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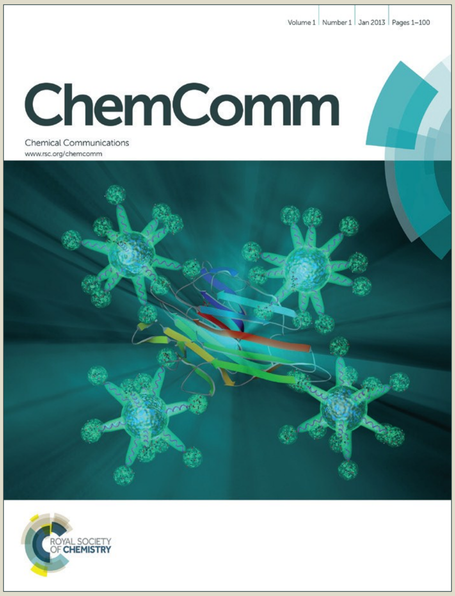

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Iridium-Catalysed Dehydrocoupling of Aryl Phosphine-Borane Adducts: Synthesis and Characterisation of High Molecular Weight Poly(phosphinoboranes)

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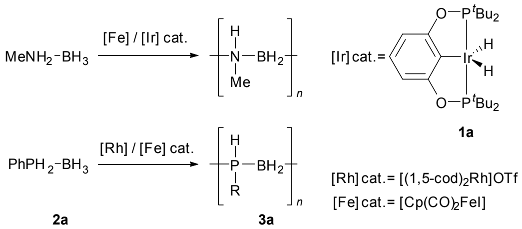
The thermal dehydrogenative coupling of aryl phosphine-borane adducts with iridium complexes bearing a bis(phosphinite) pincer ligand is reported. This catalysis produces high molecular weight poly(phosphinoboranes) $[ArPH–BH_2]_n$ (Ar = Ph, ^{p}Tol, Mes). Furthermore, we investigated the reactivity of these pincer complexes towards primary phosphines and their respective borane adducts on a stoichiometric scale.

The formation of main group element-element bonds has traditionally been achieved using methods such as salt metathesis and reductive coupling. Catalytic routes to form relatively strong homonuclear (E–E) und heteronuclear (E–E') bonds between lighter main group elements (E = B, N, Al, Si, P, S), are mainly based on dehydrocoupling of main group element hydrides (E–H). The transition metal and main group element catalysts used for this kind of bond-formation reaction usually need to be highly reactive in order to facilitate an element-hydrogen bond activation step, typically required for the dehydrocoupling.

Iridium complexes bearing the bis(phosphinite) pincer ligand ^{t}BuPOCOP (κ^3-C_6H_3-1,3-$(OP^tBu_2)_2$) have shown unique activities in the homogeneous (transfer)dehydrogenation of various substrates such as alkanes,[1a] alcohols[1b] and amines.[1c] Furthermore, the complex $[(^tBuPOCOP)IrH_2]$ (**1a**) proved to be an active (pre)catalyst in the dehydrogenation of ammonia borane $(NH_3–BH_3)$[1d-h] as well as in dehydrocoupling reactions of primary amine boranes $(RNH_2–BH_3)$ to yield soluble high molecular weight poly(aminoboranes) $[RNH\text{-}BH_2]_n$.[1h] The latter result was of particular interest, as previous studies revealed that a variety of catalysts only led to the formation of borazines and/or poorly characterised insoluble and branched oligomeric material.[2] This prompted us to investigate these iridium pincer complexes as catalysts for the dehydrogenative coupling of phosphine-borane adducts $(RPH_2–BH_3)$.



Scheme 1. Examples for catalytic dehydropolymerisation of amine[1h,4a] and phosphine[3a,4b] boranes.

