

ChemPubSoc Europe

DOI:10.1002/ejic.201300629

### Thermally Induced Dehydrogenation of Amine–Borane Adducts and Ammonia–Borane by Group 6 Cyclopentadienyl Complexes Having Single and Triple Metal–Metal Bonds

# Daniel García-Vivó,\*<sup>[a]</sup> Estefanía Huergo,<sup>[a]</sup> Miguel A. Ruiz,<sup>[a]</sup> and Raquel Travieso-Puente<sup>[a]</sup>

Keywords: Boranes / Amines / Dehydrogenation / Metal-metal bonds / Group 6 elements

Treatment of solutions of ammonia-borane (NH<sub>3</sub>·BH<sub>3</sub>, AB) with catalytic amounts (5 mol-%) of the singly bonded dimers  $[M_2Cp_2(CO)_6]$  [M = Cr (1a), Mo (1b), W (1c); Cp = cyclopentadienyl] under mild thermal activation (333 K) led to the progressive dehydrogenation of the adduct and guantitative conversions were achieved after 12, 24, and >34 h, respectively. At the initial stages of these reactions (low conversions), the major products were cyclic and branched oligomers of aminoborane (NH<sub>2</sub>=BH<sub>2</sub>). However, at longer reaction times (high conversions), the major products were, in all cases, borazine,  $[HNBH]_3$ , and polyborazylene,  $[NBH_x]$  (x < 1), whereas other minor products were derived from B-N bond-cleavage processes. Over the course of these reactions, complexes **1a-c** were transformed into the corresponding mononuclear hydrides  $[MCpH(CO)_3]$  [M = Cr (2a), Mo (2b),W (2c)], which are supposed to be the catalytically active species in these processes, as also supported by similar catalytic activity exhibited by pure samples of the dihydride  $[Mo_2Cp_2(H)_2(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_2] \quad \textbf{(2b')}. \quad Under \quad similar$ conditions, 1a-c were also active catalysts for the dehydroge-

#### Introduction

One of the biggest technological challenges of modern societies is the development of cleaner energy sources that can mitigate the current dependence on fossil fuels and alleviate the greenhouse effect associated with carbon-based technologies. Over the last decades, hydrogen has appeared as a long-term sustainable solution able to meet our future energy demands;<sup>[1]</sup> however, the safe and economical storage of hydrogen remains one of the major barriers for its broad implementation.<sup>[2]</sup> In this context, amine–borane adducts, and in particular ammonia–borane (NH<sub>3</sub>·BH<sub>3</sub>, AB), are promising candidates for the chemical storage of hydrogen for the chemical storage for hydrogen for hydrogen for hydrogen for the chemical storagen for hydrogen for the chemical storagen for hydrogen for hydrogen

nation of adducts derived from substituted amines (tBuH<sub>2</sub>N·BH<sub>3</sub> and Me<sub>2</sub>HN·BH<sub>3</sub>), although the rate of dehydrogenation was significantly lower than that of AB. This lower activity follows from deprotonation of hydrides 2 by the free amines, which are in turn generated through B-N bond-cleavage processes. The dehydrogenation products of tBuH<sub>2</sub>N·BH<sub>3</sub> are also derived from oligomerization processes of the corresponding aminoborane (tBuHN=BH<sub>2</sub>), which in this case was identified in the reaction mixtures, but even at long reaction times, the formation of the borazine-like product was not complete, and the reaction mixture contained significant amounts of (poorly defined) soluble polymeric materials. For Me<sub>2</sub>HN·BH<sub>3</sub>, the major product obtained in all of the reactions was cyclic dimer [Me<sub>2</sub>N=BH<sub>2</sub>]<sub>2</sub>. Similar studies were performed with triply bonded complexes [Mo<sub>2</sub>Cp<sub>2</sub>- $(CO)_4$  (3b) and  $[Mo_2Cp_2(\mu-Ph_2PCH_2PPh_2)(CO)_2]$  (3b'), which displayed similar catalytic activity while remaining essentially unperturbed along the reactions, and these complexes yielded product distributions that were similar to those observed for singly bonded dimers 1a-c.

gen because of their high gravimetric hydrogen capacity, stability, and controlled hydrogen release. Therefore, it is not surprising that these "simple" adducts have attracted much research recently,<sup>[3]</sup> including numerous studies related to the development of low-energy regeneration routes of the B-N spent fuels.<sup>[4]</sup> The interest in these substances also stems from their potential as precursors of new inorganic materials (i.e., polymers,<sup>[5]</sup> ceramics,<sup>[6]</sup> etc.) and as reducing and hydroborating reagents in organic chemistry.<sup>[7]</sup> Prompted by all of these promising applications, the development of novel transition-metal-based catalysts able to promote and control the dehydrocoupling/dehydrogenation reactions of amine-borane adducts has bloomed in recent years.<sup>[3]</sup> Most of the systems used so far are complexes based on second- and third-row transition metals including Rh.<sup>[8]</sup> Ir.<sup>[9]</sup> Ru.<sup>[10]</sup> Re.<sup>[11]</sup> and Pd.<sup>[12]</sup> which are expensive and in some cases act in a heterogeneous manner rather than a homogeneous manner. More scarce are the catalytic sys-



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 <sup>[</sup>a] Departamento de Química Orgánica e Inorgánica / IUQOEM, Universidad de Oviedo, 33071 Oviedo, Spain

E-mail: garciavdaniel@uniovi.es

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201300629.



tems based on first-row transition metals (i.e., Ti,<sup>[13]</sup> Cr,<sup>[14]</sup> Ni,<sup>[15]</sup> and Fe<sup>[16]</sup> catalysts). Unfortunately, many of these systems suffer from instability under the reaction conditions, which further complicates the mechanistic landscape of these reactions. Quite relevant to this work, Manners et al. recently reported the dehydrocoupling reactions of primary and secondary amine–borane adducts and of AB itself by using the [Fe<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub>] (Cp = cyclopentadienyl) iron dimer under photochemical activation.<sup>[16a]</sup> Elegant parallel experiments excluded the presence of heterogeneous process, which suggests the formation of the rather unstable mononuclear hydride [FeCpH(CO)<sub>2</sub>] over the course of these reactions; however, such a species was only detected in stoichiometric experiments and was not identified in the catalytic reactions.

