

VIP Very Important Paper

Synthesis and Reactivity of an Aluminium *N*-heterocyclic AminoalTaylor Wilde^{†, [a]}, Fáinché Murphy^{†, [a]}, Cooper R. T. Smylie,^[a] Alan R. Kennedy,^[a] and Catherine E. Weetman^{*[a]}

Tethered *N*-heterocyclic carbenes (NHCs) are an emerging class of ligand, as they feature all the desirable aspects of NHCs (ease of synthesis, high tunability) but also enable metal-ligand cooperativity when combined with Lewis acidic metal centres due to the donor-acceptor nature of the complexes formed. Herein we report a simple ethoxy-tethered NHC for the stabilisation of Al(III) hydrides, resulting in the unexpected

formation of a bicyclic *N*-heterocyclic aminoal (1). Compound 1 behaves as a metal hydride, capable of reducing benzophenone and carbodiimide to yield compounds 2 and 3, respectively. Furthermore, we show that 1 behaves as an efficient catalyst in the dehydrocoupling of amine-boranes due to the hemi-labile nature of the supporting ligand.

Introduction

Since their discovery, *N*-heterocyclic carbenes (NHCs) have become a powerful tool for the modern-day chemist, due to their ease of synthesis and highly tunable steric and electronic features.^[1–2] Their high nucleophilicity/Lewis basicity pairs well with late transition metals and have found wide reaching applications in many homogeneous catalytic transformations. In contrast, the combination of Lewis basic NHCs and Lewis acidic metals (e.g., early transition metals, group 13 and 14 elements, and lanthanides) often results in donor-acceptor type complexes.^[3–6] In several instances, particularly in combination with functionalised (also known as tethered) NHCs, metal-ligand cooperativity has been observed and has resulted in comparisons to ‘frustrated Lewis pair’ (FLP) reactivity.^[7–8] This is exemplified by the work of P. Arnold and co-workers wherein polar substrates can add across the metal-carbene bond resulting in reversible addition/elimination reactions (Figure 1).^[9]

Whilst this reactivity has been established for the lanthanides, it has yet to be fully explored with the most abundant metal found within the earth’s crust, aluminium. A recent study by Camp and co-workers showed that there is non-innocence at the Al-NHC bond when using alkoxy-functionalised NHC ligands.^[10] Here it was reported that the steric demands of the alkylaluminium reagent influenced the formation of either the expected alkoxy-NHC complex (A) or an imidazolium-aluminate

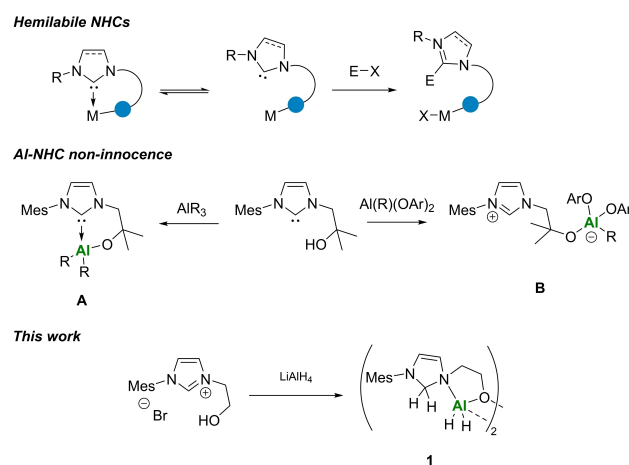


Figure 1. Overview of NHC hemilability. Top: Desired reactivity from hemilabile NHC systems; Middle: Previously reported Al-non-innocence by Camp and co-workers^[10]; Bottom: This work.

zwitterion (B), with the latter formed with sterically demanding aluminium reagents (Figure 1). Similar observations have also been made with the heavier alkylgallium analogues using a saturated-backbone NHC with alkoxy tether.^[11] However, in this instance NHC complexes were obtained by first forming the zwitterion and then subsequent deprotonation with a strong base.

Given the interest in the use of main group hydrides,^[12] in particular aluminium, we were intrigued to see if we could utilise tethered NHCs to invoke reversible transformations through metal-ligand cooperativity which could then be exploited in catalysis.

