Electronic Supplementary Information (ESI)

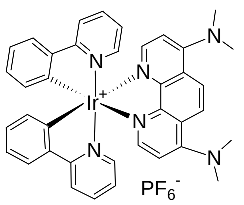
Comparison of ruthenium(II) and cyclometalated iridium(III) azacrown ether phenanthroline hybrids for the detection of metal cations by electrochemiluminescence

Hengwei Lin, Mehmet Emin Cinar, and Michael Schmittel*

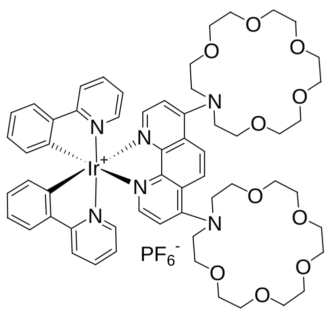
Center of Micro- and Nanochemistry and Engineering, Organische Chemie I, Universität Siegen, Adolf-Reichwein Str., D-57068 Siegen, Germany; FAX: int (+49) 271-740-3270, E-mail: schmittel@chemie.uni-siegen.de

Contents

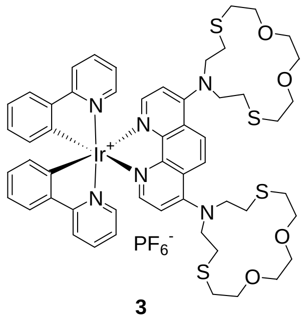
Compounds



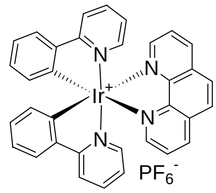
1'



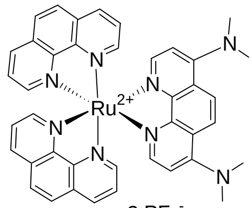
1



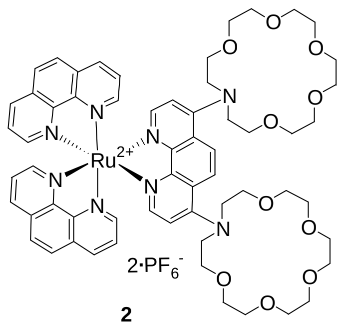
3



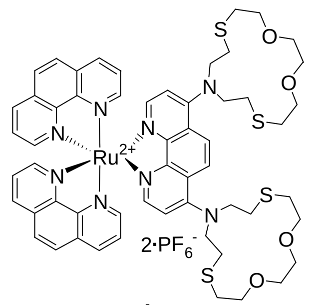
5



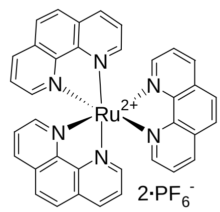
2'



