Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Supporting Information for:

Theoretical study of the activity in Rh-catalysed hydroformylation. The origin of enhanced activity of π-acceptor phosphinine ligand

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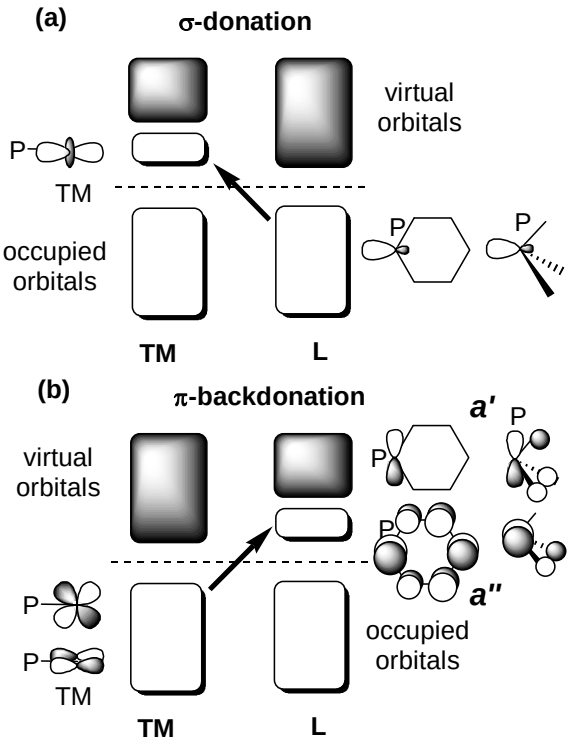
S1. **Energy decomposition analysis (EDA) and modified version based on orbital deletion procedure.** The Energy Decomposition Analysis (EDA) method[1] divides the interaction energy in three terms: (i) the classical electrostatic interaction ΔE_{elstat} between the unperturbed charges of the fragments, (ii) the Pauli term ΔE_{Pauli}, which accounts for repulsion between electrons of the same spin, and (iii) the orbital term ΔE_{orb} that accounts for charge transfer and polarization effects.[2] The sum of electrostatic and Pauli terms is often called the steric term (ΔE_{ster}). The orbital term can be separated into interactions falling in different symmetry representations, allowing in some cases, to distinguish between σ-donation and π-backdonation for example.

Recently, we have proposed a modified version of EDA procedure based on orbital deletion, allowing separation of σ and π interactions in a physically meaningful manner.[3] To account for σ-donation, referred to as $\Delta E_{\sigma}(L \rightarrow Rh)$, we repeated the EDA analysis while consecutively deleting all the virtual molecular orbitals except those metal orbitals (d_{z2}- and 5s-type) with the appropriate shape for σ-donation (see Figure S1a). Keeping the appropriate virtual orbitals of the ligand fragment provides data for the π-backdonation, referred to as $\Delta E_{\pi}(Rh \rightarrow L)$. For phosphinine we kept the usually-discussed out-of-plane p_{π}-type orbital and the additional in-plane p_{π}-type of phosphorus, while for the phosphane ligand two π*-type phosphorus orbitals perpendicular to the bond axis (see Figure S1b). This gives the energetic contribution to the bonding from the interaction between the occupied orbitals of one fragment with the selected unoccupied orbitals of the other fragment. Technically, we did this by combining the "FRAGMENT calculations" in ADF with the keyword "REMOVEFRAGORBITALS". In some cases, we had to combine "FRAGMENT calculations" because orbitals can be deleted only in blocks without holes.

Figure S1. Schematic representation of the modified EDA procedure based on orbital deletion. Evaluation of the σ-donation (a) from the phosphinine and phosphane (L) to rhodium metal fragment TM and of π-backdonation (b) from TM to L.



[1] a) Morokuma, K. *J. Chem. Phys*. **1971**, *55*, 1236; b) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1; c) Ziegler, T.; Rauk, A.; *Inorg. Chem*. **1979**, *18*, 1755; d) Ziegler, T.; Rauk, A. *Inorg. Chem*. **1979**, *18*, 1558.
[2] Bickelhaupt, F. M.; Nibbering, N. M. M.; van Wezenbeek, E. M.; Baerends, E. J. *J. Phys. Chem.* **1992**, *96*, 4864
[3] a) Antonova, N. S.; Carbó, J. J.; Poblet, J. M. *Organometallics* **2009**, *28*, 4283; b) Antonova, N. S.; Carbó, J. J.; Poblet, J. M. *Dalton Transac.* **2011**, *40*, 2975

Table S1. Overall ($\Delta E^{\neq}_{Overall}$), alkene insertion ($\Delta E^{\neq}_{inser}$) energy barriers, in kcal.mol^{-1} for the different coordination isomers of [$HRh(CO)_3(PPh_3)$] (equatorial, **e**, and apical, **a**) and [$HRh(CO)_2(PPh_3)_2$] (equatorial-equatorial, **ee**, and equatorial-apical, **ea**) systems.

	mono-phosphane		bi-phosphane	
coordination	e	a	ee	ea
$\Delta E^{\neq}_{Overall}$ (**1** → **TS**)	22.4	23.1	25.9	26.9
$\Delta E^{\neq}_{inser}$ (**3** → **TS**)	10.9	12.0	10.8	11.3

Table S2. EDA partition for the Rh-phosphorus and Rh-alkene bonds. Interaction energy (ΔE_{int}), Pauli term (ΔE_{Pauli}), electrostatic term ($\Delta E_{elestat}$), steric term (ΔE_{ster}, sum of Pauli and electrostatic terms), and orbital term (ΔE_{orb}). The σ-donation (ΔE_{σ}(L→Rh)), π-backdonation (ΔE_{π}(Rh→L)), in-plane π-backdonation of *a'* symmetry (ΔE_{π}(a')), and out-of-plane π-backdonation of *a''* symmetry (ΔE_{π}(a')) using a modified version EDA analysis based on orbital deletion.

