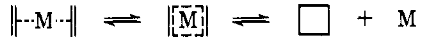
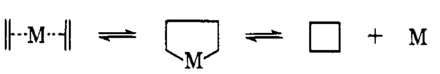
Metal-Catalyzed [2 + 2] Cycloaddition Reactions. A Metallocyclic Intermediate

Sir:

Conflicting explanations have been advanced to account for the observation that certain transition metals catalyze reactions which are thermally "forbidden" by the Woodward-Hoffmann conservation of orbital symmetry rules,[1-5] *e.g.*, as in the [2 + 2] cycloaddition of olefins to form a cyclobutane moiety or the corresponding cycloreversion reaction. On one hand it has been proposed that the new C-C bonds are formed simultaneously[6-10] (eq 1), and that the function


(1)

of the metal is to act merely as a template[11] which provides d orbitals of suitable symmetry to mix with the orbitals of the organic species, thereby rendering the reaction symmetry "allowed."[5,8-10,12] An alternative interpretation[13-16] is a nonconcerted mechanism involving the stepwise formation of an M-carbon σ-bonded intermediate followed by reductive elimination of the hydrocarbon, as shown in eq 2.


(2)

Recently such intermediates have been implicated in catalytic processes involving olefin metathesis,[13] valence isomerization of cubane to *syn*-tricyclooctadiene,[14] cycloaddition reactions of norbornadiene,[15] and rearrangements of *exo*-tricyclo[3.2.1.0^{2,4}]octene.[16] However, no metal-carbon σ-bonded species has been isolated and then proven to be a genuine intermediate by its further reaction to yield the product in question. We wish to report the results of just such an experiment involving the symmetry-"forbidden" dimerization of norbornadiene.

On reacting [Ir(1,5-cyclooctadiene)Cl]$_2$[17] with excess norbornadiene (NBD) in acetone at room temperature, 1,5-cyclooctadiene is displaced and a microcrystalline compound **1** is produced with empirical formula Ir(NBD)$_3$Cl. [*Anal.* Calcd for IrC$_{21}$H$_{24}$Cl: C, 50.05; H, 4.77; Cl, 7.06. Found: C, 49.88; H, 4.77; Cl, 6.92.] The extreme insolubility of **1** does not permit elucidation of its structure by solution methods although it is probably not monomeric. The more soluble PMe$_3$ derivative **2**, Ir(NBD)$_3$(PMe$_3$)Cl, can be readily prepared by refluxing **1** with excess PMe$_3$ in CH$_2$Cl$_2$. [*Anal.* Calcd for IrC$_{24}$H$_{33}$ClP: C, 49.70; H, 5.70; Cl, 6.12; P, 5.35. Found: C, 49.62; H, 5.59; Cl, 6.53; P, 5.44.] Similarly, refluxing **1** with 2,4-pentanedione and Na$_2$CO$_3$ in acetone yields the acetylacetonate (acac) derivative **3**, Ir(NBD)$_3$(acac).

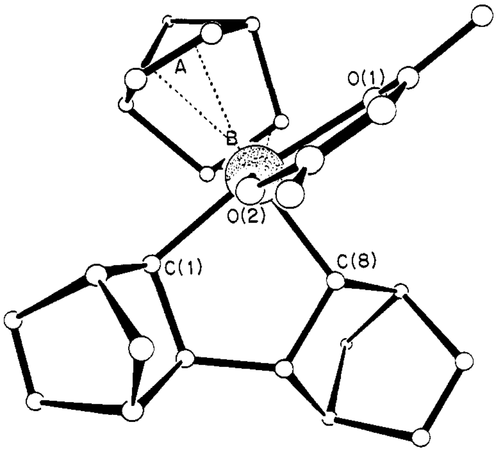


Figure 1.

Since conventional modes of chelation for NBD and acac ligands in **1**–**3** would result in unusual coordination numbers ≥7 for Ir in these compounds, a single-crystal X-ray diffraction study was undertaken on Ir(NBD)$_3$acac to determine unequivocally its structure. The compound crystallizes in space group $P\bar{1}$ (no. 2) with a = 9.239 (2), b = 14.267 (3), and c = 9.638 (2) Å, α = 111.95 (1), β = 65.77 (1), and λ = 106.70 (1)°; Z = 2. The observed and calculated densities are, respectively, 1.78 (2) and 1.771 g cm^{-3}. The reflection data were collected on a fully automated Picker Nuclear FACS 1 diffractometer using a maximum value of 45° in 2θ. In the subsequent solution and refinement of the structure by conventional Patterson, Fourier, and least-squares methods, 1906 observations (>3σ) were used. The present R value is 5.5%, with esd's of ±0.02 Å on Ir-C and Ir-O distances and ±0.03 Å on distances between light atoms.

