Carbohydrate-Modified Metal Carbenes: Synthesis and First Applications

Karl Heinz Dötz* and Richard Ehlenz

Abstract: Carbohydrate-modified carbene complexes can be synthesised by combining a sugar electrophile with a metalate nucleophile or vice versa. Acyclic sugar skeletons adopt conformations that are controlled by the minimisation of 1,3-interactions and are not significantly affected by the incorporation of a metal fragment. Thus, the latter can be used exclusively for reactivity tuning. Sugar carbene complexes undergo regio- and stereoselective ligand- and metal-centred reactions such as C_2-homologisation and benzannulation.

Keywords: asymmetric synthesis · carbene complexes · carbohydrates · glycosylidenes · spiro compounds

Introduction

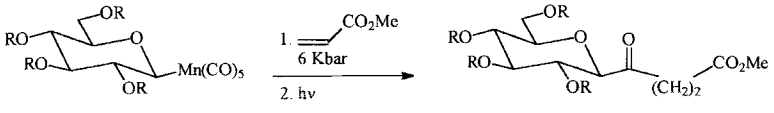
Carbohydrates are widespread compounds in nature and are of growing interest in biochemistry as well as in stereoselective synthesis. During the past two decades it has been recognised that sugars participate in important biochemical processes; for example, the carbohydrate units of glycoconjugates strongly influence biological selection processes such as molecular recognition at cell walls.[1] They also play an active role in intracellular enzyme transport,[2] infection processes[3] and cell adhesion.[4]

Up to now, a broad variety of synthetic methods have been developed for the synthesis of oligo- and polysaccharides, but it still remains a major challenge to activate the C-1 carbon atom smoothly for glycosidation reactions.[5] Whereas organometallic chemistry is widely used in stereoselective organic synthesis, its impact on carbohydrate chemistry is still underdeveloped. Carbohydrates are used as valuable auxiliaries in stereoselective synthesis.[6] As ligands bound through oxygen to titanium they facilitate Lewis acid catalyzed Diels–Alder[7] and aldol reactions.[8] However, the tuning of the anomeric centre for glycosidation reactions by means of organometallic reagents is mainly restricted to lithiation and stannylation.[9] In addition, very few transition metal complexes have been used in *C*-glycosidation reactions.[10] Stable glycosyl complexes have been reported for cobalt,[10a] manganese[10b–d] and iron,[10e,f] and manganese compounds **1** have been employed in the synthesis of *C*-glycosides, although wider application is hampered by the high-pressure conditions required (Scheme 1).

Because of the inherent polarity of the metal–alkyl bond in **1**, the anomeric centre experiences an umpolung and thus reacts as a nucleophile. On the other hand, a pronounced electrophilicity is expected when C-1 is modified to a glycosylidene carbon atom, coordinated to a metal carbonyl fragment. Such Fischer carbene complexes are promising candidates for both ligand- and metal-centred reactions, which may enlarge the scope of carbohydrate synthetic methodology.

So far, carbohydrates have been used to introduce chiral information into the carbene ligand by addition of partially protected carbohydrates to isonitrile complexes of gold or platinum,[11] to cationic manganese and rhenium carbynes[12] or to alkynyl carbene complexes of chromium or tungsten (Scheme 2).[13] These methodologies allow the modification of the carbene ligand with an *O*-linked sugar skeleton to give complexes of type **2** and **3**; however, no synthetic applications have been reported so far.

Apart from the modification of Fischer carbene complexes with carbohydrates described above, a promising strategy is the activation of sugar carbon atoms as electrophilic carbene carbons. With regard to this aim three topics are of interest:



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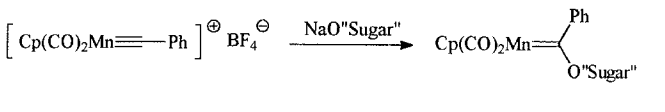
Scheme 1. High-pressure *C*-glycosidation with manganese complexes.



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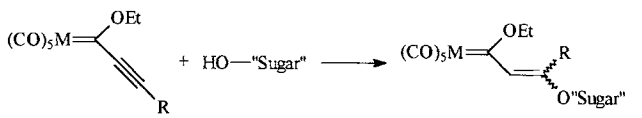

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Scheme 2. Carbene complexes modified with *O*-linked sugars.

