Dalton Transactions

PAPER

Check for updates

Cite this: DOI: 10.1039/d1dt01404h

Received 28th April 2021, Accepted 2nd August 2021 DOI: 10.1039/d1dt01404h

rsc.li/dalton

Introduction

Due to growing interest toward energy and environmental problems, the pursuit of clean energy sources for a sustainable society is intense around the world. Dihydrogen H₂ has an extremely large energy density (120 MJ kg⁻¹ ν s. 44.5 MJ kg⁻¹ for gasoline) and environment-friendly (CO₂-free) power production is possible by using fuel cells. Because of these characteristics, H₂ is one of the best candidates as a future energy source. On the other hand, it is quite difficult to store H₂ under mild conditions due to the extremely low density, the small number of intermolecular interactions, and the resultant low boiling point.

To solve this problem, many kinds of materials including metal–organic frameworks (MOFs),^{1–11} covalent organic frameworks (COFs),¹² chemical hydrides^{13–15} and hydrogen-absorbing alloys¹⁶ have been studied intensely for H₂ storage. These solid-state H₂ storage materials are roughly divided into physisorptive and chemisorptive mechanisms, and each has pros and cons. Physisorptive materials have extremely low H₂

Reversible hydrogen adsorption at room temperature using a molybdenum-dihydrogen complex in the solid state[†]

Kaiji Uchida,^a Naoki Kishimoto,^a Shin-ichiro Noro, ^b Hiroaki Iguchi ^a and Shinya Takaishi ^{*}

Reversible H₂ storage under mild conditions is one of the most important targets in the field of materials chemistry. Dihydrogen complexes are attractive materials for this target because they possess moderate adsorption enthalpy as well as adsorption without cleavage of the H–H bond. In spite of these advantages, H₂ adsorption studies of dihydrogen complexes in the solid state are scarce. We herein present H₂ adsorption properties of the 16-electron precursor complex ($[Mo(PCy_3)_2(CO)_3]$) in the solid state synthesized by two procedures. One is the direct synthesis under an Ar atmosphere (1), and the other is removal of the N₂-adduct under vacuum (2). 2 showed ideal Langmuir type reversible ad/desorption of H₂ above room temperature, whereas 1 showed irreversible adsorption. The adsorption enthalpy of 2 was larger than that in THF solution. Using DFT calculation, this difference was explained by the absence of the agostic interaction in the solid state.

uptake under ambient conditions due to low adsorption enthalpy ($|\Delta H^{\circ}| < 10 \text{ kJ mol}^{-1}$), while the interaction with hydrogen is reversible and kinetics is fast. On the other hand, chemisorptive materials can adsorb H₂ under ambient conditions by forming a strong chemical bond with hydrogen, but at the same time, this process is accompanied by the cleavage of the H–H bond, which leads to irreversible adsorption and extremely slow kinetics at room temperature. So the exploration of the intermediate of these two mechanisms is necessary for developing reversible H₂ ad/desorption materials under mild conditions.

Metal-dihydrogen complexes are appealing candidates because of their moderate adsorption enthalpy which ranges from -25 to -50 kJ mol⁻¹. First a metal-dihydrogen complex was reported by Kubas and coworkers in 1984,¹⁷ and hundreds of compounds have been reported so far.¹⁸⁻²⁷ Orbital interaction of the metal-dihydrogen complex is described in the same manner as the Dewar-Chatt-Duncanson model, namely, the η^2 type M-H₂ bond is formed by σ -donation from H₂ to metal and π -back-donation from metal to H₂. In the metaldihydrogen complex, a chemical bond is formed between the metal and dihydrogen molecule, whereas the H-H bond is kept albeit it is elongated and weakened. This can be regarded as an intermediate of physisorption and chemisorption, and therefore, large adsorption enthalpy and fast ad/desorption kinetics could be achieved. Actually, the solution calorimetry study of $[W(PCy_3)_2(CO)_3]$ (PCy₃ = tricyclohexylphosphine) revealed that this complex has moderate enthalpy (≈ -40 kJ



View Article Online

^aDepartment of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan. E-mail: shinya.takaishi.d8@tohoku.ac.jp

^bFaculty of Environmental Earth Science, Hokkaido University, Sapporo 060-0810, Japan

