reaction vessel equipped with a magnetic stirrer bar. After the mixture was stirred for 3 days at 80 °C, the solvent and volatile components were removed in vacuo. The yellow solid was then washed with hexane, filtered, and dried in vacuo. Yield: 95.6 %. Elemental analysis: calcd: C 74.25, H 9.43, N 4.44, Al 4.27; found: C 73.94, H 9.53, N 4.52, Al 4.24; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.36$ (s, 1 H), 8.15 (s, 1 H), 7.47–7.50 (dd, $J = 2.7$, 8.0 Hz, 2 H), 6.98–7.05 (dd, $J = 2.7$, 17.0 Hz, 2 H), 3.92 (t, $J = 9.6$ Hz, 1 H), 3.71 (sept, $J = 5.7$ Hz, 1 H), 3.04 (t, J 9.6 Hz, 1 H), 2.60 (br s, 1 H), 2.40 (br s, 1 H), 2.06 (b, 2 H), 1.55 (s, 9 H), 1.52 (s, 9 H), 1.47 (m, 4 H), 1.30 (s, 9 H), 1.29 (s, 9 H), 0.86 ppm (dd, $J = 5.7$, 7.5 Hz, 6 H); ^{27}Al NMR (104 MHz, toluene/[D$_8$]toluene (v/v: 2/1), $Al_2(SO_4)_3$ in D_2O): $\delta = 35.45$ ppm ($w_{1/2} = 954$ Hz).

(*rac*)-**1**: Elemental analysis: calcd: C 74.25, H 9.43, N 4.44, Al 4.27; found: C 74.28, H 9.42, N 4.50, Al 4.13; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.36$ (s, 1 H), 8.15 (s, 1 H), 7.47–7.50 (dd, $J = 2.4$, 7.5 Hz, 2 H), 6.98–7.05 (dd, $J = 3.0$, 17.1 Hz, 2 H), 3.92 (t, $J = 10.5$ Hz, 1 H), 3.71 (sept, $J = 5.7$ Hz, 1 H), 3.04 (t, $J = 10.5$ Hz, 1 H), 2.60 (br s, 1 H), 2.40 (br s, 1 H), 2.06 (br s, 2 H), 1.55 (s, 9 H), 1.52 (s, 9 H), 1.47 (m, 4 H), 1.30 (s, 9 H), 1.29 (s, 9 H), 0.86 ppm (dd, $J = 5.7$, 7.5 Hz, 6 H).

Solution polymerization (typical experiment): The catalyst (*rac*)-**1** (0.102 g, 0.162 mmol), D,L-LA (1.44 g, 10 mmol), and toluene (12 mL) were added to a dried reaction vessel equipped with a magnetic stirrer bar. The vessel was placed in an oil bath at 70 °C (thermostat control) and stirred for 12 days. Acetic acid was added to terminate the polymerization. A sample was taken for the determination of the conversion by ^{1}H NMR spectroscopy. The solvent was removed by rotary evaporation, the remaining residues were redissolved in CH_2Cl_2, and the polymer was precipitated from excess cold methanol. Filtration, followed by drying at 40 °C in vacuo yielded a white crystalline polymer. Conversion = 85.3 %, M_n (GPC) = 7.7×10^3, $M_w/M_n = 1.06$.

Solvent-free polymerization (typical experiment): The catalyst (*rac*)-**1** (0.065 g, 0.103 mmol) and D,L-LA (3.0 g, 20.8 mmol) were stirred at 130 °C for 2 days. A sample was taken for determination of the conversion by ^{1}H NMR spectroscopy. The polymer was isolated by dissolution in CH_2Cl_2, precipitation from excess ethanol, filtration, and drying at 40 °C in vacuo. Conversion = 94.8 %, M_n (GPC) = 24.9×10^3, $M_w/M_n = 1.37$.

