Organotransition Metal Modified Sugars, Part 13[+]

Furanosylidene and Iminofuranosylidene Complexes: Synthesis by Stoichiometric Olefin Metathesis and Ring-Opening/Mitsunobu-Recyclization Sequence

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Dedicated to Professor Fritz Vögtle on the occasion of his 60th birthday

Abstract: Stoichiometric olefin metathesis of highly electrophilic Fischer diphenylcarbene complexes of chromium and tungsten **3** and **4** with D-mannose- and D-gulose-derived furanoid *exo*-glycals has been applied to the synthesis of furanosylidene complexes **5**–**8**. *E*-selective ring-opening aminolysis with a range of primary amines and subsequent recyclization under Mitsunobu conditions provides an easy access to iminofuranosylidene complexes of the *talo* and *allo*-series **20**–**26**. The scope of this sequence is demonstrated by the synthesis of a novel class of organometallic glycoconjugates.

Keywords: bioorganometallic chemistry · carbene complexes · carbohydrates · glycoconjugates · Mitsunobu reaction

Introduction

Carbohydrates are of widespread use in nature and biological chemistry. In addition to their long known functions as backbone or energy storing molecules, they play an important role in intercellular molecular recognition processes, such as infection, tumor cell growth, and cell adhesion.[2] C-glycosides and imino-sugars have been the subject of intense research during the past decade as they act as carbohydrate mimetics or glycosidase inhibitors, and novel synthetic methodologies for these types of substrates have been established.[3] The development and the manifold use of transition metal organometallic compounds in organic synthesis[4] has established bioorganometallic chemistry as a new area of research, which is concerned with both the use of biomolecules as auxiliaries in metal-mediated reactions and the synthesis of biologically important molecules by means of organotransition metal chemistry.[5] Nonetheless, its influence on synthetic carbohydrate chemistry is still marginal though increasing.[6, 7]

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Fischer carbene complexes of Group 6 transition metals have been developed to valuable tools in stereoselective organic synthesis.[8, 9] Their synthetic potential is based on the electrophilic carbene carbon atom and the α-CH acidity as well as on the template properties of the metal carbonyl fragment. They undergo a variety of metal- and ligand-centred reactions like aldol-type condensation,[10] cyclopropanation,[11] alkyne insertion,[12] $[3+2+1]$ benzannulation,[8, 13] Diels–Alder reaction,[14] or photoinduced β-lactam and β-lactone formation.[15] Our aim is to activate the anomeric carbon of the carbohydrate skeleton by transforming it into a Fischer carbene centre,[1, 7, 16–19] with the aim of forming organotransition metal stabilized formal analogues of the "glycosylidene carbene" intermediates studied by Vasella and co-workers.[20]

Herein[21] we report on an efficient synthetic access to furanosylidene chromium complexes and their application to novel organometallic glycoconjugates still bearing a metal-carbene functionality.

Results and Discussion

Furanosylidene complexes: The stoichiometric olefin metathesis reaction involving well-defined metal carbenes[22] has been mainly addressed in terms of a model reaction for catalytic olefin metathesis[23] which has been recently devel-

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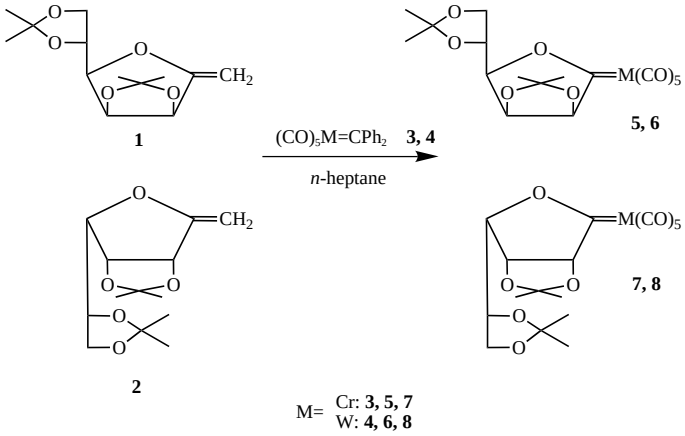
oped into a powerful synthetic methodology[24] with numerous applications as a key step in natural product synthesis.[25] Surprisingly, there are only a few examples of the stoichiometric variant aimed at the synthesis of carbene complexes otherwise difficult to obtain.[26] In our efforts to modify the sugar C-1 carbon atom into a Fischer-carbene centre we applied the olefin metathesis reaction to generate glycosylidene complexes on a multigram scale. Reaction of the hept-1-enitols **1**[27] and **2** with the highly electrophilic diphenylcarbene complexes **3** and **4**[28] afforded the glycosylidene complexes **5**–**8** in variable yields (Scheme 1). Best yields were



Scheme 1. Preparation of furanosylidene complexes. Conditions and yields. **5**: Room temperature, 90 min, 65 %; **6**: 50 °C, 90 min, 3 %; **7**: room temperature, 90 min, 66 %; **8**: 55 °C, 90 min, < 3 %.

obtained in the chromium series when a minimum amount of *n*-heptane was used as a solvent. The reaction was monitored by IR spectroscopy and TLC, and was completed within 90 minutes. As the formation of the oxa-stabilized glycosylidene complex is the driving force of the reaction, we had to make use of the reactive complexes **3** and **4**, rather than of the easier to handle methoxy(phenyl)carbene complex applied by Barluenga et al. for the formation of even more stabilized α,β-unsaturated aminocarbene complexes.[26]

The spectroscopic data of complexes **5**–**8** are characteristic for Fischer-type oxacyclopentylidene complexes. The X-ray structure analysis of complex **5** shows the typical bond lengths and angles expected for chromium oxacyclopentylidene complexes (Figure 1).[29] No significant influence of the bulky pentacarbonyl chromium fragment on the envelope conformation of the sugar ring or distortion of the dioxolane rings can be detected.

Abstract in German: *Die stöchiometrische Olefin-Metathese hochelektrophiler Fischer-Carbenkomplexe des Chroms und Wolframs **3** und **4** mit furanoiden exo-Glycalen wurde zur Darstellung der Furanosylidenkomplexe **5**–**8** mit* D-*manno-bzw.* D-*gulo-Konfiguration eingesetzt. E-selektive ringöffnende Aminolyse mit einer Reihe von primären Aminen und nachfolgender Ringschluß unter Mitsunobu-Bedingungen eröffnen einen einfachen Zugang zu Iminofuranosylidenkomplexen **20**–**26** der talo- und allo-Reihe. Die Anwendungsbreite der vorgestellten Reaktionssequenz wird anhand der Synthese einer neuartigen Klasse metallorganischer Glycokonjugate demonstriert.*

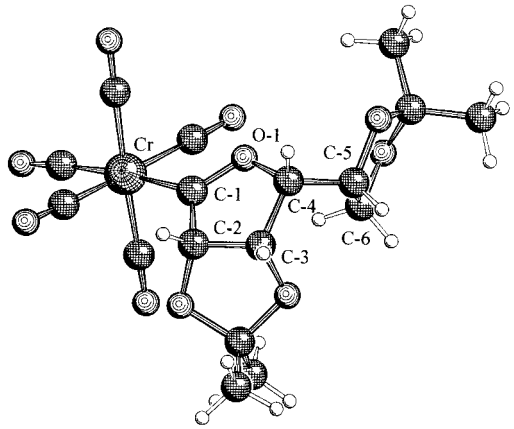
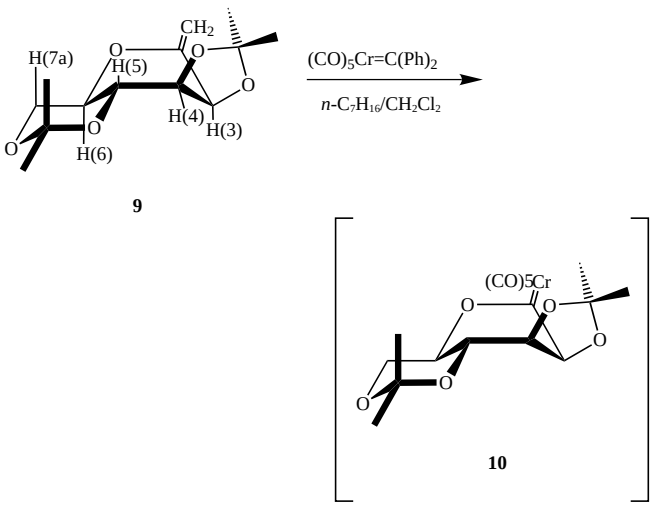


Figure 1. Schakal plot of the molecular structure of complex **5**.[21] One molecule out of two in the asymmetric unit is shown. Selected bond lengths [Å] and angles [°]: Cr–C-1 1.979(6), C-1–O-1 1.302(7), O-1–C-4 1.483(7), C-1–C-2 1.560(7), C-2–C-3 1.502(9), C-3–C-4 1.527(8); Cr–C-1–O-1 125.0(4), Cr–C-1–C-2 128.6(4), O-1–C-1–C-2 106.4(5).

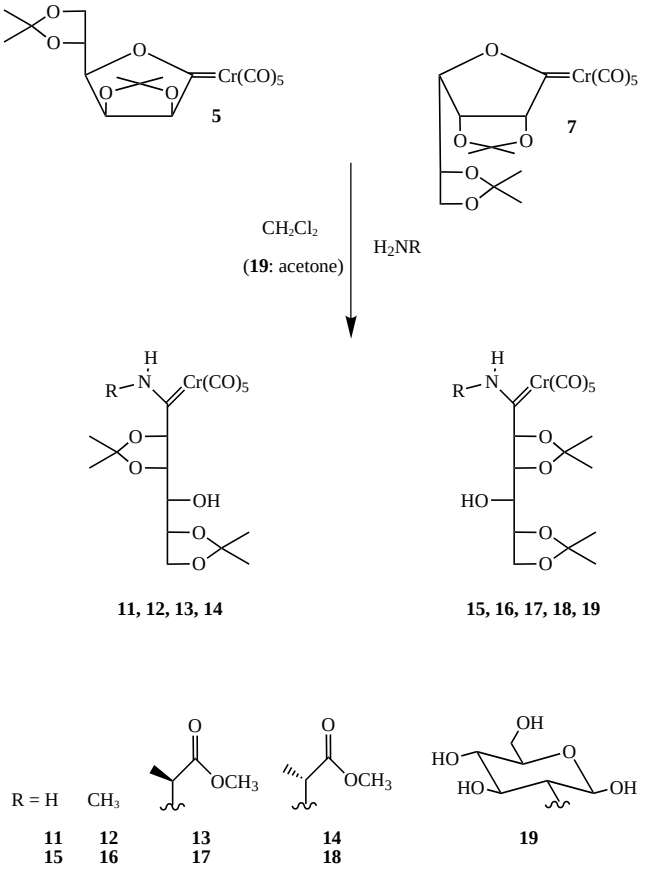
In an attempt to apply the reaction to the synthesis of pyranosylidene complexes we chose diisopropylidene-protected mannopyranoic *exo*-glycal **9**. Surprisingly, the resulting mannopyranosylidene complex **10** was extremely thermolabile. It could be identified by spectroscopic data, but it was impossible to purify it without decomposition. This lability may be due to insufficient stabilization of the carbene carbon atom by the ring oxygen atom for conformational and steric reasons.[30] As indicated by the $^3J_{H,H}$ coupling constants in the ^{1}H NMR spectrum the 4,6-*O*-isopropylidene protecting group forces the *exo*-glycal **9** into the boat conformation $B_{2,5}$ (Scheme 2). Supposed this rigid conformation still holds for



Scheme 2. Formation of pyranosylidene complex **10**. Selected spectroscopic data for **9**: ^{1}H NMR ($CDCl_3$): $^3J_{H\text{-}7a,H\text{-}6} = 10.1$ Hz, $^3J_{H\text{-}6,H\text{-}5} = 10.3$ Hz, $^3J_{H\text{-}5,H\text{-}4} = 7.4$ Hz, $^3J_{H\text{-}4,H\text{-}3} = 6.9$ Hz. Selected spectroscopic data for **10**: ^{13}C NMR ($CDCl_3$): $\delta = 352.4$ (C-1).

the glycosylidene complex **10**, it is expected to impose a destabilizing steric interaction between the 2,3-di-*O*-isopropylidene group and the pentacarbonylchromium fragment.

