ORGANOMETALLICS

Osmium-Promoted Dehydrogenation of Amine–Boranes and B–H Bond Activation of the Resulting Amino–Boranes

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Supporting Information

ABSTRACT: The five-coordinate osmium complex OsH- $(SH)(CO)(P^{i}Pr_{3})_{2}$, containing an electrophilic center bonded to the soft hydrogen sulfide ligand, promotes dehydrogenation of amine-boranes and captures the amino-borane products, forming hydrogenaminothioborate complexes.

The increased consumption of fossil sources is anticipated to have substantial negative consequences for the environment, in particular the large anthropogenic atmospheric carbon dioxide emission. Reducing our current environmental footprint will require significant changes in the way we produce, distribute, store, and use energy. A crucial step in the process is decreasing our dependence on carbon-based fossil fuels. Thus, the development of alternative sources to fossil-based energy is the most critical scientific challenge of this century.¹ However, the discontinuity of these alternative sources is a serious problem. For example, the diurnal nature of solar energy requires an effective way to store the converted energy. In this context, the high energy density offered by chemical storage provides a promising alternative: in particular, molecular hydrogen is the most efficient and clean energy carrier known.²

Homogeneous catalysts of transition metals offer great control over the kinetics of H_2 release from ammonia–borane,³ which has a hydrogen capacity of 19.6% in weight. As a consequence, amine–borane adducts are attracting a great deal of interest as vectors for hydrogen storage.⁴ Unfortunately, the ammonia–borane dehydrogenation generally leads to polymeric materials, which are difficult to recycle.⁵ A promising pathway toward the solution of this problem could be to trap the dehydrogenated monomer before the polymerization reaction. Therefore, the development of systems able to promote both ammonia–borane dehydrogenate is of general interest.

The transition-metal-promoted heterolysis of B–H bonds generally requires N and O hard bases with free electron pairs. We have recently shown that the five-coordinate osmium complex $OsH(SH)(CO)(P^iPr_3)_2^6$ (1), containing an electrophilic center bonded to the soft hydrogen sulfide ligand, promotes the heterolytic B–H activation of pinacolborane



(HBpin), catecholborane (HBcat), and the diborane 9borabicyclo[3.5.1]nonane dimer ((HBbn)₂) along with a heterolytic H–H formation, to afford dihydrogen–borylthiolate



complexes (eq 1).⁷ Now, we have observed that complex 1 catalyzes the dehydrogenation of amine-boranes and traps the



Figure 1. Monitoring of the amount of H_2 released in the catalytic dehydrogenation of a 0.167 M solution of BH_3NH_3 in THF with 5 mol % of 1.

Received: January 13, 2014 Published: February 18, 2014 Scheme 1. Preparation of Complexes 2-4





Figure 2. Molecular diagram of 2 with 50% probability ellipsoids. Hydrogen atoms, except those bonded to the osmium and nitrogen atoms, are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os-S 2.501(2), 2.479(2), 2.493(2); P-Os-P 163.05(7), 166.33(7), 164.21(7); H-Os-H 166(3), 178(3), 171(3); C-Os-S 166.8(2), 172.1(3), 168.7(2); S-Os-H(B) 75.0(15), 75.5(15), 75.8(15).



Figure 3. Contour line diagrams $\nabla^2 \rho(r)$ for complex **2** in the Os–S–B plane. Solid lines indicate areas of charge concentration ($\nabla^2 \rho(r) < 0$), while dashed lines show areas of charge depletion ($\nabla^2 \rho(r) > 0$). The black solid lines connecting the atomic nuclei are the bond paths, while the small green and red spheres indicate the corresponding bond critical points and ring critical points, respectively. The solid lines separating the atomic basins indicate the zero-flux surfaces crossing the molecular plane.

resulting amino-boranes. This communication describes the first osmium catalyst for the dehydrogenation of these

hydrogen carriers and reveals that the cooperating⁸ hydrogen sulfide ligand facilitates the capture of the dehydrogenated monomer, forming unprecedented hydrogenaminothioborate ligands. Furthermore, the bonding interactions between the metal and this novel type of ligand will be described.

