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Synthesis, Structure and Electrochemistry of Macrocyclic Tetrametallic Group 6 (Fischer) Carbene Complexes[‡]

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The 1,4-addition of diamine dinucleophiles to dimetallic carbene scaffolds **5** yields tetrametallic azamacrocycles **9** and **10** with exocyclic metal–carbene nuclei, in excellent yields and with high stereocontrol. All-Z stereoisomers are isolated in all cases, with the exception of the tungsten(0) macrocycle **10**, which is obtained as a mixture of isomers. This methodology allows the preparation of a new type of homo- and hetero-cyclophane metallomacrocycles in which the geometry and the size of the cavity can be designed as a function of the biscarbene complexes employed and the diamines used as linkers. The X-ray structure of complex **10a** showing the high stability of the Z configuration of these compounds and the electrochemistry of the metallomacrocycles prepared are also reported.

Introduction

The use of simple molecular building blocks to assemble a wide array of new chemical architectures has fascinated the chemists in the last decades. The wise combination of many different small molecular components, with covalent or (labile) coordinate bonds and supramolecular chemistry, has allowed the successful preparation of structures of high order and complexity.[2] In this context, among the different approaches reported, the combination of metal and organic fragments in the construction of 2D and 3D macrocyclic structures has been particularly fruitful.[3] It is known that macrocyclization in conventional organic synthesis is a low-yield process, generally accompanied by a considerable amount of oligomeric by-products. The only exceptions to the rule are the strategies based on reversible reactions, which overcome the formation of undesired linear/cyclic by-products (*dynamic covalent chemistry*, DCC).[4] In sharp contrast, the combination of metal and organic frameworks in the construction of macrocyclic structures through the self-assembling strategy (the so called *directional bonding approach*) has resulted in the efficient preparation of new metal-containing macrocycles with interesting properties.[5] The shape and size of the metallomacrocycles obtained by this well-established methodology relies on the geometry and length of the building blocks, and the metal fragments (generally Pt and Pd complexes) are incorporated in the corners linking the organic units (**1**–**3**, Figure 1).[6,7]

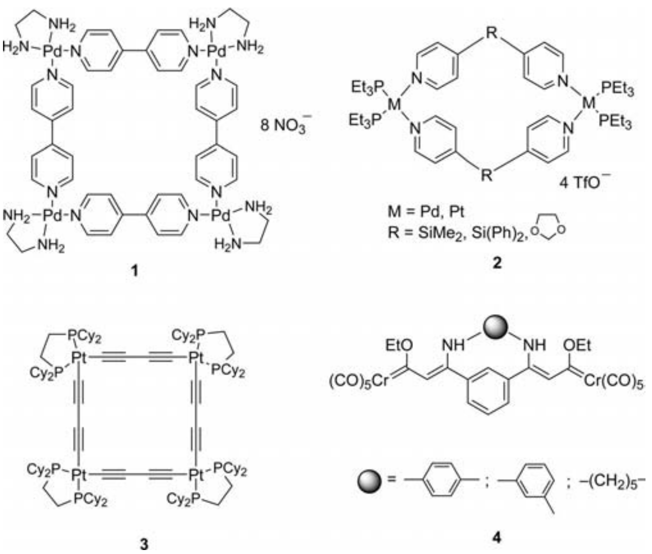

Figure 1. Metallomacrocycles **1**–**3** and examples of cyclophane-like α,β-unsaturated dimetallic (Fischer) carbene complexes.

Metallomacrocycles having pendant metal fragments are, however, rare. Our research group reported some years ago, the use of α,β-unsaturated dimetallic (Fischer) carbene complexes as scaffolds to build this type of compound, **4**.[1,8] The success of our approach derives from the reversible nature of the 1,4-addition of dinucleophiles to the α,β-unsaturated dimetallic template, which makes this strategy

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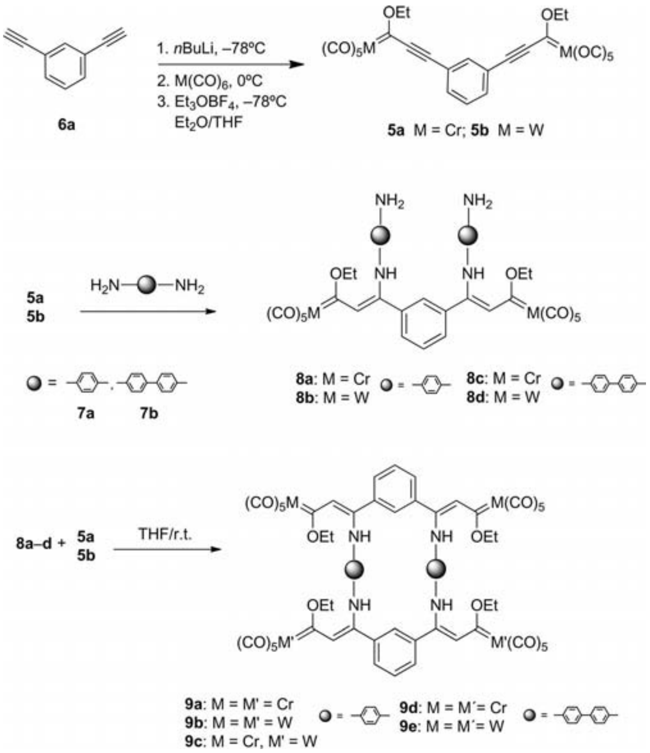
a combination of the use of metal building blocks with dynamic covalent cyclization. In this report, we expand the scope of our methodology to prepare diverse macrocyclic structures with four pendant metal–carbene subunits, modulating the tethers in the biscarbene template and the nucleophile. We also report the study of their electrochemical properties and, for the first time, the X-ray structure of one of these macrocyclic species.

