

Rhenium-Catalysed Hydroboration of Aldehydes and Aldimines

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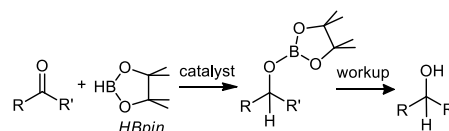
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The first examples for the rhenium-catalysed hydroboration of aldehydes, ketones and aldimines, including heteroaromatic quinoline, are reported herein. Reactions are remarkably chemoselective and tolerant of several functional groups. A wide array of rhenium complexes were efficient pre-catalysts for these hydroborations, including new low-valent complexes of the formula $[\text{Re}(\text{N-N})(\text{CO})_3(\text{L})]\text{X}$ (N-N = bipy derivative, L = labile ligand/solvent, and X = $[\text{BAR}^f_4]^-$ and $[\text{B}(3,5\text{-di-tBu-cat})_2]^-$), which have been characterized fully including an X-ray diffraction study for $[\text{Re}(\text{bipy})(\text{CO})_3(\text{quin})][\text{BAR}^f_4]$ (**2**). A new silver spiroboronate ester $\text{Ag}[\text{B}(3,5\text{-di-tBu-cat})_2](\text{NCCCH}_3)_3$ (**3**) was prepared and characterized fully, including an X-ray diffraction study, and used to make one of the new rhenium complexes.

Introduction

The catalysed hydroboration of unsaturated organic molecules using either catecholborane (HBcat: cat = 1,2- $\text{O}_2\text{C}_6\text{H}_4$) or pinacolborane (HBpin: pin = 1,2- $\text{O}_2\text{C}_2\text{Me}_4$) offers the synthetic chemist a gentle and efficient methodology for the reduction of double and triple bonds. Depending upon the nature of the substrate, fine-tuning of the catalyst system and the borane, these catalysed reactions can generate products with complementary, or opposite, chemo-, regio-, and stereoselectivities compared to those obtained in conventional hydroborations using $\text{H}_3\text{B}\cdot\text{LB}$ (LB = Lewis base), alkyl- or dialkyl boranes.¹ Although catalysed hydroborations have traditionally employed late metal catalysts (Ru, Rh, Ir, etc) and have focused on the reduction of alkenes and alkynes, a considerable amount of research has recently investigated the possibility of using alternate catalyst systems for the hydroboration of aldehydes and ketones as a gentle route for generating the corresponding alcohols (Scheme 1).² Not surprising the boron usually ends up bound to the electronegative oxygen atom of the aldehyde or ketone while the basic hydride adds to the carbon atom.² Indeed, a number of different metal complexes and Lewis acids have been found to be effective pre-catalysts for the reduction of C=O double bonds, including Zr,³ Ti,⁴ Mn,⁵ Fe,⁶ Co,⁷ Ni,⁸ Cu,⁹ Zn,¹⁰ Mo,¹¹ Ru,¹² Rh/Ir,¹³ Ge/Sn,¹⁴ P,¹⁵ Al,¹⁶ Ga/In,¹⁷ Mg,¹⁸ and La.¹⁹



Scheme 1 Hydroboration and Oxidative Workup of Ketones and Aldehydes using HBpin.

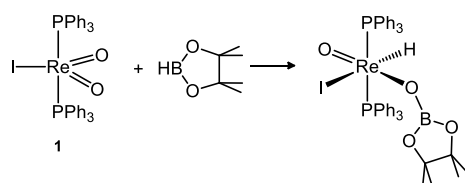
It is somewhat surprising, therefore, that the use of rhenium complexes in catalysed hydroboration reactions has been largely ignored. Indeed, the only reported examples so far have been by Fernandes and co-workers who have elegantly demonstrated that high-valent rhenium complexes, such as $[(\text{PPh}_3)_2\text{Re}(\text{O})_2]$, are effective pre-catalysts for the reduction or sulfoxides using either HBcat or HBpin.²⁰ These reactions are believed to proceed *via* initial dissociation of the phosphine ligands and coordination of two sulfoxide groups. The next step involves activation of the B-H bond by a formal addition of the borane to the rhenium-oxide bond to give the corresponding rhenium hydrides where the Lewis acid boryl group has added to the oxygen atom to form transient Re-OBcat or Re-OBpin appendages. In support of this mechanism, Fernandes and co-workers have found that stoichiometric addition of HBcat and HBpin to $[(\text{PPh}_3)_2\text{Re}(\text{O})_2]$ (**1**) cleanly affords the metal hydrides (*trans*- $[(\text{Ph}_3\text{P})_2(\text{O})(\text{I})\text{Re}(\text{H})\text{OBcat}]$ and *trans*- $[(\text{Ph}_3\text{P})_2(\text{O})(\text{I})\text{Re}(\text{H})\text{OBpin}]$) in high yields (Scheme 2). Following this remarkable chemistry, and considering our interest in rhenium chemistry²¹ and developing novel borylation strategies,²² we decided to explore the possibility of using various rhenium complexes as pre-catalysts for the hydroboration of aldehydes, ketones and aldimines, the results of which are presented within.

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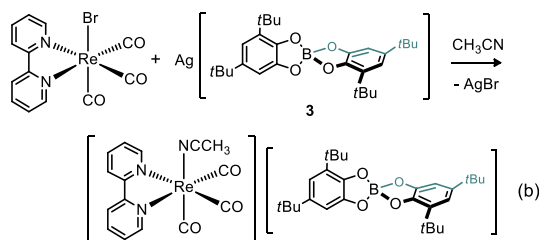
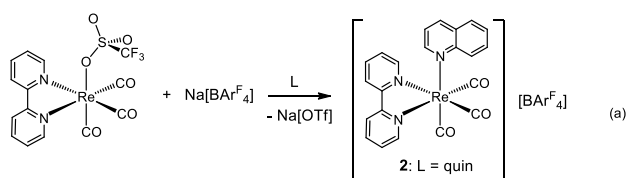
† Electronic Supplementary Information (ESI) available: experimental and catalytic data provided. See DOI: 10.1039/x0xx00000x

Scheme 2 Addition of HBpin to $[(PPh_3)_2Re(O)_2]$.