Complex 1 promotes the release of 1 mol of molecular hydrogen, per mole of substrate, from ammonia-borane and dimethylamine-borane, with turnover frequency values at 50% conversion (TOF_{50%}) of 43 and 7 h^{-1} , respectively, in tetrahydrofuran as solvent, at 31 °C. Figure 1 shows the course of the dehydrogenation of ammonia-borane, which yields borazine ($\delta_{11}{}_{B}$ 31.5, J_{B-H} = 129 Hz), polyborazylene ($\delta_{11}{}_{B}$ 27.4), and B-(cyclodiborazanyl)aminoborohydride (δ^{μ}_{B} –4.5 (J_{B-H} = 107 Hz), -10.5, and -23.4)⁹ as dehydrogenation products, according to the ¹¹B NMR spectra at 50% and at the end of the dehydrogenation. The formation of these products appears to result from off-metal processes. Recent quantum-chemical investigations have shown that nucleophilic solvents and early intermediates, such as B-(cyclodiborazanyl)aminoborohydride, catalyze the oligomerization of amino-boranes to form cyclic oligomers at low activation barriers through nucleophilic assistance.¹⁰ The ¹¹B NMR spectrum of the solution at the end of the dimethylamine-borane dehydrogenation process contains at 4.9 ppm the characteristic triplet ($J_{B-H} = 113 \text{ Hz}$) corresponding to the dimer [H₂BNMe₂]₂. This compound seems to result from an off-metal dimerization of H₂B=NMe₂. No traces of the linear diborazane H₃B-NMe₂-BH₂-NHMe₂ were observed at any point of the reaction.⁴ⁱ

Complex 1 captures the amino-borane monomers, before their coupling, to form the hydrogenaminothioborate derivatives $O_{sH}(CO) \{\kappa^2 - H_s S - [HB(S)(NR_2)]\} (P^i Pr_3)_2 \ (R = H \ (2),$ Me (3), at low concentrations of the amine-borane substrates. Thus, complexes 2 and 3 are the main metallic species at the end of the respective dehydrogenation processes, according to the ³¹P{¹H} NMR spectra of the resulting solutions. These compounds and the tert-butyl counterpart $OsH(CO){\kappa^2-H,S-[HB(S)(NH^tBu)]}(P^iPr_3)_2$ (4) were prepared as white solids in high yields (75-86%), under stoichiometric conditions, by means of the treatment of toluene solutions of 1 with 1.2 equiv of the amine-borane at room temperature. They are stable in the presence of amine-borane and do not promote the respective dehydrogenation process. Therefore, the catalysis is possible because the reaction between the metal center and the amine-borane substrates is faster than the process involving the amino-borane dehydrogenation products.

Table	1.	EDA	Results	for	Comple	x 2	Computed	l at tl	he BP86,	/TZ2P/	//BP86,	/def2-SVP	Level"
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$\Delta E_{ m int}$	$\Delta E_{ m Pauli}$	$\Delta E_{\mathrm{elstat}}^{b}$	$\Delta E_{\mathrm{orb}}{}^{b}$	$\Delta E_{\sigma}^{\ c}$	$\Delta E_{\pi}^{\ c}$	$\Delta E_{ m prep}$	$\Delta E = -D_{\rm e}$
-157.6	177.7	-220.6 (65.8)	-114.7 (34.2)	-94.1 (82.0)	-20.6 (18.0)	15.7	141.9
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^{*a*}Energy values are given in kcal/mol. ^{*b*}The values in parentheses (in %) give the contribution to the total attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$. ^{*c*}The values in parentheses (in %) give the contribution to the total orbital interactions ΔE_{orb} .



