Supporting Information for:

Quantifying the Donor-Acceptor Properties of Phosphine and N-Heterocyclic Carbene Ligand in Grubbs' Catalysts using a Modified EDA Procedure Based on Orbital Deletion.

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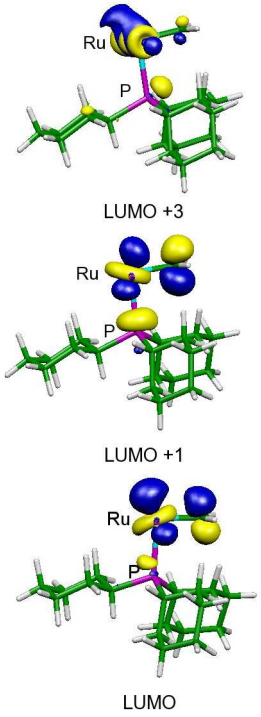

Figure S1. 3D representation of the dz^2 Ru-based LUMO and LUMO+1 orbitals, and 5s Ru-based LUMO+3 orbital of the metal fragment in **1b**.

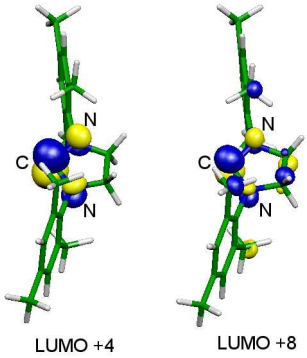

Figure S2. 3D representation of the out-of-plane p_π-type orbitals LUMO+4 and LUMO+8 molecular orbitals of the H_2IMes ligand fragment in **1b**..

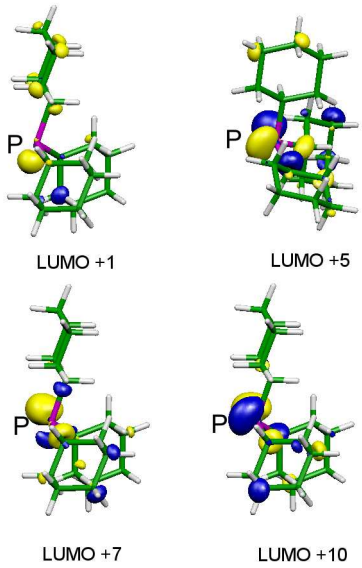

Figure S3. 3D representation of the phosphorus π*-type LUMO+1, LUMO+5, LUMO+7 and LUMO+10 molecular orbitals of PCy3 ligand fragment in **1a**.

Computational details

We used the density-functional theory (DFT) implemented in the ADF 2004.01 [1] package to study the molecules discussed in this work. The electron density is characterized by the local density approximation for the exchange electronic interactions, featuring the Xα model with Becke's gradient-corrected functional.[2] The correlation part is described by the VWN parameterization[3] together with Perdew's corrections.[4] The valence electrons of all the atoms are described with a set of Slater-type basis functions of triple-ξ + polarization quality. The innermost or *core* electrons (O, C: 1s; P, Cl: 1s2p; Ru: 1s4p;) were kept frozen. We applied scalar relativistic corrections to them—*zeroth-order regular approximation* (ZORA)—via the core potentials generated with the program DIRAC.**Error! Bookmark not defined.**

[1] ADF 2004.01. Department of Theoretical Chemistry. Vrije Universiteit. Amsterdam. Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41. Versluis, L.; Ziegler, T. *J. Chem. Phys.* **1988**, *88*, 322. Te Velde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84. Fonseca Guerra, C.; Snijders, J. G.; Te Velde, G.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 391.

[2] Becke, A. D.; *J. Chem. Phys.* **1986**, *84*, 4524; *Phys. Rev.* **1988**, *A38*, 3098.

[3] Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

[4] Perdew, J. P. *Phys. Rev.* **1986**, *B33*, 8822; *ibid*. **1986**, *B34*, 7406.

