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Cooperative carbon-atom abstraction from alkenes in the core of a pentanuclear nickel cluster

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Although the cleavage of C–C bonds in unactivated hydrocarbons by soluble transition-metal complexes remains a challenge, such reactions hold the potential to provide access to previously inconceivable skeletal transformations. For instance, one can imagine the dismantling and reassembly of C–C and C–H bonds commonly observed in surface catalysis, but with the increased control innate to homogeneous catalysis. Here we report a pentanuclear nickel cluster that is unreactive to functional groups, such as alcohols, amines and even water, but selectively cleaves the C=C bonds of simple alkenes, such as ethylene, styrene and isobutylene, at temperatures as low as −30 °C and in near-quantitative yields. The isolation of intermediates in reactions with styrene and isobutylene demonstrates that the five nickel centres cooperatively activate three C–H bonds of the alkene substrate before cleaving the C–C bond in the core of the cluster to give a pentanuclear nickel carbide. The net organic product transformation is the abstraction of a carbon atom from an alkene.

Molecular clusters have the potential to display reactivity comparable to that of metal surfaces in the catalysis of difficult bond transformations that feature multiple C–H bond activations and C–C bond skeletal rearrangements[1–6]. The low activation barriers for these transformations on surfaces can be ascribed to cooperative reactivity between metal centres; however, the presence of multiple adjacent metal sites is insufficient for cooperative catalysis, and the full potential of cooperative reactivity is rarely actualized. Even on heterogeneous surface catalysts, reaction sites are often structure sensitive[7–9]. For example, catalysis on Ni(111) surfaces frequently occurs at steps rather than on terraces; these sites are so reactive that they facilitate the room-temperature cleavage of ethylene to give nickel carbide from multiple C–H and C=C bond cleavages[10]. Model complexes for surface C–C bond cleavage and the more intriguing mechanistic microscopic reverse, C–C bond formation from C_1 feedstocks, are entirely lacking[11]. Although mononuclear complexes that cleave C–C bonds are known, many of them rely on activated substrates[12–15], or on highly reduced metal centres incompatible with the majority of functional groups[1,3,6,16,17]. Despite focused efforts to design reactive polynuclear complexes with both monodentate[18–24] and polydentate ligands[25–32], few molecular clusters are known that selectivity react with hydrocarbons via multiple C–H and C–C bond activation[2], and invariably the voracious reactivity and incompatibility of these complexes with functional groups limits their catalytic potential.

The pentanuclear cluster $[({}^{i}Pr_3P)Ni]_5H_6$ (**1**) has been shown to perform catalytic H/D exchange with unactivated arenes[33] and ultradeep hydrodesulfurization[34]. Both reactions are slow at room temperature. The cleavage of strong unactivated C=C bonds in alkenes is a difficult transformation, because of the substantial bond-dissociation energy[35] and the anticipated involvement of an intermediate with an unreactive C–C bond. These C=C cleavages are typically accomplished via oxidative processes[36]. The addition of two equivalents of ethylene to a solution of the pentanuclear hydride **1** in *n*-pentane at room temperature gave an immediate and clean conversion into $[({}^{i}Pr_3P)Ni]_5(\mu_2\text{-}H)_4(\mu_5\text{-}C)$ (**2**), as shown in Fig. 1a. Cluster **2** has two fewer hydrides than **1**, in agreement with the stoichiometric requirement of two equivalents of ethylene, one of which is hydrogenated to give ethane. The second equivalent of ethylene is converted into methane via the net loss of a carbon atom. The reaction of **1** with ethylene was conducted in an NMR probe cooled to −80 °C, and revealed that cluster **2**, ethane and methane are produced on warming above −30 °C.

An ORTEP (Oak Ridge thermal-ellipsoid plot program) depiction of the solid-state structure of **2**, as determined by X-ray crystallography, is shown in Fig. 2. The 68-electron $[Ni_5]^{8+}$ carbide cluster **2** features a central carbide, C(1), which lies 0.372 (2) Å above the approximate square base of Ni(2), Ni(3), Ni(4) and Ni(5). Ni(1) sits above this plane, bound only to C(1), Ni(3), Ni(1) and Ni(2). The Ni–C(1) distances to the Ni(2), Ni(3), Ni(4) and Ni(5) square base vary from 1.818(2) to 1.854(2) Å. The Ni(1) site is disordered, and was modelled with capping Ni(1A), Ni(1B) and Ni(1C) that bridge Ni(2) and N(3), Ni(2) and Ni(5), or Ni(4) and Ni(5), respectively.

