Electronic Supplementary Information for Dalton Transactions

The preparation and characterisation of ruthenium cyanovinylidene complexes

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Syntheses

All preparations were carried out on a double manifold vacuum/nitrogen line using standard Schlenk techniques. Solvents were dried on an Innovative Technologies SPS-400 system and degassed prior to use. The compounds [Ru(C≡CC$_6$H$_4$-4-Me)(dppe)Cp*],[S1] [Ru(C≡CH)(dppe)Cp*] [S2] and [CAP]BF$_4$ [S3] were prepared according the literature methods, noting that in the preparation of the CAP salts the use of freshly sublimed BrCN is essential. NMR spectroscopic measurements were carried out on Bruker DRX-400 (^{1}H 400.13 MHz, ^{31}P 161.98 MHz) or Varian Inova-500 (^{13}C 125.67 MHz) and referenced against solvent resonances or external H$_3$PO$_4$. Infrared spectra were recorded in solution cells fitted with CaF$_2$ widows on a Nicolet Avatar FT-IR spectrometer. Spectroelectrochemical work was conducted at room temperature using a gas-tight cell fitted with Pt gauze working electrode, Ag-wire pseudo reference and Pt counter electrodes.[S4] Electrochemical measurements (Autolab PG-STAT 30) were carried out using CH$_2$Cl$_2$ solutions containing 0.1 M NBu$_4$BF$_4$ electrolyte in a standard three-electrode cell using Pt electrodes, and potentials are reported on the SCE scale using an internal ferrocene/ferrocenium couple as reference (Fc/Fc$^+$ = 0.46 V).

[Ru{C=C(CN)C$_6$H$_4$-4-Me}(dppe)Cp*]BF$_4$ ([1]BF$_4$): A solution of [Ru{C≡CC$_6$H$_4$-4-Me}(dppe)Cp*] (0.05 g, 0.066 mmol) and [CAP]BF$_4$ (0.039 g, 0.166 mmol) in CH$_2$Cl$_2$ was stirred for 4 h. The resulting dark brown solution was evaporated to dryness and the residue extracted into acetone and the extracts purified by preparative TLC (silica gel, GF$_{254}$, 20 x 20 cm, 60/40 acetone/hexane). The red band isolated from the plates was crystallised (acetone/hexane) to give [**1**]BF$_4$ as a red crystalline material (0.038 g, 66%). IR (CH$_2$Cl$_2$) ν(C≡N) 2201, ν(C=C) 1580 cm^{-1}. ^{1}H NMR (*d*$_6$-acetone, 400 MHz) δ 1.69 (s, 3H, Me), 1.80 (s, 5H, Cp*), 3.00, 3.23 (2 x m, 2 x 2H, dppe), 6.53, 6.78 (2 x d, J_{HH} = 8 Hz, 2 x 2H, C$_6$H$_4$), 7.10 – 7.80 (m, 20H, Ph). ^{31}P NMR δ 72.7 (s, dppe). ^{13}C NMR δ 9.33 (s, Cp*-Me), 20.4 (s, Me), 29.0 (CH$_2$), 99.9

(s, Cp*), 105.8 (s, C_β), 120.9 (s, CN), 127.0 – 137.8 (m, Ph), 343.4 (t, J_{CP} = 16 Hz, C_α). ES(+)-MS 775.8, $[M]^+$.