Cartesian coordinates in Å and total electronic energies in a.u.:

(1a) $(PCy3)_2Cl_2Ru=CH_2$
E = -599.62453

C	0.279053	-1.689789	4.766602
C	-0.117432	1.633300	-4.800507
C	0.308228	-1.686935	3.229248
C	0.304581	-3.134155	5.294037
C	0.323517	1.476273	-3.328262
C	1.681366	3.077057	4.924561
C	1.137100	1.318161	3.181778
C	0.613327	2.815170	-5.473190
C	-0.504303	-3.597107	-5.287064
C	0.602219	-1.979691	-3.645309
C	1.547836	-2.436676	2.692398
C	0.510513	-3.447906	-4.108841
C	1.519165	-3.917480	4.762314
C	1.720581	-0.563828	-0.267900
C	1.856995	1.301559	-3.227097
C	3.169632	2.694916	4.874878
C	1.574417	-3.881607	3.225403
C	2.624649	0.898346	3.157608
C	2.142075	2.674683	-5.364929
C	2.581314	2.496750	-3.901642
C	3.542038	2.091187	3.488037
C	-0.788528	-1.437683	-3.236145
C	0.763229	1.888550	4.565460
C	-1.876724	-3.023010	-4.897583
C	-1.779694	-1.557297	-4.416946
C	-1.709839	0.473373	3.095871
C	-2.445023	0.904602	-2.443085
C	-2.566193	2.411102	-2.114288
C	-2.205856	1.780029	2.426147
C	-2.784286	-0.665817	2.945602
C	-3.403732	0.075333	-1.549316
C	-4.025162	2.890411	-2.238205
C	-3.566635	2.217117	2.991684
C	-4.134018	-0.200546	3.512054
C	-4.857971	0.561752	-1.676910
C	-4.616318	1.101715	2.853729
C	-4.974197	2.060684	-1.356995
Cl	0.601974	2.386795	-0.012894
Cl	-0.926712	-2.278931	0.065277
H	0.300308	3.756088	-4.981873
H	0.302948	-3.133820	6.398224
H	1.494934	3.898575	4.206207
H	1.021957	2.127106	2.432785
H	0.306320	2.892242	-6.531235
H	0.115402	0.705872	-5.353973
H	1.156097	-1.145844	5.154907
H	-0.597092	-4.657684	-5.577850
H	-0.112930	-3.054138	-6.168579
H	0.706955	-4.429169	2.810364
H	0.184052	-4.078125	-3.261230
H	1.009781	-1.370636	-4.475159
H	1.516541	-2.448914	1.591476
H	1.489594	-4.959824	5.125443
H	2.352676	3.415710	-3.330185
H	1.310471	-1.895096	-2.802475
H	2.149490	1.246628	-2.166931
H	3.383698	1.944504	5.660233
H	2.798920	0.099258	3.903137
H	1.954498	-1.611359	-0.530441
H	3.801392	3.573715	5.091965
H	2.475677	-1.918503	2.998627
H	3.432678	2.865219	2.706879

H	2.889023	0.482574	2.169830
H	2.578644	0.126144	-0.175064
H	2.174316	0.363846	-3.718216
H	2.446014	-3.467026	5.168991
H	2.638306	3.553696	-5.812866
H	2.467865	1.794205	-5.952148
H	1.507477	-3.808990	-4.418732
H	2.479340	-4.398727	2.859680
H	3.674133	2.348892	-3.841690
H	4.598450	1.769608	3.484070
H	1.415009	3.465408	5.924271
H	0.090897	2.412598	-2.781448
H	0.856964	1.107376	5.342209
H	-1.153198	-2.087723	-2.411560
H	-0.623322	-3.647949	4.976639
H	-0.566528	-2.251495	2.854385
H	-1.454758	-0.918259	-5.257919
H	-1.207840	1.780396	-4.871704
H	-2.304916	-3.634735	-4.080780
H	-0.612061	-1.169052	5.146805
H	-2.580856	-3.090652	-5.745911
H	-0.284302	2.232100	4.582367
H	-2.785477	-1.214371	-4.123886
H	-1.931595	3.008835	-2.790482
H	-1.583282	0.661072	4.180237
H	-1.461533	2.587585	2.531708
H	-2.751633	0.765213	-3.499634
H	-2.455170	-1.574585	3.476761
H	-2.188980	2.601883	-1.092438
H	-2.304535	1.610870	1.336960
H	-2.882996	-0.944183	1.880417
H	-3.331924	-1.000977	-1.780853
H	-3.083649	0.172470	-0.494339
H	-3.452438	2.481995	4.061142
H	-4.347961	2.809600	-3.294678
H	-4.036316	-0.038910	4.604019
H	-4.086975	3.960175	-1.971451
H	-3.906952	3.132858	2.476746
H	-5.216629	0.378586	-2.708618
H	-4.886139	-0.998581	3.380829
H	-4.714874	2.224640	-0.293991
H	-4.804413	0.913803	1.779129
H	-5.508560	-0.029327	-1.008636
H	-5.579208	1.421219	3.290039
H	-6.016251	2.402817	-1.484421
P	0.000000	0.000000	2.440216
P	-0.680222	0.224762	-2.334167
Ru	0.000000	0.000000	0.000000