Solution NMR spectroscopy of the crude reaction mixture demonstrates a clean conversion into **2**, which is fluxional. The $^{31}P\{^{1}H\}$ NMR spectrum has a single resonance at $\delta = 52.1$. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra confirm the conversion to a single cluster, with a set of resonances that correspond to five equivalent fluxional ${}^{i}Pr_3P$ moieties and an upfield signal at $\delta = -7.15$ that integrate to four hydride ligands. The hydride signal is a sextet from coupling to five ^{31}P nuclei with an average J_{PH} of 2.5 Hz. The ^{1}H NMR spectrum of the crude reaction mixture also has two singlets at $\delta = 0.84$ and $\delta = 0.16$ from ethane and methane, respectively. As for **1**, cooling solutions of **2** to as low as −90 °C did not slow the fluxional process enough to cause decoalescence of any of the ^{1}H or ^{31}P NMR resonances.

The reaction of **1** with ^{13}C-labelled ethylene provided the ^{13}C-labelled cluster (**2-^{13}C**). The $^{13}C\{^{1}H\}$ NMR spectrum of **2-^{13}C** has a sextet for the carbide from coupling to five phosphines, at a downfield shift of $\delta = 446.4$ with $^{2}J_{CP} = 20.5$ Hz. The $^{31}P\{^{1}H\}$ NMR spectrum of **2-^{13}C** features a doublet instead of a singlet, with $^{2}J_{CP} = 20.5$ Hz. The ^{13}C NMR spectrum of the crude reaction mixture allowed confirmation of the hydrocarbon products $^{13}CH_4$ and $^{13}C_2H_6$ as a pentet at $\delta = -4.90$ and a second-order multiplet at $\delta = 6.79$ in deuterated tetrahydrofuran (THF-d_8), respectively.

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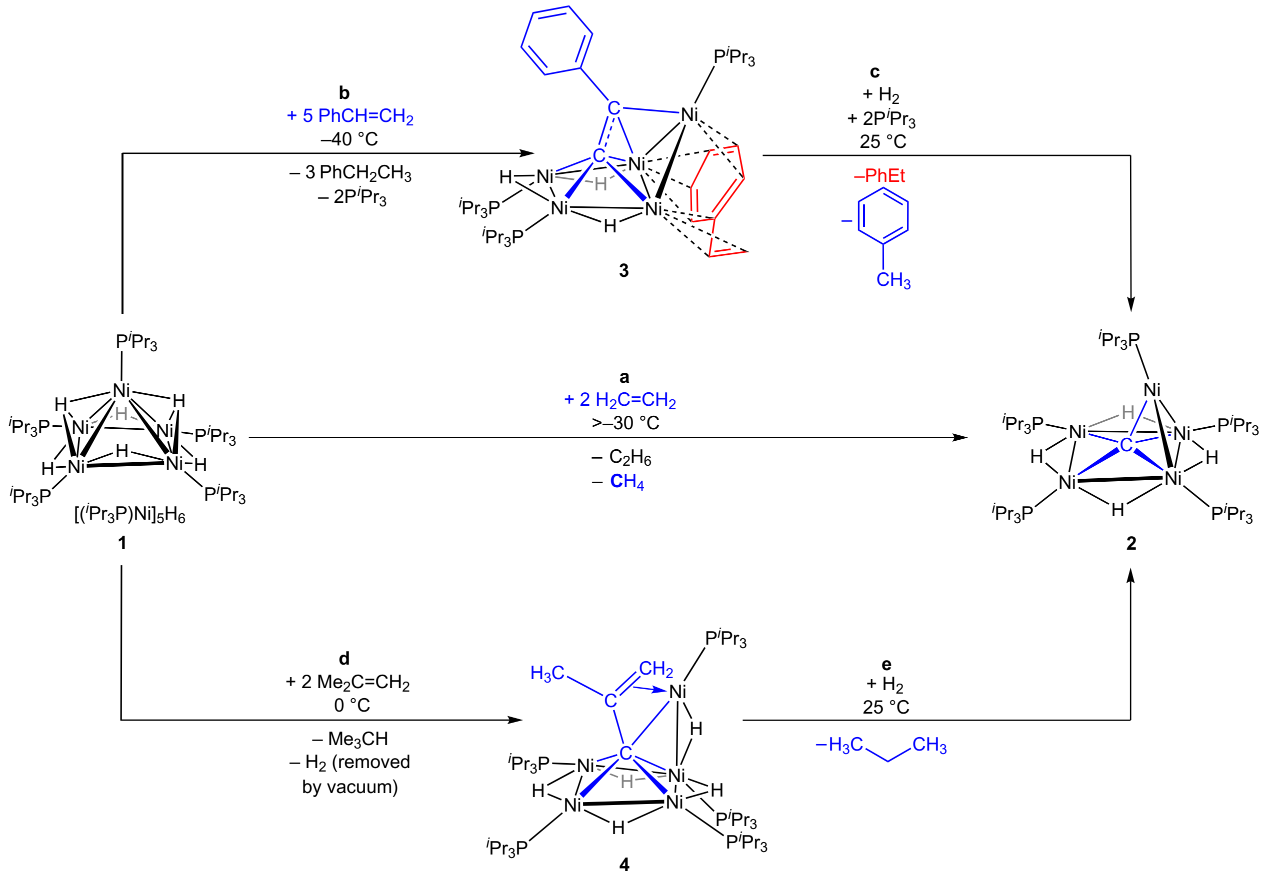

