

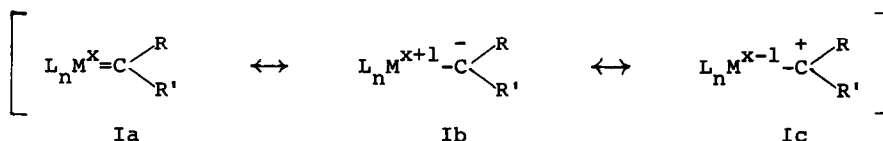
ON THE NATURE OF CARBENOIDS GENERATED FROM BICYCLO[1.1.0]BUTANES
AND TRANSITION METAL COMPLEXES¹

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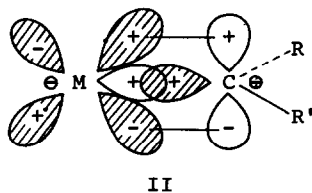
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In valence bond description, a complex of a transition metal M^xL_n (x = oxidation number, L = ligand) and a carbene $:CRR'$ ($R, R' = H$ or carbon function) exists as a resonance hybrid consisting of the ylene form Ia and the two polar contributors, the metal-bonded carbanion Ib (ylide) and the metal-bonded carbocation Ic (inverse ylide).² The relative significance of the canonical forms is determined by the nature of the metal, its ligands, and the carbene substituents



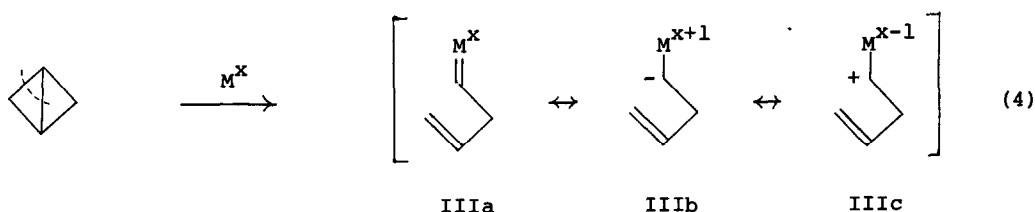
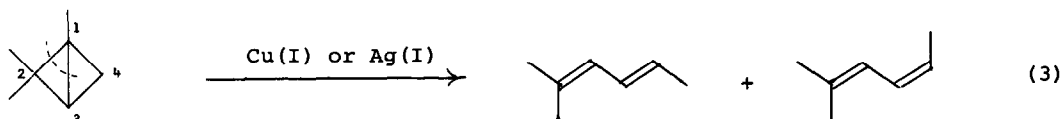
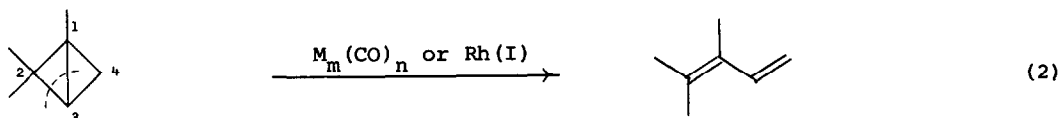
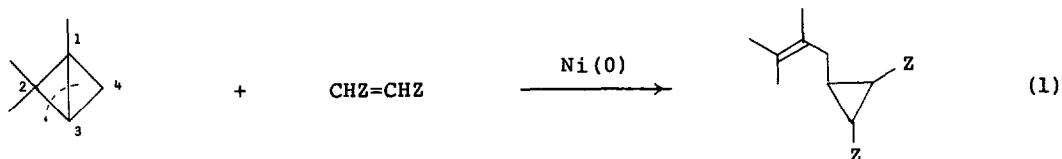
The bonding between the metal and the singlet σ^2 carbene upon the molecular orbital treatment can be best represented by the model II: lone-pair electrons in the carbene sp^2 hybrid are donated into a vacant orbital of M forming a σ bond, and simultaneous back-donation from an appropriate d or hybridized orbital of M to the vacant 2p orbital of the carbenic carbon forms a π bond. The great π -donor capacity of M is expected to offer a preference for the ylide structure Ib in the resonance hybrid. On the other hand, a carbenoid in which M has



