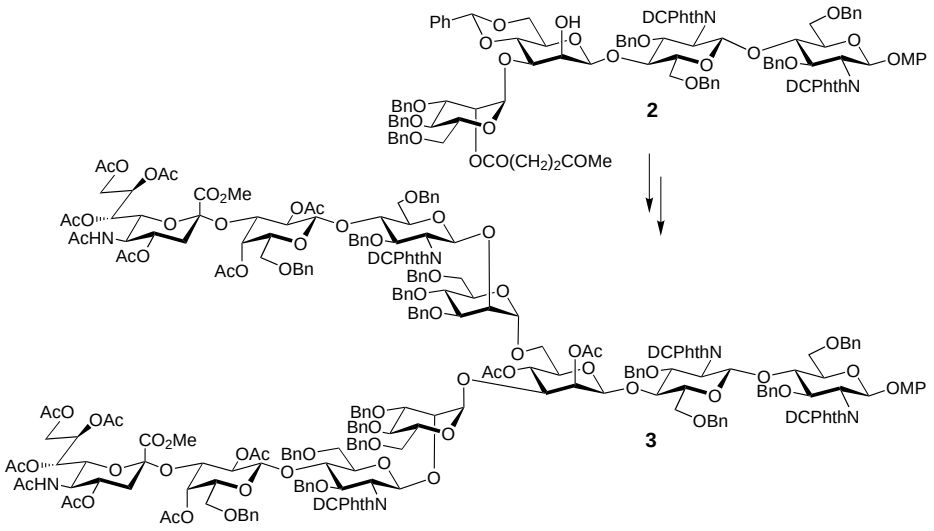
Synthesis of an α-(2,3)-Sialylated, Complex-Type Undecasaccharide**

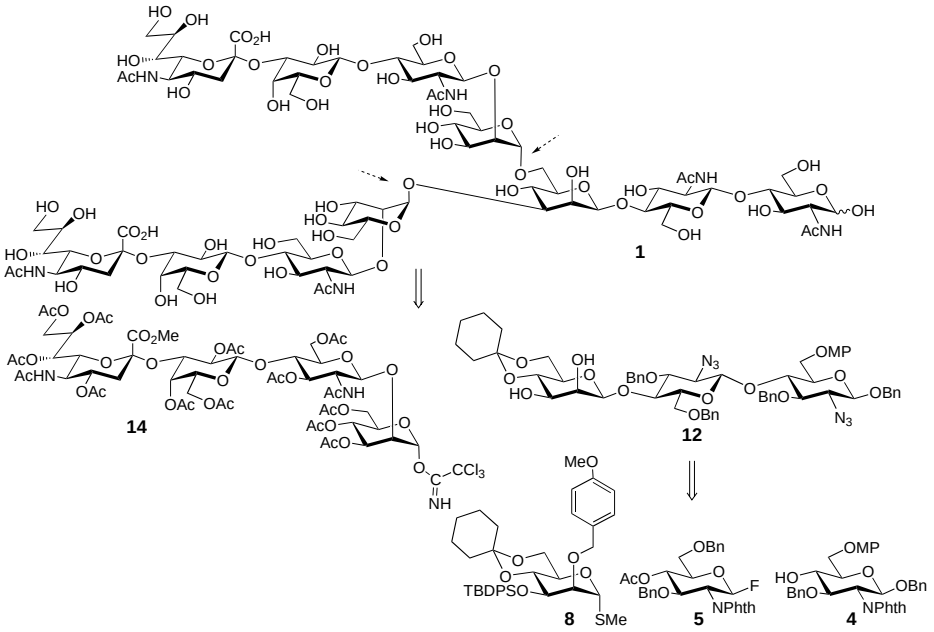
Joachim Seifert, Matthias Lergenmüller, and Yukishige Ito*