Results and discussion

Synthesis of rhenium complexes

It is well known that rhenium complexes in various oxidation states can effectively be used as pre-catalysts for the hydrosilylation of carbonyl compounds.²³ Although a number of simple neutral rhenium complexes are readily-available, we decided to prepare a series of low-valent rhenium cationic salts of the general formula $[Re(bipy)(CO)_3(L)]X$ (Lewis-base, Scheme 3) in an effort to expand the range of rhenium complexes investigated for the analogous hydroboration reactions. For complete spectroscopic data and catalytic results on these species, please see the Supporting Information section. These complexes have been designed to be strong Lewis acids, combining labile ligands and non-coordinating anions with a cationic metal centre and strongly π -acceptor carbonyl ligands.²¹ Variation of the labile monodentate L, allowed us to fine-tune the physicochemical properties of the rhenium complexes. All new complexes have been characterized fully by a number of physical techniques including multinuclear NMR spectroscopy, FT-IR spectroscopy, elemental analyses and X-ray diffraction in the case of **2**. The molecular structure of **2** is shown in Fig. 1 and bond distances and angles are similar to those reported earlier for related complexes.²¹



Scheme 3 Synthesis of Rhenium Complexes 1-9.

The counterion X^- was also altered in an effort to see if the anion plays any role in hydroboration activities. As an economically-viable and readily prepared alternative to the frequently used weakly-coordinating anion (WCA), $Na[BARF_4]$,²⁴

we have prepared the silver salt $Ag[B(3,5-di-tBu-cat)_2](NCCH_3)_3$ (**3**) from the reaction of $B_2(3,5-di-tBu-cat)_3$ ²⁵ with $[Ag(acac)]$ in acetonitrile. The reaction proceeded in the dark for 18 h to give the desired silver salt in moderate yield (61%) along with concomitant formation of $(acac)B(3,5-di-tBu-cat)$. The ¹¹B NMR spectrum for $Ag[B(3,5-di-tBu-cat)_2](NCCH_3)_3$

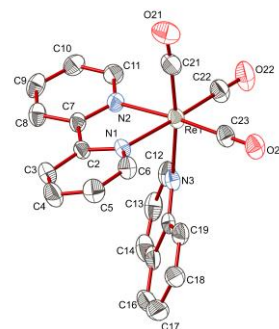


Fig. 1 The molecular structure of **2** with thermal ellipsoids shown at the 50% probability level. The anion has been omitted for clarity. Selected bond distances (Å) and angles ($^\circ$): Re(1)-C(23) 1.924(4), Re(1)-C(21) 1.925(6), Re(1)-C(22) 1.939(5), Re(1)-N(1) 2.171(3), Re(1)-N(2) 2.181(3), Re(1)-N(3) 2.257(4); C(22)-Re(1)-N(1) 173.88(15), C(23)-Re(1)-N(2) 173.74(15), C(21)-Re(1)-N(3) 172.42(16).

shows the expected sharp singlet at 14.1 ppm which is typical for four-coordinate boron bound to two catecholato groups.²⁵ To confirm the formation of this silver salt we have carried out a single crystal X-ray diffraction study on **3**, the molecular structure of which is shown in Fig. 2. As expected, the borate anion lies in a slightly distorted tetrahedral environment. The silver cation has three molecules of acetonitrile arranged in a distorted tetrahedral geometry as there appears to be significant interaction with one of the oxygen atoms of the catecholato groups of the bulky $[B(3,5-di-tBu-cat)_2]$. Indeed, the long silver-oxygen distance of 2.4333(16) Å is close to that found in related structures containing bound THF ligands, demonstrating that the anion is only weakly coordinated to the silver cation in the solid state.²⁶ No evidence was found using multinuclear NMR spectroscopy for any such coordination of the bulky $[B(3,5-di-tBu-cat)_2]$ anion to the silver cation in solution.

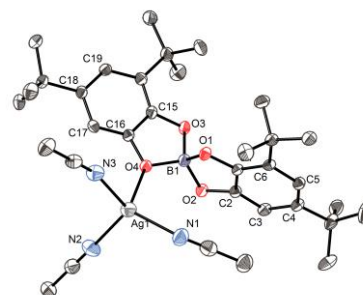


Fig. 2 The molecular structure of $Ag[B(3,5-di-tBu-cat)_2](NCCH_3)_3$ (**3**) with thermal ellipsoids shown at the 50% probability level. Selected bond distances (Å) and angles ($^\circ$): Ag(1)-N(1) 2.240(2), Ag(1)-N(3) 2.250(2), Ag(1)-N(2) 2.274(2), Ag(1)-O(4) 2.4333(16); N(1)-Ag(1)-N(3) 130.83(9), N(1)-Ag(1)-N(2) 109.49(9), N(3)-Ag(1)-N(2) 108.33(8), N(1)-Ag(1)-O(4) 101.86(7), N(3)-Ag(1)-O(4) 97.60(7), N(2)-Ag(1)-O(4) 104.84(7).

Furthermore, we have found that addition of **3** in CH₃CN to [Re(bipy)(CO)₃Br] resulted in the formation of [Re(bipy)(CO)₃(CH₃CN)][B(3,5-di-*t*Bu-cat)₂] (**4**, Scheme 3b) in high yields (88%) along with concomitant formation of AgBr. With these new rhenium complexes in hand, along with a variety of known compounds, we then decided to examine their potential to facilitate the hydroboration of compounds containing carbonyl and imine groups.

Catalytic hydroborations

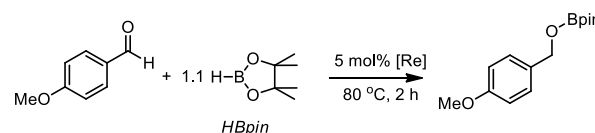
Our initial studies focused on reactions of 4-anisaldehyde using HBpin as the reducing agent as it is considerably less-reactive than its counterpart, HBcat.²⁷ Although no reaction was observed at room temperature over two hours, we have found that a variety of rhenium complexes are effective pre-catalysts for this reduction at elevated temperatures (Table 1 illustrates selected examples, where complexes **2** and **4** were chosen as representative examples of complexes of the type [Re(bipy)(CO)₃(L)]X, additional results are shown in the SI section). It should be noted, however, that under these conditions, depending upon the solvent, about 30-40% conversion to give the saturated boronate ester product is observed even in the absence of a rhenium pre-catalyst. The rhenium dimer [Re₂(CO)₁₀] (Entry 2) showed no significant improvements in conversion (as ascertained by ¹H NMR spectroscopy) in C₆D₆ but up to 90% of the starting aldehyde was reduced in reactions carried out in CD₂Cl₂, illustrating that the Re(0) species had some effectiveness in this solvent. More remarkable is that complete conversion was achieved in either solvent using the readily available rhenium(I) complex [Re(CO)₅Br] (Entry 3). Substitution of two of the carbonyl ligands with a more basic bipy group (Entry 4) in the neutral rhenium(I) complex showed reduced conversion in CD₂Cl₂ and no improvements in reactions carried out in C₆D₆. We then examined a variety of complexes of the type [Re(N-N)(CO)₃(L)]X (SI) and are pleased to report that several of these low-valent species proceeded with complete conversions in reactions carried out in both solvents. Unfortunately, complexes containing either basic pyridine or quinoline (Entry 5) gave lower conversions as considerable degradation of the borane to B₂pin₃ and H₂ was observed using multinuclear NMR spectroscopy in these cases. The base or transition-metal promoted degradation of HBpin and other hydridoboranes is well-documented.¹ It is important to note that complexes containing both boron-containing WCAs [BAR^F₄]⁻ and [B(3,5-di-*t*Bu-cat)₂]⁻ gave excellent conversions. Finally, reactions employing rhenium complexes in higher oxidation states were also examined. It is not really surprising that the oxo-rhenium complex **1** proceeded with complete conversion (Entries 12) in both solvent systems as Fernandes and co-workers have previously demonstrated the utility of this species in catalysed hydroborations.²⁰

