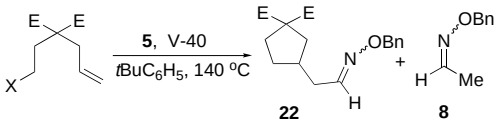
telluride group relative to that of an iodine atom.[15] Some experimental results are included in Table 1 and demonstrate the efficiency of the phenyl telluride approach. The reaction was successful with secondary and primary alkyl tellurides. We briefly examined a sequential radical reaction involving a cyclization and acylation sequence [Eq. (7)]. Reaction of **21**



(7)

	22	**8**
20: X = I	31%	55%
21: X = TePh	67%	0%

with **5** under the same conditions afforded the desired oxime ether **22** in 67% yield, whereas the use of iodide **20** gave **22** in 31% yield along with **8** (55%); this demonstrates the efficiency of the phenyl telluride group as a radical precursor.

Experimental Section

Typical procedure: A degassed solution of 1-bromo-4-iodomethyl-benzene (118 mg, 0.40 mmol), *O*-benzyl-1-(methanesulfonyl)formaldoxime (**5**, 128 mg, 0.60 mmol) and V-40 (20 mg, 0.08 mmol) in freshly distilled octane (2 mL) was heated to reflux under N_2 for 8 h. The solvent was evaporated under reduced pressure, and the residue was purified by chromatography on a silica gel column (*n*-hexane: ethyl acetate 1:15) to yield *O*-benzyl-1-(4-bromobenzyl)formaldehyde (98 mg, 0.32 mmol, 80% yield, $E:Z = 1.1:1$). ^{1}H NMR ($CDCl_3$, 200 MHz): *E* isomer: $\delta = 3.45$ (d, $J = 6.4$ Hz, 2H), 5.08 (s, 2H), 7.06 (d, $J = 2.2$ Hz, 2H), 7.32–7.43 (m, 7H), 7.49 (t, $J = 6.4$ Hz, 1H); *Z* isomer: $\delta = 3.65$ (d, $J = 5.4$ Hz, 2H), 5.15 (s, 2H), 6.80 (t, $J = 5.4$ Hz, 1H), 7.02 (d, $J = 2.2$ Hz, 2H), 7.32–7.43 (m, 7H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 31.9$, 35.3, 75.8, 76.1, 120.5, 120.8, 127.8, 127.9, 128.2, 128.4, 128.6, 128.8, 130.4, 130.5, 131.7, 131.8, 135.3, 135.8, 137.6, 137.7, 149.0, 149.3; IR (NaCl): $\tilde{\nu} = 3031$, 2928, 1656, 1586, 1488, 1454, 1367, 1276, 1072, 1012 cm^{-1}; HR-MS: [M^+] calcd for $C_{15}H_{14}BrNO$: 303.0259; found: 303.0257.

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Cyclodextrin Cavities as Probes for Ligand-Exchange Processes

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Cyclodextrins (CDs) have attracted a lot of attention as chiral building blocks for the construction of enzyme mimics because of their ability to bind a wide range of organic substrates in water.[1–4] Combining CDs with transition metals has proven a very attractive goal in terms of achieving highly selective and efficient catalysis.[5–11] One of the challenges, so far not met, is to force a metal that is covalently linked to a CD framework to be confined in the cavity where maximum interaction between the first coordination sphere of the metal and the CD walls is expected to take place so as to stabilize unusual coordination modes. In addition, cavities with introverted[12] functionalities could provide new catalysts where a metal center operates inside a spatially restricted environment.[13–15] We report here the first α-CD-based multitopic ligand (**2**) capable of hosting metal–organic fragments. As shown by NMR investigations, the complexes derived from this ligand display unique intra- and intermolecular ligand-exchange phenomena at the included metal center.

