The preparation, characterisation and electronic structures of 2,4-pentadiynylnitrile (cyanobutadiynyl) complexes

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Supporting Information

General conditions

All reactions were carried out in oven dried (110 ºC) glassware and in a dry high-purity nitrogen environment, using standard Schlenk techniques. Solvents were dried on an Innovative Technologies SPS-400 system and degassed prior to use. The compounds $[Ru(C{=}CH_2)(PPh_3)_2Cp]PF_6$,[S1] $[Ru(C{=}CH_2)(dppe)Cp^*]PF_6$,[S2] $Ru(C{\equiv}CC{\equiv}CSiMe_3(PPh_3)_2Cp$,[S3] $Ru(C{\equiv}CC{\equiv}CSiMe_3)(dppe)Cp^*$[S3] and 1-cyano-4-dimethylaminopyridinium tetrafluoroborate ($[CAP]BF_4$)[S4] were prepared according the literature methods. All other reagents were purchased and used as received.

NMR spectra were obtained using Bruker and Varian Mercury-400 (^{1}H, 399.97 MHz; ^{13}C, 100.57 MHz; ^{31}P, 161.10 MHz), Varian Inova-500 (^{1}H, 499.77 MHz, ^{13}C, 125.67 MHz; ^{31}P, 202.31 MHz) or Varian VNMRS-700 (^{1}H, 699.73 MHz, ^{13}C, 175.95 MHz ; ^{31}P, 279.89 MHz) spectrometers in $CDCl_3$, and referenced against solvent references (^{1}H, 7.26 ppm; ^{13}C, 77.0 ppm) or external H_3PO_4 (^{31}P). Mass spectra were obtained using a Bruker Daltonik Autoflex II ToF / ToF mass spectrometer equipped with a 337 nm laser, a TQD mass spectrometer and a Waters Ltd. Xevo QToF mass spectrometer. Infrared spectra were recorded in solution cells fitted with CaF_2 windows on a Thermo Nicolet FT-6700 spectrometer.

Preparation of Ru(C≡CC≡N)(PPh$_3$)$_2$Cp (**3a**)

[Ru(C=CH$_2$)(PPh$_3$)$_2$Cp]PF$_6$ (292 mg, 0.34 mmol) and KO^{t}Bu (39 mg, 0.34 mmol) were added to CH$_2$Cl$_2$ (14 ml) and stirred for 40 min. To the resulting dark coloured solution, [CAP]BF$_4$ (100 mg, 0.34 mmol) was added and the reaction stirred for a further 15 min., during which time the solution coloured darkened further. The reaction mixture was then filtered and filtrate concentrated to dryness leaving a dark brown residue, which was purified using column chromatography over silica (70 : 30, hexane : acetone). A yellow band was collected and solvent removed under reduced pressure to yield a yellow-brown solid (121 mg, 48 %). IR (CH$_2$Cl$_2$, cm^{-1}): 2181s, 1999m ν(C≡CC≡N). ^{1}H NMR δ / ppm: 4.31 (s, 5H, Cp), 7.04 - 7.63 (m, 30H, Ph). ^{31}P NMR δ / ppm: 47.8 (s, PPh$_3$). ^{13}C NMR δ / ppm: 81.8 (s, C$_\beta$), 85.4 (s, Cp), 106.5 (s, C$_\gamma$), 126.2 - 136.7 (m, Ph), 139.5 (t, J = 22 Hz, C$_\alpha$). ESI(+)-MS : *m/z* 1432 [2.M – C$_3$N]$^+$, 741 [M]$^+$, 691 [M - C$_3$N]$^+$, 479 [M - PPh$_3$]$^+$, 429 [M - C$_3$N - PPh$_3$]$^+$, 167 [M - C$_3$N - 2.PPh$_3$]$^+$.

*Preparation of Ru(C≡CC≡N)(dppe)Cp** (**3b**)

[Ru(C=CH$_2$)(dppe)Cp*]PF$_6$ (497 mg, 0.68 mmol) and KO^{t}Bu (79 mg, 0.70 mmol) were added to CH$_2$Cl$_2$ (10 ml) and stirred for 50 min. yielding a green solution. To this solution, [CAP]BF$_4$ (119 mg, 0.68 mmol) was added and the reaction stirred for a further 10 min. to afford a deep red solution. The reaction mixture was filtered and filtrate concentrated to complete dryness leaving a dark residue, which was purified using column chromatography over silica (40 : 60, hexane: acetone). A yellow band was collected and solvent removed under reduced pressure to yield a bright yellow solid (225 mg, 49 %). (49%) IR (CH$_2$Cl$_2$ / cm^{-1}): ν(C≡CC≡N) 2175s, 1994m. ^{1}H NMR δ / ppm: 1.46 (s, 15H, Cp*); 2.01 - 2.17 (m, 2H, dppe); 2.46 - 2.67

(m, 2H, dppe); 7.05 - 7.57 (m, 20H, Ph). ^{31}P NMR δ / ppm: 78.3 (s, dppe). ^{13}C NMR δ / ppm: 8.8 (s, Cp*); 28.3 (t, J = 24 Hz, dppe); 77.0 (s, C_β); 93.1 (s, Cp*); 107.3 (s, C_γ); 126.7 - 136.1 (m, Ph); 150.6 (t, J = 22 Hz, C_α). ASAP(+)-MS: *m*/*z* 686 $[M + H]^+$; 685 $[M]^+$; 635 $[M - C_3N]^+$.

Preparation of Ru(C≡CC≡CC≡N)(PPh$_3$)$_2$Cp (**4a**)

A sample of Ru(C≡CC≡CSiMe$_3$)(PPh$_3$)$_2$Cp (638 mg, 0.79 mmol) was dissolved in CH_2Cl_2 (8 ml). To the brown solution, [CAP]BF_4 (277 mg, 1.18 mmol) was added and the mixture stirred for 45 min. After this time, the solvent was removed *in vacuo* and the crude product was purified by column chromatography over neutral alumina (act. I) using CH_2Cl_2 as the initial eluent to which the first orange-brown band was discarded and the product then obtained using EtOAc : CH_2Cl_2 (3 : 97). To remove remaining impurities, the product was recrystallised twice from CH_2Cl_2 / hexane by slow layer diffusion in the freezer, yielding the product as pale brown crystals suitable for X-ray diffraction (265 mg, 44 %). ^{1}H NMR δ / ppm: 4.43 (s, 5H, Cp); 7.17 (t, J = 7 Hz, 12H, H_o); 7.28 (t, J = 7 Hz, 6H, H_p); 7.32 (m, 12H, H_m). ^{31}P NMR δ / ppm: 49.4. ^{13}C NMR δ / ppm: 53.4 (s, C_δ); 86.7 (s, Cp); 72.4 (s, C_γ); 93.4 (s (br), C_β); 108.4 (s, C_ε); 127.5 (s, C_o); 129.1 (s, C_p); 133.4 (s, C_m); 136.0 (s, C_{ipso}); 145.5 (t, J = 26 Hz, C_α). IR (CH_2Cl_2 / cm^{-1}): ν(C≡CC≡CC≡N) 2192w; 2112m; 1977w. MALDI(+)-MS: *m*/*z* 765 $[M]^+$; 691 $[M - C_5N]^+$.

*Preparation of Ru(C≡CC≡CC≡N)(dppe)Cp** (**4b**)

A sample of Ru(C≡CC≡CSiMe$_3$)(dppe)Cp* (157 mg, 0.20 mmol) was dissolved in CH_2Cl_2 (5 ml) and treated with [CAP]BF_4 (59 mg, 0.25 mmol). The mixture was

stirred for 45 min., during which a colour change of the solution from yellow to dark orange was observed. The solvent was removed *in vacuo* and the residue extracted with CH_2Cl_2 (3 x 2 ml). The extracts were filtered via cannular, concentrated and layered with hexane under an inert atmosphere yielding a brown precipitate. The mother liquor was then decanted and slowly evaporated to obtain a purer sample, yielding crystals suitable for X-ray diffraction (15 mg; 10 %), although it was not possible to purify the product completely. ^{1}H NMR δ / ppm: 1.51 (s, 15H, Cp*); 2.04 - 2.23 (2H, m, dppe); 2.53 - 2.72 (2H, m, dppe); 7.16 - 7.60 (m, 20H, Ph). ^{31}P NMR δ / ppm: 79.8. IR (CH_2Cl_2 / cm^{-1}): ν(C≡CC≡CC≡N) 2187w, sh; 2105m, sh; 1973w; 1945m. MALDI(+)-MS : *m*/*z* 709 $[M]^+$, 685 $[M + 2.H - CN]^+$.