Encouraged by these results, we reasoned that the related binuclear  $[M_2Cp_2(CO)_6]$  complexes of group 6 metals [M =Cr (1a), Mo (1b), and W (1c)] might display significant catalytic activity in these sorts of dehydrogenative processes. In particular, these dimers are known to undergo M-M bond homolysis to generate the 17-electron [MCp(CO)<sub>3</sub>]. radicals in a reaction that takes place spontaneously in solution at room temperature for the Cr substrate<sup>[17]</sup> and under photochemical conditions (or strong thermal activation) for the Mo and W complexes.<sup>[18]</sup> Moreover, the corresponding hydrides, [MCpH(CO)<sub>3</sub>] (2a-c), are relatively stable molecules that have been extensively studied,<sup>[19]</sup> and they are known to undergo dehydrogenation processes under mild conditions to regenerate the corresponding binuclear complexes.<sup>[20]</sup> Herein, we report that group 6 binuclear dimers 1a-c are effective catalysts, via mentioned mononuclear hydrides 2, for the dehydrocoupling of a range of amine-borane adducts including AB under mild thermal conditions (333 K). To extend the scope of this study, we also explored the catalytic activity of the readily accessible 30-electron complex  $[Mo_2Cp_2(CO)_4]$  (3b)<sup>[21]</sup> and that of the dppm-bridged derivatives [Mo<sub>2</sub>Cp<sub>2</sub>(µ-dppm)(CO)<sub>n</sub>] [dppm =  $Ph_2PCH_2PPh_2$ ; n = 4 (1b'), 2 (3b')].<sup>[22]</sup> Although the triply bonded complexes have stronger intermetallic bonds, the presence of the diphosphane ligand is expected to increase the electron density and increase the stability of these complexes towards degradation of the dimetal center. As discussed below, we found that the triply bonded complexes exhibit higher catalytic activity than their corresponding singly bonded analogues in some of the reactions examined, which proves, for the first time, that complexes with multiple M-M bonds can be efficient catalysts for the dehydrogenation of amine-borane adducts.

#### Results

### Dehydrogenation Reactions of AB Catalyzed by Complexes 1a-c (M-M) and 3b (Mo=Mo)

Following a procedure similar to that used by Manners and co-workers for iron dimer [Fe<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub>],<sup>[16a]</sup> we started our study by adding catalytic amounts (5 mol-%) of singly bonded complexes 1a-c to THF solutions of the unsubstituted adduct, NH<sub>3</sub>·BH<sub>3</sub> (AB, 0.23 M). The reaction progress was evaluated in situ by <sup>11</sup>B and <sup>11</sup>B{<sup>1</sup>H} NMR spectroscopy, and all of the dehydrogenation products were identified by comparison of their NMR resonances with those reported previously in the literature. Although no significant reaction was observed at room temperature, progressive dehydrogenation was observed if these mixtures were heated at 333 K to give mixtures of products (Scheme 1 and Table 1). All of the complexes under study displayed significant catalytic activity (reactions faster than the blank run) and yielded almost-quantitative conversions after 12, 24, and >34 h for 1a, 1b, and 1c, respectively. It was also evident that the metal center has a strong influence on the activity, as the activity decreased for heavier metals, which is an observation that might be rationalized on the basis of the different strengths of the M-M and M-H bonds in the species involved in these reactions (vide infra). In spite of the different rates, the products obtained in all of these reactions were quite similar, and their relative ratio evolved with the reaction time, as expected. Thus, in the initial stages of the reaction, the major dehydrogenation products observed in the presence of heavier congeners 1b and 1c were those following from the formal loss of one equivalent of H<sub>2</sub>, in particular the cyclolinear trimer, B-(cyclodiborazanyl)aminoborohydride (BCDB),<sup>[15b]</sup> and the cyclic trimer (CTB).<sup>[23]</sup> These two species are intermediates in the dehydrogenation reaction, as prolonged reaction times led to quantitative conversions of the parent adduct and, most importantly, to the formation of borazine (BH-NH)3 (formal loss of 2 equiv. of H2)[8a] and polyborazylene  $(BNH_x, x < 1, PB^{[15b]}$  loss of >2 equiv. of H<sub>2</sub>) as major dehydrogenation products. However, chromium complex 1a displayed a significantly higher reaction rate, and even at short reaction times the major dehydrogenation product was borazine. Notably, besides these major dehydrogenation products, we could also identify the presence of µ-aminodiborane,  $B_2H_5(\mu-NH_2)$  ( $\mu$ -ADB), in the reaction mixtures<sup>[24]</sup> and small amounts of the BH<sub>3</sub>·THF adduct, both of which should be formed through B-N bond-cleavage processes of



Scheme 1.



Complex	<i>t</i> [h]	Product d	istribution [%]	Conv. [%]	TOF [h <sup>-1</sup> ] <sup>[c]</sup>				
		μ-ADB	BH <sub>3</sub> ·THF	BCDB	CTB <sup>[d]</sup>	Borazine	PB <sup>[e]</sup>		
1a	6	34	2	10	20	30	4	81	
	12	26	2	7	11	49	5	94	0.8
	24	19	3	1	4	53	20	100	
1b	6	23	0	41	19	13	4	40	
	12	19	1	25	10	34	11	78	
	24	24	2	9	9	49	7	97	0.4
1c	6	4	0	56	36	4	0	14	
	12	6	0	63	19	9	2	40	
	24	10	0	41	19	24	6	66	
	34	13	0	33	17	29	8	80	0.3
3b	6	7	0	54	23	13	3	42	
	12	11	0	32	22	27	8	65	
	24	11	1	28	16	35	9	92	0.8
	34	12	3	7	13	47	18	99	
Plank	24	0	0	72	24	4	0	20	

Table 1. Thermal dehydrogenation of AB catalyzed by complexes **1a–c** and **3b** (5 mol-%).<sup>[a,b]</sup>

[a] Reactions were run with [cat] = 0.012 M and  $[AB]_0 = 0.23 \text{ M}$  in THF (0.5 mL). The conversion and product distribution were determined by integration of the corresponding signals in the <sup>11</sup>B{<sup>1</sup>H} NMR spectra. [b] Reaction times were not necessarily optimized. [c] Turnover frequency (TOF) = (% conversion/% loading)/time, with % loading = 10 (for **1a–c**) and 5 (for **3b**), see text. [d] The corresponding signal in the <sup>11</sup>B{<sup>1</sup>H} NMR spectrum overlaps one of the resonances of BCDB, and therefore, the percentage was calculated by difference. [e] The product distribution was calculated on the basis of the corresponding monomer (-BNH<sub>x</sub>-) (x < 1).

the parent adduct.<sup>[15b]</sup> Actually, the former was recently prepared in high yield from the reaction of AB with  $BH_3$ ·THF.<sup>[24c]</sup>

of singly bonded **1b**, as illustrated by the effective TOF values at 24 h (0.8 vs.  $0.4 \text{ h}^{-1}$ ).

