[14] M. E. Brown, G. M. Swallowe, *Thermochim. Acta* **1981**, *49*, 333, and references therein.
[15] B. Morosin, R. G. Dunn, R. Assink, T. M. Massis, Y. Fronabarger, E. N. Duesler, *Acta Crystallogr. Sect. C* **1997**, *53*, 1609.
[16] X. G. Zhou, Z. E. Huang, R. F. Cai, L. X. Zhang, X. F. Hou, X. J. Feng, H. Y. Huang, *J. Organomet. Chem.* **1998**, *563*, 101.
[17] R. D. Holm, P. L. Donnelly, *J. Inorg. Nucl. Chem.* **1966**, *28*, 1887.
[18] a) S. K. Debb, A. D. Yoffe, *Trans. Faraday Soc.* **1959**, *55*, 106; b) M. J. Sole, A. D. Yoffe, *Proc. R. Soc.* **1964**, *A 277*, 498.
[19] H. M. Montagu-Pollock, *Proc. R. Soc.* **1962**, *A 269*, 219.
[20] M. J. Sole, A. D. Yoffe, *Proc. R. Soc.* **1964**, *A 277*, 523, and references therein.

Novel Ternary Alkali Metal Silver Acetylides M^IAgC_2 ($M^I = Li, Na, K, Rb, Cs$)[**]

Winfried Kockelmann and Uwe Ruschewitz*

Recently we showed that Na_2PdC_2 and Na_2PtC_2 can be synthesized by the reaction of Na_2C_2 with palladium or platinum at temperatures of about 350 °C under an inert atmosphere.[1] These compounds are the first examples of ternary alkali metal transition metal acetylides. Their crystal structures are characterized by $^1_\infty[M(C_2)^{2-}_{2/2}]$ chains (M = Pd, Pt) that are separated by sodium ions. In the meantime we were able to extend this synthesis to the analogous potassium, rubidium, and cesium acetylides,[2] but attempts to synthesize ternary acetylides of transition metals other than palladium or platinum by this method were not successful up to now. In 1963 a synthesis was described by which the ternary silver acetylide $KAgC_2$ could be obtained.[3] The crystal structure of this compound was not determined, but elemental analyses and IR investigations corroborated its existence. As highly explosive Ag_2C_2 was used in this synthesis [Eq. (1)], we have tried to find a different approach, which avoids this starting material.

$$2\,KC_2H + Ag_2C_2 \longrightarrow KAgC_2 + K[Ag(C_2H)_2] \qquad (1)$$

For that purpose we treated KC_2H with AgI in liquid ammonia, which resulted in a nonexplosive complex hydrogenacetylide as intermediate [Eq. (2)], which could be transformed into the ternary silver acetylide by heating under high vacuum to temperatures of about 120–130 °C [Eq. (3)].

$$2\,KC_2H + AgI \longrightarrow K[Ag(C_2H)_2] + KI \qquad (2)$$

$$K[Ag(C_2H)_2] \longrightarrow KAgC_2 + C_2H_2 \qquad (3)$$

The by-product KI [Eq. (2)] was removed by washing with liquid ammonia so that the insoluble $KAgC_2$ could be obtained in a pure form. It was possible to extend this synthesis to ternary silver acetylides of the other alkali metals. In a variation, the synthesis of $LiAgC_2$ according to Equation (3) was performed in boiling pyridine. LiI is soluble in pyridine so that the insoluble $LiAgC_2$ could be separated by filtration. All products are colorless, nonexplosive, and sensitive to air and moisture.