N-Glycosylation is a widespread posttranslational modification of eukaryotic proteins. N-Glycans are functional constituents of glycoproteins and serve to control the intra- and intercellular distribution and three-dimensional structure of glycoproteins and also protect them against degradation. Furthermore, N-glycans are involved in important biological processes including cell differentiation, cell adhesion, and malignant transformation.[1] Here we report the synthesis of undecasaccharide **1** (see Scheme 2), one of the prototypical structures of complex-type N-glycans of mammalian origin.[2] This represents the first purely chemical synthesis of **1** achieved with strict stereochemical control.[3]

With the aim of constructing this complex molecule in a stereocontrolled fashion, our initial investigation centered around the use of tetrasaccharide **2**[4a] (Scheme 1), obtainable by *p*-methoxybenzyl-assisted intramolecular aglycon delivery (IAD), as the key intermediate, which was eventually transformed into the fully protected undecasaccharide **3**. However, deprotection of **3** turned out to be highly challenging, mainly due to the difficulty of manipulating sialic acid methyl ester in the presence of a 4,5-dichlorophthaloyl (DCPhth) group, and vice versa.



Scheme 1. The tetrasaccharide **2** served as a template for the formation of undecasaccharide **3**. The deprotection of **3** failed. Bn = benzyl, DCPhth = 4,5-dichlorophthaloyl, MP = *p*-methoxyphenyl.



Scheme 2. The undecasaccharide **1** was constructed from the β-mannosidic trisaccharide **12** and trichloroacetimidate **14**[11] as key building blocks. Compound **12** was prepared from the monosaccharides **4**,[5b,c] **5**[5d] and **8**.[5a] Phth = phthaloyl, TBDPS = *tert*-butyldiphenylsilyl.

In our revised synthetic plan (Scheme 2), the core trisaccharide **12** was designed as the key intermediate on the basis of the following considerations: First, acetamido groups were masked as azides in the hope that problems associated with the potential nucleophilicity of acetamido groups and/or the base lability of phthalimide (or DCPhth) can be largely eliminated at the stage of critical glycoside bond forming reactions and/or manipulation of the protecting groups. Additionally, to maximize the efficiency of β-mannosylation, cyclohexylidene-protected **8**[5a] was adopted as the mannosyl donor; it has proved to be the most suitable glycosyl donor for such purposes.

In practice, preparation of trisaccharide **12** was executed with monosaccharide components **4**,[5b,c] **5**,[5d] and **8**[5a] (Scheme 3) and commenced with the high-yield preparation

[*] Dr. Y. Ito, Dr. J. Seifert, Dr. M. Lergenmüller
RIKEN (The Institute of Physical and Chemical Research)
and CREST Japan Science and Technology Corporation (JST)
Hirosawa 2–1, Wako-Shi, Saitama, 351-0198 (Japan)
Fax: (+81) 48-462-4680
E-mail: yukito@postman.riken.go.jp

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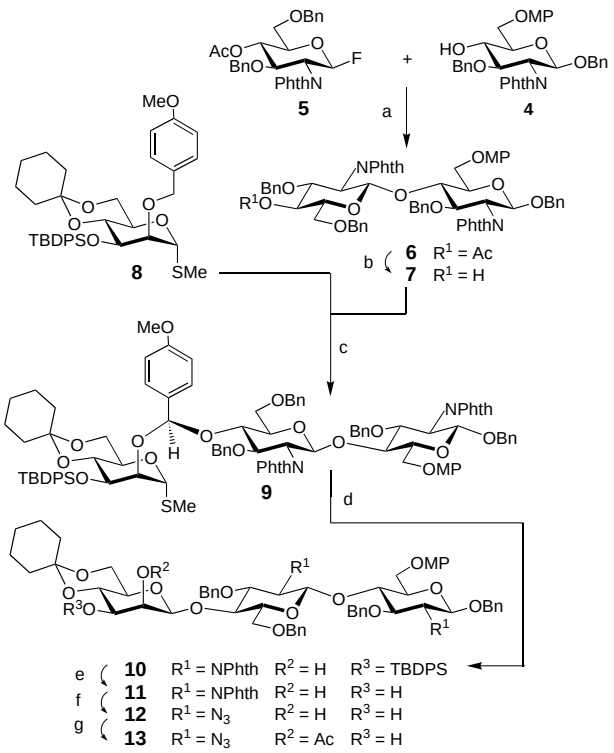