(1b) (H_2Imes)(PCy_3)Cl_2Ru=CH_2
E = -610.14717 a.u.

C	-1.789856	0.115631	-0.357788
C	6.717224	0.395569	1.581741
C	5.242996	0.280640	1.894043
C	4.616714	-0.965469	1.989365
C	4.471710	1.426712	2.123489
C	3.250626	-1.096619	2.283493
C	3.108795	1.355621	2.432251
C	2.639328	-2.470016	2.414200
C	2.498703	0.081497	2.472687
C	0.000015	0.000000	2.076355
C	2.330368	2.610809	2.724075
C	-2.411300	2.506516	2.425278
C	-4.533463	1.146912	2.055862

C	-3.144500	1.183426	2.354248
C	-6.729034	-0.058380	1.656769
C	-5.249374	-0.058868	1.983856
C	-2.481766	-0.049042	2.562790
C	-4.566086	-1.254913	2.232574
C	-3.177307	-1.274338	2.530182
C	-2.460785	-2.616547	2.782928
C	0.790558	-0.233688	4.297363
C	-0.707138	0.034607	4.337372
C	2.849503	-1.984512	-1.950806
C	3.474319	0.483322	-2.041046
C	5.304794	-1.291550	-1.832916
C	2.489944	-0.616592	-2.576523
C	-0.863800	2.134445	-3.317291
C	-1.737167	-1.267975	-3.530090
C	4.310471	-2.368103	-2.301086
C	-0.235916	-1.547150	-3.283539
C	4.932755	0.101028	-2.372864
C	0.535980	1.470871	-3.339508
C	-2.463638	-2.554993	-3.963257
C	-0.778931	3.571411	-3.887009
C	0.408569	-2.093552	-4.585983
C	-1.824097	-3.156586	-5.227585
C	1.095230	1.446884	-4.778931
C	-0.313873	-3.381485	-5.036224
C	-0.196869	3.582779	-5.310500
C	1.168411	2.874542	-5.360641
Cl	-0.119202	-2.467819	0.048431
Cl	0.280151	2.439285	-0.092087
H	-2.279083	1.085922	-0.550827
H	-2.423187	-0.786972	-0.393936
H	5.205002	-1.873611	1.834976
H	7.289978	0.687668	2.475739
H	4.944565	2.411362	2.075043
H	3.342300	-3.234894	2.060944
H	1.709091	-2.562119	1.833298
H	1.602509	2.806992	1.919403
H	-1.566269	2.538467	1.715042
H	-6.931396	0.498184	0.727417
H	3.005295	3.471786	2.809357
H	-1.626572	-2.742462	2.071640
H	-3.094100	3.335602	2.189224
H	-5.047653	2.097031	1.873520
H	2.407272	-2.705139	3.465515
H	-7.110641	-1.082092	1.530304
H	-5.103821	-2.207718	2.189423
H	-3.167694	-3.449554	2.657639
H	1.763855	2.525970	3.663147
H	-2.003555	2.688477	3.434357
H	-7.313782	0.423462	2.458130
H	-2.054260	-2.665802	3.807312
H	1.032043	-1.271454	4.573883
H	1.368851	0.441284	4.938934
H	-0.941147	1.039566	4.721542
H	-1.258514	-0.700256	4.934586
H	7.125793	-0.556137	1.218628
H	6.900894	1.160767	0.814346
H	2.732269	-1.928131	-0.854095
H	3.350891	0.579208	-0.945786
H	5.293700	-1.256104	-0.728485
H	-1.240555	2.170944	-2.284531
H	-2.209717	-0.855453	-2.621414
H	-0.180923	-2.343445	-2.513580
H	-2.415100	-3.289307	-3.137497
H	2.160767	-2.776672	-2.287933
H	4.557770	-3.344040	-1.846298
H	1.183594	2.123856	-2.719300

