Dalton
Transactions

FRONTIER

Cite this: *Dalton Trans.*, 2019, **48**, 8530

Multiple activations of CH bonds in arenes and heteroarenes

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Received 14th April 2019,
Accepted 20th May 2019

DOI: 10.1039/c9dt01584a

rsc.li/dalton

The activation of CH bonds in arenes and heteroarenes has attracted considerable attention in recent years. Examples of the activation of two or more CH bonds in arenes or heteroarenes are rare. In recent studies it has been found that certain polynuclear metal carbonyl complexes, such as $Re_2(CO)_8(\mu\text{-}C_6H_5)(\mu\text{-}H)$, **1** and $Os_3(CO)_{10}(NCMe)_2$, can react two or more times with selected arenes and heteroarenes through a series of CH activations to yield interesting new multiply-CH activated arenes and heteroarenes and can lead to the opening of ring systems in the case of heteroarenes. A summary of these novel reactions and new products is presented in this Frontier article.

Introduction

The activation of the C–H bonds in hydrocarbons has attracted the interest of organometallic chemists for many years.[1] The activation of aromatic CH bonds was actually among the first examples of CH activation transformations, Scheme 1,[2] and has been the most successfully developed over the years.[3] In this Frontier article, the CH activation process is defined as the full cleavage of a CH bond by oxidative addition to a low-valent transition metal complex to yield a hydrido ligand and an aryl ligand,[1a,b,3] but the overall process may involve intermediates or transition states in which the CH bond is coordinated to the metal prior to its cleavage.

CH activation processes are an important first step in many examples of the metal-catalyzed functionalization of aromatic hydrocarbons which has been one of the great triumphs of modern organometallic chemistry.[4]

Curiously, there have been very few examples of multiple aromatic CH activations.[5–7] Esteruelas *et al.* showed that a single osmium atom could active a CH bond on two different aryl rings (double *ortho*-metallation), *e.g.* Scheme 2.[5]

It has been shown that a single vanadium or zirconium atom can activate adjacent CH bonds on benzene to yield a benzyne C_6H_4 ligand, Scheme 3.[6]

A number of studies have shown that polynuclear metal complexes can generate benzyne ligands by 1,2-activation of CH bonds in benzene, see Scheme 4.[7]

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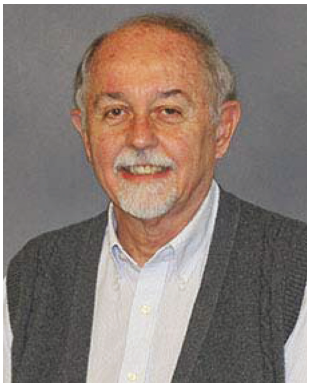

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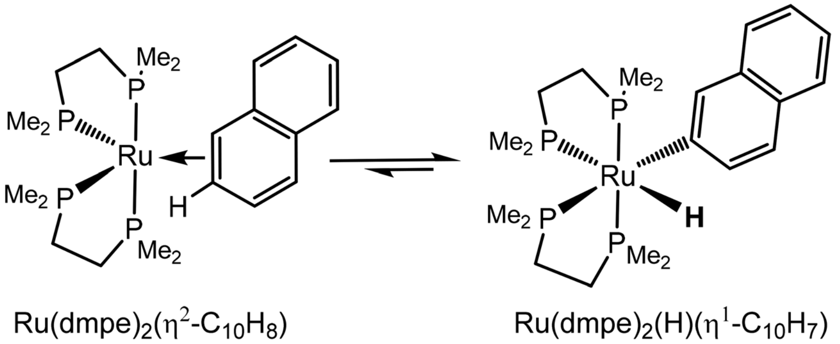
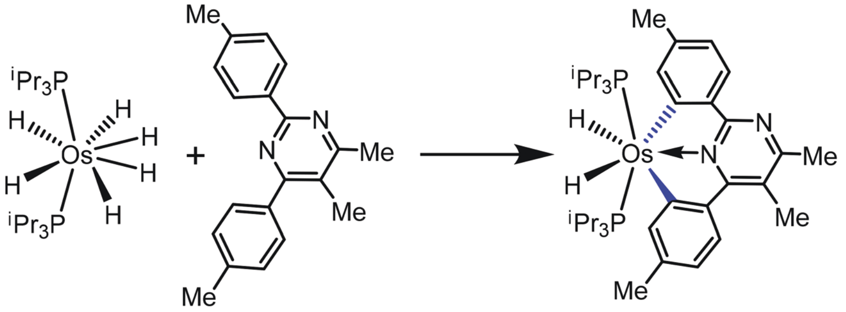
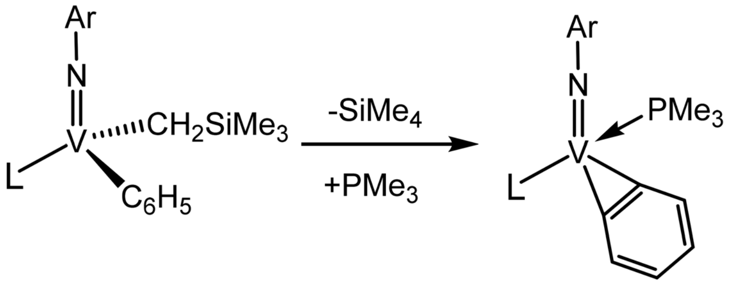


Scheme 1 A schematic of the conversion of naphthalene to a naphthyl ligand and a hydrido ligand by aromatic activation at the ruthenium of the π-coordinated naphthalene ligand in the ruthenium complex on the left.



Scheme 2 Two CH activations of a diaryl-substituted pyrimidine ligand by two *ortho*-metallations at the osmium atom of the osmium complex.