Scheme 3. a) $[Cp_2HfCl_2]$, AgOTf, molecular sieves (4 Å), CH_2Cl_2, $-30\,^\circ C$; b) NaOMe, MeOH (75%, 2 steps); c) DDQ (1.5 equiv) molecular sieves (4 Å), CH_2Cl_2, 2 h; d) MeOTf (3.4 equiv), DBMP (3.8 equiv), molecular sieves (4 Å), $ClCH_2CH_2Cl$, 45 °C, 36 h (78%); e) TBAF, HOAc, THF (78%); f) 1. ethylenediamine, *n*-BuOH, 100 °C, 24 h, 2. Tf-N_3, DMAP, CH_3CN, CH_2Cl_2, 5 h (84%); g) 1. $CH_3C(OEt)_3$, *p*-Tos-OH/OH_2, C_6H_6, 1 h, 2. 80% HOAc, 5 min (92%). DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, DBMP = 2,6-di-*tert*-butyl-4-methylpyridine, DMAP = 4-dimethylaminopyridine, OTf = trifluoromethanesulfonate, TBAF = tetrabutylammonium fluoride, *p*-Tos-OH/OH_2 = *p*-toluenesulfonic acid monohydrate, Tf-N_3 = trifluoromethanesulfonyl azide.

of chitobiose derivative **6** under Suzuki conditions.[6] Subsequent deacetylation gave **7**, which in turn was subjected to β-mannosylation. Coupling with methylthio mannoside **8** according to our two-step protocol for IAD[4, 5a] effected clean formation of β-mannoside **10** via mixed acetal **9** in 78% yield. The ^1J(C,H) coupling constant of C-1^3 (161.7 Hz, Table 1) confirmed the configuration of the newly generated β-mannosidic linkage.[7] Reaction of **10** with tetrabutylammonium fluoride (TBAF) led to the diol **11**. Subsequent removal of the phthaloyl group[8] followed by a diazo transfer reaction[9] afforded bisazido compound **12** in 84% yield. Regioselective acetylation at position C-2^3 was performed under Lemieux conditions[10] to furnish **13** in high yield.

Trichloroacetimidate **14** (Scheme 2), which corresponds to symmetric branches linked to mannose,[3] was prepared as described previously.[11] The glycosylation of 2^3-O-acetylated **13** with **14** (1.9 equiv) provided **16** in 69% yield (Scheme 4). Alternatively, a similar reaction with diol **12** gave 3-O-glycosylated **15** as the sole isolable coupling product in 61% yield, which was acetylated to **16**. Removal of the cyclohexylidene group to give diol **17** was followed by further glycosylation to undecasaccharide, again with trichloroacetimidate **14** as glycosyl donor. This reaction gave the undecasaccharide **18** in 50% yield, which was counterbalanced by recovered **17**. Acetylation of **18** gave **19**, detailed ^{1}H NMR analysis of which fully supported its regio- and stereochemical integrity (Table 1).

Table 1. Selected physical data of **1**, **10**, **15**, **16**, **18**, and **19**

