09720       YES     YES
    11        a              17.59         0.02248       YES     YES
    12        a              23.22         0.01663       YES     YES
    13        a              27.13         0.04657       YES     YES
    14        a              28.60         0.07958       YES     YES
    15        a              30.89         0.25657       YES     YES
    16        a              33.04         0.07104       YES     YES
    17        a              35.91         0.32338       YES     YES
    18        a              38.16         0.01398       YES     YES
    19        a              40.62         0.08127       YES     YES
    20        a              45.50         0.03757       YES     YES
    21        a              46.05         0.18155       YES     YES
    22        a              47.78         0.00946       YES     YES
    23        a              48.41         0.04961       YES     YES
    24        a              50.31         0.07761       YES     YES
    25        a              52.90         0.10159       YES     YES
    26        a              54.79         0.06049       YES     YES
    27        a              56.69         0.31422       YES     YES
    28        a              58.08         0.56283       YES     YES
    29        a              59.95         0.50393       YES     YES
    30        a              62.97         0.00957       YES     YES
    31        a              65.55         0.10752       YES     YES
    32        a              71.83         0.29467       YES     YES
```

33	a	72.48	0.55568	YES	YES
34	a	81.85	0.44817	YES	YES
35	a	87.00	0.02843	YES	YES
36	a	95.46	1.14590	YES	YES
37	a	98.43	1.64151	YES	YES
38	a	102.10	0.10998	YES	YES
39	a	110.04	2.56807	YES	YES
40	a	125.99	3.52001	YES	YES
41	a	132.34	1.54486	YES	YES
42	a	149.27	0.49998	YES	YES
43	a	152.12	0.26572	YES	YES
44	a	160.52	4.60297	YES	YES
45	a	163.81	0.80449	YES	YES
46	a	168.67	2.59171	YES	YES
47	a	172.54	1.24399	YES	YES
48	a	179.35	2.55938	YES	YES
49	a	183.23	0.03373	YES	YES
50	a	195.20	1.76049	YES	YES

S6.4 Complex [7a]

SCF Energy (au) (RI)BP86/SV(P) -4695.2750946450
SCF Energy (au) PBE0/def2-TZVPP -4694.560937211
SCF Energy (au) PBE0/def2-TZVPP -4694.5925251380 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.8905876
Chemical potential (kJ mol^{-1}) 2055.28
Dispersion correction (au) PBE0/def2-TZVPP -0.23267006

xyz coordinates
117

C	0.23877	-1.44444	0.25545
C	-1.05648	1.03782	-2.93215
C	1.88717	1.49137	-3.42035
C	0.79695	-1.13095	-3.50439
C	1.63236	0.38238	2.67791
C	-0.56656	2.23375	3.23655
C	-1.19038	-0.55376	3.12581
C	3.98767	0.14739	0.84814
P	-1.85848	0.68098	-1.26371