As shown in Figure 1, the octahedral Ir^{III} complex has one acac and one NBD chelating conventionally, and the remaining two NBDs are forming a saturated metallocycle by insertion of the Ir atom into the four-membered ring of an incipient norbornadiene dimer molecule of exo-trans-exo stereochemistry. Ir-ligand bond distances are as follows: Ir-O(1), 2.192; Ir-O(2), 2.067; Ir-A, 2.248; Ir-B, 2.011; Ir-C(1), 2.106; and Ir-C(8), 2.082 Å.

We have assigned analogous structures containing both an iridocycle and a normal bidentate NBD to compounds **1** and **2** based on the following observations. (1) The ir spectra of **2** and **3** are essentially identical with that of **1** in the 1300-400-cm^{-1} region except for those bands attributable to the presence of the PMe$_3$ or acac ligands, respectively. (2) The ^{1}H Fourier transform nmr (100 MHz) spectrum of **2** in CDCl$_3$ shows *inter alia* resonances at τ 3.62 (1 H), 3.98 (1 H), and 4.09 (2 H) which correspond to resonances at τ 3.68 (1 H), 3.98 (1 H), and 4.11 (2 H) in **3** which can be assigned to the four uncoordinated vinyl protons. Further, the protons β to iridium in the five-membered

[1] D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Amer. Chem. Soc.*, **87**, 2596 (1965).

[2] C. W. Bird, D. L. Colinese, R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Lett.*, 373 (1961).

[3] C. W. Bird, R. G. Cookson, and J. Hudec, *Chem. Ind.* (*London*), 20 (1960).

[4] H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeck, *J. Amer. Chem. Soc.*, **91**, 218 (1969).

[5] W. Merk and R. Pettit, *ibid.*, **89**, 4788 (1967).

[6] G. N. Schrauzer, *Advan. Catal.*, **18**, 373 (1968).

[7] G. N. Schrauzer, B. N. Bastian, and G. A. Fosselius, *J. Amer. Chem. Soc.*, **88**, 4890 (1966).

[8] F. D. Mango and J. H. Schactschneider, *ibid.*, **89**, 2484 (1967).

[9] F. D. Mango, *Advan. Catal.*, **20**, 291 (1969).

[10] N. Calderon, *Accounts Chem. Res.*, **5**, 127 (1972).

[11] G. N. Schrauzer, P. Glochner, and S. Eichler, *Angew. Chem., Int. Ed. Engl.*, **3**, 184 (1964).

[12] G. S. Lewandos and R. Pettit, *Tetrahedron Lett.*, 789 (1971).

[13] R. H. Grubbs and T. K. Brunck, *J. Amer. Chem. Soc.*, **94**, 2538 (1972).

[14] L. Cassar, P. E. Eaton, and J. Halpern, *ibid.*, **92**, 3515 (1970).

[15] T. J. Katz and N. Acton, *Tetrahedron Lett.*, **27**, 2601 (1967).

[16] T. J. Katz and S. Cerefice, *J. Amer. Chem. Soc.*, **91**, 2405 (1969).

[17] [Ir(cyclooctene)$_2$Cl]$_2$ gives an identical product from refluxing benzene.

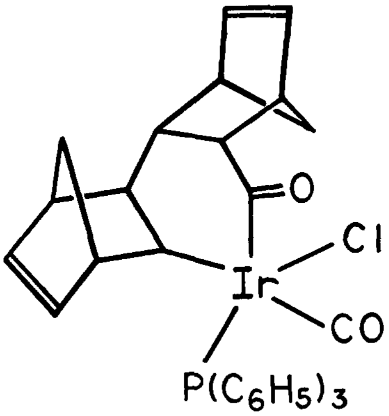


Figure 2.

iridocycle occur at τ 6.69 (1 H) and 7.21 (1 H) in **2** and τ 6.26 (1 H) and 7.62 (1 H) in **3**; the protons α to iridium could not be unambiguously assigned but occur in both **2** and **3** in the region τ 8.4–9.4.

A yellow crystalline compound **4** can be isolated by treating a suspension of **1** in CH_2Cl_2 with CO, followed by the addition of 1 mol of $P(C_6H_5)_3$. Analyses of **4** are consistent with the addition of 2 mol of CO and 1 mol of $P(C_6H_5)_3$ to **1** with the loss of one NBD ligand. [*Anal.* Calcd for $IrC_{34}H_{31}O_2ClP$: C, 56.00; H, 4.25; Cl, 4.87; P, 4.25. Found: C, 56.22; H, 3.46; Cl, 5.06; P, 4.31.]

The nmr spectrum of **4** shows the presence of the uncoordinated vinyl groups of an iridocycle, and sharp absorptions at 2020 and 1695 cm^{-1} in the infrared indicate the presence of both terminal and acyl[18,19] carbonyl groups. Further, the molecular weight (in $CHCl_3$ solution) shows **4** to be monomeric, and thus a structure as in Figure 2 is proposed which has resulted by insertion of CO into one of the Ir–C bonds of the iridocycle to form a cyclic metal acyl derivative.