Results and Discussion

Whilst several examples of alkoxy-tethered NHC complexes have been reported across the periodic table, the majority are

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2-(hydroxyisobutyl)imidazolium containing.^[13–16] In this instance we sought to use the simple 2-ethoxy tether, due to the reduced sterics and high propensity of Al–O bonds to form oligomers in solution.^[17–18] We envisioned this would provide a simple entry point to multimetallic chemistry. Notably, the pro-ligand (LOH.HBr) can easily be prepared on preparative scales (> 10 g), in yields greater than 75% and is 100% atom efficient (Scheme 1).^[19]

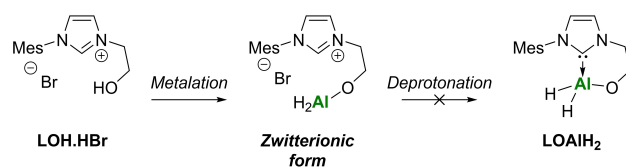
With pro-ligand in hand, we proceeded to target the isolation of the NHC ligand *via* deprotonation with a suitable base. In line with previous studies, this step was complicated due to the various species that can be formed (see SI for details). In the case of the previously reported 2-(hydroxyisobutyl)imidazolium, deprotonation with 1 eq. of KHMDS in THF, at room temperature overnight favours the hydroxy carbene form.^[20] However, following the same protocol with our 2-ethoxy tether resulted in multiple species after 2 and 18 hrs. The same was also observed after varying the base, concentration, reaction time, temperature, and solvent (see SI for screening). This is not unexpected, as previous reports have also noted unselective deprotonations with *N*-functionalised NHCs.^[21–23] Transmetalation routes, *via* silver or copper NHCs, have been suggested as a viable alternative to install metal centres into tethered systems.^[24] However, we opted against this on the grounds of atom inefficiency and mixed success when transferring to strong Lewis acids such as aluminium.^[25–26]

Seeking alternatives, we followed the suggested route reported by Horeglad for alkylgallium complexes.^[11] Reaction of LOH.HBr with Me₃N·AlH₃ resulted in rapid gas evolution (Me₃N and H₂) and concomitant precipitation of a colourless solid that was isolated in 85% yield. Similar to that reported for the alkylgallium zwitterionic species,^[11] this compound was insoluble in all common solvents, which precluded further characterization except for solid-state IR which confirmed the presence of hydrides within the zwitterionic form (Al–H found in region 1830–1716 cm⁻¹). In contrast to the previous report, deprotonation of this species failed due to the high insolubility (Scheme 2).

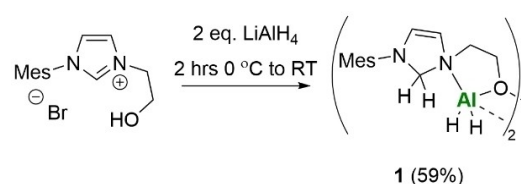
Alternatively, we sought to use LiAlH₄ as it has previously been used as a one-pot route to deprotonate and install aluminium hydrides with NHC ligands.^[26–27] A THF solution of LiAlH₄ was added dropwise to a THF solution of LOH.HBr at 0 °C (Scheme 3). After allowing reaction mixture to stir for 2 hrs at room temperature volatiles were removed and the crude product was extracted with toluene. Crystalline colourless material of **1** was obtained in 59% yield. The ¹H NMR spectrum revealed loss of both the imidazolium-*H* and hydroxy resonances, with signals corresponding to the ligand moving in accordance with aluminium complexation (i.e., NHC backbone

doublets moved upfield, whilst alkyl arm moved downfield). Notably, a broad signal at δ4.1 ppm was observed in the ¹H NMR spectrum corresponding to an aluminium hydride, along with a signal at δ104.5 ppm in the ²⁷Al NMR, thus confirming the complexation of an aluminium hydride. Complexation was also confirmed on inspection of the IR data, with Al–H stretches found at 1730 cm⁻¹.

Crystals suitable for single crystal X-ray diffraction (SC–XRD) were grown from a concentrated toluene solution at –25 °C. Compound **1** crystallises in the triclinic P-1 space group revealing a dimeric bicyclic species with an alkoxy-tethered *N*-heterocyclic *aminal* (Figure 2). The asymmetric unit consists of the monomeric ‘LH₂OAlH₂’ species, with the desired ‘head to tail’ dimerization at the Al–O bond resulting in a dimeric dihydride complex.



Scheme 2. Metalation/Deprotonation route to target isolation of a tethered-NHC alane.



