catalysts

Supplementary Materials

Sustainable Option for Hydrogen Production: Mechanistic Study of the Interaction between Cobalt Pincer Complexes and Ammonia Borane

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To prove that the method and basis sets were chosen appropriately, apart from using the method B3LYP/6-31G(d,p)//LanL2DZ (**L1**), we have also compared the result with other methods, such as M06/6-31G(d,p)//LanL2DZ (**L2**), SMD(THF)B3LYP/6-31G(d,p)//LanL2DZ (**L3**), SMD(THF)M06/6-31G(d,p)//LanL2DZ (**L4**) and SMD(THF)M06/TZVP//LanL2DZ (**L5**) to optimize the structure of the Pre-catalyst (Figure 1). The results were shown in Table S1 below. It was shown that the bond lengths are very close at different level of calculation, and also they are in close agreement with the experimental determined bond lengths. This proved that the chosen method and basis sets are appropriate.

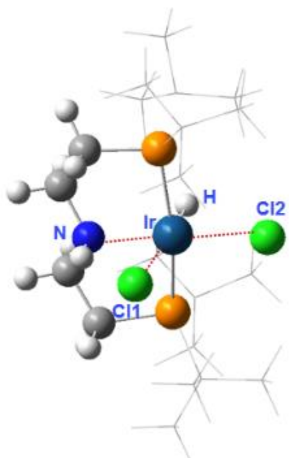

Figure S1. Optimized structures for the Pre-Cat.

Table S1. Major bond lengths calculated at different calculation levels, and the last column is the experimental values.

	L1	L2	L3	L4	L5	exp
N-Ir	2.139	2.136	2.128	2.126	2.122	2.094
Ir-H	1.558	1.564	1.551	1.559	1.555	1.53
Ir-Cl1	2.679	2.639	2.667	2.665	2.682	2.54
Ir-Cl2	2.434	2.419	2.465	2.447	2.448	2.387

The choice of calculation and basis sets are based on the consistency of the experimental values and theoretical values. Our choice of B3LYP/6-31G(d,p)-Lanl2dz(metal) is motivated by its good performance for geometry optimization and prediction of vibrational frequencies for intermediates and transition states based on previous literatures, which deal with the transition state metal (Ir, Ni, Rh, Ru) catalyzed reactions [1-6]. Moreover, for the reaction studied, this method is a balance choice in consideration of computational efficiency and accuracy.

[1] Lu, G.; Fang, C.; Xu, T.; Dong, G.; Liu, P. Computational study of Rh-catalyzed carboacylation of olefins: Ligand-promoted rhodacycle isomerization enables regioselective C–C Bond functionalization of benzocyclobutenones. *J. Am. Chem. Soc.* **2015**, *137*, 8274–8283. DOI: 10.1021/jacs.5b04691.

[2] Huang, G.; Kalek, M.; Liao, R.-Z.; Himo, F. Mechanism, reactivity, and selectivity of the iridium-catalyzed C(sp^3)–H borylation of chlorosilanes. *Chem. Sci* **2015**, *6*, 1735–1746. DOI: 10.1039/c4sc01592d.

[3] Patel, C.; Abraham, V.; Sunoj, R.B. Mechanistic insights and the origin of regioselective borylation in an iridium-catalyzed alkyl C(sp^3)−H bond functionalization. *Organometallics* **2017**, *36*, 151−158. DOI: 10.1021/acs.organomet.6b00513.

[4] Zhang, S.Q.; Taylor, B.L.H.; Ji, C.L.; Gao, Y.; Harris, M.R.; Hanna, L.E.; Jarvo,E.R.; Houk, K. N.; Hong, X. Mechanism and origins of ligand-controlled stereoselectivity of Ni-catalyzed Suzuki-Miyaura coupling with benzylic esters: A computational study. *J. Am. Chem. Soc.* **2017**, *139(37)*, 12994–13005. DOI:10.1021/jacs.7b04973.

[5] Wang, X.; Li, Y.; Knecht, T.; Daniliuc, C.G. Houk, K. N. Glorius, F. Unprecedented dearomatized spirocyclopropane in a sequential rhodium(III)-catalyzed C–H activation and rearrangement reaction. *Angew. Chem. Int. Ed.* **2018**, *57*, 5520–5524. DOI:10.1002/anie.201800803.

[6] Chen, S.; Zheng, Y.; Cui, T.; Meggers, E.; Houk, N.K. Arylketone π-conjugation controls enantioselectivity in asymmetric alkynylations catalyzed by centrochiral ruthenium complexes. *J. Am. Chem. Soc*. **2018**, *140*, 5146−5152. DOI: 10.1021/jacs.8b00485.

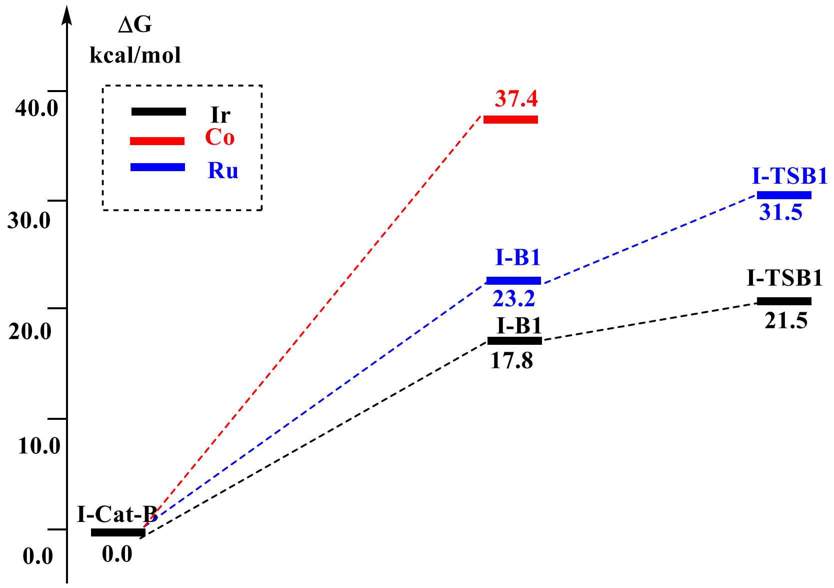

Figure S2. Reaction potential energy surface of Pathway I-B with different metal centers involved in the H_2 release reaction.

Solvent effects and effects of different PNP ligands

After optimizing the structure, M06 calculation method was then used to determine the rate of the H_2 release reaction when THF and water were used as solvents respectively. The energies calculated at the M06 level are a bit different from the experimental results. While for THF being the solvent media, as shown in Figure S3, the reactivity are P(^{t}Bu) >P(^{i}Pr) > P(Ph) when all structures in the optimal pathway I-B at the M06 level was optimized. This is consistent to our experimental observed values under dehydrogenation condition (without water). When the phosphine ligand substituent is ^{t}Bu group, the energy barrier of the first step/second step is 13.0/20.8 kcal/mol; when the ligand substituent is ^{i}Pr, the reaction energy barrier of the first step/second step is 5.4/28.5 kcal/mol; when the ligand substituent is Ph, the energy barrier of the first step/second step is 11.9/33.8 kcal/mol In all cases, the rate determining step is from the complexes I-B2 to I-Cat-B, therefore, the order of the energy barrier is as follows: P(^{t}Bu) < P(^{i}Pr) < P(Ph), so the reaction rate is P(^{t}Bu) faster than P(^{i}Pr) and P(Ph), which are consistent with the experimental results.

While for water being the solvent media, as shown in Figure 8, the reactivity are P(^{t}Bu) > P(Ph) > P(^{i}Pr) which is a bit different from the observed values. When the ligand substituent is P^{t}Bu, the energy barrier of the first step/second step of the reaction is 17.9/14.0 kcal/mol; when the ligand substituent is P^{i}Pr, the energy barrier of the first step/the reaction is 15.7/32.3 kcal/mol; when the ligand substituent is PPh, the energy barrier of the first step/second step of the reaction is 10.9/27.2 kcal/mol For ^{t}Bu group, the rate determining step is from I-Cat-B to I-TSB1 while for ^{i}Pr and Ph, the rate determining step is from I-B2 to I-Cat-B. Thus, the order of the energy barrier is as follows: P(tBu) < P(Ph) < P(iPr), so the reaction rate is P(^{t}Bu) > P(Ph) > P(^{i}Pr).

Nevertheless, the catalyst with P(tBu) substituent group on the phosphine still has the highest reaction rate in both cases. The results after optimizing each intermediates in Pathway I-B using the M06 method and calculated single point energy based on M06 geometry were shown in Figure S3 and S4 respectively.

In brief, when the solvent is THF and the method used is M06, the calculation results correlated with the experimental results, i.e. observed P(^{t}Bu) is more reactive than P(iPr) and then P(Ph). However, when the solvent is water, the calculation results are inconsistent with the experimental results. However, considering the experimental use of a mixed solvent (THF/H_2O), the specific effect of which solvent is dominant may require further testing.

