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Oxidative C(sp^3)–H bond cleavage, C–C and C═C coupling at a boron center with O$_2$ as the oxidant mediated by platinum(II)†

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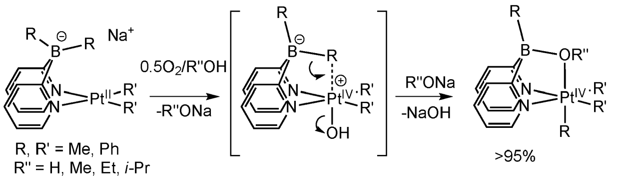
Dimethyl- and diphenylplatinum(II) fragments Pt^{II}R$_2$ (R = Me, Ph) enable facile and efficient oxidative C(sp^3)–H bond cleavage and stepwise C–C and C═C coupling at the boron atom of a coordinated 1,5-cyclooctanediyldi(2-pyridyl)borato ligand with O$_2$ as the sole oxidant.

The selective oxidation of C–H bonds using dioxygen, an inexpensive and environmentally benign reagent, catalyzed by electrophilic transition metals and pioneered by Hay[1] and Shilov[2] has recently attracted much attention.[3–7] In turn, organoboron compounds have emerged as valuable nucleophilic partners in various oxidative coupling reactions allowing for the formation of C–C and a variety of C–X bonds.[8] In spite of the great practical importance of the transition metal chemistry of organoboranes, little is known about the mechanisms of reactions of organoboron compounds and electrophilic transition metals. In the transition metal-mediated C–C coupling reactions of organoboron compounds it is usually presumed that the boron atom is only involved in the transmetallation of a boron-bound hydrocarbyl to an electrophilic metal whereas the high-valent transition metal center is solely responsible for the product-forming step.[3,8] Previously, we have characterized the direction and the nature of the migration of the methyl and phenyl groups R between an anionic boron atom of the dimethyl- and diphenyldi(2-pyridyl)borates $R_2B(C_5H_4N)_2^-$ (L) and the nearby electrophilic Pt^{IV}R$'_2$ fragment (R$'$ = Me, Ph) which can result, in particular, from the oxidation with O$_2$ of the organoplatinum(II) complexes Na[LPt^{II}R$'_2$] (see examples in Scheme 1).[9–11] In this work we report that the anionic alkylborate **1**$^-$ present in the Pt^{II} complexes Na[**2**]–Na[**5**] (Chart 1) can be involved in a Pt-mediated double oxidative cleavage of the bridgehead alkylborate C(sp^3)–H bonds accompanied by an unprecedented C═C coupling at the boron center, with O$_2$ as the sole oxidant. According to our mechanistic proposal, the C–C/C═C coupling occurs at the boron center.



Scheme 1 Oxidatively induced B-to-Pt^{IV} hydrocarbyl transfer.[9–11]

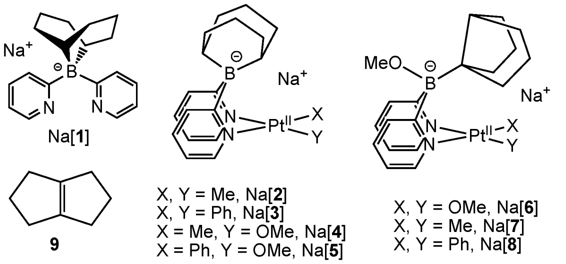


Chart 1 New borate ligand and derived compounds.

The new borate ligand and the derived anionic Pt^{II} complexes in the form of their sodium salts, Na[**2**]–Na[**5**], were prepared using standard synthetic techniques and fully characterized. The chloride salt of the doubly protonated dipyridylborate, H[**1**]·HCl, was also characterized by single crystal X-ray diffraction.

The reactivity of the new organoplatinum(II) organoborates Na[**2**]–Na[**5**] toward O$_2$ in methanolic solution was studied next. We anticipated that compounds Na[**2**]–Na[**5**] bearing one or two hydrocarbyl groups at the Pt^{II} center would be reactive toward O$_2$ in methanol.[9,10,12–14] We also expected that the 9-borabicyclo[3.3.1]-nonane (9-BBN) fragment present in these complexes would resist B-to-Pt^{IV} hydrocarbyl migration due to the constraints imposed by its bicyclic structure.