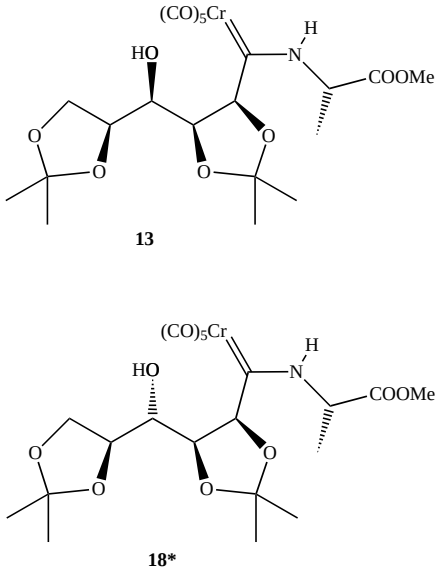
Ring-opening aminolysis: Fischer-type alkoxycarbene complexes undergo smooth aminolysis to give aminocarbene complexes.[31] The reaction is thermodynamically favoured, but may be hampered when bulky amines are used resulting in decreased yields and increased reaction times. Thus, reaction of **5** and **7** with small N-nucleophiles such as ammonia or methylamine at $-78\,^{\circ}C$ yielded immediately and quantitatively the corresponding acyclic amino(glycosyl)carbene complexes **11**, **12**, **15**, **16**, (Scheme 3) which could be obtained as



Scheme 3. Ring-opening aminolysis reactions. Reaction conditions and yields: **11**: $-78\,^{\circ}C$, instantaneously, 100%; **12**: $-78\,^{\circ}C$, instantaneously, 100%; **13**: $0\,^{\circ}C$, 2 h, 70%; **14**: $0\,^{\circ}C$, 2 h, 60%; **15**: $-78\,^{\circ}C$, instantaneously, 100%; **16**: $-78\,^{\circ}C$, instantaneously, 100%; **17**: $-78\,^{\circ}C$, instantaneously, 67%; **18**: $-78\,^{\circ}C$, instantaneously, 80%; **19**: room temperature, overnight, 50%.

analytically pure samples after evaporation of the solvents; no chromatographic workup procedure was required. When D- or L-alanine methyl ester were used as N-nucleophiles, the yields of the corresponding amino acid glycoconjugates **13**, **14**, **17**, **18** were lowered to 60–80%. Aminolysis with glucosamine resulted in a 50% yield of *N*-disaccharide **19**, a rare example of a neutral water-soluble carbene complex.[32] Tetrabenzoylated glucosamine was inert towards furanosylidene complex **5** under our standard conditions, which is likely attributed to the bulky O-protecting groups at C-1′ and C-3′.

Aminolysis with alanine ester provides a very efficient and straightforward access to organometallic equivalents of glycosoyl alanine esters, still bearing the synthetic potential of the pentacarbonylchromium fragment. Analoguous arabinoylglycinate and arabinoylglycine have recently been prepared in a multistep sequence by using N-alkylation of arabinonamide, and tested for its potential as an in vitro inhibitor against several sialidases.[33] Strikingly, reaction times of alanine methyl ester with complexes **5** and **7** were significantly different. Whereas gulofuranosylidene complex **7** almost instantaneously changed its reddish colour to yellow when mixed with the amino ester at $-78\,^{\circ}C$, indicating completion of the reaction, mannofuranosylidene complex **5** took two hours for the same reaction at $0\,^{\circ}C$, leading to comparable yields. In order to decide whether this is the result of a mismatched and a matched pair of two chiral substrates, **5** and **7** were also subjected to aminolysis with the unnatural D-alanine ester.[34] Again the aminolysis of *gulo*-complex **7** proceeded significantly faster indicating that the different reactivity of mannofuranosylidene complex **5** and gulofuranosylidene complex **7** reflects the complementary relative configuration at C-5, the only feature in which D-gulose and L-mannose differ from each other (Scheme 4).



Scheme 4. Configuration of complex **13** and the enantiomer of complex **18**.

In acyclic glycosylidene complexes the conformation of the carbohydrate skeleton has been found to be controlled by the relative 1,3-stereochemistry imposed by the O-protecting groups rather than by the bulky organometallic fragment.[7] In the case of the *manno*- and *gulo*-aminocarbene complexes **11**–**19** a $_2$G-sickle conformation is favoured by the rigidity of the acetalic protecting groups. The lack of any detectable scalar coupling in complexes **11**–**18**, and the small vicinal $^3J_{H\text{-}3,H\text{-}4}$ coupling constant of 2.7 Hz in complex **19**, suggest a preferred conformation in solution somewhere between synclinal and orthogonal orientation of the hydrogen atoms along the C-3/C-4 bond. The medium vicinal $^3J_{H\text{-}4,H\text{-}5}$ coupling constants (6.5–7.8 Hz) indicate a conformational equilibrium and rather free rotation around the C-4/C-5 bond, which is consistent with the data known for analogously protected mannonamide and gulonamide.[35] X-ray structural analysis of aminoglycosylidene complex **11** confirms these arguments and shows a $_2G^+$ conformation in the solid state (Figure 2).

0947-6539/99/0507-2016 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 7

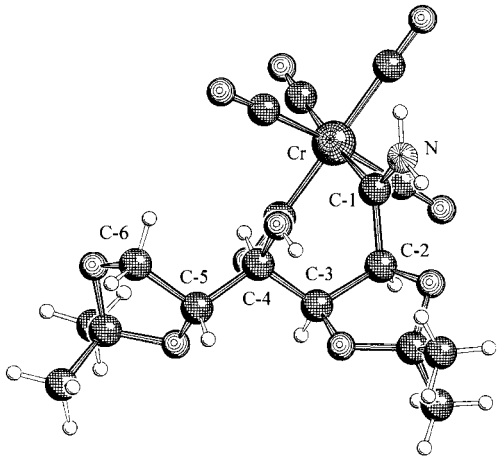


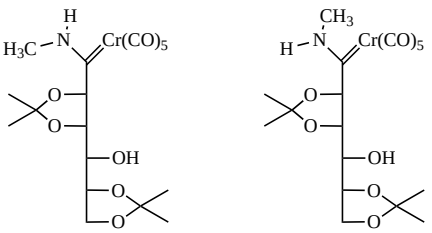
Figure 2. Schakal plot of the molecular structure of complex **11.** Selected bond lengths [Å] and angles [°]: Cr–C-1 2.086(2), C-1–N 1.299(3), C-1–C-2 1.525(3); Cr–C-1–N 125.1(2), Cr–C-1–C-2 122.8(1), N–C-1–C-2 111.9(2), C-1–C-2–C-3–C-4 –11.56 (0.25).

Again, *manno*- and *gulo*-derivatives in an achiral environment differ from each other only in the configuration at C-5. The same holds for *manno*- and *gulo*-derivatives with enantiomeric substrates. Thus, any difference in reactivity should be due to different steric impacts of the C-5/C-6-*O*-isopropylidene rotor.

The aminolysis of alkoxycarbene complexes with primary amines is expected to afford a mixture of *E/Z* isomers with respect to the C(carbene)–N bond. Surprisingly, only the reaction of furanosylidene complex **5** with excess methylamine at –78 °C results in the formation of an approximately 2:1 mixture of (*E*)-**12** and (*Z*)-**12** (Scheme 3, Table 1), whereas all other aminolysis reactions yielded a single diastereomer within the limits of NMR spectrosopy. The configuration of both isomers of **12** (Scheme 5) can be assigned on the basis of solvent-induced chemical shifts in the ^{1}H NMR spectra for the N-H and the N-$CH_{2(3)}$ hydrogen atoms observed in an isotropic and in an anisotropic solvent.[36] The shift differences $\Delta = \delta(CDCl_3) - \delta(C_6D_6)$ observed for the N-CH_2 group in the *E* isomers generally exceed those encountered for the *Z* isomers, (e.g. in this case 0.8 compared to 0.4), while the opposite trend holds for the N-H protons (0.35 compared to 1.0).[37]

Table 1. Characteristic NMR shifts of complex **12**.

	E-**12**		*Z*-**12**	
	N–H	N–CH_3	N–H	N–CH_3
$CDCl_3$	10.05	3.6	9.0	3.2
C_6D_6	9.7	2.8	8.0	2.8
Δ	0.35	0.8	1.0	0.4



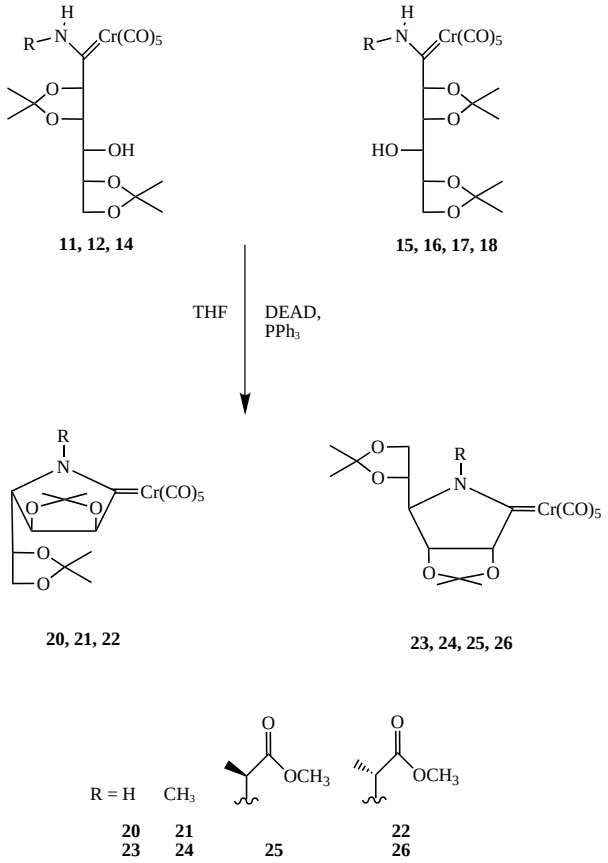
(*E*)-**12** (*Z*)-**12**

Scheme 5. *E/Z* Isomers of complex **12**.

The stereoselectivity of the aminolysis depends on the reaction and workup conditions. When aminolysis of mannofuranosylidene complex **5** was carried out with methylamine generated by slow hydrolysis of benzylidene(methyl)-imine at ambient temperature, only the *E* isomer of **12** was formed and could be isolated in 53% yield. Thus, all aminolysis reactions of chromium furanosylidene complexes **5** and **7** with primary amines could be performed with excellent stereoselectivity yielding only a single detectable isomer. The configuration of the mannose-derived aminolysis product (*E*)-**12** was determined based on the arguments outlined above. As the complexes **12**–**14** and **16**–**19** exhibit chemical shifts of the N-H protons in the range from $\delta = 10.05$ to 10.36 which corresponds to those of (*E*)-**12**, they are supposed to adopt the *E* configuration.[38]

Mitsunobu recyclization: In contrast to a variety of methods for the preparation of 4-deoxy-4-iminosugars, a general facile method for the stereospecific transformation of readily available furanonolactones into the corresponding C-4-epimeric furanonolactams is still missing. Moreover, intramolecular recyclization sequences of acyclic 4-hydroxy-aldonamides described so far require N-protection and an additional hydroxyl activation step[39, 40] or a stereochemically ambiguous oxidation/reduction sequence.[41] With the aim of synthesizing iminoglycosylidene complexes which represent organometallic analogues of sugar lactams and potential precursors of aza-*C*-glycosides which are currently receiving increased attention due to their potential as glycosidase inhibitors,[42] we were interested in a recyclization of the acyclic aminoglycosylidene complexes **11**–**19**. They bear a selectively unprotected hydroxy substituent at C-4 which might be exploited in a stereospecifical one-step recyclization using an intramolecular version of the Mitsunobu reaction.[43, 44] The analogous reaction of acyclic aldonamides suffers from competing side reactions due to the nucleophilicity of the carboxylic oxygen atom.[39] The applicability of Mitsunobu conditions in organotransition metal chemistry has recently been demonstrated.[45] When aminocarbene complexes **11**, **12**, **14** and **15**–**18** were treated with diethyl azodicarboxylate (DEAD) and triphenylphosphane in THF at room temperature cyclization to chromium 4-deoxy-4-iminofuranosylidenes **20**–**26** occurred in isolated, non-optimized yields of 23 to 67% (Scheme 6).

The X-ray structure analysis of complex **21** (Figure 3) indicates the configuration at C-4 and, in comparison with complex **5**, demonstrates that epimerization at the sterically demanding C-5/C-6-anchor has little impact on the ring conformation. As previously observed for the aminolysis the absolute configuration at C-5 also effects the propensity for recyclization. While *gulo*-complexes **17** and **18** undergo ready cyclization independent of the configuration of the amino acid ester, the *manno*-analogue **13** does not, and **14** affords only traces of iminofuranosylidene complex **22**. Evidently, the sterically demanding C-5/C-6-di-*O*-isopropylidene anchor, in



Scheme 6. Mitsunobu cyclization reactions. Reaction times and yields. **20**: overnight, 42%; **21**: overnight, 67%; **22**: 4 days, 1%; **23**: overnight, 36%; **24**: overnight, 34%; **25**: 2 days, 23%; **26**: 2 days, 54%.