H	3.240021	1.469406	-2.475845
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H	-0.141541	4.178162	-3.216721
H	-1.781067	4.035706	-3.877533
H	6.333054	-1.557831	-2.137680
H	-3.533142	-2.341949	-4.139206
H	-1.576111	1.548157	-3.925568
H	-1.849274	-0.508789	-4.327621
H	2.644485	-0.692459	-3.672546
H	-0.157578	-4.162109	-4.267792
H	4.396454	-2.499603	-3.397522
H	5.065918	0.114243	-3.472534
H	1.479553	-2.308731	-4.441772
H	1.902725	3.459869	-4.774979
H	-2.320908	-4.104736	-5.498825
H	2.095734	0.985443	-4.811508
H	0.338287	-1.336197	-5.387207
H	0.437897	0.830276	-5.418472
H	-0.102280	4.618347	-5.682709
H	-1.981171	-2.462509	-6.076096
H	-0.897827	3.064362	-5.993210
H	0.140518	-3.758957	-5.969437
H	1.546875	2.838364	-6.397781
N	1.111694	-0.000015	2.871429
N	-1.082321	-0.063141	2.910461
P	0.662750	-0.152084	-2.378647
Ru	0.000000	0.000000	0.000000

(2a) $(PCy_3)Cl_2Ru{=}CH_2$
E = -313.65723 a.u.

C	0.182335	-4.780174	-1.626950
C	0.486029	-3.267882	-1.549982
C	0.705242	-5.378097	-2.946346
C	0.926387	-5.261748	3.548925
C	1.492619	-3.467026	1.838920
C	1.732021	-3.986607	3.267913
C	1.970221	-0.249530	0.221097
C	1.995528	-2.996657	-1.728293
C	2.205711	-5.112385	-3.131395
C	2.512806	-3.611790	-3.039446
C	-0.010170	-3.239180	1.563002
C	-0.564791	-5.035497	3.271971
C	-0.812535	-4.532098	1.837603
C	-2.181067	-2.680029	-0.402820
C	-2.659310	-2.394822	-1.842815
C	-3.054129	-1.921336	0.622307
C	-4.157823	-2.711908	-2.002088
C	-4.546655	-2.245452	0.448419
C	-5.017015	-1.953112	-0.982259
Cl	-0.196457	0.197111	-2.296848
Cl	-0.728986	0.265379	2.112378
H	0.150422	-4.929774	-3.788847
H	0.497438	-6.459512	-2.971344
H	0.670450	-5.297138	-0.783419
H	1.077510	-5.591176	4.588931
H	1.296285	-6.078146	2.902863
H	1.440929	-3.203335	3.988389
H	1.891680	-4.205317	1.121257
H	2.039984	-3.088453	-3.888293
H	2.050701	-2.531104	1.691811
H	2.173566	-1.912866	-1.736512
H	2.638571	-1.117204	0.285019
H	2.452141	0.744332	0.299752
H	2.561756	-3.421650	-0.881482

