(13) This decrease is due to the production of some vinylacetylene during the irradiation of 1,3-butadiene with the Zn lamp.
(14) Irradiation (214 nm) of the significantly thicker matrix necessary for the infrared experiments produced a small amount of s-*cis*-1,3-butadiene and vinylacetylene (by IR). Internal filtering by the s-cis isomer (which has some absorption at 214 nm) produced near the surface of the matrix, however, prevented the establishment of a photostationary state throughout the entire sample.
(15) "CRC Atlas of Spectral Data and Physical Constants for Organic Compounds", J. G. Brasselli, Ed., CRC Press, Cleveland, Ohio, 1973.
(16) (a) B. Dumbacher, *Theor. Chim. Acta.*, **23,** 346 (1972); (b) A. Devaquet, R. E. Townsend, and W. J. Hehre, *J. Am. Chem. Soc.*, **98,** 4068 (1976).
(17) N. L. Allinger and M. A. Miller, *J. Am. Chem. Soc.*, **86**; 2811 (1964).
(18) Previous experimental evidence which was considered to support a gauche geometry for *s-cis*-1,3-butadiene[2b,19,20] can be interpreted equally well on the basis of a planar geometry. Lipnick and Garbisch[2b] analyzed the temperature dependence of the NMR parameters in 1,3-butadiene and claimed that the entropy required to fit the data favored a gauche geometry for the s-cis form. Unfortunately, these workers treated the errors assigned to various parameters as being independent of one another, whereas they are, in fact, highly correlated, and this results in the true error limits of $\Delta S°$ being so large that a geometric assignment can no longer be made.
(19) J. R. Durig, W. E. Buey, and A. R. H. Cole, *Can. J. Phys.*, **53,** 1832 (1976).
(20) V. I. Tyulin, *Zh. Strukt. Khim.*, **15,** 639 (1974).
(21) Rate constants of 9×10^{-5}, 5×10^{-4}, and 2×10^{-4} s^{-1} were measured at 53, 55, and 56 K respectively. The error reported is 2 std of the $\Delta G^{\ddagger}$ values obtained from the three rates of decay.
(22) S. Benson, "The Foundations of Chemical Kinetics", McGraw-Hill, New York, 1960, p 250.
(23) National Science Foundation Predoctoral Fellow, 1974–1977.

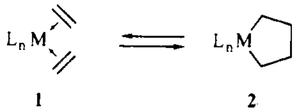
M. E. Squillacote, R. S. Sheridan,[23]
O. L. Chapman,* F. A. L. Anet*
Department of Chemistry
University of California, Los Angeles
Los Angeles, California 90024

Received January 24, 1979

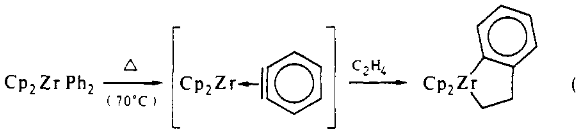
Equilibrium between Metallaindans and Aryne Olefin–Metal Complexes[1]

Sir:

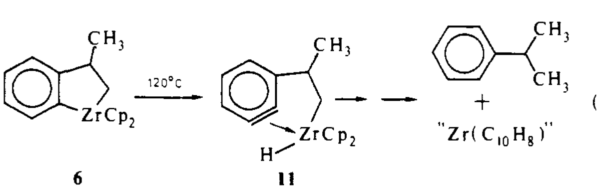
The equilibrium between bis(olefin)-transition metal complexes **1** and metallacyclopentanes **2** appears to be an important step in many catalytic reaction sequencies[2] (eq 1). This transformation has been observed with a variety of transition metals, and it has been suggested as being a quite general reaction.[3] More detailed information about this important structural relation is, however, scarce. Most of the data available has been obtained from studies on the parent systems, the unsubstituted metallacyclopentanes.[4] There is, however, very little known about how sensitive this rearrangement is to variations in the organic moieties of the complexes.