We anticipated that an easy way to ensure metal encapsulation in a cavity would be to use an α-CD derivative bearing

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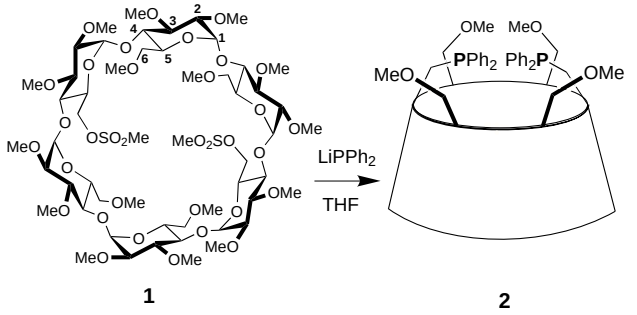
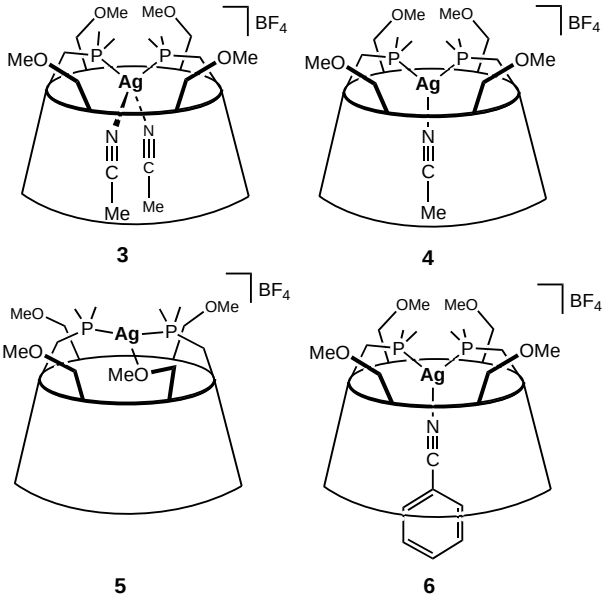
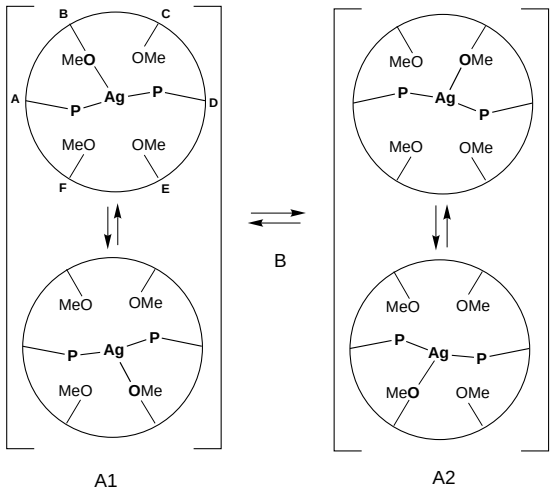




donor functions that preferentially point inside the CD. This feature is realized in diphosphane **2**, in which the orientation of the phosphorus lone pairs is controlled by steric interactions between the CD matrix and the closely appended phosphanyl groups. The presence of adjacent methoxy groups provides additional binding sites that may help metal stabilization. Two diphenylphosphanyl fragments were grafted onto the C-6 atoms of the A and D units of an α-CD platform by using a method developed by Brown et al. for the functionalization of trehalose units.[16] Thus, the reaction of the known dimesylate **1**[17] with lithium diphenyl phosphide in THF afforded compound **2** in high yield [Eq. (1)]. The ^{31}P NMR spectrum of the resulting chiral diphosphane consists of a singlet at $\delta = -17.9$ commensurate with its expected C_2 symmetry. The latter was confirmed by the presence of eight methyl signals as well as three doublets for the H-1 protons in the ^{1}H NMR spectrum. Interestingly, the proximity of the chiral cavity produces a strong differentiation between the two phenyl groups attached to each phosphorus atom as revealed by ^{13}C NMR spectroscopy. This effect is no longer observed when the coordinating atoms are separated from the C-6 atoms by longer spacers like phenylene.[18]