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1) What strategies can be developed for the synthesis of carbohydrate-functionalised carbene complexes?
2) To what extent does a bulky organometallic substituent influence the conformation of the carbohydrate skeleton?
3) Do carbohydrate-functionalised carbene complexes adhere to the typical carbohydrate reactivity patterns, and can they be used in diastereoselective reactions, in *C*-glycosidations and in the formation of non-glycosidic linkages?

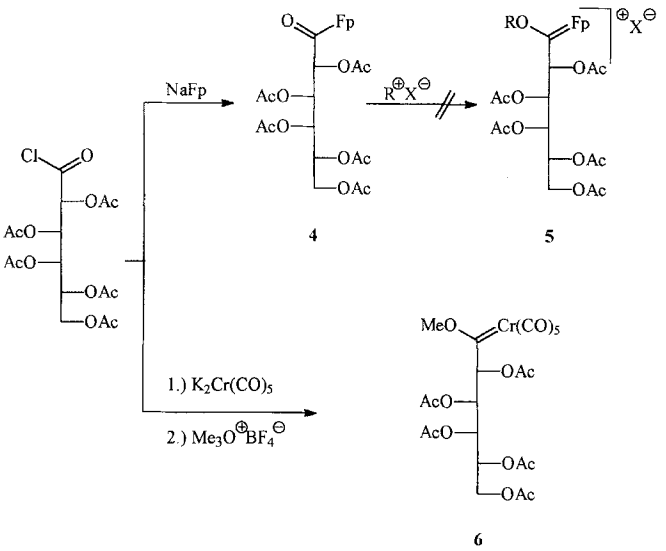
Discussion

Acyclic sugar carbene complexes: Carbene complexes are generally synthesised by combining a metal electrophile and a *C*-nucleophile[14] or vice versa.[15] The latter strategy, which has been applied to the synthesis of glycosyl complexes, can also be exploited for the transformation of the C-1 of acyclic, protected carbohydrates into a transition metal stabilised carbene centre.

Strong organometallic bases like sodium cyclopentadienyldicarbonylferrate or potassium pentacarbonylmanganate add to hexonic and pentonic acid chlorides to yield neutral sugar acyl complexes **4**,[16] as demonstrated for the D-galactose series. Contrary to the iron compounds, the manganese analogues decarbonylate under mild conditions. Whereas simple acyl complexes of iron undergo ready *O*-alkylation when treated with hard electrophiles, the transformation of **4** into cationic iron carbenes **5** is hampered by the presence of the acetyl protecting groups. However, with increased nucleophilicity of the acyl oxygen, such as in anionic acyl complexes of Group 6 or 7 metalates, clean alkylation occurs to give the neutral carbene complexes **6** (Scheme 3).[17]

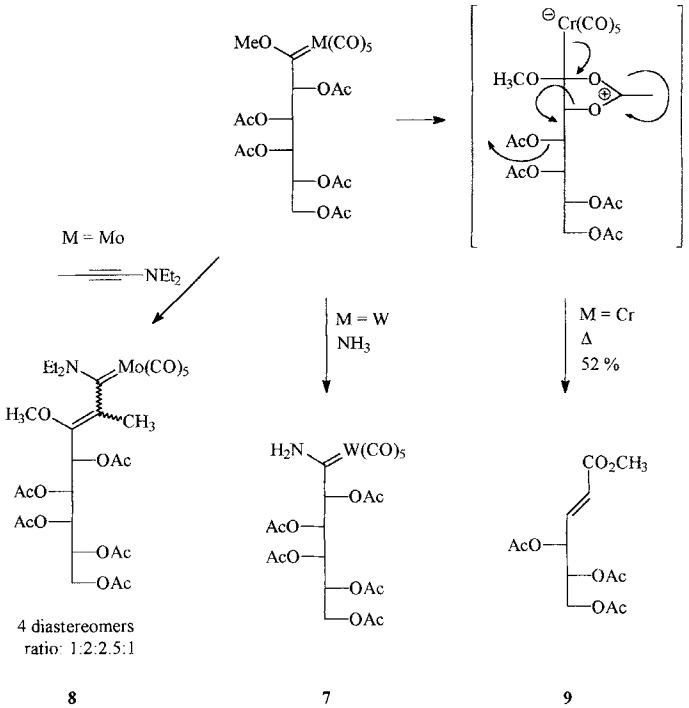
The reactivity of the neutral carbene complexes such as **6** generally resembles that known for Fischer-type carbene complexes. The addition of nucleophiles such as amines[18a] or ynamines[18b] results in the formation of aminocarbene complexes of type **7** and **8**, respectively (Scheme 4). Whereas aminolysis occurs readily with gaseous ammonia, the reaction with sterically more demanding amines is accompanied by a competing ester cleavage. Attempts to perform cyclopropanation under thermal conditions have been unsuccessful so far; instead, owing to the leaving group character and neighbouring group participation of the ester protecting groups, elimination of two vicinal acetoxy groups and the metal carbonyl fragment occurs leading to the formation of sugar enoates **9**.[18c]