Triply bonded tetracarbonyl **3b** also catalyzed the dehydrogenation of AB under the same reaction conditions. Quite remarkably, this complex achieved quantitative conversions after approximately 24 h, which led to a reaction rate and product distribution similar to those of singly bonded **1b** (vide infra), although the formation of products derived from B–N bond-cleavage processes were partially suppressed.

The fate of the metal complexes over the course of the above reactions was examined by <sup>1</sup>H NMR and IR spectroscopy, and it turned out to be different for the singly and triply bonded complexes. The former compounds were found in all cases to transform into corresponding mononuclear hydrides 2. In fact, for chromium complex 1a this transformation takes place spontaneously upon mixing with AB at room temperature. In contrast, for the heavier congeners no reaction was observed at room temperature, and the corresponding hydrides were only formed after heating these mixtures. Thus, molybdenum dimer **1b** was converted completely into hydride 2b only after 12 h of reaction, whereas the tungsten compound was converted into its hydride after nearly 34 h. In contrast, triply bonded complex 3b remained essentially unperturbed over the course of the dehydrogenation reaction. Of course, this implies the occurrence of different reaction mechanisms for the singly and triply bonded complexes, as discussed below. Moreover, the formation of mononuclear hydrides 2 as the active species in the reactions of complexes **1a**-c implies that these reactions are actually running at a higher (ideally 10 mol-%) catalyst loading. Therefore, it can be guessed that the activity of triply bonded **3b** (which is actually running at 5 mol-% loading) would be comparatively higher than that

## Dehydrogenation Reactions of AB Catalyzed by Diphosphane-Bridged Complexes

Treatment of singly bonded dppm-bridged complex 1b' with 20 equiv. (5 mol-% cat.) of AB under the same conditions as those used for complexes **1a-c** did not lead to significant dehydrogenation of the adduct. Instead, the metal complex was transformed completely into a mixture of products containing three known complexes as major organometallic species: triply bonded dicarbonyl 3b' (Figure 1), phosphanylmethyl complex [Mo<sub>2</sub>Cp<sub>2</sub>(µ-Ph<sub>2</sub>PCH<sub>2</sub>)(µ-PPh<sub>2</sub>)- $(CO)_2$ ],<sup>[22b]</sup> and dihydride [Mo<sub>2</sub>Cp<sub>2</sub>(H)<sub>2</sub>( $\mu$ -dppm)(CO)<sub>4</sub>] (2b').<sup>[22a]</sup> Whereas the first two complexes are genuine products of the thermal decarbonylation of 1b' in the absence of AB,<sup>[22b]</sup> the dihydride complex is not, and its formation should follow a pathway similar to that of mononuclear hydrides 2a-c, as discussed below. To check if the low conversions observed in the reaction of 1b' were derived from small amounts of **2b**' generated during the reaction, we decided to test the catalytic activity of pure samples of dihydride 2b' (Table 2). As it can be seen, this was the case, as the catalytic activity of 2b' at short reaction times was comparable to that of hexacarbonyl dimer 1b; however, at high conversions the rate of dehydrogenation became slower and more than 46 h was required to achieve quantitative conversion of the adduct. Although the dehydrogenation products are similar to those observed in the reactions of complexes 1a-c and 3b, there are some significant differences if dihydride 2b' is used as the catalyst. First, a comparatively lower amount of borazine is generated at high conversions (i.e., 28% at 46 h vs. 49% at 24 h for 1b), which



Complex	<i>t</i> [h]	Product dis dppm·BH <sub>3</sub>	tribution [%] µ-ADB	] BH₃•THF	BCDB	CTB <sup>[d]</sup>	Borazine	PB <sup>[e]</sup>	Conv. [%]	TOF [h <sup>-1</sup> ] <sup>[c]</sup>
2b'	6	5	0	0	76	12	5	2	46	
	12	7	0	0	55	22	12	4	67	
	24	5	1	0	39	31	18	6	78	0.3
	34	8	3	0	30	31	20	8	84	
	46	7	5	0	28	31	22	7	92	0.2
3b′	6	5	0	0	61	15	13	6	43	
	12	5	0	0	48	26	15	6	56	
	24	6	3	0	34	30	20	7	75	0.6

Table 2. Thermal dehydrogenation of AB catalyzed by complexes 2b' and 3b' (5 mol-%).<sup>[a,b]</sup>

[a] Reactions were run with [cat] = 0.012 M and  $[AB]_0 = 0.23 \text{ M}$  in THF (0.5 mL). The conversion and product distribution were determined by integration of the corresponding signals in the <sup>11</sup>B{<sup>1</sup>H} NMR spectra. [b] Reaction times were not necessarily optimized. [c] TOF = (% conversion/% loading)/time, with % loading = 10 (for **2b**') and 5 (for **3b**'). [d] The corresponding signal in the <sup>11</sup>B{<sup>1</sup>H} NMR spectrum overlaps one of the resonances of the BCDB, and therefore, the percentage was calculated by difference. [e] The product distribution was calculated on the basis of the corresponding monomer (-BNH<sub>x</sub>-) (x < 1).

implies that the dehydrogenation of the intermediate species (i.e., BCDB and CTB) is significantly slower in this case. Second, the formation of products derived from B–N bond-cleavage processes is also comparatively lower, in particular that of  $\mu$ -ADB [ $\approx 3\%$  for **2b**' vs. 24% for **1b**]. Finally, although complex **2b**' remains essentially unaltered over the course of the reaction, a minor decomposition pathway leads to the liberation of a small amount of dppm, which under the working conditions is rapidly transformed into the corresponding BH<sub>3</sub> adduct (dppm·BH<sub>3</sub>).<sup>[25]</sup>



sions the reaction mixture contained higher amounts of borazine and PB (65 vs. 27%).

