DALTON
FULL PAPER

Carbohydrates tagged with the $CCo_3(CO)_9$ cluster †

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Two synthetic routes, the direct reaction of a carbohydrate with $^{+}COCCo_3(CO)_9$, or the reaction of $Co_2(CO)_8$ with 1,1,1-tribromomethyl sugar derivatives have been used to prepare [AcOglc = tetra-*O*-acetyl-D-glucopyranose, $Co_3 = CCo_3(CO)_9$] 1-β-AcOglc-N-(CO)-Co_3,, 2-β-AcOglc-N-(CO)-Co_3,, 1-α- (**16**) and 1-β-AcOglc-OCH_2Co_3, 1-α-BnOglc-O-(CO)Co_3 and 1-α- and 1-β-AcOmaltose-OCH_2Co_3. An unusual oxazoline cluster was isolated from the reaction with 2-aminoglucose. An X-ray structure confirmed the structure and absolute configuration of **16**. Deprotection of 1-β-AcOglc-OCH_2Co_3 on ion exchange resin gave water soluble 1-β-glc-OCH_2Co_3; higher yields of water soluble complexes were obtained by direct reaction of deprotected trihalomethyl derivatives with $Co_2(CO)_8$. Dppm complexes of the OCH_2Co_3 glucose derivatives were also prepared. Reaction of $^{+}COCCo_3(CO)_9$ with methyl-α-D-glucopyranoside gave the series 1-MeOglc-3-Co_3, 1-MeOglc-3,6-$(Co_3)_2$, 1-MeOglc-2,3,6-$(Co_3)_3$ and 1-MeOglc-3,4,6-$(Co_3)_3$, structurally characterised by 2-D ^1H and ^{13}C NMR. The carbohydrate-cluster complexes show reversible redox activity in organic and aqueous media.

Introduction

Carbohydrates play an essential role in many biological events[1] and are naturally occurring, oxygen-rich, chiral ligand sources. Metal–carbohydrate interactions are expected in biological fluids but whether specific metal–carbohydrate complexes play a role in these events still remains to be determined because of the paucity of structural information. Complexation would affect the biological activity of bio-molecules such as glycoproteins or lipopolysaccharides and could ensure a particular carbohydrate configuration for metabolic processes. It is therefore not surprising that metal–carbohydrate interactions are attracting a great deal of interest.[2–7] Recent work has shown that the carbohydrate portions of nucleosides and nucleotides play a key role in complexation with both main group and transition metal ions[8] and that an oxovanadium saccharide complex inhibits Rnase activity.[9] A long-standing debate has focused on the role of the aminosugar–metal link in the cytostatic mechanism of Fe[II] and Fe[III]/bleomycin and related anti-tumor agents.[10] Plant systems are also influenced by metal–sugar interactions; for example, selectivity of metal ion binding has been discovered with citrus and sugar beet pectins.[11] The applications of metal–carbohydrate complexes are not restricted to the biomedical area and include chromatography, electrophoresis, and metal-promoted stereoselective syntheses.[7,12]

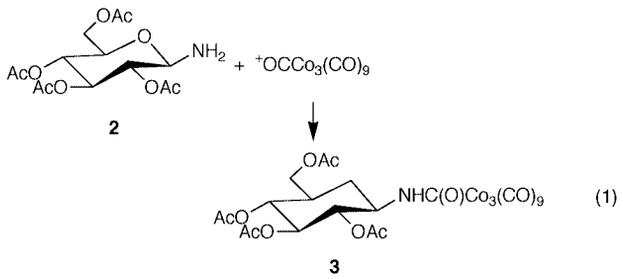
In contrast to this recent activity, organometallic–sugar chemistry, apart from ferrocenyl derivatives,[13,14] is virtually unexplored. Transition metal–carbohydrate complexation normally involves metal–oxygen bonding but, with "soft" metal ions, M–C can compete with M–O bonding.[15] Carbene complexes of deprotected and protected sugars are known.[16] Protected glycopyranosyl bromides react stereoselectively with organometallic compounds of cobalt,[17] iron,[18] and manganese[19,20] to give glycosyl complexes. Pyranosyl and furanosyl organometallic complexes undergo insertion reactions resulting in the formation of C–glycosyl derivatives with the reaction rates dependent on the configuration of the anomeric center bound to the metal.[20] Sugars serve as optically active ligands for chiral induction for reactions mediated by low-valent titanium complexes[21] and a well-studied example of carbohydrate synthesis is the decarbonylation of aldehydes (aldoses) by $Rh(PPh_3)_3Cl$[22] which involves transient sugar–rhodium complexes. There is only one report of a reaction with a metal cluster. Bhaduri *et al.* found[23] that $Ru_3(CO)_{12}$ reacted with 1,2-*O*-isopropylidene α-D-glucofuranose to give a novel molecule in which one Ru–Ru bond is cleaved and new Ru–H bonds and Ru–OH–Ru bridges formed. This reaction implies that heavy metal clusters can strip acidic protons from sugars leading to the incorporation of the cluster into the sugar.

Metal clusters have the potential to assist in elucidating structural functions and detailed mechanism of immunological responses and glycoprotein action. They are lypophilic, spectroscopically active and have a high electron density. Long-range electron transfer plays an important role in many biological processes[24] and metal sugar complexes may facilitate chemistry at a distance. The relatively simple redox chemistry of many metal clusters[25,26] could therefore be used to probe these through-space interactions and there is interest in developing small molecules that selectively target RNA and DNA. A robust cluster family with a well-defined redox system is $-CCo_3(CO)_9$ which has the added advantage of being tetherable *via* the carbyne cap. The synthesis and redox chemistry of carbohydrate complexes of this cluster as model bioprobes are described in this paper.

Results and discussion

The acylium cation $^{+}OCCCo_3(CO)_9$ **1** is a potent electrophile[27] and provides a useful precursor to tethered carbohydrates**.** Thus the reaction of **1** with the O-acetyl protected 1-β-aminoglucose **2** gave the amido complex **3** (eqn. (1)) and with *O*-acetyl protected 2-glucosamine **4**, the unstable 2-amido derivative **5**. No reaction occurred with *N*,*O*-acetylglucosamines as **1** does not react with amides. Apart from **5**, a solid, these cluster derivatives are purple syrups, soluble in most organic solvents in which they tended to be relatively unstable. Microanalyses, mass spectra, NMR and IR data for **3** and **5** were compatible with the proposed structures and stereochemistry. Dominant positive ions in the Electrospray (ES) mass spectra were MNH_4^+ and assignments were checked by recording the MK^+

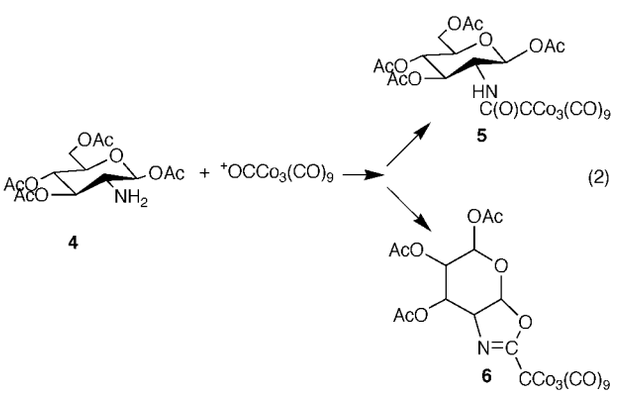
† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4165/



(1)

spectrum. With the exception of resonances for groups attached to the anomeric carbon there was little difference in the ^{1}H and ^{13}C NMR spectra of the 1-β and 2-substituted compounds: for **3** and **5** respectively OAc (δ_H 1.98–2.02, δ_C 20.5–20.6/169.6–171.4 and 2.00–2.09, 20.6–20.8/169.3–171.0), ring H_{1-6} (δ_H 3.83–5.39 and 3.86–5.94) ring C_{3-5} (δ_C 70.7–73.5 and 68.0–73.0). Significant differences in δ_H(amide) and $\delta_C(C_1)$ were observed due to the configuration about the anomeric carbon. Thus δ_H(amide) in **3** and **5** appeared as a doublet at 6.73 and 6.05 respectively clearly showing the downfield shift when the anomeric carbon in **3** carries the amide functionality. A 'normal' $\delta_C(C_1)$ at 92.6 in **5** was shifted upfield to 79.7 in **3** because of an *O*/*N* rather than *O*/*O* configuration at the anomeric carbon. In the IR the characteristic[28] three-band ν(CO) cluster spectrum was observed with the symmetrical A_1 mode shifted to higher energy (2110 cm^{-1}) due to the electronegative acyl group; the amide ν(CO) band occurred at ≈1640 cm^{-1}.

An oxazoline **6** was also isolated from the reaction with **4** if a two mole equivalent of **1** was used (eqn. (2)). The oxazoline ring



(2)

in **6** was defined by a ν(C=N) band at 1597 cm^{-1} and δ_C 178.6 for the ring carbon. Other NMR parameters indicated that the glucose skeleton is distorted by oxazoline formation, typical of oxazoline-sugars. To our knowledge this is the first reported oxazoline derivative of the $CCo_3(CO)_9$ cluster. However, oxazoline-sugars are proving to be useful precursors for glycoconjugates and oligosaccharides[29] and the applications of our cluster oxazolines will be described elsewhere.