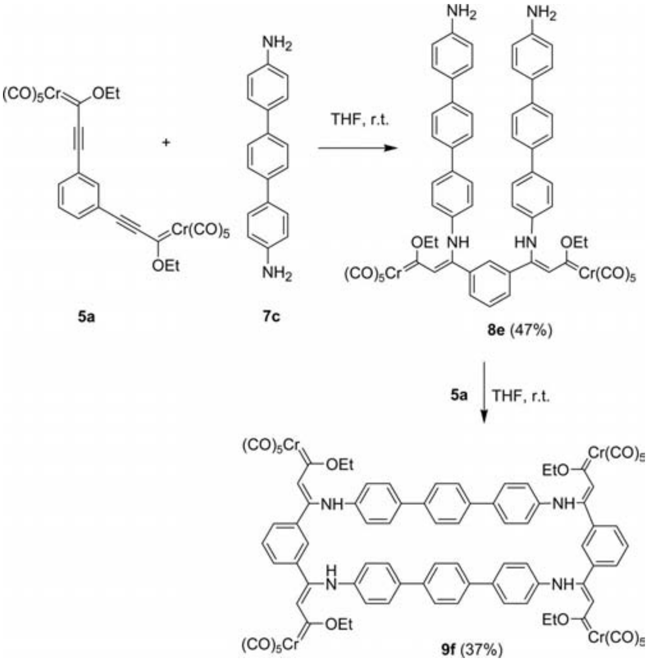
Results and Discussion

In our previous study,[1] we determined the usefulness of dimetallic carbenes **5a** and **5b** and aromatic diamines in the construction of azamacrocyclic structures having pendant metal moieties.[9] Thus, from the reaction of templates **5a** and **5b** (prepared from bisalkyne **6a**)[10] with diamines **7a** and **7b**, (*Z,Z*)-dinuclear carbene complexes **8a**–**d**[11] were obtained in high yields (Scheme 1). Further reaction of the bis(enaminocarbene) complexes **8** with the corresponding biscarbene complexes **5** yielded a series of cyclophane carbene complexes **9** as stable compounds. Tetrametallic azamacrocycles **9** constitute a new type of metallomacrocycles having pendant metal fragments and combine, in their structures, the size of the cavity with the presence of four reactive metal carbene moieties. The synthesis of the tetrametallic azamacrocycles **9** could be envisaged as an example of macrocycle peripheral functionalization, in which the functional groups [namely the pentacarbonylmetal(0) carbene fragments] are introduced during the building of the macrocycle.[12]



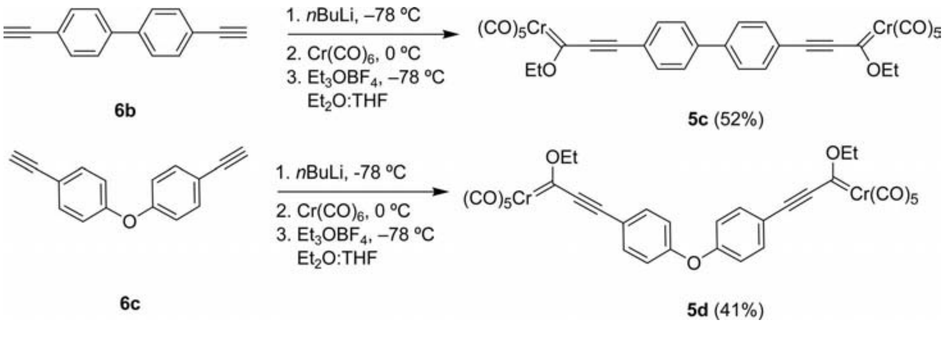
Scheme 1.

The extension of this methodology to longer polyaromatic tethers was effected by reaction of complex **5a** and diaminoterphenylene **7c**. Complex **8e** was formed in 47% yield, and subsequent reaction with biscarbene complex **5a** afforded macrocycle **9f** in 37% yield (Scheme 2).



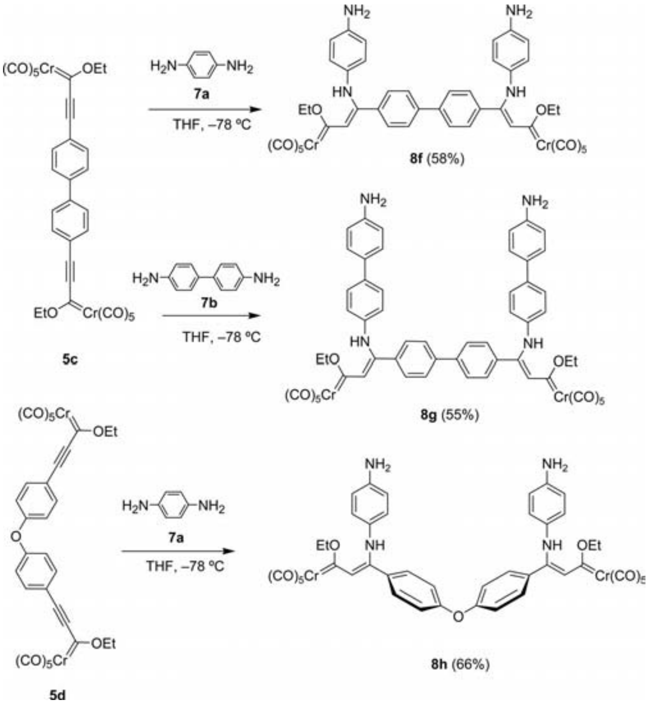
Scheme 2.

The effect of the tether joining both metallic centers in the macrocyclization was explored next. Preparation of biscarbenes **5c** and **5d** was achieved from bisalkynes **6b** and **6c** by reaction of the corresponding dilithium derivative with



Scheme 3.