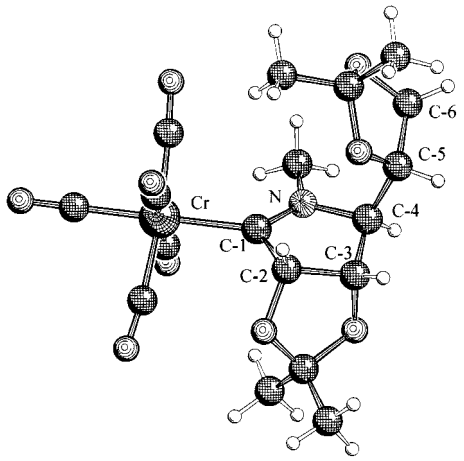
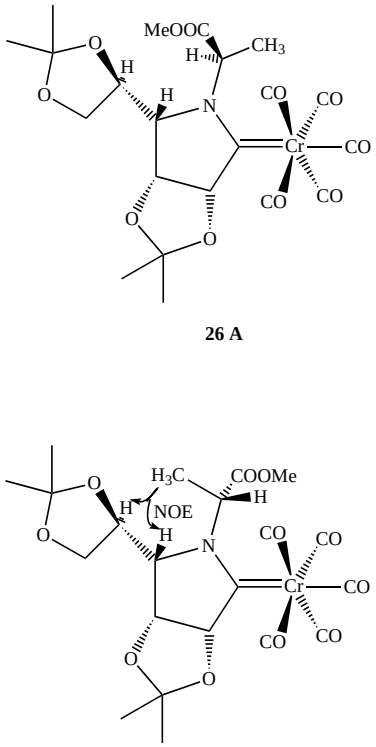


Figure 3. Schakal plot of the molecular structure of complex **21**.[21] Selected bond lengths [Å] and angles [°]: Cr–C-1 2.097(3), C-1–N 1.313(4), N–C-4 1.495(3), C-1–C-2 1.524(4), C-2–C-3 1.514(4), C-3–C-4 1.507(4); Cr–C-1–N 130.8(2); N–C-1-C-2 105.4, Cr-C-1-C-2 123.7(2).

combination with the bulky amino ester, prevents the *manno*-complexes from intramolecular nucleophilic attack at C-4. Similarly, the steric bulk of the glucosamine skeleton may be made responsible for the failure of the attempted cyclization of the *N*-disaccharide complex **19**. The different tendency towards cyclization observed for the *manno*- and *gulo*-derivatives is precedented; whereas *N*-benzyl-2,3:5,6-di-*O*-isopropylidene-4-methanesulfonyl-D-gulonamide underwent cyclization in high yield, the reaction of the *manno* analogue failed.[40,46]

Chromium 4-deoxy-4-imino-allofuranosylidene conjugate **26** was obtained in two isomeric forms **A** and **B** (Scheme 7) which are supposed to be atropisomers due to restricted rotation around the N–C-2′ bond. Their conformation was



Scheme 7. Atropisomers **26 A** and **26 B**.

assigned by NOE, no coalescence could be detected over a temperature range of 218–333 K (see Experimental Section). Metal carbenes **22**, **25** and **26** represent a novel class of organometallic glycoconjugates which may be extended to iminoglycopeptides following the same ring-opening aminolysis/recyclization methodology. Moreover, this approach provides a general strategy complementary to the sugar lactam electrophile/carbonyl metalate nucleophile route;[21, 47, 48] it avoids the use of the tedious reducing agent potassium graphite, makes both N-deprotected and N-substituted iminofuranosylidene complexes accessible, and is compatible with the synthesis of carbohydrate-anchored azacyclopentylidene complexes.[49]

We have described an efficient and multigram scale access to C-1-metal carbene modified furanoses and iminofuranoses which exhibit the characteristic properties of Fischer carbene complexes. Their scope and application in typical reactions such as C-glycosidation and cycloaddition reactions is under investigation.

Experimental Section

All operations involving organometallic compounds were performed under argon atmosphere. Reaction mixtures were degassed in three cycles prior to the start of the reaction. Solvents used for organometallic compounds were

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dried according to standard procedures: THF over sodium/potassium or LAH, diethyl ether over sodium hydride, dichloromethane and light petroleum (40–60 °C) over calcium hydride, and acetone over calcium chloride. If not mentioned otherwise, column chromatography was carried out using degassed solvents and silica gel (Merck Type 60, 0.063-0.200 mm). FT-IR: Nicolet Magna 550. MS: Kratos 1 H Concept. Melting points: Büchi SMP 20, uncorrected. Elemental analyses: Heraeus CHN-O-Rapid. NMR: Bruker AM 250, Bruker AM 400, Bruker DRX 500. Chemical shifts refer to those of residual solvent signals based on $\delta_{TMS} = 0.00$.

Preparation of the furanosylidene complexes 5–8: 2,5-Anhydro-1-deoxy-3,4:6,7-di-*O*-isopropylidene-D-gulo-hept-1-enitol (**2**) was prepared in analogy to the protocol by Csuk and Glänzer:[27] A solution of dicyclopentadienyldimethyltitanium[27] (8.36 g, 40.16 mmol)) and 2,3:5,6-di-*O*-isopropylidene-D-gulofuranonolactone[50] (4.70 g, 18.20 mmol) in toluene (100 mL) was stirred for 48 h at 65–70 °C in the dark. The reaction mixture was concentrated, and **2** was purified by column chromatography on silica gel (gradient light petroleum/ethyl acetate 20/1 to 5/1, silica gel and eluent containing 1% of triethylamine to prevent hydrolysis, $R_f = 0.61$, eluent light petroleum/ethyl acetate 3:1). Compound **2** (3.40 g, 13.27 mmol) was obtained as a waxy colourless solid in 73% yield. M.p. 47 °C; $[\alpha]_D^{20} = -103$ (584 nm, $CHCl_3$, 2.34 mM); IR (film): $\tilde{\nu} = 1688\ cm^{-1}$ (s, C=C); ^1H NMR (500.13 MHz, $CDCl_3$): $\delta = 1.31$ (s, 3H; CH_3), 1.37 (s, 3H; CH_3), 1.44 (s, 3H; CH_3), 1.45 (s, 3H; CH_3), 3.70 (dd, $^2J_{H,H} = 8.6$ Hz, $^2J_{H,H} = 7.05$ Hz, 1H; H-7a), 4.04 (dd, $^3J_{HH} = 8.44$ Hz, $^3J_{H,H} = 4.37$ Hz, 1H; H-5), 4.19 (dd, $^2J_{H,H} = 8.6$ Hz, 6.71 Hz, 1H; H-7b), 4.26 (dd, $^2J_{H,H} = 2.0$ Hz, $^4J_{H,H} = 1.0$ Hz, 1H; H-1a), 4.39 (dt*, $^3J_{H,H} = 8.44$ Hz, $^3J_{H,H} = 6.86$ Hz, 1H; H-6), 4.58 (ddd, $^2J_{H,H} = 2.0$ Hz, $^4J_{H,H} = 1.4$ Hz, $^5J_{H,H} = 0.6$ Hz, 1H; H-1b), 4.62 (dd, $^3J_{H,H} = 6.1$ Hz, $^3J_{H,H} = 4.37$ Hz, 1H; H-4), 5.04 (dt*, $^3J_{H,H} = 6.1$ Hz, $^4J_{H,H} = 1.2$ Hz, 1H; H-3); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 26.2$, 26.7, 27.5, 27.7 (4C; CH_3), 66.7 (1C; C-7), 76.8, 79.5, 81.1, 85.7 (4C; C-6, C-5, C-4, C-3), 87.9 (1 C; C-1), 110.9, 114.6 (2C, $C_{acetalic}$), 161.9 (1C, C-2); MS (EI): *m/z* (%): 256 (7) [M^+], 241 (38) [$M^+ - CH_3$], 213 (3), 198 (1) [$M^+ - (CH_3)_2CO$], 183 (10) [$M^+ - CH_3 - (CH_3)_2CO$], 141 (20), 43 (39); HRMS for $^{12}C_{13}{}^1H_{20}{}^{16}O_5$ [M^+] calcd. 256.1311; found 256.1307; $C_{13}H_{20}O_5$ (256.30): calcd. C 60.92, H 7.87; found C 60.90, H 7.93.

Pentacarbonyl(2,3:5,6-di-*O*-isopropylidene-D-mannofuranosylidene)chromium(0) (5): To pentacarbonyl(diphenylcarbene)chromium (0) (**3**)[28] (5.25 g, 14.65 mmol), *exo*-methylene sugar **1**[27] (3.45 g, 13.46 mmol) and *n*-heptane (11 mL) were added at −40 °C, allowed to warm to ambient temperature and stirred for 90 min. Column chromatography on silica gel (light petroleum/diethyl ether/dichloromethane 10/5/1; $R_f = 0.38$) afforded **5** (4.00 g, 9.21 mmol) as a dark orange solid in 68% yield. Crystals for X-ray structural analysis were grown from pentane. IR (*n*-heptane): $\tilde{\nu} = 2070$ (s, $^1A_1$; C=O), 1965 (vs, $^2A_1$/E; C=O), 1954 cm^{-1} (vs, E/$^2A_1$; C=O); ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 1.40$ (s, 3H; CH_3), 1.406 (s, 3H; CH_3), 1.41 (s, 3H; CH_3), 1.51 (s, 3H; CH_3), 4.16 (dd, $^2J_{H,H} = 9$ Hz, $^3J_{H,H} = 4.9$ Hz, 1H; H-6a), 4.20 (dd, $^2J_{H,H} = 9$ Hz, $^3J_{H,H} = 6.3$ Hz, 1H; H-6b), 4.48 (td, $^3J_{H,H} = 6.3$ Hz, $^3J_{H,H} = 4.9$ Hz, 1H; H-5), 4.71 (dd, $^3J_{H,H} = 5.5$ Hz, $^3J_{H,H} = 4$ Hz, 1H; H-3), 5.00 (dd, $^3J_{H,H} = 6.3$ Hz, $^3J_{H,H} = 4$ Hz, 1H; H-4), 5.23 (d, $^3J_{H,H} = 5.5$ Hz, 1H; H-2); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 25.4$, 25.5, 26.5, 26.8 (4 C, CH_3), 66.0, 72.6, 74.7, 97.5, 99.2 (5C, C-2, C-3, C-4, C-5, C-6), 110.0, 114.2 (2 C, $C_{acetalic}$), 215.8 (4 C, CO_{cis}), 224.0 (1 C, CO_{trans}), 342.4 (1 C, C-1); MS (EI): *m/z* (%): 434 (14) [M^+], 419 (7) [$M^+ - CH_3$], 406 (7) [$M^+ - CO$], 391 (1) [$M^+ - CO - CH_3$], 378 (1) [$M^+ - 2CO$], 350 (7) [$M^+ - 3CO$], 335 (7) [$M^+ - 3CO - CH_3$], 322 (42) [$M^+ - 4CO$], 307 (10) [$M^+ - 4CO - CH_3$], 294 (30) [$M^+ - 5CO$], 279 (5) [$M^+ - 5CO - CH_3$], 236 (1) [$M^+ - 5CO - (CH_3)_2CO$], 221 (2) [$M^+ - 5CO - CH_3 - (CH_3)_2CO$], 178 (100) [$M^+ - 5CO - 2(CH_3)_2CO$], 148 (18); HRMS for $^{12}C_{17}{}^1H_{18}{}^{16}O_{10}{}^{52}Cr$ [M^+] calcd. 434.0305; found 434.0296; $C_{17}H_{18}O_{10}Cr$ (434.32): calcd. C 47.01, H 4.18; found C 47.40, H 4.63.

Pentacarbonyl(2,3:5,6-di-*O*-isopropylidene-D-mannofuranosylidene)tungsten(0) (6): A mixture of of *exo*-methylene sugar **1**[27] (360 mg, 1.42 mmol) and pentacarbonyl(diphenylcarbene)tungsten (0) (**4**)[28] (665 mg, 1.35 mmol) in *n*-heptane (2 mL) was prepared at −20 °C, then warmed and stirred at 50 °C for 90 min. Column chromatography on silica gel (light petroleum/diethyl ether/dichloromethane 15/5/1; $R_f = 0.20$) yielded **6** (20 mg, 0.035 mmol) as a dark orange crystalline solid in 3% yield. IR: (light petroleum): $\tilde{\nu} = 2075\ cm^{-1}$ (s, $^1A_1$; C=O), 1954 cm^{-1} (vs, $^2A_1$, E; C=O); ^1H NMR (500.13 MHz, $CDCl_3$): $\delta = 1.39$ (s, 3H; CH_3), 1.40 (s, 3H; CH_3), 1.42 (s, 3H; CH_3), 1.50 (s, 3H; CH_3), 4.13 (dd, $^2J_{H,H} = 9.2$ Hz, $^3J_{H,H} = 4.8$ Hz, 1H; H-6a), 4.20 (dd, $^2J_{H,H} = 9.2$ Hz, $^3J_{H,H} = 6.3$ Hz, 1H; H-6b), 4.50 (td, $^3J_{H,H} = 6.3$ Hz, $^3J_{H,H} = 4.8$ Hz, 1H; H-5), 4.71 (dd, $^3J_{H,H} = 5.3$ Hz, $^3J_{H,H} = 3.9$ Hz, 1H; H-3), 4.95 (dd, $^3J_{H,H} = 6.3$ Hz, $^3J_{HH} = 3.9$ Hz, 1H; H-4), 4.98 (d, $^3J_{H,H} = 5.3$ Hz, 1H; H-2); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 25.3$, 25.6, 26.73, 26.75 (4C, CH_3), 66.0 (1C, C-6), 72.4, 74.8, 97.8, 101.5 (4C, C-2, C-3, C-4, C-5), 109.9, 114.0 (2C, $C_{acetalic}$), 196.5 (d, $^1J_{W,C} = 64$ Hz, 4C, CO_{cis}), 204.6 (1C, CO_{trans}), 314.1 (1C, C-1); MS (EI): *m/z* (%): 566 (10) [M^+], 538 (1) [$M^+ - CO$], 436 (1), 394 (1), 366 (1), 338 (5), 310 (7), 282 (18), 254 (5), 59 (40); HRMS for $^{12}C_{17}{}^1H_{18}{}^{16}O_{10}{}^{182}W$ [M^+] calcd. 564.0381; found 564.0386.