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Unprecedented Coupling of Allenylidene and Diynyl Metal Complexes: A Bimetallic Ruthenium System with a C_7 Conjugated Bridge**

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Jean-Luc Fillaut, Stéphane Golhen, and
Pierre H. Dixneuf

Organometallic complexes with π-conjugated bridges have gained importance in view of potential applications in the emerging field of molecular-scale electronic devices.[1,2] An attractive pursuit in this area is the design of molecular wire precursors that allow exchange of electrons through bridges between remote terminal groups.[2–6] A variety of different approaches have been applied to construct such entities, the majority of which have contained an even number of carbon atoms in the bridge.[2,3] By contrast, only a few complexes with

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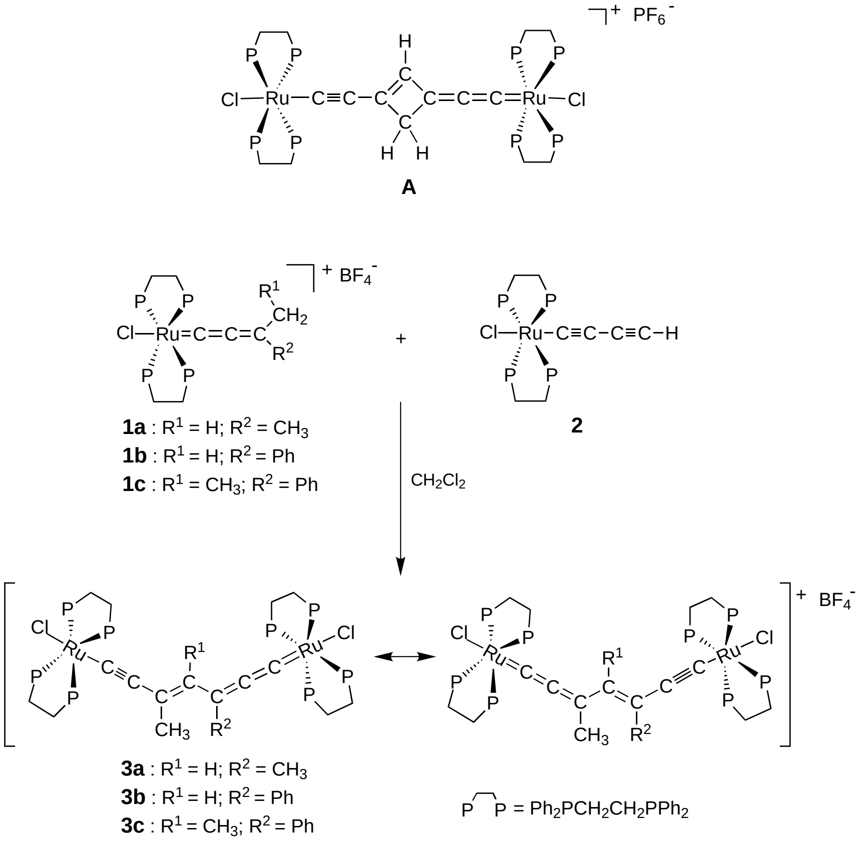
odd-numbered carbon chains or cyclic bridges have been described.[4–7] The most general process involves [2+2] cycloadditions between vinylidene [M]=C=CHR or allenylidene [M]=C=C=CR^{1}R^2 species and the C$_\alpha$≡C$_\beta$ bond of acetylides [M]−C≡C−R or diynyl complexes [M]−C≡C−C≡C−R. These reactions lead to the formation of rigid four-membered cyclic bridges with a delocalized C_3 path between the metal centers.[6] Thus, the limited number of well-defined synthetic processes limits the construction of systems with odd-numbered carbon chains from small to nanoscale devices. Recently, we reported the first complex with an annelated C_7 bridge **A** (Scheme 1); complex **A** resulted from an unprecedented electron-promoted [2+2] cycloaddition exclusively at the C$_\gamma$≡C$_\delta$ bond of a diynyl metal complex, and involved a transient radical cumulenic species.[7] These results provided impetus to investigate reactions between cationic cumulenic species and a diynyl metal complex in which steric protection at the C$_\alpha$≡C$_\beta$ bond controls the regioselective addition at the C$_\gamma$≡C$_\delta$ bond. Based on the use of the [Cl(dppe)$_2$Ru]$^+$ moiety[8] (dppe = 1,2-diphenyphosphanylethane), we now report a novel simple method for coupling metal allenylidenes with a metal diyne to obtain a new class of C_7 carbon-rich bimetallic systems *trans*-[Cl(dppe)$_2$Ru−C≡C−C(CH$_3$)=C(R^1)−C(R^2)=C=C=Ru(dppe)$_2$Cl]BF$_4$ with pendant groups on the linear conjugated bridging ligand.