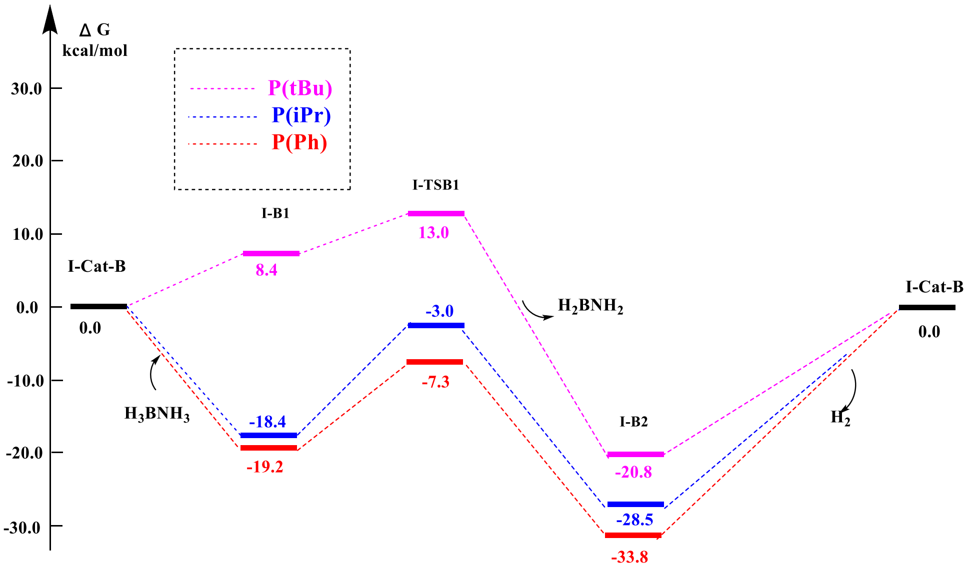

Figure S3 (a). When the solvent is THF, the potential energy surface of Pathway I-B of using phosphine ligands with various substituents optimized at the M06 level.

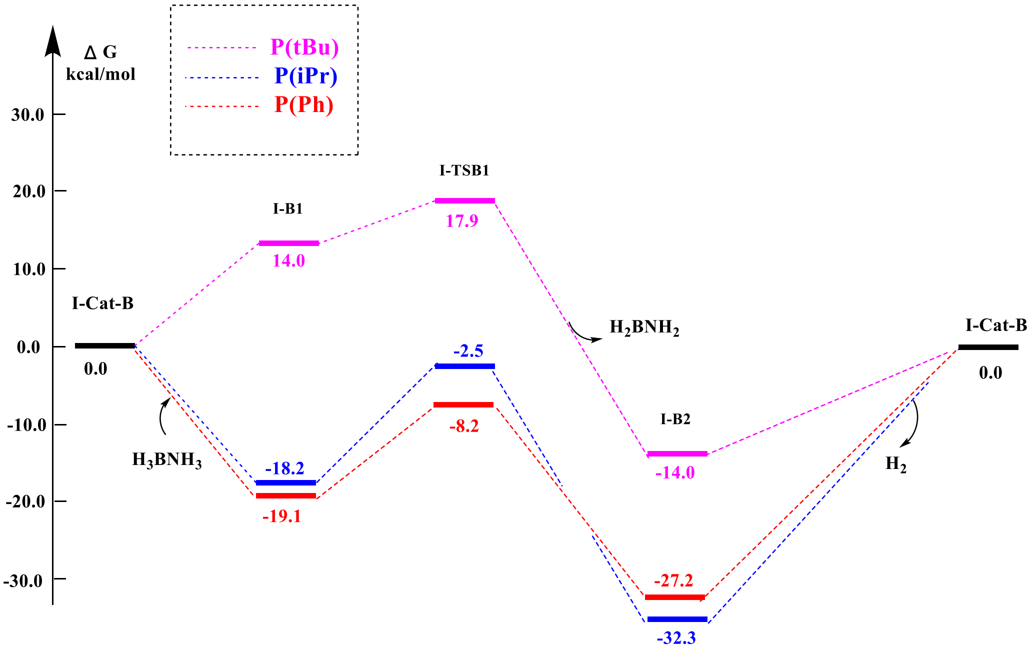

Figure S3 (b). The potential energy surface of Pathway I-B with different PNP ligands when the reaction was carried out in pure H_2O optimized at the M06 level.

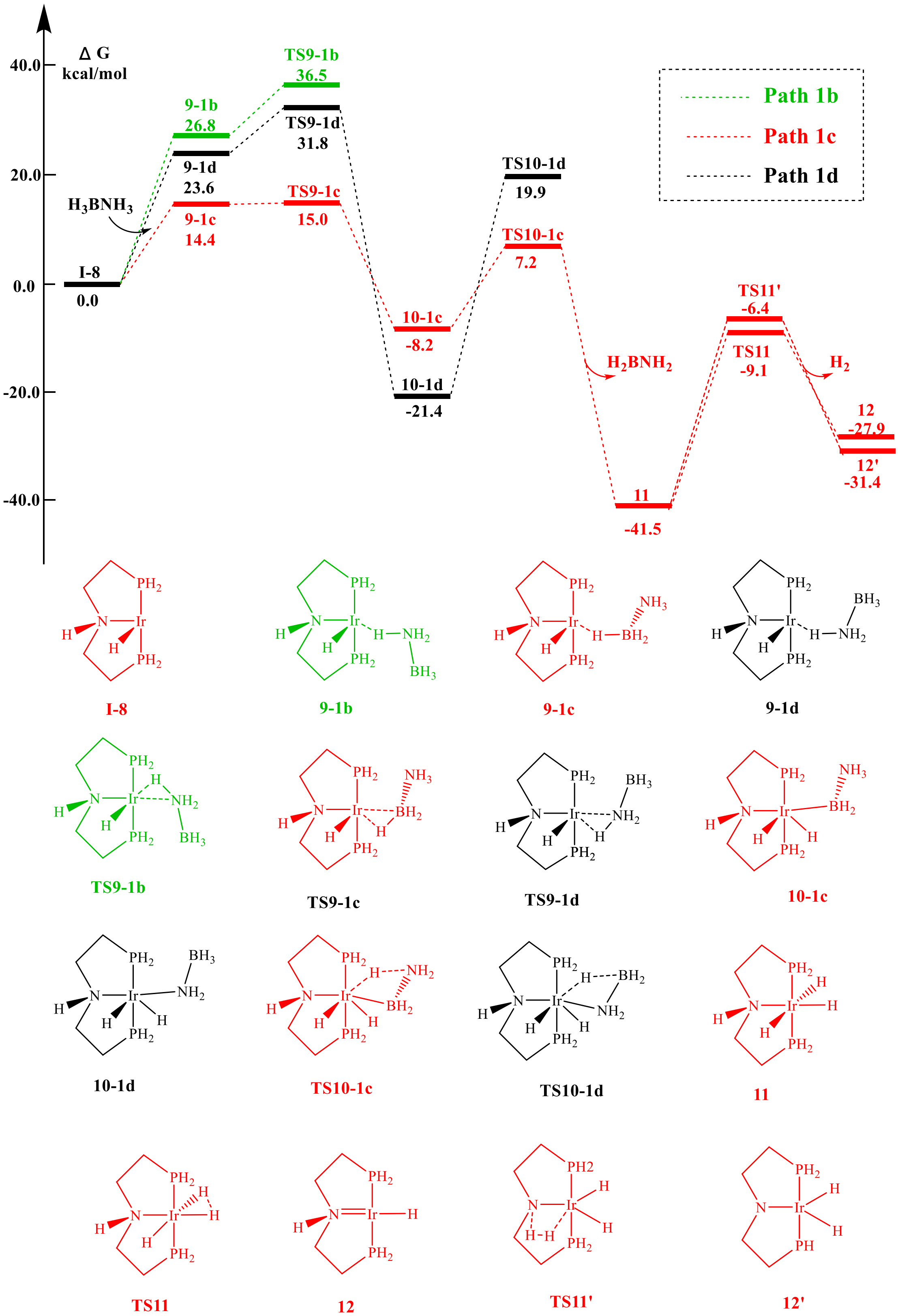

Figure S4. The other three pathway for the Stepwise Mechanism.

