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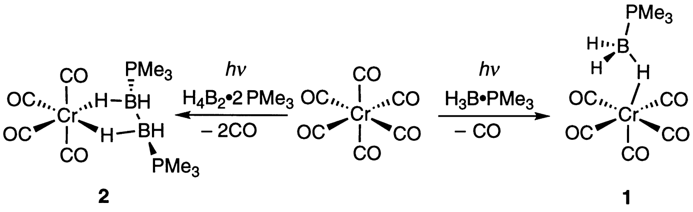
B–H Bond Activations in the Alkane Analogues $H_3B \cdot PR_3$

Warren E. Piers*

The selective, catalytic functionalization of normally inert C–H bonds has been called one of the "Holy Grails" of chemistry.[1] Consequently, much effort has been expended towards understanding the mechanism of C–H bond activation by homogeneous transition metal compounds. In contrast, comparatively little has been done on the activation of bonds in compounds which are isoelectronic to alkanes. The relationship between BH_4^- and CH_4 has been noted, but analogies between complexes formed through ligation of BH_4^- and the more elusive σ complexes of CH_4 are tenuous, based on the obvious difference in charge for these two species. For instance, with the exception of a few examples, BH_4^- tends to bind metals in an η^2 fashion, while CH_4 has been computationally predicted to assume an η^1, end-on bonding posture.[2] Thus, while the borohydride complexes $[(CO)_4M(\eta^2\text{-}BH_4)]^-$ (M = Cr, W) are known,[3] they serve as poor structural models for the methane complexes $[(CO)_5M \cdot CH_4]$ observed when $[M(CO)_6]$ is photolyzed in a methane matrix.[4]

To eliminate this difference and provide a more useful chemical analogy, Shimoi et al. have recently examined the photolysis of $[M(CO)_6]$ in the presence of $H_3B \cdot L$ (L = PMe_3, PPh_3, NMe_3),[5] methane analogues which are both isoelectronic and neutral. The products isolated, in excellent yield, are remarkable η^1-borane complexes of the $M(CO)_5$ fragment that contain an unsupported M-H-B interaction (exemplified by **1**; Scheme 1). The increased stability of these alkane-analogue σ complexes allowed for complete characterization, including four examples crystallographically.



Scheme 1.

All the structural and spectroscopic data for $[(CO)_5M(\eta^1\text{-}BH_3 \cdot L)]$ support a bonding picture in which σ donation from a B–H bond into the a_1 orbital of $M(CO)_5$ is the dominant feature of the interaction. Molecular orbital calculations show that π back donation from $M(CO)_5$ to $H_3B \cdot L$ is negligible, a combination of the poor π donating ability of the former and the high energy of the B–H σ* orbitals. These complexes are more stable than the alkane complexes due to the greater degree of polarization and electron richness inherent in the B–H bond in $H_3B \cdot L$ as opposed to the C–H bonds in CH_4. Interestingly, η^2 complexes are not observed upon further photolysis, although the same authors have shown that related species, for example **2**, are formed when $[M(CO)_6]$ is photolyzed in the presence of diborane $B_2H_4 \cdot 2PMe_3$ (Scheme 1).[6] Taken together, the experimental and computational data on the η^1 complexes provide convincing support for a valid and valuable analogy between complex **1** and the methane adducts $[(CO)_5M \cdot CH_4]$.[2, 4] The nature of these adducts also has implications for the reaction pathway for B–H bond activation, which was investigated in a subsequent paper by these same authors.[7]

Photolysis of a metal carbonyl that contains a somewhat more electron rich metal center, and also a sacrificial alkyl ligand, in the presence of the borane–phosphane alkane analogues leads to formation of Lewis base stablized boryl compounds. Photolytic loss of CO from $[Cp^*M(CO)_3CH_3]$ (M = Mo, W; Cp* = C_5Me_5) generates "$[Cp^*M(CO)_2CH_3]$", a highly reactive molecular fragment capable of interacting with X–H σ bonds. When those bonds are the B–H bonds of

