1.622 g cm^{-3}, $F(000) = 2636$, $\mu = 5.064$ mm^{-1}. Data collected as described for **2** with an irregular block ($0.35 \times 0.19 \times 0.08$ mm). 35 819 measured reflections, 12 913 unique; a multiscan absorption correction was performed (SADABS program), with min./max. transm. factors 0.421/0.727. Structure solution and refinement as described for **2**. Final agreement factors were $R1 = 0.0520$ (8227 observed reflections) and $wR2 = 0.1088$. Data/restrains/parameters 12 913/7/631; GoF = 0.949. Largest peak and 2.358 and -1.238 e Å^{-3}.

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Bis(1,2,3,4-η^4-anthracene)cobaltate(1−)[**]

William W. Brennessel, Victor G. Young, Jr., and John E. Ellis[*]

Dedicated to Professor Klaus Jonas

Polycyclic aromatic hydrocarbon (PAH or polyarene)[1] anion mediated reductions of transition metal halides and related substances provide convenient and sometimes unique routes to a variety of polyarene metal complexes and derived species.[2] Since the polyarene ligands may be labile and easily displaced by a variety of small molecules, polyarene metal complexes are potential sources of highly unsaturated metallic units in chemical synthesis.[3] Homoleptic systems are of particular interest since these species may function as "naked" metal atom reagents and are therefore valuable precursors for the general exploration of low-valent transition metal chemistry.[4] Except for the first reported homoleptic polyarene transition metal complex $[Ru(C_{10}H_8)_2]^{2+}$ ($C_{10}H_8$ = naphthalene),[5] all previous examples contained only early (Groups 4–6) transition metals.[4] However, the existence of this cationic ruthenium species suggested that related neutral and anionic polyarene complexes of later transition metals should also be accessible. We now report on the first anion of this type and the initial homoleptic polyarene complex of cobalt, bis(η^4-anthracene)cobaltate(1−) (**1**). The only previously known homoleptic anthracene transition metal complex is bis(anthracene)chromium(0), which was prepared by the reaction of chromium vapor and anthracene in a metal atom reactor.[4c]

Reduction of cobalt(II) bromide by three equivalents of potassium anthracene in tetrahydrofuran (THF) at −55 to −65 °C provided a dark red solution, from which deep red, nearly black, microcrystals of **1** as [K([2.2.2]cryptand)]$^+$ or [K([18]crown-6)(THF)$_2$]$^+$ salts were isolated in 82–87% yields (see Experimental Section for details; [Eq. (1)]). Corresponding reductions conducted with alkali metal naphthalenes provided much less thermally stable solutions of a presumably analogous bis(naphthalene)cobaltate(1−).

$$CoBr_2 + 3\,KC_{14}H_{10} \xrightarrow[-60\,^{\circ}C]{THF} \xrightarrow[-2\,KBr]{L} [KL(THF)_x][Co(C_{14}H_{10})_2]\cdot y\,THF + C_{14}H_{10} \qquad (1)$$

1a: L = [2.2.2]cryptand, $x = 0$; $y = 1/2$; 82%
1b: L = [18]crown-6, $x = 2$; $y = 0$; 87%

Although this substance is highly reactive towards a number of substrates, for example, it readily reacts with carbon monoxide at normal pressures and −60 °C° to produce $[Co(CO)_4]^-$, all attempts to isolate this interesting species have so far failed.[6] Interestingly, the reduction of cobaltocene by three equivalents of potassium naphthalene provided a similarly labile source of Co^{I-}, which also defied isolation and characterization.[7]

^{1}H and ^{13}C NMR spectra of **1** were independent of the cation and established that its stoichiometry in solution is identical to that observed in the solid state (vide infra). ^{1}H, ^{13}C correlated NMR spectra of **1** exhibited two equally intense quaternary ^{13}C signals at $\delta = 134.1$ and 146.0, which are indicative of two equivalent η^4-anthracenes bound through one peripheral ring each to cobalt.[8] ^{1}H NMR spectra of **1** are also consistent with the presence of two identical anthracene groups bound in the same fashion to cobalt (see Experimental Section). These resonance positions and patterns are consistent with those previously observed for other η^4-anthracene transition metal complexes,[9] and provide compelling evidence for the presence of discrete bis(1,2,3,4-η^4-anthracene)cobaltate(1−) units in solution.