X-ray diffractometer investigations[4] on the colorless powders of the silver acetylides resulted in the unit cells and space groups given in Table 1.[5] It is striking that in all unit cells a lattice parameter of about 5.30 Å is found. As this distance corresponds approximately to the sum of two Ag–C single bonds (2.087 and 2.108 Å in $Ag_2C_2 \cdot 2\,AgClO_4 \cdot 2\,H_2O$)[6] and one C–C triple bond (1.206 Å),[7] it was assumed that $^1_\infty[Ag(C_2)^{-}_{2/2}]$ chains run along this unit cell axis. However, the unit cells given in Table 1 suggest that at least three different packing variants of the silver–carbon chains must exist. With these assumptions, possible structural models were created, and the refinements of the X-ray powder diffractograms showed that $NaAgC_2$, $KAgC_2$, and $RbAgC_2$ are isotypic, but $LiAgC_2$ and $CsAgC_2$ crystallize in different structure types. To obtain precise bond lengths neutron powder diffraction experiments on a representative of each structure type (LiAgC2, KAgC2, and CsAgC2) were performed.[8] The resulting crystal structures are shown in Figures 1–3.[9]

Table 1. Lattice parameters of ternary silver acetylides M^IAgC_2 (M^I = Li, Na, K, Rb, Cs) at room temperature.[4]

	a [pm]	*c* [pm]	Space group
$LiAgC_2$	379.6(1)	533.0(1)	$P\bar{6}m2$
$NaAgC_2$	374.7(1)	532.0(1)	$P4/mmm$
$KAgC_2$	424.5(1)	530.7(1)	$P4/mmm$
$RbAgC_2$	447.5(1)	531.0(1)	$P4/mmm$
$CsAgC_2$	527.7(1)	857.9(1)	$P4_2/mmc$

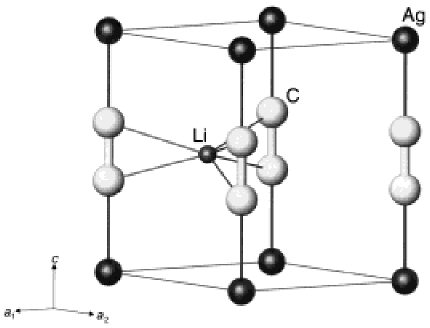

Figure 1. Crystal structure of $LiAgC_2$. The unit cell, the C–C and Ag–C bonds as well as the shortest Li–C distances are emphasized. Selected interatomic distances [Å]: Li–C 2.2786(9) (6 ×), Ag–C 2.025(3) (2 ×), C–C 1.278(6).

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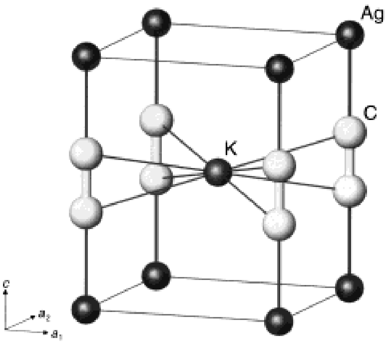

Figure 2. Crystal structure of $KAgC_2$. The unit cell, the C–C and Ag–C bonds as well as the shortest K–C distances are emphasized. Selected interatomic distances [Å]: K–C 3.0506(8) (8 ×), Ag–C 2.032(3) (2 ×), C–C 1.223(6).

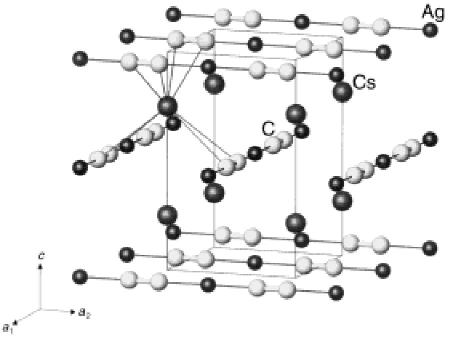

Figure 3. Crystal structure of $CsAgC_2$. The unit cell, the C–C and Ag–C bonds as well as the shortest Cs–C distances around one of the cesium ions are emphasized. Selected interatomic distances [Å]: Cs–C 3.4347(7) (8 ×), Ag–C 2.015(4) (2 ×), C–C 1.217(7).