Figure 1 | Cooperative carbon-atom abstraction from alkenes by [(^{i}Pr$_3$P)Ni]$_5$H$_6$ (1). **a**, Synthesis of 2 from the reaction of ethylene with 1. **b**, Synthesis of 3 from the reaction of styrene with 1. **c**, Conversion of 3 into 2 by reaction with H_2 and ^{i}Pr$_3$P. **d**, Synthesis of 4 from the reaction of isobutene with 1. **e**, Conversion of 4 into 2 by reaction with H_2. The cleavage of the C=C bonds in these substrates under such mild conditions is mediated by the cooperative activation of the C–H and C–C bonds by all five nickel centres, as evidenced by the structures of intermediates 3 and 4.

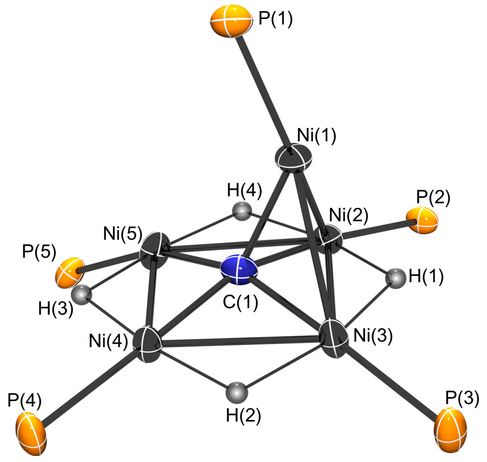

Figure 2 | ORTEP depiction of the solid-state molecular structure of 2, with 50% probability ellipsoids. Carbons and hydrogens associated with the phosphine ligands and disorder of Ni(1) are omitted for clarity. The carbon atom abstracted from the alkene is in a distorted five-coordinate geometry, with the low-coordinate Ni(1) centre shifted towards the Ni(2)–Ni(3) edge of the square base of the 68-electron $[Ni_5]^{8+}$ carbide cluster.

To demonstrate the remarkable selectivity in the C=C bond activation, cluster 1 was mixed with a variety of molecules that contained functional groups, which included *n*-butanol, diisopropylamine, 3-pentanone, isopropyl acetate, *N*,*N*-dimethylformamide, 3-hexyne and neopentyl chloride. With two exceptions, the addition of ethylene to these mixtures at –40 °C produced an equivalent of ethane, methane and the carbide cluster 2, in greater than 70% NMR yield (Supplementary Table 1). One exception was 3-hexyne, which also generated methane and 2, but an equivalent of 3-hexyne was hydrogenated to give 3-hexene in lieu of ethane. The second exception was the reaction in the presence of neopentyl chloride, which still provided ethane and methane from the selective activation of ethylene, but neopentyl chloride was observed to react with cluster 2; further work is underway to examine the reactivity of 2 and the nature of this product. Only a few functional groups were not tolerated. For example, both benzyl chloride and propionitrile were observed to react rapidly with 1 at –40 °C.

