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Synthesis and Electrochemical Properties of Novel Tetrametallic Macrocyclic Fischer Carbene Complexes

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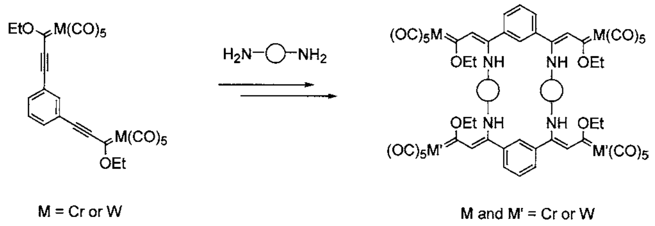
ABSTRACT



Metallomacrocyclic compounds can be easily prepared by 1,4-addition of diamines to α,*β*-unsaturated Fischer bis-carbene templates. This method allows the preparation of a new family of homo- and heterotetrametallic compounds having macrocyclic cyclophanic structures.

In the last few years, the use of transition metal centers in the construction of cyclophanes or macrocyclic structures has gained a lot of attention.[1] This is due to the fact that metal centers are an exceptional tool for constructing organic structures since they can be assembled easily with high efficiency.[2] Many of the metallocyclophanes known to date have been prepared using metals in low oxidation states I or II, in particular, square planar Cu^{II}, Pd^{II}, or Pt^{II} centers or tetrahedral Cu^{I} centers.[3] Examples of cyclophanes containing octahedral W, Mo, Re, Ru, and Rh centers have also been reported.[4] Recently, Re-based chiral square molecular systems have been prepared by using chiral bridging ligands.[5]

Fischer carbene complexes have become an excellent tool in organic chemistry because of the impressive array of processes in which they can take part.[6] Nevertheless, the potential use of this type of compounds in the construction

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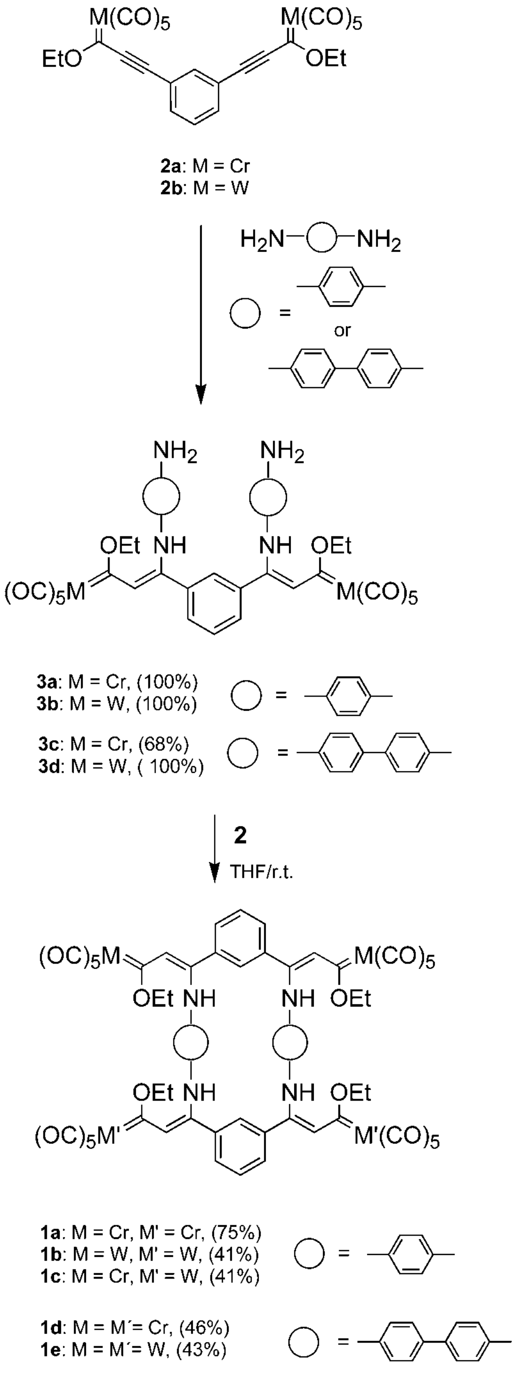
of macrocyclic and supramolecular structures remains unexplored.[7] Recently, our interest has focused on the design and development of new methods for the synthesis of cyclophanic structures using Fischer carbene complexes.[8] The incorporation of metal centers may be used to create further sophisticated structures by taking advantage of the chemistry of the complexes developed so far. Herein we report the synthesis, as well as the electrochemical properties, of new metallomacrocyclic compounds containing four centers.

