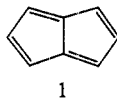# Approaches to the Synthesis of Pentalene *via* Metal Complexes

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Pentalene, which is predicted[1] to have in the ground state the polyolefin structure 1, is unstable,

1

and attempts to prepare the compound by conventional organic synthetic procedures have failed. This is presumably due to its ready dimerization since 1-methylpentalene, identified from its ultraviolet and infrared spectra at −196°, was observed to dimerize at temperatures above −140°.[2] Moreover, although photolysis at −196° of the dimer of 1,3-dimethylpentalene led to spectroscopic identification of the monomer, quantitative regeneration of the dimer occurred on warming to 20°.[3] The presence of bulky substituents on the pentalene system appears to sterically hinder dimerization, and monomeric hexaphenyl-,[4] bis(1,3-dimethylamino)-,[5] and 1,3,5-tri-*tert*-butylpentalenes[6] exhibit fair stability.

Similar behavior is shown by cyclobutadiene, which is detectable only in a matrix at low temperatures.[7-10] As with pentalene, bulky substituents enhance stability, and tri-*tert*-butylcyclobutadiene can be prepared at −70°, although it decomposes on warming to room temperature.[11]

One of the most interesting aspects of the development of organometallic chemistry has been the discovery that transition metals can form stable complexes with organic molecules which are unstable under normal conditions.[12] A classic example is provided by the work of Pettit and his coworkers[13] on cyclobutadiene. Decades of attempts to synthesize this highly reactive hydrocarbon by classical methods were unsuccessful, but in 1965 a stable tricar-

bonyliron complex (2) was obtained by dehalogenation of 3,4-dichlorocyclobut-1-ene with Fe₂(CO)₉.[14]

2
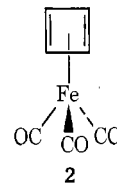
Subsequent release of cyclobutadiene from 2 with ceric ion illustrated the problem facing the early workers, for dimerization occurs at very low temperature. Considerable chemistry of cyclobutadiene is now known since 2 can be used as a source both of the free hydrocarbon and of substituted derivatives *via* electrophilic attack on the coordinated hydrocarbon.[13]

In view of the isolation of 2 it is not surprising that attention should have been given to the stabilization and characterization of pentalene through complexation with transition metals. Katz and coworkers[15]

Gordon Stone was born in Exeter, England, and received his Ph.D. degree from Cambridge University in 1952. After 2 years as a Fulbright Scholar at the University of Southern California, he spent several years at Harvard University, where his interests in organometallic chemistry began. He is now Professor of Inorganic Chemistry at Bristol University. His research has been marked by its breadth covering both the chemistry of the main-group elements and that of the transition metals.

Selby Knox was born in Newcastle-upon-Tyne, England, in 1944, and obtained B.Sc. and Ph.D. degrees from the University of Bristol. After postdoctoral work at the University of California, Los Angeles, with Professor Herbert D. Kaesz, he became a Lecturer in inorganic chemistry at Bristol University in 1972.

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(2) R. Block, R. A. Marty, and P. de Mayo, *J. Amer. Chem. Soc.*, 93, 3071 (1971).

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first synthesized the dianion 3, an aromatic ten-π-

3
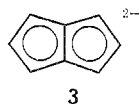
electron system, from dihydropentalene. These investigators[16] treated various transition metal halides with the dianion in reactions paralleling the successful synthesis of *pentahapto*cyclopentadienyl complexes from metal salts and the cyclopentadienide ion. However, an X-ray crystallographic study[17] has shown that an iron complex, $Fe(C_8H_6)_2$, formed from ferrous chloride, is in actuality a derivative (4) of fer-

4
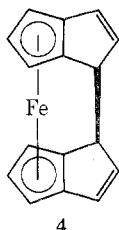
rocene, with a carbon–carbon bond joining the pair of C_5 rings not sandwiching the iron atom. Isoelectronic $[Co(C_8H_6)_2]^+$ probably has a similar structure. Binuclear metal complexes $Ni_2(C_8H_6)_2$ and $Co_2(C_8H_6)_2$ are obtained from $NiCl_2$ or $CoCl_2$ and 3, but in the absence of single-crystal X-ray crystallographic studies their nature is unclear. Reaction of the dianion with $[\eta^3-C_3H_5NiCl]_2$, however, affords[18] a product which has been shown[19] by single-crystal X-ray diffraction studies to contain an essentially planar pentalene ligand bridging two nickel atoms (5a). Although evidently diamagnetic, the molecule is overall two electrons short of satisfying the "18-electron" rule. In terms of the nickel–carbon (ring) bond lengths the structure is best represented by 5a, although in a valence bond representation (5b and 5c) the electron count is better revealed.

5a **5b** **5c**
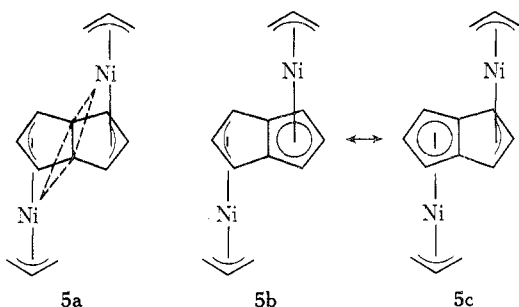
Another approach to the isolation of pentalene as a metal complex involves dehydrogenation of dihydropentalenes with iron carbonyls. In this manner complexes $Fe_2(CO)_5(C_8H_5R)$ (6) have been obtained.[20] Compound 6 (R = H) has also been prepared by treating the dimer of pentalene with

6, R = H, NMe₂, Ph

$Fe_2(CO)_9$.[21] The syntheses from dihydropentalenes again parallel cyclopentadienylmetal chemistry in that iron carbonyls dehydrogenate cyclopentadiene (C_5H_6) to give $[Fe(CO)_2(\eta^5-C_5H_5)]_2$.