	Rh-phosphorus			**Rh-alkene**		
	$P(OH)_3$	PC_5H_5	PH_3			
	-	**1e1^H**	**1Pe^H**	**3e1^H**	**3Pe^H**	**3Pee^H**
d(Rh-L)	2.334	2.372	2.410	2.277	2.262	2.238
d(C-C)	-	-	-	1.399	1.403	1.408
ΔE_{int}	-29.6	-24.8	-20.8	-30.4	-33.9	-35.9
ΔE_{Pauli}	+139.1	+114.9	+111.0	+126.4	+128.6	+140.4
$\Delta E_{elestat}$	-117.8	-94.0	-91.5	-95.1	-98.1	-69.4
ΔE_{ster}	+21.3	+20.9	+19.5	+31.3	+30.5	+32.7
ΔE_{orb}	-50.9	-45.7	-40.3	-61.8	-64.4	-68.6
ΔE_{σ}(L→Rh)	-13.1	-13.5	-13.6	-14.2	-13.7	-13.8
ΔE_{π}(Rh→L)	-10.3	-8.5	-6.9	-22.6	-24.7	-27.1
ΔE_{π}(a')	-	-3.2	-3.2	-	-	-
ΔE_{π}(a'')	-	-5.3	-3.7	-	-	-

Energies in kcal.mol^{-1} and metal-ligand bond lengths in Å. EDA partition for the Rh-phosphorus ligand bond in hydrido-carbonyl complexes **1e1^H** and **1Pe^H**, and of the Rh-alkene bond in alkene complexes of the type **3^H**. For $P(OH)_3$, values taken from ref. **¡Error! Marcador no definido.** for the [$Rh(CO)_2H(PH_3)(P(OH_3))$] complex with the $P(OH)_3$ ligand in equatorial position. For **1e1^H** and **1Pe^H**, calculations imposing C_s symmetry constrains for decomposing the energy interactions.

S2. Definition of q^2: The cross-validated correlation coefficient (q^2) is defined as follow:

$$q^2 = 1 - \frac{\sum_{n=1}^{N} (y_n - \hat{y}_n)^2}{\sum_{n=1}^{N} (y_n - \tilde{y}_n)^2}$$

where y_n is the observed activity, $\hat{y}$ is the predicted activity and $\tilde{y}$ is the mean activity value.

Cartesian coordinates in Å for some of the most representative structures:

[HRh(CO)$_3$(2,4,6-PC$_5$H$_2$Ph$_3$)] (**1e1**)

Rh	-0.945623	0.167022	0.000000
H	-0.727352	-1.410058	0.000000
C	-1.341068	2.136233	0.000000
O	-1.700663	3.230587	0.000000
C	-1.757350	-0.230660	1.731634
O	-2.277494	-0.553261	2.714363
C	-1.757350	-0.230660	-1.731634
O	-2.277494	-0.553261	-2.714363
C	2.415364	-1.356256	0.000000
C	2.620329	1.386100	0.000000
C	3.812101	-1.305607	0.000000
C	3.994194	1.134061	0.000000
C	4.584971	-0.136616	0.000000
H	4.345416	-2.260507	0.000000
H	4.661572	2.000541	0.000000
P	1.429750	0.095947	0.000000
C	2.132849	2.798995	0.000000
C	1.908075	3.476450	1.209223
C	1.908075	3.476450	-1.209223
C	1.476993	4.805410	1.208421
H	2.074807	2.954156	2.152960
C	1.476993	4.805410	-1.208421
H	2.074807	2.954156	-2.152960
C	1.260509	5.473260	0.000000
H	1.307154	5.318401	2.155805
H	1.307154	5.318401	-2.155805
H	0.920704	6.509754	0.000000
C	1.740099	-2.690873	0.000000
C	1.429697	-3.333919	1.208753
C	1.429697	-3.333919	-1.208753
C	0.829713	-4.595686	1.208320
H	1.661547	-2.838088	2.152919
C	0.829713	-4.595686	-1.208320
H	1.661547	-2.838088	-2.152919
C	0.528972	-5.230624	0.000000
H	0.596076	-5.082426	2.156155
H	0.596076	-5.082426	-2.156155
H	0.060285	-6.215719	0.000000
C	6.078003	-0.249851	0.000000
C	6.790071	-0.304976	-1.207754
C	6.790071	-0.304976	1.207754
C	8.183787	-0.413007	-1.208092
H	6.244779	-0.263505	-2.152387
C	8.183787	-0.413007	1.208092
H	6.244779	-0.263505	2.152387
C	8.884366	-0.467313	0.000000
H	8.722384	-0.454784	-2.155718
H	8.722384	-0.454784	2.155718
H	9.972053	-0.551662	0.000000

[HRh(CO)$_3$(2,4,6-PC$_5$H$_2$Ph$_3$)] (**1e2**)