Encouraged by these promising results, we decided to expand the scope of these hydroborations and initially examine various aldehyde, ketone and aldimine derivatives (Table 1)

using the readily-available high-oxidation state complex [(PPh₃)₂Re(O)₂] (**1**) as the representative catalyst precursor. Reactions of these substrates were carried out using HBpin and 5 mol% pre-catalyst in C₆D₆ at 80°C for 2 h. Benzaldehyde, 4-fluorobenzaldehyde and 4-nitrobenzaldehyde were investigated to see what effect varying the electronics on the aldehyde had on these reductions. Like 4-anisaldehyde, hydroborations of both benzaldehyde and 4-fluorobenzaldehyde proceeded smoothly with complete conversion of the aldehyde, demonstrating that these reactions work well with electron-rich and electron-poor aromatic derivatives. Reactions with 4-nitrobenzaldehyde were of singular interest as both the aldehyde and the nitro group were reduced using excess HBpin (3 equiv) under these conditions. The catalytic reduction of aromatic nitro groups has been the subject of recent considerable interest.^{19,28}

Hydroborations of

Table 1 Rhenium-Catalyzed Hydroboration of 4-Anisaldehyde with Pinacolborane

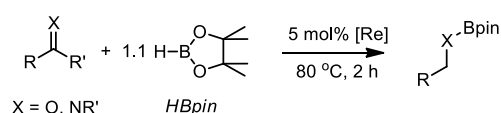




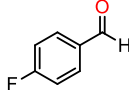
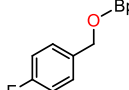
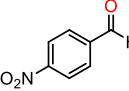
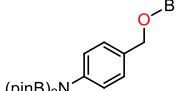
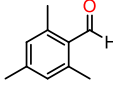
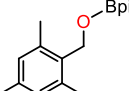
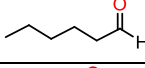
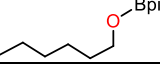


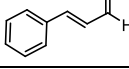
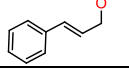




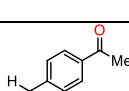
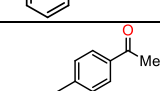




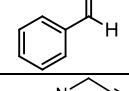
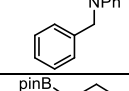
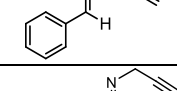
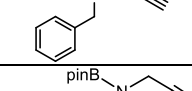
Entry	Catalyst Precursor	Conversion ^a	
		C ₆ D ₆	CD ₂ Cl ₂
1	none	30	40
2	[Re ₂ (CO) ₁₀]	30	90
3	[Re(CO) ₅ Br]	100	100
4	[Re(bipy)(CO) ₃ Br] ^b	30	95
5	[Re(bipy)(CO) ₃ (quin)][BAR ^F ₄] ^c	45	80
6	[Re(bipy)(CO) ₃ (CH ₃ CN)][BAR ^F ₄]	100	100
7	[Re(bipy)(CO) ₃ (THF)][BAR ^F ₄]	100	100
8	[Re(bipy)(CO) ₃ (CH ₃ CN)][B(3,5-di- <i>t</i> Bu-cat) ₂] ^d	100	100
9	[(PMe ₂ Ph) ₃ ReCl ₃]	30	85
10	[(PPh ₃) ₂ Re(O) ₂]	100	100

^aConversion ascertained using ¹H NMR spectroscopy averaged over three runs. Reactions were carried out in a sealed J. Young tube in a water bath heated at 80°C for two hours. ^bbipy = 2,2'-bipyridine. ^cquin = quinoline. ^d3,5-di-*t*Bu-cat = bis(3,5-di-*tert*-butyl[1,2-benzenediolato(2-)-O,O']borate

sterically-hindered mesitaldehyde (Entry x) also proved successful (100% conversion) as did the aliphatic derivative hexanal (Entry y). Reactions with thiophene-2-carbaldehyde (Entry z) proceeded with complete conversion demonstrating that this reaction is tolerant of heteroaromatic groups. More remarkable, however, is that the rhenium-catalysed hydroboration of *trans*-cinnamaldehyde gave the corresponding 1,2-addition product predominantly with only minor amounts of the 1,4-addition product (< 2%) (Entry x). Boron-element additions with this challenging substrate frequently give mixtures of both 1,2- and 1,4-addition products.²⁸ Similar results were generally observed in reactions employing the low-valent rhenium complexes and variation of the bipy (N-N) groups and labile ligand L had negligible effect on both activities and selectivities (see SI).

Table 2 Rhenium-Catalyzed Hydroboration of Aldehydes and Aldimines using 5 mol% [(PPh₃)₂Re(O)₂I] with Pinacolborane.^a



Entry	Substrate	Product	Yield ^a
1			100
2			100
3			100
4			100
5			100
6			100
7			98
8			40
9			15
10			100
11			100
12			25
13			100
14			100

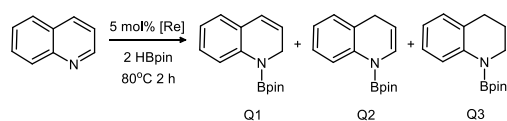
^aConversion ascertained using ¹H NMR spectroscopy averaged over three runs. Reactions were carried out in a sealed J. Young tube in a water bath heated at 80°C for two hours.

We then turned our attention to the rhenium-catalysed hydroboration of ketones using 5 mol% **1** as this precatalyst was the most efficient at reducing the more challenging substrates. Unfortunately, reactions of HBpin with acetophenone only gave 40% (by ¹H NMR spectroscopy) conversion after 2 h at 80°C and even lower conversions (15%) were observed in reactions with benzophenone. Taking advantage of these reduced activities we were able to reduce 4-acetylbenzaldehyde chemoselectively, as hydroboration occurred solely at the aldehyde group. Although aldimines derived from primary aliphatic amines, such as *N*-benzylidenemethanamine, were readily reduced under these conditions, attempts to affect the hydroboration of aldimines derived from aromatic primary amines proved more challenging. Indeed, only 25% of the bulkier aldimine, *N*-benzylidene-4-methoxyaniline, was actually reduced under these conditions.