In the light of our own work, described below, and in the absence of X-ray crystallographic studies on these molecules, it seems reasonable to formulate the metal-to-ring bonding in 6 as shown. It is important to note at this juncture that these syntheses of pentalene complexes involve organic precursors which already contain the relatively inaccessible bicyclo-[3.3.0] pentalene carbon skeleton.

Trimethylsilyl and Trimethylgermyl Derivatives of Ruthenium Carbonyl

Our own involvement in pentalene chemistry was in the first instance fortuitous. Following the discovery of convenient syntheses of dodecacarbonyltriruthenium in our laboratory[22] and elsewhere,[23] an apparently limitless area of organoruthenium chemistry has developed based on this carbonyl as a chemical reagent.[24] We have studied reactions of the carbonyl with trimethylsilane, -germane, and -stannane and characterized many polynuclear metal complexes containing ruthenium bonded to silicon, germanium, or tin.[25]

In the context of the "18-electron" rule, so commonly followed in metal carbonyl chemistry, the Me_3M ligands can be regarded formally as one-electron donors. Although complexes derived from the parent carbonyl $Ru_3(CO)_{12}$ with cyclic C_7 and C_8 olefins have been well studied, it seemed that related species formed from 7 or 8 would afford organoruthenium compounds of new structural types[26,27] because of different electronic requirements of ruthenium when coordinated with an MMe_3 ligand. In particular, compounds 7, at present somewhat rare ex-
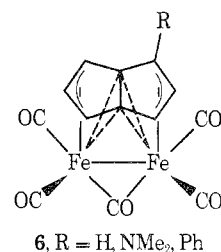
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(20) D. F. Hunt and J. W. Russell, *J. Amer. Chem. Soc.*, 94, 7198 (1972); *J. Organometal. Chem.*, 46, C22 (1972); Abstracts, 6th International Conference on Organometallic Chemistry, Amherst, 1973, P13.

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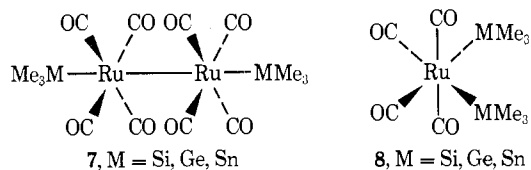(22) M. I. Bruce and F. G. A. Stone, *J. Chem. Soc. A*, 1238 (1967).

(23) F. Piacenti, P. Pino, M. Bianchi, G. Braca, and G. Sbrana, "Progress in Coordination Chemistry," M. Cais, Ed., Elsevier, Amsterdam, 1968, p 54.

(24) Those wishing to follow this rapidly developing area should refer to (a) M. A. Bennett, *Organometal. Chem.*, 1–3 (1972-1974); (b) J. A. McCleverty, *Annu. Survey 1972, J. Organometal. Chem.*, 68, 423 (1974).

(25) These complexes included the first examples of covalent compounds containing six-membered heterocyclic metal rings. See S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. A*, 2874 (1971); A. Brookes, S. A. R. Knox, and F. G. A. Stone, *ibid.*, 3469 (1971); J. A. K. Howard and P. Woodward, *ibid.*, 3468 (1971).

(26) Following the synthesis of 7 (M = Sn) by Julie Edwards it was possible to carry out a single-crystal X-ray diffraction study (Judith Howard, Susan Kellet, and P. Woodward) which revealed that the carbonyl groups are eclipsed. For a discussion of eclipsed *vs.* staggered conformations for equatorial carbonyl ligands in structures with single two- and three-center metal-metal bonds, see R. Bau, S. W. Kirtley, T. N. Sorrell, and S. Winarko, *J. Amer. Chem. Soc.*, 96, 988 (1974).

(27) It has been shown by R. K. Pomeroy and W. A. G. Graham, *J. Amer. Chem. Soc.*, 94, 274 (1972), that compounds of type 8 are nonrigid, cis-trans isomerization occurring by an intramolecular process. They therefore provide interesting examples of stereochemical nonrigidity in octahedral systems.

Figure 1. Molecular structure of the pentalene complex [Ru-(GeMe₃)(CO)₂]₂C₈H₆:[31] large open circles, germanium.
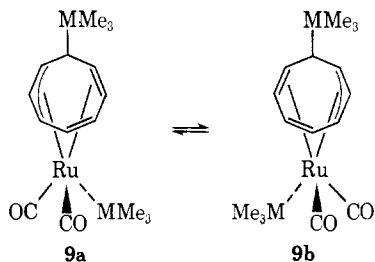
amples of binuclear ruthenium species, should coordinate with cyclooctatetraene or cycloheptatriene following loss of carbon monoxide in such a manner that these ligands bridge the two ruthenium atoms. Compounds 8, on the other hand, seemed likely precursors of mononuclear ruthenium complexes, as a result of direct replacement of carbon monoxide ligands. The possibility of insertion of C_8H_8 or C_7H_8 into the Me₃M–Ru bonds (*i.e.*, Me₃M group transfer from ruthenium to the coordinated hydrocarbon) had also to be considered in view of an interesting early observation of Gorsich.[28]

These admittedly naive ideas involving compounds 7 or 8 as precursors in organoruthenium chemistry were broadly supported by experiment.[29] However, a surprising capability of 7 and 8, and of Ru₃(CO)₁₂ itself, to yield pentaleneruthenium complexes by dehydrogenative transannular ring closure of monocyclic C₈ olefins arose, and it is the study of this and related phenomena which we describe here.