Rh	-0.979210	-0.100557	0.000000

H	-0.746433	1.478848	0.000000
C	-1.298819	-2.074551	0.000000
O	-1.490472	-3.213246	0.000000
C	-1.789410	0.324784	-1.721960
O	-2.362066	0.658794	-2.670520
C	-1.789410	0.324784	1.721960
O	-2.362066	0.658794	2.670520
C	2.531882	-0.050712	1.376322
C	2.531882	-0.050712	-1.376322
C	3.915614	0.099662	1.221623
C	3.915614	0.099662	-1.221623
C	4.595181	0.159729	0.000000
H	4.515740	0.139411	2.134611
H	4.515740	0.139411	-2.134611
P	1.440766	-0.164165	0.000000
C	1.971038	-0.092166	2.754200
C	2.269220	0.936280	3.666338
C	1.162182	-1.158208	3.182677
C	1.768890	0.900650	4.969296
H	2.882623	1.777303	3.339785
C	0.671344	-1.199171	4.489031
H	0.939276	-1.971323	2.490906
C	0.970843	-0.169198	5.385861
H	1.998194	1.714727	5.658708
H	0.054537	-2.040723	4.807698
H	0.581741	-0.199101	6.404417
C	1.971038	-0.092166	-2.754200
C	2.269220	0.936280	-3.666338
C	1.162182	-1.158208	-3.182677
C	1.768890	0.900650	-4.969296
H	2.882623	1.777303	-3.339785
C	0.671344	-1.199171	-4.489031
H	0.939276	-1.971323	-2.490906
C	0.970843	-0.169198	-5.385861
H	1.998194	1.714727	-5.658708
H	0.054537	-2.040723	-4.807698
H	0.581741	-0.199101	-6.404417
C	6.091482	0.230329	0.000000
C	6.761811	1.462487	0.000000
C	6.847010	-0.952632	0.000000
C	8.159582	1.510092	0.000000
H	6.183601	2.388457	0.000000
C	8.243864	-0.905127	0.000000
H	6.332062	-1.915183	0.000000
C	8.903718	0.327008	0.000000
H	8.668181	2.475290	0.000000
H	8.816226	-1.834110	0.000000
H	9.994028	0.365007	0.000000

$[HRh(CO)_3(2,4,6\text{-}PC_5H_2Ph_3)]$ (**1a**)

Rh	-0.8552	0.0164	0.0492
H	-0.7965	0.0220	1.6246
C	-1.9357	1.6320	0.3978
O	-2.5748	2.4829	0.8503
C	-1.9256	-1.6054	0.4132
O	-2.5561	-2.4540	0.8816

C	1.0866	0.0166	0.2290
O	2.2276	0.0166	0.4410
C	-0.9126	-1.3655	-3.4545
C	-0.9168	1.3991	-3.4546
C	-0.9696	-1.2082	-4.8439
C	-0.9734	1.2421	-4.8441
C	-0.9859	0.0170	-5.5245
P	-0.8904	0.0169	-2.3786
C	-0.9570	0.0162	-7.0227
C	-2.1416	0.0195	-7.7735
C	0.2732	0.0110	-7.6988
C	-2.0969	0.0180	-9.1713
C	0.3179	0.0103	-9.0956
C	-0.8674	0.0135	-9.8359
C	-0.9066	2.7668	-2.8627
C	-1.9931	3.6351	-3.0656
C	0.1821	3.2126	-2.0947
C	-1.9929	4.9144	-2.5063
C	0.1882	4.4983	-1.5507
C	-0.9016	5.3506	-1.7491
C	-0.8991	-2.7332	-2.8634
C	-1.9863	-3.6014	-3.0620
C	0.1938	-3.1793	-2.1020
C	-1.9823	-4.8818	-2.5048
C	0.2038	-4.4657	-1.5601
C	-0.8865	-5.3184	-1.7542

$[HRh(CO)_3(PC_5H_5)]$ (**1e1^{H}**)

Rh	-0.908384	0.015185	-0.184170
H	-0.802145	0.016595	1.407291
C	-0.977329	0.013957	-2.179409
O	-0.977727	0.012988	-3.332469
C	-1.791026	1.733611	0.143647
O	-2.367788	2.697383	0.418703
C	-1.797566	-1.698907	0.146122
O	-2.378080	-2.660509	0.420972
C	2.459750	0.012640	1.376840
C	2.631142	0.020054	-1.332484
C	3.853301	0.015732	1.333654
H	1.952156	0.009329	2.344084
C	4.008271	0.022593	-1.118490
H	2.250799	0.022282	-2.356946
C	4.598990	0.020534	0.149688
H	4.395771	0.014625	2.281888
H	4.663946	0.026585	-1.992427
H	5.687264	0.022926	0.218045
P	1.459275	0.014250	-0.045646

$[HRh(CO)_3(PC_5H_5)]$ (**1e2^{H}**)

Rh	-0.913761	0.015504	-0.129875
H	-0.948420	0.013646	1.450975
C	-1.853395	1.726540	0.096108
O	-2.388391	2.721656	0.347619
C	-1.855740	-1.693350	0.094624
O	-2.393565	-2.687815	0.343012

C	1.041680	0.022224	0.147204
O	2.157226	0.028193	0.451340
C	-0.920577	-1.347144	-3.615139
C	-0.912525	1.374785	-3.616412
C	-0.928041	-1.216671	-5.003563
H	-0.920012	-2.343300	-3.166424
C	-0.920861	1.243018	-5.004740
H	-0.906289	2.371286	-3.168488
C	-0.928493	0.012852	-5.671260
H	-0.933391	-2.128992	-5.604151
H	-0.921308	2.154657	-5.606351
H	-0.935330	0.012438	-6.761705
P	-0.913967	0.014281	-2.539040

$[HRh(CO)_3(PC_5H_5)]$ (**1a^{H}**)

