Metal-induced B—H activation in Cp*Rh, Cp*Ir, (*p*-cymene)Ru, and (*p*-cymene)Os half-sandwich complexes containing the 1,2-dicarba-*closo*-dodecaborane(12)-1,2-dichalcogenolato ligand

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The reactivity of the 16e half-sandwich complexes Cp*Rh[$E_2C_2(B_{10}H_{10})$] (**1a**,**b**), Cp*Ir[$E_2C_2(B_{10}H_{10})$] (**2a,b**) (E = S (**a**), Se(**b**)), (*p*-cymene)Ru[$S_2C_2(B_{10}H_{10})$] (**3**), (*p*-cymene)Os[$S_2C_2(B_{10}H_{10})$] (**4**) (*p*-cymene = 1-Me-4-Pr^i-benzene) towards various alkynes (acetylene, propyne, 3-methoxypropyne, methyl acetylenemonocarboxylate, dimethyl acetylenedicarboxylate, phenylacetylene, ferrocenylacetylene) was studied. The reactions start with an insertion into one of the M—E bonds, followed (except for $MeO_2C—C{\equiv}C—CO_2Me$) by intramolecular, metal-induced B—H activation, formation of an M—B bond, accompanied by simultaneous transfer of a hydrogen atom from boron *via* the metal atom to the alkyne. This leads to new complexes with a *cisoid* or *transoid* geometry (orientation of the E—C=C unit with respect to the C(1)—B bond). This geometry determines the course of further intramolecular reactions which lead selectively to carboranes mono- or disubstituted in B(3,6) positions. Numerous intermediates and final products were characterized by X-ray analysis in the solid state, and by multinuclear magnetic resonance in solution. First catalytic applications of **1a,b** became evident by cyclotrimerization reactions.

Key words: carboranes; iridium; osmium; rhodium; ruthenium, selenium; sulfur; X-ray; NMR.

Introduction

The search for activation of element—element bonds, in particular, of element—hydrogen bonds, has developed towards an active research area once it had been recognized what roles transition metal complex fragments or the metal surface itself (*e.g.*, in heterogeneous catalysis) can play in these processes.[1,2] ** B—H bond activation is readily achieved by electron deficient boron sites, and may be considered as one of the driving forces due to which polyboranes in general exist as single isomers (in contrast to their hydrocarbon congeners). Transition metal complexes with the tetrahydroborate ligand[3] are well-known examples of B—H—M bridging, and more recently, various simple boron hydride ligands have been found to interact with transition metals by B—H bond activation.[4,5] In carborane derivatives an electron deficient metal center, which at the same time is also coordinatively unsaturated, can induce B—H activation once the metal gets close to the B—H bond. Early examples have been known[6—8] and frequently carborane anions were used as ligands by which B—H—M interactions helped to stabilize the complexes. These turned out to be either extremely stable[9] or reactive with respect to fusion of the carborane units to give readily rearranged tetracarba-*nido*-octaboranes(8).[10] Recently, an interesting work has been presented in which metallacarborane anions coordinate to metal fragments by B—H—M bridging.[11]

Our work had started with the synthesis of monomeric 16e half-sandwich complexes of Cp*Rh, Cp*Ir, (*p*-cymene)Ru and (*p*-cymene)Os bearing thiolato or selenolato ligands. In this context, the 1,2-dicarba-*closo*-dodecaborane(12)-1,2-dichalcogenolato ligands appeared particularly attractive, since, in addition to kinetic stabilization of the 16e complexes, the products are sufficiently soluble to carry out extensive NMR studies in solution, and, in most cases, they readily crystallize to give solid materials suitable for X-ray analyses. Thus, complexes **1**—**4** were prepared, starting from *ortho*-carborane, following established procedures[12] to the dichalcogeno-dilithio derivatives, which react readily with the respective transition metal dichloride[13,14] to give the desired product[15—17] (Scheme 1).

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** See reviews on the activation of the H—E bond (E = H,[1a] C and Si,[1b] and Sn[1c]).