More significant is the observation that hydroborations of (*E*)-*N*-benzylideneprop-2-yn-1-amine proceeded with complete selectivity for the imine C=N bond as the alkyne group was left intact. Likewise, rhenium-catalysed reactions of (*E*)-1-(4-((prop-2-yn-1-ylimino)methyl)-phenyl)ethanone with HBpin were remarkably selective and only reduction of the imine double bond was observed. In the absence of any catalyst, only the aldehydes seemed to react with HBpin under these conditions but only gave the corresponding reduction products in around 10-40% yield.

Considering the wealth of recent interest into the catalysed hydroboration of pyridines using transition metals,³⁰ lanthanides,³¹ main-group compounds,³² as well as metal-free methodologies,³³ we decided to examine the potential of using rhenium complexes to facilitate this remarkable reduction. Although no reaction was observed in the case of pyridine itself, 5 mol% of [(PPh₃)₂Re(O)₂I] can be employed along with 2 eq of HBpin at 80°C for 2 h to afford partially reduced quinoline products while preserving the annulated carbocyclic aromatic ring (Scheme 4). When the reaction was carried out in C₆D₆, a mixture of the 1,2-addition product **Q1**, the 1,4-addition product **Q2** as well as the partially-saturated derivative **Q3** was observed in a ratio of 70:20:10 as ascertained by ¹H NMR spectroscopy. The borylated quinoline derivative **Q3** presumably arises from a subsequent hydrogenation of **Q1** and **Q2**. Dihydrogen and B₂pin₃ are well-known decomposition products frequently observed in catalysed hydroboration reactions.³⁴ Reactions of quinoline using only one equivalent of HBpin did not improve selectivities and resulted in incomplete conversion. Changing the solvent to CD₂Cl₂ gave increased amounts of both **Q2** and **Q3** in a ratio of 15:55:30. Although other rhenium complexes were also examined (see SI section), the highest selectivities were achieved using [Re(CO)₅Br] in C₆D₆ which gave a mixture of the two addition products in a ratio of 90:10:0. Unfortunately, the low valent rhenium complexes all showed poor conversion of this substrate. These results might explain why hydroborations using precatalyst **2** gave lower

conversions (Table 1, Entry 5) for all substrates as HBpin could also be reducing the labile quinoline ligand.



Scheme 4 The Rhenium Catalysed Hydroboration of Quinoline.

While it is likely that hydroborations using $[(\text{PPh}_3)_2\text{Re}(\text{O})_2\text{I}]$ proceed *via* a mechanism similar to that outlined by Fernandes and co-workers,²⁰ where the B–H bond in HBpin is activated by a sigma-bond metathesis step to generate a reactive rhenium hydride intermediate, along with a [Re]–OBpin group, it is unclear yet how these reactions occur using $[\text{Re}(\text{CO})_5\text{Br}]$ and the low-valent rhenium cationic complexes. In analogous rhenium-catalysed hydrogenation and hydrosilylation reactions,³⁵ possible mechanisms have been postulated whereby the active catalytic species involves a low-valent rhenium hydride.³⁶ Indeed, monitoring all reactions upon completion of catalysis by ^1H NMR spectroscopy in reactions employing $[\text{Re}(\text{bipy})(\text{CO})_3(\text{THF})][\text{BAR}^{\text{F}}_4]$ and $[\text{Re}(\text{bipy})(\text{CO})_3(\text{CH}_3\text{CN})][\text{B}(3,5\text{-di-}t\text{Bu-cat})_2]$ as pre-catalysts showed resonances at -9.1 and -8.8 ppm, respectively. Likewise, reactions using $[\text{Re}(\text{CO})_5\text{Br}]$ and a slight excess of HBpin (1.5 eq) showed a major hydride at -13.5 ppm in the ^1H NMR spectra. Further investigation is currently underway to elucidate the mechanism of these unique reactions, the results of which will be reported in due course.

Conclusions

In this study, we report the first examples for the rhenium-catalysed hydroboration of aldehydes, ketones and aldimines, including heteroaromatic quinoline. Reactions are remarkably chemoselective and tolerant of several functional groups. A wide array of rhenium complexes were efficient pre-catalysts for these hydroborations including the low-valent complexes of the formula $[\text{Re}(\text{bipy})(\text{CO})_3(\text{L})]\text{X}$ (L = labile ligand, and X = $[\text{BAR}^{\text{F}}_4]^-$ and $[\text{B}(3,5\text{-di-}t\text{Bu-cat})_2]^-$) prepared in this study. A new silver spiroboronate ester $\text{Ag}[\text{B}(3,5\text{-di-}t\text{Bu-cat})_2](\text{NCCH}_3)_3$ was prepared and characterized fully and used to make one of the new rhenium complexes. The possibility that low valent rhenium hydrides may play a part in some of these catalysed reactions is under further investigation.

Experimental

General conditions and methods

All reagents and solvents, unless otherwise noted, were purchased from commercial sources and used without further purification. Solvents were distilled over appropriate drying agents under dinitrogen: CH_2Cl_2 over CaH_2 , THF over Na/benzophenone, and hexane and toluene over freshly wired sodium. CD_2Cl_2 was purchased from Cambridge Isotope

Laboratories, degassed by three freeze-pump-thaw cycles, kept in a J. Young tube with potassium carbonate and stored in a dark place over oven-activated 4 Å molecular sieves. Pinacolborane (HBpin) was purified by vacuum distillation prior to use. Compounds $\text{B}_2(3,5\text{-di-}t\text{Bu-cat})_3$,²⁵ $[\text{Re}(\text{CO})_5\text{Br}]$,³⁷ $[\text{Re}(\text{bipy})(\text{CO})_3\text{Br}]$,³⁷ $[\text{Re}(\text{bipy})(\text{CO})_3(\text{THF})][\text{BAR}^{\text{F}}_4]$,³⁸ $[\text{Re}(\text{bipy})(\text{CO})_3\text{OTf}]$,³⁸ $[\text{Re}(\text{bipy})(\text{CO})_3(\text{CH}_3\text{CN})][\text{BAR}^{\text{F}}_4]$,³⁸ $[\text{Re}(\text{phen})(\text{CO})_3\text{Br}]$,³⁹ $[\text{Re}(\text{phen})(\text{CO})_3\text{OTf}]$,³⁹ $[\text{Re}(\text{bipy})(\text{CO})_3(\text{MeIm})][\text{OTf}]$,⁴⁰ and $\text{Na}[\text{BAR}^{\text{F}}_4]$ ($\text{Ar}^{\text{F}} = 3,5\text{-bis}(\text{trifluoromethyl})\text{phenyl}$),²⁴ were prepared following the reported procedures. Compounds $[\text{Re}(4,4'\text{-X}_2\text{bipy})(\text{CO})_3\text{Br}]$, $[\text{Re}(3,4,7,8\text{-Me}_4\text{phen})(\text{CO})_3\text{Br}]$ were prepared in similar way to that described for $[\text{Re}(\text{bipy})(\text{CO})_3\text{Br}]$, and $[\text{Re}(4,4'\text{-X}_2\text{bipy})(\text{CO})_3\text{OTf}]$ and $[\text{Re}(3,4,7,8\text{-Me}_4\text{phen})(\text{CO})_3\text{OTf}]$ to that for $[\text{Re}(\text{bipy})(\text{CO})_3\text{OTf}]$.³⁸ Please see the SI section for a complete list of new complexes, prepared, characterized and examined in this study.

