ARTICLE

Reactivity of triphosphinoboranes towards H₃B·SMe₂: Access to derivatives of boraphosphacycloalkanes

Anna Ordyszewska,[a]* Jarosław Chojnacki[a], and Rafał Grubba[a]*

Triphosphinoboranes activated the B–H bond in the BH_3 molecule without any catalysts at room temperature. Hydroboration reactions led to boraphosphacyloalkanes with diverse structures. The outcomes of reactions depend on the size of phosphanyl substituents on the boron atom of the parent triphosphinoborane, where derivatives of boraphosphacyclobutane and boraphosphacyclohexane were obtained. Furthermore, the precursor of triphosphinoboranes, namely bromodiphosphinoborane, also exhibited high reactivity towards $H_3B·SMe_2$, yielding bromo-substituted boraphosphacyclobutane. Hydroboration products were characterized by heteronuclear NMR spectroscopy, single crystal X-ray diffraction, and elemental analysis.

Introduction

Small-molecule activation has been a rapidly developing topic in modern chemistry for a few decades. For a very long time, this type of reactivity was dominated by transition metal complexes as they play a unique role in the cleavage of strong σ-bonds. However, main-group compounds have revealed their potential in oxidative addition and reductive elimination[1] as well as frustrated Lewis pairs (FLPs)[2]; thus, research into the topic has expanded vastly since then. Main-group bond activation is possible when two key conditions are fulfilled. Firstly, to mimic the reactivity of transition metal complexes, a main-group compound must possess a lone pair to donate and a free orbital to accept electrons. In other words, the chemical compound has to exhibit the properties of both a Lewis base and a Lewis acid. Secondly, it simply must be sterically possible.

In this paper, we decided to focus on the B–H bond activation. Although there appears to be a relatively high number of metallic systems that can activate the B–H bond,[3–9] the number of compounds of the main-group elements with such activity is rather limited. While the majority of B–H bond activation examples are based on HBpin[10–13] and HBcat,[13–15] $BH_3·L$ (L = SMe₂, THF) appears to be a better and more attractive choice as it is the substrate for obtaining those previously mentioned compounds. Borane dimethylsulfide (BMS) was used in the synthesis of boron dihydride complexes of bis(phosphinimino)amine with the release of H_2 and SMe_2.[16] The aforementioned adduct was also used in the reduction reaction of CO_2 with B–H bond cleavage using Lewis bases[17] or carbenoid species[18] as a catalyst.

Phosphenium ions possessing P–B bonds have been shown to activate not only B–H but also Si–H and C–H bonds.[19] Singlet electrophilic carbenes[20] along with carbenoids[21] are examples of compounds capable of breaking the B–H bond as a result of the 1,1-addition of BH_3. Moreover, cyclic alkyl(amino)carbenes (CAACs) have recently been used in the effective dehydrocoupling of phosphine-borane adducts yielding inorganic polymers.[22] Before, this reaction required a transition metal catalyst in the majority of reactions, but still only the dehydrocoupling of primary arylphosphine boranes $ArPH_2·BH_3$ (Ar = aryl) was reported.[23–26] Non-metallic systems, namely amine-stabilized phosphinoboranes (RR'PBH₂·NMe₃) were shown to be valuable synthons for the synthesis of poly(alkylphosphino)boranes through thermolysis at mild conditions.[27,28] Finally, tris(pentafluorophenyl)borane was used as a catalyst in the dehydrocoupling reaction of RPH_2-BH_3 (R = Ph, H) yielding the corresponding polymers.[29] All the above examples of poly(phosphino)boranes concern linear inorganic polymers; however, the cyclic ones should not be forgotten. There appear to be several reports on cyclic poly(phosphino)boranes (R₂PBR₂)ₙ with diversified substituents on the boron atom resulting from head-to-tail polymerization of the monomeric phosphinoboranes[30] although only a few cyclic polymers containing the –BH₂– unit have been described in the literature.[31–35]

