with $x = 2$, L = HMPA, $x = 1$, L = TMEDA or PMDETA, result in 83–95% yields from n-BuLi + NH_4SCN + L reactions in hexane/toluene; thermodynamic (enthalpic and, possibly more important, entropic) parameters are also being calculated.

Acknowledgment. We thank the S.E.R.C. (D.B. and R.S.), the Royal Society (R.E.M.), and the Associated Octel Co. Ltd. (R.S. and D.S.W.) for financial support and Professor R. D. Chambers for helpful discussions.

Electrochemically Induced Reversible Insertion of Ruthenium Atoms into an Eight-Carbon Chain†

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Received July 21, 1987

We report remarkable redox chemistry of an organodiruthenium complex in which reversible opening and closing of an eight-carbon chain is accompanied by formation and cleavage, respectively, of a metal–metal bond. A net two-electron transfer, accomplished either electrochemically or with a chemical redox agent, is an integral part of the reaction. This redox-initiated C–C bond activation may have relevance to the mechanism of the nickel-catalyzed tetramerization of acetylene.[1,2]

Earlier studies[3] demonstrated that the pseudo-triple-decker[4] complexes $Cp_2M_2(cot)$[5] (**1**: M = Co, Rh; see Scheme I) undergo substantial flattening of the bridging cyclooctatetraene ligand when oxidized by two electrons to give **2** (M = Co, Rh; $n = 2$). The two butadiene-like halves of the cot ring remain slightly twisted from coplanarity in **2**.[3b] In a search for even more electron-deficient members of this series, the oxidation of $Cp_2Ru_2(cot)$ (**3**) was investigated. This diruthenium complex is isoelectronic and isostructural[6] with **2** but is more readily oxidized since it is neutral.

Solutions of **3** at 298 K in acetone/0.1 M Bu_4NPF_6 display an anodic wave of two-electron height at +0.04V versus SCE when scanned in CV[5] experiments. A cathodic wave at −0.25 V arises from re-reduction of the oxidation product. Bulk coulometric oxidation of **3** released 2 faradays of charge and resulted in stable solutions of a red-brown dication, **4**. The dication was isolated either from acetone with 2 equiv of $[Cp_2Fe][PF_6]$ as oxidant or from dichloromethane with low-temperature electrolysis (**4** precipitated nearly quantitatively from CH_2Cl_2 solutions of **3** electrolyzed at 220 K).

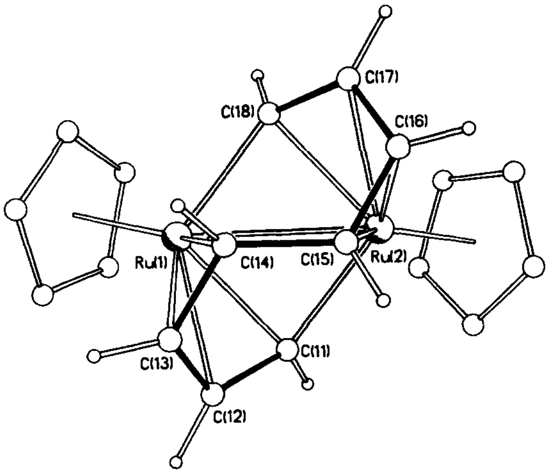
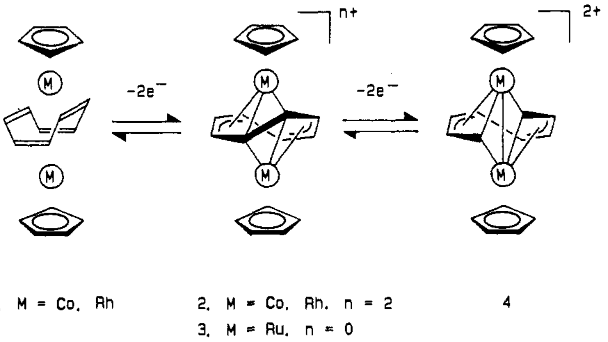


