Design and validation of non-metal oxo complexes for C–H activation†

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We use our recent discovery of the reduction-coupled oxo activation (ROA) principle to design a series of organometallic molecules that activate C–H bonds through this unique proton/electron-decoupled hydrogen abstraction mechanism, in which the main group oxo moiety binds to the proton while the electron is transferred to the transition metal. Here we illustrate this general class of catalyst clusters with several examples that are validated through quantum mechanics calculations.

The two major approaches for activating alkane C–H bonds are:

- Direct reaction with a metal centre; examples of which include oxidative addition, electrophilic substitution, σ -bond metathesis, and 1,2-addition (Scheme 1(a)). These cases lead to formation of a metal–alkyl complex.^{1,2}
- Radical rebound, involving reaction at transition metal-oxo moieties ($M=O$) (Scheme 1(b)) to form a metal hydroxide–alkyl radical pair, in which the metal is reduced by one electron during the reaction.^{3–5} The alkyl radical then can rebound with $M-OH$ to form the corresponding alcohol or for heterogeneous catalysts it can bind to other $M=O$ bonds on the catalyst surface.⁶

Recently, we determined the reaction mechanism for the highly selective direct oxidation of *n*-butane to maleic anhydride by the vanadium phosphate oxide (VPO) catalyst, in which O_2 is the oxidant.⁷ We found that the strong C–H bonds of *n*-butane are activated through a unique mechanism involving the $O=P$ rather than the $O=V$ moieties to cleave the butane C–H bond in a homolytic manner. This is most favourable because the proton transfers to $O=P$ while the electron transfers simultaneously to the neighbouring vanadium (which is coupled to the P through oxygen), reducing it from V^V to V^{IV} (Scheme 2(a), $M = V$, $n = 5$). This $PO-H$ bond is sufficiently strong that the reaction barrier to extract an H from *n*-butane is less than $14.0 \text{ kcal mol}^{-1}$. For the VPO catalyst the butyl radical gets trapped on an adjacent $V=O$ site and

Scheme 1 Existing approaches for activating alkane C–H bonds.

Scheme 2 Valence bond description for the reduction-coupled oxo activation (ROA) principle.

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subsequent C–H bond breaking occurs through successive activation by additional $P=O$ bonds, eventually producing maleic anhydride.⁷

Fig. 1 (a) Scheme for generating the active molecule **B** from its precursor **A**, and its monohydrogenation to **C**. The number below each species is the M–P bond distance in Å. (b) The actual structures investigated for group 5 and 10 metals. The number below each species is the $D_{\text{PO-H}}$ energy and the reaction barrier (E_a) for *n*-butane methylene C–H bond cleavage (in parentheses) in kcal mol⁻¹.

Activating C–H bonds in this way decreases the likelihood of unwanted side reactions on the transition metal centre, since the metal is not adjacent to the active centre. Moreover, the C–H activation power ($D_{\text{PO-H}}$, the binding energy of the P=O to a hydrogen atom, e.g., **B** → **C**, Fig. 1(a)) of the substrate depends on both the pK_a of the protonated oxo and on the reduction potential of the transition metal,⁸ and their separation from each other by two atoms (–PO–) provides some freedom to tune $D_{\text{PO-H}}$ for selective activation.

We expect that these concepts could be useful in designing new organometallic catalysts for alkane C–H activation and functionalization. However, organometallic compounds containing a transition metal bridged by oxygen to P=O are rare in the literature and might be difficult to synthesize.^{9–11} Consequently we consider here application of this principle to cases in which a transition metal atom is bound directly to O=P, so that after hydrogen binds with O=P, the P–M σ -bond becomes a donor–acceptor bond to reduce the metal by one electron (Scheme 2(b)). Organometallic complexes featuring such a structure have been synthesized recently,^{12–19} but they are not yet optimal for increased activity *via* the ROA principle. We report here newly designed organometallic molecules expected to exhibit the ROA-principle activation of alkane C–H bonds with low barriers. We then validate these predictions using density functional theory (see ESI†) and analyse the factors controlling their C–H activation power.

We first investigated the effect of the metallic centre on $D_{\text{PO-H}}$. Considering the trianionic pincer-type phosphinito [OP(O)O]³⁻ group 5 transition metal dichloride complexes (**1-V**, **-Nb**, and **-Ta**, Fig. 1(b)) in which the metal is in the +5 oxidation state, we predict $D_{\text{PO-H}}$ values of 85.6 (V), 66.0 (Nb), and 59.3 (Ta) kcal mol⁻¹. This indicates that the V case should be quite active. Indeed, we found that using **1-V** to activate *n*-butane methylene C–H bonds leads to a barrier of E_a = 24.2 kcal mol⁻¹, much lower than that using **1-Nb** (39.0 kcal mol⁻¹) or **1-Ta** (43.8 kcal mol⁻¹).