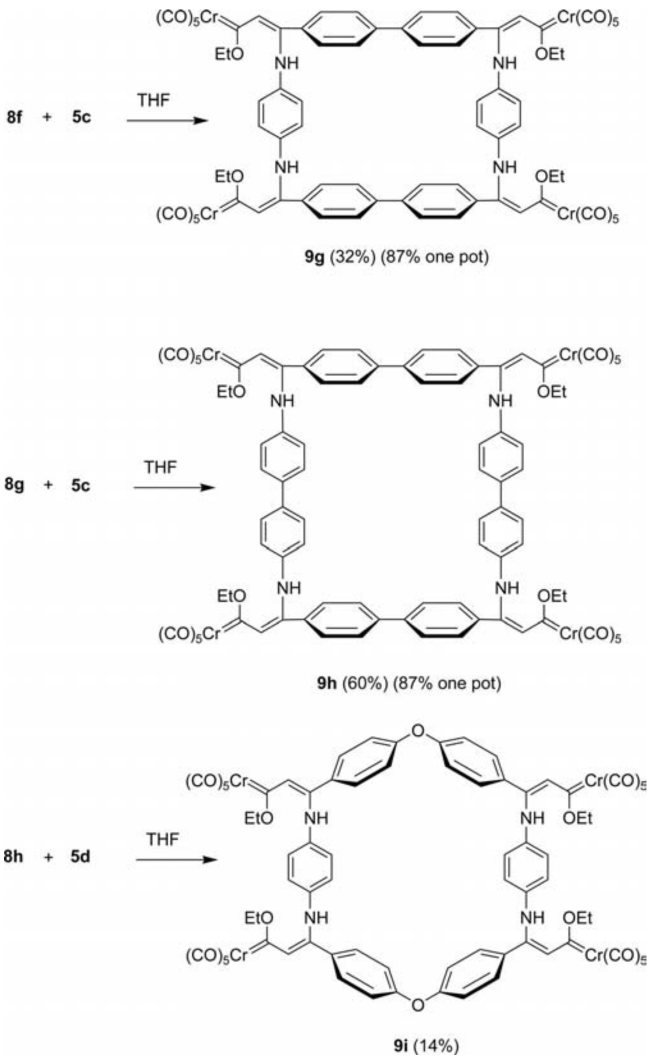
$M(CO)_6$ (M = Cr, W) and subsequent treatment with Et_3OBF_4 (Scheme 3). Dimetallic carbene complex **5c** was treated with diamines **7a** and **7b** to form enamino complexes **8f** and **8g** in moderate yields (58 and 55%, respectively). In a similar manner, the more flexible complex **5d** was treated with amine **7a** to give the corresponding biscarbene **8h** in 66% yield (Scheme 4).



Scheme 4.

The isolated complexes **8f**–**h** were treated next with an equimolar amount of the required biscarbene complex to close the symmetrical cavities **9g**–**i** (Scheme 5). Compounds **9g** and **9h** were obtained in acceptable yields (32 and 60%, respectively), but complex **9i** could only be synthesized in a 14% yield. This behavior may be related to a poorer preorganization of the biphenyl ether moiety in the starting enamino complex **8h**. Nevertheless, the yields of macrocycles **9g**–**h** was considerably improved when the assembly was carried out in one pot. Thus, treatment of biscarbene **5c** with the corresponding diamine **7a** or **7b** (1:2 ratio) in THF at –78 °C (until the disappearance of the starting material), followed by addition of an equimolar amount of the carbene complex **5c** at low temperature resulted in the formation of macrocycles **9g** and **9h**, respectively, and in 87% yield in both cases, which makes the process remarkably efficient. Interestingly, the one-pot reaction of **9i** met with no success. This fact points to the necessity of a certain degree of preorganization in the template for the formation of macrocycles in high yields.

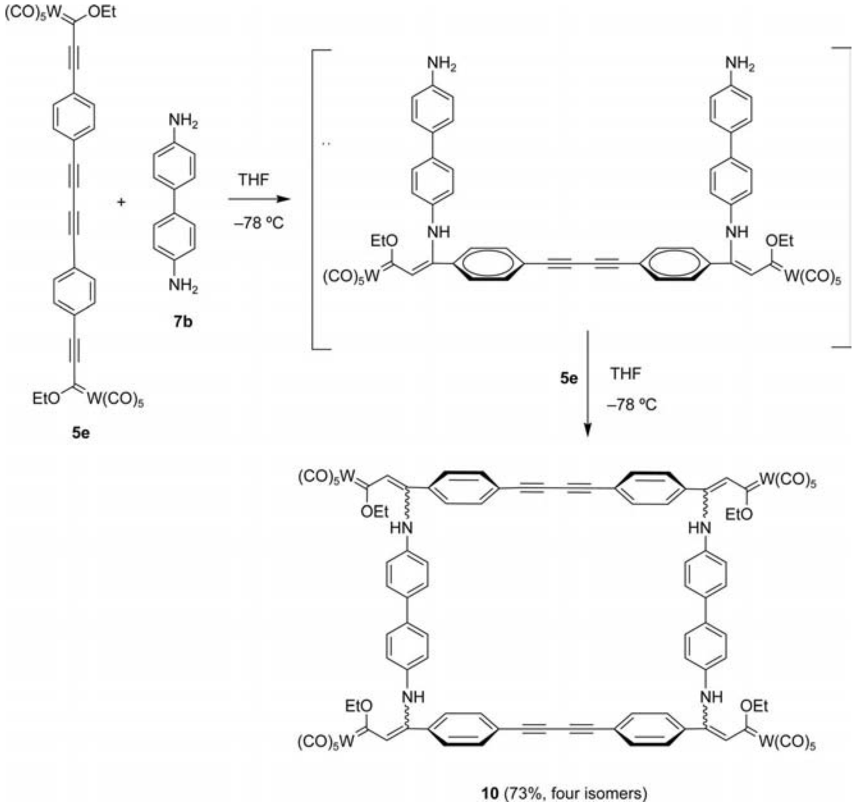
Tetrametallic macrocycles **9a**–**i** are stable compounds, which can be purified by column chromatography on silica gel. The all-*Z* stereochemistry of these compounds was assigned by comparison with literature data.[11]



Scheme 5.

Finally, tungsten(0) carbene complex **5e** was chosen as a new scaffold for the design of a new type of tetrametallic tetraazamacrocyclic structure. In the last years, there has been a rising interest in shape-persistent arylene–ethynylene macrocycles with respect to their roles as large, supramolecular building blocks that generate π-stacked structures in solution, non collapsible nanoporous solids, and tubular ordered fluid phases.[13] In this regard, we considered complex **5e** as an attractive building block for the synthesis of macrocycles with interesting properties in the development of new organic materials.