Figure 1. Molecular structure and labeling scheme for $[C_{18}H_{18}Ru_2][PF_6]_2 \cdot 0.5C_6H_6$ (distances in Å, angles in deg): Ru(1)–Ru(2), 2.7291 (4); Ru(1)–CNT(1), 1.868 (5); Ru(2)–CNT (2), 1.881 (5); Ru(1)–Cu(11), 2.131 (4); Ru(1)–C(12), 2.213 (5); Ru(1)–C(13), 2.181 (7); Ru(1)–Cu(14), 2.233 (8); Ru(1)–C(18), 2.066 (4); Ru(2)–C(11), 2.063 (4); Ru(2)–Cu(15), 2.228 (7); Ru(2)–C(16), 2.174 (7); Ru(2)–C(17), 2.216 (6); Ru(2)–C(18), 2.143 (5); C(11)–C(12), 1.417 (8); C(12)–C(13), 1.407 (10); C(13)–C(14), 1.400 (8); C(14)–C(15), 1.491 (7); C(15)–C(16), 1.366 (8); C(16)–C(17), 1.408 (10); C(17)–C(18), 1.414 (8); C(11)···C(18), 3.195 (8). C(11)–Ru(1)–C(18), 99.1 (2); C(11)–Ru(2)–C(18), 98.8 (2); Ru(1)–C(11)–Ru(2), 81.2 (2); Ru(1)–C(18)–Ru(2), 80.8 (2); Ru(1)–C(11)–C(12), 74.1 (3); Ru(2)–C(11)–C(12), 132.5 (4); Ru(1)–C(18)–C(17), 131.8 (4); Ru(2)–C(18)–C(17), 73.9 (3); C(11)–C(12)–C(13), 121.3 (4); C(12)–C(13)–C(14). 118.0 (5); C(13)–C(14)–C(15), 120.5 (5); C(14)–C(15)–C(16), 120.3 (5); C(15)–C(16)–C(17), 118.2 (5); C(16)–C(17)–C(18), 121.9 (5). CNT(1)–Ru(1)–Ru(2)–CNT(2), −31.5 (4); C(11)–C(12)–C(13)–C(14), −13.3 (6); C(12)–C(13)–C(14)–C(15), −38.3 (6); C(13)–C(14)–C(15)–C(16), 152.3 (6); C(14)–C(15)–C(16)–C(17), −36.7 (6); C(15)–C(16)–C(17)–C(18), −14.8 (6).

Scheme I



NMR spectra of the dication displayed an unusually low-field resonance in both ^1H (δ 13.4) and ^{13}C (δ 195) experiments.[7] The carbon resonance was reminiscent of those observed for bridging carbons in "flyover" complexex[8] and suggested that the eight-carbon ring had been fractured in the dication. This suspicion was confirmed by X-ray crystrallography on crystals grown from nitromethane/benzene.[9]

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† Structural Consequences of Electron-Transfer Reactions. Part 16. Part 15: Van Order, N., Jr., et al. *J. Am. Chem. Soc.* **1987**, *109*, 5680.

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[4] Lauher, J. W.; Elian, M.; Summerville, R. H.; Hoffman, R. *J. Am. Chem. Soc.* **1976**, *98*, 3219.

[5] Abbreviations used in this paper are the following: cot = cyclooctatetraene; Cp = η^5-cyclopentadienyl; CV = cyclic voltammetry.

[6] (a) Bieri, J. H.; Egolf, T.; von Philipsborn, W.; Piantini, U.; Prewo, R.; Ruppli, U.; Salzer, A. *Organometallics* **1986**, *5*, 2413. (b) **3** has been characterized by X-ray crystallography.

[7] NMR data for **4** (acetone-d_6): δ 13.40 (d, J = 6.8 Hz, 2 H, $Ru_2C\mathit{H}CHCHCH$), 7.30 (dd, J = 6.8, 5.4 Hz, 2 H, $Ru_2CHC\mathit{H}CHCH$), 6.37 (m, 2 H, $Ru_2CHCHC\mathit{H}CH$), 6.03 (s, 10 H, C_5H_5), and 4.64 (d, J = 7.6 Hz, 2 H, $Ru_2CHCHCHC\mathit{H}$).

