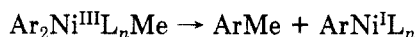
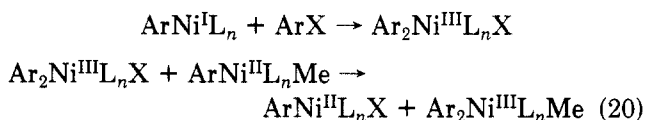


carbon-carbon double or triple bond, which is neither oxidative nor reductive.

Second, in both mechanisms discussed above, the oxidative addition of organic electrophiles to Pd or Ni complexes is a presumed key step. Indeed, in many instances, oxidative addition products have been isolated and have been shown to react with organometallic reagents to produce the expected cross-coupling products, indicating that they can be intermediates in the Pd- or Ni-catalyzed cross coupling.

Third, recent mechanistic studies indicate that various ramifications and/or modifications of the mechanisms presented above are possible. For example, although *o*-tolylmethylbis(triethylphosphine)nickel undergoes a thermal, intramolecular, first-order reaction to produce *o*-xylene in >90% yield in accordance with Scheme I, its reaction in the presence of an added aryl halide is a faster radical-chain process involving paramagnetic Ni(I) and Ni(III) species<sup>87</sup> (eq 20). On the



other hand, the Pd-catalyzed methyl-benzyl coupling<sup>69,88</sup> most likely involves the intermediacy of a hexacoordinate Pd(IV) species formed by oxidative addition of an organic halide (RX) to a diorganopalladium (II) species. While these mechanisms appear plausible for the reactions studied, their generality remains to be established. It does not appear that the mechanism represented by Scheme I has not been ruled out for a number of synthetically useful Pd-catalyzed

(87) Smith, G.; Kochi, J. K. *J. Organomet. Chem.* 1980, 198, 199, and references therein.

(88) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* 1980, 102, 4933.

reactions, in which the thermal reductive elimination step appears to be very facile. Therefore, until the overall mechanistic picture of the Pd- or Ni-catalyzed cross coupling emerges, we may still use Scheme I as a working hypothesis, with the understanding that some reactions require modifications of this scheme.

## Conclusions

A decade ago, copper was the only metal that would permit synthetic chemists to cope with unsaturated organic electrophiles in the cross-coupling reaction, and the use of nickel in this reaction has just been introduced. The unique capability of palladium began capturing the attention of synthetic chemists only as recent as the mid-1970s. Despite its short history, the Pd- or Ni-catalyzed cross coupling has already begun rivaling the Cu-promoted cross coupling in scope and synthetic utility. Perhaps more importantly, the two methods are often complementary, as discussed above. Despite the high cost of Pd, the Pd-catalyzed cross coupling, along with the Ni-catalyzed cross coupling, should find widespread use in synthesis because of its versatility and high selectivity. Finally, a number of papers related to the topics, most notably a series of pioneering works on the Ni-catalyzed cross coupling by Kumada, Tamao, Hayashi, and their co-workers, are not cited, since (a) this Account emphasizes the Pd-catalyzed cross coupling and (b) there is an excellent recent review<sup>7b</sup> mainly describing their own contributions.

*I am deeply indebted to my co-workers, whose names appear in our papers cited in this Account, especially Drs. S. Baba, A. O. King, D. E. Van Horn, N. Okukado, L. F. Valente, M. Kobayashi, and H. Matsushita. My current co-workers active in this area are C. L. Rand, S. Chatterjee, F. T. Luo, L. D. Boardman, A. T. Stoll, and M. Balestra. Our research has been supported mainly by the National Science Foundation, the National Institutes of Health, and the Petroleum Research Fund, administered by the American Chemical Society.*

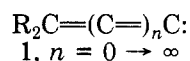
# Recent Developments in Unsaturated Carbenes and Related Chemistry<sup>1</sup>

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*Received April 9, 1982*

Carbenes are among the more useful and interesting intermediates in organic chemistry. Unsaturated carbenes, **1**, are members of an infinite homologous



series of reactive intermediates where the electron-deficient

carbenic carbon is an integral part of a  $\pi$  unsaturation. There has been much confusion in the literature on the proper nomenclature of these novel species. A consistent, logical system, in accord with current IUPAC rules, is presented, along with examples, in Table I.<sup>2</sup> This system is based upon the recommendation of Chemical Abstracts Service,<sup>3</sup> with alkylidene-carbene **2** as a root for the first member of the ho-

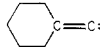
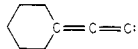
(1) Presented at the 183rd National Meeting of the American Chemical Society, Las Vegas, NV, March 1982, as part of the James Flack Norris Award Symposium in Physical Organic Chemistry honoring A. Streitwieser, Jr.