H 2.549550 -5.516710 -4.096274
H 2.768199 -5.648804 -2.346458
H 2.807898 -4.169509 3.417569
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H -0.016800 -2.764381 -2.397578
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H -0.519270 -5.319665 1.123731
H -0.897919 -4.970462 -1.535640
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H -2.472874 -1.337420 -2.091317
H -2.733908 -2.138609 1.652527
H -2.905457 -0.836797 0.489073
H -4.318275 -3.797718 -1.872863
H -4.472712 -2.469176 -3.029240
H -4.723948 -3.311045 0.680877
H -4.935528 -0.869054 -1.175032
H -5.133149 -1.662999 1.176043
H -6.079689 -2.216983 -1.101915
P -0.332633 -2.373581 -0.099125
Ru 0.154738 -0.175767 -0.008561

(2b) (H_2IMes)Cl_2Ru=CH_2
E = -323.96305157 a.u.
C 0.023041 0.204443 1.872027
C 0.169504 0.084936 -6.744980
C 0.801599 0.029512 -5.373586
C 1.000772 -1.187699 -4.717714
C 1.248410 1.197743 -4.742912
C 1.605506 -1.269334 -3.454176
C 1.847122 1.176397 -3.479642
C 1.905436 -2.626326 -2.866763
C 1.972953 -0.065685 -2.816023
C 2.107163 -0.045890 -0.272545
C 2.376112 2.452242 -2.875537
C 3.025642 2.544812 1.857727
C 3.136701 1.311474 4.084851
C 3.111339 1.265370 2.665977
C 3.187112 0.234376 6.380497
C 3.166645 0.144957 4.868678
C 3.118031 -0.003917 2.045559
C 3.173118 -1.093555 4.216409
C 3.149780 -1.191811 2.799150
C 3.124247 -2.575614 2.117713
C 4.100727 -0.354473 -1.512049
C 4.465407 -0.037018 -0.064291
Cl -0.207157 -2.314652 -0.151196
Cl -0.306002 2.167709 -0.683253
H 0.796578 0.302442 2.642600
H -1.032079 0.231921 2.218642
H 0.690026 -2.115176 -5.205440
H 0.921574 0.315982 -7.515445
H 1.137712 2.158989 -5.251611
H 1.323003 -3.401030 -3.381428
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H 2.334910 0.824301 6.754780
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H 2.228993 -2.678713 1.483498
H 2.951230 3.416243 2.523826
H 3.118918 2.292754 4.571417

H	2.970474	-2.878872	-2.999443
H	3.138701	-0.762848	6.841198
H	3.187526	-2.017195	4.804010
H	3.116685	-3.371007	2.876485
H	3.441696	2.361830	-2.614952
H	3.913367	2.686201	1.219102
H	4.106066	0.728584	6.736894
H	4.009367	-2.721217	1.476542
H	4.300534	-1.407477	-1.768246
H	4.619598	0.284452	-2.237797
H	4.902996	0.969120	0.046313
H	5.158894	-0.765691	0.374340
H	-0.296111	-0.872517	-7.010147
H	-0.600473	0.867046	-6.798284
N	2.647890	-0.092024	-1.538745
N	3.152794	-0.100075	0.612182
Ru	0.183383	-0.002828	0.066355

(1b' C_s) (Imes)(PH_3)Cl_2Ru=CH_2

E = -108.28267 a.u.

Ru	-0.103923	0.564699	0.000000
N	1.193904	-2.139295	0.000000
N	-0.960635	-2.371420	0.000000
C	-1.894070	0.907768	0.000000
C	0.029124	-1.462588	0.000000
C	1.040246	-3.603973	0.000000
C	-0.501507	-3.768971	0.000000
H	-2.450125	1.032068	0.947018
H	1.502770	-4.045909	-0.893262
H	-0.859694	-4.299348	-0.893085
H	1.502770	-4.045909	0.893262
H	-0.859694	-4.299348	0.893085
H	2.096238	-1.680696	0.000000
H	-1.933734	-2.096018	0.000000
H	-2.450125	1.032068	-0.947018
Cl	0.094933	0.600681	2.407229
Cl	0.094933	0.600681	-2.407229
P	0.594423	2.830657	0.000000
H	2.012838	2.976276	0.000000
H	0.312075	3.695094	-1.094827
H	0.312075	3.695094	1.094827