NMR spectra were recorded on Bruker AV 300, Bruker AV 400 (^1H : 400.54 MHz and ^{13}C : 100.72 MHz), or JEOL JNM-GSX400 (^1H : 400 MHz; ^{11}B : 128 MHz; and ^{13}C : 100 MHz) spectrometers. Chemical shifts (δ) are reported in ppm [relative to residual solvent peaks (^1H and ^{13}C) or external $\text{BF}_3\cdot\text{OEt}_2$ (^{11}B)]. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), multiplet (m), overlapping (ov), and broad (br). Melting points were measured uncorrected with a Stuart SMP30 apparatus. IR solution spectra were obtained using a Perkin-Elmer Spectrum 100 FT-IR spectrometer using 0.2 mm CaF_2 cells or in the solid state using a Thermo Fisher Scientific Nicolet iS5 FT-IR spectrometer in ATR mode and are reported in cm^{-1} . All manipulations were performed under an atmosphere of dinitrogen using standard Schlenk techniques or in an MBraun LabMaster glovebox.

Preparation of compounds

$[\text{Re}(\text{bipy})(\text{CO})_3(\text{quin})][\text{BAR}^{\text{F}}_4]$ (**1**). Quinoline (14 μL , 0.12 mmol) was added to a solution of $[\text{Re}(\text{CO})_3(\text{bipy})(\text{THF})][\text{BAR}^{\text{F}}_4]$ (160 mg, 0.12 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 5 hours and then concentrated to 5 mL. Addition of hexane (15 mL) caused the precipitation of a yellow solid which was washed with hexane (2×10 mL) and dried under vacuum. Compound **1** was isolated as a yellow microcrystalline solid in a 91% yield (151 mg). Slow diffusion of hexane (8 mL) into a concentrated solution of **1** in CH_2Cl_2 (4 mL) at -20°C yielded yellow crystals of **1** one of which was employed for X-ray diffraction. Yield: 89% (148 mg). Anal. Calcd. for $\text{C}_{54}\text{H}_{27}\text{BF}_4\text{N}_3\text{O}_3\text{Re}$ (1418.79) (%): C 45.71, H 1.92, N 2.96. Found: C 45.05, H 1.82, N 2.93. IR (CH_2Cl_2 , cm^{-1}): 2039, 1936 (ν_{CO}). ^1H NMR (CD_2Cl_2 , 298 K, 400 MHz): δ 9.38 (d, J = 5.6 Hz, 2H, H_6 bipy), 8.49 (m, 2H, quin), 8.30 (d, J = 8.4 Hz, 1H, quin), 8.13 (m, 4H, H_4 bipy), 8.09 (m, 2H, H_3 bipy), 7.89 (m, 2H, quin), 7.79 (m, 2H, H_5 bipy {obscured by BAR^{F}_4 signal, can be seen in COSY and HSQC spectrum}), 7.66 (m, 1H, quin), 7.24 (dd J = 8.3, 5.3 Hz, 1H, quin). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 298 K, 100 MHz): δ 195.2 (2 CO), 189.3 (CO), 155.6 (C_2 bipy), 153.9 (C_6 bipy), 153.8

(CH quin), 147.4 (QC quin), 141.3 (CH quin), 141.1 (C₄ bipy), 132.3, 129.9 (CH quin), 128.6 (C₅ bipy {obscured by BAr^F₄ signal, can be seen in HSQC and HMBC spectra}), 128.4, 126.8 (CH quin), 125.9 (QC quin), 124.1 (C₃ bipy), 121.6 (CH quin).

The resonances due to the anion [BAr^F₄][−] are: ¹H NMR (CD₂Cl₂, 298 K, 400 MHz): δ 7.77 (s, 8H, H_o), 7.52 (s, 4H, H_p). ¹³C{¹H} NMR (CD₂Cl₂, 298 K, 400 MHz): δ 161.7 (q, J_{CF} = 49.1 Hz, C_i), 134.8 (C_o), 129.0 (q, J_{CF} = 31.3 Hz, C_m), 125.1 (q, J_{CF} = 271.2 Hz, CF₃), 117.5 (C_p).

Ag[B(3,5-di-tBu-cat)₂](NCCH₃)₃ (**3**). B₂(3,5-di-tBu-cat)₃ (1.50 g, 2.20 mmol) was added in small portions as a solid to a stirred CH₃CN (20 mL) suspension of Ag(acac) (0.50 g, 2.42 mmol). The reaction mixture was stirred in the dark at RT for 18 hours. The reaction mixture was filtered to remove residual solids and the volume of solvent was reduced to 10 mL under vacuum and the clear red solution was stored at -30°C. The initial precipitate [acacB(3,5-di-tBu-cat)] was collected by suction filtration and discarded. The amount of CH₃CN was reduced to 5 mL under vacuum and the solution stored once again at -30°C. The second precipitate was collected by suction filtration to afford **9** as a white crystalline solid. Yield: 61% (0.75 g); mp: 112–113°C (decomposition). Anal. Calcd. for C₃₄H₅₈AgBN₃O₄ (691.53) (%): C 59.84, H 7.24, N 6.16. Found: C 60.08, H 7.19, N 5.98. IR (ATR, cm⁻¹): 2961, 2271 (ν_{CN}). ¹H NMR data (CD₃CN, 298 K, 400 MHz): δ 6.54 (d, J = 1.8 Hz, 2H, Ar), 6.53 (d, J = 1.8 Hz, 2H, Ar), 1.31 (s, 18H, tBu), 1.24 (s, 18H, tBu). ¹¹B NMR data (CD₃CN, 298 K, 128 MHz): δ 13.1 (sharp). ¹³C{¹H} NMR data (CD₃CN, 298 K, 100 MHz): δ 151.6 (C cat), 147.1 (C cat), 139.4 (C cat), 128.9 (C cat), 110.7 (CH cat), 104.0 (CH cat), 34.1 (C tBu), 33.7 (C tBu), 31.4 (CH₃ tBu), 28.9 (CH₃ tBu).

