

# Attempts at generating metathesis-active Fe(IV) and Co(IV) complexes via the reactions of $(\text{silox})_2\text{M}(\text{THF})_2$ , $[(\text{silox})_3\text{M}][\text{Na}(\text{THF})_2]$ ( $\text{M} = \text{Fe}, \text{Co}$ ), and related species with propellanes and triphenylboron

Gregory M. George, Peter T. Wolczanski<sup>\*</sup>, Samantha N. MacMillan

Department of Chemistry & Chemical Biology, Baker Laboratory, Cornell University, Ithaca, NY 14853, USA

## ARTICLE INFO

Dedicated to the memory of Prof. Malcolm L.H. Green, his passion for chemistry, and his delight in its practice.

**Keywords:**  
Iron  
Siloxide  
Propellane  
Boron  
Alkylidene

## ABSTRACT

Metathetical syntheses of  $(\text{silox})_2\text{M}(\text{THF})_2$  (1-M, Fe, Co),  $[(\text{silox})_3\text{M}][\text{Na}(\text{THF})_2]$  (2-M, Fe, Co), and  $(\text{silox})_3\text{Fe}(\text{THF})_2$  (3) are presented, as are X-ray structural studies of 1-Co, 2-Fe, and 2-Co. Exposure of these complexes to 1.1.1-propellane (**111P**,  $\text{C}_5\text{H}_6$ ) and 1,3-dehydroadamantane (**AdP**), which are known progenitors of ROMP-active alkylidenes with ruthenium, failed to elicit similar reactivity. A total of 28 complexes were subjected to **111P** in attempts to make “Fe(IV)” alkylidenes capable of some form of olefin metathesis with no success. At best, catalytic ring-opening to 3-*exo*-methylene cyclobutylidene was evidenced. The addition of triphenylboron as a Lewis acid failed to aid in metal complex formation of the propellanes, but an unusual rearrangement of **AdP** was noted. In addition, 2-Fe catalyzed the conversion of **111P** to 3-*exo*-methylene cyclobutylidene, which added twice to  $\text{Ph}_3\text{B}$ , affording a structurally characterized product,  $\text{Ph}(\kappa\text{-CH}=\text{CMeCH}_2\text{BPh}(\text{C}_4\text{H}_4\text{-1-Ph,3-CH}_2))$  (**4**), which features cyclobutyl-ring-opening, migration, and phenyl migration.

## 1. Introduction

Olefin metathesis (OM) as a useful catalytic process is restricted to transition metals that are predominantly in the second row [1–5]. Molybdenum is practically significant and diverse in application, and ruthenium catalysts are widely available, and tolerant to diverse functionality. Continued exploration of these systems has uncovered significant improvements in cross-metathesis (CM) and enantioselective applications [6,7]. Some 3rd-row transition metal species have also shown utility [8], but group 6 and 8 1st-row alternatives, chromium [9,10] and iron [11–25], have failed to exhibit the bond-making and -breaking steps crucial to OM. In the first row, only vanadium alkylidenes [26–29] show significant ring-opening metathesis polymerization (ROMP) activity, following seminal work on niobium and tantalum [33]. Recent work on vanadium suggests that that catalytically relevant olefin metathesis (e.g.,  $\text{RCH}=\text{CH}_2 \rightarrow \text{RCH}=\text{CHR} + \text{C}_2\text{H}_4$ ) [30] and ring-closing metathesis catalysis [31,32] may be possible, where some of the earliest catalysts base on titanium alkylidenes proved only modestly effective [34–36].

Theoretical work by Hoffmann suggests that  $d^n$  ( $n \leq 4$ ) complexes are a requirement for metathesis [37], based on the idea that at least one of the “ $t_{2g}$ ” orbitals must be empty to accommodate electron density in the

crucial  $\text{M}=\text{CHR} + \text{olefin}$  to metalacyclobutane conversion. Interestingly, while chromium metalacyclobutane complexes have been isolated from the addition of olefins to transient chromium(VI) alkylidenes [9,10], cycloreversion required for catalysis is apparently not energetically feasible. In the case of iron, a variety of formally Fe(IV) complexes have been prepared, and some are illustrated in Fig. 1. Early work revealed only cyclopropanation [38] reactivity in  $[\text{CpLL}'\text{Fe}=\text{CRR}']^+$  systems [11–22], and in a clever masked iron alkylidene system recently implemented by Deng [39]. Its transient iron alkylidene was calculated to have substantial radical character, i.e.,  $(\text{PN}_2)\text{Fe}^{\text{I}}(\text{III})(-\text{C}^1\text{Ar}_2)$ , akin to the  $(\text{PDI})\text{Fe}=\text{CPh}_2$  derivative synthesized by Chirik et al. [17] This formulation is similar to that of Groysman’s  $(\text{tBu}_2\text{Ph})_2\text{CoCPh}_2$  complex [40], which also fails to display any metathesis reactivity.

Other subsequent systems featuring Fe(IV) chelate alkylidenes prepared in these laboratories, both cations and neutral, manifested no clean olefin reactivity at all. Orbital analysis revealed that formal oxidation states descriptions belied distributions of electron density that were realistically closer to Fe(II) [23–25,41]. Iron(II) systems, being  $d^6$ , should not be capable of metathesis, but Iluc has recently prepared a diamagnetic pincer carbene capable of a 2 + 2 process with alkynes [42].

These laboratories have proffered an explanation why iron

<sup>\*</sup> Corresponding author.

E-mail address: [ptw2@cornell.edu](mailto:ptw2@cornell.edu) (P.T. Wolczanski).

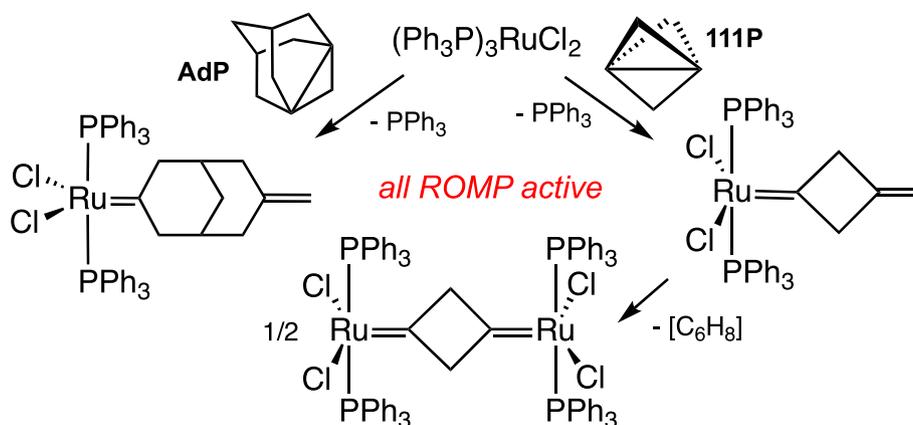
<https://doi.org/10.1016/j.poly.2022.115656>

Received 11 October 2021; Accepted 7 January 2022

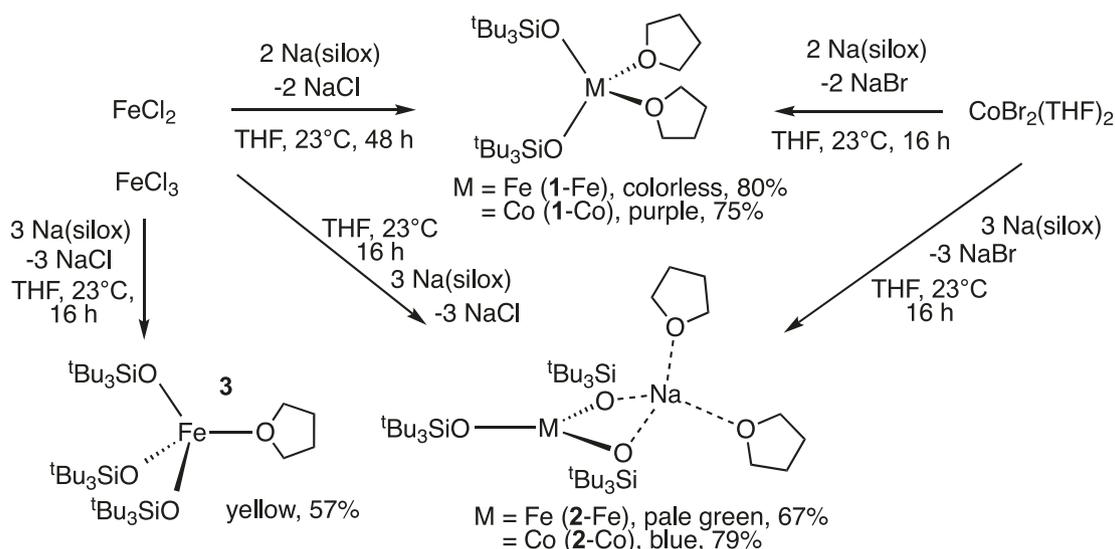
Available online 19 January 2022

0277-5387/© 2022 Elsevier Ltd. All rights reserved.





**Scheme 1.** The addition of 1.1.1-propellane (**111P**,  $\text{C}_5\text{H}_6$ ) and 1,3-dehydroadamantane (**AdP**) to  $(\text{Ph}_3\text{P})_3\text{RuCl}_2$  affords alkydienes that are ROMP active for norbornene.



**Scheme 2.** Metathetical preparations ( $\text{M} = \text{Fe}, \text{Co}$ ) of  $(\text{silox})_2\text{M}(\text{THF})_2$  (**1-M**),  $[(\text{silox})_3\text{M}]\text{Na}(\text{THF})_2$  (**2-M**) and  $(\text{silox})_3\text{Fe}(\text{THF})$  (**3**).

sodium ion, rendering their  $d(\text{M}-\text{O}(\text{Si}))$  (Fe: 1.9333(10), 1.9082(10) Å; Co: 1.9259(14), 1.8941(13) Å) 0.052–0.096 Å longer than the terminal silox  $\text{M}-\text{O}$  distances (Fe, 1.8563(10) Å; Co, 1.8308(14) Å). The  $\text{M}(\mu\text{-O})_2$  plane is  $\sim 129^\circ$  relative to the  $\text{Na}(\mu\text{-O})_2$  plane within the  $\text{M}(\mu\text{-O})_2\text{Na}$  diamond core, as the  $\text{Na}(\text{THF})_2$  group is displaced away from the bulky siloxides. Within the trigonal planes, the  $\mu\text{-O}-\text{M}-\mu\text{-O}$  angles are pinched in (Fe,  $98.48(4)^\circ$ ; Co,  $97.17^\circ$ ) due to coordination to Na, whereas the remaining  $\mu\text{-O}-\text{M}-\text{O}(\text{Si})$  are around  $130^\circ$  for both transition elements. Coordination of THF to the sodium in each case appears largely dictated by the space available, consistent with binding to an alkali metal ion.

### 2.3. Reactions of $(\text{silox})_2\text{M}(\text{THF})_2$ (**1-M**) and $[(\text{silox})_3\text{M}]\text{Na}(\text{THF})_2$ (**2-M**)

#### 2.3.1. Alkydienes attempts via 1.1.1.-propellane, 1,3-dehydroadamantane, and NBE

Given the cobalt diphenylcarbene derivative of Groyzman [40], and related work of Chirik [17] and Bukhryakov [44], the low coordinate, electron deficient  $(\text{silox})_2\text{M}(\text{THF})_2$  (**1-M**) and  $[(\text{silox})_3\text{M}]\text{Na}(\text{THF})_2$  (**2-M**,  $\text{M} = \text{Fe}, \text{Co}$ ) complexes were considered plausible candidates for butenyldiene and adamantyldiene formation. With evidence that 1.1.1.-propellane (**111P**) and 1,3-dehydroadamantane (**AdP**) can generate alkydienes capable of initiating ROMP of NBE [49], **1-M** and **2-M** were subjected to the propellanes. Scheme 3 illustrates the results with **111P**,

which was prepared *in situ* according to the method of procedure of Semmler, Szeimies, and Belzner [50]. The results were disappointing, as the transition metal compounds appeared to catalyze the known rearrangement of **111P** to 3-methylene-cyclobutyldiene, as its dimer was observed [51]. Since **111P** was generated *in situ* and added to **1-M** and **2-M** ( $\text{M} = \text{Fe}, \text{Co}$ ) via distillation (**3** also yields dimer), only amounts of organic products that were non-volatile were observed by NMR spectroscopic assay. Even with NBE present, **111P** and **1-Fe** or **2-Fe** failed to elicit any signs of ROMP or carbene transfer. These results, while not productive, were not unanticipated, as the exposure of various organometallic systems to **111P** was vetted in the early 1970's [52]. The studies revealed a rearrangement product, 3-methylene-cyclobutene, the dimer of 3-methylene-cyclobutyldiene, and its trimeric cyclopropanation product (Scheme 4), essentially the same products generated upon thermolysis of **111P**. In fact, Aggarwal has recently exploited the Ni-catalyzed generation of 3-methylene-cyclobutyldiene in a variety of cyclopropanations of synthetic organic relevance [53].