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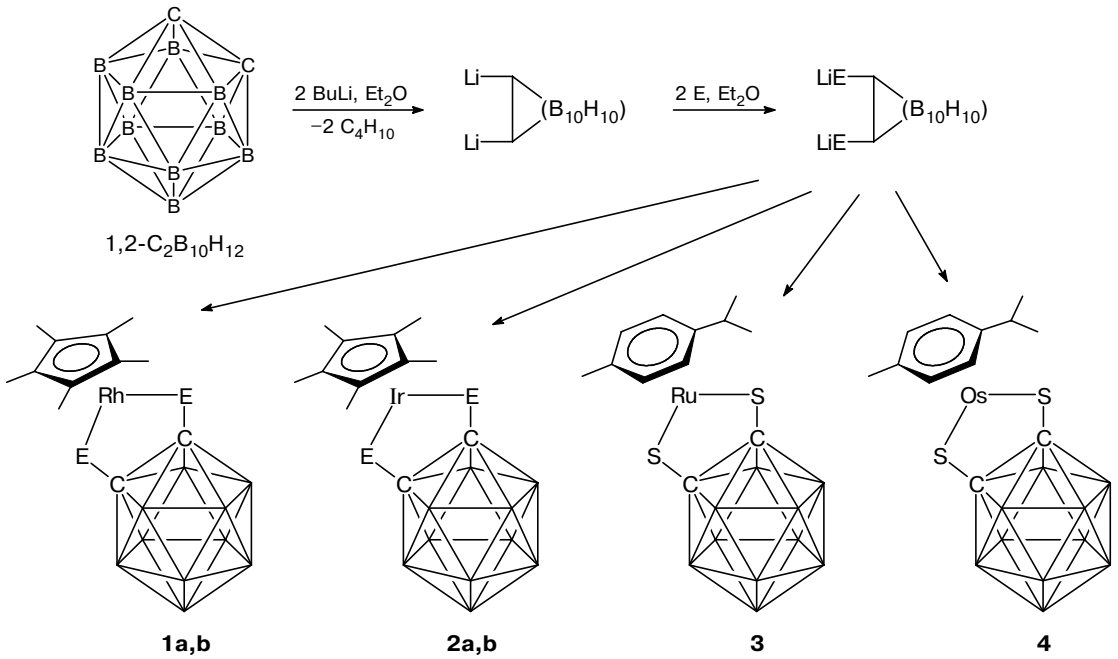
Scheme 1



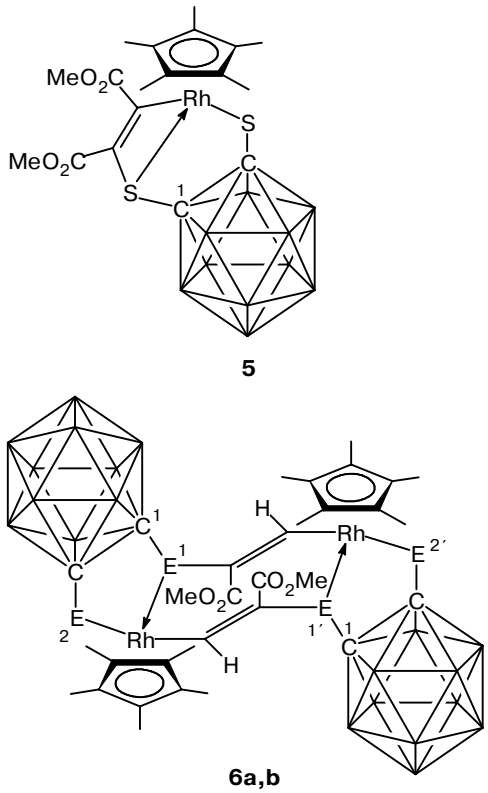
E = S (**a**), Se (**b**)

Note. The B—H and C—H bonds are not shown.

How to bring the reactivity of the starting 16e complexes 1—4 to life ?

The molecular structures of 16e complexes **1—4** [15—17] show a rigid planar arrangement of the five-membered MECCE ring which precludes any significant M..H—B interactions. However, this situation may become quite different if the reactivity at the metal center is first used for insertion reactions. Such reactions were also shown to take place for the corresponding 16e cobalt complex $CpCo[S_2C_2(B_{10}H_{10})]$.[18] When alkynes react with **1—4**, the first step can be envisaged as an oxidative addition,[19,20] although, in the present studies, the resulting intermediate was never observed. Instead, the examples isolated were the products of insertion into one of the M—E bond.[18,21] With dimethyl acetylenedicarboxylate, $MeO_2C—C{\equiv}C—CO_2Me$, this can lead to the monomeric 18e complex **5**, in which a coordinative E—M bond is present,[21] or to dimers **6**,[22] also 18e complexes (Scheme 2). The structures of complexes **5** [21] and **6b** [22] were established by X-ray analyses. The nonfirst-order signals in the ^{77}Se NMR spectrum of **6b** (Fig. 1) prove that the dimeric structure is retained in solution.* It should be noted that complexes of type **5** have not been detected so far in reactions with alkynes other than

