

Supporting information

EPR detection and characterisation of a paramagnetic Mo(III) dihydride intermediate involved in electrocatalytic hydrogen evolution

Christopher Prior,[†] Lee R. Webster,[†] Saad K. Ibrahim, Joseph A Wright, Ali F. Alghamdi, Vasily S. Oganessian^{*†} and Christopher J. Pickett^{*†}

Energy Materials Laboratory, School of Chemistry, University of East Anglia, Norwich Research Park, Norwich NR4 7TJ, United Kingdom

Synthesis of the complexes $[\text{MH}_2(\text{O}_2\text{CR})(\text{dppe})_2][\text{BPh}_4]$ ($\text{M} = \text{Mo}, \text{W}$) ($\text{R} = \text{CF}_3, \text{H}$)

All manipulations were carried out under and argon atmosphere using dry solvents. The synthetic methodology first reported by Ito was adopted whereby $[\text{MH}_4(\text{dppe})_2]$ (1 mol) was stirred for 6 h ($\text{M} = \text{Mo}$) or 20 h ($\text{M} = \text{W}$) with the appropriate neat carboxylic acid. Removal of the acid under vacuum, dissolution in ethanol and subsequent filtration into ethanol containing $\text{Na}[\text{BPh}_4]$ precipitated each complex as a purple solid which was isolated by filtration, washed with EtOH, dried and re-crystallised from tetrahydrofuran. Yields were typically 55–65%. Table S1 shows selected spectroscopic data and Table S2 summarises analytical data.

Table S1 Spectroscopic data

Complex	IR $\nu(\text{OCO}) \text{ cm}^{-1}$	IR $\nu(\text{M-H}) \text{ cm}^{-1}$	$^1\text{H-NMR}$ $\Delta(\text{M-H})$ ppm CD_2Cl_2	$^{31}\text{P-NMR}$ Chemical shift data
$[\text{WH}_2(\text{HCOO})(\text{dppe})_2][\text{BPh}_4]$	1450 s, 1409 b	1861 s	-0.95	-54.4, -48.8
$[\text{WH}_2(\text{CF}_3\text{COO})(\text{dppe})_2][\text{BPh}_4]$	1464 s, 1410 b	1887 w, br	-0.80	-53.23, -47.3
$[\text{MoH}_2(\text{HCOO})(\text{dppe})_2][\text{BPh}_4]$	1433 s, 1402 b	1889 w, br	-4.1	-76.0, -57.5
$[\text{MoH}_2(\text{CF}_3\text{COO})(\text{dppe})_2][\text{BPh}_4]$	1435 s, 1403 b	1884 w, br	-4.18	-76.5, -54.5

Table S2 Elemental analysis

Complex		% Calculated	% Found
$[\text{WH}_2(\text{HCOO})(\text{dppe})_2][\text{BPh}_4]$	C	68.66	68.61
	H	5.31	5.34
$[\text{WH}_2(\text{CF}_3\text{COO})(\text{dppe})_2][\text{BPh}_4]$	C	66.21	66.10
	H	4.99	4.90
$[\text{MoH}_2(\text{HCOO})(\text{dppe})_2][\text{BPh}_4]$	C	73.46	73.46
	H	5.68	5.71
$[\text{MoH}_2(\text{CF}_3\text{COO})(\text{dppe})_2][\text{BPh}_4]$	C	70.6	70.55
	H	5.32	5.30

X-ray crystallographic data

For each sample, crystals were suspended in oil, and one was mounted on a glass fibre and fixed in the cold nitrogen stream of the diffractometer. Data were collected using Mo-K α ($\lambda = 0.71073 \text{ \AA}$) radiation using a Bruker–Nonius KappaCCD diffractometer equipped with a Bruker–Nonius FR591 molybdenum rotating anode with confocal mirrors, and were processed using DENZO and COLLECT.¹ Structures were determined a dual-space approach in SHELXT² and refined by full-matrix least-squares methods on F^2 in SHELXL.³

Non-hydrogen atoms were refined with anisotropic thermal parameters. Metal-bound hydrogen atoms were located in the Fourier difference map and refined with the M–H distances equal; in the tungsten case the H···H distance was restrained to $1.24(2) \text{ \AA}$. All other hydrogen atoms were included in idealized positions and their U_{iso} values were set to ride on the U_{eq} values of the parent atom. In both systems the BPh₄[−] ligand was disordered and was refined with the geometry of both components restrained to the same values. In the tungsten system one dppe was also disordered and the two positions were restrained to the same geometric values.