Our group has been working intensively on tricoordinate P-B species over the past few years[36–39] as they are nonmetallic systems possessing remarkable ambiphilic properties, and are cheap and easy to obtain. We have recently synthesized a new series of tricoordinate phosphorus and boron compounds, namely triphosphinoboranes[40] (Chart 1). As we anticipated, these compounds display features of both a Lewis base and a Lewis acid and therefore are capable of breaking the B–H bond. In our preliminary study, we have shown the very first reaction of triphosphinoborane (tBu₂P)₂BPiPr₂ with BMS yielding boraphosphacyclobutane.[40] Herein, we attempted to further

a. Department of Inorganic Chemistry, Faculty of Chemistry and Advanced Materials Center, Gdańsk University of Technology, ul. Narutowicza 11/12, 80-233 Gdańsk

explore this reactivity of triphosphinoboranes **1–5** and diphosphinoborane **6** possessing diversified structures.
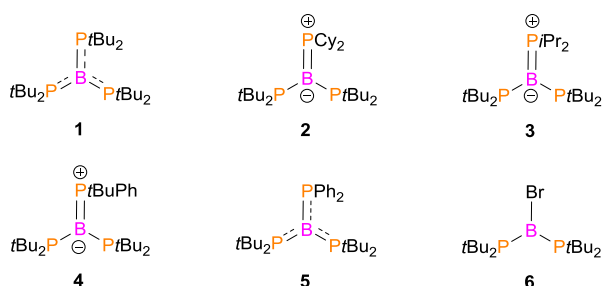
Chart 1. Triphosphinoboranes **1–5** and diphosphinoborane **6** selected for reactions with $H_3B \cdot SMe_2$.

Results and discussion

The bulkiest triphosphinoborane **1** bearing *t*Bu groups at P-atoms reacts with two equivalents of $H_3B \cdot SMe_2$ (BMS) in toluene, yielding the derivative boraphosphacyclobutane **1a** as the main product (Scheme 1). In addition, a small amount of the second compound, probably the adduct *t*Bu$_2$P(BH$_3$)-BH$_2$(SMe$_2$) (**1b**) was detected in the reaction mixture. The ^{11}B NMR spectrum of **1a** shows a broad multiplet at −27.2 ppm, which is in the typical range for tetracoordinate boron atoms. The presence of a broad quintet at 8.7 ppm ($^1J_{BP}$ = 60 Hz) in the ^{31}P{^{1}H} spectrum of **1a** indicates two equivalent boron atoms coupled with phosphorus. Furthermore, the ^{1}H NMR spectrum of **1a** contains a broad quartet at 2.58 ppm ($^1J_{BH}$ = 100 Hz), which corroborates the presence of the B–H unit in the structure of **1a**.
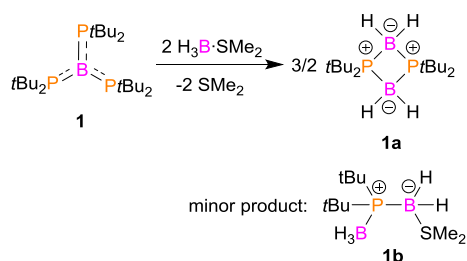
Scheme 1. The reaction of **1** with $H_3B \cdot SMe_2$.

Interestingly, Nöth and co-workers detected the formation of a small amount of **1a** together with other boron-containing compounds during the decomposition of the R$_2$B-P*t*Bu$_2$(BH$_3$) adduct (R$_2$B = 9-borabicyclo[3.3.1]nonanyl); however, the low yield of this reaction made it impossible to fully characterize the mentioned compound.[41]

X-ray-quality crystals of **1a** were obtained via evaporation of the solvent from the reaction mixture under reduced pressure and crystallization from petroleum ether solution at −20°C. The molecular structure of **1a** is presented in Figure 1.
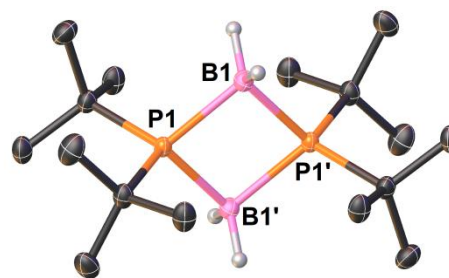
Figure 1. X-ray structure of **1a** showing the atom-numbering scheme. Ellipsoids are shown at 50% probability. H atoms have been omitted for clarity except those bound to boron atoms.

The X-ray diffraction study reveals that **1a** can be seen formally as a dimer of the elusive phosphinoborane *t*Bu$_2$P-BH$_2$. In contrast to cyclobutane which exhibits saddle conformation, the four membered-ring present in the structure of **1a** is planar with a torsion angle P1-B1-P1'-B1' of 0°. This planar conformation of **1a** results from steric repulsion of bulky *tert*-butyl groups at P atoms (a space-filling model of **1a** is depicted in Figure S1). The B–P distances are close to 2 Å and only slightly exceed the expected distance for a single covalent B–P bond (1.96 Å).[42] To the best of our knowledge this, is the first structure of boraphosphacyclobutane derivative possessing two BH$_2$ units.

