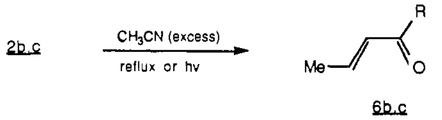
Table I

entry	RX	product (R =)	yield (%)
a	MeI	Me **2a**	74,[a] 79[b]
b	$PhCH_2Br$	$PhCH_2$ **2b**	87,[a] 93[b]
c	$Me(CH_2)_3I$	$Me(CH_2)_2CH_2$ **2c**	78[a]
d	Me_2CHBr	Me_2CH **2d**	73[a]
e	$CH_2{=}CHCH_2Br$	$CH_2{=}CHCH_2$ **2e**	61[c]

[a] Yields are based on the starting $C_3H_5Fe(CO)_3I$, **1**, generated in situ as sodium salt. [b] Yields based on reaction with pure isolated $C_3H_5Fe(CO)_3^-PPN^+$. [c] $(\pi\text{-}C_3H_5)_2Fe(CO)_2$ is also obtained as reported previously.[9]

acterized[10] at low temperature (−40 °C) by reaction of **1** with CH_3I and $PhCH_2Br$ in the absence of PPh_3. Treatment of **3a,b** with PPh_3 at −78 °C results in immediate formation of acyl complexes **4a,b** ($t_{1/2}$ < 10 min, −78 °C) which were characterized by ^1H NMR spectroscopy.[11] In a first-order process, complexes **4a,b** convert to **2a,b** via an acyl migration reaction. Rates measured by ^1H NMR were $k_{4a\rightarrow 2a} = 5.1 \times 10^{-2}\ s^{-1}$, 21 °C, $\Delta G^{\ddagger}$ = 18.9 kcal/mol for CH_3CO migration and $k_{4b\rightarrow 2b} = 6.1 \times 10^{-2}\ s^{-1}$, 21 °C, $\Delta G^{\ddagger}$ = 18.8 kcal/mol for $PhCH_2CO$ migration. No intermediates (i.e., neither **5** nor π-allylhydride species) were detected by ^1H NMR in the conversion of **4a,b** to **2a,b**.

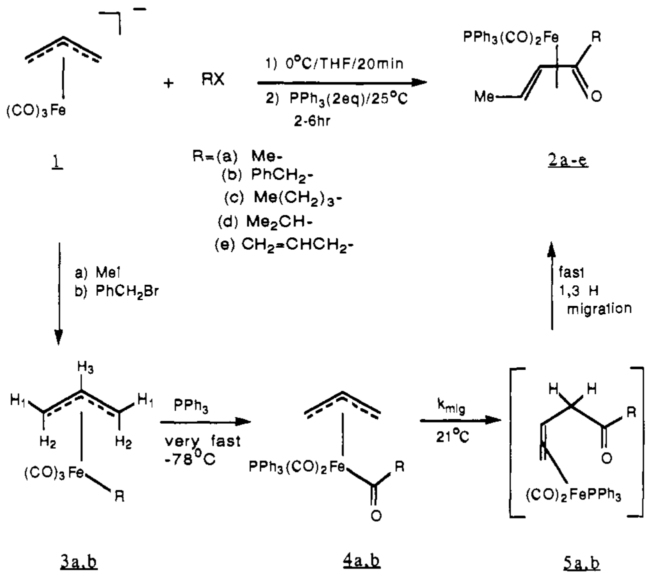
Free α,β-unsaturated ketones may be readily obtained from **2a–e**. Refluxing enone complexes **2b,c** in CH_3CN (2–6 h) gives metal-free enone compounds **6b,c** in good yields (70–77%). Alternatively irradiation (GE sunlamp) of enone complexes in CH_3CN under mild conditions (0 °C, 2–6 h) leads to **6b,c** in somewhat better yields (80–85%).