(2) Fisk, T. E. Ph.D. Dissertation, The University of Utah, 1980.

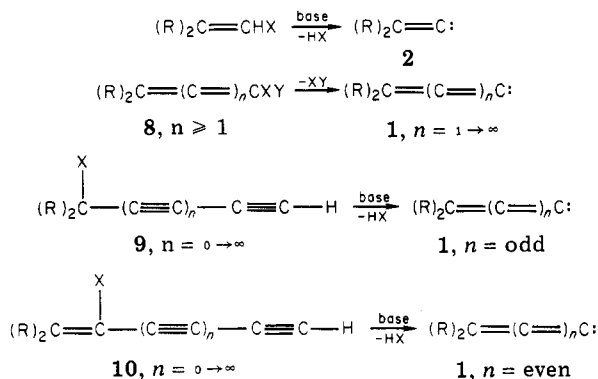
(3) See footnote 2 in: Newman, M. S.; Patrick, T. B. *J. Am. Chem. Soc.* 1970, 92, 4312.

Peter J. Stang received a B.S. in Chemistry from DePaul University in 1963 and a Ph.D. from the University of California, Berkeley, in 1966. Following 2 years of postdoctoral work at Princeton he joined the faculty at the University of Utah, where he is presently Professor of Chemistry. His research activities, besides unsaturated carbenes and vinyl cations, involve organometallic chemistry as well as certain antitumor agents and other compounds of medicinal and biological concern. His interests outside of chemistry include, *inter alia*, travel as well as geodes.

Table I  
Suggested Nomenclature for Unsaturated Carbenes

generic name	example	specific name
$R_2C=C$ : alkylidenecarbene 2	$H_2C=C$ : $(CH_3)_2C=C$ : $(C_6H_5)_2C=C$ :	methylidenecarbene isopropylidenecarbene (diphenylmethylidene)carbene
		cyclohexylidenecarbene
$R_2C=C=C$ : alkenylidenecarbene 3	$H_2C=C=C$ : $(CH_3)_2C=C=C$ : $CH_2=CHCH=C=C$ :	ethenylidenecarbene isobutenylidenecarbene 1,3-butadienylidenecarbene
		(2,2-pentamethylenethenylidene)carbene
$R_2C=C=C=C$ : alkadienylidenecarbene 4	$H_2C=C=C=C$ : $(CH_3)_2C=C=C=C$ : $(C_6H_5)_2C=C=C=C$ :	1,2-propadienylidenecarbene (3-methyl-1,2-butadienylidene)carbene (3,3-diphenyl-1,2-propadienylidene)carbene
$R_2C=C=C=C=C$ : alkatrienylidenecarbene 5	$H_2C=C=C=C=C$ : $(CH_3)_2C=C=C=C=C$ :	1,2,3-butatrienylidenecarbene (4-methyl-1,2,3-pentatrienylidene)carbene
$R_2C=C=C=C=C=C$ : alkatetraenylidenecarbene 6	$H_2C=C=C=C=C=C$ : $(CH_3)_2C=C=C=C=C=C$ :	1,2,3,4-pentatetraenylidenecarbene (5-methyl-1,2,3,4-hexatetraenylidene)carbene
$R_2C=C=C=C=C=C=C=C$ : alkaoctaenylidenecarbene 7	$H_2C=C=C=C=C=C=C=C=C$ :	1,2,3,4,5,6,7,8-nonaoctaenylidenecarbene

## Scheme I



mologous series (i.e., 1 where  $n = 0$ ).

Similar to any reactive intermediate, the major questions of interest regarding unsaturated carbenes are their mode of generation, their nature and properties, and their chemistry.

The major mode of alkylidenecarbene generation is  $\alpha$  elimination from a suitably functionalized ethylene, as shown in Scheme I. In principle, entry into the higher homologues, 1,  $n \geq 1$ , may be gained either via  $\alpha$  elimination of a suitable functionalized cumulene 8 or by means of a more elaborate elimination of an appropriately functionalized polyalkyne, 9 or 10, as illustrated in Scheme I.