X-ray crystallography

Single crystal X-ray diffraction data for compounds **4a** and **4b** were collected at 120K on a Bruker SMART 6000 CCD area detector diffractometer equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostat using graphite-monochromated Mo-Kα radiation (λ=0.71073Å). Both structures were solved by direct methods and refined by full-matrix least-squares on F^2 for all data using SHELXTL[S5] and OLEX2[S6] software. All non-disordered non-H atoms were refined with anisotropic atomic displacement parameters. H-atoms were placed in calculated positions and refined in "riding mode". Disordered atoms in the structure **4a** were refined isotropically with fixed SOF. The crystallographic and refinement parameters for studied compounds are given in Table S1. CCDC numbers 916018 and 916019 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table S1 Crystal data and structure refinement for 4a and 4b		
Identification code	4a	4b
Empirical formula	$C_{46}H_{35}NP_2Ru$ x 1.5 CH_2Cl_2 x 0.125 C_6H_{14}	$C_{41}H_{39}NP_2Ru$
Formula weight	902.92	708.74
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/n$
a/Å	8.8477(3)	10.2903(2)
b/Å	13.5114(5)	22.7951(5)
c/Å	18.6418(7)	14.8498(3)
α/°	87.912(10)	90.00
β/°	81.897(10)	108.363(10)
γ/°	72.388(10)	90.00
Volume/$Å^3$	2102.82(13)	3305.92(12)
Z	2	4
$\rho_{calc}mg/mm^3$	1.426	1.424
μ/mm^{-1}	0.675	0.602
F(000)	923.0	1464.0
2Θ range for data collection	2.2 to 57°	3.4 to 57°
Reflections collected	25093	52188
Independent reflections	10610[R(int) = 0.0467]	8382[R(int) = 0.0530]
Data/restraints/parameters	10610/0/510	8382/0/411
Goodness-of-fit on F^2	1.030	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0473, wR_2 = 0.1151	R_1 = 0.0421, wR_2 = 0.0980
Final R indexes [all data]	R_1 = 0.0700, wR_2 = 0.1293	R_1 = 0.0545, wR_2 = 0.1075

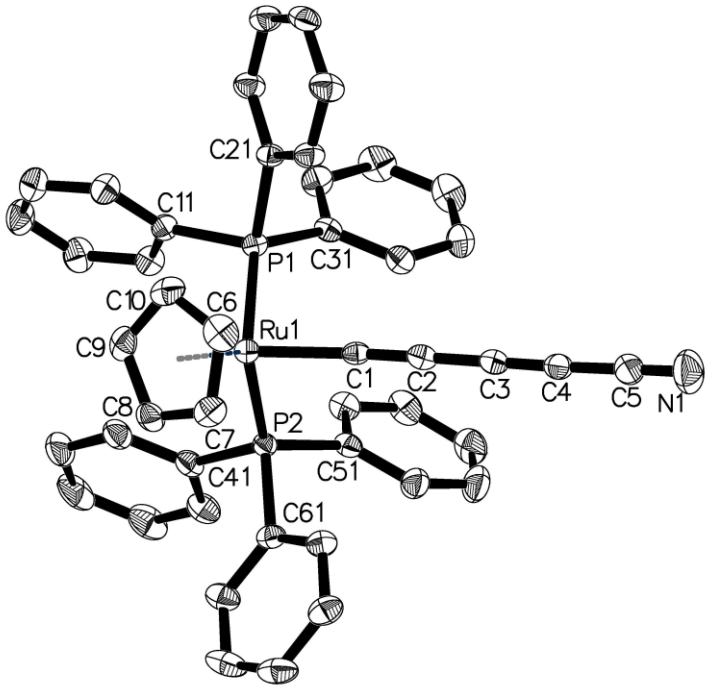


Figure S1. A plot of a molecule of **4a**, showing the atom labelling scheme

Table S2 Bond Lengths for 4a					
Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Ru1	P1	2.2947(8)	C25	C26	1.387(5)
Ru1	P2	2.3050(9)	C31	C32	1.400(4)
Ru1	C1	1.958(3)	C31	C36	1.392(5)
Ru1	C6	2.221(3)	C32	C33	1.387(5)
Ru1	C7	2.241(3)	C33	C34	1.376(6)
Ru1	C8	2.256(3)	C34	C35	1.388(5)
Ru1	C9	2.269(3)	C35	C36	1.386(5)
Ru1	C10	2.233(3)	C41	C42	1.382(5)
P1	C11	1.828(3)	C41	C46	1.404(5)
P1	C21	1.847(3)	C42	C43	1.401(5)
P1	C31	1.838(3)	C43	C44	1.372(6)
P2	C41	1.840(3)	C44	C45	1.383(6)
P2	C51	1.835(3)	C45	C46	1.378(5)
P2	C61	1.850(3)	C51	C52	1.401(5)
N1	C5	1.148(5)	C51	C56	1.389(5)
C1	C2	1.230(4)	C52	C53	1.389(5)
C2	C3	1.346(5)	C53	C54	1.375(6)
C3	C4	1.215(5)	C54	C55	1.383(6)
C4	C5	1.362(5)	C55	C56	1.399(5)
C6	C7	1.424(5)	C61	C62	1.394(5)
C6	C10	1.412(5)	C61	C66	1.391(5)
C7	C8	1.406(5)	C62	C63	1.389(5)
C8	C9	1.412(5)	C63	C64	1.390(5)
C9	C10	1.422(5)	C64	C65	1.390(6)
C11	C12	1.399(5)	C65	C66	1.385(5)
C11	C16	1.396(4)	Cl1	C1S	1.712(9)
C12	C13	1.392(5)	Cl2	C1S	1.761(9)
C13	C14	1.378(5)	C1H	C2H	1.43(2)
C14	C15	1.386(5)	C2H	C3H	1.34(2)
C15	C16	1.391(5)	C3H	C3H[1]	1.41(3)
C21	C22	1.397(4)	Cl3	C2SA	1.790(8)
C21	C26	1.391(4)	Cl3	C2SB	1.730(10)
C22	C23	1.380(5)	Cl4	C2SA	1.745(8)
C23	C24	1.391(5)	Cl4	C2SB	1.775(10)
C24	C25	1.379(5)			

[1]-X,2-Y,1-Z

Table S3 Bond Angles for 4a.							
Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
P1	Ru1	P2	100.40(3)	C6	C10	C9	108.2(3)
C1	Ru1	P1	93.66(9)	C9	C10	Ru1	72.95(19)
C1	Ru1	P2	88.87(9)	C12	C11	P1	121.1(2)
C1	Ru1	C6	91.14(14)	C16	C11	P1	120.2(2)
C1	Ru1	C7	96.61(13)	C16	C11	C12	118.3(3)
C1	Ru1	C8	130.43(13)	C13	C12	C11	120.5(3)
C1	Ru1	C9	152.58(13)	C14	C13	C12	120.6(3)
C1	Ru1	C10	120.17(14)	C13	C14	C15	119.6(3)
C6	Ru1	P1	116.87(10)	C14	C15	C16	120.3(3)
C6	Ru1	P2	142.64(10)	C15	C16	C11	120.7(3)
C6	Ru1	C7	37.23(13)	C22	C21	P1	120.5(2)
C6	Ru1	C8	61.27(14)	C26	C21	P1	120.6(2)
C6	Ru1	C9	61.49(14)	C26	C21	C22	118.7(3)
C6	Ru1	C10	36.95(14)	C23	C22	C21	120.4(3)
C7	Ru1	P1	152.03(10)	C22	C23	C24	120.8(3)
C7	Ru1	P2	105.73(10)	C25	C24	C23	118.9(3)
C7	Ru1	C8	36.43(13)	C24	C25	C26	120.8(3)
C7	Ru1	C9	61.19(13)	C25	C26	C21	120.4(3)
C8	Ru1	P1	134.80(9)	C32	C31	P1	122.2(3)
C8	Ru1	P2	91.15(10)	C36	C31	P1	118.4(2)
C8	Ru1	C9	36.36(13)	C36	C31	C32	118.9(3)
C9	Ru1	P1	99.99(9)	C33	C32	C31	120.0(3)
C9	Ru1	P2	111.60(10)	C34	C33	C32	120.9(3)
C10	Ru1	P1	90.71(9)	C33	C34	C35	119.5(3)
C10	Ru1	P2	148.33(11)	C36	C35	C34	120.3(3)
C10	Ru1	C7	61.68(13)	C35	C36	C31	120.4(3)
C10	Ru1	C8	61.09(13)	C42	C41	P2	120.4(3)
C10	Ru1	C9	36.82(14)	C42	C41	C46	118.6(3)
C11	P1	Ru1	110.50(11)	C46	C41	P2	120.9(3)
C11	P1	C21	102.61(15)	C41	C42	C43	120.0(4)
C11	P1	C31	105.21(14)	C44	C43	C42	120.2(4)
C21	P1	Ru1	114.65(10)	C43	C44	C45	120.5(4)
C31	P1	Ru1	124.23(11)	C46	C45	C44	119.3(4)
C31	P1	C21	96.96(14)	C45	C46	C41	121.2(4)
C41	P2	Ru1	119.21(12)	C52	C51	P2	118.9(3)
C41	P2	C61	102.04(15)	C56	C51	P2	122.5(3)
C51	P2	Ru1	121.61(10)	C56	C51	C52	118.6(3)
C51	P2	C41	100.04(15)	C53	C52	C51	120.8(3)
C51	P2	C61	103.70(15)	C54	C53	C52	119.9(4)
C61	P2	Ru1	107.69(11)	C53	C54	C55	120.3(3)
C2	C1	Ru1	171.9(3)	C54	C55	C56	120.1(4)
C1	C2	C3	178.9(4)	C51	C56	C55	120.2(3)
C4	C3	C2	178.7(4)	C62	C61	P2	118.9(3)
C3	C4	C5	176.6(4)	C66	C61	P2	122.2(3)

N1	C5	C4	179.8(5)	C66	C61	C62	118.6(3)
C7	C6	Ru1	72.13(19)	C63	C62	C61	120.8(3)
C10	C6	Ru1	72.00(19)	C62	C63	C64	120.2(4)
C10	C6	C7	108.0(3)	C65	C64	C63	119.0(3)
C6	C7	Ru1	70.64(19)	C66	C65	C64	120.8(4)
C8	C7	Ru1	72.38(19)	C65	C66	C61	120.5(4)
C8	C7	C6	107.5(3)	Cl1	C1S	Cl2	111.9(5)
C7	C8	Ru1	71.19(19)	C3H	C2H	C1H	125.2(17)
C7	C8	C9	109.1(3)	C2H	C3H	C3H[1]	143(2)
C9	C8	Ru1	72.32(19)	C2SB	Cl3	C2SA	20.9(4)
C8	C9	Ru1	71.32(19)	C2SA	Cl4	C2SB	21.0(4)
C8	C9	C10	107.2(3)	Cl4	C2SA	Cl3	112.0(4)
C10	C9	Ru1	70.23(19)	Cl3	C2SB	Cl4	113.5(6)
C6	C10	Ru1	71.05(19)				