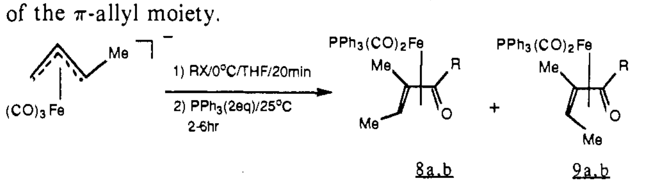


On the basis of the mechanism in Scheme I, if the 16-electron olefin complexes, **5a–e**, could be intercepted and displaced prior to its isomerization to **2a–e**, then a reaction sequence would be available to prepare not only α,β-enones but also the less readily available unconjugated β,γ-isomers. This proved possible using the following procedure: After alkylation of anion **1** (R = CH_2Ph, $-CHMe_2$, 0 °C, 30 min), the reaction mixture was quenched with excess CH_3CN. Irradiation of this mixture at 0 °C for 2–6 h gave the β,γ-unsaturated ketones in good yields (75–80%). The products were contaminated by small amounts of α,β-unsaturated ketone (<10%).

Preliminary results using a substituted allyl system indicate that substantial regioselectivity in the migration reaction is observed. For example, in situ generation of $\eta^3\text{-}(CH_2{\cdots}CH{\cdots}CHCH_3)Fe(CO)_3^-Na^+$ from the (η^3-methallyl)iron tricarbonyl iodide followed by treatment with CH_3I or $PhCH_2Br$ and then with PPh_3 yields complexes **8** and **9** in an ca. 2:1 ratio (75–81% yield).[12] Isolation of complexes **8** and **9** indicates that acyl migration occurs regioselectively to the more hindered methyl-substituted carbon of the π-allyl moiety.

Scheme I





Acknowledgment is made to the National Institutes of Health (GM 28938) for support of this research.

Supplementary Material Available: ^1H, ^{13}C NMR, IR, and microanalytical data for **2c**, **2d**, **2e**, **6b**, **8a**, **9a**, **8b**, **9b**, η^4-$[CH_2{=}C(CH_2CH_3)COCH_3]Fe(CO)_2PPh_3$, η^4-$[CH_2{=}C(CH_2CH_3)COCH_2Ph]Fe(CO)_2PPh_3$, and $CH_3CH{=}CHCOCH_2CH_2CH_2CH_3$ and ^1H, NMR, and high resolution mass spectroscopic data for $CH_3CH{=}CHCOCH_2Ph$ and $CH_2{=}CHCH_2COCH_2Ph$ (4 pages). Ordering information is given on any current masthead page.

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(9) Nesmeyanov, A. N.; Kristskaya, I. I.; Ustynyuk, Y. A.; Fedin, E. I. *Dokl. Akad. Nauk. SSSR* **1968**, *176*, 341.

(10) $\eta^3\text{-}C_3H_5Fe(CO)_3(CH_3)$, **3a**: Obtained as a mixture of two isomers (15:1 at −58 °C); IR ν_{max} (THF) 2050, 1985 cm^{-1}; ^1H NMR ($CDCl_3$, −58 °C, δ) major isomer 3.92 (m, 1 H, 3-H), 3.04 (d, *J* = 7.5 Hz, 2 H, 1-H), 2.18 (d, *J* = 12.2 Hz, 2 H, 2-H), −0.51 (s, 3 H, CH_3); minor isomer, 4.20 (m, 1 H, 3-H), 3.52 (d, *J* = 7.6 Hz, 2 H, 1-H), 1.74 (d, *J* = 12.5 Hz, 2 H, 2-H), −0.42 (s, 3 H, CH_3). $\eta^3\text{-}C_3H_5Fe(CO)_3(CH_2Ph)$, **3b**: obtained as a mixture of two isomers (5:1 at −13 °C); IR ν_{max} (THF) 2057, 1994, 1711 cm^{-1}; ^1H NMR (CD_2Cl_2, −13 °C, δ) major isomer 7.18–6.92 (m, 5 H, Ph), 3.92 (m, 1 H, 3-H), 3.16 (d, *J* = 7.5 Hz, 2 H, 1-H), 2.36 (d, *J* = 12.4 Hz, 2 H, 2-H), 1.80 (s, 2 H, CH_2Ph); minor isomer, 7.18–6.92 (m, 5 H, Ph), 4.21 (m, 1 H, 3-H), 3.58 (d, *J* = 7.5 Hz, 2 H, 1-H), 1.90 (d, *J* = 12.5 Hz, 2 H, 2-H), 1.80 (s, 2 H, CH_2Ph).