Since the early 2000s, detailed studies on rhodium-catalysed dehydropolymerisation of a broad range of primary phosphine boranes[3] have been reported, giving polydisperse, soluble, branched polymers ($M_n > 10\,000$) as well as crosslinked, swellable, but insoluble materials, depending on the specific conditions and substituents of the phosphine. Though sufficient results were only obtained when the polymerisation was carried out as a melt reaction at elevated temperatures (ca. 130 °C).[3a-e, 3g-h] In marked contrast, Manners *et al.* reported recently an iron-catalysed dehydrocoupling of $PhPH_2–BH_3$ (**2a**) in solution to yield the respective soluble poly(phosphinoborane) (**3a**) with control over the molecular weight (M_n 42 000 to 80 000) by varying the catalyst loading (Scheme 1).[4b] The iron complex $[Cp(CO)_2FeI]$ investigated is one of the rare examples[5] of a catalyst which was successfully applied in the dehydrogenation of both amine-[4a] and phosphine-borane[4b] adducts, a fact that further encouraged us to conduct our studies. Interestingly, the substrate scope of this dehydrogenative coupling reaction is limited to aryl substituted phosphine boranes, while alkyl substituted poly(phosphinoboranes) are accessible through metal-free addition/polymerisation of suitable Lewis base stabilised monomeric phosphinoboranes, as recently reported by Scheer *et al.*[6]

Treatment of primary phosphine boranes $ArPH_2–BH_3$ (Ar = Ph **2a**, ^{p}Tol **2b**, Mes **2c**) with 5 mol% of $[(^tBuPOCOP)IrH_2]$ (**1a**) in toluene at 100 °C results in the complete consumption of the starting materials within 24 hours and, as monitored by ^{11}B

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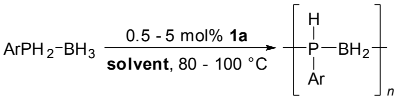
and ^{31}P NMR spectroscopy, in the selective formation of the respective poly(phosphinoborane) $[ArPH–BH_2]_n$ (Ar = Ph **3a**, ^{p}Tol **3b**, Mes **3c**) (Table 1).[7] The polymeric products were isolated as off-white solids by precipitation into cold pentane and subsequently characterised by multinuclear NMR as well as IR spectroscopy and elemental analysis.

Table 1. Iridium-catalysed dehydrocoupling of primary phosphine-borane adducts **2a-c** to polymers **3a-c**.



2 **3**

Ar = Ph **a**, ^{p}Tol **b**, Mes **c**

	Adduct	Mol% **1a**	Method[a]	Time	M_n/M_w	PDI
1	**2a**	5	**A**	24 h	10 000/ 216 000	21.6
2	**2b**	5	**A**	24 h	5 000/ 66 000	13.2
3	**2c**	5	**A**	24 h	10 000/ 300 000	30.0
4	**2c**	2.5	**A**	24 h	5 000/ 13 000	2.6
5	**2c**	2.5	**B**	24 h	33 000/ 59 000	1.8
6	**2c**	2.5	**B**	6 h	20 000/ 116 000	5.8
7	**2c**	0.5	**B**	24 h	5 000/ 10 000	2.0

[a] Reaction conditions for methods **A**: 5 mL of toluene, 100 °C and **B**: 0.6 mL of benzene, 80 °C.

In good agreement with previous reports for polymer **3a**,[3a,b] the ^{31}P NMR spectra of the isolated products show one broad singlet at $\delta(^{31}P) = -48.7$ (**3a**)/ -49.8 (**3b**)/ -73.0 ppm (**3c**), which splits into a doublet ($^{1}J_{PH} = 352$ (**3a**)/ 355 (**3b**)/ 355 Hz (**3c**)) in the ^{1}H-coupled spectrum and thus confirms the presence of one single hydrogen substituent at phosphorus (Figure 1). The ^{1}H NMR spectra were also consistent with the assigned structures and contain a broad doublet at $\delta(^{1}H) = 4.64$ (**3a**)/ 4.73 (**3b**)/ 4.93 ppm (**3c**) for the PH group ($^{1}J_{PH} = 352$ (**3a**)/ 353 (**3b**)/ 356 Hz (**3c**)) as well as a broad signal for the BH$_2$ protons ($\delta(^{1}H\{^{11}B\}) = 2.12$-1.56 ppm) besides the peaks for the aromatic protons ($\delta(^{1}H) = 7.39$-6.50 ppm) and the methyl groups bound to the aryl substituents ($\delta(^{1}H) = 2.41$-2.01 ppm), in the case of **3b** and **3c**. The ^{11}B NMR spectra show a single broad resonance at $\delta(^{11}B) = -33.9$ (**3a**)/ -33.5 (**3b**)/ -34.3 ppm (**3c**), which lies in the expected range of a four-coordinate boron center and is slightly downfield shifted compared to the starting materials **2a-c** (Figure 1). The ^{13}C NMR resonances appear in the expected region. In the IR spectra of the polymers **3a-c** strong absorptions were observed around 2443 and 2382 cm^{-1}, which is in the expected range for both P–H and B–H stretching vibrations.