CCDC 1407344 and 1407345 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for [(H)₂Mo(dppe)₂(O₂CH)][BPh₄]: C₅₃H₅₁MoO₂P₄, C₂₄H₂₀B, $M = 1259.0$, Monoclinic, space group $P2_1/n$, $a = 17.4817(5) \text{ \AA}$, $b = 20.7047(5) \text{ \AA}$, $c = 17.5343(5) \text{ \AA}$, $\beta = 93.3380(10)^\circ$, $V = 6335.8(3) \text{ \AA}^3$, $Z = 4$, $D_c = 1.320 \text{ g cm}^{-3}$, $F(000) = 2624$, $T = 120(2) \text{ K}$, $\mu(\text{Mo-K}\alpha) = 0.356 \text{ mm}^{-1}$, $\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$. Total no. of reflections recorded, to $\theta_{\text{max}} = 25.0^\circ$, was 50 365 of which 11 116 were unique ($R_{\text{int}} = 0.095$); 7278 were 'observed' with $I > 2\sigma_I$. At the conclusion of the refinement, $wR_2 = 0.176$ for all 11 116 reflections; for the 'observed' data only, $R_1 = 0.089$.

Crystal data for [(H)₂W(dppe)₂(O₂CH)][BPh₄]: C₅₃H₅₁O₂P₄W, C₂₄H₂₀B, $M = 1346.9$,

Monoclinic, space group $P2_1/n$, $a = 17.4968(6) \text{ \AA}$, $b = 20.7324(8) \text{ \AA}$, $c = 17.5670(7) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 93.337(2)^\circ$, $\gamma = 90^\circ$, $V = 6361.6(4) \text{ \AA}^3$, $Z = 4$, $D_c = 1.406 \text{ g cm}^{-3}$, $F(000) = 2752$, $T = 120(2) \text{ K}$, $\mu(\text{Mo-K}\alpha) = 1.964 \text{ mm}^{-1}$, $\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$. Total no. of reflections recorded, to $\theta_{\text{max}} = 25.0^\circ$, was 44 369 of which 11159 were unique ($R_{\text{int}} = 0.113$); 6935 were 'observed' with $I > 2\sigma_I$. At the conclusion of the refinement, $wR_2 = 0.201$ for all 11 159 reflections; for the 'observed' data only, $R_1 = 0.098$.

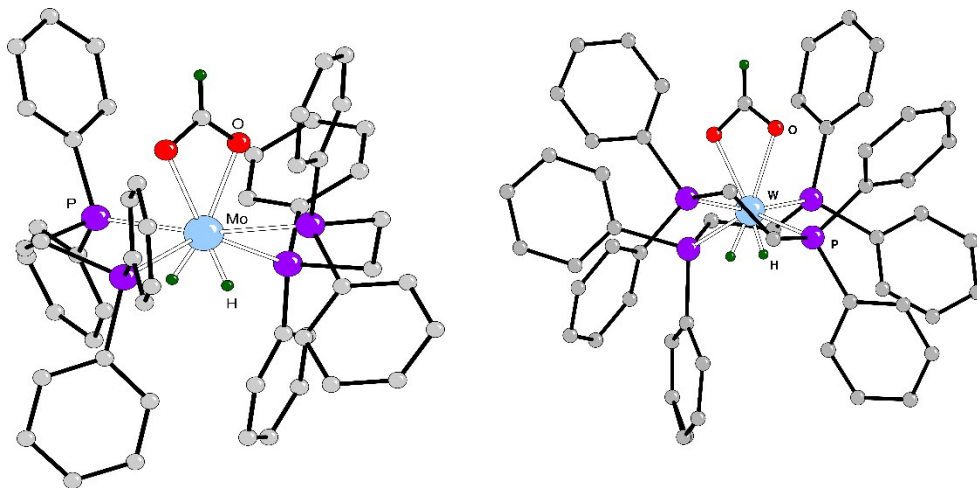


Figure S1. ORTEP representations of the cations of $[\text{MoH}_2(\text{O}_2\text{CH})(\text{dppe})_2]^+$ (left) and $[\text{WH}_2(\text{O}_2\text{CH})(\text{dppe})_2]^+$ (right); hydrogen atoms not bound to the metal or formate ligand have been omitted for clarity.

Electrochemical measurements and simulation.