1: $[\alpha]_D^{20} = -2.1$ ($c = 0.33$ in H_2O); ^{1}H NMR (500 MHz, D_2O, 25 °C, *t*BuOH): $\delta = 5.19$ (d, $^3J(1,2) = 2.7$ Hz, 0.67 H; H-1$^1\alpha$), 5.11 (d, $^3J(1,2) <$ 1.0 Hz, 1 H; H-1^4), 4.92 (d, $^3J(1,2) < 1.0$ Hz, 1 H; H-1$^{4'}$), 4.75 (d, $^3J(1,2) <$ 1.0 Hz, 1 H; H-1^3), 4.69 (d, $^3J(1,2) = 7.8$ Hz, 0.33 H; H-1$^1\beta$), 4.61 (d, $^3J(1,2) = 7.8$ Hz, 0.67 H; H-1$^2\beta$, α form), 4.60 (d, $^3J(1,2) = 7.6$ Hz, 0.33 H; H-1$^2\beta$, β form), 4.57 (d, $^3J(1,2) = 8.0$ Hz, 2 H; H-1$^{5/5'}\beta$), 4.55 (d, $^3J(1,2) =$ 7.8 Hz, 1 H; H-1$^{6'}\beta$), 4.54 (d, $^3J(1,2) = 7.8$ Hz, 1 H; H-1$^6\beta$), 4.24 (dd, $^3J(2,3) = 2.4$ Hz, 1 H; H-2^3), 4.19 (dd, $^3J(2,3) = 3.0$ Hz, 1 H; H-2^4), 4.13–4.10 (m, 3 H; H-2$^{4'}$, H-3$^{6/6'}$), 2.75 (dd, $^3J(3,4) = 4.3$ Hz, $^2J_{gem} = 12.3$ Hz, 2 H; H-3eq$^{N/N'}$), 2.08–2.03 (6s, 18 H; NAc), 1.80 (t, $^3J(3,4) \approx {}^2J_{gem} = 12.0$ Hz, 2 H; H-3ax$^{N/N'}$); ^{13}C NMR (125 MHz, D_2O, 25 °C, *t*BuOH): $\delta = 175.71$–174.53 (C=O), 103.34 (C-1^6), 103.30 (C-1$^{6'}$), 102.06 (C-1^2), 101.08 (C-1^3), 100.52 (C-2$^{N/N'}$), 100.23 (C-1^4, C-1^5), 100.17 (C-1$^{5'}$), 97.77 (C-1$^{4'}$), 95.50 (C-1$^1\beta$), 91.12 (C-1$^1\alpha$), 40.33 (C-3$^{N/N'}$), 23.03–22.57 (NAc); ESI-MS (neg. mode, MeOH/H_2O = 1/1): *m*/*z*: 1110.7 [($M^{2-} - 2$H)/2]; calcd for $C_{84}H_{136}N_6O_{62}$/2 [($M^{2-} -$ 2H)/2]: 1110.9

10: $[\alpha]_D^{20} = 19.9$ ($c = 2.67$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 5.17$ (d, $^3J(1,2) = 8.2$ Hz, 1 H; H-1$^1\beta$), 4.96 (d, $^3J(1,2) = 8.1$ Hz, 1 H; H-1$^2\beta$), 4.33 (d, $^3J(1,2) < 1.5$ Hz, 1 H; H-1^3), 1.08 (s, 9 H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 100.04$ (C-1^3, ^1J(C,H) = 161.7 Hz), 99.70 (cyclohexylidene), 97.07 (C-1^1), 96.87 (C-1^2), 26.96 (C(CH_3)$_3$), 19.39 (C(CH_3)$_3$)

15: $[\alpha]_D^{20} = -14.9$ ($c = 0.5$ in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 4.99$ (d, $^3J(1,2) = 2.1$ Hz, 1 H; H-1^4), 4.68 (d, $^3J(1,2) = 8.1$ Hz, 1 H; H-1$^6\beta$), 4.50 (d, $^3J(1,2) < 1.5$ Hz, 1 H; H-1^3), 4.43 (m, 1 H; H-1^5), 4.35 (m, 1 H; H-1^1), 4.28 (m, 1 H; H-1^2), 3.91 (m, 1 H; H-2^3); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 101.08$ (C-1^1), 101.01 (C-1^6), 100.45 (C-1^2), 100.20 (cyclohexylidene), 99.97 (C-1^5), 99.32 (C-1^3, ^1J(C,H) = 162.2 Hz), 98.78 (C-1^4, ^1J(C,H) = 172.8 Hz), 96.80 (C-2^N), 70.76 (C-2^3); FAB-MS (pos. mode, NBA[a]): *m*/*z*: 2461.0 [M^++H+Na]; calcd for $C_{115}H_{145}N_8NaO_{50}$ [M^++H+Na]: 2460.9