Cl	0.11846	3.05075	-0.67829
P	2.32346	0.95105	1.03165
P	0.67065	0.42946	-2.49334
P	-0.16788	0.70896	2.23935
Ru	0.23941	0.57222	-0.10942
C	-0.81660	-2.30910	0.40569
H	-1.78204	-1.78348	0.30715
C	-1.01730	-3.73825	0.67389
C	-3.02566	-0.72490	-1.62233
C	-3.07508	2.05464	-1.00877
C	2.88921	2.70040	1.27276
H	-1.04340	2.13920	-3.05900
H	-1.52865	0.55429	-3.81327
H	2.00785	0.83050	3.62258
H	1.79686	-0.71684	2.68829
C	-2.88254	-2.40971	4.42496
C	-1.48828	-2.51970	4.54544
C	-0.64570	-1.59703	3.90041
C	-2.59452	-0.45355	3.00443
C	-3.43420	-1.37248	3.65204
H	-3.54060	-3.13819	4.92638
H	-1.04651	-3.33599	5.14011
H	0.44503	-1.70777	4.00399
H	-3.03929	0.35282	2.39669
H	-4.52804	-1.28071	3.54754
C	-1.06431	4.54896	4.78060
C	-1.11065	3.27763	5.38132
C	-0.86667	2.12625	4.61573
C	-0.51694	3.51187	2.63948
C	-0.76800	4.66061	3.41255
H	-1.26124	5.45209	5.38256
H	-1.34424	3.17905	6.45480
H	-0.91722	1.13605	5.09733

H	-0.28187	3.60529	1.56396
H	-0.72704	5.65235	2.93225
C	6.57170	-0.93778	0.51348
C	5.78212	-0.63517	-0.60935
C	4.49436	-0.10018	-0.44313
C	4.78623	-0.15005	1.97165
C	6.06993	-0.69613	1.80409
H	7.58005	-1.36459	0.38308
H	6.16802	-0.82503	-1.62471
H	3.87067	0.11769	-1.32550
H	4.41052	0.04452	2.99015
H	6.68357	-0.93112	2.68986
C	3.91700	5.32382	1.50367
C	3.83024	4.70679	0.24295
C	3.31234	3.40869	0.12546
C	2.97318	3.32687	2.53211
C	3.48333	4.63284	2.64600
H	4.31937	6.34666	1.59412
H	4.15787	5.24460	-0.66200
H	3.23559	2.94326	-0.86988
H	2.63796	2.80914	3.44401
H	3.53990	5.10905	3.63898
C	0.97017	-3.46282	-5.09576
C	1.30921	-3.50812	-3.73488
C	1.22496	-2.34859	-2.94014
C	0.47003	-1.08969	-4.88167
C	0.55276	-2.24702	-5.67005
H	1.03279	-4.37356	-5.71455
H	1.63934	-4.45418	-3.27523
H	1.49985	-2.39771	-1.87602
H	0.15737	-0.14102	-5.35027
H	0.29340	-2.19912	-6.74094
C	3.83599	3.04780	-4.76746
C	2.66547	3.64728	-4.27310
C	1.69920	2.88064	-3.59842
C	3.06908	0.89620	-3.92199
C	4.03631	1.66873	-4.58595
H	4.59104	3.65370	-5.29553
H	2.49749	4.72879	-4.40858
H	0.81018	3.37447	-3.17974
H	3.23135	-0.18834	-3.81077
H	4.94863	1.18432	-4.97222
C	-4.78871	-2.89145	-2.09884
C	-5.16229	-1.85511	-1.22679
C	-4.28800	-0.78075	-0.98839
C	-2.65185	-1.78247	-2.48145
C	-3.52921	-2.85265	-2.72094
H	-5.47551	-3.73279	-2.28867
H	-6.14711	-1.87553	-0.73073
H	-4.60283	0.03106	-0.31306
H	-1.66285	-1.78589	-2.96581
H	-3.21837	-3.66642	-3.39616
C	-4.98877	4.09324	-0.61457
C	-4.88006	3.46143	-1.86643
C	-3.93289	2.44299	-2.06137
C	-3.18384	2.69792	0.23846

C	-4.14157	3.70732	0.43765
H	-5.73440	4.89119	-0.46132
H	-5.54023	3.76062	-2.69766
H	-3.86824	1.94376	-3.04295
H	-2.49855	2.42310	1.05486
H	-4.21229	4.20351	1.41953