#### Dehydrogenation Reactions of tBuNH<sub>2</sub>·BH<sub>3</sub> (tBuAB)

To evaluate the scope of amine-borane adducts that might be efficiently dehydrogenated with the binuclear complexes under study, we tested the catalytic activity of some of these complexes (the most active ones) in the dehydrogenation of the primary  $tBuNH_2 \cdot BH_3$  (tBuAB) adduct. In agreement with previous studies, we found that this adduct is significantly more thermally robust than AB,<sup>[3g]</sup> as a 1.3 M solution of tBuAB in THF remained stable under the reaction conditions used in our work (333 K). However, addition of catalytic amounts (5 mol-%) of complexes **1a**, **1b**, **2b'**, **3b**, and **3b'**<sup>[26]</sup> to these solutions induced dehydrogenation of tBuAB to yield a mixture of products (Scheme 2 and Table 3). We note, however, that these reactions were comparatively slower than those observed for AB.



Figure 1. Complexes used in this work.

The second diphosphane-bridged complex tested as a catalyst was triply bonded  $[Mo_2Cp_2(\mu-dppm)(CO)_2]$ (**3b**'),<sup>[22,26]</sup> which is a diphosphane-substituted analogue of **3b**. This complex also promoted the dehydrogenation of AB (Table 2). In the initial stages of the reaction, this complex induced conversions that were slightly higher than those found for **3b**, but both complexes required approximately 24 h to achieve almost quantitative conversions. However, even if the conversions were similar, the degree of dehydrogenation was higher for tetracarbonyl **3b**, as at high conversions.

Scheme 2.

In terms of conversion, chromium complex 1a was found to be again the most active catalyst among the electronprecise complexes, and it achieved nearly quantitative conversions after roughly 50 h of reaction. Analogous molybdenum complex 1b was less active, with only about 62%conversion after 44 h. Even lower activity was exhibited in this case by diphosphane-bridged dihydride 2b', for which less than 3% conversion was achieved after 12 h, and there-



Complex	t	Product dist	ribution [%]								Conv.	TOF <sup>[d]</sup>
-	[h]	dppm∙ BH <sub>3</sub>	$B_2H_4(\mu-NHtBu)(\mu-H)$	HB(NH <i>t</i> Bu) <sub>2</sub>	<i>t</i> BuHN=BH <sub>2</sub>	$(H_2B-NHtBu)_n^{[c]}$	Poly. I <sup>[c]</sup>	Poly. II <sup>[c]</sup>	(H <sub>2</sub> B– NH <i>t</i> Bu) <sub>2–3</sub>	(HB– NtBu) <sub>3</sub>	[%]	$[h^{-1}]$
1a	14	_	37	8	4	10	0	8	33	0	42	
	44	_	24	16	1	30	2	12	10	5	82	
	148	_	4	11	0	29	9	22	1	24	94	0.06
1b	14	_	50	4	4	6	0	5	31	0	20	
	44	_	28	16	3	38	0	4	9	2	62	
	50	_	23	14	1	42	0	2	9	9	72	
	62	_	15	16	1	49	1	2	6	10	90	0.15
2b'	12	0	0	100	0	0	0	0	0	0	3	
3b	14	_	52	32	8	0	0	0	8	0	9	
	108	_	16	17	2	3	0	14	32	16	88	0.16
3b'	12	1	18	35	1	_	0	25	20	0	46	
	24	1	13	27	1	_	0	21	34	3	62	
	70	1	4	17	2	0	1	20	43	12	90	0.26

Table 3. Thermal dehydrogenation of tBuAB catalyzed by complexes 1a, 1b, 2b', 3b, and 3b' (5 mol-%).<sup>[a,b]</sup>

[a] Reactions were run with [cat] = 0.07 M and  $[tBuAB]_0 = 1.3 \text{ M}$  in THF (0.7 mL). Conversion and product distribution were determined by integration of the corresponding signals in the <sup>11</sup>B{<sup>1</sup>H} NMR spectra. [b] Reaction times were not necessarily optimized. [c] Product distribution was calculated on the basis of the corresponding monomer. [d] TOF = (% conversion/% loading)/time, with % loading = 10 (for 1a, 1b, and 2b') and 5 (for 3b and 3b').

fore, it was not further explored in this reaction. As for the triply bonded complexes, tetracarbonyl **3b** required longer reaction times than singly bonded **1b**, with conversions close to 90% after approximately 108 h of reaction; in contrast, related diphosphane-bridged complex **3b'** exhibited remarkably high activity, with quantitative conversions after about 70 h, and it was the most active catalyst among all of the binuclear compounds here examined.

The dehydrogenation products formed in the above reactions (Scheme 2) were slightly different from those observed for the AB reactions, although they are similar to those reported for other catalytic systems.<sup>[14,27]</sup> The most striking differences are the identification of small amounts of the simplest dehydrogenation product, the aminoborane tBuHN=BH<sub>2</sub>,<sup>[14]</sup> and the presence of poorly defined, presumably polymeric species [<sup>11</sup>B NMR:  $\delta = 41$  (polymer I) and 21 ppm (polymer II)].<sup>[27a]</sup> Notably, aminoboranes are key intermediates in the formation of other reaction products by oligomerization<sup>[16a]</sup> or redistribution reactions.<sup>[28]</sup> In any case, these products were also accompanied by the corresponding borazine-like and cycloborazane products, and the former was favored at long reaction times but was never obtained quantitatively. As found in the AB reactions, we also identified some products derived from B-N bondcleavage processes, such as  $\mu$ -aminodiborane [B<sub>2</sub>H<sub>4</sub>( $\mu$ - $NHtBu)(\mu-H)$ ] and diaminoborane  $[HB(NHtBu)_2]$ ,<sup>[14b]</sup> which were formed in significant amounts.

A second critical difference in the reactions of unsubstituted AB was found for the metallic species present in the reaction media. In the *t*BuAB reactions, singly bonded complexes **1a** and **1b** were again completely transformed after 14 h, but the major organometallic species present were mononuclear anions  $[MCp(CO)_3]^-$  (**4a**, **4b**) along with small amounts of expected hydrides **2a** and **2b**. As discussed below, these anions are inactive in the dehydrogenation of amine-borane adducts, and therefore, their formation under the catalytic conditions is a drawback to the use of complexes **1a** and **1b**, because it actually represents a deactivation pathway (by progressively reducing the amount of hydrides 2 in solution). In contrast, triply bonded complexes 3b and 3b' remained essentially unperturbed over the course of these reactions in a similar way to that observed for the AB dehydrogenations, which thus allows the presence of roughly constant amounts of active metallic species in the solutions.