 $[\]dagger\,Electronic$ supplementary information (ESI) available: Experimental details, adsorption measurements, kinetic analyses and DFT calculations. See DOI: 10.1039/d1dt01404h

 mol^{-1}) of H₂ binding in THF or toluene solution.²⁸ Also about the other metals, variable-temperature spectroscopic studies were also performed and their thermodynamic properties were thoroughly investigated in the solution state.^{29–32}

Recently, the η^2 coordination motif has been widely utilized in solid-state hydrogen storage materials. $^{5,9,33-41}$ As for the conventional dihydrogen complexes, on the other hand, there is only one example of the H₂ adsorption study on [Mn(CO) (dppe)₂][BAr^F₄] (Ar^F = 3,5-(CF₃)₂C₆H₃)⁴² in the solid state though several papers reported the dihydrogen complex formation, $^{43-45}$ to the best of our knowledge.

In this study, we studied the H₂ adsorption of [Mo $(PCy_3)_2(CO)_3$], a 16-electron precursor of one of the conventional dihydrogen complexes, in the solid state. We synthesized $[Mo(PCy_3)_2(CO)_3]$ in two different methods, namely a direct synthesis under an Ar atmosphere (1) and the removal of the N_2 -adduct under vacuum (2). Details are shown in the ESI.[†] H_2 adsorption isotherms of each sample were measured at various temperatures. Isotherms changed dramatically depending on the synthetic procedures, and a large difference of adsorption enthalpy was found between that in the solid state (this work) and in THF or toluene solution (ref. 28). According to the density functional theory (DFT) calculation of $[Mo(PR_3)_2(CO)_3]$ (R = methyl, isopropyl and cyclohexyl), the enthalpy difference between them was reasonably explained by the absence of the agostic interaction in the solid state. In this paper, we report the synthesis, H₂ adsorption measurements and DFT calculation of [Mo(PCy₃)₂(CO)₃].

Results and discussion

The H₂ ad/desorption isotherm at 333 K of **1** and **2** is shown in Fig. 1. The adsorption behaviours of **1** and **2** are quite different. 2 showed a type-I adsorption isotherm with a good linearity in a Langmuir plot (Fig. S2[†]), indicating the existence of site-specific interaction between the coordinatively unsaturated Mo atom and dihydrogen molecule. Ad/desorption iso



Fig. 1 H_2 adsorption isotherms of 1 and 2 at 333 K. Red diamond represents the data of 1 and black square represents the data of 2. Filled and hollow symbols represent adsorption and desorption, respectively.

therms were fully reversible in the measured pressure range. These data show that the H_2 adsorption of 2 occurred by site-specific metal-dihydrogen complex formation in the solid state.

On the other hand, **1** showed an irreversible isotherm. This irreversible isotherm and increase of adsorbed amount in the pressure-reducing process indicates that the ad/desorption was quite slow and that equilibrium was not reached. The isotherms at other temperatures also showed irreversible adsorption behaviour (Fig. S4[†]). Due to the non-equilibrium adsorption behaviour, it was impossible to analyse the thermodynamic properties of **1**.

In order to clarify the origin of this difference, we measured the N₂ adsorption of **1** and **2** at 77 K (Fig. S6 and S7†). The BET surface area of **2** (3.6 m² g⁻¹) was three times larger than that of **1** (1.2 m² g⁻¹). In addition, the adsorption amount of **2** largely increased at $P/P_0 > 0.95$, suggesting that **2** was highly pulverized probably during the N₂ removal process, and it enabled the H₂ molecule to approach the Mo centre at the polycrystalline surface.

To investigate the thermodynamic properties of 2, variabletemperature H₂ adsorption isotherms were measured. The data between 313 and 373 K are shown in Fig. 3 (see Fig. S1[†] for all the data). Saturation values of the adsorbed amount are in the range of 1.14–1.24 cm³ (STP) g⁻¹ at all temperature, corresponding to ~0.04 H₂ per Mo centre. This small value is attributed to the nonporous nature of [Mo(PCy₃)₂(CO)₃], which was confirmed by the N₂ adsorption isotherm at 77 K (Fig. S6[†]). The Ad/desorption cycle was repeated 4 times and no significant decrease of the adsorbed amount was observed (Fig. S3[†]), which indicates that [Mo(PCy₃)₂(CO)₃] is stable up to 373 K in the solid state.