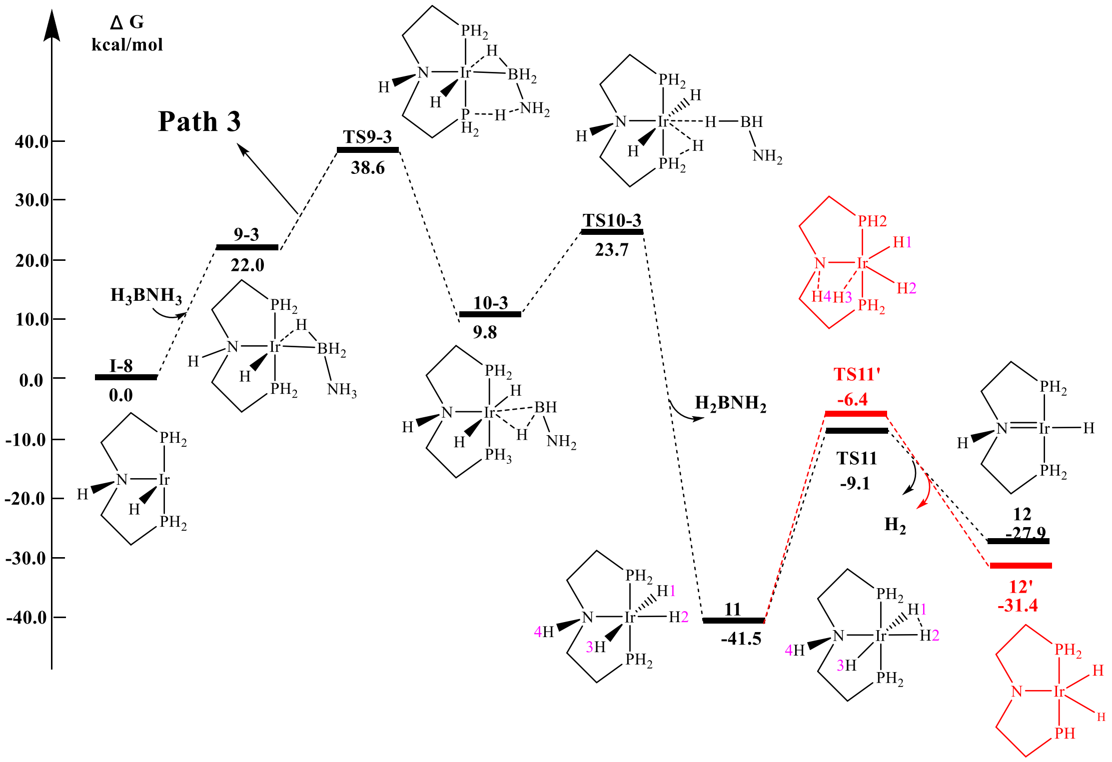

Figure S5. Potential energy transfer surface of proton transfer reaction starting from intermediate 8.

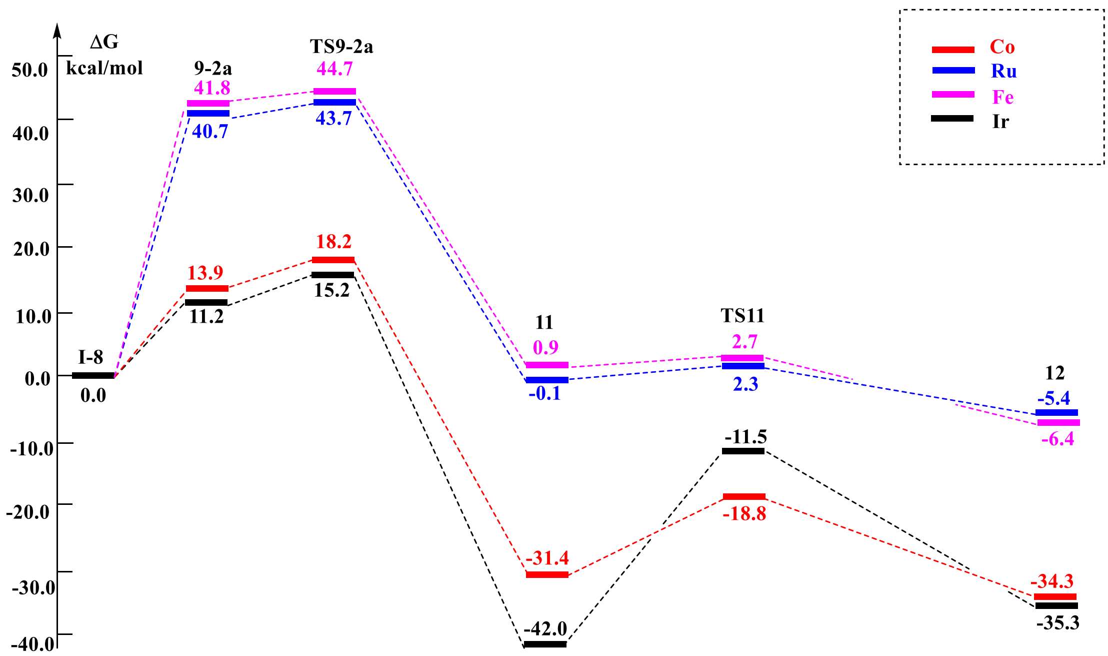

Figure S6 (a). ^{t}Bu being the substituent, the potential energy surface corresponding to the intermediates 8→12.

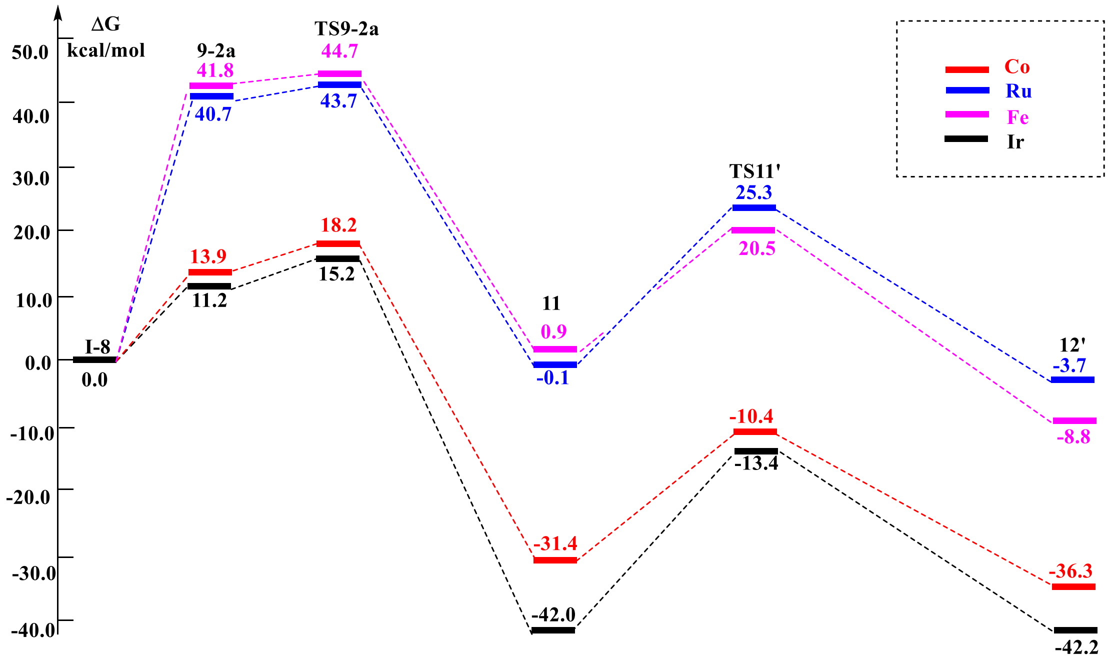

Figure S6 (b). ᵗBu being the substituent, the potential energy surface corresponding to the intermediates 8→12′.

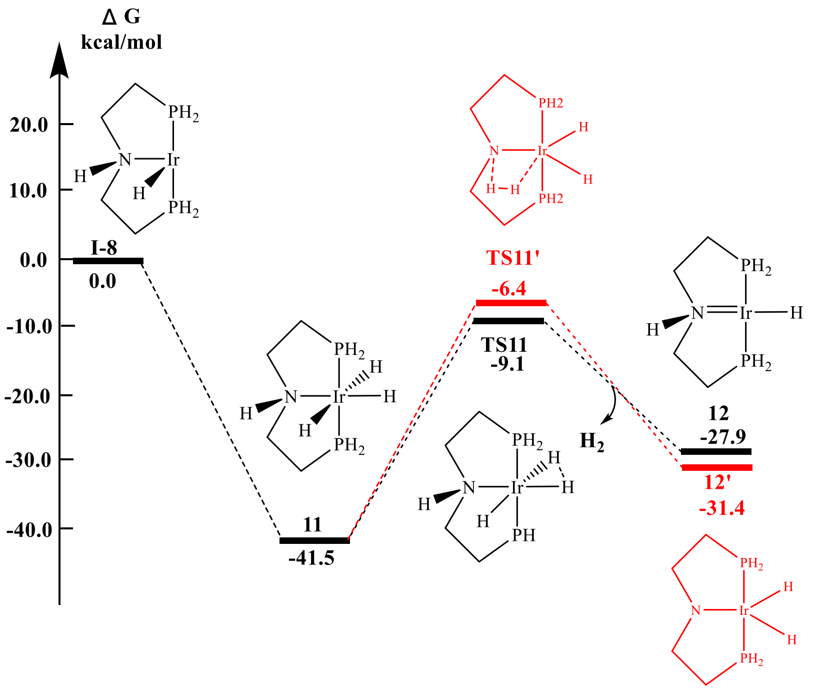

Figure S7. Difference in the energy profile between intermediate complex 12 and complex 12′.