Scheme 2



E = S (**a**), Se (**b**)

* This follows from the appearance of the ^{77}Se signals as a pseudotriplet and pseudodoublet due to the spin system AA′X (neglecting the isotope-induced interaction with ^{103}Rh).

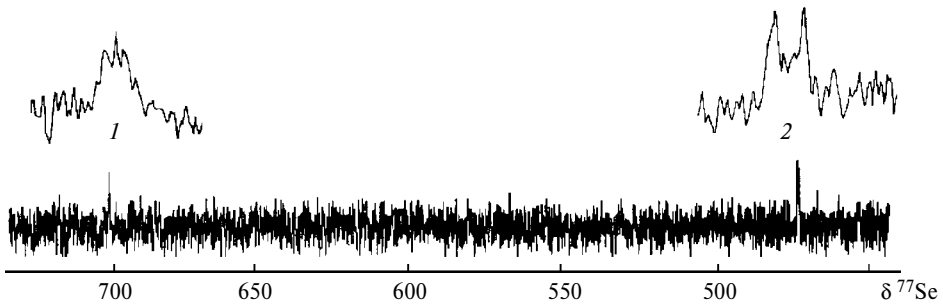


Fig. 1. The ^{77}Se NMR spectrum (at 95.4 MHz) of dimeric rhodium complex **6b**: *1*, signal from Se(1) ($^1J(^{103}Rh, ^{77}Se)$ + $^3J(^{103}Rh, ^{77}Se)$ = 29 Hz); *2*, signal from Se(2) ($^1J(^{103}Rh, ^{77}Se)$ = 46 Hz).

$MeO_2C—C{\equiv}C—CO_2Me$, and complexes of the type **6** were only observed and isolated in small quantities in addition to numerous products, which may have their origin in complexes of the type **5** or **6**.

Either monomers of the type **5** or dimers of the type **6** react further to give new products, and their formation can only be explained by assuming intramolecular metal-induced B—H activation. If the coordinative E—M bonds in the complexes of type **5** or **6** are weak, an equilibrium between 16e and 18e complexes is conceivable, and the ring structures of the 16e complexes should then become sufficiently flexible in order to allow for close M..H—B contacts at the 3- or 6-positions of the carborane cage.

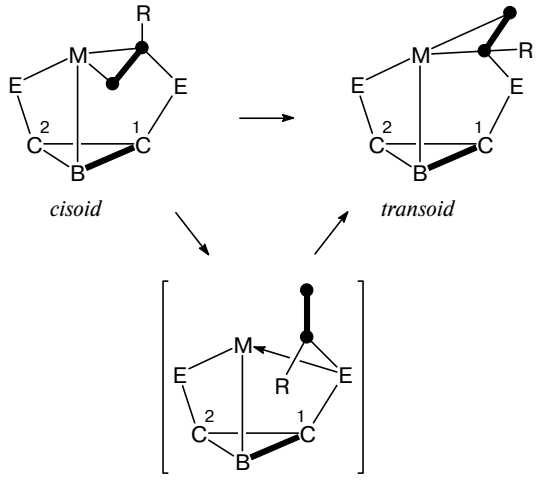
Intramolecular metal-induced B—H activation

The crucial step following metal-induced B—H activation is the formation of the M—B bond and transfer of a hydrogen atom to the metal. In the present cases, the hydrogen atom is immediately passed on *via* the metal to one of the alkynyl carbon atoms, converting the alkyne after its insertion into one of the M—E bonds to an olefin which is η^2-coordinated to the metal. Scheme 3 shows that this can afford, in principle, two isomers called *cisoid* and *transoid* according to the arrangement of the E—C=C moiety with respect to the orientation of the C(1)—B bond.