Scheme 3. Synthesis of an Aluminium *N*-heterocyclic Aminal (Compound 1).

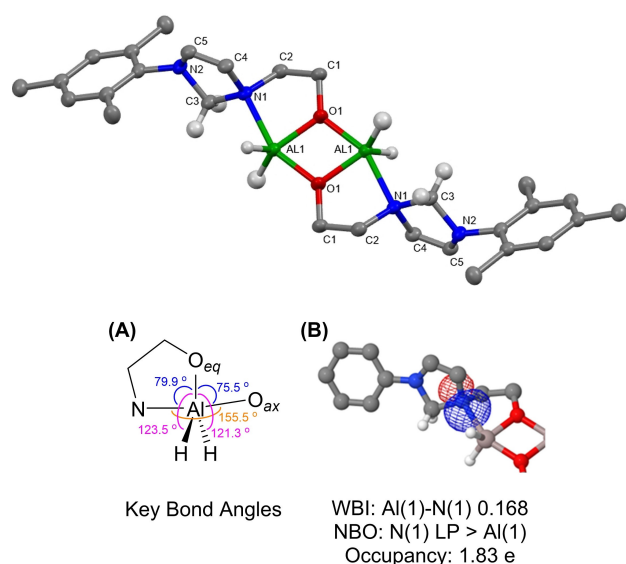
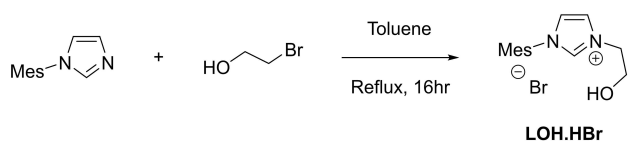


Figure 2. Solid state structure of compound **1**. Solvent and hydrogen atoms other than those on Al(1) and C(3) have been omitted for clarity. Selected bond lengths (Å): Al(1)–O(1) 1.899(2), Al(1)–O(1)′ 1.845(2), Al(1)–N(1) 2.175(2), O(1)–C(1) 1.412(3), C(1)–C(2) 1.514(4), C(2)–N(1) 1.498(3), H–Al(1)–H 115.1(16). (A) Selected bond angles. (B) Visual representation of N(1)–Al(1) NBO.



Scheme 1. Synthesis of pro-ligand.

The aluminium centre is 5-coordinate with *pseudo*-trigonal bipyramidal geometry. N(1), O(1)_{ax} and O(1)_{eq} atoms are in the same plane as the Al atom with the two hydride ligands above and below the plane. Rather than coordination to the expected C(3) carbene carbon, the Al is coordinated to the now four coordinate nitrogen (N(1)) of the *N*-heterocycle. The Al(1)–N(1) bond length (2.1752(2) Å) is longer than expected for Al–N bond lengths (mean for reported structures in CSD, N–Al in *N*-coordinated Al–H is 1.947 Å, sum of covalent radii is 1.92 Å), suggesting more dative type character from N(1) to Al(1). The former *N*-heterocyclic ring is no longer planar, due to the *pseudo*-tetrahedral geometry at N(1) and C(3), whilst N(2) retains its trigonal planar geometry. Comparison of the bond lengths around the *N*-heterocycle also highlight the change from the imidazolium character to aminal, with the bond distances now in line with C–N single bond character [C–N single bonds 1.47 Å vs. partial double 1.35 Å; C(3)–N(1) 1.487(3) and C(3)–N(2) 1.471(3) Å]. It is of note that this is a rare example of a structurally characterised *N*-heterocyclic aminal with *N*-coordination to a metal centre. The only other reported example to our knowledge is by Kaiho and Suzuki with a bimetallic ruthenium complex.^[28] Again the key structural features here show that one of the N-substituents is tilted out of plane from the heterocyclic ring as it is now four coordinate and bound to the Ru centre. Additionally, the heterocyclic ring acts as a four-electron donor ligand as it bridges the dinuclear ruthenium complex (2 e from N lone pair and 2 e from C–C π -bond).