Attempts to deprotect **3** on an ion exchange resin to achieve the desired water solubility for biological work were unsuccessful leading to complete declusterfication from the cluster. The instability of the amido-linked cluster in solution led us to consider the direct reaction of **1** with sugar hydroxyl groups. To define the reaction site **1** was reacted initially with the benzylated sugar **7** which has the hydroxyl functionality in the 1-α position. This gave the ester **8** in poor yield as a purple oil (eqn. (3)). Surprisingly, no deprotection occurred when **8** was hydrogenated over Pd or under thiolysis conditions, nor was the majority of the cluster decomposed by the severe treatment. As the ester link proved to be more stable than the amide link in solution this encouraged us to react the cluster directly with deprotected sugars. Methyl-α-D-glucopyranoside **9** was chosen as the carbohydrate substrate in order to reduce the number of

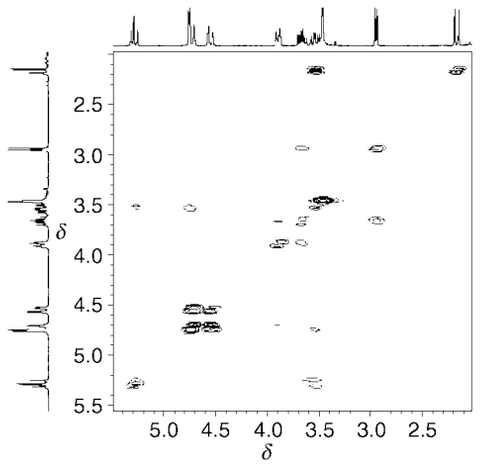
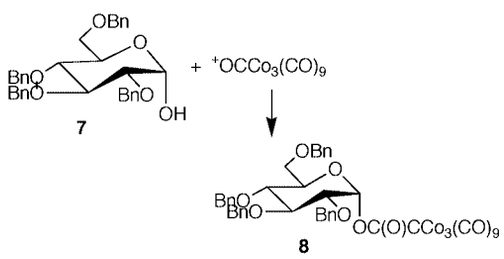


Fig. 1 COSY spectrum of **10b** in $CDCl_3$.



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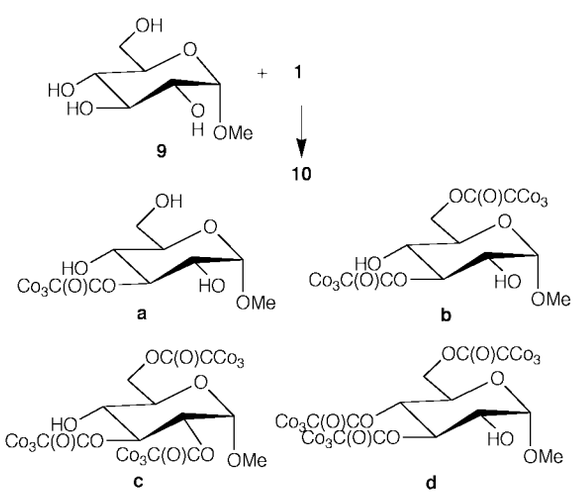


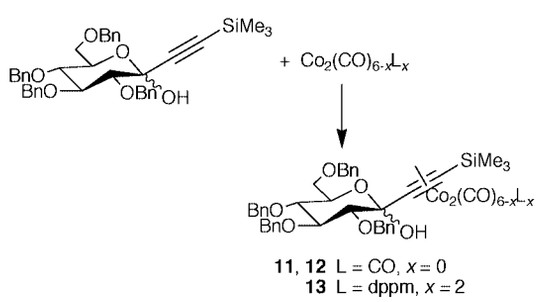
(4)

coordination sites. Direct reaction with **1** gave a sequence of sugar-clusters, **10a**–**d** (eqn. (4), $Co_3 = Co_3(CO)_9$) isolated as purple syrups, including two isomers where there are three cluster units per sugar **10c**,**d**. All had the typical ν(CO) spectrum of an acyl cluster species with the *sym*-A_1 M–CO and acyl ν(CO) bands at 2109 and ≈1730 cm^{-1} respectively. Their stoichiometry and stereochemistry were deduced from mass spectra and detailed 2-D NMR as the syrups were difficult to get analytically pure. Attachment of the clusters reduces the hydrogen-bonding associated with the sugar OH groups, consequently, the OH ^{1}H resonances were remarkably sharp in $CDCl_3$ featuring δ_H (OH) as well-defined doublets. This enabled the ^{1}H connectivity to be unambiguously obtained from COSY spectra and is illustrated for **10b** (Fig. 1). Comparable shifts for the carbon resonances permitted a complete assignment by a combination of ^{13}C, DEPT and HMQC spectra; detailed assignments are given in the experimental.

Because of the likelihood of adverse steric interactions it had been anticipated that the coordination positions on the opposite side to the 1-α OMe substituent, that is 3- and 6-, would have been preferred, and that multiple addition of clusters to a carbohydrate skeleton would have been unlikely. Indeed, the

complex with two cluster units **10b** was formed in highest yield with the expected 3-β, 6-β stereochemistry; this was the only bis-cluster product identified. The doublet at δ_H 2.18 in the ^{1}H NMR of **10b** (Fig. 1) is assigned to the 2-OH group; this is coupled to the 2-proton at δ_H 3.54. The doublet at δ_H 2.97 is similarly assigned to the 4-OH. Hydrogen atoms in close proximity to the electron-withdrawing cluster were deshielded, as expected. A similar procedure using the assignments for **10b** enabled the stereochemistry of the other products to be elucidated. Furthermore, because individual δ_C(COAc) resonances were clearly delineated in the ^{13}C NMR of **10** the number of these resonances defined the number of cluster units per glucose moiety. More than one product with one cluster per glucose was formed, all in very small yields, but the 4-isomer **10a** was dominant. Two complexes with three cluster units per glucose **10c**,**d** were isolated, again in low yields. The 3-β, 6-β-positions were also occupied in **10c** and **10d** but the surprise was the occupation, in **10c,** of the 2-α site adjacent to the axial 1-OMe; the sterically undemanding 4-α site is occupied in **10d**. To accommodate the 3-β, 6-β, 2-α stereochemistry in **10c** models show that there must be considerable distortion about the C(1)–C(2) bond. An indication of this distortion comes from the ^{13}C NMR data. In **10c** resonances for the anomeric carbon, C1, and C2 occur at δ_C 96.4 and 74.4 respectively whereas the equivalent chemical shifts for **10a**,**b**,**d** are nearly the same (δ_C 99.5 ± 0.2 and 77.5 ± 0.3 respectively). It does appear that the carbohydrate is able to mould itself to accommodate a bulky cluster. From these analyses a 2,3,6 and 3,4,6 stereochemistry was deduced for **10c** and **10d** respectively.

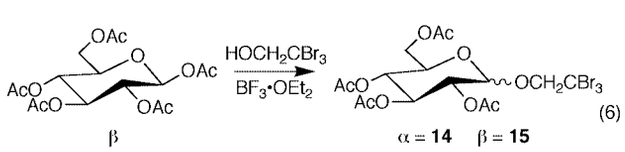
Because of the difficulty in controlling the stoichiometry of the reactions of **1** with deprotected sugars, and noting the increased stability of the protected esters, we approached the water-solubilisation problem by assembling the cluster on the carbohydrate. The tricobaltcarbon skeleton can be assembled either by acid treatment of $Co_2(CO)_6$(–C≡CH) complexes or from trihalomethyl derivatives.[28] $Co_2(CO)_6$ complexes of benzyl-protected 1-α- and 1-β-trimethylsilylethynylglucopyranosides **11**, **12** and the dppm compound **13** (eqn. (5)) were



(5)

11, **12** L = CO, x = 0
13 L = dppm, x = 2

characterised; similar compounds have been reported by Armstrong and Daly.[30] Desilylation of **11** and **12** by K_2CO_3 gave the terminal alkyne but treatment with methanolic sulfuric acid did not give the expected[28] cluster product. The alternative route from trihalomethyl sugars was more successful. The new compounds, 1-α-**14** and 1-β-*O*-1′,1′,1′-tribromoethyl-2,3,4,6-tetra-*O*-acetylglucopyranose **15** were synthesised by similar routes (eqn. (6)) to those used for –CCl_3 analogues[31] and reacted with



(6)

β α = **14** β = **15**

$Co_2(CO)_8$ in THF at room temperature to give the 1-α **16** and 1-β **17** clusters (eqn. (7)). The ^{1}H and ^{13}C NMR data for the glucopyranose portion of **16** and **17** were similar to **3** with the exception that δ_C (1-C) has moved from 79.7 downfield

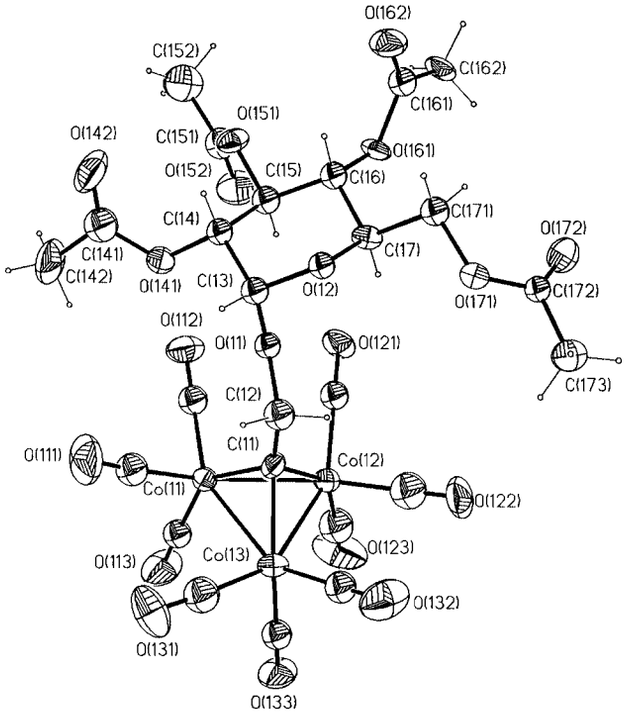
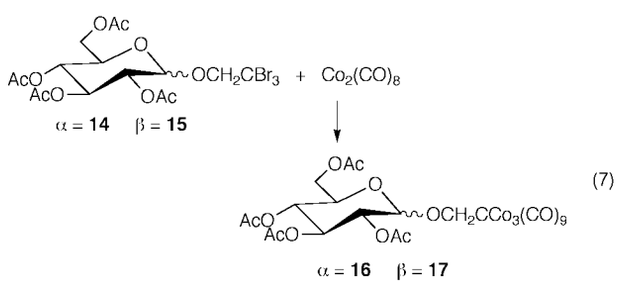


Fig. 2 Structure of molecule 1 of compound **16** showing the atom numbering scheme. For clarity only the O atoms of the carbonyl ligands have been labelled, the carbonyl C atoms have the same number as the O to which they are bound. Molecule 2 is numbered similarly, except that each atom number begins with 2.