#### Dehydrogenation Reactions of Me<sub>2</sub>HN·BH<sub>3</sub> (MeAB)

The next step was to test our complexes in the dehydrogenation of borane adducts of secondary amines, for which we used Me<sub>2</sub>NH·BH<sub>3</sub> (MeAB). This adduct has been widely used in studies of this type, because in most cases its dehydrogenation is quite simple and yields almost exclusively the cyclic aminoborane  $[H_2BNMe_2]_2^{[13c]}$  and possible reaction intermediates usually remain soluble.<sup>[3]</sup>

As observed for *t*BuAB, THF solutions of MeAB (1.3 M) remained stable under our particular reaction conditions, but dehydrogenation could be induced by the dimetal complexes (Table 4 and Scheme 3). Remarkably, the most active

Table 4. Thermal dehydrogenation of MeAB catalyzed by complexes 1a, 1b, 2b', 3b, and 3b' (5 mol-% catalyst loading).<sup>[a,b]</sup>

Complex	<i>t</i> [h]	Product dist Me <sub>2</sub> N=BH <sub>2</sub>	ribution [%] HB(NMe <sub>2</sub> ) <sub>2</sub>	(H <sub>2</sub> B-NMe <sub>2</sub> ) <sub>2</sub>	Conv. [%]	TOF [h <sup>-1</sup> ] <sup>[c]</sup>
1a	14	2	5	93	90	0.64
1b	14	0	0	100	11	
	40	0	0	100	99	0.25
2b'	24	3	5	92	18	
3b	14	0	0	100	15	
	68	0	0	100	88	0.26
3b'	12	0	1	99	100	1.67

[a] Reactions were run with [cat] = 0.07 M and [MeAB]<sub>0</sub> = 1.3 M in THF (0.7 mL). Conversion and product distribution were determined by integration of the corresponding signals in the <sup>11</sup>B{<sup>1</sup>H} NMR spectra. [b] Reaction times were not necessarily optimized. [c] TOF = (%conversion/%loading)/time, with %loading = 10 (for 1a, 1b, and 2b') and 5 (3b and 3b').



catalyst for the dehydrogenation of this adduct was again diphosphane-bridged triply bonded complex **3b**', which achieved quantitative conversions at comparatively short reaction times ( $\approx$ 12 h).<sup>[26]</sup> As found in the other reactions discussed above, chromium complex **1a** was also remarkably active, and it provided almost quantitative conversions after only 14 h of reaction.



Scheme 3.

In contrast, slower reactions were observed in the presence of molybdenum complexes **1b**, **2b**', and **3b**. In any case, irrespective of the catalyst used, the major dehydrogenation product was  $[H_2BNMe_2]_2$ .<sup>[13c]</sup> For some of the complexes, this was the only product observed in the reactions. Albeit in very small amounts, two other dehydrogenation species were observed for some of the systems: the monomeric aminoborane  $H_2B=NMe_2$  (a precursor of the corresponding cyclic dimer just mentioned)<sup>[13c,29]</sup> and the diaminoborane  $HB(NMe_2)_2$ .<sup>[13c,30]</sup>

As for the metallic species present over the course of the catalytic reactions, an analogous situation to that discussed for the *t*BuAB reactions was found. Thus, the triply bonded complexes remained essentially unperturbed over the course of the reactions, as did dihydride complex 2b'. However, singly bonded complexes 1a and 1b were completely transformed into a mixture of mononuclear hydrides 2 and corresponding anions 4. In this case, however, the formation of anions 4a and 4b was not as favorable as that found in the *t*BuAB reactions, and in the reactions of molybdenum complex 1b, hydride 2b remained as the major species, whereas for the chromium complex an approximately equimolar mixture of 2a/4a was observed.

#### Discussion

As noted in the preceding section, two different species are involved in the dehydrogenation reactions studied. For the singly bonded complexes, mononuclear hydrides **2** are invariably formed in all of the reactions studied, in a way similar to that observed by Manners and co-workers for  $[Fe_2Cp_2(CO)_4]$  in stoichiometric experiments.<sup>[16a]</sup> Moreover, pure samples of dihydride **2b**' exhibits activity similar to that observed for molybdenum dimer **1b**, but it remains essentially unaltered. Also, in the reactions of adducts derived from substituted amines, we observed the formation of significant amounts of mononuclear anions **4**, which were accompanied by a significant decrease in the rates of the dehydrogenation reaction. Therefore, it seems reasonable to assume that the hydrides are either the true catalysts or the catalyst precursors in these reactions. In contrast, the triply bonded complexes remained essentially stable over the course of their reactions, and therefore, these species should be the active catalysts in the corresponding dehydrogenation reactions. Thus, two alternative pathways should be formulated for these reactions, depending on the dimetal complex being used.

#### Proposed Reaction Mechanism for Singly Bonded Complexes 1a-c and 2b'

For tricarbonyl dimers 1a-c, the catalytic reactions should start with the formation of mononuclear hydrides 2 (Scheme 4). This can be fully rationalized by recalling the well-established trend of the parent dimers to undergo homolytic M-M bond cleavage to yield metal-centered radicals of formula [MCp(CO)<sub>3</sub>] (A in Scheme 4).<sup>[17,18]</sup> These 17-electron radicals are highly reactive, and they can evolve through a number of reactions such as simple recombination (to give the parent dimers)<sup>[31]</sup> or hydrogen/halogen abstraction,<sup>[31a,32]</sup> among others. In our case, hydrogen abstraction from the amine-borane adducts would take place rapidly owing to the large excess amount of these adducts present in the initial stages of the reaction, which would generate hydrides 2a-c (Scheme 4). By assuming that hydrogen abstraction is a fast process, the extent of the formation of the corresponding hydrides would then be related to the strength of the respective intermetallic bonds in the metal dimers ( $Cr \ll Mo \ll W$ ). This is actually supported by our experimental observations, as fast conversion into hydride



Scheme 4.