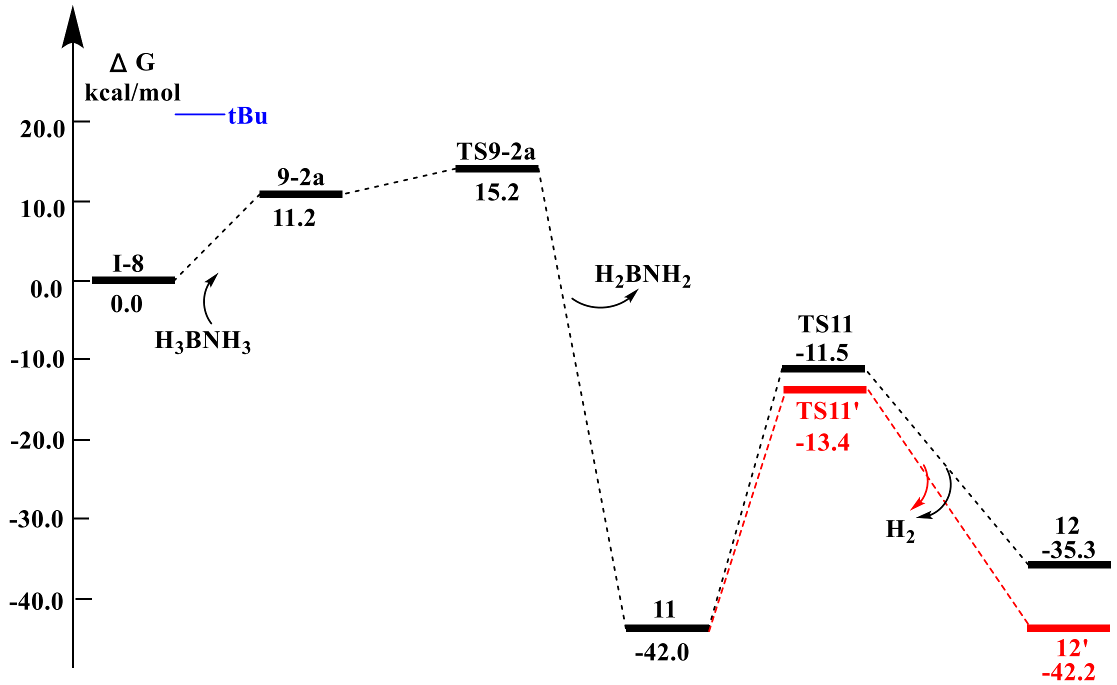

Figure S8 (a). The potential energy surface corresponding to the intermediates **8** → **12(12′)** with ᵗBu-being the phosphine substituent.

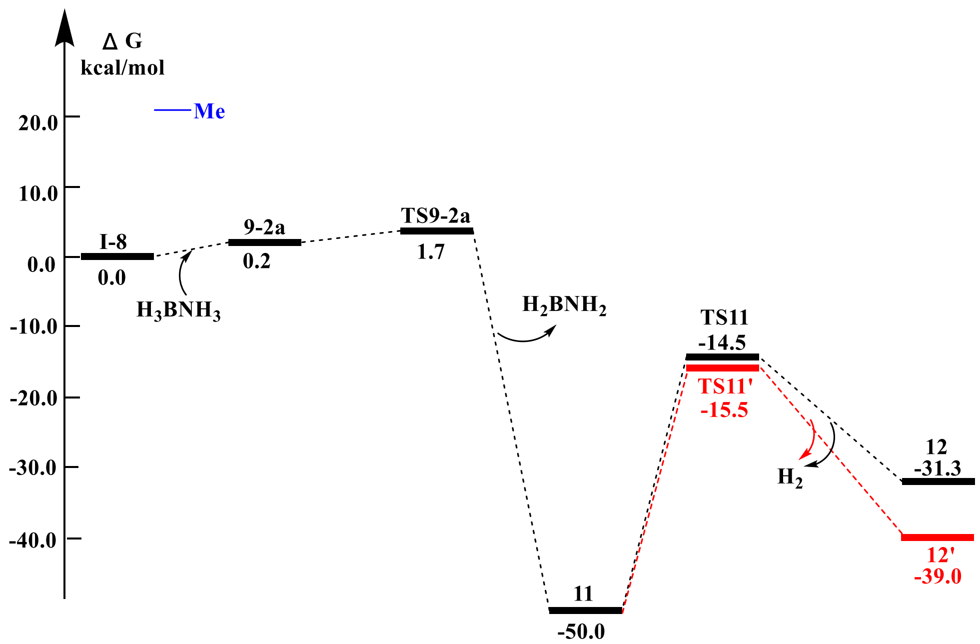

Figure S8 (b). The potential energy surface corresponding to the intermediates **8** → **12(12′)** with Me-being the phosphine substituent.

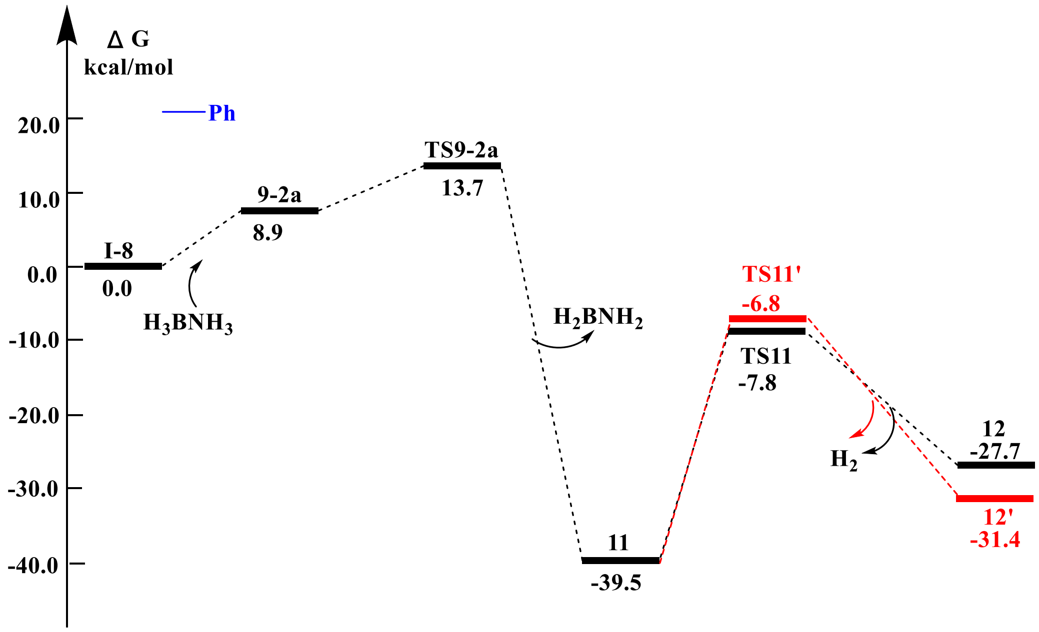

Figure S8 (c). The potential energy surface corresponding to the intermediates **8** → **12(12′)** with Ph- being the phosphine substituent.

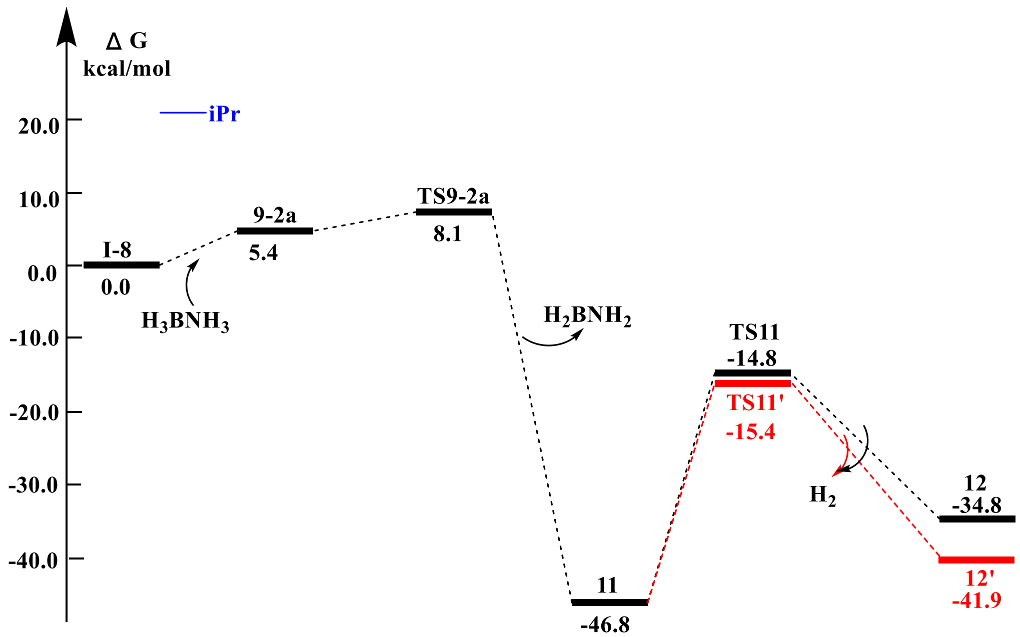

Figure S8 (d). The potential energy surface corresponding to the intermediates **8** → **12(12′)** with ^{i}Pr- being the phosphine substituent.