2



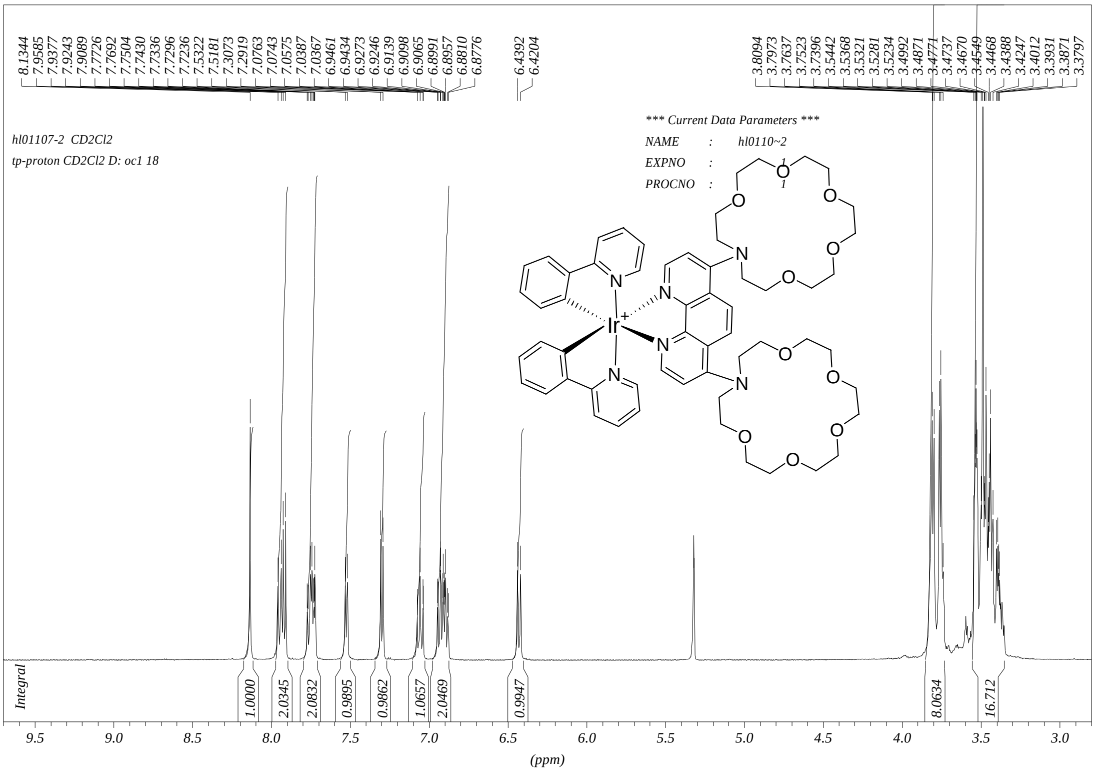
4



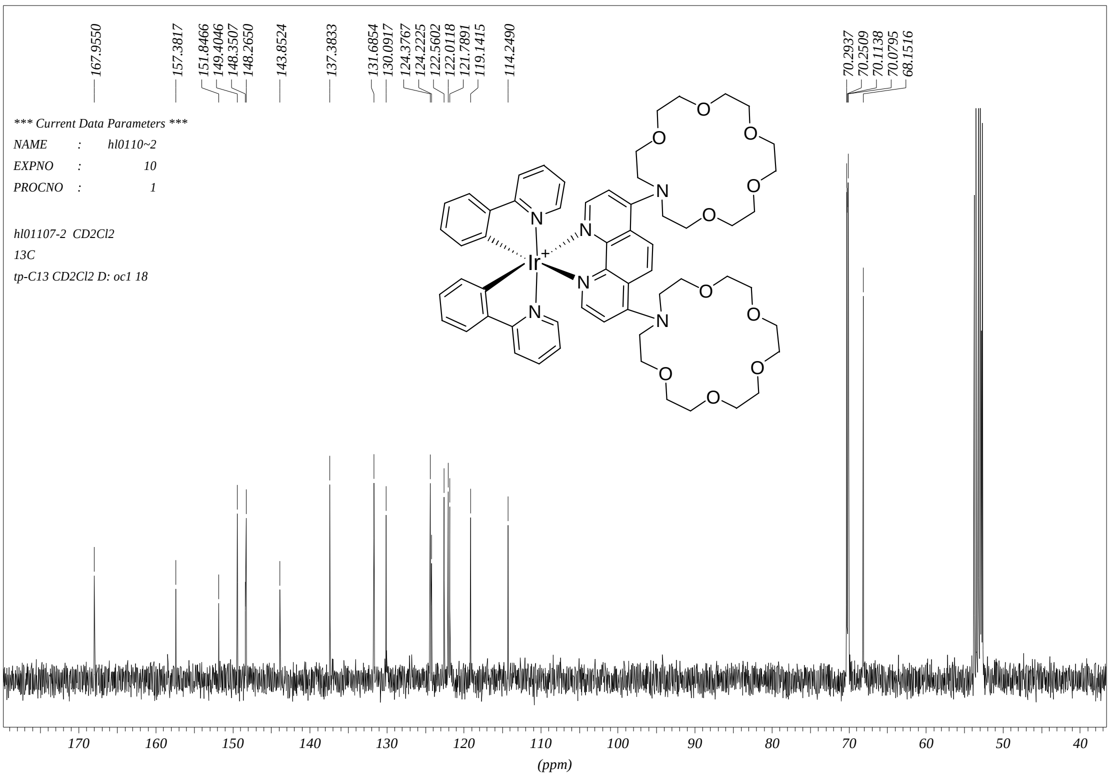
6

Characterisation of the new complex **1** p 2 – p 3
Luminescence Data p 4
Computational Results p 5 – p 9