(7)

back to a 'normal' position (δ 95–100) for an *O*/*O* configuration around the anomeric carbon. Interesting features were associated with the AB system of the diastereotopic methylene protons in all compounds with a –OCH_2–X link from the anomeric carbon, **14**–**31** (*vide infra*). Surprisingly, δ_H (X = CBr_3, 4.2–4.6) is ≈1 ppm upfield of δ_H (X = cluster, 5.2–6.0) whereas there is no difference in δ_C (CH_2, 83.5 ± 1) or the separation between the diastereotopic protons. This is likely to be a through-space rather than inductive effect. Substitution of two cluster CO groups by dppm, however, significantly increases the diastereotopic proton separation from ≈0.3 to 0.7 ppm presumably due to the increased congestion around the sugar–OCH_2–X link.

Although most of the glucose-cluster complexes were obtained as syrups poor quality crystals were isolated for **16** and its X-ray crystal structure is shown in Fig. 2. Compound **16** crystallises with two unique molecules in the asymmetric unit of the triclinic unit cell. Selected bond distances and angles for both molecules are given in Table 1 with the overall molecular geometry and numbering scheme for molecule 1 displayed in Fig. 2. Small differences in bond lengths and angles between the independent molecules can best be assigned to crystal packing effects. The structure consists of an approximately tetrahedral CCo_3 cluster capped with a 2-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyloxy) moiety bound *via* a methylene group to the apical C atom of the cluster unit. The Co atoms of the cluster core carry nine carbonyl ligands, six equatorial and three axial

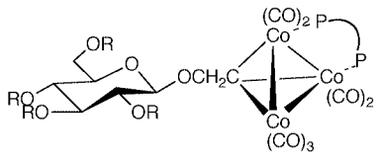
Table 1 Selected bond lengths (Å) and angles (°) for **16**

Molecule 1		Molecule 2	
O(12)–C(13)	1.456(15)	O(22)–C(23)	1.438(15)
O(12)–C(17)	1.425(17)	O(22)–C(27)	1.433(18)
O(171)–C(171)	1.496(17)	O(271)–C(271)	1.441(17)
C(171)–C(17)	1.528(18)	C(271)–C(27)	1.505(18)
C(17)–C(16)	1.505(19)	C(27)–C(26)	1.519(19)
O(161)–C(16)	1.444(18)	O(261)–C(26)	1.431(18)
C(16)–C(15)	1.545(19)	C(26)–C(25)	1.533(18)
O(151)–C(15)	1.453(17)	O(251)–C(25)	1.461(16)
C(15)–C(14)	1.48(2)	C(25)–C(24)	1.51(2)
O(141)–C(14)	1.430(15)	O(241)–C(24)	1.433(15)
C(14)–C(13)	1.504(19)	C(24)–C(23)	1.503(19)
C(13)–O(11)	1.415(16)	C(23)–O(21)	1.408(15)
O(11)–C(12)	1.463(18)	C(22)–O(21)	1.444(16)
C(12)–C(11)	1.49(2)	C(22)–C(21)	1.478(18)
C(11)–Co(11)	1.874(14)	C(21)–Co(21)	1.897(13)
C(11)–Co(12)	1.880(16)	C(21)–Co(22)	1.882(14)
C(11)–Co(13)	1.912(14)	C(21)–Co(23)	1.924(14)
Co(11)–Co(12)	2.478(2)	Co(21)–Co(22)	2.487(3)
Co(11)–Co(13)	2.471(3)	Co(21)–Co(23)	2.478(3)
Co(12)–Co(13)	2.461(3)	Co(22)–Co(23)	2.475(3)
C(17)–O(12)–C(13)	113.0(10)	C(27)–O(22)–C(23)	112.5(11)
O(171)–C(171)–C(17)	108.9(10)	O(271)–C(271)–C(27)	108.7(12)
O(12)–C(17)–C(16)	110.3(11)	O(22)–C(27)–C(271)	107.5(12)
O(12)–C(17)–C(171)	106.6(11)	O(22)–C(27)–C(26)	107.9(11)
C(16)–C(17)–C(171)	108.7(11)	C(271)–C(27)–C(26)	114.4(12)
O(161)–C(16)–C(17)	111.3(11)	O(261)–C(26)–C(27)	110.3(11)
O(161)–C(16)–C(15)	108.8(12)	O(261)–C(26)–C(25)	108.6(12)
C(17)–C(16)–C(15)	108.8(11)	C(27)–C(26)–C(25)	109.7(11)
O(151)–C(15)–C(14)	109.2(11)	O(251)–C(25)–C(24)	108.7(10)
O(151)–C(15)–C(16)	108.3(11)	O(251)–C(25)–C(26)	109.2(11)
C(14)–C(15)–C(16)	109.5(12)	C(24)–C(25)–C(26)	108.3(12)
O(141)–C(14)–C(15)	110.1(12)	O(241)–C(24)–C(23)	108.7(10)
O(141)–C(14)–C(13)	108.1(11)	O(241)–C(24)–C(25)	107.8(11)
C(15)–C(14)–C(13)	112.7(12)	C(23)–C(24)–C(25)	110.8(11)
O(11)–C(13)–O(12)	110.7(10)	O(21)–C(23)–O(22)	111.9(10)
O(11)–C(13)–C(14)	107.8(12)	O(21)–C(23)–C(24)	109.0(11)
O(12)–C(13)–C(14)	110.2(10)	O(22)–C(23)–C(24)	110.3(11)
C(13)–O(11)–C(12)	112.4(11)	O(21)–C(22)–C(21)	108.9(12)
O(11)–C(12)–C(11)	106.1(13)	C(23)–O(21)–C(22)	113.2(10)
C(12)–C(11)–Co(11)	130.9(10)	C(22)–C(21)–Co(22)	131.6(11)
C(12)–C(11)–Co(12)	132.2(11)	C(22)–C(21)–Co(21)	131.1(9)
Co(11)–C(11)–Co(12)	82.6(6)	Co(22)–C(21)–Co(21)	82.3(5)
C(12)–C(11)–Co(13)	129.8(12)	C(22)–C(21)–Co(23)	130.7(11)
Co(11)–C(11)–Co(13)	81.5(5)	Co(21)–C(21)–Co(23)	80.8(5)
Co(12)–C(11)–Co(13)	80.9(5)	Co(22)–C(21)–Co(23)	81.1(5)
Co(13)–Co(11)–Co(12)	59.66(8)	Co(23)–Co(21)–Co(22)	59.79(8)
Co(13)–Co(12)–Co(11)	60.03(8)	Co(23)–Co(22)–Co(21)	59.91(8)
Co(12)–Co(13)–Co(11)	60.31(8)	Co(22)–Co(23)–Co(21)	60.30(8)

with respect to the Co_3 triangle. The structure confirms that the anomeric configuration of the sugar is α. Further, refinement of the Flack parameter[32] indicates that the structural parameters represent the correct absolute structure for the chiral molecule and that the configuration of the carbohydrate unit is D as expected. The poor quality of the diffraction data and resulting high esd's preclude detailed examination of the molecular parameters but, in general, bond lengths and angles in both the sugar[33] and cluster[28,34] moieties are unremarkable.

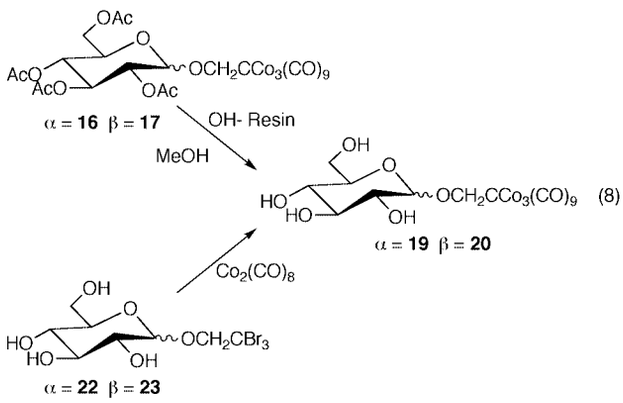
Carbonyl substitution of a cluster fragment of **17** by $P(Cy)_3$ was attempted in order to obtain a solid material but the cluster was removed from the sugar. Apparently, there is sufficient clutter at the cluster terminus to destabilise the molecule on coordination of a bulky phosphine in the axial position as the direct reaction of **17** with dppm in benzene gave high yields of **18** where the chelate is clamping a Co–Co bond. An oxidisable cluster centre is also generated by coordination of the dppm.[25]

Deprotection of **17** on a basic ion exchange resin gave the fully deprotected water-soluble 1-β **20** glucose clusters in low yield together with partially deprotected compounds. Surprisingly, the dppm complex **21** derived from **20**, was crystalline



18 R = Ac **21** R = H

even though its acetylated analogue **18**, was an oil. A more direct route to **20** was from the new sugar 1-β-*O*-1′,1′,1′-tribromoethylglucopyranose **23** and $Co_2(CO)_8$ which gave a single water soluble product in good yield (eqn. (8)). Attempts



α = **16** β = **17**

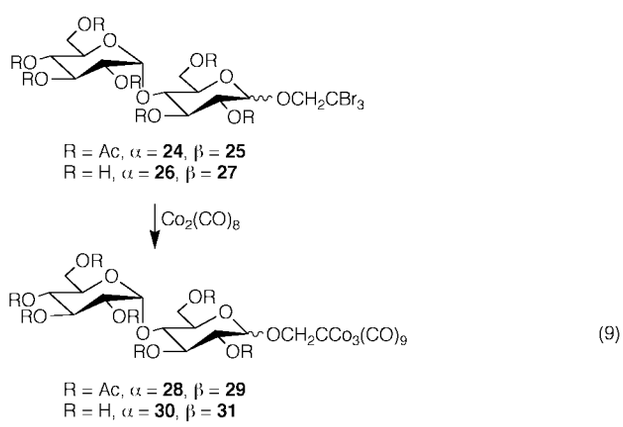
α = **19** β = **20**

α = **22** β = **23**

(8)

to prepare the deprotected 1-α-**19** from **16** or **22** were unsuccessful as it appeared that it was very unstable in solution (see also maltose situation below).

