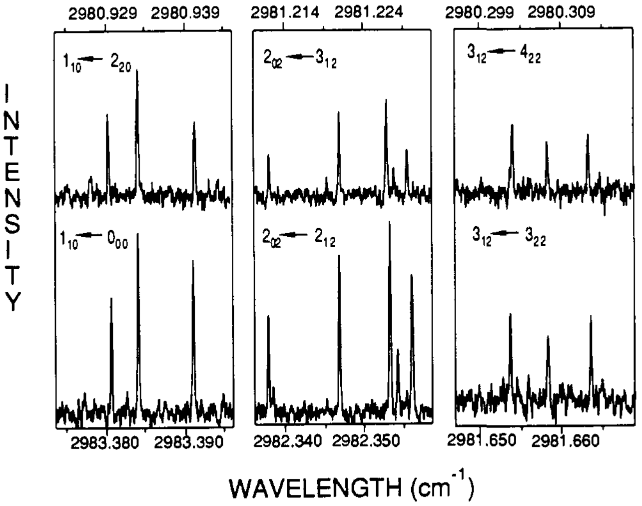

Figure 1. Each panel in the figure shows two sets of transitions to the same excited state. The transitions are labeled with the J, K_a, and K_c quantum numbers as $J_{K_aK_c}$ corresponding to the labels of the zeroth-order uncoupled states. The left panel shows two sets of transitions to the 1_{10} excited state. The middle and right panels are to the 2_{02} and 3_{12} excited states, respectively. In each case the similarity of the patterns of peak positions and intensities is apparent, demonstrating the presence of vibrational mode coupling.

between the peaks in these clusters is 0.004 cm^{-1}. Therefore, the magnitude of the matrix element need not be very large in order to have a significant effect in mixing states.

To veryify that a cluster of peaks is, in fact, caused by mixing of states, one can compare two sets of transitions to the same excited state. The same pattern of peak spacing and intensities should appear for two different transitions to the same excited rotational state. Shown in Figure 1 are several spectral regions consisting of pairs of transitions to the same excited state. The similarity of the patterns is apparent, and we conclude that mode coupling is causing these clusters of peaks.

From a simple state-counting algorithm that treats the normal modes in 2FE as harmonic oscillators,[18] with the exception that the C–C torsion and the O–H torsion are treated as hindered rotors,[19] 2FE has 58 states/cm^{-1} at the CH stretching region. With this density of states, virtually all modes must be coupled to the optically active mode. The fact that all modes appear to couple to the optically active mode is similar to the results of previous studies of terminal acetylenes.[13,14] In contrast, however, the average matrix element that couples the asymmetric CH stretch to other modes is 0.0029 ± 0.0011 cm^{-1}, which is a factor of 2–3 smaller than those calculated for the terminal acetylenes.[19] The small magnitude of the matrix element in 2FE relative to butyne is particularly surprising given that the acetylenic CH stretch would be expected to couple poorly to the other modes in butyne, as the authors note. The small amount of coupling in 2FE is consistent with the slow rate of isomerization observed when this CH stretch was excited in a matrix. Further experiments are necessary to fully quantify the relationship between mode coupling and isomerization rates. In particular, the high-resolution infrared spectrum of the OH stretch is essential for comparison with the current high-resolution spectrum of the CH region. One might expect that the mode coupling would be more substantial in the OH stretch to account for the faster reaction rate upon excitation of this mode in matrices. Such experiments are currently underway in our laboratory. The results presented here demonstrate the power of high-resolution spectroscopy to resolve the controversy surrounding the role of mode-selective chemistry in the isomerization reaction of 2FE.