The isolation of intermediates in the reactions with alkenes other than ethylene gave insight into how the five nickel centres cooperatively abstract C from alkenes. When 1 was reacted with styrene, the immediate ^{1}H and ^{31}P{^{1}H} NMR spectra displayed an intermediate that converted into 2 over the course of 16 hours. The addition of excess styrene to 1 in a solution of *n*-pentane at –40 °C followed by recrystallization provided the intermediate to the C=C bond cleavage, (^{i}Pr$_3$P)$_3$Ni$_5$(μ_2-H)$_3$(CCPh)(H$_2$C=CHPh) (3), as shown in Fig. 1b. The stoichiometry of the reaction involves five equivalents of styrene. Two equivalents of styrene are incorporated in the product. One is triply C–H activated to give a bent PhCC fragment, and the second styrene acts as bridging ligand π bound over three nickel centres. The complex has only three hydride ligands, and along with the three hydrogens lost from the activated styrene, the total of six hydrogens lost are all incorporated into ethyl benzene from the hydrogenation of three equivalents of styrene, as quantified by integration of

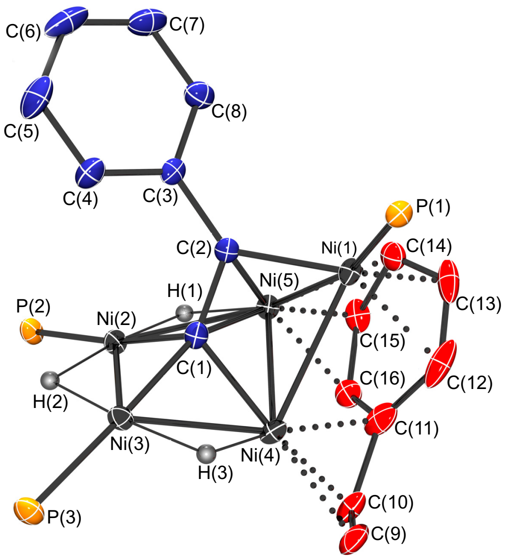

Figure 3 | ORTEP depiction of the solid-state molecular structure of 3, with 50% probability ellipsoids. Carbons and hydrogens associated with the phosphine ligands and disorder of C(9) and C(10) are omitted for clarity. This 72-electron $[Ni_5]^{6+}$ cluster reveals the triple C–H bond activation of one styrene vinyl moiety, shown in blue, which is coordinated to all five nickel centres prior to C–C cleavage. Two $^{i}Pr_3P$ groups are replaced by a coordinated styrene moiety, shown in red.

the ^1H NMR spectrum of the crude reaction mixture. The unactivated bridging styrene displaces two $^{i}Pr_3P$ ligands from the cluster.

The solid-state structure of 3 was determined by X-ray crystallography, and is displayed in Fig. 3. The solid-state structure of cluster 3 features many similarities to that of cluster 2. The capping Ni(1) bonds to C(2) and retains short distances to only two of the nickel centres in the base, which opens up the cluster to provide a binding pocket for the substrate. The Ni(2), Ni(3), Ni(4) and Ni(5) centres distort away from a square planar to a butterfly geometry, and all bind to the terminal C(1) of the PhCC fragment. Ni(5) features nearly equal bond lengths to both C(1) and C(2). The C(1)–C(2) bond length of 1.397(5) Å along with the bent C(1)–C(2)–C(3) bond angle are suggestive that some double-bond character of styrene is maintained after the triple C–H bond activation. The *π*-bound styrene exhibits disorder where the two different faces of the vinyl group are bound. This disorder is maintained in solution, and results in a major and a minor isomer being observed by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy. Unlike 1 and 2, the C_1 symmetric 72-electron $[Ni_5]^{6+}$ cluster 3 is not fluxional, and all the anticipated resonances were accounted for and are in agreement with the presence of two isomers in the solid-state structure of 3. In an attached proton test $^{13}C\{^1H\}$ NMR spectrum, the α and β carbons of the PhCC moiety, located at $\delta = 150.4$ (d) and $\delta = 242.2$ (dd) for the major isomer, were phased consistent with the absence of attached hydrogens. A ^1H-^{13}C heteronuclear single-quantum correlation (HSQC) NMR experiment also showed no proton correlation to the α and β carbons.