A similar fate occurred when 1,3-dehydroadamantane (**AdP**) was exposed to  $(\text{silox})_2\text{M}(\text{THF})_2$  (**1-M**) and  $[(\text{silox})_3\text{M}]\text{Na}(\text{THF})_2$  (**2-M**) ( $\text{M} = \text{Fe}, \text{Co}$ ) as shown in Scheme 5. At temperatures  $>100^\circ\text{C}$ , no transition metal reactivity was noted, but the known polymerization of **AdP** was likely evidenced by the decline of **AdP** in the  $^1\text{H}$  NMR spectrum and the deposition of a white solid [54].

Given Bukhryakov's curious result [44], the possibility of NBE-

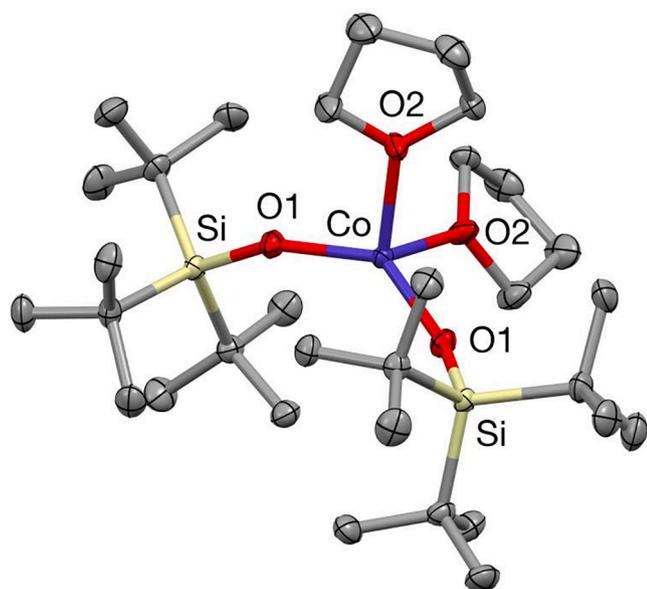


Fig. 2. Molecular view of  $(\text{silox})_2\text{Co}(\text{THF})_2$  (**1-Co**); pertinent metric parameters are listed in Table 1.

initiated ROMP [55–56] was checked via thermolyses ( $130\text{ }^\circ\text{C}$ ) of **1-M**, **2-M** (Fe, Co) and **3** in the presence of NBE, and no reaction was noted. Precedent exists for NBE adduct rearrangement to norbornylidene for  $(\text{silox})_3\text{M}(\text{NBE})$  ( $\text{M} = \text{Nb}, \text{Ta}$ ) [57], as shown in Scheme 6, but the NBE binding and the type of CH activation necessary to conduct this rearrangement has little precedent for base metals. As shown, extended thermolyses at high temperatures failed to elicit alkylidene formation, ROMP, or any significant reactivity; **3** also failed to bind or show reactivity with NBE.

### 2.3.2. Attempts at $\text{BPh}_3$ assisted propellane activation

It is perhaps unreasonable for  $(\text{silox})_2\text{M}(\text{THF})_2$  (**1-M**) and  $[(\text{silox})_3\text{M}]\text{Na}(\text{THF})_2$  (**2-M**,  $\text{M} = \text{Fe}, \text{Co}$ ) to incur the ligand reactivity that could isomerize an olefin adduct of weak field iron and cobalt complexes, especially since olefin complexes cannot be isolated or discerned by  $^1\text{H}$  NMR spectroscopy. As a consequence,  $\text{Ph}_3\text{B}$ , chosen as a representative Lewis acid, was utilized in an attempt to activate the propellanes for potential ligation.

Attempts to activate **AdP** with  $\text{Ph}_3\text{B}$  and phenyl boronic acid proved successful, as indicated in Scheme 7, which reveals rapid scission of the 1,3-connectivity at room temperature. Unfortunately, no involvement of the transition metal centers was noted, and their absence had no impact on the rate or conditions of the reaction. Ring opening of **AdP** generates (7-methylene-3-phenylbicyclo[3.3.1]nonan-3-yl)diphenylborane, which apparently results from insertion of an incipient carbene into a Ph-B bond. This direct insertion is unlikely as initial electrophilic ring-

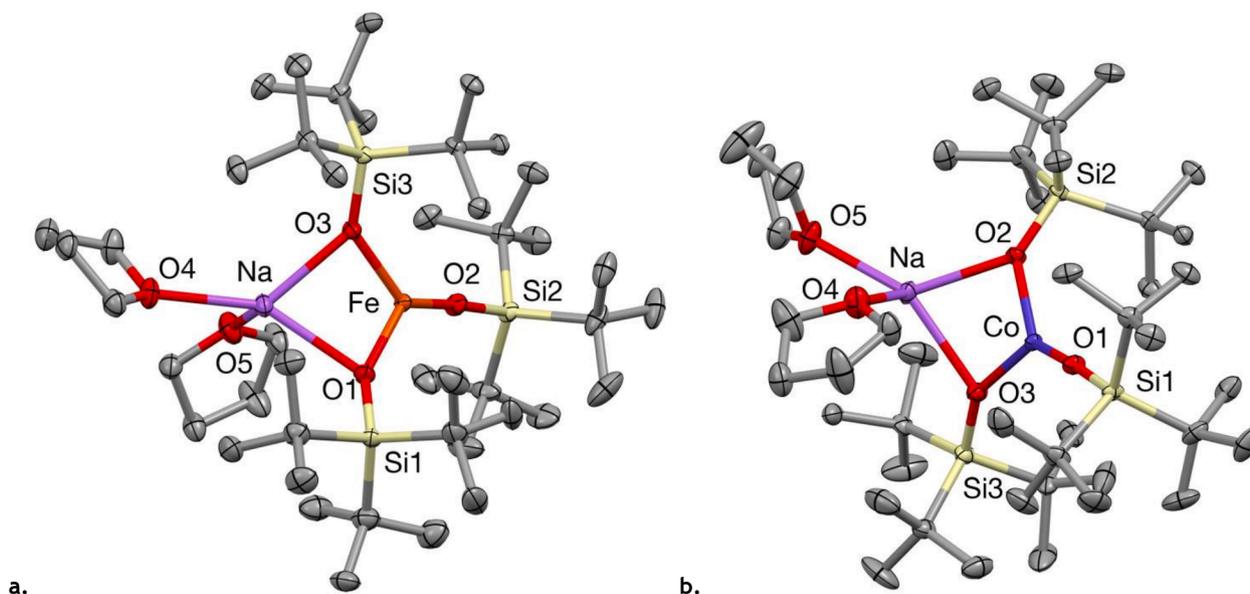
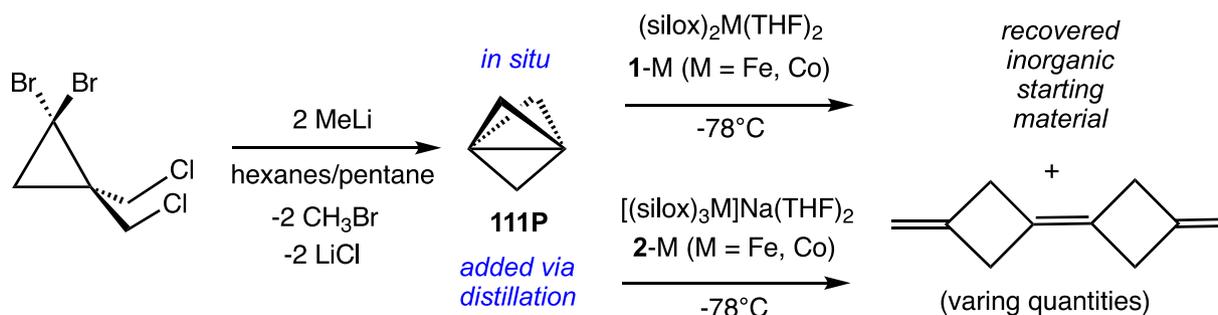
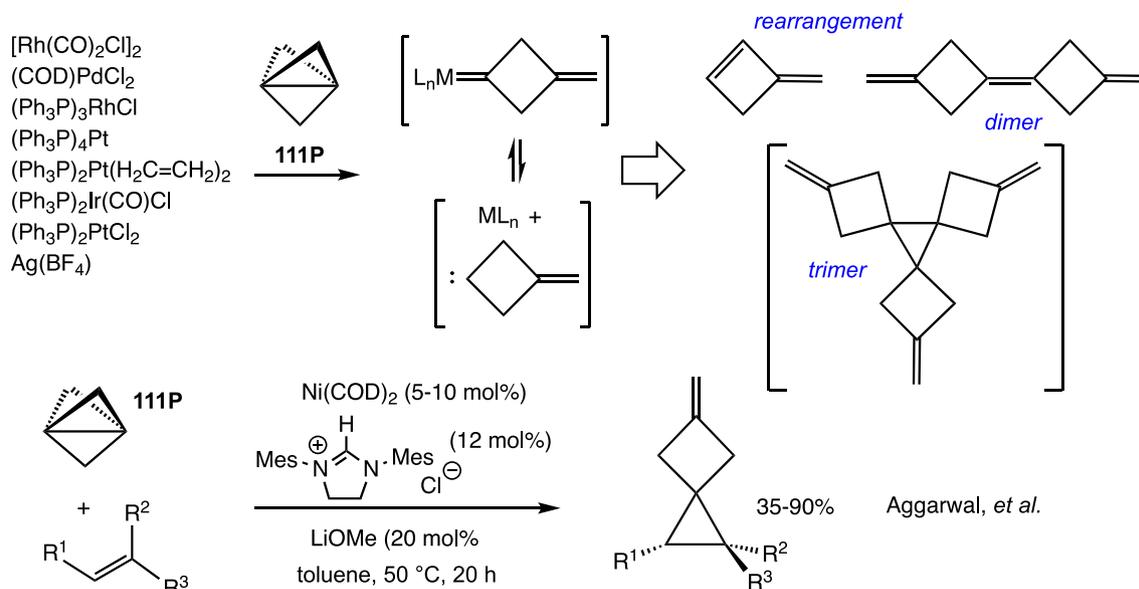


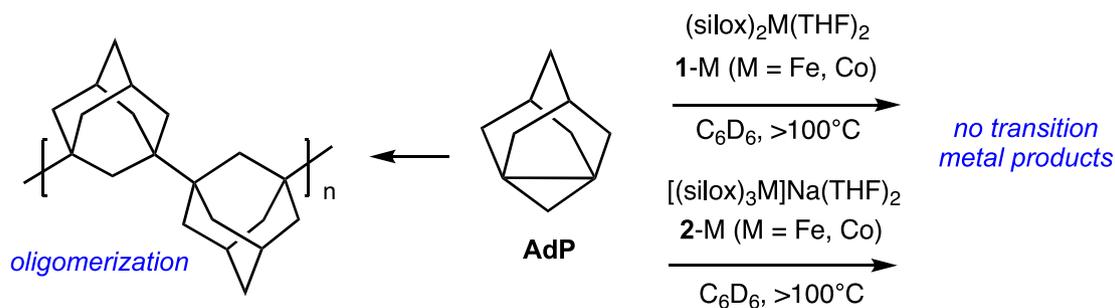
Fig. 3. Molecular views of  $[(\text{silox})_3\text{M}]\text{Na}(\text{THF})_2$  (**2-M**,  $\text{M} = \text{Fe}$ , a.;  $\text{Co}$ , b.); core interatomic distances and angles are listed in Table 1.