Numerous experiments have provided evidence that the *transoid* isomer is the product of thermodynamic control, although there are some examples where a complete rearrangement from the *cisoid* to the *transoid* structure could not be achieved, since alternative reactions were found to be competitive or the *cisoid* isomer turned out to be markedly stabilized by kinetic effects. Examples for complexes with *transoid* (**7**, **8**)[23] and *cisoid* (**9**,[23] **10**[24]) structures, revealed by X-ray structural analysis, are shown in Scheme 4. In solution, the isomers can readily be distinguished by their significantly different NMR parameters.

An inspection of Schemes 3 and 4 indicates that the M—B bond must be regarded as an reactive center inviting for further intramolecular activities. Indeed,

Scheme 3

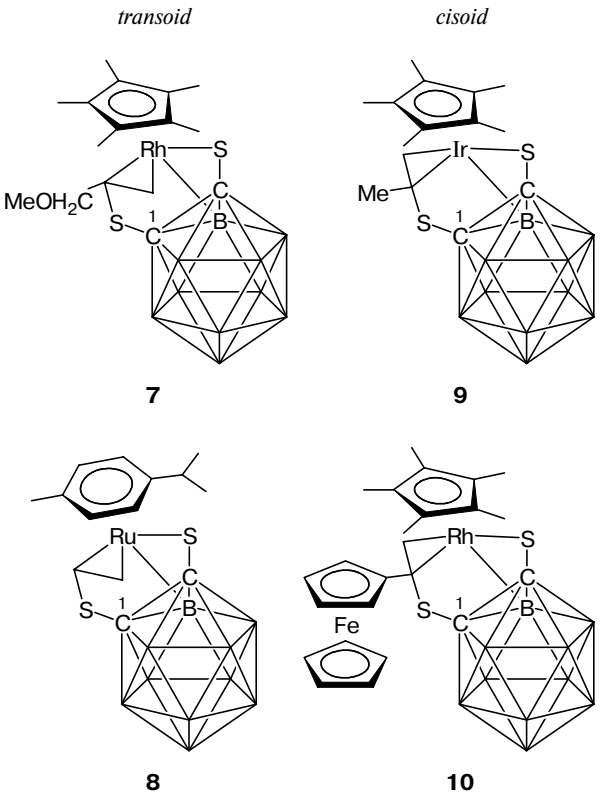


this proved to be the source of interesting transformations leading to completely new types of complexes.

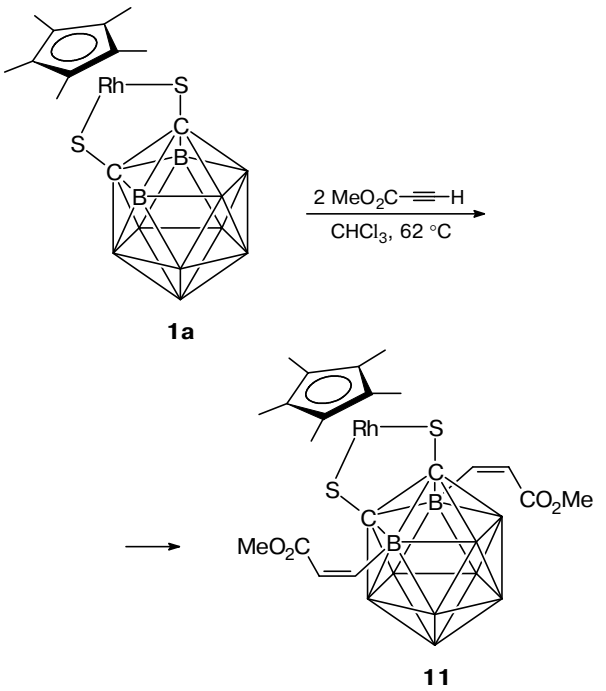
Selective and stepwise B(3), B(6)-substitution of *ortho*-carborane derivatives

The selective substitution of *ortho*-carborane at the sites of the boron atoms is still a formidable problem.[12] Recently, polyalkyl-substitution has been achieved using Friedel—Crafts conditions[25]; however, halogenation usually does not take place in 3,6-positions.[12] Therefore, the complexes shown in Scheme 4 are unique, since they open the way to introduce substituents selectively in the 3,6-positions. This was shown in our initial attempt to make use of these complexes.[21] Complex **11** was formed in good yield (>65 %; Scheme 5)[21] and characterized by X-ray analysis, and the proposed mechanism was confirmed in detail later on. The substituents in both 3- and 6-positions possess (*Z*)-configuration. Compound **11** is again a 16e complex. Clearly, the reaction has to go first to monosubstitution (16e complex) and then the cascade of insertion, B—H activation, the formation of the M—B bond, *etc.* repeats itself.

