A Class III asymmetric binuclear cyanido-bridged mixed-valence complex

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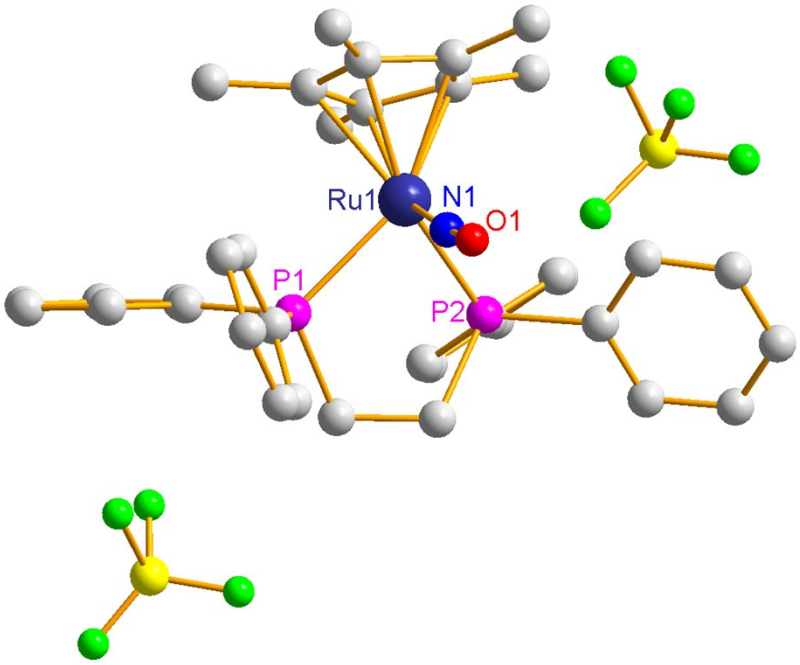

Figure S1. Molecular structure of compound **[Cp*(dppe)Ru(NO)][BF_4]$_2$**. Hydrogen atoms , and solvent molecules have been omitted for clarity. Ru dark blue, P pink, C white, N blue, F green, B yellow, O red. The Ru-P bond length are 2.3792(7) and 2.4119(6) Å.

Table S1. Crystallographic data for **1[BF_4]** and **1[BF_4]$_2$**.

	1[BF_4]·CH_2Cl_2	**1[BF_4]$_2$**	**[Cp*(dppe)Ru (NO)][BF_4]$_2$**
Empirical formula	$C_{58}H_{57}BCl_3F_4N_5P_2Ru_2$	$C_{58}H_{57}B_2Cl_3F_8N_5P_2Ru_2$	$C_{36}H_{39}B_2F_8NOP_2Ru$
Color and Habit	Red purple block	Dark red block	Light orange plate
Crystal Size (mm)	0.230×0.150×0.230	0.230×0.130×0.120	0.230×0.110×0.110
Temperature(K)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	*$P2_1/n$*	*P-1*	*P-1*
a (Å)	11.0409(3)	12.2343(4)	8.87820(10)
b (Å)	12.7863(4)	13.0543(4)	12.3726(2)
c (Å)	39.5972(12)	21.7618(3)	18.0161(2)
alpha (deg.)	90	86.764(2)	84.1790(10)
beta (deg.)	91.115(2)	78.308(2)	78.8260(10)
gamma (deg.)	90	62.126(3)	73.611(2)
Volume(Å ^3)	5589.0(3)	3005.65(16)	1860.30(5)
Z	4	2	2
Formula weight	1281.32	1368.13	838.31
Density(cal.)(Mg/m^3)	1.523	1.512	1.497
μ(mm^{-1})	4.504	4.274	3.243
F(000)	2600.0	1382.0	852.0
Theta range (deg.)	3.88 to 121.284	6.666 to 121.182	9.166 to 121.82
Reflections collected / unique	47272 / 12488 [R(int) = 0.0596]	41976 / 13232 [R(int) = 0.0957]	25889 / 8310 [R(int) = 0.0368]
Index range	-14<=h<=10, -16<=k<=15, -51<=l<=51	-15<=h<=15, -16<=k<=16, -27<=l<=27	-11<=h<=11, -12<=k<=16, -23<=l<=22
Data/restraints/parameters (obs.)	12488/0/681	13232/47/736	8310/19/538