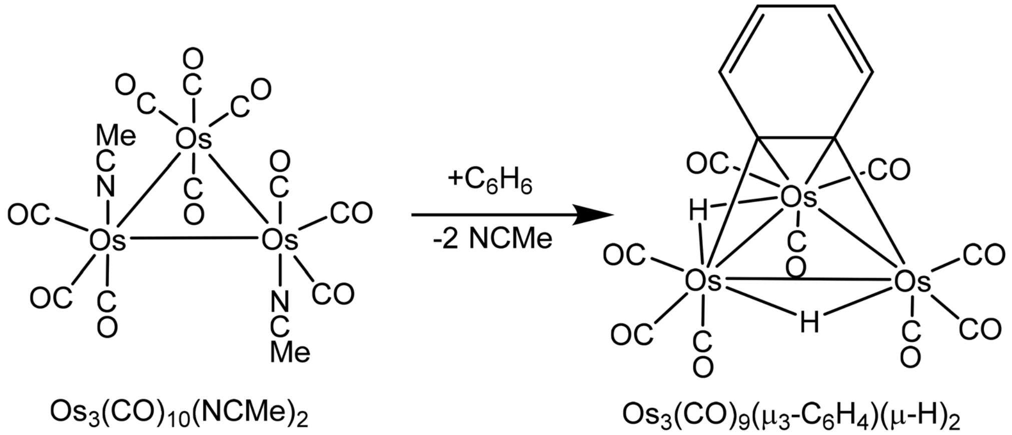


Scheme 3 A schematic of the conversion of a phenyl ligand to a benzyne ligand by CH activation at a neighboring carbon atom in the phenyl ring.

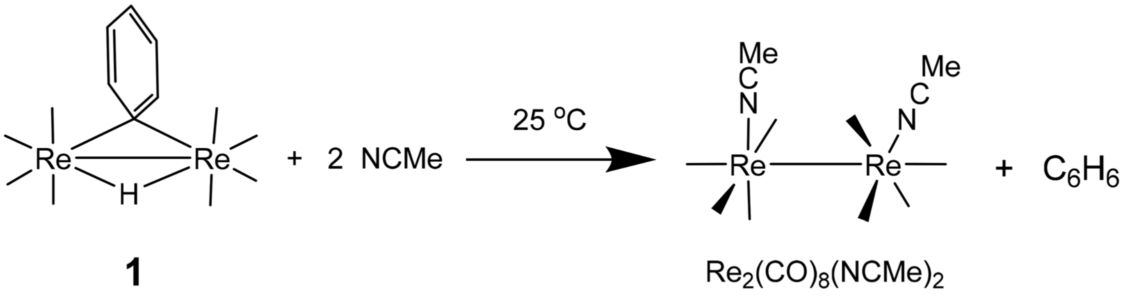
Our journey into the study of the activation of aromatic CH bonds with polynuclear metal complexes began with our synthesis of the compound $Re_2(CO)_8(\mu\text{-}C_6H_5)(\mu\text{-}H)$, **1**, by the reaction of $Re_2(CO)_8(\mu\text{-}C_6H_5)[\mu\text{-}Au(PPh_3)]$ with $HSnPh_3$.[8] To our surprise, the $SnPh_3$ group combined with the $Au(PPh_3)$ group and removed it from the complex to yield the compound $[Ph_3SnAuPPh_3]_2$. In this process, the hydrogen atom from the stannane was transferred to the dirhenium group to yield the coproduct **1** which contains an η^1-bridging phenyl group and a bridging hydrido ligand across the Re–Re bond. The η^1-bridging phenyl group and the hydrido ligand both serve as 1-electron donors, thus compound **1** contains a total of 32 valence electrons and is formally unsaturated by the amount of two electrons. We immediately realized that compound **1** should readily accept donor ligands and should probably also reductively eliminate C_6H_6 by formation of a CH bond between the phenyl and hydrido ligands. This was readily accomplished quantitatively by the addition of two equivalents of NCMe to **1**, see Scheme 5.[8]

More importantly, it was found shortly thereafter that even benzene itself was sufficiently "nucleophilic" to induce the reductive elimination of C_6H_6 from **1** and in the process an added molecule of benzene was converted to a new bridging phenyl ligand and bridging hydrido ligand by the oxidative addition of one of its C–H bonds to the dirhenium carbonyl group.[9] This exchange reaction was confirmed by an isotope-labeling experiment as illustrated in Scheme 6.

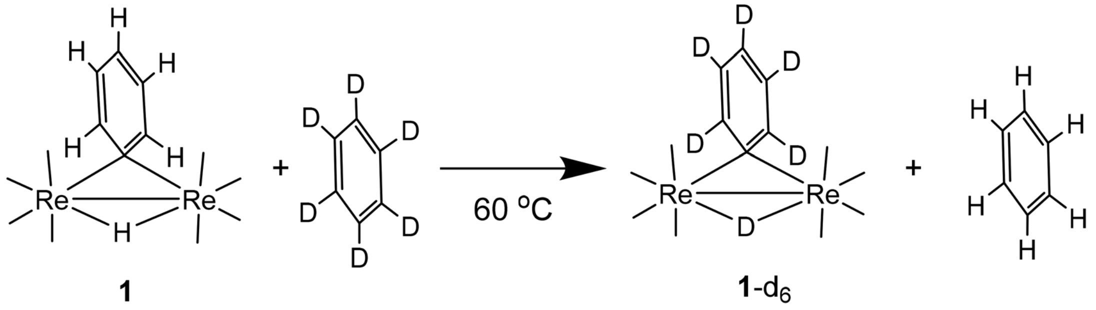
Computational analyses revealed that the oxidative addition of the C–H bond to the dirhenium group proceeded *via* transition state **TS** containing a binuclear η^2-CH coordinated C_6H_6



Scheme 4 A schematic of the conversion of benzene into a benzyne ligand by 1,2-CH activation by a triosmium carbonyl cluster complex.



Scheme 5 A schematic of the reductive elimination of benzene from compound **1** by the addition of NCMe.