16: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 5.10$ (m, 1 H; H-2^3)

18: $[\alpha]_D^{20} = -9.8$ ($c = 1.0$ in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS):[b] $\delta = 5.10$, 4.64, 4.63, 4.59, 4.56, 4.43, 4.34, 4.30, 4.24 (H-1^1–H-1^6 and H-1$^{4'}$–H-1$^{6'}$, not assigned), 3.74 (m, 1 H; H-4^3); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 101.17$, 100.88, 100.69, 100.47, 100.32, 99.95, 99.65 (^1J(C,H) = 177.3 Hz), 97.96, 97.79 (^1J(C,H) = 170.8 Hz), (C-1^1–C-1^6 and C-1$^{4'}$–C-1$^{6'}$, not assigned), 96.74 (C-2$^{N/N'}$), 68.61 (C-4^3); FAB-MS (pos. mode, NBA[a]): *m*/*z*: 3759.8 [M^++H+Na], calcd for $C_{167}H_{215}N_{10}NaO_{86}$ [M^++H+Na]: 3759.3

19: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 5.03$ (dd, $^3J(3,4) \approx {}^3J(4,5) = 8.8$ Hz, 1 H; H-4^3)

[a] NBA = *m*-nitrobenzyl alcohol. [b] δ(^{1}H) was determined from a ^{1}H/^{13}C HMQC-COSY spectrum.

Having obtained the full backbone structure of the target undecassaccharide, we executed complete deprotection of **19** (Scheme 5). First, the *p*-methoxyphenyl group at the reducing end GlcNAc residue was removed with ammonium cerium(IV) nitrate[12] to afford **20**. Azido groups were converted into acetamides by a two-step procedure to give **21** in 82% yield.[13] Cleavage of the methyl ester and *O*-acetyl groups was performed under alkaline conditions to give **22**, which was finally subjected to hydrogenation over 10% Pd/C. After purification by size exclusion chromatography (Biogel P-2, H_2O), the target molecule was isolated in 98% yield. The ^{1}H NMR spectrum (500 MHz, Table 1) revealed that all chemical shifts of synthetic **1** are essentially identical with those reported for the reference compound **1** isolated from human chorionic gonadotropin.[2a]