As assumed, the title compounds have $_{\infty}^{1}[\mathrm{Ag}(\mathrm{C}_2)_{2/2}^{-}]$ chains as their common structural element. The C–C bond lengths in $KAgC_2$ and $CsAgC_2$ are 1.223(6) and 1.217(7) Å, respectively. This is close to the expected value for a C–C triple bond (acetylene 1.205 Å[10]; CaC_2 1.191 Å[11]). For $LiAgC_2$ a surprisingly long C–C distance of 1.278(6) Å was obtained. This distance is probably an artifact of the structural refinement, as the investigated sample contained about 13 wt % Li_2C_2[12] and $LiAgC_2$ showed strong anisotropic reflection broadening, so that a strong overlap of reflections resulted. A C–C bond length in $LiAgC_2$ similar to those found in $KAgC_2$ and $CsAgC_2$ is strongly supported by the results of Raman spectroscopic investigations (see below). The determination of the lithium positions was also not clear-cut. In Figure 1 the crystal structure which gave the best R values ($P\bar{6}m2$, $Z = 1$) is shown, but other structural models gave only slightly worse agreement factors.[13]

In $LiAgC_2$ (Figure 1) and $KAgC_2$ (Figure 2) the $_{\infty}^{1}[\mathrm{Ag}(\mathrm{C}_2)_{2/2}^{-}]$ chains run parallel to each other along the crystallographic *c* axis. In $CsAgC_2$ (Figure 3), however, the $_{\infty}^{1}[\mathrm{Ag}(\mathrm{C}_2)_{2/2}^{-}]$ chains are aligned in layers perpendicular to the *c* axis, and the layers are rotated by 90° to each other. Thus the hexagonal and the two tetragonal packings of the silver–carbon chains correspond to the three simplest rod packings as described by O'Keeffe and Andersson.[15] The alkali metal ions lie between these chains.[16] The lithium ions in $LiAgC_2$ are coordinated *side-on* by three C_2 dumbbells, which sit in distorted Li_3Ag_2 trigonal bipyramids. The Li–C distances of 2.2786(9) Å are in good agreement with the corresponding distances in Li_2C_2 (2.2122(6) and 2.4017(6) Å).[17] The larger alkali metal ions Na^+, K^+, Rb^+, and Cs^+ are coordinated *side-on* by four C_2 dumbbells, which are surrounded by distorted $M^{I}_4Ag_2$ octahedra. Again the agreement of the alkali metal–carbon distances in the title compounds with those in binary acetylides is very good: 3.0506(8) ($KAgC_2$), 3.009(3)–3.146(3) (K_2C_2),[18] 3.4347(7) ($CsAgC_2$), 3.31(1)–3.83(2) Å (CsC_2H).[19]

Neutron diffraction investigations on Na_2PdC_2 resulted in a C–C distance of 1.264(3) Å.[2] This value is—even considering the standard deviations—distinctly larger than those found in $KAgC_2$ and $CsAgC_2$. Therefore we have performed Raman spectroscopic investigations with a particular interest in the frequencies of the C–C stretching vibrations. The results are summarized in Table 2. It is obvious that a correlation between the C–C distance and the frequency of the C–C stretching vibration exists. The ternary palladium acetylides with longer C–C bond lengths have distinctly smaller frequencies, indicating weaker C–C bonding, than the silver acetylides. Moreover the Pd–C distance (2.001(1) Å) is shortened compared to the sum of the covalent radii (2.055 Å),[20] whereas a very good agreement is found for both values in the ternary silver acetylides ($KAgC_2$: Ag–C 2.032(3) Å; sum of covalent radii 2.032 Å).[20] We think that stronger backbonding from palladium to carbon is responsible for the increase in the C–C bond length. The fact that almost the same frequencies of the C–C stretching vibration have been found for all title compounds (Table 2) supports the assumption of similar C–C distances in these compounds. Therefore the longer C–C distance in $LiAgC_2$ must be an artifact of the structural refinement (see above). It is unlikely that the different cation environments can account for an increase in the C–C distance by more than 5 pm.