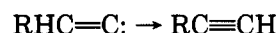
Since, other than allenes, cumulenes of type 8 functionalized with suitable leaving groups (halogens, sulfonates, etc.) are neither known nor readily accessible, in practice the polyalkynes 9 or 10 are more realistic progenitors of extended unsaturated carbenes 1,  $n \geq 1$ .

The alkylidenecarbenes, prototypes of the extended members of the series, have been extensively investigated and reported on.<sup>4</sup> Previous studies, here as well as by other groups, have established that these species are unencumbered electrophilic intermediates with a

singlet ground state and with some definite steric requirements for interaction with olefins.<sup>4</sup> However, interesting new developments have occurred in at least three areas of this field in the last few years since our previous Account:<sup>5</sup> (a) theoretical investigations; (b) generation and chemistry of more extended species; (c) transition-metal complexes and related compounds. These recent developments will be the focus of the present Account.

## Theoretical Developments

It is well-known<sup>4</sup> that  $\beta$ -hydrogen-containing alkylidenecarbenes undergo rapid rearrangement to the corresponding acetylenes:



The most recent and sophisticated calculations<sup>6-8</sup> all agree that the barrier to this rearrangement is very low. Using Møller-Plesset perturbation theory with an extended polarized basis set and inclusion of zero-point vibrational corrections, Pople, Schleyer, and co-workers<sup>7</sup> predict a methylidenecarbene-to-acetylene rearrangement barrier of only 0.9 kcal/mol. A low barrier is in agreement with recent experimental results of Steinfeld and co-workers,<sup>9</sup> using multiple infrared photon excitation (MIRPE) of  $\alpha$ -chloro olefins by intense CO<sub>2</sub> laser pulses as a means of alkylidenecarbene generation in the gas phase. In fact, Pople and Schleyer suggest that the methylidenecarbene should be considered as the effective transition structure, rather than a discrete intermediate, for the degenerate rearrangement on the C<sub>2</sub>H<sub>2</sub> surface, with an activation energy of about 45 kcal/mol. This interesting hypothesis is in accord with

(5) Stang, P. J. *Acc. Chem. Res.* 1978, 11, 107.

(6) Schaefer, H. F. *Acc. Chem. Res.* 1979, 12, 288.

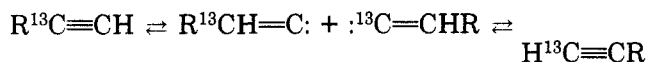
(7) Krishnan, R.; Frisch, M. J.; Pople, J. A.; Schleyer, P. v. R. *Chem. Phys. Lett.* 1981, 79, 408.

(8) Osamura, Y.; Schaefer, H. F.; Gray, S. K.; Miller, W. H. *J. Am. Chem. Soc.* 1981, 103, 1904.

(9) Reiser, C.; Steinfeld, J. I. *J. Phys. Chem.* 1980, 84, 680. Reiser, C.; Lussier, F. M.; Jensen, C. C.; Steinfeld, J. I. *J. Am. Chem. Soc.* 1979, 101, 350.

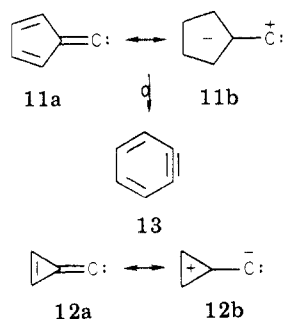
(4) For reviews see: (a) Hartzler, H. D. In "Carbenes"; Moss R. A., Jones, M., Eds.; Wiley-Interscience: New York, 1975; Vol. II, Chapter 2, pp 43-100. (b) Stang, P. J. *Chem. Rev.* 1978, 78, 383.

long-known data of Brown and co-workers<sup>10</sup> on such degenerate acetylene rearrangements upon flash vacuum pyrolysis, between 700 and 850 °C, of labeled alkynes:



In contrast to the parent and other  $\beta$ -hydrogen-containing alkylidene carbenes, the difluoromethylidene carbene to difluoroacetylene rearrangement is calculated<sup>11</sup> to have a considerable barrier of 36 kcal/mol. This higher barrier for the  $F_2C=C:$  rearrangement is in agreement with the fact that this carbene, unlike  $H_2C=C:$ , may be intermolecularly trapped by suitable substrates.<sup>12</sup>