2 takes place only for chromium dimer 1a (weakest M–M bond), whereas for the molybdenum and tungsten complexes this transformation only goes to completion at longer reaction times. In addition, separate experiments proved that molybdenum hydride 2b was formed rapidly and quantitatively upon photochemical irradiation (10 min, 298 K) of a typical reaction mixture of AB and 1b (5 mol-% loading) without causing significant dehydrogenation of the adduct; even more importantly, heating these mixtures led to a dehydrogenation reaction that was somewhat faster than that of the dark reactions.

Notably, abstraction of hydrogen from amine- and phosphane-borane adducts by different radical species has been extensively studied by Roberts and co-workers,<sup>[33]</sup> who observed preferential activation of the B-H bonds of the amine-borane adducts in all cases to yield B-centered radicals of formula  $[R_xH_{3-x}N-BH_2]$  (**B** in Scheme 4) as products of kinetic control. Depending on the substituents and on the particular experimental variables, these transient amine-boryl species were observed to evolve through various pathways, which all led to the quenching of the boryl radical. Among these pathways, they observed the isomerization to aminyl-borane radicals (thermodynamically more stable) and the release of hydrogen to yield aminoboranes  $[R_xH_{2-x}N=BH_2]$ .<sup>[33]</sup> In a similar way, tricarbonyl radicals A would abstract hydrogen from the amine-borane adducts to yield hydrides 2 and the corresponding monomeric aminoboranes, which is consistent with the detection of significant amounts of these monomers in the catalytic reactions of the substituted amine-borane tBuAB and MeAB adducts. Moreover, the liberation of free aminoborane species would account for the formation of most of the dehydrogenation products observed in our catalytic reactions through off-metal processes such as oligomerization [i.e.,  $(\mathbf{R}_{x}\mathbf{H}_{2-x}\mathbf{N}-\mathbf{B}\mathbf{H}_{2})_{n}$  by reaction with unreacted adduct (i.e., BCDB) or by redistribution processes.<sup>[28]</sup> Such off-metal processes of aminoboranes have been recently proposed to occur in reactions of photoactivated precatalysts  $[Fe_2Cp_2(CO)_4]^{[16a]}$  and  $[M(CO)_6]$  (M = Cr, Mo, W).<sup>[14a]</sup>

Up to this point, only stoichiometric conversion of the amine-borane adducts into aminoborane and hydrogen would be attained. To explain the observed full conversions of the amine-borane adducts, a catalytic cycle should take place on the basis of hydrides 2. For this, however, two reaction pathways are conceivable. First, hydrides 2 could experience thermal dehydrogenation to regenerate 17-electron radicals A, which then would react again with more amineborane to yield parent hydrides 2 (pathway I in Scheme 4). Indeed, hydrides 2a-c have been reported to undergo thermal dehydrogenation to yield dimers 1a-c via radicals A.<sup>[20]</sup> As an alternative route (pathway II in Scheme 4), direct reaction of hydrides 2a-c with the amine-borane adducts might liberate hydrogen to generate unstable amine-stabilized boryl intermediate C (Scheme 4). Notably, we cannot exclude the alternative activation of an N-H bond of the amine-borane adduct to yield a borane-stabilized amido complex; however, we reasoned that such a process would be of higher energy by taking into account the different

bond energies involved (N–H > B–H). Even if we have not been able to identify this type of species in our reactions, we note that the coordination mode of the boryl ligand in C has been previously observed in related species,<sup>[3b]</sup> such as the mononuclear complexes of formula [MX(CO)<sub>3</sub>- $(BH_2PMe_3)$  [X = Cp, C<sub>5</sub>Me<sub>5</sub> (Cp\*); M = Mo, W] previously reported by Shimoi and co-workers.<sup>[34]</sup> Interestingly, the latter complexes were prepared through photolysis of the methyl derivatives  $[MX(CO)_3Me]$  in the presence of the phosphane-borane adducts with concomitant evolution of CH<sub>4</sub>. Two other important observations were reported by Shimoi: (1) The Cp derivatives were found to be rather thermally unstable. (2) The use of the Me<sub>3</sub>N·BH<sub>3</sub> adduct instead of Me<sub>3</sub>P·BH<sub>3</sub> did not yield stable boryl complexes. Therefore, it seems reasonable that, under our reaction conditions, intermediates C would be rather unstable species. In this case, a simple  $\beta$ -elimination step of the coordinated amine-boryl ligand would regenerate hydrides 2 while releasing aminoborane, in a process which would likely involve reversible loss of CO to generate unsaturated species akin to those proposed for the related reactions of the methyl derivative just mentioned. We should finally note that, although all of the preceding discussion explains the formation of products in which only one equivalent of hydrogen is lost, it can be assumed that similar processes occurring for already dehydrogenated species would then account for the formation of products in which two or more equivalents of hydrogen were released, such as borazine or polyborazylene.

We should stress that both pathways I and II (Scheme 4) would imply the consumption of the amine-borane adduct with production of only hydrogen and the corresponding aminoboranes as primary products, so we cannot rule out either mechanism. However, there are two experimental observations that would suggest the prevalence of pathway II. First, in the reaction with molybdenum complex 1b, even at long reaction times (when the concentration of unreacted amine-borane is low), the only metal-containing species in solution is hydride 2b (or its deprotonated anion 4b); however, if pathway I was to be dominant we would expect the presence of the parent dimer (generated through radical coupling reactions) at long reaction times. Second, as mentioned above, amine-boryl radicals are liberated in pathway I rather than aminoboranes, and it is known that these species can evolve through various reaction paths to yield different products,<sup>[33]</sup> that is, radical homocoupling reactions; however, in all of our reactions, the formation of these products was not observed.