We also calculated the $D_{\text{PO-H}}$'s of the monoanionic pincer-type phosphinito [PP(O)P]¹⁻ group 10 transition metal monochloride complexes (**2-Ni**, **-Pd**, and **-Pt**), in which the metal is at the +2 oxidation state. This leads to $D_{\text{PO-H}}$ values of 46.8 (Ni), 36.7 (Pd), and 30.7 (Pt) kcal mol⁻¹, none of which are capable of breaking alkane C–H bonds. This is further supported by the high E_a of 58.6 kcal mol⁻¹ for **2-Ni**. Methods for synthesizing these complexes^{13–15,18,19} or their precursors^{12,16,17} (**A**, Fig. 1) are known, and oxidation of the precursors (**A** → **B**)^{15,18,19} leads to the target molecules (DFT predicts the reaction energy from **A** to **B** to be downhill by 57.3, 58.6, and 59.8 kcal mol⁻¹ for **2-Ni**, **-Pd**, and **-Pt**, respectively).

According to the valence bond description (Scheme 2(b)), the M–P bond distance should increase by ~half a bond order or ~0.1 Å after hydrogen abstraction since it changes from a covalent bond to a donor–acceptor bond. This is consistent with our calculated results showing $R_{\text{M-P}}$ values of **B** at 2.52 and 2.21 Å for **1-V** and **2-Ni**, respectively, which are lengthened in **C** to 2.64 and 2.29 Å, respectively.

Evidently, as the metal changes from a 1st- to 2nd- to 3rd-row transition metal, the $D_{\text{PO-H}}$ decreases significantly, with vanadium and nickel representing the best choices of the metallic centre for groups 5 and 10, respectively. This trend is due to the decrease in the reduction potential going down the periodic table, since the role that the metallic ion plays in the hydrogen abstraction is to host the added electron.²⁰

The Mulliken analysis shows that the spin density on the metal of the hydrogenated complex **C** decreases from 1.06 and 0.78 for **1-V** and **2-Ni** to 0.87 and 0.36 for **1-Nb** and **2-Pd**, and further to 0.79 and 0.26 for **1-Ta** and **2-Pt**, indicating that as the metal changes from a 1st- to 2nd-, to 3rd-row transition metal, its reduction potential decreases. Moreover, our calculations show that group 5 early transition metals possesses a much larger $D_{\text{PO-H}}$ (and as a result a lower E_a) than does group 10 of late transition metals, clearly indicating that it is more beneficial to have an early transition metal with a high oxidation state as the metallic centre.

Fig. 2 Proposed early and late transition metal complexes for evaluating the C–H activation power. The numbers below the notations are $D_{\text{PO-H}}$ values and E_a values in parentheses.

Fig. 3 Potential energy surface of using (a) **4-V** and (b) the Mn dioxo porphyrin complex to activate *n*-butane secondary C–H bonds. Energies are in kcal mol^{−1}, and bond distances are in Å.

We then studied the influence of organic ligands on $D_{\text{PO-H}}$. Two additional ligands were chosen for vanadium (Fig. 2). We predict $D_{\text{PO-H}} = 80.6$ and $E_a = 26.9$ kcal mol^{−1} for **3-V**, and $D_{\text{PO-H}} = 89.7$ and $E_a = 20.4$ kcal mol^{−1} for **4-V**. For the nickel complexes, we predict $D_{\text{PO-H}} = 58.6$, 58.3 and 43.0 kcal mol^{−1} for **5-Ni**, **6-Ni**, and **7-Ni**, and $E_a = 51.5$ and 47.2 kcal mol^{−1} for **5-Ni** and **6-Ni**, respectively. Thus, the vanadium complexes are more favourable for cleaving C–H bonds than the nickel complexes. Nevertheless we found the replacement of the [PP(O)P] ligand significantly affects $D_{\text{PO-H}}$ as well as E_a .

Next we compared the E_a of **4-V** to that of the Mn^V *trans*-dioxo porphyrin complex (Fig. 3), a known catalyst for alkane C–H activation.²¹ We found the two barriers to be nearly identical (20.4 versus 20.8 kcal mol^{−1}). This suggests that the C–H activation ability of the molecules proposed in this study is similar to that of existing catalysts. As expected, the calculated C–H activation barriers correlate well with $D_{\text{PO-H}}$ ($R^2 = 0.98$) (see ESI†). This suggests that C–H activation barriers of this type of organometallic complexes can be estimated accurately by their $D_{\text{PO-H}}$'s.

The C–H activation power of these proposed molecules can be further increased by using those high oxidation state metals having the largest reduction potentials. This might be accomplished by modifying the organic ligand to make the metal more electron-deficient. Another way to enhance the C–H activation ability is to replace O=P with other motifs with higher basicity, such as RN=P.