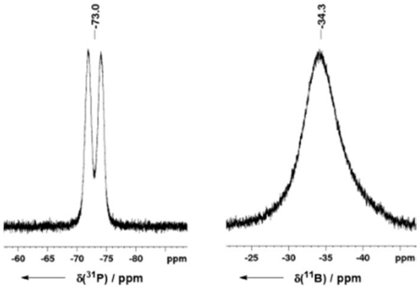


Figure 1. ^{31}P (162 MHz, C_6D_6, 298 K) and ^{11}B NMR spectrum (128 MHz, C_6D_6, 298 K) of the isolated polymerisation-product **3c**.

We investigated the molecular weights of the polymers **3a-c** through gel permeation chromatography (GPC) experiments (Table 1 and Figure S1-S3 in the SI).[8] In the case of $[PhPH–BH_2]_n$ (**3a**) and $[^{p}TolPH–BH_2]_n$ (**3b**) the GPC traces show a very broad distribution of molecular weights (entries 1-2). The same observation was made for $[MesPH–BH_2]_n$ (**3c**) (entry 3 and Figure S1). The high molecular weight obtained for the mesityl-substituted polymer encouraged us to further optimise the catalysis with MesPH$_2$–BH$_3$ (**2c**) as starting material (entries 4-7 and Figure S2). Lowering the catalyst loading to 2.5 mol% results in a more-defined GPC trace with narrower molecular weight distribution (entry 4) but lower overall weights. Furthermore, quantitative dehydrocoupling of **2c** already takes place at 80 °C in benzene within 24 hours[9] giving high molecular weight **3c** (entry 5 and Figure S3). When only 0.5 mol% of **1a** is used as catalyst under similar conditions the molecular weight of polymer **3c** further decreases (entry 7). This dependence of the molecular weight on the catalyst loading (higher loadings lead to higher molecular weights) would suggest a step-growth mechanism of the investigated iridium catalysed polymerisation of phosphine boranes. The presence of high molecular weight polymers even at low conversion (6 h, ≈ 36 %, entry 6), however, rather indicates a chain-growth character of this reaction.

These contrary results would be consistent with a two-stage polymerisation mechanism, as already reported for the dehydrocoupling of primary amine boranes.[1h] According to this, in the first step dehydrogenation proceeds slowly through hydrogen cleavage from the parent phosphine borane by the iridium bis(phosphinite) pincer complex.[1i] The so formed monomer phosphinoborane ArPH–BH$_2$ subsequently undergoes (conceivably metal assisted) fast chain-growth polymerisaton to the respective poly(phosphinoborane) $[ArPH–BH_2]_n$ in the second step. In such a reaction sequence the availability of the monomer phosphinoborane would be the limiting factor (for the progress of the polymerisation), thus, explaining the observed dependence of the polymer molecular weight on the catalyst loading.

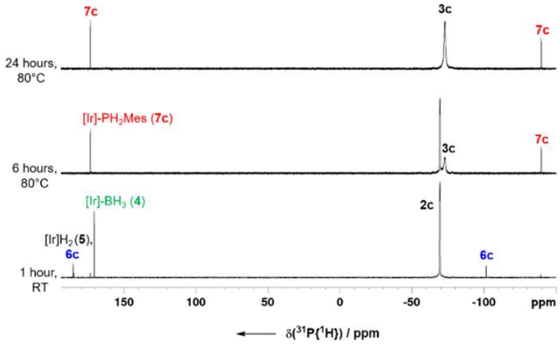


Figure 2. Time dependent ^{31}P NMR spectra (162 MHz, C_6D_6, 298 K) of the dehydrogenation reaction of adduct **2c** with complex **1a** as catalyst.