Final R indices (obs.)	R_1 = 0.0420, wR_2 = 0.1042	R_1 = 0.0760, wR_2 = 0.2063	R_1 = 0.0403, wR_2 = 0.1085
R indices (all)	R_1 = 0.0582, wR_2 = 0.1120	R_1 = 0.0895, wR_2 = 0.2178	R_1 = 0.0444, wR_2 = 0.1111
Goodness-of-fit	1.057	1.051	1.034

$R_1 = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|$;
$wR_2 = [\mathbf{\Sigma}w(|F_0^2| - |F_c^2|)^2/\Sigma w|F_0^2|^2]^{1/2}$

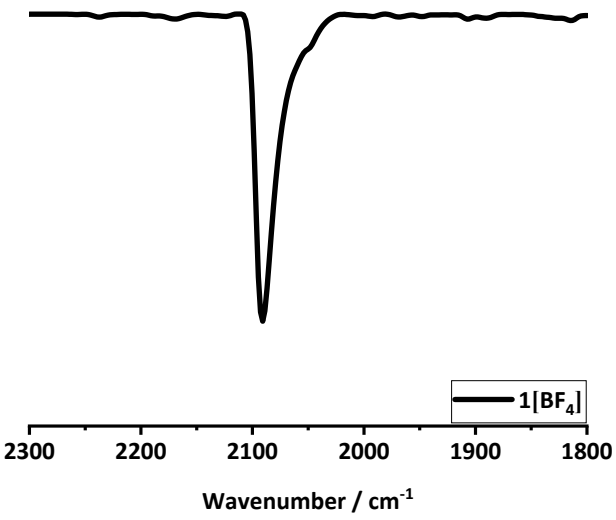

Figure S2. IR_{KBr} spectra of **1[BF$_4$]** (2090 cm^{-1}).

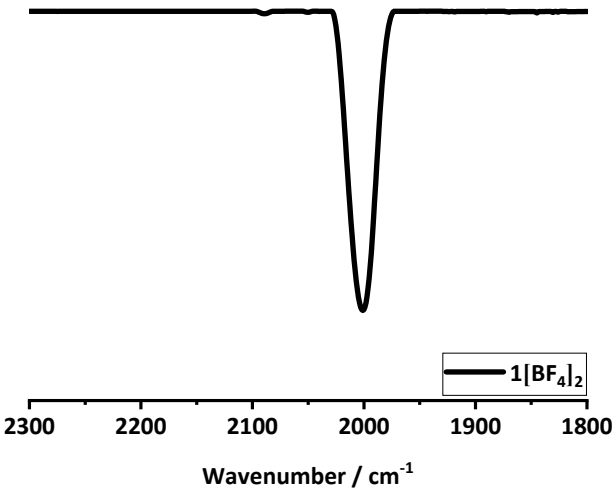

Figure S3. IR_{KBr} spectra of **1[BF$_4$]$_2$** (2000 cm^{-1}).

Table S2. Experimental data and TDDFT data of the MMCT band (in CH_2Cl_2) for MV complex **1[BF_4]$_2$**.

	λ (cm^{-1})
Experimental data	8461 cm^{-1}, (ε = 4116 $M^{-1}cm^{-1}$)
TDDFT data	7255 cm^{-1}

Table S3. Data of the electron spin density for MV complex **1[BF_4]$_2$**.

complexes	Ru(1)	Ru(2)
1[BF_4]$_2$	0.473	0.406

Table S4. Calculated and experimental electronic absorption in CH_2Cl_2 of **1[BF_4]$_2$** (MMCT).