The reaction of ligand **2** with one equivalent of $AgBF_4$ in MeCN leads to the quantitative formation of the complex $[Ag(\mathbf{2})(CH_3CN)_2]BF_4$ (**3**), which is only stable in the presence of a large excess of MeCN (>15 equiv). The formulation of **3** was inferred from its ES-MS spectrum, which revealed the presence of a strong peak for the $[M+H_2O]^+$ ion[19] together with fragmentation peaks resulting from loss of one and two molecules of MeCN. The ^{1}H, ^{13}C, and ^{31}P NMR spectra are all consistent with a C_2-symmetrical complex. Furthermore, the 2D ROESY spectrum of **3** in a $CDCl_3$ solution containing 15 equivalents of MeCN clearly shows cross-peaks corresponding to NOEs between the coordinated MeCN molecules[20] and all the H-3 CD protons as well as two types of H-5 CD proton[21] but no through-space correlations between MeCN with protons outside the cavity.[22] These observations are fully consistent with coordinated MeCN molecules that are located inside the cavity.

Upon evaporation of MeCN, **3** loses coordinated MeCN to produce complexes **4** and **5** in a 80:20 mixture whose ratio does not decrease significantly after prolonged drying in vacuo at 90 °C. However, as confirmed by ^{31}P NMR spectroscopy and microanalysis, quantitative formation of **5** occurs when acetone is added to the mixture prior to evaporation. Coordination of one of the four MeO-6 groups to the silver atom in **5** was inferred from a temperature-dependent ^{1}H NMR study. Thus, at room temperature, the ^{1}H NMR spectrum of **5**, recorded in $C_2D_2Cl_4$, reveals the presence of two distinctive species (45:55 ratio) both of which have averaged C_2 symmetry. As the sample is heated, the signals first broaden, then coalesce near 70 °C, and finally sharpen to produce a spectrum with half the number of signals, consistent with a rapid equilibration of the (B,E)[23] and (C,F) glucose units (Scheme 1, equilibrium B). The calculated energy barrier for this process is about 67.8 kJ mol^{-1}. Upon cooling a CD_2Cl_2 solution of **5** to -20 °C, the room-temperature



Scheme 1. Hemilabile behavior of ligand **2** in complex **5**. A1 and A2, low-energy dynamics; B, high-energy exchange processes.

spectrum no longer persists. Indeed, two new sets of signals emerge that correspond to two C_1-symmetrical species, reflecting a slow exchange on the ^{1}H NMR time scale between diametrically opposed MeO-6 groups (Scheme 1, equilibria A1 and A2).[24] Overall, our findings are best rationalized in terms of ligand fluxionality about a tricoordinate silver ion, the dynamics involving alternative binding of

all four ether groups. Unsurprisingly, the hemilabile[25] behavior of ligand **2** allows substitution of the coordinated oxygen atom by stronger donors.

The addition of 5–10 equivalents of MeCN to a solution of **5** in $CDCl_3$ led to a mixture of complexes **3** and **4**, both of which interconvert with **5**, as revealed by NMR experiments. A larger excess of MeCN causes **4** to bind an extra MeCN molecule to give **3** exclusively. Conversely, dilution of solutions containing **3** with $CDCl_3$ regenerated compounds **4** and **5**. The C_2 symmetry of the trigonal complex **4** was confirmed by NMR spectroscopy as well as by a single-crystal X-ray diffraction study (Figure 1). As anticipated, the two

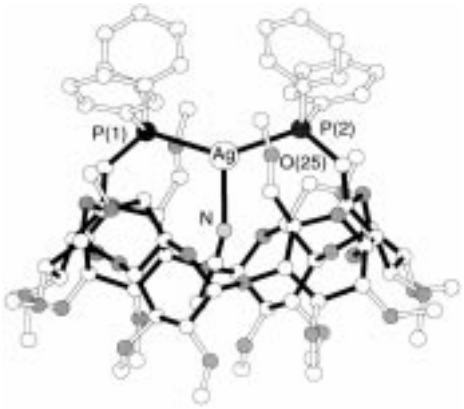


Figure 1. X-ray structure of **4** showing the encapsulated MeCN ligand. The BF_4^- ion and the solvent molecules are not shown. Selected bond lengths [Å] and angles [°]: Ag-P(1) 2.570(4), Ag-P(2) 2.558(4), Ag-N(1) 2.41 (1), P(1)-Ag-P(2) 142.9(1), P(1)-Ag-N(1) 108.9(4), P(2)-Ag-N(1) 108.2(4), Ag-N(1)-C(1) 158.3 (2), N(1)-C(1)-C(2) 173.2 (2). Shortest Ag···O separation: 3.86(1) Å (Ag-O(25)).

