Supplementary Material for PCCP

Catalytic homogeneous hydrogenation of compounds containing X→O semipolar bonds (X = N, S, P) with *para*-hydrogen as a promising route for preparation of *para*-water†

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Electronic Supplementary Information (ESI)

Calculations details.

Stationary points were identified by an analysis of Hessians. The energies of the stationary points are corrected to zero-point vibrations (ZPVE). The statistical formulas of rigid rotator and harmonic oscillator were used for the calculation of the thermodynamic functions. Construction of internal reaction coordinate (IRC) was used to check the observed transition states.

Table 1. Calculated thermodynamic functions of the reactants, intermediates, and reaction products (all Hessian eigenvalues are positive, and the stationary points are minima on the PES)

	E, a.u**	E_0, a.u	S^0_{298}, cal*mol^{-1}*K^{-1}	U^0_{298}-E, kcal*mol^{-1}	H^0_{298}-E, kcal*mol^{-1}	G^0_{298}-E, kcal*mol^{-1}
$ClRh(PPh_3)_3$	-478.116	-477.312	323.5	539.1	539.7	443.3
$ClRh(PPh_3)_2$(**1**)	-360.433	-359.899	243.7	359.5	360.1	287.4
$ClRh(PPh_3)_2$ (**1**T)*	-360.408	-359.873	255.0	360.0	360.6	284.6
$ClRh(PPh_3)_2H_2$(**2**)	-361.645	-361.094	255.1	370.5	371.0	295.0
$ClRh(PPh_3)_2H_2$ (**2**T)	-361.586	-361.038	252.0	369.0	369.6	294.4
$ClRh(PPh_3)_2(OH)H$(**4**)	-377.661	-377.104	256.1	375.0	375.6	299.2
$ClRh(PPh_3)_2(OH)H$ (**4**T)	-377.624	-377.068	257.1	374.2	374.8	298.2
$ClRh(PPh_3)_2(OH_2)$(**6**)	-377.667	-377.106	252.1	377.4	377.9	302.8
H_2	-1.166	-1.157	32.6	7.6	8.2	-1.5
H_2O	-17.213	-17.192	46.5	14.9	15.5	1.6
C_5H_5NO	-57.255	-57.165	73.8	59.9	60.5	38.5
C_5H_5N	-41.285	-41.199	69.2	56.8	57.4	36.8
$C_5H_5N*H_2O$	-58.511	-58.401	89.3	74.0	74.6	48.0
Ph_3PO	-133.693	-133.423	140.8	180.5	181.1	139.1
Ph_3P	-117.644	-117.378	135.5	177.0	177.6	137.2
$(CH_3)_2SO$	-41.077	-41.000	74.9	51.7	52.2	29.9
$(CH_3)_2S$	-25.090	-25.017	69.4	49.2	49.8	29.1
N_2O	-35.835	-35.825	52.6	8.5	9.0	-6.6
N_2	-19.888	-19.883	47.2	4.8	5.4	-8.6

*The index (T) is used to designate the triplet state.
**a.u. = 627.52 kcal/mol