$\beta = 1.49$ Å^{-1}.[3a] This value is practically identical to that observed in the present study. However, our data is quite different from that of Murphy et al. ($\beta = 0.2$ Å^{-1}),[8a] although the same mediator was used. This large discrepancy could not be explained with the above description.

In conclusion, we measured the long-range electron transfer through a DNA helix and its distance dependence by introducing a dye precisely into a DNA helix. Since these modified DNA are readily prepared by a DNA synthesizer, it is easy to introduce the second or third dyes into the DNA structure and to change the base sequence. We are now in the position to use this system to delineate the reorganization energy, the reverse electron transfer, and the effect of base stacking[16] in a DNA π frame.

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Overcoming a Longstanding Challenge: X-Ray Structure of a $[Co_2(CO)_6]$-Complexed Propargyl Cation**

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The ability of mono- and polynuclear transition metal clusters to dramatically enhance the stability of neighboring carbocationic centers is well documented.[1–3] NMR spectroscopy has been widely used to structurally characterize homo- and heteronuclear metal complexes;[4] on the contrary, X-ray crystallography has been used to a lesser extent because of the thermal lability and low crystallinity of organometallic cations. Chronologically, ferrocenyl-[5] and bis(tricarbonylcyclobutadienyliron)-stabilized[6] methyl cations were characterized first, followed by a variety of organometallic species[7–11] with tetrahedral (or quasi tetrahedral) metal cores (Mo_2C_2,[7] $MoCoC_2$,[7a, 8, 11] W_2C_2,[9] and $CoFeC_2$[11]). The synthesis and structure of the propargyl cation stabilized by the $[Co_2(CO)_6]$ cluster have been thoroughly investigated.[12] NMR studies[13–15] revealed two modes of fluxionality, a low-energy *antara*-facial motion of the cationic center between metal atoms, and a high-energy rotation around the bond between the cationic center and the cluster (apical C – C

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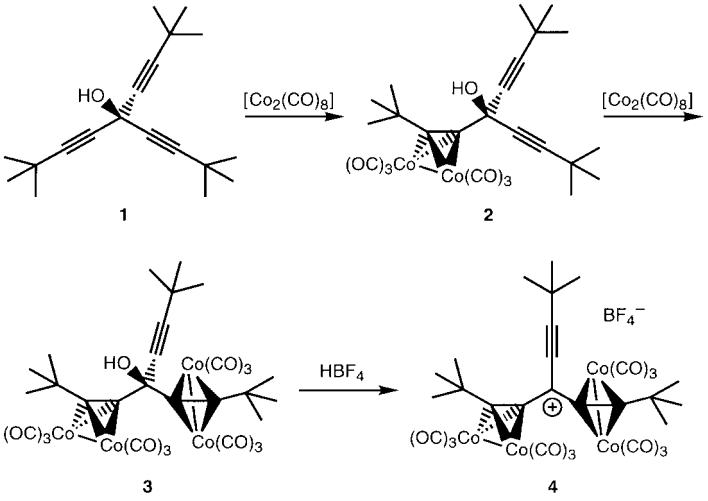
double bond).[14] Although a $[Co_2(CO)_6]$-complexed propargyl cation was isolated two decades ago,[13a] the X-ray crystal structure of such a cation was hitherto unknown.[2, 12]

As a part of a continuing study of the chemistry of π-bonded organometallic radicals and carbocations,[16] we report herein the synthesis and the first X-ray characterization of a doubly stabilized $[Co_2(CO)_6]$-complexed propargyl cation. The adopted strategy consists of introducing two charge-stabilizing metallaalkyne moieties in the α position to the cationic center to enhance the thermal stability and crystallinity of target species. The starting material **1** was synthesized by a modified literature procedure[17] in 55% yield (Scheme 1). Alkyne moieties of the latter were consecutively protected with $[Co_2(CO)_6]$ groups[18] to generate mono- and diclusters **2** and **3**[19] (Figure 1), respectively. Treatment of **3** with HBF_4 resulted in the salt **4** of the corresponding complex cation, a black solid stable at ambient temperature under aerobic conditions, which rapidly decomposes in solution (CH_2Cl_2, acetone).



Scheme 1. Synthesis of **4** from the triyne **1**.