negligible π -donor ability can be viewed as the inverse ylide Ic. Therefore, the bonding situation is closely related to the promotion energy of the metal M (π -interaction)³ and its electron affinity (σ -interaction). The formal charge in resonance structure, however, does not necessarily indicate the reactivity of the carbene complex, because the rules do not take into account details of electronic distribution (the description is concerned with only π -interaction). The actual charge distribution in the covalent M=C bond is determined by a net balance between the π - and σ -components. The direction of the bond dipole is dominated by a variety of factors, but could be inferred primarily by comparing the electronegativity of M with that of carbon atom.⁴

This paper describes an attempt to interpret the divergence of the transition metal catalyzed reactions of bicyclo[1.1.0]butanes which involve carbene-metal complexes as a reaction intermediate.⁵ The mode of bond rupture of bicyclobutanes is markedly dependent on the nature of the transition metal catalysts. For instance, Ni(0) complexes catalyze a coupling reaction of 1,2,2-trimethylbicyclo[1.1.0]butane and electron-poor olefins producing the cyclopropane derivatives (eq 1).⁶ Apparently cleavage of the C-1--C-3 and C-2--C-3 bonds of the bicyclobutane is involved. In the presence of certain metal carbonyls⁷ or Rh(I) complexes,⁸ the bicyclobutane undergoes the same type of bond fission to afford the isomerized diene (eq 2). By contrast, Cu(I)⁷ and Ag(I)⁹ complexes promote the isomerization via C-1--C-3 and C-1--C-2 cleavage yielding a mixture of conjugated dienes (eq 3). The mode of the Pd(II) catalysis is dependent on the metal ligand.⁷ These two-bond cleavage reactions could be best explained in terms of the carbene-metal complexes, in which the original C-1 or C-3 carbon is incorporated as the carbenic carbon (see eq 4).^{5,10} The dual reactivities of the intermediates are also worthy of remark: the allyl-carbene-Ni(0) intermediates exhibit an eminent nucleophilic reactivity, whereas other metal ion carbenoids appear to behave as an electrophile.¹¹ The discussion is divided into two parts, dealing first with the mode of the catalysis, then with the reactivity of the organometallic intermediates.

The observed choice of the reaction mode could reasonably be explained in terms of the nature of the resulting allylcarbene-metal complexes. If bicyclo-



butanes are unsymmetrically substituted, the two-bond breakage reaction would take place in such a way to produce a carbenoid⁵ most preferable in view of the resonance stabilization; effects concerning the stability of the carbenic center and the olefinic moiety are the dominating factor. As shown in Table I, Ni(0) atom as well as Rh(I) and Ir(I) ions is an efficient π -donor, and therefore promotes the reaction leading to the carbenoids which have a substantial ylide character (IIIb), as is consistent with the observations.^{6-8,12} Although only the ylene—inverse ylide hybrid (IIIa \leftrightarrow IIIc) has been considered for the Rh(I) carbenoid,⁸ the ylide form of type IIIb would be also, or even more, important as the polar contributor in resonance. The other extreme is the case of Cu(I) and Ag(I) carbenoids (if formed⁵). Since these ions are poor π -donors, the catalysis of bicyclobutanes produces the inverse ylides of type IIIc.^{7,9} Pt(II) and Pd(II) ions locate intermediate between these two extremes, and the catalysis mode would be subtly influenced by various secondary factors such as kind of

Table I. Properties of Certain Transition Metal Atom and Ions

Atom or ion	Electronic configuration	Promotion energy, eV ^{a,b}	Electron affinity, eV ^a	Electro-negativity, χ^c
Ni(0)	d ¹⁰	1.72	1.2	1.1
Rh(I)	d ⁸	~ 1.60	7.31	4.1
Ir(I)	d ⁸	~ 2.4	7.95	4.0
Pt(II)	d ⁸	~ 3.05	18.56	7.5
Pd(II)	d ⁸	~ 3.39	19.42	8.5
Cu(I)	d ¹⁰	8.25	7.72	4.4
Ag(I)	d ¹⁰	9.94	7.57	4.6