Rh	0.188367	1.579787	-3.945703
C	-0.244775	0.244779	-2.565684
O	-0.618824	-0.515077	-1.777356
C	3.483809	1.481654	-2.164938
C	3.810090	1.576958	-4.865846
C	4.877980	1.458703	-2.130099
H	2.919480	1.456940	-1.229863
C	5.172561	1.545149	-4.570652
H	3.483702	1.622609	-5.907555
C	5.687295	1.488363	-3.270830
H	5.365652	1.415239	-1.153809
H	5.878505	1.566219	-5.403859
H	6.769797	1.466415	-3.141108
P	2.578485	1.548177	-3.643739
H	-1.377012	1.580189	-4.168690
C	-0.109397	3.472693	-3.473858
O	-0.410866	4.559040	-3.216298
C	0.206346	1.075731	-5.842175
O	0.101372	0.787966	-6.958716

$[HRh(CO)_3(PH_3)]$ (**1Pe^{H}**)

Rh	-0.073443	-0.211649	0.000000
H	-1.670458	-0.190931	0.000000
O	-0.647019	-1.454195	2.788383
C	-0.382943	-0.975062	1.768840
C	1.923290	-0.328897	0.000000
C	-0.382943	-0.975062	-1.768840
O	-0.647019	-1.454195	-2.788383
O	3.071842	-0.431289	0.000000
P	-0.290236	2.199163	0.000000
H	-1.597161	2.765988	0.000000
H	0.216578	3.018399	1.055117
H	0.216578	3.018399	-1.055117

Alkene complex $[HRh(CO)_2(2,4,6\text{-}PC_5H_2Ph_3)(C_2H_4)]$ (**3e1**)

Rh	-0.930385	0.275013	0.231432
C	-1.363143	2.213632	-0.031440
O	-1.775665	3.280568	-0.191160
C	-1.672343	0.087829	2.002503
O	-2.122877	-0.117552	3.052680
C	2.386158	-1.281495	-0.070416

C	2.632227	1.450275	0.109744
C	3.779164	-1.243561	-0.182340
C	4.000063	1.181062	0.024985
C	4.573045	-0.090862	-0.108598
H	4.295471	-2.202442	-0.282859
H	4.679235	2.037618	0.057938
P	1.417682	0.176667	0.107348
C	2.182255	2.871708	0.162167
C	1.635905	3.424764	1.331278
C	2.322538	3.690103	-0.972260
C	1.255354	4.768614	1.369379
H	1.522848	2.796797	2.216433
C	1.929147	5.029420	-0.936702
H	2.733749	3.263712	-1.889138
C	1.397721	5.573618	0.235983
H	0.843772	5.186972	2.288709
H	2.034091	5.647009	-1.829543
H	1.093279	6.620878	0.264848
C	1.706927	-2.609899	-0.113750
C	1.084509	-3.138197	1.029357
C	1.704787	-3.370610	-1.294672
C	0.483160	-4.398107	0.994976
H	1.086596	-2.558478	1.953399
C	1.092441	-4.625991	-1.332676
H	2.178684	-2.965954	-2.191020
C	0.481123	-5.144495	-0.186955
H	0.014476	-4.796422	1.895906
H	1.092828	-5.200001	-2.260581
H	0.006750	-6.126446	-0.214076
C	6.058495	-0.224925	-0.127501
C	6.731557	-0.717852	-1.256868
C	6.811610	0.132242	1.003667
C	8.123456	-0.842252	-1.258539
H	6.158571	-0.985020	-2.146421
C	8.200869	-0.011400	1.010037
H	6.296336	0.501674	1.892378
C	8.861978	-0.494887	-0.123545
H	8.632632	-1.208488	-2.150914
H	8.766787	0.249224	1.905540
H	9.947741	-0.602011	-0.121348
H	-0.738258	-1.294132	0.386479
C	-1.302989	-0.246353	-1.968381
C	-2.506737	-0.354810	-1.263339
H	-2.874450	-1.331796	-0.953258
H	-3.257316	0.432632	-1.330291
H	-0.723687	-1.139157	-2.198885
H	-1.099361	0.627273	-2.587607

Alkene complex $[HRh(CO)_2(PPh_3)(C_2H_4)]$ (**3Pe**)

C	0.327523	-0.836294	5.048074
C	1.329262	1.439056	8.430712
C	1.366208	2.232178	9.590335
C	0.855530	1.745519	10.794918
C	0.299583	0.461531	10.856199
C	0.260216	-0.333763	9.708217
C	0.772566	0.153714	8.501553

C	3.783578	2.305755	7.138466
C	4.540198	3.097721	6.252213
C	5.921154	3.221698	6.413282
C	6.572961	2.544359	7.451957
C	5.831240	1.748587	8.329011
C	4.445045	1.630190	8.176399
C	1.337286	3.793365	6.739525
C	1.996861	4.856923	7.379248
C	1.470729	6.151318	7.332302
C	0.276689	6.401679	6.648906
C	-0.388841	5.349738	6.011606
C	0.139440	4.057170	6.053826
H	0.108895	1.452879	4.883237
H	1.786487	3.236861	9.552627
H	0.884631	2.373388	11.687083
H	-0.107432	0.085640	11.796382
H	-0.176622	-1.333360	9.745632
H	0.736280	-0.458683	7.599756
H	4.043424	3.626362	5.437217
H	6.491238	3.846867	5.724374
H	7.653717	2.636215	7.572822
H	6.328577	1.213570	9.139421
H	3.877543	1.007571	8.869433
H	2.936375	4.678648	7.902977
H	2.000027	6.965581	7.828918
H	-0.130484	7.413584	6.607389
H	-1.318002	5.535660	5.470875
H	-0.372588	3.241534	5.540828
O	-0.445760	-1.704178	5.090067
P	1.981560	2.051222	6.802562
Rh	1.505383	0.674434	4.878348
C	2.185625	2.252740	3.384190
C	1.524805	1.230090	2.689067
H	0.491387	1.360531	2.370171
H	2.093446	0.478198	2.141687
H	1.671247	3.188238	3.602890
H	3.274978	2.303382	3.369586
C	3.209358	-0.345411	4.842992
O	4.161993	-0.999410	4.800717