While the platinum-free compound Na[**1**] dissolved in methanol showed no change under 1 atm O$_2$ after 4 days at 20 °C, the aerobic oxidation of the hydrocarbyl methoxo Pt^{II} complexes Na[**4**] and Na[**5**] in methanol-*d*$_4$ was facile and took

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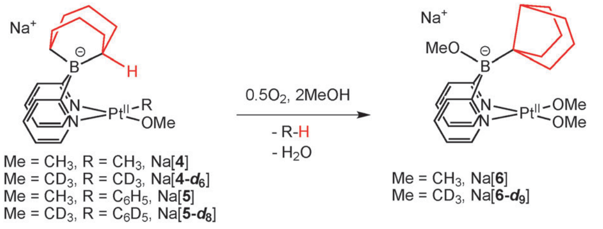


Scheme 2 Oxidative C–C coupling of Na[**4**] and Na[**5**].

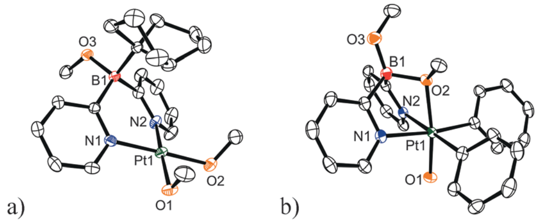


Fig. 1 ORTEP drawings (50% probability ellipsoids) of: (a) the anionic fragment of Na[**6**], (b) complex **11**. Hydrogen atoms are omitted for clarity.

less than 5 min under the conditions indicated above (Scheme 2). Both reactions led to the formation of a platinum-containing product Na[**6**] in >96% NMR yield, H_2O and a hydrocarbon, methane or benzene, respectively, identified by means of NMR spectroscopy. The identity of Na[**6**] was confirmed using the Electro-Spray Ionization Mass-Spectrometry (ESI-MS) and single crystal X-ray diffraction. This characterization revealed that the 1,5-cyclooctanediyl fragment present in Na[**4**] and Na[**5**] is converted to the bicyclo[3.3.0]octyl group (Fig. 1a) as a result of the cleavage of one of the ligand bridgehead C–H bonds and an intramolecular C(sp^3)–C(sp^3) coupling. The dimethoxoplatinum(II) complex Na[**6**] is completely inert under 1 atm O_2 in methanol at 20 °C for at least 2 days.

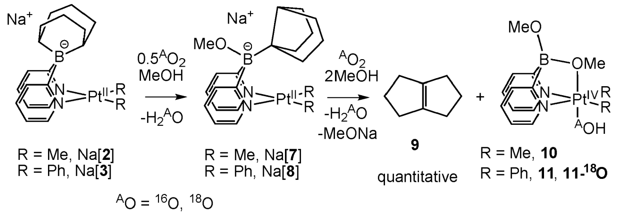
Further exploration of the unusual aerobic C–C coupling reactivity of the Pt^{II} complexes derived from Na[**1**] involved the diphenylplatinum(II) complex Na[**3**]. The reaction of Na[**3**] under 1 atm O_2 in methanol was complete after 10 min at 20 °C and led to a virtually quantitative formation of the bicycloolefin **9**, as confirmed using ^{1}H and ^{13}C NMR spectroscopy and GS-MS, dimethoxodi(2-pyridyl)borato[15] diphenylplatinum(IV) hydroxo complex **11** (isolated yield 95%) and two moles of H_2O (Scheme 3). In contrast to the monophenyl complex Na[**5**], no benzene was formed in this reaction. Solid reaction residues were strongly alkaline confirming the formation of sodium methoxide. The identity of **11** was proven using ESI-MS and single crystal X-ray diffraction (Fig. 1b). Hence, a double oxidative cleavage of the ligand **1**$^-$ bridgehead C–H bonds and an intramolecular oxidative C=C coupling were observed in the reaction of O_2 with the diphenylplatinum(II) complex Na[**3**] in methanol.‡

The stepwise character of the oxidative C=C coupling in Scheme 3 was proven in the following experiments. When reaction of Na[**3**] with O_2 was performed under conditions of starvation of oxygen using only 0.5 equiv. O_2 the cleavage of one of the ligand **1**$^-$ bridgehead C–H bonds and the selective formation of a C–C coupled product Na[**8**] (94% NMR yield), the diphenylplatinum(II) analog of Na[**7**], was observed.