Reactions of Cyclooctatetraenes

Both iron and ruthenium carbonyls are known to react with cyclooctatetraene (COT) to give several complexes whose study has done much to add to our knowledge of fluxional behavior.[30] For both metals, compounds of formula (COT)M(CO)₃, (COT)M₂(CO)₆, and (COT)M₂(CO)₅ have been thoroughly characterized. In addition, ruthenium forms a novel cluster complex of formula (COT)₂Ru₃(CO)₄ containing two cyclooctatetraene molecules. It was therefore with this hydrocarbon that we chose to initiate studies with 7 and 8.

In refluxing hexane, complexes of formula Ru(MMe₃)(CO)₂(C₈H₈MMe₃) were isolated (quantitatively for M = Si) from the reaction of COT with 8 (M = Si, Ge). An X-ray diffraction study completed on Ru(SiMe₃)(CO)₂(C₈H₈SiMe₃) recently established structure 9, the result of an MMe₃ migration to the C₈ ring and with one double bond not to the ruthenium

9a   9b

atom. These are fluxional molecules, with temperature-variable ¹H and ¹³C nmr spectra (between limits of +100 and −60°) consistent with the oscillatory process 9a ⇌ 9b shown.

If these complexes are refluxed in heptane, or if 8 and COT are heated in heptane or octane, crystalline compounds Ru₂(MMe₃)₂(CO)₄(C₈H₆) (10) are

10, M = Si, Ge
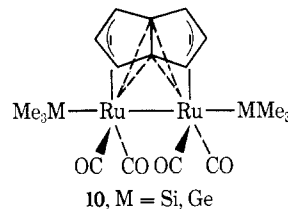
obtained in about 30% yield.[31] The properties of these complexes, including their nmr spectra which showed equivalent MMe₃ groups and a triplet (2 H) and doublet (4 H) (J_{HH} = 2.5 Hz) signal for the ring protons, suggested that they contained pentalene as a ligand. This was confirmed by a single-crystal X-ray diffraction study on 10 (M = Ge),[31] which revealed a nonplanar conformation for the two fused five-membered rings, these being hinged to one another at an angle of 173° away from the Ru–Ru bond (Figure 1). There are two sets of Ru–C (ring) distances, with C(1)–C(3) and C(5)–C(7) on average 2.21 Å from their nearest Ru atom, while C(4) and C(8) are equidistant (2.53 Å) from each Ru atom. The bonding can therefore be approximately represented as involving two η^3-allyl units, each bonded to one ruthenium, coupled with a four-center four-electron interaction between the two ruthenium atoms and C(4) and C(8). A very related bonding scheme was earlier proposed for the cyclooctatetraene complex Fe₂(CO)₅(COT).[30]

The role of the apparent intermediates 9 in the formation of the pentalene complexes 10 is as yet not understood. The process appears to occur with specific elimination of the MMe₃ group.

Although formation of 10 (M = Si) from Ru(SiMe₃)₂(CO)₄ occurs without by-products, the analo-

(28) R. D. Gorsich studied the reaction between Mn(SnPh₃)(CO)₅ and tetraphenylcyclopentadienone (*J. Amer. Chem. Soc.*, 84, 2486 (1962)) and obtained a compound formulated with a manganese-tin bond and a η⁴-cyclopentadienone ligand. Subsequent study (R. D. Gorsich, *J. Organometal. Chem.*, 5, 105 (1966)) revealed that the complex was a substituted cyclopentadienyl derivative Mn(C₅H₄OSnPh₃)(CO)₃, *i.e.*, the Ph₃Sn group had transferred from the manganese atom to the organic moiety.

(29) The tin compounds 7 and 8 are less reactive and do not afford under similar conditions complexes analogous to those formed from the silicon and germanium compounds.

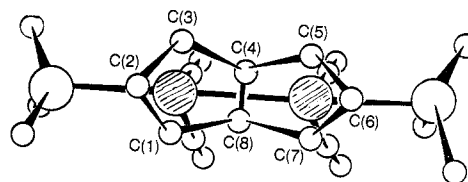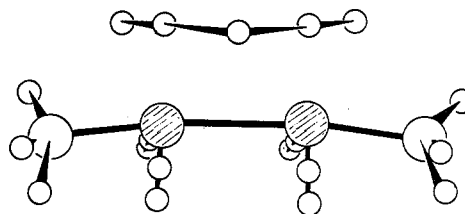(30) For a review and summary of leading references, see F. A. Cotton, *Accounts Chem. Res.*, 1, 257 (1968).