Table 2. Frequencies of the C–C stretching vibrations of ternary palladium and silver acetylides.

	$\tilde{\nu}_{C\equiv C}$ [cm^{-1}]		$\tilde{\nu}_{C\equiv C}$ [cm^{-1}]
$LiAgC_2$[14]	1962		
$NaAgC_2$	1965	Na_2PdC_2	1862
$KAgC_2$	1963	K_2PdC_2	1850
$RbAgC_2$	1961		
$CsAgC_2$	1965		

Band-structure calculations[21] showed that Na_2PdC_2 is a semiconductor with a very small, indirect band gap of about 0.1 eV, whereas $KAgC_2$ and $CsAgC_2$ have distinctly larger band gaps ($CsAgC_2$: 2 eV). Considering that density functional calculations typically provide band gaps which are too small,[22] these results correspond nicely to the colors of the compounds: Na_2PdC_2 is black, while the ternary silver acetylides are colorless. Measurements of the electrical conductivity (PPMS, Quantum Design, powder pellet with four silver contacts) confirmed these findings: Na_2PdC_2 showed semiconducting and $CsAgC_2$ insulating behavior. An analysis of the crystal orbital Hamilton population (COHP)[23] from the band structures above confirmed the assumption that the Pd–C backbonding in Na_2PdC_2 is stronger than the Ag–C backbonding in the ternary silver acetylides, as the integrated COHPs of the π-M-C bonding—mainly consisting of overlaps of the metal d-π orbitals with carbon p-π orbitals—are larger in Na_2PdC_2 than in $KAgC_2$ and $CsAgC_2$.

At the moment we are investigating the analogous copper and gold compounds which can also be prepared by the synthetic route given above. They crystallize in structures analogous to those of the ternary silver acetylides.

Experimental Section

All preparations were carried out under an inert argon atmosphere using Schlenk techniques.

$LiAgC_2$: Lithium (69 mg, 10 mmol) was dissolved in liquid ammonia (approx. 30 mL, cooled with a CO_2/acetone bath). Acetylene was passed over the blue stirred solution until it decolorized. A surplus of acetylene must be avoided to prevent the formation of Ag_2C_2 in the next step. After addition of AgI (587 mg, 2.5 mmol)—a surplus of lithium prevents the formation of Ag_2C_2—the mixture was stirred for another hour and the solution was allowed to warm up. The white residue was dried under high vacuum at room temperature and then refluxed in pyridine overnight. After filtration the product could be obtained as a colorless residue. The sample for the neutron diffraction investigation was synthesized using enriched ^7Li.

$NaAgC_2$/$KAgC_2$: The synthesis was analogous to the synthesis of $LiAgC_2$, but the residue obtained after the evaporation of ammonia was dried and then, as a solid, heated to 120–130°C under high vacuum. Pure samples could be obtained by repeated washings with liquid ammonia.

$RbAgC_2$/$CsAgC_2$: Ammonia was condensed into a Schlenk flask loaded with the alkali metal. The further steps of the synthesis were analogous to the preparation of $NaAgC_2$ and $KAgC_2$.

Raman spectroscopic investigations: BIO-RAD-FT-Raman spectrometer, Nd-YAG-laser ($\lambda = 1064$ nm, 50 mW laser power); the samples were sealed and measured in NMR tubes ("Economy", Wilmad) under an argon atmosphere.

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[1] M. Weiss, U. Ruschewitz, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1208–1210.

[2] S. Hemmersbach, Dissertation, RWTH Aachen, **1998**.

[3] R. Nast, H. Schindel, *Z. Anorg. Allg. Chem.* **1963**, *326*, 201–208.

[4] STOE Stadi P2 powder diffractometer, Ge monochromator, $Cu_{K\alpha 1}$ radiation ($\lambda = 1.54059$ Å), capillaries (diameter 0.3 mm), linear position sensitive OED detector.