(11) $\eta^3\text{-}C_3H_5Fe(CO)_3(COCH_3)$, **4a**: IR ν_{max} (CH_2Cl_2) 1991, 1932, 1639 cm^{-1}; ^1H NMR (CD_2Cl_2, −40 °C, δ) 7.56–7.24 (m, 15 H, 3Ph), 4.20 (m, 1 H, 3-H), 2.92 (s, 3 H, $COCH_3$), 2.86 (d, *J* = 6.9 Hz, 2 H, 1-H), 1.92 (dd, $J_{H\text{-}P}$ = 3.7 Hz, *J* = 12.2 Hz, 2 H, 2-H); $\eta^3\text{-}C_3H_5Fe(CO)_3(COCH_2Ph)$, **4b**: IR ν_{max} (CH_2Cl_2) 1990, 1930, 1630 cm^{-1}; ^1H NMR (CD_2Cl_2, −45 °C, δ) 7.80–7.12 (m, 20 H, 4Ph), 4.81 (s, 2 H, CH_2Ph), 4.38–4.04 (m, 1 H, 3-H), 2.98 (d, *J* = 7.5 Hz, 2 H, 1-H), 2.04 (dd, $J_{H\text{-}P}$ = 3.5 Hz, *J* = 12.3 Hz, 2 H, 2-H).

(12) A minor product is η^4-$[CH{=}C(CH_2CH_3)COR]Fe(CO)_2PPh_3$.

Metallabenzene: Synthesis, Structure, and Spectroscopy of a 1-Irida-3,5-dimethylbenzene Complex

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Replacement of a methine group in benzene with a nitrogen, phosphorus,[1] or arsenic[1] atom leads to stable heterocyclic compounds in which aromaticity is retained. However, little is known about analogous replacements involving transition metals and their associated ligands. Particularly intriguing is the question of whether such "metallabenzenes" would exhibit aromatic properties.[2]

To date, only one family of stable metallabenzenes has been reported.[3,4] These species, obtained via a cyclization reaction involving acetylene and an osmium–thiocarbonyl complex, were reported by Roper in 1982.[3] The X-ray crystal structure of Roper's parent compound, $[\overline{\mathrm{Os{\cdots}C(S){\cdots}CH{\cdots}CH{\cdots}CH{\cdots}CH}}]$-

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(1) Ashe, III, A. J. *J. Am. Chem. Soc.* **1971**, *93*, 3293.

(2) For a theoretical discussion of delocalization in metallacycles, see: Thorn, D. L.; Hoffmann, R. *Nouv. J. Chem.* **1979**, *3*, 39.

(3) Elliot, G. P.; Roper, W. R.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 811.

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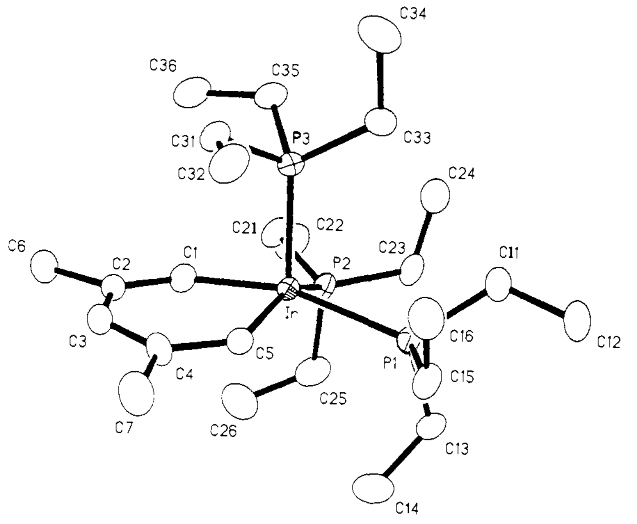
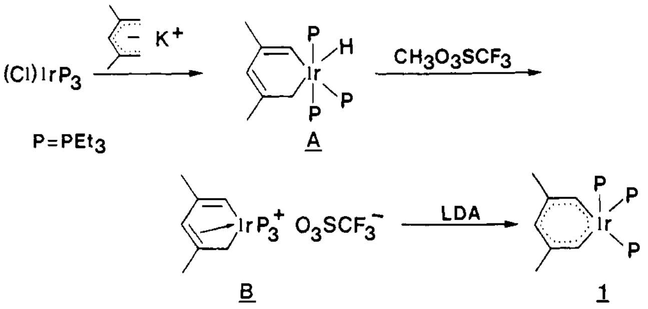


Figure 1. ORTEP drawing of $[\overline{\mathrm{Ir{\cdots}CH{\cdots}C(Me){\cdots}CH{\cdots}C(Me){\cdots}CH}}](\mathrm{PEt_3})_3$ (**1**) with 30% thermal ellipsoids.

