Supporting computational data for

A Highly Reactive Ruthenium Phosphido Complex Exhibiting Ru-P π-Bonding

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Results from DFT and TD-DFT calculations[1]

Table 1. Total energy (in hartrees) and optimized cartesian coordinates (in Å) for **2a**

E(RPBE+HF-PBE) = _2274.40197162

44	0.0863360	_1.1067690	_0.4148330
15	_1.7824780	_0.1269230	0.0724260
15	1.4106070	0.7022570	_0.0849400
6	_0.5712350	_3.1396100	_0.9921710
1	_1.5844230	_3.5181530	_0.9435560
6	0.0296060	_2.4734100	_2.1055490
1	_0.4630210	_2.2239270	_3.0406630
6	1.3995840	_2.2089440	_1.7953760
1	2.1218050	_1.7604870	_2.4671690
6	1.6863710	_2.8037720	_0.5102360
6	2.8769940	_2.9361890	0.2473940
1	3.8188310	_2.5828170	_0.1605360
6	2.8280170	_3.5787350	1.4633990
1	3.7422700	_3.7084560	2.0409250
6	1.6052230	_4.0779030	1.9833390
1	1.6024110	_4.5679730	2.9561930
6	0.4296030	_3.9629280	1.2779460
1	_0.5047770	_4.3614150	1.6715490
6	0.4501970	_3.3468400	_0.0002090
6	_2.1624440	1.6824530	0.3224770
1	_1.1730660	2.1752450	0.3237670
6	_2.8278930	1.9526980	1.7012770
1	_3.8039290	1.4446290	1.7514340
1	_2.1906910	1.5456160	2.5024860
6	_3.0313860	3.4736550	1.9161360
1	_3.5355700	3.6448740	2.8791960
1	_2.0444150	3.9610840	1.9654760
6	_3.8573600	4.0966850	0.7672600
1	_4.8724100	3.6693760	0.7748320
1	_3.9542830	5.1818290	0.9225370
6	_3.1976180	3.8189660	_0.6031230
1	_2.2153510	4.3170740	_0.6464220
1	_3.8176970	4.2347570	_1.4116210
6	_3.0018960	2.2989540	_0.8295690
1	_2.4916640	2.1293410	_1.7917420
1	_3.9881830	1.8117800	_0.8767810
6	_3.4708870	_0.9146070	_0.0628770
1	_4.2176070	_0.1513230	0.2260960
6	_3.5922810	_2.0986260	0.9310150

1	_2.7845820	_2.8249230	0.7259760
1	_3.4430340	_1.7304520	1.9590920
6	_4.9651540	_2.8028590	0.8089420
1	_4.9958860	_3.6662450	1.4902070
1	_5.7597050	_2.1050030	1.1179150
6	_5.2249210	_3.2624570	_0.6433200
1	_4.4694580	_4.0146150	_0.9295440
1	_6.2119390	_3.7440140	_0.7148560
6	_5.1492270	_2.0662810	_1.6182820
1	_5.9477390	_1.3467840	_1.3764350
1	_5.3096260	_2.4087330	_2.6515610
6	_3.7761820	_1.3576350	_1.5183280
1	_3.7523810	_0.4799500	_2.1846900
1	_2.9821880	_2.0482620	_1.8574080
6	1.1713120	1.4914520	1.5466990
6	0.9173020	0.6013270	2.6219270
1	0.8669940	_0.4782990	2.4179160
6	0.6937950	1.0954760	3.9156130
1	0.4982990	0.3965700	4.7378720
6	0.7091020	2.4794600	4.1489260
1	0.5252360	2.8673410	5.1573200
6	0.9513200	3.3665730	3.0906030
1	0.9585450	4.4469560	3.2722600
6	1.1876270	2.8793920	1.7966020
1	1.3711670	3.5836580	0.9784690
6	1.3423540	2.0137910	_1.3526270
6	0.4228130	1.8539780	_2.4132700
1	_0.2232890	0.9640740	_2.4082510
6	0.3581470	2.8019230	_3.4478530
1	_0.3583480	2.6669610	_4.2671330
6	1.2140740	3.9114890	_3.4341470
1	1.1653130	4.6525460	_4.2403680
6	2.1485970	4.0668660	_2.3977740
1	2.8303480	4.9244820	_2.3991000
6	2.2214160	3.1213970	_1.3671360
1	2.9774410	3.2330860	_0.5806640
6	3.1797210	0.2524490	_0.1063810
6	3.8217580	0.0699390	_1.3575910
1	3.2864150	0.3199720	_2.2829420
6	5.1381790	_0.4091510	_1.4187780
1	5.6228110	_0.5434750	_2.3927710
6	5.8363850	_0.7007940	_0.2355030
1	6.8663330	_1.0717000	_0.2847040
6	5.2180180	_0.5066840	1.0087040
1	5.7643210	_0.7215520	1.9341320
6	3.8969620	_0.0391840	1.0767700
1	3.4200390	0.1012840	2.0540720

Table 2. Energies, oscillator strengths and molecular orbital assignments for the ten lowest TD-DFT calculated excitations.