The synthetic route to the new ruthenium bimetallic complexes is outlined in Scheme 1. The allenylidene complexes **1a–c** were synthesized by reaction of the 16-electron species [Cl(dppe)$_2$Ru]BF$_4$ with the appropriate propargylic alcohol. These cationic complexes **1a–c** were allowed to react overnight, at room temperature, with one equivalent of the neutral diyne compound **2.** Consequently, a metal-assisted C−C bond-forming reaction took place and stable dark green crystals of **3a–c** were isolated in good yields (69–75%) after several crystallizations. The complexes **3a–c** were also obtained in similar yields when the reaction was performed with the protected diyne *trans*-[Cl(dppe)$_2$Ru−C≡C−C≡C−SiMe$_3$][7] as starting material instead of **2**. Thus, spontaneous deprotection occurs in the reaction medium in the presence of the ruthenium allenylidene salt, and prior desilylation is not necessary. Compounds **3a–c** were fully characterized on the basis of their NMR, IR, UV/Vis, and HR-MS (FAB) data. The FTIR spectra for all compounds display an intense absorption around 1900 cm^{-1}, characteristic of the cumulenic character of the chain. The ^{31}P NMR spectrum of **3a** shows one singlet at $\delta = 47.1$ ppm typical for a symmetrical structure, indicating that the two metal sites are equivalent with a *trans* disposition of the chlorine atom to the chain on each metal center. The ^{1}H NMR spectrum of **3a** displays a singlet at $\delta = 5.50$ ppm for the proton (R^1 = H) on the C$_\delta$ atom of the chain, and a single signal for two methyl groups at $\delta = 1.35$ ppm. Conversely, NMR analyses indicate an unsymmetrical structure for the systems **3b** and **3c**. Indeed, the ^{31}P NMR spectrum of **3c** displays two singlets at $\delta = 43.8$ and 49.6 ppm, and the ^{1}H NMR spectrum shows two signals for the two methyl groups at $\delta = 1.27$ and 1.06 ppm. Furthermore the ^{13}C NMR spectrum displays seven different signals for the delocalized carbon chain.[9] It is noteworthy that the resonance signals for the carbon atoms C$_\alpha$ and C$_\alpha$′ of these compounds (**3a**: $\delta = 224$ ppm) are found upfield to that of an allenylidene complex (**1a**: $\delta = 320$ ppm) and downfield to that of an acetylide complex (**2**: $\delta = 123$ ppm), indicating a highly delocalized structure (Scheme 1).



Scheme 1. Synthesis of **3a–3c**.

The structure of complex **3a** was confirmed by X-ray structure analysis (Figure 1).[10] Owing to the inversion center, the structure can be described as two identical bulky ruthenium fragments [RuCl(dppe)$_2$]$^+$ that are connected by a planar "W"-shaped C_9H_7 bridge to minimize steric repulsions. The Cl-Ru1-C53-C54-C55 arrangement is almost linear. As observed for the annelated compound **A**,[7] the Ru1−C53 (1.923(9) Å) and C54−C55 (1.390(13) Å) bonds are significantly shorter than the related single bonds in a ruthenium alkyne system and longer than the corresponding double bonds in a metal allenylidene.[11] On the other hand, the C53−C54 bond length (1.218(12) Å) is intermediate between the values found in these mononuclear systems. The different angles about C55 and C56 are close to 120° showing the high sp^2 nature of these carbon atoms. Along with the C55−C56 bond length (1.401(11) Å),

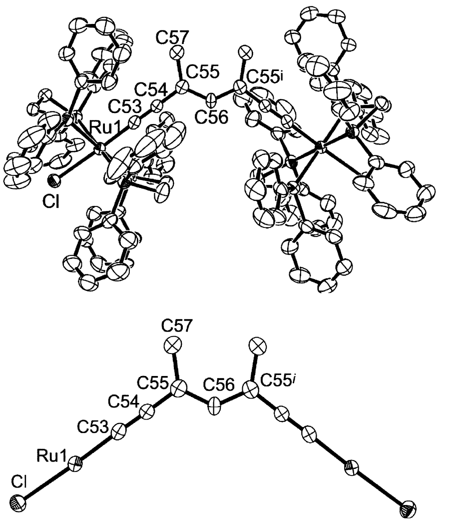


Figure 1. Molecular structure of **3a**. Selected bond lengths [Å] and angles [°]: Ru1-C53 1.923(9), C53-C54 1.218(12), C54-C55 1.390(13), C55-C56 1.401(11), C55-C57 1.528(12); C53-Ru1-Cl 177.3(2), C54-C53-Ru1 178.0(8), C53-C54-C55 178.1(11), C54-C55-C56 118.0(9), C54-C55-C57 118.5(8), C56-C55-C57 123.6(9), C55-C56-C55^i 129.8(13).

these data reveal extended π conjugation along this bridge which bears two identical methyl groups (C55−C57 1.528(12) Å) as indicated by the NMR data.