Pentacarbonyl(2,3:5,6-di-*O*-isopropylidene-D-gulofuranosylidene)chromium(0) (7): To pentacarbonyl(diphenylcarbene)chromium (0) (**3**)[28] (5.80 g, 16.19 mmol), *exo*-methylene sugar **2** (2.05 g, 8.00 mmol) and *n*-heptane (10 mL) were added at −40 °C. The mixture was warmed up to ambient temperature and stirred for 90 min. Column chromatography on silica gel (light petroleum/diethyl ether/dichloromethane 15/5/1; $R_f = 0.28$) afforded **7** (2.3 g, 5.30 mmol) as a red oil in 66% yield. IR: (light petroleum): $\tilde{\nu} = 2070\ cm^{-1}$ (s, $^1A_1$; C=O), 1965 (vs, $^2A_1$/E; C=O), 1956 (vs, E/$^2A_1$; C=O); ^1H NMR (500.13 MHz, $CDCl_3$): $\delta = 1.36$ (s, 3H; CH_3), 1.37 (s, 3H; CH_3), 1.42 (s, 3H; CH_3), 1.51 (s, 3H; CH_3), 3.82 (dd, $^2J_{H,H} = 8.95$ Hz, $^3J_{H,H} = 6.26$ Hz, 1H; H-6a), 4.22 (dd, $^2J_{H,H} = 8.95$ Hz, $^3J_{H,H} = 6.76$ Hz, 1H; H-6b), 4.41 (dt*, $^3J_{H,H} = 8.14$, $^3J_{H,H} = 6.56$, 1H; H-5), 4.59 (dd, $^3J_{H,H} = 5.56$, $^3J_{H,H} = 4.27$, 1H; H-3), 4.92 (dd, $^3J_{H,H} = 8.2$ Hz, $^3J_{H,H} = 4.22$, 1H; H-4), 5.24 (d, $^3J_{H,H} = 5.66$, 1H; H-2); ^{13}C NMR (100.62 MHz, C_6D_6): $\delta = 25.9$, 26.0, 27.1, 27.5 (4C, CH_3), 66.5, 75.4, 75.4, 100.2, 101.9 (5C, C-2, C-3, C-4, C-5, C-6), 111.3, 114.6 (2C, $C_{acetalic}$), 217.1 (4C, CO_{cis}), 225.1 (1C, CO_{trans}), 342.1 (1C, C-1); MS (EI): *m/z* (%): 434 (32) [M^+], 419 (18) [$M^+ - CH_3$], 406 (9) [$M^+ - CO$], 391 (2) [$M^+ - CH_3 - CO$], 378 (6) [$M^+ - 2CO$], 350 (8) [$M^+ - 3CO$], 335 (13) [$M^+ - CH_3 - 3CO$], 322 (82) [$M^+ - 4CO$], 307 (7) [$M^+ - CH_3 - 4CO$], 294 (18) [$M^+ - 5CO$], 279 (12) [$M^+ - CH_3 - 5CO$], 178 (100) [$M^+ - 5CO - 2(CH_3)_2CO$], 126 (34); HRMS for $^{12}C_{17}{}^1H_{18}{}^{16}O_{10}{}^{52}Cr$ [M^+] calcd. 434.0306; found 434.0306.

Pentacarbonyl(2,3:5,6-di-*O*-isopropylidene-D-gulofuranosylidene)tungsten(0) (8): A mixture of *exo*-methylene sugar **2** (482.4 mg, 1.88 mmol) and pentacarbonyl(diphenylcarbene)tungsten (0) (**4**)[28] (1.00 g, 2.04 mmol) in *n*-heptane (2 .5 mL) was prepared at −20 °C, and stirred at 55 °C for 90 min. Column chromatography on silica gel (light petroleum/diethyl ether/dichloromethane 15/5/1; $R_f = 0.42$) yielded **8** (29 mg, < 0.05 mmol) as a dark orange oil in < 3% yield. IR (light petroleum): $\tilde{\nu} = 2077\ cm^{-1}$ (s, $^1A_1$; C=O), 1962 cm^{-1} (vs, $^2A_1$, E; C=O); ^1H NMR (500.13 Hz, $CDCl_3$): $\delta = 1.36$ (s, 3H; CH_3), 1.39 (s, 3H; CH_3), 1.42 (s, 3H; CH_3), 1.51 (s, 3H; CH_3), 3.83 (dd, $^2J_{H,H} = 8.95$ Hz, $^3J_{H,H} = 6.3$ Hz, 1H; H-6a), 4.23 (dd, $^2J_{H,H} = 8.95$ Hz, $^3J_{H,H} = 6.76$ Hz, 1H; H-6b), 4.42 (dt*, $^3J_{H,H} = 8.2$ Hz, $^3J_{H,H} = 6.56$ Hz, 1H; H-5), 4.58 (dd, $^3J_{H,H} = 5.6$ Hz, $^3J_{H,H} = 4.2$ Hz, 1H; H-3), 4.87 (dd, $^3J_{H,H} = 8.2$ Hz, $^3J_{H,H} = 4.2$ Hz, 1H; H-4), 5.00 (d, $^3J_{H,H} = 5.6$ Hz, 1H; H-2); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 25.3$, 25.8, 26.8, 26.9 (4C, CH_3), 66.0, 74.7, 74.9, 101.2, 101.8 (5C, C-2, C-3, C-4, C-5, C-6), 110.7, 114.1 (2C, $C_{acetalic}$), 196.6 (d, $^1J_{W,C} = 63.6$ Hz, 4C, CO_{cis}), 204.7 (d, $^1J_{W,C} = 58.3$ Hz, 1C, CO_{trans}), 313.1 (d, $^1J_{W,C} = 54.0$ Hz, 1C, C-1); MS (EI): *m/z* (%): 566 (5) [M^+], 551 (1) [$M^+ - CH_3$], 538 (1) [$M^+ - CO$], 482 (4) [$M^+ - 3CO$], 467 (1) [$M^+ - 3CO - CH_3$], 408 (12), 310 (5), 282 (8); HRMS for $^{12}C_{16}{}^1H_{15}{}^{16}O_{10}{}^{182}W$ [$M^+ - CH_3$] calcd. 549.0147; found 549.0141.

Attempted preparation of pyranosylidene complex 10: 2,6-Anhydro-1-deoxy-3,4:5,7-di-*O*-isopropylidene-D-manno-hept-1-enitol (**9**) was prepared in analogy to the protocol by Csuk and Glänzer:[27] A solution of dicyclopentadienyldimethyltitanium[27] (3.33 g, 16.00 mmol) and 2,3:4,6-di-*O*-isopropylidene-D-mannopyranonolactone[51] (2.00 g, 7.74 mmol) in toluene (40 mL) was stirred for 48 h at 65–70 °C in the dark. The reaction mixture was concentrated and **9** was purified by column chromatography on silica gel (light petroleum/ethyl acetate 5/1, silica gel and eluent containing 1% of triethylamine to prevent hydrolysis of the double bond; $R_f = 0.50$). Compound **9** (1.70 g, 6.63 mmol) was obtained as a waxy yellowish oil in 86% yield. IR (film): $\tilde{\nu} = 1655\ cm^{-1}$ (s, C=C); ^1H NMR (500.13 MHz, $CDCl_3$): $\delta = 1.38$ (s, 3H; CH_3), 1.41 (s, 3H; CH_3), 1.51 (s, 3H; CH_3), 1.52 (s, 3H; CH_3), 3.50 (td, $^3J_{H,H} = 10.23$ Hz, $^3J_{H,H} = 5.66$ Hz, 1H; H-6), 3.75 (dd, $^2J_{H,H} = 11.02$ Hz, $^3J_{H,H} = 10.14$ Hz, 1H; H-7a), 3.84 (dd, $^3J_{H,H} = 10.33$ Hz, $^3J_{H,H} = 7.35$ Hz, 1H; H-5), 3.98 (dd, $^2J_{H,H} = 11.03$ Hz, $^3J_{H,H} = 5.67$ Hz, 1H; H-7b), 4.23 (t*, $^3J_{H,H} = 7.1$ Hz, 1H; H-4), 4.53 (t*, $^{2/4}J_{H,H} = 1.20$ Hz, 1H; H-1a), 4.63 (t*, $^{2/4}J_{H,H} = 0.99$ Hz, 1H; H-1b), 4.70 (d, $^3J_{H,H} = 6.85$ Hz, 1H; H-3); ^{13}C NMR (125.76 Hz, C_6D_6): $\delta = 19.3$, 26.5, 28. 4, 29.8 (4C, CH_3), 63.2 (1C, C-7), 67.7, 73.5, 73.8, 78.1 (4C, C-3, C-4, C-5, C-6), 92.2 (1C, C-1), 100.1, 111.6 (2C, $C_{acetalic}$), 156.9 (1C, C-2); MS (EI): *m/z* (%): 256 (19) [M^+], 241 (100) [$M^+ - CH_3$], 199 (5) [$M + H^+ - (CH_3)_2CO$],

183 (15) [$M^+ - CH_3 - (CH_3)_2CO$], 141 (19). HRMS for $^{12}C_{13}{}^{1}H_{20}{}^{16}O_5$ [M^+] calcd. 256.1311; found 256.1297; for $^{12}C_{12}{}^{1}H_{17}{}^{16}O_5$ [$M^+ - CH_3$] calcd. 241.1075; found 241.1071; $C_{13}H_{20}O_5$ (256.30): calcd. C 60.92, H 7.87; found C 60.77, H 7.85.

Pentacarbonyl(2,3:4,6-di-*O*-isopropylidene-D-mannopyranosylidene)chromium(0) (10): A solution of *exo*-methylene sugar **9** (439 mg, 1.71 mmol) in *n*-heptane/dichloromethane (4.3 mL, 1/1) was added to pentacarbonyl(diphenylcarbene)chromium (0) (**3**)[28] (920 mg, 2.57 mmol) at $-50\,^{\circ}C$. The solution was stirred at ambient temperature for 90 min until TLC indicated that the starting material **3** had been consumed. The solvent was evaporated below $-20\,^{\circ}C$, and the reaction mixture was submitted to column chromatography on silica gel (light petroleum/diethyl ether 3/2) at $-20\,^{\circ}C$. The crude orange product complex **10** ($R_f = 0.28$, eluent light petroleum/diethyl ether 3/2) could not be purified due to rapid decomposition even at $-78\,^{\circ}C$. IR (light petroleum): $\tilde{\nu} = 2068\ cm^{-1}$ (s, $^1A_1$; C=O), 1962 (s, $^2A_1$/E; C=O), 1948 (vs, E/$^2A_1$; C=O); ^{13}C NMR (62.9 MHz, $CDCl_3$, 253 K): $\delta = 216.0$ (4C, CO_{cis}), 225.2 (1C, CO_{trans}), 352.4 (1C, C-1).

Aminolysis reactions to acyclic aminoglycosylidene complexes 11–19:

General procedure for the preparation of the complexes 11, 12, 15 and 16: Into a solution of the glycosylidene complex (**5** for **11** and **12**; **7** for **15** and **16**) in dichloromethane (ca. 10 mL/0.1 mmol) the gaseous amine (ammonia for **11** and **15**; methylamine for **12** and **16**) was condensed at $-78\,^{\circ}C$. The colour changed from orange to yellow instantaneously. Excess amine and solvent were evaporated at low temperature affording a quantitative yield of pure product.

Pentacarbonyl(1-amino-1-deoxy-2,3:5,6-di-*O*-isopropylidene-D-mannitol-1-ylidene)chromium(0) (11): Yellowish crystalline solid, m.p. 150–152 °C (decomp), $R_f = 0.65$ (eluent light petroleum/diethyl ether 1/6). Crystals for X-ray structure analysis were grown from hexane/dichloromethane; IR (KBr): $\tilde{\nu} = 2058\ cm^{-1}$ (s, $^1A_1$; C=O), 1969 cm^{-1} (s, B_1; C=O), 1925 cm^{-1} (vs, $^2A_1$/E; C=O), 1915 cm^{-1} (vs, E/$^2A_1$; C=O); ^1H NMR (500.13 MHz, $CDCl_3$): $\delta = 1.33$ (s, 3H; CH_3), 1.39 (s, 3H; CH_3), 1.44 (s, 3H; CH_3), 1.53 (s, 3H; CH_3), 1.72 (d, $^3J_{H,H} = 8.65$ Hz, 1H; OH), 3.63 (dd, $^3J_{H,H} = 8.64$ Hz, $^3J_{H,H} = 7.05$ Hz, 1H; H-4), 3.91 (dd, $^2J_{H,H} = 8.3$ Hz, $^3J_{H,H} = 6.2$ Hz, 1H; H-6a), 3.96 (q*, $^3J_{H,H} = 6.4$ Hz, 1H; H-5), 4.05 (dd, $^2J_{H,H} = 8.3$ Hz, $^3J_{H,H} = 6.1$ Hz, 1H; H-6b), 4.92 (d, $^3J_{H,H} = 7.75$ Hz, 1H; H-3), 5.61 (d, $^3J_{H,H} = 7.85$ Hz, 1H; H-2), 8.9 (br, 1H; NH-a), 9.55 (br, 1H; NH-b); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 25.0, 25.3, 26.2, 26.4$ (4C, CH_3), 66.7, 70.7, 76.1, 76.2 (4C, C-3, C-4, C-5, C-6), 87.7 (1C, C-2), 108.9, 109.4 (2C, $C_{acetalic}$), 216.9 (4C, CO_{cis}), 221.5 (1C, CO_{trans}), 276.5 (1C, C-1); MS (EI): *m/z* (%): 451 (4) [M^+], 436 (9) [$M^+ - CH_3$], 423 (2) [$M^+ - CO$], 408 (4) [$M^+ - CO - CH_3$], 378 (3) [$M^+ - CH_3 - (CH_3)_2CO$], 367 (5) [$M^+ - 3CO$], 339 (18) [$M^+ - 4CO$], 311 (48) [$M^+ - 5CO$], 57 (100); HRMS for $^{12}C_{17}{}^{1}H_{21}{}^{16}O_{10}{}^{14}N\ ^{52}Cr$ [M^+] calcd. 451.0570; found 451.0574; $C_{17}H_{21}O_{10}NCr$ (451.35): calcd. C 45.24, H 4.69, N 3.10; found C 45.34, H 4.91, N 2.76.