Scheme 4



Scheme 5



We have attempted to stop the reaction at the stage of monosubstitution. This was only partially successful with the rhodium complexes. However, the iridium complexes react somewhat more slowly, and it proved possible to isolate the respective intermediates, two of which are shown in Fig. 2 (see also Scheme 4), and transform them into monosubstituted carboranes **12**—**15**. The latter could finally be converted (Scheme 6)[26] into 3*B*,6*B*-disubstituted derivatives **16**, **17**, and **18b** (compound **18a** was not detected).

The structures of compounds **15a**, **17b**, and **19b** were confirmed by X-ray analyses.[26] The formation of compound **19** is due to a different intramolecular rearrangement typical of the *cisoid* configuration.

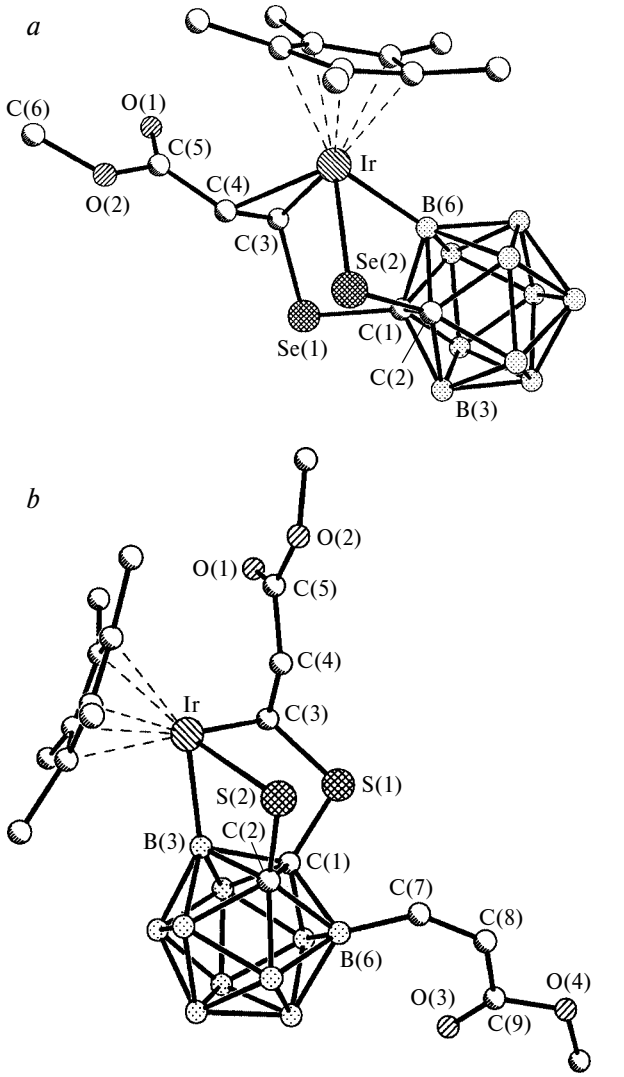
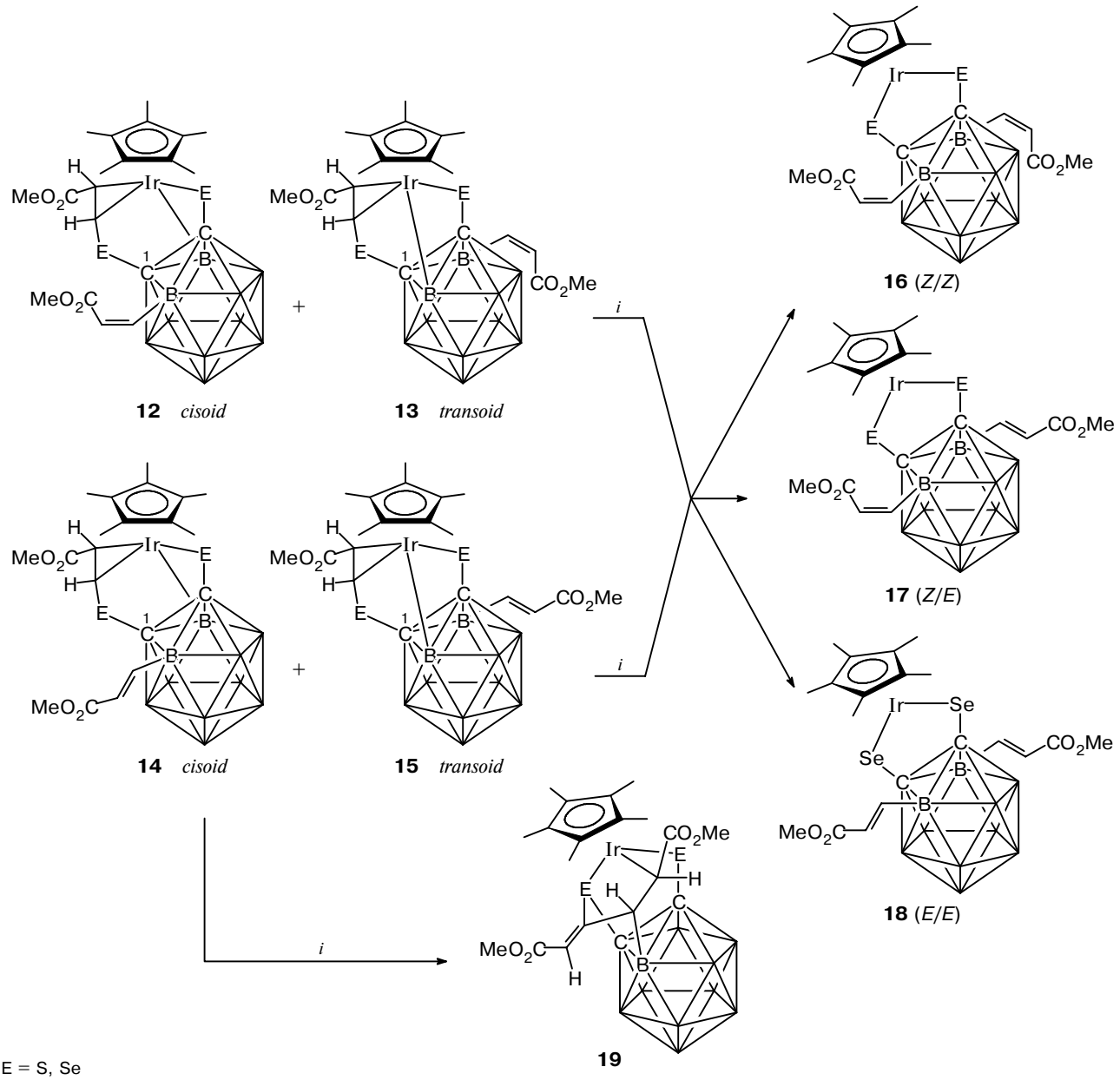