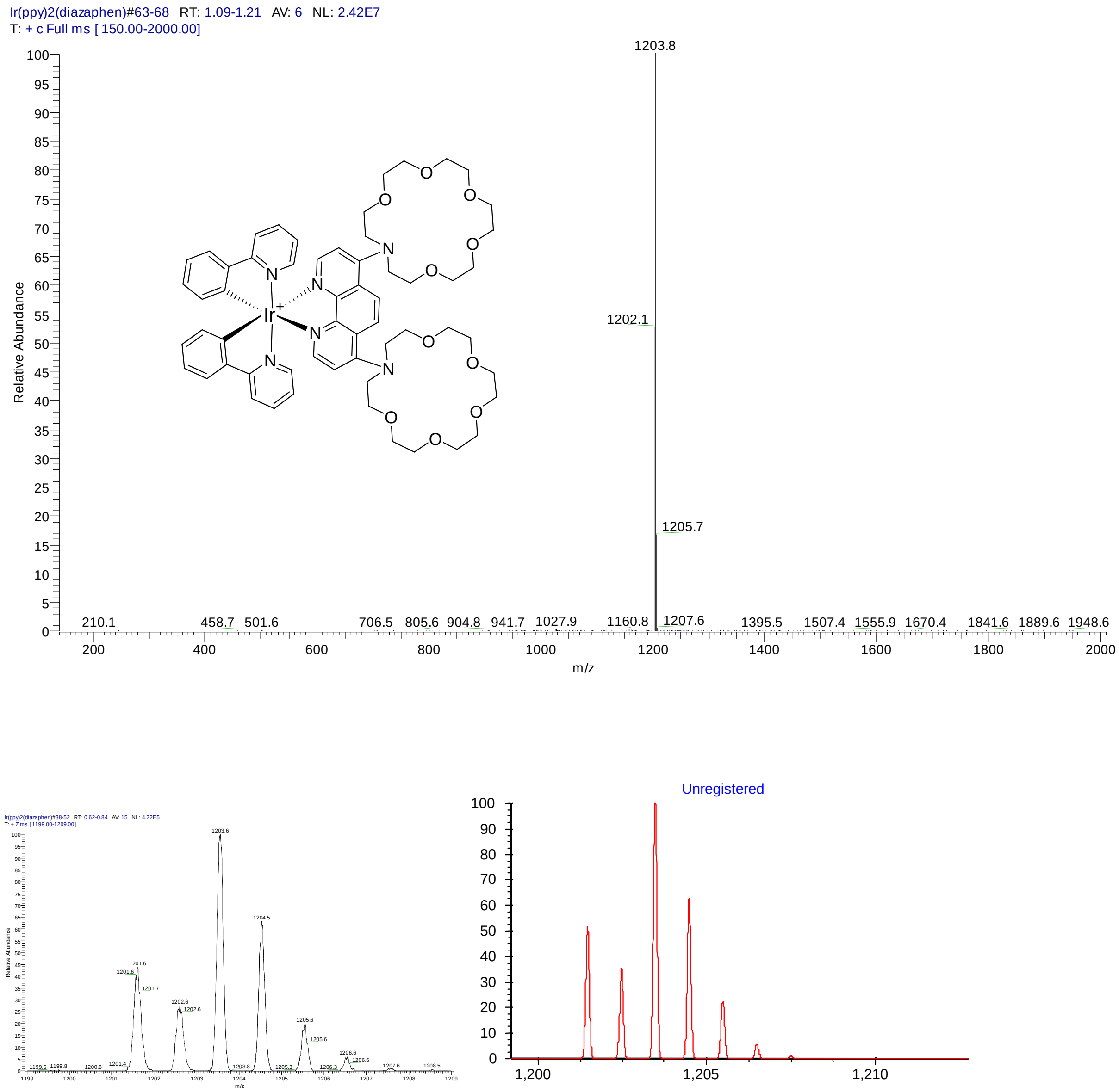
* Fax: int (+49) 271-740-3270, E-mail: schmittel@chemie.uni-siegen.de



^{1}H NMR (400 MHz) spectrum of iridium complex **1** in CD_2Cl_2.



^{13}C NMR (100 MHz) spectrum of iridium complex **1** in CD_2Cl_2.



ESI MS of iridium complex **1** along with the experimental (left) and simulated (right) isotopic splitting.