phosphorus atoms point towards the interior of the cavity. The trigonal-planar coordination mode forces the coordinated MeCN molecule to be included in the CD cavity which does not undergo significant deformation upon complexation. However, compared to the related complex $[Ag(PPh_3)_2(NCMe)]BF_4$,[26] the Ag–P bonds are unusually long (av 2.56 Å vs. 2.44 Å), reflecting the shortness of the two phosphane arms. Incidentally, the stereochemistry of the silver atom significantly deviates from an ideal trigonal geometry; the P-Ag-P angle (142.9(1)°) is considerably larger than 120°. This geometry is comparable to those observed in trigonal-planar silver complexes obtained with Venanzi's *trans*-spanning ligands.[27] Interestingly, the Ag–N bond is also longer than usual (2.41(1) Å vs. 2.321(2) Å in $[Ag(PPh_3)_2(NCMe)]BF_4$), consistent with a weakly bonded nitrile. Finally, we note that the nitrile rod is slightly bent with respect to the Ag–N axis (Ag-N(1)-C(1) 158.3(2)°).

The aforementioned experiments provide, for the first time, spectroscopic evidence for dinitrile complexes of the type $[Ag(phosphane)_2(MeCN)_2]^+$, although such species have already been proposed.[28] In contrast, related monoacetonitrile silver cations are well documented.[26] Subtle interactions between the cavity and the acetonitrile ligand may contribute to the unexpected stabilization of the "$Ag(MeCN)_2$" unit by cavitand **2**.

Finally, the addition of benzonitrile (ca. 8 equiv) to a solution of **3** in a $CHCl_3$/MeCN mixture (**3**/MeCN = 1:15) resulted in the quantitative formation of complex **6** in which a single benzonitrile molecule is coordinated to the silver ion, as revealed by the corresponding ES-MS spectrum. A range of correlations between some H-3 as well as MeO-3 protons[29] and aromatic protons belonging to the entrapped guest in the 2D ROESY spectrum of **6** confirmed the inclusion of benzonitrile in the CD cavity. Careful examination of the 2D spectra reveals that, upon complexation, the orientation of the benzonitrile plane must be close to that of the P-Ag-P plane. In addition, as a result of the magnetic field anisotropy created by the included phenyl ring, the MeO-3 and MeO-2 signals in the ^{1}H NMR spectrum ($CDCl_3$) are considerably more spread out in **6** than in **3** ($\Delta\delta = 0.65$ vs. 0.2). Clearly, the CD cavity does not allow the coordination of more than one benzonitrile molecule, but can easily accomodate two smaller nitrile ligands such as MeCN. Favorable van der Waals interactions between the inner walls of the CD torus and the cavity-matching phenyl residue, together with the better electron-donating ability of benzonitrile, are likely to account for the higher stability of **6** compared to **4**.