Cyclic voltammetry was performed on complexes **3a–c**, and the results are reported in Table 1. The three compounds undergo a well-defined one-electron reversible oxidation wave followed by an almost reversible or irreversible second oxidation wave consistent with the doubly oxidized species undergoing subsequent chemical reactions. To a first approximation, these two oxidation steps could be viewed as essentially involving the two Ru^{II}/Ru^{III} couples.[5b,8d,12] The large separation of the processes ($\Delta E^\circ = 650$ mV, $K_c = \exp(\Delta E^\circ F/RT) = 1.27 \times 10^{11}$ for **3b**[2a]) is attributable to a combination of phenomena such as strong electronic coupling, columbic repulsion, and/or structural distortion through the oxidations. The singly oxidized compounds (mixed valence) should be stable and isolatable for further studies. These complexes also undergo a well-defined one-electron reduction wave attributable to the reduction of the unsaturated carbon chain,[7,8c] the rather negative values show that the new compounds are electron-rich. This assignment is also supported by the fact that the reduction potential is highly influenced by the introduction of the phenyl group (compare **3b** and **3c** with **3a**). UV/Vis spectra of **3a–c**, which were recorded from the deep green solutions in CH_2Cl_2, show a strong charge transfer band with a significant absorption coefficient (Table 1), and the λ_{max} values are clearly influenced by the nature of the pendant groups on the bridge. These results are consistent with those on the C_5 "V"-shaped compound [CpRu(PPh$_3$)$_2$=C=C=CH−C≡C−Ru(PPh$_3$)$_2$Cp]-BF$_4$, which shows an intense band at lower wavelength ($\lambda_{max} = 600$ nm, $\varepsilon = 72\,000$ mol^{-1} L cm^{-1}), in accord with its shorter conjugated path.[5a] The optical band gaps roughly correlate with the electrochemical band gaps and are indicative of the metal-to-ligand charge transfer (MLCT) nature of the transitions. For example, for **3a** the optical band gap is 1.70 eV and $\Delta E^\circ = 1.69$ V. It is worth noting that for complex **A** a band was observed at $\lambda_{max} = 633$ nm (1.95 eV, $\varepsilon = 141\,000$ mol^{-1} L cm^{-1}) and that this red shift (100 nm, 0.25 eV) matches the observed difference in the electrochemical band gap of 0.21 eV ($\Delta E^\circ = 1.90$ V for **A**). Thus, these preliminary results show that a slight structural variation in the C_7 bridges, that is, the "bridging CH$_2$" in **A** is replaced by two methyl groups in **3a**, induces a significant difference in their optical and redox properties. The new linear systems display the highest conjugation and this could be related to the absence of a cycle constraint in the delocalized path by contrast with **A**. These observations support the necessity to tune a general system to find the best physical properties.