Biscarbene complex **5e** was obtained by Cu-catalyzed alkyne dimerization following our reported procedure.[10] Starting from **5e** and amine **7b** and by using the one-pot method described above, the tungsten(0) tetrametallic macrocyclic complex **10** was synthesized as a mixture of four isomers (Scheme 6). The fast atom bombardment mass spectrometric analysis of the mixture (FABMS) showed a peak at m/z = 2389.6, which corresponds to the $[M + H]^+$ species, which excludes the presence of oligomers. The exis-



Scheme 6.

tence of rotamers in the mixture of **10** was also disregarded through NMR experiments ($CDCl_3$) at low temperature (–35 °C) and by heating the sample up to 54 °C, which show no significant changes in the signals of the spectra.

Two of the four isomers **10** could be isolated by chromatography and analyzed by FABMS and spectroscopic techniques. Isomers **10a** (13%) and **10b** (31%) show the expected $[M + H]^+$ peak at m/z = 2389.6 and a single signal characteristic of the carbene carbon atom at δ = 281.8 ppm in the ^{13}C NMR spectra. The other two isomers could not be separated and were obtained as a 1:1.3 mixture in 30% yield. By considering all the experimental evidence, the isomeric mixture **10** may comprise geometrical *Z*/*E* isomers. This point was confirmed by X-ray diffraction study of suitable crystals obtained by slow diffusion of isomer **10a** in *n*-pentane/CH_2Cl_2 at room temperature (Figure 2). The compound shows the all-*Z* configuration for the C=C bonds, with short N···O distances of 2.61 and 2.64 Å. The strong N–H···O hydrogen bonds may be responsible for the high stability of the observed *Z* configuration. Furthermore, the distances in the N–C=C–C_{carbene} unit clearly show the delocalization of the lone pair of the nitrogen atom and of the π electrons in the stabilization of the electron deficiency at the carbene center. This deficit is also compensated by the oxygen atom, as evidenced by short C–O distances of 1.37 and 1.32 Å and by a very open C–O–C angle of 122°, which is in perfect agreement with sp^2 hybridization of the oxygen atom, necessary for such stabilization. The fixed geometry around the alkene carbon atoms leads to deformations of the C_6H_4–C≡C–C≡C–C_6H_4 linkers, which are slightly bent toward the inside of the cavities formed by the macrocycles (Figure 2). In the solid state, the macrocycles form channels hosting mobile solvent mole-

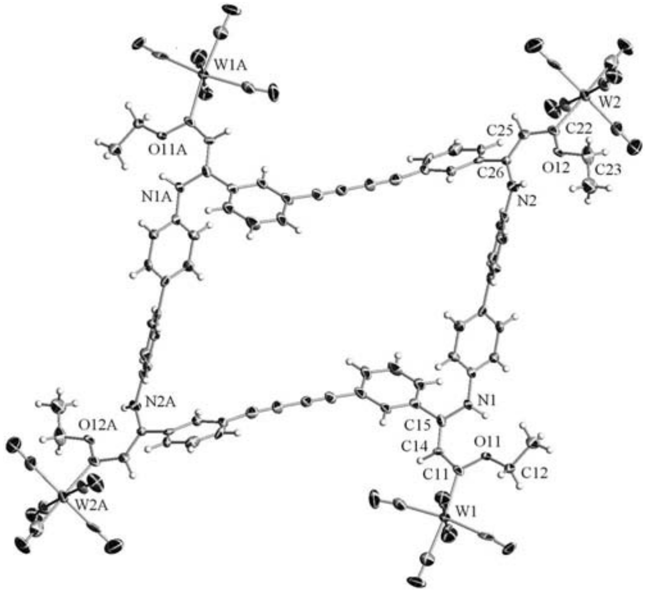


Figure 2. Crystal structure of **10a**. Thermal ellipsoids are depicted at the 50% level. Solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–C15 1.38(2), C15–C14 1.38(2), C14–C11 1.40(2), C11–O11 1.37(2), C11–W1 2.23(2), N1···O11 2.61, N2–C26 1.36(2), C26–C25 1.38(2), C25–C22 1.44(2), C22–O12 1.32(2), C22–W2 2.21(2), N2···O12 2.64, C11–O11–C12 122.2(10), C22–O12–C23 122.5(10).

cules. This mobility explains the high instability of the crystals, which rapidly lose the solvent (see Figure 3).[14]

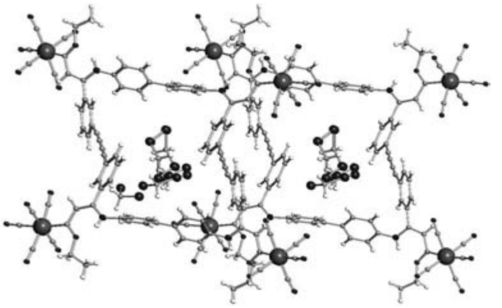


Figure 3. Crystal packing of **10a**.

Finally, the redox properties of the metallomacrocyclic compounds **9** were studied to estimate the effect of the tethers joining the metallic nuclei on the electron-donating and electron-accepting abilities of the metal–carbene moieties.

All homometallic chromium(0) carbenes **9** having different aromatic spacers show an irreversible oxidation wave in the range E_{pa} = 0.84–0.92 V (Table 1). These data are in accordance with the delocalization of the enamino moiety into the carbene carbon that diminishes the oxidation potential values reported for alkoxy carbenes.[15] The analogous homometallic tungsten(0) carbene complex **9b** behaves in a similar way, but shows an irreversible one-step oxidation at higher potential (E_{pa} = 1.04 V). There are no significant differences between the redox behavior of complexes **9a**–**e** and **9g**–**i**, which have more conjugated tethers.

Table 1. Redox properties of macrocycles **9**.[a]

Compound	First E_{pa}	Second E_{pa}	First E_{pc}	Second E_{pc}
9a	0.88		–1.34	–1.60
9b	1.04		–1.28	–1.57
9c	0.92	1.05	–1.33	–1.59
9d	0.91	1.20	–1.33	–1.46
9e	1.03		–1.24	–1.44
9g	0.84		–1.32	–1.51
9h	0.91		–0.81	
9i	0.85	1.08	–0.82	–0.86

[a] Data in V, measured in 0.1 M Bu_4NClO_4/CH_2Cl_2 at a scan rate of 0.1 V/s at 25 °C.