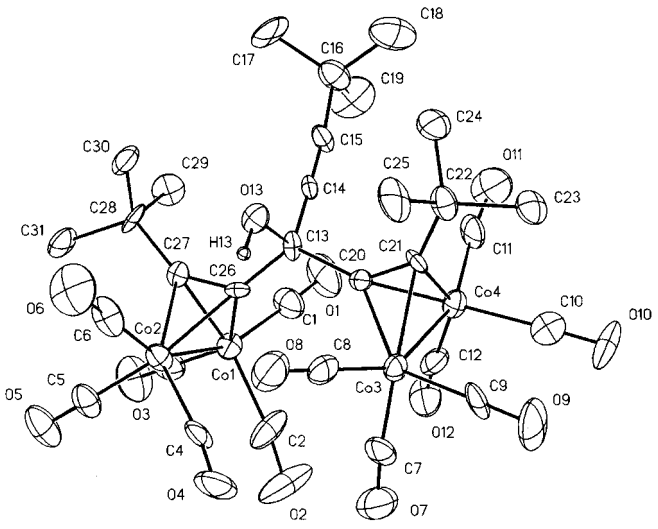


Figure 1. Molecular structure of **3** (30% probability ellipsoids). Selected interatomic distances [Å] and angles [°]: C13–C20 1.49(2), C13–C26 1.53(2), C13–C14 1.43(2), C13–Co1 3.29(1), C13–Co2 3.25(1), C13–Co3 3.26(1), C13–Co4 3.25(1); C14-C13-C20 108.9(11), C14-C13-C26 108.0(10), C20-C13-C26 119.5(12), C14-C13-O13 108.0(12), C20-C13-O13 106.0(10), C26-C13-O13 105.9(10), C27-C26-C13 133.6(12), C21-C20-C13 134.8(13), C28-C27-C26-C13 4.8(1), C22-C21-C20-C13 4.4(1); angle between the bonds C26–C27 and Co1–Co2 89.2(5), between C20–C21 and Co3–Co4 90.1(5), between Co1–Co2 and Co3–Co4 24.2(4).

The structure of **4** was characterized by low-temperature ^1H and ^{13}C NMR spectroscopy (−80 °C) and X-ray crystallography (−105 °C). In the ^1H NMR spectrum, the *tert*-butyl groups are deshielded compared to those in the neutral bis-cluster **3**. The absolute values of $\Delta\delta$ of 0.128 and 0.076 ppm for substituents at the uncomplexed and complexed triple bonds respectively, indicate a higher sensitivity of the former towards developing cationic center. Single crystals of **4** (Figure 2) were obtained by its slow precipitation from an

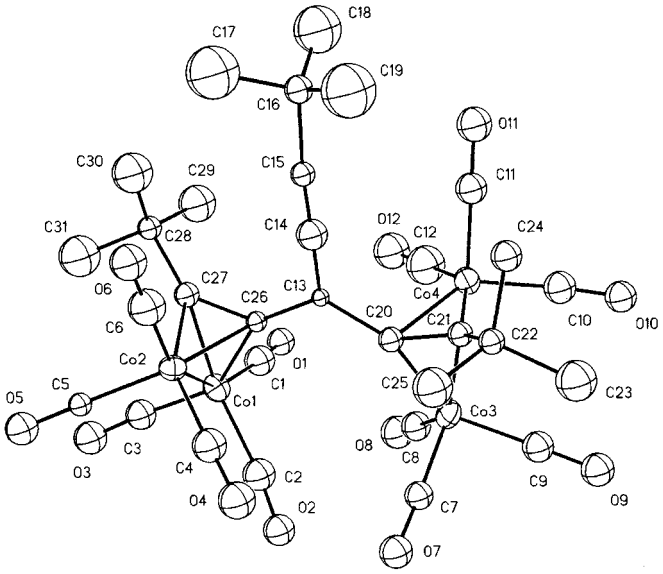


Figure 2. Molecular structure of **4** (30% probability ellipsoids; anisotropic refinement for Co atoms only).Selected interatomic distances [Å] and angles [°]: C13–C20 1.45(2), C13–C26 1.51(2), C13–C14 1.34(2), C13–Co1 3.07(1), C13-Co2 2.81(1), C13-Co3 3.27(1), C13-Co4 2.89(1), C14-C13-C20 120.5(11), C14-C13-C26 118.6(11), C20-C13-C26 120.9(10), C27-C26-C13 135.5(12), C21-C20-C13 135.9(12), C28-C27-C26-C13 55(1), C22-C21-C20-C13 43(1); angle between the bonds C26–C27 and Co1–Co2 82.3(6), between C20–C21 and Co3–Co4 89.7(6), between Co1–Co2 and Co3–Co4 88.0(5).