C	-1.70793	-6.49562	1.18563
C	-0.35620	-6.06367	1.15399
C	-0.02018	-4.72969	0.90623
C	-2.37114	-4.18944	0.70962
C	-2.71307	-5.51890	0.95583
C	-2.04503	-7.86119	1.43930
H	0.44337	-6.80157	1.33035
H	1.03919	-4.44461	0.89546
H	-3.17550	-3.45661	0.53108
H	-3.77211	-5.82290	0.97284
C	-2.33469	-9.03426	1.65751
H	-2.58880	-10.06805	1.84921
Cl	1.90365	-2.24347	0.48309

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules	
#		cm**(-1)	km/mol	IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	11.46	0.09051	YES	YES
8	a	14.57	0.22798	YES	YES
9	a	17.44	0.04176	YES	YES
10	a	20.32	0.04996	YES	YES
11	a	25.64	0.19661	YES	YES
12	a	27.28	0.05764	YES	YES
13	a	28.52	0.07562	YES	YES
14	a	30.12	0.02200	YES	YES
15	a	32.80	0.17401	YES	YES
16	a	34.96	0.07762	YES	YES
17	a	38.18	0.12244	YES	YES
18	a	38.60	0.01575	YES	YES
19	a	40.99	0.10523	YES	YES
20	a	42.24	0.06453	YES	YES
21	a	44.58	0.02708	YES	YES
22	a	46.74	0.05860	YES	YES
23	a	47.95	0.08373	YES	YES
24	a	50.62	0.19003	YES	YES
25	a	52.25	0.05663	YES	YES
26	a	56.19	0.22327	YES	YES
27	a	59.08	0.19641	YES	YES
28	a	62.37	0.02910	YES	YES
29	a	63.91	0.41600	YES	YES
30	a	67.51	0.06962	YES	YES
31	a	71.28	0.22429	YES	YES

32	a	73.41	0.03722	YES	YES
33	a	83.78	0.18139	YES	YES
34	a	93.30	0.10262	YES	YES
35	a	97.58	2.14227	YES	YES
36	a	104.34	0.29405	YES	YES
37	a	108.15	0.44763	YES	YES
38	a	117.48	1.08050	YES	YES
39	a	120.88	2.98637	YES	YES
40	a	132.96	2.98292	YES	YES
41	a	142.27	0.30493	YES	YES
42	a	145.23	2.75125	YES	YES
43	a	147.15	0.93087	YES	YES
44	a	155.02	2.72625	YES	YES
45	a	163.76	1.37085	YES	YES
46	a	167.29	1.70259	YES	YES
47	a	168.60	0.47369	YES	YES
48	a	175.52	0.87708	YES	YES
49	a	182.68	10.56224	YES	YES
50	a	189.89	2.30958	YES	YES

S6.5 Complex $[1a]^+ + Cl^-$, C-Cl distance 2.5 Å

SCF Energy (au) (RI)BP86/SV(P) -4695.2584701700
SCF Energy (au) PBE0/def2-TZVPP -4694.536678317
SCF Energy (au) PBE0/def2-TZVPP -4694.5721281055 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.8891414 0.8886137
Chemical potential (kJ mol^{-1}) 2054.74
Dispersion correction (au) PBE0/def2-TZVPP -0.23245125

xyz coordinates
117

C	0.13597	-1.35925	0.25350
Cl	2.37397	-2.43325	0.56050
C	-1.07253	0.96667	-2.93066
C	1.84451	1.41215	-3.45591
C	0.78257	-1.24059	-3.38918
C	1.63216	0.24444	2.67308
C	-0.48521	2.24379	3.24739
C	-1.26275	-0.50487	3.13796
C	4.02951	0.18648	0.82852
P	-1.87849	0.70242	-1.25086
Cl	0.12208	2.99351	-0.70321
P	2.34250	0.89389	1.07022
P	0.65455	0.36969	-2.48285
P	-0.14732	0.69228	2.27714
Ru	0.24991	0.54469	-0.08863
C	-0.77197	-2.35023	0.41558
H	-1.77008	-1.85817	0.39176
C	-0.92372	-3.79471	0.61003
C	-3.08682	-0.67972	-1.54447
C	-3.03825	2.13064	-1.03772