To gain further insight into the mechanism of this iridium-promoted dehydrogenation, we monitored the reaction of MesPH$_2$–BH$_3$ (**2c**) with catalytic amounts of **1a** by ^{31}P{^{1}H} NMR spectroscopy (Figure 2). The signal for **1a** vanishes

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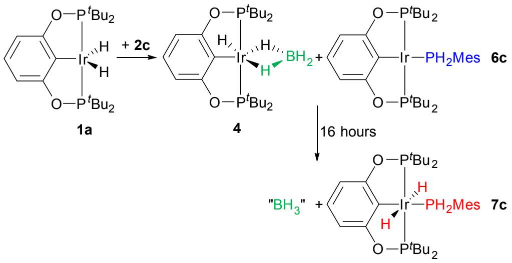
upon addition of the adduct $MesPH_2$-BH_3 (**2c**) and four different iridium species can be observed, namely the iridium borohydride complex $[(^tBuPOCOP)Ir(H)_2(BH_3)]$ (**4**),[1d] minor amounts of the tetrahydride complex $[(^tBuPOCOP)IrH_4]$ (**5**)[10] and two additional species **6c** and **7c**. These complexes were considered to be $[(^tBuPOCOP)Ir(PH_2Mes)]$ (**6c**) and $[(^tBuPOCOP)Ir(H)_2(PH_2Mes)]$ (**7c**) as each of them show one doublet for the pincer ligand ($\delta(^{31}P)$ = 185.2/173.4 ppm with $^2J_{PP}$ = 9.2/11.9 Hz) and one triplet ($\delta(^{31}P)$ = -101.6/-139.7 ppm with $^2J_{PP}$ = 9.2/11.9 Hz) in the region expected for the primary mesitylphosphine coordinating to a transition metal. Upon heating the reaction mixture to 80 °C the signals for complexes **4**, **5** and **6c** disappear completely and compound **7c** can be observed as the only iridium containing species in solution and therefore might be described as the resting state of the catalytically active species. This is supported by the observation that the catalysis can be resumed through addition of a further equivalent of adduct **2c** to this reaction mixture and subsequent heating (Figure S4).

Similar results are obtained when reacting $[(^tBuPOCOP)IrH_2]$ (**1a**) with a stoichiometric amount of the phosphine-borane adduct $MesPH_2$-BH_3 (**2c**) at room temperature (Scheme 2).



Scheme 2. Stoichiometric reaction of $MesPH_2$-BH_3 (**2c**) with complex $[(^tBuPOCOP)IrH_2]$ (**1a**).

According to $^{31}P\{^1H\}$ NMR spectroscopical data, complex **1a** is immediately converted equally into $[(^tBuPOCOP)Ir(H)_2(BH_3)]$ (**4**) and compound **6c** and within further 16 hours the latter complex **6c** is quantitatively converted into compound **7c**. (Figure 3) During this reaction, the ^{11}B NMR spectrum reveals only signals for starting material **2c** and borohydride complex **4**. Furthermore, with the formation of **7c** the ^1H NMR spectrum reveals a new hydride resonance ($\delta(^1H)$ = -10.98 ppm) besides those assigned for compound **4** ($\delta(^1H)$ = -20.36, -6.14, -4.95 ppm).

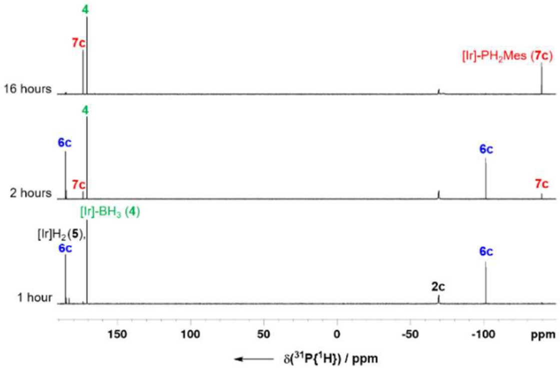
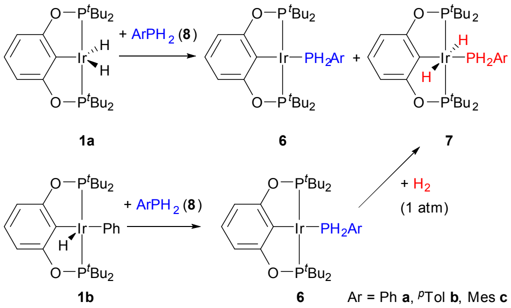


Figure 3. Time dependent ^{31}P NMR spectra (162 MHz, C_6D_6, 298 K) of the stoichiometric reaction of adduct **8c** with complex **1a**.