ethereal solution at −20 °C.[20] Generation of the cation leads to a rehybridization of the central carbon atom (C13) into sp^2, which is substantiated by its nearly flat geometry (out-of-plane $<0.5°$) and nearly ideal trigonal planar arrangement (119–121°). Covalent bonds around the cationic center are shortened slightly because of an increased s-character in hybridized orbitals; remarkably, the C13–C14 bond to the uncoordinated triple bond is more sensitive to the formation of the cation (1.43 Å in **3** vs. 1.34 Å in **4**) than the bonds to the coordinated triple bonds (C13–C20 1.49 vs. 1.45 Å; C13–C26 1.53 vs. 1.51 Å). Unexpectedly, the geometry of coordinated triple bonds (C27-C26-C13, C21-C20-C13) proved indifferent towards charge/hybridization changes of the central carbon atom (**3**: 134–135°, **4**: 136°). One of the important structural characteristics of binuclear metal complexes is the range of possible orientations of the C≡C and metal–metal bonds

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from perpendicular to each other to nearly parallel and σ-bonded.[3] In **3**, the corresponding angles are 89.2° and 90.1°. The development of positive charge at the central carbon atom makes the metal clusters nonequivalent (the angle between C26 – C27 and Co1 – Co2 is 82.3°, that between C20 – C21 and Co3 – Co4 is 89.7°) with one of them adopting a skew geometry, that is a twist from a perpendicular orientation by 7.7°. Among the configurational changes, attendant with generation of a cation in the α-position to the cobalt cluster, is a deviated linearity of the π-bonded ligand and a shift of the cationic center towards one of the vertices. The former is quantified by the magnitude of dihedral angles C28-C27-C26-C13 and C22-C21-C20-C13. In precursor **3** both values are small (4.8° and 4.4°, respectively), indicating a nearly undistorted linear arrangement. The build-up of positive charge at C13 results in preferential coordination of the cationic center with one of the metal atoms in each cluster, and consequently, a significant departure from linearity (55° and 43°, respectively). These findings are further confirmed by analysis of nonbonding distances between the cationic center C13 and all four cobalt atoms. In **3** the central carbon is equidistant from both metal atoms (differences in bond lengths are 0.04 Å for C13 – Co1 and C13 – Co2, and 0.01 Å for C13 – Co3 and C13 – Co4); in contrast, in **4** C13 is shifted 0.26 Å closer towards Co2 and, even more, 0.38 Å towards Co4; the shortest distances are 2.81 Å and 2.89 Å for C13 – Co2 and C13 – Co4, respectively.

Experimental Section

2: a) **1**: Synthesized according to protocol given in reference [17] in a yield of 54.6 %. R_f (TLC, petroleum ether/ether 10/1) = 0.40; m.p. 101 – 102 °C (sealed capillary) (in ref. [17] m.p. 102 – 103 °C); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.24 (s, 27 H; *t*Bu), 2.64 (s, 1 H; OH).

b) Monocomplexation of **1**. A solution of $[Co_2(CO)_8]$ (376 mg, 1.1 mmol) in dry ether (15 mL) was added dropwise to a vigorously stirred solution of **1** (272 mg, 1 mmol) in dry ether (20 mL) at ambient temperature under an inert atmosphere. After the addition (55 min), the reaction mixture was stirred for 2 h (monitored by TLC). Ether was evaporated in vacuum, and the residue was chromatographed on silica gel to afford **2** (483 mg, 86.5 %) as dark red crystals. R_f (TLC, petroleum ether/ether 15/1) = 0.74; m.p. 110 – 122 °C (decomp; sealed capillary); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.21 (s, 18 H; 2*t*Bu), 1.41 (s, 9 H; *t*Bu), 2.70 (s, 1 H; OH); MS-FAB: *m*/*z* (%): 557 (16) [M^+ – H], 530 (100) [M^+ – CO], 390 (15) [M^+ – 6 CO]; C,H analysis ($C_{25}H_{28}O_7Co_2$, 558.4): calcd. C 53.78, H 5.05; found C 53.89, H 5.09.