Crystal data for 11: $C_{17}H_{21}CrNO_{10}$, $M_r = 451.35$, orthorhombic, space group $P2_12_12_1$ (No. 19), yellow prisms, dimensions $0.20 \times 0.20 \times 0.15\ mm^3$, $a = 10.752(1)$, $b = 12.336(1)$, $c = 15.712(1)$ Å, $V = 2084.0(3)$ Å^3, $\rho_{calcd} = 1.439\ Mg\,m^{-3}$, $Z = 4$, $\mu(Cu_{K\alpha}) = 5.001\ mm^{-1}$, $T = 293(2)$ K, $F(000) = 936$; 9673 reflections were collected on a MACH3 diffractometer ($2\theta_{max} = 150°$; $-13 \le h \le 13$, $-15 \le k \le 15$, $-2 \le l \le 19$), 4264 symmetry-independent reflections ($R_{int} = 0.0342$) were used for the structure solution (direct methods)[52] and refinement (full-matrix least-squares on F^2,[53] 270 parameters, 2 restraints), non-hydrogen atoms were refined anisotropically, H atoms localized by difference electron density and refined using a riding model; $wR2 = 0.0734$ [$R_1 = 0.0295$ for $I > 2\sigma(I)$]. The absolute configuration was determined by refinement of Flack's *x* parameter ($x = 0.002(4)$).[54] A semi-empirical absorption correction on the basis of Ψ scans (min./max. transmission 0.253/0.811) was applied. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114498. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Pentacarbonyl(1-*N*-methylamino-1-deoxy-2,3:5,6-di-*O*-isopropylidene-D-mannitol-1-ylidene)chromium(0) (12): The procedure described above afforded an approximately 2:1 mixture of (*E*)-**12** and (*Z*)-**12**. Pure (*E*)-**12** was obtained by stirring a solution of glycosylidene complex **5** (229 mg, 0.53 mmol) and partially hydrolyzed benzylidene(methyl)imine (0.13 mL, 1.05 mmol) in degassed dichloromethane (6 mL) at ambient temperature for several days. Column chromatography on silica gel (light petroleum/dichloromethane/diethyl ether 10/1/5, $R_f = 0.25$) afforded pure (*E*)-**12** (132 mg, 0.28 mmol) as a yellowish solid in 53% yield, m.p. 45–47 °C; IR (light petroleum): $\tilde{\nu} = 2058\ cm^{-1}$ (s,$^1A_1$; C=O), 1971cm^{-1} (m, B_1; C=O), 1938 cm^{-1} (vs, $^2A_1$/E; C=O), 1929 cm^{-1} (vs, E/$^2A_1$; C=O); ^1H NMR (500.13 Mz, $CDCl_3$): $\delta = 1.32$ (s, 3H; CH_3), 1.36 (s, 3H; CH_3), 1.42 (s, 3H; CH_3), 1.53 (s, 3H; CH_3), 1.76 (d, $^3J_{H,H} = 7.8$ Hz, 1H; OH), 3.41 (dd, $^3J_{H,H} = 7.7$ Hz, $^3J_{H,H} = 6.5$ Hz, 1H; H-4), 3.61 (d, $^3J_{H,H} = 5.17$ Hz, 3H; NCH_3), 3.87 (dd, $^2J_{H,H} = 8.3$ Hz, $^3J_{H,H} = 6.6$ Hz, 1H; H-6a) 3.93 (q*, $^3J_{H,H} = 6.3$ Hz, 1H; H-5), 4.02 (dd, $^2J_{H,H} = 8.3$ Hz, $^3J_{H,H} = 6.1$ Hz, 1H; H-6b), 4.83 (d, $^3J_{H,H} = 7.35$ Hz, 1H; H-3), 5.61 (d, $^3J_{H,H} = 7.25$ Hz, 1H; H-2), 10.08 (br, 1H; NH). ^1H NMR (250.13 MHz, C_6D_6): $\delta = 1.07$ (s, 3H; CH_3), 1.25 (s, 3H; CH_3), 1.28 (s, 3H; CH_3), 1.39 (s, 3H; CH_3), 1.68 (d, $^3J_{H,H} = 7.8$ Hz, 1H; OH), 2.78 (d, $^3J_{H,H} = 4.9$ Hz, 3H; NCH_3), 3.55 (t*, 6 Hz, 1H), 3.80–4.00 (m, 4H; H-4, H-5, H-6a, H-6b), 4.92 (d, $^3J_{H,H} = 7.32$ Hz, 1H; H-3), 5.66 (d, $^3J_{H,H} = 7.33$ Hz, 1H; H-2), 9.67 (br, 1H; NH); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 25.2$, 25.3, 26.1, 26.3 (4C, CH_3), 39.2 (1C, NCH_3), 66.3 (1C, C-6), 70.2, 76.1, 76.4, 88.0 (4C, C-2, C-3, C-4, C-5), 108.9, 109.1 (2C, $C_{acetalic}$), 217.3 (4C, CO_{cis}), 222.0 (1C, CO_{trans}), 262.5 (1C, C-1); ^{13}C NMR (62.5 Hz, C_6D_6): $\delta = 25.5, 26.1, 26.5, 27.3$ (4C, CH_3), 39.3 (1C, NCH_3), 67.4, 71.4, 77.3, 77.5, 89.0 (5C, C-2, C-3, C-4, C-5, C-6), 109.5, 110.0 (2C, $C_{acetalic}$), 218.6 (4C, CO_{cis}), 223.1 (1C, CO_{trans}), 262.6 (1C, C-1); MS (EI): *m/z* (%): 465 (10) [M^+], 450 (10) [$M^+ - CH_3$], 381 (3) [$M^+ - 3CO$], 353.2 (22) [$M^+ - 4CO$], 325.2 (77) [$M^+ - 5CO$], 310.2 (12) [$M^+ - 5CO - CH_3$]; HRMS for $^{12}C_{18}{}^{1}H_{23}{}^{16}O_{10}{}^{14}N\ ^{52}Cr$ [M^+] calcd. 465.0727; found 465.0719.

(*Z*)-**12** was obtained in an approximately 1:2 mixture with the *E* isomer, following the general procedure. Characteristic spectroscopic data: ^1H NMR (500.13 MHz, $CDCl_3$): $\delta = 1.31$ (s, 3H; CH_3), 1.37 (s, 3H; CH_3), 1.45 (s, 3H; CH_3), 1.69 (s, 3H; CH_3), 2.20 (d, $^3J_{H,H} = 10.7$ Hz, 1H; OH), 3.17 (d, $^3J_{H,H} = 5.3$ Hz, 3H; NCH_3), 8.99 (br, 1H; NH); ^1H NMR (250.13 MHz, C_6D_6): $\delta = 1.04$ (s, 3H; CH_3), 1.19 (s, 3H; CH_3), 1.24 (s, 3H; CH_3), 1.53 (s, 3H; CH_3), 2.06 (d, $^3J_{H,H} = 10.9$ Hz, 1H; OH), 2.79 (d, $^3J_{H,H} = 5.1$ Hz, 3H; NCH_3), 8.0 (br, 1H; NH).

Pentacarbonyl(1-amino-1-deoxy-2,3:5,6-di-*O*-isopropylidene-D-gulitol-1-ylidene)chromium(0) (15): Yellowish powder, m.p. 155 °C (decomp); IR (light petroleum): $\tilde{\nu} = 2058\ cm^{-1}$ (s, $^1A_1$; C=O), 1967 cm^{-1} (m, B_1; C=O), 1936 cm^{-1} (vs, $^1A_1$/E; C=O), 1923 cm^{-1} (vs, E/$^2A_1$; C=O); ^1H NMR (500.13 MHz, $CDCl_3$): $\delta = 1.35$ (s, 3H; CH_3), 1.37 (s, 3H; CH_3), 1.41 (s, 3H; CH_3), 1.55 (s, 3H; CH_3), 2.24 (d, $^3J_{H,H} = 4.6$ Hz, 1H; OH), 3.49 (dd, $^3J_{H,H} = 7$ Hz, $^3J_{H,H} = 4.6$ Hz, 1H; H-4), 3.78 (dd, $^2J_{H,H} = 8.6$ Hz, $^3J_{H,H} = 5.6$ Hz, 1H; H-6a), 4.05 (dd, $^2J_{H,H} = 8.6$ Hz, $^3J_{H,H} = 6.4$ Hz, 1H; H-6b), 4.17 (dt*, $^3J_{H,H} = 7$ Hz, $^3J_{H,H} = 6$ Hz, 1H; H-5), 4.57 (d, $^3J_{H,H} = 7.25$ Hz, 1H; H-3), 5.56 (d, $^3J_{H,H} = 7.25$ Hz, 1H; H-2), 8.89 (br, 1H; NH-a), 9.68 (br, 1H; NH-b); ^{13}C NMR (125.76 MHz, $CDCl_3$): 25.5, 25.9, 26.1, 26.7 (4C, CH_3), 65.8, 71.2, 76.7, 77.0, 88.1 (5C, C-2, C-3, C-4, C-5, C-6), 109.75, 109.84 (2C, $C_{acetalic}$), 217.1 (4C, CO_{cis}), 221.4 (1C, CO_{trans}), 275.0 (1C, C-1); MS (EI): *m/z* (%): 451 (7) [M^+], 436.0 (18) [$M^+ - CH_3$], 423 (14) [$M^+ - CO$], 408.2 (12) [$M^+ - CO - CH_3$], 378 (5) [$M^+ - CH_3 - (CH_3)_2CO$], 367 (24) [$M^+ - 3CO$], 339 (67) [$M^+ - 4CO$], 311 (92) [$M^+ - 5CO$], 296 (17) [$M^+ - 5CO - CH_3$]; HRMS for $^{12}C_{17}{}^{1}H_{21}{}^{16}O_{10}{}^{14}N^{52}Cr$ [M^+] calcd. 451.0571; found 451.0569; $C_{17}H_{21}O_{10}NCr$ (451.35): calcd. C 45.24, H 4.69, N 3.10; found C 46.14, H 4.95, N 2.59.

(*E*)-Pentacarbonyl(1-*N*-methylamino-1-deoxy-2,3:5,6-di-*O*-isopropylidene-D-gulitol-1-ylidene)chromium(0) (16): Light orange oil; IR (light petroleum): $\tilde{\nu} = 2056\ cm^{-1}$ (s, $^1A_1$; C=O), 1971 cm^{-1} (m, B_1; C=O), 1936 cm^{-1} (vs, $^1A_1$/E; C=O), 1919 cm^{-1} (vs, E/$^2A_1$; C=O); ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 1.34$ (s, 3H; CH_3), 1.37 (s, 3H; CH_3), 1.41 (s, 3H; CH_3), 1.55 (s, 3H; CH_3), 2.21 (d, $^3J_{H,H} = 5.09$ Hz, 1H; OH), 3.30 (dd, $^3J_{H,H} = 7.2$ Hz, $^3J_{H,H} = 5.09$ Hz, 1H; H-4), 3.61 (d, $^3J_{H,H} = 5.2$ Hz, 3H; NCH_3), 3.77 (dd, $^2J_{H,H} = 8.6$ Hz, $^3J_{H,H} = 5.68$ Hz, 1H; H-6a), 4.02 (dd, $^2J_{H,H} = 8.5$ Hz, $^3J_{H,H} = 6.4$ Hz, 1H; H-6b), 4.14 (dt*, $^3J_{H,H} = 7.2$ Hz, $^3J_{H,H} = 6.2$ Hz, 1H; H-5), 4.53 (d, $^3J_{H,H} = 7.04$ Hz, 1H; H-3), 5.56 (d, $^3J_{H,H} = 7.04$, 1H; H-2), 10.21 (br, 1H; NH); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 25.4$, 25.8, 26.0, 26.6 (4C, CH_3), 39.1 (1C, NCH_3), 65.8, 71.0, 76.8, 77.02, 88.2 (5C, C-2, C-3, C-4, C-5, C-6), 109.5, 109.7 (2C, $C_{acetalic}$), 217.5 (4C, CO_{cis}), 221.8 (CO_{trans}), 260.8 (1C, C-1); MS (EI): *m/z* (%): 465.1 (3) [M^+], 450.0 (4) [$M^+ - CH_3$], 437.0 (2) [$M^+ - CO$], 381 (4) [$M^+ - 3CO$], 353.1 (1) [$M^+ - 4CO$], 325.1 (3) [$M^+ - 5CO$]; HRMS for $^{12}C_{18}{}^{1}H_{23}{}^{16}O_{10}{}^{14}N^{52}Cr$ [M^+] calcd. 465.0728; found 465.0730.