All measurements were made under an atmosphere of argon at a vitreous carbon electrode in the toluene electrolyte at 303 K using an Autolab potentiostat type PGSTAT30. An Ag/ AgCl reference and a Pt counter electrode were employed. Table S3 shows the parameters obtained by digital simulation of the experimental cyclic voltammetric data for the cyclic voltammetry of the set of Mo and W complexes studied in the toluene electrolyte.

Table S3 Electrochemical simulation parameters

M	R	E^0 / V	α / eV	$k_s / 10^{-4} \text{ cm s}^{-1}$	$D / 10^{-7} \text{ cm}^2 \text{ s}$	$C / \text{ mM}$
Mo	H	-0.94	0.50	2	3	1.11
W	H	-1.09	0.55	0.2	3	1.13
Mo	CH ₃	-1.10	0.50	1	3	1.12
W	CH ₃	-1.27	0.62	0.2	3	1.10
W	CF ₃	-0.76	0.50	2	3	0.60
Mo ^a	CH ₃	-1.15	0.50	6	10	1.11

Digital simulation of electrochemical values for complexes $[\text{MH}_2(\eta^2\text{-O}_2\text{CR})(\text{dppe})_2]^+$ in 1:3 molar ratio $[\text{NBu}_4][\text{BF}_4]$ -toluene electrolyte (a = in 0.1 M $[\text{Bu}_4\text{N}][\text{BF}_4]$ -MeCN electrolyte) at 303 K at a vitreous carbon electrode ($A = 0.071 \text{ cm}^2$) (E^0 = potential, α = electron transfer coefficient, k_s = electron transfer rate constant, D = diffusion coefficient, C = concentration).

EPR experimental measurements and simulation of spectra

Room temperature EPR spectra were measured using an X-band (9.5 GHz) Bruker EMX spectrometer fitted with the ER4102ST resonator. The following conditions were used: microwave frequency of 9.562 GHz; microwave power of 2 mW; modulation frequency of 100 kHz; modulation amplitude of 1.0 G. The magnetic field was calibrated using the signal of Mn(II) ion doped in MgO powder. The reduction of the dihydride A^+ ($M = \text{Mo}$; $R = \text{Me}$) was carried out in the cavity of an EPR spectrometer by controlled-potential electrolysis at a platinum wire working electrode in tetrahydrofuran containing 0.2M $[\text{NBu}_4][\text{BF}_4]$ as the supporting electrolyte under an atmosphere of argon.

A computational model assuming a fast rotational motional regime has been applied for the simulation of EPR spectra.⁴ Simulation and fitting of EPR spectra were performed using Easyspin.⁵