Single-crystal X-ray studies on **1a** and **1b** were carried out[10] and confirmed the formulation of **1** based on NMR data and elemental analyses. The cations in these salts are unexceptional and well separated from anions in the crystalline lattices. Since the structures of **1** in both salts show nearly identical features, but the cobaltate in **1a** suffered from slight disorder in one anthracene ring, only **1b** will be described herein. The coordination environment about the cobalt is distorted tetrahedral, as defined by midpoints of the outer C–C bonds of the coordinated diene units (Figure 1), and resembles that previously observed in [Co(η^4-1,4-di-*tert*-butylbuta-1,3-diene)$_2$]$^-$ (**2**).[11] Analogous Co–C and C–C distances of the cobalt-diene units in **1b** and **2** are also very similar, suggesting that the Co–C interactions in both species are closely related. For example, the respective C–C distances of the coordinated diene units in **1b** and **2** show no significant variation.[12] This situation is typical of later transition metal conjugated diene complexes, such as the d^8 Fe^0 complex, η^4-butadiene iron tricarbonyl,[13] in which metal π donation (backbonding) is not so important as it is in related early

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[**] Highly Reduced Organometallics, part 56. This work was supported by the U.S. National Science Foundation and the donors of the Petroleum Research Fund, Administered by the American Chemical Society. We thank Ms. Christine Lundby for expert assistance in the preparation of this manuscript. Part 55: J. M. Allen, W. W. Brennessel, C. E. Buss, J. E. Ellis, M. E. Minyaev, M. Pink, G. F. Warnock, M. L. Winzenburg, V. G. Young, Jr., *Inorg. Chem.* **2001**, *40*, 5279.

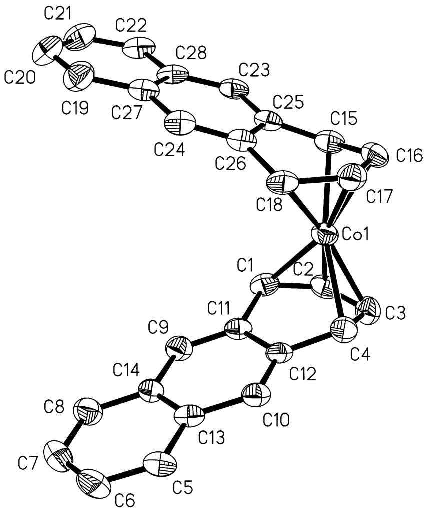
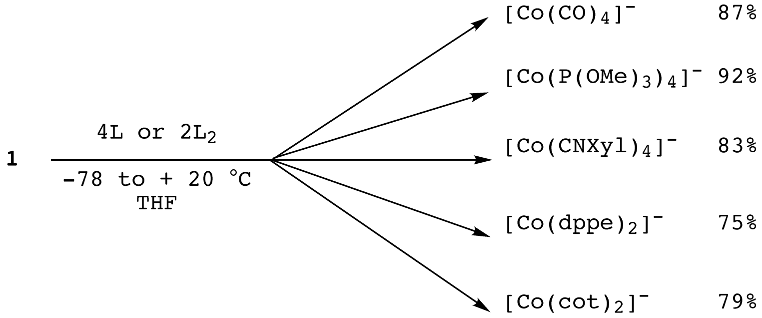


Figure 1. Molecular structure of the anion in **1b**. Thermal ellipsoids are set at the 50% probability level, with hydrogen atoms omitted for clarity. Important dimensions [Å and °]: Co1-C1 2.125(4), Co1-C2 1.978(4), Co1-C3 2.011(4), Co1-C4 2.132(4), Co1-C15 2.154(4), Co1-C16 2.010(4), Co1-C17 1.974(4), Co1-C18 2.112(4), C1-C2 1.406(5), C2-C3 1.424(5), C3-C4 1.422(5), C15-C16 1.413(5), C16-C17 1.416(5), C17-C18 1.422(5), Co-centroid(η^4) 1.64; centroid(η^4)-Co-centroid(η^4) 172.5.