Apeloig and Schreiber<sup>13</sup> have shown by calculations at the STO-3G and 4-31G level and by a set of isodesmic reactions that electronegative substituents ( $NH_2$ ,  $OH$ ,  $F$ ,  $CN$ ,  $Cl$ ) in the  $\beta$  position destabilize alkylidene carbenes, whereas electropositive substituents ( $BeH$ ,  $BH_2$ ,  $CH_3$ ,  $SiH_3$ ) stabilize them relative to the parent methylenecarbene. Thus,  $F_2C=C:$  is calculated to be almost 17 kcal/mol less stable than  $H_2C=C:$ ; whereas  $(H_3Si)_2C=C:$  is found to be 19 kcal/mol more stable. Similarly, calculations predict<sup>14</sup> carbene 11 to be



strongly electrophilic, due to the importance of resonance form 11b, whereas carbene 12 is predicted to be nucleophilic, due to 12b. Calculations also indicate<sup>14</sup> that *o*-benzyne 13 is 14 kcal/mol more stable than carbene 11 and hence that carbene 11 may well rearrange to 13. These interesting predictions await experimental testing.

An extensive set of calculations at the MNDO as well as ab initio levels on the interaction of unsymmetrical alkylidene carbenes with unsymmetrical olefins indicates that the preferred approach of the carbene to an olefin is the anti, semiperpendicular one shown in Figure 1a, with the large carbenic substituent pointing up and away from the olefin. This approach results in the formation of the favored (major) *E* adduct, whereas the minor *Z* isomer arises from the anti, semiperpendicular approach shown in Figure 1b. The calculated difference in energy between these two approaches is a function of both the olefinic (*R*) and carbenic (*L*, *S*) substituents, but for  $R = L = t\text{-Bu}$  and  $S = Me$  it is 5.0 kcal/mol.<sup>15</sup>

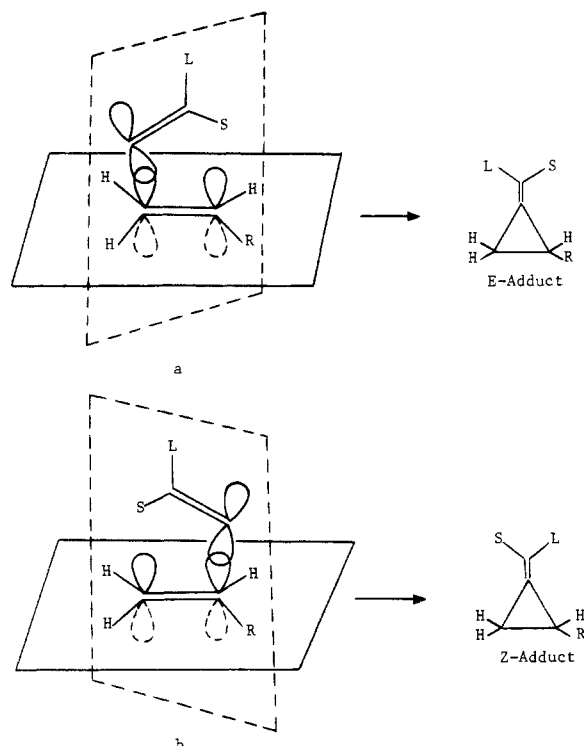
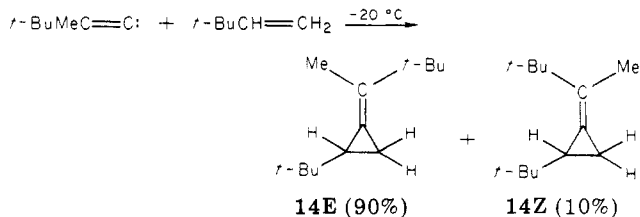


Figure 1.

Table II  
Relative Reactivity of  $(CH_3)_2C=C:$   
with Various Olefins at  $-20^\circ C$

substrate	relative reactivity
<i>cis</i> -2-butene	8.7
2-methyl-2-butene	2.7
<i>trans</i> -2-butene	1.6
1-butene	1.5
isobutylene	1.0
2,3-dimethyl-2-butene	0.25

All other approaches and pathways are higher in energy. Such an approach maximizes the favorable 2-electron LUMO(carbene)–HOMO(olefin) interaction, minimizes the repulsive 4-electron HOMO(carbene)–HOMO(olefin) interaction, and avoids the unfavorable steric interaction between the large (*L*) carbenic substituent and the alkyl group on the ethylene. This model correctly accounts for the preferred formation of the *E* adduct 14E over 14Z in the addition of (*tert*-butylmethylmethylidene)carbene to *tert*-butylethylene:<sup>15</sup>



Moreover, this approach nicely explains the previously observed<sup>16</sup> relative reactivities of alkylidene carbenes with substituted olefins summarized in Table II. In particular, the “anti” approach explains why *cis* olefins react faster than the *trans* isomers as well as the slower

(10) Brown, R. F. C. “Pyrolytic Methods in Organic Chemistry”; Academic Press: New York, 1980; pp 124–127 and references therein.