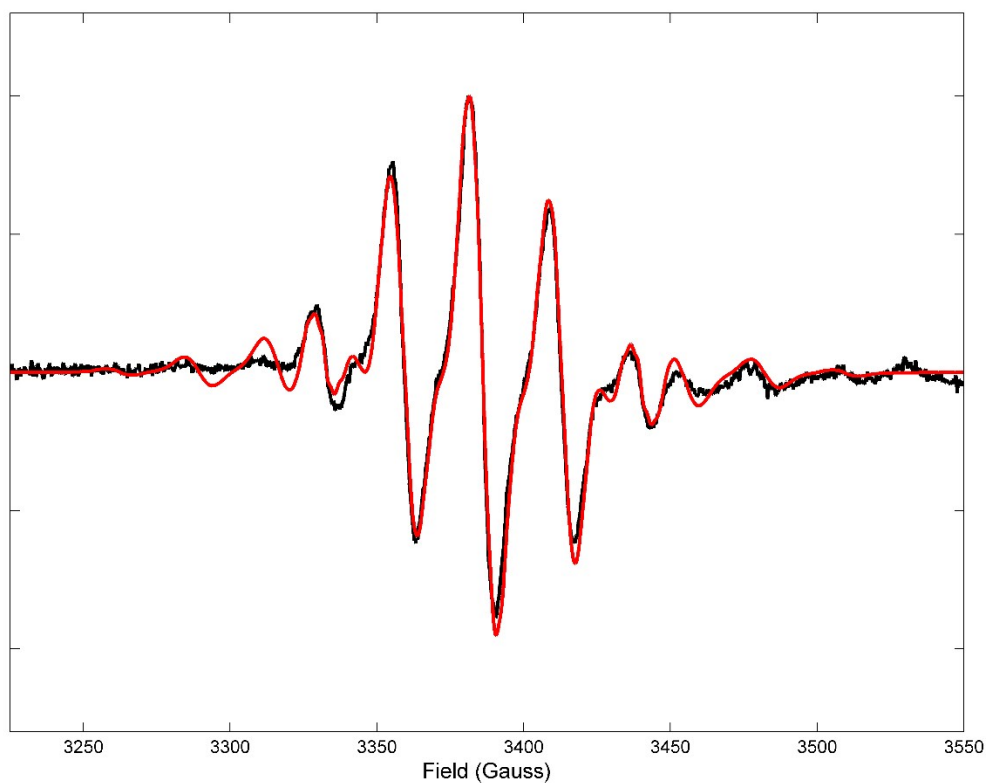


Figure S2. EPR spectrum of the deuterated form of A^0 with contributions from Mo hyperfine coupling included. Black and red lines correspond to experimental and fitted spectra, respectively. Contributions from Mo to the hyperfine occur from the Mo^{95} ($I=5/2$, 15.92%) and Mo^{97} ($I=5/2$, 9.55%) isotopes and result in characteristic low intensity features visible either side of the five lines arising from phosphorous splitting. The fitted value of the Mo hyperfine coupling is 78 MHz (2.78 mT).

Details of DFT calculations

All calculations were performed using the Gaussian 09 (Revision C01) set of programs⁶ in the gas phase based on the methods of Ndiay⁷ and Hadt.⁸ Geometry optimisations were carried out using the Tao–Perdew–Staroverov–Scuseria⁹ (TPSS) density functional. Molybdenum, phosphorous and chlorine atoms are described by the Hay and Wadt LANL2DZ^{10,11} basis set with effective core potential (ECP) and carbon, oxygen and hydrogen atoms described by the 6-31+G** basis set. EPR magnetic parameters were calculated using the optimised structures and the O3LYP¹² hybrid functional with molybdenum, phosphorous and chlorine atoms described with the DZVP basis set with completely uncontracted s and d terms to accurately predict the Fermi contact of these heavy atoms. Carbon, oxygen and hydrogen were described using the 6-311+G** basis set. EPR magnetic parameters, namely *g* and *A* tensors spectra were calculated from DFT results and used in Easyspin suite⁵ for the prediction of EPR spectra. The process was repeated with the deuterated form.

Table S4. Optimised atomic coordinates (in angstrom) of complex $[\text{Mo}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2(\text{H})_2(\text{O}_2\text{CH}_3)]^{2+}$ (A°)

C	-0.4075	2.4842	-1.7098
C	-0.6918	-1.4005	-3.1956
C	0.7828	-1.7779	-2.9745
C	-0.6384	1.4768	3.2788
C	0.6029	0.6114	3.5499
H	-0.7686	-0.4487	-3.7365
H	-1.2215	-2.1775	-3.7668
H	1.3397	-1.7943	-3.9230
H	-0.3386	2.5129	3.0633
H	0.8628	-2.7764	-2.5202
H	-1.3109	1.5021	4.1492
H	0.6017	-1.6893	0.0098

H	-0.4729	-1.2256	1.2546
H	1.2445	1.0594	4.3232
H	0.3058	-0.3888	3.8972
O	-0.9060	1.7685	-2.6089
O	0.0361	2.0502	-0.5619
P	-1.5605	-1.1047	-1.5377
P	-1.5860	0.8674	1.7355
P	1.6147	-0.5764	-1.7630
P	1.5888	0.3450	1.9457
Mo	0.0283	-0.0520	0.0792
C	-0.2487	3.9913	-1.9264
H	0.7728	4.1948	-2.2775
H	-0.9509	4.3405	-2.6896
H	-0.3932	4.5435	-0.9907
C	-2.0294	-2.9184	-1.2121
C	-1.3719	-3.6917	-0.2381
C	-2.9879	-3.5553	-2.0316
C	-1.6656	-5.0562	-0.0774
H	-0.6228	-3.2162	0.3923
C	-3.2835	-4.9162	-1.8728
H	-3.5144	-2.9846	-2.7956
C	-2.6236	-5.6734	-0.8919
H	-1.1435	-5.6322	0.6864
H	-4.0298	-5.3829	-2.5149
H	-2.8541	-6.7306	-0.7673
C	-3.2506	-0.4656	-2.0355
C	-4.3406	-0.7275	-1.1769
C	-3.4722	0.2935	-3.2008
C	-5.6240	-0.2587	-1.4849
H	-4.1872	-1.3029	-0.2652
C	-4.7612	0.7576	-3.5098
H	-2.6426	0.5535	-3.8516
C	-5.8399	0.4823	-2.6574
H	-6.4511	-0.4717	-0.8091
H	-4.9153	1.3409	-4.4169
H	-6.8376	0.8459	-2.9001
C	-2.9125	-0.1968	2.5490
C	-2.8919	-1.5964	2.4120
C	-3.9405	0.3880	3.3188
C	-3.8650	-2.3960	3.0322
H	-2.1138	-2.0579	1.8077
C	-4.9119	-0.4088	3.9405

