Organometallics **2001,** *20,* 4304−4306

Synthesis of Cyclophanic Chromium(0) Bis(carbene) Complexes

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Received June 25, 2001

Summary: Double Michael addition of 1,4- and 1,3-xylylene diamines and 1,5-diaminobutane to the bimetallic α,β*-unsaturated alkoxychromium(0) carbene complex* ***4*** *produces in good to excellent yields the corresponding cyclophane bimetallic complexes* ***5*−*7*** *as single isomers. In contrast, the reaction with 1,4-diaminobutane produces a different cyclophane complex,* ***8****, derived from a 1,2- + 1,4-addition process.*

The synthesis of chromium(0) bis(carbene) complexes as well as the study of their reactivity is far behind those of their mononuclear counterparts.[1] In fact, although the first of these compounds was reported by Fischer in 1982,[2] little work has been directed toward the transformation of simple bimetallic complexes into structurally more sophisticated bis(carbenes). Thus, some examples of this kind of transformation can be found in the aminolysis of group 6 alkoxy carbenes with different amines[3] or in the deprotonation and further alkylation of bis(carbene) **1** with $[(CO)_3Fe(C_6H_7)BF_4]$ and $[(CO)_5Re(C_2H_4)BF_4]$ to yield the tetranuclear derivatives **2a** and **2b**, respectively. Compound **3** was also obtained by oxidation of the bis anion formed in the deprotonation process (Figure 1).[4] Aumann has also prepared an impressive array of complex chromium(0) bis(carbenes) while studying 1,4-nucleophilic additions to α,β-unsaturated chromium(0) and tungsten(0) carbene complexes,[1a,i,5] and Macomber has prepared a series of chromium(0) and tungsten(0) bis(carbene) complexes by reaction of the α-anions of group 6 carbene complexes and α,ω-dihaloalkanes.[6] Additionally, Hegedus has reported the preparation of different homo-bis(carbene) complexes in his approach to the synthesis of cyclams.[7]

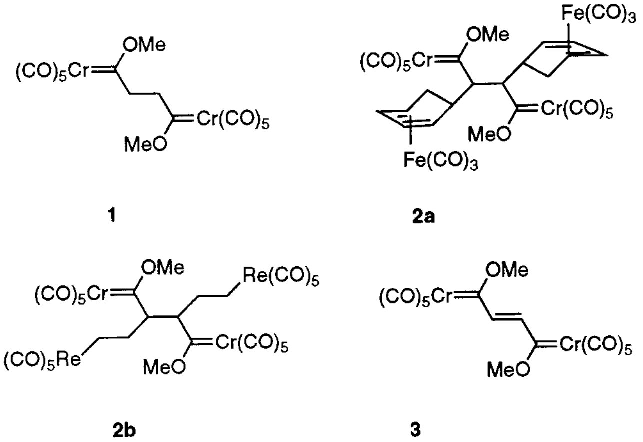
1 **2a** **2b** **3**

Figure 1.

The chemistry of chromium(0) bis(carbene) complexes reported to this moment is that expected for both metal nuclei reacting as isolated centers,[8] although some anomalous results have been obtained in the regiochemistry of Dötz-type reactions[9] and during the Pd-catalyzed dimerization of alkylchromium(0) bis(carbenes).[10] These results may point to some kind of interaction between the metal centers during the reac-

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10.1021/om010561e CCC: $20.00
Publication on Web 09/18/2001

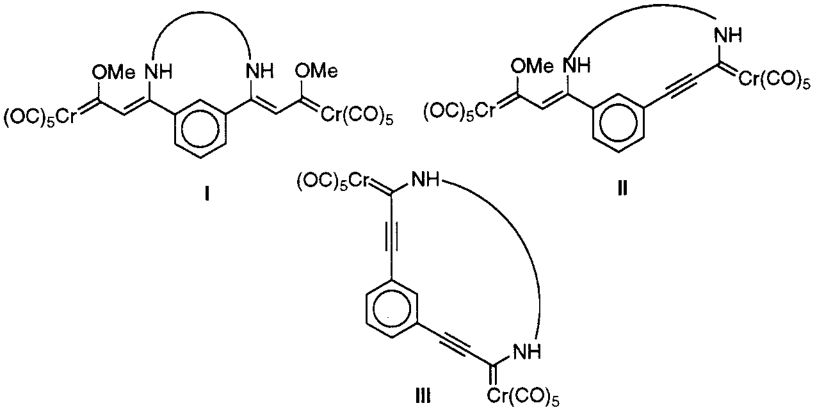

Figure 2.

tion process. In this regard, tethered chromium(0) bis(carbene) complexes with a cyclophanic structure would be of interest. Should their preparation be viable, they would offer a good opportunity to study the reactivity of bimetallic alkoxychromium(0) carbene complexes having severe structural constraints. Here, we report the achievement of the first goal: a general procedure to prepare chromium(0) bis(carbene) complexes having a cyclophane structure.