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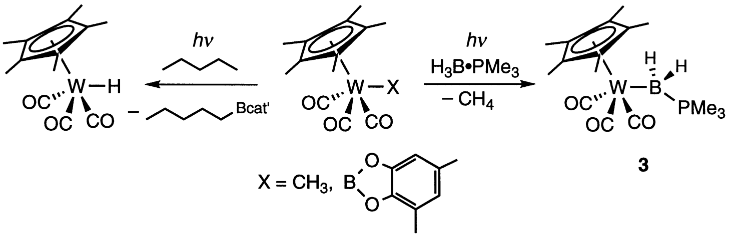
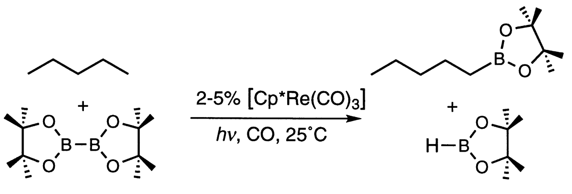
$H_3B \cdot L$, methane loss ensues with production of a phosphane-stabilized boryl species (exemplified by **3**; Scheme 2). Unlike the extensive chemistry known for the parent alkyl ligand CH_3, there are no known compounds containing an unligated BH_2 ligand; even base-stabilized examples are exceedingly rare.[8] In **3**, the W–B bond is the longest known at 2.476(7) Å, presumably because the stabilizing phosphane ligand precludes π bonding between W and B. The relatively low stretching frequencies for the CO ligands, however, suggest that the boryl ligand is a stronger σ donor than the methyl group of the starting materials.



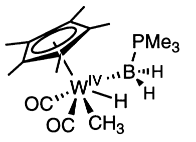
Scheme 2.

As Scheme 2 further suggests, this chemistry is closely related to the stoichiometric alkane functionalization reactions reported by Hartwig and Waltz in 1997,[9] a discovery which stands as an important milestone in the search for this particular Holy Grail. In this instance, it is a boryl ligand which assumes the role of the sacrificial species while the alkane solvent is activated. However, one crucial difference is notable: B–C bond formation is observed with elimination of R–Bcat′ rather than H–Bcat′ (cat′ = 3,5-dimethylcatechol), allowing for further functionalization of the alkane fragment. Very recently, the Hartwig group has reported a catalytic version of this reaction, employing a rhenium-based catalyst and a diborane(4) compound as shown in Scheme 3.[10]



Scheme 3.

Mechanistically, the reactions shown in Schemes 2 and 3 bring to light a conundrum for the key steps in the reactions: oxidative addition or σ-bond metathesis? This question has also arisen within the context of C–H activation reactions.[11] Clearly, in the reaction producing compound **3**, the B–H bond is in some way activated; the experimental data does not, however, distinguish between full oxidative addition (producing intermediate **4**) or a concerted methane elimination process (via transition state **5**). Distinguishing these mechanistic possibilities experimentally is nontrivial and computational studies[12] have proven helpful for the cationic iridium system of Bergman and Arndtsen.[11] Probably the choice between the two pathways will depend on the variables inherent to the system in question, that is, metal, ligands, and bond being activated. For formation of **3**, the authors speculate, quite reasonably, that σ bond metathesis is more likely given the high energy of the B–H σ* orbitals, which would need to be populated in a mechanism based on oxidative addition. Whatever the mechanism of methane loss, the initial work with $M(CO)_5$ (Scheme 1) provides a firm foundation for the notion that η^1-$H_3B \cdot L$ adducts would be the initial products in $[Cp^*M(CO)_3CH_3]$ chemistry.



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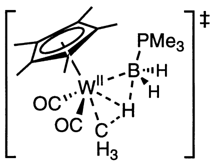
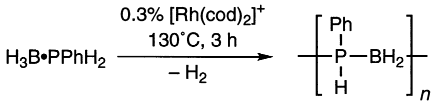


5

The work of Shimoi et al.[5–7] provides an excellent model system for alkane activation, but it also has implications for chemistry aimed at the activation and functionalization of the $H_3B \cdot L$ adducts themselves. The Manners group has recently reported the dehydropolymerization of $H_3B \cdot PPhH_2$ to high molecular weight poly(phosphinoborane) at 130 °C using Rh^I-based catalyst precursors (Scheme 4).[13] By performing the reaction in neat monomer, molecular weights of 31 000, corresponding to a degree of polymerization of 254, were achieved. The authors point out that this polymer is a structural analogue of polystyrene, which raises intriguing questions about its properties. Little mechanistic investigation has been presented to date, but clearly the results of Shimoi et al. have a bearing on possible mechanistic steps in the polymerization process. The apparent lack of B–B or P–P bond formation in this reaction suggests that, despite the higher temperatures in the Rh-catalyzed reaction, the borane–phosphane adduct reacts without dissociation into its constituents. Since Rh^I is involved, an oxidative addition of a B–H or P–H bond is a plausible first step in the polymerization reaction; the work of Shimoi and co-workers points to the former. Subsequent B–P bond formation could then occur by a σ-bond metathesis reaction involving P–H bonds. Of course, there are several possible mechanistic scenarios which await further investigation.