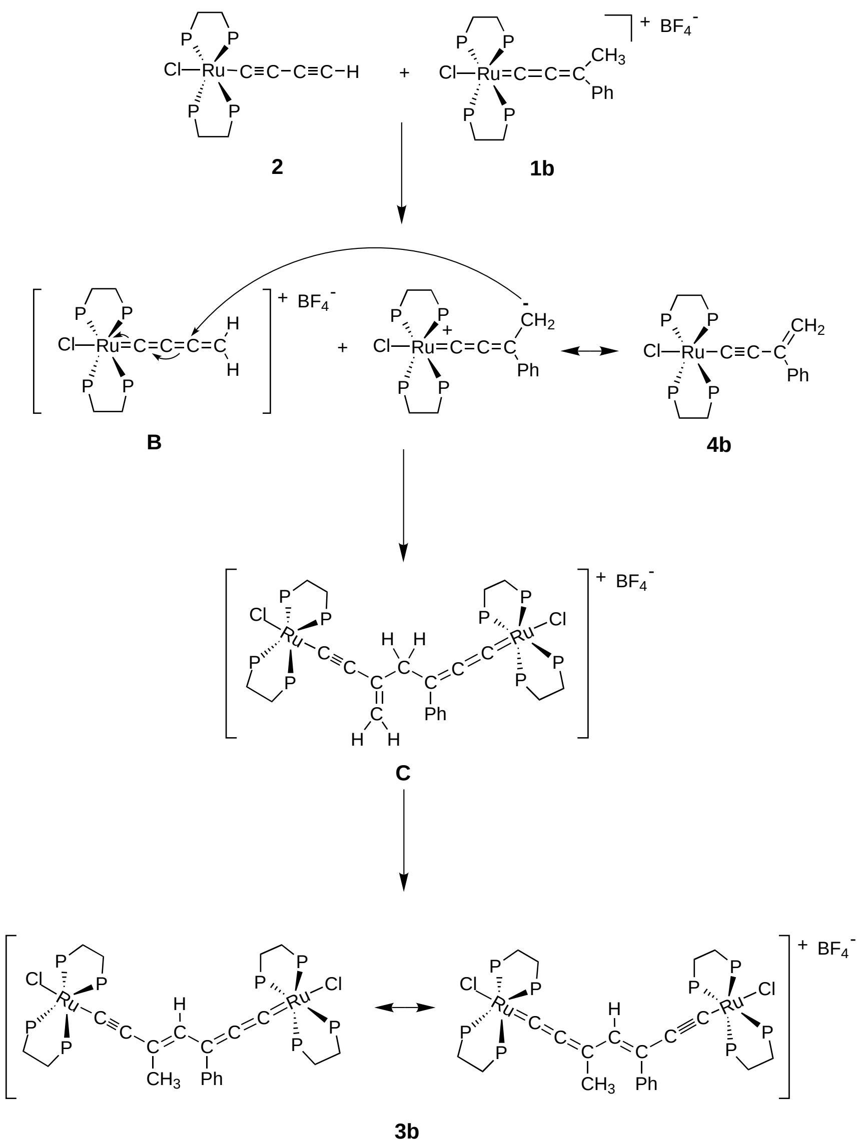
Table 1. Cyclic voltammetry[a] and UV/Vis data for complexes **3a–c**.

	E°_{red} [V][b]	E°_{ox1} [V][b]	E°_{ox2} [V]	λ_{max} [nm]	ε [mol^{-1} L cm^{-1}][e]
3a	−1.38	0.31	0.99[d]	730	122 000
3b	−1.24	0.32	0.97[e]	746	98 000
3c	−1.25	0.23	1.06[d]	764	109 000

[a] Sample, 1 mM; Bu$_4$NPF$_6$ (0.1M) in CH_2Cl_2; $\upsilon = 100$ mV s^{-1}; potentials are reported in Volt versus ferrocene as an internal standard. [b] Reversible redox processes $\Delta E_p \approx 60$ mV, $I_{pc}/I_{pa} \approx 1$. [c] In CH_2Cl_2. [d] Peak potential of an irreversible process. [e] Partially reversible peak $\Delta E_p \approx 95$ mV, $I_{pc}/I_{pa} < 1$.

A possible mechanism for the reaction was established by monitoring the formation of **3b** by ^{31}P NMR spectroscopy. Two features were observed: 1) at the beginning of the reaction, the appearance of two signals of similar intensity at $\delta = 53.6$ and 43.2 ppm and a signal of weak intensity at $\delta = 51.2$ ppm; 2) the gradual disappearance of these peaks and the emergence of two new signals corresponding to the final complex **3b**. The signal at $\delta = 51.2$ ppm can be attributed to the transient formation of the acetylide **4b** as the initial step of the reaction (Scheme 2). Indeed, ruthenium allenylidenes with a -CHRR′ group at the C_γ atom are easily deprotonated into stable ruthenium acetylides by the action of weak bases.[13] As **4** can be easily protonated at the C_δ atom,[8a] the transfer of this proton from **3b** could transform **4** into the unstable butatrienylidene complex **B**. A fast addition of the nucleophilic C_δ atom of **4b** at the electrophilic C_γ atom[12b] of **B** could lead to the intermediate **C**, which formally bears an enyne moiety ($\delta = 53.6$ ppm) and an allenylidene moiety ($\delta = 43.2$ ppm). ^{1}H NMR spectroscopy revealed two broad signals at $\delta = 4.20$ and 5.05 ppm, which were attributable to the ethylenic protons of **C**. They progressively disappeared and were replaced by a unique signal at $\delta = 5.79$ ppm for complex **3b**. The formation of **3b** would result from an allylic hygrogen transfer in the intermediate **C**. This mechanism can be applied to **3a** and **3c**, and is supported by the fact that the reaction does not work with allenylidene complexes such as *trans*-[(dppe)$_2$(Cl)Ru=C=C=CR^{3}Ph]BF$_4$ with R^3 = H, Ph, or CH(CH$_3$)$_2$. Hence, two hydrogen atoms on one group at the C_γ atom of the allenylidene are required: one for the proton exchange between **1** and **2** and another one for the final transfer in **C**.