Next, we tested the reactivity of triphosphinoboranes with diversified substituents, where the central boron atom is connected to two bulky *t*Bu$_2$P fragments and a less crowded phosphanyl group such as Cy$_2$P (**2**), *i*Pr$_2$P (**3**), *t*BuHP (**4**), or Ph$_2$P (**5**) (Chart 1). Similar to the reaction involving **1**, triphosphinoborane **2** reacts with two equivalents of BMS in toluene with the formation of **2a** containing a four-membered B$_2$P$_2$ ring (Scheme 2). The evaporation of the solvent from the reaction mixture under vacuum, followed by washing the crude product with petroleum ether and crystallization from concentrated toluene solution yielded analytically pure **2a** as colourless crystals in moderate yield (64%).
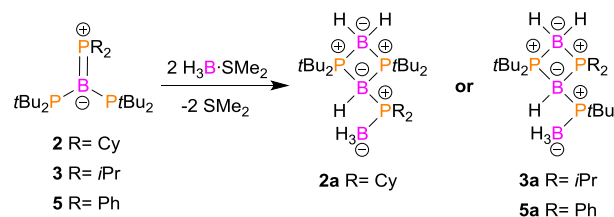

Scheme 2. Reactions of **2-5** with $H_3B \cdot SMe_2$.

Collectively, the heteronuclear NMR analysis and X-ray diffraction study revealed that, similarly to **1a**, the mentioned ring includes two *t*Bu$_2$P fragments linked by boron hydride fragments; however, unlike **1a**, one hydrogen atom of the BH$_2$ unit is substituted by a Cy$_2$P-BH$_3$ moiety (Figure 2). The phosphaboracyclobutane ring of **2a** exhibits analogous structural features to those observed in **1a**, such as almost planar conformation (P1-B1-P2-B2 torsion: 3.88°) and B–P bond distances of approximately 2 Å. In contrast with **1a**, the ^{31}P{^{1}H} spectrum of **2a** consists of three very broad singlets at 38.3 ppm (*t*Bu$_2$P), 30.3 ppm (*t*Bu$_2$P), and −3.4 ppm (Cy$_2$P), indicating three

inequivalent phosphorus centres. The ^{11}B NMR spectrum of **2a** shows a broad multiplet for the BH moiety at −25.6 ppm and two overlapping signals attributable to BH$_2$ and BH$_3$ fragments at approximately −36 ppm.
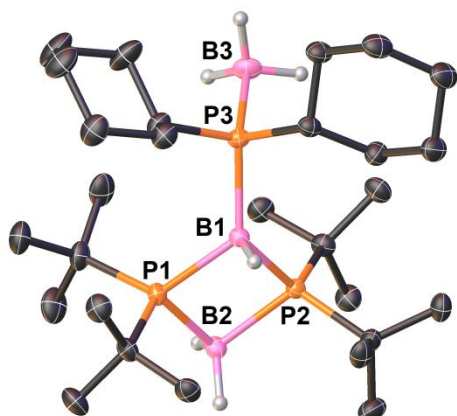
Figure 2. X-ray structure of **2a** showing the atom-numbering scheme. Ellipsoids are shown at 50% probability. H atoms, except those bound to boron atoms, have been omitted for clarity.

The influence of substituents on reaction outcome is visible in the case of the analogous experiment using **5**, which contains the least crowded Ph$_2$P fragment. The product of reaction (**5a**) was isolated in moderate yield (52%) from concentrated petroleum ether solution at −20°C as large colourless crystals. At the first glance, the obtained product of reaction with BMS (**5a**) is similar to those observed in a reaction involving **2**. However, careful analysis of the molecular structure of **5a** revealed substantial differences between **2a** and **5a** (Figure 3).
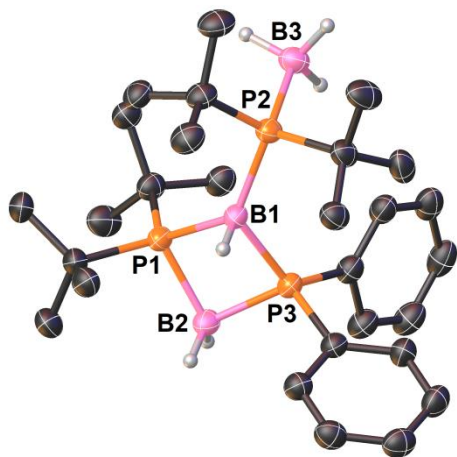

Figure 3. X-ray structure of **5a** showing the atom-numbering scheme. Ellipsoids are shown at 50% probability. H atoms, except those bound to boron atoms, have been omitted for clarity.