Conclusions

On the basis of the reversible nature of the 1,4-addition of aromatic diamine dinucleophiles[16] to α,β-unsaturated dimetallic (Fischer) carbene complexes, we have developed a novel approach to the synthesis of metallomacrocycles. Our strategy allows the preparation of a wide range of tetrametallic macrocycles having four pendant metal–carbene moieties in good yields, and, with the exception of macrocycles **10**, in a stereocontrolled manner. This methodology allows the control of the geometry and the size of the cavity of the cyclophane, which can be designed as a function of the biscarbene complexes employed and the diamine used as linker. Moreover, the sequential building of these macrocyclic entities allows the obtainment of homo- and heterotetrametallic derivatives. Efforts to explore the versatility of this method to access other metallic complexes and organic structures are currently underway in our laboratories.

Experimental Section

General Procedure: ^1H NMR and ^{13}C NMR spectra were recorded at room temperature on BrukerAvance 500 MHz (500.1 MHz and 125.7 MHz), BrukerAvance DPX 300 MHz (300.1 MHz and 75.4 MHz), and Bruker DPX 300 MHz-BACS60 (300.1 MHz and 75.4 MHz) spectrometers. Chemical shifts are given in ppm relative to TMS (^1H, NMR 0.00 ppm) and $CDCl_3$ (^{13}C, 77.0 ppm). All NMR samples were filtered through a small pad of Celite 545 just before recording the NMR spectra. IR spectra were taken on a Perkin–Elmer 781 and on a Bruker Tensor 27 (MIR 8000–400 cm^{-1}), spectrometers. Cyclic voltammetry experiments were performed in CH_2Cl_2 at room temperature with 0.1 M tetrabutyl ammonium perchlorate as the supporting electrolyte and glassy carbon as the working electrode. A platinum wire was used as the counter electrode and Ag/Ag^+ as the reference electrode. All the measurements were done with potentiostat/galvanostat Autolab PGSTAT30 o PGSTATAT302N, and ferrocene was used as internal standard. Solvents were distilled and dried under argon before use. THF and Et_2O were distilled from sodium/benzophenone. Flame-dried glassware and standard Schlenk techniques were used for moisture-sensitive reactions. Merck silica gel (230–400 Mesh) was used as the stationary phase for purification of the crude reaction mixtures by flash column chromatography. Identification of products was made by TLC (kiesegel 60F-254). UV light (λ = 254 nm) and 5% phosphomolybdic acid solution in 95% EtOH were used to develop the plates. Mass experiments were carried out on a MAT95XP/THERMOFISHER spectrometer. All commercially available compounds were used without further purification. Compounds 4,4′-diethynyl-1,1′-biphenyl,[17] 4,4′-diethynyl-1,1′-biphenyl ether,[10] alkynylcarbene complexes **5a**,[8] **5b**,[1] **5e**,[10] and complexes **8a**–**d** and **9a**–**e**[1] were synthesized following methods previously reported.

General Method for the Synthesis of Biscarbene Complexes 5c and 5d: To a solution of the corresponding diethynyl compound **6** in dry Et_2O at –78 °C was added dropwise *n*BuLi (1.6 M in hexanes, 2.2 equiv.). The mixture was stirred at –78 °C for 45 min, and then $Cr(CO)_6$ (2 equiv.) was added at 0 °C in one portion. After stirring the mixture at this temperature for 15 min, dry THF was also added to dissolve the mixture, which was left to stir at room temperature overnight. Afterwards, $Et_3O^+BF_4^-$ in excess (4 equiv.) was added in one portion at –78 °C. The solution was stirred at this temperature for 20 min and then allowed to reach room temperature over an hour. The mixture turned purple. The solvents were removed under reduced pressure, and the residue was dissolved in Et_2O and filtered through a small pad of silica gel. The solvent was evaporated under vacuum, and the residue was submitted to flash column chromatography under argon pressure (SiO_2, hexane/AcOEt mixtures) to give the corresponding biscarbene **5**, together with different amounts of the analogous monocarbene complex.

Compound 5c: Following the general method, from **6b** (300 mg, 1.48 mmol) in dry Et_2O (14 mL), *n*BuLi (1.6 M in hexanes, 2.1 mL, 3.36 mmol)), $Cr(CO)_6$ (653 mg, 2.97 mmol), THF (7.5 mL), and $Et_3O^+BF_4^-$ (1.13 g, 5.93 mmol),a dark purple solid identified as biscarbene **5c** was obtained (538 mg, 52%), together with the analogous monocarbene complex (233 mg, 35%).[10] Biscarbene **5c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74–7.67 (m, 8 H, ArH), 4.79 [q, ^{3}J(H,H) = 7.1 Hz, 4 H, OCH_2], 1.61 [t, ^{3}J(H,H) = 7.1 Hz, 6 H, CH_3] ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 313.3 (C=Cr), 225.7 (CO *trans*), 216.3 (CO *cis*), 142.6, 133.3, 127.6, 120.9 (C and CH aromatics), 92.5 (C≡C), 75.9 (OCH_2), 15.0 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 1925, 1956, 2058, 2150 cm^{-1}. $C_{32}H_{18}Cr_2O_{12}$ (698.48): calcd. C 55.03, H 2.60; found C 54.79, H 2.38.

Compound 5d: Following the general method, from compound **6c** (520 mg, 2.38 mmol) in dry Et_2O (52 mL), *n*BuLi (1.6 M in hexanes, 3.3 mL, 5.28 mmol), $Cr(CO)_6$ (1.05 g, 4.76 mmol), THF (26 mL), and $Et_3O^+BF_4^-$ (1.81 g, 9.52 mmol),a dark purple–red solid identified as biscarbene **5d** was obtained (742 mg, 41%), together with the analogous monocarbene complex (218 mg, 20%).[10] Biscarbene **5d**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 [d, ^{3}J(H,H) = 8.7 Hz, 4 H, ArH], 7.12 [d, ^{3}J(H,H) = 8.7 Hz, 4 H, ArH], 4.76 [q, ^{3}J(H,H) = 7.2 Hz, 4 H, OCH_2], 1.60 [t, ^{3}J(H,H) = 7.2 Hz, 6 H, CH_3] ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 312.8 (C=Cr), 225.6 (CO *trans*), 216.3 (CO *cis*), 158.9, 135.0, 119.5, 116.6 (C and CH aromatics), 92.2 (C≡C), 75.8 (OCH_2), 14.9 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 1954, 2060, 2150 cm^{-1}. $C_{32}H_{18}Cr_2O_{13}$ (714.48): calcd. C 53.79, H 2.54; found C 53.35, H 2.86.