(11) Frisch, M. J.; Krishnan, R.; Pople, J. A.; Schleyer, P. v. R. *Chem. Phys. Lett.* 1981, 81, 421.

(12) Sharp, K. G.; Schwager, F. *Inorg. Chem.* 1976, 15, 1697. Norstrom, R. J.; Gunning, H. E.; Strausz, D. P. *J. Am. Chem. Soc.* 1976, 98, 1454.

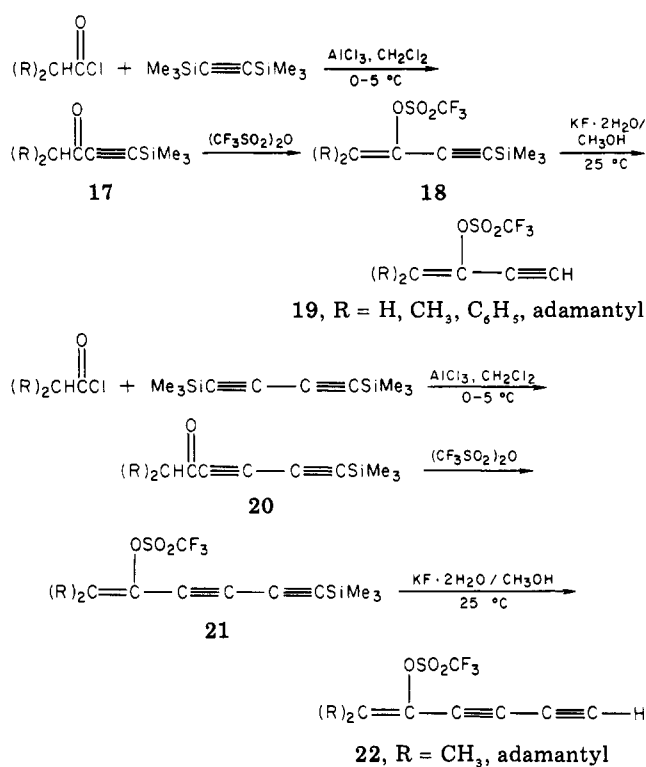
(13) Apeloig, Y.; Schreiber, R. *Tetrahedron Lett.* 1978, 4555.

(14) Apeloig, Y.; Schreiber, R.; Stang, P. J. *Tetrahedron Lett.* 1980, 411.

(15) Stang, P. J.; Fox, D. P.; Apeloig, Y.; Karni, M. *J. Am. Chem. Soc.*, submitted for publication.

(16) Stang, P. J.; Madsen, J. R.; Mangum, M. G.; Fox, D. P. *J. Org. Chem.* 1977, 42, 1802.

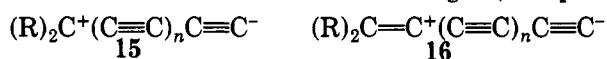
Scheme II



reactivity of isobutylene compared to 1-butene and 1-octene. The model also accounts for the very slow reactivity of tetramethylethylene, despite the fact that it is the most electron-rich alkyl-substituted olefin investigated.<sup>15,16</sup>

### Extended Unsaturated Carbenes

The second member of the homologous series (1,  $n = 1$ ), alkenylenecarbenes **3**, has been known and investigated for some time. Their properties and behavior are similar to those of alkylidenecarbenes,<sup>4</sup> with both theoretical<sup>17</sup> and experimental<sup>18</sup> data suggesting that these odd carbon-containing species have larger dipole moments than the even carbenes. This is presumably due to the greater contribution of charged resonance forms **15** for the odd-membered homologues, compared



to the even ones **16**, ascribable to the lower stability of vinyl cations<sup>19</sup> relative to trisubstituted carbenium ions. Here we wish to emphasize and discuss the generation and some chemistry of even more extended members, with four, five, and six carbons (i.e., 1,  $n = 2, 3, 4$ ).