In the case of **5a**, a less crowded phosphanyl group is incorporated into the B$_2$P$_2$ ring, whereas tBu$_2$P moiety is included in the tBu$_2$P(BH$_3$) fragment bonded via the P atom to B1 atom of the B$_2$P$_2$ ring. Moreover, in contrast to **2a**, the B$_2$P$_2$ ring of **5a** is folded along B1-B2 and exhibits saddle conformation with torsion P2-B1-P3-B2 of −17.88(9)°.

As expected, ^{31}P{^{1}H} and ^{11}B NMR spectra of **5a** show three well-separated broad signals in the ranges from −7.8 ppm to

30.3 ppm and from −36.8 ppm to −18.3 ppm, respectively. It is worth mentioning that our previous preliminary studies revealed that the reaction of **3** possessing a iPr$_2$P group with BMS yielded product **3a**, with analogous structural features to those observed in **5a** such as a folded B$_2$P$_2$ ring containing a less crowded phosphanyl fragment iPr$_2$P (Scheme 2).[40]

In comparison to reactions **1**, **2**, **3**, or **5** with BMS, the analogous reaction involving **4** did not give only one major product, but a mixture of several species containing B–P moieties. Monitoring the progress of the reaction by heteronuclear NMR spectroscopy indicated the formation of four main products together with small amounts of other unidentified boron and phosphorus species (Scheme 3). The compounds **4a**, **4b**, **1a**, and **1b** were identified by NMR spectroscopy, and the structures of **4a**, **4b**, and **1a** were additionally confirmed by X-ray crystallography. The mix of **4a**, **4b**, **1a**, and **1b** in a molar ratio of 1:1:0.5:1 was obtained from concentrated petroleum ether at −20°C. Owing to the very similar solubility of the aforementioned compounds in common organic solvents, the separation of reaction products via fractional crystallization was not possible.
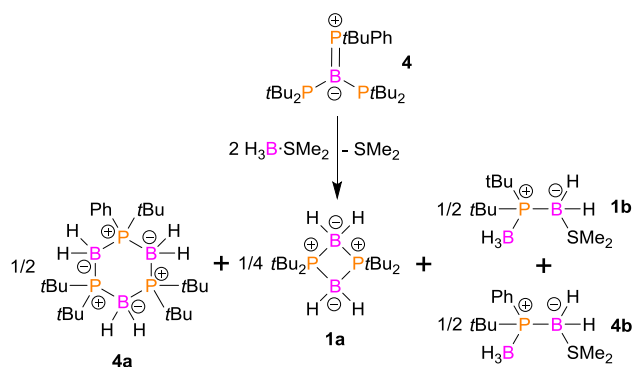
Scheme 3. The reaction of **4** with H$_3$B·SMe$_2$.

The most fascinating product of this reaction is the derivative boraphosphacyclohexane **4a**. It displays two ^{31}P{^{1}H} resonances at 13.7 ppm and −4.6 ppm, which are assigned to phosphorus atoms of tBu$_2$P and tBuPhP fragments. Furthermore, it shows two ^{11}B resonances at −14.2 ppm and −20.9 ppm attributed to inequivalent BH$_2$ groups. The molecular structure of **4a** is depicted in Figure 4. Owing to the low quality of crystals of **4a** (R_1 = 11.79%), we will not discuss in detail the metric parameters of the X-ray structure of **4a**. However, crucial structural features of **4a** can be easily identified based on these data. The molecule of **4a** consists of a six-membered ring composed of tBuPhP moiety and two tBu$_2$P fragments linked by boron atoms of three BH$_2$ groups. The six-membered ring is folded along the P1-P3 and B2-B3 vectors, which leads to a boat conformation. The compound **4a** can be treated as an adduct of one molecule of tBuPhP-BH$_2$ and two molecules of tBu$_2$P-BH$_2$.
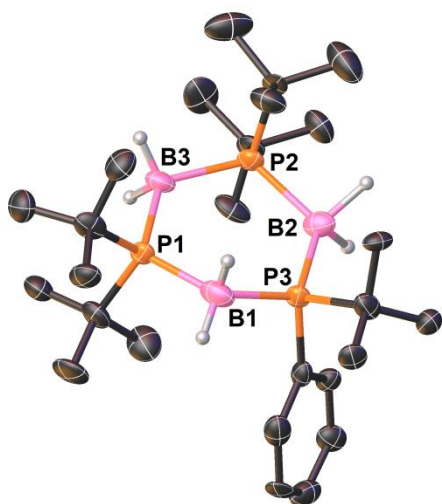
Figure 4. X-ray structure of **4a** showing the atom-numbering scheme. Ellipsoids are shown at 50% probability. H atoms, except those bound to boron atoms, have been omitted for clarity.