To confirm that cluster 3 is an intermediate of the C–C bond cleavage rather than a result of a non-productive side reaction, an isolated sample of 3 in a solution of deuterated benzene (C_6D_6) was exposed to $^{i}Pr_3P$ and an atmosphere of dihydrogen, as shown in Fig. 1c. After four hours, ^1H and $^{31}P\{^1H\}$ NMR spectra revealed the conversion of cluster 3 into cluster 2 along with ethyl benzene and toluene. The ethyl benzene is probably formed from hydrogenation of the *π*-bound styrene fragment, whereas the toluene is generated from C–C bond cleavage of the PhCC fragment and the incorporation of three hydrogen atoms.

Cluster 3 demonstrates how the Ni_5 core of 1 can open to cooperatively triply C–H activate alkenes, and ultimately facilitate C–C bond cleavage to give 2 and the formation of three new C–H bonds to give toluene; however, the additional *π*-bound styrene is a factor in the isolation of 3 that may not be relevant to the activation of ethylene or other alkenes. To demonstrate the scope of substituted alkenes that can undergo carbon-atom abstraction using 1 and to reveal mechanistic similarities, the isolation of an intermediate using a different substrate was explored. The reaction of 1 with isobutylene yielded 2 along with an equivalent of both isobutane and propane; however, a short-lived intermediate (4) was also observed when the reaction was monitored by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. Under typical reaction conditions, the isolation of 4 was impossible because of its rapid conversion into 2; however, the reaction of a large excess of isobutylene with 1 at 0 °C followed by the application of a vacuum allowed the characterization of $[(^{i}Pr_3P)Ni]_5(\mu_2\text{-}H)_5(CC(Me)=CH_2)$ (4), as shown in Fig. 1d. The removal of H_2 gas from the reaction using a vacuum is necessary for the crystallization of 4, although the thermal instability of 4 prevented its isolation in the absence of 2. When hydrogen gas is added to a solution of 4, conversion into 2 along with propane occurs via C–C bond cleavage and the formation of three new C–H bonds, as shown in Fig. 1e.

The solid-state structure of 4 is shown in Fig. 4. The structure features multiple similarities to clusters 2 and 3, but with Ni(1) attached only to Ni(2). A hydride bridges this connection to the approximately square base of Ni(2), Ni(3), Ni(4) and Ni(5). As for cluster 3, triple C–H bond activation of isobutylene is observed, which includes the vinylic $C=CH_2$ bonds and an sp^3 C–H bond of one of the Me groups. Two-site disorder was modelled for the bound isobutylene fragment. The C(2)–C(3) bond distance is 1.380(14) Å and the C(1)–C(2) bond distance is 1.475(9) Å. Short bonding contacts are observed between C(1) and all the nickel centres, with Ni(1) η^3 bound to the C(1)–C(2)–C(3) fragment.

The $^{31}P\{^1H\}$ NMR spectrum of the 70-electron $[Ni_5]^{8+}$ intermediate 4 features a singlet at $\delta = 47.3$, and selective ^1H decoupling of the isopropyl substituent hydrogens resulted in a sextet with a J_{PH} of 6.5 Hz. The ^1H NMR spectrum displays a similar 6.5 Hz sextet at $\delta = -22.05$ for the hydrides. This is consistent with the solid-state structure undergoing a rapid fluxional exchange of the five hydride and phosphine environments. The ^1H NMR spectrum of