Alkene complex $[HRh(CO)(PPh_3)_2(C_2H_4)]$ (**3Pee**)

C	4.806092	-0.284278	3.281373
C	5.265373	0.984400	3.670792
C	6.377341	1.559270	3.049288
C	7.038075	0.877007	2.022494
C	6.582891	-0.384038	1.621745
C	5.474178	-0.961848	2.246784
C	1.644001	1.590586	3.438636
C	4.069257	-2.262997	5.291034
C	5.369415	-2.761396	5.110332
C	5.879731	-3.745407	5.963321
C	5.095061	-4.254447	7.002100
C	3.797126	-3.767019	7.188966
C	3.292475	-2.775046	6.344823
C	2.659144	-2.104588	2.793906
C	2.051233	-1.502294	1.674633

C	1.517501	-2.280633	0.646840
C	1.566309	-3.678387	0.722110
C	2.164169	-4.285805	1.827791
C	2.710291	-3.505282	2.855347
C	1.124368	2.033645	8.251985
C	0.985962	3.116093	9.138698
C	0.376498	2.946594	10.382770
C	-0.102560	1.689133	10.766314
C	0.040089	0.603377	9.898858
C	0.650718	0.775512	8.651404
C	3.651315	2.788096	7.176662
C	3.957899	4.093341	7.596866
C	5.237997	4.405403	8.062785
C	6.224011	3.414818	8.126547
C	5.925239	2.110661	7.718647
C	4.649169	1.801203	7.240289
C	1.206531	3.850242	6.013287
C	-0.138400	4.155672	6.290042
C	-0.744890	5.284667	5.730221
C	-0.021172	6.125857	4.880072
C	1.313337	5.824509	4.587077
C	1.920357	4.695212	5.143257
H	1.829783	-0.414373	6.368236
H	4.734572	1.523945	4.456375
H	6.720273	2.546583	3.361934
H	7.899383	1.330738	1.527842
H	7.086394	-0.917211	0.813587
H	5.115810	-1.937313	1.917306
H	5.991218	-2.378224	4.302579
H	6.896422	-4.112734	5.812351
H	5.494415	-5.021227	7.667993
H	3.177984	-4.153061	8.000573
H	2.290757	-2.376824	6.507563
H	1.995596	-0.414886	1.603923
H	1.054849	-1.794234	-0.213885
H	1.138103	-4.287237	-0.076108
H	2.208621	-5.373612	1.898527
H	3.179682	-3.997505	3.707117
H	1.350412	4.102771	8.854854
H	0.277432	3.798881	11.056636
H	-0.580357	1.558069	11.739156
H	-0.326126	-0.381661	10.190412
H	0.772956	-0.070496	7.974664
H	3.199815	4.874923	7.547996
H	5.464248	5.425788	8.376479
H	7.223267	3.660616	8.490773
H	6.688102	1.332598	7.764161
H	4.416798	0.787888	6.906222
H	-0.717257	3.509460	6.951268
H	-1.788755	5.504408	5.961747
H	-0.494461	7.007948	4.444215
H	1.885252	6.469186	3.918314
H	2.959243	4.469675	4.896425
O	1.644578	2.233033	2.467822
P	3.320170	-0.997752	4.146153
P	1.961594	2.259038	6.596596

Rh	1.698085	0.489546	5.040633
C	-0.142173	-0.810437	4.656418
C	-0.569367	0.347558	5.311050
H	-0.259248	-0.917822	3.578016
H	-0.033262	-1.744170	5.208112
H	-1.025146	1.161753	4.747232
H	-0.805742	0.328083	6.374806

Alkene complex $[HRh(CO)_2(PC_5H_5)(C_2H_4)]$ (**3e1^{H}**)

Rh	-0.807739	-0.079297	0.477542
H	-0.925241	1.507741	0.612104
C	-0.620650	-2.051144	0.287276
O	-0.526724	-3.196790	0.163391
C	-2.100961	-0.060104	1.922813
O	-2.844202	0.006563	2.808754
C	-2.061847	1.898127	-2.341876
C	-2.219828	-0.753816	-2.889832
C	-2.635838	2.060987	-3.601814
H	-1.824443	2.779065	-1.740877
C	-2.778982	-0.340553	-4.097731
H	-2.100062	-1.822803	-2.696089
C	-2.981343	0.999594	-4.445510
H	-2.828737	3.078350	-3.950559
H	-3.078993	-1.108822	-4.814434
H	-3.428055	1.226046	-5.414089
P	-1.696914	0.346892	-1.644458
C	1.217536	0.238509	1.440141
C	1.400793	0.350858	0.057488
H	1.499750	-0.675788	1.962543
H	1.145506	1.131745	2.059466
H	1.829396	-0.473765	-0.512272
H	1.468753	1.332700	-0.409191

Alkene complex $[HRh(CO)_2(PH_3)(C_2H_4)]$ (**3Pe^{H}**)

Rh	-0.073443	-0.211649	0.000000
H	-1.670458	-0.190931	0.000000
O	-0.647019	-1.454195	2.788383
C	-0.382943	-0.975062	1.768840
C	1.923290	-0.328897	0.000000
C	-0.382943	-0.975062	-1.768840
O	-0.647019	-1.454195	-2.788383
O	3.071842	-0.431289	0.000000
P	-0.290236	2.199163	0.000000
H	-1.597161	2.765988	0.000000
H	0.216578	3.018399	1.055117
H	0.216578	3.018399	-1.055117