Surprisingly, the incorporation of the bulky metal carbonyl fragment has no significant impact on the conformation adopted by the sugar backbone. Low-temperature NMR studies show



Scheme 3. Carbohydrate-modified acyl and carbene complexes (Fp = $CpFe(CO)_2$).

that the per-*O*-acetylated iron acyl complexes with D-galacto and L-arabino configurations adopt planar zigzag conformations, whereas the D-gluco and D-ribo compounds suffer from unfavourable 1,3-interactions, which force the sugar skeletons to adopt sickle-shaped conformations. X-ray studies indicate that the D-galacto and D-gluco acyl complexes show the same preferences in the solid state (Scheme 5).[16] Similar observations have been made for acyclic sugar carbene complexes; comparative X-ray structure analyses of the D-galacto chromium complex and its isolobal analogue methyl galactonate demonstrate that the conformation of the sugar backbone is controlled by 1,3-interactions of the protecting groups rather than by the bulky organometallic substituent at C-1.[18a]



Scheme 4. Reactions involving the C-1 carbon of acyclic sugar carbene complexes.

Abstract in German: *Kohlenhydrat-modifizierte Carbenkomplexe sind durch die Kombination von Zucker-Elektrophil mit Metallat-Nucleophil oder umgekehrt zugänglich. Acyclische Zuckergerüste bevorzugen Konformationen entlang der Zuckerkette, die durch eine Minimierung von 1,3-Wechselwirkungen der Schutzgruppen bestimmt sind. Somit kann das Metallkomplexfragment ausschließlich zur Modifizierung der Reaktivität des Zuckers herangezogen werden. Die Zucker-modifizierten Carbenkomplexe gehen regio- und stereoselektive Ligand- und Metall-zentrierte Reaktionen wie C_2-Homologisierungen und Benzanellierungen ein.*

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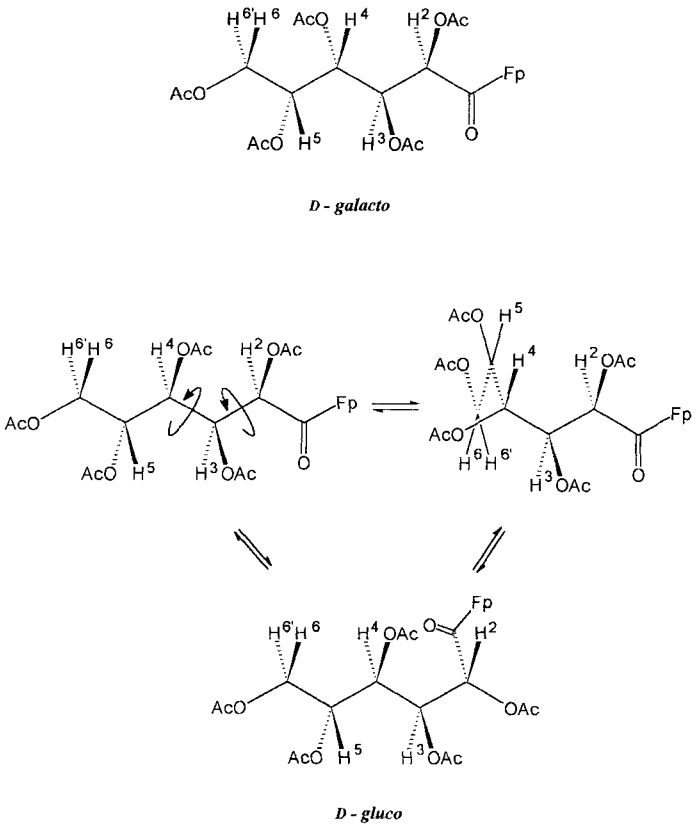
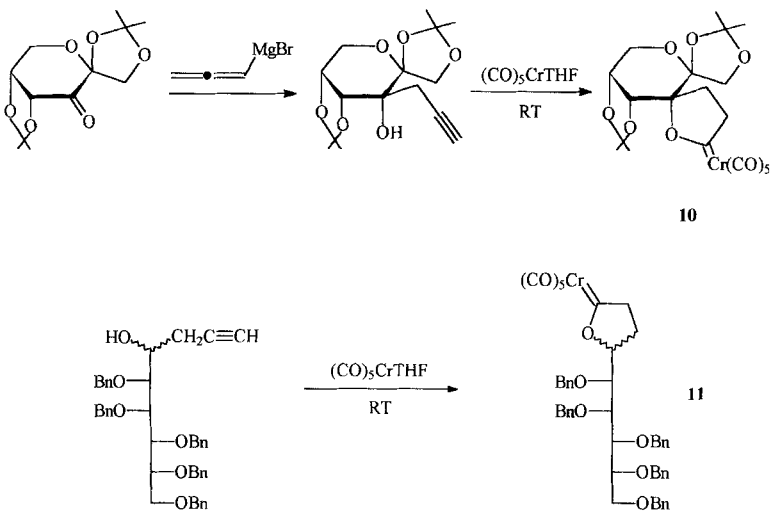