(31) A. Brookes, J. A. K. Howard, S. A. R. Knox, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 587 (1973).
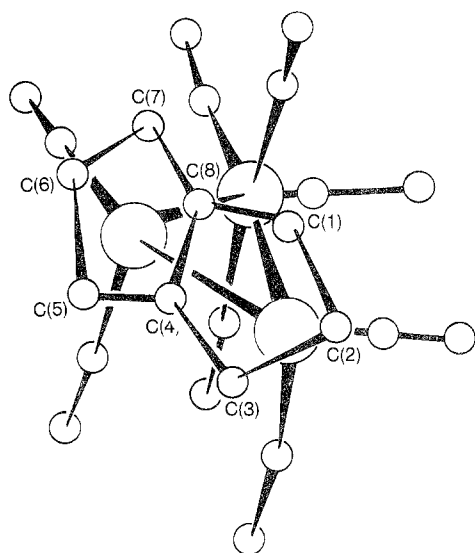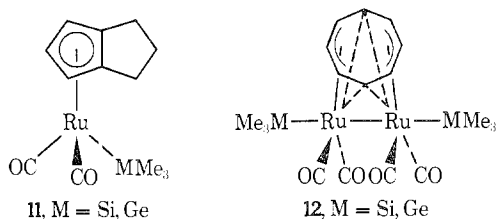
Figure 2. Molecular structure of the pentalene complex $Ru_3(CO)_8C_8H_6$.[34,36]

gous reaction between $Ru(GeMe_3)_2(CO)_4$ and COT, in addition to giving **10** (M = Ge), yields several other complexes, two of which have been identified as Ru-(GeMe₃)(CO)₂(C₈H₉) (**11**; M = Ge) and Ru₂(Ge-Me₃)₂(CO)₄(C₈H₈) (**12**; M = Ge). The former is again


11, M = Si, Ge

12, M = Si, Ge

the consequence of a ring-closure process, but here COT has abstracted a hydrogen from some source to give the tetrahydropentalenyl ligand,[32] a derivative of the cyclopentadienyl group.

Complexes **12** are of more interest. The mode of attachment of the C_8H_8 ring to the two metal atoms is likely to be similar to that in $Fe_2(CO)_5(COT)$, referred to above. As in **10**, the metal–ring bonding can be envisaged to involve two interannular η^3-allyl units and a four-center interaction. Because of this it was attractive to believe that **12** would lead to pentalene complexes **10** by loss of H from the central bridging carbons with concomitant C–C bond formation, but attempts to induce such a transformation have so far been unsuccessful. Complexes **12** can be prepared more easily by heating COT in hexane with **7**, compounds which already contain the $Ru_2(MMe_3)_2$ unit.

Formation of **10** by dehydrogenative transannular cyclization of COT prompted a more detailed study of reactions between cyclooctatetraene or its derivatives and ruthenium carbonyl complexes. In view of the inaccessibility of organic precursors containing a preformed pentalene C_8 skeleton, the development of syntheses of pentalene complexes from cyclooctatetraenes was attractive. Substituted cyclooctatetraenes can be fairly readily prepared, and if reactions of the type which gave **10** could be extended to

these derivatives a variety of pentalene complexes might be identified. It was also necessary to establish whether pentaleneruthenium complexes could only be formed using the complexes **8** or whether ruthenium carbonyl itself could bring about similar dehydrogenation of COT. With this in mind, a reexamination [33] of the reaction of cyclooctatetraene with dodecacarbonyltriruthenium led to the discovery, albeit in very small yield, of two new trinuclear ruthenium complexes, in addition to the complexes previously obtained.[30] The formulas of the new crystalline compounds were $Ru_3(CO)_6(C_8H_9)_2$ and $Ru_3(CO)_8(C_8H_6)$.

The compound $Ru_3(CO)_8(C_8H_6)$ proved to be, as its formula suggested, a pentalene complex (**13**; R^1
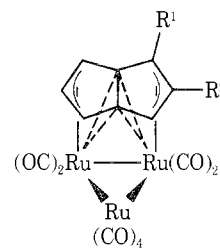
13, $R^1 = R^2 = H$; $R^1 = Me$ or Ph, $R^2 = H$;
$R^1 = H$, $R^2 = Me$ or Ph

= R^2 = H). An X-ray diffraction study[34] revealed a nearly planar pentalene ligand, the angle between the planes of the two C_5 rings being 177°, with the rings again bending away from the molecular center (Figure 2). As in $Ru_2(GeMe_3)_2(CO)_4(C_8H_6)$ (**10**), the Ru–C (ring) distances fall into two groups, with C(1)–C(3) and C(5)–C(7) at a mean distance of 2.23 Å and the junction atoms C(4) and C(8) at 2.48 Å, so that the bonding can be similarly represented as in **10**. The most significant feature of the structure, however, is that the plane of the Ru_3 triangle makes an angle of 50° with the mean plane of the pentalene.

It was of considerable interest that the ^1H nmr spectrum of $Ru_3(CO)_8(C_8H_6)$ varied with temperature (Figure 3). The data indicate a degenerate rearrangement producing a time-averaged molecular plane of symmetry, and we favor the unique oscillatory rearrangement shown in Scheme I, compatible with the ground-state structure revealed by X-ray diffraction. One may note that such a process also requires the complementary "swinging" of the terminal CO ligands of the $Ru(CO)_2$ groups. The activation energy for the process is 12.8 ± 0.3 kcal/mol.

Scheme I
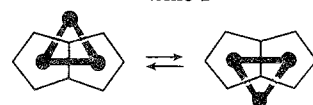
● = Ru, with CO groups omitted

The other new product of the reaction of $Ru_3(CO)_{12}$ and cyclooctatetraene, $Ru_3(CO)_6(C_8H_9)_2$, has recently been identified by an X-ray diffraction study[35] and is illustrated schematically as **14**. Again,

(32) Several years ago it was observed (T. H. Coffield, K. G. Ihrman, and W. Burns, *J. Amer. Chem. Soc.*, 82, 4209 (1960)) that $Mn_2(CO)_{10}$ and COT reacted to give $Mn(CO)_3(C_8H_9)$.