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Rhodium(II) Acetate Catalyzed Alkyne Insertion Reactions of α-Diazo Ketones: Mechanistic Inferences

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Readily prepared α-diazo ketones bearing tethered alkyne units have shown potential for the construction of polycyclic skeletons.[2,3] Exposure of compounds like **1** (Scheme I) to a variety of transition-metal catalysts results in cycloisomerization of an initially formed α-keto carbene (**2**) to an intermediate in which carbene-like reactivity has been transferred to one of the alkyne carbons (cf. **3** and/or **5**). A second strategically disposed functional group G may then trap this monocyclic intermediate via known carbene chemistry[4] to give various products. The specific role of certain metals throughout this type of transformation has been of interest to us. We report here the results of a study that addresses the fundamentally important mechanistic question of whether the metal moiety actually migrates to the alkyne carbon in the $Rh_2(OAc)_4$-catalyzed reactions of **1**.

Likely metal-containing intermediates lie within the continuum represented by **2**–**5**.[5] We recognized that this manifold could also be entered from the vinylogous α-diazo ketones **6**. Presumably the distribution of products arising via **3**[6] would be different from that via **5**. If metal migration were to occur in the conversion of **1**, then the reactions of isomeric **1** and **6** would both proceed via the common intermediate **5** and identical product distributions would result. Such is not the case; distincly *different* product distributions arise. This strongly implies that migration of rhodium

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[1] Rohm & Haas Graduate Fellow, 1989–1990. Graduate Fellow of the ACS Division of Organic Chemistry, sponsored by Glaxo Research Laboratories, 1990–1991.

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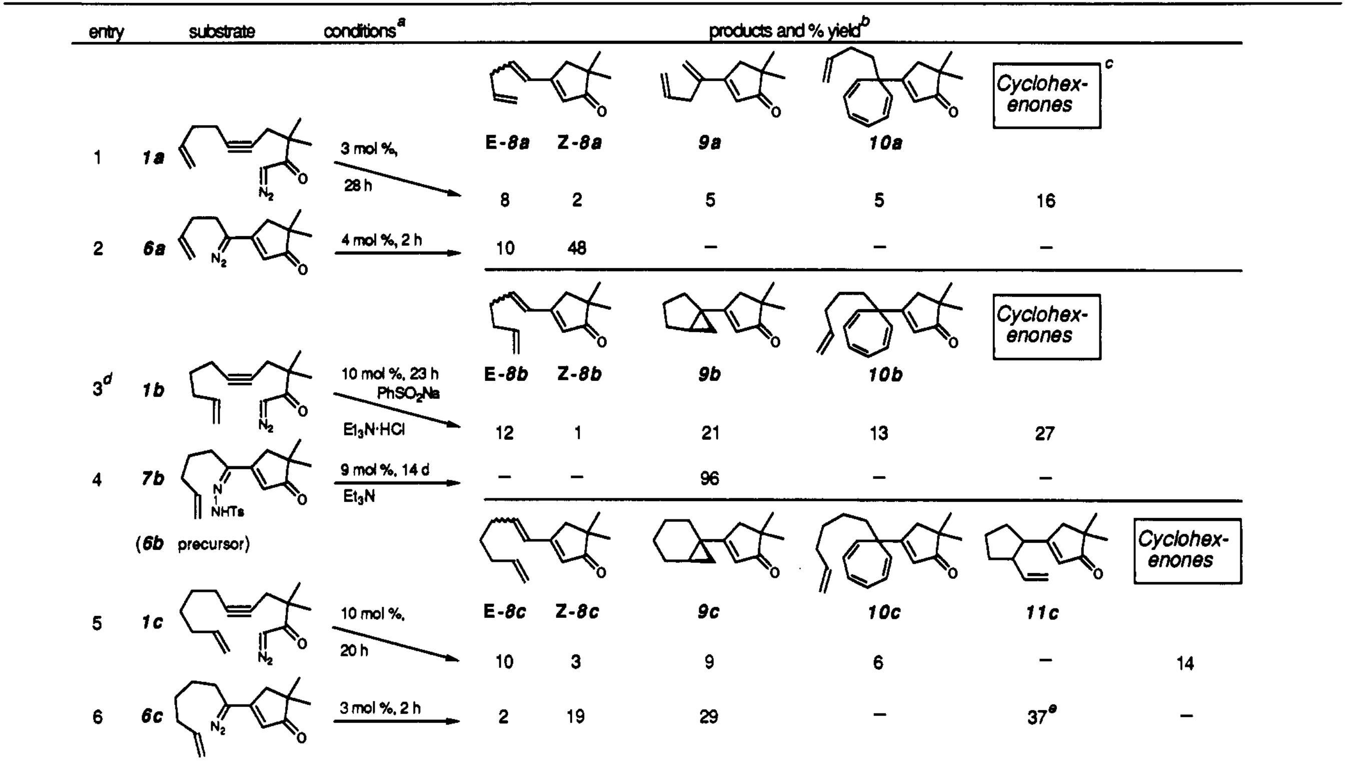
[5] (a) Any of **3**, **4**, or **5** could reversibly lose the metal moiety to give the corresponding strained cyclopropene.[2,3,5b] (b) Müller, P.; Pautex, N.; Doyle, M. P.; Bagheri, V. *Helv. Chim. Acta* **1990**, *73*, 1233.