General Method for the Synthesis of Tetrametallic Macrocycles 9 and 10: To a solution of the biscarbene complex in dry THF was added in one portion the diamine (1:2 molar ratio, respectively). The reaction mixture was stirred at room or low temperature, as indicated for each case, under argon until the disappearance of the starting material (checked by TLC). An appreciable change in the color to deep red was always observed in the reaction mixture after the addition of the diamine. The solvent was removed under reduced pressure, and the crude reaction was purified by flash column chromatography on silica gel under argon pressure to give the corresponding product **8**.

Method A: The bis(enaminocarbene) **8** then formed was dissolved in dry THF and reacted with an equimolar amount of the corresponding biscarbene complex **5** at room or low temperature, as indicated for each case, under argon until the disappearance of the starting material (checked by TLC). The solvent was removed under reduced pressure, and the crude reaction was purified by flash column chromatography under argon pressure to give pure tetranuclear macrocycles **9** or **10**.

Method B (One Pot): The corresponding diamine was added to a solution of the biscarbene complex in dry THF in one portion (2:1 molar ratio, respectively). The reaction mixture was stirred at low temperature under argon until the disappearance of the starting material (checked by TLC). An equimolar amount of the corresponding biscarbene complex was then added at low temperature under argon, and the mixture was stirred until the disappearance of the starting material (checked by TLC). The solvent was removed under reduced pressure, and the crude reaction was purified by flash column chromatography under argon pressure to give pure tetranuclear macrocycles **9g**–**h** or **10**.

Compound 8e: Following the general method, from biscarbene complex **5a** (100 mg, 0.16 mmol), **7c** (84 mg, 0.32 mmol), and THF (10 mL) and after 2 h at room temperature and purification by flash column chromatography (SiO_2, hexane/AcOEt mixtures), complex **8e** was obtained as a red solid (86 mg, 47%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.35 (br., 2 H, NH), 7.57–7.33 (m, 24 H, ArH), 6.77–6.53 (m, 4 H, ArH), 6.51 (s, 2 H, C=CH), 5.00 [q, ^{3}J(H,H) = 6.9 Hz, 4 H, OCH_2], 3.69 (br., 4 H, NH_2), 1.70 [t, ^{3}J(H,H) = 7.0 Hz, 6 H, CH_3] ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 305.1 (C=Cr), 224.0 (CO *trans*), 218.0 (CO *cis*), 146.0, 144.6, 140.3, 137.9, 137.2, 136.1, 130.7, 130.5, 129.5, 129.0, 127.8, 127.5, 126.9, 126.7, 123.2, 122.2, 115.4 (C=CH and C and CH aromatics), 74.7 (OCH_2), 15.7 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 1182, 1375, 1490, 1539, 1911, 2050, 3385 cm^{-1}. $C_{62}H_{46}Cr_2N_4O_{12}$ (1143.06): calcd. C 65.15, H 4.06; found C 64.84, H 4.31.

Compound 8f: Following the general method, from biscarbene complex **5c** (50 mg, 0.07 mmol), **7a** (16 mg, 0.14 mmol), and THF (8 mL) and after 1.5 h at –78 °C and purification by flash column chromatography (SiO_2, hexane/AcOEt mixtures), the bis(enaminocarbene) complex **8f** was obtained as a red solid (37 mg, 58%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.51 (br., 2 H, NH), 7.53 [d, ^{3}J(H,H) = 8.3 Hz, 4 H, ArH], 7.41 [d, ^{3}J(H,H) = 8.3 Hz, 4 H, ArH], 6.60–6.54 (m, 2 H, C=CH and 8 H, ArH), 4.95 [q, ^{3}J(H,H) = 7.1 Hz, 4 H, OCH_2], 3.66 (br., 4 H, NH_2), 1.65 [t, ^{3}J(H,H) = 7.0 Hz, 6 H, CH_3] ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 296.6 (C=Cr), 224.1 (CO *trans*), 218.5 (CO *cis*), 148.0, 144.5, 141.2, 134.5, 129.7, 129.0, 127.0, 124.7, 121.0, 115.3 (C=CH and C and CH aromatics), 74.1 (OCH_2), 15.8 (CH_3) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1200, 1516, 1916, 2049, 3392 cm^{-1}. $C_{44}H_{34}Cr_2N_4O_{12}$ (914.76): calcd. C 57.77, H 3.75; found C 57.99, H 3.57.

Compound 8g: Following the general method, from biscarbene complex **5c** (50 mg, 0.07 mmol), **7b** (26 mg, 0.14 mmol), and THF (8 mL) and after 2.5 h at –78 °C and purification by flash column chromatography (SiO_2, CH_2Cl_2/AcOEt mixtures), the bis(enaminocarbene) complex **8g** was obtained as a red solid (41 mg, 55%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.54 (br., 2 H, NH), 7.60–7.32 (m, 16 H, ArH), 6.78–6.70 (m, 2 H, C=CH and 8 H, ArH), 5.04–4.99 (m, 4 H, OCH_2), 3.77 (br., 4 H, NH_2), 1.72 [t, ^{3}J(H,H) = 7.0 Hz, 6 H, CH_3] ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 301.0 (C=Cr), 224.1 (CO *trans*), 218.2 (CO *cis*), 146.2, 146.1, 141.4, 138.1, 136.4, 134.4, 129.7, 127.6, 127.2, 126.7, 123.0, 122.0, 115.3 (C=CH and C and CH aromatics), 74.4 (OCH_2), 15.7 (CH_3) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1201, 1376, 1537, 1917, 2049, 3453 cm^{-1}. $C_{56}H_{42}Cr_2N_4O_{12}$ (1066.96): calcd. C 63.04, H 3.97; found C 63.28, H 4.27.