Tetrametallic macrocyclic compounds **1** were prepared by Michael addition of different amines to α,*β*-unsaturated Fischer carbene complexes **2**, according to Scheme 1.[9] Biscarbene complexes **2a** and **2b** were selected as templates for the macrocyclic structures. Reaction of these bis-carbene complexes **2** with diamines (2:1 ratio) in THF solution at room temperature afforded the binuclear carbene complexes **3** in high yields. These complexes were obtained as a single stereoisomer (*Z*,*Z*) in accordance with the data reported in the literature.[8,10] Further reaction of the bis-enaminocarbene complexes **3**, with an equimolecular amount of the corresponding bis-carbene complex **2**, yielded cyclophane carbene complexes **1** in good yields.[11]

The tetranuclear macrocycles are quite stable, can be easily purified by flash column chromatography on silica, and were characterized by spectroscopic and analytical methods. ^{1}H NMR and ^{13}C NMR spectra for all complexes exhibit the same features. Significantly, the ^{13}C NMR spectra show a single signal in the range of 283.9−308.7 ppm attributable to the carbene carbon, indicating the presence of one single steroisomer (all-(*Z*)). The stereochemistry was assigned by comparison of their spectroscopic data with reported analogue structures.[10] Chromium or tungsten macrocyclic carbenes can be prepared in this way, and diverse diamines can be used as linkers to join the two bis-carbene moieties.

Scheme 1



The versatility of the method also enables the facile synthesis of heterotetrametallic complexes. This is an important aspect because the introduction of different metals in the same system may further control the reactivity and properties of the complexes formed. Thus, reaction of bistungsten enaminocarbene complex **3b** with chromium biscarbene complex **2a**, in a stoichiometric ratio, afforded complex **1c** in 41% yield. Compound **1c** was isolated as an inseparable mixture of stereoisomers in the chromium moieties in a 1:2 ratio, as it can be deduced from the

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Schimer, H.; Duesch, M. *Angew. Chem., Int. Ed.* **2000**, *100*, 3591. (g) Sierra, M. A. *Chem. Rev.* **2000**, *100*, 3591. (h) Barluenga, J.; Fañanas, F. J. *Tetrahedron* **2000**, *56*, 457. (i) Barluenga, J.; Flórez, J.; Fañanas, F. J *J. Organomet. Chem.* **2001**, *624*, 5.