1,3-Diethynylbenzene was the template selected to build the cyclophanic skeleton. This compound was transformed into the corresponding bis(carbene) complex **4** (26% overall yield) by sequential reaction with BuLi and $[Cr(CO)_6]$ and final quenching of the lithium ate complex thus formed with Et_3OBF_4 (together with complex **4**, the corresponding mono(carbene) complex was obtained in 21% yield, see the Supporting Information for a detailed experimental procedure). The cyclophanic skeleton would be built on complex **4** through a double Michael addition. This assumption was based on the known fact that α,β-unsaturated complexes are exceptional Michael acceptors. However, the regiochemistry of their reaction with amines (namely the 1,4- vs 1,2-addition) is highly influenced by steric and electronic effects. This fact was early demonstrated by Fischer,[11] and it has been extensively studied recently by one of us.[12] In our case, the problem is exacerbated by the necessity to effect the ring closure into the second Michael acceptor, once the first addition has occurred. In fact, taking into account only regiochemical considerations, there are three different types of compounds that could be formed, with generic structures I−III (Figure 2). Nevertheless, we were confident that the double 1,4-adduct would be the main reaction product. This hypothesis was based on the known fact that usually 1,4-addition is obtained when the reaction is carried out at room temperature. As matters evolved, compounds having structures I and II were obtained in these reactions, depending on the nature of the diamine nucleophile.

Complex **4** was reacted with 1,4-xylylenediamine in CH_2Cl_2 at room temperature. The violet solution of complex **4** became deep red instantaneously upon addition of the diamine. After the solvent was removed, the ^1H NMR spectrum of the solid residue showed only the expected cyclophane bis(carbene) complex **5**, formed as a single isomer. No further purification was required, since the product was obtained in analytically pure form. The structure of complex **5** was determined by standard spectroscopic techniques. Since ^1H NMR spectra of complex **5** (and as a matter of fact ^1H NMR spectra of all the cyclophanic complexes obtained through this work) showed ill-resolved broad signals, the well-resolved ^{13}C NMR spectra were decisive in establishing the cyclophane structure (this was also true for the remaining cyclophane complexes synthesized through this work). Thus, a single signal corresponding to the carbene carbon appeared at 297.6 ppm, with additional signals at 223.8 ppm (trans-CO) and 218.4 ppm (cis-CO) which unambiguously established the nature of the alkoxycarbene complex for **5**. Therefore, a double 1,4-addition had occurred (Scheme 1).[13] Analogously, results were obtained with *m*-xylylenediamine and cadaverine (1,5-diaminopentane) that yielded complexes **6** and **7** almost instantaneously. However, in these cases the reactions were slightly dirtier and column chromatography was needed to obtain pure compounds. Complexes **6** and **7** were obtained in 61 and 53% yields, respectively. The spectroscopic pattern in these cases was analogous to that observed with complex **5**, with signals assignable to carbene carbons bearing alkoxy substituents at 297.9 and 294.1 ppm, respectively (Scheme 1). A *Z*,*Z* stereochemistry was assigned to complexes **5**−**7** by comparison of their spectroscopic data with those of their reported noncyclophane analogues.[12]

The reaction between complex **4** and putrescine (1,4-diaminobutane) produced a different outcome. The starting complex was consumed quantitatively, and the crude material was submitted to column chromatography, to yield a red solid having spectroscopic data clearly distinguishable from those discussed for complexes **5**−**7**. In fact, in this case the ^{13}C NMR spectra of the product