To the best of our knowledge, this is the first example of a derivative of boraphosphacyclohexane bearing diversified substituents at phosphorus atoms. Interestingly, the great majority of boraphosphacyclohexanes were obtained via dehydrocoupling of phosphine-boranes and they have a trimeric structure with a general formula of $(R_2P\text{-}BH_2)_3$. Only a few examples of such trimers were investigated by X-ray diffraction.[43,44,35] In contrast to **4a**, they exhibit armchair conformation, such as the cases of $(Me_2P\text{-}BH_2)_3$[43] and $(Ph_2P\text{-}BH_2)_3$[44], or the almost planar conformation observed for $((Me_3Si)_2P\text{-}BH_2)_3$.[35]

Regarding other products of the reaction of **4a** with BMS, **4b** is an adduct of elusive tBuPhB-BH$_2$ and BMS (Figure 4), whereas **1a** and **1b** were identified by us as products of the previously mentioned reaction of **1** with BMS.
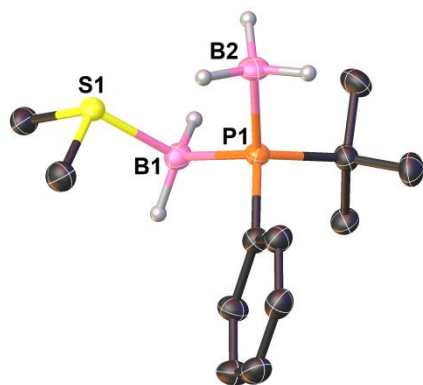
Figure 5. X-ray structure of **4b** showing the atom-numbering scheme. Ellipsoids are shown at 50% probability. H atoms, except those bound to boron atoms, have been omitted for clarity.

The high reactivity of triphosphinoboranes towards BMS encourages us to expand our study to other species with B−P bonds. For the synthesis of triphosphinoboranes with diversified substituents (**2**–**5**), we used bromo-substituted diphosphinoborane **6** (Chart 1). We were curious if the precursor of triphosphinoboranes would also activate the BH$_3$

molecule. To our delight, the reaction of **6** with BMS in toluene in a molar ratio of 1:1 proceeded smoothly and resulted in only one product **6a** (Scheme 4).
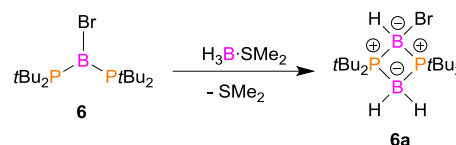
Scheme 4. The reaction of **6** with $H_3B\cdot SMe_2$.

The X-ray quality crystals of **6a** were obtained via low-temperature crystallization from concentrated petroleum ether solution in a high yield (82%). NMR spectroscopy and single crystal X-ray diffraction both confirmed the formation of a bromo-substituted boraphosphacyclobutane structure. The ^{11}B NMR spectrum of **6a** shows two broad signals at −31.1 ppm (BH$_2$) and −17.8 ppm (BBrH), whereas the ^{31}P{^{1}H} NMR spectrum of **6a** contains only one broad resonance at 10.1 ppm (tBu$_2$P). These data corroborate well with the results of X-ray diffraction analysis, which indicated the presence of two inequivalent boron centres and two equivalent phosphorus centres. The X-ray structure of **6a** is depicted in Figure 6.