General procedure for the preparation of the amino acid derivatives 13,14, 17 and 18:

0947-6539/99/0507-2020 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 7

To a solution of amino acid methyl ester hydrochloride (3 equiv) in dichloromethane (4 mL per mmol hydrochloride) triethylamine (1.2 mL per mmol hydrochloride) was added, and the solution was stirred for 5 min. Then the mixture was added to a solution of one equivalent of glycosylidene complex **5** (at 0 °C) or **7** (at −78 °C) in dichloromethane (9.3 mL per mmol complex). The reaction was monitored by TLC (completion: **13**, **14** after 2 h of stirring at 0 °C; **17**, **18** instantaneously at −78 °C). After evaporation of the solvent the products were purified by column chromatography on silica gel (light petroleum/diethyl ether 1:1).

(*E*)-Pentacarbonyl([*N*-2′-(*S*)-1′-methoxycarbonylprop-2′-yl]-1-amino-1-deoxy-2,3:5,6-di-*O*-isopropylidene-D-mannitol-1-ylidene)chromium(0) (13): 442 mg (0.82 mmol, 70 %), yellowish oil, $R_f = 0.48$ (eluent light petroleum/diethyl ether 1/3); IR (light petroleum): $\tilde{\nu} = 2058\ cm^{-1}$ (s, $^1A_1$; C=O), 1971 cm^{-1} (m, B_1;C=O), 1938 cm^{-1} (vs, E/$^2A_1$; C=O); ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 1.31$ (s, 3H; CH_3), 1.36 (s, 3H; CH_3), 1.43 (s, 3H; CH_3), 1.55 (s, 3H; CH_3), 1.62 (d, $^3J_{H,H} = 7.15$ Hz, 3H; CH_3-3′), 1.74 (d, $^3J_{H,H} = 8.6$ Hz, 1H; OH), 3.40 (dd, $^2J_{H,H} = 8.6$ Hz, $^3J_{H,H} = 7.0$ Hz, 1H; H-6a), 3.80 (s, 3H; OCH_3), 3.84 (dd, $^3J_{H,H} = 8.4$ Hz, $^3J_{H,H} = 6.6$ Hz, 1H; H-4), 3.92 (q*, $^3J_{H,H} = 6.6$ Hz, 1H; H-5), 4.02 (dd, $^2J_{H,H} = 8.5$ Hz, $^3J_{H,H} = 6.2$ Hz, 1H; H-6b), 4.86 (d, $^3J_{H,H} = 7.45$ Hz, 1H; H-3), 5.12 (dq, $^3J_{H,H} = 9.3$ Hz, $^3J_{H,H} = 7.2$ Hz, 1H; H-2′), 5.63 (d, $^3J_{H,H} = 7.55$, 1H; H-2), 10.35 (d, br, $^3J_{H,H} = 7$ Hz, NH); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 18.4$ (1C, CH_3-3′), 25.0, 25.2, 26.1, 26.3 (4C, CH_3), 53.0 (1C, C-2′), 59.9 (1C, OCH_3), 66.7, 70.3, 76.1, 76.2, 88.2 (5C, C-2, C-3, C-4, C-5, C-6), 109.0, 109.3 (2C, $C_{acetalic}$), 171.6 (1C, C-1′), 216.9 (4C, CO_{cis}), 221.6 (1C, CO_{trans}), 263.2 (1C, C-1); MS (EI): *m/z* (%): 537 (2) [M^+], 522 (5) [$M^+ - CH_3$], 509 (4) [$M^+ - CO$], 397 (18) [$M^+ - 5CO$]; HRMS for $^{12}C_{21}{}^1H_{27}{}^{16}O_{12}{}^{14}N^{52}Cr$ [M^+] calcd. 537.0938; found 537.0942.

(*E*)-Pentacarbonyl([*N*-2′-(*R*)-1′-methoxycarbonylprop-2′-yl]-1-amino-1-deoxy-2,3:5,6-di-*O*-isopropylidene-D-mannitol-1-ylidene)chromium(0) (14): 260 mg (0.48 mmol, 60 %), light orange oil, $R_f = 0.84$ (eluent light petroleum/diethyl ether 1/3); IR (light petroleum): $\tilde{\nu} = 2058\ cm^{-1}$ (s, $^1A_1$; C=O), 1973 cm^{-1} (m, B_1; C=O), 1944 cm^{-1} (vs, E, $^2A_1$; C=O); ^{1}H NMR (400.13 MHz, C_6D_6): $\delta = 1.00$ (d, $^3J_{H,H} = 7.04$ Hz, 3H; CH_3-3′), 1.19 (s, 3H; CH_3-b), 1.28 (s, 3H; CH_3-a), 1.45 (s, 3H; CH_3-d),1.59 (s, 3H; CH_3-c), 3.14 (s, 3H; OCH_3), 3.51 (d, $^3J_{H,H} = 7.82$ Hz, 1H; OH), 3.71 (t*, $^3J_{H,H} = 7.83$ Hz, 1H; H-4), 4.0-4.1 (m, 2H; H-6a, H-6b), 4.23 (q*, $^3J_{H,H} = 6.7$ Hz, 1H; H-5), 5.13 (dq, $^3J_{H,H} = 9.1$ Hz, $^3J_{H,H} = 7.1$ Hz, 1H; H-2′), 5.15 (d, $^3J_{H,H} = 7$ Hz, 1H; H-3), 5.82 (d, $^3J_{H,H} = 7$ Hz, 1H; H-2), 10.34 (d, br, $^3J_{H,H} = 8$ Hz, 1H; NH); ^{13}C NMR (100.62 MHz, C_6D_6): $\delta = 18.0$ (1C, CH_3-3′), 26.2 (1C, CH_3-a), 26.4 (1C, CH_3-b), 26.6 (1C, CH_3-c), 27.4 (1C, CH_3-d), 53.7 (1C, OCH_3), 60.9 (1C, C-2′), 68.3 (1C, C-6), 71.8 (1C, C-4), 77.0 (1C, C-5), 78.2 (1C, C-3), 89.9 (1C, C-2), 110.29, 110.32 (2C, $C_{acetalic}$), 173.7 (1C, C-1′), 218.0 (4C, CO_{cis}), 222.7 (1C, CO_{trans}), 269.6 (1C, C-1); MS (EI): *m/z* (%): 537 (4) [M^+], 522 (8) [$M^+ - CH_3$], 509 (6) [$M^+ - CO$], 494 (2) [$M^+ - CO - CH_3$], 453 (2) [$M^+ - 3CO$], 425 (10) [$M^+ - 4CO$], 397 (13) [$M^+ - 5CO$], 382 (12) [$M^+ - 5CO - CH_3$]; HRMS for $^{12}C_{20}{}^1H_{24}{}^{16}O_{12}{}^{14}N^{52}Cr$ [M^+] calcd. 522.0704; found 522.0706.

(*E*)-Pentacarbonyl([*N*-2′-(*S*)-1′-methoxycarbonylprop-2′-yl]-1-amino-1-deoxy-2,3:5,6-di-*O*-isopropylidene-D-gulitol-1-ylidene)chromium(0) (17): 353 mg (0.71 mmol, 67 %), orange oil, $R_f = 0.88$ (eluent light petroleum/diethyl ether 1/6); IR (light petroleum): $\tilde{\nu} = 2058\ cm^{-1}$ (s, $^1A_1$; C=O), 1971 cm^{-1} (m, B_1; C=O), 1938 cm^{-1} (vs, $^1A_1$/E; C=O), 1924 cm^{-1} (vs, E/$^1A_1$; C=O); ^{1}H NMR (400.13 MHz, C_6D_6): $\delta = 1.10$ (d, $^3J_{H,H} = 7.1$ Hz, 3H; CH_3-3′), 1.23 (s, 3H; CH_3), 1.30 (s, 3H; CH_3), 1.40 (s, 3H; CH_3), 1.63 (s, 3H; CH_3), 3.19 (s, 3H; OCH_3), 3.68 (dd, $^3J_{H,H} = 7.3$ Hz, $^3J_{H,H} = 5$ Hz, 1H; H-4), 3.89-3.98 (m, 2H; H-6a, H-6b), 4.34 (q*, $^3J_{H,H} = 7$ Hz, 1H; H-5), 4.69 (d, $^3J_{H,H} = 6.85$ Hz, 1H; H-3), 5.14 (dt, $^3J_{H,H} = 9$ Hz, $^3J_{H,H} = 7.2$ Hz, 1H; H-2′), 5.80 (d, $^3J_{H,H} = 6.85$ Hz, 1H; H-2), 10.57 (d, br, $^3J_{H,H} = 7$ Hz, 1H; NH), OH not observed; ^{13}C NMR (100.62 MHz, C_6D_6): $\delta = 17.8$ (q, $^1J_{C,H} = 132.7$ Hz, 1C, CH_3-3′), 25.8, 25.96, 25.99, 26.9 (4C, CH_3), 52.6 (q, $^1J_{C,H} = 148.4$ Hz, 1C, OCH_3), 60.5 (d, $^1J_{C,H} = 143.7$ Hz, 1C, C-2′), 65.8 (t, $^1J_{CH} = 147.5$ Hz, 1C, C-6), 71.4 (d, $^1J_{C,H} = 141.1$ Hz, 1C, C-3/C-4/C-5), 77.4 (d, $^1J_{CH} = 150.0$ Hz, 1C, C-3/C-4/C-5), 77.8 (d, $^1J_{CH} = 153.9$ Hz, 1C, C-3/C-4/C-5), 89.3 (dd, $^1J_{CH} = 156.4$ Hz, $^2J_{CH} = 7.6$ Hz, 1C, C-2), 109.5, 110.0 (2C, $C_{acetalic}$), 171.5 (1C, C-1′), 217.6 (4C, CO_{cis}), 221.8 (1C, CO_{trans}), 265.6 (C-1); MS (EI): *m/z* (%): 537 (1) [M^+], 522 (4) [$M^+ - CH_3$], 509 (4) [$M^+ - CO$], 425 (11) [$M^+ - 4CO$], 397 (12) [$M^+ - 5CO$], 382 (12) [$M^+ - 5CO - CH_3$]; HRMS for $^{12}C_{21}{}^1H_{27}{}^{16}O_{12}{}^{14}N^{52}Cr$ [M^+] calcd. 537.0939; found 537.0932; $C_{21}H_{27}O_{12}NCr$ (537.44): calcd. C 46.93, H 5.06, N 2.61; found C 47.57, H 5.53, N 3.22.

(*E*)-Pentacarbonyl([*N*-2′-(*R*)-1′-methoxycarbonylprop-2′-yl]-1-amino-1-deoxy-2,3:5,6-di-*O*-isopropylidene-D-gulitol-1-ylidene)chromium(0) (18): 553 mg (1.029 mmol, 80 %), light orange oil. IR (light petroleum): $\tilde{\nu} = 2058\ cm^{-1}$ (s, $^1A_1$;C=O), 1973 (m, B_1; C=O), 1936 cm^{-1} (vs, $^2A_1$, E; C=O); ^{1}H NMR (500.13 MHz, C_6D_6): 1.14 (s, 3H; CH_3-a), 1.22 (s, 3H; CH_3-b), 1.30 (s, 3H; CH_3-c), 1.36 (d, $^3J_{H,H} = 7.16$ Hz, 3H; CH_3-3′), 1.46 (s, 3H; CH_3-d), 2.31 (d, $^3J_{H,H} = 4$ Hz, 1H; OH), 3.25 (s, 3H; OCH_3), 3.48 (dd, $^3J_{H,H} = 7.7$ Hz, $^3J_{H,H} = 4$ Hz, 1H; H-4), 3.70-3.85 (m, 2H; H-6a/b), 4.16 (q*, $^3J_{H,H} = 5.8$ Hz, 1H; H-5), 4.52 (d, $^3J_{H,H} = 6.5$ Hz, 1H; H-3), 5.19 (quint*, $^3J_{H,H} = 7.3$ Hz, 1H; H-2′), 5.69 (d, $^3J_{H,H} = 6.5$ Hz, 1H; H-2), 10.67 (d, br, $^3J_{H,H} = 6.0$ Hz, 1H; NH); ^{13}C NMR (125.76 Hz, C_6D_6): $\delta = 18.7$ (1C, CH_3-3′), 26.3 (1C, CH_3-b), 26.5 (1C, CH_3-a), 26.6 (1C, CH_3-d), 27.7 (1C, CH_3-c), 53.1 (1C, OCH_3), 61.1 (1C, C-2′), 66.6 (1C, C-6), 72.1 (1C, C-4), 77.92 (1C, C-3), 78.00 (1C, C-5), 89.7 (1C, C-2), 110.5, 110.6 (2C, $C_{acetalic}$), 171.7 (1C, C-1′), 218.5 (4C, CO_{cis}), 222.6 (1C, CO_{trans}), 262.2 (1C, C-1); MS (EI): *m/z* (%): 537 (2) [M^+], 522 (6) [$M^+ - CH_3$], 509 (5) [$M^+ - CO$], 425 (8) [$M^+ - 4CO$], 397 (25) [$M^+ - 5CO$], 382 (13) [$M^+ - 5CO - CH_3$], 339 (20) [$M^+ - 5CO - (CH_3)_2CO$]; HRMS for $^{12}C_{21}{}^1H_{27}{}^{16}O_{12}{}^{14}N\ ^{52}Cr$ [M^+] calcd. 537.0939; found 537.0952.