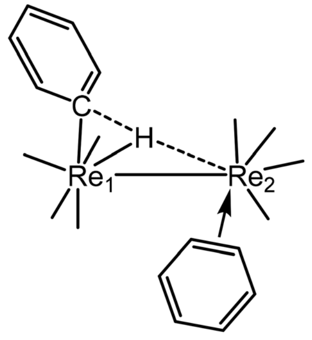


Scheme 6 A benzene–benzene exchange reaction involving compound **1** performed by using isotopically labeled benzene.

ligand. The H atom of the activated CH bond in **TS** interacts with both rhenium atoms, and the electron density from the metal–metal bond is fed into the σ*-orbital of the CH bond to facilitate its cleavage (Scheme 7).[9]

It was soon found that CH activation reactions could be achieved through reactions of **1** and other arenes, such as naphthalene and *N*,*N*-diethylaniline in particular.[9] The reaction of $Re_2(CO)_8(\mu\text{-}C_6H_5)(\mu\text{-}H)$, **1**, with naphthalene yielded the naphthyl complex $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}C_{10}H_7)(\mu\text{-}H)$, **2**, which contains an η^2-σ + π-coordinated bridging naphthyl ligand that serves as a 3-electron donor to the dirhenium group.[9] Thus, compound **2** contains 34 valence electrons at the two mutually bonded metal atoms and it is electronically saturated, *i.e.* each metal atom formally has an 18 electron configuration. The reaction involves a reductive-elimination of benzene from **1**[9] and an oxidation addition of the CH bond at the 2-position of the naphthalene molecule to the incipient $Re_2(CO)_8$ group formed by the elimination of benzene from **1**, see Scheme 8.[10]

Most interestingly, it was found that the reaction of naphthalene with an excess of **1** yielded two doubly CH activated, bis-$Re_2(CO)_8(\mu\text{-}H)$ naphthalendiyl coproducts: $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}\mu\text{-}\eta^2\text{-}3,4\text{-}C_{10}H_6)Re_2(CO)_8(\mu\text{-}H)$, **3**, in 47% yield and $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}\mu\text{-}\eta^2\text{-}5,6\text{-}C_{10}H_6)Re_2(CO)_8(\mu\text{-}H)$, **4**, in 8% yield, Scheme 8. These products can also be obtained



TS

Scheme 7 A line structure of the transition state **TS**.

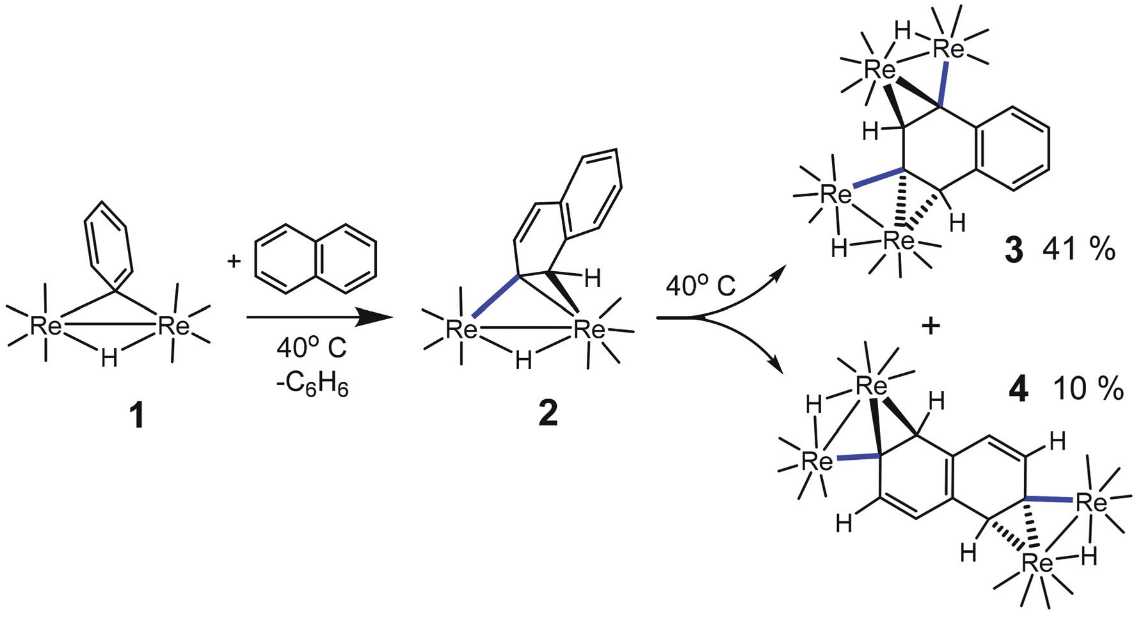
in similar yields from the reaction of **2** with **1**. Compound **3** contains two $Re_2(CO)_8(\mu\text{-}H)$ groups on the naphthalendiyl ligand which undergoes CH activation at both the 2- and 4-positions. Compound **4** also contains two σ + π-coordinated $Re_2(CO)_8(\mu\text{-}H)$ groups on the bridging naphthalendiyl ligand, but the CH activations occurred on different rings, specifically at the 2- and 6-positions, one on each ring. Compound **4** is structurally centrosymmetrical.