Figure 6. X-ray structure of **6a** showing the atom-numbering scheme. Ellipsoids are shown at 50% probability. H atoms, except those bound to boron atoms, have been omitted for clarity.
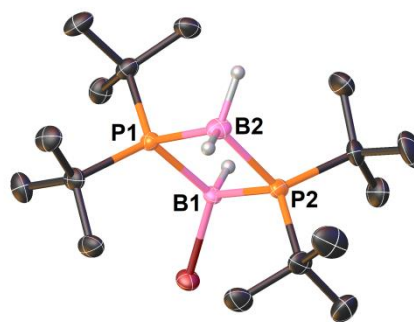
The **6a** structure is very similar to **1a**; however, in the case of **6a**, one hydrogen atom at the B1 atom is substituted by a bromine atom. The central B$_2$P$_2$ ring of **6a** is slightly more distorted in comparison to those observed in **1a** with a P1-B1-P2-B2 torsion angle of 4.4(2)°.

Conclusions

Triphosphinoboranes smoothly activate the B−H bond in BMS owing to the presence in their structures of both Lewis acidic and Lewis basic reactive centres. The steric effect has a strong influence on the outcomes of described reactions. Depending on the substituents at phosphorus atoms in the starting B−P compounds, four- or six-membered cyclic products were obtained. The resulting cyclic compounds can be seen as derivatives of boraphosphocyclobutane or boraphosphacyclohexane, respectively. These results not only confirmed the applicability of triphosphinoboranes in the activation of covalent bonds but also provide new synthetic access to cyclic B−P species.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