[8] (a) Knox, S. A. R.; Stansfield, F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1978**, 221. (b) Knox, S. A. R.; Stansfield, F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 173. (c) Boileau, A. M.; Orpen, A. G.; Stansfield, R. F. D.; Woodward, P. *Ibid.* **1982**, 187; (d) Green, M.; Kale, P. A.; Mercer, R. J. *J. Chem. Soc., Chem. Commun.* **1987**, 375.

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The main features of $[Cp_2Ru_2(C_8H_8)]^{2+}$ (**4**) are as follows (Figure 1). The eight-carbon ring of the neutral precursor has opened, giving a chain whose termini now bridge the newly formed Ru–Ru bond. The metals have inserted into a C–C bond of the original cot ring and two new Ru–C σ bonds have formed. Each metal is bonded to five carbons of the chain (by two σ and three π bonds) and to the other metal (Ru–Ru distance 2.7291 (4) Å). The central structure is basically that of a ten-membered dimetallacyclic ring; the Cp rings adopt a cis configuration.

The flyover dication **4** shows CV behavior complementary to that of **3**. Thus, it reduces at -0.28 V and has a coupled anodic wave at +0.02 V. Coulometric reduction of **4** in acetone consumes two electrons and gives solutions with the same electrochemical behavior as **3**. Extraction of the reduced solutions with benzene allowed isolation of **3**, confirming that reduction of **4** results in re-formation of the cyclooctatetraene ring. Thus, it is clear that **3** and **4** constitute a chemically reversible redox couple involving an overall two-electron transfer.[10]

$$\underset{\mathbf{3}}{Cp_2Ru_2(cot)} \rightleftarrows \underset{\mathbf{4}}{Cp_2Ru_2(C_8H_8)^{2+}} + 2e^-$$

Dimetallacycles have been viewed as key intermediates in the formation of cyclooctatetraenes from alkynes,[11] accounting in part for the interest in flyover-type metallacycles.[8,11-13] Up to the present, however, no examples of reversible zipping and unzipping of the final C–C link of the *n*-carbon chain appear to have been reported.[14] The present data show that electron-transfer processes may initiate such intramolecular coupling and uncoupling reactions. This observation should spur investigations of the redox reactions of other metallacyclic complexes.

Acknowledgment. This work was generously supported at Vermont by the National Science Foundations (CHE 86-03728) and at Zürich by the Swiss National Science Foundation (2.846-0.85). A gift of cyclooctatetraene from BASF is gratefully acknowledged. We thank U. Piantini and W. von Philipsborn (University of Zürich) for recording and simulating the NMR spectra of **4**.

Supplementary Material Available: Tables of atomic coordinates, isotropic and anisotropic parameters, bond distances, and bond angles (6 pages); listing of structure factors (33 pages). Ordering information is given on any current masthead page.

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(9) For $[C_{18}H_{18}Ru_2][PF_6]_2 \cdot 0.5C_6H_6$: triclinic, $P1$, $a = 9.237$ (3) Å, $b = 9.234$ (3) Å, $c = 16.151$ (5) Å, $\alpha = 80.31$ (3)°, $\beta = 74.09$ (2)°, $\gamma = 68.09$ (2)°, $V = 1225.8$ (7) Å^3, $Z = 2$, D(calcd) = 2.074 g cm^{-3}, μ(Mo Kα) = 14.4 cm^{-1}, $T = 293$ K, and crystal dimensions = 0.24 × 0.26 × 0.30 mm. A deep red crystal mounted on a glass fiber was found to have no symmetry higher than triclinic. Of 5891 reflections collected ($4° \leq 2\theta \leq 55°$, Nicolet R3m/μ), 5605 were independent [R(int) = 1.60%] and 4558 with $F_o \geq 3\sigma(F_o)$ were considered observed. The two metal atoms were located by direct methods; subsequent difference Fourier syntheses located all atoms. With all non-hydrogen atoms anisotropic and all hydrogen atoms isotropic: $R(F) = 3.89\%$ [all data R(F) = 4.86%], $R(wF) = 4.57\%$, GOF = 1.44, $\Delta/\sigma = 0.07$, $\Delta(\rho) = 0.77$ e Å^{-3} (in PF_6^- ion), $N_o/N_v = 11.2$. SHELXTL (5.1) software (Nicolet Corp., Madison, WI) was used for all computations.

