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Intramolecular C−H Insertion Reactions of Boroxy Fischer Carbene Complexes

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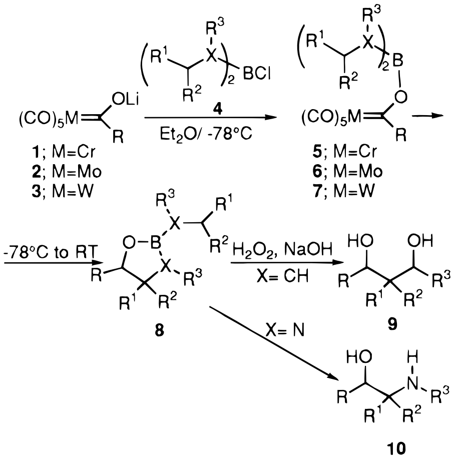
The great variety of synthetically engaging transformations that are known and continuously being described for Fischer carbene complexes has served to establish the usefulness of these complexes for synthesis of novel organic compounds.[1] On the other hand, the chemistry of bimetallic systems in which the carbene heteroatom is bound to a second, electron-deficient, metal offers the opportunity to control the carbene reactivity by steric and electronic variation of the Lewis acidic component.[2] Although two examples of boroxy Fischer carbene complexes have been described, they are found to decompose to a mixture of unidentified products upon standing at room temperature.[3] Whereas some C−H insertion reactions are known for cationic iron carbene complexes,[4] only two examples that involve group 6 nonheteroatom-stabilized Fischer carbene complexes have been reported.[5] In the present communication we describe, for the first time, the preparation of boroxy Fischer carbene complexes and their transformation into oxaborolane or oxazaborolidine derivatives *via* a C−H insertion process. Oxidation of these compounds leads to 1,3-diol and 1,2-aminoalcohol derivatives. This process is amenable for synthesizing enantiomerically pure compounds.

The treatment of pentacarbonylmetal acylate intermediates **1**−**3**, formed by reaction of metal hexacarbonyl and the corresponding organolithium compound,[6] with dialkylchloroboranes **4** (X = CH)[7] in diethyl ether at −78 °C readily led to dialkylboroxycarbene complexes **5**−**7**. On warming to room temperature, these compounds underwent loss of the metal fragment affording the oxaborolane derivatives **8** (X = CH). This transformation involves the insertion of the carbene into the boron C_β−H bond. Further oxidation of **8** yielded 1,3-diols **9** as mixtures of diastereoisomers (Scheme 1 and Table 1, entries 1−4). We have observed that oxaborolanes **8** are produced in moderate yield when either R^1 and R^2 are alkyl groups (entry 1) or R^1 and R^2 are H and a donor group, respectively (entries 2−4). Conversely, the reaction does not work for R^1 = H and R^2 = alkyl (c-C_6H_{11} or n-C_6H_{13}) or electron-withdrawing groups (4-ClC_6H_4), and complex mixtures are obtained. On the other hand, starting from diaminochloroborane **4e** (X = N),[8] oxazaborolidine **8e** and 1,2-aminoalcohol **10** can be prepared (entry 5). It is interesting to note that the nature of metal plays a role in the reaction rate, while the product distribution remains unaffected. Thus, 2 or 3 h and around 12 h were required for the formation of oxaborolanes **8a,b** at room temperature by starting from carbenes **6a,b** (M = Mo) and **7a,b** (M = W), respectively.

Scheme 1



In order to study the influence of the chiral dialkylborane bearing a tertiary C_β−H bond on the diastereoselectivity of the reaction, a set of experiments using the commercially available (−)-chlorodiisopinocampheylborane [(−)-Ipc_2BCl] was envisaged (Scheme 2 and Table 1, entries 6−11). To our delight, diastereoselectivities higher than 99% were then reached in the case of **13c** and **13d** (entries 8, 9). In addition, dialkylboroxycarbene complexes **11** and oxaborolane derivatives **12** were clearly identified by NMR spectroscopy. The absolute configuration of the new stereogenic centers in the major and minor diastereoisomers was assigned by NOE experiments of the corresponding acetonides **14**.[9] It is interesting to point out that a quaternary carbon center has been created in a enantioselective way[10] and that the diastereoselectivity depends exclusively on the way that the C−H is approaching the metal−carbon double bond.

A reasonable mechanism that accounts for the formation of oxaborolanes **8** is outlined in Scheme 3 and involves intramolecular hydride transfer to the carbene carbon atom in the complex **7**, favored presumably by an interaction between the boron atom and the metal of carbene complex as depicted in the transition state **I**, to give formally the carbocation intermediate **II**, which rapidly affords the oxaborolane derivatives **8** likely by simultaneous formation of a carbon−carbon bond and loss of the metal fragment. The results are in agreement with the proposed mechanism. In fact, the hydride transfer is only

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[†] NMR studies.