Alkene complex $[HRh(CO)(PH_3)_2(C_2H_4)]$ (**3Pee^{H}**)

Rh	-0.939180	0.161984	-0.326550
H	-0.880198	0.315591	1.276657
C	-1.024694	-0.022593	-2.288686
O	-1.083400	-0.119662	-3.440716
C	-1.917782	1.816983	-0.175142
O	-2.498478	2.813405	-0.042881
P	1.406486	0.030503	-0.041036
H	2.014072	-0.926026	0.831103

P	-1.851036	-1.940255	0.268114
H	-1.199896	-2.805158	1.202675
H	-3.124708	-2.005801	0.913793
H	2.113334	1.148884	0.497547
H	2.313570	-0.190105	-1.122691
H	-2.133891	-2.969452	-0.682087

Transition state for alkene rotation **TS_{rot}e1**

Rh	-0.960245	0.386937	0.533651
C	-1.338142	2.289846	0.097709
O	-1.684451	3.367995	-0.133634
C	-2.055747	0.295292	2.095676
O	-2.661476	0.191025	3.082842
C	2.284628	-1.251167	-0.018973
C	2.562212	1.478678	0.176166
C	3.672968	-1.223521	-0.165538
C	3.915833	1.195115	-0.004721
C	4.485292	-0.078629	-0.156309
H	4.169977	-2.192411	-0.254326
H	4.591253	2.053416	-0.024484
P	1.329728	0.216057	0.195470
C	2.152082	2.903065	0.316701
C	1.443494	3.350957	1.444943
C	2.509099	3.839419	-0.670629
C	1.109294	4.699699	1.584681
H	1.164358	2.634415	2.218084
C	2.164926	5.185493	-0.534468
H	3.049110	3.499477	-1.556335
C	1.464664	5.620533	0.595069
H	0.565309	5.031191	2.469993
H	2.440596	5.895338	-1.315702
H	1.195901	6.672497	0.701064
C	1.606756	-2.579618	-0.084243
C	0.923841	-3.115141	1.020818
C	1.678690	-3.343689	-1.262642
C	0.327229	-4.376255	0.947360
H	0.880326	-2.544789	1.948606
C	1.081360	-4.604693	-1.336509
H	2.203843	-2.936303	-2.128763
C	0.400851	-5.124306	-0.231410
H	-0.191504	-4.778361	1.818548
H	1.147238	-5.180955	-2.260438
H	-0.065021	-6.109331	-0.286962
C	5.959156	-0.214899	-0.273033
C	6.540517	-1.216857	-1.073074
C	6.820197	0.652631	0.426435
C	7.926548	-1.345374	-1.171415
H	5.898583	-1.889611	-1.643312
C	8.206203	0.526074	0.327269
H	6.397001	1.415757	1.080547
C	8.767587	-0.474018	-0.472426
H	8.352289	-2.125257	-1.804250
H	8.850267	1.204781	0.888207
H	9.851087	-0.575102	-0.548215
H	-0.684962	-1.122213	0.987827
C	-1.876983	-1.152446	-1.204220

C	-2.055173	0.081327	-1.752499
H	-2.999835	0.614753	-1.640656
H	-1.320462	0.510407	-2.433998
H	-2.679754	-1.646836	-0.658112
H	-1.004233	-1.758193	-1.448071

Transition state for alkene rotation **TS_{rot}Pe**

C	4.881078	-0.512107	3.276792
C	5.495512	0.664821	3.741225
C	6.695327	1.107485	3.180894
C	7.297403	0.383578	2.145359
C	6.697811	-0.791039	1.682651
C	5.498998	-1.240077	2.247245
C	2.528423	2.169387	3.630435
C	3.918401	-2.021681	5.534610
C	5.084981	-2.799781	5.422759
C	5.563971	-3.521076	6.518737
C	4.884549	-3.477240	7.741554
C	3.724122	-2.707973	7.861410
C	3.247985	-1.979683	6.766625
C	2.678130	-2.362275	2.929873
C	2.304527	-1.987050	1.623961
C	1.752447	-2.919128	0.744152
C	1.545138	-4.240611	1.159587
C	1.899879	-4.619505	2.456225
C	2.464694	-3.688468	3.336222
H	1.193340	-0.566535	5.499884
H	5.024283	1.237393	4.542131
H	7.155550	2.026051	3.547458
H	8.228375	0.736809	1.698436
H	7.159560	-1.362628	0.875944
H	5.039831	-2.156424	1.875799
H	5.629812	-2.832969	4.478885
H	6.476404	-4.110993	6.418943
H	5.265243	-4.032494	8.600821
H	3.191857	-2.660481	8.812754
H	2.356899	-1.359216	6.866831
H	2.457645	-0.957539	1.293468
H	1.477816	-2.613667	-0.266648
H	1.106372	-4.968293	0.474924
H	1.740951	-5.646010	2.790369
H	2.743281	-3.999180	4.343842
O	2.967364	3.104609	3.104188
P	3.293459	-1.043115	4.080533
Rh	1.728588	0.657519	4.595150
C	-0.005155	0.764717	2.726190
C	-0.376138	-0.246600	3.557524
H	-0.394003	1.775017	2.853414
C	1.248351	1.631642	6.170200
O	1.004573	2.156813	7.180269
H	-0.115641	-1.281328	3.334067
H	0.568126	0.566200	1.820680
H	-1.088122	-0.076872	4.364429