Scheme 4. cod = 1,5-cyclooctadiene.

One of the joys of chemistry is the seemingly endless games one can play with the periodic table. In the various papers reported here, the close relationship between alkanes and borane–phosphane adducts has been exploited to reveal some remarkable chemistry. The work addresses some mechanistic questions and raises others concerning the fundamental bond activation chemistry involved, but also has exciting prospects for new materials and practical alkane functionalization processes.

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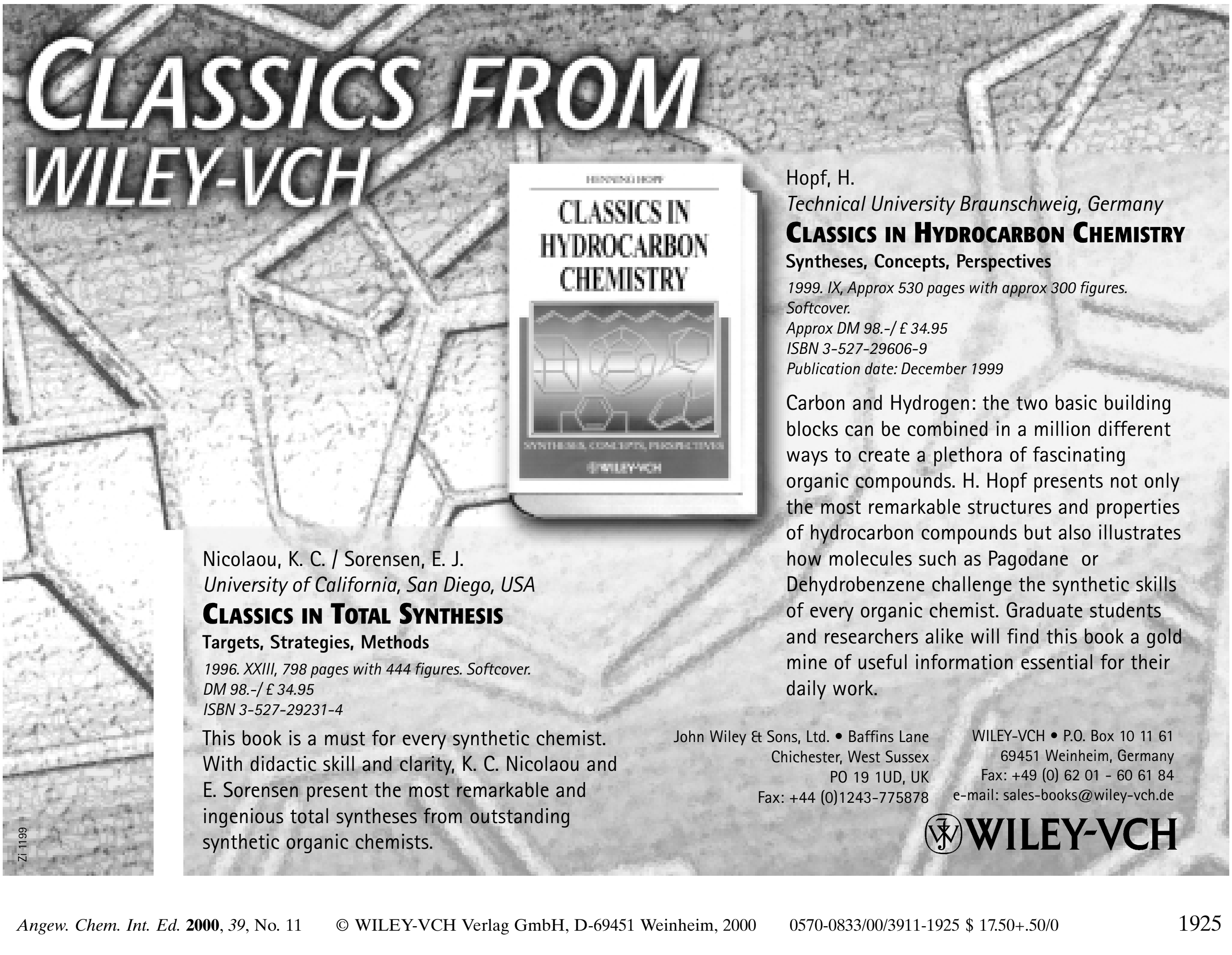

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