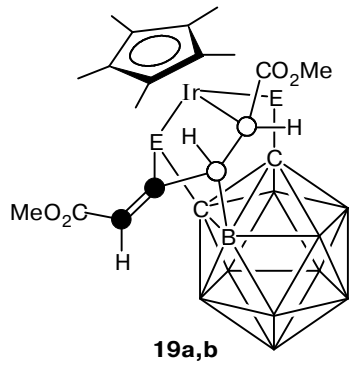
Fig. 2. Molecular structures of intermediates with the Ir—B bond: (*a*) *transoid* iridium complex (see for the mutual orientation of the Se(1)C(3)=C(4) and C(1)—B(6) fragments, the intermediate in the formation of the 16e iridium complex with the monosubstituted carborane ligand[26]; and (*b*) *cisoid* iridium complex **13a** (see for the mutual orientation of the S(1)C(3)=C(4) and C(1)—B(3) fragments, the intermediate in the formation of the disubstituted carborane derivatives **16a** and **17a**.[26]

Scheme 6



Below we present intramolecularly rearranged complex **19** [26] obtained from the monosubstituted carborane complexes after the reaction with the second equivalent of $MeO_2C—C{\equiv}CH$ and heating in toluene at 110 °C. Note the transformation of the initial alkynyl carbon atoms into two olefinic (dark circles) and two aliphatic sites (light circles).

