Electrical Supplementary Information for

Reversible Hydrogen Adsorption at Room Temperature using Molybdenum-Dihydrogen Complex in Solid State

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Contents

I. General experimental information

All chemicals were used without further purification. Thermogravimetric (TG) analysis was measured using Shimadzu DTG-60H under a constant argon gas flow (100 ml/min) with a sweep rate of 5 K/min. H_2 and N_2 sorption isotherm was performed using microtracbel Belsorp Max. Detail of adsorption measurement and kinetic analysis are written later. IR

spectra were recorded as KBr pellets on a JASCO FT/IR-4200 spectrometer at room temperature. For acquiring IR spectra under inert atmosphere, the KBr pellets were fabricated in glove box (MBRAUN UNILAB1200/780) filled with Ar gas, and then the pellets were set into a specially designed sealed optical cell individually. ^{1}H NMR measurements were performed on Bruker AV500 at room temperature. Elemental analyses were performed using J-Science Lab JM-10 equipped in the research and analytical center for giant molecules at Tohoku University.

II. Adsorption measurement

The detail of sample loading is described in the synthetic procedure of **2**. Similar procedure was used for **1** in the Ar-filled grove box. H_2 sorption isotherm was measured by using G1 grade (> 99.99999 %) H_2 gas. Sorption measurement was performed by volumetric method, and the volume of adsorbed H_2 gas was calculated from the ideal gas equation with second virial coefficient of 3.436×10^{-9}. H_2 sorption isotherm was measured for **1** at the temperature of 293, 313 and 333 K, and for **2** at the temperature of 273, 283, 293, 303, 313, 333, 343, 353, 363 and 373 K, respectively. Temperature control during sorption measurement was done by using Dewar bottle, circulating water cooler and brass block heater for 273K, 283-313 K and 333-373 K, respectively. Adsorption isotherm was measured in the pressure range of $P/P_0 = 10^{-5}$-0.997 (P_0 = 101.325 kPa) and desorption isotherm was measured down to P/P_0 = 0.01. The volume of sample space was measured after sorption measurement by using G2 grade (> 99.999 %) He gas, and dead volume correction was applied to the raw data. For N_2 adsorption measurement, G3 grade (> 99.9995 %) N_2 gas was used. For H_2 adsorption, 802.3 and 499.6 mg of **1** and **2** were used. For N_2 adsorption, 189.0 and 499.6 mg of **1** and **2** were used.

III. Kinetic analysis

Kinetic analysis of **2** was performed at the temperature of 273, 283, 293 and 303 K. H_2 gas was introduced into sample tube at the pressure of 90-100 Pa. Pressure of the Adsorption rate was determined as a pressure decrease rate inside of the sample tube. The data was obtained from the trend graph of BELSOPR-MAX. The detail of analysis is written in main text.

IV. DFT calculation

DFT calculation was performed to investigate the thermodynamic properties of hydrogen adsorption with using GAUSSIAN 16 software.[S1] Geometry optimization and vibrational analysis were performed using B3LYP/LanL2DZ level of theory. Effective core potentials representing the 36 core electrons for molybdenum atom and 10 core electrons for phosphorus atom was used. Thermodynamic parameters were obtained by following procedure.

Geometry optimization and vibrational analysis were performed for the singlet state of coordinatively-unsaturated (16-electron) complexes $[Mo(PR_3)_2(CO)_3]$ (R = Me, iPr, and Cy), H_2-adduct of each complex $[Mo(\eta^2\text{-}H_2)(PR_3)_2(CO)_3]$ and free H_2 molecule. For 16-electron complexes, initial structures were made in the Gauss View 6.1[S2] by adding two trialkylphosphine PR_3 and three carbonyl ligands to Oh symmetric Mo atom. For H_2-adduct, initial structures were made by adding a H_2 molecule to the initial structure of 16-electron complexes.

Standard molar Gibbs free energy change ΔG°, standard molar enthalpy change ΔH° and standard molar entropy change ΔS° of adsorption were calculated by following equation

$$\Delta E(T) = E_{M-H_2}(T) - E_{H_2}(T) - E_M(T)$$

where the subscript M-H_2, H_2 and M represent H_2-adduct, free H_2 molecule and 16-electron complexes, respectively.

V. Syntheses

Synthesis of [Mo(cht)(CO)$_3$] (Mo-cht)[S3]

Nitrogen-purged 2-necked flask was charged with molybdenum hexacarbonyl $Mo(CO)_6$ (4.0 g, 15.15 mmol), 1,3,5-Cycloheptatriene (9.0 ml, 86.74 mmol) and 40 ml of N_2-saturated heptane. The white suspension was refluxed at 130 ℃ for 24 h and cooled down to room temperature, which gave red precipitate. The reaction mixture was filtered and washed with heptane. Residual red solid was extracted with hexane and combined with red heptane solution. Solvent was removed by rotary evaporator and resultant red solid was subject to vacuum sublimation at 40 ℃ to remove the unreacted $Mo(CO)_6$, which gave analytically pure red crystalline solid of target compound.

Yield: 86 %

^{1}H NMR($CDCl_3$, 500 MHz) δ = 2.467 (1H), 3.027 (1H), 3.607 (2H), 4.927 (2H), 6.071 (2H)

IR (KBr): ν(CO) = 2039, 1841(br) cm^{-1}

Elemental analysis: Calculated for MoC10H8O3 C: 44.141 H: 2.963 N: 0.000

Found C: 43.761 H: 2.963 N: 0.000

Synthesis of [Mo(PCy$_3$)$_2$(CO)$_3$] (1)[24]

In the argon-filled glove box, 10 ml vial was charged with **Mo-cht** (326 mg, 1.2 mmol) and tricyclohexylphosphine PCy_3 (688 mg, 2.45 mmol). 8.0 ml of diethyl ether Et_2O was added to this solid mixture and stirred at room temperature for 1 day. The resulting brown purple precipitate was filtered off and washed with Et_2O and dried at argon atmosphere. The product was identified by KBr-IR and elemental analysis. Although the small amount of [$Mo(PCy_3)_2(CO)_4$] byproduct was detected by IR spectrum, the product was used for adsorption measurement without further purification because this 18-electron complex does not affect the thermodynamic parameters of adsorption.

Yield: 65 %

IR (KBr): ν(CO) = 1952, 1834, 1796 cm^{-1} ([$Mo(PCy_3)_2(CO)_4$]: 1863 cm^{-1})

Elemental analysis: Calculated for MoC39H66P2O3 C: 63.230 H: 8.980 N: 0.000

Found C: 62.820 H: 8.806 N: 0.000

Synthesis of [Mo(PCy$_3$)$_2$(CO)$_3$(N$_2$)][24]

N_2-purged 2-necked flask was charged with **Mo-cht** (272 mg, 1.0 mmol), PCy_3 (574 mg, 2.05 mmol) and 4.0 ml of N_2-saturated toluene. The reaction mixture was stirred at room temperature for 4 h, and then, 10 ml of N_2-saturated heptane was added and further stirred for 45 min. The resulting yellow brown suspension was filtered and residual yellow solid was washed with heptane/toluene = 3/1. The product was identified by ATR-IR and elemental analysis. The product was

used for adsorption measurement without further purification.

Yield: 65 %

IR (ATR): ν(CO) = 1956, 1835 cm^{-1}, ν(N ≡ N) = 2153 cm^{-1}

Elemental analysis: Calculated for $MoC_{39}H_{66}P_2O_3N_2$ C: 60.925 H: 8.652 N: 3.644

Found C: 61.675 H: 8.457 N: 3.076

Synthesis of $[Mo(PCy_3)_2(CO)_3]$ (2) from $[Mo(PCy_3)_2(CO)_3(N_2)]$

Freshly synthesized $[Mo(PCy_3)_2(CO)_3(N_2)]$ (553.6 mg) was loaded into a glass tube for adsorption measurement. First, sample space was evacuated by rotary oil pump at room temperature and turbo-molecular pump was also used after the pressure reached 3.0 kPa. Heating was initiated after the pressure reached 20 kPa and temperature was raised to 80 ℃ with the rate of 5 ℃/min. As soon as the temperature reached 80 ℃, evolution of N_2 gas was detected as the increase of pressure and the color of the sample changed from yellow to purple, which indicates the formation of five-coordinate complex $[Mo(PCy_3)_2(CO)_3]$. This color change is consistent with the result of TD-DFT calculation (Fig. S14). The weight of the sample was measured again after the adsorption measurement and it was determined to be 499.6 mg. Removal of N_2-ligand and formation of the target compound were confirmed by IR measurement.