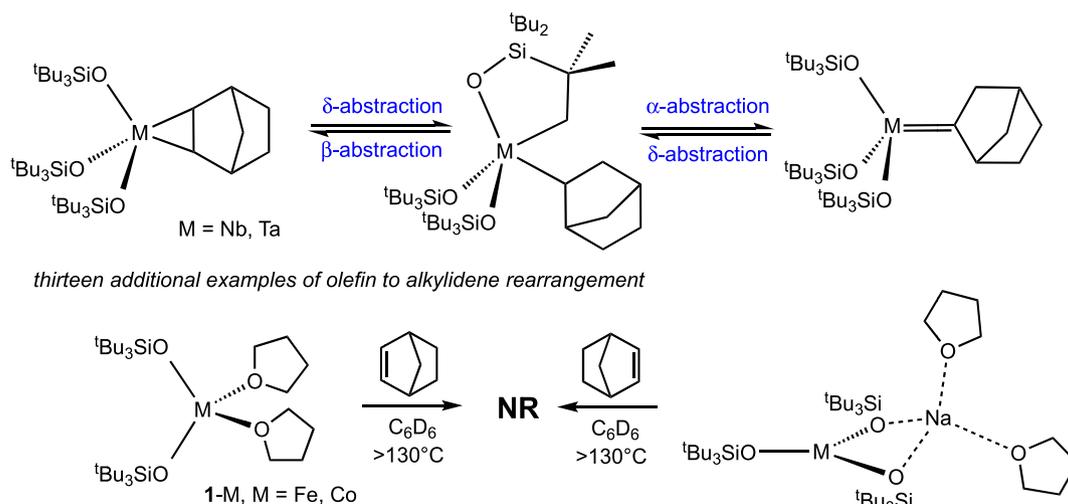
Scheme 3. Addition of **111P** to  $(\text{silox})_2\text{M}(\text{THF})_2$  (**1-M**) and  $[(\text{silox})_3\text{M}]\text{Na}(\text{THF})_2$  (**2-M**,  $\text{M} = \text{Fe}, \text{Co}$ ) via distillation. The only inorganics identified after **111P** was consumed were **1-M** and **2-M**.



Scheme 4. Early studies of 111P with  $L_nM$ , and a recent Ni catalyzed carbene transfer application by Aggarwal et al.



Scheme 5. Exposure of AdP to  $(silox)_2M(THF)_2$  (1-M) and  $[(silox)_3M]Na(THF)_2$  (2-M,  $M = Fe, Co$ ) led to simple thermal oligomerization.

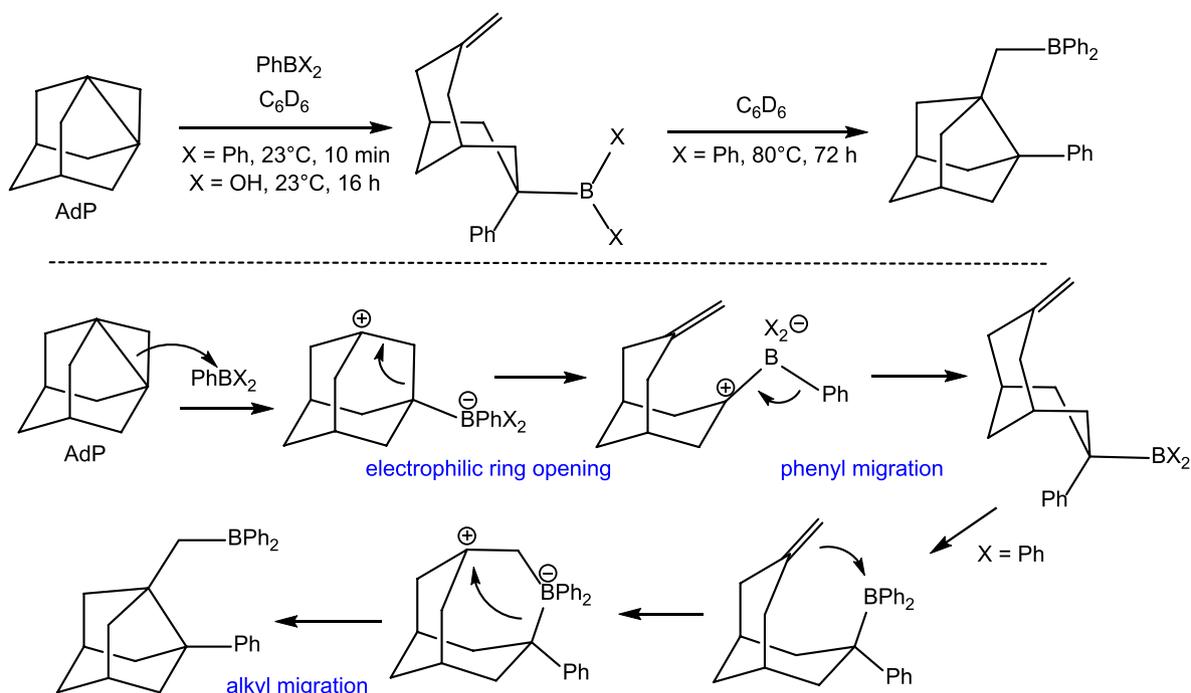


Scheme 6. Precedent for alkylidene formation from norbornene (NBE) adducts via reversible ligand CH-activation, and the non-reactivity of NBE in the iron and cobalt systems.

opening should generate a zwitterion susceptible to bond migration followed by phenyl migration, as Scheme 7 portrays. Continued thermolysis surprisingly led to a tricyclic product via  $-BPh_2$  activation of the

pendant olefin, and subsequent phenyl-cyclohexyl migration [58].

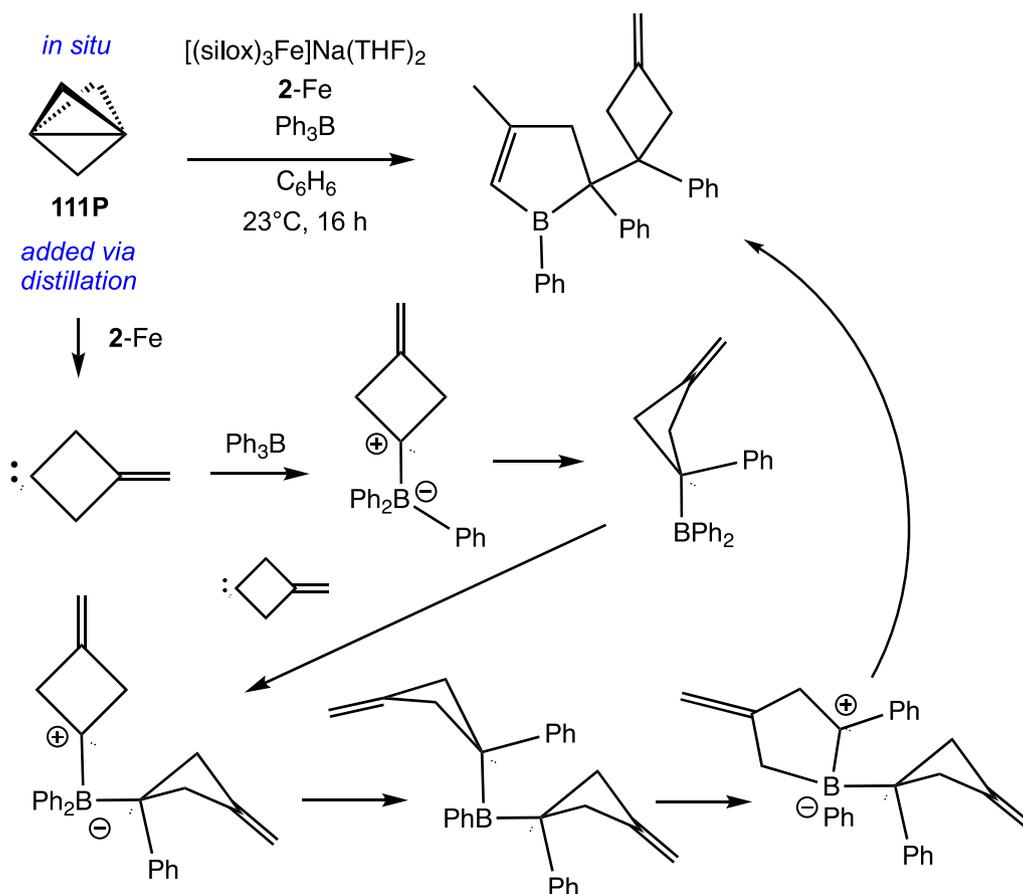
The successful implementation of 2-D NMR spectroscopic techniques permitted identification of the products in Scheme 7, and similar



**Scheme 7.** Electrophilic opening of AdP by  $\text{Ph}_3\text{B}$  and  $\text{PhB}(\text{OH})_2$ , and a postulated mechanism featuring plausible rearrangements.

analyses were put to the test upon assay of the product of **111P** in the presence of  $\text{Ph}_3\text{B}$  and  $[(\text{silox})_3\text{Fe}]\text{Na}(\text{THF})_2$  (**2-Fe**). Under the conditions indicated **Scheme 8**, a colorless major product crystallized from a

solution containing several products. Control reactions indicated that both  $\text{Ph}_3\text{B}$  and **2-Fe** were required to generate the diamagnetic compound, which possessed complicated  $^1\text{H}$  NMR spectra that had two



**Scheme 8.** **111P** decomposition product in the presence of  $\text{Ph}_3\text{B}$  and  $[(\text{silox})_3\text{Fe}]\text{Na}(\text{THF})_2$  (**2-Fe**), and a postulated mechanism of formation. Colorless 4-methyl-2-(3-methylene-1-phenylcyclobutyl)-1,2-diphenyl-2,3-dihydro-1H-borole was isolated in 35% yield.

components of **111P** (typically added in excess) and one of  $\text{Ph}_3\text{B}$ , and included phenyl migration from boron and eventual cyclobutane ring opening. X-ray crystallography corroborated the product (*vide infra*).

A plausible mechanism is also illustrated in [Scheme 8](#). It is likely that **2-Fe** catalyzes the rearrangement of **111P** to 3-methylene-cyclobutylidene, which is trapped by  $\text{Ph}_3\text{B}$ , resulting in Ph migration from boron to provide a neutral  $\text{Ph}_2\text{B}(\text{C}_4\text{H}_4\text{-1-Ph,3-CH}_2)$ . This species is electrophilic enough for a similar sequence to give  $\text{PhB}(\text{C}_4\text{H}_4\text{-1-Ph,3-CH}_2)_2$ , where it is possible that steric crowding results in alkyl migration to boron [\[58\]](#), thereby relieving some ring strain. A subsequent group migration of  $(\text{C}_4\text{H}_4\text{-1-Ph,3-CH}_2)$  alleviates considerable strain at B, leaving only isomerization of the *exo*-methylene to an internal ring position to afford the ultimate product,  $\text{Ph}(\kappa\text{-CH}=\text{CMeCH}_2\text{BPh}(\text{C}_4\text{H}_4\text{-1-Ph,3-CH}_2))$  (**4**). Given the presence of Lewis acid (e.g.,  $\text{Ph}_3\text{B}$ ) and possible Brønsted acid sources (trace hydrolysis), the olefin isomerization step may occur via many paths.

### 2.3.3. Structure of $\text{Ph}(\kappa\text{-CH}=\text{CMeCH}_2\text{BPh}(\text{C}_4\text{H}_4\text{-1-Ph,3-CH}_2))$ (**4**)

In [Fig. 4](#), the NMR-determined structure of  $\text{Ph}(\kappa\text{-CH}=\text{CMeCH}_2\text{CPh}(\text{C}_4\text{H}_4\text{-1-Ph,3-CH}_2))$  (**4**) was verified by single crystal X-ray crystallography, and its salient metric parameters are listed in the caption. The B-C12 bond of the five-membered ring is 1.6314(15) Å, which is long compared to the boron-phenyl-carbon (C23) distance of 1.5642(16) Å, and  $d(\text{B-C19}) = 1.5310(16)$  [\[59\]](#). Steric factors regarding this tertiary carbon are a likely influence, in addition to hybridization, as C(23) is an  $\text{sp}^3$ -carbon, whereas C23 and C19 are  $\text{sp}^2$ . Note that  $\text{C19-C20} = 1.3455(16)$  Å and  $\text{C20-C22} = 1.4930(15)$  Å, confirming the isomerization of the *exo*-methylene as [Scheme 8](#) shows. The *exo*-methylene of the four-membered ring is 1.3185(15) Å, and ring distances manifest the

influence of its  $\text{sp}^2$ -carbon, as  $d(\text{C2-C3})$  and  $d(\text{C2-C5})$  average 1.515(2) Å, compared to the remaining two distances, which average 1.583(2) Å [\[53\]](#). All angles reflect the sterics and hybridizations involved. For example,  $\text{C5-C2-C3}$  is  $92.71(8)^\circ$ , followed by the angles  $\text{C2-C3-C4}$  and  $\text{C2C5-C4}$  at  $89.33(8)^\circ$  and  $89.13(8)$ , respectively, and the  $\text{C3-C4-C5}$  angle is  $87.68(7)$ .