Anthracene reacts with **1** in a similar series of steps to yield a mono CH activated dirhenium complex $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}C_{14}H_9)$, **5**, and two doubly CH activated complexes $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}\mu\text{-}\eta^2\text{-}3,4\text{-}C_{14}H_8)Re_2(CO)_8(\mu\text{-}H)$, **6**, and $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}\mu\text{-}\eta^2\text{-}5,6\text{-}C_{14}H_8)Re_2(CO)_8(\mu\text{-}H)$, **7**, that are structurally analogous to **3** and **4** but contain the three ring anthracendiyl ligand instead, Scheme 9.[10]

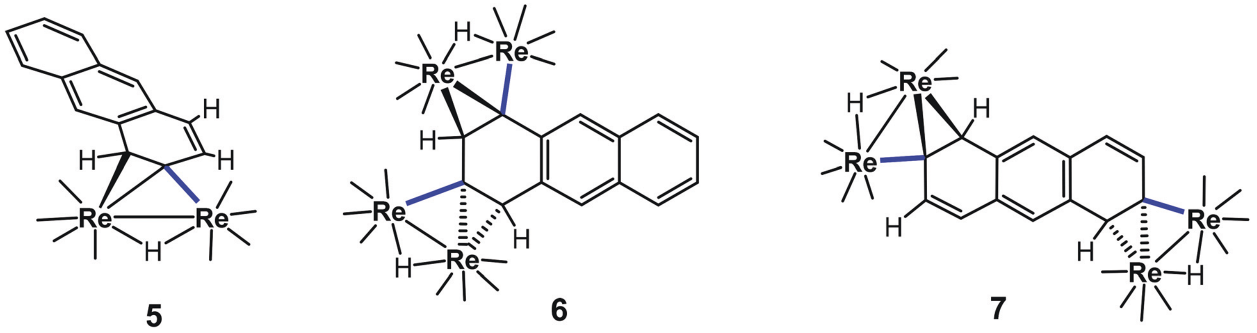
However, the most remarkable product from the anthracene reaction was the tetra-$Re_2(CO)_8(\mu\text{-}H)$ anthracenetetrayl complex $[Re_2(CO)_8(\mu\text{-}H)]_4(\mu\text{-}\eta^2\text{-}1,2\text{-}\mu\text{-}\eta^2\text{-}3,4\text{-}\mu\text{-}\eta^2\text{-}5,6\text{-}\mu\text{-}\eta^2\text{-}7,8\text{-}C_{14}H_6)$, **8**, formed in low yield by the activation of four of the aromatic CH bonds on the two outer rings of a single molecule of anthracene. All four $Re_2(CO)_8(\mu\text{-}H)$ groups possess the η^2-bridging σ + π-coordination to the ring system. Two of the $Re_2(CO)_8(\mu\text{-}H)$ groups lie on one side of the C_{14} plane and two on the other side. Overall, the molecule has C_2-rotational symmetry with the C_2-axis passing through the center of the central ring perpendicular to the C_{14} plane of the anthracenetetrayl ligand, see Fig. 1.

Interestingly, we found that compound **1** will even react with itself by loss of benzene to yield the doubly-metalated benzene compound $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}1,\mu\text{-}3\text{-}C_6H_4)Re_2(CO)_8(\mu\text{-}H)$, **9**, which contains two $Re_2(CO)_8(\mu\text{-}H)$ groups bridged by a single C_6H_4 ring metalated at *ortho*-related carbon atoms, see Fig. 2. Compound **9** contains an approximate C_2-symmetry with the 2-fold rotation axis passing through the ring carbon atoms C2 and C5. As in compound **1**, only one carbon atom of the C_6 ring is bonded to each pair of rhenium atoms.

To extend our studies of these CH activation reactions, we investigated the reactions of **1** with the bowl-shaped aromatic compound corannulene, $C_{20}H_{10}$.[11] These studies provided the first examples of CH activation reactions in corannulene. Four products were obtained, one mono CH activated compound, $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}C_{20}H_9)$, **10**, and three doubly-CH activated compounds: $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}\mu\text{-}\eta^2\text{-}10,11\text{-}C_{20}H_8)Re_2(CO)_8(\mu\text{-}H)$, **11**, $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}2,1\text{-}\mu\text{-}\eta^2\text{-}10,11\text{-}C_{20}H_8)Re_2(CO)_8(\mu\text{-}H)$, **12** and $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}1,2\text{-}\mu\text{-}\eta^2\text{-}11,10\text{-}C_{20}H_8)Re_2(CO)_8(\mu\text{-}H)$, **13**. In all of the products, the $Re_2(CO)_8(\mu\text{-}H)$ group bridges a single double bond in one of the rim locations



Scheme 8 Activation of the CH bonds in naphthalene in its reactions with compound **1**. The blue lines indicate the locations of the rhenium–carbon σ-bonds. CO ligands are represented only as lines from the Re atoms.



5 6 7

Scheme 9 Line structures of compounds 5–7.