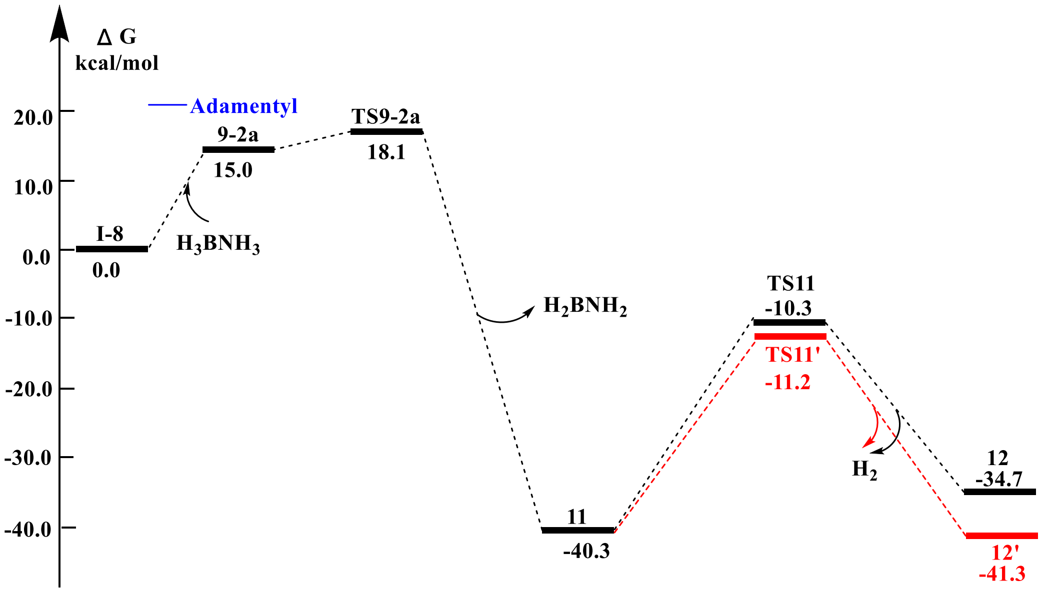

Figure S9. Potential energy profile for reaction between iridium PNP complex with (adamantly)$_2$P-substituents and ammonia borane.

Table S2. Preliminary test on the chelation of NH_3 to intermediate **I-8** (simplified PH$_2$P– model). For 8-Xnh3-Y, X denotes the number of NH_3 molecules; Y denotes the chelation of NH_3 at different orientation to the metal.

NH_3 chelation	Species	Relative energies (kcal/mol)
without NH_3 chelation	I-8	0.0
one NH_3 chelation	8-1nh3-1	−1.7
	8-1nh3-2	−1.0
two NH_3 chelation	8-2nh3-1	5.2
	8-2nh3-2	6.4
	8-2nh3-3	6.6
	8-2nh3-4	6.9
	8-2nh3-5	7.0
	8-2nh3-6	10.9
	8-2nh3-7	11.2
three NH_3 chelation	8-3nh3-1	14.1
	8-3nh3-2	16.5
	8-3nh3-3	17.1
	8-3nh3-4	20.3
	8-3nh3-5	20.5
	8-3nh3-6	24.3

Table S3 (a). The effect of H_2O, NH_3 and THF chelation to the stabilization of complex **I-8** ([t]Bu-PNP-Ir).

Chelation	Species	Relative energy （kcal/mol）
No chelation	I-8-bu	0.0
	Ir-8-h2o-1	16.8
	Ir-8-h2o-2	2.8
H_2O	Ir-8-h2o-3	6.8
	Ir-8-h2o-4	3.8
	Ir-8-h2o-5	16.4
	Ir-8-h2o-6	16.6
	Ir-8-nh3-1	7.5
	Ir-8-nh3-2	8.1
NH_3	Ir-8-nh3-3	8.3
	Ir-8-nh3-4	9.0
	Ir-8-nh3-5	10.6
	Ir-8-nh3-6	10.0
	Ir-8-thf-1	20.1
	Ir-8-thf-2	20.1
THF	Ir-8-thf-3	19.7
	Ir-8-thf-4	14.0
	Ir-8-thf-5	20.6
	Ir-8-thf-6	20.6

Table S3 (b). The effect of H_2O, NH_3 and THF to the stabilization of complex **I-8** ([t]Bu-PNP-Fe).

Chelation	Species	Relative energy （kcal/mol）
No chelation	Fe-8	0.0
	Fe-8-h2o-1	11.2
	Fe-8-h2o-2	26.1
H_2O	Fe-8-h2o-3	34.6
	Fe-8-h2o-4	9.5
	Fe-8-h2o-5	42.4
	Fe-8-h2o-6	42.4
	Fe-8-nh3-1	32.2
	Fe-8-nh3-2	31.9
NH_3	Fe-8-nh3-3	32.1
	Fe-8-nh3-4	10.3
	Fe-8-nh3-5	36.9
	Fe-8-nh3-6	36.9
	Fe-8-thf-1	47.0
	Fe-8-thf-2	10.5
THF	Fe-8-thf-3	10.5
	Fe-8-thf-4	11.7
	Fe-8-thf-5	47.5
	Fe-8-thf-6	46.2

Table S3 (c). The effect of H_2O, NH_3 and THF to the stabilization of complex **I-8** (^{t}Bu-PNP-Ru).

Chelation	Species	Relative energy (kcal/mol)
No chelation	Ru-8	0.0
	Ru-8-h2o-1	19.4
	Ru-8-h2o-2	9.1
H_2O	Ru-8-h2o-3	11.1
	Ru-8-h2o-4	21.8
	Ru-8-h2o-5	42.9
	Ru-8-h2o-6	42.1
	Ru-8-nh3-1	13.1
	Ru-8-nh3-2	29.5
NH_3	Ru-8-nh3-3	29.5
	Ru-8-nh3-4	25.3
	Ru-8-nh3-5	37.8
	Ru-8-nh3-6	37.9
	Ru-8-thf-1	44.6
	Ru-8-thf-2	10.9
THF	Ru-8-thf-3	12.2
	Ru-8-thf-4	45.5
	Ru-8-thf-5	45.5

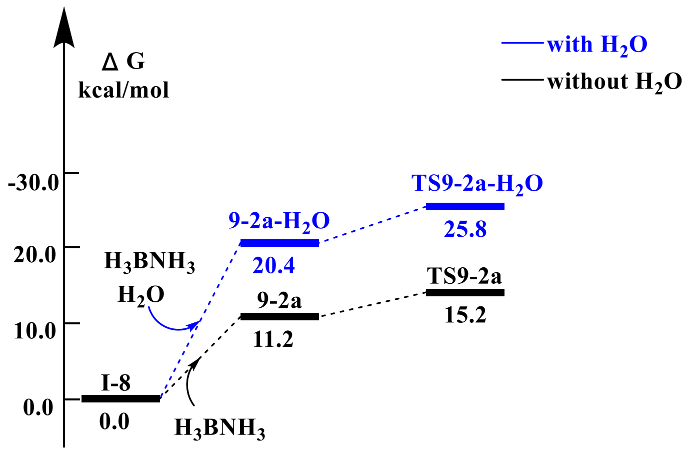

Figure S10. The energy profile (kcal/mol) of the NH_3BH_3 activation reaction with and without the chelation of H_2O to the Ir metal center.

Table S4. Testing the stability of H_2O chelation to the Ir complexes.