Scheme 1. Reactions of **1** with L = CO (1 atm P), P(OMe)$_3$, CNXyl, and L$_2$ = dppe, cot, with isolated percentage yields of products.

transition metal dienes.[14] Another measure of metal π donation in cyclic η^4-diene complexes is the magnitude of the dihedral (or fold) angle, defined by the intersection of the planes of the η^4-diene and the uncoordinated group attached to the outer diene carbon atoms,[15] that is, the exo-naphthalene unit in the case of η^4-anthracene complexes. In **1b** this angle is 27.8° and similar to the one of 26.2° found in the formally Ni^0 complex [Ni(η^4-C$_{14}$H$_{10}$)(η^2-Et$_2$PCH$_2$CH$_2$-PEt$_2$)].[16] In contrast, early transition metal η^4-anthracene complexes have significantly larger dihedral angles,[17] which is indicative of a greater degree of metal to anthracene back-bonding than that present in the cobalt or nickel species. For these reasons, as in the case of **2**,[11] **1** appears to be best formulated as a substituted conjugated diene complex of d^{10} Co(I −).

Although certain η^4-anthracene complexes, notably [Ta(η^4-C$_{14}$H$_{10}$)(dmpe)$_2$Cl] (dmpe = 1,2-bis(dimethylphosphanyl)-ethane),[9c] and [Co(η^4-C$_{14}$H$_{10}$)(PMe$_3$)$_2$(SnPh$_3$)][18] are inert towards carbon monoxide under normal conditions, solutions of **1** in THF readily absorb CO at atmospheric pressure and temperatures ≥ -30 °C to give high yields (87%) of [Co(CO)$_4$]$^-$. To further establish the utility of **1** as a precursor to low-valent cobalt complexes, it was treated with a variety of ligands, including 2,6-dimethylphenyl isocyanide (CNXyl), trimethylphosphite (P(OMe)$_3$), 1,2-bis(diphenylphosphanyl)-ethane (dppe), and 1,3,5,7-cyclooctatetraene (cot) as shown in Scheme 1. All reactions proceeded completely within minutes at temperatures ≥ -30 °C to provide the respective [CoL$_4$]$^-$ (L = CNXyl, P(OMe)$_3$) or [CoL$_2$]$^-$ (L = dppe or cot) in 75–92% yields. While [Co(CNXyl)$_4$]$^-$ [7] and [Co(P(OMe)$_3$)$_4$]$^-$ [19] have been fully characterized previously, [Co(dppe)$_2$]$^-$ (**3**) has been only identified in solution by cyclic voltammetry,[20] and [Co(cot)$_2$]$^-$, **4**, is a new substance and the first homoleptic cot complex of cobalt. Single-crystal X-ray studies of **3** and **4** were carried out to confirm their natures. Cations were well separated from the anions in these salts and appeared to have no significant influence on the structures of **3** and **4**.[21, 10b]

Deep red **3** is the first structurally characterized homoleptic triorganophosphanecobaltate(1 −),[22] and has a slightly distorted tetrahedral geometry about the cobalt center (Figure 2) similar to that recently reported for [Co(η^2-tmbp)$_2$]$^-$ (tmbp = 4,4′,5,5′-tetramethyl-2,2′-biphosphinine).[23] For example, **3** has a twist angle, θ, between planes, defined by the two CoP$_2$ units, of 85°, where $\theta = 90°$ would correspond to tetrahedral coordination, while those observed for two independent anions in the biphosphinine complex are $\theta = 78$ and 83°. Also, average Co–P distances in these two cobaltates, both of which are best formulated as a d^{10} Co^{I-} species, are experimentally indistinguishable, that is, 2.109(6) Å for **3** and 2.100(11) Å for the biphosphinine complex.