(10) Low-temperature CV measurements suggest that the oxidation consists of two one-electron processes with very similar $E°$ values. The mechanism is under scrutiny.

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(13) (a) Geibel, W.; Wilke, G.; Goddard, R.; Kruger, C.; Mynott, R. *J. Organomet. Chem.* **1978**, *160*, 139. (b) Goddard, R.; Kruger, C. In *Electron Distributions and the Chemical Bond*; Coppens, P., Hall, G., Eds.; Plenum: New York, 1982; p 297. (c) Wilke, G. In *Fundamental Research in Homogeneous Catalysis*; Tsutsui, M., Ed.; Plenum: New York, 1978; Vol. 3, p 1.

(14) The flyover complex $Cp_2Cr_2(C_8H_8)$,[13a] structurally similar to **4** but with two fewer valence electrons, was originally believed to reversibly rearrange to a complex with a closed cot ring[11] an interpretation which was later discarded.[13a] Unusual line-broadening in its NMR spectra are now established as due to temperature-dependent paramagnetism (Dr. J. Heck, personal communication to A.S., 1987). Non-reversible thermal rearrangement to the closed-chain isomer has been observed.[13b,c] Arewgoda et al.[15] have identified hexakis(trifluoromethyl)benzene in the decomposition of the flyover radical anion $Co_2(CO)_4[\mu\text{-}C_6(CF_3)_6]^-$.

(15) Arewgoda, C. M.; Bond, A. M.; Dickson, R. S.; Mann, T. F.; Moir, J. E.; Rieger, P. H.; Robinson, B. H.; Simpson, J. *Organometallics* **1985**, *4*, 1077.

Rigid Molecular Tweezers: Synthesis, Characterization, and Complexation Chemistry of a Diacridine

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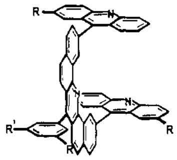
Received August 21, 1987

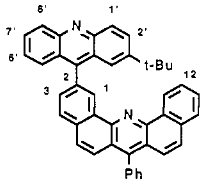
Synthetic receptors containing two aromatic (complexing) chromophores connected by a single spacer have been referred to as *molecular tweezers*.[1] These nonmacrocyclic receptors can have distinct advantages over their cyclic relatives (cyclophanes[2]) in terms of the size and *topology* of the guest which can be complexed.[3] Thus, a molecular tweezer with an ca. 7-Å interchromophore distance can complex guests of unrestricted length and width provided they have the thickness of a single aromatic ring. With respect to topology it is not surprising that both natural and synthetic DNA bis intercalators possess the molecular tweezer structure type.[4-6]

Little is known about the structural and electronic requirements for optimum complexation by a molecular tweezer. Chen and Whitlock have shown that in aqueous medium the spacer unit should be rigid in order to prevent self-association of the complexing chromophores.[1] Molecular tweezers studied thus far have contained spacers of varying degrees of rigidity but none have *preorganized* the cavity for complexation since they are conformationally mobile.[1,5,6] The importance of preorganization in the complexation of metal ions by crown ethers is now well appreciated as a result of Cram's studies of spherands.[7]

Herein we describe the synthesis of the first molecular tweezer **1** in which a rigid spacer enforces a syn–cofacial orientation of the two complexing (acridine) chromophores. The acridine moieties in **1** show remarkable cooperativity in complexation while a flexible, yet noncollapsing diacridine **7** complexes very weakly. The dibenz[*c*,*h*]acridine spacer was chosen since its C-2 to C-12 distance is 7.24 Å and chromophores attached at these positions appeared likely to lie in parallel planes.[8,9] The synthesis began



1a: R, R' = H
1b: R = t-Bu, R' = Me
1c: R, R' = t-Bu



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