Transition state for alkene rotation **TS_{rot}Pee**

C	4.897061	-0.482092	3.242913

C	5.533947	0.714938	3.613301
C	6.719913	1.111900	2.990873
C	7.284865	0.321083	1.984573
C	6.660317	-0.873046	1.610045
C	5.475437	-1.274057	2.236300
C	2.496864	2.042415	3.373617
C	3.923495	-2.134263	5.421873
C	5.160847	-2.790742	5.305226
C	5.589427	-3.686759	6.289733
C	4.784372	-3.950936	7.401602
C	3.547063	-3.310269	7.523626
C	3.125433	-2.406405	6.545479
C	2.607048	-2.162536	2.866823
C	2.041295	-1.641025	1.686204
C	1.491471	-2.488272	0.722907
C	1.478115	-3.873927	0.929051
C	2.024864	-4.400787	2.101224
C	2.589053	-3.552182	3.061657
C	1.240115	1.849189	8.188402
C	1.576629	2.544059	9.362529
C	1.069873	2.139369	10.600016
C	0.211991	1.037349	10.683610
C	-0.131579	0.339963	9.521559
C	0.384022	0.741441	8.285057
C	3.562773	3.048436	7.005073
C	3.820074	4.395640	7.305051
C	5.111832	4.808162	7.654198
C	6.153270	3.878424	7.724394
C	5.900493	2.530201	7.441060
C	4.617630	2.120452	7.074482
C	0.919120	3.977418	6.278803
C	-0.119164	4.378837	7.134683
C	-0.856263	5.539781	6.871529
C	-0.566748	6.320885	5.750975
C	0.465393	5.930514	4.888620
C	1.194924	4.768409	5.144982
H	1.736962	-0.164848	6.032848
H	5.082255	1.345665	4.380536
H	7.193558	2.050112	3.283893
H	8.203266	0.639149	1.487383
H	7.089931	-1.493251	0.821486
H	4.992048	-2.201671	1.929491
H	5.800067	-2.597128	4.444447
H	6.559928	-4.174915	6.186439
H	5.122802	-4.644454	8.173304
H	2.912851	-3.500797	8.390787
H	2.174865	-1.884330	6.661066
H	2.042524	-0.561549	1.519437
H	1.067459	-2.067393	-0.190378
H	1.041093	-4.536673	0.180061
H	2.019204	-5.478493	2.273573
H	3.023782	-3.979969	3.964914
H	2.247346	3.401680	9.311102
H	1.352289	2.683313	11.502751
H	-0.179053	0.719759	11.651999
H	-0.795537	-0.524587	9.576574

H	0.140468	0.180459	7.383603
H	3.014117	5.128998	7.256759
H	5.300675	5.861271	7.870000
H	7.160123	4.202522	7.994245
H	6.706458	1.796727	7.493389
H	4.420957	1.076089	6.824471
H	-0.357526	3.786404	8.017386
H	-1.659286	5.830269	7.551124
H	-1.142491	7.225332	5.546505
H	0.699136	6.530057	4.007254
H	1.988459	4.476519	4.456165
O	2.824373	2.774467	2.525997
P	3.315336	-0.955709	4.105761
P	1.885645	2.399218	6.526900
Rh	1.953557	0.826214	4.775424
C	-0.374595	-0.096858	4.546907
C	-0.266323	0.864518	3.587069
H	-0.196013	-1.146861	4.318394
H	-0.840107	0.130928	5.504304
H	0.008590	0.602905	2.565351
H	-0.613865	1.883139	3.761331

Transition state for alkene insertion into the Rh-H bond **TSe1**

Rh	-1.098266	0.260764	0.366306
C	-1.606287	2.087865	-0.122690
O	-2.011415	3.123463	-0.447859
C	-1.843917	0.324004	2.139686
O	-2.321999	0.333470	3.199163
C	2.315278	-1.359687	0.116030
C	2.523547	1.369359	0.271729
C	3.694100	-1.303959	-0.100879
C	3.877700	1.124785	0.037461
C	4.469815	-0.134822	-0.142046
H	4.218485	-2.258278	-0.193465
H	4.532816	1.997945	-0.009356
P	1.316942	0.081137	0.342982
C	2.067662	2.777395	0.414526
C	1.256013	3.175444	1.491146
C	2.455356	3.747095	-0.528688
C	0.849677	4.504205	1.624161
H	0.955289	2.435895	2.233703
C	2.042239	5.074096	-0.398868
H	3.066975	3.447582	-1.381712
C	1.238001	5.457777	0.678798
H	0.225362	4.794750	2.469948
H	2.342516	5.808482	-1.147628
H	0.912588	6.494245	0.778629
C	1.658418	-2.696692	0.138691
C	0.847473	-3.094973	1.216639
C	1.857289	-3.604415	-0.918010
C	0.253879	-4.358984	1.235420
H	0.701399	-2.411440	2.053241
C	1.262738	-4.868036	-0.900009
H	2.472924	-3.305088	-1.768071
C	0.456604	-5.249846	0.176773
H	-0.363534	-4.651464	2.085776

H	1.426234	-5.554224	-1.732102
H	-0.007214	-6.237136	0.192761
C	5.938218	-0.231647	-0.343081
C	6.491382	-1.194532	-1.207474
C	6.818015	0.636085	0.331066
C	7.871380	-1.285167	-1.393477
H	5.829526	-1.863025	-1.759751
C	8.198207	0.545366	0.146778
H	6.415788	1.369892	1.030500
C	8.732078	-0.415537	-0.716996
H	8.276024	-2.032890	-2.076908
H	8.860125	1.221319	0.689808
H	9.811020	-0.487333	-0.860541
H	-1.135850	-1.370750	0.495827
C	-1.836564	-1.463475	-1.016085
C	-1.302055	-0.409305	-1.786275
H	-1.981008	0.312873	-2.239553
H	-0.339741	-0.537963	-2.280897
H	-2.910050	-1.520582	-0.841541
H	-1.314884	-2.423617	-1.007896