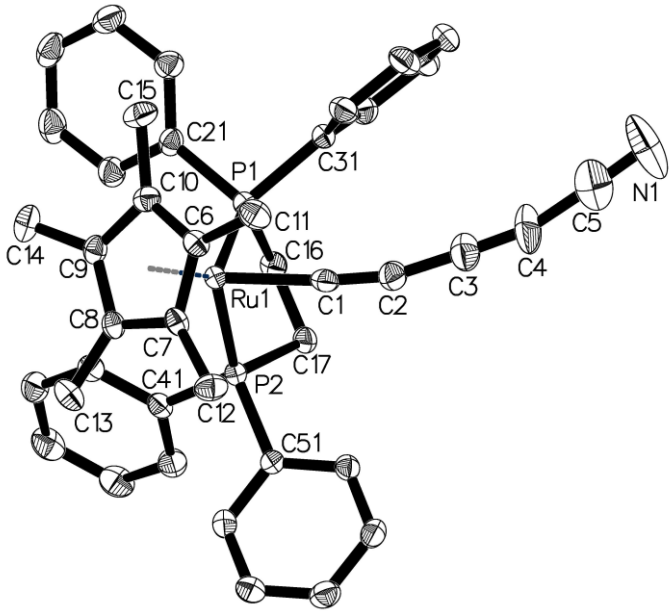


Figure S2. A plot of a molecule of **4b**, showing the atom labelling scheme.

Table S3 Bond Lengths for 4b.					
Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Ru1	P1	2.2914(7)	C9	C14	1.497(4)
Ru1	P2	2.2647(7)	C10	C15	1.496(4)
Ru1	C1	1.968(3)	C16	C17	1.532(4)
Ru1	C6	2.250(3)	C21	C22	1.407(4)
Ru1	C7	2.226(3)	C21	C26	1.400(4)
Ru1	C8	2.256(2)	C22	C23	1.391(4)
Ru1	C9	2.276(3)	C23	C24	1.386(5)
Ru1	C10	2.269(3)	C24	C25	1.385(5)
P1	C16	1.854(3)	C25	C26	1.386(4)
P1	C21	1.834(3)	C31	C32	1.396(4)
P1	C31	1.841(3)	C31	C36	1.395(4)
P2	C17	1.836(3)	C32	C33	1.388(4)
P2	C41	1.829(3)	C33	C34	1.387(5)
P2	C51	1.824(3)	C34	C35	1.384(4)
N1	C5	1.176(5)	C35	C36	1.393(4)
C1	C2	1.223(4)	C41	C42	1.401(4)
C2	C3	1.364(4)	C41	C46	1.387(4)
C3	C4	1.198(5)	C42	C43	1.384(4)
C4	C5	1.411(6)	C43	C44	1.383(5)
C6	C7	1.436(4)	C44	C45	1.386(4)
C6	C10	1.421(4)	C45	C46	1.392(4)
C6	C11	1.495(4)	C51	C52	1.399(4)
C7	C8	1.436(4)	C51	C56	1.393(4)
C7	C12	1.497(4)	C52	C53	1.385(4)
C8	C9	1.428(4)	C53	C54	1.391(4)
C8	C13	1.490(4)	C54	C55	1.378(4)
C9	C10	1.444(4)	C55	C56	1.396(4)

Table S4 Bond Angles for 4b.								
Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**
P2	Ru1	P1	83.25(3)		C8	C7	C12	126.0(2)
P2	Ru1	C9	119.87(7)		C12	C7	Ru1	125.51(19)
P2	Ru1	C10	156.90(7)		C7	C8	Ru1	70.18(14)
C1	Ru1	P1	85.28(8)		C7	C8	C13	124.2(2)
C1	Ru1	P2	85.69(8)		C9	C8	Ru1	72.42(14)
C1	Ru1	C6	90.10(10)		C9	C8	C7	108.5(2)
C1	Ru1	C7	98.62(10)		C9	C8	C13	126.8(3)
C1	Ru1	C8	134.47(10)		C13	C8	Ru1	129.46(19)
C1	Ru1	C9	151.46(10)		C8	C9	Ru1	70.85(14)
C1	Ru1	C10	116.51(10)		C8	C9	C10	107.5(2)
C6	Ru1	P1	129.38(7)		C8	C9	C14	127.9(3)
C6	Ru1	P2	146.67(7)		C10	C9	Ru1	71.19(15)
C6	Ru1	C8	61.85(10)		C10	C9	C14	123.7(3)
C6	Ru1	C9	61.68(10)		C14	C9	Ru1	131.98(19)
C6	Ru1	C10	36.66(9)		C6	C10	Ru1	70.97(15)
C7	Ru1	P1	165.67(7)		C6	C10	C9	108.2(2)
C7	Ru1	P2	110.71(7)		C6	C10	C15	126.8(3)
C7	Ru1	C6	37.42(9)		C9	C10	Ru1	71.76(15)
C7	Ru1	C8	37.37(9)		C9	C10	C15	124.3(3)
C7	Ru1	C9	62.16(9)		C15	C10	Ru1	130.37(19)
C7	Ru1	C10	62.06(10)		C17	C16	P1	109.81(18)
C8	Ru1	P1	140.22(7)		C16	C17	P2	105.78(17)
C8	Ru1	P2	98.83(7)		C22	C21	P1	120.8(2)
C8	Ru1	C9	36.74(9)		C26	C21	P1	120.7(2)
C8	Ru1	C10	61.57(9)		C26	C21	C22	118.2(3)
C9	Ru1	P1	108.66(7)		C23	C22	C21	120.3(3)
C10	Ru1	P1	103.83(7)		C24	C23	C22	120.5(3)
C10	Ru1	C9	37.05(10)		C25	C24	C23	119.9(3)
C16	P1	Ru1	109.36(9)		C24	C25	C26	120.1(3)
C21	P1	Ru1	118.64(9)		C25	C26	C21	121.1(3)
C21	P1	C16	104.67(12)		C32	C31	P1	121.7(2)
C21	P1	C31	100.93(12)		C36	C31	P1	119.7(2)
C31	P1	Ru1	117.52(9)		C36	C31	C32	118.6(2)
C31	P1	C16	104.07(12)		C33	C32	C31	120.8(3)
C17	P2	Ru1	107.22(9)		C34	C33	C32	119.9(3)
C41	P2	Ru1	120.49(9)		C35	C34	C33	120.0(3)
C41	P2	C17	100.15(12)		C34	C35	C36	120.0(3)
C51	P2	Ru1	117.22(9)		C35	C36	C31	120.5(3)
C51	P2	C17	106.87(12)		C42	C41	P2	121.4(2)
C51	P2	C41	102.97(12)		C46	C41	P2	119.8(2)
C2	C1	Ru1	174.1(2)		C46	C41	C42	118.6(3)
C1	C2	C3	166.1(3)		C43	C42	C41	120.5(3)
C4	C3	C2	178.1(4)		C44	C43	C42	120.3(3)
C3	C4	C5	166.1(5)		C43	C44	C45	119.9(3)
N1	C5	C4	175.4(5)		C44	C45	C46	119.9(3)
C7	C6	Ru1	70.35(15)		C41	C46	C45	120.8(3)

C7	C6	C11	124.9(2)		C52	C51	P2	120.8(2)
C10	C6	Ru1	72.37(15)		C56	C51	P2	120.6(2)
C10	C6	C7	108.4(2)		C56	C51	C52	118.4(2)
C10	C6	C11	126.6(3)		C53	C52	C51	120.4(2)
C11	C6	Ru1	126.15(19)		C52	C53	C54	120.7(3)
C6	C7	Ru1	72.23(15)		C55	C54	C53	119.5(3)
C6	C7	C8	107.5(2)		C54	C55	C56	120.1(3)
C6	C7	C12	126.2(2)		C51	C56	C55	120.9(3)
C8	C7	Ru1	72.45(14)					

Computational details

All ground state structures and properties were obtained using a version of the TURBOMOLE 6.4 code[S7] locally modified by the Berlin group. The DFT optimisations were performed with the global hybrid functional BLYP35:[S8a]

$$E_{XC} = (1-a)(E_X^{LSDA} + \Delta E_X^{B88}) + aE_X^{exact} + E_C^{LYP}, \qquad (1)$$

with a = 0.35. While this is not a thermochemically optimised functional, BLYP35 has proven to provide a good balance between reduced self-interaction errors and a simulation of static correlation, thus providing good agreement with ground- and excited-state experimental data of previously organic mixed-valence systems[S8] as well as mixed-valence transition metal complexes.[S9] It is thus expected to provide a good description of localisation / delocalisation for the systems studied here. As experiments were mainly carried out in dichloromethane (permittivity ε = 8.93), this solvent was considered by the conductor-like-screening solvent model (COSMO).[S10]

For all calculations, split valence basis sets def2-SVP on the lighter atoms and the corresponding def2-SVP effective-core potentials with a corresponding valence basis for ruthenium were employed.[S11] Calculated harmonic vibrational frequencies were scaled by an empirical factor of 0.95.[S12] Spin density and molecular orbital plots were obtained using the Molekel program.[S13]