[6] (a) Formation of **3** is analogous to the Doyle mechanism[4e,6b] for Rh(II)-catalyzed cyclopropanation involving an electrophilic attack of the carbene carbon on the alkene. (b) Doyle, M. P.; Griffin, J. H.; Bagheri, V.; Dorow, R. L. *Organometallics* **1984**, *3*, 53.

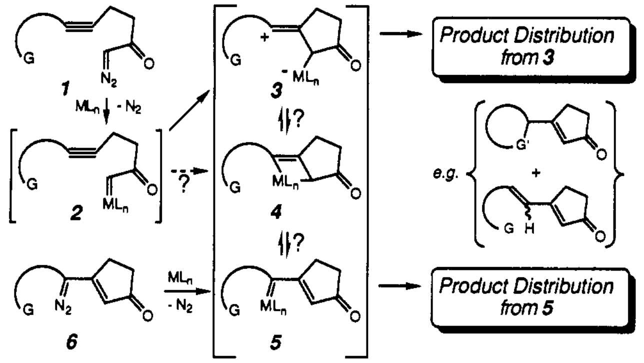
Table I. $Rh_2(OAc)_4$-Induced Reactions of Isomeric Diazo Ketones **1** and **6**



entry	substrate	conditions[a]	E-8	Z-8	9	10	11	Cyclohexenones
			E-8a	**Z-8a**	**9a**	**10a**		Cyclohexenones[c]
1	**1a**	3 mol %, 28 h	8	2	5	5		16
2	**6a**	4 mol %, 2 h	10	48	–	–		–
			E-8b	**Z-8b**	**9b**	**10b**		Cyclohexenones
3[d]	**1b**	10 mol %, 23 h $PhSO_2Na$ $Et_3N{\cdot}HCl$	12	1	21	13		27
4	**7b** (**6b** precursor)	9 mol %, 14 d Et_3N	–	–	96	–		–
			E-8c	**Z-8c**	**9c**	**10c**	**11c**	Cyclohexenones
5	**1c**	10 mol %, 20 h	10	3	9	6	–	14
6	**6c**	3 mol %, 2 h	2	19	29	–	37[e]	–

[a] Described in supplementary material, along with relevant control experiments. [b] MPLC or HPLC on SiO_2. [c] See ref 3. [d] Also 18% of 1-chloro-3,3-dimethyl-10-undecen-5-yn-2-one. [e] A single diastereomer of undetermined stereochemistry.

Scheme I

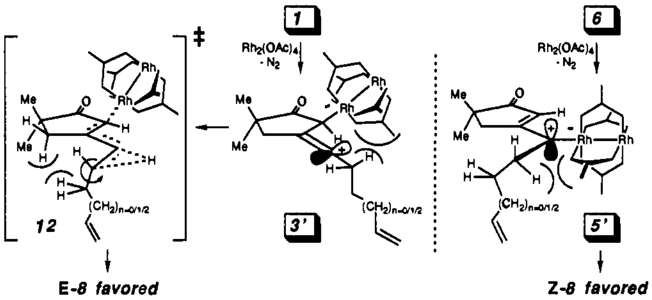


to the remote alkyne carbon does *not* take place in these alkyne insertion reactions of **1**.