In conclusion, a novel rational synthesis has been developed to obtain the first bimetallic complexes containing a "W"-shaped C_7 bridge that display remarkable stabilities, and



Scheme 2. Proposed mechanism for the formation of **3a**–**3c**.

interesting spectroscopic and structural properties. To gain a better understanding of the properties of these complexes, theoretical calculations and isolation of mixed-valence species are in progress. The reaction also shows the potential of allenylidene systems as pronucleophiles for further syntheses. In addition, these systems could serve as valuable models for new functionalized one-dimensional wirelike arrangements with the introduction of functional pendant groups on the chain through exhange of R^1 and R^2.

Experimental Section

General procedure for the synthesis of **3a:** CH_2Cl_2 (30 mL) was added to a Schlenk tube containing **1a** (163 mg, 0.15 mmol), and in another tube, **2** (158 mg, 0.15 mmol) was dissolved in CH_2Cl_2 (100 mL). The latter solution was slowly added to the first one over 6 h, using a dropping funnel. This mixture was stirred for an additional 18 h at room temperature. After filtration, the solution was evaporated and the residue was washed with diethyl ether (3 × 25 mL). Crystallization in a CH_2Cl_2/pentane mixture yielded dark green crystals of **3a** (233 mg; 75%), which were characterized by spectroscopic analysis (see Supporting Information).

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[9] Selected data for **3c**: $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, TMS): δ = 245.26 and 220.37 (quint., $^2J(P,C) = 14$ Hz; C_α and $C_{\alpha'}$), 170.47 and 158.22 (s; C_β and $C_{\beta'}$), 157.99 and 146.64 (s; C_γ and $C_{\gamma'}$), 152.11 (s; C_δ-CH_3), 31.01 and 28.97 (m, $|^1J(P,C) + {}^3J(P,C)| = 23$ Hz; CH_2), 30.70 (s; C_γ-CH_3), 22.47 ppm (s; C_δ-CH_3).

[10] Data for X-ray structure analysis of **3a**: $C_{113}H_{103}BCl_2F_{3.5}OP_8Ru_2$: ($M_r = 2075.06$); crystal size $0.20 \times 0.15 \times 0.10$ mm^3, orthorhombic, space group *Pbna*, $a = 13.5145(1)$, $b = 23.8041(3)$, $c = 33.4320(4)$ Å, $V = 10755.1(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.282$ g cm^{-3}, $2\theta_{max} = 25.35°$, $T =$

293(2) K; 18793 reflections measured, 9847 unique (R(int) = 0.0612) and 5293 $I > 2\sigma(I)$; Nonius Kappa CCD, Mo$_{K\alpha}$ radiation (λ = 0.71073 Å), graphite monochromator, Lp correction. The structure was solved by direct methods and refined against F^2 with the full-matrix, least-squares method (G. M. Sheldrick, SHELXS-98, Program for Crystal Structure Analysis, University of Göttingen, Göttingen (Germany), **1998**), 583 parameters, $R1 = 0.1578$, $wR2 = 0.2990$ for all data and $R1 = 0.0892$, $wR2 = 0.2574$ for $I > 2\sigma(I)$; residual electron density 2.104/−0.579 e Å^{-3}. Owing to disorder in the BF$_4^-$ ion, restrain distances were introduced and an occupation factor of 0.5 was applied to all B and F atoms in general positions; the highest residual electron density peaks are localized near this anion. CCDC-188436 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[13] Complex **4b** has been separately obtained and characterized by the deprotonation of **1b**, see: P. Haquette, D. Touchard, L. Toupet, P. H. Dixneuf, *J. Organomet. Chem.* **1998**, *565*, 63–73.