(33) V. Riera, S.A. R. Knox, and F. G. A. Stone, to be published.
(34) J. A. K. Howard, S. A. R. Knox, V. Riera, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 452 (1974).
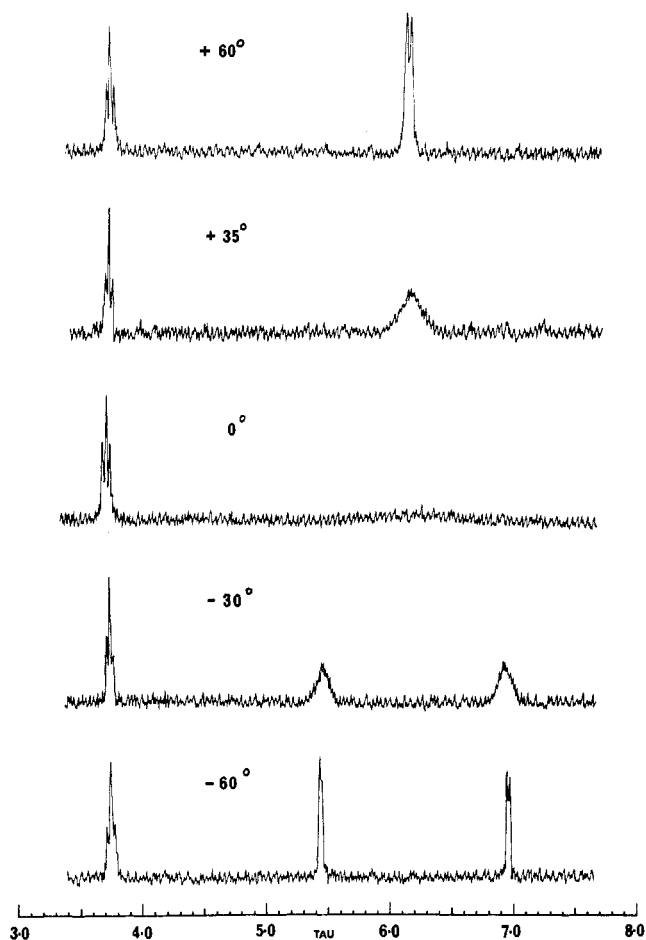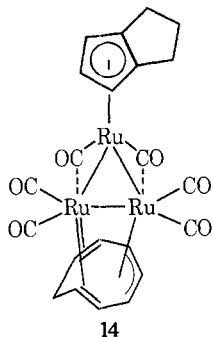(35) R. Bau and B. Chaw-Kuo Chou, private communication.

Figure 3. Variable-temperature ^1H nmr spectrum of Ru_3-$(CO)_8(C_8H_6)$.

a ring closure is evident in the formation of the tetrahydropentalenyl ligand.

14

Phenyl- and methylcyclooctatetraenes react with **7** (M = Si) and with $Ru_3(CO)_{12}$ to give many organoruthenium complexes.[33] Several of these are of the pentalene type, and some are, as with COT, common to reactions involving both **7** (M = Si) and $Ru_3(CO)_{12}$. The former compound thus undergoes fission of its Ru–Si bonds, possibly with loss of Me_3SiH. Within the context of this Account four complexes are of interest. Each of **13** (R^1 = H, R^2 = Me or Ph; R^1 = Me or Ph, R^2 = H) was isolated, showing that during dehydrogenative ring closure of cyclooctatetraenes C_8H_7R, the position of central σ-bond formation is apparently not greatly influenced by the substituent. In fact, formation of 2-substituted pentalenes (2–7%) is marginally favored over 1-substituted pentalenes ($\sim$1%).

An interesting situation arises in that the 2-substituted complexes **13** (R^1 = H, R^2 = Me or Ph) are fluxional, while the 1-substituted isomers **13** (R^1 = Me or Ph, R^2 = H) are not. The two fluxional complexes appear from their nmr spectra to be undergoing a process analogous to that of $Ru_3(CO)_8(C_8H_6)$, with free energy of activation being essentially independent of the 2-substituent, at 12.8 ± 0.3 kcal/mol for each of the three.

A degenerate fluxional process of this type is not possible for complexes of the unsymmetrical 1-methyl- and 1-phenylpentalene, since the two components of the oscillation would be inequivalent. However, the possibility of a nondegenerate oscillation remains, but we have so far observed the population of only one form. The structure of $Ru_3(CO)_8$-$[C_8H_4(SiMe_3)_2]$, to be discussed later, suggests that the favored species is that in which the $Ru(CO)_4$ group is furthest from the substituent.