C	2.82249	2.65743	1.38433
H	-1.05771	2.05623	-3.13301
H	-1.55315	0.43104	-3.77571
H	2.04159	0.58392	3.64853
H	1.74351	-0.85988	2.55663
C	-3.09769	-2.29442	4.33008
C	-1.74689	-2.65312	4.19253
C	-0.83212	-1.76647	3.59685
C	-2.62661	-0.15513	3.26998
C	-3.53719	-1.04262	3.86444
H	-3.81198	-2.99488	4.79343
H	-1.39745	-3.63930	4.53804
H	0.21614	-2.07983	3.47592
H	-2.98382	0.82572	2.91411
H	-4.59633	-0.75215	3.96445
C	-0.98322	4.59110	4.74137
C	-0.94954	3.33999	5.38501
C	-0.70433	2.17243	4.64483
C	-0.50948	3.50211	2.60962
C	-0.76038	4.66731	3.35747
H	-1.18399	5.50650	5.32312
H	-1.12220	3.27098	6.47223

H	-0.69720	1.19744	5.15934
H	-0.32594	3.56876	1.52297
H	-0.77775	5.64314	2.84448
C	6.68148	-0.67122	0.42439
C	5.88408	-0.30359	-0.67313
C	4.56137	0.12049	-0.47348
C	4.83235	-0.17250	1.92936
C	6.15167	-0.60630	1.72473
H	7.71794	-1.01244	0.26631
H	6.29077	-0.35700	-1.69654
H	3.93240	0.38717	-1.33845
H	4.42857	-0.12801	2.95425
H	6.77010	-0.89744	2.59009
C	3.71927	5.31385	1.74928
C	3.62062	4.77262	0.45541
C	3.17116	3.45625	0.27174
C	2.92598	3.20650	2.67818
C	3.37131	4.52794	2.85934
H	4.06612	6.35110	1.89172
H	3.88621	5.38342	-0.42321
H	3.08771	3.04921	-0.74766
H	2.65825	2.61180	3.56499
H	3.44285	4.94209	3.87858
C	0.97186	-3.67234	-4.80707
C	1.40065	-3.59604	-3.47278
C	1.30829	-2.38551	-2.75842
C	0.37120	-1.31515	-4.74217
C	0.46105	-2.52557	-5.44469
H	1.03664	-4.62589	-5.35769
H	1.80712	-4.48649	-2.96632
H	1.65605	-2.34397	-1.70918
H	-0.01343	-0.42027	-5.26053
H	0.13377	-2.57280	-6.49692
C	3.73538	2.93694	-4.91210
C	2.56746	3.54079	-4.41706
C	1.63049	2.78999	-3.68659
C	3.02220	0.81136	-3.95894
C	3.96126	1.56997	-4.67682
H	4.46870	3.53049	-5.48285
H	2.37866	4.61243	-4.59666
H	0.74198	3.28931	-3.27316
H	3.20201	-0.26495	-3.80444
H	4.87153	1.08295	-5.06412
C	-4.93129	-2.78138	-1.98757
C	-5.29514	-1.67808	-1.19756
C	-4.37997	-0.63494	-0.97430
C	-2.72116	-1.80647	-2.31596
C	-3.64011	-2.84470	-2.53928
H	-5.65235	-3.59526	-2.17000
H	-6.30422	-1.61987	-0.75617
H	-4.68685	0.23043	-0.36559
H	-1.70952	-1.88693	-2.74466
H	-3.33781	-3.71287	-3.14688
C	-4.87314	4.25306	-0.71185
C	-4.70718	3.65269	-1.97226
C	-3.80024	2.59193	-2.13387

C	-3.20556	2.74132	0.21969
C	-4.12404	3.79232	0.38422
H	-5.58568	5.08527	-0.58554
H	-5.28985	4.01033	-2.83772
H	-3.69172	2.12107	-3.12530
H	-2.59518	2.40807	1.07344
H	-4.24087	4.26357	1.37387
C	-1.50543	-6.58457	0.98181
C	-0.17131	-6.11945	0.83143
C	0.11514	-4.76291	0.64748
C	-2.25898	-4.27008	0.76354
C	-2.54857	-5.62253	0.94305
C	-1.79862	-7.97231	1.16073
H	0.65273	-6.85084	0.85793
H	1.15570	-4.42038	0.53826
H	-3.08967	-3.54491	0.73280
H	-3.59349	-5.95463	1.05272
C	-2.06384	-9.16138	1.31290