Complex	Excitation (percentage)
1[BF_4]$_2$	HOMO (239B) → LUMO (240B) (65%)
	HOMO-2 (237B) → LUMO (240B) (22%)
	HOMO-3 (236B) → LUMO (240B) (7%)
	HOMO-1 (238B) → LUMO (240B) (3%)

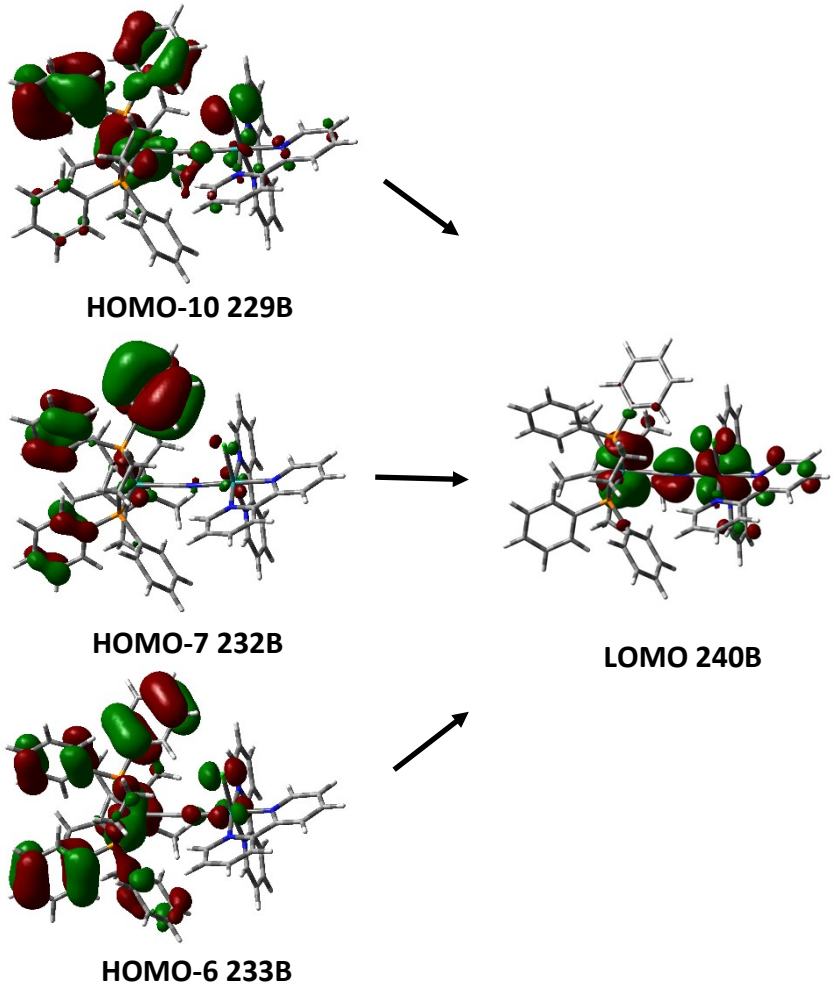

Figure S4. Molecular orbital diagrams of HOMO-10 (229B), HOMO-7 (232B), HOMO-6 (233B) and LUMO (240B) of **1[BF_4]$_2$** in dichloromethane (isocontour value: 0.02 [e/b3]1/2).

Table S5. Calculated and experimental electronic absorption in CH_2Cl_2 of **$1[BF_4]_2$** (LMCT).

Complex	Excitation (percentage)
$1[BF_4]_2$	HOMO-10 (229B) → LUMO (240B) (12%)
	HOMO-7 (232B) → LUMO (240B) (23%)
	HOMO-6 (233B) → LUMO (240B) (36%)

Table S6. Theoretical bond lengths (Å) for **$1[BF_4]$** and **$1[BF_4]_2$**.