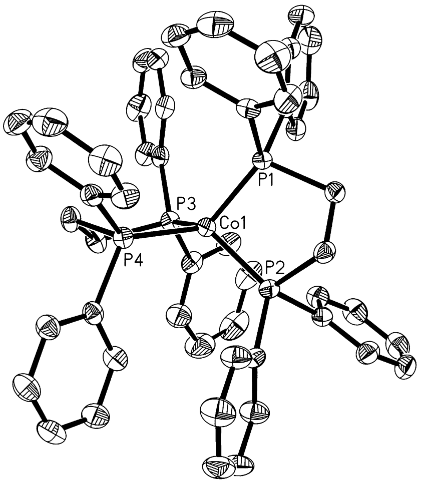


Figure 2. Molecular structure of **3**, cation not shown. Thermal ellipsoids are set at the 50% probability level, with hydrogen atoms omitted for clarity. Important dimensions [Å and °]: Co1-P1 2.1124(5), Co1-P2 2.1156(6), Co1-P3 2.1045(5), Co1-P4 2.1037(5), P-C$_{av}$ for phenyl carbon atoms 1.86(1), P-C$_{av}$ for ethane carbon atoms 1.873(6); P1-Co1-P2 89.14(2), P3-Co1-P4 89.86(2).

Deep green **4** is noteworthy in that it represents only the third well-characterized anionic homoleptic cot transition metal complex,[24] which is surprising in view of the good acceptor ability of this ligand. To our knowledge, the only other structurally authenticated homoleptic cot complexes of the later (Groups 7–11) transition metals are [Fe(cot)$_2$],[25] [Ru(cot)$_2$],[26] and [Ag(cot)]$^+$.[27] Although attempts to prepare neutral homoleptic cot complexes of cobalt (by metal vapor syntheses) were unsuccessful,[28] two nickel species are well characterized, [{Ni(cot)}$_2$] and [Ni(cot)$_2$].[29a] Related phenylcyclooctatetraene (Phcot) nickel complexes have been structurally characterized, that is, [{Ni(Phcot)}$_2$] and [Ni(Phcot)$_2$], where the latter contains the tetrahedral coordination about nickel expected of d^{10} Ni^0.[29b] Solutions of **4** in tetrahydrofuran and acetonitrile had virtually identical ^{1}H and ^{13}C{^{1}H} NMR solution spectra and showed sharp singlets at $\delta_H = 5.18$ and $\delta_C = 91.0$, respectively, with $J_{C,H} = 149.7$ Hz. These spectra were temperature independent (down to -80 °C in [D$_8$]THF) and indicate that **4** is highly fluxional, as are all other known η^4-cot complexes.[30] The δ_C and $J_{C,H}$ values for **4** are intermediate between those of free cot, $\delta_C = 132.7$ and $J_{C,H} = 154.4$ Hz, and cot^{2-} (as K$^+$ salt), $\delta_C = 89.9$ and $J_{C,H} = 143.3$ Hz,[31] and suggest that the coordinated cot groups in **4** remove substantial electron density from cobalt.

An X-ray structural analysis also indicates that the η^4-cot groups in **4** function as substantially better acceptor ligands than the η^4-diene units in **1b** and **2** (Figure 3). For example, the distinctive long–short–long pattern in the C−C lengths of the coordinated diene unit in **4** is absent in **1b** and **2**, and suggests that there is a significant metallacyclopentene or $\sigma^2\pi$ contribution to the cobalt–cot bonding.[13] The relatively large dihedral angle of 38.6°[15] of the cot ligands in **4**, compared to the corresponding 27.8° angle present in **1b**, is also in accord with this view. However, the most persuasive evidence that the cot groups in **4** are superb acceptors is the surprising *planar* geometry observed for cobalt, which is consistent with the presence of d^8 Co^I, in contrast to the corresponding tetrahedral geometry of cobalt in **1b**, indicative of d^{10} Co^{I-}.[32] The interaction of **1** with two equivalents of cot to give **4** may be regarded as a reaction in which each cot ligand functions formally as a one-electron oxidizing agent. However, the highly nonplanar η^4-cot ligand in **4** is substantially different in character from the recently reported planar η^2-cot ligands in formal d^{10} Ni^0 complexes, for example, [Ni(η^2-cot)(η^2-iPr$_2$PCH$_2$CH$_2$PiPr$_2$)], which are formulated to contain semiaromatic planar C$_8$H$_8$ radical anions.[31] Both this latter report and our results demonstrate that coordinated cot, *regardless of its geometry or hapticity*, is able to function as an outstanding acceptor in later transition metal chemistry.