These observations supported the assumption that compounds **6c** and **7c** might be products upon coordination of free mesitylphosphine to the iridium center, resulting in the formation of $[(^tBuPOCOP)Ir(PH_2Mes)]$ (**6c**) or $[(^tBuPOCOP)Ir(H)_2(PH_2Mes)]$ (**7c**).

To confirm our assignment of complexes **6c** and **7c**, we studied the reactivity of $[(^tBuPOCOP)IrH_2]$ (**1a**) towards different primary phosphines $ArPH_2$ (Ar = Ph **8a**, ^{p}Tol **8b**, Mes **8c**) (Scheme 3). Addition of one equivalent of $MesPH_2$ (**8c**) to a solution of complex **1a** resulted in the liberation of dihydrogen and formation of a mixture of two products, which were identified by comparison of $^{31}P\{^1H\}$ NMR spectroscopical data as the two compounds already described above as iridium(I) phosphine $[(^tBuPOCOP)Ir(PH_2Mes)]$ (**6c**) and iridium(III) dihydrido phosphine complex $[(^tBuPOCOP)Ir(H)_2(PH_2Mes)]$ (**7c**).



Scheme 3. Reaction of primary phosphines **8a-c** with complexes **1a** and **1b** to give the iridium(I) phosphine **6a-c** and iridium(III) dihydrido phosphine complexes **7a-c**, respectively.

The same results were obtained for the analogous reactions of $PhPH_2$ (**8a**) and ^{p}TolPH_2 (**8b**) with **1a**, giving rise to mixtures of $[(^tBuPOCOP)Ir(PH_2Ar)]$ (Ar = Ph **6a**, ^{p}Tol **6b**) and $[(^tBuPOCOP)Ir(H)_2(PH_2Ar)]$ (Ar = Ph **7a**, ^{p}Tol **7b**). All of these iridium phosphine complexes can be synthesised selectively by variation of the starting material. Reacting the phosphines **8a-c** with the bis(phosphinite) stabilised iridium complex $[(^tBuPOCOP)IrHPh]$ (**1b**)[10] instead, the phosphine complexes $[(^tBuPOCOP)Ir(PH_2Ar)]$ (Ar = Ph **6a**, ^{p}Tol **6b**, Mes = **6c**) are formed quantitatively (Scheme 3). Subsequent pressurising of the iridium(I) complexes **6a-c** with dihydrogen (1 atm) at room temperature yields the respective iridium (III) dihydrides $[(^tBuPOCOP)Ir(H)_2(PH_2Ar)]$ (Ar = Ph **7a**, ^{p}Tol **7b**, Mes **7c**). Compounds **6a-c** and **7a-c** were characterised by multinuclear NMR spectroscopy and single-crystal X-ray diffraction (Figure 4). Furthermore, the iridium (phosphine) complexes **1b**, **6c** and **7c** serve as (pre)catalysts for the dehydrogenation of adduct **2c** (Figure S5), hence corroborating our assumption of the phosphine complexes being a resting state rather than a dormant form of the catalytically active species.

During the course of this study, we found no evidence for the formation of boryl, phosphido or phosphido-borane complexes, which were proposed as the catalytic intermediates that undergo the P–B bond formation processes in the respective rhodium[11] and iron[4] based systems. Thus, further investigations are needed to shed light into the precise

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order of the P–H/B–H activation process and P–B bond formation in particular.

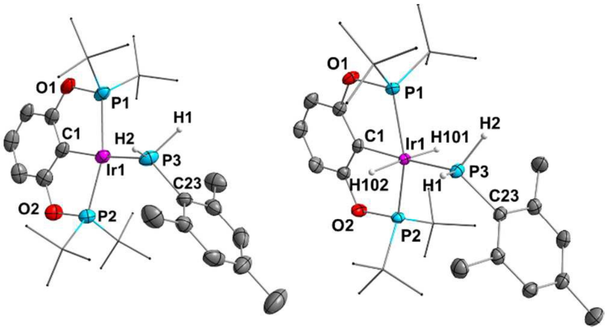

Figure 4. Molecular structure of [(^{t}BuPOCOP)Ir(PH$_2$Mes)] **6c** (left) and [(^{t}BuPOCOP)Ir(H)$_2$(PH$_2$Mes)] **7c** (right); thermal ellipsoids set at 50 % probability level. Some hydrogen atoms have been omitted for clarity. Selected bond lengths [pm] and angles [°]: **6c:** Ir1–C1 205.1(4), Ir1–P1 226.90(11), Ir1–P2 228.48(12), Ir1–P3 228.92(12); C1-Ir1-P3 171.88(12), P1-Ir1-P2 156.29(4), P1-Ir1-C1 78.58(13), Ir1-P3-C23 130.08(14); **7c**: Ir1–C1 206.5(2), Ir1–P1 229.35(6), Ir1–P2 231.33(6), Ir1–P3 231.48(6); C1-Ir1-P3 171.88(6), P1-Ir1-P2 155.94(2), P1-Ir1-C1 78.48(6), Ir1-P3-C23 126.85(7).