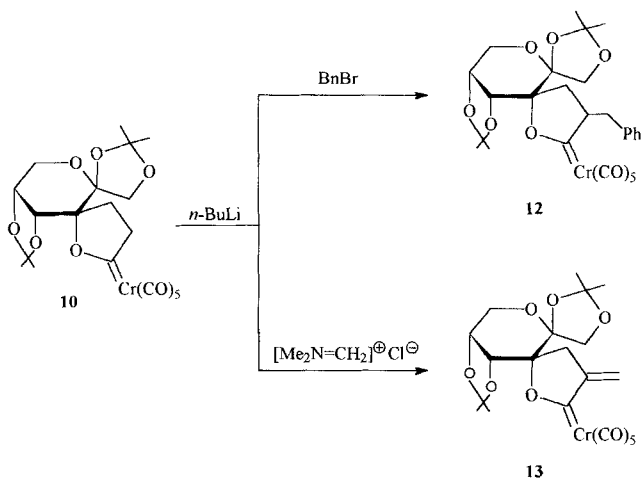
Scheme 5. Preferred conformations of D-galacto and D-gluco iron acyl complexes.

Carbohydrate oxacyclopentylidene complexes: An elegant method for the preparation of oxacyclopentylidene complexes is based on the cyclisation of alkynols.[19] This methodology has been exploited for the preparation of spirocyclic tetrahydrofuranyl ethers,[20] which are important structures in natural product synthesis, because of their pharmacological reactivity patterns; calyculine, for example, is a phosphatase inhibitor,[21a] and papulacandines inhibit (1→3)-β-glucansynthase.[21b, c]

Generally, butynols are readily accessible by the addition of propargylic organometallics to carbonyl compounds. In the synthesis of carbohydrate-functionalised butynols, however, allenylmagnesium bromide turns out to be the reagent of choice,



Scheme 6. Metal-assisted sugar alkynol cycloisomerisation.



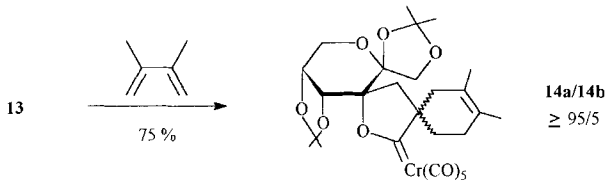
Scheme 7. α-Functionalisation of spiro pyranosyl carbene complexes.