In order to explore the application of this synthetic strategy to higher saccharides the new tribromomethyl compounds **24**–**27** (eqn. (9)) were prepared from maltose by the same



R = Ac, α = **24**, β = **25**
R = H, α = **26**, β = **27**

R = Ac, α = **28**, β = **29**
R = H, α = **30**, β = **31**

(9)

method given in ref. 6. The reaction of the acetylated **24**, **25** with $Co_2(CO)_8$, as a mixture of anomers, gave both 1-α **28** and 1-β **29** as purple solids. However, the analogous reaction with deprotected **26**, **27** gave only 1-β **31**. As with the glucose reactions there was no evidence of an α anomer. We have no explanation for why the deprotected α anomers are unstable particularly as the acetylated parents are stable solids and there are no obvious close contacts between the carbohydrate skeleton and the cluster. The deprotected representative **31** was soluble in alcohols, acetone and water–alcohol mixtures, but insoluble in chlorinated or hydrocarbon solvents; the opposite holds for **28** and **29**. The ^1H NMR of the maltose complexes are complicated due to overlapping resonances from sixteen sugar protons but COSY, HMQC and DEPT sequences enabled an assignment of the ^1H and ^{13}C NMR spectra and confirmation of the structures. The chemical shifts were similar to the glucopyranose analogues.

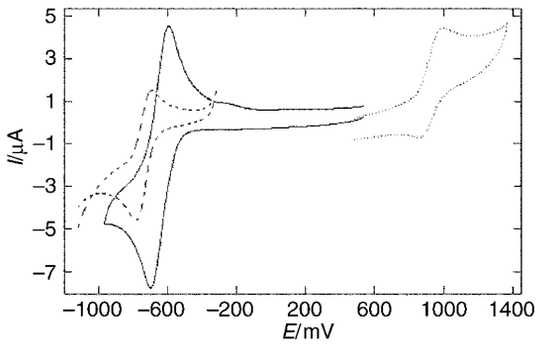


Fig. 3 Cyclic voltammogram (ran at a 100 mV s^{-1} scan rate) of: (——) **20** in CH_2Cl_2, Pt, 0.1 M $Bu^n_4NPF_6$; (----) **20** in MeOH–H_2O, Pt, 0.1 M Et_4NClO_4 and (····) **18** in CH_2Cl_2, Pt, 0.1 M $Bu^n_4NPF_6$, 100 mV s^{-1}.

Redox chemistry

Recently we showed by SNIFTIRS (subtractively normalized interfacial FTIR spectroscopy) that the redox processes of the $CCo_3(CO)_9$ cluster at an electrode surface are unchanged in water;[35] indeed a trace of water is adventitious in removing passive cluster material from the electrode surface. The redox chemistry of water soluble phosphine complexes also mirrored that of analogues in organic solvents.[36] Nevertheless, physiological conditions may provide a more testing environment and it was therefore of interest to look at the redox chemistry of the sugar derivatives in various media.

In dichloromethane, the cluster complexes undergo the typical[25] chemically reversible, one-electron reduction process to form the radical anion $[sugar–CCo_3(CO)_9]^{\bullet -}$ (Fig. 3) . It is of significance that there was no evidence for the CO-dissociative step to form the $CCo_3(CO)_8^{2-}$ species which is a feature of $RCCo_3(CO)_9$ electrochemistry.[37] The $E_{1/2}$ values were dependent on the electronic character of the link between cluster and sugar. Thus, $E_{1/2}$ for those with an electron-withdrawing –O(CO)– link were 0.65 ± 0.02 V *vs.* SCE; whereas with a $–OCH_2–$ they were 0.75 ± 0.01 V. For the multi-substituted species **10b**,**c** there was clearly very slow diffusion at the electrode surface as the $E_a - E_c$ values for the reversible couples were up to 130 mV at 50 mV s^{-1} and 300 mV at 400 mV s^{-1}, even with a microelectrode. The dppm compounds **18** and **21** displayed a one-electron oxidation step with only partial chemical reversibility at 293 K for **18** (Fig. 3) and irreversibility for **21**. Reduction of **16** over sodium in THF produced the radical anion $\mathbf{16}^{\bullet -}$ identified by its isotropic EPR spectrum[25] ($g = 2.02$, $a^{Co} = 35$ G); the anion was remarkably stable in the absence of oxygen.

The electrochemistry of one deprotected complex **20** was studied in 1:1 water–methanol. The slow electrode kinetics increased the $E_a - E_p$ separation (Fig. 3) but the couple was still chemically reversible at scan rates >400 mV s^{-1}. Below 400 mV s^{-1} I_a/I_p decreased with decreasing scan rate, being 0.6 at 50 mV s^{-1}. $E_{1/2}$ was 0.80 V; that is, a shift of ≈−50 mV from that in dichloromethane. Strong association of M^+, NH_4^+ ions with the parent ions of the glycosides, including **20**, was a feature of both FAB and ES-MS, which led us to consider whether cationic association or coordination occurred in solution. If these interactions were adjacent to the redox centre then the redox potential could be affected—that is, they could act as sensors. In fact, there was virtually no change in the electrochemical behavior of **20** when M^+ (M = Na, K, Ag), M^{2+} (Cu, Ni, Mg) were added in up to 100 mol equivalent excess. Aggregates are not uncommon in alkali and alkaline earth–carbohydrate chemistry[3,4] and further work is in progress with a view to defining the site of interaction in the cluster derivatives.

Conclusion

This work demonstrates that the tricobalt cluster can be used to regio- and stereo-selectively tag carbohydrates and hence probe structure and function of these substrates. There are several strategies which would be applicable to biological substrates. Direct cluster formation *via* the formation of 1,1,1-tribromomethyl intermediates is the preferred option for reducing sugars; it is not viable for non-reducing sugars as a reactive anomeric carbon is required. Electrophilic attack by the acylium cation $^+COCCo_3(CO)_9$ on a sugar offers a viable alternative for non-reducing sugars although *in situ* delivery is a problem. In principle, the relative instability of carbohydrate complexes of the cluster with an amide link compared to those with an acyl link could be used to selectively target functional groups in biological molecules and to deamidate sugars. Coordination of the cluster also offers a means of changing the functionality of the carbon atom to which the cluster is attached. For example, oxidation of the acylcluster–carbohydrate will lead to a carboxylic acid functional group. Applications include the determination of structure and chain length of polysaccharides by electron microscopy and X-ray techniques, incorporation of the cluster tagged glycosoamines into neoglycoproteins to probe ligand–acceptor interactions, and cellular recognition studies. Examples of these concepts will be described in succeeding publications.

Experimental

All cluster reactions were carried out under nitrogen in dry solvents in oven-dried glassware. Methyl-α-D-glucopyranoside **9**, β-D-glucose pentaacetate, dicobalt octacarbonyl and tribromoethanol were used as received (Aldrich). Compound **1**,[27] $EtOC(O)CCo_3(CO)_9$,[27] **2**,[38] **4**,[39] **7**,[40] 2,3,4,6-tetra-*O*-benzyl-*C*-trimethylsilylethyn-1-ylglucopyranoside,[41] and peracetylated maltose[42] were prepared by literature methods. IR and NMR spectra were recorded on a Digilab FX60 and Varian VXR 500, 300 MHz /Gemini 200 MHz spectrometers respectively. Microanalyses were carried out by the Campbell Microanalytical Laboratory, University of Otago. In common with sugar complex chemistry compounds were often prepared as analytically-reproducible solvated syrups. FAB mass spectra were recorded on a Kratos MS80RFA instrument with an Iontech ZN11NF atom gun. Electrospray mass spectra were recorded on a VG Platform II spectrometer in a 1:1 v/v acetonitrile–water or methanol–water mobile phase (0.1 mM in compound). Electrochemical measurements were performed with a three-electrode cell using a computer controlled EG & G PAR 273A potentiostat/galvanostat at scan rates 0.05–10 V s^{-1}. A polished Pt disc electrode was employed; the reference was SCE uncorrected for junction potentials ($E_{1/2}$ $[ferrocene]^{+/0} = 0.466$ V in acetone) or decamethylferrocene (CH_2Cl_2); the supporting electrolyte (0.1 M) was Et_4NClO_4 (aqueous solvents) or Bu^n-NPF_6 (CH_2Cl_2) and the substrate ≈1 × 10^{-3} M.

Preparation of 3

$EtOC(O)CCo_3(CO)_9$ (0.717 g, 1.4 mmol) was dissolved in propionic anhydride (15 ml). Hexafluorophosphoric acid (0.35 g, 0.32 ml of 65%, 2.4 mmol) was added and the mixture stirred for 30 min, while a black precipitate formed. The precipitate was filtered under N_2 and washed with dichloromethane. 1-amino-β-glucopyranoside **2** (0.804 g, 2.3 mmol) in 15 ml dichloromethane was added to the precipitate and the mixture stirred for 1 h at room temperature. The purple solution was washed with water (2 × 20 ml), dried ($MgSO_4$), and the solvent removed *in vacuo* to obtain a purple oil which was purified by silica gel preparative plate chromatography (2:1 ether–hexane). Compound **3** was obtained as a purple oil (36%). The compound was soluble in organic solvents except hydrocarbons (Found: C, 37.55; H, 2.57; N, 2.33; FAB, 816 MH^+. $C_{25}H_{20}Co_3O_{19}N$ requires: C, 36.83; H, 2.47; N, 1.72%; M 815). $\nu(CH_2Cl_2, cm^{-1})$ 2110, 2064, 2048 (M–CO), 1750 (OAc), 1640

(CO amide). $\delta_H(CDCl_3)$ 1.98, 2.00, 2.01, 2.02 (4 × 3H, 4 × s, 4 × OAc), 3.83 (1H, dq, J = 2 and 10 Hz, 5-H), 4.10 (1H, dd, J = 2 and 12 Hz, 6-H), 4.30 (1H, dd, J = 4 and 12 Hz, 6′-H), 4.93–5.39 (4H, m, 1, 2, 3, 4-H), 6.73 (1H, d, J = 9 Hz, NH); $\delta_C(CDCl_3)$ 20.5, 20.7 (4 × acetate CH_3), 61.7 (6-C), 68.6, 70.7, 72.7, 73.5 (2, 3, 4, 5-C), 79.7 (1-C), 169.6, 169.9, 170.6, 171.4 (4 × acetate CO), 178.5 (amide CO), 198.5 (M–CO).