^a Taken from R. S. Nyholm, *Proc. Chem. Soc.*, 273 (1961). ^b Energy required for the (n-1)d → np transition. ^c Mulliken-type value adjusted to Pauling's scale, (ionization potential + electron affinity)/(2 x 3.15).

the metal ligand.^{7,13,14}

Reactivity of the carbenoid intermediates could be interpreted as follows. As is evident from Table I, Ni(0) atom is more electropositive than carbon atom ($\chi \sim 2.6$), and thence its carbenoids behave as a nucleophile.^{6,12} By contrast, Rh(I), Ir(I), Pt(II), and Pd(II) ions are highly electronegative, and consequently the carbenoids undergo typical electrophilic reactions. Therefore, it is not surprising that Rh(I) catalysts effect the Ni(0)-type catalysis of bicyclobutanes (eq 2), but that the resulting carbenoids exhibits electrophilic characters. The best known electrophilic behavior is the isomerization of substituted III ($M^x = Rh(I)$) with loss of the metal ion leading to conjugated dienes; migratory aptitudes to the carbenic center are H > vinyl > CH₃.⁸ Another example is the rearrangement of phenyl-substituted bicyclobutanes to hydroazulenes and hydronaphthalenes which involves intramolecular carbene reactions to the phenyl ring (addition to C=C bond and insertion to C-H bond, respectively).¹⁵ The electrophilic nature of the intermediates of type IIIc⁹ would need no explanation.

Finally, the nucleophilic character of the Ni(0) carbenoids should be

emphasized, since catalyses of diazoalkane, a conventional method for the generation of carbenoids, are usually accomplished using metal ions with a high oxidation number and produce electrophilic species, Ic or $Ia \leftrightarrow Ic$.^{16,17}

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13. Cf. W. G. Dauben and A. J. Kielbania, Jr., J. Amer. Chem. Soc., 93, 7345 (1971).
14. The present discussion is made mainly in terms of electronic properties of the central metals. The catalysis mode is also sensitive to the nature of the ring system of the strained hydrocarbons. Steric factors controlling the direction of metal approach may reflect on the product. Rh(I)- and Cu(I)-catalyses of a tricyclic substrate, 1-methyltricyclo[4.1.0.0^{2,7}]heptane

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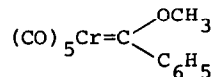
i



ii



iii



iv

The chemistry of the Fischer's stable carbene complex iv is well documented (ref. 2). The carbenic center is electron-deficient (cmr evidence) due to the presence of an oxygen function on the carbenic carbon, and strongly π -accepting CO ligands on the Cr atom. The electrophilic character was also illustrated by the facile reactions (below room temperature) with phenyllithium, amines, thiols, and Wittig reagents.¹⁸ Methoxyphenylcarbene cleaved upon heating the complex at elevated temperature is known to cycloadd to electron-poor olefins.^{2a} Fischer postulated the cyclopropane formation is a result of the direct interaction between the complex iv and olefins. In our opinion, however, a mechanism which involves free carbenes as major reactive species or "an intimate pair of methoxyphenylcarbene and $\text{Cr}(\text{CO})_5$ " (where the carbene behaves like a free species) could also accommodate the experimental findings. The following points would be in accord with this view: (1) the reaction conditions ($>90^\circ$), (2) the eminent nucleophilic character of the carbene,¹⁹ (3) other carbene reactions under the comparable reaction conditions, *viz.*, "dimerization" producing dimethoxystilbenes,²⁰ insertion to Si-H bond,²⁰ and its ability to induce *cis*-*trans* isomerization of diethyl maleate,²¹ (4) the stereoselectivity observed in the reaction with methyl *trans*-crotonate which could be ascribed to the "steric attraction" effect,²² and (5) the fact that independently generated free methoxyphenylcarbene exhibits the same reactivity.²³

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