(*E*)-Pentacarbonyl(*N*-2′-glucosyl-1-amino-1-deoxy-2,3:5,6-di-*O*-isopropylidene-D-gulitol-1-ylidene)chromium(0) (19): Glucosamine hydrodrochloride (501.6 mg, 2.33 mmol) was suspended in acetone (6 mL), and triethylamine (2.7 mL) was added. After stirring for 5 min, a solution of gulofuranosylidene complex **7** (348.2 mg, 0.80 mmol) in acetone (6 mL) was added at ambient temperature. The reaction mixture was stirred at ambient temperature overnight and subjected to column chromatography on silica gel (acetone/dichloromethane 1/3). The first orange fraction ($R_f = 0.88$) contained **7** (113.6 mg, 0.262 mmol; 67 % turnover), the second orange fraction ($R_f = 0.15$) yielded **19** (64.2 mg, 0.268 mmol; 50 % referring to turnover) as a yellowish powder, m.p. 108 °C; IR (acetone): $\tilde{\nu} = 2058\ cm^{-1}$ (s, $^1A_1$; C=O), 1975 cm^{-1} (m, B_1; C=O), 1938 cm^{-1} (vs, $^2A_1$/E; C=O), 1919 cm^{-1} (vs, E/$^2A_1$; C=O); ^{1}H NMR (500.13 MHz, THF-D_8): $\delta = 1.27$ (s, 3H; CH_3-a), 1.29 (s, 3H; CH_3-b), 1.40 (s, 3H; CH_3-c), 1.58 (s, 3H; CH_3-d), 3.48 (br, 1H; H-4′), 3.55 (t*, $^3J_{H,H} = 6.0$ Hz, 1H; H-5), 3.68 (br, 1H; H-6a′), 3.74 (br, 1H; H-6b′), 3.76 (t*, br, $^{2/3}J_{H,H} = 6.4$ Hz, 1H; H-6a), 3.85 (br, 1H; H-5′), 3.92 (br, 1H; OH), 3.95 (t*, br, $^{2/3}J_{H,H} = 6$ Hz, 1H; H-6b), 3.98 (br, 1H; H-3′), 4.08 (q*, br, $^{2/3}J_{H,H} = 7$ Hz, 1H; H-4), 4.30 (t*, br, $^3J_{H,H} = 7.5$ Hz, 1H; H-2′), 4.60 (dd, $^3J_{H,H} = 7.0$ Hz, $J_{H,H} = 2.7$ Hz, 1H; H-3), 4.82 (br, 1H; OH), 4.91 (br, 1H; OH), 5.30 (br, 1H; H-1′), 5.33 (br, 1H; OH), 5.65 (dd, $^3J_{H,H} = 6.8$ Hz, 1H; H-2), 6.39 (br, 1H; OH), 10.36 (d, $^3J_{H,H} = 6.7$ Hz, 1H; NH); ^{13}C NMR (62.9 Hz, [D_8]THF): $\delta = 26.4$ (2C, CH_3-a, CH_3-c), 26.6 (1C, CH_3-d), 27.3 (1C, CH_3-b), 63.2 (1C, C-6′), 66.8 (1C, C-6), 69.0 (1C, C-2′), 71.7 (1C, C-4′), 72.2 (1C, C-5), 72.4 (1C, C-3′), 73.7 (1C, C-5′), 78.3 (1C, C-3), 78.9 (1C, C-4), 90.1 (1C, C-2), 92.8 (1C, C-1′), 218.3 (4C, CO_{cis}), 222.9 (1C, CO_{trans}), 260.8 (1C, C-1); MS (FAB): *m/z* (%): 636 (20) [$M^+ + Na$], 613 (5) [M^+], 580 (3) [$M^+ + Na - 2CO$], 552 (24) [$M^+ + Na - 3CO$], 473 (19) [$M^+ - 5CO$], 415 (47) [$M^+ - 5CO - (CH_3)_2CO$], 397 (21).

General procedure for Mitsunobu cyclization reactions to iminoglycosylidene complexes 20–26: The acyclic aminoglycosylidene complex (0.25–0.94 mmol) was dissolved in THF (10 mL per mmol complex for **20**, **21**, **23** and **24**; ca. 40 mL per mmol complex for **22**, **25** and **26**); 1.5 equivalents triphenylphosphane and 1.3 equivalents of diethyl azodicarboxylate (DEAD) were added. The reaction mixture was stirred at ambient temperature until TLC indicated consumption of the starting complex material. For reaction times and purification see below.

4-Amino-4-deoxy-2,3:5,6-di-*O*-isopropylidene-D-talofuranosylidene(pentacarbonyl)chromium(0) (20): The reaction was complete after stirring overnight. Column chromatography on silica gel (light petroleum/diethyl ether 1/1, $R_f = 0.34$) and recrystallization from pentane afforded **20** (77.9 mg, 0.18 mmol) as a light yellow powder in 42 % yield, m.p. 109–113 °C (decomp); IR (light petroleum): $\tilde{\nu} = 2056\ cm^{-1}$ (s, $^1A_1$; C=O), 1973 cm^{-1} (s, B_1; C=O), 1931 cm^{-1} (vs, $^2A_1$/E; C=O); ^{1}H NMR (500.13 Mz, $CDCl_3$): $\delta = 1.32$ (s, 3H; CH_3), 1.36 (s, 3H; CH_3),1.37 (s, 3H; CH_3), 1.41 (s, 3H; CH_3), 3.91 (dd, $^2J_{H,H} = 8.8$ Hz, $^3J_{H,H} = 4.8$ Hz, 1H; H-6a), 4.12–4.14, 4.18 (m, br, 3H; H-4, H-5, H-6b), 4.41 (d, $^3J_{H,H} = 5.27$ Hz, 1H; H-3), 5.17 (d, $^3J_{H,H} = 5.27$ Hz, 1H; H-2), 8.87 (br, 1H; NH); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 24.8$, 25.7, 26.3, 26.8 (4 C, CH_3), 65.9, 75.3, 75.7, 77.4, 95.2 (5 C, C-2, C-3, C-4, C-5, C-6), 110.8, 112.1 (2 C, $C_{acetalic}$), 217.4 (4 C, CO_{cis}), 222.8 (1 C, CO_{trans}), 279.4 (1 C, C-1); MS (EI): *m/z* (%): 433 (9) [M^+], 418 (6) [$M^+ - CH_3$], 349 (1) [$M^+ - 3CO$], 334 (2) [$M^+ - 3CO - CH_3$], 321 (16) [$M^+ - 4CO$], 306 (3) [$M^+ - 4CO - CH_3$], 293 (100) [$M^+ - 5CO$], 278 (11) [$M^+ - 5CO - CH_3$]; HRMS for $^{12}C_{17}{}^1H_{19}{}^{16}O_9{}^{14}N^{52}Cr$ [M^+] calcd. 433.0465; found 433.0460.

Pentacarbonyl(4-deoxy-4-methylamino-2,3:5,6-di-*O*-isopropylidene-D-talofuranosylidene)chromium(0) (21): The reaction was complete after stirring overnight. Column chromatography on silica gel (light petroleum/diethyl ether 1/1, $R_f = 0.34$) and recrystallization from pentane afforded **21** (75.9 mg, 0.17 mmol) as a light yellow cystalline solid in 67% yield, m.p. 105-107 °C (decomp). Crystals for X-ray structural analysis were grown from pentane; IR (light petroleum): $\tilde{\nu} = 2058\ cm^{-1}$ (s, $^1A_1$; C≡O), 1977 cm^{-1} (w, B_1; C≡O), 1931 (vs, $^2A_1$/E; C≡O); ^1H NMR (500.13 MHz, $CDCl_3$): $\delta = 1.32$ (s, 3H; CH_3), 1.33 (s, 3H; CH_3), 1.36 (s, 3H; CH_3) 1.45 (s, 3H; CH_3), 3.79 (s, 3H; NCH_3), 3.89 (dd, $^2J_{H,H} = 9$ Hz, $^3J_{H,H} = 5$ Hz, 1H; H-6a), 4.06–4.11, 4.14–4.17 (m, 3H; H-4, H-5, H-6b), 4.25 (d, $^3J_{H,H} = 5.07$ Hz, 1H; H-3), 5.20 (d, $^3J_{H,H} = 5.07$ Hz, 1H; H-2); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 24.6$, 26.1, 26.3, 27.0 (4C, CH_3), 43.8 (1C, NCH_3), 66.3, 75.8, 78.0, 82.0, 96.6 (5C, C-2, C-3, C-4, C-5, C-6), 110.9, 111.6 (2C, $C_{acetalic}$), 217.7 (4C, CO_{cis}), 223.1 (1C, CO_{trans}), 272.3 (1C, C-1); MS (EI): *m/z* (%): 447 (45) [M^+], 432 (32) [$M^+ - CH_3$), 419 (28) [$M^+ - CO$], 391 (8) [$M^+ - 2CO$], 363 (8) [$M^+ - 3CO$], 335 (15) [$M^+ - 4CO$], 307 (100) [$M^+ - 5CO$], 292 (8) [$M^+ - 5CO - CH_3$]; HRMS for $^{12}C_{18}{}^1H_{21}{}^{16}O_9{}^{14}N^{52}Cr$ [M^+] calcd. 447.0622; found 447.0617; $C_{18}H_{21}O_9NCr$ (447.36): calcd. C 48.33, H 4.73, N 3.13; found C 48.21, H 4.80, N 3.31.

Pentacarbonyl[4-deoxy-2,3:5,6-di-*O*-isopropylidene-4-(1′-methoxycarbonylprop-2′-(*R*)-2′-yl)-amino-D-talofuranosylidene)chromium(0) (22): After four days of stirring the reaction was terminated. Column chromatography on silica gel (light petroleum/diethyl ether 2/1) afforded **22** (<2.6 mg, <5 μmol) ($R_F = 0.60$) as a yellow oil in 1% yield. Major amounts of starting material **14** were recovered in a second band ($R_f = 0.50$). Selected NMR spectroscopic data: ^1H NMR (250.13 MHz, C_6D_6): $\delta = 4.43$ (d, $^3J_{H,H} = 5.8$ Hz, 1H; H-3), 4.98 (d, $^3J_{H,H} = 5.6$ Hz, 1H; H-2), 5.77 (q*, $^3J_{H,H} = 7.2$ Hz, 1H; H-2′); ^{13}C NMR (62.5 MHz, C_6D_6): 15.06, 15.14, 15.9, 16.2 (4C, CH_3), 97.1 (1C, C-2/C-4), 111.3, 112.2 (2C, $C_{acetalic}$), 172.0 (1C, C-1′), 218.8 (4C, CO_{cis}), 232.1 (1C, CO_{trans}), 280.8 (1C, C-1).

4-Amino-4-deoxy-2,3:5,6-di-*O*-isopropylidene-D-allofuranosylidene(pentacarbonyl)chromium(0) (23): The reaction was complete after stirring overnight. Complex **23** was purified by column chromatography on silica gel (light petroleum/diethyl ether 1/1, $R_f = 0.25$), and hydrazine-*N,N*-dicarboxylate formed in the Mitsunobu reaction was removed by subsequent crystallization from hexane/dichloromethane, leaving complex **23** (131.4 mg, 0.30 mmol) as a yellow oil in 36% yield; IR (KBr): $\tilde{\nu} = 2058\ cm^{-1}$ (s, $^1A_1$; C≡O), 1976 cm^{-1} (s, B_1; C≡O), 1927 cm^{-1} (vs, E, $^2A_1$; C≡O); ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 1.30$ (s, 3H; CH_3), 1.35 (s, 3H; CH_3), 1.37 (s, 3H; CH_3), 1.41 (s, 3H; CH_3), 3.63 (br, 1H;) 4.09 (br, 1H), 4.18-4.32 (m, 2H) (H-4, H-5, H-6a, H-6b), 4.43 (d, $^3J_{H,H} = 4.7$ Hz, 1H; H-3), 5.14 (4.9 Hz, 1H; H-2), 8.98 (br, 1H; NH); ^{13}C NMR (125.76 MHz, C_6D_6): $\delta = 24.8$, 26.3, 26.6, 27.6 (4C, CH_3), 65.8, 74.6, 76.5, 76.6, 96.5 (5C, C-2, C-3, C-4, C-5, C-6), 110.8, 112.5 (2C, $C_{acetalic}$), 218.8 (4C, CO_{cis}), 224.1 (1C, CO_{trans}), 276.7 (1C, C-1); MS (EI): *m/z* (%): 433 (4) [M^+], 418 (4) [$M^+ - CH_3$], 405 (1) [$M^+ - CO$], 377 (1) [$M^+ - 2CO$], 349 (1) [$M^+ - 3CO$], 334 (1) [$M^+ - 3CO - CH_3$], 321 (18) [$M^+ - 4CO$], 306 (3) [$M^+ - 4CO - CH_3$], 293 (100) [$M^+ - 5CO$], 278 (11) [$M^+ - 5CO - CH_3$]; HRMS for $^{12}C_{17}{}^1H_{19}{}^{16}O_9{}^{14}N^{52}Cr$ [M^+] calcd. 433.0465; found 433.0452; $C_{17}H_{19}O_9NCr$ (433.33): calcd. C 47.12, H 4.42, N 3.23; found C 46.85, H 5.08, N 3.09.