As noted above, for all of the borane adducts studied we observed the formation of products with B/N ratios different from unity, which necessarily are formed through B–N bond-cleavage reactions. These products were observed previously in other transition-metal-catalyzed dehydrogenation reactions, and they are presumably formed through reactions of the free amine or borane entities with the aminoborane<sup>[15b]</sup> or amine–borane.<sup>[24c]</sup> However, in the reactions of complexes **1a–c**, the presence of free amines has an additional negative consequence: the formation of variable

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amounts of anions 4, particularly in the reactions of the tBuAB and MeAB adducts. As it can be seen from the data in Table 5, hydrides 2a-c are moderately acidic molecules that are susceptible to undergo deprotonation if confronted with bases, and then, the presence of free amine in the reaction media could explain the formation of anions 4 by simple deprotonation (Scheme 5). Indeed, an independent experiment revealed that the addition of diisopropylamine to a freshly prepared solution of molybdenum hydride 2b led immediately to the corresponding anion 4b. However, if we keep in mind that ammonia is only slightly less basic than the substituted tBuNH<sub>2</sub> or Me<sub>2</sub>NH amines, the fact that we did not observe the formation of anions 4 in the reactions of AB must be attributed to its higher volatility, especially in reactions running at 333 K, which would effectively reduce its presence in solution. In agreement with this, the reactions of the tBuAB adduct (which would liberate the amine with the highest boiling point) are those for which higher amounts of anions 4 were observed. In any case, the formation of these anions is always accompanied by a drastic decrease in rate of dehydrogenation.

Table 5. pK values and boiling points for free amines and hydrides **2a**-c.

Compound	pK <sub>a</sub>	$pK_b$	b.p. [K]
NH <sub>3</sub> <sup>[a]</sup>		4.79	240
tBuNH <sub>2</sub> <sup>[a]</sup>		3.55	317
Me <sub>2</sub> NH <sup>[a]</sup>		3.36	280
<i>i</i> Pr <sub>2</sub> NH <sup>[a]</sup>		2.95	357
[CrCpH(CO) <sub>3</sub> ] <sup>[b]</sup>	13.3		_
[MoCpH(CO) <sub>3</sub> ] <sup>[b]</sup>	13.9		_
[WCpH(CO) <sub>3</sub> ] <sup>[b]</sup>	16.1		_

[a] Values in  $\rm H_2O$  solution taken from ref.^{[35]} [b] Values in NCMe solution taken from ref.^{[36]}



Scheme 5.

### Proposed Reaction Mechanism for Triply Bonded Complexes 3b and 3b'

As noted above, the catalytic reactions of the triply bonded complexes should involve a mechanism that is different from the one just discussed for the singly bonded compounds, as complexes 3b and 3b' undergo no net transformation over the course of their catalytic reactions. Presumably, the first step in this case would be the simple coordination of the amine-borane adduct to the dimetal center through one or two of the B–H bonds (D in Scheme 6). Clearly, this step would be greatly facilitated by the electronic and coordinative unsaturation of the dimetal center in these 30-electron complexes. Although we could not identify any intermediate in our reactions, we note that such a coordination mode has been previously observed for the tetrahydroborate ligand<sup>[37]</sup> {i.e.,  $[Mn_2(\mu-\eta^2:\eta^2-BH_4)(\mu-H)-$ (CO)<sub>6</sub>(µ-dppm)]<sup>[37a]</sup> and [Mo<sub>2</sub>Cp<sub>2</sub>(µ-SMe)<sub>2</sub>(µ-CCH<sub>2</sub>Ph)(µ- $\kappa^{1}$ : $\kappa^{1}$ -BH<sub>4</sub>]<sup>[37b]</sup>, and it has been recently substantiated in the borane- and boryl-bridged dirhodium cation [Rh<sub>2</sub>H<sub>2</sub>(µ- $\kappa^{1}:\eta^{2}-H_{2}BNMe_{3})_{2}(\mu-\eta^{2}:\eta^{2}-H_{3}BNMe_{3})(PCy_{3})_{2}]^{2+.[38]}$  In any case, the coordination of these ligands (formally acting as four-electron donors) converts intermediate D into a saturated 34-electron complex with a single intermetallic bond. The next step might involve the oxidative addition of one of the coordinated B-H bonds to yield complex E with hydride and amine-boryl ligands akin to that proposed for the singly bonded complexes. Although the presence of two metal centers increases the number of possible coordination modes of this group, a simple  $\beta$ -elimination step would lead again to the liberation of the corresponding aminoborane and the generation of dihydride complex F. Such an intermediate would be related to  $[Mo_2Cp*_2(CO)_4(\mu-H)_2]$ , a complex reported some time ago by Alt and co-workers as a product of the hydrogenation of  $[Mo_2Cp_2(CO)_4]$  under photolytic conditions in a process found to be fully reversible.<sup>[39]</sup> These authors noticed that no dihydride complex was formed for the analogous Cp complex [Mo<sub>2</sub>Cp<sub>2</sub>-(CO)<sub>4</sub>] under similar conditions, and therefore, it would not be surprising that in our reactions putative dihydrides F would quickly release hydrogen to regenerate catalytically active species 3.



Scheme 6.

Overall, this catalytic cycle would consume the amineborane adducts to produce hydrogen and free aminoboranes as primary products. Further interaction of complexes **3b** and **3b**' with the oligomerization products of the latter aminoboranes would be much slower if we take into account the significantly slower dehydrogenations observed for the *t*BuAB and MeAB adducts (relative to AB) in the presence of complexes **3**. If we keep in mind that the first step of the mechanism is the coordination of the amineborane adducts to the dimetal center, we can guess that all of this might have a steric origin, that is, a more difficult



approach to the dimetal center because of unfavorable interactions with the alkyl chains.

A related observation that might be counterintuitive is that complex 3b' (having a bulky dppm bridging ligand) displays higher dehydrogenation rates than its tetracarbonyl relative 3b for some adducts. However, we must recall that although these two complexes are isoelectronic, they are not isostructural: in complex 3b four carbonyl ligands bridge the dimetallic center, whereas in 3b' there are only two CO bridging ligands and the diphosphane ligand occupies two essentially terminal positions in a forced *cis* disposition. Eventually, this renders a more accessible dimetal center in dppm-bridged complex 3b'.