Transition state for alkene insertion into the Rh-H bond **TSPe**

C	4.843197	-0.474303	3.304792
C	5.350279	0.775548	3.700704
C	6.559739	1.247417	3.185732
C	7.274215	0.482074	2.257648
C	6.776043	-0.760831	1.854811
C	5.570443	-1.239077	2.377608
C	1.983046	2.168273	3.238787
C	3.811086	-2.054826	5.498233
C	4.962172	-2.858955	5.433640
C	5.361894	-3.615481	6.537477
C	4.617646	-3.580688	7.722487
C	3.473575	-2.782034	7.798467
C	3.077180	-2.020961	6.694229
C	2.671237	-2.328754	2.853039
C	2.403399	-1.940778	1.524105
C	1.857744	-2.845919	0.612858
C	1.546796	-4.151047	1.015513
C	1.792560	-4.540855	2.334329
C	2.351842	-3.638564	3.246903
H	0.907419	-0.251199	5.605503
H	4.782332	1.383073	4.407333
H	6.937382	2.221511	3.500276
H	8.211957	0.857014	1.843862
H	7.323967	-1.362016	1.127510
H	5.186633	-2.205638	2.049446
H	5.555911	-2.886899	4.519751
H	6.261947	-4.229075	6.473864
H	4.934768	-4.167711	8.586277
H	2.892955	-2.740187	8.721285
H	2.196764	-1.380256	6.759676
H	2.626669	-0.921369	1.202817
H	1.666989	-2.529566	-0.413871
H	1.112604	-4.856330	0.305011
H	1.553464	-5.554519	2.659986

H	2.546590	-3.960550	4.270851
O	2.137445	3.007634	2.451278
P	3.239519	-1.034999	4.049980
Rh	1.647476	0.779322	4.558641
C	-0.071042	-0.035948	3.344848
C	-0.467630	-0.216265	4.687404
H	-0.572286	-1.235308	5.066618
H	-1.107408	0.519643	5.173185
H	0.206071	-0.903291	2.743804
H	-0.453756	0.827907	2.800041
C	2.156057	1.821836	6.088800
O	2.398021	2.464679	7.028328

Transition state for alkene insertion into the Rh-H bond **TSPee**

C	4.860384	-0.488302	3.329725
C	5.406276	0.769115	3.637608
C	6.611430	1.181416	3.062543
C	7.284160	0.346297	2.164473
C	6.748453	-0.907222	1.850259
C	5.546265	-1.323315	2.430554
C	2.227665	2.130220	3.318716
C	3.845149	-2.047729	5.549596
C	5.061474	-2.750711	5.515545
C	5.447514	-3.557030	6.589888
C	4.619883	-3.682033	7.710928
C	3.408300	-2.985773	7.756650
C	3.030814	-2.167109	6.687762
C	2.649816	-2.273260	2.946898
C	2.291196	-1.859328	1.646754
C	1.766098	-2.767182	0.725838
C	1.568336	-4.105772	1.089461
C	1.907212	-4.524454	2.378517
C	2.445855	-3.617420	3.299769
C	1.344997	1.504405	8.136385
C	1.973108	1.922104	9.321075
C	1.561579	1.424572	10.562018
C	0.511189	0.505845	10.640341
C	-0.122719	0.082886	9.466908
C	0.294723	0.574974	8.228323
C	3.473097	2.916678	6.804917
C	3.764304	4.282531	6.665160
C	5.070779	4.752452	6.850300
C	6.097541	3.867571	7.187933
C	5.815761	2.501898	7.328131
C	4.519400	2.028915	7.124745
C	0.704589	3.711407	6.443997
C	0.552623	4.535232	7.573078
C	-0.286047	5.651307	7.532143
C	-0.989187	5.961464	6.361645
C	-0.849177	5.147314	5.234678
C	-0.010973	4.027701	5.278647
H	0.886960	-0.328247	5.511697
H	4.874973	1.431707	4.322859
H	7.015475	2.164740	3.307377
H	8.217536	0.674828	1.703236
H	7.262649	-1.563369	1.145868

H	5.131774	-2.297722	2.170070
H	5.715489	-2.662477	4.648260
H	6.400348	-4.087492	6.550703
H	4.923767	-4.311149	8.549764
H	2.761249	-3.066102	8.631269
H	2.101541	-1.596525	6.737600
H	2.435331	-0.816925	1.354878
H	1.505205	-2.428362	-0.278384
H	1.151980	-4.815019	0.371813
H	1.760605	-5.565301	2.673011
H	2.718757	-3.965024	4.297134
H	2.797650	2.633623	9.275264
H	2.066711	1.758433	11.469856
H	0.190091	0.118778	11.609034
H	-0.943197	-0.635165	9.515284
H	-0.197938	0.229895	7.319409
H	2.971217	4.985521	6.408411
H	5.280117	5.816707	6.728925
H	7.114546	4.235957	7.334763
H	6.610603	1.799635	7.583432
H	4.315287	0.959197	7.207203
H	1.086700	4.301880	8.493385
H	-0.396101	6.277869	8.419031
H	-1.648326	6.831241	6.332622
H	-1.397227	5.378275	4.319551
H	0.091234	3.379469	4.406372
O	2.536057	2.932121	2.526753
P	3.258601	-0.977380	4.137150
P	1.799093	2.191537	6.461149
Rh	1.669575	0.795848	4.554554
C	-0.094828	0.180377	3.285937
C	-0.416171	-0.319568	4.564726
H	-0.434102	-1.402697	4.705932
H	-1.115583	0.233913	5.191307
H	0.209441	-0.517077	2.503815
H	-0.546211	1.115848	2.953063