Towards Stepwise Cluster Assembly: A Decacopper(II) Complex Obtained by Controlled Expansion of a Metallasiloxane Cage[**]

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The synthesis of new magnetic clusters with unprecedented spin topologies is a central topic in the field of molecular magnetism. Among different strategies that have been developed, serendipitous assembly[1] and rational design[2] represent opposite limiting approaches. The rational construction of heptanuclear clusters with high-spin ground states has been reported starting from hexacyanometalates $[M(CN)_6]^{3-}$ (M = Cr, Fe) and mononuclear complexes bearing a capping ligand.[2] The use of robust, preformed clusters as central cores represents an even more appealing approach, which we are currently pursuing. In particular, we are focusing on metallasiloxane cages such as $[Cu_6\{(PhSiO_2)_6\}_2L_6]$[3] (where L = monodentate ligand). The $[Cu_6\{(PhSiO_2)_6\}_2]$ skeleton features a layer of six coplanar metal ions, sandwiched between two $[(PhSiO_2)_6]^{6-}$ ligands. Similar architectures containing other first-row divalent metal ions and encapsulating a chloride ion are known.[3a,4] The twelve six-membered chelate rings in the $[Cu_6\{(PhSiO_2)_6\}_2]$ structure convey a remarkable inertness and thermodynamic stability to the cluster core. In contrast, the monodentate ligands which surround the Cu$_6$ cage are labile and can be easily replaced in solution by open-shell units bearing suitable bridging groups. In principle, this allows a fully controlled organization of a second shell of magnetic centers around the Cu$_6$ unit, Figure 1.

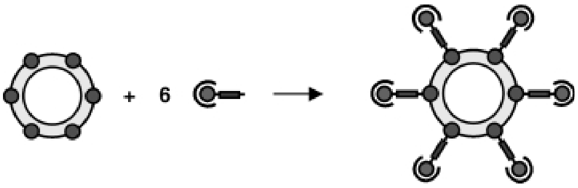

Figure 1. Addition of a second shell of magnetic centers to a central Cu$_6$ core.

Herein we report the successful expansion of the hexacopper(II) cage **1** through the addition of four $[Cu(tmpa)CN]^+$ (tmpa = tris(2-pyridylmethyl)amine)[5,6] units from **3** to give a decacopper(II) cluster **2**.

$[Cu_6\{(PhSiO_2)_6\}_2(n\text{BuOH})_{6-x}(H_2O)_x]$ **1**

$[Cu(tmpa)CN]PF_6$ **3**

$[Cu_6\{(PhSiO_2)_6\}_2\{NCCu(tmpa)\}_4](PF_6)_4$ **2**

Compound **2** was synthesized by reaction of **1**[3b] with the copper cyanide complex **3**[5a] in a methanol–chloroform solvent mixture (see Experimental Section).

The composition of the crystalline compound, **2**$\cdot 2\,CHCl_3 \cdot 2.75\,MeOH \cdot 0.25\,H_2O$, was established by elemental analysis and a low-temperature single-crystal X-ray diffraction investigation. The molecular structure of the cation of **2** has idealized D_2 point-group symmetry (Figures 2 and 3). The metal topology comprises an hexagonal, almost planar Cu$_6$ array (within ± 0.0108(6) Å), plus four peripheral Cu(tmpa) units linked to the central core through cyanide bridges. Formation of the cyanide bridge induces only minor structural changes in the $[Cu(tmpa)CN]^+$ unit, the bond lengths of which are equal to within 3σ of those in **3**. On the other hand, the trigonal-bipyramidal (TB) coordination geometry of the copper(II) ion of **2** is slightly more distorted, with τ values[7] in the range 0.843(7)–0.902(7), compared with 0.943(3) in **3**.[5a] The arrangement of the bulky Cu(tmpa) units around the Cu$_6$ core of **2** results in significant departures from linearity in the Cu-N-C-Cu(tmpa) moieties, which have a *cisoid* conformation with N-C-Cu(tmpa) and Cu-N-C angles in the range 168.8(7)–

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