H	-2.29693	-10.20951	1.44307

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1	a	-94.34	0.00000	YES	YES
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7		0.00	0.00000	-	-
8	a	13.07	0.26859	YES	YES
9	a	16.41	0.61386	YES	YES
10	a	18.44	0.05075	YES	YES
11	a	24.36	0.00971	YES	YES
12	a	26.48	0.41784	YES	YES
13	a	27.49	0.23949	YES	YES
14	a	30.26	0.12206	YES	YES
15	a	32.30	0.03409	YES	YES
16	a	34.91	0.55374	YES	YES
17	a	35.03	0.30263	YES	YES
18	a	38.91	0.09839	YES	YES
19	a	40.23	0.03016	YES	YES
20	a	41.11	0.34225	YES	YES
21	a	43.72	0.23155	YES	YES
22	a	46.39	0.27853	YES	YES
23	a	48.89	0.05056	YES	YES
24	a	50.79	0.15072	YES	YES
25	a	53.38	0.17542	YES	YES
26	a	54.93	0.21758	YES	YES
27	a	58.82	0.78956	YES	YES
28	a	59.67	0.16534	YES	YES
29	a	63.48	0.03424	YES	YES
30	a	67.89	0.30869	YES	YES
31	a	68.25	0.33188	YES	YES

32	a	75.30	0.19248	YES	YES
33	a	76.29	2.06882	YES	YES
34	a	84.58	1.24899	YES	YES
35	a	94.46	0.23955	YES	YES
36	a	98.39	4.93460	YES	YES
37	a	103.49	1.55262	YES	YES
38	a	105.66	0.17388	YES	YES
39	a	112.09	3.70983	YES	YES
40	a	124.17	4.06085	YES	YES
41	a	134.74	6.55020	YES	YES
42	a	141.94	3.05020	YES	YES
43	a	143.19	1.40835	YES	YES
44	a	148.87	0.40580	YES	YES
45	a	155.65	3.76085	YES	YES
46	a	163.95	1.03244	YES	YES
47	a	165.31	0.37542	YES	YES
48	a	168.00	0.89374	YES	YES
49	a	171.17	1.05720	YES	YES
50	a	182.28	13.38740	YES	YES

S6.6 Complex $[2a]^+ + Cl^-$, C-Cl distance 2.5 Å

SCF Energy (au) (RI)BP86/SV(P) -4695.2611714000
SCF Energy (au) PBE0/def2-TZVPP -4694.540889117
SCF Energy (au) PBE0/def2-TZVPP -4694.5795424415 (CH_2Cl_2 Correction)
Zero Point Energy (au) 0.8886137
Chemical potential (kJ mol^{-1}) 2050.14
Dispersion correction (au) PBE0/def2-TZVPP -0.22601327

xyz coordinates
117

C	0.89682	-7.71594	1.91580
Cl	-0.09818	-9.41494	0.36780
C	0.06139	-1.03320	0.14725
C	-1.42365	0.90614	-3.06730
C	1.38578	1.69632	-3.63790
C	0.75428	-1.09691	-3.28111
C	1.27567	0.95384	2.59420
C	-0.95013	2.88664	2.81031
C	-1.58590	0.10730	3.02918
C	3.35616	-0.21901	0.82710
P	-2.15723	0.80500	-1.33693
Cl	-0.04651	3.31251	-0.92380
P	2.04549	1.07956	0.87478
P	0.36994	0.57208	-2.58244
P	-0.50311	1.25394	2.05654
Ru	-0.03714	0.89806	-0.24719
C	0.18339	-2.26043	0.38827
C	0.35957	-3.62927	0.70561
C	-3.20344	-0.72070	-1.34089
C	-3.45702	2.12634	-1.21693
C	3.02328	2.65171	0.90002
H	-1.49161	1.94671	-3.44725
H	-1.85612	0.20919	-3.81640
H	1.67391	1.64860	3.36435
H	1.39561	-0.09373	2.94272
C	-3.35615	-1.65468	4.36090
C	-2.05964	-2.07699	4.02120
C	-1.18100	-1.20596	3.35363
C	-2.89407	0.52317	3.37077
C	-3.77135	-0.35294	4.03077
H	-4.04383	-2.34089	4.88266
H	-1.72472	-3.09770	4.26872
H	-0.18142	-1.57020	3.07177