The thermodynamic properties of H₂ adsorption were studied by analysing the adsorption isotherms. First, the adsorption enthalpy (ΔH°) evaluated from the isosteric differential heat of adsorption was calculated from the adsorption isotherms, and it was almost constant around -49 kJ mol⁻¹ regardless of the surface coverage (Fig. 2). This indicates that H₂ adsorption in **2** is a single site adsorption and each site is independent of each other, which well obeys the Langmuir model. All isotherms were accurately fitted ($R^2 > 0.998$) by the Langmuir adsorption isotherm,



Fig. 2 (a) H_2 adsorption isotherms of 2 at 293, 333 and 373 K. (b) Adsorption enthalpy (ΔH) of 2 estimated using data at 293, 333, and 373 K.



Fig. 3 Variable-temperature H_2 adsorption isotherms of 2. Symbols represent the measured data and lines represent the fitting curves by the Langmuir adsorption isotherm. Vertical axis is normalized to the surface coverage of the adsorbent.

$$\theta = \frac{V_{\rm a}}{V_{\rm m}} = \frac{KP}{1 + KP} \tag{1}$$

where θ is the adsorbed fraction of the adsorbent, $V_{\rm m}$ is the mono-layer adsorption capacity and *K* is the Langmuir equilibrium constant. The obtained fitting parameters are listed in Table S1.[†]

van't Hoff plot was made by using these values and fitted by the following equation,

$$\ln K = -\frac{\Delta H^{\circ}}{R} \frac{1}{T} + \frac{\Delta S^{\circ}}{R}$$
(2)

where ΔH° is the standard molar enthalpy change of adsorption, ΔS° is the standard molar entropy change of adsorption and *R* is the ideal gas constant. Fitting of the van't Hoff plot gave the following parameters; $\Delta H^{\circ} = -48.1$ kJ mol⁻¹ and $\Delta S^{\circ} = -113.5$ J K mol⁻¹ (Fig. 4).

The absolute value of ΔS° is slightly smaller than the standard molar entropy of the free dihydrogen molecule (130.7 J K mol⁻¹), which indicates that most of the entropic terms derive from the suppression of translational and rotational motion of hydrogen, and the small deviation is due to the newly appeared 6 vibrational modes by addition of the two hydrogen



Fig. 4 van't Hoff plot of **2**. Black square represents the Langmuir equilibrium constant obtained from fitting and the red line represents the fitted line by eqn (2).

atoms to form $[Mo(\eta^2-H_2)(PCy_3)_2(CO)_3]$, as well as the relatively free rotational motion of the η^2-H_2 ligand. It is noteworthy that the absolute value of ΔH° is significantly larger than the reported value of $\Delta H^\circ = -27.2$ kJ mol⁻¹ in the variable-temperature spectroscopic study in THF solution.²⁸ To clarify the origin of the energy difference between the solid state and solution state, DFT calculation was performed.

DFT calculation was performed to evaluate the energy difference between $[Mo(PR_3)_2(CO)_3]$ (R = alkyl group) with and without agostic interaction. It has been reported that [Mo (PCy₃)₂(CO)₃] shows Mo-P-C-C-H···Mo type agostic interaction, in which β -hydrogen interacts with the Mo centre (β -agostic interaction).⁴⁶ We selected R = Cy and isopropyl (iPr) as a molecule with the agostic interaction, while R = methyl (Me) as a model without agostic interaction because PMe₃ has no β-hydrogen. The details of the calculation method are shown in the Experimental section (see the ESI[†]). The optimized structures of [Mo(PCy₃)₂(CO)₃] (Mo-PCy₃), [Mo $(PiPr_3)_2(CO)_3$ (Mo-PiPr₃) and $[Mo(PMe_3)_2(CO)_3]$ (Mo-PMe₃) are shown in Fig. S13-S15.† As can be seen from the figure, Mo-PCy₃ (and Mo-PiPr₃) have a highly distorted structure with a P-Mo-P angle of 166.2° (166.4°), and the nearest C-H bond exists in the distance of 3.06 Å (3.09 Å) from the Mo atom. This structural distortion occurred to relieve the instability of the coordinatively unsaturated Mo centre (16-electron complex) by forming an agostic interaction. This structural distortion was directly observed by single crystal X-ray diffraction measurement for various metals including Cr, Mn, Re and W.^{27,47-49} In the case of Mo-PMe₃, on the other hand, structural distortion is not observed and the P-Mo-P angle is 175°. The nearest C-H bond is too far (3.90 Å) to interact with the Mo vacant site, so there is no agostic interaction to stabilize.