To investigate the electronic nature of **1**, we performed DFT calculations at the M062x/6-311 + g(d,p) level of theory (see SI for details).^[29] The optimised structure is in good agreement with the experimentally determined structure. The HOMO and HOMO–1 consist of the *N*-heterocycle ligand (with a lone pair on N(2)) and the HOMO–2 and HOMO–3 consisting of Al-hydrides. HOMO–4 shows a lone pair on N(1) which is orientated along the expected bond path towards the Al centre. This is also supported by Natural bond orbital (NBO) analysis,^[30] with second-order perturbation theory (SOPT) revealing donation from the N(1) lone pair to the empty Al(1) orbital (LP N(1) > LV Al(1) 32.7 kcal mol^{–1}).

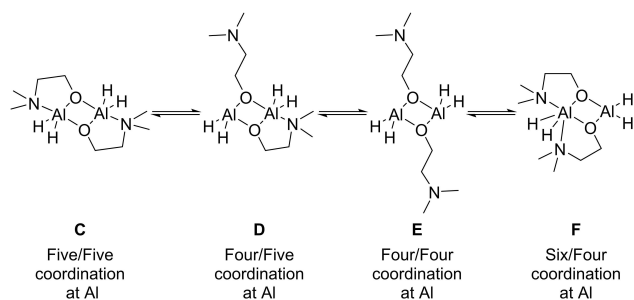
With a clearer understanding of the identity of compound **1** we re-examined the initial NMR data. The ¹H NMR at room temperature contains two 1H doublets at δ 4.62 and 4.56 ppm (J = 4.3 Hz), which correlate to δ 73.7 ppm in the ¹³C{¹H} NMR spectrum by HSQC. These peaks are assigned as the CH₂ aminal resonances, as the protons in the C(3) position are diastereotopic owing to the now chiral N(1) atom. Upon cooling to 220 K, the Al–H resonances become sharper, along with further splitting of the alkyl tether. Here the C(1) and C(2) protons resolve into four multiplets at δ 3.64, 3.52, 3.46 and 2.47 ppm each with an integral of 1H in the asymmetric unit. ¹H DOSY NMR indicates that the dimeric nature of **1** is retained in solution based on estimated molecular weight (see SI for details).^[31]

Aminoalkoxyalanes of type R₂N(X)_nOAlH₂ have previously been reported by Nöth and co-workers.^[32] In the solid-state the characteristic Al₂O₂ ring system, due to dimerization, is

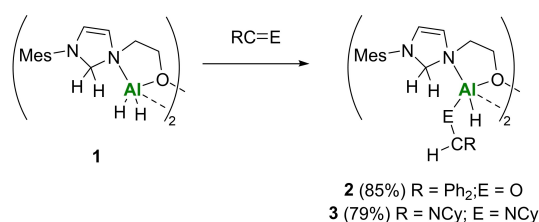
observed along with pentacoordinate Al centres. In a similar manner to **1**, solution studies with *N,N*-dimethylaminoethoxyalane also revealed ligand flexibility (Scheme 4). However, owing to the smaller ligand size, exchange between four-, five- and six-coordinate Al complexes were observed in the ²⁷Al NMR (Compounds **C** to **F**) highlighting the dynamic nature of aminoalkoxyalanes in solution. It is therefore likely that similar coordination modes are possible with compound **1**.

The combined experimental and theoretical studies support a degree of lability in the N–Al bond. This hemi-lability is consistent with the ligand design albeit at N(1) rather than the C(3) carbene position. As such we were interested to see if compound **1** behaved as a metal hydride or if alternate reactivity would be observed. NMR scale reactions of **1** with 1 eq. of benzophenone and *N,N'*-dicyclohexylcarbodiimide (DCC) were performed. In both cases, metal hydride-based reactivity was observed with reduction of the C=E bond (E=O or N) to form CH–E species (Scheme 5). IR spectroscopy shows that only one Al–H undergoes insertion reactivity as there is retention of Al–H stretch in the spectrum (1732 (**2**) and 1802 cm^{–1} (**3**)). Preparative scale experiments with benzophenone and DCC resulted in the isolation of compounds **2** (85% yield) and **3** (79% yield), respectively. In the case of **2** we were able to grow single crystals suitable for SC–XRD from a concentrated benzene solution at room temperature (Figure 3).

The solid-state structure of **2** retains the dimeric unit and five-coordinate aluminium centre. The *pseudo*-trigonal bipyramidal geometry is slightly more distorted due to the increased steric congestion at the Al centre. The N(1), O(1)_{ax} and O(1)_{eq} atoms are still in the same plane as the Al atom, with the hydride and reduced carbonyl unit (C(15)–O(2)) above and below this plane. The carbonyl has been reduced to 1.748(14) Å in line with the now single bond character. This structure



Scheme 4. Dynamic coordination modes of aminoalkoxyalanes in solution.^[32]



Scheme 5. Reactivity of compound **1** towards unsaturated substrates, benzophenone and carbodiimide.