[5] a) P. E. Werner, *Z. Kristallogr.* **1964**, *120*, 375–387; b) P. E. Werner, Programm TREOR90, Stockholm (Sweden), **1990**.

[6] G.-C. Guo, Q.-G. Wang, G.-D. Zhou, T. C. W. Mak, *Chem. Commun.* **1998**, 339–340.

[7] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, **1960**, p. 224.

[8] ROTAX time-of-flight diffractometer[24] at the ISIS spallation source (Rutherford Appleton Laboratory, UK); samples in vanadium cylinders (diameter 8 mm, height approx. 50 mm, wall thickness approx. 0.1 mm) with aluminum screw caps and indium seals closed air-tight.

[9] Structure refinement of $LiAgC_2$: crystal system: hexagonal, space group $P\bar{6}m2$ (no. 187), $a = 3.7882(5)$, $c = 5.328(3)$ Å, $\rho_{calcd} = 3.482$ g cm^{-3}, $Z = 1$, Ag on 1(a), C on 2(g) with $z = 0.3800(5)$, Li on 1(d), 22 reflections on the forward and 36 reflections on the back scattering bank, 4 positional and thermal parameters refined, $wR_P = 0.0146/0.0211$, $R_P = 0.0111/0.0197$, $R_F = 0.0072/0.0158$; the investigated sample contained 12.8(2) wt% Li_2C_2 as an impurity. Structure refinement of $KAgC_2$: crystal system: tetragonal, space group $P4/mmm$ (no. 123), $a = 4.2267(8)$, $c = 5.287(2)$ Å, $\rho_{calcd} = 3.006$ g cm^{-3}, $Z = 1$, Ag on 1(a), C on 2(g) with $z = 0.3843(6)$, K on 1(d), 37 reflections on the forward and 60 reflections on the back scattering bank, 4 positional and thermal parameters refined, $wR_P = 0.0183/0.0273$, $R_P = 0.0151/0.0337$, $R_F = 0.0286/0.0433$. Structure refinement of $CsAgC_2$: crystal system: tetragonal, space group $P4_2/mmc$ (no. 131), $a = 5.2467(6)$, $c = 8.528(1)$ Å, $\rho_{calcd} = 3.746$ g cm^{-3}, $Z = 2$, Ag on 2(b), C on 4(k) with $x = 0.1159(7)$, Cs on 2(e), 110 reflections on the forward and 120 reflections on the back scattering bank, 4 positional and thermal parameters refined, $wR_P = 0.0323/0.0335$, $R_P = 0.0266/0.0368$, $R_F = 0.0461/0.0624$; the investigated sample contained 37.1(5) wt% of a second modification of $CsAgC_2$, which crystallizes isotypic to $KAgC_2$ in space group $P4/mmm$ ($a = 4.7149(8)$, $c = 5.259(3)$ Å). All refinements were carried out with the GSAS suite of programs.[25] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository numbers CSD-410868 ($LiAgC_2$), -410874 ($KAgC_2$), and -410873 ($CsAgC_2$).

[10] G. Herzberg, J. W. T. Spinks, *Z. Physik* **1934**, *91*, 386.

[11] M. Atoji, *J. Chem. Phys.* **1961**, *35*, 1950–1960.

[12] In all preparations, a surplus of the alkali metal was used to prevent the formation of Ag_2C_2. The excess hydrogen acetylide M^IC_2H (M^I = Na–Cs) is soluble in liquid ammonia and can be removed by washing. LiC_2H, however, decomposes irreversibly to Li_2C_2 at temperatures of boiling ammonia. Li_2C_2 is insoluble in liquid ammonia and therefore cannot be removed.

[13] a) Space group $P6/mmm$ (no. 191), $Z = 1$ with Ag on 1(a), C on 2(e), and Li on 2(d) with an occupancy of 0.5: $wR_P = 0.0148/0.0214$ and $R_F = 0.0084/0.0170$; b) space group $P6_3/mmc$ (no. 194), $Z = 2$ (the c axis is doubled compared to the two other structural models) with Ag on 2(a), C on 4(e), and Li on 2(c): $wR_P = 0.0155/0.0214$ and $R_F = 0.0078/0.0169$.