A product isolated[33] in very low yield from the reaction between phenylcyclooctatetraene and $Ru_3(CO)_{12}$, which we initally believed to be a pentalene complex, has been characterized[36] by X-ray diffraction as a complex of bicyclooctatetraenyl, best represented by **15**. This complex has not been ob-
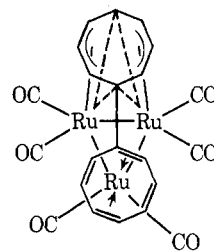
15

served in reactions involving COT, and may be formed *via* elimination of phenyl groups, since C–C bond formation between two rings has been observed in the reaction of cyclohexa-1,3-diene with $Ru_3(CO)_{12}$.[37] We cannot, however, discount the possibility that **15** arises from some bicyclooctatetraenyl impurity in the phenylcyclooctatetraene employed. The structure is unique with one COT ring in a "tub" conformation, coordinated as a 1,5-diene, an unprecedented mode for metals of the iron triad. The complex is formed readily from the direct reaction of $Ru_3(CO)_{12}$ and bicyclooctatetraenyl in refluxing toluene.[38]

Reactions of Cyclooctatrienes

In the context of the above results involving COT, and following an observation[39] (discussed below) that cycloocta-1,5-diene formed the tetrahydropentalenyl ligand in reactions with **7** and **8**, we initiated a study of reactions of cyclooctatrienes with ruthenium carbonyl complexes. We were especially hopeful that the yields of any pentalene complexes of the type **13** would exceed those obtained from cyclooctatetraenes.
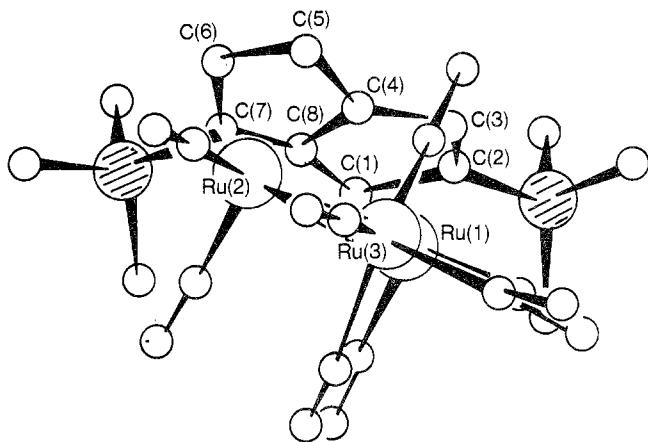
Reduction of COT affords an isomeric mixture of

(36) J. A. K. Howard and P. Woodward, to be published.
(37) T. H. Whitesides and R. A. Budnik, *J. Chem. Soc., Chem. Commun.,* 87 (1973).
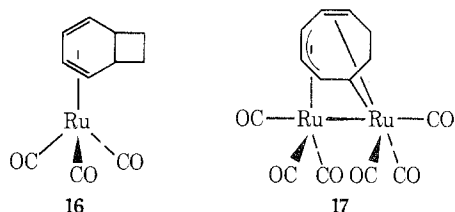(38) J. Edwards, S. A. R. Knox, and F. G. A. Stone, unpublished observations.
(39) S. A. R. Knox, R. P. Phillips, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.,* 658 (1974).

Figure 4. Molecular structure of the pentalene complex Ru$_3$-(CO)$_8$[C$_8$H$_4$(SiMe$_3$)$_2$].[36,43]

cycloocta-1,3,5-triene, cycloocta-1,3,6-triene, and bicyclo[4.2.0]octa-2,4-diene.[40] Under heptane reflux this mixture did not yield a pentalene complex upon reaction with **7** or **8**. The observed products were **11** and complexes Ru(CO)$_3$(C$_8$H$_{10}$) (**16**) and Ru$_2$-(CO)$_6$(C$_8$H$_{10}$) (**17**) of the two tautomers of cy-

cloocta-1,3,6-triene. Not unexpectedly, both **16** and **17** are much more readily obtained from Ru$_3$(CO)$_{12}$ and the C$_8$H$_{10}$ mixture.[41]

Since traces of Ru$_3$(CO)$_8$(C$_8$H$_6$) were detected when the cyclooctatriene isomeric mixture was heated with Ru$_3$(CO)$_{12}$ in octane, it was decided to carry out studies on substituted cyclooctatrienes. The presence of bulky substituents appears to stabilize the pentalene system, as referred to earlier, and it seemed possible that pentalene complex formation might also be so favored. This work is at a preliminary stage, but the novel hydrocarbon 5,8-bis(trimethylsilyl)cycloocta-1,3,6-triene (**18**)[42] reacts with **7**
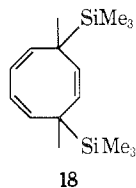
(M = Si) or Ru$_3$(CO)$_{12}$ to give a separable mixture of Me$_3$Si-containing analogs of **16** and **17,** and the bis(trimethylsilyl)pentalene complex Ru$_3$(CO)$_8$-[C$_8$H$_4$(SiMe$_3$)$_2$] (**19**)[43] in 10% yield, the structure of which has been established[36] by X-ray diffraction. The molecular configuration (Figure 4) is nearly identical with that of Ru$_3$(CO)$_8$(C$_8$H$_6$): Ru(1)–Ru(3)

(40) A. C. Cope, A. C. Haven, F. L. Ramp, and E. R. Trumbull, *J. Amer. Chem. Soc.*, **74**, 4867 (1952).

(41) A. C. Szary, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 66 (1974).

(42) We are indebted to Drs. J. M. Bellama and J. B. Davison of the University of Maryland for synthesizing this ligand during a visit to our laboratory.

(43) J. A. K. Howard, S. A. R. Knox, F. G. A. Stone, A. C. Szary, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, in press.