Compound 8h: Following the general method, from biscarbene complex **5d** (100 mg, 0.14 mmol), **7a** (30 mg, 0.28 mmol), and THF (15 mL) and after 3 h at –78 °C and purification by flash column chromatography (SiO_2, hexane/AcOEt mixtures), the bis(enaminocarbene) complex **8h** was obtained as a red solid (86 mg, 66%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.48 (br., 2 H, NH), 7.33 [d, ^{3}J(H,H) = 8.7 Hz, 4 H, ArH], 6.94 [d, ^{3}J(H,H) = 8.6 Hz, 4 H, ArH], 6.59–6.48 (m, 2 H, C=CH and 8 H, ArH), 4.93 [q, ^{3}J(H,H) = 7.0 Hz, 4 H, OCH_2], 3.68 (br., 4 H, NH_2), 1.64224.1 (CO *trans*), 218.5 (CO *cis*), 157.7, 147.9, 144.5, 131.0, 130.2, 129.0, 124.7, 120.9, 118.9, 115.2 (C=CH and C and CH aromatics), 74.0 (OCH_2), 15.7 (CH_3) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1096, 1200, 1373, 1477, 1515, 1542, 1897, 2048 cm^{-1}. $C_{44}H_{34}Cr_2N_4O_{13}$ (930.76): calcd. C 56.78, H 3.68; found C 56.67, H 3.39.

Compound 9f: Following the general method A, from complex **5a** (22 mg, 0.035 mmol), bis(enaminocarbene) complex **8e** (40 mg, 0.035 mmol), and THF (4 mL) and after 1 h at room temperature and purification by flash column chromatography (SiO_2, hexane/AcOEt mixtures), tetrametallic complex **9f** was obtained as a red solid (23 mg, 37%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.20 (br., 4 H, NH), 7.44–7.28 (m, 24 H, ArH), 6.66–6.63 (m, 4 H, C=CH and 8 H, ArH), 5.05–5.03 (m, 8 H, OCH_2),1.73–1.69 (m, 12 H, CH_3) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 307.9 (C=Cr), 223.9 (CO *trans*), 217.9 (CO *cis*), 144.1, 138.4, 138.1, 137.0, 136.6, 130.6, 129.6, 127.4, 127.0, 123.2, 123.0 (C=CH and C and CH aromatics), 74.8 (OCH_2), 15.7 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 1182, 1350, 1541, 1911, 2052, 3421 cm^{-1}. $C_{88}H_{60}Cr_4N_4O_{24}$ (1765.44): calcd. C 59.87, H 3.43; found C 60.21, H 3.29.

Compound 9g: Following the general method A, from bis(enaminocarbene) complex **8f** (37 mg, 0.04 mmol), **5c** (28 mg, 0.04 mmol), and THF (10 mL) at –78 °C and after 7 d at room temperature and purification by flash column chromatography (SiO_2, hexane/AcOEt mixtures), tetrametallic complex **9g** was obtained as a red solid (21 mg, 32%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.51 (s, 4 H, NH), 7.53–7.40 (m, 16 H, ArH), 6.58–6.49 (m, 4 H, C=CH and 8 H, ArH), 4.96–4.95 (m, 8 H, OCH_2), 1.65 (s, 12 H, CH_3) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 296.6 (C=Cr), 224.1 (CO *trans*), 218.5 (CO *cis*), 148.0, 144.5, 141.2, 134.5, 129.7, 129.0, 127.0, 124.7, 121.0, 115.3 (C and CH aromatics and C=CH), 74.1 (OCH_2), 15.8 (CH_3) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1067, 1201, 1374, 1476, 1536, 1561, 1898, 2048 cm^{-1}. FABMS: *m*/*z* = 1614.6 $[M + H]^+$.

Following the general method B, from biscarbene complex **5c** (400 mg, 0.57 mmol), **7a** (62 mg, 0.57 mmol), and THF (30 mL) at –78 °C and after 1.5 h (first part) and one night (second part) and purification by flash column chromatography (SiO_2, hexane/AcOEt mixtures), tetrametallic complex **9g** was obtained as a red solid (407 mg, 87%).

Compound 9h: Following the general method A, from bis(enaminocarbene) complex **8g** (41 mg, 0.038 mmol), **5c** (27 mg, 0.038 mmol), and THF (10 mL) at–78 °C and after 7 d at room temperature and purification by flash column chromatography (SiO_2, hexane/AcOEt mixtures), tetrametallic complex **9h** was obtained as a red solid (40 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.51 (br., 4 H, NH), 7.60–7.30 (m, 24 H, ArH), 6.79–6.70 (m, 4 H, C=CH and 8 H, ArH), 5.01–4.99 (m, 8 H, OCH_2), 1.70 [t, ^{3}J(H,H) = 7.0 Hz, 12 H, CH_3] ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 301.3 (C=Cr), 224.0 (CO *trans*), 218.2 (CO *cis*), 146.6, 141.5, 138.2, 136.4, 134.5, 129.7, 127.6, 127.3, 126.7, 123.0, 122.0, 115.3 (C=CH and C and CH aromatics), 74.4 (OCH_2), 15.7 (CH_3) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1096, 1200, 1351, 1501, 1537, 1903, 2048 cm^{-1}. FABMS: *m*/*z* = 1766.6 $[M + H]^+$.

Following the general method B, from biscarbene complex **5c** (400 mg, 0.57 mmol), **7b** (106 mg, 0.57 mmol), and THF (30 mL) at –78 °C and after 1.10 h (first part) and one night (second part) and purification by flash column chromatography (SiO_2, hexane/AcOEt mixtures), tetrametallic complex **9h** was obtained as a red solid (443 mg, 87%).