1 **2** (1)



3 **4** **5** (2)



6 **11** (3)

Table I. Thermolysis of Biscyclopentadienylzirconaindans

compd	neat, dec temp, °C[a]	in the presence of olefins $\Delta G^{\ddagger}_{80.5°C}$, kcal/mol[b]	solvent
5	130	29.9 ± 0.4	1-octene
		30.3 ± 0.4	norbornene
6	120	27.8 ± 0.3	1-octene
7	105	27.6 ± 0.3	isooctane–1-octene
			isooctane–norbornene
8	115	29.4 ± 0.9	norbornene
9	170	31.6 ± 0.8	isooctane–5,5-dimethylnorbornene

[a] Half life of 1 h. [b] For the formation of aryne olefin zirconocenes at 80.5 °C, obtained from the initial slope of the first-order plot. [c] 3,3-Dimethyl-1-[bis(η^5-cyclopentadienyl)zircona]indan.

A severe perturbation of the system would presumably result, if one of the olefinic ligands of **1** could be replaced by dehydrobenzene, because the energy content of the bis(olefin) structure should be increased by this structural change relative to the metallacycle. Moreover, this would hopefully lead to thermally more stable compounds and simpler overall kinetics, since dissociation of the aryne ligand from the complex should be an unfavorable process.[5] Consequently we developed a synthetic route to 1-metallaindans. The reaction of dehydrobenzenezirconocene (**4**, generated from diphenylzirconocene[6]) with ethylene (20 bar) produces a 95% yield of metallaindan **5** (eq 2). Likewise metallaindans regioselectively (≥95%) bearing the substituent in the 3 position are obtained from substituted olefins.[7]

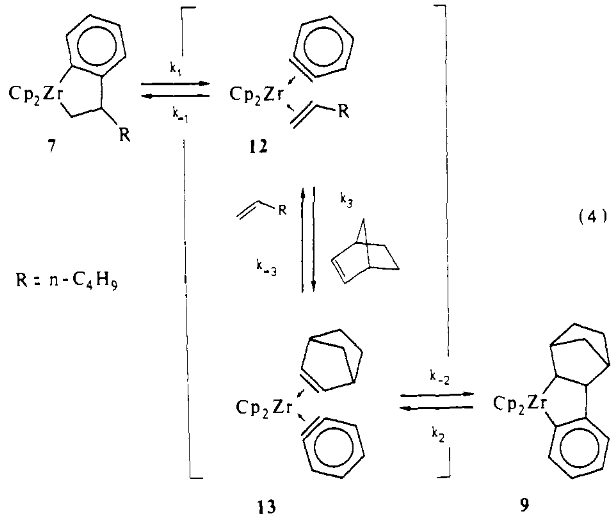
In contrast to most metallacyclopentanes, temperatures above 100 °C are required to start the decomposition of the zirconaindans (Table I). In solution the corresponding phenylalkanes are the only organic compounds obtained. When the zirconaindans **7**-d_4 or **9**-d_4, containing labeled aromatic rings, are thermolyzed in saturated hydrocarbon solution, labeled phenylalkanes are obtained. ^{1}H NMR analysis shows the average presence of only three deuterium atoms. No deuterium can be found in the alkyl substituents. Mass spectroscopic analyses of these phenylalkanes reveal the presence of a mixture of products containing one to five deuterium atoms in a distribution which is almost statistical if it derives from initially pure phenylalkanes-d_3. Equally, thermolyses of unlabeled zirconaindans in benzene-d_6 produce phenylalkanes containing some of the isotope bound to the phenyl groups. Thermolyses of the solvent-free zirconaindans under vacuum (10^{-3} Torr) proceed alike, except with 3-*n*-butylzirconaindan (**7**) which produces 2-phenylhexane accompanied by a low yield (~10%) of 1-hexene.

In the presence of olefins, the thermal reactivity of the zirconaindans appears markedly changed. At temperatures significantly lower than required for the decomposition (vide supra), liberation of alkene from the complex is observed. At the same time formation of a new zirconaindan containing the added olefin takes place (eq 4; see below). Upon thermolysis of 3-*n*-butylzirconaindan (**7**) with excess norbornene (1.1 to 20 molar equiv), **9** is almost exclusively obtained (>98%). Equilibration of **7** with the less reactive olefin 1-octene (1 molar equiv) leads to a nearly equimolar mixture of 3-*n*-hexylzirconaindan (**10**) and the starting material. This ratio is shifted in favor of **10** with an increasing 1-octene concentration (9:1 with 5 molar equiv of 1-octene). The pronounced effect of the olefins on the equilibrium stands in contrast to the influences of the olefins on the reaction rate. The rate of decrease in **7**, obtained at the beginning of the reaction, has been found to be independent both of the structure and of the concentration of the added alkene. All zirconaindans studied show a similar behavior.