## 3. Conclusions

### 3.1. Structures of $(\text{silox})_2\text{Co}(\text{THF})_2$ (**1-Co**) and $[(\text{silox})_3\text{M}]\text{Na}(\text{THF})_2$ (**2-M**; $\text{M} = \text{Fe, Co}$ )

Low coordinate bulky alkoxide, siloxide, and various amide complexes, especially homoleptic or pseudo-homoleptic examples, are a class of hard-donor, high-spin complexes that comprise a cornerstone of inorganic synthesis. The pseudo-tetrahedral and pseudo-trigonal geometries of  $(\text{silox})_2\text{Co}(\text{THF})_2$  (**1-Co**) and  $[(\text{silox})_3\text{M}]\text{Na}(\text{THF})_2$  (**2-M**;  $\text{M} = \text{Fe, Co}$ ) harbor no surprises, as deviations are readily explained by steric factors. While lacking the steric bulk necessary to restrict the coordination number, the *bis*-siloxide, *bis*-THF species provide entries into sterically saturated  $\text{L}_2\text{M}(\text{silox})_2$  and  $[\text{M}(\text{silox})_3\text{L}]\text{M}'$  derivatives. The Dewar-Chart-Duncanson olefin-binding model has come unto question for first row transition metals, in which ionic contributions may predominate in what is essentially just a simple donor-acceptor interaction [\[41\]](#). The failure to achieve NBE coordination to these weak field complexes is perhaps a testament to the inability of olefins in general to bind to metal centers possessing contracted 3d orbitals. In this instance, the synthesis of anions, thought to expand the 3d orbitals and provide greater donor-acceptor overlap for either olefin or alkylidene binding, also failed to elicit the desired reactivity.

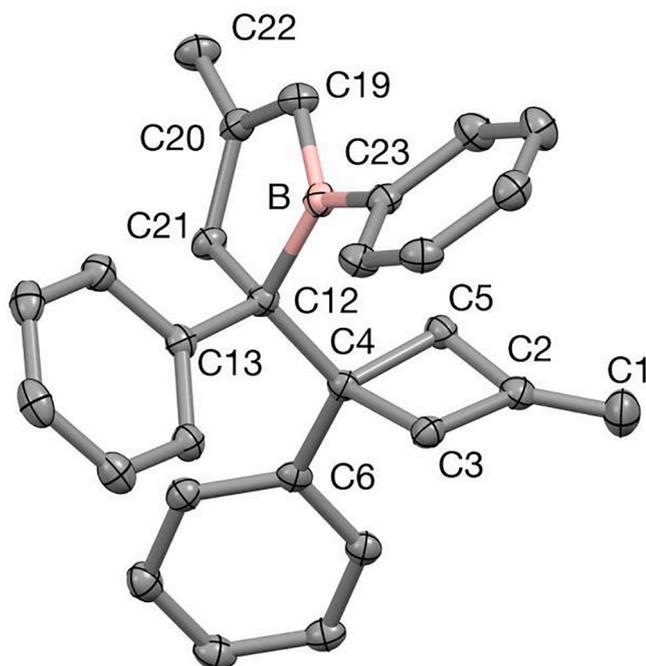
### 3.2. Propellane non-reactivity

Given previous comments related to formally Fe(IV) alkylidenes and olefin metathesis, it is not surprising that no reactivity of consequence with  $(\text{silox})_2\text{M}(\text{THF})_2$  (**1-M**) or  $[(\text{silox})_3\text{M}]\text{Na}(\text{THF})_2$  (**2-M**) was observed [\[43\]](#). Aside from the curious results of Bukhryakov [\[44\]](#), none would be anticipated. The question of whether there is an alternative mechanism for the  $(\text{HMTO})_2\text{Fe}$  ( $\text{HMTO} = \text{O-2,6-(2,4,6-Me}_3\text{C}_6\text{H}_2)\text{C}_6\text{H}_3$ )/NBE/  $(\text{Ph}(\text{CF}_3)_2\text{COH})$  system has not been answered, and there remains the potential for metal contamination, even though Bukhryakov has done a credible job of investigating this possibility.

The compounds herein are not the only iron and cobalt derivatives subjected to **111P** as a potential alkylidene precursor to 3-*exo*-methylene cyclobutylidene complexes. [Table 2](#) lists the slew of coordinatively unsaturated inorganic and organometallic compounds that have been subjected to **111P** under standard conditions (typically  $23^\circ\text{C}$ , THF,  $>1$  equiv). The results corroborate the problems generating an “Fe(IV)” (or “Co(IV)”) alkylidene, when the metals are incapable of making true covalent interactions [\[43\]](#). When **111P** reactivity was observed, like **1-M** and **2-M**, the compounds generally served to catalyze the rearrangement to free 3-*exo*-methylene cyclobutylidene, as its dimerization product was most commonly observed. In four cases, paramagnetic metal-containing products were observed, but  $^1\text{H}$  NMR spectral analyses were insufficient to ascribe signals to derivatives of **111P**, and despite concerted efforts, crystallizations have failed thus far. It is noteworthy that two of the reactions involved starting materials  $(\text{PDI})\text{Fe}(\text{N}_2)_2$  [\[17\]](#) and  $\text{Co}(\text{OC}^t\text{Bu}_2\text{Ph})_2(\text{THF})_2$  [\[40\]](#) are precursors for the aforementioned diphenyl carbene species with radical character from the Chirik and Groyzman labs, respectively. The remaining two compounds are 3- and 4-coordinate dineopentyl complexes  $(\text{MeIPr})\text{Fe}(\text{neopPe})_2$  and  $(\text{TMEDA})\text{Fe}(\text{neopPe})_2$  with the potential for carbene insertion chemistry.

### 3.3. Final comments

Previous strong field, formally iron(IV) alkylidenes, both cationic



**Fig. 4.** Molecular view of  $\text{Ph}(\kappa\text{-CH}=\text{CMeCH}_2\text{BPh}(\text{C}_4\text{H}_4\text{-1-Ph,3-CH}_2))$  (**4**). Selected interatomic distances (Å) and angles( $^\circ$ ): B-C12, 1.6314(15); B-C19, 1.5310(16); B-C23, 1.5642(16); C19-C20, 1.3455(16); C20-C22, 1.4930(15); C20-C21, 1.5042(15); C12-C21, 1.5619(14); C12-C13, 1.5275(14); C4-C12, 1.5520(14); C3-C4, 1.5814(14); C4-C6, 1.5349(14); C4-C5, 1.5835(14); C2-C5, 1.5163(15); C1-C2, 1.3185(15); C2-C3, 1.5129(15); C12-B-C19, 106.96(9); C12-B-C23, 128.98(9); C19-B-C23, 124.05(10); B-C12-C21, 101.45(8); C12-C21-C20; 107.93(9); C21-C20-C19, 113.86(9); C21-C20-C22, 118.51(10); C19-C20-C22; 127.63(10); B-C19-C20, 109.75(10); B-C12-C13, 103.77(8); B-C12-C4, 113.71(8); C12-C4-C3, 117.04(8); C12-C4-C5, 112.09(8); C12-C4-C6, 115.56(8); C3-C4-C5, 87.68(7); C4-C5-C2, 89.13(8); C5-C2-C3; 92.71(8); C5-C2-C1, 134.17(11); C1-C2-C3, 132.87(11); C2-C3-C4, 89.33(8).

**Table 1**Metric parameters (d(Å), angles(°)) associated with (silox)<sub>2</sub>Co(THF)<sub>2</sub> (1-Co) and [(silox)<sub>3</sub>M]Na(THF)<sub>2</sub> (2-M, M = Fe, Co).

M = Fe, Co	1-Co	2-Fe	2-Co
M–O(Si)	1.8628(9)	1.9333(10) 1.8563(10) 1.9082(10)	1.9259(14) 1.8308(14) 1.8941(13)
M–O(THF)	2.0718(10)		
M...Na		2.8900(6)	2.9133(8)
Na–O(Si)		2.46781(11)	2.4389(15)
		2.3288(11)	2.3153(18)
Na–O(THF)		2.3485(12)	2.3582(17)
		2.3112(13)	2.3153(18)
Si–O	1.6045(1)	1.6257(10) 1.6183(10) 1.6299(10)	1.6234(14) 1.6279(14) 1.6230(14)
(Si)O–M–O(Si)	133.48(6)	130.00(4) 98.48(4) 129.71(4)	130.63(6) 97.17(6) 130.48(8)
(Si)O–M–O(THF)	144.05(4) 96.65(4)		
(THF)O–M–O(THF)	97.03		
M–O(Si)–Na		84.85(4) 81.57(4)	86.38(5) 83.45(5)
O(Si)–Na–O(Si)		74.63(4)	74.12
O(Si)–Na–O(THF)		147.09(5) 103.45(4) 132.25(4) 111.15(4)	148.24(7) 102.46(6) 132.38(7) 109.80(6)
O(THF)–Na–O(THF)		85.22(4)	85.60(6)

**Table 2**Complexes subjected to **111P** under standard conditions, and products if observed.

Cmpd	Observable Products		
	R/ NR	bis(3-methylene- cyclobutylidene)	metal or 1- containing
(silox) <sub>2</sub> Fe(THF) <sub>2</sub> (1-Fe)	R	✓	1-Fe
(silox) <sub>2</sub> Co(THF) <sub>2</sub> (1-Co)	R	✓	1-Co
[(silox) <sub>3</sub> Fe]Na(THF) <sub>2</sub> (2-Fe)	R	✓	2-Fe
[(silox) <sub>3</sub> Co]Na(THF) <sub>2</sub> (2-Co)	R	✓	2-Co
(silox) <sub>3</sub> Fe (3)	R	✓	3
(MeIPr)Fe( <sup>neo</sup> Pe) <sub>2</sub> [60]	R		unidentified paramagnetic Fe(0)
“(PMe <sub>3</sub> ) <sub>4</sub> Fe” [61]	R		
( <sup>Ph</sup> PMe <sub>3</sub> N <sup>Ph</sup> P)FeCl <sub>2</sub> [43]	NR		
(PMe <sub>3</sub> ) <sub>2</sub> FeCl <sub>2</sub> [62]	NR		
(Me <sub>2</sub> Pr)Fe(dvtms) [63]	R	✓	Fe(0), dvtms
(PMe <sub>3</sub> ) <sub>2</sub> Fe(1-nor) <sub>2</sub> [64]	NR		
(TMEDA)Fe( <sup>neo</sup> Pe) <sub>2</sub> [60]	R		unidentified paramagnetic
[( <sup>t</sup> Bu <sub>3</sub> Si) <sub>2</sub> Fe] <sub>2</sub> [65]	NR		
{(Me <sub>3</sub> Si) <sub>2</sub> N} <sub>2</sub> Fe [66]	R	✓	starting material
(PMe <sub>3</sub> ) <sub>2</sub> FeMes <sub>2</sub> [67]	R	✓	starting material
FeBr <sub>2</sub> (THF) <sub>2</sub> [68]	NR		
(PDI)Fe(N <sub>2</sub> ) <sub>2</sub> [69]	R		unidentified paramagnetic starting material
{(Me <sub>3</sub> Si) <sub>2</sub> N} <sub>2</sub> FeTHF [70]	R	✓	
[Fe(Me <sub>6</sub> porph)] Na <sub>2</sub> (THF) <sub>2</sub> [71]	NR		
Fe(dadi) [72]	NR		
Fe(acac) <sub>2</sub>	NR		
FeI <sub>2</sub>	NR		
Co(OC <sup>t</sup> Bu <sub>2</sub> Ph) <sub>2</sub> (THF) <sub>2</sub> [40]	R	✓	unidentified paramagnetic
Fe(OC <sup>t</sup> Bu <sub>2</sub> Ph) <sub>2</sub> (THF) <sub>2</sub> [40]	R	✓	
[(2,4,6 <sup>t</sup> BuC <sub>6</sub> H <sub>2</sub> S) <sub>2</sub> Fe] <sub>2</sub> [73]	NR		
[(2,4,6 <sup>t</sup> BuPh) <sub>3</sub> Fe]Li [74]	NR		
{(Me <sub>3</sub> Si) <sub>2</sub> N} <sub>2</sub> CoTHF [75]	NR		
CoCl <sub>2</sub> THF <sub>2</sub> [76]	NR		

and neutral, have failed to elicit any olefin metathesis reactivity, and attempts to exploit **111P** in the synthesis of additional systems has failed. For an iron complex to be capable of olefin metathesis, an “Fe(IV)” alkylidene must be “oxidizing” enough for a true covalent interaction. In all cases thus far, so-called iron-carbon double bonds are either polarized to the extent that “Fe(IV)” is really an Fe(II) stabilized carbocation, or the carbon at most possesses radical character, especially within weak fields. Even the  $\pi$ -bonding in “Fe(IV)” imido complexes, where nitrogen is significantly more “oxidizing” than carbon, is highly delocalized or imidyl-like that the the oxidation state is nebulous. Assuming the Bukhryakov ROMP case is valid, an alternative to the Chauvin mechanism seems plausible.