IR (KBr): ν(CO) = 1953, 1922, 1837, 1798 cm^{-1}

Elemental analysis: Calculated for $MoC_{39}H_{66}P_2O_3N_2$ C: 63.226 H: 8.980 N: 0.000

Found C: 61.650 H: 8.420 N: 0.000

VI. Thermal transpiration correction

In our measurements, we used the correction of thermal transpiration using the following empirical formula.

$$\frac{P_2}{P_1} = \frac{AX^2 + BX + C\sqrt{X} + \sqrt{(T_2/T_1)}}{AX^2 + BX + C\sqrt{X} + 1}$$

$$A = 1.4 \times 10^4 exp(1.17 \times D \times 10) \times (T)^{-2}$$

$$B = 5.6 exp(1.40 \times D \times 10) \times (T)^{-1}$$

$$C = ((1.10 \times 10/D) - 14) \times (T)^{-0.5}$$

$$T = \frac{T_1 + T_2}{2}$$

Where P_1 is pressure in the sample cell, P_2 is pressure in the manifold, T_1 is the temperature in the sample cell, T_2 is the temperature in the manifold, d is the inner diameter of the sample cell (9 mm), D is the diameter of the hydrogen molecule (0.269 nm).

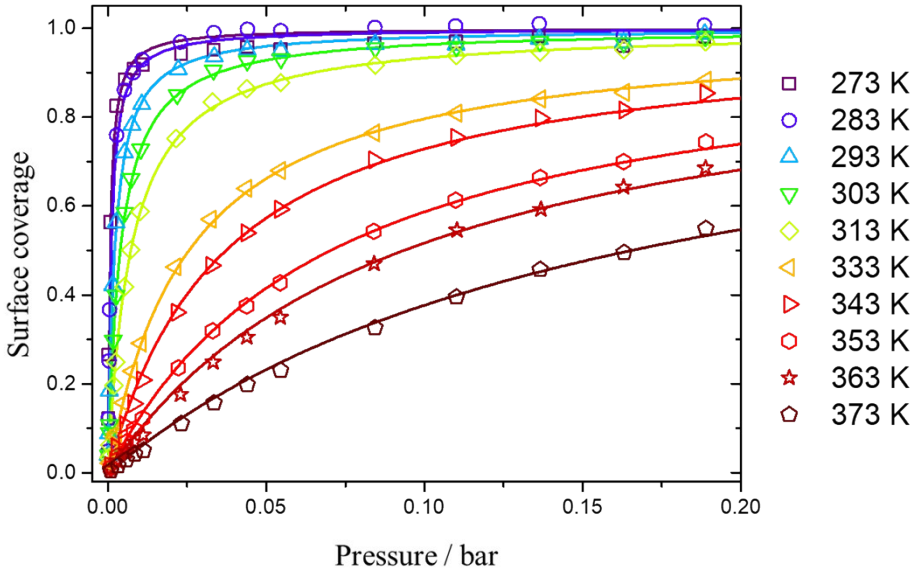

Fig. S1 Variable-temperature H_2 adsorption isotherms of **2** at 273-373 K. Plots represent data and lines represent the fitting by Langmuir adsorption isotherm.

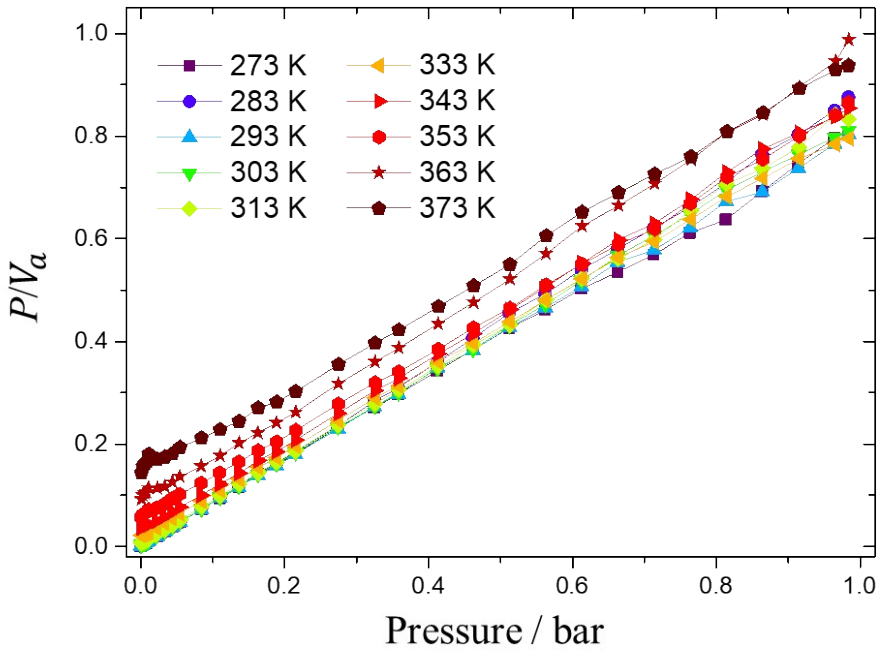

Fig. S2 Langmuir plots of **2** at 273-373 K. The lines are visual aid.

Table S1 Fitting parameters of **2** obtained from the Langmuir analysis of H_2 adsorption isotherms.

Temperature (K)	K	R^2	V_m ($cm^3(STP)g^{-1}$)
273	1502.60	0.9901	1.20
283	1015.88	0.9970	1.15
293	465.76	0.9978	1.21
303	254.86	0.9991	1.20
313	137.11	0.9991	1.19
333	38.57	0.9991	1.23
343	26.47	0.9987	1.19
353	14.02	0.9993	1.24
363	10.56	0.9978	1.14
373	5.97	0.9990	1.22

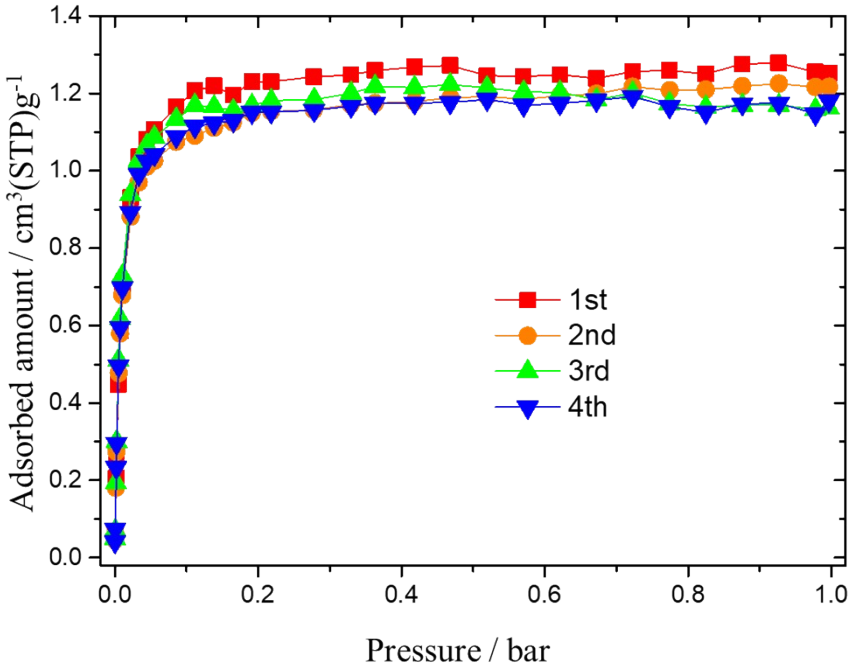

Fig. S3 Repetition of the H_2 adsorption isotherms of **2** at 313 K. The lines are visual aid.

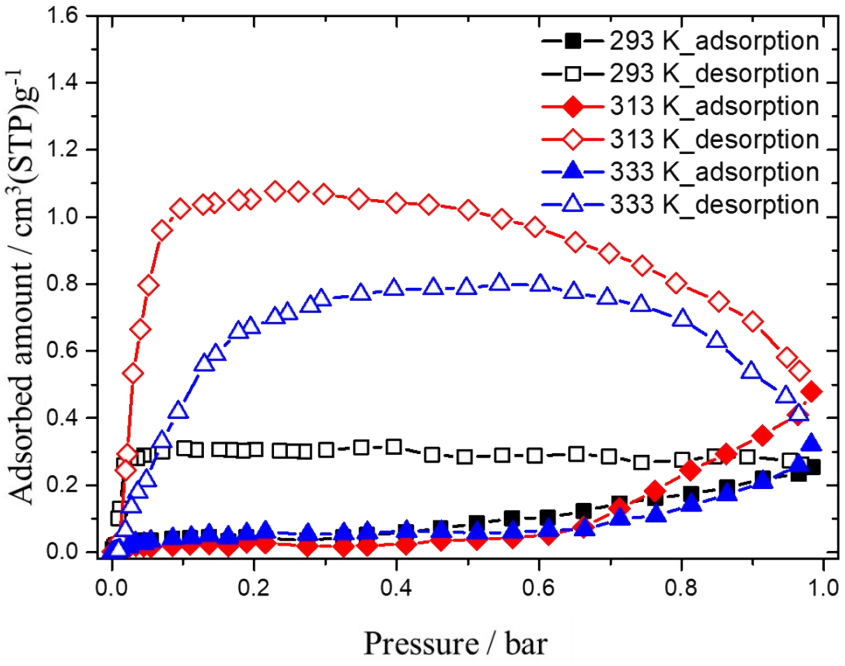

Fig. S4 Variable-temperature H_2 adsorption isotherms of **1** at 313-333 K. Plots represent data and lines are visual aid.

