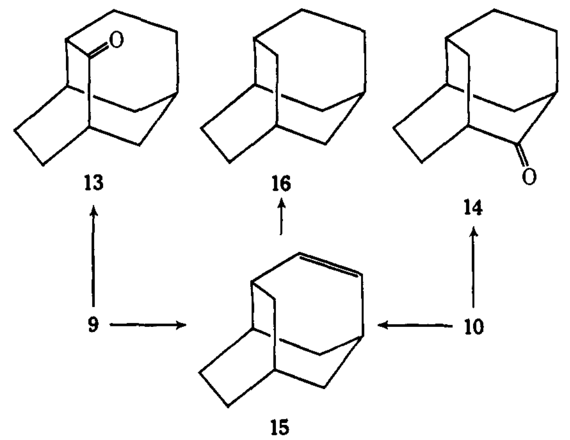
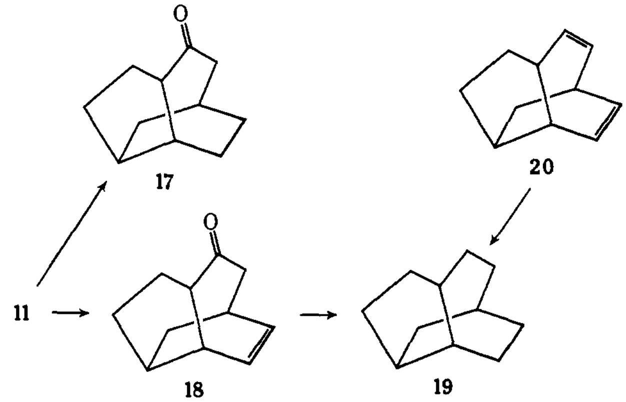
and **5**;[1] in particular, due to the rigidity of the ring structure about the double bond, the resonances of the vinyl protons which appear as "triplets" are very revealing. The separation of 48 Hz for **9** is identical with that for **4**, while the 20 Hz for **10** compares well with the 22 Hz for **5**. In addition the unobscured triplet (τ 7.06)[11] assignable to the allylic bridgehead proton adjacent to the carbonyl in **9** has identical multiplicity and essentially the same chemical shift as the corresponding proton of **4** (τ 7.09).[1]

Hydrogenation of **9** gave saturated ketone **13** (mp 207–208.6°, $\nu_{\max}^{\mathrm{CCl_4}}$ 1702, 1717 cm^{-1}) while **10** gave the isomeric ketone **14** (mp 188–190°, $\nu_{\max}^{\mathrm{CCl_4}}$ 1694, 1715 cm^{-1}). Wolff-Kishner reduction of **9** and **10** each gave olefin **15** (mp 164.7–165.3°), which was converted by hydrogenation to tricyclo$[4.4.1.0^{3,8}]$ undecane (**16**) (mp 181–183°).[12]



The tricyclic ketone **11** (mp 123–125°, $\nu_{\max}^{\mathrm{CCl_4}}$ 1700 cm^{-1}) exhibited nearly equivalent vinyl proton resonances (Figure 1) presumably due to the more symmetrical disposition of the carbonyl group relative to the double bond.[13] Hydrogenation of **11** gave **17** (mp 170.3–171.8°, $\nu_{\max}^{\mathrm{CCl_4}}$ 1696 cm^{-1}) while modified Wolff-Kishner reduction[15] gave olefin **18** (mp 133.3–134°), which was converted by hydrogenation to tricyclo$[5.3.1.0^{4,8}]$undecane (**19**) (mp 165–167°). The latter material was identical with that obtained upon hydrogenation of **20**, which is a minor cycloaddition product observed in the pyrolysis of 7-(3-butenyl)cycloheptatriene.[17]



Studies concerned with extensions of this approach to the synthesis of other new bridged polycyclics are in progress.[19]

Acknowledgment. We are grateful to the National Science Foundation for support of this work under Grant No. NSF GP-24392.