which adds diastereoselectively to sugar-based lactones and ketones. The subsequent reaction of the sugar butynols with a solvent-stabilised pentacarbonylchromium template yields spirocyclic 2-oxacycloalkylidene complexes, as demonstrated in the psicose series for carbene complex **10** (Scheme 6).[22] The cycloisomerisation strategy can be similarly applied to acyclic carbohydrates. In contrast, the diastereoselectivity of the allenyl Grignard addition to sugar aldehydes is considerably lower. Separation of the diastereoisomers can most readily be achieved after cycloisomerisation at the chromium template to give pentose- or hexose-modified chromium oxacyclopentylidenes, as depicted for the mannose derivative **11** (Scheme 6).[23]

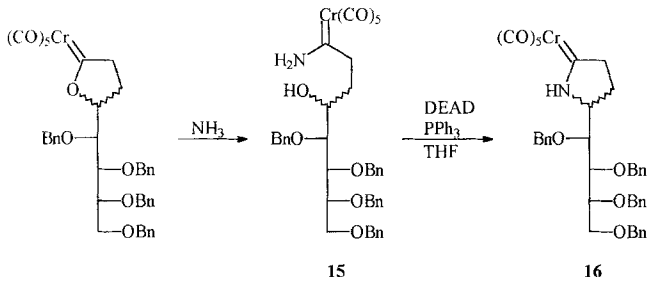
The potential of metal carbenes in stereoselective synthesis is based both on the pronounced acidity of the α-CH in the alkyl side chain of the carbene[24] and on the cycloaddition reactions centred on the metal[25] or carbene ligand.[26] The incorporation of the sugar backbone into the carbene ligand leads to an asymmetric modification of these carbon–carbon bond forming reactions. For example, on α-benzylation of psicose complex **10**, the monoalkylated compound **12** is obtained as a single diastereomer (Scheme 7), along with a minor amount of the bisalkylation product.

The conjugated base generated from psicose complex **10** can be modified into the α-*exo*-methylene derivative **13** upon reaction with methylenedimethyliminium chloride (Scheme 7). This type of transition metal complex bears a carbon–carbon double bond activated by the metal carbene moiety for cycloaddition reactions. The Diels–Alder reaction with 2,3-dimethylbutadiene gives the bis-spiro carbene complex **14a/b** in ≥90% *de* (Scheme 8).[22b] A sterically more demanding dienophile, however, may fail to undergo a [4+2] cycloaddition, as demonstrated for the benzylidene analogue. 2-Oxacyclopentylidene complexes with acyclic sugar side chains show similar high diastereoselectivities in alkylation and Diels–Alder reactions. Whereas the *exo*-methylene oxacyclopentylidene complexes are susceptible to ligand-centred cycloaddition reactions, the metal-centred benzannulation reaction of **13** fails under our standard conditions.

The pronounced electrophilicity of the metal-coordinated carbene carbon atom is the most remarkable fea-



Scheme 8. Bisspiro carbene complexes by diastereoselective Diels–Alder reaction.



Scheme 9. 2-Azacyclopentylidene complexes formed by ring opening/recyclisation.

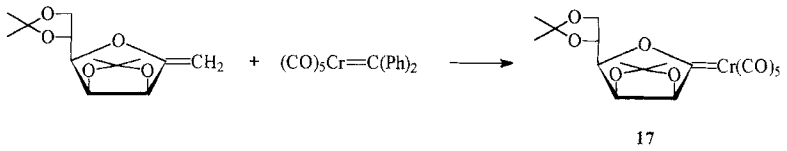
ture of the Fischer carbene complexes, and this can be exploited in an exchange of alkoxy for amino substituents at this position. The aminolysis of diastereopure 2-oxacycloalkylidene complexes (although with unknown configuration at the ring carbon atom bearing the sugar side chain) results in a ring-opening reaction to give acyclic aminocarbene complexes **15** bearing an unprotected hydroxyl group in the γ-position. This substitution pattern allows a recyclisation under Mitsunobu conditions to give 2-azacyclopentylidene complexes **16** with concomitant epimerisation at the former C-1 position of the carbohydrate chain (Scheme 9).[23]

Glycosylidene complexes: Attempts to synthesize glycosylidene complexes, which are promising reagents for novel *C*- and heteroatom glycosidation reactions, by means of the classical Fischer or the pentacarbonyl metalate dianion procedure failed. However, the stoichiometric olefin metathesis reaction, in which an electron-rich alkene is coupled with an electron-deficient metal carbene, allowed the *exo*-methylene furanoses to be modified into furanosylidene complexes such as **17** in good yields (Scheme 10).[27]