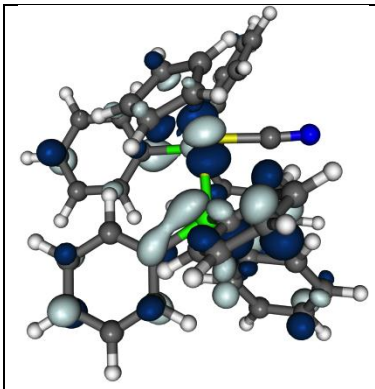
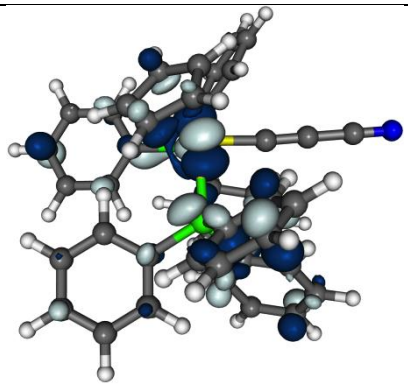
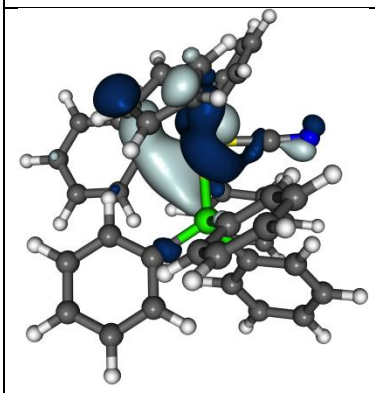
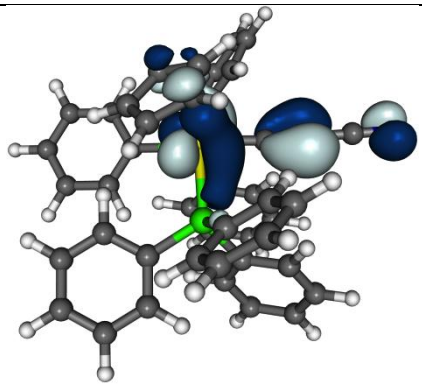
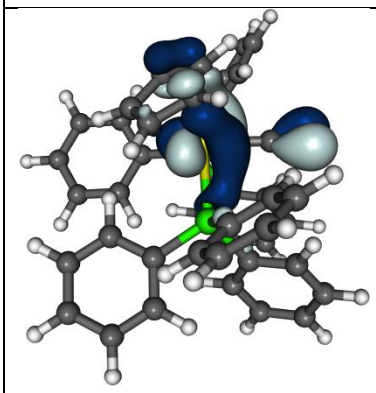
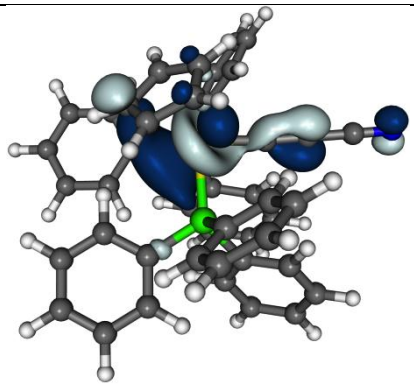
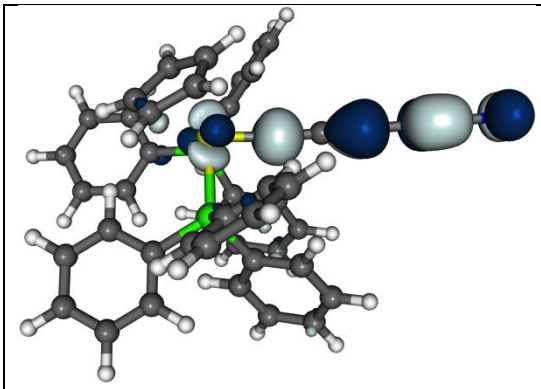
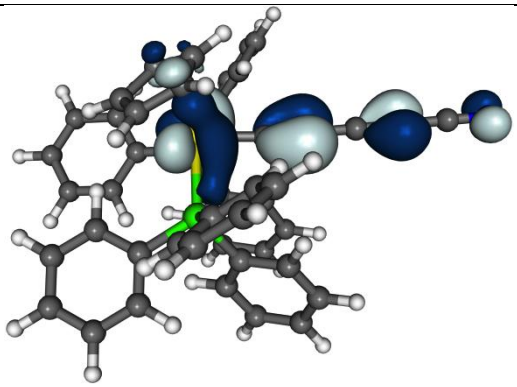
	
LUMO	**LUMO**
	
HOMO	**HOMO**
	
HOMO–1	**HOMO–1**

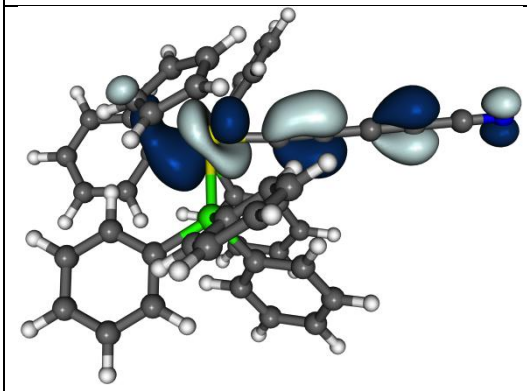
Fig. S3 Isosurface plots (± 0.04 a.u.) of the frontier orbitals of **2a´** (left) and **3a´** (right).



LUMO



HOMO



HOMO–1

Fig. S4 Isosurface plots (± 0.04 a.u.) of the frontier orbitals of **4a´**.

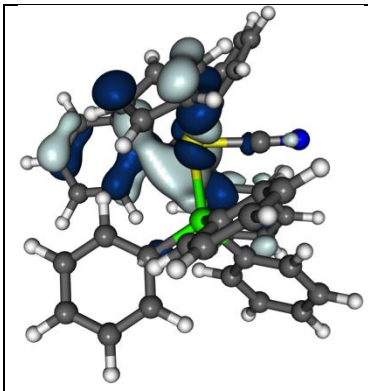
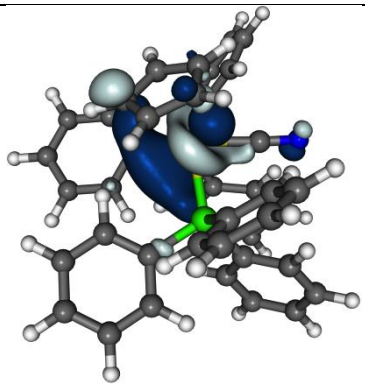
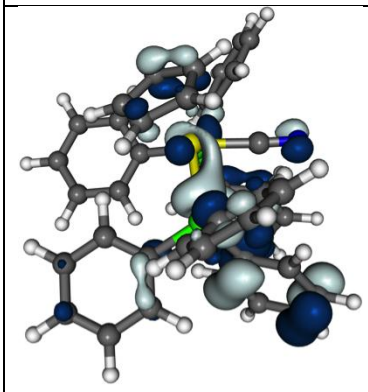
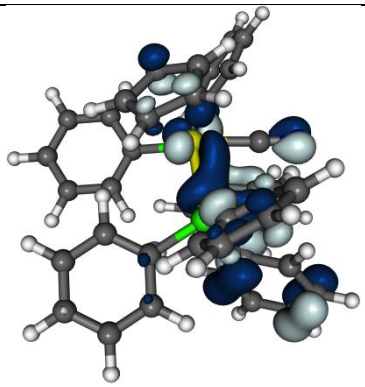
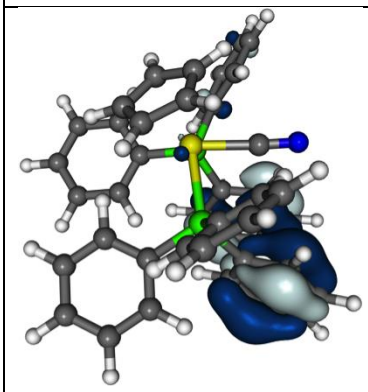
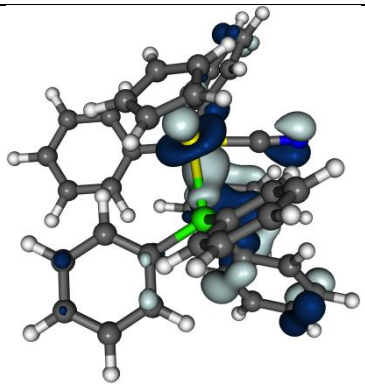
	
α-SOMO	**β-SOMO (unoccupied)**
	
α–HOMO	**β-HOMO**
	
α-HOMO–1	**β-HOMO–1**

Fig. S5 Isosurface plots (± 0.04 a.u.) of the frontier orbitals of **[2a´]**$^{+}$.