[14] The frequency of the C–C stretching vibration of Li_2C_2 was found at 1872 cm^{-1},[17] and can therefore clearly be distinguished from the frequency of $LiAgC_2$.

[15] M. O'Keeffe, S. Andersson, *Acta Crystallogr. Sect. A* **1977**, *A33*, 914–923.

[16] Simple geometric calculations show that a hexagonal packing of cylinders (space filling 90.7%) is denser than a tetragonal packing (space filling 78.5%). However, for the intercalation of spheres (alkali metal ions) the space filling of the tetragonal packing becomes larger than the hexagonal packing when the ratio of the radius of the sphere to the radius of the cylinder reaches a fixed value. This makes the structural change from the lithium compound to the sodium compound plausible.

[17] U. Ruschewitz, R. Pöttgen, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1599–1603.

[18] S. Hemmersbach, B. Zibrowius, U. Ruschewitz, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1440–1446.

[19] U. Ruschewitz, W. Kockelmann, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1041–1046.

[20] L. Pauling, *The Nature of the Chemical Bond*, 3rd. ed., Cornell University Press, Ithaca, NY, **1960**, pp. 224, 256, 514.

[21] Calculations of the electronic structure were performed using the LMTO method[26] within the local density approximation (LDA), taking the von Barth–Hedin approximation.[27] Atomic sphere radii used in the TB-LMTO-ASA calculations were chosen using an automated procedure. Scalar relativistic corrections were included and the calculations were checked for k-point convergence. Differing to most MO methods, employing Gaussian basis sets, the wave functions of the valence electrons are expanded into Hankel envelope functions. In proximity of the nuclei, Schrödinger's equation is solved numerically.

[22] R. O. Jones, O. Gunnarsson, *Rev. Mod. Phys.* **1989**, *61*, 689.

[23] R. Dronskowski, P. E. Blöchl, *J. Phys. Chem.* **1993**, *97*, 8617–8624.

[24] W. Kockelmann, H. Tietze-Jaensch, E. Jansen, W. Schäfer, *ROTAX Activity Report 95/96*, Rutherford Appleton Laboratory (UK), **1997**.

[25] A. C. Larson, R. B. v. Dreele, *Los Alamos Laboratory, Rep. No. LA-UR* **1987**, *86*, 748; PC version **1996**.

[26] O. K. Andersen, C. Arcangeli, R. W. Tank, T. Saha-Dasgupta, G. Krier, O. Jepsen, I. Dasgupta, *Tight-Binding Approach to Computational Materials Science*, MRS Symposia Proceedings, no. 491, MRS, Pittsburgh, **1998**; G. Krier, O. Jepsen, A. Burkhardt, O. K. Andersen, *Das TB-LMTO-ASA-Programm*, Version 4.7.

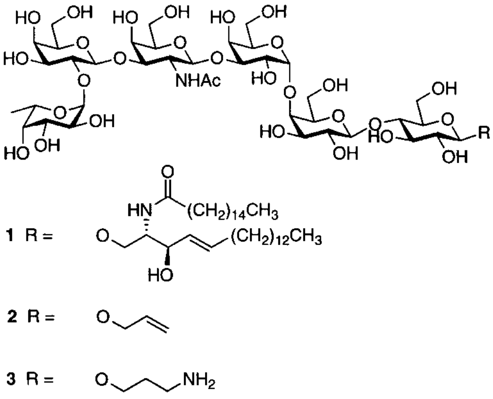
[27] U. von Barth, L. Hedin, *J. Phys. C* **1972**, *5*, 1629.