These results indicate that the zirconaindans studied are

0002-7863/79/1501-3659$01.00/0

subjected to two different types of thermally induced reaction paths. The high activation energy process leading to phenylalkanes most likely does not reflect a reaction mode typical of a five-membered metallacycle. It rather resembles the thermal decomposition of acyclic group 4 transition metal-aryl complexes.[6,9] The loss of one deuterium atom from the aryl group, the isotopic scrambling of the already formed phenylalkane, and the participation of aromatic solvents in the reaction can sufficiently be accounted for by an intermediate aryne-zirconocene complex. The formation of such a species (e.g., **11** from **6**) by a β-hydride elimination from the aromatic ring is an attractive mechanistic possibility[10] (eq 3). A different intramolecular reaction pathway with a lower activation energy, however, becomes apparent in the presence of alkenes. In the thermolysis of the zirconaindans, a reactive intermediate is formed which can only revert to the starting material, if not intercepted by an added olefin. A reasonable structure of this intermediate is the 18-electron species aryne olefin zirconocene (e.g., **12** from **7**)[11] (eq 4). The introduction of the dehydrobenzene ligand into this type of intermediate, as expected, leads to an extraordinary high thermal stability of the corresponding five-membered metallacycle. Moreover, the initial ring opening of the metallaindan represents the rate-determining step in the reaction sequence (eq 4).[12] This feature can be used to obtain information about the influence of structural changes or substituent effects on the transformation between metallacyclic and bis(olefin) structure by this exchange reaction. The $\Delta G^{\ddagger}$ differences observed (Table I) reflect a pronounced influence of the olefinic ligand on the intermediate—the formation of the more strained olefins makes the ring opening of the metallacycle less favorable.[13] The unexpected deviation of **8** from this behavior seems to indicate the sensitivity of this reaction to steric hindrance, here introduced by the geminal two methyl groups.



(4)

The thermal reactions of the zirconaindans demonstrate that these metallacycles exhibit a reactivity which is markedly dependent on the substitution, but, nevertheless, still follow a reaction pattern typical of a five-membered metallacycle. The unique features of the equilibrium between metallacycle and bis(olefin) complex should make these readily available metallaindans useful model systems to study the influence of structural changes on carbon-carbon bond formation processes in transition metal complexes.