Experimental Section

2: Selected data: ^{1}H NMR (400.1 MHz, $CDCl_3$, 25 °C; assignment by COSY): $\delta = 2.18$, 3.29 (AB, $^2J_{AB} = 10.4$ Hz, 4H; H-6$^{C,F\ or\ B,E}$), 2.50, 2.67 (br AB, 4H; H-6^{A,D}), 2.76 (s, 6H; CH_3O-6), 2.99 (s, 6H; CH_3O-6), 3.10 (dd, 2H; H-2$^{C,F\,or\,B,E}$), 3.15 (dd, 2H; H-2$^{B,E\,or\,C,F}$), 3.22 (dd, 2H; H-2^{A,D}), 3.28, 4.05 (AB, $^2J_{AB} = 10.5$ Hz, 4H; H-6$^{B,E\ or\ C,F}$), 3.40 (t, 2H; H-4^{A,D}), 3.45 (s, 6H; OCH_3), 3.47 (s, 6H; OCH_3), 3.51 (s, 6H; OCH_3), 3.57 (t, 2H; H-3^{A,D}), 3.58 (t, 2H; H-3$^{C,F\ or\ B,E}$), 3.59 (t, 2H; H-3$^{B,E\ or\ C,F}$), 3.61 (s, 6H; OCH_3), 3.63 (s, 6H; OCH_3), 3.64 (t, 2H; H-4$^{C,F\,or\,B,E}$), 3.64 (t, 2H; H-5$^{C,F\ or\ B,E}$), 3.65 (s, 6H; OCH_3), 3.71 (t, $^3J = 8.9$ Hz, 2H; H-4$^{B,E\ or\ C,F}$), 3.79 (m, 2H, $^3J = 9.6$ Hz, 2H; H-5$^{B,E\ or\ C,F}$), 4.39 (m, $^3J = 8.8$ Hz, 2H; H-5^{A,D}), 4.93 (d, $^3J_{H\text{-}2,H\text{-}1} = 2.9$ Hz, 2H; H-1^{A,D}), 5.01 (d, $^3J_{H\text{-}2,H\text{-}1} = 3.2$ Hz, 2H; H-1$^{B,E\,or\,C,F}$), 5.03 (d, $^3J_{H\text{-}2,H\text{-}1} = 3.6$ Hz, 2H; H-1$^{C,F\,or\,B,E}$), 7.22–7.64 (m, 20H; arom. H); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25 °C): $\delta = -17.8$ (s). Elemental analysis (%): calcd for $C_{76}H_{110}O_{28}P_2$ (1533.62): C 59.52, H 7.23; found: C 59.80, H 7.48.

3: The ^{31}P NMR spectrum in $CDCl_3$ reveals the presence of a mixture of **3**, **4**, and **5** (^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25 °C): $\delta = 7.7$ (2d, $^{107}J_{Ag,P} = 458$, $^{109}J_{Ag,P} = 529$ Hz; **3**), 6.1 (2d, $^{107}J_{Ag,P} = 417$, $^{109}J_{Ag,P} = 480$ Hz; **4**), −3.5 (2d, $^{107}J_{Ag,P} = 503$, $^{109}J_{Ag,P} = 581$ Hz; **5**)). When the spectrum was recorded in pure CD_3CN, only **3** was detected. ^{1}H NMR (400.1 MHz, CD_3CN, 25 °C): $\delta = 2.52$ (d, 2H, $^2J = 10.6$ Hz; H-6b^{A,D}, tentative assignment), 2.78 (s, 6H; CH_3O-6), 2.83 (s, 6H; CH_3O-6), 3.43 (s, 6H; OCH_3), 3.44 (s, 6H; OCH_3), 3.49 (s, 6H; OCH_3), 3.56 (s, 6H; OCH_3), 3.57 (s, 6H; OCH_3), 3.60 (s, 6H; OCH_3), 2.84–3.69 (32H; H-2, H-3, H-4, H-5^{B,C,E,F}, H-6a, H-6b^{B,C,E,F}), 4.44 (m, 2H; H-5^{A,D}), 4.79 (d, $^3J_{H\text{-}2,H\text{-}1} = 2.6$ Hz, 2H; H-1), 4.95 (d, $^3J_{H\text{-}2,H\text{-}1} = 3.2$ Hz, 2H; H-1), 5.14 (d, $^3J_{H\text{-}2,H\text{-}1} = 3.2$ Hz, 2H; H-1), 7.35–7.80 (m, 20H; arom. H); ^{31}P{^{1}H} NMR (121.5 MHz, CD_3CN, 25 °C): $\delta = 7.6$ (2d, $^{107}J_{Ag,P} = 458$, $^{109}J_{Ag,P} = 529$ Hz); MS (ES): m/z (%): 1741.3 (13) [$M^+ - BF_4 + H_2O$]. As deduced from 2D NMR experiments, the Me signals of free and coordinated MeCN overlap ($\delta = 1.90$–2.10). All protons of **3** could be assigned by a COSY experiment ($CDCl_3$/CH_3CN). The latter experiment also allowed to unambiguously distinguish protons of **3** from those of **4**.

