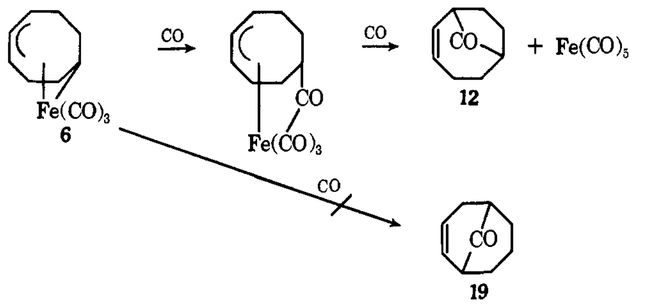

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[13] On leave of absence from Laboratório de Física e Engenharia Nucleares, Sacavem, Portugal.

F. A. Cotton
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

A. J. Deeming, P. L. Josty, S. S. Ullah
Department of Chemistry, University College, London
London, W.C.1., England

A. J. P. Domingos,[13] B. F. G. Johnson, J. Lewis*
University Chemical Laboratory
Cambridge, CB2 1EW, England.

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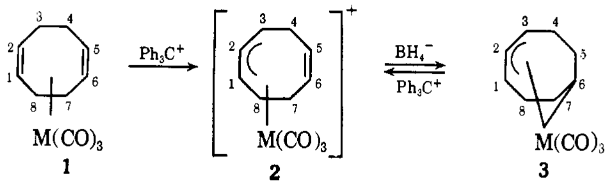
Structural Characterization of a Novel Complex Derived from Tricarbonyl(cyclooctadiene)ruthenium

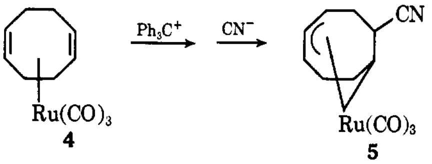
Sir:

In a previous communication[1] it has been proposed that one important reaction sequence beginning with tricarbonyl(cycloocta-1,5-diene)metal(0) complexes is the one shown in eq 1. It was also noted that the intermediates **2** can be treated with nucleophiles other than H^- (in the form of BH_4^-). The use of other nucleophiles, such as CN^-, whose location in the products can be ascertained, is of interest because of the information thus provided about the detailed course of the reactions. We report here on one example, namely the transformation of **4** into **5** and the characterization of the product **5**. The structure confirms the general views which have been given[1] as to the course of this and related reactions.



(1)

Compound **5** can be obtained in the form of air-stable crystals which belong to the orthorhombic system. The space group is *Pbca*, and the unit cell dimensions are: $a = 22.76$ (1), $b = 8.296$ (5), $c = 13.19$ (1) Å. The observed density, 1.69 g/cm^3, may be compared with 1.70 g/cm^3 calculated for eight formula units per cell. Mo Kα radiation filtered by zirconium foil was used to collect 1896 independent reflections on a GE XRD-5 counter diffractometer in a manner previously described.[2] The data were corrected for a slight decomposition observed during data collection and for absorption ($\mu = 12.29$ cm^{-1}). The structure was solved by standard Patterson and Fourier procedures and refined by full-matrix least-squares methods employing anisotropic temperature factors for all nonhydrogen atoms. At the current state of refinement, the conventional R factor is 4.8%.



(2)

The carbocyclic ligand is attached to the ruthenium atom by a σ bond (2.16 Å) from C(6) and by coordination of a π-allyl group formed by C(1), C(2), and C(3) (Ru–C(1), 2.25 Å; Ru–C(2), 2.21 Å; Ru–C(3), 2.28 Å). The cyano group occupies the exo position on C(5). The manner of attachment of the ring to the metal naturally requires extensive folding of the ring, and this can be seen in Figure 1. All bond lengths within the ring system have reasonable values, *viz.*, C(5)–C(9), 1.48 Å; C(9)–N, 1.15 Å; C–C single bonds, 1.52–1.55 Å; C–C bonds in the π-allyl group, 1.41 Å. The Ru–C–O groups have Ru–C(av) = 1.94 Å and C–O(av) = 1.12 Å. The C–Ru–C angles average 94.8°.

As often happens when seven- or eight-membered carbocyclic rings have a multiple attachment to a single metal atom, all C–C–C angles within the ring are greater than the ideal values for sp^2 or sp^3 hybridization. In this molecule, the former average 124.6° and the latter range from 110.6 to 114.7°. The C–C–H angles are correspondingly smaller.

The only previous indication that a cyclooctapolyene ring can bind to a metal in this 1,2,3,6-tetrahapto fashion is found in a cyclooctatetraene complex of tricarbonylosmium, where such a structure has been inferred from the ^{1}H nmr spectrum.[3] With the COT compound the 1,2,3,6-tetrahapto structure rearranges thermally to a 1,2,3,4-tetrahapto one, whereas with 1,5-cyclooctadiene the 1,2,3,6-tetrahapto structure appears to be thermodynamically favored over the 1,2,5,6- or 1,2,3,4-tetrahapto ones, according to results in the preceding communication.

