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Synthesis of a Nickel(0) Complex of a Methoxy-Substituted Tribenzocyclotriyne. X-ray Crystallographic Evidence for an *Inter*molecular C–H–Ni Agostic Interaction

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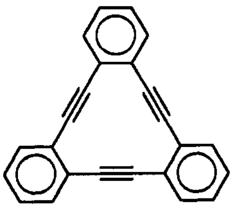
Summary: The synthesis and characterization of a nickel(0) complex of 5,6,11,12,17,18-hexadehydro-1,4,7,10,13,16-hexamethoxytribenzo[a,e,i]cyclododecene (2) is described. The crystal structure revealed the presence of intermolecular agostic C–H---Ni and intermolecular C–H---O interactions.

Cyclotriynes[3] such as TBC (1) are extensively conjugated, planar, anti-aromatic molecules. The cavity of TBC is of sufficient size to form complexes with low-oxidation-state first-row transition metals Ni(0),[4] Cu(I),[5] and Co(0).[6] With the larger Ag(I) cation a sandwich compound is formed.[7] The arrangement of the alkynes allows for the templating of three or four metal moieties to form aggregates[8] and clusters.[6] When it is partially reduced with alkali metals, Ni(TBC) increases its conductivity by 4 orders of magnitude.[9,10] With lithium metal TBC undergoes a novel alkyne cyclization reaction.[11]



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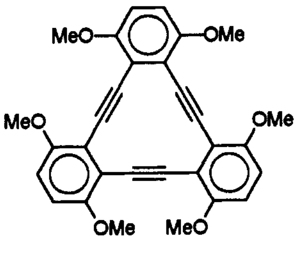

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The unprecedented versatility of TBC as a ligand has encouraged us to make derivatives and related compounds. We are synthesizing a variety of new cyclotriynes, including derivatives of TBC substituted with electron-withdrawing or -releasing groups on the benzo rings and cyclotriynes with heterocycles instead of benzo rings. For example, we have reported the synthesis of tribenzocyclotriynes substituted with methoxy groups[12] and a cyclotriyne with thiophenes[13] instead of benzo rings. Varying the substituents on the cyclotriyne ring should affect the ability of the ligand to undergo the cyclization reaction, the reactivity of the ligand with transition metals, the reactivity of the metallocyclotriyne molecules formed with small molecules, and the conductivity of both the doped ligand and metallocyclotriynes. In this paper we wish to report the synthesis of a new metallocyclotriyne molecule, nickel(0) 5,6,11,12,17,18-hexadehydro-1,4,7,10,13,16-hexamethoxytribenzo[*a*,*e*,*i*]cyclododecene (3). The low-temperature X-ray crystal structure of 3[14] shows unusual intermolecular interactions which appear to govern the stacking of molecules in the solid state.

Combining 2[12] with $Ni(COD)_2$ in benzene results in the formation of 3 in an 81% yield.[15] The bonding geometry around the central nickel is virtually identical to that in Ni(TBC),[4] with Ni–C(alkyne) distances averaging 1.955(3) Å and the C(alkyne)–C(alkyne) distances averaging 1.244(5) Å (Figure 1). The nickel atom is essentially in the plane described by the six alkyne carbons (0.0105 Å above the plane). The crystal structure of 3 shows that two methyls (C28 and C30) of the methoxy groups are significantly out of the least-squares plane of the molecule defined by C1–C24. The methoxy carbon C(28) is 1.065 Å below and methoxy carbon C(30) is 0.691 Å above the previously described plane.

The packing diagram for 3 shows that 3 stacks in layers similar to graphite with an interplanar distance of 3.43 Å. This is in contrast with the slipped-stacked herringbone pattern of Ni(TBC). Whereas Ni(TBC) shows no close contacts, the packing diagram of 3 shows the presence of *inter*molecular agostic C–H---Ni and intermolecular C–H---O interactions. These are shown in the portion of the packing diagram given in Figure 2. These interactions appear to be responsible for the differences between the packing of 3 and Ni(TBC). All hydrogen atoms were visible on an electron density map and were refined isotropically.

Intermolecular interaction A (Figure 2) is an agostic interaction between the 16-electron, 3-coordinate nickel(0) atom and hydrogen atom H25A on the methoxy carbon

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[3] (a) Nakagawa, M. In *The Chemistry of the Carbon-Carbon Triple Bond*; 2; Patai, S., Ed.; Wiley-Interscience: New York, 1978; Part 2, pp 635–712, and references therein. (b) Sondheimer, F. *Acc. Chem. Res.* **1972**, *5*, 81–91.