The mass spectra of these species are of some interest. **1** shows no parent peak corresponding to $Ir(NBD)_3Cl^+$ or any multiple thereof; the highest *m/e* isotopic cluster corresponds to the fragment $[Ir(NBD)Cl]_2^+$ (relative intensity, 4.6). In addition, however, a peak of high relative abundance (42.2) appears at *m/e* 184 corresponding to a NBD dimer liberated from the iridocycle species. Likewise, **2** shows no molecular ion, the only peaks of interest being due to $[Ir(NBD)Cl]_2^+$, $(NBD)_2^+$, and PMe_3^+ (relative intensities 2.8 : 16.8 : 66.3). The most intense peak in both **1** and **2** is $C_5H_6^+$. However, the mass spectrum of **3** has the parent peak (*m/e* 568, relative intensity 48.2), but unlike **1** and **2**, no dimer of NBD is observed. Further significant peaks corresponded to products resulting from two stepwise retro-Diels–Alder reactions of the iridocycle moiety, *i.e.*, $Ir(NBD)(acac)(C_9H_{10})^+$, $Ir(NBD)(acac)(C_4H_8)^+$, and $C_5H_6^+$ (relative intensities 55.2 : 89.6 : 100)

Evidence that these metallocyclic complexes can be regarded as stabilized intermediates in the metal-promoted dimerization of NBD, rather than artifacts of no mechanistic significance, is provided by the following experiment. When **1** is refluxed in $CHCl_3$ with a fivefold excess of $P(C_6H_5)_3$, ring closure is induced and the NBD dimer is displaced from the iridium atom in *ca.* 35% yield. The dimer is extracted from the reaction mixture with pentane, and its nmr spectrum is identical with that of the exo-trans-exo dimer.[1] No other isomers were detected.

The observation that NBD dimerization proceeds *via* a metal–carbon σ-bonded intermediate adds to the accumulating evidence[13,14,20–22] that concerted mechanisms proposed for transition metal catalyzed symmetry forbidden processes must be carefully evaluated.

Acknowledgments. This work has been supported by the National Research Council of Canada (P. H. B. and A. R. F.), by the National Science Foundation in the form of predoctoral fellowships (S. A. B. and J. R. S) and the Henry and Camille Dreyfus Foundation (J. A. O.).

---

(18) *Cf.* acyl carbonyl frequencies of other cyclic metal acyls: 1703,[14] 1700,[4] and 1670 cm^{-1}.[19]

(19) D. M. Roundhill, D. N. Lawson, and G. Wilkinson, *J. Chem. Soc. A*, 845 (1968).

(20) T. J. Katz and S. A. Cerefice, *J. Amer. Chem. Soc.*, **91**, 6519 (1969).

(21) R. R. Schrock and J. A. Osborn, *ibid.*, **93**, 3089 (1971).

(22) N. Acton, R. J. Roth, T. J. Katz, J. K. Frank, C. A. Maier, and I. C. Paul, *ibid.*, **94**, 5446 (1972).

A. R. Fraser, P. H. Bird
Department of Chemistry, Sir George Williams University
Montreal 107, Quebec, Canada

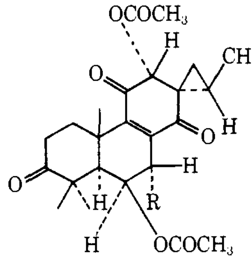
S. A. Bezman, J. R. Shapley, R. White, J. A. Osborn*
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

Received September 5, 1972

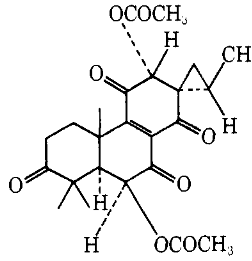
Structure and Absolute Stereochemistry of the Diterpenoid Barbatusin

Sir:

Barbatusin is a novel diterpenoid isolated from the leaves of *Coleus barbathus* (*Labiatae*) and its molecular structure I has been established by X-ray and spectrochemical investigations.



I, R = OH
II, R = $OCOCH_3$
III, R = $OCOC_6H_4Br$



IV

Barbatusin, mp 224–228°, has the molecular formula $C_{24}H_{30}O_8$, assigned on the basis of elemental analysis and mass spectrometry ($M^+ = 446$). The absorption maximum at 235 nm (ε 15,000) indicates a conjugated ketone, and in alkaline ethanolic solution is replaced by two other maxima at 223 (ε 26,800) and 272 nm (sh) (ε 4600), typical of an enolate. The ir spectrum shows the presence of a hydroxyl, an ester, a ketone in a six-membered ring, and an α,β-unsaturated ketone (3500, 1740, 1705, 1670, and 1605 cm^{-1}). The nmr spectrum ($CDCl_3$) was particularly informative in that it revealed three *C*-methyl groups (s at 1.21, 1.24, and