H	-3.23112	1.54317	3.12540
H	-4.78657	-0.01091	4.29264
C	-1.69686	5.33277	4.00200
C	-1.10007	4.32419	4.78191
C	-0.73231	3.10624	4.19121
C	-1.54837	3.89950	2.03258
C	-1.91941	5.11790	2.63241
H	-1.98768	6.28954	4.46715
H	-0.92646	4.48546	5.85902

H	-0.28441	2.31495	4.81655
H	-1.68064	3.74693	0.94962
H	-2.38170	5.90563	2.01539
C	5.35943	-2.20213	0.72582
C	4.43108	-2.08459	-0.32218
C	3.42911	-1.09921	-0.27095
C	4.29411	-0.34006	1.87791
C	5.28913	-1.32934	1.82762
H	6.13960	-2.98048	0.68730
H	4.47266	-2.77172	-1.18274
H	2.68525	-1.02737	-1.07972
H	4.25450	0.34838	2.73949
H	6.01686	-1.41803	2.65193
C	4.46055	5.08732	0.84915
C	5.03422	3.91914	0.32032
C	4.32096	2.70800	0.34331
C	2.44509	3.83606	1.40976
C	3.16510	5.04111	1.39239
H	5.02268	6.03596	0.83600
H	6.05093	3.94385	-0.10688
H	4.78755	1.79721	-0.06517
H	1.42371	3.82711	1.82095
H	2.70128	5.95439	1.80022
C	1.37679	-3.69153	-4.21908
C	2.27890	-2.63366	-4.42054
C	1.97168	-1.34294	-3.95506
C	-0.14006	-2.17011	-3.06809
C	0.16727	-3.45508	-3.54325
H	1.61673	-4.70360	-4.58482
H	3.22987	-2.80844	-4.95114
H	2.68377	-0.52063	-4.12901
H	-1.08085	-2.00986	-2.51786
H	-0.54109	-4.28207	-3.37218
C	2.97350	3.36612	-5.26442
C	3.23400	3.26817	-3.88746
C	2.44011	2.44153	-3.07376
C	1.12796	1.79733	-5.02342
C	1.91674	2.63140	-5.83204
H	3.59331	4.02070	-5.89972
H	4.05296	3.85031	-3.43384
H	2.62618	2.39303	-1.99002
H	0.30962	1.21499	-5.48032
H	1.70704	2.70501	-6.91217
C	-4.85976	-3.00617	-1.27268
C	-4.02348	-2.70919	-0.18404
C	-3.19372	-1.57264	-0.21697
C	-4.05775	-1.01823	-2.42773
C	-4.87651	-2.15783	-2.39570
H	-5.50245	-3.90187	-1.24779
H	-4.00474	-3.36834	0.69887
H	-2.52313	-1.35409	0.62779
H	-4.09792	-0.34999	-3.30468
H	-5.53643	-2.38322	-3.25005
C	-5.44163	4.12395	-0.92122
C	-4.28109	4.38285	-1.66966
C	-3.28950	3.39719	-1.81263

C	-4.62405	1.87656	-0.45828
C	-5.60699	2.86903	-0.31105
H	-6.21707	4.90032	-0.81235
H	-4.13831	5.36637	-2.14761
H	-2.36952	3.63414	-2.36717
H	-4.77616	0.89281	0.01447
H	-6.51340	2.65380	0.27892
C	0.71837	-6.39407	1.42448
C	1.64056	-5.38979	1.86303
C	1.44888	-4.05147	1.53537
C	-0.51768	-4.65463	0.21779
C	-0.35342	-5.99119	0.57283
H	2.49664	-5.68455	2.49229
H	2.16133	-3.29396	1.89966
H	-1.34148	-4.36168	-0.45404
H	-1.01835	-6.78343	0.18886
C	1.35138	-8.43182	2.93853
H	1.60742	-7.92946	3.89278
H	1.46251	-9.52534	2.88209

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules	
#		cm**(-1)	km/mol	IR	RAMAN
1	a	-184.97	0.00000	YES	YES
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7		0.00	0.00000	-	-
8	a	14.23	0.31876	YES	YES
9	a	15.99	0.38862	YES	YES
10	a	17.59	0.04022	YES	YES
11	a	21.11	0.36741	YES	YES
12	a	24.16	0.03247	YES	YES
