Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

A Normal Equilibrium Isotope Effect For Oxidative Addition of H_2 to (η^6–Anthracene)Mo(PMe_3)$_3$

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Experimental data; computational data for calculation of equilibrium isotope effects.

Experimental Details

General Considerations

All manipulations were performed using a combination of dry glovebox, high vacuum, and Schlenk techniques under an argon atmosphere.[i] Solvents were purified and degassed by standard procedures. (η^6–AnH)Mo(PMe_3)$_3$ (AnH = anthracene) was prepared by the literature method.[ii] ^1H NMR spectra were measured on Bruker 300wb DRX, Bruker Avance 400 DRX and Bruker Avance 500 DMX spectrometers.

Determination of the Equilibrium Isotope Effects for Oxidative Addition of H_2/D_2 to (η^6-Anthracene)Mo(PMe_3)$_3$

In a typical experiment, a solution of (η^6–AnH)Mo(PMe_3)$_3$ (2 mg) in toluene-d_8 (0.5 mL) in a J-Young NMR tube was saturated with H_2 (1 atm at 24°C). The sample was placed in a constant temperature bath and removed periodically to monitor the conversion to a mixture with (η^4–AnH)Mo(PMe_3)$_3H_2$ by ^1H NMR spectroscopy. In each case, the equilibrium was quenched by placing the NMR tube immediately in a dry ice-acetone bath at –78°C prior to recording the ^1H NMR spectrum at 10°C. Analogous experiments were performed by saturating a solution of (η^6–AnH)Mo(PMe_3)$_3$ (2 mg) in toluene-d_8 (0.5 mL) with different pressures of H_2 (0.4, 0.6, and 0.8 atm respectively). The equilibrium constant at each temperature, $K = [(\eta^4\text{–AnH})\text{Mo}(\text{PMe}_3)_3\text{H}_2]/[(\eta^6\text{–AnH})\text{Mo}(\text{PMe}_3)_3][\text{H}_2]$ was determined by using ^1H NMR spectroscopy to give the ratio $[(\eta^4\text{–AnH})\text{Mo}(\text{PMe}_3)_3\text{H}_2]/[(\eta^6\text{–AnH})\text{Mo}(\text{PMe}_3)_3]$ while the molar concentration of H_2 was obtained by using a combination of Henry's law and the ideal gas law by a method similar to that described previously.[iii]

In brief, the calculation of equilibrium constants requires knowledge of the total amount of H_2 initially present in the closed system, which is the sum of that in the gas phase above the solution and that in solution. The number of moles of H_2 in the gas phase is determined by using the ideal gas law and knowledge of the partial pressure of H_2 (*i.e.* the total pressure minus the partial pressure of the solvent[iv]) and the volume of the headspace above the solution, while the number of moles of H_2 initially in solution is calculated from the solubility expression given by Clever,[v] adjusting for the partial pressure of H_2 according to Henry's law.[vi]

At equilibrium, the concentration of H_2 is determined from the total number of moles of H_2 present at equilibrium which is obtained by using the ratio $[(\eta^4\text{–AnH})Mo(PMe_3)_3H_2]/[(\eta^6\text{–AnH})Mo(PMe_3)_3]$ to indicate how much of the H_2 initially present has been consumed. The concentration of H_2 in solution at equilibrium at each temperature is obtained by solving the two simultaneous equations that relate the partial pressure of H_2 in the gas phase to *(i)* the number of moles of H_2 in the gas phase *via* the ideal gas law, and *(ii)* the number of moles of H_2 in solution *via* Henry's law.

The equilibrium constant (K_H) was measured as a function of temperature and ΔH and ΔS were determined from a van't Hoff plot over the temperature range 30–90°C (Table 1). An analogous procedure was used to determine K_D as a function of temperature for the corresponding reaction between $(\eta^6\text{–AnH})Mo(PMe_3)_3$ and D_2.[vii] To minimize systematic errors, the deuterium equilibrium isotope effect was determined at each temperature by evaluating the ratio K_H/K_D for each pair of samples prepared with the same initial partial pressures of H_2 and D_2. The equilibrium isotope effects listed in Table S1 correspond to an average of the values for all pairs.

Table S1. Equilibrium Constant and Equilibrium Isotope Effect Data for Oxidative Addition of H_2 and D_2 to (η^6-AnH)Mo(PMe_3)$_3$. The EIEs correspond to the average of the K_H/K_D values for pairs of samples prepared with similar partial pressures of H_2 and D_2.