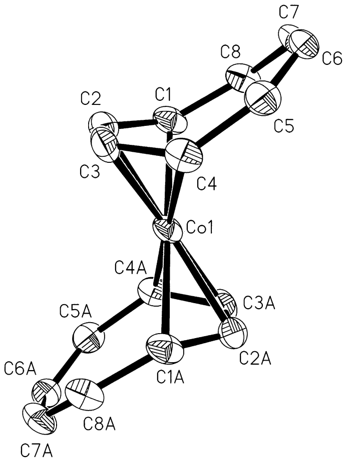


Figure 3. Molecular structure of **4**, cation not shown. Thermal ellipsoids are set at the 50% probability level, with hydrogen atoms omitted for clarity. Important dimensions [Å and °]: Co1-C1 2.152(3), Co1-C2 1.991(3), Co1-C3 1.989(3), Co1-C4 2.199(3), C1-C2 1.429(4), C2-C3 1.398(4), C3-C4 1.437(4), C4-C5 1.454(4), C5-C6 1.364(4), C6-C7 1.405(4), C7-C8 1.383(4), C1-C8 1.447(4), Co1-centroid(η^4) 1.61, centroid(η^4)-Co-centroid(η^4) 180.

In summary, we have established the existence of the first homoleptic polyarene complex of cobalt, bis(1,2,3,4-η^4-anthracene)cobaltate(1−), and have shown that it functions as an effective and facile source of "naked" atomic cobalt anion, Co^{I-}, in several reactions. In this regard, **1** is related to [Co(C$_2$H$_4$)$_4$]$^-$ and [Co(1,5-cyclooctadiene)$_2$]$^-$, prepared and studied by Klaus Jonas more than 20 years ago.[33] Extensions of this investigation to other polyarenes and later transition metals are currently in progress in this laboratory.

Experimental Section

1a: A solution of anhydrous CoBr$_2$ (0.528 g, 2.42 mmol) in THF (100 mL, -78 °C) was added by cannula to a magnetically stirred solution of KC$_{14}$H$_{10}$ (7.24 mmol) in THF (100 mL, -78 °C), containing a slight excess of anthracene (1.2 mmol). The reaction mixture turned deep red during the transfer and was slowly warmed to 20 °C over a 12 h period, and then filtered into a vessel containing a solution of [2.2.2]cryptand (1.00 g, 2.66 mmol) in THF (50 mL). The filtrate was stirred for 2 h at 20 °C and then heptane (30 mL) was added. After all but about 30 mL of solvent mixture was removed in vacuo, diethyl ether (75 mL) was added, whereupon a dark solid formed. The latter was thoroughly washed with diethyl ether (40 mL) and pentane (2 × 40 mL) to remove anthracene, dried in vacuo, and recrystallized from THF/diethyl ether to provide satisfactorily pure deep red-black microcrystalline **1a** (1.72 g; 82% based on CoBr$_2$). Elemental analysis calcd for C$_{48}$H$_{60}$CoKN$_2$O$_{6.5}$ (%): C 66.49, H 6.98, N 3.23; found: C 66.05, H 7.09, N 2.89; m.p. 131–132 °C (decomp); ^{1}H NMR (300 MHz [D$_8$]THF, 20 °C, THF and [2.2.2]cryptand resonances omitted): $\delta = 3.07$ (br m, 4H; H$_{1,4}$), 5.06 (br m, 4H; H$_{2,3}$), 6.64 (m, 4H; H$_{5,8}$ or H$_{6,7}$), 6.87 (m, 4H; H$_{6,7}$ or H$_{5,8}$); ^{13}C{^{1}H}NMR (75.4 MHz, [D$_8$]THF, 20 °C, THF and [2.2.2]cryptand resonances omitted): $\delta = 108.8$ (s; C$_{9,10}$), 121.2 (s; C$_{5,8}$ or C$_{6,7}$), 124.7 (s; C$_{6,7}$ or C$_{5,8}$), 134.1 (s; C$_{13,14}$), 146.0 (s; C$_{11,12}$). The metal-coordinated carbon atoms could not be resolved. Assignment of C,H resonances was established by ^{1}H–^{13}C heteronuclear multiple quantum correlation (HMQC) and trends previously established for η^4-anthracene or naphthalene complexes,[2, 8] but no unique assignment of C$_{5,8}$, C$_{6,7}$, or corresponding hydrogen atoms was possible. X-ray quality single crystals of **1a** were grown as deep red-black blocks from pentane–THF at 0 °C for 24 h under an argon atmosphere.