References and Notes

(1) The financial support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.
(2) R. H. Grubbs and A. Miyashita, *J. Am. Chem. Soc.*, **100**, 7416 (1978); M. J. Doyle, J. McMeeking, and P. Binger, *J. Chem. Soc., Chem. Commun.*, 376 (1976); R. Noyori, Y. Kumagai, and H. Takaya, *J. Am. Chem. Soc.*, **96**, 634 (1974); L. Cassar, P. E. Eaton, and J. Halpern, *ibid.*, **92**, 3515 (1970).
(3) R. H. Grubbs and A. Miyashita, *J. Organomet. Chem.*, **161**, 371 (1978), and references cited therein.
(4) J. X. McDermott, J. F. White, and G. M. Whitesides, *J. Am. Chem. Soc.*, **98**, 6521 (1976); J. X. McDermott, M. E. Wilson, and G. M. Whitesides, *ibid.*, **98**, 6529 (1976); G. B. Young and G. M. Whitesides, *ibid.*, **100**, 5808 (1978); R. H. Grubbs and A. Miyashita, *ibid.*, **100**, 1300 (1978); R. H. Grubbs, A. Miyashita, M. Liu, and P. Burk, *ibid.*, **100**, 2418 (1978); P. Diversi, G. Ingrosso, and A. Lucherini, *J. Chem. Soc., Chem. Commun.*, 735 (1978).
(5) Typical reaction products of free arynes, to our knowledge, have never been observed from transition metal-aryne complexes: H. Masal, K. Sonogashira, and N. Hagihara, *Bull. Chem. Soc. Jpn.*, **41**, 750 (1968); V. B. Shur, E. G. Berkovitch, L. B. Vasiljeva, R. V. Kudryavtsev, and M. E. Volpin, *J. Organomet. Chem.*, **78**, 127 (1974).
(6) G. Erker, *J. Organomet. Chem.*, **134**, 189 (1977).
(7) The description of **5** as 1-[bis(η^5-cyclopentadienyl)zircona]indan is consistent with its spectroscopic properties and chemical reactivity—reactions with protic acid, halogen, or carbon monoxide give products expected for the five-membered metallacycle: ^{1}H NMR (in C_6D_6) δ 7.20-6.55 (m, 4 H, aromatic), 5.95 (s, 10 H, cyclopentadienyl), 3.25 (t, 2 H, benzylic), 1.25 (t, 2 H); ^{13}C NMR (in C_6D_6) δ 183.8, 150.2, 136.8, 127.2, 125.6, 124.0 (6 C, aromatic), 112.0 (10 C, cyclopentadienyl), 43.0 (1 C, α to the metal), 34.4 (1 C, benzylic). The ^{1}H NMR spectrum of 3-methyl-1-zirconaindan (**6**) indicates a strong deviation of the five-membered ring from planarity:[8] δ 7.50-6.90 (m, 3 H), 6.65-6.30 (m, 1 H, aromatic), 5.95 (s, 5 H), 5.90 (s, 5 H, cyclopentadienyl), 3.50, 2.15, 0.25 (AMX system, J_{AM} = 12.5, J_{MX} = 11.0, J_{AX} = 5.5 Hz, 3 H), 1.45 (d, 3 H).
(8) C. G. Biefeld, H. A. Eick, and R. H. Grubbs, *Inorg. Chem.*, **12**, 2166 (1973).
(9) P. J. Davidson, M. F. Lappert, and R. Pearce, *Chem. Rev.*, **76**, 219 (1976); R. R. Schrock and G. W. Parshall, *ibid.*, **76**, 243 (1976).
(10) It is not without precedence that alkyl hydride-metal complexes are not subjected to direct reductive elimination: L. Abis, A. Sen, and J. Halpern, *J. Am. Chem. Soc.*, **100**, 2915 (1978); J. Evans, S. J. Okrasinski, A. J. Pribula, and J. R. Norton, *ibid.*, **98**, 4000 (1976); K. I. Gell and J. Schwartz, *ibid.*, **100**, 3246 (1978); D. R. McAlister, D. K. Erwin, J. E. Bercaw, *ibid.*, **100**, 5966 (1978). In the special case of **11** a *cis* relationship of the alkyl and the hydride ligand has to be established before reductive elimination could occur. Such a process (e.g., cleavage of the aryne to metal bond, or pseudorotational reorganization of the ligands) is not supported by the results obtained. All three additional hydrogen atoms found in the product phenylalkane in this decomposition originate from the cyclopentadienyl ligands.
(11) The exchange of the olefinic ligand should be described by a dissociative process with the intermediate formation of the aryne zirconocene complex **4**. In solution the rapid reverse reaction precludes the direct observation of this process. Under special conditions (vide supra) the thermally induced dissociation of 1-hexene from **12** can indeed be observed.
(12) The rate at the beginning of the reaction (eq 4) can be expressed by $v_0 = k_1[\mathbf{7}](1 + k_{-1}/k_3[\text{norbornene}])^{-1}$; v_0 is independent of the norbornene concentration for $k_{-1} \ll k_3$[norbornene].
(13) J. L. Jensen, *Prog. Phys. Org. Chem.*, **12**, 189 (1976).

Gerhard Erker,* Kurt Kropp
Lehrstuhl für Organische Chemie
der Ruhr-Universität Bochum
D-4630 Bochum, West Germany
Received February 5, 1979

Non-Br^--Controlled Oscillations in the Belousov-Zhabotinskii Reaction of Malonic Acid

Sir:

The principal features of the chemical mechanism for the temporal oscillations in the Belousov-Zhabotinskii[1-3] reaction have been elucidated by Field, Körös, and Noyes.[4-6] Their mechanism applies a hypothesis originally proposed by Zhabotinskii. According to that supposition in the course of the oscillations, the oxidation of Ce^{3+} by acidic bromate is inhibited periodically by bromide whenever the concentration of bromide exceeds a critical value. That is, in the classical oscillations the bromide ion is a key reference reactant, a control intermediate, the concentration variation of which "turns on" and "turns off" certain chemical processes. In our experiments we could detect oscillations of the redox potential when the bromide concentration was much below its critical value. During these oscillations the potential of a bromide-ion-specific electrode changes monotonically or undergoes very small amplitude oscillations.

The aim of the experiments was to observe the classical BZ system when the natural bromide concentration was depleted

0002-7863/79/1501-3660$01.00/0