Figure 4. (a) π molecular orbital HOMO-4. (b, c) NBO orbitals responsible for the (b) B-H-Os(p) and (c) LP(S)-Os(p) interactions. Orbitals were computed at the BP86/def2-SVP level (isosurface of 0.035 au).

The formation of 2-4 can be rationalized according to Scheme 1. The reactions of 1 with the amino-boranes generated from the dehydrogenation of the amine-boranes could initially lead to dihydrogen- κ^1 -S-hydrogenaminothioborate intermediates $OsH{\kappa^1-S-[HB(S)(NR_2)]}(CO)(\eta^2-H_2)$ - $(P^{i}Pr_{3})_{2}$ (a), analogous to the dihydrogen-borylthiolate compounds shown in eq 1. The reaction should follow a four-step mechanism similar to that reported for the reaction between 1 and pinalcolborane, / including (i) interaction of one of the B-H bonds of the amino-borane with the Os-S bond of 1, (ii) elongation of the B–H bond, (iii) rupture of the B–H bond to form a *trans*-dihydride species, and (iv) hydrogen transfer from the S atom to one of the hydride ligands via an $Os\{\eta^2$ -H-S-[BH(NR₂)] transition state. The dissociation of the dihydrogen ligand of the dihydrogen- κ^1 -S-hydrogenaminothioborate intermediates **a** and the κ^1 -S into κ^2 -H,S transformation of the hydrogenaminothioborate groups should finally afford the isolated compounds.¹¹

The formation of the novel hydrogenaminothioborate ligands is demonstrated by the X-ray structure of 2, which further proves the existence of this type of compound. The structure has three chemically equivalent but crystallographically independent molecules in the asymmetric unit. Figure 2 shows one of them. The coordination geometry around the metal center can be rationalized as a distorted octahedron with trans phosphines $(P-Os-P = 163.05(7)-166.33(7)^{\circ})$. The hydride and carbonyl ligands lie at the perpendicular plane disposed trans to the hydrogen and sulfur atoms, respectively, of the hydrogenaminothioborate group (H-Os-H = 166(3)- $178(3)^{\circ}$ and C-Os-S = 166.8(2)-172.1(3)^{\circ}, which acts with a bite angle between 75.0(15) and 75.8(15)°. The angles around the boron, between 104.6(8) and $132.8(7)^{\circ}$, suggest an sp² hybridization for this atom. The separation between the latter and the metal center (2.319(9)-2.356(11)Å) is about 0.4 Å longer than that in the complex $OsH_2Cl\{\eta^2-H-B(NMe_2)\}$ - $(P^{i}Pr_{3})_{2}$ (1.923(6) Å),¹² suggesting no interaction between the osmium and boron atoms. The ¹H, ³¹P{¹H}, and ¹¹B NMR spectra of 2-4 are consistent with the structure shown in Figure 2. In agreement with the presence of the hydride ligand, the ¹H NMR spectra show at about -9.5 ppm triplets with H-P coupling constants of about 20 Hz, whereas the B-H hydrogen atom displays broad signals at about -7.6 ppm. As

expected for equivalent phosphine ligands, the ${}^{31}P{}^{1}H$ NMR spectra contain singlets at about 27 ppm. Broad signals between 33 and 38 ppm in the ${}^{11}B$ NMR spectra are also a characteristic feature of these compounds.

The bonding situation of complex **2** was analyzed by means of DFT calculations at the BP86/def2-SVP level using the AIM (atoms in molecules), NBO (natural bond orbital), and energy decomposition analysis (EDA) methods (see the Supporting Information).