Preparation of 5

Compound **5** was obtained as a purple oil in 9% yield from **4** using the same procedure as for **3**. Unstable in solution with solubilities similar to **3**. Found: ES-MS (positive ion) 832 (MNH_4^+); (negative ion) 814 ($M - H^-$). $\nu(CH_2Cl_2, cm^{-1})$ 3053 (NH), 2110, 2066, 2046 (M–CO), 1757 (OAc), 1605 (CO amide). $\delta_H(CDCl_3)$ 2.00, 2.03, 2.08, 2.09 (4 × 3H, 4 × s, 4 × OAc), 3.86 (1H, dq, J = 2 and 10 Hz, 5-H), 4.10–4.31 (3H, m, 2, 6-H_2), 5.15 (1H, t, J = 10 Hz, 3 or 4-H), 5.41 (1H, t, J = 10 Hz, 3 or 4-H), 5.94 (1H, d, J = 9 Hz, 1-H), 6.05 (1H, d, J = 8 Hz, NH). $\delta_C(CDCl_3)$ 20.6, 20.7, 20.8, 20.8 (4 × acetate CH_3), 55.0 (6-C), 61.8, 68.0, 72.4, 73.0 (2, 3, 4, 5-C), 92.6 (1-C), 169.3, 169.4, 170.7, 171.0 (4 × acetate CO), 171.9 (amide CO), 198.6 (M–CO).

When 2 × mole equivalent of **1** was used with **4**, in the same procedure as above, the oxazoline **6** only was produced in 11% yield as a purple solid (Found: C, 36.59; H, 2.03; N, 1.90. $C_{23}H_{16}Co_3O_{17}N$ requires: C, 36.58; H, 2.14; N, 1.86%). $\nu(CH_2Cl_2, cm^{-1})$ 2110, 2063, 2046 (M–CO), 1746 (OAc), 1597 (CN). $\delta_H(CDCl_3)$ 1.95, 2.05, 2.14 (3 × 3H, 3 × s, 3 × OAc), 3.71 (1H, dq, J = 2 and 4 Hz, 5-H), 4.16 (2H, m, 6-H_2), 4.38 (1H, dq, J = 1 and 7 Hz, 2-H), 4.88 (1H, d, J = 9 Hz, 4-H), 5.43 (1H, d, J = 3 Hz, 3-H), 6.13 (1H, d, J = 7 Hz, 1-H). $\delta_C(CDCl_3)$ 20.5, 20.7, 21.1 (3 × acetate CH_3), 64.1, 66.5, 67.7, 68.7, 69.5 (2, 3, 4, 5, 6-C), 100.4 (1-C), 169.2, 169.7, 170.7 (3 × acetate CO), 178.6 (oxazoline NCO), 198.6 (M–CO).

Preparation of 8

The acylium cation **1** was prepared from $EtOC(O)CCo_3(CO)_9$ (0.459 g, 0.9 mmol) as described for **3**. The sugar **7** (0.772 g, 1.4 mmol) in 15 ml dichloromethane was added and the mixture stirred for 1 h at ambient temperature. The purple solution was washed with water, dried ($MgSO_4$), and the solvent removed *in vacuo* to obtain a purple oil which was purified by silica gel preparative plate chromatography (2:1 ether–hexane). Compound **8** was obtained as a purple oil (10%) (Found: C, 53.47; H, 3.56; FAB, 924 ($M^+ - 3CO$). $C_{45}H_{35}Co_3O_{16}$ requires: C, 53.59; H, 3.50%; M 1009). $\nu(CH_2Cl_2, cm^{-1})$ 2111, 2064, 2047 (M–CO), 1747 (ester CO). $\delta_H(CDCl_3)$ 3.66–3.96 (6H, m, 6 of sugar or CH_2Ph), 4.45–4.90 (8H, m, 8 of sugar or CH_2Ph), 6.65 (1H, d, J = 2 Hz, 1-H), 7.15–7.32 (20H, m, Ph). $\delta_C(CDCl_3)$ 68.1 (6-C), 73.3, 73.5 (2 × CH_2Ph), 73.7 (1 of 2, 3, 4 or 5-C), 74.7, 75.7 (2 × CH_2Ph), 76.7, 79.1, 82.0 (3 of 2, 3, 4 and 5-C), 92.1 (1-C), 127.4, 127.6, 127.7, 127.8, 127.9, 128.0, 128.3, 128.4 (20 × Ph), 137.8, 137.9, 138.6, 138.6 (4 × Ph), 177.4 (ester CO), 198.5 (M–CO).

Preparation of 10

A 1:1 mole ratio of **1** to the methyl-α-D-glucopyranoside **9**, following the procedure used to prepare **3**, produced a large number of products. These were separated on preparative silica gel plates as purple oils; only 4 were identified. In order of R_f (2:1 ether–hexane):

Compound 10c. (yield 2%). Found: ES-MS 1616 (MNH_4^+). $\nu(CH_2Cl_2, cm^{-1})$ 2111, 2068, 2046 (M–CO), 1730 (CO ester). $\delta_H(CDCl_3)$ 2.98 (1H, d, J = 5 Hz, 4-OH), 3.36 (3H, s, OMe), 3.64–3.78 (1H, m, 4-H), 3.92 (1H, dt, J = 0.5 and 10 Hz, 5-H), 4.56 (1H, dd, J = 2.5 and 12 Hz, 6-H), 4.69 (1H, dd, J = 3 and 12 Hz, 6′-H), 4.91 (1H, dd, J = 4 and 10 Hz, 2-H), 5.15 (1H, d, J = 4 Hz, 1-H), 5.65 (1H, t, J = 10 Hz, 3-H). $\delta_C(CDCl_3)$ 54.9 (OMe), 63.8 (6-C), 69.8, 70.7, 72.5, 74.4 (2, 3, 4, 5-C), 96.4 (1-C), 178.1, 179.5, 179.8 (3 × ester CO), 198.5 (M–CO).

Compound 10d. (yield 3.5%). Found: ES-MS 1616 (MNH_4^+), 1598 (M^+). $\nu(CH_2Cl_2, cm^{-1})$ 2111, 2069, 2046 (M–CO), 1727 (CO ester). $\delta_H(CDCl_3)$ 2.06 (1H, d, J = 12 Hz, 2-OH), 3.48 (3H, s, OMe), 3.48–3.70 (1H, m, 2-H), 4.02 (1H, dt, J = 9.5 and 2.5 Hz, 5-H), 4.09 (1H, dd, J = 2 and 12 Hz, 6-H), 4.50 (1H, dd, J = 3 and 12 Hz, 6′-H), 4.77 (1H, d, J = 4 Hz, 1-H), 5.41 (1H, t, J = 9.5 Hz, 4-H); 5.56 (1H, t, J = 9.5 Hz, 3-H). $\delta_C(CDCl_3)$ 56.1 (OMe), 63.1 (6-C), 68.5, 69.1, 72.1, 75.3 (2, 3, 4, 5-C), 99.5 (1-C), 176.7, 178.4, 179.1 (3 × ester CO), 199.7 (M–CO).

Compound 10b. (yield 9%). Found: ES-MS 1148 (MNH_4^+). $\nu(CH_2Cl_2, cm^{-1})$ 2110, 2065, 2047 (M–CO), 1735 (CO ester). $\delta_H(CDCl_3)$ 2.18 (1H, d, J = 11 Hz, 2-OH), 2.97 (1H, d, J = 5 Hz, 4-OH), 3.47 (3H, s, OMe), 3.50–3.58 (1H, m, 2-H), 3.59–3.70 (1H, m, 4-H), 3.90 (1H, dt, J = 10 and 2.5 Hz, 5-H), 4.54 (1H, dd, J = 2 and 12 Hz, 6-H), 4.72 (1H, dd, J = 3 and 11 Hz, 6′-H), 4.75 (1H, d, J = 4 Hz, 1-H), 5.29 (1H, t, J = 10 Hz, 3-H). $\delta_C(CDCl_3)$ 55.7 (OMe), 63.9 (6-C), 68.9, 70.6, 71.2, 77.8 (2, 3, 4, 5-C), 99.7 (1-C), 179.7, 180.4 (2 × ester CO), 198.5 (M–CO).

Compound 10a. (yield 2%). $\nu(CH_2Cl_2, cm^{-1})$ 2111, 2074, 2047 (M–CO) 1740 (CO ester). $\delta_H(CDCl_3)$ 2.13 (d, J = 9 Hz, 2-OH), 2.44 (br s, 2 × OH), 3.38–3.60 (1H, m, 2-H), 3.45 (3H, s, OMe), 3.89 (1H, t, J = 9 Hz, 3-H), 3.98 (1H, d, J = 10 Hz, 3-H), 4.41 (1H, dd, J = 2 and 12 Hz, 6-H), 4.56 (1H, dd, J = 4 and 12 Hz, 6′-H), 4.78 (1H, d, J = 4 Hz, 1-H), 5.14 (1H, t, J = 10 Hz, 4-H); $\delta_C(CDCl_3)$ 56.0 (OMe), 63.2 (6-C), 68.5, 71.2, 72.9, 73.5 (2, 3, 4, 5-C), 99.4 (1-C), 178.4, (1 × ester CO), 198.7 (M–CO).

Preparation of 11 and 12

Racemic 2,3,4,6-tetra-O-benzyl-C-trimethylsilylethyn-1-yl-glucopyranoside[41] (0.223 g, 0.35 mmol) was dissolved in benzene (25 ml), and dicobalt octacarbonyl (0.120 g, 0.35 mmol) added. The mixture was stirred for 3 h at ambient temperature then washed with water (2 × 25 ml), dried ($MgSO_4$) and the solvent removed *in vacuo*. The red-brown oil was purified by silica gel column chromatography (3:1 hexane–ether) to obtain **11** and **12** as red-brown oils (53% and 14% respective yields).