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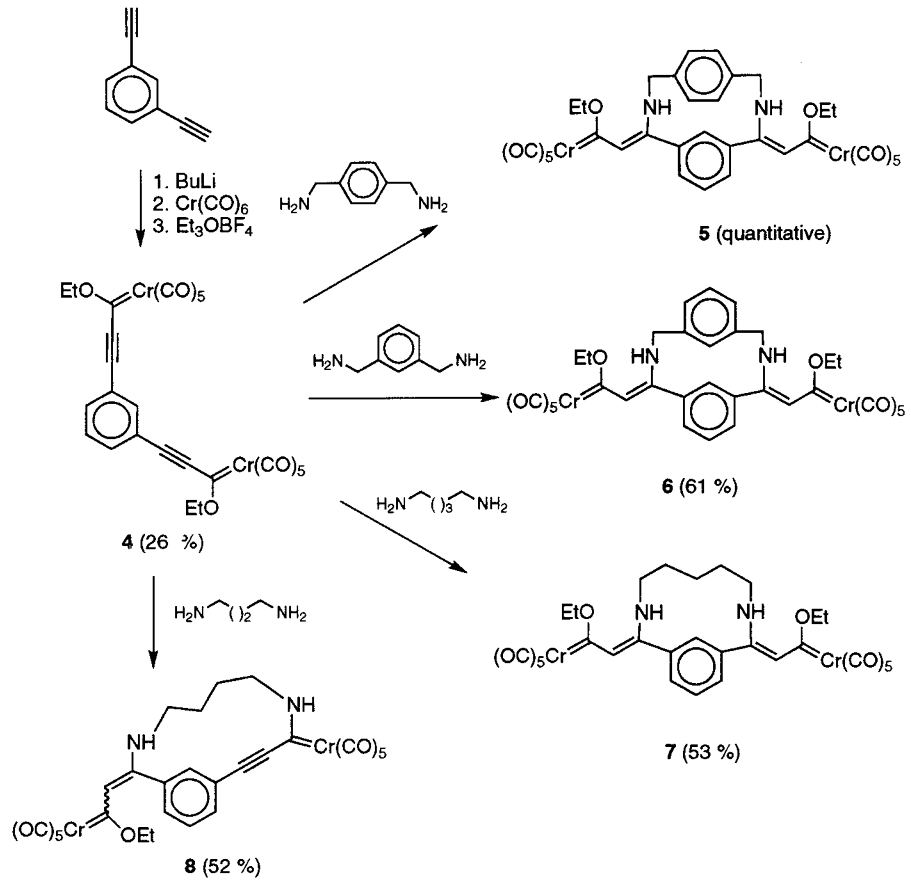
[13] The preparation of bimetallic cyclophane **5** is representative: to a solution of 750 mg (1.21 mmol) of complex **4** in dry CH_2Cl_2 was added *via cannula* at room temperature 164 mg (1.21 mmol) of *p*-xylylenediamine in 75 mL of dry CH_2Cl_2. The reaction mixture was stirred for about 30 min (all the reactions were monitored by TLC until the disappearance of the starting material). An appreciable change of color to deep red was always observed in the reaction mixture. The solvent was removed under reduced pressure to obtain 916 mg (quantitative yield) of complex **5** as a red solid. No further purification was required. ^1H NMR ($CDCl_3$): δ 1.25 (m, 6H), 4.28 (s, 4H), 4.73 (q, 4H, $J = 6.5$ Hz), 6.20 (s, 2H), 7.13−7.46 (m, 8H), 9.04 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 15.5, 49.5, 74.2, 119.6, 127.4, 128.2, 129.7, 135.4, 136.7, 151.5, 218.4, 223.8, 297.6. IR (KBr): ν 2050, 1896 cm^{-1}.

Scheme 1



showed two different signals at 297.8 and 258.6 ppm, indicating that one of the alkoxychromium carbene nuclei had reacted with the amine to produce an aminochromium carbene (signal at 258.6 ppm), while the second amine group reacted as expected in a 1,4-fashion, maintaining the second alkoxychromiumcarbene nucleus (signal at 297.8 ppm). Therefore, the alkoxyamino–bis(carbene) complex **8** (type II in Figure 2) was obtained in this case. This structure is fully consistent with the presence of two different sets of cis- and trans-CO ligands surrounding two different chromium nuclei. This results in four signals at 223.7, 222.9 ppm (trans-CO) and 218.3, 217.0 ppm (cis-CO). The two carbons of the intact triple bond appeared at 88.9 and 119.4 ppm in complex **8**. Furthermore, compound **8** was obtained as an inseparable 1:1 mixture of isomers around the newly formed double bond. The reasons for this anomalous selectivity obtained with putrescine are not clear at this moment.

In conclusion, a new class of bimetallic bis(carbene) complexes having a cyclophanic structure has been prepared, taking advantage of the high Michael reactivity of the bimetallic α,β-unsaturated alkoxychromium(0) carbene complex **4**. The double 1,4-addition occurrs easily with *p*- and *m*-xylylenediamines and cadaverine to form cyclophane bis(carbenes) of type I (Figure 2). However, the reaction with putrescine produces a different cyclophane complex derived from 1,2- + 1,4-addition (type II in Figure 2). The extension of this methodology to prepare other cyclophane bi- and polymetallic complexes as well as the study of their reactivity is actively underway in our laboratories.

Acknowledgment. Support for this work under Grants PB97-0323 and 2FD97-0314-CO2-02 from the Dirección General de Enseñanza Superior e Investigación Científica y Técnica (MEC-Spain) and the European Commission is acknowledged. I.F. acknowledges the MEC for a predoctoral (FPI-MEC) fellowship.

Supporting Information Available: Text describing the full experimental procedure and characterization of compounds **5**–**8**. This material is available free of charge via the Internet at http.//pubs.acs.org.

OM010561E