The goal of the analysis is to suggest how to develop new classes of organometallic complexes for activating C–H bonds by using the new ROA proton/electron-decoupled hydrogen transfer principle, found to be responsible for the high reactivity of the VPO system.^{7,22} Towards this end, we have designed several organometallic molecules to illustrate how to achieve activation of strong C–H bonds of alkanes, which we then validated using

density functional theory. These molecules activate C–H bonds through the new ROA principle involving a proton/electron-decoupled hydrogen transfer mechanism that combines a main group element-oxo moiety with a reducible transition metal. We also analyse the factors controlling the C–H activation power of these molecules.

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Notes and references

- (a) D. Balcells, E. Clot and O. Eisenstein, *Chem. Rev.*, 2010, **110**, 749–823; (b) B. G. Hashiguchi, S. M. Bischof, M. M. Konnick and R. A. Periana, *Acc. Chem. Res.*, 2012, **45**, 885–898.
- (a) M. L. Steigerwald and W. A. Goddard, *J. Am. Chem. Soc.*, 1984, **106**, 308–311; (b) J. Kua, X. Xu, R. A. Periana and W. A. Goddard, *Organometallics*, 2002, **21**, 511–525; (c) C. J. Jones, D. Taube, V. R. Ziatdinov, R. A. Periana, R. J. Nielsen, J. Ongaard and W. A. Goddard, *Angew. Chem., Int. Ed.*, 2004, **43**, 4626–4629; (d) D. H. Ess, W. A. Goddard and R. A. Periana, *Organometallics*, 2010, **29**, 6459–6472.
- W. Liu, X. Y. Huang, M. J. Cheng, R. J. Nielsen, W. A. Goddard and J. T. Groves, *Science*, 2012, **337**, 1322–1325.
- J. T. Groves and G. A. McCluskey, *J. Am. Chem. Soc.*, 1976, **98**, 859–861.
- M. Filatov, N. Harris and S. Shaik, *J. Chem. Soc., Perkin Trans. 2*, 1999, 399–410.
- (a) J. N. Allison and W. A. Goddard, *ACS Symp. Ser.*, 1985, **279**, 23–36; (b) Y. H. Jang and W. A. Goddard, *Top. Catal.*, 2001, **15**, 273–289; (c) Y. H. Jang and W. A. Goddard, *J. Phys. Chem. B*, 2002, **106**, 5997–6013.
- M. J. Cheng and W. A. Goddard, *J. Am. Chem. Soc.*, 2013, **135**, 4600–4603; (b) M. J. Cheng, R. J. Nielsen, J. Tahir-Kheli and W. A. Goddard, *Phys. Chem. Chem. Phys.*, 2011, **13**, 9831–9838.
- K. A. Gardner and J. M. Mayer, *Science*, 1995, **269**, 1849–1851.
- N. Marino, S. K. Hanson, P. Muller and R. P. Doyle, *Inorg. Chem.*, 2012, **51**, 10077–10079.
- N. Herron, D. L. Thorn, R. L. Harlow and G. W. Coulston, *J. Am. Chem. Soc.*, 1997, **119**, 7149–7150.
- D. Solis-Ibarra, J. S. Silvia, V. Jancik and C. C. Cummins, *Inorg. Chem.*, 2011, **50**, 9980–9984.
- R. C. Bauer, Y. Gloaguen, M. Lutz, J. N. H. Reek, B. de Bruin and J. I. van der Vlugt, *Dalton Trans.*, 2011, **40**, 8822–8829.
- E. J. Derrah, S. Ladeira, G. Bouhadir, K. Miqueu and D. Bourissou, *Chem. Commun.*, 2011, **47**, 8611–8613.
- E. J. Derrah, C. Martin, S. Mallet-Ladeira, K. Miqueu, G. Bouhadir and D. Bourissou, *Organometallics*, 2013, **32**, 1121–1128.
- Y. Gloaguen, W. Jacobs, B. de Bruin, M. Lutz and J. I. van der Vlugt, *Inorg. Chem.*, 2013, **52**, 1682–1684.
- M. Mazzeo, M. Lamberti, A. Massa, A. Scettri, C. Pellecchia and J. C. Peters, *Organometallics*, 2008, **27**, 5741–5743.
- M. Mazzeo, M. Strianese, O. Kuhl and J. C. Peters, *Dalton Trans.*, 2011, **40**, 9026–9033.
- B. F. Pan, M. W. Bezpalko, B. M. Foxman and C. M. Thomas, *Organometallics*, 2011, **30**, 5560–5563.
- B. F. Pan, M. W. Bezpalko, B. M. Foxman and C. M. Thomas, *Dalton Trans.*, 2012, **41**, 9083–9090.
- M. Martelli, G. Pilloni, G. Zotti and S. Daolio, *Inorg. Chim. Acta*, 1974, **11**, 155–158.
- N. Jin, M. Ibrahim, T. G. Spiro and J. T. Groves, *J. Am. Chem. Soc.*, 2007, **129**, 12416–12417.
- Y. Schuurman and J. T. Gleaves, *Ind. Eng. Chem. Res.*, 1994, **33**, 2935–2941.