The results presented here support the general scheme in eq 1 and, specifically, substantiate the correctness of structures of type **3**. The location of the cyano group in **5** implies that this nucleophile attacks the intermediate **2** from the exo direction at ring carbon atom 5. There is, of course, no certainty that all other nucleophiles, especially one as unique as H^-, do the same, but

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(3) M. I. Bruce, M. Cooke, M. Green, and D. J. Westlake, *J. Chem. Soc. A*, 987 (1969).

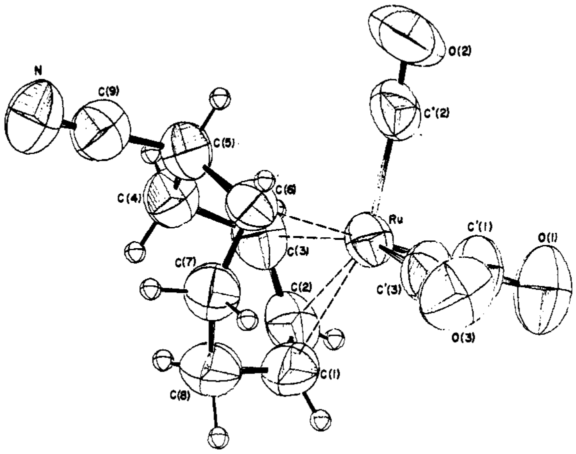

Figure 1. A perspective view of the 1,2,3,6-*tetrahapto*(5-cyanocyclooctadienyl)tricarbonylruthenium molecule.

it seems likely that most of them will behave in the same way.[4]

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F. A. Cotton,* M. D. LaPrade
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

B. F. G. Johnson, J. Lewis
University Chemical Laboratory
Cambridge, CB2 1EW, England

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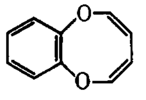
A Synthesis of 1,4-Dithiocins. 1,6-Benzodithiocin[1]

Sir:

A great deal of effort has been devoted to the synthesis of ten-π-electron systems in recent years.[2] Aromaticity has been demonstrated in certain carbocyclic ring systems but the predictions of the $4n + 2$ rule are not, with one exception,[3] borne out by the ten-π-electron heterocycles synthesized thus far. Following the analogy which furan, pyrrole, and thiophene have with benzene, various heterocyclic analogs of the cyclononatetraenyl anion[4] and the cyclooctatetraene dianion[5] have been prepared and studied. Of the heterocyclic analogs[6] of the former, only 1-H azonine exhibits appreciable aromatic character.[3] Three neutral[7] heterocyclic analogs of the latter have been reported (**1**,[8] **2**,[9] and **3**[10]), none of which exhibits nmr spectral properties consistent with aromaticity in the heterocyclic ring.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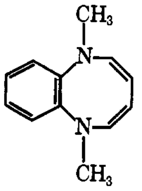

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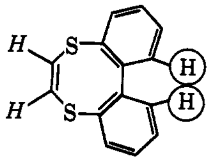
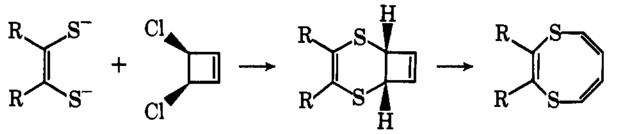


3

Despite the nonaromatic character imputed to compound **3** (the italicized protons resonate at 6.26 ppm[10] but steric interactions between the circled protons could destabilize the planar form), there are two good reasons for believing that eight-membered rings with two sulfur atoms may be the best candidates for ten-π-electron aromatic heterocycles. The aromaticity of the cyclooctatetraene dianion demonstrates that 135° bond angles can be accommodated and a sulfur atom is more nearly equivalent to a carbon–carbon double bond than other heteroatoms.[11]

With this incentive we have undertaken a study of 1,4-dithiocins based on the following synthetic scheme and report in preliminary form our results which, contrary to our original expectations, mitigate against the existence of aromatic character in this system.



Salts of the appropriate *cis*-1,2-dimercaptoethenes[12] were found to condense smoothly with *cis*-3,4-dichlorocyclobutene[13] to give 1,4-dithiocin precursors **4** [50%; mp 178–179°; nmr (CDCl$_3$) δ 4.84 and 6.09 ppm (2 H, m, $W_{1/2} \simeq 2$ Hz); and mass spectrum m/e 116, 165, and 192 (M$^+$)], **5** [61%; mp 102–103°; nmr

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(1) This research was supported by the National Science Foundation (GP-10950) and the Cities Service Oil Co. Presented at the 23rd IUPAC Congress, Boston, Mass., July 1971.

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(11) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962, p 28. This is perhaps best illustrated by the close resemblance which thiophene bears to benzene. The rationalization of this resemblance in terms of d orbital contributions to the π-bonding *via* pd^2 hybrids would be applicable to the 1,4-dithiocins. However, this question of d orbital involvement is a highly contentious one. For recent reviews see W. G. Salmond, *Quart. Rev., Chem. Soc.*, **22**, 253 (1968), and D. T. Clark in "Organic Compounds of Sulphur, Selenium, and Tellurium," Vol. 1, The Chemical Society, London, 1970, p 9.

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