5: ^{1}H NMR (500.1 MHz, $C_2D_2Cl_4$, 27 °C): $\delta = 2.81$ (s, 3H; CH_3O-6), 2.90 (s, 3H; CH_3O-6), 3.07 (s, 3H; CH_3O-6), 3.24 (s, 3H; CH_3O-6), 3.36 (s, 3H; OCH_3), 3.42 (s, 3H; OCH_3), 3.47 (s, 6H; OCH_3), 3.49 (s, 6H; OCH_3), 3.51 (s, 3H; OCH_3), 3.59 (s, 3H; OCH_3), 3.63 (s, 6H; OCH_3), 3.64 (s, 3H; OCH_3), 3.74 (s, 3H; OCH_3), 2.80–4.30 (36H, H-2, H-3, H-4, H-5, H-6), 4.67 (d, $^3J_{H\text{-}1,H\text{-}2} = 2.0$ Hz, 2H; H-1), 4.79 (d, $^3J_{H\text{-}1,H\text{-}2} = 4.2$ Hz, 2H; H-1), 4.90 (d, $^3J_{H\text{-}1,H\text{-}2} = 2.6$ Hz, 2H; H-1), 5.09 (d, $^3J_{H\text{-}1,H\text{-}2} = 3.0$ Hz, 2H; H-1), 5.39 (d, $^3J_{H\text{-}1,H\text{-}2} = 3.0$ Hz, 2H; H-1), 5.45 (d, $^3J_{H\text{-}1,H\text{-}2} = 3.6$ Hz, 2H; H-1), 7.10–7.65 (20H; arom. H); ^{31}P{^{1}H} NMR (121.5 MHz, $C_2D_2Cl_4$, 25 °C): $\delta = 11.37$ (2d, $^{107}J_{Ag,P} = 488$, $^{109}J_{Ag,P} = 565$ Hz; **5a**), 11.60 (2d, $^{107}J_{Ag,P} = 483$, $^{109}J_{Ag,P} =$

  1433-7851/01/4013-2528 $ 17.50+.50/0

559 Hz; **5b**). Elemental analysis (%): calcd for $C_{76}H_{110}O_{28}P_2BF_4Ag$ (1728.30): C 52.82, H 6.41; found: C 53.08, H 6.45; MS (FAB): *m/z* (%): 1657.4 (60) $[M^+ - BF_4 + O]$, 1641.4 (100) $[M^+ - BF_4]$.

6: ^{1}H NMR (400.1 MHz, $CDCl_3/C_6H_5CN$, 25 °C; assignment by COSY): $\delta = 2.28$, 3.60 (AB, $^2J_{AB} = 10.2$ Hz, 4H; H-6$^{B,E \text{ or } C,F}$), 2.73 (s, 6H; OCH_3), 2.76, 3.30–3.35 (br AB (×2), 8H; H-6^{A,D} and H-6$^{C,F \text{ or } B,E}$), 2.93 (s, 6H; OCH_3), 2.95 (t, 2H; H-3$^{B,E \text{ or } C,F}$), 2.95 (t, 2H; H-3$^{C,F \text{ or } B,E}$), 3.00 (d, 2H; H-2$^{C,F \text{ or } B,E}$), 3.03 (s, 6H; OCH_3), 3.05 (d, 2H; H-5$^{C,F \text{ or } B,E}$), 3.05 (d, 2H; H-2$^{B,E \text{ or } C,F}$), 3.32 (s, 6H; OCH_3), 3.35 (d, 2H; H-2^{A,D}), 3.37 (s, 6H; OCH_3), 3.40 (d, 2H; H-5$^{B,E \text{ or } C,F}$), 3.50 (s, 6H; OCH_3), 3.50 (br, 2H; H-4^{A,D}), 3.52 (s, 6H; OCH_3), 3.55 (d, 2H; H-4$^{B,E \text{ or } C,F}$), 3.65 (d, 2H; H-4$^{C,F \text{ or } B,E}$) 3.70 (s, 6H; OCH_3), 3.75 (t, 2H; H-3^{A,D}), 4.70 (m, 2H; H-5^{A,D}), 4.84 (d, $^3J_{H\text{-}2,H\text{-}1} = 2.2$ Hz, 2H; H-1$^{C,F \text{ or } B,E}$), 4.88 (d, $^3J_{H\text{-}2,H\text{-}1} = 2.6$ Hz, 2H; H-1^{A,D}), 5.16 (d, $^3J_{H\text{-}2,H\text{-}1} = 3.3$ Hz, 2H; H-1$^{B,E \text{ or } C,F}$), 7.35–7.90 (m, 20H, arom. H); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3/C_6H_5CN$, 25 °C): $\delta = 8.7$ (2d, $^{107}J_{Ag,P} = 458$, $^{109}J_{Ag,P} = 529$ Hz); MS (ES): *m/z* (%): 1744.7 (22) $[M^+ - BF_4]$.