Chelation	Species	Relative energy （kcal/mol）
H_2O	9-2a-H_2O	20.4
	9-2a-H_2O-1	21.0
	9-2a-H_2O-2	20.9
	9-2a-H_2O-3	21.7
	TS9-2a-H_2O	25.8
	TS9-9-2a-H_2O-1	27.3
	TS9-9-2a-H_2O-2	25.9

Table S5 (a). Energies of each compounds for the simplified model (H_2P-) with NH_3 chelation for Ir complexes. G_corr = Thermal correction to Gibbs Free Energy; E = Absolute single-point energies; G = Gibbs free energies.

species	G_corr	E	G
8-1nh3-1	0.171311	−1059.751451	−1059.580140
8-1nh3-2	0.17045	−1059.751742	−1059.581292
8-2nh3-1	0.205193	−1116.340042	−1116.134849
8-2nh3-2	0.203345	−1116.345025	−1116.141680
8-2nh3-3	0.205627	−1116.339968	−1116.134341
8-2nh3-4	0.201212	−1116.345075	−1116.143863
8-2nh3-5	0.203903	−1116.345007	−1116.141104
8-2nh3-6	0.203924	−1116.345196	−1116.141272
8-2nh3-7	0.203111	−1116.345030	−1116.141919
8-3nh3-1	0.23667	−1172.940103	−1172.703433
8-3nh3-2	0.237663	−1172.931097	−1172.693434
8-3nh3-3	0.238028	−1172.931182	−1172.693154
8-3nh3-4	0.234922	−1172.933571	−1172.698649
8-3nh3-5	0.234133	−1172.933652	−1172.699519
8-3nh3-6	0.238949	−1172.926072	−1172.687123

Table S5 (b). Energies of each compounds for the complete model ($^tBu_2P$-) with H_2O, NH_3 and THF chelation. G_corr = Thermal correction to Gibbs Free Energy; E = Absolute single-point energies; G = Gibbs free energies.

species	G_corr	E	G
Ir-8-h2o-1	0.589065	−1708.780295	−1708.191230
Ir-8-h2o-2	0.586351	−1708.799866	−1708.213515
Ir-8-h2o-3	0.588042	−1708.795181	−1708.207139
Ir-8-h2o-4	0.587122	−1708.799071	−1708.211949
Ir-8-h2o-5	0.58874	−1708.780593	−1708.191853
Ir-8-h2o-6	0.590482	−1708.781990	−1708.191508
Ir-8-nh3-1	0.600848	−1688.916959	−1688.316111
Ir-8-nh3-2	0.601766	−1688.916795	−1688.315029
Ir-8-nh3-3	0.601917	−1688.916739	−1688.314822
Ir-8-nh3-4	0.599167	−1688.912898	−1688.313731
Ir-8-nh3-5	0.60728	−1688.918407	−1688.311127
Ir-8-nh3-6	0.605957	−1688.918004	−1688.312047
Ir-8-thf-1	0.678843	−1864.838313	−1864.159470
Ir-8-thf-2	0.678566	−1864.837948	−1864.159382
Ir-8-thf-3	0.677897	−1864.837902	−1864.160005
Ir-8-thf-4	0.672992	−1864.842139	−1864.169147
Ir-8-thf-5	0.67932	−1864.837995	−1864.158675
Ir-8-thf-6	0.679421	−1864.838009	−1864.158588
Co-8-h2o-1	0.590048	−1749.089156	−1748.499108
Co-8-h2o-2	0.589841	−1749.088912	−1748.499071
Co-8-h2o-3	0.590007	−1749.089121	−1748.499114
Co-8-h2o-4	0.590398	−1749.139143	−1748.548745
Co-8-h2o-5	0.588704	−1749.089376	−1748.500672
Co-8-h2o-6	0.59093	−1749.090657	−1748.499727
Co-8-nh3-1	0.604243	−1729.223385	−1728.619142
Co-8-nh3-2	0.604313	−1729.223414	−1728.619101
Co-8-nh3-3	0.604325	−1729.223415	−1728.619090
Co-8-nh3-4	0.60086	−1729.259149	−1728.658289
Co-8-nh3-5	0.60494	−1729.224435	−1728.619495
Co-8-nh3-6	0.604888	−1729.224436	−1728.619548
Co-8-thf-1	0.680181	−1905.144879	−1904.464698
Co-8-thf-2	0.676345	−1905.142732	−1904.466387
Co-8-thf-3	0.678972	−1905.142902	−1904.463930
Co-8-thf-4	0.672656	−1905.153694	−1904.481038
Co-8-thf-5	0.680279	−1905.145247	−1904.464968
Co-8-thf-6	0.679826	−1905.144883	−1904.465057
Fe-8-h2o-1	0.590269	−1727.488394	−1726.898125
Fe-8-h2o-2	0.587855	−1727.462258	−1726.874403
Fe-8-h2o-3	0.588807	−1727.449565	−1726.860758
Fe-8-h2o-4	0.587752	−1727.488615	−1726.900863

Fe-8-h2o-5	0.588076	−1727.436518	−1726.848442
Fe-8-h2o-6	0.588599	−1727.437063	−1726.848464
Fe-8-nh3-1	0.603839	−1707.578463	−1706.974624
Fe-8-nh3-2	0.603325	−1707.578476	−1706.975151
Fe-8-nh3-3	0.603686	−1707.578463	−1706.974777
Fe-8-nh3-4	0.598244	−1707.607721	−1707.009477
Fe-8-nh3-5	0.603368	−1707.570496	−1706.967128
Fe-8-nh3-6	0.603359	−1707.570496	−1706.967137
Fe-8-thf-1	0.677967	1883.492395	−1882.814428
Fe-8-thf-2	0.669764	−1883.542448	−1882.872684
Fe-8-thf-3	0.670335	−1883.543040	−1882.872705
Fe-8-thf-4	0.670092	−1883.540918	−1882.870826
Fe-8-thf-5	0.678168	−1883.491831	−1882.813663
Fe-8-thf-6	0.676542	−1883.492322	−1882.815780
Ru-8-h2o-1	0.59073	−1697.965560	−1697.374830
Ru-8-h2o-2	0.588659	−1697.979910	−1697.391251
Ru-8-h2o-3	0.587331	−1697.975428	−1697.388097
Ru-8-h2o-4	0.587623	−1697.958658	−1697.371035
Ru-8-h2o-5	0.587188	−1697.924552	−1697.337364
Ru-8-h2o-6	0.586224	−1697.924848	−1697.338624
Ru-8-nh3-1	0.601459	−1678.096242	−1677.494783
Ru-8-nh3-2	0.605483	−1678.074231	−1677.468748
Ru-8-nh3-3	0.605571	−1678.074248	−1677.468677
Ru-8-nh3-4	0.598606	−1678.074010	−1677.475404
Ru-8-nh3-5	0.602093	−1678.057499	−1677.455406
Ru-8-nh3-6	0.602174	−1678.057495	−1677.455321
Ru-8-thf-1	0.674534	−1853.982585	−1853.308051
Ru-8-thf-2	0.671485	−1854.033256	−1853.361771
Ru-8-thf-3	0.672414	−1854.032192	−1853.359778
Ru-8-thf-4	0.676058	−1853.982642	−1853.306584
Ru-8-thf-5	0.676027	−1853.982638	−1853.306611

Table S5 (c). Energies of each compounds for the complete model (Ada$_2$P-) with H_2O, NH_3 and THF chelation. G_corr = Thermal correction to Gibbs Free Energy; E = Absolute single-point energies; G = Gibbs free energies.

species	G_corr	E	G
Ir-8-h2o-1	1.023496	−2638.069623	−2637.046127
Ir-8-h2o-2	1.021922	−2638.084185	−2637.062263
Ir-8-h2o-3	1.020554	−2638.084919	−2637.064365
Ir-8-h2o-4	1.01834	−2638.088362	−2637.070022
Ir-8-h2o-5	1.020851	−2638.084174	−2637.063323
Ir-8-h2o-6	1.022499	−2638.069227	−2637.046728
Ir-8-nh3-1	1.039089	−2618.204452	−2617.165363
Ir-8-nh3-2	1.040021	−2618.205379	−2617.165358
Ir-8-nh3-3	1.037204	−2618.204595	−2617.167391
Ir-8-nh3-4	1.03247	−2618.203925	−2617.171455
Ir-8-nh3-5	1.040013	−2618.207049	−2617.167036
Ir-8-nh3-6	1.039999	−2618.206294	−2617.166295
Ir-8-thf-1	1.111952	−2794.124934	−2793.012982
Ir-8-thf-2	1.113933	−2794.126029	−2793.012096
Ir-8-thf-3	1.104493	−2794.133369	−2793.028876
Ir-8-thf-4	1.112085	−2794.125762	−2793.013677
Ir-8-thf-5	1.111066	−2794.125614	−2793.014548
Co-8-h2o-1	1.025592	−2678.378690	−2677.353098
Co-8-h2o-2	1.023393	−2678.378506	−2677.355113
Co-8-h2o-3	1.023816	−2678.379631	−2677.355815
Co-8-h2o-4	1.023978	−2678.428265	−2677.404287
Co-8-h2o-5	1.024273	−2678.374516	−2677.350243
Co-8-h2o-6	1.02355	−2678.375193	−2677.351643
Co-8-nh3-1	1.03861	−2658.512678	−2657.474068
Co-8-nh3-2	1.037657	−2658.512080	−2657.474423
Co-8-nh3-3	1.034658	−2658.548820	−2657.514162
Co-8-nh3-4	1.035512	−2658.493837	−2657.458325
Co-8-nh3-5	1.037823	−2658.511366	−2657.473543
Co-8-thf-1	1.110804	−2834.431381	−2833.320577
Co-8-thf-2	1.11081	−2834.431380	−2833.320570
Co-8-thf-3	1.105272	−2834.438950	−2833.333678
Co-8-thf-4	1.105656	−2834.438281	−2833.332625
Co-8-thf-5	1.112483	−2834.432078	−2833.319595

Table S6. Cartesian coordinates for the molecules involved in Pathway I-B and Pathway 2a.