Luminescence Data

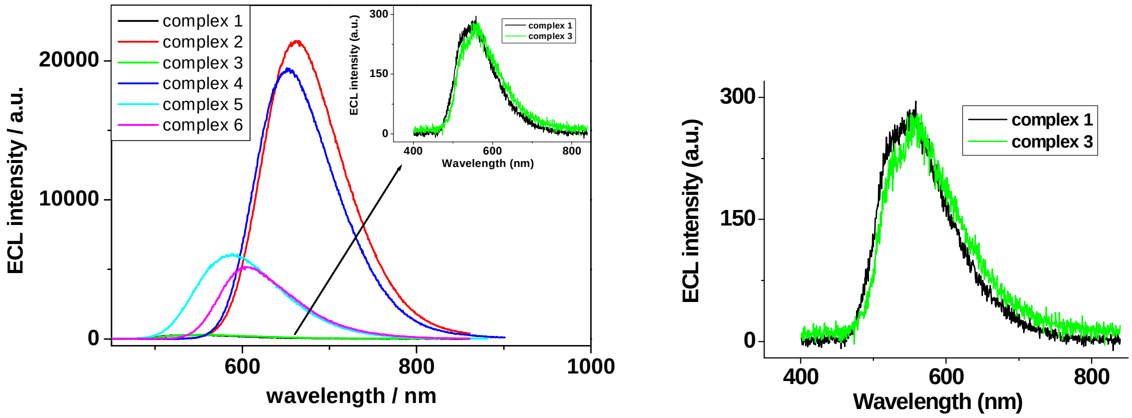


Figure S1. (left) ECL emission spectra of complexes **1-6** (10 µM) in MeCN. 50 mM TPrA and 0.1 M $^{n}Bu_4PF_6$ were used as coreactant and electrolyte, respectively. The electrode potential was swept between 0 to 1.6 V (*vs.* silver wire) at a scan rate of 100 mV s^{-1}. (right) Inset enlarged.