Ru(C≡CC≡N)(dppe)Cp* (2): To a solution of BrCN (250 mg 2.36 mmol) in CH_2Cl_2 (40 ml) was added 4-dimethylaminopyridine (610 mg 2.36 mmol). The solution was stirred for 5 min before addition of [Ru(C≡CH)(dppe)Cp*] (1.00 g, 1.52 mmol). The reaction was stirred for 5 min, after which time the solvent was removed *in vacuo* and the crude product purified via silica column chromatography (acetone/hexane 3:7, 25 cm). The yellow band was collected and dried *in vacuo* to give a yellow powder of the title product. Yield: 763 mg (1.11 mmol, 73 %). IR (acetone, cm^{-1}): ν(C≡C) 1993, ν(C≡N) 2179. ^{1}H-NMR: δ 1.51 (s, 15H, Cp*), 2.15 (m, 2H, dppe), 2.62 (m, 2H, dppe), 7.12-7.61 (m, 20H, Ph). ^{31}P{H}-NMR: δ 80.2 (s, dppe). ES(+)MS (*m/z*) 686.4 $[M+H]^+$ (Literature:[S5] IR (acetone, cm^{-1}): ν(C≡C) 1994, ν(C≡N) 2176. ^{1}H-NMR: δ 1.51 (s, 15H, Cp*), 2.14 (m, 2H, dppe), 2.62 (m, 2H, dppe), 7.16-7.61 (m, 20H, Ph). ^{31}P{H}-NMR: δ 80.2 (s, dppe). ES(+)MS (*m/z*) 686.2 $[M+H]^+$).

[Ru{C=C(CN)$_2$}(dppe)Cp*]BF$_4$ ([3]BF$_4$): To a solution of **2** (0.05 g, 0.073 mmol) in acetonitrile (10 ml), [CAP]BF_4 (0.043 g, 0.18 mmol) in acetonitrile (3 ml) was added. The mixture was allowed to stir for 2 h, before the solvent was removed and the residue extracted (acetone) and purified by preparative TLC (acetone/hexane 4:6). The peach-orange coloured band was collected and isolated as a solid by precipitation (acetone/diethyl ether) (0.017 g, 36%). Crystals suitable for X-ray diffraction were obtained by crystallisation from acetone/hexane. IR (CH_2Cl_2) ν(C≡N) 2221, ν(C=C) 1539 cm^{-1}.^{1}H NMR (*d*$_6$-acetone, 400 MHz) δ 1.82 (s, 5H, Cp*), 3.09, 3.24 (2 x m, 2 x 2H, dppe), 7.22 – 7.34 (m, 20H, Ph). ^{31}P NMR δ 70.9 (s, dppe). ^{13}C NMR 9.55, (s, Cp*-Me), 29.2 (CH_2), 81.3 (s, Cp*), 103.3 (s, C_β), 107.9 (s, CN), 128.6, 129.9 (2 x dd, J_{CP} = 6 Hz, 2 x C_i), 129.7 130.1 (m, $J_{CP} = J_{CP'}$ = 5 Hz, 2 x C_m), 132.9 (s, 2 x C_p), 133.3 (t, J_{CP} = 6 Hz, C_o), 330.0 (t, J_{CP} = 15 Hz, C_α). ES(+)-MS 710.6, $[M]^+$.

Crystallography

Single-crystal X-ray data were collected on a Bruker SMART CCD 6000 3-circle diffractometer using graphite-monochromated Mo-K_a radiation (λ = 0.71073Å). The data collections were carried out at 120 K maintained by a Cryostream (Oxford cryosystems) open-flow N_2 cryostat. Reflection intensities were integrated using the SAINT V6.45 program and corrected for absorption by the SADABS program. [S6] Structures were solved by direct method and refined by full matrix least squares against F^2 of all data using SHELXTL software. [S6] All non-hydrogen atoms were refined in anisotropic approximation. Hydrogen atoms were placed in the calculated positions and refined isotropically using a riding model. CCDC reference numbers 660903 and 660904.

Computations

All *ab initio* computations were carried out with the Gaussian 03 package.[S7] The model geometries, [**1-H**]$^+$, **1-H·**, [**3-H**]$^+$ and **3-H·**, discussed here were optimised using the B3LYP,[S8] BP86,[S9] MPW1K,[S10] or PBE1PBE [S11] functionals with no symmetry constraints. The 3-21G* basis sets (all atoms),[S12] or the pseudopotentials LANL2DZ [S13] for the Ru atom and 6-31G* basis set for all other atoms were used.[S14] Frequency calculations on these optimised geometries at the corresponding levels have no imaginary frequencies.