Pre-Cat

Ir	-0.26482700	0.07975300	7.23029500
H	0.51133500	-0.80939400	6.18350000
Cl	-1.61784800	1.33456200	9.06177900
Cl	0.56776200	1.99514100	6.02542800
P	-2.19764600	-0.14232200	6.00306500
P	1.51518900	-0.06919600	8.67990200
N	-1.05135900	-1.56536300	8.36723800
H	-1.56833900	-1.02189000	9.07613400
C	0.95974100	-1.44167700	9.82196900
H	1.79502800	-2.01223100	10.23604300
H	0.43214000	-0.96091800	10.65220600
C	0.00322900	-2.36379000	9.05351000
H	0.53961100	-2.92443800	8.28165600
H	-0.46379700	-3.08438400	9.73800300
C	-2.02372500	-2.39809000	7.60392000
H	-2.50868100	-3.11461900	8.28011600
H	-1.45336100	-2.96314500	6.86032900
C	-3.07563700	-1.50983400	6.92592300
H	-3.69964200	-1.02312500	7.68257700
H	-3.72650000	-2.10651700	6.28162900
H	1.86050700	0.98196200	9.55202800
H	2.79702700	-0.46779500	8.24266900
H	-3.15607700	0.88724700	5.92455900
H	-2.17919400	-0.57531700	4.65935400

I-Cat-B

Ir	-0.21974900	0.13061800	7.17510200
H	0.32592600	1.37985100	6.38541600
Cl	-1.33586800	1.51956500	8.68700400
P	-2.20387900	-0.14721800	5.96404700
P	1.56204700	-0.08097900	8.67890900
N	-1.07147600	-1.60599700	8.39978200
H	-1.59694700	-1.09455800	9.11451500
C	0.95662400	-1.42659100	9.82714200
H	1.79013200	-1.98166200	10.26542500
H	0.43123700	-0.92437100	10.64704500
C	0.00287000	-2.37755800	9.08478000
H	0.53883300	-2.95282800	8.32228200
H	-0.42627000	-3.09403400	9.79637100
C	-2.03987600	-2.41433900	7.60788200
H	-2.56168500	-3.13507600	8.24980400
H	-1.46921600	-2.98525900	6.86771500
C	-3.06877100	-1.49966800	6.92210600
H	-3.69424900	-1.00195700	7.67156900
H	-3.73311400	-2.08202000	6.27829600
H	-3.14497500	0.88986500	5.83774800
H	-2.12090900	-0.62357600	4.63893000
H	2.80216900	-0.54020900	8.18776100
H	1.95879000	0.97960100	9.51254500

I-B1

Ir	-0.23957600	0.35951300	7.48300600
H	0.34634300	1.59375900	6.68377000
Cl	-1.48643400	1.87094700	8.90818300
P	-2.20122200	0.10132400	6.25236800
P	1.38778900	0.28453100	9.15513300
N	-1.19472000	-1.24952800	8.76513700

H	-1.74533200	-0.65925800	9.39714300
C	0.70034400	-0.99080600	10.33654300
H	1.49817700	-1.51183800	10.87156600
H	0.10969600	-0.44098200	11.07700500
C	-0.19145800	-1.98564400	9.57849900
H	0.39970400	-2.60493700	8.89685300
H	-0.68848400	-2.65293000	10.29418300
C	-2.13599100	-2.09725400	7.98667100
H	-2.68971800	-2.77130000	8.65284500
H	-1.54281200	-2.71249900	7.30339800
C	-3.12413200	-1.20991600	7.21543300
H	-3.78267500	-0.68141800	7.91271000
H	-3.75641600	-1.81314100	6.55914000
H	-3.10812500	1.17173800	6.15563400
H	-2.18282800	-0.37123200	4.92468300
H	2.69938200	-0.15849800	8.87977400
H	1.64518800	1.41510700	9.95076500
B	1.01335900	-0.98312900	5.42911400
H	1.79887000	-1.86622900	5.63304200
H	0.73950900	-0.77936500	6.70597700
N	1.78817100	0.27274500	4.80538100
H	2.57563800	0.57176200	5.38202300
H	2.15659900	0.02886900	3.88304800
H	1.17172800	1.08122700	4.70657400
H	0.06861900	-1.25402700	4.75620200

I-TSB1

Ir	-0.19841800	0.05860900	7.46467100
H	0.50186200	1.13852000	6.46494600
Cl	-1.19258000	2.03127700	8.66214600
P	-2.18103900	-0.16030100	6.26921300
P	1.48945300	0.02090400	9.06779200
N	-1.30888900	-1.04392500	8.99257100
H	-1.73006100	-0.24730700	9.48854700
C	0.65077500	-0.83293000	10.49671400
H	1.36343200	-1.37655400	11.12151500
H	0.19860300	-0.04522700	11.10806000
C	-0.42933500	-1.77390600	9.95168900
H	0.01493200	-2.61631100	9.41403100
H	-1.03143000	-2.17336800	10.77669100
C	-2.41182300	-1.87841500	8.43219100
H	-3.02313300	-2.28208500	9.24835300
H	-1.95135100	-2.71767500	7.90299600
C	-3.28173600	-1.03983400	7.48898100
H	-3.81367600	-0.26283300	8.04751200
H	-4.02664200	-1.66318600	6.98858000
H	-2.91258500	0.97560700	5.87593500
H	-2.24302000	-0.93910100	5.09475600
H	2.68232000	-0.70304400	8.86055600
H	1.99336000	1.21826100	9.60859800
B	2.05797000	-1.21362800	4.74988400
H	2.93049400	-1.68164100	5.40206600
H	0.36173400	-1.28818500	6.80184900
N	1.88693200	0.24580100	4.77936500
H	2.70786100	0.80037300	5.01881100
H	1.39935000	0.66783600	3.99015100
H	1.06842400	0.45103400	5.79982800
H	1.29461200	-1.84877000	4.10258500

I-B2

Ir	0.10609200	0.11350500	-0.18508600
H	0.78285500	1.32445900	-1.15119400
Cl	-0.81031800	2.09809900	1.04777200
P	-1.91153600	-0.05347900	-1.37273200
P	1.86926900	0.01209100	1.36270700
N	-0.96747000	-0.94138300	1.32414300
H	-1.35699900	-0.14070300	1.84293000
C	1.03190600	-0.81943700	2.79974100
H	1.73644300	-1.39840200	3.40161400
H	0.62355500	-0.02271000	3.42991100
C	-0.09021400	-1.71372500	2.26394500
H	0.31011300	-2.56720000	1.71039700
H	-0.70047200	-2.09420100	3.09048000
C	-2.11573200	-1.75046500	0.79743600
H	-2.70174200	-2.13020600	1.64168400
H	-1.69397900	-2.60400800	0.25978600
C	-2.99580200	-0.89380200	-0.11792000
H	-3.49138000	-0.10142600	0.45224500
H	-3.76956500	-1.50236100	-0.59209300
H	-2.60119700	1.10757400	-1.76283600
H	-1.97367000	-0.84132500	-2.53750600
H	3.01246700	-0.75680200	1.07435000
H	2.42873600	1.19573200	1.87432800
H	0.58315900	-1.27012400	-0.82103900
H	1.05809900	0.53825100	-1.50920500
8			
Ir	-0.98562200	-0.69889900	8.92973700
P	-2.90833700	-1.46031100	8.03237200
P	0.72941600	-1.17893000	10.31223800
N	-1.98429400	-3.20719000	10.82677300
H	-2.51725900	-3.21127700	11.68901900
C	0.25961400	-2.46397100	11.59815500
H	1.17879900	-2.85886100	12.04613300
H	-0.28880900	-1.94017500	12.38872300
C	-0.60635700	-3.61593100	11.04562300
H	-0.19497600	-3.95131800	10.08777400
H	-0.51746000	-4.47302800	11.73766700
C	-2.74194700	-3.77930500	9.72480800
H	-3.31712400	-4.67540300	10.02006500
H	-2.03345600	-4.11036200	8.95804400
C	-3.72644300	-2.76334300	9.10880900
H	-4.25141400	-2.23131100	9.90967700
H	-4.48434300	-3.28093600	8.50946700
H	-1.80170400	-0.28825200	10.17714600
H	-4.07656800	-0.70892700	7.70035900
H	-2.85007600	-2.17246600	6.80020000
H	1.44390500	-0.28710000	11.16885500
H	1.88887000	-1.80283300	9.76880200
9-2a			
Ir	0.53574300	0.00292900	-0.35178300
P	-0.04494800	-2.18018900	-0.27167000
P	-0.01311900	2.19314400	-0.23351000
N	-2.55841700	0.01747500	0.16953400
H	-3.28075000	0.03414000	-0.54195600
C	-1.86512900	2.38537600	0.03995600
H	-2.05688500	3.36756300	0.48672300
H	-2.33393000	2.38303300	-0.95043500
C	-2.48942900	1.26834400	0.90250800
H	-1.87414800	1.10415700	1.79341900