Notes and references

1 T. Chu, S. F. Vyboishchikov, B. M. Gabidullin and G. I. Nikonov, *J. Am. Chem. Soc.*, 2017, **139**, 8804–8807.
2 D. W. Stephan, *J. Am. Chem. Soc.*, 2015, **137**, 10018–10032.
3 I. M. Riddlestone, J. A. B. Abdalla and S. Aldridge, *Coordination and activation of E-H Bonds (E=B, Al, Ga) at transition metal centers*, Elsevier Inc., 1st edn., 2015, vol. 63.
4 T. Higashi, S. Kusumoto and K. Nozaki, *Chem. Rev.*, 2019, **119**, 10393–10402.
5 M. Zafar, R. Ramalakshmi, A. Ahmad, P. K. S. Antharjanam, S. Bontemps, S. Sabo-Etienne and S. Ghosh, *Inorg. Chem.*, 2021, **60**, 1183–1194.
6 M. A. Esteruelas, M. Oliván and A. Vélez, *Organometallics*, 2015, **34**, 1911–1924.
7 Y. Kawano, T. Yasue and M. Shimoi, *J. Am. Chem. Soc.*, 1999, **121**, 11744–11750.
8 W. E. Piers, *Angew. Chemie - Int. Ed.*, 2000, **39**, 1923–1925.
9 L. T. Scharf, J. Weismann, K. S. Feichtner, F. Lindl and V. H. Gessner, *Chem. - A Eur. J.*, 2018, **24**, 3439–3443.
10 Q. Zhu, P. Wang, J. Zhu, C. Zhu and G. Zeng, *Inorg. Chem.*, 2020, **59**, 15636–15645.
11 V. S. V. S. N. Swamy, K. V. Raj, K. Vanka, S. S. Sen and H. W. Roesky, *Chem. Commun.*, 2019, **55**, 3536–3539.
12 Y. C. Lin, E. Hatzakis, S. M. McCarthy, K. D. Reichl, T. Y. Lai, H. P. Yennawar and A. T. Radosevich, *J. Am. Chem. Soc.*, 2017, **139**, 6008–6016.
13 M. K. Bisai, V. Sharma, R. G. Gonnade and S. S. Sen, *Organometallics*, 2021, **40**, 2133–2138.
14 S. Würtemberger-Pietsch, H. Schneider, T. B. Marder and U. Radius, *Chem. - A Eur. J.*, 2016, **22**, 13032–13036.
15 A. Kassymbek, D. G. Gusev, A. Dmitrienko, M. Pilkington and G. I. Nikonov, *Chem. - A Eur. J.*, , DOI:10.1002/chem.202103455.
16 K. Jaiswal, B. Prashanth, D. Bawari and S. Singh, *Eur. J. Inorg. Chem.*, 2015, **2015**, 2565–2573.
17 M. A. Légaré, M. A. Courtemanche and F. G. Fontaine, *Chem. Commun.*, 2014, **50**, 11362–11365.
18 S. Y. F. Ho, C. W. So, N. Saffon-Merceron and N. Mézailles, *Chem. Commun.*, 2015, **51**, 2107–2110.
19 N. Dordević, R. Ganguly, M. Petković and D. Vidović, *Inorg. Chem.*, 2017, **56**, 14671–14681.
20 D. N. Lastovickova and C. W. Bielawski, *Organometallics*, 2016, **35**, 706–712.
21 H. Heuclin, S. Y. F. Ho, X. F. Le Goff, C. W. So and N. Mézailles, *J. Am. Chem. Soc.*, 2013, **135**, 8774–8777.
22 N. L. Oldroyd, S. S. Chitnis, V. T. Annibale, M. I. Arz, H. A. Sparkes and I. Manners, *Nat. Commun.*, 2019, **10**, 1–9.
23 H. Dorn, R. A. Singh, J. A. Massey, J. M. Nelson, C. A. Jaska, A. J. Lough and I. Manners, *J. Am. Chem. Soc.*, 2000, **122**, 6669–6678.
24 S. Pandey, P. Lönnecke and E. Hey-Hawkins, *Eur. J. Inorg. Chem.*, 2014, 2456–2465.
25 F. High, M. Weight, H. Dorn, R. A. Singh, J. A. Massey, A. J. Lough and I. Manners, *Angew. Chemie - Int. Ed.*, 1999, **38**, 3321–3323.
26 T. J. Clark, J. M. Rodezno, S. B. Clendenning, S. Aouba, P. M. Brodersen, A. J. Lough, H. E. Ruda and I. Manners, *Chem. - A Eur. J.*, 2005, **11**, 4526–4534.
27 C. Marquardt, T. Jurca, K. C. Schwan, A. Stauber, A. V. Virovets, G. R. Whittell, I. Manners and M. Scheer, *Angew. Chemie - Int. Ed.*, 2015, **54**, 13782–13786.
28 A. Stauber, T. Jurca, C. Marquardt, M. Fleischmann, M. Seidl, G. R. Whittell, I. Manners and M. Scheer, *Eur. J. Inorg. Chem.*, 2016, **2016**, 2684–2687.
29 J.-M. Denis, H. Forintos, H. Szelke, L. Toupet, T.-N. Pham, P.-J. Madec and A.-C. Gaumont, *Chem. Commun.*, 2003, 54–55.
30 D. C. Pestaña and P. P. Power, *J. Am. Chem. Soc.*, 1991, **113**, 8426–8437.
31 N. N. Pham-Tran, N. H. T. Huy, P. C. Nam, L. Ricard and M. T. Nguyen, *J. Organomet. Chem.*, 2006, **691**, 4058–4064.
32 A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, 1953, **75**, 3872–3877.
33 W. Gee, R. A. Shaw, B. C. Smith and G. J. Bullen, *Proc. Chem. Soc.*, 1961, 432.
34 D. Dou, M. Westerhausen, G. L. Wood, G. Linti, E. N. Duesler, H. Noth and R. T. Paine, *Chem. Ber.*, 1993, **126**, 379–397.
35 G. Lynn Wood, D. Dou, C. K. Narula, E. N. Duesler, R. T. Paine and H. Nöth, *Chem. Ber.*, 1990, **123**, 1455–1460.
36 N. Szynkiewicz, A. Ordyszewska, J. Chojnacki and R. Grubba, *RSC Adv.*, 2019, **9**, 27749–27753.
37 N. Szynkiewicz, A. Ordyszewska, J. Chojnacki and R. Grubba, *Inorg. Chem.*, 2021, **60**, 3794–3806.
38 A. Ordyszewska, N. Szynkiewicz, E. Perzanowski, J. Chojnacki, A. Wiśniewska and R. Grubba, *Dalton Trans.*, 2019, **48**, 12482–12495.
39 N. Szynkiewicz, J. Chojnacki and R. Grubba, *Inorg. Chem.*, 2020, **59**, 6332–6337.
40 A. Ordyszewska, N. Szynkiewicz, J. Chojnacki and R. Grubba, *Inorg. Chem.*, 2022, **61**, 4361–4370.
41 H. Nöth, S. Staude, M. Thomann and R. T. Paine, *Chem. Ber.*, 1993, **126**, 611–618.
42 P. Pyykkö and M. Atsumi, *Chem. - A Eur. J.*, 2009, **15**, 186–197.
43 W. C. Hamilton, *Acta Crystallogr.*, 1955, **8**, 199–206.
44 G. J. Bullen and P. R. Mallinson, *J. Chem. Soc. Dalt. Trans.*, 1973, 1295.