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(11) Nmr spectra were obtained on a Varian HA-100 spectrometer. Spectra were obtained in CCl$_4$ with chemical shifts reported as τ in parts per million relative to internal TMS.

(12) That **9** and **10** are nonenolizable was shown by the fact that no deuterium was incorporated under exchanging conditions. See ref 13.

(13) Deuterium exchange[14] of **11** (D$_2$O, K$_2$CO$_3$, dioxane, 48 hr, 100°) gave 78% d_2, 15% d_1, and 7% d_0 (by mass spectroscopic analysis), showing that it was enolizable, in contrast to **9** and **10**.

(14) H. W. Whitlock, Jr., and M. W. Siefken, *J. Amer. Chem. Soc.*, **90**, 4929 (1968).

(15) Reduction of the semicarbazone with sodium methoxide in ethanol at 200° (sealed tube).[16]

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(18) The formation of **20** from 7-(3-butenyl)cycloheptatriene is analogous to the formation of 7% tricyclic ether observed in the pyrolysis of **1**.[1]

(19) The approach outlined in this report also constitutes an alternative synthetic entry to **4** and **5**. We have found, however, that the overall yield is higher when **1** is pyrolyzed directly.

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Tricarbonyl(cyclooctadiene) Complexes of Iron(0), Ruthenium(0), and Osmium(0)

Sir:

Cycloocta-1,5-diene- and cycloocta-1,3-dieneiron tricarbonyl complexes have been reported previously.[1–3] However, the corresponding ruthenium and osmium complexes have not been established. We find that the reactivity of these adducts varies markedly with the metal and, for the cycloocta-1,5-diene derivatives, contrasts with the reactivity of the isoelectronic cobalt(I), rhodium(I), and iridium(I) cyclopentadienyl adducts.

The reaction of cycloocta-1,3-diene with dodecacarbonyltriruthenium has been studied under a variety of conditions. The organometallic product isolated from these reactions was always $\mathrm{C_8H_{12}Ru_3(CO)}_n$ (n = 9 or 10[4]). In contrast, reaction of cycloocta-1,5-diene with the same carbonyl in benzene under reflux led, after limited periods (up to 8 hr), to a reaction mixture containing the three isomeric forms of cyclooctadiene and a complex of composition $\mathrm{C_8H_{12}Ru(CO)_3}$ (**3**). Isolation of **3** and analysis of its ^{1}H nmr spectrum showed it to be tricarbonyl(cycloocta-1,5-diene)ruthenium. Over more extended periods (~10 hr), complex **3** underwent slow conversion to a second isomer **7**, the ^{1}H nmr spectrum of which establishes that both a carbon–ruthenium σ bond and h^3-allyl–ruthenium bond had been formed. A related product from the photochemical reaction of dodecacarbonyltriosmium and cyclooctatetraene had been observed previously.[5]

In contrast, reactions of dodecacarbonyltriosmium with either cycloocta-1,3-diene or cycloocta-1,5-diene

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(1) J. E. Arnet and R. Pettit, *J. Amer. Chem. Soc.*, **83**, 1954 (1961).

(2) R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, **1**, 1 (1964); M. A. Bennett, *ibid.*, **4**, 353 (1966).

(3) E. K. von Gustorf and J. C. Hogan, *Tetrahedron Lett.*, 3191 (1968).

(4) J. P. Candlin, K. K. Joshi, and D. T. Thompson, *Chem. Ind. (London)*, 1960 (1966).

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

in benzene under reflux led to substitution with retention of the triosmium skeleton. No evidence for the formation of monomers was found. Prolonged irradiation (90 hr) of a suspension of dodecacarbonyltriosmium in benzene with cycloocta-1,5-diene did not yield simply tricarbonyl(cycloocta-1,5-diene)osmium, but rather a mixture of products of general formula $C_8H_{12}Os(CO)_3$. We were unable to separate the components of this mixture; however, ^1H nmr and infrared spectroscopic data indicate that both tricarbonyl(cycloocta-1,5-diene)-osmium and tricarbonyl(cycloocta-1,3-diene)osmium were present. Under the experimental conditions employed, isomerization of the diene also occurred. The photochemical reaction of cycloocta-1,3-diene with dodecacarbonyltriosmium gave, as the single organometallic product, tricarbonyl(cycloocta-1,3-diene)osmium (**13**). The ^1H nmr spectrum of this derivative is in agreement with the proposed structure.