Product distributions from three homologous pairs of enynyl α-diazo ketones **1a–c** and their isomers **6a–c** were compared (see Table I). Enones **6a** and **6c**[7] were sufficiently stable at room temperature, but study of **6b** required in situ preparation from **7b** in the presence of $Rh_2(OAc)_4$ to prevent its otherwise facile intramolecular 1,3-dipolar cyclization to a pyrazoline.

The differences in product identity and ratios (see Table I) can perhaps best be rationalized through the intermediacy of the zwitterion **3′** and its isomeric Rh(II)–carbene complex **5′** (Scheme II): specific renditions of the generic **3** and **5**. With respect to alkyne insertion/1,2-hydrogen migration to give dienones **8**, α-diazo ketone **1** yielded mostly trans olefins (entries 1, 3, and 5), while **6** favored cis stereoselectivity[8] (entries 2 and 6). This divergence likely follows from steric demands within the transition states leading from **3′** (i.e., **12**) vs **5′**. α-Diazo enyne **1a** gave the unusual dienone **9a** (entry 1), but **6a** did not; thus, vinylogous

Scheme II



Wolff rearrangement[9] within **5′** was not observed. Cyclopropanation[10] to give **9b** was the only mode of carbene trapping from **7b** (via **6b**, entry 4), but **1b** pursued additional pathways (entry 3). The α-diazo enynes **1** consistently reacted with the benzene solvent after alkyne insertion (but never before)[11] to give cylcoheptatrienes **10** and also cyclized to the distal alkyne carbon to yield cyclohexenone isomers[3] (entries 1, 3, and 5), while the vinylogous diazo ketones **6** did neither. Finally, **1c** failed to provide **11c** by insertion into an allylic C–H bond[12] after cyclization, but this was the major product from reaction of **6c** (entry 6).

As is often the case with metal–carbene complex mediated transformations of organic substrates, mechanistic inferences are most readily, if not only, available through product analysis. The clear differences in product distributions from the isomeric diazo

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(7) The syntheses of **6a–c** are described in the supplementary material.

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precursors **1** and **6** reported here prove the lack of a common intermediate in these two reaction manifolds. This is most consistent with the lack of rhodium migration to an alkyne carbon in the alkyne insertion reactions of **1**.

Acknowledgment. This investigation was supported by Grant GM-38854 awarded by the DHHS. We also thank Rohm & Haas and Glaxo for fellowship support.[1]

Supplementary Material Available: Summary of the syntheses of **6a/c** and **7b**, representative experimental procedures for $Rh_2(OAc)_4$-catalyzed reactions, characterization of all new compounds (**1a**, **6a**, **6c**, **7b**, (*E*)- and (*Z*)-**8a**, **9a**, **10a**, and **11c**), and descriptions of relevant control experiments (5 pages). Ordering information is given on any current masthead page.

Radical Cation–Arene π-Molecular Complexes. Thioether Radical Cations in Aromatic Solvents[†]

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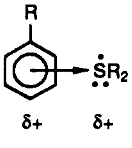
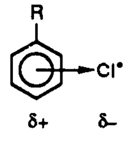
Thioether radical cations are known to be stabilized by coordination of the unpaired p electron of the oxidized sulfur atom to free p-electron pairs. Complex radical cations coupled by a three-electron $(\sigma)^2(\sigma^*)^1$ S–S bond are usually the only radical-cation species observed in liquid-phase studies of the oxidation of alkyl sulfides.[1-3] The dimer radical cations are more stable

$$R_2S \overset{+}{\therefore} SR_2$$

than the monomer radical cations, which in aqueous solutions undergo fast deprotonation reactions.[1,4] Monomer thioether radical cations have previously only been observed in rigid matrices by EPR.[5-10]