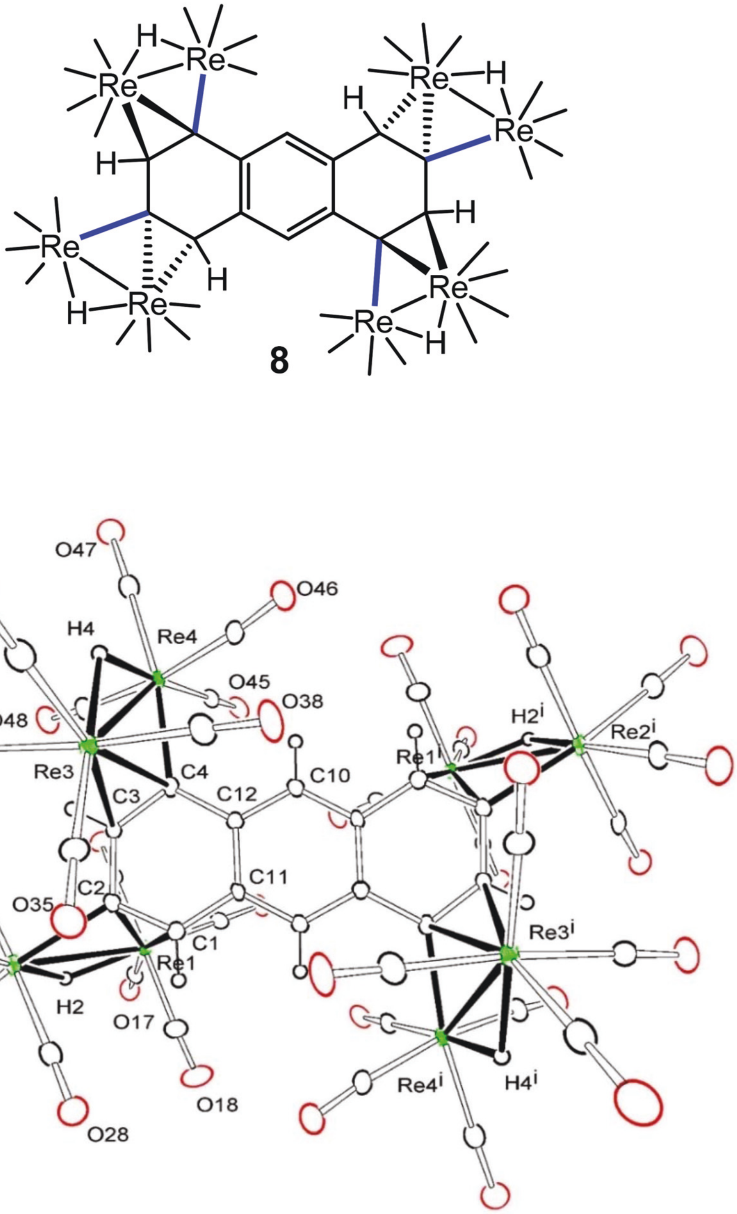


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Fig. 1 A line structure (upper) and an ORTEP diagram (lower) of the molecular structure of compound **8**, a quadruply CH activated anthracene complex. Reproduced with permission from the American Chemical Society, ref. 10*a*.

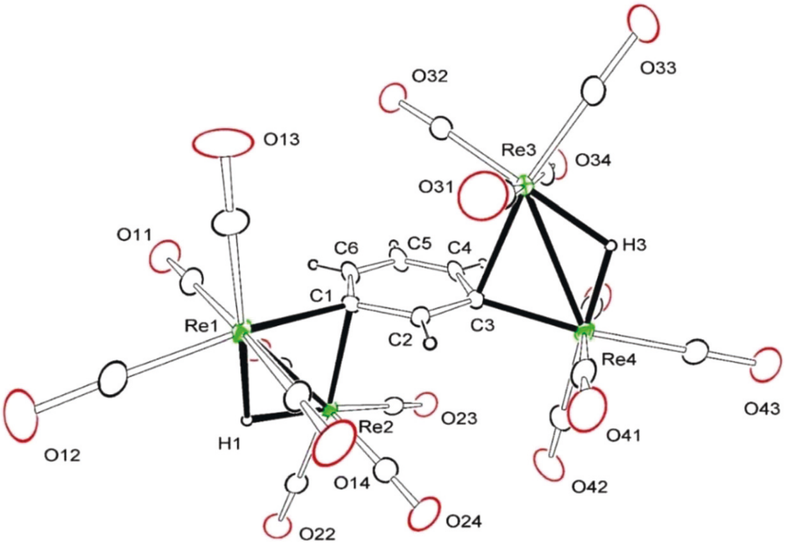


Fig. 2 An ORTEP diagram of the molecular structure of $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}1,\mu\text{-}3\text{-}C_6H_4)Re_2(CO)_8(\mu\text{-}H)$, **9**. Reproduced with permission from the American Chemical Society, ref. 10*a*.

in the standard σ + π coordination to a pair of rhenium atoms. Compounds **11–13** are isomers and can be obtained directly from **10** by reaction with a second equivalent of **1**. In each case, the $Re_2(CO)_8(\mu\text{-}H)$ group is coordinated to a rim C–C double bond at the 1,2 and 10,11 positions of the outer ring. Fig. 3 shows the molecular structure of **11** obtained from a single-crystal X-ray diffraction analysis. For steric reasons, the dirhenium groups are coordinated on the outside of the corannulene bowl in all cases.

The doubly-metalated isomers **11–13** differ according to which of the CH bonds were activated. In compound **11** the CH bonds were activated at the carbon atoms at the C1 and C10 positions. In **12** the CH bonds were activated at the C2 and C10 positions and in **13** the CH bonds were activated at the C1 and C11 positions. The isomers are shown schematically in Scheme 10. The blue lines show the locations of the Re–C σ-bonds which signify the locations of the CH activation sites.

Furans are an important family of heteroarenes that are derived from biomass and serve as platform chemicals and precursors of a range of higher-value compounds including biofuels.[12] There are a number of examples of the activation of CH bonds of furan C_4H_4O by mononuclear metal complexes.[13] σ-Bonded furyl complexes formed by CH activation at the 2-position of the furan molecule are the typical result. In recent studies, we have found that **1** reacts readily with furan, C_4H_4O, to yield two dirhenium furyl isomers, $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}2,3\text{-}C_4H_3O)(\mu\text{-}H)$, **14**, and $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}3,2\text{-}C_4H_3O)(\mu\text{-}H)$, **15**,