Comparison between the optimised geometries of [**1-H**]$^+$ and [**3-H**]$^+$ at various levels of theory and experimental geometries for [**1**]$^+$ and [**3**]$^+$ reveals very good agreement between the geometries optimised at the MPW1K/3-21G* level of theory,[S10] and the experimental geometries. The full geometries of [**1**]$^+$, **1·**, [**3**]$^+$ and **3·** were then carried out at the MPW1K/3-21G* level of theory with no symmetry constraints. Frequency calculations were computed on these optimised geometries and shown to have no imaginary frequencies. A scaling factor of 0.90 was applied to the calculated vibrational frequencies.[S15] The electronic structures were also computed at the same level of theory. The optimised geometries of [**1**]$^+$ and [**3**]$^+$ were shown to agree very well with experimental geometries of [**1**]$^+$ and [**3**]$^+$ as shown in Table S1. Atomic composition of orbitals (%) in [**1**]$^+$ and [**3**]$^+$ are given in Tables S2 and S3, respectively

Table S1. Selected calculated and crystallographically determined bond lengths.

[1]$^+$	Ru-P	Ru-C	C=C	C-C	C-N
MPW1K/3-21G*	2.325 2.302	1.836	1.329	1.420	1.157
X-ray	2.3260(3) 2.3140(3)	1.8134(13)	1.3343(17)	1.4356(19)	1.151(2)
[3]$^+$	Ru-P	Ru-C	C=C	C-C	C-N
MPW1K/3-21G*	2.343 2.312	1.809	1.339	1.416 1.415	1.156 1.156
X-ray	2.3652(6) 2.3237(6)	1.781(2)	1.358(3)	1.434(4) 1.434(4)	1.144(4) 1.146(4)

Table S2 Orbital composition (%) for [**1**]$^+$ (MPW1K/3-21G*)

MO		eV	Ru	C(1)	C(2)	C(3)	N(1)	Tol	Cp	dppe
225	L+23	0.88	16	0	1	4	3	1	3	73
224	L+22	0.59	19	2	0	1	1	0	6	70
223	L+21	0.49	26	4	5	23	23	5	2	12
222	L+20	0.45	58	0	0	7	6	2	8	18
221	L+19	0.22	73	-1	1	1	2	2	9	14
220	L+18	0.08	68	0	0	1	1	3	1	26
219	L+17	-0.18	25	1	0	0	0	0	16	57
218	L+16	-0.29	8	0	1	3	3	1	71	14
217	L+15	-0.45	72	1	0	1	1	1	10	13
216	L+14	-0.5	5	1	0	0	0	0	64	29
215	L+13	-0.92	4	4	5	9	12	59	0	7
214	L+12	-1.27	1	0	0	0	0	86	0	11
213	L+11	-1.59	4	0	0	1	1	3	3	88
212	L+10	-1.73	11	2	0	0	0	1	7	79
211	L+9	-1.75	11	3	0	0	0	5	6	75
210	L+8	-1.98	17	2	0	0	0	2	7	71
209	L+7	-2.13	2	0	0	0	0	2	1	94
208	L+6	-2.32	3	0	0	0	0	0	2	94
207	L+5	-2.35	8	18	5	2	3	14	2	48
206	L+4	-2.63	7	4	1	0	1	3	4	80
205	L+3	-2.76	16	11	3	1	2	8	7	52
204	L+2	-2.82	4	4	2	0	1	5	1	82
203	L+1	-3.28	28	0	0	0	0	0	21	51
202	LUMO	-3.93	26	47	4	3	3	6	5	6
201	HOMO	-9.13	14	10	14	0	5	51	3	2
200	H-1	-9.63	23	6	1	0	0	0	56	15
199	H-2	-9.78	8	6	0	0	0	5	42	38
198	H-3	-10.12	0	0	0	0	0	89	0	11
197	H-4	-10.45	4	0	0	1	1	1	3	90
196	H-5	-10.55	4	1	0	0	1	1	3	90
195	H-6	-10.69	5	0	2	0	1	10	2	80
194	H-7	-10.73	15	1	10	2	7	28	5	32
193	H-8	-10.82	3	0	0	0	0	2	2	92
192	H-9	-10.9	3	0	1	0	1	8	2	86
191	H-10	-10.98	2	0	0	0	0	2	3	93
190	H-11	-11.03	4	0	0	0	0	0	1	95
189	H-12	-11.1	8	0	1	0	1	2	8	80
188	H-13	-11.34	61	1	1	0	1	1	19	17
187	H-14	-11.7	50	15	0	2	2	2	14	15
186	H-15	-12.28	32	13	2	7	11	2	13	19
185	H-16	-12.61	7	3	2	16	19	15	9	30
184	H-17	-12.65	8	1	0	16	18	8	23	27