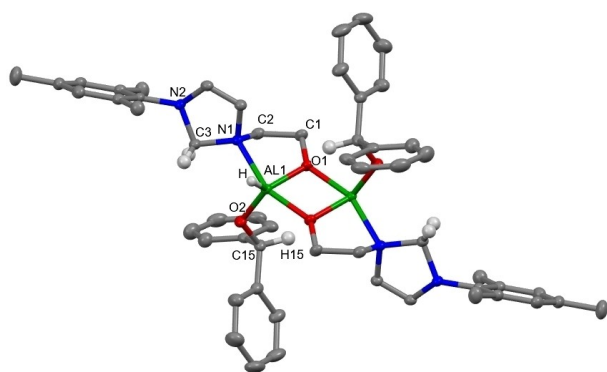


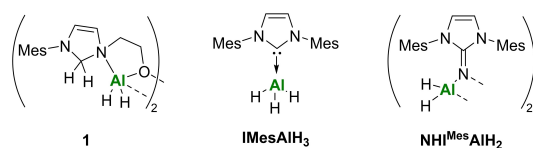
Figure 3. Solid state structure of compound 2. Solvent and hydrogen atoms other than those on Al(1), C(3) and C(15) have been omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)–O(1) 1.842(9), Al(1)–O(1)′ 1.898(9), Al(1)–N(1) 2.122(10), Al(1)–O(2) 1.748(9), O(2)–C(15) 1.407(14). N(1)–Al(1)–O(1)_{eq} 79.94(4), N(1)–Al(1)–O(1)_{ax} 155.05(4), O(2)–Al(1)–H 119.4(5).

confirms that the metal-hydride is still an active site and capable of reducing unsaturated substrates.

Given interests in aluminium catalysis, and how to influence catalytic performance, we turned our attention to benchmarking the catalytic activity of this flexible *N*-heterocyclic ligand system vs. non-flexible *N*-heterocyclic derived ligands. As NHC and *N*-heterocyclic imine (NHI) supported aluminium hydrides have been used in amine-borane dehydrocoupling chemistry,^[33] this provided an ideal system to compare the differences in the ligands and their influence on catalytic performance (Scheme 6).

To establish a base level of activity $\text{Me}_3\text{N}\cdot\text{AlH}_3$ was used as a control (i.e., no ligand), and after 48 hrs at 50 °C approximately 60% consumption of the amine-borane starting material was noted. Further conversion is possible but beyond 48 hrs the reaction drastically slows, and metallic precipitate is observed indicating alane decomposition. As previously reported, the NHI stabilised alane requires elevated temperatures of 80 °C to turn over vs. milder conditions for the NHC stabilised alane (50 °C). However, the NHC catalysts were prone to deactivation pathways and over the course of the catalysis the remaining ‘active’ species diminishes resulting in prolonged reaction times.^[33]

Using the same conditions as previously reported, we found that **1** notably reduces reaction times (Table 1) and achieves full consumption of starting material. We believe this enhanced reactivity is due to (i) increased ligand flexibility and (ii) aminal incorporation into the ligand. Whilst the NHI-ligand provides kinetic and thermodynamic stabilisation to the alane, the dimeric nature of the system hinders incoming substrates. In the case of **1**, the hemilabile nature of the Al–N bond allows for flexibility and the ligand can effectively move out of the way for incoming substrates whilst still providing necessary electronic stabilisation. For point (ii) in the



Scheme 6. Al(III)-Hydrides used in this dehydrocoupling study.^[33]

Table 1. Dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ with 5 mol% Al(III) hydride catalyst.^[33]