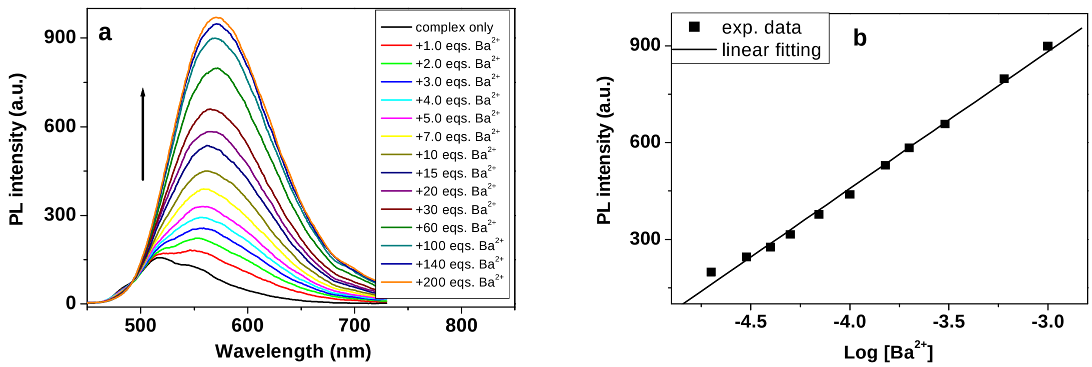
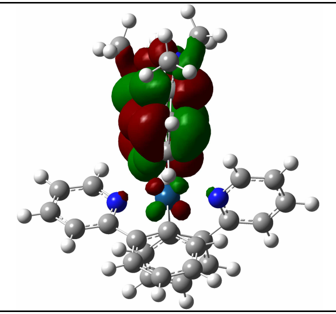
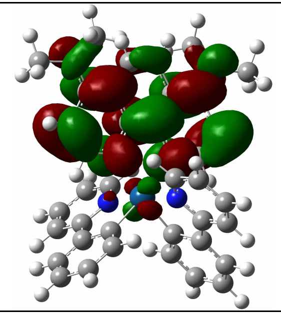
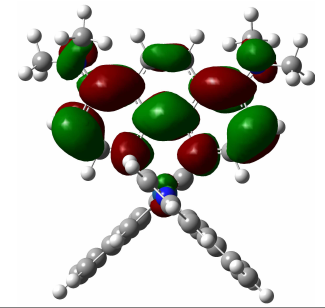
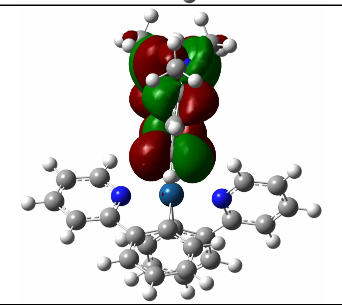
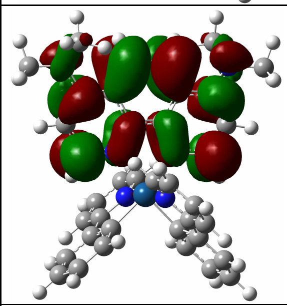
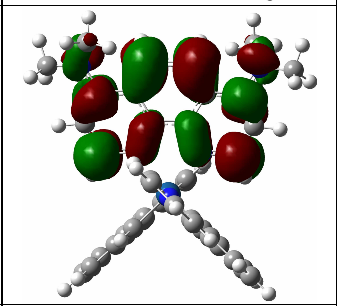
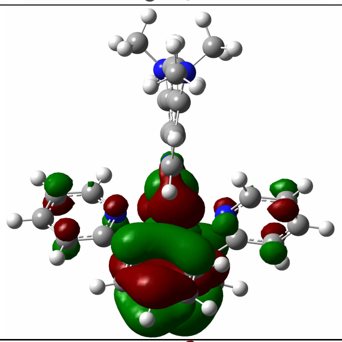
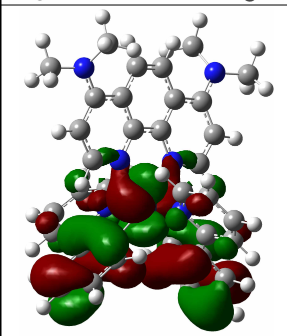
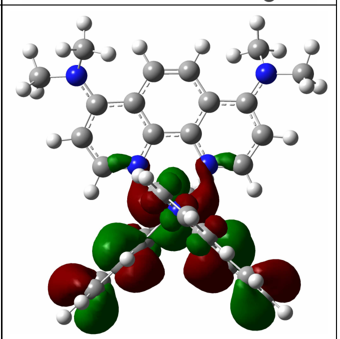
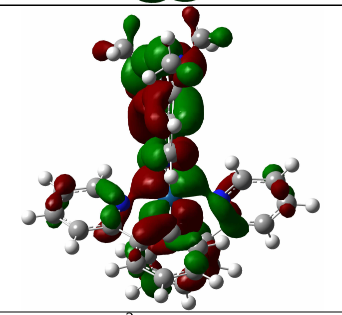
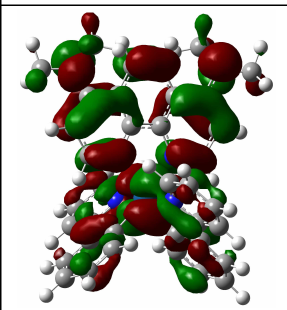
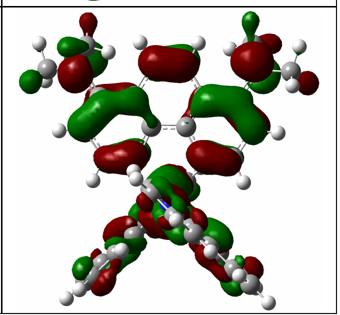


Figure S2 (a) PL responses of **1** (10 µM in MeCN) with increasing concentrations of Ba^{2+} addition (λ_{exc} = 374 nm). (b) Linear fitting of PL emission intensity of **1** (10 µM in MeCN) at 572 nm with respect to log $[Ba^{2+}]$.