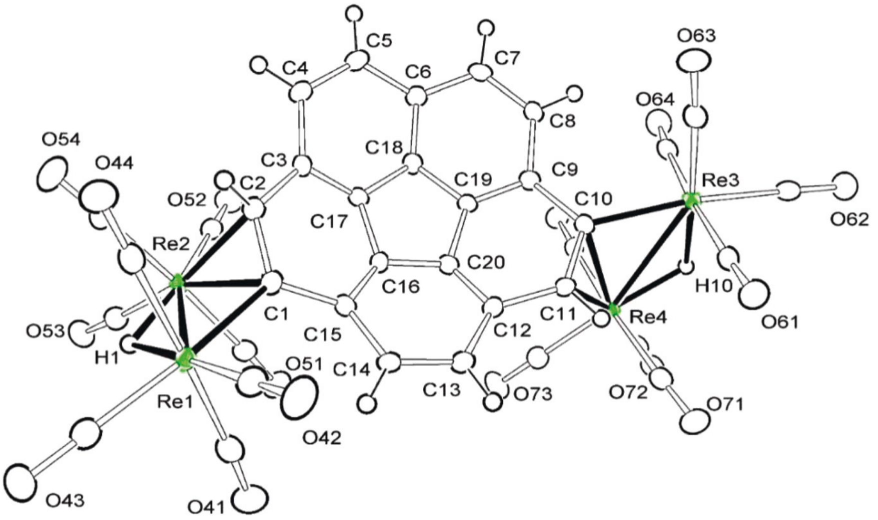
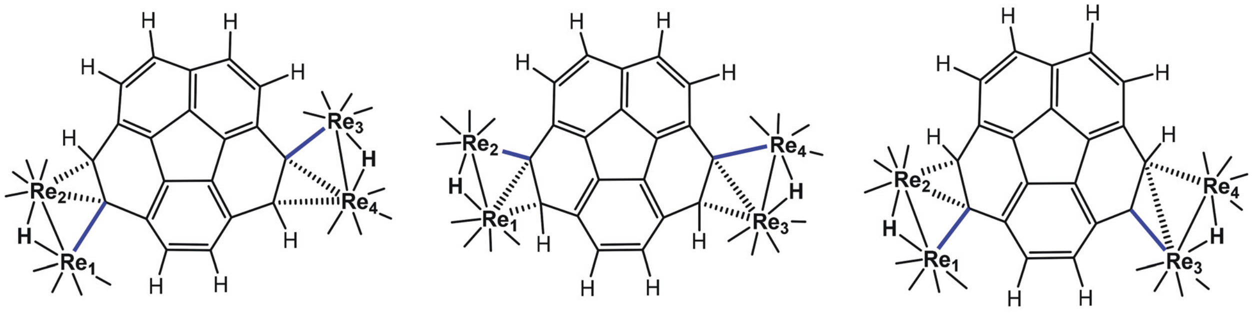


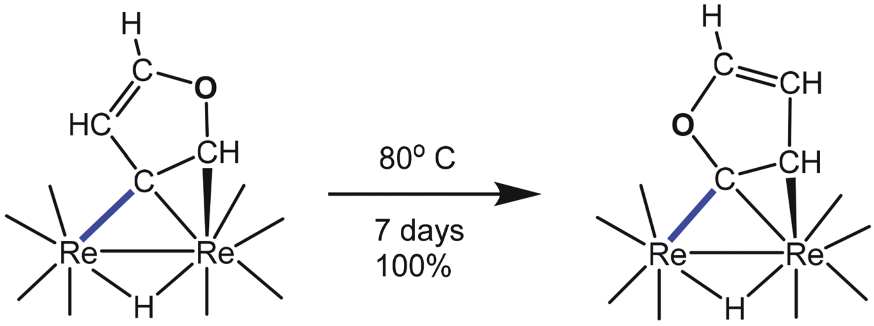
Fig. 3 A structural diagram of the molecular structure of $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\mu\text{-}\eta^2\text{-}1,2\text{-}\mu\text{-}\eta^2\text{-}10,11\text{-}C_{20}H_8)Re_2(CO)_8(\mu\text{-}H)$, **11**. Reproduced with permission from the Wiley VCH Publishers, ref. 11.



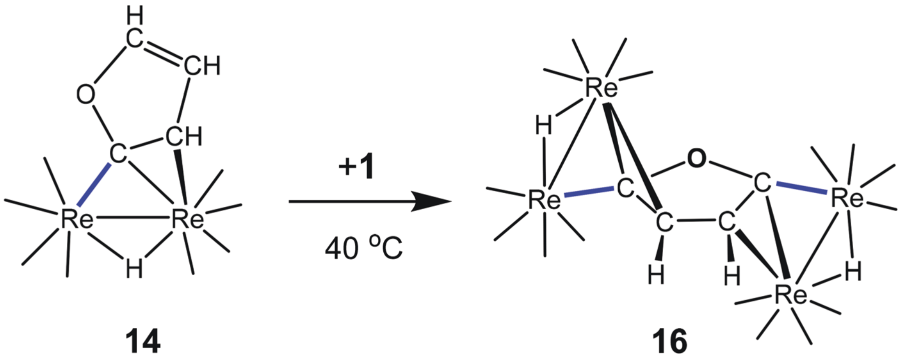
Scheme 10 Line structures of the three isomers of the doubly CH activated corannulene complexes **11–13**. The blue lines indicate the locations of the rhenium–carbon σ-bonds. CO ligands are represented only as lines from the Re atoms.

which differ according to which of the two furan CH bonds were activated to form them.[14] Compound **14** was formed by CH activation at the furan 2-position and compound **15** was formed by activation at the 3-position. In both cases, the CH activated C–C double bond is σ + π-coordinated to the two rhenium atoms as a bridging ligand. Compound **15** can be isomerized quantitatively to **14** by heating to 80 °C in solution for 7 days, see Scheme 11. The mechanism of this transformation has not yet been established.

Compound **14** reacts with a second equivalent of **1** to yield the doubly metalated furan complex $[Re_2(CO)_8(\mu\text{-}H)]_2(\mu\text{-}\eta^2\text{-}2,3\text{-}\mu\text{-}\eta^2\text{-}5,4\text{-}C_4H_2O)$, **16**, by a CH activation at the carbon atom at the 5-position of the furyl ligand in **14**, see Scheme 12. Compound **16** has a C_2 symmetry.



Scheme 11 Line structures of the two CH activated furan isomers **14** and **15** and their thermal isomerization. The blue lines indicate the locations of the rhenium–carbon σ-bonds. CO ligands are represented only as lines from the Re atoms.