Crystal structure analysis of $\mathbf{4} \cdot H_2O \cdot 3CH_3CN$: crystals suitable for X-ray diffraction were obtained by slow diffusion of diisopropyl ether into a butanone–acetonitrile (100:1, v/v) solution of the complex; $M_r = 1910.56$, triclinic, space group $P\bar{1}$, $a = 13.7530(4)$, $b = 14.4944(6)$, $c = 15.0189(6)$ Å, $V = 2447.8(6)$ Å^3, $Z = 1$, $\rho = 1.30$ g cm^{-3}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu = 0.321$ mm^{-1}. Data were collected on a Kappa CCD Enraf Nonius system at 173 K. The structure was solved by direct methods and refined on F_o^2 by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically. The absolute structure was determined by refining Flack's *x* parameter. $R1 = 0.069$ and $\omega R2 = 0.089$ for 5753 data with $I > 3\sigma(I)$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157445. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[19] Complex **5** crystallized with a water molecule located outside the cavity. The latter is hydrogen-bonded to the BF_4^- ion and a MeO-3 oxygen atom. Similar noncovalent aggregates are known to withstand the conditions used for this ES-MS experiment.
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[23] Owing to C_2 symmetry, the B and C glucose units are equivalent to the E and F units, respectively.
[24] The whole variable-temperature NMR study required the use of two distinct solvents, CD_2Cl_2 (−40–20 °C) and $C_2D_2Cl_4$ (20–100 °C). The coalescence temperature for the two low-energy processes is close to the boiling point of CD_2Cl_2 and hence the corresponding activation barriers could not be determined accurately.
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Ruthenium Nitrides: Redox Chemistry and Photolability of the Ru–Nitrido Group**

Lucia Bonomo, Euro Solari, Rosario Scopelliti, and Carlo Floriani*

The metal nitride[1] group plays a key role in nitrogen transfer to organic[2–4] and inorganic[5] substrates. Such reactivity exists when the nitrido group is associated with a labile metal, which generally displays catalytic properties. To this end we considered the ruthenium ion in *meso*-octamethylporphyrinogen,[6] which is related to porphyrin—the macrocycle par excellence in ruthenium chemistry. Ruthenium nitride chemistry[7] has received considerable attention in the recent past, and some major issues are considered here: 1) the formation of the Ru≡N group by cleavage of N–N bonds[7] which mimic the N_2 molecule; 2) the redox chemistry associated with the [Ru≡N] fragment, with the intent of tuning the nucleophilic–electrophilic properties of the nitrido group;[7a,b] 3) the relationship between the terminal [Ru≡N] and the bridging [Ru=N=Ru] groups; 4) the photolabilization of Ru–N bonds; and 5) the use of a tetrapyrrolic macrocycle related to porphyrin, a key ligand in Ru chemistry and one with which the Ru≡N group has so far not been associated.

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