The AIM method locates bond critical points (BCPs) between the transition metal and the sulfur and hydrogen atoms associated with bond paths (BPs) running between these atoms (Figure 3). In contrast, there are no BCPs (or BPs) between the osmium and the boron atoms, confirming that the Os…B interaction is not significant. This agrees with the computed Os-B NBO-Wiberg bond index (WBI) of 0.30; this is similar to that found for the vinylaminoborane complex $Cr{\kappa^{3}-H,C,C[HB(CH=CHMe)N(SiMe_{3})_{2}]}(CO)_{4}$ (0.23), which in addition to the coordinated C-C double bond shows a Cr-HB interaction.¹³ However, the WBI in 2 is clearly lower than the value computed for the Os-B bond in the osmium-boryl complex $[OsH_2(Bpin)(\eta^6-p-cymene)(IPr)]^+$ (IPr = 1,3-bis(2,6-diisopropylphenylimidazolylidene); 0.58),¹⁴ which features a distinctive metal-boron single σ bond. Moreover, the Laplacian distribution in the Os-S-B bonding region exhibits an area of charge concentration ($\nabla^2 \rho(r) < 0$, solid lines) at the sulfur atom directed toward the osmium atom, which carries an area of charge depletion ($\nabla^2 \rho(r) > 0$, dashed lines). This is typical for a closed-shell donor-acceptor bond.¹⁵ Therefore, according to the AIM analysis complex 2 should be viewed as an acceptor $[(P^{i}Pr_{3})_{2}(CO)OsH]^{+}$ fragment interacting with the $[HB(S)(NH_2)]^-$ donor ligand.

Quantitative insight into the bonding situation in 2 can be obtained with the EDA method (Table 1). The computed high dissociation energy in the gas phase indicates a strong interaction between the [(PⁱPr₃)₂(CO)OsH]⁺ and [HB(S)- (NH_2) ⁻ fragments. The main contribution to the total attractions comes from the electrostatic term (ca. 66% to the total bonding), which is not surprising if we take into account that charged fragments are used. Despite that, the orbital term is also quite significant (ca. 34%), indicating a substantial covalent character. Further partitioning of the ΔE_{orb} term indicates that although σ bonding becomes the main contributor to the total orbital attractions (82%), significant π bonding (18%) is also present. This becomes evident from the inspection of the HOMO-4 (Figure 4a), which can be viewed as a π molecular orbital involving the sulfur and osmium atoms. According to second-order perturbation theory (SOPT) of the NBO method, the σ bonding is the result of two main contributions, that involving the 2e of the Os-H-B bond and 2e donation from the sulfur lone pair to a vacant osmium p atomic orbital (associated SOPT energies $\Delta E^{(2)}$ of -133.6 and -94.6 kcal/mol, respectively; Figure 4b,c, respectively).

The perpendicular disposition of the $[HB(S)(NH_2)]^-$ ligand with regard to the P–Os–P axis resembles that found for the boryl groups in the Os–bis(boryl) complex OsH(Bcat)₂Cl-

(PⁱPr₃)₂, which exhibits stabilizing CH– π interactions between the closest methyl groups of the phosphines and the vacant p_z (π^*) atomic orbital of the boron atoms.¹⁶ For complex **2**, the SOPT of the NBO method locates similar stabilizing delocalizations (σ -C–H \rightarrow p_z-B, one interaction per phosphine; see the Supporting Information) with a computed $\Delta E^{(2)}$ energy of –1.9 kcal/mol (CH…B bond distance of 2.568 Å). Moreover, the lone pairs of sulfur and nitrogen atoms produce an additional stabilization of the [HB(S)(NH₂)]⁻ ligand, as they can delocalize into the atomic p_z boron orbital as well (associated SOPT energy $\Delta E^{(2)} = -57.6$ and -65.1kcal/mol, respectively). As a consequence of these electronic delocalizations, the atomic p_z-B orbital presents a significant electronic occupation (0.58e).

In conclusion, our results demonstrate that unsaturated complexes containing an electrophilic metal center coordinated to a soft base with free electron pairs not only promote the release of molecular hydrogen from amine—boranes but also capture the amino—borane dehydrogenation products, before their coupling to form polymers or oligomers.

ASSOCIATED CONTENT

S Supporting Information

Text, figures, a table, and a CIF file giving experimental details and characterization data, X-ray data, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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