Treatment of complexes **1**, **2**, **3**, **6**, **7**, or **13** with triphenylmethyl tetrafluoroborate results in hydride ion abstraction in all cases. These reactions are summarized in Figure 1. With complexes of the conjugated diene (**2** and **13**), the products of the reaction were the dienyl salts **14**[6] and **15**. With complexes of the nonconjugated diene (**1** and **3**), the products were the allyl-olefin salts **4** and **5**. Cations **14** and **15** are related to the previously reported tricarbonyl(cyclohexadienyl)-derivatives of iron[7] and ruthenium[8] and cations **4** and **5** to the 1,2,3,5,6-*pentahapto*cyclooctadienyl derivatives of cobalt, rhodium, and iridium.[9] Reduction of **4** with sodium borohydride gave two products. One was the initial cycloocta-1,5-diene complex **2** (10%) and the other a σ,h^3-allyl complex **6** (90%). Reduction of **5** gave **7** as the sole product. These results are in distinct contrast to those obtained in the reduction of the isoelectronic ions $[C_8H_{11}MCp]^+$ (M = Co or Rh) in which nucleophilic attack occurs at the h^3-allyl fragment, and the cycloocta-1,5-diene derivative is the only reaction product. This change emphasizes the importance in these systems of the overall charge of the metal and reflects a change in charge density within the $C_8H_{11}^+$ species with change in the coordinated metal unit. Somewhat similar results were obtained in the reduction of $[C_8H_{11}Os(CO)_3]^+$ (**15**) with sodium borohydride. This reduction produced, as the sole product, the σ,h^3-allyl complex **17**. However, in contrast to complexes **6** and **7** described above, analysis of the ^1H nmr spectrum of **17** indicated that it was of the 1,2,3,5-tetrahapto type. Some experimental support for this structure came from the reaction of **17** with triphenylmethyl tetrafluoroborate to give the 1,2,3,5,6-pentahapto ion **18** and not the simple 1,2,3,4,5-pentahaptodienyl salt **15**. Reduction of the corresponding iron salt **14** followed a different reaction path. The major product obtained was the cycloocta-1,3-diene complex **2**, but in addition a second product of composition $(C_{12}H_{24}O)$-$Fe(CO)_3$ (**16**) was isolated. The structure and stereochemistry of this second compound are under investigation.

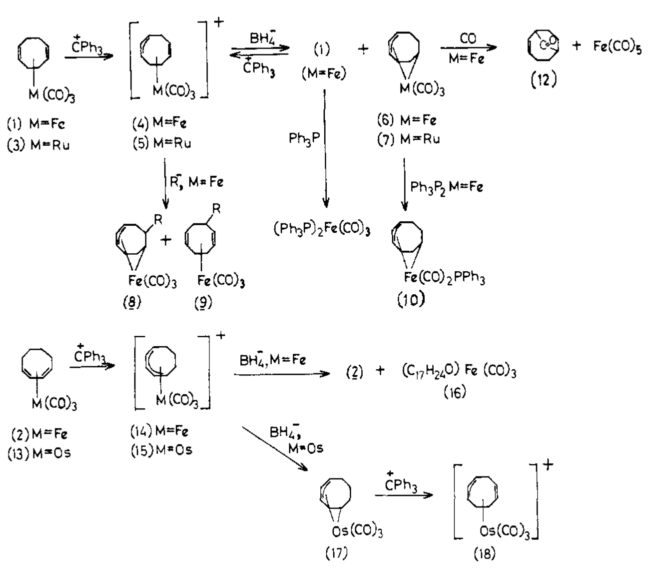

Figure 1.