Here we show that thioether radical cations are stabilized by electron donation from aromatic solvents, and we have observed their EPR spectra in the liquid phase by time-resolved fluorescence-detected magnetic resonance (FDMR) spectroscopy. The thioether radical cation EPR parameters are strongly solvent dependent and are a sensitive probe of the solvent to radical cation (electron) charge transfer. This is the first example of saturated radical cations that form complexes with π-electron donors. Perhaps the closest analogue is the complexation of chlorine atoms with benzene, which was noted for the first time in the classical studies of the photochlorination of alkanes.[11-15]





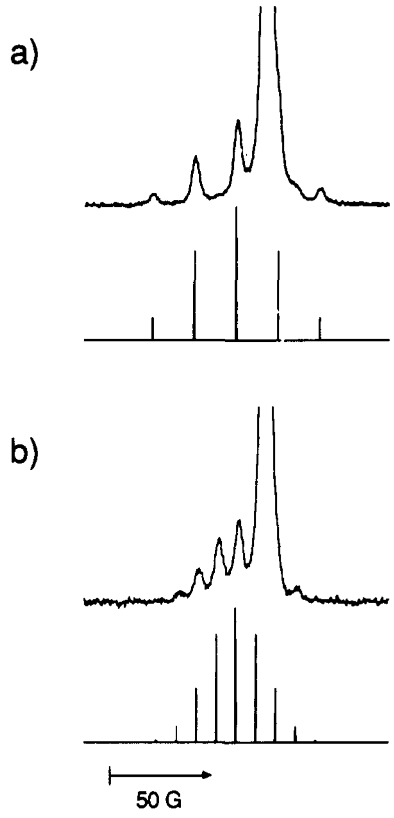


Figure 1. FDMR spectra observed in toluene/thietane mixtures: (a) 3×10^{-3} M thietane, $T = 205$ K; (b) 10^{-2} M thietane, $T = 290$ K. The anthracene-d_{10} scintillator concentration was 10^{-3} M. The microwave pulse was applied from $t = 0$ to $t = 150$ ns. The multiplet spectrum ($a = 20.8$ G, 4 H) in part a is assigned to thietane radical cations which are formed via electron transfer to toluene radical cations formed by electron radiolysis. The multiplet spectrum ($a = 9.8$ G, 8 H) in part b is assigned to thietane dimer radical cations formed by reaction of thietane radical cations with neutral thietane molecules.

Table I. EPR Parameters for Thioether Radical Cations

radical cation	matrix or solvent	T, K	a, G	$g^{a,b}$	ref
$(CH_3)_2S^{\cdot+}$	toluene	205	13.1 (6 H)	2.010	*e*
	CF_3CCl_3	81	20.4 (6 H)	2.013	7
	$CF_2ClCFCl_2$	81	20.4 (6 H)	2.017	8
	$CFCl_3$	130	21 (6 H)	2.014	9
$(CH_2)_3S^{\cdot+}$	toluene	205	20.8 (4 H)	2.013	*e*
	$CFCl_3$	90	31.1 (4 H)	2.019	7
	$CFCl_3$	ca. 120	31 (4 H)	2.016	9
$(CH_2)_4S^{\cdot+}$	toluene	205	21.2 (4 H)	2.011	*e*
	$CF_2ClCFCl_2$	81	28.4 (4 H)[c]		8
	$CFCl_3$	77	30 (4 H)[d]	2.014	9

[a] The g factors in toluene are relative to that of the anthracene radical anion ($g = 2.0027$) (Segal, B. G.; Kaplan, M.; Fraenkel, G. K. *J. Chem. Phys.* **1965**, *12*, 4191). [b] The g factors in Freons are averages of g_x, g_y, and g_z. [c] Average of 37.8 (2 H) and 18.9 (2 H). [d] Average of 40 (2 H) and 20 (2 H). [e] This work.

Figure 1 shows FDMR spectra obtained in toluene solvent containing thietane (trimethylene sulfide). In the pulse radiolysis/FDMR method, fluorescence from the recombination reaction between spin-correlated pairs of radical cations and aromatic scintillator radical anions, eq 1, is modulated at resonant magnetic field by a microwave pulse.[16] The plot of the magnetic field

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