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(11) The following preparation of tetrametallic macrocyclic **1a** is representative. To a solution of chromium carbene complex **2a** in THF was added 1,4-diamino benzene in one portion (2:1 molar ratio). The mixture was stirred at room temperature under argon until the dissappearance of the starting material (checked by TLC). The solvent was removed under reduced pressure to yield compound **3a** (100%). **3a**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.57 (t, 6H, $J = 7.0$ Hz), 3.61 (br s, 4H, NH_2), 4.85 (q, 4H, $J = 7.0$ Hz), 6.22 (s, 2H), 6.40−6.51 (m, 8H, ar), 7.19−7.24 (m, 4H, ar), 10.33 (s, 2H, NH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.7, 74.2, 115.3, 116.7, 120.8, 124.7, 128.6, 129.0, 130.3, 135.6, 144.7, 147.1, 218.3, 224.2, 298.1; IR (KBr) ν 2048, 1909, 1541, 1514, 1198 cm^{-1}. Anal. Calcd for $C_{38}H_{30}Cr_2N_4O_{12}$: C, 54.42; H, 3.61; N, 6.68. Found: C, 54.55; H, 3.76; N, 6.51. The bis-enaminocarbene **3a** was dissolved in dry THF and reacted with an equimolar amount of the chromium complex **2a**. The mixture was stirred for 1 h. The solvent was reduced in vacuo and the macrocyclic purified by flash column chromatography under argon to yield pure tetranuclear complex **1a** (75% yield). **1a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.65 (t, 12H, $J = 7.0$ Hz), 4.95 (m, 8H), 6.38 (s, 8H, ar), 6.64 (s, 4H), 6.96 (m, 4H, ar), 7.74 (s, 2H, ar), 10.24 (s, 4H, NH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.7, 74.8, 122.4, 122.9, 127.6, 127.7, 131.3, 135.0, 136.2, 142.7, 217.8, 224.1, 308.5; IR (KBr) ν 2052, 1975, 1931, 1535, 1371, 1350, 1192 cm^{-1}. Anal. Calcd for $C_{64}H_{44}Cr_4N_4O_{24}$: C, 52.61; H, 3.04; N, 3.83. Found: C, 52.85; H, 3.26; N, 3.68.

spectroscopic data. ^{13}C NMR spectrum of **1c** displays two signals at δ 308.2 and 308.4 ppm attributable to different chromium moieties. However, the tungsten carbene carbons exhibit a single signal at δ 283.3 ppm. The stereochemistry of this mixture could not be assigned unequivocally.

It should be noted that this methodology allows control of the geometry and the size of the cavity of the cyclophane. They can be designed as a function of the bis-carbene complexes employed and the diamine used as a linker. To evaluate the geometry and the size of the cavity created in tetranuclear macrocyclic complexes **1a**−**c**, a semiempirical PM3 calculation[12] was performed using the corresponding nonmetallic macrocyclic tetraethyl ester as a model. From the data obtained, the size of the cavity allows accommodation of molecules of about 6 Å.

Redox properties of compounds **1a**−**e** were also examined in order to evaluate the interaction among the metallic centers of the macrocyclic complexes, as well as the influence of the metal and the spacer on their electron-donating and -accepting abilities. Cyclic voltammograms of macrocycles **1a**−**e** in $Bu_4NClO_4-CH_2Cl_2$ are displayed in Figure 1.[13] The electrochemical properties are summarized in Table 1.

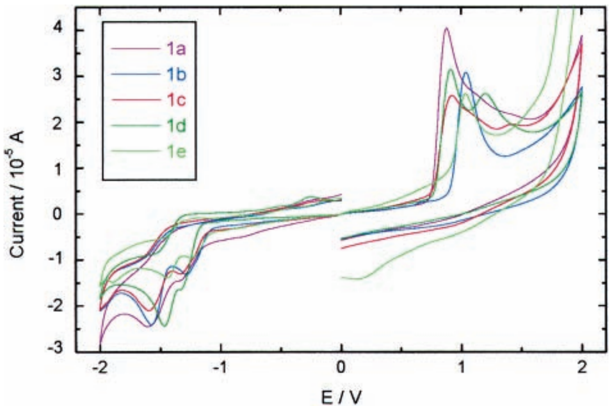

Figure 1. Cyclic voltammograns of complexes **1** in 0.1 M $Bu_4ClO_4-CH_2Cl_2$ at a scan rate of 0.1 V/s at 25 °C.

Table 1. Electrochemical Data Obtained for Complexes **1**

compound	1st E_{pa}	2nd E_{pa}	1st E_{pc}	2nd E_{pc}
1a	0.88		−1.34	−1.60
1b	1.04		−1.28	−1.57
1c	0.92	1.05	−1.33	−1.59
1d	0.91	1.20	−1.33	−1.46
1e	1.03		−1.24	−1.44

All homometallic chromium carbenes show an irreversible oxidation wave of the metal moieties in a range of $E_{\mathrm{pa}} = 0.88-0.92$ V. The analogous homometallic tungsten carbene complexes behave in a similar way, showing a further irreversible one-step oxidation in the range of $E_{\mathrm{pa}} = 1.03-1.04$ V. All tungsten carbene complexes in Table 1 exhibit higher oxidation potentials than the related chromium complexes, following the reported pattern for this kind of complexes.[14]