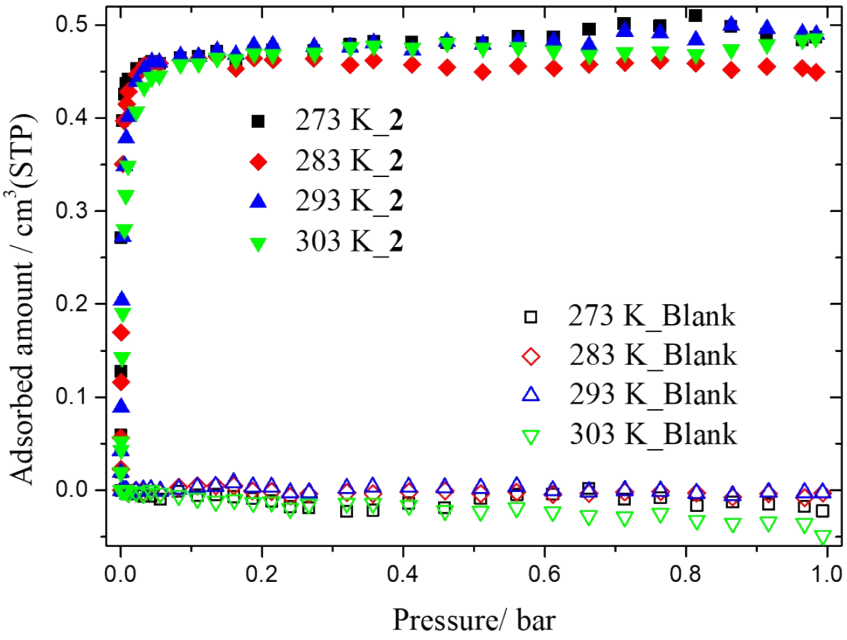

Fig. S5 H_2 uptake to the sample bottle with powder sample of **2** (499.6 mg) and empty bottle (blank).

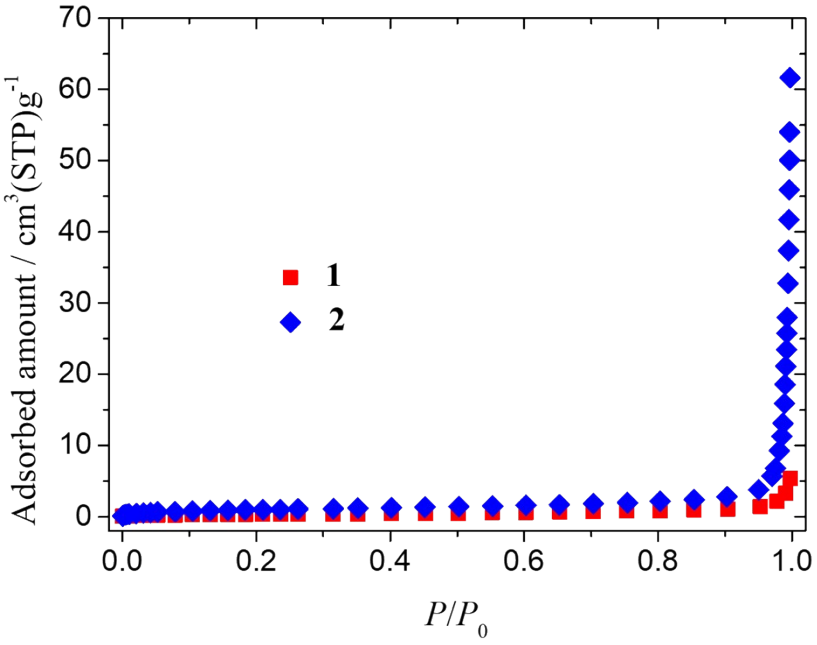

Fig. S6 Comparison of N_2 ad/desorption isotherms of **1** and **2** at 77 K.

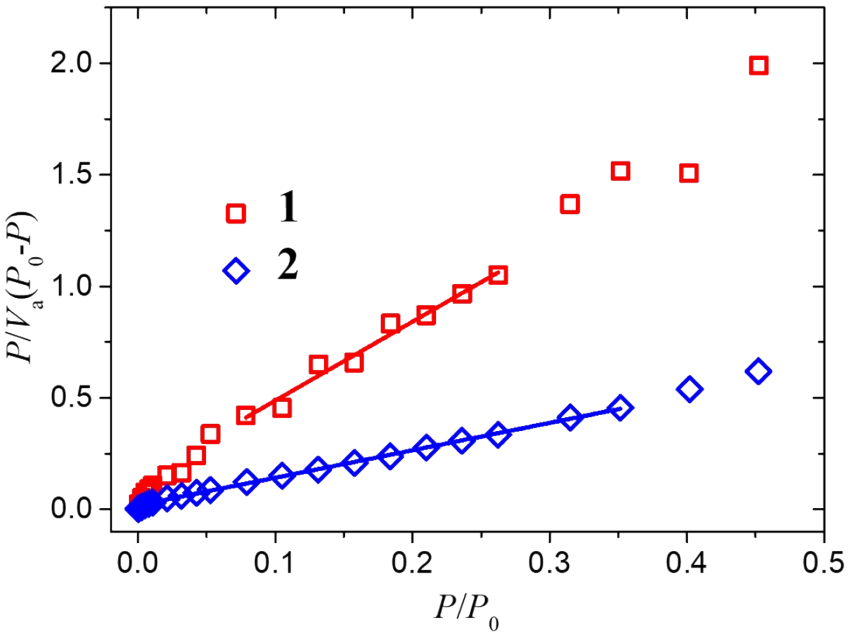

Fig. S7 BET plot of **1** and **2**. Lines represent the fitting by BET method.

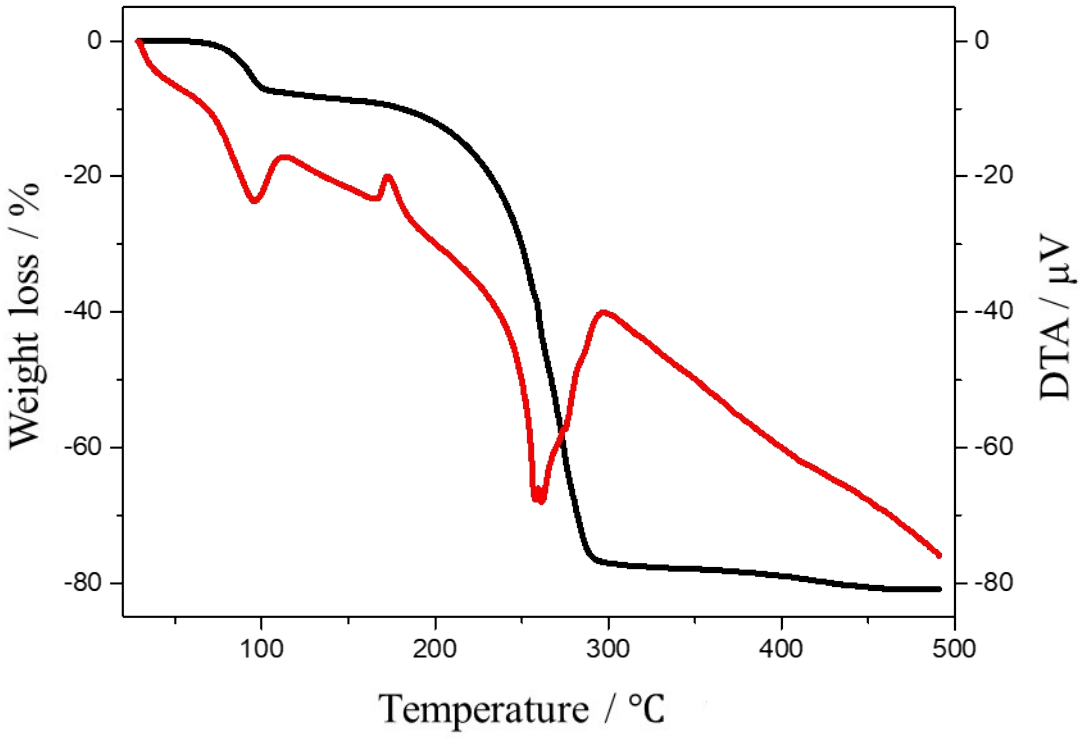

Fig. S8 TGA (black line) and DTA (red line) analysis of $[Mo(PCy_3)_2(CO)_3(N_2)]$.