## 4. Experimental

### 4.1. General considerations

All manipulations were performed using either glovebox, Schlenk, or high vacuum line techniques, unless stated otherwise. All glassware was oven dried at 180 °C. THF and ether were distilled under nitrogen from purple sodium benzophenone ketyl and vacuum transferred from the same prior to use. Hydrocarbon solvents were treated in the same manner with the addition of 1–2 mL/L tetraglyme. Benzene-*d*<sub>6</sub> was dried over sodium, vacuum transferred and stored over sodium. THF-*d*<sub>8</sub> was dried over sodium, and vacuum transferred from sodium benzophenone ketyl prior to use. Acetonitrile-*d*<sub>3</sub> was dried over refluxing CaH<sub>2</sub>, vacuum distilled and stored over CaH<sub>2</sub>, and chloroform-*d*<sub>1</sub> (Cambridge Isotope Laboratories) was used as received.

NMR spectra were obtained using Varian 300 MHz (Mercury), 400 MHz (Inova), 500 MHz (Inova) and 600 MHz (Inova) spectrometers. <sup>1</sup>H and <sup>13</sup>C NMR shifts are referenced to benzene-*d*<sub>6</sub> (<sup>1</sup>H,  $\delta$  7.16 ppm; <sup>13</sup>C,  $\delta$  128.39 ppm), toluene-*d*<sub>8</sub> (<sup>1</sup>H,  $\delta$  2.09 ppm; <sup>13</sup>C,  $\delta$  20.40 ppm), acetonitrile-*d*<sub>3</sub> (<sup>1</sup>H,  $\delta$  1.94 ppm; <sup>13</sup>C,  $\delta$  118.26 ppm), tetrahydrofuran-*d*<sub>8</sub> (<sup>1</sup>H,  $\delta$  3.58 ppm; <sup>13</sup>C,  $\delta$  67.57 ppm), dichloromethane-*d*<sub>2</sub> (<sup>1</sup>H,  $\delta$  5.32 ppm; <sup>13</sup>C,  $\delta$  53.84 ppm), deuterium oxide (<sup>1</sup>H,  $\delta$  4.79 ppm; <sup>13</sup>C, CH<sub>3</sub>CN spike,  $\delta$  1.79 ppm). The 2D experiments utilized were <sup>1</sup>H–<sup>13</sup>C HSQC (Heteronuclear Single Quantum Coherence), <sup>1</sup>H–<sup>13</sup>C HMBC (Heteronuclear Multiple Bond Correlation), and <sup>1</sup>H–<sup>1</sup>H COSY (CORrelated Spectroscopy). Solution magnetic measurements were conducted via Evans' method [50].

### 4.2. Procedures

#### 4.2.1. (silox)<sub>2</sub>Fe(THF)<sub>2</sub> (1-Fe)

To a 25 mL round bottom flask charged with FeCl<sub>2</sub> (0.250 g, 1.97 mmol) and Na(silox) (0.941 g, 3.94 mmol) was added 15 mL of freshly distilled THF at –78 °C. The mixture was allowed to warm slowly to 23 °C and stirred for 48 h, resulting in a yellow solution. The volatiles were evaporated, and the residue was triturated in the presence of pentane (2 × 10 mL), which was then removed *in vacuo*. Pentane (15 mL) was added to the residue, which was filtered, and washed with additional pentane until the filtrate was clear. The solution was concentrated to 5 mL, cooled to –78 °C and stirred for 30 min. The solution was filtered to yield 1-Fe as a colorless solid (0.997 g, 80%).  $\mu_{\text{eff}}$  (Evans, C<sub>6</sub>D<sub>6</sub>) = 5.2  $\mu_{\text{B}}$ . <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  12.99 (54H,  $\nu_{1/2} \approx$  280 Hz, CH<sub>3</sub>), 1.78 (8H,  $\nu_{1/2} \approx$  74 Hz, THF), –3.79 (8H,  $\nu_{1/2} \approx$  512 Hz, THF). An NMR tube sample was opened to air, one drop (~0.05 mL) of deionized H<sub>2</sub>O was added, and the tube was shaken. The contents were filtered through a plug of MgSO<sub>4</sub>, and assayed by <sup>1</sup>H NMR spectroscopy: (C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.11 (54H), 1.40 (8.41H), 3.57 (8.41H), indicating a 1.05:1 ratio of THF:(silox)H.

#### 4.2.2. (silox)<sub>2</sub>Co(THF)<sub>2</sub> (1-Co)

To a 25 mL round bottom flask charged with CoBr<sub>2</sub>(THF)<sub>2</sub> (0.265 g, 0.730 mmol) and Na(silox) (0.348 g, 1.46 mmol) was added 15 mL of freshly distilled THF at –78 °C. The mixture was allowed to warm slowly to 23 °C and stirred for 16 h, resulting in a purple solution. The volatiles

were evaporated, and the residue was triturated in the presence of pentane ( $2 \times 10$  mL), which was then removed *in vacuo*. Pentane (15 mL) was added to the residue, which was filtered, and washed with additional pentane until the filtrate was clear. The solution was concentrated to 5 mL, cooled to  $-78$  °C and stirred for 30 min. The solution was filtered to yield 1-Co as a purple solid (0.350 g, 75%).  $\mu_{\text{eff}}$  (Evans,  $\text{C}_6\text{D}_6$ ) = 4.0  $\mu_{\text{B}}$ .  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  12.53 (54H,  $\nu_{1/2} \approx 75$  Hz,  $\text{CH}_3$ ),  $-4.70$  (8H,  $\nu_{1/2} \approx 40$  Hz, THF),  $-8.25$  (8H,  $\nu_{1/2} \approx 220$  Hz, THF). An NMR tube sample was opened to air, one drop ( $\sim 0.05$  mL) of deionized  $\text{H}_2\text{O}$  was added, and the tube was shaken. The contents were filtered through a plug of  $\text{MgSO}_4$ , and assayed by  $^1\text{H NMR}$  spectroscopy: ( $\text{C}_6\text{D}_6$ )  $\delta$  1.11 (54H), 1.40 (8.20H), 3.57 (8.20H), indicating a 1.03:1 ratio of THF:(silox)H.

#### 4.2.3. $[(\text{silox})_3\text{Fe}]\text{Na}(\text{THF})_2$ (2-Fe)

To a 25 mL round bottom flask charged with  $\text{FeCl}_2$  (0.142 g, 1.12 mmol) and  $\text{Na}(\text{silox})$  (0.800 g, 3.36 mmol) was added 15 mL of freshly distilled THF at  $-78$  °C. The mixture was allowed to warm slowly to 23 °C and stirred for 16 h, resulting in a pale green solution. The volatiles were evaporated, and the residue was triturated in the presence of pentane ( $2 \times 10$  mL), which was then removed *in vacuo*. Pentane (15 mL) was added to the residue, which was filtered, and washed with additional pentane until the filtrate was clear. The solution was concentrated to 5 mL, cooled to  $-78$  °C and stirred for 30 min. The cold solution was filtered to yield 2-Fe as a pale green solid (0.656 g, 67%).  $\mu_{\text{eff}}$  (Evans,  $\text{C}_6\text{D}_6$ ) = 5.1  $\mu_{\text{B}}$ .  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  6.53 (81H,  $\nu_{1/2} \approx 300$  Hz,  $\text{CH}_3$ ),  $-4.79$  (8H,  $\nu_{1/2} \approx 42$  Hz, THF),  $-8.70$  (8H,  $\nu_{1/2} \approx 231$  Hz, THF).

#### 4.2.4. $[(\text{silox})_3\text{Co}]\text{Na}(\text{THF})_2$ (2-Co)

To a 25 mL round bottom flask charged with  $\text{CoBr}_2(\text{THF})_2$  (0.265 g, 0.730 mmol) and  $\text{Na}(\text{silox})$  (0.522 g, 2.2 mmol) was added 15 mL of freshly distilled THF at  $-78$  °C. The mixture was allowed to warm slowly to 23 °C and stirred for 16 h, resulting in a blue solution. The volatiles were evaporated, and the residue was triturated in the presence of pentane ( $2 \times 10$  mL), which was then removed *in vacuo*. Pentane (15 mL) was added to the residue, which was filtered, and washed with additional pentane until the filtrate was clear. The solution was concentrated to 5 mL, cooled to  $-78$  °C and stirred for 30 min. The cold solution was filtered to yield 2-Co as a blue solid (0.503 g, 79%).  $\mu_{\text{eff}}$  (Evans,  $\text{C}_6\text{D}_6$ ) = 4.8  $\mu_{\text{B}}$ .  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  11.67 (81H,  $\nu_{1/2} \approx 52$  Hz,  $\text{CH}_3$ ),  $-7.39$  (8H,  $\nu_{1/2} \approx 28$  Hz, THF),  $-16.73$  (8H,  $\nu_{1/2} \approx 117$  Hz, THF).

#### 4.2.5. $(\text{silox})_3\text{Fe}(\text{THF})$ (3)

To a 25 mL round bottom flask charged with  $\text{FeCl}_3$  (0.182 g, 1.12 mmol) and  $\text{Na}(\text{silox})$  (0.800 g, 3.36 mmol) was added 15 mL of freshly distilled THF at  $-78$  °C. The mixture was allowed to warm slowly to 23 °C and stirred for 16 h, resulting in a yellow solution. The volatiles were evaporated, and the residue was triturated in the presence of pentane ( $2 \times 10$  mL), which was then removed *in vacuo*. Pentane (15 mL) was added to the residue, which was filtered, and washed with additional pentane until the filtrate was clear. Volatiles were removed, a minimal amount of pentane was added and slow evaporation of the concentrated solution at  $-35$  °C yielded the product as a yellow solid (0.495 g, 57%).  $\mu_{\text{eff}}$  (Evans,  $\text{C}_6\text{D}_6$ ) = 5.9  $\mu_{\text{B}}$ .  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  12.24 (81H,  $\nu_{1/2} \approx 2400$  Hz,  $\text{CH}_3$ ), 3.33 (8H,  $\nu_{1/2} \approx 210$  Hz, THF), 2.10 (8H,  $\nu_{1/2} \approx 260$  Hz, THF).