At least in the case of the iridium complexes, a straightforward way is now open for the first time to prepare selectively mono- and 3,6-disubstituted *ortho*-carborane derivatives. Scheme 3 suggests that the *transoid* isomers are more likely than the *cisoid* isomers to undergo the reaction at the M—B bond to give first



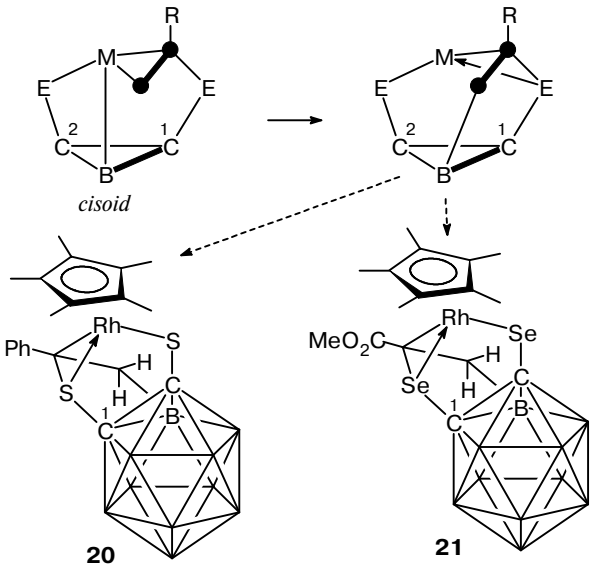
the monosubstituted and then the disubstituted derivatives.

Other variants of intramolecular reactions involving the M—B bond

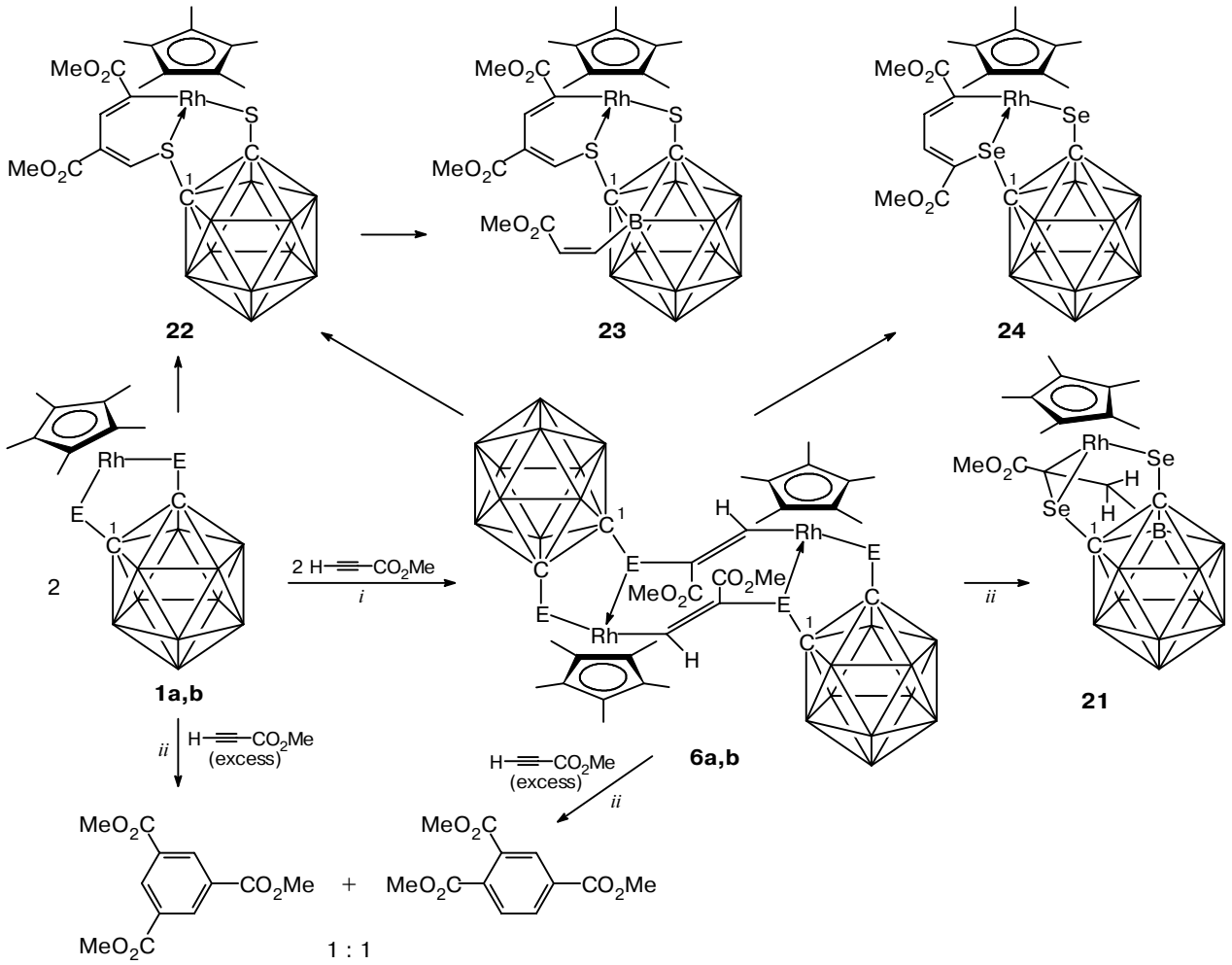
Are there other possibilities for the M—B bond to undergo intramolecular reactions, *e.g.*, starting from the *cisoid* isomer (Scheme 3)? If the *cisoid-transoid* rearrangement is slow, the terminal alkyne carbon atom can react at the M—B bond as shown in Scheme 7. Both compounds **20** [27] and **21** [28] were structurally characterized by X-ray analysis and NMR. Thus, there are additional ways to form selectively new carbon—boron bonds.