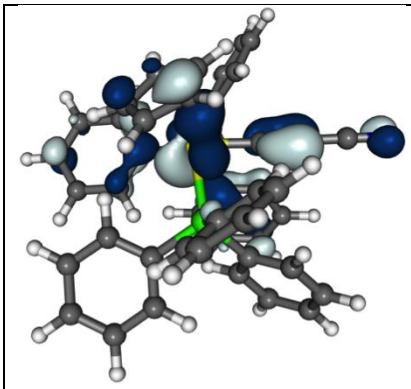
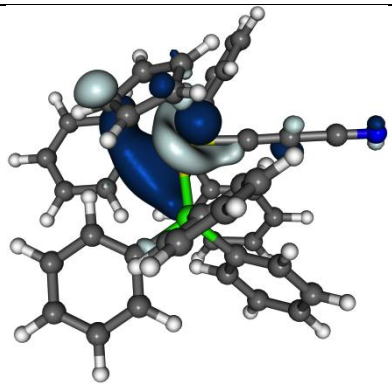
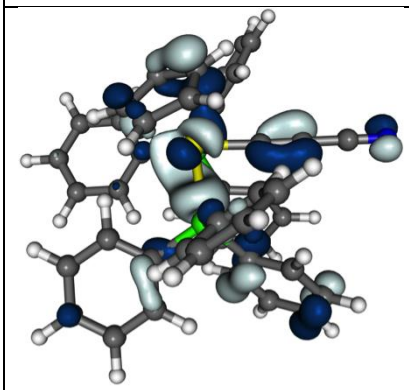
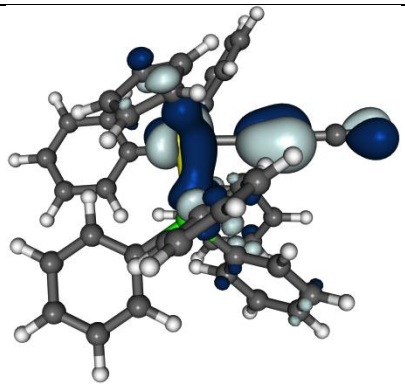
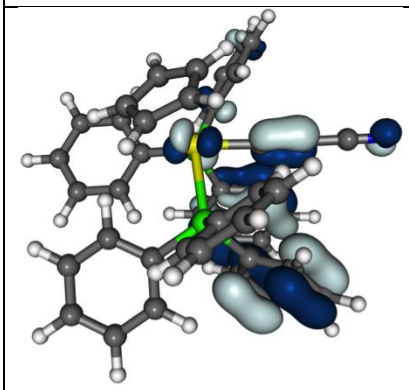
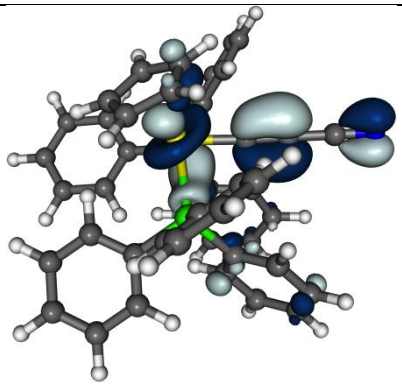
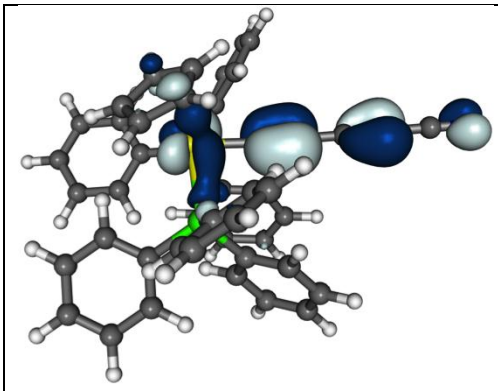
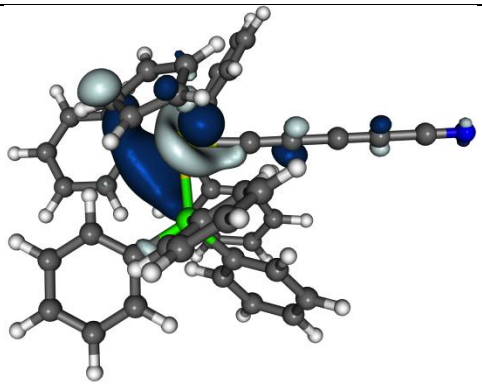
	
α-SOMO	**β-SOMO (unoccupied)**
	
α–HOMO	**β-HOMO**
	
α-HOMO–1	**β-HOMO–1**

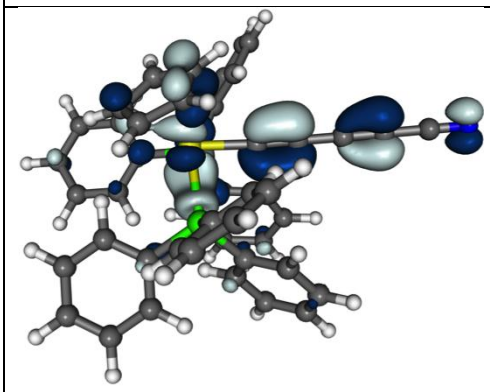
Fig. S6 Isosurface plots (± 0.04 a.u.) of the frontier orbitals of **[3a´]**$^{+}$.



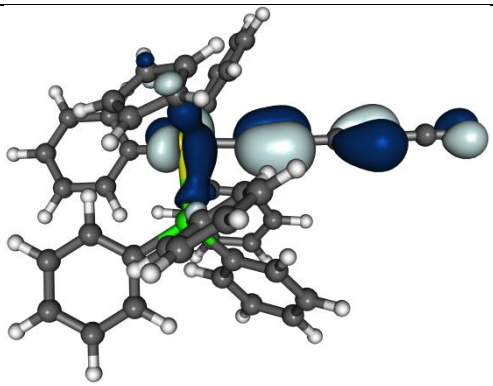
α-SOMO



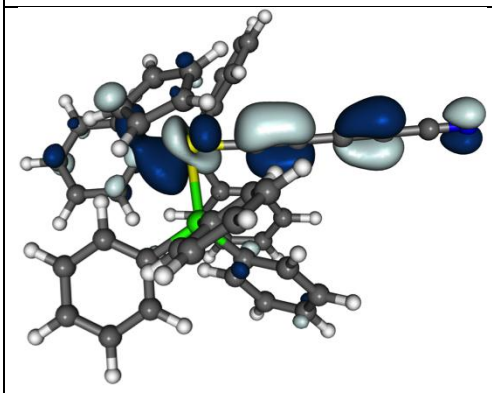
β-SOMO (unoccupied)



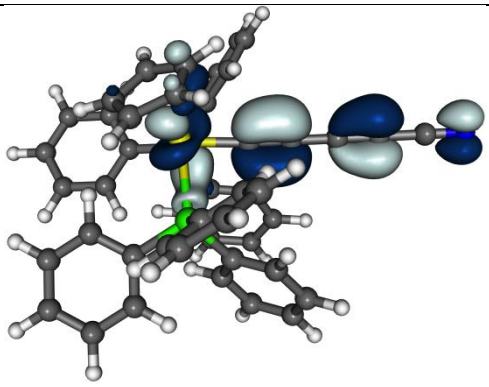
α–HOMO



β-HOMO



α-HOMO–1



β-HOMO–1

Fig. S7 Isosurface plots (± 0.04 a.u.) of the frontier orbitals of **[4a´]**$^{+}$.

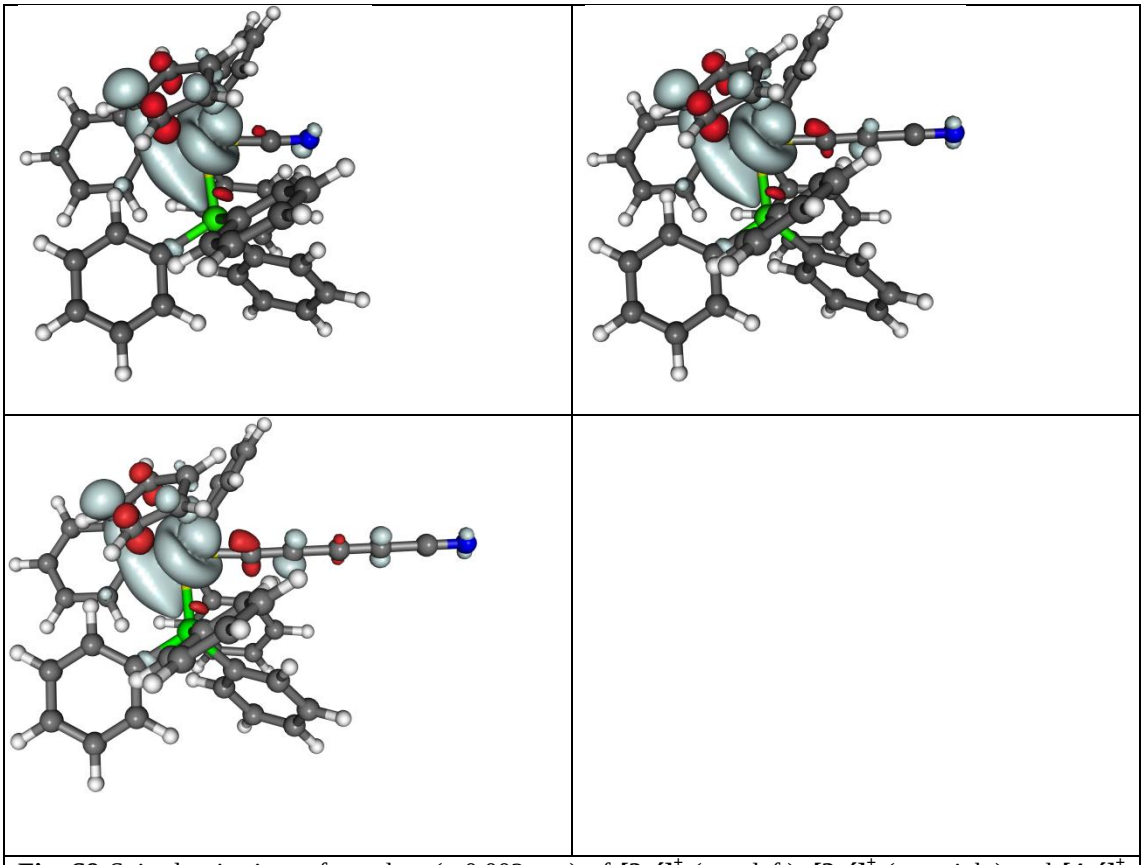


Fig. S8 Spin density isosurface plots (± 0.002 a.u.) of **[2a´]**$^+$ (top, left), **[3a´]**$^+$ (top, right) and **[4a´]**$^+$ (bottom).