13	a	25.95	0.14825	YES	YES
14	a	28.34	0.13931	YES	YES
15	a	30.31	0.16311	YES	YES
16	a	32.81	0.15185	YES	YES
17	a	35.21	0.24358	YES	YES
18	a	39.11	0.01853	YES	YES
19	a	40.86	0.10213	YES	YES
20	a	44.01	0.03828	YES	YES
21	a	46.36	0.06230	YES	YES
22	a	48.58	0.00329	YES	YES
23	a	49.91	0.01743	YES	YES
24	a	51.11	0.32898	YES	YES
25	a	53.25	0.03426	YES	YES
26	a	54.10	0.02502	YES	YES
27	a	56.65	0.03999	YES	YES
28	a	58.47	0.86655	YES	YES
29	a	58.82	0.35364	YES	YES
30	a	62.03	0.12092	YES	YES
31	a	64.50	0.35903	YES	YES

32	a	70.00	0.08568	YES	YES
33	a	73.06	2.41551	YES	YES
34	a	81.60	0.84816	YES	YES
35	a	88.27	0.94784	YES	YES
36	a	89.55	2.58097	YES	YES
37	a	92.90	0.04069	YES	YES
38	a	98.22	0.07744	YES	YES
39	a	101.93	0.07931	YES	YES
40	a	111.71	2.68077	YES	YES
41	a	128.27	2.90384	YES	YES
42	a	133.15	2.89115	YES	YES
43	a	136.11	2.89804	YES	YES
44	a	148.32	0.98124	YES	YES
45	a	152.31	0.85345	YES	YES
46	a	163.44	0.39700	YES	YES
47	a	166.59	4.18839	YES	YES
48	a	170.97	0.61832	YES	YES
49	a	178.30	4.25957	YES	YES
50	a	183.83	1.04220	YES	YES

Complex	bp86_SVP SCF energy (a.u.)	bp86_SVP Zero Point Energy (a.u.)	bp86_SVP Chem Pot (KJ mol^{-1})	D3 correction tzvpp	pbe0_TZVVP_sp SCF energy (a.u.)	pbe0_TZVVP_sp SCF energy (a.u.) COSMO	Rel. H_sp (kJ mol-1) pbe0/TZVPP COSMO + D3	Rel. G_sp (kJ mol-1) pbe0/TZVPP COSMO + D3	C-Cl distance	imaginary freq /cm-1
[6a]	-4695.312894	0.891071	2046.62	-0.226758	-4694.606199	-4694.635062	0	0	1.77	
[7a]	-4695.275095	0.890588	2055.28	-0.232670	-4694.560937	-4694.592525	95	105	1.86	
[2a] + Cl-										
1.90	-4695.308608	0.890641	2054.52	-0.226565	-4694.599075	-4694.628602	16	25	1.90	0
2.00	-4695.301566	0.890160	2053.03	-0.226409	-4694.589960	-4694.620198	38	46	2.00	0
2.10	-4695.293143	0.889624	2050.31	-0.226253	-4694.579266	-4694.610435	62	70	2.10	0
2.2	-4695.284386	0.889135	2052.25	-0.226094	-4694.568505	-4694.600893	86	97	2.2	-107
2.3	-4695.275846	0.888909	2051.44	-0.225976	-4694.557984	-4694.591942	110	120	2.3	-161
2.40	-4695.268209	0.888859	2049.87	-0.226156	-4694.549507	-4694.585636	126	135	2.40	-179
2.5	-4695.261171	0.888614	2050.14	-0.226013	-4694.540889	-4694.579542	141	151	2.5	-185
2.6	-4695.254689	0.888550	2048.64	-0.225869	-4694.533896	-4694.575669	152	160	2.6	-180
2.70	-4695.248826	0.888433	2047.63	-0.225703	-4694.527662	-4694.572893	159	167	2.70	-176
2.80	-4695.243771	0.888325	2047.56	-0.225550	-4694.522506	-4694.571463	163	171	2.80	-170
2.9	-4695.239298	0.888230	2047.09	-0.225384	-4694.518207	-4694.570987	164	172	2.9	-164
3.00	-4695.235198	0.888150	2045.94	-0.225222	-4694.514652	-4694.571343	164	171	3.00	-157