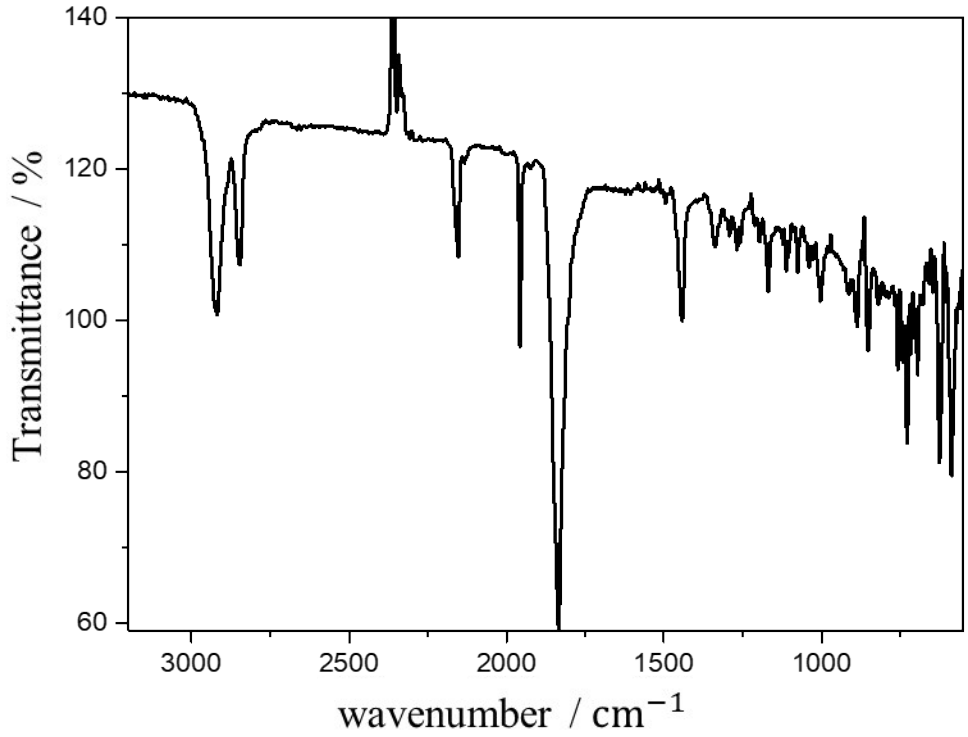

Fig. S9 FT-IR spectrum of $[Mo(PCy_3)_2(CO)_3(N_2)]$ (ATR method).

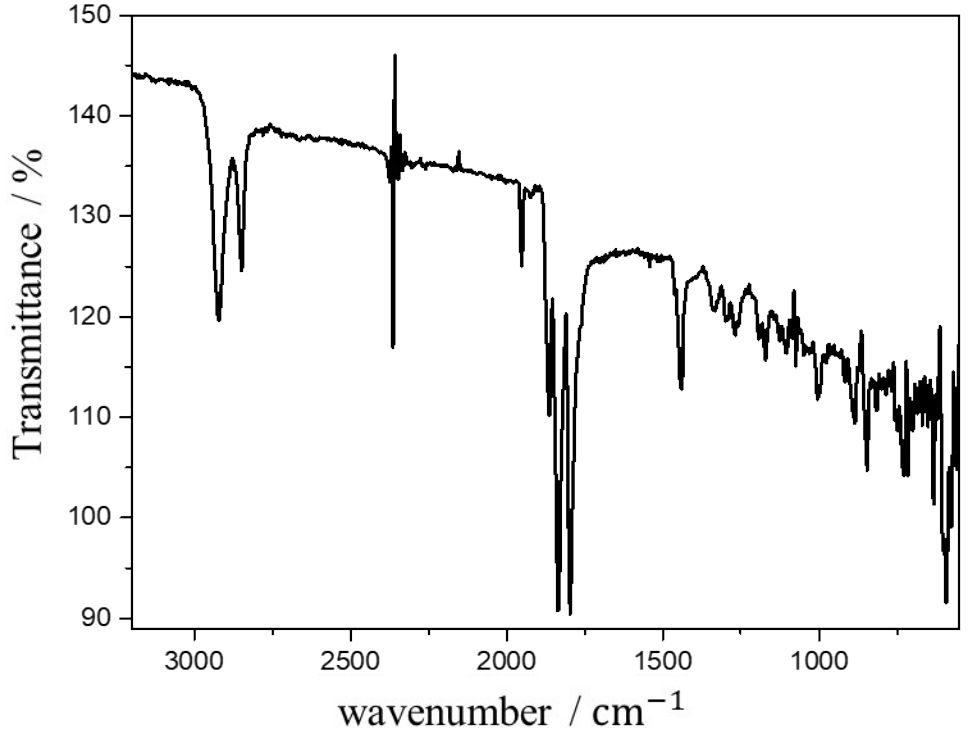

Fig. S10 FT-IR spectrum of **1** (KBr pellet).

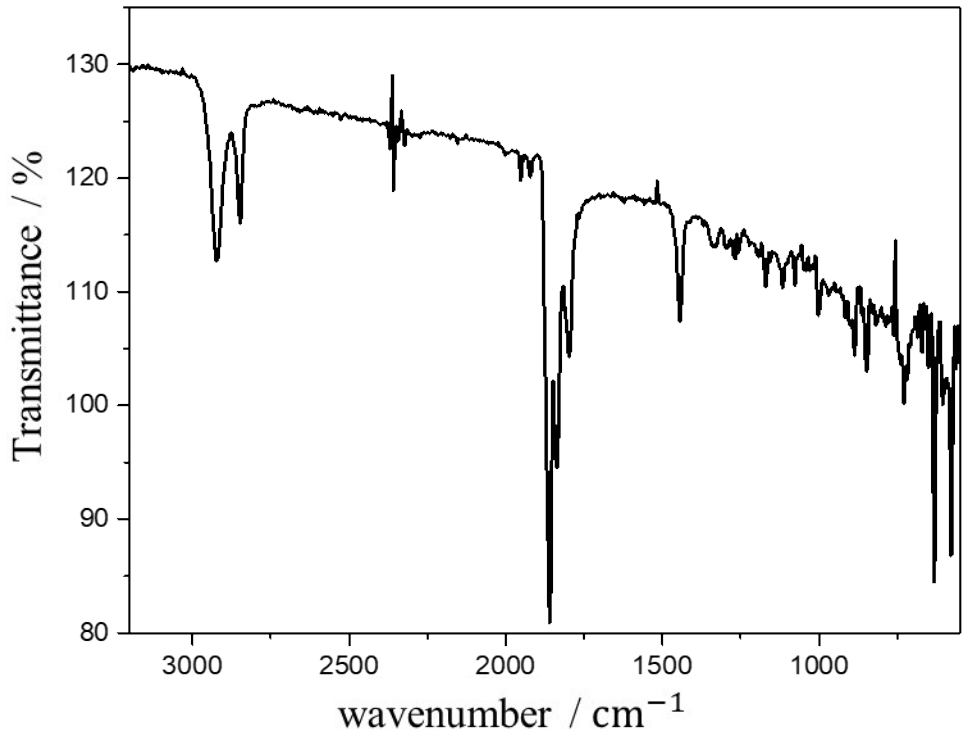

Fig. S11 FT-IR spectrum of **2** (KBr pellet).

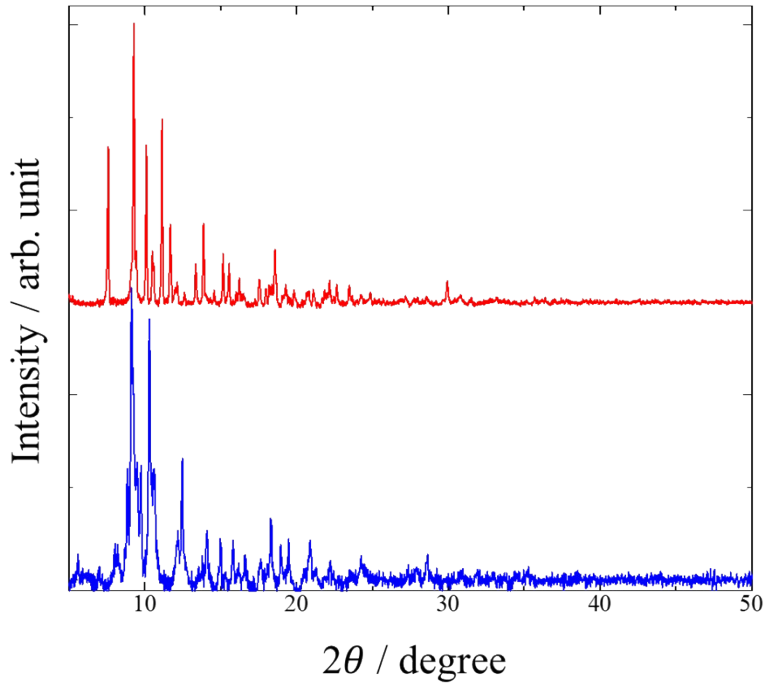

Fig. S12 PXRD pattern of **1** (red) and **2** (blue).