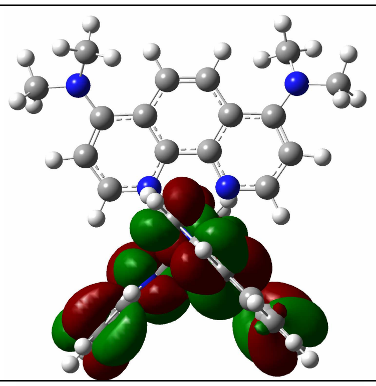
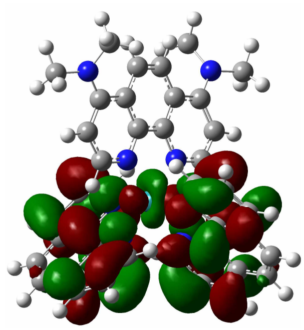
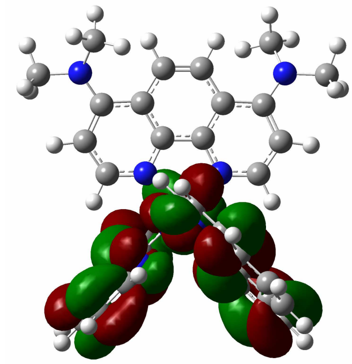
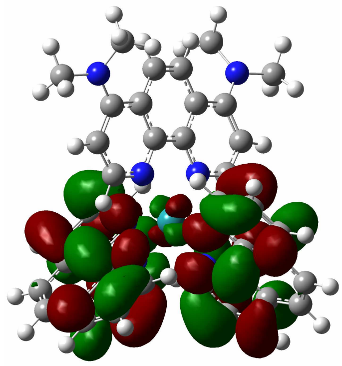
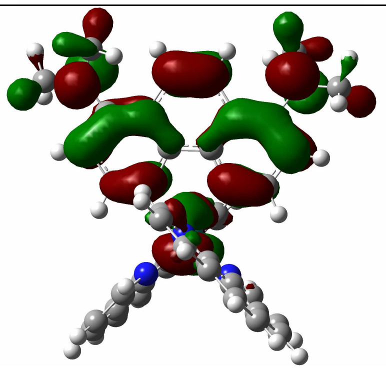
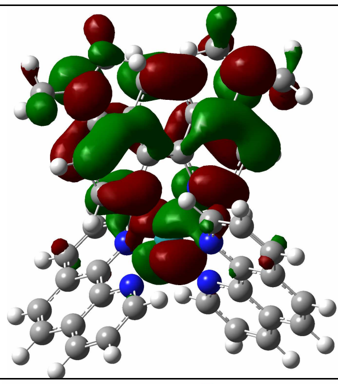
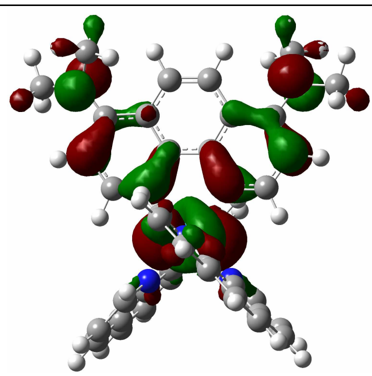
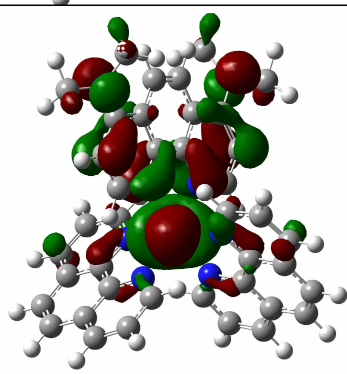
Computational Results

Table 1. Molecular orbitals calculated of **1’** at B3LYP/6-311+G(d)/LANL2DZ//B3LYP/6-31G(d)/LANL2DZ level (views on to the MOs from three different angles).

LUMO+1 **(162)** -0.16531 au			
LUMO **(161)** -0.16559 au			
HOMO **(160)** -0.28063 au			
HOMO-1 **(159)** -0.30140 au			

*Isocontour plots (0.02 ebohr $^{-3}$) **(1 Hartree= 27.2116 eV).

Table 2. Molecular orbitals calculated of **2'** at B3LYP/6-311+G(d)/LANL2DZ//B3LYP/6-31G(d)/LANL2DZ level (views on to the MOs from two different angles).

LUMO+1 **(174)** -0.25835 au		
LUMO **(173)** -0.26113 au		
HOMO **(172)** -0.37143 au		
HOMO-1 **(171)** -0.38047 au		

*Isocontour plots (0.02 ebohr $^{-3}$) **(1 Hartree= 27.2116 eV), calculated HOMO-LUMO gap is 3.001 eV.

Geometry optimization of symmetric Ru-complex was performed within C_2 symmetry constraints at the DFT level by using the Gaussian 03 program.[1] B3LYP[2] method with 6-31G(d) basis set on H, C, N atoms, and double-ζ quality basis set (LANL2DZ)[3], containing the Hay and Wadt's effective core potential (ECP), on Ru atom was applied. Fast multipole method (FMM),[4] implemented in Gaussian 03 and default for big molecules, was used to solve the self-consistent field problem.[5] The minima was verified by analyzing the harmonic vibrational frequencies, using analytical second derivatives, which have NIMAG=0. Single point calculation on the optimized geometry was performed at B3LYP/6-311+G(d)/LANL2DZ level. The visualization of orbitals was done with GaussView 3.07.