= Ru(2)–Ru(3) = 2.806 (1) Å, Ru(1)–Ru(2) = 2.930 (1) Å; the mean Ru–C(1)–C(3) and Ru–C(5)–C(7) distance is 2.23 (1) Å and the mean Ru–C(4)–C(8) distance is 2.48 (1) Å. The C–C distances in the pentalene are all equal at 1.44 (1) Å mean, and the angle between the Ru$_3$ plane and the mean plane of the pentalene is again 50°. Like Ru$_3$(CO)$_8$ complexes of unsymmetrical 1-substituted pentalenes, the asymmetric pentalene confers nonfluxional character on **19**. Presumably for steric reasons the preferred


19
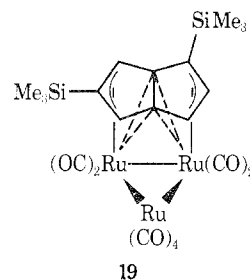
conformation is that in which the Me$_3$Si group on C(1) is furthest from Ru(3).

This route to substituted pentalene complexes is promising. The triene **20** reacts with Ru$_3$(CO)$_{12}$ to

20
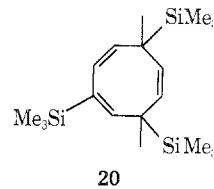
afford the 1,3,6-tris(methylsilyl)pentalene complex Ru$_3$(CO)$_8$[C$_8$H$_3$(SiMe$_3$)$_3$] (**21**) in 15% yield.[43]

This symmetrically trisubstituted pentalene complex is fluxional, as expected, and able to undergo a degenerate oscillatory process similar to that invoked in Scheme I for Ru$_3$(CO)$_8$(C$_8$H$_6$), so that at the high-temperature limit a time-averaged molecular plane of symmetry is generated (Figure 5). The free energy of activation for the oscillation (9.2 ± 0.2 kcal/mol) is appreciably lower than that for Ru$_3$-(CO)$_8$(C$_8$H$_6$) or 2-substituted pentalene complexes. A determination of the ground-state molecular structure of **21** would be of interest, in perhaps showing

21
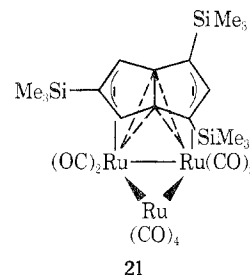
steric crowding by the SiMe$_3$ groups constraining the Ru$_3$ plane to make a larger angle than 50° with the pentalene plane, consistent with a lower energy oscillation.

Reactions of Cycloocta-1,5-diene

Cycloocta-1,5-diene does not yield a complex of pentalene upon reaction with either Ru$_3$(CO)$_{12}$, **7**, or **8**. A ring-closure process is in evidence, however, in that a major product from **7** or **8** is the tetrahydropentalenyl complex Ru(MMe$_3$)(CO)$_2$(C$_8$H$_9$) (**11**).[39]
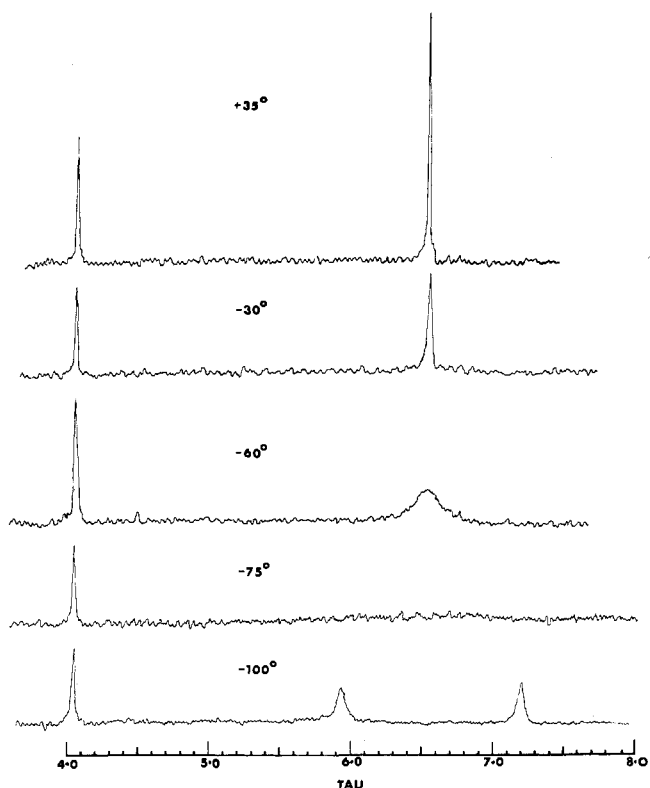
Figure 5. Variable-temperature ^1H nmr spectrum of Ru_3-$(CO)_8[C_8H_3(SiMe_3)_3]$.

With **8** (M = Ge), additional products are Ru-$(GeMe_3)_2(CO)_2(C_8H_{12})$ (**22**) and $Ru_2(GeMe_3)(\mu$-

22   **23**
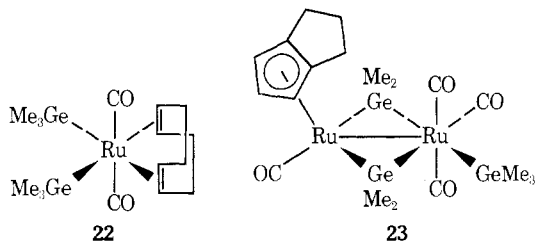
$GeMe_2)_2(CO)_4(C_8H_9)$ (**23**), another tetrahydropentalenyl complex. Heating **22** revealed it to be the precursor of both **11** (M = Ge) and **23**.