H	-3.47508500	1.62132800	1.26008400
C	-2.51538000	-1.25354100	0.86993600
H	-3.50994900	-1.59912200	1.20906800
H	-1.90657800	-1.12325800	1.77087300
C	-1.90000000	-2.35719000	-0.01592700
H	-2.36329000	-2.32506900	-1.00842400
H	-2.10688600	-3.34725800	0.40615100
H	0.15297600	3.14624300	-1.27659300
H	0.46800900	3.03477700	0.81007100
H	0.11914600	-3.11829700	-1.32802600
H	0.43128800	-3.02712000	0.76646200
H	0.05608100	0.02108800	-1.86906600
B	2.30360800	-0.23827100	1.83648700
H	2.37541500	-1.41127600	2.09641600
H	2.50553500	0.50070500	2.76846200
N	3.37360400	0.08577500	0.65446500
H	2.80290200	-0.04701300	-0.22278800
H	3.69562400	1.05145400	0.66731300
H	4.18511100	-0.53072600	0.66913000
H	1.12946200	0.05544700	1.42883400
TS9-2a			
Ir	-0.99801800	-1.00707700	8.98167400
P	-3.00887600	-1.49096900	8.04298100
P	0.76478000	-1.20735000	10.40178900
N	-1.83159300	-3.03277000	10.56132400
H	-2.34611100	-2.61406100	11.33065000
C	0.33901900	-2.56999000	11.62919600
H	1.25155400	-3.03268900	12.01855500
H	-0.16186300	-2.08589600	12.47624200
C	-0.59049200	-3.63978000	11.02576200
H	-0.10755700	-4.11055300	10.16220100
H	-0.74916300	-4.43262800	11.77889600
C	-2.71498900	-3.79949100	9.69169000
H	-3.23204500	-4.62444700	10.21431700
H	-2.09711400	-4.25194900	8.90815800
C	-3.77505200	-2.87966500	9.05725200
H	-4.36656600	-2.40300300	9.84827700
H	-4.46983400	-3.46261700	8.44430700
H	1.23075400	-0.21178200	11.29847800
H	2.03688800	-1.63680300	9.94262000
H	-4.11996900	-0.61338900	7.95545500
H	-3.10401900	-2.02323000	6.73101800
H	-1.70927700	0.01378800	9.99258700
B	0.49332200	-1.58117600	6.67187200
H	-0.10375600	-2.09779600	5.75781700
H	1.62382000	-1.97493700	6.83391500
N	0.40584300	-0.00644400	6.63100600
H	-0.31444300	0.08562300	7.76130100
H	1.29937100	0.47004400	6.71201500
H	-0.09387800	0.36957400	5.83044000
H	-0.13970600	-2.06656500	7.74766800
11			
Ir	0.00000000	-0.69360800	0.00341300
P	-2.25191700	-0.42701200	0.03975300
P	2.25191700	-0.42701000	0.03975000
N	-0.00000100	1.58438000	-0.27604900
H	0.00000100	1.70246300	-1.28820600
C	2.47627500	1.41823500	-0.24388000
H	3.38485800	1.80198700	0.22931400

H	2.58137500	1.56689400	-1.32487100
C	1.24346000	2.17016500	0.27553600
H	1.17794500	2.07799100	1.36382300
H	1.32087500	3.23931500	0.02476600
C	-1.24346400	2.17016600	0.27553100
H	-1.32087900	3.23931400	0.02475400
H	-1.17795100	2.07799800	1.36381800
C	-2.47627700	1.41823200	-0.24388300
H	-2.58137700	1.56688600	-1.32487600
H	-3.38486100	1.80198400	0.22930800
H	3.16550000	-0.96046500	-0.90182400
H	3.03103200	-0.65685800	1.19957100
H	-3.16549900	-0.96047100	-0.90181800
H	-3.03102900	-0.65685600	1.19957600
H	-0.00000200	-0.96283100	-1.65354500
H	0.00000100	-2.26096800	0.18067400
H	0.00000300	-0.54970800	1.67667100

TS11

Ir	-0.27904200	0.04300400	7.25736400
H	0.53367400	-0.95046000	6.15206900
P	-2.40324300	0.02106900	6.41009500
P	1.19762200	0.08664900	9.00138300
N	-1.07146100	-1.74283600	8.39999900
H	-1.60742100	-1.27362900	9.12943100
C	0.83131300	-1.51584800	9.93904000
H	1.74901100	-1.99505900	10.29029100
H	0.24716900	-1.24906700	10.82760400
C	0.02861900	-2.48284300	9.05589600
H	0.65568100	-2.90045200	8.26381800
H	-0.36784900	-3.31110900	9.66326000
C	-2.02191800	-2.52150300	7.57705300
H	-2.45187600	-3.35093300	8.15966100
H	-1.45925300	-2.93997200	6.73832700
C	-3.13741900	-1.58950400	7.08102800
H	-3.80048600	-1.32557700	7.91338100
H	-3.75055300	-2.09559100	6.33066100
H	1.30953200	0.97271100	10.11175300
H	2.60072400	-0.02395200	8.79623700
H	-3.51312100	0.88384000	6.64377600
H	-2.65203200	-0.11750800	5.01664700
H	-0.13200800	1.61399200	7.01567200
H	0.67934200	0.16936800	5.92197500

12

Ir	-0.09113500	0.73155800	0.10601900
P	-1.87846800	0.37068800	-1.20965000
P	1.72916000	0.44242500	1.39389700
N	-0.69410700	-1.29060800	0.99663600
H	-1.27455600	-1.02778600	1.79447400
C	1.39293900	-1.14612800	2.34677700
H	2.30918100	-1.68036900	2.61605500
H	0.89084500	-0.86597100	3.28037500
C	0.48250200	-2.04308200	1.50199100
H	1.02651600	-2.40393700	0.62359400
H	0.16336700	-2.92177000	2.08349700
C	-1.52458000	-2.08312900	0.05470900
H	-1.95382400	-2.96321100	0.55802500
H	-0.85312000	-2.44268200	-0.73108500
C	-2.63581200	-1.22641500	-0.56148100
H	-3.37283400	-0.95122000	0.20228000

H	-3.16417400	-1.78940600	-1.33698600
H	2.20461100	1.27190400	2.44776800
H	3.00276100	0.17647700	0.82116800
H	-3.04938300	1.16804200	-1.34350400
H	-1.72873100	0.08323300	-2.59370300
H	0.31044100	2.15402700	-0.48995400
TS11′			
Ir	-0.20227200	0.06393100	7.14310500
H	0.68543900	-0.43834900	5.92478500
P	-2.05856100	-0.32247400	5.85914900
P	1.61433700	-0.25186900	8.50516600
N	-0.98741200	-1.74078500	8.28334800
H	-1.29016000	-0.32614900	8.66548400
C	1.05150100	-1.60169800	9.67024600
H	1.89228900	-2.17004000	10.07791900
H	0.55023400	-1.09342400	10.50148900
C	0.05434400	-2.51257000	8.93450500
H	0.61024700	-3.13027000	8.20189400
H	-0.37276300	-3.21564200	9.67278300
C	-1.92204100	-2.54668100	7.51965000
H	-2.47082900	-3.24807500	8.17433000
H	-1.39319200	-3.16886600	6.77097300
C	-2.95591500	-1.67023300	6.79221000
H	-3.59245500	-1.15942700	7.52336300
H	-3.60058400	-2.26476300	6.13864900
H	2.16987100	0.70983100	9.38183400
H	2.81305600	-0.74127600	7.94220400
H	-3.08662200	0.61077900	5.58668000
H	-1.89222400	-0.83947500	4.55594800
H	-1.25515100	0.63398600	8.58920700
H	0.19859800	1.48910600	6.54815800
12′			
Ir	-0.21071900	-0.00476900	7.15834200
H	0.65046600	0.53681200	5.94615900
P	-2.11239700	-0.29882600	5.93121300
P	1.56225000	-0.22879700	8.57761900
N	-0.86629800	-1.67633900	8.11173800
C	0.94490800	-1.49490800	9.79535400
H	1.75572200	-2.05264400	10.27288700
H	0.41363400	-0.92712200	10.56612100
C	-0.04158100	-2.41930600	9.06382200
H	0.51882200	-3.23100400	8.56505600
H	-0.67964100	-2.91123600	9.81757800
C	-2.01673800	-2.45247000	7.65025700
H	-2.51664500	-2.93762200	8.50581800
H	-1.70649300	-3.27186600	6.97638000
C	-3.04365700	-1.56268200	6.93122900
H	-3.61412000	-0.99041800	7.67002700
H	-3.74480800	-2.14681300	6.32816700
H	-0.18588700	1.59010600	7.08320000
H	-3.07904200	0.69585600	5.65686500
H	-2.02899200	-0.86556200	4.63641800
H	2.09696600	0.79422000	9.39398700
H	2.78147300	-0.76537400	8.09771500