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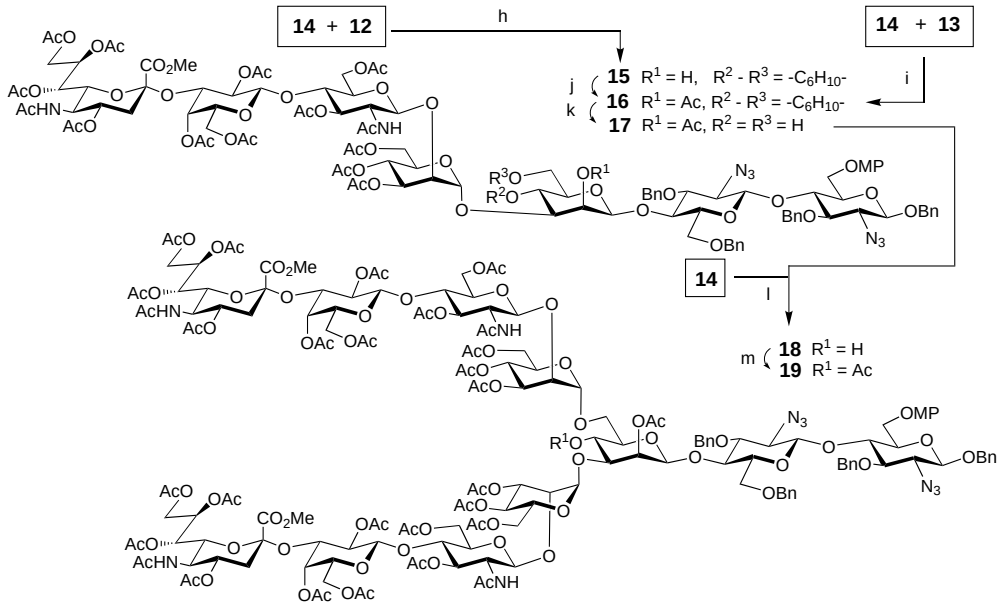
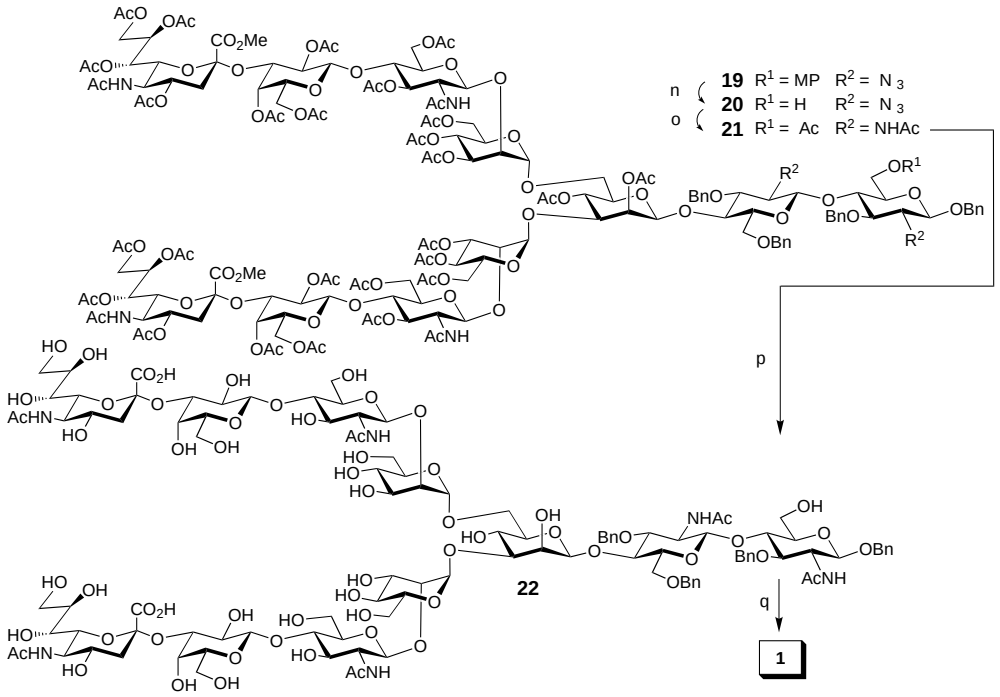


Scheme 4. h) TMS-OTf (0.2 equiv), molecular sieves (4 Å), CH_2Cl_2, $-20\,^{\circ}C$ (61 %); i) BF_3/OEt_2 (1.5 equiv), CH_2Cl_2, molecular sieves (4 Å), $-15\,^{\circ}C$ (69 %); j) Ac_2O, pyridine, DMAP (quantitative); k) *p*-Tos-OH/OH_2 (2.7 equiv), CH_3CN (92 %); l) BF_3/OEt_2(2 equiv), molecular sieves (4 Å, AW 300), CH_2Cl_2, $-20\,^{\circ}C$ (50 %); m) Ac_2O, pyridine, DMAP (92 %). TMS-OTf = trimethylsilyl trifluoromethanesulfonate.