	$1[BF_4]$	**$1[BF_4]_2$**
Ru(1)-C(1)	2.0039	1.9743
Ru(1)-P(1)	2.4193	2.4573
Ru(1)-P(2)	2.4223	2.4586
Ru(1)-N(1)	2.0966	2.0116
Ru(2)-N(3)	2.0665	2.0791
Ru(2)-N(4)	2.0771	2.0895
Ru(2)-N(5)	2.0757	2.0948
Ru(2)-N(6)	2.0554	2.0972
Ru(2)-Cl(1)	2.5073	2.4708
N(1)≡C(1)	1.1939	1.2016

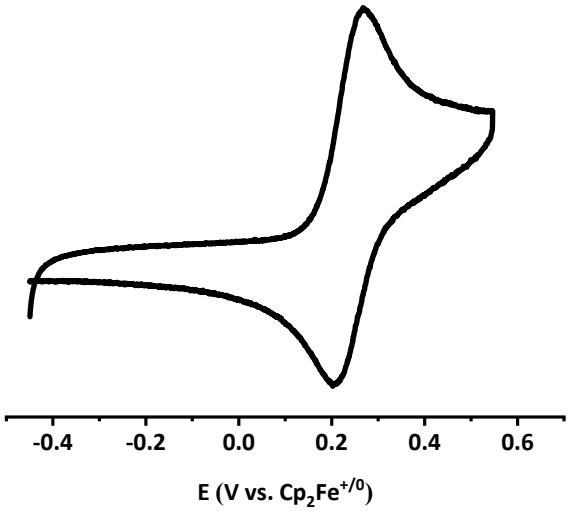

Figure S5. Cyclic voltammogram of **[Cp*(dppe)RuCN]** recorded in CH_2Cl_2 / 0.1M $[TBA]PF_6$ at 100 mV s^{-1} scan rate.

Author Contributions

X.-L. L. synthesized and characterized the molecules. T.-L. S. performed and analysed the DFT/TDDFT calculations. Y. L. contributed to the determination of single crystal structure. T.-L. S. and X.-L. L. wrote the text. T.L.S. conceived and supervised the project. All authors discussed the results and contributed to the writing of the manuscript.