Pentacarbonyl(4-deoxy-4-methylamino-2,3:5,6-di-*O*-isopropylidene-D-allofuranosylidene)chromium(0) (24): The reaction was complete overnight. Column chromatography on silica gel (light petroleum/diethyl ether 1/4; $R_f = 0.52$, light petroleum/diethyl ether 1/6) afforded complex **24** (54 mg, 0.12 mmol) as a yellowish oil in 34% yield; IR (light petroleum): $\tilde{\nu} = 2056\ cm^{-1}$ (s, $^1A_1$; C≡O), 1975 cm^{-1} (s, B_1; C≡O), 1931 cm^{-1} (vs, E, $^2A_1$; C≡O); ^1H NMR (250.13 MHz, $CDCl_3$): $\delta = 1.29$ (s, 3H; CH_3-a), 1.31 (s, 3H; CH_3-b), 1.37 (s, 3H; CH_3-c), 1.39 (s, 3H; CH_3-d), 3.70 (d, $^5J_{H,H} = 0.6$ Hz, 1H; NCH_3), 3.84 (dd , $^2J_{H,H} = 9$ Hz, $^3J_{H,H} = 5$ Hz, 1H; H-6a), 4.03 (d, $^3J_{H,H} = 2.0$ Hz, 1H; H-4), 4.18 (dd, $^2J_{H,H} = 9$ Hz, $^3J_{H,H} = 7.7$ Hz, 1H; H-6b), 4.43 (d, $^3J_{H,H} = 5.5$ Hz, 1H; H-3), 4.47 (ddd, $^3J_{H,H} = 7.5$ Hz, $^3J_{H,H} = 5.0$ Hz, $^3J_{H,H} = 2.0$ Hz, 1H; H-5), 5.19 (dd, $^3J_{H,H} = 5$ Hz, $^5J_{H,H} = 0.6$ Hz, 1H; H-2); ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 23.6$ (1C, CH_3-a), 25.7 (1C, CH_3-d), 26.1 (1C, CH_3-c), 27.1 (1C, CH_3-b), 41.2 (1C, NCH_3), 65.4 (1C, C-6), 70.9 (1C, C-5), 75.3 (1C, C-3), 82.4 (1C, C-4), 97.2 (1C, C-2), 110.6, 111.3 (2C, $C_{acetalic}$), 217.8 (4C, CO_{cis}), 223.3 (1C, CO_{trans}), 271.1 (1C, C-1); MS (EI): *m/z* (%): 447 (3) [M^+], 432 (2) [$M^+ - CH_3$), 419 (2) [$M^+ - CO$], 391 (1) [$M^+ - 2CO$], 363 (2) [$M^+ - 3CO$], 335 (20) [$M^+ - 4CO$], 320 (2) [$M^+ - 4CO - CH_3$], 307 (100) [$M^+ - 5CO$], 292 (8) [$M^+ - 5CO - CH_3$]; HRMS for $^{12}C_{18}{}^1H_{21}{}^{16}O_9{}^{14}N^{52}Cr$ [M^+] calcd. 447.0622; found 447.0626.

Pentacarbonyl[4-deoxy-2,3:5,6-di-*O*-isopropylidene-4-(1′-methoxycarbonylprop-2′-(*S*)-2′-yl)-amino-D-allofuranosylidene)chromium(0) (25): After stirring overnight TLC indicated the formation of two yellow products (**A**: $R_f = 0.73$, **B**: $R_f = 0.61$, eluent light petroleum/diethyl ether 1/6). When the reaction mixture was stirred for two days, the formation of a single isomer was indicated by TLC ($R_f = 0.53$, eluent light petroleum/diethyl ether 1/2). In both cases column chromatography on silica gel (light petroleum/diethyl ether gradient 2/1–1/2) afforded a single isomer of **25** (53 mg, 0.10 mmol) as a yellowish oil in 23% yield; IR (light petroleum): $\tilde{\nu} = 2058\ cm^{-1}$ (s, $^1A_1$; C≡O), 1979 cm^{-1} (m, B_1; C≡O), 1940 cm^{-1} (vs, E/$^2A_1$; C≡O), 1923 cm^{-1} (s, $^2A_1$/E, C≡O); ^1H NMR (250.13 MHz, C_6D_6): $\delta = 0.85$ (s, 3H; CH_3-a), 1.10 (s, 3H; CH_3-b), 1.20 (s, 3H; CH_3-c), 1.23 (d, $^3J_{H,H} = 7.7$ Hz, 3H; CH_3-3′), 1.30 (s, 3H; CH_3-d), 3.25 (m, 1H; H-6a), 3.30 (m, 1H; H-6b), 3.37 (s, 1H; OCH_3), 3.80 (t*d, $^3J_{H,H} = 6$ Hz, $^3J_{H,H} = 1.4$ Hz, 1H; H-5), 3.90 (d, $^3J_{H,H} = 1.4$ Hz, 1H; H-4), 4.38 (d, $^3J_{H,H} = 5.1$ Hz, 1H; H-3), 5.39 (d, $^3J_{H,H} = 5.1$ Hz, 1H; H-2), 5.73 (q, $^3J_{H,H} = 7.4$ Hz, 1H; H-2′); ^{13}C NMR (62.9 MHz, C_6D_6): $\delta = 15.9$ (1C, CH_3-3′), 24.0 (1C, CH_3-a), 26.2 (1C, CH_3-b), 26.7 (1C, CH_3-c), 28.1 (1C, CH_3-d), 52.8 (1C, OCH_3), 63.0 (1C, C-2′), 66.2 (1C, C-6), 72.4 (1C, C-5), 76.2 (1C, C-3), 77.5 (1C, C-4), 97.5 (1C, C-2), 111.0, 111.7 (2C, $C_{acetalic}$), 170.4 (1C, C-1′), 218.9 (4C, CO_{cis}), 224.6 (1C, CO_{trans}), 280.7 (1C, C-1); MS (EI): *m/z* (%): 519 (2) [M^+], 504 (3) [$M^+ - CH_3$], 491 (4) [$M^+ - CO$], 463 (2) [$M^+ - 2CO$], 435 (2) [$M^+ - 3CO$], 433 (3) [$M^+ - CO - (CH_3)_2CO$], 407 (23) [$M^+ - 4CO$], 379 (12) [$M^+ - 5CO$], 321 (40) [$M^+ - 5CO - (CH_3)_2CO$]; HRMS for $^{12}C_{21}{}^1H_{25}{}^{16}O_{11}{}^{14}N^{52}Cr$ [M^+] calcd. 519.0832; found 519.0819.

Pentacarbonyl[4-deoxy-2,3:5,6-di-*O*-isopropylidene-4-(1′-methoxycarbonylprop-2′-(*R*)-2′-yl)-amino-D-allofuranosylidene)chromium(0) (26): After two days of stirring the reaction was complete. Column chromatography on silica gel (light petroleum/diethyl ether 1/2) gave two isomers of complex **26** (major isomer: $R_f = 0.63$; minor isomer: $R_f = 0.51$, eluent light petroleum/diethyl ether 1/2), presumably atropisomers around the N-C-2′ bond, in an approximately 1:1 ratio (total yield: 262 mg, 0.51 mmol, 54%). No coalescence of NMR signals could be detected in the temperature range of 218–333 K. Both isomers had to be further purified by column chromatography on silica gel (light petroleum/chloroform 1/40; first isomer: $R_f = 0.32$; second isomer: $R_f = 0.28$).

Major isomer (still containing certain amounts of the second isomer): yellowish oil, 160 mg (0.31 mmol, 33%); IR (light petroleum): $\tilde{\nu} = 2058\ cm^{-1}$ (s, $^1A_1$; C≡O), 1969 cm^{-1} (s, B_1; C≡O), 1935 cm^{-1} (vs, $^2A_1$/E; C≡O), 1917 cm^{-1} (sh, E/$^1A_1$;C≡O); ^1H NMR (500.13 MHz, C_6D_6): $\delta = 0.90$ (s, 3H; CH_3-a), 1.12 (s, 3H; CH_3-b), 1.21 (s, 3H; CH_3-c), 1.25 (br, 3H; CH_3-3′), 1.31 (s, 3H; CH_3-d), 3.24-3.30 (m, br, 1H; H-6a), 3.38-3.45 (m, br, 1H; H-6b), 3.40 (s, 3H; OCH_3), 3.83 (br, 1H; H-5), 3.95 (br, 1H; H-4), 4.39 (br, 1H; H-3), 5.37 (d, $^3J_{H,H} = 5$ Hz, 1H; H-2), 5.71 (br, 1H; H-2′); ^{13}C NMR (125.76 MHz, C_6D_6): $\delta = 15.6$ (1C, CH_3-3′), 23.9 (1C, CH_3-a), 26.2 (1C, CH_3-b), 26.6 (1C, CH_3-c), 28.0 (1C, CH_3-d), 52.8 (1C, OCH_3), 63.1 (1C, C-2′), 66.3 (1C, C-6), 72.3 (1C, C-5), 76.2 (1C, C-3), 77.5 (1C, C-4), 97.5 (1C, C-2), 111.0, 111.7 (2C, $C_{acetalic}$), 170.3 (1C, C-1′), 218.9 (4C, CO_{cis}), 224.7 (1C, CO_{trans}), 280.3 (1C, C-1); MS (EI): *m/z* (%): 519 (1) [M^+], 504 (2) [$M^+ - CH_3$], 491 (2) [$M^+ - CO$], 463 (1) [$M^+ - 2CO$], 435 (1) [$M^+ - 3CO$], 433 (4) [$M^+ - CO - (CH_3)_2CO$], 407 (14) [$M^+ - 4CO$], 379 (6) [$M^+ - 5CO$], 321 (27) [$M^+ - 5\ CO - (CH_3)_2CO$]; HRMS for $^{12}C_{21}{}^1H_{25}{}^{16}O_{11}{}^{14}N^{52}Cr$ [M^+] calcd. 519.0832; found 519.0843.

Minor isomer: yellowish oil, 102 mg (0.20 mmol, 21%); IR (light petroleum): 2058 cm^{-1} (s, $^1A_1$; C≡O), 1979 (s, B_1; C≡O), 1938 cm^{-1} (vs, E/$^2A_1$; C≡O), 1922 cm^{-1} (sh, $^2A_1$/E; C≡O); ^1H NMR (500.13 MHz, C_6D_6): $\delta = 0.86$ (s, 3H; CH_3), 1.12 (s, 3H; CH_3), 1.24 (s, 3H; CH_3), 1.34 (s, 3H; CH_3), 1.57 (d, 3H; CH_3-3′), 3.21 (dd, $^2J_{H,H} = 9$ Hz, $^3J_{H,H} = 4$ Hz, 1H; H-6a), 3.32 (s, 3H; OCH_3), 3.34 (t*, $^{2/3}J_{H,H} = 8$ Hz, 1H; H-6b), 4.03-4.08 (m, br, 2H; H-4, H-5), 4.37 (d, $^3J_{H,H} = 4.96$ Hz, 1H; H-3), 5.41 (d, $^3J_{H,H} = 4.96$ Hz, 1H; H-2), 5.82-5.91 (m, br, 1H; H-2′). H-4/H-5 show a strong NOE upon irradiation at CH_3-3′, indicating a *syn* conformation along the N-C-2′ bond; ^{13}C NMR (125.76 MHz, C_6D_6): $\delta = 17.8$ (1C, CH_3-3′), 23.6 , 26.0, 26.9, 27.6 (4C, CH_3), 52.9 (1C, OCH_3), 64.8 (1C, C-2′), 65.9 (1C, C-6), 73.5 (1C, C-5), 76.6 (1C, C-3), 79.8 (1C, C-4), 97.3 (1C, C-2), 111.0, 111.8 (2C, $C_{acetalic}$), 169.8 (1C, C-1′), 218.6 (4C, CO_{cis}), 224.3 (1C, CO_{trans}), 280.0 (1C, C-1), ^{13}C assignments in analogy to the major isomer; MS (EI): *m/z* (%): 519 (2) [M^+], 504 (5) [$M^+ - CH_3$], 491 (8) [$M^+ - CO$], 463 (5) [$M^+ - 2CO$], 435 (1) [$M^+ - 3CO$], 407 (35) [$M^+ - 4CO$], 379 (25) [$M^+ - 5CO$], 364 (11) [$M^+ - 5CO - CH_3$], 321 (41) [$M^+ - 5CO - (CH_3)_2CO$]; HRMS for $^{12}C_{21}{}^1H_{25}{}^{16}O_{11}{}^{14}N^{52}Cr$ [M^+] calcd. 519.0832; found 519.0842.

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