Thermodynamic parameters obtained by the DFT calculation are listed in Table S2.[†] From these data, the strength of H₂ adsorption is in the following order; $PMe_3 > PCy_3 \approx PiPr_3$. This result seems counterintuitive because the order of the electron donating ability of the phosphine ligand is opposite; $PCy_3 \approx PiPr_3 > PMe_3$ (Tolman electronic parameter).⁵⁰ Usually a stronger electron donating ability of the phosphine ligand leads to stronger back donation and stronger binding of the dihydrogen ligand. On the basis of experimental and calculation results, the energy diagram of H₂ adsorption is shown



Reaction coordinate

Fig. 5 Energy diagram of H₂ adsorption in the solution state and solid state (2). The value of ΔH_1° was quoted from ref. 28.

Paper

in Fig. 5. In the solution state, molecular motion is relatively free and agostic interaction occurs to stabilize the 16-electron complex, which lowers the energy gap between the 16-electron complex and metal-dihydrogen complex (ΔH_1° in Fig. 5). In the case of 2, on the other hand, the coordinatively unsaturated site, which is formed by N₂ removal, should be fully exposed due to the restricted motion of the PCy₃ ligand in the solid state. Therefore, there is no stabilization of the 16-electron complex, which leads to a significantly large energy gap between the 16-electron complex and metal-dihydrogen complex (ΔH_2° in Fig. 5).

Here we discuss the difference in the H₂ adsorption isotherms of 2 and the previously reported [Mn(CO) $(dppe)_2$ [BAr^F₄].⁴² Although the ΔH° value is similar (-49 kJ mol^{-1} for 2 and -52 kJ mol^{-1} for $[Mn(CO)(dppe)_2][BAr^F_4]$), there is a large difference in the adsorbed amount of H₂. The utilization fraction for H_2 adsorption in [Mn(CO) $(dppe)_2$ [BAr^F₄] (0.35) is much higher than that of 2 (0.04). This value is too much to be the surface adsorption. Recently, Weller and co-workers reported the reversible encapsulation of CH₂Cl₂ and Xe into a non-porous organometallic framework $[Rh(Cy_2PCH_2PCy_2)(NBD)][BAr_4]$ (NBD = norbornadiene).⁵¹ They showed that the non-covalent interaction of the CF₃ group and the hydrophobic pathway made by the $[BAr_4^F]^$ anion play an important role in the dynamic porosity. In the case of $[Mn(CO)(dppe)_2][BAr_4^F]$, the $[BAr_4^F]^-$ anion should also contribute to the dynamic porosity.

Conclusions

In conclusion, we presented the H_2 adsorption properties of $[Mo(PCy_3)_2(CO)_3]$ in the solid state synthesized by the two procedures. The sample synthesized *via* the removal of the N₂-adduct showed a Langmuir type reversible ad/desorption of H_2 above room temperature. Although the adsorption density of H_2 is quite low (0.01 wt%), the N₂ elimination of N₂-adducts is widely applicable. Thus, the current method will be a facile method for evaluating thermodynamic parameters in a series of dihydrogen complexes.

Author contributions

K. Uchida: investigation, writing-original draft. N. Kishimoto: computation. S. Noro: Gas adsorption. H. Iguchi: conceptualization, writing-review and editing. S. Takaishi: conceptualization, funding, supervision, writing-review and editing, project administration.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was partially supported by a JSPS KAKENHI Grant (B) 19H02729, Institute for Quantum Chemical Exploration (IQCE), Adaptable and Seamless Technology Transfer Program through Target-Driven R and D (A-STEP, JST) and Tohoku university molecule & material synthesis platform in nanotechnology platform project sponsored by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