$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{Me}-\text{N}-\text{B}-\text{H} \\ \quad \\ \text{Me} \quad \text{H} \end{array} \xrightarrow[\text{- H}_2]{\begin{array}{c} 5 \text{ mol\% [Al-H]} \\ \text{C}_6\text{D}_6 \end{array}} \begin{array}{c} \text{Me} \quad \text{H} \\ \quad \\ \text{Me}-\text{N}-\text{B}-\text{H} \\ \quad \\ \text{H}-\text{B}-\text{N}-\text{Me} \\ \quad \\ \text{H} \quad \text{Me} \end{array} + \text{other dehydrocoupled products}$			
Catalyst	Temp/°C	Time/h	Conversion ^[a] /%
$\text{Me}_3\text{N}\cdot\text{AlH}_3$	50	48	59
1	50	12	> 99
IMesAlH_3	50	26	92
$\text{NHI}^{\text{Mes}}\text{AlH}_2$	80	34	84
Reaction conditions: 5 mol% [Al–H] (0.012 mmol), $\text{Me}_2\text{NH}\cdot\text{BH}_3$ (0.24 mmol), 0.5 mL C_6D_6 . [a] Conversion of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ determined by ^{11}B NMR relative integrals.			

previous NHCAIH_3 catalysis, aminal formation was part of a deactivation pathway as this resulted in loss of the coordinated ligand and free AlH_3 being part of the active catalytic cycle. As highlighted from the control reaction of $\text{Me}_3\text{N}\cdot\text{AlH}_3$, the turnover is notably slower than when combined with organic ligands. In the case of **1** the aminal is part of the ligand framework, and due to the anionic tether, the ligand stays coordinated throughout the catalysis.

Conclusions

Synthetic routes to isolate a tethered-NHC Al(III)hydride complex resulted in the formation of a bicyclic Al(III)hydride coordinated to a *N*-heterocyclic aminal, with a five coordinate aluminium centre. The desired hemi-lability was still obtained albeit at the Al–N bond rather than the expected Al–Carbene bond. Compound **1** was found to react as a metal-hydride in a series of archetypal reactions, wherein reduction of unsaturated substrates was observed. Compound **1** readily dehydrocoupled amine-borane with enhanced reactivity observed compared to analogous Al(III)hydrides. This is thought to be due to the increased ligand flexibility, which due to the hemi-labile nature can effectively move out of the way for incoming substrate coordination yet still provide the necessary thermodynamic and kinetic stabilisation. We are currently looking to further exploit this ligand flexibility in the development of new catalytic cycles based upon earth abundant metal centres.

Supporting Information

The data that support the findings of this study are available in the supplementary material of this article and available from the University of Strathclyde KnowledgeBase at <https://doi.org/10.15129/22b66cde-d7b9-48a8-8e5b-af26a0581730>. The authors have cited additional references within the Supporting Information.^[22–28]

Deposition Number(s) 2310547 (for Compound 1), 2310548 (for Compound 2) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint

Cambridge Crystallographic Data Centre and Fachinfor-mationszen-trum Karlsruhe Access Structures service.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are openly available in University of Strathclyde KnowledgeBase at <https://doi.org/10.15129/22b66cde-d7b9-48a8-8e5b-af26a0581730>, reference number 0.