Compound 11 (major anomer). (Found: C, 58.88; H, 4.75; FAB, 923 (M^+). $C_{45}H_{44}Co_2O_{12}Si$ requires: C, 58.57; H, 4.81; M 923). ν(hexane, cm^{-1}) 3350 (OH), 2090, 2051, 2025 (M–CO). $\delta_H(CDCl_3)$ 0.26 (9H, s, $SiMe_3$), 3.68 (1H, dd, J = 1,5 and 10.5 Hz, 6-H), 3.76 (1H, d, J = 9 Hz, 1 of 2, 3, 4-H), 3.85 (1H, dd, J = 3 and 11 Hz, 6′-H), 3.94 (1H, d, J = 10 Hz, 1 of 2, 3, 4-H), 4.10–4.17 (2H, 5-H and 1 of 2, 3, 4-H), 4.48 (2H, dd, J = 12 and 39 Hz, 1 × CH_2Ph), 4.60–4.85 (4H, m, 2 × CH_2Ph), 4.98 (1H, d, J = 11 Hz, 1 of a CH_2Ph), 5.28 (1H, d, 11 Hz, 1 of a CH_2Ph); $\delta_C(CDCl_3)$ 0.92, 0.96 (3 × $SiMe_3$), 68.8 (6-C), 72.2 (2, 3, 4 or 5-C), 72.9, 73.3, 74.9, 75.2 (4 × CH_2Ph), 78.4 (2, 3, 4 or 5-C), 79.3 (alkyne), 82.7, 84.6 (2 of 2, 3, 4 and 5-C), 98.6 (1-C), 112.5 (alkyne), 126.4, 127.2, 127.5, 127.7, 127.8, 128.3, 128.4, 128.5 (20 × Ph), 138.1, 138.2, 138.4 (4 × Ph), 200.2 (M–CO).

Compound 12 (minor anomer). FAB, 922 (M^+); $C_{45}H_{44}Co_2O_{12}Si$ requires: M 923. ν(hexane, cm^{-1}) 3350 (OH), 2090, 2051, 2025 (M–CO). $\delta_H(CDCl_3)$ 0.41 (9H, s, $SiMe_3$), 3.39–4.05 (6H, m, 6 of sugar or CH_2Ph), 4.35–5.01 (8H, m, 8 sugar or CH_2Ph), 7.15–7.42 (20H, m, Ph).

Desilylation of 11

Compound **11** (0.13 g, 0.14 mmol), was dissolved in methanol (10 ml) and 0.02 g of K_2CO_3 added. The mixture was stirred for 15 minutes, when a sample for ^{1}H NMR was taken. The

$SiMe_3$ resonance was absent, so the reaction mixture was washed with water and extracted into ether. The solvent was removed *in vacuo* to obtain an orange-red oil (0.096 g, 80%). The oil was dissolved in a small amount of methanol, conc. H_2SO_4 (3 ml) added, and the mixture stirred at ambient temperature. No cluster product was identified.

Preparation of 13

Diphenylphosphinomethane (dppm) (0.054 g, 0.14 mmol) was added to **11** (0.117 g, 0.13 mmol) dissolved in benzene and the mixture heated under reflux for 1 h. The solvent was removed *in vacuo* and the resulting red-brown oil was purified by silica gel column chromatography (2:1 diethyl ether: hexane) to obtain **13** as a red-brown oil (36%), soluble in hexane, benzene and chlorinated solvents. (Found: FAB *m/z* 1251 (M^+). $C_{68}H_{66}Co_2O_{10}P_2Si$ requires: M 1251). $\nu(CH_2Cl_2, cm^{-1})$ 2027, 2000, 1973 (M–CO). $\delta_H(CDCl_3)$: 0.13 (9H, s, $SiMe_3$), 2.69 (1H, d, $J = 5$ Hz, OH), 3.25–4.09 (7H, m, 7 of sugar, CH_2P and CH_2Ph protons), 4.26–5.22 (9H, m, 9 of sugar, CH_2P and CH_2Ph protons), 7.02–7.65 (40H, m, Ph protons). $\delta_C(CDCl_3)$ 1.8 ($3 \times SiMe_3$), 37.1 (CH_2P), 71.4 (5-C), 71.4 (6-C), 71.8, 73.2, 74.0, 74.7 ($4 \times CH_2Ph$), 78.9, 80.9 (2 of 2, 3, 4, 5-C), 82.5, 84.2 ($2 \times$ alkyne), 85.8 (1 of 2, 3, 4, 5-C), 91.5 (1-C), 127.1, 127.3, 127.6, 127.7, 127.8, 127.9, 128.1, 128.3, 128.4, 129.2, 129.3, 129.7, 129.8, 130.5, 130.9, 131.0, 132.7 ($40 \times$ Ph), 138.1, 138.5, 138.6 (Ph), 202.9 (M–CO).

Preparation of tribromomethyl sugars[31]

$BF_3{\cdot}OEt_2$ (6 ml) and tribromoethanol (8.69 g, 30.7 mmol) was added to β-D-glucose pentaacetate (4.0 g, 10.2 mmol), dissolved in dry dichloromethane (20 ml). The mixture was stirred at ambient temperature for 21 h. Pyridine (6 ml) was added cautiously, followed by water (60 ml). The organic layer was separated and the aqueous extracted with dichloromethane (2×30 ml). The organic extracts were combined, washed with water (1×50 ml), 10%HCl (2×50 ml) and water (2×50 ml); dried ($MgSO_4$) and the solvent removed *in vacuo*. The resulting pale yellow syrup was purified by silica gel column chromatography (2:1 ether–hexane) to obtain a white solid (63%) soluble in chlorinated and ether solvents. This is a mixture of anomers with approximate ratio of 1:5 α **14**: β **15** which can be separated by careful chromatography. The mixture was used in most reactions. **14** (Found: C, 31.58; H, 3.35. $C_{16}H_{21}Br_3O_{10}$ requires: C, 31.35; H 3.45%). $\delta_H(CDCl_3)$ 2.03, 2.05, 2.08, 2.10 ($4 \times 3H$, $4 \times$ s, $4 \times$ OAc), 4.12–4.31 (4H, m, 5-H, 6-H_2, 1 of OCH_2CBr_3), 4.43 (1H, d, $J = 12$ Hz, 1 of OCH_2CBr_3), 4.92 (1H, dd, $J = 4$ and 10 Hz, 1 of 2, 3, 4-H), 5.10 (1H, t, $J = 10$ Hz, 1 of 2, 3, 4-H), 5.50 (1H, d, $J = 4$ Hz, 1-H), 5.58 (1H, t, $J = 10$ Hz, 1 of 2, 3, 4-H). **15** (Found: C, 31.63; H, 3.28. $C_{16}H_{21}Br_3O_{10}$ requires: C 31.35; H, 3.45%). $\delta_H(CDCl_3)$ 2.02, 2.03, 2.08, 2.11 ($4 \times 3H$, $4 \times$ s, $4 \times$ OAc), 3.75 (1H, dq, $J = 2$ and 10 Hz, 5-H), 4.17 (1H, dd, $J = 2.5$ and 12 Hz, 6-H), 4.24–4.30 (1H, m, 6′-H), 4.29 (1H, d, $J = 12$ Hz, OCH_2CBr_3), 4.59 (1H, d, $J = 12$ Hz, OCH_2CBr_3), 4.93 (1H, d, $J = 8$ Hz, 1-H), 5.08–5.32 (3H, m, 2, 3, 4-H).

From the same procedure the acetylated maltose precursors **24**, **25** were obtained in 61% yield (anomeric mixture, approximately 1:5 α:β) from peracetylated maltose[42] as white solids. (Found: C, 38.16; H, 4.10. $C_{28}H_{37}Br_3O_{18}{\cdot}0.25C_6H_{14}$ requires: C, 38.39; H, 4.42%).

Compound 25. $\delta_H(CDCl_3)$ 2.00, 2.02, 2.02, 2.04, 2.05, 2.10, 2.16 ($7 \times 3H$, $7 \times$ s, $7 \times$ OAc), 3.73 (1H, dq, $J = 2$ and 10 Hz, 5-H), 3.91–4.14 (3H, m, 3 sugar protons), 4.17–4.33 (2H, m, 3 sugar protons), 4.28 (1H, d, $J = 12$ Hz, 1 of OCH_2), 4.41–4.57 (1H, m, 1 sugar proton), 4.57 (1H, d, $J = 12$ Hz, 1 of OCH_2), 4.74–5.12 (4H, m, 4 sugar protons), 5.25–5.44 (3H, m, 2, 3, 4-H). $\delta_C(CDCl_3)$ 20.6, 20.7, 20.9, 20.9 ($7 \times$ OAc), 61.5, 62.5 (6, 6′-C), 68.0, 68.6, 69.3, 70.0, 71.7, 72.4, 72.5, 74.9 (2, 2′, 3, 3′, 4, 4′, 5, 5′-C), 83.1 (OCH_2), 95.6, 100.5 (1, 1′-C), 169.4, 169.5, 170.0, 170.2, 170.4, 170.5, 170.5 ($7 \times$ OAc).

Compound 24. $\delta_C(CDCl_3)$ 20.6, 20.7, 20.9, 20.9 ($7 \times$ OAc), 61.5, 62.4 (6, 6′-C), 68.6, 68.9, 70.0, 71.1, 72.4, 72.0, 72.7 (2, 2′, 3, 3′, 4, 4′, 5, 5′-C), 82.2 (OCH_2), 95.7, 96.1 (1, 1′-C), 169.4, 169.7, 169.9, 170.5, 170.6 ($7 \times$ OAc).

Preparation of 16 and 17

Dicobalt octacarbonyl (0.295 g, 0.86 mmol) was added to **15** (0.265 g, 0.43 mmol), dissolved in dry THF (25 ml). The mixture was stirred for 1 h at ambient temperature and then for 2 h at 30 °C. This mixture was filtered and the filtrate was treated with 20 ml of 10% HCl. The organic layer was separated and washed with water (2×25 ml), dried ($MgSO_4$) and the solvent removed *in vacuo*. The purple oil obtained was purified by silica gel preparative plate chromatography (3:2 ether–hexane) to obtain **17** (0.140 g, 40%) as a purple oil, soluble in organic solvents except hexane. (Found: C, 37.75; H, 2.46; FAB, 802 (M^+). $C_{25}H_{21}Co_3O_{19}$ requires: C, 37.43; H, 2.64%; M 802). $\nu(CH_2Cl_2, cm^{-1})$ 2104, 2055, 2038 (M–CO), 1758 (acetate CO). $\delta_H(CDCl_3)$: 1.99, 2.01, 2.03, 2.06 ($4 \times 3H$, $4 \times$ s, $4 \times$ OAc), 3.76 (1H, dq, $J = 2$ and 10 Hz, 5-H), 4.17 (1H, dd, $J = 3$ and 12 Hz, 6-H), 4.25 (1H, dd, $J = 5$ and 12 Hz, 6′H), 4.86 (1H, d, $J = 8$ Hz, 1-H), 5.00–5.30 (4H, 2, 3, 4-H and 1 of OCH_2), 5.45 (1H, d, $J = 14$ Hz, 1 of CH_2. $\delta_C(CDCl_3)$ 20.6, 20.7 ($4 \times$ acetate CH_3), 62.0 (6-C), 68.5, 71.5, 72.0, 73.3 (2, 3, 4, 5-C), 83.0 (OCH_2), 99.7 (1-C), 169.1, 169.4, 170.4, 170.7 ($4 \times$ acetate CO), 199.6 (M–CO).