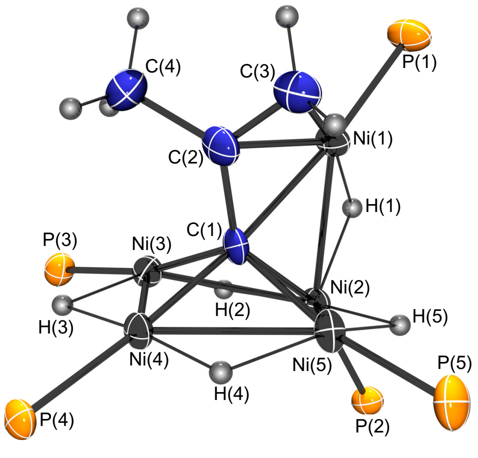

Figure 4 | ORTEP depiction of the solid-state structure of cluster 4, with 50% probability ellipsoids. Carbons and hydrogens on the phosphine ligands along with the two-site disorder on the top nickel centre and the bound isobutylene fragment are omitted for clarity. This 70-electron $[Ni_5]^{8+}$ intermediate reveals triple C–H bond activation of one sp^3 and both vinylic C–H bonds of isobutylene. The resultant moiety, shown in blue, is cooperatively bound by all five nickel centres prior to C–C bond cleavage.

cluster 4 also reveals resonances for the triply C–H activated isobutylene, with the methyl group at $\delta = 2.05$ and a singlet at $\delta = 2.90$ for one of the inequivalent coordinated $C{=}CH_2$ hydrogens. The second $C{=}CH_2$ hydrogen features a temperature-dependent shift that ranges from $\delta = 1.62$–1.78 between 283 and 288 K. Low-temperature $^{13}C\{^{1}H\}$-DEPT-Q (distortionless enhancement by polarization transfer) and $^{13}C\{^{1}H\}$-^{1}H-HSQC NMR spectra were collected to confirm these assignments.

Although carbide formation is often viewed as a detrimental step for heterogeneous Ni catalysis[37], there is a modern interest in the use of surface nickel carbides in reactions that involve C–H and C–C bond transformations[38,39], with the belief that reactivity occurs at four-coordinate square-planar carbide sites[40]. The facile transformations of the C–H and C–C bonds at $[(^{i}\mathrm{Pr}_3\mathrm{P})\mathrm{Ni}]_5\mathrm{H}_6$ demonstrate the dramatic effect of cooperativity by five metals, and offer a possible insight into unforeseen mechanisms of C–C bond making and breaking on metal surfaces at higher coordinate sites.

Data availability. Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under the deposition numbers 1559374 (2), 1559375 (3) and 1559376 (4). Copies of these data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif. All other data supporting the findings of this study are available within the article and Supplementary Information.