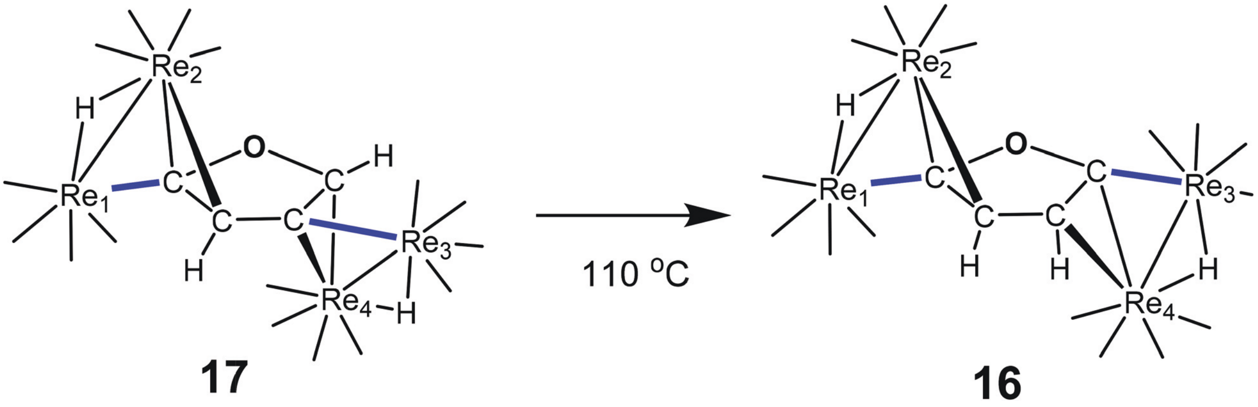


Scheme 12 A schematic of the synthesis and structure of the doubly CH activated furandiyl complexes **16** from **14**. The blue lines indicate the locations of the rhenium–carbon σ-bonds. CO ligands are represented only as lines from the Re atoms.

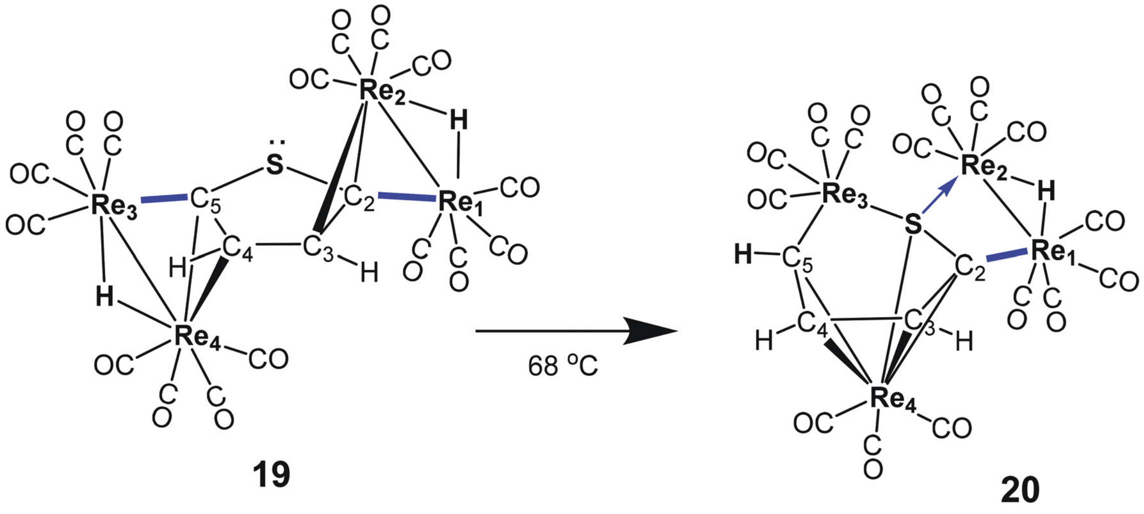
Compound **15** reacts with **1** to yield the doubly-metalated compound $[Re_2(CO)_8(\mu\text{-}H)]_2(\mu\text{-}\eta^2\text{-}2,3\text{-}\mu\text{-}\eta^2\text{-}4,5\text{-}C_4H_2O)$, **17**, by a CH activation at the 5-position in **15**. Compound **17** is an isomer of **16** and it can be isomerized to **16** by heating to 110 °C for 10 h, see Scheme 13. The mechanism of the 1,2-H-shift that occurs in this process has not yet been established.

Compound **1** reacts with thiophene (the sulfur homolog of furan) to yield the dirhenium complex $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}SC_4H_3)(\mu\text{-}H)$ **18,** the thienyl homolog of **14** and $[Re_2(CO)_8(\mu\text{-}H)]_2(\mu\text{-}\eta^2\text{-}2,3\text{-}\mu\text{-}\eta^2\text{-}4,5\text{-}C_4H_2S)$, **19**, the doubly CH activated thiendiyl homolog of **16.**[15] Interestingly, the heated compound **19** underwent a ring-opening transformation of the bridging thiendiyl ligand by cleavage of the heteroatomic C–S bond to yield the compound $Re(CO)_4[\mu\text{-}\eta^5\text{-}\eta^2\text{-}SCC(H)C(H)C(H)][Re(CO)_3][Re_2(CO)_8(\mu\text{-}H)]$, **20**, this could be regarded as the first step in a potential process for the desulfurization of the thiendiyl ligand, see Scheme 14. Compound **20** contains a doubly-metalated 1-thiapentadienyl ligand that is π–coordinated to a $Re(CO)_3$ group and edge-bridged by a $Re_2(CO)_8(\mu\text{-}H)$ group and has a $Re(CO)_4$ group that was inserted into the C5–S bond of **19**.