Compound **16** was obtained from the same reaction as above in 9% yield from the alpha anomer **14** contained in the starting sugar. Crystallisation from ether–hexane or benzene–hexane gave purple needles. (Found: C, 37.54; H, 2.44; FAB, 802 (M^+). $C_{25}H_{21}Co_3O_{19}$ requires: C, 37.43; H, 2.64%; M 802). $\nu(CH_2Cl_2, cm^{-1})$ 2104, 2055, 2039 (M–CO), 1753 (acetate CO). $\delta_H(CDCl_3)$ 1.98, 2.00, 2.02, 2.05 ($4 \times 3H$, $4 \times$ s, $4 \times$ OAc), 4.10 (1H, dq, $J = 2$ and 10 Hz, 5-H), 4.15 (1H, dd, $J = 2.5$ and 10 Hz, 6-H), 4.24 (1H, dd, $J = 5$ and 12 Hz, 6′-H), 4.93–5.11 (3H, 2 of 2-H, 3-H, 4-H and 1 of OCH_2), 5.45 (3H, m, 1-C, 1 of 2, 3, 4-H and 1 of OCH_2). $\delta_C(CDCl_3)$ 20.5, 20.7 ($4 \times$ acetate CH_3), 62.2 (6-C), 68.2 (5-C), 68.6, 70.0, 70.7 (2, 3, 4-C), 83.0 (OCH_2), 95.9 (1-C), 169.7, 169.7, 170.3, 170.6 ($4 \times$ acetate CO), 199.5 (M–CO).

Deprotection of 8, 14, 15, 24 and 25

A mixture of **14** and **15** (3.39 g, 5.5 mmol) was dissolved in methanol (50 ml) and Amberlite IRA400(OH) resin (3.6 g) added. The mixture was left for 5 days, filtered and the solvent removed *in vacuo* to give a mixture of **22** and **23** as a clear syrup (81%). (Found: C, 21.84; H, 3.05. $C_8H_{13}Br_3O_5$ requires: C, 22.40; H 3.06%). $\delta_H(d_6\text{-acetone})$ 2.90 (4H, br s, $4 \times$ OH), 3.30–3.50 (4H, m, 4 of 1, 2, 3, 4, 5-H), 3.68 (1H, dd, $J = 5$ and 12 Hz, 6-H), 3.90 (1H, dd, $J = 2$ and 12 Hz, 6′-H), 4.42 (1H, d, $J = 12$ Hz, 1 of OCH_2CBr_3), 4.64 (1H, d, $J = 12$ Hz, 1 of OCH_2CBr_3) 4.68–4.95 (1H, m, 1 of 1, 2, 3, 4, 5-H).

The maltose–CBr_3 analogues **26**, **27** were prepared by deprotection of the anomeric mixture of **24**, **25** by the same procedure as above. The crude reaction mixture was purified by column chromatography (1:1 MeOH–CH_2Cl_2); the solvent was removed and the residue dissolved in acetone and filtered. Removal of the acetone gave **26**, **27** in 61% yield as a mixture of anomers, (approximately 1:5 α:β) as white syrups. (Found: C, 35.61; H, 5.65; FAB, 630 (MNa^+). $C_{28}H_{37}Br_3O_{18}{\cdot}3C_3H_6O$ requires: C, 35.36; H, 5.29; M, 607). Individual spectroscopic data:

Compound 26. $\delta_C(CDCl_3)$ 20.6, 20.7, 20.9, 20.9 ($7 \times$ OAc), 61.5, 62.4 (6, 6′-C), 68.6, 68.9, 70.0, 71.1, 72.4, 72.0, 72.7 (2, 2′, 3, 3′, 4, 4′, 5, 5′-C), 82.2 (OCH_2), 95.7, 96.1 (1, 1′-C), 169.4, 169.7, 169.9, 170.5, 170.6 ($7 \times$ OAc).

Compound 27. $\delta_H(CDCl_3)$ 2.00, 2.02, 2.02, 2.04, 2.05, 2.10, 2.16 (7 × 3H, 7 × s, 7 × OAc), 3.73 (1H, dq, J = 2 and 10 Hz, 5-H), 3.92–4.09 (3H, m, 4, 5′, 6-H), 4.21–4.28 (2H, m, 6, 6′-H), 4.28 (1H, d, J = 12 Hz, 1 of OCH_2), 4.49–4.54 (1H, m, 6′-H), 4.57 (1H, d, J = 12 Hz, 1 of OCH_2), 4.85 (1H, dd, J = 4 and 10 Hz, 2′-H), 4.94 (1H, d, J = 8 Hz, 1-H), 4.99 (1H, dd, J = 8 and 9 Hz, 2-H), 5.06 (1H, t, J = 10 Hz, 4′-H), 5.30 (1H, t, J = 9 Hz, 3-H), 5.36 (1H, t, J = 10 Hz, 3′-H), 5.43 (1H, d, J = 4 Hz, 1′-H). $\delta_C(CDCl_3)$ 20.6, 20.7, 20.9, 20.9 (7 × OAc), 61.5 (6-C), 62.5 (6′-C), 68.0 (4′-C), 68.6 (5′-C), 69.3 (3′-C), 70.0 (2-C), 71.7 (2-C), 72.4 (5-C), 72.5 (4-C), 74.9 (3-C), 83.1 (OCH_2), 95.6 (1′-C), 100.5 (1-C), 169.4, 169.5, 170.0, 170.2, 170.4, 170.5, 170.5 (7 × OAc).

Deprotection of 8. Debenzylation was attempted both *via* hydrogenation (H_2, Pd/C, ethanol, 20 °C) and thiolysis (ethanethiol, boron trifluoride etherate, dichloromethane, 20 °C). Both reactions returned **8**.

Preparation of 19 and 20

Dicobalt octacarbonyl (0.225 g, 0.66 mmol) was added to the anomeric mixture of **22**, **23** (0.165 g, 0.38 mmol), dissolved in dry THF (15 ml). The mixture was stirred for 1 h at ambient temperature and then for 2 h at 30 °C. This mixture was filtered and the filtrate was treated with 20 ml of 10% HCl. The organic layer was separated and washed with water (2 × 25 ml), dried ($MgSO_4$) and the solvent removed *in vacuo*. The purple oil obtained was purified by silica gel preparative plate chromatography (1 : 2 : 4 methanol–hexane–CH_2Cl_2) to obtain **20** only (0.076 g, 31%) as a purple oil. (Found: C, 31.16; H, 2.01; FAB, 550 ($M^+ - 3CO$). $C_{17}H_{13}Co_3O_{15}\cdot 0.25CH_2Cl_2$ requires: C, 31.07; H, 2.09%, M 634). $\nu(CH_2Cl_2, cm^{-1})$ 2104, 2055, 2038 (M–CO). $\delta_H(d_6$-acetone) 2.93 (4H, br s, 4 × OH), 3.20–3.50 (4H, m, 2, 3, 4, 5-H), 3.70 (1H, dd, J = 5 and 11 Hz, 6-H), 3.85 (1H, dd, J = 2 and 11 Hz, 6′-H), 4.66 (1H, d, J = 8 Hz, 1-H), 5.27 (1H, d, J = 15 Hz, 1 of OCH_2), 5.57 (1H, d, J = 15 Hz, 1 of OCH_2). $\delta_C(d_6$-acetone) 62.6 (6-C), 70.6, 75.7, 76.3, 76.4 (2, 3, 4, 5-C), 83.8 (OCH_2), 102.4 (1-C), 199.7 (M–CO). Compound **20** was also prepared by deprotection of **17**. Compound **17** (0.253 g, 0.32 mmol) was dissolved in methanol (50 ml) and Amberlite IRA400(OH) resin (0.50 g) added. The mixture was left for 5 days, then filtered and the solvent removed *in vacuo* to give a purple syrup, which was purified by silica gel plate chromatography to give **20** (0.003 g, 1.5%), along with other fractions which were identified as partially deacetylated clusters.

Compound **19** was unable to be prepared as the product appeared to be unstable in solution. Both preparation methods were attempted—the deprotection of **16** with ion exchange resin in methanol (as above) and the addition of dicobalt octacarbonyl to the deprotected –CBr_3 sugar in THF as for **16** and **17**.

Preparation of 28 and 29

Dicobalt octacarbonyl (0.655 g, 1.90 mmol) was added to **24**, **25** (1.08 g, 1.20 mmol), dissolved in dry THF (50 ml). The mixture was stirred for 1 h at ambient temperature and then for 2 h at 30 °C. This mixture was filtered and the filtrate was treated with 20 ml of 10% HCl. The organic layer was separated and washed with water (2 × 25 ml), dried ($MgSO_4$) and the solvent removed *in vacuo*. The purple oil obtained was purified by silica gel preparative plate chromatography (1 : 1 hexane–ether) to obtain **28** and **29** as purple oils in 4% and 12% yield respectively.

Compound 28. (Found: C, 42.22; H, 3.89; FAB, 1006 ($M^+ - 3CO$). $C_{37}H_{37}Co_3O_{27}\cdot C_4H_{10}O$ requires: C, 42.28; H, 4.07%; M 1090). $\nu(CH_2Cl_2, cm^{-1})$ 2105, 2057, 2040 (M–CO), 1750 (CO acetate). $\delta_H(CDCl_3)$ 1.93, 2.00, 2.01, 2.03, 2.07, 2.10, 2.10 (7 × 3H, 7 × s, 7 × OAc), 3.64 (1H, m, 1 sugar proton), 3.86–4.16 (4H, m, 4 sugar protons), 4.19–4.35 (2H, m, 2 sugar protons), 4.45 (1H, dd, J = 11 and 2 Hz, 1 of 6, 6′-H_2), 4.80–4.91 (1H, m, 1 sugar proton), 4.98–5.20 (3H, m, 3 sugar protons), 5.25–5.50 (3H, m, 3 sugar protons), 5.55 (1H, d, J = 4 Hz, 1 of 1, 1′-H). $\delta_C(CDCl_3)$ 20.4, 20.5, 20.6, 20.6, 20.7, 20.9 (7 × acetate CH_3), 63.0, 65.9 (6, 6′-C), 68.1, 68.7, 69.5, 69.9, 71.1, 72.6, 72.7 (2, 2′, 3, 3′, 4, 4′, 5, 5′-C), 83.1 (OCH_2), 95.4, 95.8 (1, 1′-C), 169.5, 169.5, 170.0, 170.4, 170.5, 170.6, 170.8 (7 × acetate C=O), 199.6 (M–CO).