Coordinates of 1' after minimisation

C	-0.0000	2.9971	0.3596
C	0.4054	4.3184	0.4698
C	1.4350	4.6246	1.3649
C	2.0097	3.6044	2.1092
C	1.5623	2.2816	1.9650
N	0.5566	2.0028	1.0792
C	2.0674	1.1208	2.6950
C	3.1118	1.1921	3.6337
C	3.5340	0.0450	4.2951
C	2.9091	-1.1764	4.0190
C	1.8720	-1.2509	3.0866
C	1.4255	-0.1124	2.3974
C	-1.8720	1.2509	3.0866
C	-2.9091	1.1764	4.0190
C	-3.5340	-0.0450	4.2951
C	-3.1118	-1.1921	3.6337
C	-2.0674	-1.1208	2.6950
C	-1.4255	0.1124	2.3974
C	-1.5623	-2.2816	1.9650
C	-2.0097	-3.6044	2.1092
C	-1.4350	-4.6246	1.3649
C	-0.4054	-4.3184	0.4698
C	0.0000	-2.9971	0.3596
N	-0.5566	-2.0028	1.0792
Ir	-0.0000	0.0000	0.9680
H	-0.7966	2.7016	-0.3120
H	-0.0769	5.0838	-0.1281
H	1.7804	5.6475	1.4817
H	2.8044	3.8239	2.8123
H	3.5974	2.1390	3.8537
H	4.3384	0.0995	5.0225

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian 03, Gaussian, Inc., Wallingford CT, 2004.

[2] (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372-1377. (b) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652. (c) C. Lee, W. Yang and R.G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.

[3] (a) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270-283. (b) W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, ***82***, 284-298. (c) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, ***82***, 299-310.

[4] (a) L. Greengard and V. Rokhlin, *J. Comput. Phys.*, 1987, **73**, 325-348. (b) L. Greengard, *Science*, 1994, **265**, 909-914. (c) C. A. White and M. Head-Gordon, *J. Chem. Phys.*, 1994, **101**, 6593-6605. (d) J. C. Burant, M. C. Strain, G. E. Scuseria and M. J. Frisch, *Chem. Phys. Lett.*, 1996, **248**, 43-49. (e) M. C. Strain, G. E. Scuseria and M. J. Frisch, *Science*, 1996, **271**, 51-53.

[5] a) J. M. Millam and G. E.Scuseria, *J. Chem. Phys.*, 1997, **106**, 5569. b) A. D. Daniels, J. M. Millam and G. E. Scuseria, *J. Chem. Phys.*, 1997, **107**, 425.

H	3.2308	-2.0755	4.5391
H	1.4044	-2.2140	2.9026
H	-1.4044	2.2140	2.9026
H	-3.2308	2.0755	4.5391
H	-4.3384	-0.0995	5.0225
H	-3.5974	-2.1390	3.8537
H	-2.8044	-3.8239	2.8123
H	-1.7804	-5.6475	1.4817
H	0.0769	-5.0838	-0.1281
H	0.7966	-2.7016	-0.3120
H	5.4561	-1.7244	-3.8002
C	4.9820	-0.8563	-4.2844
N	3.5262	-0.9561	-4.3221
H	5.3495	-0.7996	-5.3130
H	5.2868	0.0553	-3.7654
C	2.8038	-0.6675	-3.1836
C	3.0473	-1.9364	-5.3051
C	3.4109	-0.6138	-1.9212
C	1.3957	-0.3462	-3.2348
H	3.0921	-1.5305	-6.3226
H	3.6805	-2.8333	-5.2668
H	2.0252	-2.2427	-5.0866
C	2.6455	-0.4030	-0.7759
H	4.4692	-0.8076	-1.8011
C	0.7074	-0.1491	-2.0125
C	0.6643	-0.1611	-4.4497
N	1.3249	-0.2173	-0.7943
H	3.1063	-0.4246	0.2066
C	-0.7074	0.1491	-2.0125
C	-0.6643	0.1611	-4.4497
H	1.1772	-0.2522	-5.3981
N	-1.3249	0.2173	-0.7943
C	-1.3957	0.3462	-3.2348
H	-1.1772	0.2522	-5.3981
C	-2.6455	0.4030	-0.7759
C	-2.8038	0.6675	-3.1836
C	-3.4109	0.6138	-1.9212
H	-3.1063	0.4246	0.2066
N	-3.5262	0.9561	-4.3221
H	-4.4692	0.8076	-1.8011
C	-4.9820	0.8563	-4.2844
C	-3.0473	1.9364	-5.3051
H	-5.4561	1.7244	-3.8002
H	-5.3495	0.7996	-5.3130
H	-5.2868	-0.0553	-3.7654
H	-3.0921	1.5305	-6.3226
H	-3.6805	2.8333	-5.2668
H	-2.0252	2.2427	-5.0866