In summary, we have demonstrated that the bis(phosphinite) pincer ligated iridium complexes [(^{t}BuPOCOP)IrH$_2$] (**1a**) and [(^{t}BuPOCOP)IrHPh] (**1b**) can be used as catalysts in the dehydrogenative coupling of primary phosphine-borane adducts **2a-c** in solution to yield the respective poly(phosphinoboranes) **3a-c** as readily soluble, high molecular weight polymers. (Stoichiometric) reactions of [(^{t}BuPOCOP)IrH$_2$] (**1a**) with ArPH$_2$–BH$_3$ (**2c**) lead to cleavage of the phosphine boranes[11] with formation of [(^{t}BuPOCOP)Ir(H)$_2$(BH$_3$)] (**4**), iridium(I) phosphine complexes [(^{t}BuPOCOP)Ir(PH$_2$Ar)] (Ar = Ph **6a**, ^{p}Tol **6b**, Mes **6c**) and iridium(III) dihydrido phosphine complexes [(^{t}BuPOCOP)Ir(H)$_2$(PH$_2$Ar)] (Ar = Ph **7a**, ^{p}Tol **7b**, Mes **7c**). The latter complexes have also been prepared directly from the metal precursor and the corresponding phosphine. Due to the observed dependence of the polymer molecular weight on the catalyst loading we assume that the iridium catalysed dehydrocoupling of phosphine-borane adducts proceeds through a two-stage polymerisation mechanism, likewise postulated for the respective reaction with amine boranes.[1h]

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Notes and references

1 a) I. Göttker-Schnettmann, P. S. White and M. Brookhart, *J. Am. Chem. Soc.*, 2004, **126**, 1804-1811; b) A. V. Polukeev, P. V. Petrovskii, A. S. Peregudov, M. G. Ezernitskaya and A. A. Koridze, *Organometallics*, 2013, **32**, 1000-1015; c) W. H. Bernskoetter and M. Brookhart, *Organometallics*, 2008, **27**, 2036-2045; d) M. C. Denney, V. Pons, T. J. Hebden, D. M. Heinekey and K. I. Goldberg, *J. Am. Chem. Soc.*, 2006, **128**, 12048-12049; e) A. Staubitz, A. P. Soto and I. Manners, *Angew. Chem. Int. Ed.*, 2008, **47**, 6212-6215; f) V. Pons and R. T. Baker, *Angew. Chem. Int. Ed.*, 2008, **47**, 9600-9602; g) B. L. Dietrich, K. I. Goldberg, D. M. Heinekey, T. Autrey and J. C. Linehan, *Inorg. Chem.*, 2008, **47**, 8583-8585; h) A. Staubitz, M. E. Sloan, A. P. M. Robertson, A. Friedrich, S. Schneider, P. J. Gates, J. Schmedt auf der Günne and I. Manners, *J. Am. Chem. Soc.*, 2010, **132**, 13332-13345; i) A. Paul and C. B. Musgrave, *Angew. Chem. Int. Ed.*, 2007, **46**, 8153-8156.

2 a) C. A. Jaska, K. Temple, A. J. Lough and I. Manners, *J. Am. Chem. Soc.*, 2003, **125**, 9424-9434; b) [Ru]: N. Blaquiere, S. Diallo-Garcia, S. I. Gorelsky, D. A. Black and K. Fagnou, *J. Am. Chem. Soc.*, 2008, **130**, 14034-14035; c) [Rh]: C. A. Jaska, K. Temple, A. J. Lough and I. Manners, Chem. Commun., 2001, 962-963; d) [Ni]: R. J. Keaton, J. M. Blacquiere and R. T. Baker, *J. Am. Chem. Soc.*, 2007, **129**, 1844-1845; e) [Pt heterogen]: R. P. Shrestha, H. V. K. Diyabalanage, T. A. Semelsberger, K. C. Ott and A. K. Burrell, *Int. J. Hydrogen Energy*, 2009, **34**, 2616-2621.