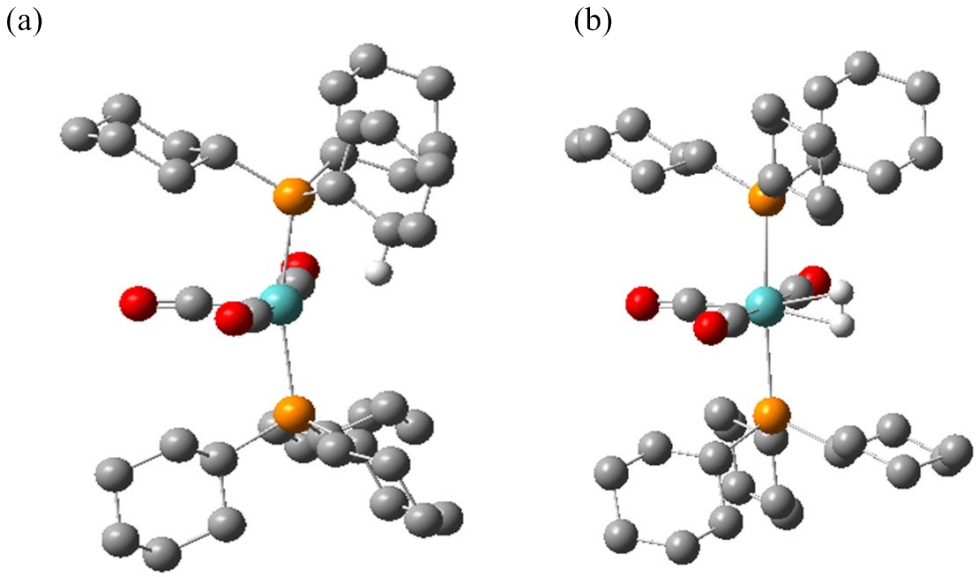

Fig. S13 Optimized structure of (a) Mo-PCy_3 and (b) Mo-PCy_3-H_2. Hydrogen atoms of cyclohexyl groups without the agostic interaction are omitted for clarity.

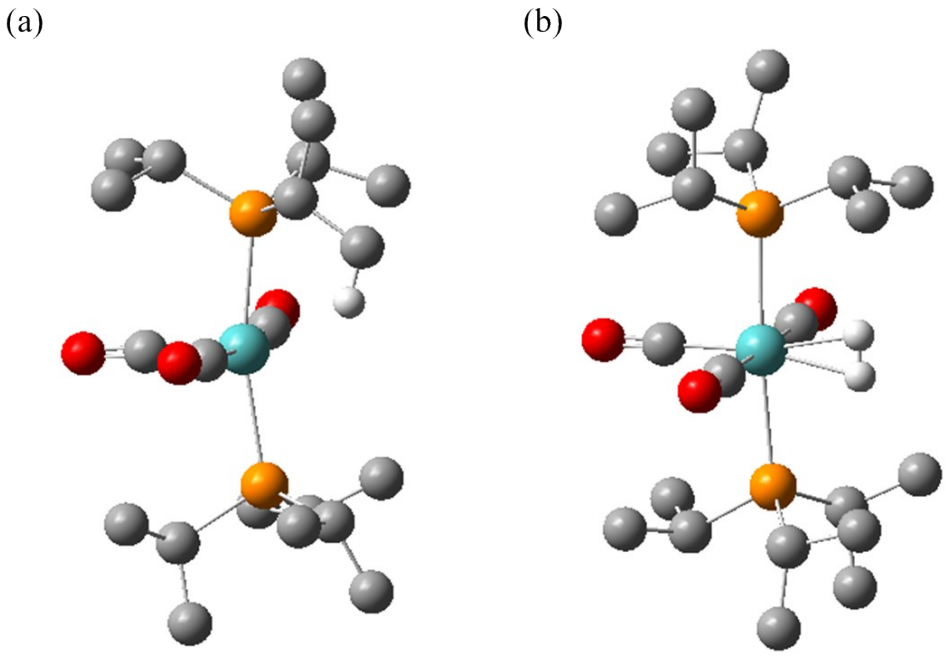

Fig. S14 Optimized structure of (a) Mo-iPr_3 and (b) Mo-$PiPr_3$-H_2. Hydrogen atoms of isopropyl groups without the agostic interaction are omitted for clarity.

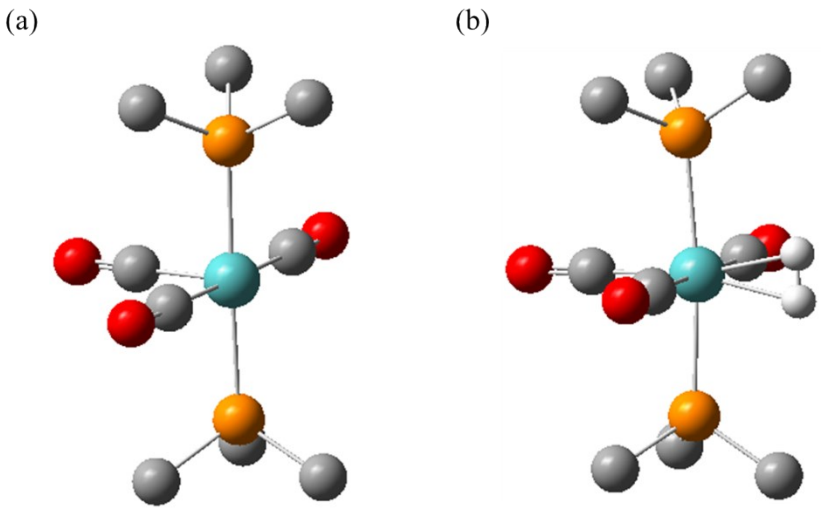

Fig. S15 Optimized structure of (a) Mo-PMe_3 and (b) Mo-PMe_3-H_2. Hydrogen atoms of methyl groups are omitted for clarity.

Table S2 Thermodynamic parameters of dihydrogen complex formation.

	ΔG° / kJ/mol	ΔH° / kJ/mol	ΔS° / kJ/mol
Mo-PCy_3	+9.50	–27.04	–122.57
Mo-$PiPr_3$	+2.71	–28.94	–106.04
Mo-PMe_3	–4.46	–37.69	–111.33

Table S3 Enthalpy and free energy of Mo-PR_3 and Mo-PR_3-H_2.

	Enthalpy / Hartree	Free energy / Hartree
Mo-PCy_3	-1830.889032	-1831.027317
Mo-PCy_3-H_2	-1832.060288	-1832.199434
Mo-$PiPr_3$	-1131.009782	-1131.121564
Mo-$PiPr_3$-H_2	-1132.181760	-1132.296283
Mo-PMe_3	-659.727861	-659.808648
Mo-PMe_3-H_2	-660.903172	-660.986098

Table S4 Frequency of carbonyl and dihydrogen ligand in Mo-PR_3 and Mo-PR_3-H_2.

	ν_1(C≡O) / cm^{-1}	ν_2(C≡O) / cm^{-1}	ν_3(C≡O) / cm^{-1}	ν(H-H) / cm^{-1}
Mo-PCy_3	1776.01	1783.78	1890.45	
Mo-PCy_3-H_2	1797.69	1801.10	1902.51	3552.46
Mo-$PiPr_3$	1781.02	1790.43	1895.00	
Mo-$PiPr_3$-H_2	1802.63	1806.74	1905.93	3545.17
Mo-PMe_3	1796.28	1811.81	1911.28	
Mo-PMe_3-H_2	1817.28	1825.58	1917.09	3521.95

Table S5 Atomic coordinates of Mo-PCy_3 in optimized structure.

1	Mo1	0.0273	0.1328	-0.2949 Mo
2	P2	2.6163	0.1467	0.0130 P
3	O3	0.4912	-2.2788	-2.3573 O
4	C4	0.2711	-1.4264	-1.5461 C
5	C5	3.6185	1.4387	-1.0096 C
6	C6	3.1690	2.8922	-0.7171 C
7	C7	3.9990	3.9084	-1.5394 C
8	C8	3.9248	3.6083	-3.0531 C
9	C9	4.3586	2.1556	-3.3501 C
10	C10	3.5287	1.1386	-2.5290 C
11	C11	3.4844	-1.5221	-0.4456 C
12	C12	3.0104	-2.6938	0.4521 C
13	C13	3.4915	-4.0509	-0.1158 C
14	C14	5.0281	-4.0776	-0.2838 C
15	C15	5.5209	-2.8838	-1.1333 C
16	C16	5.0302	-1.5298	-0.5596 C
17	C17	3.0515	0.6046	1.8401 C
18	C18	2.1535	-0.1444	2.8596 C
19	C19	2.3369	0.4339	4.2841 C
20	C20	3.8200	0.4028	4.7213 C
21	C21	4.7268	1.1115	3.6887 C
22	C22	4.5363	0.5205	2.2691 C
23	H23	4.6684	1.3331	-0.6940 H
24	H24	2.1074	3.0027	-0.9735 H
25	H25	3.2670	3.1262	0.3516 H
26	H26	3.6347	4.9252	-1.3352 H
27	H27	5.0509	3.8735	-1.2116 H
28	H28	2.8911	3.7540	-3.4010 H
29	H29	4.5561	4.3147	-3.6112 H
30	H30	5.4281	2.0374	-3.1101 H
31	H31	4.2455	1.9373	-4.4214 H
32	H32	2.4800	1.1914	-2.8474 H
33	H33	3.8799	0.1216	-2.7489 H
34	H34	3.0822	-1.7092	-1.4528 H
35	H35	1.9145	-2.6946	0.5369 H