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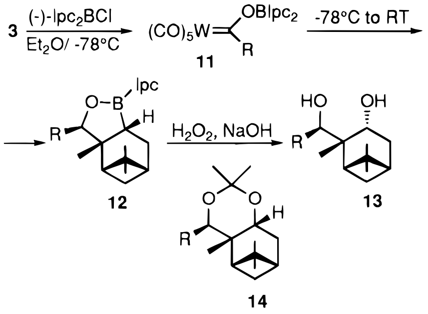
Table 1. Diols **9**, **13**, and Aminoalcohol **10** from C−H Insertion in the Boroxy Fischer Carbene Complexes **5**, **6**, **7**, **11** and Further Oxidation

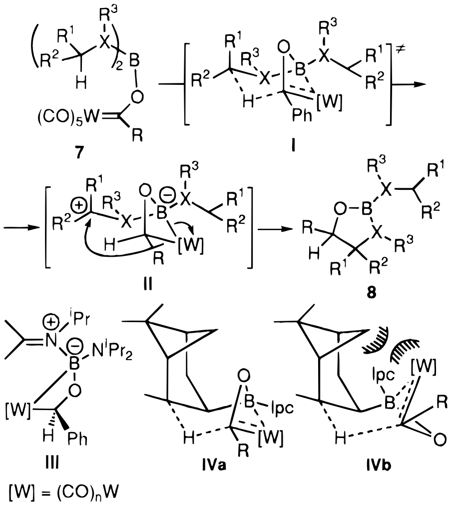
entry	carbene complex	R	X	R^1	R^2	R^3	product	yield[a]	de[b]
1	**6a**[c]	(*E*)−PhCH=CH	CH	Me	Me	Me	**9a**	53	12
2	**6b**[c]	Ph	CH	H	Ph	H	**9b**	52	10
3	**6c**	(*E*)−PhCH=CH	CH	H	Ph	H	**9c**	64	32
4	**6d**	Me	CH	H	4-MeOC_6H_4	H	**9d**	49	20
5	**6e**[d]	Ph	N	Me	Me	^{i}Pr	**10**	65	
6	**11a**[e]	Ph			Ipc[f]		**13a**	87	51
7	**11b**	2-Naph			Ipc[f]		**13b**	85	72
8	**11c**	(*E*)−PhCH=CH			Ipc[f]		**13c**	81	>99
9	**11d**	CH_2=C(Ph)			Ipc[f]		**13d**	83	>99
10	**11e**	Me_2C=CH			Ipc[f]		**13e**	75	97
11	**11f**[e]	CH_2=C(Me)			Ipc[f]		**13f**[g]	78	86

[a] Based on $M(CO)_6$. [b] Determined by NMR. [c] Also carried out with the corresponding carbene complex **7**. [d] Also carried out with the carbene complexes **5e** and **7e**. [e] Also carried out with the corresponding chromium and molybdenum carbene complexes. [f] (−)-Ipc_2BCl was used as dialkylchloroborane. [g] Both diastereoisomers have been isolated.

Scheme 2



Scheme 3



observed in the cases in which the early developing carbocation can be stabilized. Moreover, NMR monitoring of the reaction course of **7e** (X = N) at −50 °C allowed identification of the intermediate **III** (Scheme 3). The 2D ^1H, ^{13}C HMBC spectrum[11] showed correlations of the methine proton at 5.31 ppm with aromatic carbons (119.4, 157.3 ppm) and one of the carbonyl groups bound to tungsten (203.6 ppm), while the diastereotopic methyl groups (2.68, 2.74 ppm) correlate with a carbon at 189.2 ppm. The ^{183}W chemical shift of **III** (−66.8 ppm) measured from the ^1H, ^{183}W HMBC spectrum[12] is unusually high compared with other related tungsten complexes,[13] and suggests that the metal actually coordinates to the boron atom.

The high stereoselectivity of the hydride attack leading to oxaborolanes **12** may be tentatively accounted for by considering transition states **IVa** and **IVb** (Scheme 3). Assuming that a boron−metal interaction takes place, the chairlike transition state **IVa** would explain the formation of the major diastereoisomer. This stereochemical course should be favored over that one involving the boat conformation **IVb**, which exibits severe hindrance between the metal fragment and the ring moiety. Moreover, the higher diastereoselectivity found for R = alkenyl groups (entries 8−11) can be rationalized in terms of coordination of the metal to the carbon−carbon double bond, which would result in increasing the transition state rigidity.[14] Thus, **IVb** is more disfavored than **IVa**.

In conclusion, we have described an efficient and diastereoselective conversion of boroxycarbene complexes to oxaborolane, oxazaborolidine, 1,3-diol, and 1,2-aminoalcohol derivatives, representing, as far as we know, the first example of an intramolecular C−H insertion reaction in a stabilized Fischer carbene complex. In addition, an intermediate of this reaction has been characterized by NMR spectroscopy. Further studies on the mechanism and synthetic applications of this novel transformation as well as the likely influence of the Lewis acidic component on the carbene reactivity will be reported in due course.

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Supporting Information Available: Synthetic procedures and listing of spectral data for **7**−**14** and NMR spectra of intermediate **III** and the fate of **11c** (30 pages). See any current masthead page for ordering and Internet access instructions.

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[14] This coordination has been observed by NMR during the transformation of **11c** as an intermediate species formed at −30 °C. The olefinic carbon atoms are highly shielded (79.51, 81.17 ppm) related to the starting carbene, and the corresponding protons (5.21, 5.32 ppm) show cross peaks in the 2D ^1H, ^{13}C HMBC spectrum with a carbonyl carbon at 196.91 ppm.