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References

1. Takemori, T., Inagaki, A. & Suzuki, H. A novel type of carbon–carbon double bond cleavage of 1,1-disubstituted alkenes on a triruthenium polyhydrido cluster. *J. Am. Chem. Soc.* **123,** 1762–1763 (2001).
2. Hu, S., Shima, T. & Hou, Z. Carbon–carbon bond cleavage and rearrangement of benzene by a trinuclear titanium hydride. *Nature* **512,** 413–415 (2014).
3. Suzuki, H., Takaya, Y., Takemori, T. & Tanaka, M. Selective carbon–carbon bond cleavage of cyclopentadiene on a trinuclear ruthenium pentahydride complex. *J. Am. Chem. Soc.* **116,** 10779–10780 (1994).
4. Matsubara, K., Inagaki, A., Tanaka, M. & Suzuki, H. Regioselective C–H bond activation of alkanes by a trinuclear ruthenium trihydride complex having a μ_3-sulfido ligand. *J. Am. Chem. Soc.* **121,** 7421–7422 (1999).
5. Buchowicz, W. *et al.* Triple C–H bond activation of a nickel-bound methyl group: synthesis and X-ray structure of a carbide cluster $(\mathrm{NiCp})_6(\mu_6\text{-C})$. *Inorg. Chem.* **51,** 8292–8297 (2012).
6. Chamberlin, R. L., Rosenfeld, D. C., Wolczanski, P. T. & Lobkovsky, E. B. Ethylene and alkyne carbon–carbon bond cleavage across tungsten–tungsten multiple bonds. *Organometallics* **21,** 2724–2735 (2002).
7. Calle-Vallejo, F. *et al.* Finding optimal surface sites on heterogeneous catalysts by counting nearest neighbors. *Science* **350,** 185–189 (2015).
8. Van Santen, R. A. Complementary structure sensitive and insensitive catalytic relationships. *Acc. Chem. Res.* **42,** 57–66 (2008).
9. Siaj, M. & McBreen, P. H. Creating, varying, and growing single-site molecular contacts. *Science* **309,** 588–590 (2005).
10. Vang, R. T. *et al.* Ethylene dissociation on flat and stepped Ni(111): a combined STM and DFT study. *Surf. Sci.* **600,** 66–77 (2006).
11. Guo, X. *et al.* Direct, nonoxidative conversion of methane to ethylene, aromatics, and hydrogen. *Science* **344,** 616–619 (2014).
12. Gozin, M., Weisman, A., Ben-David, Y. & Milstein, D. Activation of a carbon–carbon bond in solution by transition-metal insertion. *Nature* **364,** 699–701 (1993).
13. Rybtchinski, B. & Milstein, D. Metal insertion into C–C bonds in solution. *Angew. Chem. Int. Ed.* **38,** 870–883 (1999).
14. Eisch, J., Piotrowski, A., Han, K., Krüger, C. & Tsay, Y. Oxidative addition of nickel(0) complexes to carbon–carbon bonds in biphenylene: formation of nickelole and 1,2-dinickelecin intermediates. *Organometallics* **4,** 224–231 (1985).
15. Gunay, A. & Jones, W. D. Cleavage of carbon–carbon bonds of diphenylacetylene and its derivatives via photolysis of Pt complexes: tuning the C–C bond formation energy toward selective C–C bond activation. *J. Am. Chem. Soc.* **129,** 8729–8735 (2007).
16. Xi, Z., Sato, K., Gao, Y., Lu, J. & Takahashi, T. Unprecedented double C=C bond cleavage of a cyclopentadienyl ligand. *J. Am. Chem. Soc.* **125,** 9568–9569 (2003).
17. Sattler, A. & Parkin, G. Cleaving carbon–carbon bonds by inserting tungsten into unstrained aromatic rings. *Nature* **463,** 523–526 (2010).
18. Ohki, Y. *et al.* $\mathrm{Co}_6\mathrm{H}_8(\mathrm{P}^{i}\mathrm{Pr}_3)_6$: a cobalt octahedron with face-capping hydrides. *Angew. Chem.* **128,** 16053–16057 (2016).
19. Shima, T. *et al.* Dinitrogen cleavage and hydrogenation by a trinuclear titanium polyhydride complex. *Science* **340,** 1549–1552 (2013).
20. Camacho-Bunquin, J., Ferguson, M. J. & Stryker, J. M. Hydrocarbon-soluble nanocatalysts with no bulk phase: coplanar, two-coordinate arrays of the base metals. *J. Am. Chem. Soc.* **135,** 5537–5540 (2013).
21. Goodfellow, R. J., Hamon, E. M., Howard, J. A., Spencer, J. L. & Turner, D. G. Cationic platinum hydride clusters: X-ray crystal structures of $[\mathrm{Pt}_4\mathrm{H}_2(\mathrm{P}^{t}\mathrm{Bu}_3)_4][\mathrm{BF}_4]_2[\mathrm{HBF}_4]_2$ and $[\mathrm{Pt}_4\mathrm{H}_7(\mathrm{P}^{t}\mathrm{Bu}_3)_4][\mathrm{BPh}_4]$. *J. Chem. Soc. Chem. Commun.* 1604–1606 (1984).