Scheme 5. Deprotection of undecasaccharide **19** gives the target compound **1**. n) $(NH_4)_2Ce(NO_3)_6$, CH_3CN/toluene/H_2O (8/7/7), 0 °C, 15 h (80 %); o) 1. 1,3-propanedithiol, DIEA, pyridine/H_2O (7/3), 2. Ac_2O/pyridine (82 %); p) 1. NaOMe/MeOH, 12 h, 2. H_2O, 50 °C, 1 h; q) Pd/C (10 % Pd), H_2, MeOH/H_2O/HOAc (4/2/2), 5 h (98 %). DIEA = *N*,*N*-diisopropylethylamine.

In summary, we have achieved the convergent and stereocontrolled synthesis of the diantennary complex-type N-glycan **1**, which consists of eleven sugar residues and includes synthetically challenging sequences such as α-linked sialic acids and β-linked mannose. Our basic strategy may well be flexible enough to provide access to other decorated structures. Since undecasaccharide intermediates **18** and **20** have hydroxy groups that can be specifically liberated, synthetic routes to bisecting GlcNAc- and 6-*O*-Fuc- containing structures can be readily conceived.

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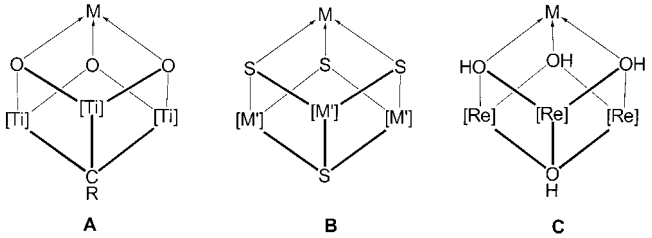
Construction of Heterometallic Cubanes $[\{Ti_3Cp^*_3(\mu_3\text{-}CR)\}(\mu_3\text{-}O)_3\{Mo(CO)_3\}]$ ($R = H$, Me; $Cp^* = \eta^5\text{-}C_5Me_5$) and $[\{Ti_3Cp^*_3(\mu_3\text{-}N)\}(\mu_3\text{-}NH)_3\{M(CO)_3\}]$ ($M = Cr$, Mo, W); Crystal Structure of $[\{Ti_3Cp^*_3(\mu_3\text{-}CMe)\}(\mu_3\text{-}O)_3\{Mo(CO)_3\}]$**

Angel Abarca, Mikhail Galakhov, Pilar Gómez-Sal, Avelino Martín, Miguel Mena,* Josep-M. Poblet, Cristina Santamaría, and Jose Pedro Sarasa

Dedicated to Alexander von Humboldt on the occasion of his commemorative year 1999

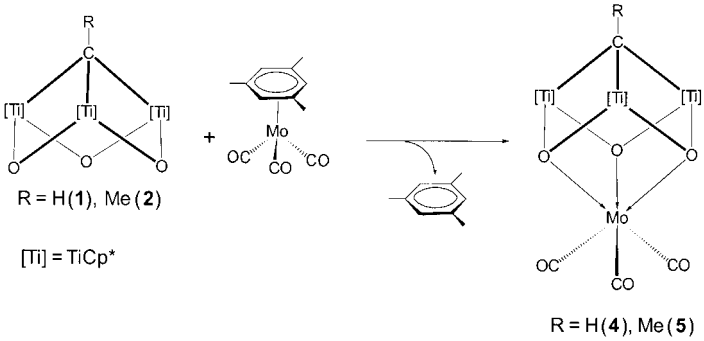
Until now we have focused on the rich chemistry of alkylidyne groups on a trinuclear support without metal – metal bonds $[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ ($R = H$ (**1**), Me (**2**); $Cp^* = \eta^5\text{-}C_5Me_5$). We showed that metal carbonyl hydrides and unsaturated molecules such as carbon monoxide, isocyanides, and ketones are incorporated into the Ti_3O_3 core with direct participation of the alkylidyne units.[1] In the course of our studies, we discovered that these complexes can also act as macrocyclic, tridentate six-electron donor ligands (Scheme 1, **A**) and thus provide an effective route to heterocubanes with $MTi_3(\mu_3\text{-}CR)(\mu\text{-}O)_3$ cores. To our knowledge, the only comparable behavior is the incorporation of metal ions by the M'_3S_4 ($M' = Fe$, Mo) precubane clusters (Scheme 1, **B**), which leads to heterometallic cubane-type MM'_3S_4 cores,[2] and the hydroxymetalate complex $[Re_3(CO)_9(\mu\text{-}OH)_3(\mu_3\text{-}OH)]$, which acts as a tripodal ligand (Scheme 1, **C**) to form "double-cubane" structures.[3] Furthermore, the $(\mu_3\text{-}CR)Ti_3(\mu_3\text{-}O)_3Mo(CO)_3$ cores described here could be invaluable as discrete and ideal models of oxide-supported metal carbonyl complexes for studying the catalyst – support interaction.[4]