#### 4.2.6. $(\text{silox})_2\text{Fe}(\text{THF})_2$ (1-Fe) + 1.1.1.-propellane

To an oven dried 25 mL two neck flask equipped with a dropping funnel and charged with 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (0.132 g, 0.445 mmol) was added 5 mL pentane at  $-78$  °C. 1.6 M MeLi solution in hexanes (0.56 mL, 0.445 mmol) was added dropwise at  $-78$  °C with vigorous stirring. The reaction mixture was stirred at  $-78$  °C for 15 min, allowed to warm to 0 °C, and stirred another hour. The propellane solution was then freeze-pumpthaw degassed 3 times with the thawing temperature not exceeding 0 °C. The propellane was distilled into a 25 mL flask charged with  $(\text{silox})_2\text{Fe}(\text{THF})_2$  (1-Fe, 0.109

g, 0.172 mmol) and cooled to  $-78$  °C. The solution was allowed to warm slowly to 23 °C and stirred for 16 h, resulting in a pale-yellow solution. The volatiles were evaporated and the residue was subjected to dynamic vacuum for 1 h. 1-Fe was recovered quantitatively, and bis(3-methylenecyclobutylidene) was present in 54% yield ( $^1\text{H NMR}$  assay) relative to initial 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane.

#### 4.2.7. $(\text{silox})_2\text{Co}(\text{THF})_2$ (1-Co) + 1.1.1.-propellane

To an oven dried 25 mL two neck flask equipped with a dropping funnel and charged with 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (0.132 g, 0.445 mmol) was added 5 mL pentane at  $-78$  °C. 1.6 M MeLi solution in hexanes (0.56 mL, 0.445 mmol) was added dropwise at  $-78$  °C with vigorous stirring. The reaction mixture was stirred at  $-78$  °C for 15 min, allowed to warm to 0 °C, and stirred another hour. The propellane solution was then freeze-pumpthaw degassed 3 times with the thawing temperature not exceeding 0 °C. The propellane was distilled into a 25 mL flask charged with  $(\text{silox})_2\text{Co}(\text{THF})_2$  (0.110 g, 0.173 mmol) and cooled to  $-78$  °C. The solution was allowed to warm slowly to 23 °C and stirred for 16 h, resulting in a purple solution. The volatiles were evaporated and the residue was subjected to dynamic vacuum for 1 h. 1-Co was recovered quantitatively and bis(3-methylenecyclobutylidene) was present in 45% yield relative to initial 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane.

#### 4.2.8. $[(\text{silox})_3\text{Fe}][\text{Na}(\text{THF})_2]$ (2-Fe) + 1.1.1.-propellane

To an oven dried 25 mL two neck flask equipped with a dropping funnel and charged with 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (0.132 g, 0.445 mmol) was added 5 mL pentane at  $-78$  °C. 1.6 M MeLi solution in hexanes (0.56 mL, 0.445 mmol) was added dropwise at  $-78$  °C with vigorous stirring. The reaction mixture was stirred at  $-78$  °C for 15 min, allowed to warm to 0 °C and stirred another hour. The propellane solution was then freeze-pumpthaw degassed 3 times with the thawing temperature not exceeding 0 °C. The propellane was distilled into a 25 mL flask charged with 0.4 equivalents of  $[(\text{silox})_3\text{Fe}][\text{Na}(\text{THF})_2]$  (0.150 g, 0.173 mmol) cooled to  $-78$  °C. The solution was allowed to warm slowly to 23 °C and stirred for 16 h, resulting in a pale-yellow solution. The volatiles were evaporated and the residue was subjected to dynamic vacuum for 1 h. 2-Fe was recovered quantitatively and bis(3-methylenecyclobutylidene) was present in 10% yield relative to initial 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane.

#### 4.2.9. $[(\text{silox})_3\text{Co}][\text{Na}(\text{THF})_2]$ (2-Co) + 1.1.1.-propellane

To an oven dried 25 mL two neck flask equipped with a dropping funnel and charged with 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (0.132 g, 0.445 mmol) was added 5 mL pentane at  $-78$  °C. 1.6 M MeLi solution in hexanes (0.56 mL, 0.445 mmol) was added dropwise at  $-78$  °C with vigorous stirring. The reaction mixture was stirred at  $-78$  °C for 15 min, allowed to warm to 0 °C, and stirred another hour. The propellane solution was then freeze-pumpthaw degassed 3 times with the thawing temperature not exceeding 0 °C. The propellane was distilled into a 25 mL flask charged with  $[(\text{silox})_3\text{Co}][\text{Na}(\text{THF})_2]$  (0.150 g, 0.173 mmol) cooled to  $-78$  °C. The solution was allowed to warm slowly to 23 °C and stirred for 16 h, resulting in a blue-green solution. The volatiles were evaporated and the residue was subjected to dynamic vacuum for 1 h, yielding 2-Co quantitatively and bis(3-methylenecyclobutylidene) in a 40% yield relative to initial 1,1-dibromo-2,2-bis(chloromethyl)-cyclopropane.

#### 4.2.10. AdP and $\text{BPh}_3$ to 7-methylene-3-phenylbicyclo[3.3.1]nonan-3-yl diphenylborane

To a J Young NMR tube charged with AdP (5 mg, 0.037 mmol) and  $\text{BPh}_3$  (9 mg, 0.037 mmol) was added  $\text{C}_6\text{D}_6$  (300  $\mu\text{L}$ ) at 23 °C and the mixture was allowed to react for 10 min, resulting in quantitative formation of (7-methylene-3-phenylbicyclo[3.3.1]nonan-3-yl)diphenylborane.  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  1.16 (m, 1H,  $\text{H}_{1\text{-eq}}$ ), 1.76 (m, 1H,  $\text{H}_{1\text{-ax}}$ ), 2.11 (bs, 2H,  $\text{H}_2$ ), 2.19 (m, 2H,  $\text{H}_{3\text{-ax}}$ ), 2.26 (m, 2H,  $\text{H}_{3\text{-eq}}$ ), 2.37 (dd,  $J =$

7.58, 14.35 Hz, 2H, H<sub>6-ax</sub>), 2.61 (dd,  $J = 2.85$ , 14.35 Hz, 2H, H<sub>6-eq</sub>), 4.86 (s, 2H, H<sub>5</sub>), 7.01 (t,  $J = 7.09$  Hz, 1H, H<sub>8</sub>), 7.12 (dd,  $J = 7.09$ , 7.56 Hz, 2H, H<sub>9</sub>), 7.15 (dd,  $J = 6.74$ , 7.01 Hz, 4H, H<sub>13</sub>), 7.20 (t,  $J = 6.74$  Hz, 2H, H<sub>12</sub>), 7.36 (d,  $J = 7.56$  Hz, 2H, H<sub>10</sub>), 7.44 (d,  $J = 7.01$  Hz, 4H, H<sub>14</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  28.54 (2C, C<sub>2</sub>), 31.34 (1C, C<sub>1</sub>), 36.72 (2C, C<sub>6</sub>), 39.88 (1C, C<sub>7</sub>), 41.35 (2C, C<sub>3</sub>), 114.32 (1C, C<sub>5</sub>), 124.93 (1C, C<sub>8</sub>), 126.01 (4C, C<sub>13</sub>), 127.46 (2C, C<sub>9</sub>), 127.47 (2C, C<sub>12</sub>), 130.00 (2C, C<sub>10</sub>), 133.87 (4C, C<sub>14</sub>), 143.56 (1C, C<sub>4</sub>), 144.34 (2C, C<sub>15</sub>), 144.97 (1C, C<sub>11</sub>). <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  68.83 (Fig. 5).

#### 4.2.11. Diphenyl(6a-phenylhexahydro-2,5-methanopentalen-3a(1H)-yl)methylborane

A J. Young tube charged with (7-methylene-3-phenylbicyclo[3.3.1]nonan-3-yl)diphenylborane (14 mg, 0.037 mmol) in C<sub>6</sub>D<sub>6</sub> (300  $\mu$ L) was placed in a preheated 80 °C oil bath for 72 h, resulting in quantitative formation of diphenyl(6a-phenylhexahydro-2,5-methanopentalen-3a(1H)-yl)methylborane. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.25 (m, 1H, H<sub>4</sub>), 1.30 (m, 2H, H<sub>5</sub>), 1.37 (m, 1H, H<sub>4</sub>), 1.63 (m, 2H, H<sub>2</sub>), 1.65 (s, 2H, BCH<sub>2</sub>), 1.69 (m, 2H, H<sub>5</sub>), 2.00 (m, 2H, H<sub>3</sub>), 2.28 (m, 2H, H<sub>2</sub>), 7.08 (t,  $J = 6.90$  Hz, 1H, CPh-H<sub>15</sub>), 7.14 (dd,  $J = 6.88$ , 7.09 Hz, 4H, BPh-H<sub>10</sub>), 7.17 (t,  $J = 6.88$  Hz, 2H, BPh-H<sub>11</sub>), 7.26 (dd,  $J = 6.90$ , 7.55 Hz, 2H, CPh-H<sub>14</sub>), 7.36 (d,  $J = 7.55$  Hz, 2H, CPh-H<sub>13</sub>), 7.56 (d,  $J = 7.09$  Hz, 4H, BPh-H<sub>9</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  33.81 (1C, C<sub>4</sub>), 35.67 (1C, BCH<sub>2</sub>), 36.24 (2C, C<sub>3</sub>), 49.35 (2C, C<sub>2</sub>), 52.22 (2C, C<sub>5</sub>), 56.08 (1C, C<sub>1</sub>), 58.11 (1C, C<sub>6</sub>), 125.55 (1C, CPh-C<sub>15</sub>), 127.28 (4C, BPh-C<sub>10</sub>), 127.71 (2C, CPh-C<sub>13</sub>), 127.85 (2C, CPh-C<sub>14</sub>), 130.80 (2C, BPh-C<sub>11</sub>), 135.70 (4C, BPh-C<sub>9</sub>), 144.58 (2C, BPh-C<sub>8</sub>), 146.36 (4C, CPh-C<sub>12</sub>). <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  75.13.

#### 4.2.12. AdP and BPh<sub>3</sub> to (7-methylene-3-phenylbicyclo[3.3.1]nonan-3-yl)boronic acid

A J. Young tube charged with AdP (5 mg, 0.037 mmol) and BPh<sub>3</sub> (9 mg, 0.037 mmol) was added C<sub>6</sub>D<sub>6</sub> (300  $\mu$ L) at 23 °C, and the mixture was allowed to react for 16 h, resulting in quantitative formation of (7-methylene-3-phenylbicyclo[3.3.1]nonan-3-yl)boronic acid. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.45 (m, 1H, H<sub>1</sub>), 1.48 (m, 1H, H<sub>1</sub>), 1.82 (m, 2H, H<sub>6</sub>), 2.09 (m, 2H, H<sub>2</sub>), 2.26 (m, 2H, H<sub>3</sub>), 2.51 (m, 2H, H<sub>3</sub>), 3.18 (m, 2H, H<sub>6</sub>), 4.49 (s, 2H, H<sub>5</sub>), 6.97 (t,  $J = 6.97$  Hz, 1H, Ph-H<sub>12</sub>), 7.36 (s, 2H, B(OH)<sub>2</sub>), 7.64 (dd,  $J = 6.97$ , 7.73 Hz, 2H, Ph-H<sub>13</sub>), 8.22 (d,  $J = 7.73$  Hz, 2H, Ph-H<sub>14</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  30.03 (2C, C<sub>2</sub>), 31.87 (1C, C<sub>7</sub>), 33.83 (1C, C<sub>1</sub>), 38.92 (2C, C<sub>6</sub>), 39.14 (2C, C<sub>3</sub>), 114.61 (1C, C<sub>5</sub>), 125.59 (1C, Ph-C<sub>12</sub>), 127.27 (2C, Ph-C<sub>13</sub>), 135.58 (2C, Ph-C<sub>14</sub>), 146.36 (1C, C<sub>4</sub>), 148.54 (1C, Ph-C<sub>15</sub>). <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  29.96.