22. Brayshaw, S. K. *et al.* Holding onto lots of hydrogen: a 12-hydride rhodium cluster that reversibly adds two molecules of H_2. *Angew. Chem. Int. Ed.* **44,** 6875–6878 (2005).
23. Brayshaw, S. K. *et al.* Sequential reduction of high hydride count octahedral rhodium clusters $[\mathrm{Rh}_6(\mathrm{PR}_3)_6\mathrm{H}_{12}][\mathrm{BArF}_4]_2$: redox-switchable hydrogen storage. *J. Am. Chem. Soc.* **129,** 1793–1804 (2007).
24. Araake, R., Sakadani, K., Tada, M., Sakai, Y. & Ohki, Y. $[\mathrm{Fe}_4]$ and $[\mathrm{Fe}_6]$ hydride clusters supported by phosphines: synthesis, characterization, and application in N_2 reduction. *J. Am. Chem. Soc.* **139,** 5596–5606 (2017).
25. Tsui, E. Y., Tran, R., Yano, J. & Agapie, T. Redox-inactive metals modulate the reduction potential in heterometallic manganese–oxido clusters. *Nat. Chem.* **5,** 293–299 (2013).
26. Kanady, J. S., Tsui, E. Y., Day, M. W. & Agapie, T. A synthetic model of the $\mathrm{Mn}_3\mathrm{Ca}$ subsite of the oxygen-evolving complex in photosystem II. *Science* **333,** 733–736 (2011).
27. Fout, A. R., Zhao, Q., Xiao, D. J. & Betley, T. A. Oxidative atom-transfer to a trimanganese complex to form Mn_6 $(\mu^6\text{-}E)(E = \mathrm{O, N})$ clusters featuring interstitial oxide and nitride functionalities. *J. Am. Chem. Soc.* **133,** 16750–16753 (2011).
28. Lee, Y. *et al.* Dinitrogen activation upon reduction of a triiron(II) complex. *Angew. Chem.* **127,** 1519–1523 (2015).
29. Lee, Y. *et al.* Reactivity of hydride bridges in high-spin $[3\mathrm{M}\text{–}3(\mu\text{-H})]$ clusters ($\mathrm{M} = \mathrm{Fe}^{\mathrm{II}}, \mathrm{Co}^{\mathrm{II}}$). *J. Am. Chem. Soc.* **137,** 10610–10617 (2015).
30. Murray, L. J., Weare, W. W., Shearer, J., Mitchell, A. D. & Abboud, K. A. Isolation of a (dinitrogen) tricopper (I) complex. *J. Am. Chem. Soc.* **136,** 13502–13505 (2014).
31. Powers, T. M. & Betley, T. A. Testing the polynuclear hypothesis: multi-electron reduction of small molecules by triiron reaction sites. *J. Am. Chem. Soc.* **135,** 12289 (2013).
32. Ishikawa, Y. *et al.* Modulation of benzene or naphthalene binding to palladium cluster sites by the backside-ligand effect. *Angew. Chem.* **127,** 2512–2516 (2015).
33. Beck, R., Shoshani, M. & Johnson, S. A. Catalytic hydrogen/deuterium exchange of unactivated carbon–hydrogen bonds by a pentanuclear electron-deficient nickel hydride cluster. *Angew. Chem.* **124,** 11923–11926 (2012).
34. Shoshani, M. M. & Johnson, S. A. Facile deep and ultradeep hydrodesulfurization by the $[(^{i}\mathrm{Pr}_3\mathrm{P})\mathrm{Ni}]_5\mathrm{H}_6$ cluster compared to mononuclear Ni sources. *Inorg. Chem.* **54,** 11977–11985 (2015).
35. Ervin, K. M. *et al.* Bond strengths of ethylene and acetylene. *J. Am. Chem. Soc.* **112,** 5750–5759 (1990).
36. Kalyani, D., Deprez, N. R., Desai, L. V. & Sanford, M. S. Oxidative C–H activation/C–C bond forming reactions: synthetic scope and mechanistic insights. *J. Am. Chem. Soc.* **127,** 7330–7331 (2005).
37. Bartholomew, C. H. Mechanisms of catalyst deactivation. *Appl. Catal. A* **212,** 17–60 (2001).
38. Solymosi, F., Cserényi, J., Szöke, A., Bánsági, T. & Oszko, A. Aromatization of methane over supported and unsupported Mo-based catalysts. *J. Catal.* **165,** 150–161 (1997).
39. Oyama, S. Preparation and catalytic properties of transition metal carbides and nitrides. *Catal. Today* **15,** 179–200 (1992).
40. Nandula, A., Trinh, Q. T., Saeys, M. & Alexandrova, A. N. Origin of extraordinary stability of square-planar carbon atoms in surface carbides of cobalt and nickel. *Angew. Chem. Int. Ed.* **54,** 5312–5316 (2015).

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Author contributions

M.M.S. conducted the experiments and analysed the data. M.M.S. and S.A.J. conceived and designed the project and prepared the manuscript

Additional information

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Competing financial interests

The authors declare no competing financial interests.