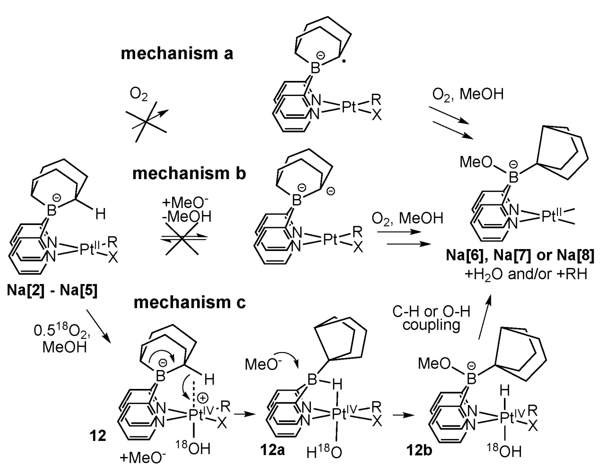
The identity of Na[**8**] was confirmed using ^{1}H NMR spectroscopy and ESI-MS. A small amount of **11** (6% NMR yield) and the equivalent quantity of **9** were also detected, presumably because of a non-ideal control of the reaction stoichiometry. When more oxygen was admitted to the reaction mixture containing Na[**8**], all of the complex was cleanly converted to **9** and **11**.

A similar reaction of O_2 with the dimethylplatinum(II) complex Na[**2**] was more challenging to characterize. A low temperature of −60 °C was required to avoid fast protonolysis of Na[**2**] as well as the protonolysis of the expected intermediate Na[**7**]. After warming from −60 °C up to 20 °C a solution of the dimethylplatinum(II) complex Na[**2**] in MeOH while bubbling slowly O_2 through it the formation of **9** and **10** (88% isolated yield), the dimethyl analog of **11**, was observed. No methane was detected.

An oxidative C–C coupling of lithium salts containing *B*,*B*-dialkyl-9-boratobicyclo[3.3.1]nonane anions to form bicyclo[3.3.0]octylboranes using acyl chlorides as oxidants was reported in the mid-1970s but it was never explored mechanistically.[16] To the best of our knowledge, the examples of the platinum-mediated oxidative C–H cleavage are very rare[17] and the C=C coupling in Scheme 3 is unique.[8,18] These considerations motivated us to carry out some mechanistic tests. To probe if free alkyl radicals are involved in the oxidative C–H bond cleavage/C–C coupling of Na[**2**]–Na[**5**] (Scheme 4, mechanism a), the oxidation with O_2 of two representative compounds, Na[**3**] and Na[**4**], was performed in the presence of 2 equiv. of a radical trap TEMPO. These reactions produced no *O*-alkyl TEMPO derivatives that might have resulted from the recombination of TEMPO and transient free alkyl species. The reactions also were not inhibited. These facts do not support mechanism a. In addition, no H/D exchange at the ligand bridgehead carbon atoms in Na[**3**] dissolved in CD_3OD was observed



Scheme 3 Aerobic C=C coupling of Na[**2**] and Na[**3**].



Scheme 4 Possible mechanisms of the C–H bond cleavage.

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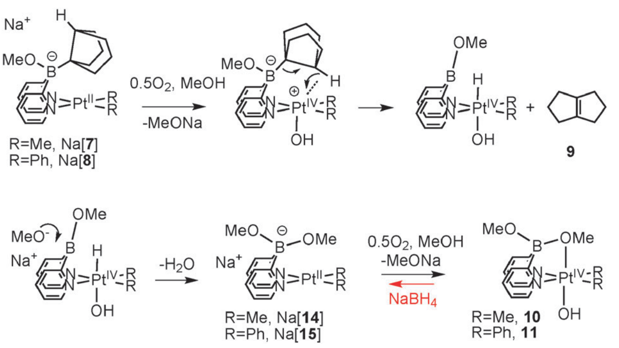
for at least 3 days so arguing against an initial deprotonation of the ligand bridgehead C–H bonds and subsequent oxidation of the resulting carbanions (Scheme 4, mechanism b).