Compound 29. (Found: C, 41.37; H, 3.64; FAB, 1006 ($M^+ - 3CO$). $C_{37}H_{37}Co_3O_{27}\cdot 0.5\ C_4H_{10}O$ requires: C, 41.54, H, 3.75%; M 1090). $\nu(CH_2Cl_2, cm^{-1})$ 2105, 2057, 2040 (M–CO), 1750 (CO acetate). $\delta_H(CDCl_3)$ 1.95, 1.97, 1.98, 1.99, 2.02, 2.04, 2.09 (7 × 3H, 7 × s, 7 × OAc), 3.73 (1H, m, 5-H), 3.94–4.06 (4H, m, 2 × 6, 6′-H_2, and 2 sugar protons), 4.22–4.27 (2H, m, 1 of 6, 6′-H_2 and 1 sugar proton), 4.49 (1H, dd, J = 11 and 2 Hz, 1 of 6, 6′-H_2), 4.82–4.89 (2H, m, 1 of 1, 1′-H and 1 sugar proton), 4.99–5.07 (1H, m, 1 sugar proton), 5.14 (1H, d, J = 14 Hz, 1 of OCH_2), 5.24–5.46 (4H, m, 1 of OCH_2 and 3 sugar protons). $\delta_C(CDCl_3)$ 20.4, 20.5, 20.6, 20.6, 20.7, 20.9 (7 × acetate CH_3), 61.5, 62.7 (6, 6′-C), 68.1, 68.5, 69.4, 70.1, 72.3, 72.3, 72.8, 75.8 (2, 2′, 3, 3′, 4, 4′, 5, 5′-C), 83.1 (OCH_2), 95.7, 99.2 (1, 1′-C), 169.5, 169.5, 170.0, 170.4, 170.5, 170.6, 170.8 (7 × acetate CO), 199.6 (M–CO).

Preparation of 31

Dicobalt octacarbonyl (0.435 g, 1.27 mmol) was added to the anomeric mixture **26**, **27** (0.40 g, 0.66 mmol), dissolved in dry THF (40 ml). The mixture was stirred for 1 h at ambient temperature and then for 2 h at 30 °C. This mixture was filtered and the filtrate was treated with 20 ml of 10% HCl. The organic layer was separated and washed with water (2 × 25 ml), dried ($MgSO_4$) and the solvent removed *in vacuo*. The purple oil obtained was purified by silica gel preparative plate chromatography (1 : 1 : 4 hexane–methanol–CH_2Cl_2) to obtain **31** in 7% yield as a purple solid. (Found: C, 35.02; H, 4.53, FAB, 819 (MNa^+). $C_{23}H_{23}Co_3O_{20}\cdot 4CH_3OH$ requires: C, 35.08; H, 4.25%, M 796). $\nu(CH_2Cl_2, cm^{-1})$ 2106, 2056 (M–CO). $\delta_H(d_6$-acetone) 2.98 (br d, 7 × OH), 3.25–3.47 (2H, sugar protons), 3.48–3.92 (9H, m, sugar protons), 4.11–4.17 (1H, m, sugar proton), 5.11 (1H, d, J = 4 Hz, 1 of 1, 1′-H), 5.24 (1H, d, J = 5 Hz, 1 of OCH_2), 5.74 (1H, d, J = 4 Hz, 1 of 1, 1′-H), 6.03 (1H, d, J = 5 Hz, 1 of OCH_2). $\delta_C(d_6$-acetone) 62.4, 63.2 (6, 6′-C), 72.1 75.0, 75.1, 75.3, 75.3, 79.0, 80.1 (2, 2′, 3, 3′, 4, 4′, 5, 5′-C), 84.8 (OCH_2), 100.1, 103.6 (1, 1′-C), 201.6 (M–CO). No α anomer **30** was found from this reaction.

Preparation of 18 and 21

Dppm (0.120 g, 0.31 mmol) was added to **17** (0.180 g, 0.29 mmol), dissolved in benzene (10 ml). The mixture was heated under reflux for 30 min. The solvent was removed *in vacuo* and the brown oil purified by silica gel preparative plate chromatography (6 : 1 ethyl acetate–hexane); yield, 57%. A sample of **18** for microanalysis was obtained from CH_2Cl_2 as a brown oil. (Found: C, 48.98; H, 4.25; FAB, $M^+ - 2CO$ 1074. $C_{48}H_{43}Co_3O_{17}P_2\cdot 0.75CH_2Cl_2$ requires: C, 49.09; H, 3.76; M 1130). $\nu(CH_2Cl_2, cm^{-1})$ 2059, 2006, 1984 (M–CO). $\delta_H(CDCl_3)$ 1.90, 2.03, 2.07, 2.10 (4 × 3H, 4 × s, 4 × OAc), 3.49 (1H, m, 1 of CH_2P), 3.67 (1H, m, 5-H), 4.03–4.28 (3H, m, 6-H_2 and 1 of CH_2P), 4.77 (1H, d, J = 8 Hz, 1-H), 4.94 (1H, d, J = 14 Hz, 1 of OCH_2), 5.04–5.26 (3H, m, 2, 3, 4-H), 5.45 (1H, d, J = 14 Hz, 1 of OCH_2), 7.25–7.45 (20H, m, Ph). $\delta_C(CDCl_3)$ 47.3 (t, $J_{(C\text{-}P)}$ = 22 Hz, CH_2P), 62.1 (6-C), 68.7 (2, 3 or 4-C), 71.7 (5-C), 71.7, 73.7 (2 of 2, 3 or 4-C), 85.4 (OCH_2), 99.8 (1-C), 128.6, 130.1, 130.2 (Ph), 131.2, 131.4, 131.8, 132.3 (4 × m, quaternary Ph), 204.8 (M–CO). $\delta_P(CDCl_3)$ 36.6.

Table 2 Crystal data and structure refinement for **16**

Empirical formula	$C_{25}H_{21}Co_3O_{19}$
Formula weight	802.21
Crystal system	Triclinic
Space group	*P*1
μ/mm^{-1}	1.600
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0734$, $wR2 = 0.1807$
R indices (all data)	$R1 = 0.0943$, $wR2 = 0.1896$
Absolute structure parameter	0.07(3)
a/Å	7.6191(15)
b/Å	12.213(2)
c/Å	18.533(4)
α/°	70.909(2)
β/°	85.774(2)
γ/°	83.702(2)
V/Å^3	1618.5(6)
T/K	158(2)
Z	2
Reflections collected	6703
Independent reflections	6324 [R(int) = 0.0184]

Dppm (0.039 g, 0.10 mmol) was added to **20** (0.053 g, 0.29 mmol), dissolved in dichloromethane (10 ml). The mixture was heated under reflux for 1.5 h. The solvent was removed *in vacuo* and the brown oil purified by silica gel preparative plate chromatography (6:1 ethylacetate–hexane); yield, 76%. A sample of **21** for microanalysis was obtained from acetone as a brown powder. (Found: C, 50.58; H, 4.13; ES-MS, MNa^+ 984 [dimer M_2Na^+ 1947, sequence $(M - 2CO)^+$, $(MNa - nCO)^+$ n = 1–6 were the other major peaks]. $C_{40}H_{35}Co_3O_{13}P_2{\cdot}C_3H_6O$ requires: C, 50.61; H, 4.05; M 962). $\nu(CH_2Cl_2, cm^{-1})$ 2058, 2004, 1962 (M–CO). δ_H(d_6-acetone) 3.08 (br s, OHs), 3.30–3.37 (2H, m, 2 of 2, 3, 4, and 5-H), 3.40–3.53 (2H, m, 2 of 2, 3, 4, and 5-H), 3.37–3.82 (2H, m, 6-H_2), 3.95 (1H, dt, J = 3 and 14 Hz, 1 of CH_2P), 4.54 (1H, d, J = 8 Hz, 1-H), 4.89 (1H, dt J = 3 and 14 Hz, 1 of CH_2P), 5.04 (1H, d, J = 14 Hz, 1 of OCH_2), 5.71 (1H, d, J = 14 Hz, 1 of OCH_2), 7.28–7.70 (20H, m, Ph). $\delta_C(CDCl_3)$ 46.8 (t, $J_{(C\text{-}P)}$ = 22 Hz, CH_2P), 63.1 (6-C), 72.0, 75.3, 77.2, 78.1 (2, 3, 4, 5-C), 86.1 (OCH_2), 103.4 (1-C), 129.3, 129.4 (Ph), 131.1, 132.1, 132.3, 133.1 (quaternary Ph), 206.7 (M–CO). $\delta_P(CDCl_3)$ 37.5.

X-Ray data collection, reduction and structure solution for 16

Crystal data for **16** are given in Table 2. The compound was recrystallised from ether–hexane and a dark red plate was used for data collection. Data were collected from the weakly diffracting crystals on a Bruker SMART CCD diffractometer, processed using SMART[43] and empirical absorption corrections applied using SADABS.[44]

The structure was solved using SHELXS-96[45] and refined by full-matrix least squares on F^2 using SHELXL-97.[45] Due to limitations in the data only the Co and C atoms of the cluster core, the carbonyl O atoms and the C and O atoms of the acetyl substituents on the sugar residue were assigned anisotropic temperature factors, with the remaining atoms refined isotropically. Hydrogen atoms were included in calculated positions. The final difference Fourier map had maxima at 2.62, −0.72 e Å^3 but no physical significance could be attached to the remaining high peaks.

CCDC reference number 186/1702.

See http://www.rsc.org/suppdata/dt/1999/4165/ for crystallographic files in .cif format.

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