1b: By essentially the same procedure as described for **1a**, reduction of CoBr$_2$ (0.507 g, 2.32 mmol) by KC$_{14}$H$_{10}$ (6.95 mmol), followed by addition of [18]crown-6 (0.674 g, 2.55 mmol), work up and recrystallization provided satisfactorily pure deep red microcrystalline **1b** (1.74 g; 87% based on CoBr$_2$). Elemental analysis calcd for C$_{48}$H$_{60}$CoKO$_8$ (%): C 67.04, H 7.03; found: C 66.41, H 6.65; m.p. 139–140 °C (decomp). NMR spectral properties of **1b** were identical for those of **1a**, except for absorptions due to cations. X-ray quality single crystals of **1b** were grown as red-black needles from pentane–THF at 0 °C for 24 h under an argon atmosphere.

3: A solution of dppe (0.508 g, 1.28 mmol) in cold THF (70 mL, -78 °C) was added by cannula to **1b** (0.500 g, 0.579 mmol) in THF (30 mL, -78 °C). Upon slowly warming with stirring, the solution first changed from dark red to deep green at about -30 °C. After further stirring at room temperature for 6 h it assumed the deep red hue of **3**. After filtration, heptane (40 mL) was added and all but about 40 mL of solvent mixture was removed in vacuo. Additional heptane (80 mL) was added to completely precipitate the product, which was separated by filtration, washed with pentane (2 × 20 mL) and dried in vacuo to provide magenta microcrystals of **3** (0.538 g; 75% yield based on **1b**). Elemental analysis calcd for C$_{68}$H$_{80}$CoKO$_7$P$_4$ (%): C 66.33, H 6.55; found: C 66.54, H 6.57; m.p. 216–218 °C (decomp). ^{1}H NMR (300 MHz, [D$_8$]THF, 20 °C, THF and [18]crown-6 resonances omitted): $\delta = 7.27$ (br m, 16H; C$_6$H$_5$ of dppe), 6.70 (br m, 24H; C$_6$H$_5$ of dppe), 1.94 (br m, 8H; C$_2$H$_4$ of dppe); ^{31}P{^{1}H} NMR (121.5 MHz, [D$_8$]THF, 20 °C, ref: 85% H$_3$PO$_4$): $\delta = 72.3$ (br, dppe).

4: Excess cot (0.5 mL) in cold THF (20 mL, −78 °C) was added by cannula to a deep red solution of **1a** (0.317 g, 0.366 mmol) in cold THF (60 mL, −78 °C). The reaction mixture slowly warmed to room temperature over a period of about 12 h. At about −30°, the color changed to a deep green. Following filtration at room temperature, the solvent was removed in vacuo. Addition of pentane (150 mL) and subsequent washing with pentane (30 mL) provided deep green-black microcrystalline **4** (0.198 g; 79 % yield based on **1a**). Elemental analysis calcd for $C_{34}H_{52}CoKN_2O_6$ (%): C 59.81, H 7.68, N 4.10; found: C 60.47, H 7.36, N 3.90; m.p. 175–177 °C (decomp); ^1H NMR (300 MHz, [D$_8$]THF, 20 °C): $\delta = 5.18$ (s, 16 H), 3.34 (br, 24 H, cryptand), 2.36 (br, 12 H, cryptand); $^{13}C\{^1H\}$ NMR (75.5 MHz, [D$_8$]THF, 20 °C): $\delta = 91.0$ (s, C_8H_8), 71.3 (s, cryptand), 68.5 (s, cryptand), 54.9 (s, cryptand).