Coordinates of 2’ after minimisation

Ru	-0.0000	0.0000	0.7216
N	-2.1060	0.2105	0.8419
N	0.0170	1.3245	-0.9300
N	2.1060	-0.2105	0.8419
N	-0.0170	-1.3245	-0.9300
N	-0.1925	1.4776	2.2402
N	0.1925	-1.4776	2.2402
C	0.0434	0.7187	-2.1608
C	-0.0434	-0.7187	-2.1608
C	-1.4924	1.8028	2.5190
C	-2.5122	1.1327	1.7684
C	2.5122	-1.1327	1.7684
C	1.4924	-1.8028	2.5190
C	0.0000	-2.6619	-0.9085
C	-0.0878	-3.4576	-2.0434
C	-0.2395	-2.8816	-3.3197
C	-0.1370	-1.4363	-3.3783

C	0.0000	2.6619	-0.9085
C	0.0878	3.4576	-2.0434
C	0.2395	2.8816	-3.3197
C	0.1370	1.4363	-3.3783
C	-0.7723	-2.0898	2.9323
C	-0.5069	-3.0494	3.9239
C	0.8024	-3.3883	4.2103
C	1.8495	-2.7603	3.4995
C	3.0424	0.4227	0.1301
C	4.4169	0.1839	0.2987
C	4.8386	-0.7416	1.2349
C	3.8760	-1.4324	2.0044
C	0.7723	2.0898	2.9323
C	-3.0424	-0.4227	0.1301
C	0.5069	3.0494	3.9239
C	-0.8024	3.3883	4.2103
C	-1.8495	2.7603	3.4995
C	-4.4169	-0.1839	0.2987
C	-4.8386	0.7416	1.2349
C	-3.8760	1.4324	2.0044
C	4.2108	-2.4088	3.0030
C	3.2401	-3.0440	3.7204
C	-3.2401	3.0440	3.7204
C	-4.2108	2.4088	3.0030
C	-0.0613	-0.6814	-4.5895
C	0.0613	0.6814	-4.5895
H	1.7908	1.8102	2.6870
H	1.3351	3.5111	4.4507
H	-1.0333	4.1277	4.9717
H	-3.5054	3.7793	4.4743
H	-5.2590	2.6322	3.1780
H	-5.8955	0.9423	1.3844
H	-5.1288	-0.7316	-0.3093
H	-2.6856	-1.1451	-0.5951
H	5.8955	-0.9423	1.3844
H	5.2590	-2.6322	3.1780
H	3.5054	-3.7793	4.4743
H	5.1288	0.7316	-0.3093
H	2.6856	1.1451	-0.5951
H	1.0333	-4.1277	4.9717
H	-1.3351	-3.5111	4.4507
H	-1.7908	-1.8102	2.6870
H	-0.0492	3.1245	0.0713
H	0.1154	4.5312	-1.9112
N	0.4253	3.6626	-4.4258
H	0.0753	1.1926	-5.5417
H	-0.0753	-1.1926	-5.5417
N	-0.4253	-3.6626	-4.4258
H	-0.1154	-4.5312	-1.9112
H	0.0492	-3.1245	0.0713
C	1.3286	3.3009	-5.5260
C	0.1212	5.0928	-4.3662
C	-1.3286	-3.3009	-5.5260
C	-0.1212	-5.0928	-4.3662
H	-0.7886	-3.1790	-6.4724
H	-1.8761	-2.3869	-5.2983
H	-2.0623	-4.1047	-5.6554
H	0.0146	-5.4574	-5.3874
H	-0.9288	-5.6741	-3.8982
H	0.8105	-5.2624	-3.8222
H	0.7886	3.1790	-6.4724
H	1.8761	2.3869	-5.2983
H	2.0623	4.1047	-5.6554
H	-0.0146	5.4574	-5.3874
H	0.9288	5.6741	-3.8982
H	-0.8105	5.2624	-3.8222