[Re(bipy)(CO)₃(CH₃CN)][B(3,5-di-tBu-cat)₂] (**4**). To a stirred CH₃CN (5 mL) yellow suspension of [Re(bipy)(CO)₃Br] (200 mg, 0.39 mmol) in a foil covered 25 mL RB was added a colourless CH₃CN (2 mL) solution of **3** (220 mg, 0.47 mmol). The reaction was allowed to proceed for 18 hours at RT at which point a grey solid (AgBr) was removed by filtration and discarded. The resulting orange filtrate was collected and the solvent was removed under vacuum to afford an oily orange solid. Trituration of the oily solid with hexanes (3 x 10 mL) afforded an orange-yellow solid which was collected by suction filtration and washed with hexanes (2 x 5 mL) to afford [Re(bipy)(CO)₃(CH₃CN)][B(3,5-di-tBu-cat)₂]. Yield: 88% (305 mg); mp: 189–191°C (decomposes to a brown solid). Anal. Calcd. for C₄₃H₅₁N₃BO₇Re (918.90) (%): C 56.20, H 5.59, N 4.57. Found: C 56.27, H 5.52, N 4.48. IR (ATR, cm⁻¹): 2951, 2036 (ν_{CO}), 1925 (ν_{CO}). ¹H NMR (CD₂Cl₂, 298 K, 400 MHz): δ 8.86 (dd, J = 5.5, 1.4 Hz, 2H, Ar), 8.37 (d, J = 8.2 Hz, 2H, Ar), 7.78 (ov ddd, J = 8.2, 7.8, 1.4 Hz, 2H, Ar), 7.40 (ddd, J = 7.8, 5.5, 1.4 Hz, 2H, Ar), 6.54 (d, J = 1.4 Hz, 2H, Ar), 6.24 (d, J = 1.4 Hz, 2H, Ar), 1.83 (s, 3H, CH₃CN), 1.27 (br s, 36H, tBu). ¹¹B NMR (CD₂Cl₂, 298 K, 120 MHz): δ 13.1 (sharp). ¹³C{¹H} NMR (CD₂Cl₂, 298 K, 100 MHz): δ 193.8 (2 CO), 190.1 (CO), 156.2 (C bipy), 152.7 (CH bipy), 151.3 (C cat), 147.2 (C cat), 141.1 (CH bipy), 139.3 (C cat), 129.4 (C cat), 127.7 (CH bipy), 125.3 (CH bipy), 122.2 (C CH₃CN), 111.0

(CH cat), 104.2 (CH cat), 34.4 (C tBu), 33.9 (C tBu), 31.9 (CH₃ tBu), 29.3 (CH₃ tBu), 3.0 (CH₃ CH₃CN).

General rhenium catalysed hydroborations

To a stirred solution of substrate (0.18 mmol) and the appropriate rhenium complex (5 mol%) in C₆D₆ or CD₂Cl₂ (0.5 mL) was added a C₆D₆ or CD₂Cl₂ (0.5 mL) solution of pinacolborane (26 mg, 0.20 mmol). The mixture was stirred for 5 minutes at which point the solution was transferred to a J. Young NMR tube and heated in a water bath at 80°C for 2 hours and then monitored by multi-nuclear NMR spectroscopy.

X-ray crystallography

Data collection was performed on a Bruker X8 KappaAPEXII single crystal diffractometer, using Cu-Kα radiation (λ = 1.54184 Å). Images were collected at a 65 mm fixed crystal-detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image (4–16 s). Data collection strategy was calculated with the program CrysAlisPro CCD.⁴¹ Data reduction and cell refinement was performed with the program CrysAlisPro RED.⁴² An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlisPro RED.⁴¹ Crystal structure was solved by direct methods, using the program SIR-92.⁴² Anisotropic least-squares refinement was carried out with SHELXL-97.⁴³ All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed riding on their parent atoms with isotropic displacement parameters set to 1.2 times the U_{eq} of the atoms to which they are attached (1.5 for methyl groups). Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers 1544620 and 1544621.

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Notes and references

- (a) C. M. Crudden and D. Edwards, *Eur. J. Org. Chem.*, 2003, 4695–4712. (b) C. M. Vogels and S. A. Westcott, *Curr. Org. Chem.*, 2005, **9**, 687–699.
- (a) I. P. Query, P. A. Squier, E. M. Larson, N. A. Isley and T. B. Clark, *J. Org. Chem.*, 2011, **76**, 6452–6456. (b) C. C. Chong and R. Kinjo, *ACS Catal.*, 2015, **5**, 3238–3259.
- N. Eedugurala, Z. Wang, U. Chaudhary, N. Nelson, K. Kandel, T. Kobayashi, I. I. Slowing, M. Pruski and A. D. Sadow, *ACS Catal.*, 2015, **5**, 7399–7414.