#### Conclusions

We have found that readily accessible group 6 binuclear cyclopentadienyl complexes having single and triple M-M bonds are efficient catalysts for the dehydrogenation of a range of amine-borane adducts, including ammonia-borane, under mild thermal activation (333 K). The activity observed for these complexes is comparable to that reported by Manners and co-workers for the [Fe<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub>] iron dimer under photochemical conditions<sup>[16a]</sup> with the advantage that in our case these reactions occur under thermal conditions rather than photochemical activation. Although these systems are not close to the fastest catalysts developed so far (based on Rh and Ir complexes, with TOF values close to  $6000 \text{ h}^{-1}$ ,  $[^{3h,5a,8e]}$  their activity is comparable to a broad range of mononuclear transition-metal complexes used to induce these transformations (with TOF values of 0.1-2.8 h<sup>-1</sup>).<sup>[3h]</sup>

For all of the adducts studied, the dehydrogenation products are similar to those observed for other transition-metal catalysts and their formation can be rationalized by the occurrence of two alternative reaction pathways: (1) neat dehydrogenation processes (dominant) and (2) B-N bondcleavage processes. The latter leads to products in which the ratio B/N is different from unity, whereas the former implies the metal-mediated generation of the corresponding  $(R_xH_{2-})$  $_{x}$ N=BH<sub>2</sub>) aminoboranes as intermediate species, which could be identified for the tBuNH<sub>2</sub> and Me<sub>2</sub>NH adducts. Once formed, however, the aminoboranes would evolve through essentially off-metal processes (oligomerization or redistribution). In turn, some of the products thus generated are able to undergo further dehydrogenation mainly leading to the formation of borazine-like products, which then represent a net loss of two equivalents of hydrogen. In the case of the  $[M_2Cp_2(CO)_6]$  (M = Cr, Mo, W) singly bonded complexes, the metal center and, in particular, the different M-M bond strengths have a strong influence on the final catalytic activity, which drops significantly when going down in the group. Under the reaction conditions used, these complexes are transformed into the catalytically active mononuclear hydrides [MCpH(CO)<sub>3</sub>], in a reaction which is instantaneous and complete only for the Cr dimer, whereas it is significantly slower for the Mo and W derivatives. This different behavior correlates with the corresponding M–M bond strength (W > Mo>> Cr) in the parent dimers. In the reactions with adducts derived from substituted amines, B-N bond dissociation of the adduct causes a significant decrease in the rate of dehydrogenation, because the liberated amine deprotonates the hydride complexes to yield the inactive mononuclear anions [MCp- $(CO)_3$ , which then reduces the concentration of hydride complexes in solution. In contrast, multiple metal-metal bonding confers higher stability to the dinuclear systems in these reactions, as deduced from the fact that the  $[Mo_2Cp_2(CO)_2(L_2)][L_2 = (CO)_2 \text{ and } \mu\text{-dppm}] \text{ complexes re-}$ mained essentially stable during the catalytic reactions. In spite of this, these complexes displayed similar or even higher activity than their singly bonded relatives in the dehydrogenation of some of the adducts studied, which proves that the electronic and coordinative unsaturation associated with the triple intermetallic bonds have a beneficial effect in terms of catalytic activity. Moreover, to the best of our knowledge, those unsaturated complexes are the first complexes with multiple M-M bonds shown to display catalytic activity in the dehydrogenation of amine-borane adducts, which then raises the question whether other complexes with multiple intermetallic bonds might display similar or even higher activity in these types of processes, a question

that we are currently addressing in our laboratory.

#### **Experimental Section**

General Procedures: All reactions and manipulations were performed under a nitrogen atmosphere by using standard Schlenk or glove box techniques. Solvents were purified according to literature procedures<sup>[40]</sup> and distilled under a nitrogen atmosphere prior to use.  $NH_3 \cdot BH_3$ ,<sup>[41]</sup> [M<sub>2</sub>Cp<sub>2</sub>(CO)<sub>6</sub>] [M = Cr (1a), W (1c)],<sup>[42]</sup>  $[Mo_2Cp_2(\mu-dppm)(CO)_2]$  (3b'),<sup>[22]</sup> and  $[Mo_2Cp_2H_2(\mu-dppm)(CO)_4]$ (2b')<sup>[22a]</sup> were prepared as described previously. All other reagents were obtained from the usual commercial suppliers and used as received, except for the Me<sub>2</sub>NH·BH<sub>3</sub> and tBuNH<sub>2</sub>·BH<sub>3</sub> adducts, which were sublimed twice and stored under a nitrogen atmosphere. IR stretching frequencies were measured in solution by using CaF<sub>2</sub> windows. NMR spectra were routinely recorded at 300.13 (1H), 121.50  $({}^{31}P{}^{1}H{})$ , and 161.47 MHz  $({}^{11}B$  and  ${}^{11}B{}^{1}H{})$  at 290 K in THF solutions unless otherwise stated. To eliminate the B-O broad resonance arising from the borosilicate glass of the NMR tube and probe, all of the <sup>11</sup>B FIDs were processed with back linear prediction (≈24 points) by using the MestReNova program.<sup>[43]</sup> Under these processing conditions, total conversions and relative distributions of the dehydrogenation products in the catalytic reactions might be slightly affected by the different relaxation times of the B nuclei involved, so the data provided in Tables 1-4 must be taken as approximate product distributions rather than quantitative determination of all the species present.

**Example of Dehydrogenation Reaction for AB:** In a typical experiment, the required amount of catalyst (0.006 mmol) was added to an NMR tube fitted with a Young valve. Then, a solution of AB [0.23 M in THF/C<sub>6</sub>D<sub>6</sub> (10:0.1), 0.5 mL, 0.115 mmol] was added, and the valve was closed. The sample was then heated at 333 K for a fixed time (6, 12 h, etc.), and the overall conversion and product distribution were evaluated by <sup>11</sup>B NMR spectroscopy.



**Example of Dehydrogenation Reaction for tBuAB and MeAB:** In a typical experiment, the required amount of catalyst (0.046 mmol) and the corresponding adduct (0.91 mmol) were dissolved in THF/ $C_6D_6$  (10:0.1, 0.7 mL). The resulting solution was then transferred to an NMR tube fitted with a Young valve, and the valve was closed. The headspace volume was vacuumed by freeze–pump cycles, and the tube was sealed under static vacuum in the final cycle. The sample was then heated at 333 K for a fixed time (6, 12 h, etc.), and the overall conversion and product distribution were evaluated as above.

Supporting Information (see footnote on the first page of this article):  ${}^{11}B{}^{1}H{}$  NMR stacking plots for selected dehydrogenation reactions.

#### Acknowledgments

We thank the European Commission (Project PERG08-GA-2010-276958) for supporting this work and the Consejería de Educación of Asturias for a "Clarín" postdoctoral reintegration grant (D. G.-V.).

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Received: May 15, 2013 Published Online: August 9, 2013