Scheme I

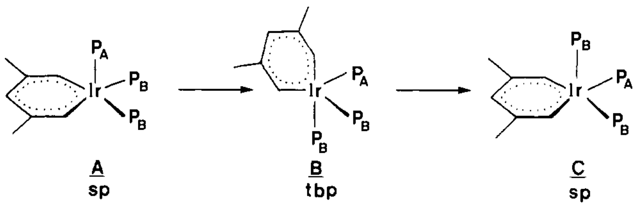


$(\mathrm{CO})(\mathrm{PPh_3})_2$, indicated a planar six-membered ring with delocalized bonding around the ring. However, no NMR spectra were reported for Roper's compounds, and the question of whether they exhibit ring currents was not addressed. Furthermore, the asymmetry of these molecules made it difficult to compare directly the structural and spectroscopic features of the two sides of the ring.

We now report the synthesis, solid-state structure, and full spectral characterization of a new, highly symmetrical metallabenzene complex, $[\overline{\mathrm{Ir{\cdots}CH{\cdots}C(Me){\cdots}CH{\cdots}C(Me){\cdots}CH}}](\mathrm{PEt_3})_3$ (**1**). Compound **1** is obtained via the three-step sequence shown in Scheme I. The first two steps were described in an earlier communication.[5] The final step, abstraction of a proton from B with lithium diisopropylamide, proceeds in high yield to produce red **1**.[6]

The solid-state structure of **1**, derived from a single-crystal X-ray diffraction study is shown in Figure 1.[7] Overall, the compound exhibits square-pyramidal coordination geometry with C1, C5, P1, and P2 occupying the four basal sites and P3 residing in the axial site. The six-membered ring is nearly planar, with no atom deviating by more than 0.08 Å from the best mean plane. Furthermore, there is delocalization of bonding within the ring (C1–C2 = 1.37 (1) Å, C2–C3 = 1.40 (1) Å, C3–C4 = 1.37 (1) Å, C4–C5 = 1.39 (1) Å, Ir–C1 = 2.024 (8) Å, Ir–C5 = 1.985 (8) Å). The bond angles within the carbon portion of the ring are 122.6 (7)° (C1–C2–C3), 125.3 (7)° (C2–C3–C4), and 121.8 (7)° (C3–C4–C5), while the Ir–C1–C2 and C4–C5–Ir angles are 131.2 (6)° and 132.9 (6)°, respectively, and the C1–Ir–C5 angle is 84.7 (3)°.

Scheme II



The ^{1}H NMR spectrum[8] of **1** clearly shows the presence of a ring current. Protons H1 and H5 (which are equivalent) resonate at δ 10.91, while H3 resonates at δ 7.18. Interestingly, the H1/H5 signal is a quartet (J = 7.30 Hz) due to coupling to three *equivalent* phosphorus nuclei (vide infra). The ^{13}C{^{1}H} NMR signals[8] of the ring carbon atoms also appear quite far downfield. Equivalent carbon atoms C1 and C5 resonate at δ 167.3, while C2 and C4 resonate at δ 132.0, and C3 resonates at δ 129.8. The C1/C5 signal is a quartet (J = 30.2 Hz) due to C–P coupling.

The ^{31}P{^{1}H} NMR signal[8] is a sharp singlet, which shows no broadening even upon cooling the sample to −60 °C. This indicates that **1** is stereochemically nonrigid and that the axial and basal phosphines are exchanging rapidly in solution. The most likely mechanism for this exchange is a Berry-type process, as shown in Scheme II.[9] The square-pyramidal complex A isomerizes to a trigonal-bipyramidal intermediate B in which one ring carbon atom and one basal phosphine ligand ($\mathrm{P_B}$) assume trans-axial positions. This intermediate then reisomerizes back to square-pyramidal complex C, causing $\mathrm{P_A}/\mathrm{P_B}$ exchange.