Received: November 26, 2001 [Z 18269]

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Peptide-Templated Saccharide Synthesis on a Solid Support**

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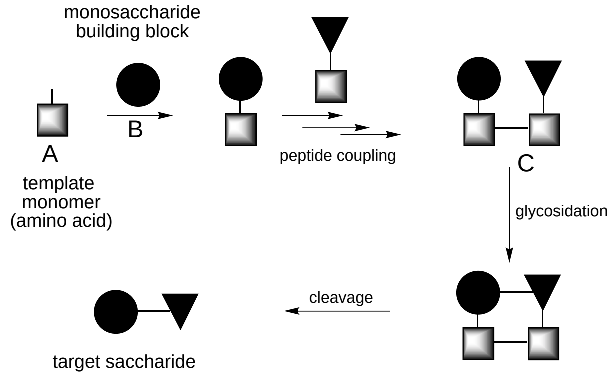
The chemical synthesis of oligosaccharides remains a major challenge in synthetic chemistry. Of particular importance is the development of new strategies for the stereoselective synthesis of oligosaccharides and the incorporation of these methods into the overall process of the assembly of target glycosides. Following the pioneering work of Hindsgaul and Barresi[1] a number of authors have investigated the use of temporary molecular tethers to control the regio- and/or stereoselectivity of glycosidation reactions.[2, 3] We were intrigued by the possibilities of extending these concepts of tethered intramolecular glycosidation reactions to an overall approach for the synthesis of saccharides. Such an approach requires the challenging construction of a molecular template bearing different monosaccharides at different points along its length. This problem is greatly simplified if the template is based upon a peptide skeleton. In following this strategy a suitably functionalized amino acid **A** is first conjugated to the monosaccharide building blocks **B** through a cleavable linker (Scheme 1). These units are then coupled by means of standard peptide synthesis protocols to provide the suitably functionalized template **C**. We then envisaged a glycosidation reaction which would "zip up" the carbohydrate with the template and thus control the steroselectivity of the glycosidation process. The product is then cleaved from the template to furnish the target saccharide.



Scheme 1. Peptide-templated saccharide synthesis.

An additional advantage of using peptide templates is that it should be possible to assemble **C** on solid support by using standard peptide synthesis protocols which opens the door to automation of the whole process. Fairbanks et al. have recently reported on independent studies on the use of peptide tethers to control the solution-phase synthesis of mannose-containing disaccharides.[4] Here we describe our initial studies of the peptide-templated synthesis of disaccharides on solid support.

The amino acid hydroxyproline (HyP) was chosen as the core of our peptide template as coupling of these units should provide a relatively rigid skeleton. Linkage of the amino acid with the monosaccharide was envisaged by means of a mixed carbonate link between the HyP hydroxy group and the 6-hydroxy group of the sugar unit. Our initial studies focussed on the synthesis of disaccharides by using this methodology, which required the preparation of a peptide template bearing a single glycosyl donor and glycosyl acceptor.

The required building block **3** was prepared in 80% yield by formation of a mixed carbonate linkage between glucosyl donor **2**[5] and protected HyP derivative **1**[6] in phosgene solution (Scheme 2). The room-temperature NMR spectrum of building blocks such as **3** is complicated by the observation of two Fmoc group rotamers in approximately equal quantities. The acceptor unit **5** was prepared in a similar manner by selective coupling of the 6-hydroxy group of the BDA-protected[7, 8] methyl glucoside **4** with **1** in 81% yield (Scheme 2; BDA = butanedione-2,3-diacetal). Protection of the secondary hydroxy group was not necessary.

With the required units in hand, we turned our attention to the solid-phase synthesis of the peptide template. As isolation of the final peptide was not required, the peptides were attached directly to an aminomethyl polystyrene-based resin, aminomethyl Novagel,[9] which had a nominal loading capacity of 0.74 mmol g^{-1}. Peptide synthesis was performed on a semiautomated peptide synthesizer in the presence of 1-hydroxy-7-azabenzotriazole (HOAt).[10]

The peptide template sequence was initiated by the addition of a glycine unit onto the resin backbone to minimize

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[**] This work was supported by the Engineering and Physical Sciences Reseach Council, the University of Leeds, and the Royal Society.

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