Temp/˚C	K_H/mol L^{-1} [(a)]	K_D/mol L^{-1} [(b)]	EIE [(c)]
30	$1.59(5) \times 10^4$	$1.60(6) \times 10^4$	0.99(1)
40	$8.18(42) \times 10^3$	$7.95(53) \times 10^3$	1.03(2)
50	$4.07(27) \times 10^3$	$3.80(30) \times 10^3$	1.07(3)
60	$2.21(18) \times 10^3$	$1.97(21) \times 10^3$	1.13(5)
70	$1.18(13) \times 10^3$	$9.9(11) \times 10^2$	1.20(4)
80	$6.46(90) \times 10^2$	$5.07(60) \times 10^2$	1.27(8)
90	$3.50(68) \times 10^2$	$2.84(69) \times 10^2$	1.25(9)

(a) $\Delta H = -13.9(2)$ kcal mol^{-1}, $\Delta S = -26.5(6)$ e.u..

(b) $\Delta H = -14.8(2)$ kcal/mol, $\Delta S = -29.5(6)$ e.u..

(c) To minimize systematic errors, the deuterium equilibrium isotope effect was determined at each temperature by evaluating the ratio K_H/K_D for each pair of samples prepared with the same initial partial pressures of H_2 and D_2, rather than comparing the average values of K_H and K_D, each of which was measured by evaluating samples prepared with different concentrations.

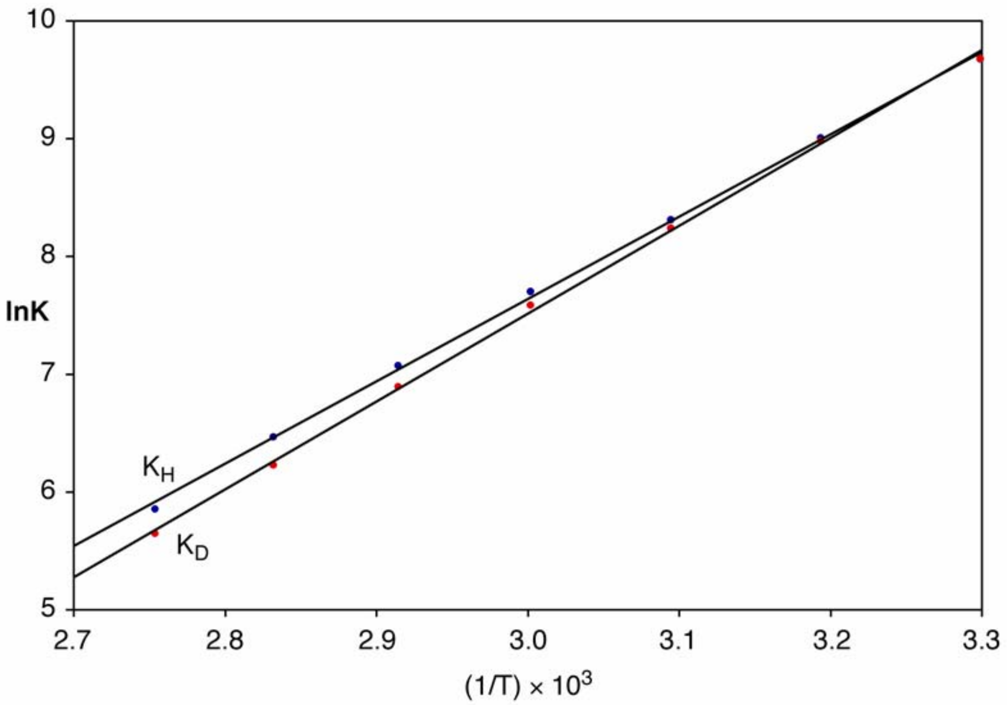

Figure S1. van't Hoff plot for Oxidative Addition of H_2 and D_2 to (η^6-AnH)Mo(PMe_3)$_3$

Computational Details and Calculation of Equilibrium Isotope Effects

All calculations were carried out using DFT as implemented in the Jaguar 4.0, 4.1 and 6.0 suites of *ab initio* quantum chemistry programs.[viii] Geometry optimizations and frequency calculations were performed with the B3LYP density functional[ix] and the 6-31G** basis set for C, H, N, O, Si, and P, while Mo and W were represented using the Los Alamos LACVP basis set[x] that includes relativistic effective core potentials. For (η^4–AnH)Mo(PH_3)$_3$$H_2$, the geometry used for the frequency calculations of (η^4–AnH)Mo(PH_3)$_3$$H^*_2$ (H^* = H, D) was taken from the literature;[ii,xi] the geometries and frequencies of Ir(PH_3)$_2$(CO)H^*_2Cl,[xii] [H_2Si(C_5H_4)$_2$]WH^*_2,[xiii] and W(CO)$_5$$H^*_2$[xiv] were also taken from the literature.