Notes and references

- 1 J. Camp, V. Stavila, M. D. Allendorf, D. Prendergast and M. Haranczyk, *J. Phys. Chem. C*, 2018, **122**, 18957.
- 2 S. Rostami, A. N. Pour, A. Salimi and A. Abolghasempour, *Int. J. Hydrogen Energy*, 2018, **43**, 7072.
- 3 R. K. Ahluwalia, T. Q. Hua and J. K. Peng, *Int. J. Hydrogen Energy*, 2012, **37**, 2891–2910.
- 4 K. M. Thomas, Dalton Trans., 2009, 1487-1505.
- 5 D. E. Jaramillo, H. Z. H. Jiang, H. A. Evans, R. Chakraborty, H. Furukawa, C. M. Brown, M. Head-Gordon and J. R. Long, *J. Am. Chem. Soc.*, 2021, **143**, 6248.
- 6 Y. Liu, H. Kabbour, C. M. Brown, D. A. Neumann and C. C. Ahn, *Langmuir*, 2008, 24, 4772.
- 7 M. D. Allendorf, Z. Hulvey, T. Gennett, A. Ahmed, T. Autrey, J. Camp, E. S. Cho, H. Furukawa, M. Haranczyk, M. Head-Gordon, S. Jeong, A. Karkamkar, D. Liu, J. R. Long, K. R. Meihaus, I. H. Nayyar, R. Nazarov, D. J. Siegel, V. Stavila, J. J. Urban, S. P. Veccham and B. C. Wood, *Energy Environ. Sci.*, 2018, 11, 2784.
- 8 M. Dinca and J. R. Long, Angew. Chem., Int. Ed., 2008, 47, 6766–6779.
- 9 D. Denysenko, M. Grzywa, J. Jelic, K. Reuter and D. Volkmer, *Angew. Chem., Int. Ed.*, 2014, **53**, 5832.
- N. Li, Z. Chang, H. Huang, R. Feng, W.-W. He, M. Zhong,
 D. G. Madden, M. J. Zaworotko and X.-H. Bu, *Small*, 2019, 15, 1900426.
- 11 D.-S. Zhang, Z. Chang, Y.-F. Li, Z.-Y. Jiang, Z.-H. Xuan, Y.-H. Zhang, J.-R. Li, Q. Chen, T.-L. Hu and X.-H. Bu, *Sci. Rep.*, 2013, **3**, 3312.
- 12 S. B. Kalidindi and R. A. Fischer, *Phys. Status Solidi B*, 2013, **250**, 1119.
- 13 A. T. Wijayanta, T. Oda, C. W. Purnomo, T. Kashiwagi and M. Aziz, *Int. J. Hydrogen Energy*, 2019, 44, 15026–15044.
- M. V. Lototskyy, M. W. Davids, I. Tolj, Y. V. Klochko,
 B. S. Sekhar, S. Chidziva, F. Smith, D. Swanepoel and
 B. G. Pollet, *Int. J. Hydrogen Energy*, 2015, 40, 11491.
- 15 R. B. Biniwale, S. Rayalu, S. Devotta and M. Ichikawa, *Int. J. Hydrogen Energy*, 2008, **33**, 360.
- 16 T. R. Somo, T. C. Maponya, M. W. Davids, M. J. Hato, M. V. Lototskyy and K. D. Modibane, *Metals*, 2020, **10**, 562.
- 17 G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini and H. J. Wasserman, *J. Am. Chem. Soc.*, 1984, **106**, 451.
- 18 G. J. Kubas, Chem. Rev., 2007, 107, 4152-4205.
- 19 G. J. Kubas, J. Organomet. Chem., 2009, 694, 2648-2653.