Optimized Cartesian Coordinates of **$1[BF_4]_2$**

Ru	-1.90613	-0.26395	0.940226	C	-6.53034	2.764315	-0.79301
Ru	3.112906	-0.13269	-0.31981	H	-7.39839	2.426624	-1.35276
P	-2.44009	-1.43751	-1.1517	C	-6.62712	-1.53377	-1.34507
P	-2.48025	1.682492	-0.44771	H	-7.46116	-1.21128	-0.72687
Cl	2.718884	-1.43951	-2.3794	C	-5.05626	0.143948	2.573206
N	3.159189	1.523292	-1.60187	H	-5.1906	1.072025	2.007519
N	1.149872	-0.05475	0.112456	H	-5.39139	0.339773	3.601774
N	3.64189	0.780907	1.471315	H	-5.73194	-0.61039	2.159153
N	3.264883	-1.78048	0.955965	C	3.7538	-2.52599	3.20615
C	-1.63211	-3.10083	-1.4532	H	4.042009	-2.30155	4.226843
C	-0.02314	-0.11293	0.36642	C	4.454706	1.81858	3.949026
N	5.125155	-0.1131	-0.91051	H	4.776933	2.217473	4.905786
C	-4.15215	2.543247	-0.26291	C	4.234418	2.673461	2.851488
C	-3.62436	-0.3282	2.583975	H	4.381372	3.745089	2.933938
C	5.449029	0.822512	-1.86321	C	4.472944	2.7233	-3.24174
C	-4.26798	3.637498	0.625918	H	5.411695	2.871178	-3.76223
H	-3.39792	4.00918	1.159867	C	2.08671	2.296608	-1.91161
C	4.35115	1.72587	-2.25795	H	1.174508	2.088377	-1.36963
C	-1.74153	-1.72727	2.729612	C	3.828359	2.118759	1.631623
C	-4.21765	-1.73237	-1.6967	H	3.648606	2.736644	0.760431
C	-1.78862	-0.25255	-2.49065	C	-4.46138	-2.37088	-2.93561
H	-0.69868	-0.22351	-2.40518	H	-3.63493	-2.71803	-3.55114
H	-2.04564	-0.64812	-3.47951	C	-6.86701	-2.16952	-2.57667
C	-2.40651	1.147895	-2.2965	H	-7.88552	-2.34343	-2.91296
H	-3.42637	1.172929	-2.6906	C	3.511248	-3.85576	2.823573
H	-1.82526	1.898188	-2.84194	H	3.613652	-4.6598	3.545823
C	-3.15843	-1.6779	2.399052	C	-6.63962	3.852981	0.091645
C	-1.32466	3.170207	-0.32945	H	-7.59162	4.360452	0.220264
C	-4.00134	-2.89013	2.107622	C	7.718792	-0.03753	-1.97432
H	-3.42969	-3.67155	1.597876	H	8.720441	-0.00924	-2.39155
H	-4.8813	-2.66039	1.502255	C	-1.45152	4.233156	-1.25382
H	-4.35953	-3.31789	3.05556	H	-2.18831	4.185	-2.05256
C	3.849259	-0.06611	2.537603	C	3.021512	-3.06612	0.585269
C	-2.49712	0.469609	3.058297	H	2.742747	-3.21125	-0.45196
C	-5.30558	-1.31313	-0.90906	C	7.373825	-0.99182	-0.99958
H	-5.12747	-0.80791	0.03329	H	8.093414	-1.72077	-0.64318
C	-1.34557	-0.40178	3.17045	C	-0.43583	-5.62411	-1.88216
C	-0.90343	-2.97532	2.801611	H	0.016858	-6.59501	-2.06624
H	-1.07154	-3.49645	3.756154	C	-1.74983	-5.5417	-1.37945
H	0.165332	-2.74781	2.732497	H	-2.31264	-6.4477	-1.17088
H	-1.14674	-3.67762	1.99747	C	3.13687	-4.12833	1.494213
C	-0.02496	-0.04162	3.795699	H	2.938583	-5.14106	1.160395
H	-0.04257	-0.28	4.869205	C	-5.77986	-2.58437	-3.37321
H	0.193496	1.027454	3.701872	H	-5.95864	-3.07689	-4.32504

H	0.802215	-0.59855	3.344813	C	3.364694	3.522967	-3.5603
C	-5.29655	2.108498	-0.96556	H	3.445396	4.291739	-4.32237
H	-5.25237	1.268431	-1.65063	C	-5.50326	4.286275	0.80173
C	-0.31168	-3.18444	-1.93842	H	-5.57423	5.13188	1.480597
H	0.277373	-2.29845	-2.1541	C	-0.66084	5.388732	-1.12052
C	3.623088	-1.49717	2.254849	H	-0.7792	6.20771	-1.82518
C	-0.4011	3.281818	0.728015	C	0.383694	4.443784	0.866891
H	-0.29987	2.468447	1.439976	H	1.07507	4.531295	1.701699
C	6.068658	-0.99656	-0.49237	C	2.152631	3.306803	-2.88101
H	5.760342	-1.7255	0.245502	H	1.271577	3.902322	-3.09103
C	4.257626	0.438879	3.786611	C	0.278234	-4.44345	-2.16107
H	4.428257	-0.23223	4.620524	H	1.284898	-4.48902	-2.56852
C	6.745684	0.876539	-2.40589	C	0.256273	5.499076	-0.05513
H	6.996344	1.613037	-3.15997	H	0.849288	6.402536	0.060322
C	-2.34802	-4.28705	-1.16794	H	-1.66312	2.42325	3.521754
H	-3.3762	-4.24268	-0.81891	H	-2.88188	1.840448	4.660385
C	-2.60562	1.871078	3.595832	H	-3.38026	2.444111	3.078736

The theoretically calculated bond length of **1[BF_4]**.