#### 4.2.13. 1.1.1-Propellane and BPh<sub>3</sub> to 4-methyl-2-(3-methylene-1-phenylcyclobutyl)-1,2-diphenyl-2,3-dihydro-1H-borole

To an oven dried 25 mL two neck flask equipped with a dropping funnel and charged with 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (0.142 g, 0.48 mmol) was added 5 mL pentane at -78 °C. A 1.6 M MeLi solution in hexanes (0.6 mL, 0.96 mmol) was added dropwise at

-78 °C with vigorous stirring. The reaction mixture was stirred at -78 °C for 15 min, allowed to warm to 0 °C and stirred another hour. The propellane solution was then freeze-pump-thaw degassed 3 times with the temperature not exceeding 0 °C. To a separate 25 mL round bottom flask charged with BPh<sub>3</sub> (0.093 g, 0.38 mmol) and (silox)<sub>3</sub>FeNa(THF)<sub>2</sub> (0.330 g, 0.38 mmol) was added 15 mL of freshly distilled toluene at -78 °C. The propellane solution was vacuum distilled into this flask at -78 °C and the reaction mixture was allowed to warm slowly to 23 °C. It was stirred for 16 h, resulting in a yellow solution. The volatiles were evaporated, and the residue was dissolved in minimal Et<sub>2</sub>O. Slow evaporation at -35 °C yielded colorless crystals of 4-methyl-2-(3-methylene-1-phenylcyclobutyl)-1,2-diphenyl-2,3-dihydro-1H-borole (0.050 g, 35%). <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.81 (s, 3H, H<sub>3</sub>), 2.98 (m, 2H, H<sub>7</sub>), 3.10 (m, 1H, H<sub>4</sub>), 3.19 (m, 2H, H<sub>7</sub>), 3.80 (m, 1H, H<sub>4</sub>), 4.63 (br s, 1H, H<sub>10</sub>), 4.85 (br s, 1H, H<sub>10</sub>), 6.36 (s, 1H, H<sub>1</sub>), 6.99–7.10 (m, 9H, Ph), 7.23 (m, 4H, Ph), 7.49 (d,  $J = 7.70$  Hz, 2H, Ph).

#### 4.3. X-ray crystal structure determinations

##### 4.3.1. (silox)<sub>2</sub>Co(THF)<sub>2</sub> (1-Co)

A purple block measuring 0.14 × 0.132 × 0.109 mm<sup>3</sup> was obtained from slow evaporation of a THF solution. Crystal data for C<sub>32</sub>H<sub>70</sub>O<sub>4</sub>Si<sub>2</sub>Co,  $M = 633.99$ , monoclinic,  $I 2/a$ ,  $a = 18.1246(2)$ ,  $b = 9.20760(10)$ ,  $c = 22.7039(2)$  Å,  $\beta = 96.4670(10)^\circ$ ,  $V = 3764.81(7)$  Å<sup>3</sup>,  $T = 100.0(2)$  K,  $\lambda = 1.54184$  Å,  $Z = 4$ ,  $\rho_{\text{calc}} = 1.119$  Mg/m<sup>3</sup>,  $\mu = 4.407$  mm<sup>-1</sup>, 24,134 reflections, 3945 independent ( $R_{\text{int}} = 0.0351$ ),  $R_1$  (all data) = 0.0307,  $wR_2 = 0.0798$ ,  $R_1 (I > 2\sigma(I)) = 0.0304$ ,  $wR_2 = 0.0795$ , GOF = 1.044.

##### 4.3.2. [(silox)<sub>3</sub>Fe][Na(THF)<sub>2</sub>] (2-Fe)

A pale green plate measuring 0.245 × 0.182 × 0.132 mm<sup>3</sup> was obtained from slow evaporation of a THF solution. Crystal data for C<sub>44</sub>H<sub>97</sub>O<sub>5</sub>Si<sub>3</sub>NaCo,  $M = 869.32$ , monoclinic,  $P2_1/n$ ,  $a = 12.47370(10)$ ,  $b = 17.31430(10)$ ,  $c = 23.96080(2)$  Å,  $\beta = 91.0820(10)^\circ$ ,  $V = 5173.97(6)$  Å<sup>3</sup>,  $T = 99.9(2)$  K,  $\lambda = 1.54184$  Å,  $Z = 4$ ,  $\rho_{\text{calc}} = 1.116$  Mg/m<sup>3</sup>,  $\mu = 3.370$  mm<sup>-1</sup>, 71,941 reflections, 10,829 independent ( $R_{\text{int}} = 0.0407$ ),  $R_1$  (all data) = 0.0357,  $wR_2 = 0.0897$ ,  $R_1 (I > 2\sigma(I)) = 0.0334$ ,  $wR_2 = 0.0882$ , GOF = 1.061.

##### 4.3.3. [(silox)<sub>3</sub>Co][Na(THF)<sub>2</sub>] (2-Co)

A blue block measuring 0.277 × 0.218 × 0.189 mm<sup>3</sup> was obtained from slow evaporation of a THF solution. Crystal data for C<sub>44</sub>H<sub>97</sub>O<sub>5</sub>Si<sub>3</sub>NaCo,  $M = 872.40$ , monoclinic,  $P2_1/n$ ,  $a = 12.47360(10)$ ,  $b = 17.33840(10)$ ,  $c = 23.93010(2)$  Å,  $\beta = 91.2410(10)^\circ$ ,  $V = 5174.20(6)$  Å<sup>3</sup>,  $T = 100.0(3)$  K,  $\lambda = 1.54184$  Å,  $Z = 4$ ,  $\rho_{\text{calc}} = 1.120$  Mg/m<sup>3</sup>,  $\mu = 3.633$  mm<sup>-1</sup>, 76,615 reflections, 10,567 independent ( $R_{\text{int}} = 0.0696$ ),  $R_1$  (all data) = 0.0510,  $wR_2 = 0.1348$ ,  $R_1 (I > 2\sigma(I)) = 0.0487$ ,  $wR_2 = 0.1330$ , GOF = 1.059.

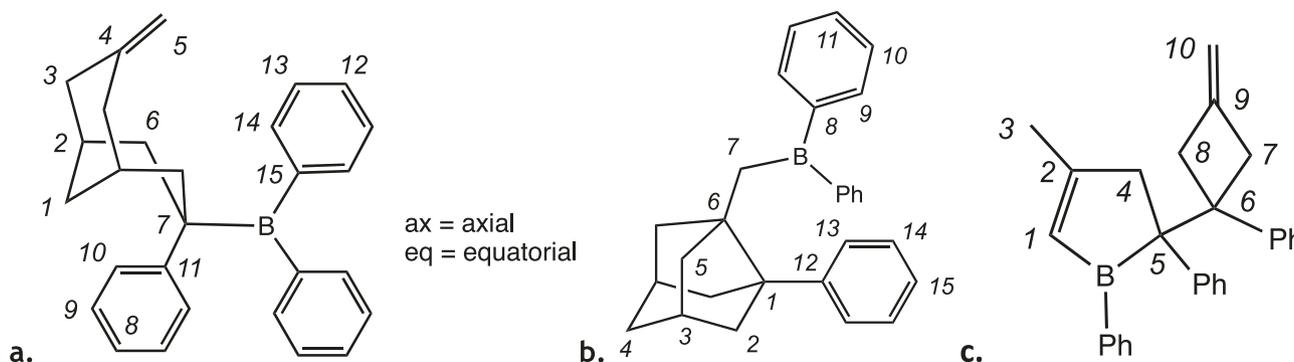


Fig. 5. Keys for NMR spectra of: a. 7-methylene-3-phenylbicyclo[3.3.1]nonan-3-yl)diphenylborane and boronic acid; b. Diphenyl(6a-phenylhexahydro-2,5-methanopentalen-3a(1H)-yl)methylborane; c. 4-methyl-2-(3-methylene-1-phenylcyclobutyl)-1,2-diphenyl-2,3-dihydro-1H-borole (4).

#### 4.3.4. *Ph*( $\kappa$ -CH=CMeCH<sub>2</sub>CPh(<sup>c</sup>C<sub>4</sub>H<sub>4</sub>-1-Ph,3-CH<sub>2</sub>)) (4)

A colorless plate measuring 0.153 × 0.12 × 0.08 mm<sup>3</sup> was obtained from slow evaporation of a benzene solution. Crystal data for C<sub>28</sub>H<sub>27</sub>B, M = 374.30, triclinic, P(1 bar), a = 8.4894(2), b = 9.9730(2), c = 13.2576(2) Å, α = 73.793(2)°, β = 74.831(2)°, γ = 86.835(2)°, V = 1040.10(5) Å<sup>3</sup>, T = 99.9(4) K, λ = 1.54184 Å, Z = 2, ρ<sub>calc</sub> = 1.195 Mg/m<sup>3</sup>, μ = 0.495 mm<sup>-1</sup>, 22,851 reflections, 4374 independent (R<sub>int</sub> = 0.0375), R<sub>1</sub> (all data) = 0.0419, wR<sub>2</sub> = 0.1026, R<sub>1</sub> (I > 2σ(I)) = 0.0387, wR<sub>2</sub> = 0.1001, GOF = 1.082.

#### 5. Author credit

Primary experimental work, and certain intellectual work excluding crystal structures was conducted by G. M. George. Funding and primary intellectual work was by P. T. Wolczanski, and crystallographic work was conducted by S. N. MacMillan.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

Support from the National Science Foundation (CHE-1953884) and Cornell University is gratefully acknowledged.