Scheme 1. Precubane systems as tripodal ligands.

Here we report the formation of the heterometallic cubanes $[\{Ti_3Cp^*_3(\mu_3\text{-}CR)\}(\mu_3\text{-}O)_3\{Mo(CO)_3\}]$ ($R = H$ (**4**), Me (**5**)) and $[\{Ti_3Cp^*_3(\mu_3\text{-}N)\}(\mu_3\text{-}NH)_3\{Mo(CO)_3\}]$ (**6**) from $[Mo(CO)_3(1,3,5\text{-}Me_3C_6H_3)]$ and the alkylidyne complexes **1** and **2** and the isoelectronic $[\{TiCp^*(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**3**), respectively. Treatment of **3** with the hexacarbonyl complexes $[M(CO)_6]$ ($M = Cr$, Mo, W) also leads to **6** and the analogous heterocubane derivatives $[\{Ti_3Cp^*_3(\mu_3\text{-}N)\}(\mu_3\text{-}NH)_3\{M(CO)_3\}]$ ($M = W$ (**7**), Cr (**8**)).

Reaction of the trimetallic starting materials **1** and **2** with one equivalent of $[Mo(CO)_3(1,3,5\text{-}Me_3C_6H_3)]$[5] in hexane at 80 °C for four days led to displacement of the mesitylene ligand from molybdenum to afford in good yield the dark green crystalline heterocubanes **4** and **5**, respectively (Scheme 2). The solid compounds are stable under argon at room temperature but decompose slowly (months) in $[D_6]$benzene with formation of **1** or **2.**[6]



Scheme 2. Synthesis of the heterometallic cubane complexes **4** and **5**.

The ^{13}C NMR spectra of both complexes show one signal at $\delta \approx 227$ for the three equivalent terminal carbonyl groups and exhibit a downfield shift of the alkylidyne carbon signals ($\delta(\mu_3\text{-}CR) = 410.3$ (**4**), 434.8 (**5**)) relative to **1** ($\delta(\mu_3\text{-}CH) = 383.2$) and **2** ($\delta(\mu_3\text{-}CMe) = 401.7$). In the IR spectra of these compounds, the three terminal CO groups give rise to two strong bands between 1915 and 1815 cm^{-1}, as expected for complexes containing a *fac*-$Mo(CO)_3$ group.[7]

[*] Dr. M. Mena, A. Abarca, Dr. M. Galakhov, Dr. P. Gómez-Sal, Dr. A. Martín, Dr. C. Santamaría
Departamento de Química Inorgánica
Universidad de Alcalá, Campus Universitario
28871 Alcalá de Henares-Madrid (Spain)
Fax: (+349) 1-88-54-683
E-mail: miguel.mena@uah.es
Dr. J.-M. Poblet
Departament de Química Física i Inorgánica
Universitat Rovira i Virgili, Imperial Tarraco 1
43005 Tarragona (Spain)
Fax: (+349) 7-75-59-563
E-mail: poblet@argo.urv.es
Dr. J. P. Sarasa
Departamento de Química Física y Química Orgánica, Universidad de Zaragoza
Ciudad Universitaria s/n. 50009 Zaragoza (Spain)

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