3: Analogously, treatment of **2** (407 mg, 0.73 mmol) in dry ether (20 mL) with $[Co_2(CO)_8]$ (250 mg, 0.73 mmol) in dry ether (15 mL) afforded **3** (439 mg, 71.3 %) as dark red crystals. R_f (TLC, petroleum ether) = 0.23; m.p. 84 – 101 °C (decomp; sealed capillary); ^{1}H NMR (500 MHz, CD_2Cl_2, – 80 °C, TMS): δ = 1.09 (s, 9 H; *t*Bu), 1.40 (s, 18 H; 2*t*Bu), 3.11 (s, 1 H; OH); ^{13}C NMR (125 MHz, CD_2Cl_2, – 70 °C, TMS): δ = 27.32, 29.00, 32.41, 36.26, 71.50, 84.34, 92.68, 100.41, 115.04, 200.25; MS-FAB: *m*/*z* (%): 843 (6) [M^+ – H], 788 (6) [M^+ – 2 CO], 508 (14) [M^+ – 12 CO]; C,H analysis ($C_{31}H_{28}O_{13}Co_4$, 844.3): calcd. C 44.10, H 3.34; found C 43.98, H 3.41. Single crystals suitable for X-ray structure analysis (Figure 1) were obtained by methanol vapor diffusion into a solution of **3** in pentane.

4: $HBF_4 \cdot Et_2O$ (58 mg, 0.36 mmol) was added dropwise (15 min) to a solution of **3** (101 mg, 0.12 mmol) in dry ether (30 mL) at – 20 °C under an inert atmosphere. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. The ethereal layer was removed with a syringe, and the precipitate was thoroughly washed with dry ether (4 × 20 mL). The resulting complex **4** (96 mg, 88.1 %) was obtained as a black solid. ^{1}H NMR (500 MHz, CD_2Cl_2, – 80 °C, TMS): δ = 1.22 (s, *t*Bu), 1.48 (s, 2 *t*Bu); ^{13}C NMR (125 MHz, CD_2Cl_2, – 70 °C, TMS): δ = 12.25; 14.90; 32.00 (br.), 65.74; 83.58, 194 – 200 (br.). Single crystals suitable for X-ray structure analysis (Figure 2) were obtained by slow addition of HBF_4 to an ethereal solution of **3** at – 20 °C.

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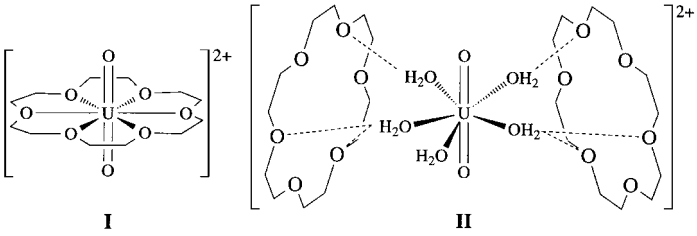
[19] a) Crystal data for **3**: crystal dimensions $0.12 \times 0.20 \times 0.37$ mm, orthorhombic space group *Pbca* (No. 61), $a = 17.277(5)$, $b = 19.393(7)$, $c = 21.190(8)$ Å, $V = 7100(4)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.58$ g cm^{-3}, $\mu = 1.90$ mm^{-1}, $F(000) = 3408$; 10912 reflections with $3.7 < 2\theta < 40.0°$. Structure solution and refinement for 3316 independent reflections with $I > 2\sigma(I)$ and 433 parameters, max./min. empirical absorption correction 0.999/0.878; $R = 0.077$; $R_w = 0.168$; max./min. residual electron density 0.64/ − 1.13 e Å^{-3}. b) Nonius CAD4 diffractometer, $Mo_{K\alpha}$ radiation, graphite monochromator. Structure solution and refinement carried out on DEC 3000 and PC computers by using the programs Open MolEN and SHELXTL Version 5.0 and the Patterson–Fourier method. Hydrogen atoms were included in calculated positions (HFIX). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Centre as supplementary publication no. CCDC-100541. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (UK) (fax: int. code + (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

[20] Crystal data for **4**: crystal dimensions $0.07 \times 0.10 \times 0.23$ mm, tetragonal space group $P4_32_12$(No. 96), $a = 16.562(6)$, $c = 26.637(11)$ Å, $V = 7307(5)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.66$ g cm^{-3}, $\mu = 1.86$ mm^{-1}, $F(000) = 3664$; 9927 reflections with $2.9 < 2\theta < 35.0°$. The crystal was mounted in Paratone oil and all measurements were performed at $-105\,°C$. Structure solution and isotropic refinement, except Co atoms, for 2469 independent reflections with $I > 2\sigma(I)$ and 227 parameters, no absorption correction, DAMP 1000, $R = 0.104$; $R_w = 0.175$; max./min. residual electron density 0.75/ − 0.59 e Å^{-3}.[19b]

Synthesis and Structure of the First Transuranium Crown Ether Inclusion Complex: $[NpO_2([18]Crown\text{-}6)]ClO_4$**