3 a) H. Dorn, R. A. Singh, J. A. Massey, A. J. Lough and I. Manners, *Angew. Chem. Int. Ed.*, 1999, **38**, 3321-3323; b) 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; c) H. Dorn, E. Vejzovic, A. J. Lough and I. Manners, *Inorg. Chem.*, 2001, **40**, 4327-4331; d) H. Dorn, J. M. Rodezno, B. Brunnhöfer, E. Rivard, J. A. Massey and I. Manners, *Macromolecules*, 2003, **36**, 291-297; e) T. J. Clark, J. M. Rodezno, S. B. Clendenning, S. Aouba, P. M. Brodersen, A. J. Lough, H. E. Ruda and I. Manners, *Chem. Eur. J.*, 2005, **11**, 4526-4534; f) E. M. Leitao, T. Jurca and I. Manners, *Nat. Chem.*, 2014, **5**, 817-829; g) S. Pandey, P. Lönnecke and E. Hey-Hawkins, *Inorg. Chem.*, 2014, **53**, 8242-8249; h) S. Pandey, P. Lönnecke and E. Hey-Hawkins, *Eur. J. Inorg. Chem.*, 2014, 2456-2465; i) H. C. Johnson, T. N. Hooper and A. S. Weller, *Top. Organomet. Chem.*, 2015, **49**, 153-220.

4 a) J. R. Vance, A. Schäfer, A. P. M. Robertson, K. Lee, J. Turner, G. R. Whittell and I. Manners, *J. Am. Chem. Soc.*, 2014, **136**, 3048–3064; b) A. Schäfer, T. Jurca, J. Turner, J. R. Vance, K. Lee, V. An Du, M. F. Haddow, G. R. Whittell and I. Manners, *Angew. Chem. Int. Ed.*, 2015, **54**, 4836-4841.

5 Further example for a rhodium-based system: a) R. Dallanegra, A. P. M. Robertson, A. B. Chaplin, I. Manners and A. S. Weller, *Chem. Commun.*, 2011, **47**, 3763-3765; b) M. A. Huertos and A. Weller, *Chem. Sci.*, 2013, **4**, 1881-1888.

6 a) K.-C. Schwan, A. Y. Timoshkin, M. Zabel and M. Scheer, *Chem. Eur. J.*, 2014, **12**, 4900-4908; b) C. Marquardt, A. Adolf, A. Stauber, M. Bodensteiner, A. V. Virovets, A. Y. Timoshkin and M. Scheer, *Chem. Eur. J.*, 2013, **19**, 11887-11891; c) C. Thoms, C. Marquardt, A. Y. Timoshkin, M. Bodensteiner and M. Scheer, *Angew. Chem, Int. Ed.*, 2013, **52**, 5150-5154; d) C. Marquardt, C. Thoms, A. Stauber, G. Balázs, M. Bodensteiner and M. Scheer, *Angew. Chem. Int. Ed.*, 2014, **53**, 3727-3730; e) C. Marquardt, T. Jurca, K.-C. Schwan, A. Stauber, A. V. Virovets, G. R. Whittell, I. Manners and M. Scheer, *Angew. Chem. Int. Ed.*, 2015, **54**, 13782-13786.

7 Similar to amine boranes, no dehydrogenative coupling was observed for secondary phosphine boranes.[1h]

8 GPC analysis in THF as eluent needs to be considered carefully, as GPC studies might be hampered by column adsorption effects and/or the formation of aggregates in solution.[3a-e]

9 The catalytic dehydrocoupling of phosphine boranes **2a** and **2b** also proceeds at 80 °C in benzene, but requires 3 days for completion.

10 I. Göttker-Schnettmann, P. S. White and M. Brookhart, *Organometallics*, 2004, **23**, 1766-1776.

11 a) T. N. Hooper, M. A. Huertos, T. Jurca, S. S. Pike, A. S. Weller and I. Manners, *Inorg. Chem.*, 2014, **53**, 3716-3729; b) T. N. Hooper, A. S. Weller, N. A. Beattie and S. A. Macgregor, *Chem. Sci.*, 2016, **7**, 2414-2426.