Table S3 Orbital composition (%) for [**3**]$^+$ (MPW1K/3-21G*)

MO		eV	Ru	C(1)	C(2)	C(3)	N(1)	C(4)	N(2)	Cp	dppe
205	L+21	0.26	27	1	0	0	0	1	1	5	64
204	L+20	0.18	25	0	0	16	15	17	15	2	10
203	L+19	0.13	50	0	0	8	6	5	5	7	19
202	L+18	-0.14	84	0	0	1	1	0	0	4	11
201	L+17	-0.22	49	0	0	4	3	4	3	1	35
200	L+16	-0.47	30	1	0	0	0	0	0	15	53
199	L+15	-0.59	10	0	0	0	0	1	1	70	16
198	L+14	-0.73	70	0	1	1	1	1	2	0	24
197	L+13	-0.84	6	0	0	0	0	0	0	77	17
196	L+12	-1.02	12	0	9	14	18	14	18	3	13
195	L+11	-1.86	1	0	0	0	0	0	0	1	96
194	L+10	-1.91	3	0	1	1	1	1	1	3	88
193	L+9	-2.06	12	2	0	0	1	0	1	8	75
192	L+8	-2.26	9	2	0	0	0	0	0	4	85
191	L+7	-2.34	8	1	0	0	0	0	0	4	87
190	L+6	-2.56	3	1	0	0	0	0	0	2	94
189	L+5	-2.71	2	4	1	0	1	1	1	1	90
188	L+4	-2.9	9	2	0	0	0	0	0	4	84
187	L+3	-3.11	21	19	5	1	4	1	3	10	36
186	L+2	-3.18	15	25	8	2	5	2	5	3	36
185	L+1	-3.64	30	0	0	0	0	0	0	22	47
184	LUMO	-4.43	27	46	4	3	2	3	2	6	7
183	HOMO	-10.02	24	5	2	0	1	0	1	51	17
182	H-1	-10.11	9	6	4	0	2	0	2	38	39
181	H-2	-10.45	21	8	23	1	11	1	11	10	14
180	H-3	-10.68	1	0	0	0	0	0	1	1	96
179	H-4	-10.75	2	0	1	0	0	0	1	2	94
178	H-5	-10.88	5	1	0	0	0	0	0	5	88
177	H-6	-10.91	1	0	0	0	0	0	0	1	97
176	H-7	-11.06	1	0	0	0	0	0	0	3	96
175	H-8	-11.2	1	0	0	0	0	0	0	1	98
174	H-9	-11.28	5	1	0	0	0	0	0	5	90
173	H-10	-11.34	6	1	0	0	0	0	0	10	83
172	H-11	-11.78	65	1	0	0	0	0	0	18	15
171	H-12	-12.27	49	17	0	2	3	1	1	12	16
170	H-13	-12.77	28	12	1	3	5	3	4	16	27
169	H-14	-12.93	14	2	0	1	2	6	8	18	50
168	H-15	-13.06	4	2	0	22	25	15	19	2	11
167	H-16	-13.18	20	2	0	0	0	3	4	11	60
166	H-17	-13.31	2	1	0	14	16	14	15	3	35
165	H-18	-13.33	2	1	0	20	21	17	18	4	18
164	H-19	-13.37	4	1	0	5	6	9	9	2	65
163	H-20	-13.47	3	0	0	2	2	2	3	5	83

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