In the cases of *cisoid* complexes **14a** and **14b**, heating at 110 °C in toluene affords another new type of complexes in which two alkyne units are linked together and only one boron atom of the carborane bears an organic substituent (see Scheme 6 and compound **19**). This is a remarkable example of B—C and C—C bond

Scheme 7



Scheme 8



E = S (**a**), Se (**b**)

Reagents and conditions: *i.* CH_2Cl_2, 25 °C; *ii.* toluene, 70 °C.

formation in the sphere of the transition metal, and both intermediates with an Ir—B bond (one before the monosubstitution and the second intermediate **14a** or **14b**) could be isolated (see Fig. 2).[26]

Catalytic activities of 16e complexes 1—4

Rhodium complexes **1** show catalytic activity which, so far, has been investigated in the reactions with methyl acetylenemonocarboxylate, $MeO_2C—C{\equiv}CH$,[22] phenylacetylene, Ph—C≡CH,[22] and ferrocenylacetylene, Fc—C≡CH.[24] In the first two cases, cyclotrimerization is the preferred reaction. In the reaction with $MeO_2C—C{\equiv}CH$ (toluene, 70 °C)[22] in the presence of **1a** or **1b**, intermediates **22**, **23**, and **24b** (Scheme 8*) were isolated and structurally characterized.[27,29] Analogous results were obtained for Ph—C≡CH; however, intermediates were not detected. In the case of Fc—C≡CH, cyclotrimerization products were not found. Instead, noncyclic dimers of Fc—C≡CH were observed when **1b** was used; however, it was difficult to reproduce high yields from >70% in repeated experiments under apparently similar conditions.[24] In the case of the reaction of **1a** with Fc—C≡CH, complex **10** (see Scheme 4) was the sole product.[24]

Conclusion

The 16e complexes **1—4** proved to be versatile reagents in their reactions with a number of terminal alkynes, such as methyl acetylenemonocarboxylate, phenylacetylene, ferrocenylacetylene, but also acetylene itself, propyne and 3-methoxy-1-propyne. This is promising for future studies, using other alkynes or comparable unsaturated substrates. The rhodium complexes **1a** and **1b** were the most reactive species. The activation of B—H bonds and the formation of M—B bonds (*ortho*-metalation) followed by selective mono- and disubstitution of the carborane cage in B(3) and B(6) positions is an interesting aspect in carborane chemistry. Together with promising aspects in catalysis, which have been by far not fully explored, these carborane derivatives deserve further attention.

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* Intermediates **22**, **23**,[29] and **24b**[27] can be isolated under milder conditions.