- 4 (a) C. W. Lindsley and M. DiMare, *Tetrahedron Lett.*, 1994, **35**, 5141–5144. (b) F. Almqvist, L. Torstensson, A. Gudmundsson and T. Frejd, *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 376–377. (c) I. Sarvary, F. Almqvist and T. Frejd, *Chem. Eur. J.*, 2001, **7**, 2158–2166. (d) A. A. Oluyadi, S. Ma and C. N. Muhoro, *Organometallics*, 2013, **32**, 70–78.
- 5 G. Zhang, H. Zeng, J. Wu, Z. Yin, S. Zheng and J. C. Fettinger, *Angew. Chem. Int. Ed.*, 2016, **55**, 14369–14372.
- 6 S. Chakraborty, P. Bhattacharya, H. Dai and H. Guan, *Acc. Chem. Res.*, 2015, **48**, 1995–2003.
- 7 (a) J. Guo, J. Chen and Z. Lu, *Chem. Commun.*, 2015, **51**, 5725–5727. (b) T. Zhang, K. Manna and W. Lin, *J. Am. Chem. Soc.*, 2016, **138**, 3241–3249.
- 8 A. E. King, S. C. E. Stieber, N. J. Henson, S. A. Kozimor, B. L. Scott, N. C. Smythe, N. C. Sutton and J. C. Gordon, *Eur. J. Inorg. Chem.*, 2016, **11**, 1635–1640.
- 9 S. Bagherzadeh and N. P. Mankad, *Chem. Commun.*, 2016, **52**, 3844–3846.
- 10 (a) M. Bandini, P. G. Cozzi, M. de Angelis and A. Umani-Ronchi, *Tetrahedron Lett.*, 2000, **41**, 1601–1605. (b) S.-G. Roh, Y.-C. Park, D.-K. Park, T.-J. Kim and J.-H. Jeong, *Polyhedron*, 2001, **20**, 1961–1965. (c) M. Locatelli and P. G. Cozzi, *Angew. Chem. Int. Ed.*, 2003, **42**, 4928–4930. (d) S.-G. Roh, J.-U. Yoon and J.-H. Jeong, *Polyhedron*, 2004, **23**, 2063–2067. (e) P. A. Lummis, M. R. Momeni, M. W. Lui, R. McDonald, M. J. Ferguson, M. Miskolzie, A. Brown and E. Rivard, *Angew. Chem. Int. Ed.*, 2015, **53**, 9347–9351.
- 11 A. Y. Khalimon, P. Farha, L. G. Kuzmina and G. I. Nikonov, *Chem. Commun.*, 2012, **48**, 455–457.
- 12 (a) L. Koren-Selfridge, H. N. Londino, J. K. Vellucci, B. J. Simmons, C. P. Casey and T. B. Clark, *Organometallics*, 2009, **28**, 2085–2090. (b) A. Kaithal, B. Chatterjee and C. Gunanathan, *Org. Lett.*, 2015, **17**, 4790–4793.
- 13 M. W. Drover, L. L. Schafer and J. A. Love, *Angew. Chem. Int. Ed.*, 2016, **55**, 3181–3186.
- 14 T. J. Hadlington, M. Hermann, G. Frenking and C. Jones, *J. Am. Chem. Soc.*, 2014, **136**, 3028–3031.
- 15 C. C. Chong, H. Hirao and R. Kinjo, *Angew. Chem. Int. Ed.*, 2015, **54**, 190–194.
- 16 (a) Z. Yang, M. Zhong, X. Ma, S. De, C. Anusha, P. Parameswaran and H. W. Roesky, *Angew. Chem. Int. Ed.*, 2015, **54**, 10225–10229. (b) V. K. Jakhar, M. K. Barman and S. Nembenna, *Org. Lett.*, 2016, **18**, 4710–4713.
- 17 A. J. Blake, A. Cunningham, A. Ford, S. J. Teat and S. Woodward, *Chem. Eur. J.*, 2000, **6**, 3586–3594.
- 18 (a) M. Arrowsmith, T. J. Hadlington, M. S. Hill and G. Kociok-Köhn, *Chem. Commun.*, 2012, **48**, 4567–4569. (b) D. Mukherjee, A. Ellern and A. D. Sadow, *Chem. Sci.*, 2014, **5**, 959–964.
- 19 V. L. Weidner, C. J. Barger, M. Delferro, T. L. Lohr and T. J. Marks, *ACS Catal.*, 2017, **7**, 1244–1247.
- 20 (a) A. C. Fernandes, J. A. Fernandes, F. A. A. Paz and C. C. Romão, *Dalton Trans.*, 2008, 6686–6688. (b) I. Cabrita, S. C. A. Sousa and A. C. Fernandes, *Tetrahedron Lett.*, 2010, **51**, 6132–6135. (c) A. C. Fernandes, J. A. Fernandes, C. C. Ramão, L. F. Veiros and M. J. Calhorda, *Organometallics*, 2010, **29**, 5517–5525. (d) S. C. A. Sousa, I. Cabrita and A. C. Fernandes, *Chem. Soc. Rev.*, 2012, **41**, 5641–5653.
- 21 (a) M. E. Viguri, M. A. Huertos, J. Pérez, L. Riera and I. Ara, *J. Am. Chem. Soc.*, 2012, **134**, 20326–20329. (b) M. A. Huertos, J. Pérez and L. Riera, *Chem. Eur. J.*, 2012, **18**, 9530–9533. (c) M. E. Viguri, M. A. Huertos, J. Pérez, L. Riera and I. Ara, *Chem. Eur. J.*, 2013, **19**, 12974–12977. (d) R. Arévalo, J. Pérez and L. Riera, *Inorg. Chem.*, 2013, **52**, 6785–6787. (e) M. E. Viguri, J. Pérez and L. Riera, *Chem. Eur. J.*, 2014, **20**, 5732–5740. (f) H. Martínez-García, D. Morales, J. Pérez, M. Puerto and I. del Río, *Chem. Eur. J.*, 2014, **20**, 5821–5834. (g) R. Arévalo, J. Pérez and L. Riera, *Chem. Eur. J.*, 2015, **21**, 3546–3549.
- 22 E. N. Daley, C. M. Vogels, S. J. Geier, A. Decken, S. Doherty and S. A. Westcott, *Angew. Chem. Int. Ed.*, 2015, **54**, 2121–2125.
- 23 (a) J. J. Kennedy-Smith, K. A. Nolin, H. P. Gunterman and F. D. Toste, *J. Am. Chem. Soc.*, 2003, **125**, 4056–4057. (b) W. Huang and H. Berker, *Chimia*, 2005, **59**, 113–115. (c) B. Royo and C. C. Romão, *J. Mol. Catal. A: Chem.*, 2005, **236**, 107–112. (d) G. Du and M. M. Abu-Omar, *Organometallics*, 2006, **25**, 4920–4923. (e) W.-G. Zhao and R. Hua, *Eur. J. Org. Chem.*, 2006, 5495–5498. (f) K. A. Nolin, J. R. Krumper, M. D. Pluth, R. G. Bergman and F. D. Toste, *J. Am. Chem. Soc.*, 2007, **129**, 14684–14696. (g) H. Dong and H. Berke, *Adv. Synth. Catal.*, 2009, **351**, 1783–1788. (h) K. A. Nolin, R. W. Ahn, Y. Kobayashi, J. J. Kennedy-Smith and F. D. Toste, *Chem. Eur. J.*, 2010, **16**, 9555–9562. (i) J. L. Smeltz, P. D. Boyle and E. A. Ison, *Organometallics*, 2012, **31**, 5994–5997. (j) P. Gu, W. Wang, Y. Wang and H. Wei, *Organometallics*, 2013, **32**, 47–51. (k) L. Huang, Y. Zhang and H. Wei, *Eur. J. Inorg. Chem.*, 2014, 5714–5723. (l) H. Dong, Y. Jiang and H. Berke, *J. Organomet. Chem.*, 2014, **750**, 17–22.
- 24 M. Brookhart, B. Grant and A. F. Volpe Jr., *Organometallics*, 1992, **11**, 3920–3922.
- 25 N. R. Halcovitch, C. M. Vogels, A. Decken and S. A. Westcott, *Can. J. Chem.*, 2009, **87**, 139–145.
- 26 (a) G. L. Ning, M. Munakata, L. P. Wu, M. Maekawa, Y. Suenaga, T. Kurodo-Sawa and K. Sugimoto, *Inorg. Chem.*, 1999, **38**, 5668–5673. (b) J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos and D. Pascual, *Organometallics*, 2015, **34**, 3029–3038.
- 27 C. E. Tucker, J. Davidson and P. Knochel, *J. Org. Chem.*, 1995, **57**, 3482–3485.
- 28 (a) C. M. Vogels, A. Decken and S. A. Westcott, *Tetrahedron Lett.*, 2006, **47**, 2419–2422. (b) S. M. Ansar and C. L. Kitchens, *ACS Catal.*, 2016, **6**, 5553–5560. (c) K. Yang, F. Zhou, Z. Kuang, G. Gao, T. G. Driver and Q. Song, *Org. Lett.*, 2016, **18**, 4088–4091.
- 29 (a) E. C. Neeve, S. J. Geier, I. A. I. Mkhalid, S. A. Westcott and T. B. Marder, *Chem. Rev.*, 2016, **116**, 9091–9161. (b) A. B. Cuenca, R. Shishido, H. Ito and E. Fernández, *Chem. Soc. Rev.*, 2017, **46**, 415–430.
- 30 (a) K. Oshima, T. Ohmura and M. Suginome, *J. Am. Chem. Soc.*, 2012, **134**, 3699–3902. (b) A. Kaithal, B. Chatterjee and C. Gunanathan, *Org. Lett.*, 2016, **18**, 3402–3405.
- 31 A. S. Dudnik, V. L. Weidner, A. Motta, M. Delferro and T. J. Marks, *Nature Chem.*, 2014, **6**, 1100–1107.
- 32 (a) M. Arrowsmith, M. S. Hill, T. Hadlington and G. Kociok-Köhn, *Organometallics*, 2011, **30**, 5556–5559. (b) J. Intemann, M. Lutz and S. Harder, *Organometallics*, 2014, **33**, 5722–5729.
- 33 (a) P. Eisenberger, A. M. Bailey and C. M. Crudden, *J. Am. Chem. Soc.*, 2012, **134**, 17384–17387. (b) K. Oshima, T. Ohmura and M. Suginome, *Chem. Commun.*, 2012, **48**, 8571–8573. (c) X. Fan, J. Zheng, Z. H. Li and H. Wang, *J. Am. Chem. Soc.*, 2015, **137**, 4916–4919.
- 34 E. C. Keske, B. D. Moore, O. V. Kenkina, R. Wang, G. Schatte and C. M. Crudden, *Chem. Commun.*, 2014, **50**, 9883–9886.
- 35 (a) E. A. Ison, R. A. Corbin and M. M. Abu-Omar, *J. Am. Chem. Soc.*, 2005, **127**, 11938–11939. (b) G. Alcaraz and S. Sabo-Etienne, *Coord. Chem. Rev.*, 2008, **252**, 2395–2409. (c) H. Dong and H. Berke, *Adv. Synth. Catal.*, 2009, **351**, 1783–1788. (d) Y. Jiang, J. Hess, T. Fox and H. Berker, *J. Am. Chem. Soc.*, 2010, **132**, 18233–18247. (e) Y. Jiang, O. Blacque, T. Fox and H. Berke, *J. Am. Chem. Soc.*, 2013, **135**, 7751–7760.
- 36 (a) D. Guisto, *Inorg. Chim. Acta Rev.*, 1972, **6**, 91–101. (b) M. A. Andrew, S. W. Kirtley and H. D. Kaesz, *Inorg. Chem.*, 1977, **16**, 1556–1561. (c) G. Jia, A. J. Lough and R. H. Morris, J.