Metallabenzenes have been implicated as intermediates in the formation of a variety of cyclopentadienyl–metal complexes.[10,5] In fact, it has been suggested that metallabenzenes (or metallacyclohexadienes) may *in general* be unstable with respect to cyclopentadienyl–metal formation.[10a] However, compound **1** is quite robust. In the solid state or in solution at room temperature (under an $\mathrm{N_2}$ atmosphere), it is stable indefinitely. Furthermore, heating **1** in refluxing benzene for short periods causes little or no decomposition.

The $\mathrm{C_5H_3Me_2}$ unit in compound **1** can perhaps best be viewed as a monoanionic ligand. As such, it possesses eight valence electrons, in addition to skeletal electrons which form its σ framework. Four of these valence electrons are used to form σ bonds to iridium, while the remaining four are π-electrons and occupy the ligand's $1\pi_s$ and $1\pi_a$ orbitals.[11] The d^8 iridium center contributes two electrons to the π-system via overlap of a filled

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[4] In addition, there is a recent report of a metallabenzene *coordinated* to a second metal center. The metallabenzene moiety in this species is obtained via an ill-defined "dehydrogenation" of a 2,4-dimethylpentadienyl ligand. See: Kralik, M. S.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1987**, *6*, 2612.

[5] Bleeke, J. R.; Peng, W.-J. *Organometallics* **1987**, *6*, 1576.

[6] In an inert atmosphere glovebox, $\{[\overline{\mathrm{Ir{-}CH{=}C(Me){-}CH{=}C(Me){-}CH_2}}](\mathrm{PEt_3})_3\}^+\mathrm{O_3SCF_3}^-$ (0.50 g, 6.3 × 10^{-4} mol) was mixed with lithium diisopropylamide (0.068 g, 6.3 × 10^{-4} mol) and dissolved in 10 mL of cold (−40 °C) acetone. The resulting solution was shaken by hand for a minute and then stored in a −40 °C freezer for 1 h. After removal of the solvent under vacuum, the red residue was redissolved in a minimal quantity of acetone and cooled to −40 °C. Red crystals of **1** (0.30 g, 75% yield) were obtained overnight. Anal. ($\mathrm{IrP_3C_{25}H_{54}}$) C, H.

[7] Crystal data for **1**: monoclinic, space group $P2_1/n$, a = 11.738 (4) Å, b = 15.643 (3) Å, c = 16.329 (3) Å, β = 95.81 (2)°, V = 2983 (1) Å^3, Z = 4, d_{calcd} = 1.42 g/cm^3, μ = 46.3 cm^{-1}; Nicolet P3 diffractometer, Mo Kα radiation, 22 °C; 5284 unique reflections with $3° < 2\theta < 50°$ collected, 3678 reflections with $I > 3\sigma(I)$ used in refinement; empirical absorption correction; R = 0.035, R_w = 0.038, GOF = 1.33.

[8] Spectroscopic data for **1**: ^{1}H NMR (acetone-d_6, 17 °C, 300 MHz) δ 10.91 (quartet, $J_{\mathrm{H\text{-}P}}$ = 7.30 Hz, 2, H1/H5), 7.18 (s, 1, H3), 2.49 (s, 6, $\mathrm{CH_3}$'s of ring), 1.85–1.74 (m, 18, $\mathrm{CH_2}$'s of $\mathrm{PEt_3}$'s), 0.94–0.81 (m, 27, $\mathrm{CH_3}$'s of $\mathrm{PEt_3}$'s); ^{13}C{^{1}H} NMR (acetone-d_6, 17 °C, 125 MHz) δ 167.3 (quartet, $J_{\mathrm{C\text{-}P}}$ = 30.2 Hz, C1/C5), 132.0 (s, C2/C4), 129.8 (s, C3), 28.4 (s, $\mathrm{CH_3}$'s of ring), 22.4 (d, $J_{\mathrm{C\text{-}P}}$ = 15.9 Hz, $\mathrm{CH_2}$'s of $\mathrm{PEt_3}$'s), 9.2 (d, $J_{\mathrm{C\text{-}P}}$ = 9.2 Hz, $\mathrm{CH_3}$'s of $\mathrm{PEt_3}$'s); ^{31}P{^{1}H} NMR (acetone-d_6, 17 °C, 202 MHz, referenced to $\mathrm{H_3PO_4}$) δ −4.8 (s, $\mathrm{PEt_3}$'s).