Table S5 Orbital energies and contributions from ruthenium and the CN- (**2a´** and **[2a´]**$^+$), C_3N- (**3a´** and **[3a´]**$^+$) or C_5N-ligand (**4a´** and **[4a´]**$^+$) from Mulliken population analysis and spin expectation value $<S>^2$ (The "spin-pure" value would be 0.00 for the neutral and 0.75 for the cationic systems) of **2a´ - 4a´** and cations [**2a´ - 4a´**]$^+$.

	2a´	**3a´**	**4a´**		**[2a´]**$^+$	**[3a´]**$^+$	**[4a´]**$^+$
Orbital	**E [eV] (composition Ru/C_nN [%])**			**Orbital**	**E [eV] (composition Ru/C_nN [%])**		
LUMO+1	-0.30 (8/0)	-0.37 (7/0)	-0.63 (4/89)	α–LUMO β–LUMO	-1.94 (37/0) -1.72 (37/0)	-1.99 (37/0) -1.76 (37/0)	-2.00 (37/0) -1.77 (35/3)
LUMO	-0.44 (12/0)	-0.52 (16/0)	-0.69 (8/64)	α–SOMO β–SOMO	-7.54 (20/1) -3.87 (64/4)	-7.52 (17/17) -3.90 (63/6)	-7.34 (15/53) -3.94 (61/7)
HOMO	-5.95 (55/5)	-5.86 (42/32)	-5.78 (35/43)	α–HOMO β–HOMO	-7.69 (8/3) -7.65 (10/4)	-7.60 (18/13) -7.48 (20/32)	-7.54 (16/35) -7.26 (19/54)
HOMO−1	-6.05 (52/14)	-6.02 (56/15)	-5.99 (47/40)	α–HOMO−1 β-HOMO−1	-7.92 (1/0) -7.88 (20/4)	-7.88 (5/12) -7.64 (28/36)	-7.66 (22/43) -7.40 (21/57)
$<S>^2$	0.00	0.00	0.00		0.76	0.76	0.76

Table S6 Atomic Mulliken spin densities for the cations with BLYP35 and B3LYP functionals.

[2a´]$^+$							
	Ru	**C1**	**N1**				
BLYP35	0.83	0.01	0.01				
B3LYP	0.77	0.01	0.01				
[3a´]$^+$							
	Ru	**C1**	**C2**	**C3**	**N1**		
BLYP35	0.84	-0.01	0.03	-0.01	0.01		
B3LYP	0.77	-0.01	0.04	-0.01	0.02		
[4a´]$^+$							
	Ru	**C1**	**C2**	**C3**	**C4**	**C5**	**N1**
BLYP35	0.83	-0.03	0.05	-0.02	0.03	-0.01	0.02
B3LYP	0.77	-0.03	0.06	-0.03	0.04	-0.01	0.02

Table S7 Cartesian coordinates for **2a´** (left) and [**2a´**]$^+$ (right)

C	-6.0540156	-0.9754685	0.9819301	-6.1131627	-0.9668396	0.9305903
C	-4.7064888	-0.5960264	0.9973643	-4.7809419	-0.5359753	0.8935705
C	-3.8869914	-0.9733979	-0.0769392	-3.9854589	-0.8619568	-0.2151804
C	-4.4087377	-1.7002278	-1.1429396	-4.5176582	-1.6017533	-1.2661748
C	-5.7518025	-2.0761081	-1.1499138	-5.8436581	-2.0323535	-1.2229621
C	-6.5703419	-1.7165537	-0.0824118	-6.6370726	-1.7165503	-0.1228371
P	-3.9628679	0.5255633	2.2723204	-4.0698861	0.5965714	2.1550948
C	-4.0171073	2.0986262	1.2783783	-4.0316716	2.1812039	1.224905
C	-5.2221892	2.528721	0.7006927	-5.2288386	2.6777754	0.6845332
C	-5.2690088	3.6837351	-0.0734262	-5.2283658	3.8477314	-0.0670566
C	-4.1066813	4.4250954	-0.2968041	-4.0324848	4.5288954	-0.3032683
C	-2.9033241	4.0005483	0.2586952	-2.8390481	4.0321671	0.2125987
C	-2.8598726	2.8449029	1.042045	-2.8375354	2.8625899	0.973924
Ru	-1.8970984	0.1366389	3.3453398	-2.0605973	0.0716417	3.4213747
C	-0.9982326	-0.0418695	1.5730274	-1.1515313	-0.1489919	1.6543324
N	-0.3987527	-0.093322	0.5729775	-0.5694445	-0.2333278	0.6527592
P	-1.8558453	-2.2241483	3.5166017	-1.8198704	-2.3458733	3.5624805
C	-2.8817433	-3.0297735	4.8344513	-2.8586118	-3.1141546	4.8726251
C	-2.9816516	-4.4281243	4.9314718	-3.001639	-4.5108761	4.9215408
C	-3.7226058	-5.0203528	5.9494643	-3.7448572	-5.1086314	5.9341768
C	-4.3790098	-4.2272942	6.8929907	-4.3604844	-4.3242425	6.9109304
C	-4.2906082	-2.8411586	6.8064465	-4.2277358	-2.9391104	6.8702086
C	-3.5486903	-2.2493085	5.7820762	-3.4803236	-2.3386324	5.8568694
C	-2.2301239	-3.3150577	2.0644496	-2.1857519	-3.3873058	2.0929252
C	-1.2504203	-3.6661768	1.1280497	-1.1815574	-3.8846673	1.2547331
C	-1.5612473	-4.4907878	0.0472058	-1.5094423	-4.6929809	0.1668611
C	-2.8555719	-4.9780519	-0.1173032	-2.8387433	-5.0160526	-0.093914
C	-3.8436491	-4.6193711	0.7977744	-3.8454039	-4.5192769	0.7332092
C	-3.5351737	-3.7900604	1.8724085	-3.5227021	-3.7056802	1.8144059
C	-0.1289886	-2.7374336	3.9992582	-0.0857961	-2.7408735	4.0522477
C	0.9561361	-2.2806026	3.2322793	0.9840368	-2.2918625	3.2599427
C	2.2637688	-2.6239596	3.5672937	2.2983444	-2.5740548	3.6231364
C	2.5208414	-3.4103894	4.6905434	2.5681099	-3.2912536	4.7889381
C	1.4567281	-3.8489156	5.4731328	1.5144935	-3.7258815	5.5883184
C	0.1442501	-3.5179046	5.1300945	0.195015	-3.4556619	5.2240393
C	-0.1175262	0.796768	4.5702442	-0.1904622	0.7645196	4.4515978
C	-0.6470302	1.9393966	3.8949509	-0.7447089	1.8904263	3.7716997
C	-1.9625277	2.1642958	4.3705867	-2.007383	2.1808047	4.3511419
C	-2.2595292	1.1733291	5.362766	-2.2355625	1.2486577	5.4019912
C	-1.1184444	0.3372372	5.4759347	-1.1180573	0.369098	5.4605792
C	-5.3087254	0.7844584	3.5145678	-5.3393367	0.798772	3.4660794
C	-5.8622479	-0.3217944	4.1755881	-5.8099006	-0.3372029	4.1437016
C	-6.8092651	-0.1542972	5.1827769	-6.700774	-0.2095527	5.2061556
C	-7.2088038	1.1267953	5.5642049	-7.122864	1.0542223	5.6175407
C	-6.6546288	2.234736	4.9273678	-6.6497468	2.1888038	4.9604733
C	-5.7154749	2.0656808	3.909116	-5.7629847	2.0653197	3.8921071
H	-2.6164989	2.9753235	4.0685622	-2.668547	2.9920949	4.0660968