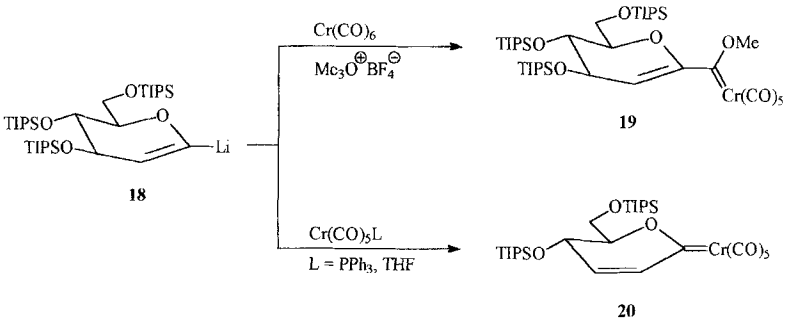
α,β-Unsaturated carbene complexes have many applications in organic synthesis. They undergo 1,2 or 1,4 nucleophilic additions, and metal-centred benzannulation or cyclopentannulation reactions. Their carbohydrate-based analogues can be formed from glycals, which can be incorporated into the carbene ligand according to the Fischer route.[14] The addition of lithioglucals such as **18** to binary metal carbonyls and subsequent alkylation provide a straightforward access to unsaturated carbohydrate carbene complexes **19**.[28] The addition of the glucal nucleophile to the metal carbonyl electrophile is controlled by the ligands in the coordination sphere of the latter. If a ligand combining donor and leaving group properties such as PPh_3 or THF is present in the metal carbonyl electrophile, the addition of the lithioglucal occurs at the metal centre rather than at the carbonyl ligand. Cleavage of the donor ligand and concomitant or subsequent elimination of the 3-silyloxy group result in the formation of unsaturated pyranosylidene complexes **20** (Scheme 11).

The aminolysis/recyclisation sequence can also be applied to metal furanosylidenes.[27] This route provides a novel approach to azasugars with inversion of configuration at the carbon atom C-4 (Scheme 12). X-ray structure analyses of the isopropylidene-protected mannosylidene complex **17** and its epimeric aza analogue **21** demonstrate that this transformation has no significant impact on the conformation of the sugar ring. A complementary approach to metal azacyclopentylidenes uses a combination of a sugar electrophile and a carbonyl metalate nucleophile. According to the procedure reported by Hegedus[29] the protected erythrono lactam **22** is modified into the corresponding furanosylidene complex **23** upon addition of dipotassium pentacarbonylchromate and deoxygenation assisted by TMS chloride (Scheme 12).[27]

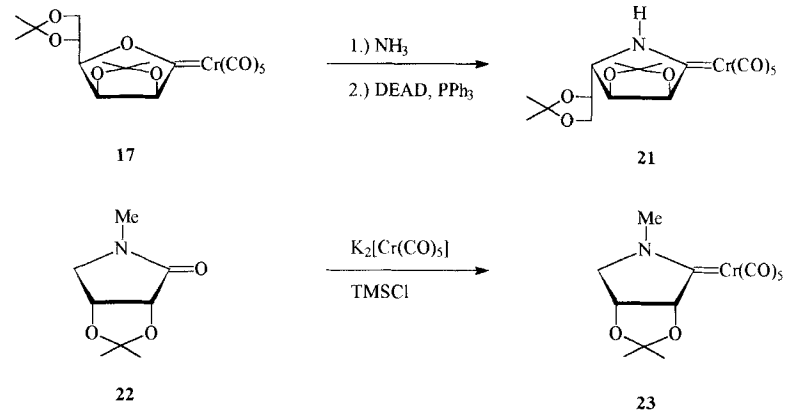
The electrophilicity of the metal carbene centre can be exploited for the homologisation of the glycosylidene ligands. Electron-rich alkynes undergo insertion into the metal carbene bond to give the C_2 homologue containing a new metal carbene



Scheme 10. Furanosylidene complexes by stoichiometric olefin metathesis.



Scheme 11. Access to glucal carbene and pyranosylidene complexes .



Scheme 12. Syntheses of azaglycosylidene complexes.