- Organomet. Chem.*, 1993, **461**, 147–156. (d) M. Bergamo, T. Beringhelli, G. D'Alfonso, G. Ciani, M. Moret and A. Sironi, *Organometallics*, 1996, **15**, 3876–3884. (e) Y. Ruiz-Morales, G. Schreckenbach and T. Ziegler, *Organometallics*, 1996, **15**, 3920–3923. (f) G. Albertin, S. Antoniutti, S. García-Fontán, R. Carballo and F. Padoan, *J. Chem. Soc., Dalton Trans.*, 1998, 2071–2081. (g) S. Ghosh, X. Lei, C. L. Cahill and T. P. Fehlner, *Angew. Chem. Int. Ed.*, 2000, **39**, 2900–2902. (h) N. Masciocchi, G. D'Alfonso, L. Garavaglia and A. Sironi, *Angew. Chem. Int. Ed.*, 2000, **39**, 4478–4480. (i) I. del Rosal, M. R. Poteau and F. Jolibois, *Dalton Trans.*, 2008, 3959–3970. (j) S. Bolaño, J. Bravo, J. Castro, M. del Carmen Marín and S. García-Fontán, *Inorg. Chem. Commun.*, 2009, **12**, 916–918. (k) S. Bolaño, J. Bravo, F. Fernández-García, S. García-Fontán and M. del Carmen Marín, *J. Organomet. Chem.*, 2009, **694**, 2994–2999. (l) N. Li, Y. Xie, R. B. King and H. F. Schaeffer III, *J. Phys. Chem. A*, 2010, **114**, 11670–11680. (m) N. Li, Y. Xie, R. B. King and H. F. Schaeffer III, *Eur. J. Inorg. Chem.*, 2011, 4626–4636.
- 37 S. P. Schmidt, W. C. Trogler and F. Basolo, *Inorg. Synth.*, 1990, **28**, 160–165.
- 38 E. Hevia, J. Pérez, V. Riera, D. Miguel, S. Kassel and A. Rheingold, *Inorg. Chem.*, 2002, **41**, 4673–4679.
- 39 E. Hevia, J. Pérez, L. Riera, V. Riera, I. del Río, S. García-Granda and D. Miguel, *Chem. Eur. J.*, 2002, **8**, 4510–4521.
- 40 M. A. Huertos, J. Pérez and L. Riera, *J. Am. Chem. Soc.*, 2008, **130**, 5662–5663.
- 41 Oxford Diffraction (2008). CrysAlisProCCD, CrysAlisProRED. Oxford Diffraction Ltd., Abingdon, Oxfordshire, UK.
- 42 A. Altomare, G. L. Casciarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Cryst.*, 1994, **27**, 435.
- 43 G. M. Sheldrick, SHELXL97, University of Göttingen, Germany, 1997.