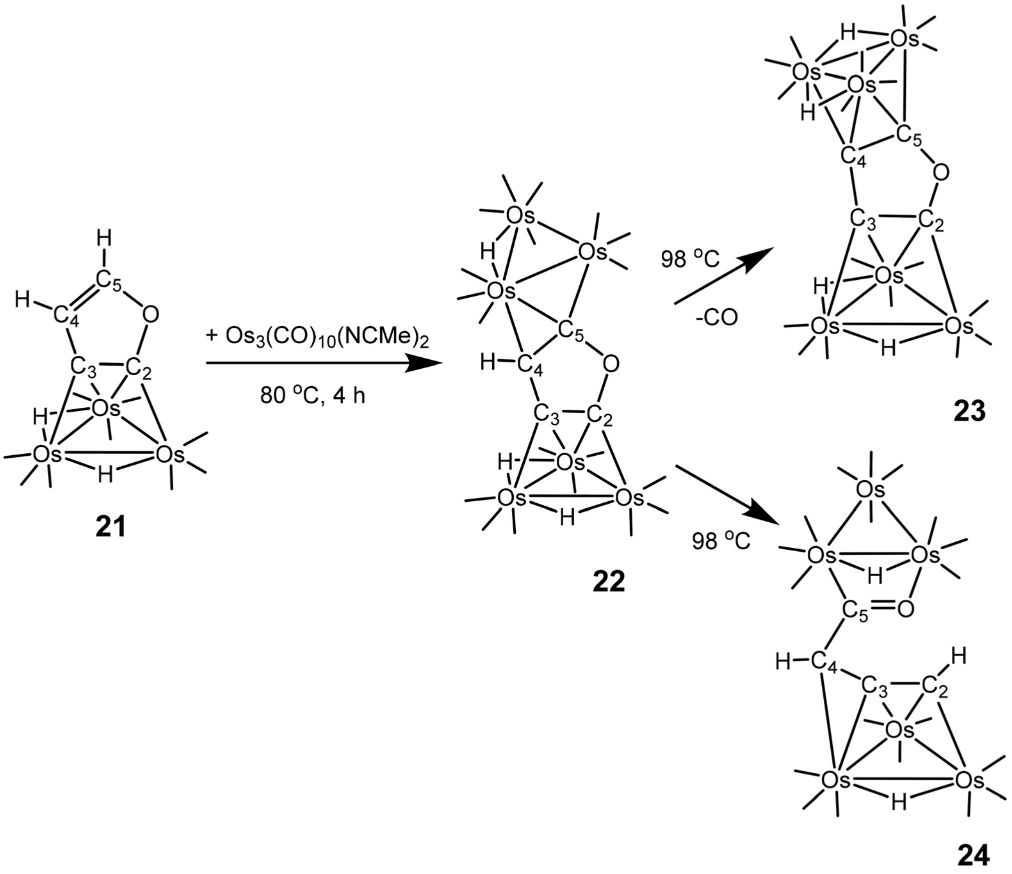
In an effort to take the multiple CH activation concept to the limit in a heteroarene, we investigated the reaction of the triosmium furyne complex $Os_3(CO)_9(\mu_3,\eta^2\text{-}C_4H_2O)(\mu\text{-}H)_2$,[16] **21**, with $Os_3(CO)_{10}(NCMe)_2$. Three products: $Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}2,3\text{-}\mu\text{-}\eta^2\text{-}4,5\text{-}C_4HO)Os_3(CO)_{10}(\mu\text{-}H)$, **22**, $Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}2,3\text{-}\mu_3\text{-}\eta^2\text{-}4,5\text{-}C_4O)Os_3(CO)_9(\mu\text{-}H)_2$, **23**, and $Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2,\mu\text{-}\eta^2\text{-}CHCCHC{=}O)Os_3(CO)_{10}(\mu\text{-}H)$, **24** were obtained. Compounds **22** and **23** were formed by a series of CH activation steps upon the addition of a second $Os_3(CO)_{10}$ group to the uncoordinated C–C double bond of the furyne ligand in **21**, see Scheme 15.[17] Compound **22** was formed by a CH activation at atom C5 of the furyne ring and **23** would formed from **22** by a CH acti-



Scheme 13 A schematic of the structures and isomerization of the doubly CH activated furandiyl complexes **17** and **16**. The blue lines indicate the locations of the rhenium–carbon σ-bonds. CO ligands are represented only as lines from the Re atoms. Reproduced with permission from the American Chemical Society, ref. 14.



Scheme 14 A schematic of the ring-opening transformation of compound **19** into **20**. The blue lines indicate the locations of the rhenium–carbon σ-bonds.



Scheme 15 A schematic of the synthesis of the furdiyne complex **23**. CO ligands are represented only as lines from the Os atoms.

vation at the C4 position of the ring. Product **23** contains what could be described as the first example of a "furdiyne" ligand which has had all four of the hydrogen atoms removed from the original furan molecule that was used to form **21**.

Compound **22** also underwent a competitive opening of its furynyl ligand to yield the ring-opened hexaosmium complex $Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2,\mu\text{-}\eta^2\text{-}CHCCHC{=}O)Os_3(CO)_{10}(\mu\text{-}H)$, **24**, see Scheme 15.

Conclusions and prospects

Our recent studies reveal that certain polynuclear metal carbonyl complexes have a special ability to perform multiple-aromatic CH activation reactions. It has been shown that these polynuclear metal complexes can readily activate more than one aromatic CH bond in a variety of arenes and heteroarenes. The $\sigma + \pi$ coordination of the bridging aromatic ring to two metal atoms obviously produces a greater stabilization of the activated species than a single metal atom can and may also increase the potential for a second CH activation on the same ring system. In a few cases, it has been shown that the multiply CH activated heteroarenes can undergo opening of their rings. This could pave the way for deeper and richer chemistry of the aromatic precursors and lead to useful new organic transformations and functionalizations of the ring systems, especially if they could be performed catalytically by the polynuclear metal complexes or at polynuclear metal sites on metal surfaces.[18]

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

This research was supported by grants 1464596 and 1764192 from the U. S. National Science Foundation.

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