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- [1] P. Bellotti, M. Koy, M. N. Hopkinson, F. Glorius, *Nat. Chem. Rev.* **2021**, *5*, 711–725.
- [2] M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, *510*, 485–496.
- [3] V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt, S. Inoue, *Chem. Rev.* **2018**, *118*, 9678–9842.
- [4] C. Fliedel, G. Schnee, T. Avilés, S. Dagorne, *Coord. Chem. Rev.* **2014**, *275*, 63–86.
- [5] C. Romain, S. Bellemin-Laponnaz, S. Dagorne, *Coord. Chem. Rev.* **2020**, *422*, 213411.
- [6] P. L. Arnold, S. T. Liddle, *Chem. Commun.* **2006**, 3959–3971.
- [7] K. J. Evans, S. M. Mansell, *Chem. Eur. J.* **2020**, *26*, 5927–5941.
- [8] S. T. Liddle, I. S. Edworthy, P. L. Arnold, *Chem. Soc. Rev.* **2007**, *36*, 1732–1744.
- [9] Z. R. Turner, R. Bellabarba, R. P. Tooze, P. L. Arnold, *J. Am. Chem. Soc.* **2010**, *132*, 4050–4051.
- [10] V. Dardun, L. Escomel, E. Jeanneau, C. Camp, *Dalton Trans.* **2018**, *47*, 10429–10433.
- [11] P. Horeglad, O. Ablialimov, G. Szczepaniak, A. M. Dąbrowska, M. Dranka, J. Zachara, *Organometallics* **2014**, *33*, 100–111.
- [12] M. M. D. Roy, A. A. Omaña, A. S. S. Wilson, M. S. Hill, S. Aldridge, E. Rivard, *Chem. Rev.* **2021**, *121*, 12784–12965.
- [13] P. L. Arnold, A. J. Blake, C. Wilson, *Chem. Eur. J.* **2005**, *11*, 6095–6099.
- [14] P. L. Arnold, I. J. Casely, Z. R. Turner, R. Bellabarba, R. B. Tooze, *Dalton Trans.* **2009**, 7236–7247.
- [15] R. Srivastava, M. Jakoobi, C. Thieuleux, E. A. Quadrelli, C. Camp, *Dalton Trans.* **2021**, *50*, 869–879.
- [16] R. Srivastava, E. A. Quadrelli, C. Camp, *Dalton Trans.* **2020**, *49*, 3120–3128.
- [17] R. J. Wehmschulte, P. P. Power, *J. Am. Chem. Soc.* **1997**, *119*, 8387–8388.
- [18] H. Zhu, J. Chai, V. Jancik, H. W. Roesky, W. A. Merrill, P. P. Power, *J. Am. Chem. Soc.* **2005**, *127*, 10170–10171.
- [19] J. Wolf, A. Labande, J.-C. Daran, R. Poli, *J. Organomet. Chem.* **2006**, *691*, 433–443.
- [20] R. Srivastava, R. Moneuse, J. Petit, P.-A. Pavard, V. Dardun, M. Rivat, P. Schiltz, M. Solari, E. Jeanneau, L. Veyre, C. Thieuleux, E. A. Quadrelli, C. Camp, *Chem. Eur. J.* **2018**, *24*, 4361–4370.
- [21] D. S. McGuinness, K. J. Cavell, *Organometallics* **2000**, *19*, 741–748.
- [22] D. J. Nielsen, K. J. Cavell, B. W. Skelton, A. H. White, *Organometallics* **2001**, *20*, 995–1000.
- [23] P. L. Arnold, A. C. Scarisbrick, A. J. Blake, C. Wilson, *Chem. Commun.* **2001**, 2340–2341.
- [24] H. M. J. Wang, I. J. B. Lin, *Organometallics* **1998**, *17*, 972–975.
- [25] V. N. Mikhaylov, I. V. Kazakov, T. N. Parfeniuk, O. V. Khoroshilova, M. Scheer, A. Y. Timoshkin, I. A. Balova, *Dalton Trans.* **2021**, *50*, 2872–2879.
- [26] F. Murphy, A. R. Kennedy, C. E. Weetman, in *Inorganics*, Vol. 11, **2023**, pp. 1–11.
- [27] M. D. Francis, D. E. Hibbs, M. B. Hursthouse, C. Jones, N. A. Smithies, *Journal of the Chemical Society-Dalton Transactions* **1998**, 3249–3254.
- [28] A. Kaiho, H. Suzuki, *Angew. Chem. Int. Ed.* **2012**, *51*, 1408–1411.
- [29] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215–241.
- [30] E. D. Glendening, C. R. Landis, F. Weinhold, *J. Comput. Chem.* **2013**, *34*, 1429–1437.
- [31] S. Bachmann, B. Gernert, D. Stalke, *Chem. Commun.* **2016**, *52*, 12861–12864.
- [32] H. Nöth, A. Schlegel, B. Singaram, J. Knizek, P. Mayer, T. Seifert, *Eur. J. Inorg. Chem.* **2001**, *2001*, 173–180.
- [33] C. Weetman, N. Ito, M. Unno, F. Hanusch, S. Inoue, in *Inorganics*, Vol. 7, **2019**.
- [34] 2018, CrysAlisPro Software system, version 1.171.39.46, Rigaku Corporation, Oxford, UK Rigaku Oxford Diffraction Rigaku Oxford Diffraction, 2018.
- [35] G. M. Sheldrick, *Acta Crystallographic a Section C Structural Chemistry* **2015**, *71*, 3–8.
- [36] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
- [37] G. W. T. M. J. Frisch, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, 2016, Gaussian 16 Revision A.03.
- [38] G. W. T. M. J. Frisch, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2013, Gaussian 09 Revision D.01.
- [39] Y. Zhao, D. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215–241.
- [40] Jmol, an open-source Java viewer for chemical structures in 3D. <http://www.jmol.org>.

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