The C–H bond cleavage/C–C coupling mechanism (Scheme 4, mechanism c) involving the formation of a Pt^{IV} center and the hydride abstraction by Pt^{IV} allows us to account for the available observations as explained below. First, the oxidation of Pt^{II} hydrocarbyl complexes with O_2 and H_2O_2‡ in hydroxylic solvents produces Pt^{IV} hydroxo species with an axial hydroxo ligand, such as **12**, with the oxygen atom of the hydroxo ligand originating from the oxidant.[12–14] Indeed, we observed the formation of the ^{18}O-labeled product **11-^{18}O** in the reaction of Na[**3**] and $^{18}O_2$ (Scheme 3). Second, the intermediates **12** derived from the complexes Na[**2**]–Na[**5**] transfer the hydride anion from a bridgehead C–H bond of the 9-BBN fragment to the Pt^{IV} center to form Pt^{IV} hydrides **12a** and then **12b**. Third, the hydride ligand at the Pt^{IV} atom of **12b** is oxidatively coupled with either the hydrocarbyl R to produce methane or benzene along with Na[**6**] or with the OH ligand to form H_2O along with the hydrocarbyl Pt^{II} complex Na[**7**] or Na[**8**]. Overall, the reactions of Na[**4**] and Na[**5**] with O_2 lead to Na[**6**], H_2O and R–H as the final products (Scheme 4, mechanism c); the dimethoxoplatinum(II) complex Na[**6**] is too electron-poor to further react with O_2.

In support of the C-to-Pt^{IV} hydride transfer mechanism c, the origin of the protium atom in the hydrocarbon R–H resulting from the oxidation of complexes Na[**4**] and Na[**5**] (Scheme 2) was revealed using the partially deuterated compounds Na[**4**-d_6] and Na[**5**-d_8]. The oxidation of the labeled complexes in methanol-d_4 leads to the formation of CD_3H or C_6D_5H, respectively, along with Na[**6**-d_9]. The only source of protium in the reaction mixtures above that could be involved in the formation of CD_3H and C_6D_5H is the 9-BBN fragment. The facile hydride abstraction from the 9-BBN moiety may be due to the rigid structure of **12** that positions the hydrogen atom of one ligand bridgehead C–H bond in the close proximity of the Pt^{IV} center, so helping to diminish the reaction activation barrier. Some metal complexes derived from 1,5-cyclooctanediylbis-(1-pyrazolyl)borate, a dipyrazolyl analogue of $\mathbf{1}^-$ having the 9-BBN framework, were reported to have an enhanced C–H agostic interactions of their bridgehead C–H bonds with the metal.[19] In support of this hypothesis, a stable trimethylplatinum(IV) complex **13**, [**1**]$PtMe_3$, was prepared as a model of **12**. Complex **13** was characterized using single crystal X-ray diffraction and found to have a short 1.99 Å agostic (δ-C)H–Pt^{IV} bond.§



Scheme 5 Proposed mechanism of the oxidative C–H bond cleavage/C=C coupling of Na[**7**] (R = Me) and Na[**8**] (R = Ph).

As opposed to the reaction of Na[**4**] and Na[**5**] with O_2, the reaction of Na[**2**] and Na[**3**] with O_2 does not stop at the formation of the C–C coupled product. The dihydrocarbyl platinum(II) complexes Na[**7**] and Na[**8**] are much more reducing compared to Na[**6**] and can be involved in another O_2 activation/hydride abstraction-oxidative C–C coupling/O_2 activation reaction sequence to produce **9** along with **10** and **11**, respectively (Scheme 5). In support of the mechanism in Scheme 5, Na[**15**] was produced *in situ* by reacting the diphenylplatinum(IV) complex **11** with $NaBH_4$ or $NaBH(OMe)_3$ in methanol. The solution of Na[**15**] then reacted with O_2 to form **11** at a fast rate in a quantitative NMR yield.

The observed reactivity suggests that **11** may be a good catalyst for the oxidation with O_2 of some hydride donors. Indeed, the oxidation with O_2 of 0.7 M Na[$BH(OMe)_3$] or $NaBH_4$ in methanol–NaOMe solutions is catalyzed efficiently by 0.5 mol% **11** with a turnover frequency of ~170 h^{-1} and ~216 h^{-1}, respectively, at 20 °C.

In summary, we have characterized a rare oxidative Pt-mediated C(sp^3)–H bond cleavage accompanied by an unprecedented C=C coupling at the boron center of the platinum(II) complexes Na[**2**]–Na[**5**]. Up to three O_2 activation steps at a single Pt^{II} atom may be involved in these facile transformations. Further study of this novel system might lead to some practical applications utilizing O_2 in catalytic oxidation and C=C coupling of organoboron and similar compounds.

We thank the National Science Foundation (CHE-0614798, CHE-1112019) for the financial support of this work.

Notes and references

‡ The use of H_2O_2 instead of O_2 in the reaction with Na[**3**] also leads to a fast formation of **9** and **11** (90% NMR yield).

§ In ^1H NMR spectra (CD_2Cl_2) the agostic proton resonance is at −3.36 ppm with the large coupling constant J_{Pt-H} = 208 Hz.

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