H	-3.1680688	1.1167358	5.9517454	-3.1090052	1.2246953	6.0464703
H	-1.0125651	-0.5038608	6.1537821	-0.9699505	-0.430135	6.1794415
H	0.8778141	0.3846993	4.4511158	0.7806713	0.3215267	4.2636848
H	-0.1251672	2.5326042	3.1513075	-0.2660028	2.4368264	2.9665948
H	-0.6619242	-3.8732791	5.7641917	-0.6075829	-3.8071405	5.8655521
H	1.6408551	-4.4533949	6.3601697	1.7128519	-4.2809377	6.5034966
H	0.7838624	-1.6397492	2.3713304	0.8001286	-1.7160315	2.356443
H	-2.4764975	-5.0644869	4.2084339	-2.5293202	-5.1389467	4.1699544
H	-3.7878392	-6.105814	6.0070375	-3.8438196	-6.1922708	5.959803
H	-4.959376	-4.6915348	7.6888964	-4.9439012	-4.794211	7.7007422
H	-4.8047573	-2.2127777	7.5318927	-4.7072434	-2.3193289	7.625481
H	-3.5004425	-1.1677244	5.7094106	-3.3948073	-1.2566935	5.8403585
H	-6.1363776	1.9582356	0.8529128	-6.1678451	2.1517779	0.8456218
H	-6.2144003	4.0038426	-0.5090275	-6.1638892	4.2255951	-0.4755441
H	-4.1414219	5.3265148	-0.9070246	-4.033117	5.4419475	-0.8962537
H	-1.9891462	4.5653246	0.0821066	-1.9007513	4.5492982	0.020864
H	-1.9140996	2.5127341	1.4576577	-1.8963969	2.4742382	1.3479791
H	-5.3037993	2.94651	3.4228313	-5.4105197	2.9638925	3.3921859
H	-6.9548338	3.240332	5.2182791	-6.9736667	3.1789596	5.2758859
H	-7.9462389	1.2592478	6.3543279	-7.8186771	1.1541482	6.4486658
H	-7.2315811	-1.0291347	5.6747071	-7.0637584	-1.1013606	5.713552
H	-5.5537308	-1.3292383	3.9068694	-5.4904025	-1.3327425	3.8437155
H	-4.324102	-3.5258922	2.5721326	-4.3238389	-3.3375938	2.4510829
H	-4.8626961	-4.981746	0.6749089	-4.8873233	-4.763534	0.5372703
H	-3.0944915	-5.6299348	-0.956356	-3.0908238	-5.6549381	-0.9386894
H	-0.7807951	-4.7565953	-0.6643963	-0.716047	-5.0770337	-0.4718926
H	-0.2311906	-3.3095392	1.2344202	-0.1361779	-3.6640848	1.445881
H	-6.7207911	-0.6867738	1.7897019	-6.7600796	-0.7127605	1.7653167
H	-7.6214012	-2.0023905	-0.0765878	-7.674719	-2.043477	-0.0824967
H	-6.1574023	-2.6481189	-1.9833194	-6.2575718	-2.6114734	-2.0468307
H	-3.757912	-1.9809529	-1.9692444	-3.8907779	-1.8442321	-2.1221904
H	-2.8356008	-0.6953233	-0.0850384	-2.9497067	-0.5362231	-0.2656012
H	3.5439714	-3.6715936	4.9566232	3.5966499	-3.5059196	5.0737343
H	3.086476	-2.2652626	2.9503414	3.1145331	-2.2259777	2.9925099

Table S8 Cartesian coordinates for **3a´** (left) and [**3a´**]$^+$ (right)

C	-6.0867416	-0.9721559	1.0155945	-6.1396108	-1.0564296	1.0854224
C	-4.7374612	-0.5982136	1.007856	-4.8527096	-0.5242761	0.940532
C	-3.9396614	-0.9789726	-0.080709	-4.1449158	-0.761084	-0.247362
C	-4.4812376	-1.7021544	-1.1389038	-4.7146149	-1.5135172	-1.2684968
C	-5.8259906	-2.0713698	-1.1230706	-5.995577	-2.0447989	-1.117419
C	-6.6240428	-1.7097498	-0.0407147	-6.7031913	-1.8170027	0.0601
P	-3.9681447	0.5258075	2.2649773	-4.0853345	0.6077344	2.1702943
C	-4.0268958	2.0954386	1.267861	-4.0508351	2.177742	1.2154017
C	-5.2377726	2.5248725	0.7017	-5.2498366	2.6543355	0.6604694
C	-5.2922129	3.6797032	-0.0720607	-5.2582939	3.8176247	-0.101154
C	-4.1323689	4.4215209	-0.306308	-4.0694151	4.5123255	-0.3334446
C	-2.923555	3.9974198	0.2375251	-2.874022	4.0354329	0.1962819
C	-2.8718635	2.841619	1.0201259	-2.8638797	2.8723628	0.9675475
Ru	-1.8869007	0.1370543	3.3214139	-2.0431245	0.076601	3.3918025
C	-0.9999717	-0.0170343	1.5712572	-1.1658382	-0.1353538	1.6225871
C	-0.3613878	-0.0376587	0.5120896	-0.5665347	-0.2241091	0.5569471
C	0.3358107	-0.0641999	-0.6599195	0.0888809	-0.3367931	-0.6414403
N	0.9327821	-0.0855682	-1.6599858	0.6422702	-0.4328137	-1.6566738
P	-1.8392939	-2.2290048	3.5053268	-1.7897479	-2.343441	3.5316988
C	-2.886685	-3.0303494	4.8085005	-2.8820689	-3.1244211	4.7911003
C	-3.0103037	-4.4278937	4.8888286	-3.1218075	-4.5078238	4.7602107
C	-3.7602151	-5.0196368	5.9006605	-3.8963038	-5.111797	5.7464245
C	-4.4015115	-4.227313	6.8548391	-4.4424492	-4.34774	6.778111
C	-4.2896248	-2.8419074	6.7848474	-4.2087621	-2.9754828	6.819868
C	-3.5392588	-2.2504182	5.7667303	-3.43407	-2.3687003	5.8320025
C	-2.1834659	-3.3217356	2.0492009	-2.0573671	-3.3810451	2.0399566
C	-1.1788324	-3.6911528	1.1466427	-0.9975945	-3.9376256	1.3143704
C	-1.4672788	-4.512323	0.0569565	-1.2504149	-4.7390414	0.2017108
C	-2.762945	-4.9808373	-0.1471338	-2.5601799	-5.0016997	-0.1918598
C	-3.7736686	-4.6084661	0.7373795	-3.6209431	-4.4519914	0.5270497
C	-3.4881665	-3.7798733	1.8188371	-3.3723138	-3.6409669	1.6298471
C	-0.1216024	-2.7389624	4.0202163	-0.0813344	-2.7353724	4.1047658
C	0.977592	-2.253469	3.293061	1.0225836	-2.2447961	3.3888029
C	2.279599	-2.60096	3.6450894	2.3197186	-2.534968	3.8029799
C	2.5152795	-3.4219879	4.7479737	2.5360248	-3.3054812	4.9458883
C	1.4362716	-3.890329	5.4921825	1.4474395	-3.7857972	5.6687592
C	0.12999	-3.5548117	5.1309345	0.145456	-3.5064282	5.2519252
C	-0.119395	0.8096213	4.572454	-0.1676904	0.7936584	4.4124708
C	-0.6468389	1.9481435	3.8915174	-0.7379281	1.9130067	3.7377519
C	-1.9688902	2.1659911	4.3530207	-2.0011623	2.1870729	4.3236997
C	-2.2685449	1.1768398	5.3462066	-2.2114834	1.2523445	5.3765764
C	-1.126463	0.3467339	5.4706921	-1.0845944	0.3862431	5.4270171
C	-5.2942741	0.7950141	3.5256016	-5.3194956	0.8489347	3.5094572
C	-5.8443735	-0.3064705	4.1971204	-5.7407156	-0.2641777	4.2542004
C	-6.7788296	-0.1310776	5.2146524	-6.6083263	-0.1084659	5.3320388
C	-7.1690645	1.1530905	5.5951318	-7.055007	1.162443	5.6927027
C	-6.6181254	2.2563421	4.9473402	-6.6295665	2.275168	4.9694287

C	-5.6912956	2.0795905	3.919247	-5.7669043	2.1230508	3.8847648
H	-2.6230982	2.9745804	4.0453001	-2.6734709	2.9910099	4.0440947
H	-3.1838215	1.1146025	5.923963	-3.0818962	1.2160825	6.0245026
H	-1.0217516	-0.492995	6.1503716	-0.9209498	-0.411844	6.1436997
H	0.8795231	0.4029581	4.465914	0.808957	0.3647179	4.2225227
H	-0.1211516	2.5437679	3.1525808	-0.2701351	2.4656468	2.9305866
H	-0.6881289	-3.9342979	5.7349383	-0.6863806	-3.8953612	5.8320325
H	1.6040924	-4.5220853	6.3632431	1.6048854	-4.3844138	6.5641993
H	0.8180837	-1.5854139	2.4508084	0.8748983	-1.632542	2.5026931
H	-2.5161387	-5.0644149	4.158592	-2.7008061	-5.1222611	3.968477
H	-3.8439955	-6.1044155	5.9447471	-4.0721195	-6.1852895	5.7081077
H	-4.9883378	-4.6911748	7.6461728	-5.0489433	-4.8225351	7.5473802
H	-4.7917546	-2.2136278	7.5187118	-4.6303401	-2.371119	7.6208358
H	-3.4736434	-1.1691176	5.7088783	-3.2685078	-1.297077	5.882943
H	-6.1504442	1.9545498	0.8630799	-6.1831319	2.1173245	0.8185648
H	-6.2418539	3.9995018	-0.4984451	-6.1951763	4.179735	-0.5206187
H	-4.1732544	5.3228788	-0.9161977	-4.076924	5.4201169	-0.9343888
H	-2.0114029	4.562568	0.0520757	-1.94086	4.5627166	0.0072321
H	-1.9215072	2.5096225	1.4255053	-1.9213485	2.4988662	1.3525703
H	-5.2821433	2.9568638	3.4245736	-5.4510202	3.0052741	3.3342403
H	-6.9113274	3.2642332	5.2372818	-6.9715173	3.2709288	5.2456955
H	-7.8968486	1.291673	6.3930736	-7.7319918	1.2847274	6.5362811
H	-7.1988984	-1.0023134	5.7147856	-6.9333365	-0.9835626	5.8916808
H	-5.5437485	-1.3163159	3.9286311	-5.3989281	-1.2642802	3.996699
H	-4.2948328	-3.5029836	2.4930164	-4.2155765	-3.2282462	2.1785589
H	-4.7928652	-4.9585044	0.584249	-4.6478366	-4.651595	0.2286705
H	-2.9851012	-5.6297683	-0.9929958	-2.7552331	-5.6354837	-1.0553329
H	-0.6687291	-4.7911917	-0.6289329	-0.4152271	-5.1654615	-0.3510698
H	-0.1566872	-3.3546214	1.2888479	0.0319026	-3.7671675	1.6135664
H	-6.738784	-0.6812261	1.8343552	-6.7242246	-0.8716804	1.9815844
H	-7.6760417	-1.9909307	-0.0171357	-7.7067229	-2.2204642	0.1837836
H	-6.2488951	-2.6395143	-1.9504072	-6.442131	-2.6312711	-1.9186772
H	-3.8459695	-1.9850733	-1.9764755	-4.1553064	-1.6843082	-2.1864426
H	-2.8880479	-0.7047133	-0.1034008	-3.1494619	-0.3470306	-0.3831876
H	3.5335443	-3.6870275	5.0283574	3.5507459	-3.5274541	5.2716403
H	3.1140277	-2.2192322	3.0585368	3.1639413	-2.1537512	3.2311445