Compound 9i: Following the general method A, from bis(enaminocarbene) complex **8h** (100 mg, 0.11 mmol), biscarbene **5d** (77 mg, 0.11 mmol), and THF (20 mL) at –78 °C and after 2.5 d at room temperature and purification by flash column chromatography (SiO_2, hexane/AcOEt mixtures), tetrametallic complex **9i** was obtained as a red solid (26 mg, 14%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.21 (s, 4 H, NH), 7.20 [d, ^{3}J(H,H) = 8.7 Hz, 8 H, ArH], 6.94 [d, ^{3}J(H,H) = 8.7 Hz, 8 H, ArH], 6.64 (s, 4 H, C=CH), 6.58 (s, 8 H, ArH), 5.00 [q, ^{3}J(H,H) = 6.9 Hz, 8 H, OCH_2], 1.67 [t, ^{3}J(H,H) = 6.9 Hz, 12 H, CH_3] ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 304.6 (C=Cr), 223.8 (CO *trans*), 218.1 (CO *cis*), 157.8, 145.4, 135.8, 131.1, 129.9, 124.3, 121.9, 118.8 (C=CH and C and CH aromatics), 74.6 (OCH_2), 15.8 (CH_3) ppm. IR (CCl_4): $\tilde{\nu}$ = 1541, 1932, 2050, 3327 cm^{-1}. $C_{76}H_{52}Cr_4N_4O_{26}$ (1645.24): calcd. C 55.48, H 3.19; found C 55.27, H 3.42.

Compound 10: Following the general method B, from biscarbene complex **5e** (84 mg, 0.08 mmol), **7b** (15.3 mg, 0.08 mmol), and THF (15 mL) at –78 °C, were obtained after 30 min (first part) and 2 h (second part), tetrametallic complex **10** as a mixture of isomers (70 mg, 73%). The different isomers were separated by flash column chromatography (SiO_2, hexane/AcOEt mixtures). Isomer **10a**: Yield: 12 mg, 13%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.47 (s, 4 H, NH), 7.57–7.30 (m, 24 H, ArH), 6.70 [d, ^{3}J(H,H) = 8.6 Hz, 8 H, ArH], 6.64 (s, 4 H, C=CH), 4.86 [q, ^{3}J(H,H) = 7.1 Hz, 8 H, OCH_2], 1.69 [t, ^{3}J(H,H) = 7.0 Hz, 12 H, CH_3] ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 281.8 (C=W), 203.6 (CO *trans*), 199.2, 198.7, 198.2 (CO *cis*), 147.9, 137.5, 137.0, 135.7, 134.3, 132.1, 129.4, 129.3, 127.8, 125.4, 122.7, 122.4 (C=CH and C and CH aromatics), 80.9 ($C\equiv C$), 77.4 (OCH_2), 74.8 ($C\equiv C$), 15.5 (CH_3) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1538, 1903, 2058 cm^{-1}. FABMS: *m*/*z* = 2389.6 $[M + H]^+$. **10b**: Yield: 29 mg, 31%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.48 (br., 4 H, NH), 7.57–7.32 (m, 24 H, ArH), 6.73–6.62 (m, 4 H, C=CH and 8 H, ArH), 4.87–4.82 (m, 8 H, OCH_2), 1.71–1.66 (m, 12 H, CH_3) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 281.8 (C=W), 203.7, 203.6 (CO *trans*), 199.2, 198.9, 198.7, 198.2 (CO *cis*), 147.9, 147.8, 137.5, 137.0, 136.6, 135.7, 135.6, 134.3, 134.2, 132.2, 132.1, 129.6, 129.4, 129.3, 129.1, 127.8, 127.6, 127.5, 126.9, 125.4, 123.0, 122.9, 122.7, 122.6, 122.4, 122.3, 115.4 (C=CH and C and CH aromatics), 81.0 ($C\equiv C$), 80.9 ($C\equiv C$), 80.8 ($C\equiv C$), 77.4 (OCH_2), 75.0 ($C\equiv C$), 74.9 ($C\equiv C$), 74.8 ($C\equiv C$), 15.5 (CH_3) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1540, 1906, 2058 cm^{-1}. FABMS: *m*/*z* = 2389.6 $[M + H]^+$. Mixture of Isomers **10c** and **10d** (28 mg, 30%, ratio 1:1.3): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.57, 10.48 (br., 4 H, NH), 7.55–7.32 (m, 28 H, ArH), 6.72–6.62 (m, 4 H, C=CH and 8 H, ArH), 4.86–4.85 (m, 8 H, OCH_2), 1.69–1.68 (m, 12 H, CH_3) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 281.5, 279.3 (C=W), 203.8, 203.7 (CO *trans*), 199.4, 199.3, 198.9, 198.8, 198.4, 198.2 (CO *cis*), 148.9, 148.8, 148.0, 146.2, 138.5, 137.5, 136.6, 136.0, 135.6, 135.5, 134.3, 134.2, 132.2, 129.8, 129.7, 129.6, 129.5, 129.1, 127.8, 127.7, 127.5, 126.9, 125.4, 124.9, 123.0, 122.8, 122.6, 122.4, 115.4, 115.3 (C=CH and C and CH aromatics), 81.0 ($C\equiv C$), 80.9 ($C\equiv C$), 80.8 ($C\equiv C$), 77.4 (OCH_2), 75.0 ($C\equiv C$), 74.9 ($C\equiv C$), 74.8 ($C\equiv C$), 15.5 (CH_3) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1019, 1096, 1540, 1905, 2058 cm^{-1}.

Crystal Data for 10a: X-ray diffraction data for **10a** were collected at low temperatures with use of an oil-coated shock-cooled crystal on a Bruker-AXS APEX2 diffractometer with Mo-K_a radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXS-97),[18] and all non-hydrogen atoms were refined anisotropically by the least-squares method on F^2.[17] $C_{99}H_{66}Cl_6N_4O_{24}W_4$: M_r = 2643.66; crystal size = 0.60 × 0.40 × 0.10 mm; triclinic; space group $P\bar{1}$; a = 10.778(2) Å, b = 13.180(2) Å, c = 20.225(3) Å, α = 71.228(8)°, β = 77.758(8)°, γ = 79.755(9)°; V = 2639.5(7) $Å^3$; Z = 1; λ = 0.71073 Å; T = 93(2) K; 30977 reflections collected; 7428 unique reflections (R_{int} = 0.0799); R_1 = 0.0538, wR_2 = 0.1016 [$I > 2\sigma(I)$]; R_1 = 0.1215, wR_2 = 0.1443 (all data); residual electron density = 2.986 e$Å^{-3}$. CCDC-775626 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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