The reactions of cations **4** and **5** with a variety of nucleophiles were investigated. Results from these experiments and others,[10] some still in progress, indicate that the production of both the 1,2,3,6-tetrahapto complex **8** and the substituted cycloocta-1,5-diene complex **9** is a general effect, although the ratio of products obtained depends to a large extent on the nucleophile employed. It is possible that steric effects are responsible for this variation.

There is a marked difference in reactivity of the isomers **1** and **6** toward replacement reactions. Thus, substitution in complex **6** with triphenylphosphine occurs at a rate considerably higher than that in complex **1** to give a product identified as dicarbonyl(triphenylphosphine)[1,2,3,6-*tetrahapto*cyclooctadiene]iron (**10**), the carbonyl group replaced being trans to the metal–carbon σ bond. The kinetic data indicate that the reaction is independent of phosphine concentration for both iron and ruthenium derivatives, and the kinetic parameters are comparable with those obtained for reaction of nickel carbonyl with phosphines.[11] In marked contrast, complex **1** losses the organic ligand and $(Ph_3P)_2Fe(CO)_3$ (**11**) is produced. No further replacement of CO or cleavage of the organic group occurred on treating **10** with excess triphenylphosphine in cyclohexane under reflux for 8 hr, reflecting the stability of the metal–carbon σ bond in this system.

Since transition metal–carbon σ bonds are known to undergo insertion reactions with particular ease, we examined the reaction of **6** with carbon monoxide. Under mild conditions, complex **6** gave $Fe(CO)_5$ and an organic product $C_9H_{12}O$. This organic compound has been tentatively assigned structure **12** on the basis of the ir spectrum and ketone characterization reactions. These clearly demonstrated that this product was not the previously reported[12] [3.3.1]bicyclo derivative **19**, and we consider that it is produced by the insertion of carbon monoxide into the iron–carbon bond followed by transannular addition of the π-allylic grouping.

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(9) J. Lewis and A. Parkins, *J. Chem. Soc. A*, 1150 (1967); 953 (1969).

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(11) F. Basolo, J. P. Day, and R. G. Pearson, *ibid.*, **90**, 6927 (1968).

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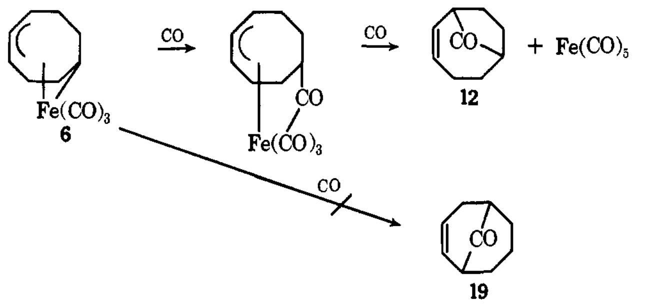

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(13) On leave of absence from Laboratório de Física e Engenharia Nucleares, Sacavem, Portugal.

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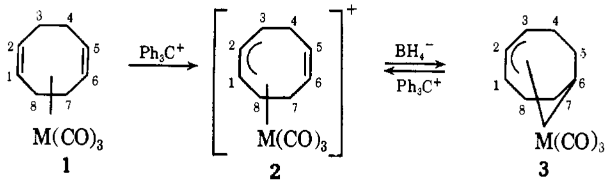
Received May 12, 1971

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

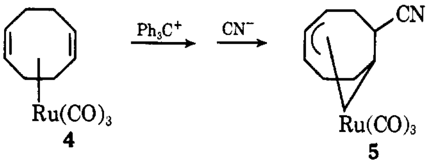
Sir:

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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[1] F. A. Cotton, A. J. Deeming, P. L. Josty, S. S. Ullah, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Amer. Chem. Soc.*, **93**, 4624 (1971).

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