[4] Ferrara, J. D.; Tessier-Youngs, C.; Youngs, W. J. *J. Am. Chem. Soc.* **1985**, *107*, 6719.

[5] Ferrara, J. D.; Tessier-Youngs, C.; Youngs, W. J. *Organometallics* **1987**, *6*, 676.

[6] Djebli, A.; Ferrara, J. D.; Tessier-Youngs, C.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1988**, 548.

[7] Ferrara, J. D.; Djebli, A.; Tessier-Youngs, C.; Youngs, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 647.

[8] Ferrara, J. D.; Tessier-Youngs, C.; Youngs, W. J. *Inorg. Chem.* **1988**, *27*, 2201.

[9] Ferrara, J. D.; Tessier-Youngs, C.; Youngs, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 3326.

[10] Ferrara, J. D.; Tanaka, A. A.; Fierro, C.; Tessier-Youngs, C. A.; Youngs, W. J. *Organometallics* **1989**, *8*, 2089.

[11] (a) Youngs, W. J.; Djebli, A.; Tessier, C. A. *Organometallics* **1991**, *10*, 2089. (b) Malaba, D.; Djebli, A.; Chen, L.; Zarate, E. A.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1993**, *12*, 1266.

[12] Kinder, J. D.; Tessier, C. A.; Youngs, W. J. *Synlett* **1993**, *2*, 149.

[13] Solooki, D.; Kennedy, V. O.; Tessier, C. A.; Youngs, W. J. *Synlett* **1990**, 427.

[14] X-ray crystallographic data for 3: Mo Kα radiation (λ = 0.710 73 Å); triclinic; $P\bar{1}$; T = 133 K; a = 8.927(2) Å, b = 9.115(2) Å, c = 15.149(3) Å; α = 97.15(3)°, β = 98.20(3)°, γ = 107.69(3)°; V = 1143.8(4) Å^3; Z = 2. Refinement on 3173 unique reflections with $|F_o| \geq 4.0\sigma(|F_o|)$ from 3.5 to 50° in 2θ converged to R = 3.85% and R_w = 4.34%; all unique data (4047) gave R = 5.67% and R_w = 4.74%. All hydrogen atoms were located from difference-Fourier maps and refined isotropically.

[15] ^1H NMR ($CDCl_3$): δ 6.25, 3.47. ^{13}C NMR ($CDCl_3$): δ 153.19, 133.10, 114.23, 113.79, 56.96. IR data (Nujol): $\nu(C\equiv C)$ 1968 (vw) cm^{-1}.

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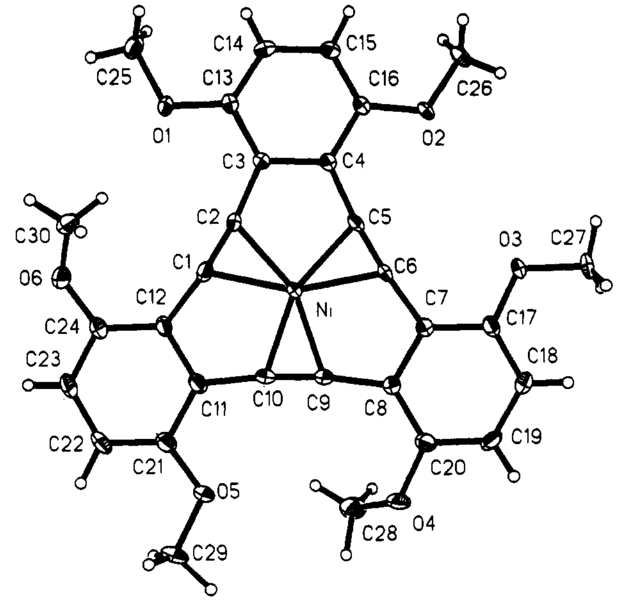

Figure 1. Thermal ellipsoid diagram of 3 drawn at 50% probability.

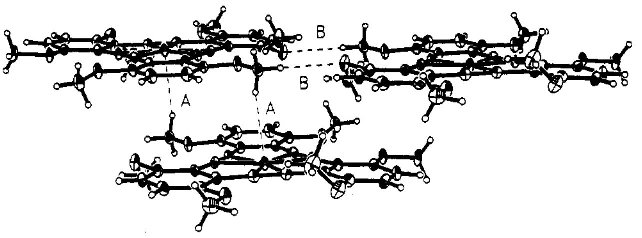

Figure 2. Agostic (A) and hydrogen-bonding (B) interactions for 3.