36	H36	3.4162	-2.5702	1.4675 H
37	H37	3.1688	-4.8671	0.5467 H
38	H38	3.0117	-4.2213	-1.0914 H
39	H39	5.5028	-4.0358	0.7099 H
40	H40	5.3414	-5.0246	-0.7458 H
41	H41	5.1495	-2.9945	-2.1642 H
42	H42	6.6192	-2.8858	-1.1883 H
43	H43	5.4854	-1.3756	0.4274 H
44	H44	5.3823	-0.7162	-1.2054 H
45	H45	2.7552	1.6643	1.8793 H
46	H46	2.4049	-1.2143	2.8708 H
47	H47	1.0961	-0.0614	2.5638 H
48	H48	1.9736	1.4730	4.2992 H
49	H49	1.7203	-0.1307	4.9983 H
50	H50	4.1450	-0.6446	4.8291 H
51	H51	3.9315	0.8729	5.7086 H
52	H52	5.7811	1.0257	3.9888 H
53	H53	4.4862	2.1860	3.6696 H
54	H54	5.1818	1.0517	1.5566 H
55	H55	4.8620	-0.5296	2.2800 H
56	P56	-2.5628	-0.2009	-0.0601 P
57	O57	-0.1538	1.8899	-2.8567 O
58	O58	0.0331	2.9120	1.3096 O
59	C59	-0.0744	1.2050	-1.8635 C
60	C60	-0.0087	1.8502	0.7590 C
61	C61	-3.2889	-1.8209	-0.8300 C
62	C62	-3.2175	-1.8263	-2.3783 C
63	C63	-3.7933	-3.1395	-2.9644 C
64	C64	-3.0954	-4.3846	-2.3741 C
65	C65	-3.1794	-4.3819	-0.8316 C
66	C66	-2.5961	-3.0759	-0.2387 C
67	C67	-3.1051	-0.3719	1.8061 C
68	C68	-3.0253	0.9718	2.5763 C
69	C69	-3.2019	0.7529	4.0982 C
70	C70	-4.5310	0.0318	4.4153 C
71	C71	-4.6513	-1.2868	3.6195 C

72	C72	-4.4640	-1.0624	2.0972 C
73	C73	-3.6442	1.1594	-0.9175 C
74	C74	-3.1949	2.6099	-0.6089 C
75	C75	-3.9455	3.6161	-1.5153 C
76	C76	-5.4788	3.4757	-1.3834 C
77	C77	-5.9302	2.0215	-1.6484 C
78	C78	-5.1770	1.0188	-0.7382 C
79	H79	-4.3506	-1.8508	-0.5444 H
80	H80	-2.1761	-1.7115	-2.7043 H
81	H81	-3.7773	-0.9770	-2.7917 H
82	H82	-3.6862	-3.1271	-4.0583 H
83	H83	-4.8730	-3.1929	-2.7494 H
84	H84	-2.0383	-4.3871	-2.6803 H
85	H85	-3.5502	-5.3009	-2.7770 H
86	H86	-4.2325	-4.4863	-0.5237 H
87	H87	-2.6391	-5.2461	-0.4188 H
88	H88	-1.5212	-3.0349	-0.4598 H
89	H89	-2.6964	-3.0951	0.8557 H
90	H90	-2.3143	-1.0270	2.2112 H
91	H91	-2.0742	1.4785	2.3814 H
92	H92	-3.8232	1.6412	2.2234 H
93	H93	-3.1608	1.7213	4.6167 H
94	H94	-2.3603	0.1521	4.4790 H
95	H95	-5.3725	0.6925	4.1523 H
96	H96	-4.6089	-0.1679	5.4936 H
97	H97	-3.8871	-1.9963	3.9756 H
98	H98	-5.6291	-1.7548	3.8047 H
99	H99	-5.2869	-0.4385	1.7232 H
100	H100	-4.5375	-2.0289	1.5858 H
101	H101	-3.4101	0.9817	-1.9786 H
102	H102	-3.3954	2.8564	0.4428 H
103	H103	-2.1172	2.7123	-0.7647 H
104	H104	-3.6500	3.4453	-2.5620 H
105	H105	-3.6342	4.6392	-1.2616 H
106	H106	-5.7850	3.7701	-0.3665 H
107	H107	-5.9845	4.1610	-2.0785 H

108 H108	-7.0141	1.9235	-1.4897 H
109 H109	-5.7375	1.7677	-2.7028 H
110 H110	-5.5125	-0.0024	-0.9631 H
111 H111	-5.4455	1.2250	0.3083 H

Table S6 Atomic coordinates of Mo-PCy_3-H_2 in optimized structure.

1 Mo1	-0.0037	-0.0520	-0.0152 Mo
2 P2	-2.6334	-0.1304	0.0192 P
3 O3	0.0043	0.1041	3.1930 O
4 C4	0.0026	0.0710	1.9983 C
5 C5	-3.4396	-1.8789	0.1972 C
6 C6	-3.0730	-2.5544	1.5432 C
7 C7	-3.7383	-3.9470	1.6726 C
8 C8	-3.3816	-4.8593	0.4783 C
9 C9	-3.7622	-4.1862	-0.8590 C
10 C10	-3.0946	-2.7964	-1.0042 C
11 C11	-3.4424	0.5032	-1.6308 C
12 C12	-3.1116	1.9843	-1.9441 C
13 C13	-3.5257	2.3486	-3.3909 C
14 C14	-5.0238	2.0624	-3.6401 C
15 C15	-5.3798	0.6017	-3.2827 C
16 C16	-4.9586	0.2487	-1.8333 C
17 C17	-3.4104	0.8034	1.5357 C
18 C18	-2.9259	2.2681	1.6821 C
19 C19	-3.3576	2.8572	3.0480 C
20 C20	-4.8866	2.7642	3.2521 C
21 C21	-5.3879	1.3149	3.0611 C
22 C22	-4.9511	0.7396	1.6901 C
23 H23	-4.5269	-1.7115	0.1915 H
24 H24	-1.9848	-2.6699	1.6154 H
25 H25	-3.3870	-1.9264	2.3882 H
26 H26	-3.4227	-4.4144	2.6163 H
27 H27	-4.8329	-3.8275	1.7252 H
28 H28	-2.3002	-5.0612	0.4867 H
29 H29	-3.8935	-5.8276	0.5749 H
30 H30	-4.8579	-4.0757	-0.9123 H

31 H31	-3.4642	-4.8232	-1.7040 H
32 H32	-2.0083	-2.9282	-1.0689 H
33 H33	-3.4186	-2.3361	-1.9474 H
34 H34	-2.9057	-0.1069	-2.3741 H
35 H35	-2.0392	2.1755	-1.8118 H
36 H36	-3.6495	2.6416	-1.2448 H
37 H37	-3.3049	3.4084	-3.5841 H
38 H38	-2.9180	1.7615	-4.0964 H
39 H39	-5.6313	2.7446	-3.0235 H
40 H40	-5.2800	2.2690	-4.6890 H
41 H41	-4.8696	-0.0783	-3.9829 H
42 H42	-6.4597	0.4335	-3.4048 H
43 H43	-5.5404	0.8662	-1.1358 H
44 H44	-5.2165	-0.7973	-1.6279 H
45 H45	-2.9697	0.2424	2.3749 H
46 H46	-3.3485	2.8867	0.8769 H
47 H47	-1.8343	2.3193	1.5938 H
48 H48	-2.8465	2.3063	3.8525 H
49 H49	-3.0286	3.9040	3.1198 H
50 H50	-5.3911	3.4203	2.5244 H
51 H51	-5.1584	3.1307	4.2522 H
52 H52	-6.4837	1.2778	3.1459 H
53 H53	-4.9835	0.6806	3.8655 H
54 H54	-5.3181	-0.2900	1.5930 H
55 H55	-5.4286	1.3287	0.8945 H
56 P56	2.6051	0.2446	-0.0344 P
57 O57	-0.0567	-0.3770	-3.2114 O
58 O58	0.2824	-3.1759	0.2287 O
59 C59	-0.0319	-0.2341	-2.0253 C
60 C60	0.1689	-1.9821	0.1362 C
61 C61	3.2250	2.0803	-0.1017 C
62 C62	2.8408	2.7950	-1.4215 C
63 C63	3.3714	4.2499	-1.4518 C
64 C64	2.8952	5.0590	-0.2249 C
65 C65	3.2785	4.3455	1.0907 C
66 C66	2.7412	2.8940	1.1257 C