A Two-Directional and Highly Convergent Approach for the Synthesis of the Tumor-Associated Antigen Globo-H[**]

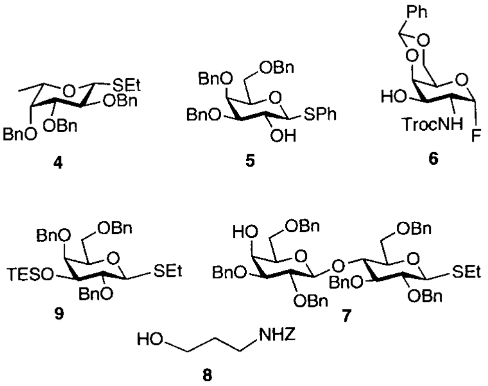
Tong Zhu and Geert-Jan Boons[*]

Human cancer cells are often characterized by the presence of tumor-associated glycosphingolipids (GSL).[1] Several GSL antigens have been identified as adhesion molecules that may promote tumor cell metastases. Active immunization with GSL can induce or enhance antibody titers and several studies indicate that these antibodies can suppress metastasis.[2]

Danishefsky and co-workers synthesized the saccharide moiety of the tumor-associated antigen Globo-H[3] (**1**) using the glycal assembly strategy. The final product was substituted with an anomeric allyl moiety (→**2**), which after oxidation to an aldehyde moiety, allowed coupling to the carrier protein keyhole limpet hemocyanin (KLH, *Megathura crenulata*). High levels of antibodies in patients with progressive and recurrent prostrate cancer could be raised by vaccination with the conjugate.[4] Schmidt and co-workers prepared the protected Globo-H hexasaccharide by employing the trichloroacetimidate methodology.[5]



Herein we report an alternative approach for a highly efficient synthesis of the Globo-H hexasaccharide **3**. For the first time we demonstrate that a hexasaccharide can be assembled in five consecutive glycosylations without the need for any intermediate protecting group manipulations. The new approach gives the readily available building blocks **4, 5**, **6**, **7**, **8**, and **9** (Scheme 1) of the protected hexasaccharide **19**, which was deprotected to yield target compound **3** (Scheme 3). The key feature of the new glycosylation sequence is a combination of two-directional glycosylation approaches (see below) with chemoselective and orthogonal glycosylations.[6] These strategies exploit both the differences in the reactivities of anomeric leaving groups and the subtle control of nucleophilicities of sugar hydroxyl groups and silyl ethers. The aminopropyl spacer was incorporated for well-defined conjugation to a carrier protein.[7]



Scheme 1. Building blocks for **3**.

Classic strategies for oligosaccharide assembly are characterized by the manipulation of protecting groups between each glycosylation step. Such manipulations increase the linearity and decrease the efficiency of oligosaccharide assembly. Two-directional glycosylation strategies and chemoselective- or orthogonal-glycosylation approaches condense the process of oligosaccharide synthesis by removing the need for unmasking procedures. In a two-directional glycosylation strategy a saccharide derivative first acts as a glycosyl donor and the resulting product is immediately used as a glycosyl acceptor in the next coupling step.[8] This reaction sequence can be performed with glycosyl donors and acceptors that both have a free hydroxyl group. It is critical that the hydroxyl group of the glycosyl acceptor is significantly more reactive than the hydroxyl group of the glycosyl donor to avoid self-condensation of the glycosyl donor. A complementary method exploits the finding that a thioglycoside protected as a silyl ether (for example, triethylsilyl, *tert*-butyldimethylsilyl) can act both as a glycosyl donor and acceptor. In general, silyl ethers are sufficiently stable under *N*-iodosuccinimide/trimethylsilyl trifluoromethanesulfonate (NIS/TMSOTf)[9] or iodonium dicollidine perchlorate (IDCP)[10] mediated glycosylations. Thioglycosides of these derivatives, therefore, can act as glycosyl donors. However, the products of these coupling reactions are suitable acceptors[11] when glycosylated with glycosyl fluorides in the presence of [Cp_2ZrCl_2]/AgOTf (Cp=cyclopentadienyl, Tf = trifluoromethanesulfonyl).[12] Chemoselective glycosylation strategies are

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