R(1,3)	2.5073	R(41,42)	1.0829
R(1,6)	2.0966	R(41,119)	1.3987
R(1,7)	2.0665	R(43,44)	1.0958
R(1,8)	2.0757	R(43,45)	1.0938
R(1,9)	2.0771	R(43,52)	1.5446
R(1,10)	2.0554	R(46,47)	1.0875
R(2,4)	2.4193	R(46,50)	1.4072
R(2,5)	2.4223	R(46,105)	1.4094
R(2,12)	2.0039	R(48,49)	1.0823
R(2,28)	2.3454	R(48,73)	1.3992
R(2,33)	2.3017	R(50,51)	1.0872
R(2,35)	2.3622	R(50,57)	1.4087
R(2,36)	2.2829	R(52,53)	1.0951
R(2,40)	2.3338	R(52,54)	1.0944
R(4,11)	1.8922	R(55,56)	1.0856
R(4,16)	1.8962	R(55,73)	1.4083
R(4,52)	1.931	R(57,58)	1.0853
R(5,27)	1.8911	R(59,60)	1.0848
R(5,29)	1.8805	R(59,63)	1.4088
R(5,43)	1.9079	R(61,62)	1.0877
R(6,12)	1.1939	R(61,103)	1.4072
R(7,15)	1.3772	R(63,64)	1.0858
R(7,48)	1.3608	R(63,75)	1.4034
R(8,17)	1.3614	R(65,66)	1.088
R(8,37)	1.3779	R(65,95)	1.4068

R(9,19)	1.3595	R(67,68)	1.0862
R(9,32)	1.3769	R(67,91)	1.4069
R(10,34)	1.3813	R(69,70)	1.0945
R(10,41)	1.3633	R(69,71)	1.1003
R(11,23)	1.4084	R(69,72)	1.0944
R(11,65)	1.4136	R(73,74)	1.0849
R(13,14)	1.084	R(75,76)	1.0844
R(13,15)	1.4075	R(77,78)	1.0869
R(13,55)	1.4017	R(77,105)	1.406
R(15,32)	1.4728	R(79,80)	1.0943
R(16,30)	1.412	R(79,81)	1.1007
R(16,67)	1.4139	R(79,82)	1.0953
R(17,18)	1.084	R(83,84)	1.0951
R(17,59)	1.4014	R(83,85)	1.1003
R(19,20)	1.0815	R(83,86)	1.0965
R(19,25)	1.4009	R(87,88)	1.0872
R(21,22)	1.084	R(87,97)	1.4072
R(21,32)	1.407	R(89,90)	1.0844
R(21,38)	1.4026	R(89,107)	1.4094
R(23,24)	1.086	R(91,92)	1.0872
R(23,61)	1.4092	R(91,97)	1.4079
R(25,26)	1.0841	R(93,94)	1.0872
R(25,38)	1.4075	R(93,107)	1.4067
R(27,89)	1.4069	R(93,109)	1.4103
R(27,101)	1.4141	R(95,96)	1.0874
R(28,35)	1.4442	R(95,103)	1.4102
R(28,36)	1.4503	R(97,98)	1.0869
R(28,69)	1.5067	R(99,100)	1.0843
R(29,57)	1.4091	R(99,121)	1.4018
R(29,77)	1.4144	R(101,102)	1.0875
R(30,31)	1.0852	R(101,109)	1.4058
R(30,87)	1.4077	R(103,104)	1.0873
R(33,36)	1.4606	R(105,106)	1.0874
R(33,40)	1.4393	R(107,108)	1.0875
R(33,115)	1.5057	R(109,110)	1.0871
R(34,37)	1.4732	R(111,112)	1.0952
R(34,99)	1.4083	R(111,113)	1.1013
R(35,40)	1.4584	R(111,114)	1.0954
R(35,83)	1.5094	R(115,116)	1.0958
R(36,111)	1.5065	R(115,117)	1.1006
R(37,75)	1.408	R(115,118)	1.0945
R(38,39)	1.0858	R(119,120)	1.0852
R(40,79)	1.5065	R(119,121)	1.4098
		R(121,122)	1.0856

The theoretically calculated bond length of **1[BF_4]$_2$**.