The equilibrium isotope effects (EIEs) were determined by the expression EIE = K_H/K_D = SYM • MMI • EXC • ZPE where SYM is the symmetry factor,[xv] MMI is the mass-moment of inertia term, EXC is the excitation term, and ZPE is the zero point energy term (Scheme S1).[xvi] The SYM term is determined by the symmetry number ratio of the species involved and is unity for oxidative addition of H_2/D_2 to L_nM; the MMI term is determined by their structures (*i.e.* their masses and moments of inertia);[xvii] and the EXC and ZPE terms are determined by their vibrational frequencies. The EIE was determined at 1 degree intervals over the range 0 – 3000 K.

$$\mathrm{EIE} = K_H/K_D = \mathrm{SYM} \bullet \mathrm{MMI} \bullet \mathrm{EXC} \bullet \mathrm{ZPE}$$

$$\mathrm{SYM} = \frac{\{(\sigma n)^R{}_H/(\sigma n)^R{}_D\}}{\{(\sigma n)^P{}_H/(\sigma n)^P{}_D\}} \qquad \mathrm{MMI} = \frac{(M^P{}_H/M^R{}_H)^{3/2}(I^P{}_H/I^R{}_H)^{1/2}}{(M^P{}_D/M^R{}_D)^{3/2}(I^P{}_D/I^R{}_D)^{1/2}}$$

$$\mathrm{EXC} = \frac{\Pi\,\{[1-\exp(-u^R{}_{iH})]/[1-\exp(-u^R{}_{iD})]\}}{\Pi\,\{[1-\exp(-u^P{}_{iH})]/[1-\exp(-u^P{}_{iD})]\}} \qquad \mathrm{ZPE} = \frac{\exp\{\Sigma\,(u^R{}_{iH}-u^R{}_{iD})/2\}}{\exp\{\Sigma\,(u^P{}_{iH}-u^P{}_{iD})/2\}}$$

where $u_{iX} = h\nu_{iX}/k_BT$, $R = H^*_2$, and $P = L_nMH^*_2$ ($H^* = H, D$)

Scheme S1. Calculation of EIEs.

Cartesian Coordinated for Geometry Optimized Structures

(η^4–AnH)Mo(PH_3)$_3H_2$

atom	x	y	z
Mo1	-0.01203	0.190553	0.223757
P2	-2.35893	0.237951	0.938487
P3	2.331904	0.69204	0.741411
P4	0.162514	-2.09281	1.104067
C5	2.893721	-0.29308	-3.06816
C6	2.260459	2.440152	-2.83993
C7	3.799929	0.673289	-3.60449
C8	5.014507	0.304427	-4.23582
H9	5.259278	-0.75196	-4.32067
C10	5.876332	1.261599	-4.73796
H11	6.801915	0.960939	-5.22125
C12	5.556692	2.633867	-4.62495
H13	6.237733	3.381573	-5.02222
C14	4.38157	3.024215	-4.01077
H15	4.134097	4.079527	-3.92071
C16	3.476924	2.066028	-3.48774
C17	1.404564	1.489235	-2.33355
C18	0.147973	1.782308	-1.62396
H19	-0.07149	2.826103	-1.42292

C20	-0.95044	0.889384	-1.75255
H21	-1.97628	1.241937	-1.76617
C22	-0.63935	-0.50148	-1.855
H23	-1.41276	-1.25183	-1.97525
C24	0.760606	-0.81928	-1.81348
H25	1.030787	-1.87295	-1.81259
C26	1.726072	0.093149	-2.45132
H27	0.012369	0.185897	1.962877
H28	-0.11597	1.728124	0.947288
H29	-3.40783	-0.05487	0.025319
H30	-2.82603	-0.59985	1.985425
H31	-2.92345	1.436827	1.444391
H32	3.316194	0.696376	-0.28203
H33	2.651527	1.94255	1.32069
H34	3.046642	-0.10604	1.675111
H35	1.340198	-2.54991	1.767666
H36	-0.75447	-2.58201	2.077022
H37	0.051408	-3.18785	0.194505
H38	3.145981	-1.34851	-3.14982
H39	2.01947	3.497054	-2.74693