Bis-carbene **4** and mononuclear enaminocarbene **5** display the same features ($E^1_{\mathrm{pa}} = 0.83$ and 0.95 V, respectively) (Figure 2). This means that the interaction among the metal centers of the cyclophane is practically nonexistent.[15]

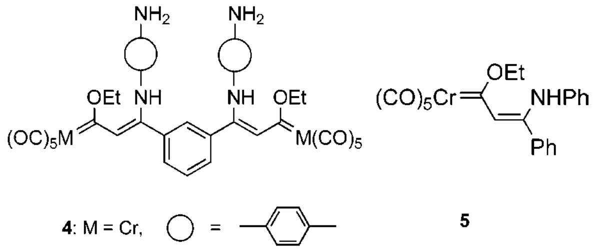

Figure 2.

The voltammogram of cyclophane **1d** displays a second clear oxidation wave at 1.20 V that could be attributable either to the diamine used as a spacer or to a second oxidation step in the Fischer carbene moiety. Oxidation of the diamine bridge may be discarded because the corresponding tungsten carbene cyclophane **1e** voltammetry shows only the usual one oxidation step of the metal center. Moreover, the diamines used through this work have lower oxidation potentials that are not observed for macrocycles **1** ($E^1_{\mathrm{pa}} = 0.49$ V and $E^2_{\mathrm{pa}} = 1.03$ V for 1,4-diaminobenzene and $E^1_{\mathrm{pa}} = 0.57$ V, $E^2_{\mathrm{pa}} = 0.75$ V, $E^3_{\mathrm{pa}} = 1.00$ V, and $E^4_{\mathrm{pa}} = 1.17$ V for

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(12) Calculations were carried out using the GAUSSIAN 98 suite of programs. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

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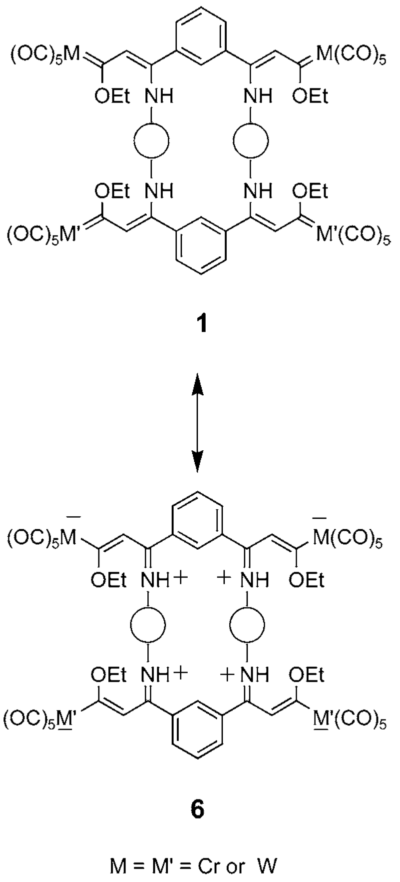

1

6

M = M' = Cr or W

Figure 3.

benzidine).[16] These results suggest an important contribution of the resonance structures **6** in complexes **1** (Figure 3).[9]

Reduction potentials are a good measurement of the electron-accepting ability of these complexes.[17] Although there are no significant changes in the values obtained for all compounds, tungsten cyclophanes **1b** and **1e** present less negative E_{pc} values, which is in accordance with the higher polarizability of tungsten compared to chromium.[18]

In summary, a methodology for preparing a family of new polynuclear and heterometallomacrocyclic compounds is described. This methodology allows the design and synthesis of novel metallocyclophanic structures at will. Further work is in progress in order to study the reactivity and host properties of these compounds.

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Supporting Information Available: Spectral data (^{1}H NMR, ^{13}C NMR, IR, and elemental analysis) for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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