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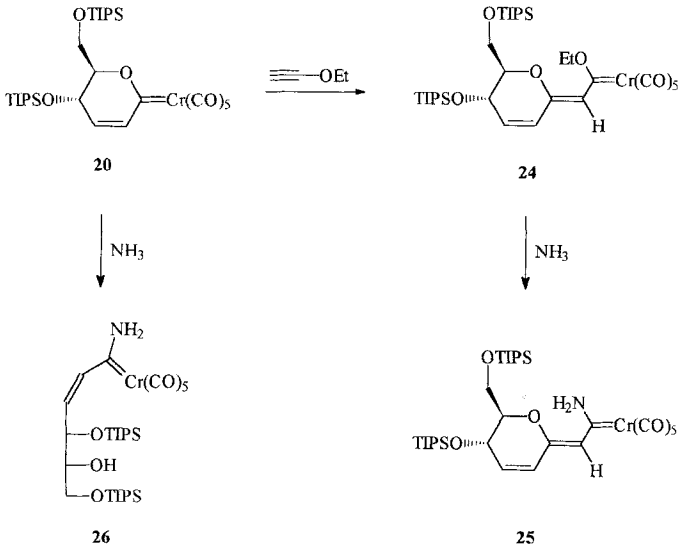
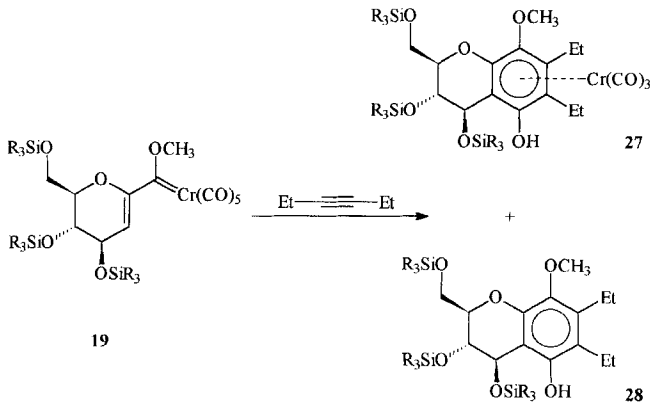
moiety.[30] While the insertion of ynamines leads to the formation of both isomers across the *exo*-alkylidene bond, the reaction with ethoxyethyne provides a stereoselective access to the (*Z*) isomer.[28] The metallatriene system **24** resulting from the C_2-homologisation of **20** offers a choice of three conjugated centres for the addition of nucleophiles. Under kinetic control ammonia adds regioselectively to the hard metal–carbene centre to give **25**; conjugate addition at the oxygenated β-position or at the C-3 carbon atom in the unsaturated sugar ring are suppressed under these conditions (Scheme 13). Similarly, upon addition of amines, the glucal-derived chromium carbene **20** favours aminolysis at the carbene carbon over Michael addition to the glucal, yielding the acyclic unsaturated carbene complex **26**.



Scheme 13. Homologisation by two carbon atoms and regioselective aminolysis of pyranosylidene complexes (TIPS = triisopropylsilyl).

The glucal carbene **19** is a promising candidate for diastereoselective benzannulation. Upon reaction with 3-hexyne the $Cr(CO)_3$-coordinated benzoglucal **27** is formed along with a comparable amount of the uncoordinated benzannulation product **28** (Scheme 14).[18b, 28] In addition to the chiral centres originating from the sugar moiety, the $Cr(CO)_3$–arene complex contains a plane of chirality. A single diastereomer (with still unknown configuration at the chromium arene bond) is obtained from the benzannulation reaction. This might be the result of a diastereoselective benzannulation; however, at present, it cannot be excluded that the decomplexed annulation product arises from the other diastereomeric annulation product in which the chromium is bound to the opposite face of the arene ring.



Scheme 14. Benzannulation of glucal carbene complexes.

Outlook

Successful carbohydrate synthesis requires a variety of tunable experimental procedures. Organometallic reagents, which have already played a major role in the development of stereoselective organic synthesis, provide an ample choice for the optimisation of metal–ligand combinations and promise to become equally successful in the preparation and modification of multifunctional sugar skeletons. In particular, metal carbene complexes are useful tools, which offer unconventional reaction patterns and thus are well-suited to extend the scope of established synthetic methodologies.

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