H	-3.9985	1.4705	3.4208
C	-4.8775	-1.8051	3.8002
H	-3.8308	-3.4772	2.9047
H	-5.6997	0.0631	4.5266
H	-5.6360	-2.4229	4.2791
C	-2.5729	2.4093	1.3275
C	-2.7974	3.4624	2.2387
C	-3.1265	2.5060	0.0374
C	-3.5674	4.5764	1.8696
H	-2.3792	3.4287	3.2433
C	-3.9000	3.6156	-0.3307
H	-2.9326	1.7174	-0.6858
C	-4.1242	4.6542	0.5847
H	-3.7297	5.3800	2.5872
H	-4.3147	3.6677	-1.3361
H	-4.7206	5.5195	0.2986
C	2.2830	0.7849	-2.8675
C	2.7296	1.9667	-2.2428
C	2.4277	0.6699	-4.2643
C	3.3250	2.9945	-2.9894
H	2.5957	2.0871	-1.1703
C	3.0062	1.7042	-5.0144
H	2.0969	-0.2254	-4.7858
C	3.4640	2.8678	-4.3789
H	3.6700	3.8952	-2.4827
H	3.1022	1.5961	-6.0941
H	3.9185	3.6680	-4.9615
C	2.7772	1.7871	1.9122
C	3.9171	1.6930	1.0846
C	2.5695	2.9768	2.6367
C	4.8312	2.7516	0.9995
H	4.0982	0.7809	0.5163
C	3.4771	4.0431	2.5395
H	1.7031	3.0850	3.2855
C	4.6117	3.9339	1.7237
H	5.7106	2.6522	0.3645
H	3.2958	4.9557	3.1058
H	5.3178	4.7599	1.6532
C	2.6844	-1.0384	2.6027
C	2.1789	-2.3531	2.5666
C	3.9189	-0.8055	3.2393
C	2.8857	-3.4087	3.1589

H	1.2286	-2.5395	2.0685
C	4.6343	-1.8660	3.8173
H	4.3276	0.2019	3.2890
C	4.1195	-3.1695	3.7827
H	2.4759	-4.4178	3.1262
H	5.5909	-1.6681	4.2996
H	4.6735	-3.9901	4.2366
C	3.1985	-1.5437	-1.4450
C	4.4695	-1.0741	-1.8330
C	3.1128	-2.8003	-0.8111
C	5.6208	-1.8412	-1.5932
H	4.5668	-0.1122	-2.3320
C	4.2602	-3.5712	-0.5838
H	2.1426	-3.1734	-0.4847
C	5.5210	-3.0937	-0.9725
H	6.5932	-1.4585	-1.9017
H	4.1691	-4.5397	-0.0937
H	6.4137	-3.6903	-0.7907

References

1. Z. Otwinowski and W. Minor, in *Methods in Enzymology*, Academic Press, 1997, vol. Volume 276, pp. 307-326.
2. G. Sheldrick, *Acta. Cryst. C.*, 2015, **71**, 3-8.
3. G. Sheldrick, *Acta. Cryst. A.*, 2015, **71**, 3-8.
4. D. L. Hughes, D. J. Lowe, M. Y. Mohammed, C. J. Pickett and N. M. Pinhal, *J. Chem. Soc. Dalton Trans.*, 1990, 2021-2027.
5. S. Stoll and A. Schweiger, *J. Mag. Res.*, 2006, **178**, 42-55.
6. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian Inc.: Wallingford CT*, 2009.
7. H. Sidorenkova, T. Berclaz, B. Ndiaye, A. Jouaiti and M. Geoffroy, *J. Phys. Chem. Solids*, 2009, **70**, 713-718.

8. R. G. Hadt, V. N. Nemykin, J. G. Olsen and P. Basu, *Phys. Chem. Chem. Phys.*, 2009, **11**, 10377-10384.
9. J. Tao, J. P. Perdew, V. N. Staroverov and G. E. Scuseria, *Phys. Rev. Lett.*, 2003, **91**, 146401.
10. P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270-283.
11. P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 284-298.
12. W.-M. Hoe, A. J. Cohen and N. C. Handy, *Chem. Phys. Lett.*, 2001, **341**, 319-328.