R(1,3)	2.4573	R(42,44)	1.0952
R(1,4)	2.4586	R(42,45)	1.0944
R(1,11)	1.9743	R(46,47)	1.0849
R(1,14)	2.3787	R(46,65)	1.4079
R(1,19)	2.3174	R(48,49)	1.0856
R(1,27)	2.3866	R(48,119)	1.4081
R(1,34)	2.3181	R(50,73)	1.4073
R(1,37)	2.3037	R(51,52)	1.0857
R(2,5)	2.4708	R(51,115)	1.409
R(2,6)	2.0948	R(53,54)	1.0821
R(2,7)	2.0116	R(53,99)	1.4003
R(2,8)	2.0791	R(55,56)	1.0839
R(2,9)	2.0895	R(55,75)	1.4031
R(2,12)	2.0972	R(57,58)	1.0835
R(3,10)	1.8736	R(57,93)	1.4031
R(3,20)	1.8825	R(59,60)	1.0867
R(3,21)	1.903	R(59,103)	1.406
R(4,13)	1.8895	R(61,62)	1.0948
R(4,24)	1.9259	R(61,63)	1.1002
R(4,28)	1.8875	R(61,64)	1.0935
R(6,18)	1.3756	R(65,66)	1.0867
R(6,81)	1.358	R(65,91)	1.407
R(7,11)	1.2016	R(67,68)	1.0871
R(8,33)	1.3775	R(67,87)	1.4066
R(8,83)	1.3603	R(69,70)	1.0952
R(9,50)	1.3768	R(69,71)	1.0994
R(9,97)	1.36	R(69,72)	1.0941
R(10,48)	1.4092	R(73,74)	1.0841
R(10,59)	1.4146	R(73,89)	1.4048
R(12,15)	1.374	R(75,76)	1.0855
R(12,53)	1.3585	R(75,77)	1.4085
R(13,16)	1.4145	R(77,78)	1.0848
R(13,46)	1.4115	R(77,83)	1.4002
R(14,27)	1.4398	R(79,80)	1.0835
R(14,34)	1.4602	R(79,109)	1.4033
R(14,69)	1.5078	R(81,82)	1.0813
R(15,18)	1.4755	R(81,117)	1.4016
R(15,57)	1.4067	R(83,84)	1.0831
R(16,17)	1.0864	R(85,86)	1.0874
R(16,111)	1.4063	R(85,107)	1.4055
R(18,79)	1.4063	R(87,88)	1.0866
R(19,27)	1.4558	R(87,107)	1.4101

R(19,37)	1.4519	R(89,90)	1.0856
R(19,38)	1.5051	R(89,105)	1.4077
R(20,35)	1.407	R(91,92)	1.0864
R(20,85)	1.4149	R(91,111)	1.4083
R(21,22)	1.0937	R(93,94)	1.0854
R(21,23)	1.0956	R(93,99)	1.407
R(21,24)	1.543	R(95,96)	1.0877
R(24,25)	1.0936	R(95,113)	1.4065
R(24,26)	1.0947	R(97,98)	1.0838
R(27,29)	1.505	R(97,105)	1.4028
R(28,51)	1.4084	R(99,100)	1.0845
R(28,95)	1.4144	R(101,102)	1.0869
R(29,30)	1.0942	R(101,103)	1.4093
R(29,31)	1.0925	R(101,119)	1.4077
R(29,32)	1.0999	R(103,104)	1.0868
R(33,50)	1.4762	R(105,106)	1.0846
R(33,55)	1.4078	R(107,108)	1.0865
R(34,37)	1.4484	R(109,110)	1.0855
R(34,61)	1.5049	R(109,117)	1.4061
R(35,36)	1.084	R(111,112)	1.0867
R(35,67)	1.409	R(113,114)	1.0869
R(37,42)	1.5049	R(113,121)	1.4101
R(38,39)	1.1004	R(115,116)	1.0875
R(38,40)	1.0949	R(115,121)	1.4071
R(38,41)	1.095	R(117,118)	1.084
R(42,43)	1.0998	R(119,120)	1.087
		R(121,122)	1.0868