Table S9 Cartesian coordinates for **4a´** (left) and [**4a´**]$^{+}$ (right)

C	-6.0815207	-0.9741711	1.0117402	-6.1134505	-1.0407505	1.0437935
C	-4.7334251	-0.5959505	1.0044716	-4.8181495	-0.5220904	0.927364
C	-3.9341983	-0.9722486	-0.0845515	-4.0862428	-0.7678311	-0.2439399
C	-4.4731319	-1.6962619	-1.1434957	-4.6410061	-1.5151515	-1.277059
C	-5.8164477	-2.0706554	-1.1277473	-5.9304887	-2.0329211	-1.1543315
C	-6.6159797	-1.7127738	-0.0452491	-6.6618186	-1.7966841	0.0069166
P	-3.9696606	0.5289007	2.2631511	-4.0713579	0.6082941	2.1710663
C	-4.0300087	2.1004097	1.270427	-4.0422287	2.1856307	1.2271675
C	-5.2423274	2.5278739	0.7057898	-5.2405334	2.6556068	0.6652056
C	-5.3000333	3.6844091	-0.0651018	-5.2531051	3.8247394	-0.0874157
C	-4.1422761	4.4299478	-0.297815	-4.0687158	4.5320991	-0.3038611
C	-2.9320816	4.007692	0.2443152	-2.8738252	4.0623187	0.233337
C	-2.8770132	2.8501761	1.0241199	-2.8597899	2.8935513	0.9959524
Ru	-1.8841135	0.1404924	3.3166374	-2.0361539	0.0900558	3.4037509
C	-1.0015652	-0.0100901	1.5797476	-1.1386519	-0.0950783	1.6480747
C	-0.3529316	-0.0236556	0.5180795	-0.5170826	-0.1531586	0.5868263
C	0.347881	-0.0375236	-0.6322668	0.1569312	-0.22252	-0.5895194
C	0.9924801	-0.045431	-1.6800338	0.7652554	-0.280715	-1.6480152
C	1.7111357	-0.0517764	-2.8377923	1.450391	-0.3439118	-2.8305837
N	2.3260066	-0.0565823	-3.825494	2.0319286	-0.3974151	-3.8327541
P	-1.8381764	-2.2283228	3.5041446	-1.7895811	-2.3295902	3.5322127
C	-2.8879267	-3.0268818	4.8060011	-2.8747496	-3.1150675	4.7950601
C	-3.0137031	-4.4243613	4.8844923	-3.0899453	-4.502909	4.7768366
C	-3.7641736	-5.0159709	5.8959276	-3.8599442	-5.1105199	5.7640799
C	-4.4039883	-4.2236762	6.8511003	-4.4272418	-4.3455951	6.7838616
C	-4.2896644	-2.8383879	6.7829675	-4.2186128	-2.9691486	6.8127436
C	-3.5386981	-2.2468821	5.7653798	-3.4472782	-2.3589199	5.8241428
C	-2.1813958	-3.3188031	2.0468361	-2.0703318	-3.3613936	2.0385994
C	-1.1751668	-3.6905161	1.1470609	-1.0160305	-3.8843979	1.2808003
C	-1.4627298	-4.5114644	0.0570089	-1.2772265	-4.6824246	0.1676672
C	-2.7588276	-4.9774579	-0.1498941	-2.5896614	-4.9744545	-0.1950621
C	-3.7710073	-4.6027741	0.7319914	-3.6451028	-4.4568303	0.5548417
C	-3.4865215	-3.7743803	1.8138397	-3.3885682	-3.6495908	1.658528
C	-0.1212206	-2.7364115	4.0210706	-0.078004	-2.725883	4.094935
C	0.9791121	-2.252117	3.2949334	1.0234603	-2.233673	3.376282
C	2.2803569	-2.6015503	3.6477896	2.3222682	-2.5252858	3.7842762
C	2.5138708	-3.4233708	4.7505102	2.543351	-3.2980707	4.9246322
C	1.4336827	-3.8901423	5.494004	1.457519	-3.7788576	5.6512417
C	0.1281745	-3.5527343	5.1319842	0.1539424	-3.4985513	5.2401429
C	-0.1183694	0.8145449	4.572085	-0.1682263	0.8033955	4.4505857
C	-0.6465895	1.9532733	3.8927461	-0.7309005	1.9274543	3.7767371
C	-1.9700067	2.1674924	4.3525874	-2.0011603	2.1971644	4.348265
C	-2.2686385	1.1765203	5.3440013	-2.2239927	1.2543905	5.3916649
C	-1.1254984	0.3483368	5.4685369	-1.0967966	0.3888857	5.4508481
C	-5.2940408	0.7919822	3.526043	-5.3199201	0.8335349	3.49972
C	-5.8428269	-0.311972	4.1945288	-5.7532854	-0.287417	4.2254131
C	-6.7762734	-0.1399398	5.2135804	-6.6320568	-0.1422322	5.2956912

C	-7.166519	1.1429057	5.5983136	-7.0783206	1.12552	5.6676494
C	-6.6170828	2.248457	4.9531325	-6.641224	2.2458924	4.9632727
C	-5.6913203	2.0753201	3.9235643	-5.7671533	2.1044219	3.886435
H	-2.6251815	2.9756708	4.0459075	-2.6700214	3.003229	4.0665968
H	-3.1846309	1.1116413	5.9203007	-3.1023262	1.2133156	6.0285246
H	-1.0198014	-0.4922523	6.1469702	-0.941853	-0.4141381	6.1639746
H	0.8812658	0.4095424	4.4658319	0.8100321	0.3746931	4.2681204
H	-0.1208491	2.5514255	3.1559207	-0.2544991	2.4845868	2.9777194
H	-0.6909635	-3.9312551	5.7352022	-0.6750375	-3.8876875	5.8239738
H	1.5999811	-4.5224209	6.3649464	1.6182687	-4.3783523	6.5455087
H	0.8215562	-1.5838864	2.4524575	0.8726941	-1.6167277	2.4941097
H	-2.5211327	-5.0608234	4.1531658	-2.6532423	-5.1176808	3.9938285
H	-3.8493845	-6.100656	5.9389916	-4.01603	-6.1873699	5.7361323
H	-4.9913458	-4.6875012	7.642037	-5.0308578	-4.8232343	7.5536295
H	-4.79052	-2.2101845	7.5177322	-4.6572483	-2.3640252	7.603917
H	-3.4716616	-1.1656526	5.7094394	-3.3015403	-1.2840507	5.864706
H	-6.1534551	1.9547796	0.8659898	-6.1703613	2.1092138	0.8111378
H	-6.2506342	4.0025927	-0.4904852	-6.1896248	4.1815476	-0.5122061
H	-4.1858881	5.3329742	-0.9050081	-4.0792393	5.4442876	-0.8980808
H	-2.0214822	4.5755861	0.0597608	-1.9440409	4.6000192	0.0573372
H	-1.9254006	2.5204792	1.428419	-1.9176106	2.5265383	1.3880575
H	-5.2835064	2.9542653	3.4307711	-5.442474	2.9924187	3.3504328
H	-6.9105854	3.2552851	5.2463493	-6.9830794	3.2392383	5.2482263
H	-7.893433	1.278745	6.3975004	-7.7642491	1.2394811	6.5051501
H	-7.1955679	-1.0127746	5.7114827	-6.9660765	-1.0232108	5.8405848
H	-5.5422228	-1.3209282	3.9228035	-5.4128046	-1.2854415	3.958482
H	-4.2941998	-3.4957266	2.4860318	-4.227586	-3.2624931	2.2318442
H	-4.7904548	-4.9510048	0.576585	-4.6740534	-4.6789739	0.2803443
H	-2.9801178	-5.6267603	-0.9956811	-2.7907988	-5.6059952	-1.0587939
H	-0.6632169	-4.7921104	-0.6270074	-0.4461497	-5.0835605	-0.4097106
H	-0.1524651	-3.3567765	1.2919236	0.0162577	-3.6913963	1.555744
H	-6.7347273	-0.6861362	1.8305651	-6.7159003	-0.8490093	1.9266242
H	-7.6669321	-1.9977433	-0.0220187	-7.6717455	-2.1901922	0.1087236
H	-6.2371513	-2.6398327	-1.9554705	-6.3649588	-2.6158094	-1.9648001
H	-3.8370251	-1.9759257	-1.9814737	-4.0632176	-1.6931582	-2.1820755
H	-2.8835811	-0.6941345	-0.1076503	-3.0830774	-0.3655872	-0.3567035
H	3.5314975	-3.6902805	5.0313454	3.5593465	-3.520772	5.2458626
H	3.1157972	-2.2207688	3.0621206	3.1641725	-2.1426693	3.2099541

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