David L. Clark,* D. Webster Keogh, Phillip D. Palmer, Brian L. Scott, and C. Drew Tait

Crown ether ligands[1, 2] have been studied as potential actinide extractants for many years, and they have been shown to influence the partitioning of actinides in two-phase aqueous systems.[3–5] Although many examples of crown ether ligands that extract actinides in hydrocarbon/water systems are known,[6, 7] relatively few actinide crown ether complexes in which the actinide ion is coordinated by one or more donor atoms of the crown ether have been reported.[8] There are only two inclusion compounds of *trans*-dioxoactinide cations AnO_2^{n+} in which the actinide ion is completely encapsulated by a crown ether ligand and the counterions (perchlorate[9, 10] or triflate[11]) are uncoordinated in the crystal lattice: $[UO_2([18]crown\text{-}6)]^{2+}$ (**I**) and $[UO_2(dicyclohexano[18]\text{-}crown\text{-}6)]^{2+}$. It has been claimed that synthesis of inclusion complexes from uranyl ions UO_2^{2+} and crown ether ligands requires the use of weakly coordinating anions, nonaqueous conditions, and proper choice of cavity size.[8] Indeed, the majority of actinide crown ether complexes exhibit second-sphere hydrogen bonding between the oxygen atoms of the crown ether and water molecules coordinated to the actinide center.[12–19] Well-known examples include $[UO_2(H_2O)_5([18]crown\text{-}6)_2(H_2O)(CH_3CN)_2][ClO_4]_2$ (central unit: **II**)[15] and $[UO_2(H_2O)_5([18]crown\text{-}6)][CF_3SO_3]_2$.[17]



I **II**

Crown ether inclusion complexes of a transuranic ion in any oxidation state are unknown.

On attempting to employ this well-known ability of crown ether ligands to form second-sphere hydrogen-bonded complexes of *trans*-dioxometal ions (as in **II**), we were surprised to observe the complete encapsulation of the NpO_2^+ ion by the [18]crown-6 ligand. Addition of one equivalent of [18]crown-6 to a stirred solution of NpO_2^{2+} in 1 M HX ($X = ClO_4^-$, $CF_3SO_3^-$) resulted in reduction of Np^{VI} to Np^V and formation of large turquoise crystals of $[NpO_2([18]crown\text{-}6)][X]$ (**1**[X]) over 12–24 h. The presence of an absorption band at 980 nm ($\varepsilon = 395$ M^{-1} cm^{-1}), characteristic of the NpO_2^+ ion,[20] in the NIR spectra of the crystalline solids dissolved in 1 M $HClO_4$ confirms that reduction of Np^{VI} to Np^V has occurred. Even in the presence of O_3, the Np^{VI} was reduced to **1**[X] on addition of [18]crown-6. Finally, solutions of Np^V compounds in 1 M HX, which are present as hydrated NpO_2^+ ions, react smoothly with [18]crown-6 to give **1**[X] in almost quantitative yield.

A single-crystal X-ray diffraction study of **1**[ClO_4] revealed an NpO_2^+ ion completely encapsulated by a disordered [18]crown-6 ligand.[21] The Np center of the $[NpO_2([18]crown\text{-}6)]^+$ ion is coordinated by two *trans* oxo ligands and six approximately coplanar crown ether O atoms to give an approximate hexagonal bipyramidal coordination environment (Figure 1). In the crown ether ligand, all C-O-C-C units have an *anti* (a), and the O-C-C-O units a *gauche* conformation (g), and this results in a distorted $g^-g^+g^+g^-g^+g^+$ conformation,[22] similar to that reported for **I**.[11] The Np=O bond length of 1.800(5) Å is unusually short for an NpO_2^+ ion; 1.85 Å is usual.[23, 24] The average equatorial Np–O distance of 2.594(10) Å is unusually long for a neutral oxygen-donor ligand when compared with the U–OH_2 distance of 2.43 Å in $[UO_2(OH_2)_5]^{2+}$ complexes.[15, 17] Coordination of σ-donor ligands in the equatorial plane of an *trans*-dioxo actinide ion generally results in a slight lengthening of the An=O bond, accompanied by decreased intensity of the Raman-active ν_1 O=An=O stretching band.[25] However, in **1**[ClO_4] the Np=O bond is shorter, and presumably stronger, than in the uncomplexed cation. Similar structural changes are observed in the uranyl system, for which encapsulation by [18]crown-6 results in a significant shortening of the U=O bond from 1.758(2) to 1.64(4) Å.[15, 17]

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