[9] Jesson, J. P.; Muetterties, E. L. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; pp 253–316.

[10] (a) Ferede, R.; Allison, N. T. *Organometallics* **1983**, *2*, 463. (b) Ferede, R.; Hinton, J. F.; Korfmacher, W. A.; Freeman, J. P.; Allison, N. T. *Ibid.* **1985**, *4*, 614. (c) Egan, J. W., Jr.; Hughes, R. P.; Rheingold, A. L. *Ibid.* **1987**, *6*, 1578.

[11] For drawings of these orbitals, see: Albright, T. A.; Hoffmann, R.; Tse, Y.-C.; D'Ottavio, T. *J. Am. Chem. Soc.* **1979**, *101*, 3812.

d orbital (a d_{xz}/d_{yz} combination orbital)[12] with the $2\pi_s$ orbital of the $C_5H_3Me_2$ unit. This brings the total π-electron count to six and explains, in a qualitative fashion, the observed aromatic character of **1**. A more detailed molecular orbital treatment of **1** will be forthcoming.

In summary, we conclude that iridacycle **1** is, in fact, a metallabenzene with all of the usual aromatic properties. In particular, (a) the six-membered ring is planar and the bonding is delocalized, (b) a ring current is present, causing the ring protons to be shifted significantly downfield in the ^{1}H NMR spectrum, and (c) the compound is very robust, surviving in refluxing benzene with no apparent decomposition.

We have begun to explore the chemical reactivity of **1** and will report the results of this study in a future communication.

Acknowledgment. Support from the National Science Foundation (Grant CHE-8520680) and a loan of $IrCl_3{\cdot}3H_2O$ from Johnson Matthey, Inc. are gratefully acknowledged. Washington University's X-ray Crystallography Facility was funded by the National Science Foundation's Chemical Instrumentation Program (Grant CHE-8811456).

Supplementary Material Available: Tables of final atomic coordinates, thermal parameters, bond lengths, and bond angles (4 pages); listings of observed and calculated structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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[12] We define the following coordinate axis system: the axial ligand lies along the z axis, while the four basal ligands, when projected onto the xy-plane, lie along the x, $-x$, y, and $-y$ axes.

The 10-Membered Ring Analogues of Neocarzinostatin Chromophore: Design, Synthesis, and Mode of Decomposition[†]

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Received January 30, 1989

The labile nonprotein chromophore[1,2] of the antitumor antibiotic neocarzinostatin (NCS), isolated from the culture filtrate of *Streptomyces carzinostaticus* by Ishida and co-workers in 1965,[3] is essentially responsible for the biological activity of NCS.[2,4] Goldberg et al. proposed that the thiol activation of the chromophore produces a free-radical intermediate which cleaves DNA via abstraction of 5′-hydrogen from DNA on aerobic incubation.[5] However, extreme instability and structural ambiguity of the chromophore hampered the establishment of precise mechanisms for its radical generation and the DNA cleavage at the molecular level. The breakthrough came in 1985: Edo and his collaborators assigned the planar structure of the NCS chromophore as an unprecedented epoxybicyclo[7.3.0]dodecadienediyne nucleus **1**,[6] which was recently supported by the elegant synthesis of the parent carbocyclic core by Wender and co-workers.[7] Furthermore, Myers proposed both the structure of the chromophore-methyl thioglycolate adduct **4** and the mechanism of its formation (Scheme I).[8,9] As a part of our studies on the mechanism of chemical and biological action of the NCS complex, we designed and synthesized the NCS chromophore analogues **6** and **7b** to answer the questions: (i) whether the ring strain inherent in the unsaturated nine-membered ring system is essential to such novel molecular transformation generating free radical and (ii) whether the epoxide functionality is also essential to it.[10]