$W(PH_3)_4I_2H_2$

atom	x	y	z
W1	0	0	0.911053
I2	-1.97333	0	-1.32427
I3	1.973334	0	-1.32427
P4	2.237027	0	1.925073
P5	-2.23703	0	1.925073
P6	0	2.434724	0.466404
P7	0	-2.43472	0.466404
H8	0	0.894016	2.364558
H9	0	-0.89402	2.364558
H10	2.285243	0	3.341769
H11	3.131439	1.069418	1.687589
H12	3.131439	-1.06942	1.687589
H13	-2.28524	0	3.341769
H14	-3.13144	-1.06942	1.687589
H15	-3.13144	1.069418	1.687589
H16	1.066238	3.234284	0.951239
H17	-1.06624	3.234284	0.951239
H18	0	2.863603	-0.87464
H19	1.066238	-3.23428	0.951239
H20	0	-2.8636	-0.87464

H21	-1.06624	-3.23428	0.951239

$Mo(CO)_5H_2$

atom	**x**	**y**	**z**
H1	-1.42028	-0.91131	0.403994
C2	-1.32614	1.34585	-1.06939
C3	1.494009	0.577417	-1.44163
Mo4	-0.03057	0.029091	-0.12568
H5	0.970518	1.361878	0.434422
C6	1.233556	-1.27109	0.881451
C7	-0.56431	-1.50655	-1.43834
C8	-0.70383	0.730654	1.687352
O9	-2.04674	2.073963	-1.59079
O10	2.341342	0.922657	-2.13195
O11	1.932452	-1.99124	1.44161
O12	-1.07953	1.121964	2.69654
O13	-0.89346	-2.36748	-2.11901