67 C67	3.4764	-0.3951	1.5827 C
68 C68	3.4070	-1.9365	1.7322 C
69 C69	3.8452	-2.3702	3.1518 C
70 C70	5.2645	-1.8602	3.4875 C
71 C71	5.3689	-0.3314	3.2874 C
72 C72	4.9206	0.0953	1.8657 C
73 C73	3.4858	-0.5079	-1.5901 C
74 C74	3.1286	-1.9931	-1.8529 C
75 C75	3.6436	-2.4379	-3.2434 C
76 C76	5.1648	-2.2079	-3.3911 C
77 C77	5.5416	-0.7420	-3.0780 C
78 C78	5.0193	-0.3065	-1.6853 C
79 H79	4.3226	2.0308	-0.0602 H
80 H80	1.7463	2.8091	-1.5338 H
81 H81	3.2381	2.2492	-2.2873 H
82 H82	3.0470	4.7399	-2.3810 H
83 H83	4.4728	4.2335	-1.4685 H
84 H84	1.8004	5.1764	-0.2688 H
85 H85	3.3246	6.0706	-0.2480 H
86 H86	4.3757	4.3310	1.1890 H
87 H87	2.8893	4.9032	1.9544 H
88 H88	1.6419	2.9208	1.1419 H
89 H89	3.0537	2.4101	2.0601 H
90 H90	2.8249	0.0326	2.3605 H
91 H91	2.3968	-2.3044	1.5289 H
92 H92	4.0768	-2.4080	0.9979 H
93 H93	3.8064	-3.4660	3.2297 H
94 H94	3.1286	-1.9728	3.8873 H
95 H95	5.9946	-2.3621	2.8321 H
96 H96	5.5304	-2.1250	4.5209 H
97 H97	4.7348	0.1755	4.0320 H
98 H98	6.4007	0.0060	3.4650 H
99 H99	5.6147	-0.3331	1.1302 H
100 H100	4.9978	1.1861	1.7821 H
101 H101	3.0206	0.0737	-2.4020 H
102 H102	3.5812	-2.6323	-1.0826 H

103 H103	2.0466	-2.1439	-1.7952 H
104 H104	3.1095	-1.8724	-4.0228 H
105 H105	3.4036	-3.4990	-3.4008 H
106 H106	5.7016	-2.8748	-2.6973 H
107 H107	5.4932	-2.4742	-4.4060 H
108 H108	6.6329	-0.6118	-3.1216 H
109 H109	5.1103	-0.0831	-3.8483 H
110 H110	5.2991	0.7393	-1.5013 H
111 H111	5.5188	-0.9142	-0.9174 H
112 H112	0.2258	1.9198	-0.1958 H
113 H113	-0.5644	1.8552	-0.1796 H

Table S7 Atomic coordinates of Mo-$PiPr_3$ in optimized structure.

1 Mo1	-0.0132	0.0109	-0.1668 Mo
2 P2	-2.6015	-0.0406	0.1248 P
3 O3	-0.3766	3.0203	-1.2157 O
4 C4	-0.1949	1.9264	-0.7673 C
5 C5	-3.6326	-0.8632	-1.2841 C
6 C6	-3.2148	-2.3313	-1.5184 C
7 C7	-3.5168	-0.0505	-2.5948 C
8 C8	-3.4270	1.7077	0.2851 C
9 C9	-2.9287	2.4597	1.5411 C
10 C10	-4.9688	1.7717	0.1850 C
11 C11	-3.0701	-1.1015	1.6773 C
12 C12	-2.1644	-0.7630	2.8855 C
13 C13	-4.5587	-1.1195	2.0889 C
14 H14	-4.6779	-0.8448	-0.9433 H
15 H15	-2.1672	-2.3980	-1.8307 H
16 H16	-3.3478	-2.9586	-0.6288 H
17 H17	-2.4868	-0.0480	-2.9657 H
18 H18	-3.8419	0.9903	-2.4788 H
19 H19	-3.0129	2.2256	-0.5908 H
20 H20	-1.8375	2.4096	1.6441 H
21 H21	-3.3831	2.0605	2.4565 H
22 H22	-5.4588	1.3094	1.0478 H
23 H23	-5.3519	1.2925	-0.7224 H

24	H24	-2.7975	-2.1124	1.3431 H
25	H25	-2.3818	0.2296	3.2960 H
26	H26	-1.1004	-0.8006	2.6138 H
27	H27	-5.2263	-1.3257	1.2437 H
28	H28	-4.8625	-0.1685	2.5422 H
29	P29	2.5814	0.1514	0.1536 P
30	O30	0.1282	-0.6992	-3.1930 O
31	O31	-0.0894	-3.1577	0.3332 O
32	C32	0.0636	-0.4219	-2.0187 C
33	C33	-0.0259	-1.9707	0.1985 C
34	C34	3.3605	1.9197	0.0427 C
35	C35	3.3024	2.4907	-1.3918 C
36	C36	2.6878	2.8816	1.0490 C
37	C37	3.1346	-0.4105	1.9406 C
38	C38	3.0541	-1.9442	2.1270 C
39	C39	4.5024	0.1129	2.4421 C
40	C40	3.6287	-0.8150	-1.1634 C
41	C41	3.1390	-2.2615	-1.3976 C
42	C42	5.1592	-0.7806	-0.9459 C
43	H43	4.4153	1.8053	0.3249 H
44	H44	2.2776	2.5168	-1.7765 H
45	H45	3.9168	1.9142	-2.0932 H
46	H46	1.6372	3.0513	0.7900 H
47	H47	2.7297	2.5085	2.0804 H
48	H48	2.3537	0.0421	2.5723 H
49	H49	2.1138	-2.3659	1.7606 H
50	H50	3.8790	-2.4496	1.6103 H
51	H51	5.3317	-0.2638	1.8344 H
52	H52	4.5594	1.2060	2.4582 H
53	H53	3.3966	-0.2485	-2.0760 H
54	H54	3.3266	-2.9084	-0.5339 H
55	H55	2.0712	-2.2945	-1.6264 H
56	H56	5.5457	0.2328	-0.7855 H
57	H57	5.4569	-1.4026	-0.0930 H
58	H58	3.1960	3.8557	1.0270 H
59	H59	3.6831	3.5218	-1.3908 H

60	H60	4.6622	-0.2380	3.4720 H
61	H61	3.1390	-2.1866	3.1957 H
62	H62	-2.3237	-1.4978	3.6870 H
63	H63	-3.2057	3.5203	1.4695 H
64	H64	-5.2812	2.8256	0.1539 H
65	H65	-4.1488	-0.5116	-3.3666 H
66	H66	-3.8318	-2.7599	-2.3203 H
67	H67	-4.7219	-1.9069	2.8387 H
68	H68	3.6779	-2.6868	-2.2561 H
69	H69	5.6596	-1.1875	-1.8360 H

Table S8 Atomic coordinates of Mo-$PiPr_3$-H_2 in optimized structure.

1	Mo1	0.0067	0.0274	0.0112 Mo
2	P2	2.6341	0.0277	-0.0105 P
3	O3	-0.0263	0.8697	-3.0885 O
4	C4	-0.0119	0.5812	-1.9294 C
5	C5	3.4909	-1.6284	-0.5276 C
6	C6	3.1588	-2.0162	-1.9857 C
7	C7	3.1416	-2.7731	0.4502 C
8	C8	3.4211	0.3360	1.7439 C
9	C9	3.0846	1.7344	2.3098 C
10	C10	4.9332	0.0478	1.8969 C
11	C11	3.4074	1.2687	-1.2930 C
12	C12	2.8479	2.7037	-1.1644 C
13	C13	4.9512	1.3009	-1.3764 C
14	H14	4.5704	-1.4360	-0.4618 H
15	H15	2.0827	-2.1516	-2.1310 H
16	H16	3.5134	-1.2701	-2.7074 H
17	H17	2.0723	-3.0019	0.4325 H
18	H18	3.4252	-2.5426	1.4843 H
19	H19	2.8764	-0.4008	2.3508 H
20	H20	2.0165	1.9656	2.2316 H
21	H21	3.6497	2.5242	1.7995 H
22	H22	5.5471	0.7732	1.3529 H
23	H23	5.2105	-0.9562	1.5589 H
24	H24	3.0245	0.8588	-2.2384 H

25	H25	3.1853	3.1944	-0.2438 H
26	H26	1.7535	2.7177	-1.1845 H
27	H27	5.3973	0.3022	-1.4427 H
28	H28	5.3893	1.8157	-0.5134 H
29	P29	-2.6072	0.2235	0.0822 P
30	O30	0.0604	-0.9760	3.0632 O
31	O31	-0.1982	-2.9717	-0.9191 O
32	C32	0.0359	-0.5820	1.9357 C
33	C33	-0.1131	-1.8272	-0.5615 C
34	C34	-3.2837	1.9777	0.5571 C
35	C35	-2.9214	2.3683	2.0071 C
36	C36	-2.8054	3.0557	-0.4421 C
37	C37	-3.4714	-0.0732	-1.6375 C
38	C38	-3.3983	-1.5519	-2.0850 C
39	C39	-4.9152	0.4607	-1.7954 C
40	C40	-3.4645	-0.8846	1.4287 C
41	C41	-3.0529	-2.3722	1.3474 C
42	C42	-5.0021	-0.7562	1.5313 C
43	H43	-4.3768	1.9073	0.4865 H
44	H44	-1.8364	2.3538	2.1724 H
45	H45	-3.3816	1.7015	2.7455 H
46	H46	-1.7173	3.1863	-0.4022 H
47	H47	-3.0711	2.8160	-1.4783 H
48	H48	-2.8222	0.5061	-2.3087 H
49	H49	-2.4022	-1.9833	-1.9556 H
50	H50	-4.1160	-2.1718	-1.5334 H
51	H51	-5.6233	-0.0687	-1.1492 H
52	H52	-5.0002	1.5331	-1.5900 H
53	H53	-3.0238	-0.4789	2.3508 H
54	H54	-3.4798	-2.8685	0.4694 H
55	H55	-1.9682	-2.4983	1.3122 H
56	H56	-5.3452	0.2836	1.5858 H
57	H57	-5.5005	-1.2388	0.6824 H
58	H58	-0.2729	1.9091	0.6056 H
59	H59	0.5191	1.8682	0.5768 H
60	H60	-3.2658	4.0220	-0.1931 H