Scheme I. Myers' Proposed Mechanism for the Formation of **4**

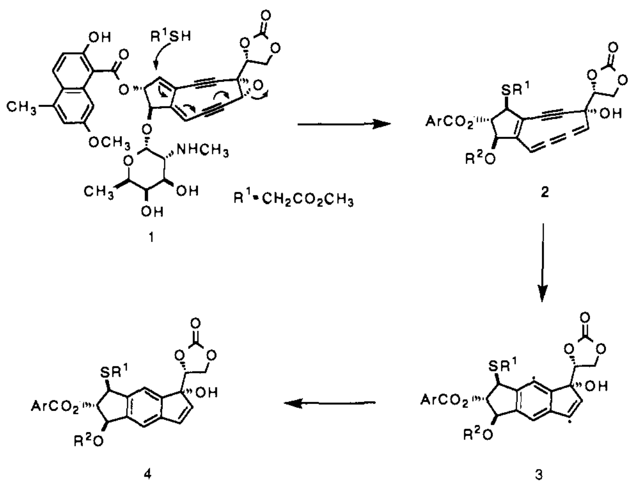
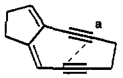
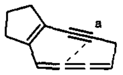
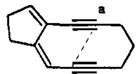
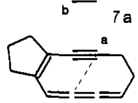


Table I. Calculated Strain Energies and Distances ab of Model Compounds **5**, **8**, **7a**, and **9**

Entry	Compound	MM2 (85) Strain Energy (kcal/mol)	MM2 (85) ab (Å)	MNDO Heat of Formation (kcal/mol)	MNDO ab (Å)
1	 5	25.85	2.95	117.5	2.97
				Δ10.3	
2	 8	Δ11.02	—[a]	127.8	3.03
3	 7a	14.83	3.12	101.1	3.20
				Δ9.7	
4	 9		—[a]	110.8	3.20

[a] Calculation parameters for cumulene are not available.

Molecular mechanics calculations [MM2(85)] indicated that the strain energy of the 10-membered ring analogue **7a** was much less than that of the parent hydrocarbon **5** (entries 3 and 1, Table I).[11] On the other hand, the increase of heat of formation from diyne **7a** to enynecumulene **9**, a 10-membered ring analogue of Myers' intermediate **2**,[8] calculated by MNDO (entries 3 and 4)

[†] Dedicated to Professor Nakao Ishida.

[‡] Tohoku University.

[§] Hiroshima University.

[1] Napier, M. A.; Holmquist, B.; Strydom, D. J.; Goldberg, I. H. *Biochem. Biophys. Res. Commun.* **1979**, *89*, 635.

[2] Koide, Y.; Ishii, F.; Hasuda, K.; Koyama, Y.; Edo, K.; Katamine, S.; Kitame, F.; Ishida, N. *J. Antibiot.* **1980**, *33*, 342.

[3] Ishida, N.; Miyazaki, K.; Kumagai, K.; Rikimaru, M. *J. Antibiot.* **1965**, *18*, 68.

[4] Kappen, L. S.; Napier, M. A.; Goldberg, I. H. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 1970.

[5] Hensens, O. D.; Dewey, R. S.; Liesch, J. M.; Napier, M. A.; Reamer, R. A.; Smith, J. L.; Albers-Schöberg, G.; Goldberg, I. H. *Biochem. Biophys. Res. Commun.* **1983**, *113*, 538. Kappen, L. S.; Goldberg, I. H. *Nucleic Acids Res.* **1985**, *13*, 1637.

[6] Edo, K.; Mizugaki, M.; Koide, Y.; Seto, H.; Furihata, K.; Otake, N.; Ishida, N. *Tetrahedron Lett.* **1985**, *26*, 331.

[7] Wender, P. A.; Harmata, M.; Jeffrey, D.; Mukai, C.; Suffert, J. *Tetrahedron Lett.* **1988**, *29*, 909.

[8] Myers, A. G. *Tetrahedron Lett.* **1987**, *28*, 4493.

[9] Myers, A. G.; Proteau, P. J.; Handel, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 7212.

[10] (a) Koide, Y.; Ito, A.; Edo, K.; Ishida, N. *Chem. Pharm. Bull. (Tokyo)* **1986**, *34*, 4425. Edo, K.; Akiyama-Murai, Y.; Saito, K.; Mizugaki, M. *J. Antibiot.* **1988**, *41*, 1272. (b) Lee, S. H.; Goldberg, I. H. *Mol. Pharmacol.* **1988**, *33*, 396.

[11] Since strainless bond enthalpy constants of $-\mathrm{C}\equiv\mathrm{C}-$ delocalized and $=\mathrm{C}-\mathrm{C}\equiv$ delocalized were assumed to be identical with those of normal bond enthalpy, the calculated strain energies themselves should be taken as indicative only, but their difference will be meaningful.

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