H_2

atom	x	y	z
H1	0	0	0.371283125
H2	0	0	-0.371283125

Vibrational Frequencies

Frequencies (cm^{-1})
(η^4–AnH)Mo(PH_3)$_3H_2$

60.91

63.26

86.69

97.3

104.45

109.88

132.73

142.35

148.69

153.13

172.95

196.01

247.79

249.02

265.15

286.4

292.27

316.94

323.7

362.37

380.24

398.55

456.08

486.25

493.8

500.98

523

524.33

534.15

549.41

563.28

569.13

580.75

596.24

601.6

635.35

642.77

682.84

740.7

747.41

762.89

770.98

775.48

807.73

825.34

827.25

846.47

865.58

877.57

883.83

891.55

906.35

910.76

939.98

951.05

982.75

983.92

1033.01

1050.83

1053.13

1065.18

1066.11

1084.83

1126.29

1135.11

1137.76

1142.39

1147.01

1153.41

1162.36

1167.09

1179.48

1191.18

1204.39

1265.33

1272.29

1286.53

1320.1

1371.42

1378.28

1393.19

1444.71

1462.82

1469.06

1506.99

1511.59

1553.38

1624.57

1655.11

1666.75

1755.04

1863.1

2352.1

2366.87

2383.53

2399.49

2401.63

2403.47

2411.5

2419.89

2448.02

3160.75

3165.02

3167.34

3168.46

3172.19

3185.45

3190.57

3199.09

3202.26

3214.01

Frequencies (cm^{-1})
(η^4–AnH)Mo(PH_3)$_3D_2$

60.8

63.07

86.68

97.2

104.19

109.73

132.65

142.14

148.57

152.73

172.28

195.69

247.37

247.69

265.02

282.52

286.73

315.49

320.78

361.03

378.73

398.34

419.35

437.4

481.48

492.1

501.16

515.73

527.92

543.17

550.15

562.47

564.87

580.58

585.12

598.98

604.69

624.7

637.48

640.69

680.1

746.11

762.99

770.55

775.48

821.97

825.74

846.44

865.64

880.68

891.31

906.28

910.25

937.29

951.03

982.6

983.88

1032.87

1050.82

1052.9

1065.07

1065.9

1084.61

1126.24

1134.84

1137.51

1142.25

1147.00

1153.23

1162.17

1165.66

1179.46

1191.16

1204.34

1249.35

1265.38

1272.28

1286.53

1320.04

1326.45

1371.42

1378.37

1393.19

1444.72

1462.95

1469.03

1506.94

1511.56

1553.38

1624.57

1655.12

1666.77

2352.06

2366.73

2383.45

2399.47

2401.61

2403.4

2411.5

2419.78

2447.94

3160.75

3165.02

3167.34

3168.46

3172.19

3185.45

3190.56

3199.09

3202.25

3214.01

Frequencies (cm^{-1})

$W(PH_3)_4I_2H_2$

10.79

66.61

77.63

79.89

82.65

106.00

109.44

114.53

128.11

145.46

155.00

163.25

165.15

241.43

245.31

280.36

284.73

293.05

316.48

504.32

550.40

564.02

569.96

588.14

599.75

625.16

626.00

687.03

884.75

889.93

1045.51

1052.52

1069.55

1076.90

1096.34

1128.80

1132.64

1136.87

1138.28

1139.47

1140.37

1147.64

1149.03

1918.19

1931.57

2420.05

2421.41

2422.67

2424.43

2427.83

2430.90

2443.44

2444.04

2444.42

2447.29

2502.80

2504.27

Frequencies (cm^{-1})
$W(PH_3)_4I_2D_2$
10.91
66.59
77.57
79.81
82.58
105.71
109.41
114.44
127.98
145.37
154.64
163.24
165.15
240.80
244.25
280.33
281.63
292.97
316.44
437.67
535.83

550.43

561.65

568.34

570.61

602.84

621.14

625.04

662.04

668.99

767.49

1045.46

1055.91

1068.92

1091.25

1128.79

1132.23

1136.82

1138.26

1139.38

1140.05

1147.52

1148.20

1359.22

1372.92
2420.05
2421.39
2422.65
2424.42
2427.81
2430.65
2443.37
2444.02
2444.42
2447.27
2502.73
2504.20

Frequencies (cm^{-1})
Mo(CO)$_5$H$_2$
55.99
61.23
76.04
82.77
88.54
94.77

98.74

286.06

328.47

347.07

352.17

372.61

374.53

384.93

404.42

432.04

440.18

457.45

468.83

507.42

535.99

568.07

572.29

590.59

669.34

759.52

1711.86

1732.83

2082.83

2106.88
2128.6
2129.37
2188.91

Frequencies (cm^{-1})
Mo(CO)$_5$D$_2$
55.42
61.22
76.03
82.31
88.54
94.69
98.45
234.23
296.29
301.58
319.93
369.44
372.38
381.94
384.56

403.54

408.12

449.67

464.43

486.72

501.54

507.4

544.32

589.14

609.56

629.56

1225.72

1231.94

2082.74

2106.5

2127.28

2128.61

2188.86

Frequencies (cm^{-1})

H_2

4469.80

Frequencies (cm^{-1})

D_2

3161.92

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(v) Mole fraction solubility of H_2 in toluene at 1 atmosphere partial pressure of H_2: $\ln x = -6.0373 - 603.07/(T/K)$. See: Clever, H. L. in *Solubility Data Series*, Young, C. L., Ed.; Pergamon Press: Oxford, 1981; Volume 5/6: Hydrogen and Deuterium, p 169.

(vi) According to Henry's law, $p(H_2) = k\bullet x(H_2)$. The proportionality constant may be determined at a given temperature from the solubility expression listed in reference v for 1 atmosphere partial pressure..

(vii) Mole fraction solubility of D_2 in toluene: $\ln x = -6.0781 - 580.52/(T/K)$. See: Clever, H. L. in *Solubility Data Series*, Young, C. L., Ed.; Pergamon Press: Oxford, 1981; Volume 5/6: Hydrogen and Deuterium, p 288.

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(xi) The most stable geometry of (η^4–AnH)Mo(PH_3)$_3$$H_2$ was used in the computation of deuterium equilibrium isotope effect for oxidative addition of dihydrogen to (η^6–AnH)Mo(PH_3)$_3$ reported here. However, an analogous calculation to give (η^4–AnH)Mo(PH_3)$_3$$H_2$ with the second most stable geometry indicates that the EIE has a similar temperature dependence.

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