#### References

- H. Jeong, J.M. John, R.R. Schrock, A.H. Hoveyda, *J. Am. Chem. Soc.* **137** (2015) 2239–2242.
- R.R. Schrock, *Angew. Chem. Int. Ed.* **45** (2006) 3748–3759; (b) R.R. Schrock, A.H. Hoveyda, *Angew. Chem. Int. Ed.* **42** (2003) 4592–4633; (c) T.T. Nguyen, M.J. Koh, F. Romiti, R.R. Schrock, A.H. Hoveyda, *Science* **352** (2016) 569–575.
- V.M. Marx, A.H. Sullivan, M. Melaimi, S.C. Virgil, B.K. Keitz, D.S. Weinberger, G. Bertrand, R.H. Grubbs, *Angew. Chem. Int. Ed.* **54** (2015) 1919–1923.
- R.H. Grubbs, *Angew. Chem. Int. Ed.* **45** (2006) 3760–3765.
- Y. Chauvin, *Angew. Chem. Int. Ed.* **45** (2006) 3740–3747.
- S.J. Malcolmsom, S.J. Meek, E.S. Sattely, R.R. Schrock, A.H. Hoveyda, *Nature* **471** (2011) 933–937; (b) S.J. Meek, R.V. O'Brien, J. Llaveria, R.R. Schrock, A.H. Hoveyda, *Nature* **471** (2011) 461–466.
- Y. Xu, J.J. Wong, A.E. Samkian, J.H. Ko, S. Chen, K.N. Houk, R.H. Grubbs, *J. Am. Chem. Soc.* **142** (2020) 20987–20993; (b) J.-A. Song, G.I. Peterson, K.-T. Bang, T.S. Ahmed, J.-C. Sung, R.H. Grubbs, *J. Am. Chem. Soc.* **142** (2020) 10438–10445; (c) J. Hartung, P. K. Dorman, R. H. Grubbs, *Science* **366** (2014) 13029–13037.
- R. Toreki, R.R. Schrock, *J. Am. Chem. Soc.* **112** (1990) 2448–2449; (b) A.M. LaPointe, R.R. Schrock, *Organometallics* **14** (1995) 1875–1884.
- M.P. Coles, V.C. Gibson, W. Clegg, M.R. Elsegood, P.A. Porrelli, *P. Chem. Commun.* (1996) 1963–1964.
- P. Wu, G.P.A. Yap, K.H. Theopold, *J. Am. Chem. Soc.* **140** (2018) 7088–7091.
- M. Brookhart, J.R. Tucker, G.R. Husk, *J. Am. Chem. Soc.* **105**, (1983) 258–264; (b) M. Brookhart, J.R. Tucker, *J. Am. Chem. Soc.* **103** (1981) 979–981; (c) M. Brookhart, D. Timmers, J.R. Tucker, G.D. Williams, G.R. Husk, H. Brunner, B. Hammer, *J. Am. Chem. Soc.* **105** (1983) 6721–6723.
- G. Poignant, S. Nlate, V. Guerschais, A.J. Edwards, P.R. Raithby, *Organometallics* **16** (1997) 124–132.
- V. Mahias, S. Cron, L. Toupet, C. Lapinte, *Organometallics* **15** (1996) 5399–5408.
- A. Klose, E. Solari, C. Floriani, N. Re, A. Chiesi-Villa, C. Rizzoli, *Chem. Commun.* (1997) 2297–2298.
- V. Esposito, E. Solari, C. Floriani, N. Re, C. Rizzoli, A. Chiesi-Villa, *Inorg. Chem.* **39** (2000) 2604–2613.
- Y. Li, J.-S. Huang, Z.-Y. Zhou, C.-M. Che, X.-Z. You, *J. Am. Chem. Soc.* **124** (2002) 13185–13193.
- S.K. Russell, J.M. Hoyt, S.C. Bart, C. Milsmann, S.C.E. Stieber, S.P. Semproni, S. DeBeer, P.J. Chirik, *Chem. Sci.* **5** (2014) 1168–1174.
- K.A.M. Kremer, G.-H. Kuo, E.J. O'Connor, P. Helquist, R.C. Kerber, *J. Am. Chem. Soc.* **104** (1982) 6119–6121; (b) G.-H. Kuo, P. Helquist, R.C. Kerber, *Organometallics* **3** (1984) 806–808.
- T. Bodnar, A.R. Cutler, *J. Organomet. Chem.* **213** (1981) C31–C36.
- A. Davison, J.P. Selegue, *J. Am. Chem. Soc.* **100** (1978) 7763–7765; (b) R.D. Adams, A. Davison, J.P. Selegue, *J. Am. Chem. Soc.* **101** (1979) 7232–7238.
- M.I. Bruce, A.G. Swincer, *Aust. J. Chem.* **33** (1980) 1471–1483.
- C.P. Casey, W.H. Miles, H. Tukada, J.M. O'Connor, *J. Am. Chem. Soc.* **104** (1982) 3761–3762.
- B.M. Lindley, A. Swidan, E.B. Lobkovsky, P.T. Wolczanski, M. Adelhardt, J. Sutter, K. Meyer, *Chem. Sci.* **6** (2015) 4730–4736.
- B.M. Lindley, B.P. Jacobs, S.N. MacMillan, P.T. Wolczanski, *Chem. Commun.* **52** (2016) 3891–3894.
- B.P. Jacobs, R.G. Agarwal, P.T. Wolczanski, T.R. Cundari, *Polyhedron* **116** (2016) 47–56.
- K.M. Dawood, K. Nomura, *Adv. Synth. Catal.* **363** (2021) 1970–1997; (b) K. Nomura, S. Zhang, *Chem. Rev.* **111** (2011) 2342–2362; (c) X. Hou, K. Nomura, *Dalton Trans.* **46** (2017) 12–24.
- X. Hou, K. Nomura, *J. Am. Chem. Soc.* **137** (2015) 4662–4665; (b) X.H. Hou, K. Nomura, *J. Am. Chem. Soc.* **138** (2016) 11840–11849.
- Y. Kawamoto, I. Elser, M.R. Buchmeiser, K. Nomura, *Organometallics* **40** (2021) 2017–2022; (b) K. Nomura, Y. Onishi, M. Fujiki, J. Yamada, *Organometallics* **27** (2008) 3818–3824; (c) J. Yamada, M. Fujiki, K. Nomura, *Organometallics* **24** (2005) 2248–2250; (d) K. Suzuki, Y. Matsumoto, K. Nomura, *J. Organomet. Chem.* **696** (2011) 4057–4063.
- H. Hayashibara, X. Hou, K. Nomura, *Chem. Commun.* **54** (2018) 13559–13562.
- S.M. Rocklage, J.D. Fellmann, G.A. Rupprecht, L.W. Messerle, R.R. Schrock, *J. Am. Chem. Soc.* **103** (1981) 1440–1447; (b) K.C. Wallace, A.H. Liu, J.C. Dewan, R.R. Schrock, *J. Am. Chem. Soc.* **110** (1988) 4964–4977.
- W.S. Ferrell, *Z. Anorg. Allg. Chem.* **647** (2021) 584–592.
- D.S. Belov, G. Tejada, K.V. Bukhryakov, *ChemPlusChem* **86** (2021) 924–937.
- D.S. Belov, G. Tejada, C. Tsay, K.V. Bukhryakov, *Chem. Eur. J.* **27** (2021) 4578–4582; (b) D.S. Belov, D.A. Fenoll, I. Chakraborty, X. Solans-Monfort, K.V. Bukhryakov, *Organometallics* **40** (2021) 4578–4582.
- F.N. Tebbe, G.W. Parshall, D.W. Ovenall, *J. Am. Chem. Soc.* **101** (1979) 5074–5075; (b) U. Klabunde, F.N. Tebbe, G.W. Parshall, R.L. Harlow, *J. Mol. Catal.* **8** (1980) 37–51.
- T.R. Howard, J.B. Lee, R.H. Grubbs, *J. Am. Chem. Soc.* **102** (1980) 6876–6878.
- Y. L. Qian, D. F. Zhang, J. L. Huang, H. Y. Ma, A. S. C. Chan, A. S. C. J. Molec. Catal. **A 133** (1988) 135–138. (b) J. F. Liu, D. F. Zhang, J. L. Huang, Y. L. Qian, A. S. C. Chan, A. S. C. J. Molec. Catal. **A 142** (1999) 301–304. (c) J. F. Liu, D. F. Zhang, J. L. Huang, Y. L. Qian, A. S. C. Chan, *J. Polym. Sci. Par A*. **38** (2000) 1639–1640.
- O. Eisenstein, R. Hoffmann, A.R. Rossi, *J. Am. Chem. Soc.* **103** (1981) 5582–5584.
- H.M.L. Davies, E.G. Antoulinakis, "Intermolecular Metal-Catalyzed Carbenoid Cyclopropanations" in *Organic Reactions*, Ed. L. E. Overman, John Wiley & Sons: New York, 2001; (b) H.M.L. Davies, R.E.J. Beckwith, *Chem. Rev.* **103** (2003) 2861–2903.
- J. Liu, L. Hu, L. Wang, H. Chen, L. Deng, *J. Am. Chem. Soc.* **139** (2017) 3876–3888.
- J.A. Bellow, S.A. Stoian, J. van Tol, A. Ozarowski, R.L. Lord, S. Groysman, *J. Am. Chem. Soc.* **138** (2016) 5531–5534; (b) J.A. Bellow, M. Yousif, D. Fang, E.G. Kratz, G.A. Cisneros, S. Groysman, *Inorg. Chem.* **54** (2015), 5624–5633.
- P.T. Wolczanski, *Organometallics* **36** (2017) 622–631.
- M.R. Hoffbauer, V.M. Iluc, *J. Am. Chem. Soc.* **143** (2021) 5592–5597.
- G.M. George, P.T. Wolczanski, S.N. MacMillan, T.R. Cundari, *Polyhedron* **181** (2020), 114460.
- D.S. Belov, L. Mathivathanan, M.J. Beazley, W.B. Martin, K.V. Bukhryakov, *Angew. Chem. Int. Ed.* **60** (2021) 2934–2938.
- M.D. Levin, P. Kaszynski, J. Michl, *Chem. Rev.* **100** (2000) 169–234; (b) A.M. Dilmaç, E. Spuling, A. de Meijere, S. Bräse, *Angew. Chem. Int. Ed.* **56** (2017) 5684–5718.
- J. Kanazawa, M. Uchlyama, *Synlett.* **30** (2019) 1–11.
- K. Semmler, G. Szeimies, J. Belzner, *J. Am. Chem. Soc.* **107** (1985) 6410–6411; (b) J. Belzner, B. Gareiss, K. Polborn, W. Schmid, K. Semmler, G. Szeimies, *Chem. Ber.* **122** (1989) 1509–1529; (c) J. Belzner, U. Bunz, K. Semmler, G. Szeimies, K. Opitz, A.-D. Schlüter, B. Gareiss, K. Polborn, W. Schmid, K. Semmler, G. Szeimies, *Chem. Ber.* **122** (1989) 397–398; (d) K.M. Lynch, W.P. Dailey, *J. Org. Chem.* **60** (1995) 4666–4668.
- R.E. Pincock, E. Torupka, *J. Am. Chem. Soc.* **91** (1969) 4593.
- G.M. George, P.T. Wolczanski, S.N. MacMillan, *Organometallics* **40** (2021) 3389–3396; (b) Wolczanski, P.T.; George, G.M. "Propellanes as Olefin Metathesis and Romp Initiators; US Provisional No. 63/012,191, April 19, 2020.
- D.F. Evans, *J. Chem. Soc.* (1959) 2003–2005; (b) E.M. Schubert, *J. Chem. Educ.* **69** (1992) 62.
- O. Jarosh, R. Walsh, G. Szeimies, *J. Am. Chem. Soc.* **122** (2000) 8490–8494; (b) K. B. Wiberg, S.T. Waddell, *J. Am. Chem. Soc.* **122** (1990) 2194–2216.
- P.G. Gassman, F. Williams, *J. Am. Chem. Soc.* **94** (1972) 7733–7741; (b) P.G. Gassman, G.R. Meyer, F. Williams, *J. Am. Chem. Soc.* **94** (1972) 7741–7748; (c) P. G. Gassman, T.J. Atkins, *J. Am. Chem. Soc.* **94** (1972) 7748–7756.
- S. Yu, A. Noble, R.B. Bedford, V.K. Aggarwal, *J. Am. Chem. Soc.* **141** (2019) 20325–20334.
- R.E. Pincock, J. Schmidt, W.B. Scott, E.J. Torupka, *Can. J. Chem.* **50** (1972) 3958–3964.
- A. Hafner, A. Mühlenbach, P.A. van der Schaaf, *Angew. Chem. Int. Ed.* **36** (1997) 2121–2124.
- J.L. Brumaghim, G.S. Girolami, *Organometallics* **18** (1999) 1923–1929.
- K.F. Hirsekorn, A.S. Veige, M.P. Marshak, Y. Koldobskaya, P.T. Wolczanski, T. R. Cundari, E.B. Lobkovsky, *J. Am. Chem. Soc.* **127** (2005) 4809–4830.
- M.E. Gurskii, I.D. Gridnev, A.V. Buevich, Y.N. Bubnov, *Organometallics* **13** (1994) 4658–4660.
- F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans. I* **1** (1987) S1–S19.
- B.P. Jacobs, P.T. Wolczanski, Q. Jiang, T.R. Cundari, S.N. MacMillan, *J. Am. Chem. Soc.* **139** (2017) 12145–12148.
- H.H. Karsch, *Chem. Ber.* **110** (1977) 2699–2711.
- H.H. Karsch, *Chem. Ber.* **110** (1977) 2222–2235.
- H. Zhang, Z. Ouyang, Y. Liu, Q. Zhang, L. Wang, L. Deng, *Angew. Chem. Int. Ed.* **53** (2014) 8432–8436.

- [64] T.R. Cundari, B.P. Jacobs, S.N. MacMillan, P.T. Wolczanski, Dalton Trans. 47 (2018) 6025–6030.
- [65] O.L. Sydora, T.P. Henry, P.T. Wolczanski, E.B. Lobkovsky, E. Rumberger, D. N. Hendrickson, Inorg. Chem. 45 (2006) 609–626.
- [66] R.A. Anderson, K. Faegri Jr., J.C. Green, A. Haaland, M.F. Lappert, W.-P. Leungand, K. Rypdal, Inorg. Chem. 27 (1988) 1782–1786.
- [67] E.J. Hawrelak, W.H. Bernskoetter, E. Lobkovsky, G.T. Yee, E. Bill, P.J. Chirik, Inorg. Chem. 44 (2005) 3103–3111.
- [68] S.D. Ittel, A.D. English, C.A. Tolman, J.P. Jesson, Inorganica Chim. Acta 33 (1979) 101–106.
- [69] S.C. Bart, E. Lobkovsky, P.J. Chirik, J. Am. Chem. Soc. 126 (2004) 13794–13807.
- [70] M.M. Olmstead, P.P. Power, S.C. Shoner, Inorg. Chem. 30 (1991) 2547–2551.
- [71] J. Bachmann, D.G. Nocera, J. Am. Chem. Soc. 127 (2005) 4730–4743.
- [72] S.P. Heins, W.D. Morris, P.T. Wolczanski, E.B. Lobkovsky, T.R. Cundari, Angew. Chem. Int. Ed. 54 (2015) 14407–14411.
- [73] P.P. Power, S.C. Shoner, Angew. Chem. Int. Ed. 30 (1991) 330–332.
- [74] F.M. MacDonnell, K. Ruhlandt-Senge, J.J. Ellison, R.H. Holm, P.P. Power, Inorg. Chem. 34 (1995) 1815–1822.
- [75] A.M. Bryan, G.J. Long, F. Grandjean, P.P. Power, Inorg. Chem. 52 (2013) 12152–12160.
- [76] R.J. Kern, J. Inorg. Nucl. Chem. 24 (1962) 1105–1109.