3.10	-4695.232560	0.888160	2044.26	-0.225582	-4694.514334	-4694.575890	151	156	3.10	-145
3.2	-4695.229859	0.888098	2043.10	-0.225426	-4694.511767	-4694.575982	151	155	3.2	-135
3.30	-4695.227399	0.887845	2036.13	-0.225397	-4694.510772	-4694.578068	145	143	3.30	-129
[1a]+ + Cl										
1.90	-4695.274860	0.890443	2055.36	-0.232600	-4694.559913	-4694.591540	97	108	1.90	0
2.00	-4695.272600	0.890005	2054.01	-0.232412	-4694.555830	-4694.587773	107	117	2.00	0
2.10	-4695.269057	0.889568	2051.19	-0.232246	-4694.550717	-4694.583229	118	126	2.10	0
2.2	-4695.265668	0.889263	2054.57	-0.231984	-4694.545908	-4694.579212	128	141	2.2	-70
2.3	-4695.262392	0.889178	2055.09	-0.231991	-4694.541454	-4694.575761	137	150	2.3	-94
2.40	-4695.260489	0.889278	2054.78	-0.232163	-4694.538825	-4694.573906	142	155	2.40	-97
2.5	-4695.258470	0.889141	2054.74	-0.232451	-4694.536678	-4694.572128	145	158	2.5	-94
2.6	-4695.255952	0.889105	2053.40	-0.232956	-4694.534865	-4694.572445	143	155	2.6	-82
2.70	-4695.255387	0.889014	2052.77	-0.232822	-4694.534303	-4694.572699	142	154	2.70	-70
2.75	-4695.253317	0.889027	2053.21	-0.233118	-4694.532720	-4694.571584	145	157	2.75	-64
2.80	-4695.245619	0.888695	2053.14	-0.231592	-4694.524003	-4694.564032	168	180	2.80	-82
2.83	-4695.250940	0.888650	2051.23	-0.231766	-4694.531630	-4694.571835	147	157	2.83	-53
2.85	-4695.251207	0.888624	2049.11	-0.231790	-4694.531522	-4694.571667	147	156	2.85	-51
2.9	-4695.251951	0.888820	2053.78	-0.232518	-4694.532015	-4694.572542	143	156	2.9	-59
3.00	-4695.248745	0.888644	2052.98	-0.232993	-4694.529555	-4694.571619	144	157	3.00	-51
3.10	-4695.248586	0.888636	2050.84	-0.233311	-4694.530611	-4694.572966	139	150	3.2	-45
3.2	-4695.247185	0.888493	2053.64	-0.233026	-4694.529241	-4694.572899	140	154	3.2	-35
3.30	-4695.246238	0.888499	2052.66	-0.232817	-4694.529308	-4694.574146	137	150	3.30	-31
[**1a**]+	-4234.97960	0.889723	2056.13	-0.22488	-4234.309749	-4234.365766	1208438	1208451		
Chloride	-460.23742			0.000000	-460.117339	-460.225625	11115698	11115991		
sum	-4695.217015	0.889723	2056.130000	-0.224882	-4694.427087	-4694.591390	116	129		
[**2a**]+	-4234.97588	0.889117	2051.94	-0.22208	-4234.29748	-4234.351335	1208482	1208493		
Chloride	-460.23742			0.000000	-460.117339	-460.225625	11115698	11115991		
sum	-4695.213303	0.889117	2051.940000	-0.222083	-4694.414819	-4694.576960	160	170		

Table S3 Collated energies, C-Cl distances and imaginary frequencies for complexes studies by DFT.

S7 References

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3. S. Takahashi, Y. Kuroyama, K. Sonogashira and N. Hagihara, *Synthesis-Stuttgart*, 1980, 627.
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