C25. The Ni---H-C distance is 2.822(1) Å, and the Ni---H-C angle is 163.5(2)°. The Ni-C25 distance is 3.750(4) Å. Numerous examples of intramolecular M---H-C agostic bonding in transition-metal complexes have been reported.[16] The intramolecular M---H-C bond distances range from as close as 1.84 Å for a manganese[17] complex to 2.92 Å for a palladium[18] complex. M-H-C *intermolecular* agostic interactions have been suggested as intermediates in chemical reactions.[16,19] The crystallographic characterizations of M-H-C close contracts between square-planar Pd(2) and Pt(2) metal centers and the α-C-H group of tetralkylammonium cations have been previously reported.[18,20]

Analysis of the packing diagram of 3 reveals the presence of a C-H---O close contact. This interaction involves oxygen atom O6 of one molecule and hydrogen atom H25B on the methoxy carbon C25 of a second molecule, as shown by interaction B in Figure 2. The hydrogen-oxygen distance is 2.551(2) Å, and the carbon-oxygen distance is 3.447(4) Å. The C-H---O angle is 158.7(2)°. There are a number of crystal structures that contain C-H---O hydrogen bonds.[21] The existence of intermolecular C-H---X interactions (where X is O, N, Cl, or S) has been supported by quantum-mechanical[22] and potential energy calculations,[23] spectroscopy,[24] and crystallographic data.[21b,23,25] It has been suggested that, owing to the frequency of C-H---O interactions in known crystal structures, they play a significant role in determining packing arrangements.[23,26]

We have found that different substituents on the cyclotriyne ligands have a strong influence on the chemistry of the ligand. The reaction chemistry of small molecules, particularly CO, with nickel cyclotriynes is very dependent upon the substituents around the central ring.[27] Work is under way to explore the reaction chemistry of 3, the conductivity of 3, and the synthesis of other complexes of 2.

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Supplementary Material Available: Tables of data collection and structure solution details, bond distances and angles, atomic coordinates, and thermal parameters (13 pages). Ordering information is given on any current masthead page.

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(16) (a) Brookhart, M.; Green, M. L. H.; Wong, L. In *Progress In Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1988; Vol. 36, pp 1-124.

(17) Lamanna, W.; Brookhart, M. *J. Am. Chem. Soc.* **1981**, *103*, 989.

(18) Dehand, J.; Fischer, J.; Pfeffer, M.; Mitschler, A.; Zinsius, M. *Inorg. Chem.* **1976**, *15*, 2675.

(19) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332.

(20) Brammer, L.; Charnock, J. M.; Goggin, P. L.; Goddfellow, R. J.; Orpen, A. G.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1991**, 1789.

(21) (a) Desiraju, G. *Acc. Chem. Res.* **1991**, *24*, 290. (b) Desiraju, G. *J. Chem. Soc., Chem. Commun.* **1990**, 454. (c) Jeffrey, G. A.; Maluszynska, H. *Int. J. Biol. Macromol.* **1982**, *4*, 173. (d) Takusagawa, F.; Koetzle, T.; Strikrishnan, T.; Parthasarathy, R. *Acta Crystalogr.* **1979**, *B35*, 1388.

(22) (a) Kollman, P.; McKelvey, J.; Johansson, A.; Rothenberg, S. *J. Am. Chem. Soc.* **1975**, *97*, 955. (b) Umeyama, H.; Morokuma, K. *J. Am. Chem. Soc.* **1977**, *99*, 1316. (c) Vishveshwara, S. *Chem. Phys. Lett.* **1978**, *59*, 26. (d) Gay, R.; Vanderkooi, G. *J. Chem. Phys.* **1981**, *75*, 2281.

(23) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063.

(24) Green, R. D. *Hydrogen Bonding by C-H Groups*; Wiley-Interscience: New York, 1974.

(25) Sutor, D. J. *J. Chem. Soc.* **1963**, 1105.

(26) (a) Berkovitch-Yellin, Z.; Leiserowitz, L. *J. Am. Chem. Soc.* **1982**, *104*, 4052. (b) Sarma, J. A. R. P.; Desiraju, G. R. *Acc. Chem. Res.* **1986**, *19*, 222. (c) Sarma, J. A. R. P.; Desiraju, G. R. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1195. (d) Desiraju, G. R.; Kishan, K. V. R. *J. Am. Chem. Soc.* **1989**, *111*, 4838.

(27) Youngs, W. J.; Tessier, C. A.; Kinder, J. D. U.S. Patent 5 132 231, July 1992.