- 20 D. M. Heinekey and W. J. Oldham, Chem. Rev., 1993, 93, 913.
- 21 R. H. Crabtree, Acc. Chem. Res., 1990, 23, 101.
- 22 R. H. Morris, Coord. Chem. Rev., 2008, 252, 2381-2394.
- 23 M. Grellier, L. Vendier and S. Sabo-Etienne, *Angew. Chem., Int. Ed.*, 2007, **46**, 2613–2615.
- 24 P. G. Jessop and R. H. Morris, *Coord. Chem. Rev.*, 1992, **121**, 155–284.
- 25 R. H. Crabtree, Chem. Rev., 2016, 116, 8750-8769.
- 26 S. J. C. Robinson and D. M. Heinekey, *Chem. Commun.*, 2017, 53, 669–676.
- 27 F. Maseras, A. Lledós, E. Clot and O. Eisenstein, *Chem. Rev.*, 2000, **100**, 601.
- 28 A. A. Gonzalez, K. Zhang, S. P. Nolan, R. L. de la Vega, S. L. Mukerjee, C. D. Hoff and G. J. Kubas, *Organometallics*, 1988, 7, 2429.
- 29 A. A. Gonzalez and C. D. Hoff, Inorg. Chem., 1989, 28, 4295.
- 30 R. C. Cammarota, J. Xie, S. A. Burgess, M. V. Vollmer, K. D. Vogiatzis, J. Ye, J. C. Linehan, A. M. Appel, C. Hoffmann, X. Wang, V. G. Young and C. C. Lu, *Chem. Sci.*, 2019, **10**, 7029.
- 31 D. L. M. Suess, C. Tsay and J. C. Peters, J. Am. Chem. Soc., 2012, 134, 14158.
- 32 D. E. Prokopchuk, G. M. Chambers, E. D. Walter, M. T. Mock and R. M. Bullock, *J. Am. Chem. Soc.*, 2019, **141**, 1871.
- 33 A. Hamaed, M. Trudeau and D. M. Antonelli, J. Am. Chem. Soc., 2008, 130, 6992–6999.
- 34 T. K. A. Hoang, M. I. Webb, H. V. Mai, A. Hamaed, C. J. Walsby, M. Trudeau and D. M. Antonelli, *J. Am. Chem. Soc.*, 2010, **132**, 11792–11798.
- 35 A. Hamaed, T. K. A. Hoang, G. Moula, R. Aroca, M. L. Trudeau and D. M. Antonelli, *J. Am. Chem. Soc.*, 2011, 133, 15434–15443.
- 36 A. I. Cooper and M. Poliakoff, Chem. Commun., 2007, 2965.

- 37 L. Morris, J. Hales, M. Trudeau, P. Georgiev, J. Embs, J. Eckert, N. Kaltsoyannis and D. A. Antonelli, *Energy Environ. Sci.*, 2019, **12**, 1580–1591.
- 38 S. E. Trentowsky, A. J. Lough and R. H. Morris, *Polyhedron*, 2018, **156**, 342–349.
- 39 S. K. Brayshaw, J. C. Green, N. Hazari, J. S. McIndoe, F. Marken, P. R. Raithby and A. S. Weller, *Angew. Chem.*, *Int. Ed.*, 2006, 45, 6005–6008.
- 40 W. Yang, X. Lin, J. Jia, A. J. Blake, C. Wilson, P. Hubberstey, N. R. Champness and M. Schroder, *Chem. Commun.*, 2008, 359.
- 41 G. Alcaraz, M. Grellier and S. Sabo-Etienne, *Acc. Chem. Res.*, 2009, **42**, 1640–1649.
- 42 D. G. Abrecht and B. Fultz, J. Phys. Chem. C, 2012, 116, 22245.
- 43 R. H. Crabtree, M. Lavin and L. Bonneviot, J. Am. Chem. Soc., 1986, **108**, 4032.
- 44 J. Eckert, G. J. Kubas and R. P. White, *Inorg. Chem.*, 1992, **31**, 1550.
- 45 L. R. Doyle, D. J. Scott, P. J. Hill, D. A. X. Fraser, W. K. Myers, A. J. P. White, J. C. Green and A. E. Ashley, *Chem. Sci.*, 2018, 9, 7362.
- 46 M. Brookhart, M. L. Green and L.-L. Wong, *Prog. Inorg. Chem.*, 1988, **36**, 1.
- 47 K. Zhang, A. A. Gonzalez, S. L. Mukerjee, S. J. Chou,
 C. D. Hoff, K. A. Kubat-Martin, D. Barnhart and
 G. J. Kubas, *J. Am. Chem. Soc.*, 1991, 113, 9170.
- 48 A. Toupadakis, G. J. Kubas, W. A. King, B. L. Scott and J. Huhmann-Vincent, *Organometallics*, 1998, **17**, 5315.
- 49 D. M. Heinekey, B. M. Schomber and C. E. Radzewich, J. Am. Chem. Soc., 1994, 116, 4515.
- 50 C. A. Tolman, Chem. Rev., 1977, 77, 313.
- 51 A. J. Martínez-Martínez, N. H. Rees and A. S. Weller, *Angew. Chem.*, *Int. Ed.*, 2019, **58**, 16873.