61	H61	-3.2763	3.3874	2.2149 H
62	H62	-5.3462	-1.2651	2.4430 H
63	H63	-5.2375	0.3022	-2.8347 H
64	H64	-3.6573	-1.6195	-3.1508 H
65	H65	-3.4232	-2.8964	2.2399 H
66	H66	3.2024	3.3089	-2.0107 H
67	H67	5.2531	1.8566	-2.2757 H
68	H68	3.3541	1.7718	3.3744 H
69	H69	5.2038	0.1198	2.9603 H
70	H70	3.6812	-3.6833	0.1531 H
71	H71	3.6489	-2.9692	-2.2291 H

Table S9 Atomic coordinates of Mo-PMe_3 in optimized structure.

1	Mo1	-0.0000	0.0001	0.2078 Mo
2	C2	-0.0001	-2.0419	0.1856 C
3	C3	0.0000	2.0421	0.1860 C
4	C4	-0.0000	0.0002	-1.7159 C
5	P5	2.4907	-0.0001	0.2436 P
6	P6	-2.4907	-0.0000	0.2435 P
7	O7	-0.0000	-3.2146	0.1309 O
8	O8	0.0004	0.0006	-2.9019 O
9	O9	0.0000	3.2147	0.1315 O
10	C10	3.3364	-1.4349	-0.5864 C
11	H11	4.4331	-1.3344	-0.5418 H
12	H12	3.0337	-2.3721	-0.0964 H
13	H13	3.0159	-1.4766	-1.6378 H
14	C14	3.3475	0.0003	1.9056 C
15	H15	4.4439	-0.0007	1.7908 H
16	H16	3.0474	0.8942	2.4739 H
17	H17	3.0459	-0.8922	2.4752 H
18	C18	3.3367	1.4341	-0.5872 C
19	H19	3.0329	2.3718	-0.0989 H
20	H20	4.4334	1.3343	-0.5411 H
21	H21	3.0175	1.4742	-1.6391 H
22	C22	-3.3476	-0.0004	1.9055 C
23	H23	-4.4440	-0.0009	1.7907 H

24	H24	-3.0464	-0.8935	2.4744 H
25	H25	-3.0472	0.8929	2.4744 H
26	C26	-3.3365	-1.4345	-0.5871 C
27	H27	-3.0335	-2.3719	-0.0978 H
28	H28	-4.4332	-1.3342	-0.5422 H
29	H29	-3.0162	-1.4756	-1.6387 H
30	C30	-3.3367	1.4345	-0.5867 C
31	H31	-4.4334	1.3344	-0.5411 H
32	H32	-3.0333	2.3719	-0.0975 H
33	H33	-3.0170	1.4754	-1.6384 H

Table S10 Atomic coordinates of Mo-PMe_3-H_2 in optimized structure.

1	Mo1	-0.0000	0.0001	-0.2874 Mo
2	C2	-0.0002	-2.0382	-0.3074 C
3	C3	0.0004	2.0383	-0.3078 C
4	C4	-0.0001	0.0004	1.6826 C
5	P5	-2.4701	0.0000	-0.1528 P
6	P6	2.4700	-0.0002	-0.1528 P
7	O7	-0.0002	-3.1937	-0.2961 O
8	O8	-0.0001	0.0007	2.8455 O
9	O9	0.0007	3.1938	-0.2967 O
10	C10	-3.2156	-1.4217	0.7504 C
11	H11	-4.3061	-1.3207	0.8353 H
12	H12	-2.9766	-2.3536	0.2236 H
13	H13	-2.7760	-1.4762	1.7540 H
14	C14	-3.4683	-0.0019	-1.7046 C
15	H15	-4.5470	-0.0017	-1.4965 H
16	H16	-3.2149	0.8871	-2.2964 H
17	H17	-3.2148	-0.8922	-2.2942 H
18	C18	-3.2161	1.4234	0.7474 C
19	H19	-2.9771	2.3544	0.2188 H
20	H20	-4.3066	1.3224	0.8321 H
21	H21	-2.7768	1.4799	1.7510 H
22	C22	3.4683	-0.0004	-1.7046 C
23	H23	4.5470	-0.0006	-1.4964 H
24	H24	3.2147	-0.8901	-2.2953 H

25 H25	3.2149	0.8892	-2.2954 H
26 C26	3.2156	-1.4228	0.7490 C
27 H27	2.9766	-2.3543	0.2213 H
28 H28	4.3061	-1.3219	0.8338 H
29 H29	2.7761	-1.4782	1.7526 H
30 C30	3.2160	1.4223	0.7488 C
31 H31	4.3064	1.3212	0.8336 H
32 H32	2.9771	2.3537	0.2210 H
33 H33	2.7765	1.4780	1.7524 H
34 H34	0.4145	-0.0004	-2.1730 H
35 H35	-0.4149	0.0004	-2.1729 H

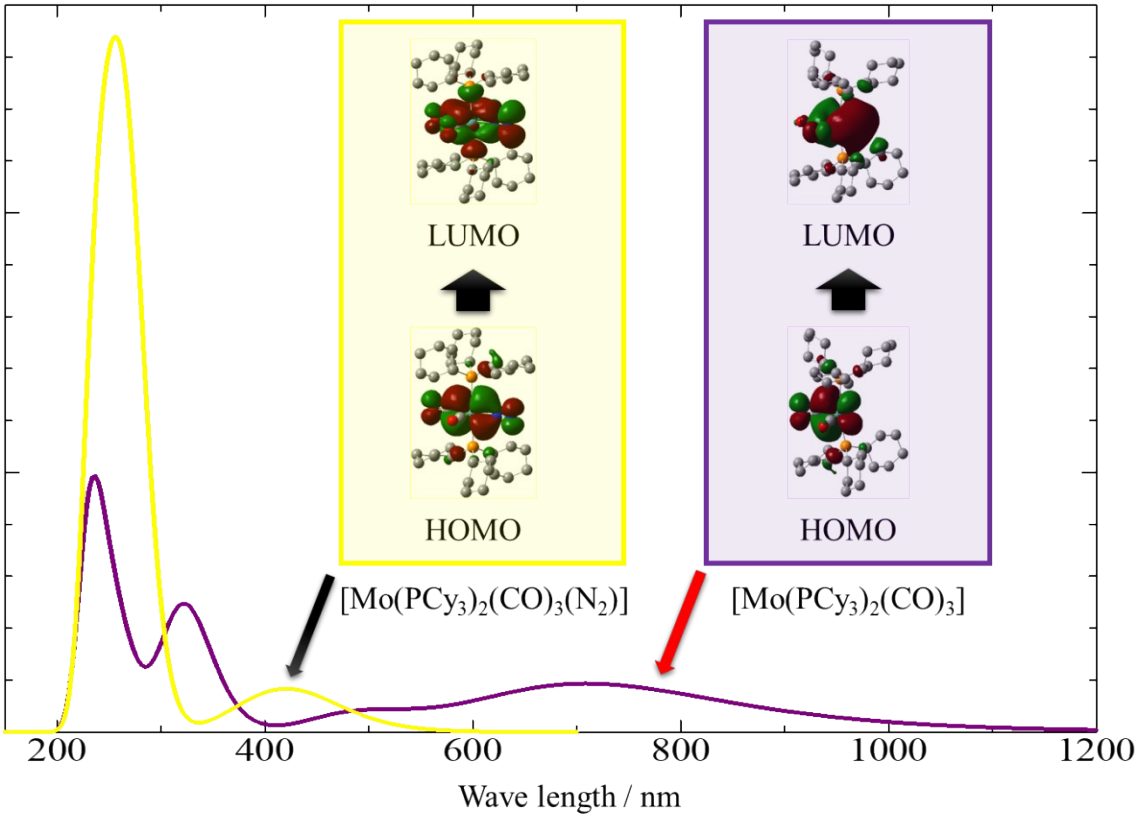

Fig. S16 Absorption spectra of $[Mo(PCy_3)_2(CO)_3(N_2)]$ and $[Mo(PCy_3)_2(CO)_3]$ by time dependent (TD)-DFT calculation.

References

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