Neither was a pentalene complex obtained from reactions with cyclooctene. Apparently these carbonylruthenium complexes are incapable of effecting the extensive dehydrogenation of cyclooctadiene and cyclooctene which would be necessary for pentalene formation.

Comments on Transannular Ring Closure

We have observed the capability of several carbonylruthenium complexes to effect transannular cyclization of cyclooctatetraenes, cyclooctatrienes, and cycloocta-1,5-diene to give pentalene and/or tetrahydropentalenyl complexes. Conversion of C_8H_8[32] or C_8H_{12}[44-46] to the bicyclic C_8H_9 tetrahydropentalenyl ligand has been observed previously, the former process involving addition of a hydrogen atom and the latter the removal of three hydrogen atoms per mole-

(44) H. Lehmkuhl, W. Leuchte, and E. Janssen, *J. Organometal. Chem.*, **30**, 407 (1971).

(45) S. Otsuka and T. Taketomi, *J. Chem. Soc., Dalton Trans.*, 1879 (1972).

(46) K. K. Joshi, R. H. B. Mais, F. Nyman, P. G. Owston, and A. M. Wood, *J. Chem. Soc. A*, 318 (1968).

cule of reactant hydrocarbon. The mechanisms of these reactions are not clear. Otsuka and Taketomi[45] found that dehydrogenative ring closure of the cycloocta-1,5-diene ligand in $Co(C_8H_{13})(C_8H_{12})$ is brought about by excess C_8H_{12} which is thereby converted to cyclooctene.

$$Co(C_8H_{13})(C_8H_{12}) + 2C_8H_{12} \rightarrow Co(C_8H_9)(C_8H_{12}) + 2C_8H_{14}$$
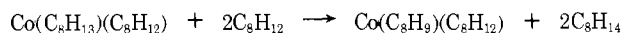
The mechanism of pentalene complex formation by dehydrogenative ring closure is similarly obscure, and probably varies according to the carbonylruthenium complex employed. Complexes of pentalenes with the $Ru_3(CO)_8$ fragment can be prepared from either $Ru_3(CO)_{12}$ or **7**, so that the presence of MMe_3 ligands in the carbonylruthenium complex appears to be of no account. Formation of the pentalene complexes **10** from COT and **8**, however, appears to involve a crucial MMe_3 migration leading to **9** as an intermediate.

Such migrations are common in reactions of **7** and **8**. Thus the bis(trimethylsilyl)pentalene complex **19** is the major product (30%) from trimethylsilylcyclooctatetraene and **7** (M = Si), while **20** on reaction with **7** (M = Si) affords **19** but no **21**.[43] Curiously, **18** and **17** (M = Si) gave **19** cleanly. This lability of MMe_3 groups inhibits mechanistic discussion of ring closure *via* **7** or **8**. Ring closure of both cyclooctatrienes and -tetraenes induced by $Ru_3(CO)_{12}$ is, however, less complicated and allows scope for the study of reactions of various derivatives of these hydrocarbons in order to gain insight into the factors controlling the process.

It is noteworthy to record at this stage that we have observed migration of MMe_3 ligands from ruthenium to other hydrocarbons. The complexes $Ru(MMe_3)_2(CO)_4$ (**8**) are most adept in this respect, giving **24** and **25** in high yield with cyclohepta-

24   **25**   **26**
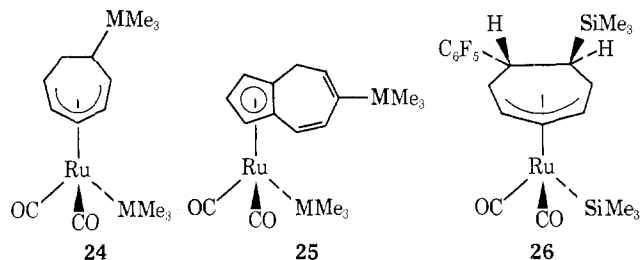
triene[47] and azulene,[48] respectively. In order to confirm the MMe_3 transfer implicit in the formulation **24**, a crystalline ring-substituted pentafluorophenyl derivative, **26**, was prepared from $7\text{-}C_6F_5C_7H_7$ and **8** (M = Si). The molecular structure was established by an X-ray diffraction study.[47] Surprisingly, an exo configuration was observed for the $SiMe_3$ group on the hydrocarbon and an endo configuration for the C_6F_5 group, although further experiments have suggested the migration is *intramolecular*.

Conclusion

A major objective in preparing pentalene metal complexes must be a study of the chemistry of the pentalene system, either by its reactions while stabilized by coordination or by its release and subse-

(47) J. A. K. Howard, S. A. R. Knox, V. Riera, B. A. Sosinsky, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 673 (1974).

(48) B. A. Sosinsky, Ph.D. Thesis, Bristol University, 1974.

quent trapping with various reagents. Thus far there have been no literature reports of experiments of this nature. However, it can be said that synthetic procedures are now at hand to make such studies imminent. Our own work has progressed to the point where pentalene complexes can be obtained in 30% yields, making 200–300-mg quantities readily available, and attention is now directed to such investigations. It should be appreciated, however, that with these complexes the pentalenes comprise a relatively small fraction of the total weight of complex, so that progress in this direction is perhaps likely to be slow.

Additions and Corrections

Selby A. R. Knox and F. Gordon A. Stone: Approaches to the Synthesis of Pentalene via Metal Complexes.

Page 323. In ref 28, line 6, the formula should read: $Mn(C_5Ph_4OSnPh_3)(CO)_3$.