E, nm (eV)	*f*	MO transitions (H = HOMO, L = LUMO)
714 (1.73)	0.001	H_1 → L (83%)
600 (2.06)	0.024	H → L (67%), H_2 → L (8%)
439 (2.82)	0.005	H_3 → L (63%), H_2 → L (13%)
390 (3.18)	0.008	H_1 → L+1 (49%), H → L+1 (25%), H_2 → L (8%)
378 (3.28)	0.017	H → L+1 (50%), H_1 → L+1 (26%)
352 (3.52)	0.139	H_2 → L (55%), H_4 → L (10%), H_3 → L (9%)
330 (3.76)	0.064	H_4 → L (41%), H → L+2 (18%), H_0 → L+3 (18%)
322 (3.85)	0.024	H_1 → L+2 (33%), H_1 → L+3 (28%), H → L+2 (16%)
313 (3.97)	0.017	H → L+2 (57%), H_4 → L (13%), H_1 → L+2 (8%), H_1 → L+3 (7%)
304 (4.08)	0.002	H_3 → L+1 (26%), H_1 → L+2 (25%), H → L+3 (15%), H_2 → L+1 (10%)

Table 3. Total energies (in hartrees) and optimized cartesian coordinates (in Å) for the simplified models of species **2** and **3**, and the transition state for their interconversion.

Model of **2**:
E(RPBE+HF-PBE) = -1012.91203199

44	-0.161744	-0.020776	-0.000044
15	1.719241	-1.111302	-0.000067
15	0.803375	2.022369	-0.000009
6	-1.690707	-1.577282	0.000361
1	-1.481562	-2.638436	0.000625
6	-1.863484	-0.748741	1.157676
1	-1.789954	-1.069104	2.188334
6	-2.163713	0.574407	0.717031
1	-2.363702	1.423423	1.356972
6	-2.163741	0.574047	-0.717403
1	-2.363782	1.422722	-1.357778
1	-1.790024	-1.070241	-2.187848
6	-1.863527	-0.749334	-1.157358
1	1.885491	-2.520654	0.000018
1	-0.082342	3.129331	0.000136
1	1.638021	2.491284	-1.050534
1	1.638208	2.491131	1.050431
6	3.484404	-0.578165	0.000086
1	3.537094	0.513861	0.000084
1	4.007246	-0.947370	0.888424
1	4.007417	-0.947388	-0.888143

Model of **3**:
E(RPBE+HF-PBE) = -1012.89620749

44	0.124987	0.055083	-0.178499
15	-0.876532	2.034920	0.139618
15	-1.725519	-1.067547	0.187843
6	1.648052	-1.584132	-0.212254
1	1.440419	-2.602418	-0.512531
6	2.085189	-0.533769	-1.069765
1	2.234170	-0.610390	-2.138119
6	2.278011	0.635842	-0.280698
1	2.639701	1.590801	-0.637606
6	1.968893	0.298555	1.085275
1	2.037869	0.965129	1.935129
1	1.315816	-1.623357	2.013409
6	1.590731	-1.065702	1.127714
1	-2.276760	2.098290	0.352257
1	-0.810369	3.049544	-0.849896
1	-0.498694	2.861272	1.231902
1	-1.702653	-2.287345	0.914395
1	-0.450561	0.266172	-1.649048
6	-3.341487	-0.907170	-0.170913
1	-4.073204	-1.631682	0.170178
1	-3.700726	-0.072012	-0.764200

Transition State:
Imaginary frequency = -2002.8072
E(RPBE+HF-PBE) = -1012.79943012

44	-0.093027	0.041794	-0.194779
15	0.942395	2.027403	-0.050443
15	1.666960	-1.202744	-0.471808
6	-1.676465	-1.525289	0.013033
6	-1.443364	-0.903720	1.279933
6	-1.777990	0.477308	1.138950
6	-2.304219	0.682591	-0.192924
6	-2.242062	-0.548624	-0.872408
1	-1.529386	-2.572945	-0.216163
1	-1.088293	-1.388005	2.179552
1	-1.745598	1.218480	1.927143
1	-2.682211	1.614958	-0.590906
1	-2.526473	-0.722659	-1.902248
1	1.669942	2.577587	-1.139059
1	1.932977	2.292110	0.937576
1	0.140520	3.167334	0.209033
1	1.527232	-2.608436	-0.266410
6	2.923498	-0.833081	0.712898
1	3.512351	-1.626961	1.169484
1	3.428673	0.125905	0.611807
1	1.436723	-0.381316	1.007345

References

(1) Full citation for *Gaussian 03* (Revision B.03): Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C. Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.;

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