Because of the superior nucleofugacity<sup>20</sup> of the trifluoromethanesulfonate anion (triflate,  $\text{CF}_3\text{SO}_3^-$ ), the (1-ethynyl)vinyl triflates **19** and (1-butadiynyl)vinyl triflates **22** were chosen as suitable precursors for alkadienylenecarbenes **4** and alkatetraenylenecarbenes **6**, respectively. These triflates were prepared<sup>21,22</sup> as shown in Scheme II. Friedel-Crafts acylation

(17) Dykstra, C. E.; Parsons, C. A.; Oates, C. L. *J. Am. Chem. Soc.* **1979**, *101*, 1962.

(18) le Noble, W. J.; Chiou, D. M.; Okaya, Y. *J. Am. Chem. Soc.* **1979**, *101*, 3244 and references therein.

(19) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. "Vinyl Cations"; Academic Press: New York, 1979.

(20) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85.

(21) Stang, P. J.; Fisk, T. E. *Synthesis* **1979**, 438.

(22) Stang, P. J.; Ladika, M. *Synthesis* **1981**, 29.

of bis(trimethylsilyl)acetylene or bis(trimethylsilyl)diacetylene gave ketones **17** and **20**, respectively. Conversion to the vinyl triflates **18** and **21** was carried out by standard procedures developed in our laboratories.<sup>23</sup> Desilylation with KF in methanol to **19** and **22** was nearly quantitative. Hence, a variety of substituted ethynyl (**19**) and butadiynyl vinyl triflates (**22**) can be prepared in 40–70% isolated yield in three simple steps.<sup>21,22</sup>

Reaction of alkynylvinyl triflates **19** and **22** with *t*-BuOK in a mixture of 1,2-dimethoxyethane (DME) and excess olefin proceeds<sup>24,25</sup> as shown in Schemes III and IV. Rapid equilibrium formation of anions **23** and **28** is indicated by reisolation of deuterium-incorporated precursors **19** and **22**, respectively, in deuterated media. Subsequent slow loss of triflate anion gives extended carbenes **4** and **6**, respectively. Hence, unlike the generation of alkylidenecarbenes **2** from primary vinyl triflates via a concerted elimination of  $\text{CF}_3\text{SO}_3\text{H}$ , the formation of **4** and **6** is a two-step process. The subsequent fate of these carbenes depends both on their substituents and on the olefin employed as trap. With tetramethylethylene (TME) as substrate, cumulenes **24** and **29** are isolated as adducts. With cyclohexene as trap, the reaction takes a different course. In both cases, the initial cumulene adducts **25** and **30** are not observed, but rather cyclodimers are isolated as stable crystalline compounds.<sup>24,25</sup> Although there are numerous cyclodimers possible from such cumulenes, only a single compound was isolated from each reaction. In the case of carbene **4**, based on related precedent<sup>26</sup> and on somewhat ambiguous spectral data, we initially reported [4]radialenes **26** as products. Recent X-ray data<sup>27</sup> reveals the compounds to be the head-to-head dimers **27**. In the case of adduct **30**, the isolated cyclodimer was identified by spectral means as the highly strained cyclododecatetrayne (cyclyne) **31**. Other known members of this cyclyne family include the parent<sup>28</sup> and the permethyl<sup>29</sup> analogue of **31**. In the absence of X-ray data the regiochemistry of cyclyne **31** is unknown, although we favor the head-to-head isomer.<sup>25</sup>

Relative rates with a set of standard olefins, in conjunction with the elegant Moss<sup>30</sup> "carbenic selectivity index", results in an  $m = 0.77$  for carbene **4**. This establishes the electrophilic nature of alkadienylenecarbene **4** and provides indirect evidence for the singlet nature of these species in accord with theoretical predictions.<sup>31</sup> Unfortunately, the required olefin adducts for carbene **6** proved to be too unstable to experimentally establish an  $m$  value and its electrophilicity. However, expectations are that all extended homologues **1** ( $n \geq 1$ ) are electrophilic. Since in all extended members of the series (1,  $n \geq 1$ ) the substituents are far

(23) Stang, P. J.; Treptow, W. *Synthesis* **1980**, 283.

(24) Stang, P. J.; Fisk, T. E. *J. Am. Chem. Soc.* **1980**, *102*, 6813; **1979**, *101*, 4772.

(25) Stang, P. J.; Ladika, M. *J. Am. Chem. Soc.* **1981**, *103*, 6437; **1980**, *102*, 5406.

(26) Hartzler, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 4527. Inou, T.; Kaneda, T.; Misumi, S. *Tetrahedron Lett.* **1974**, 2969.

(27) Kaftory, M., private communication.

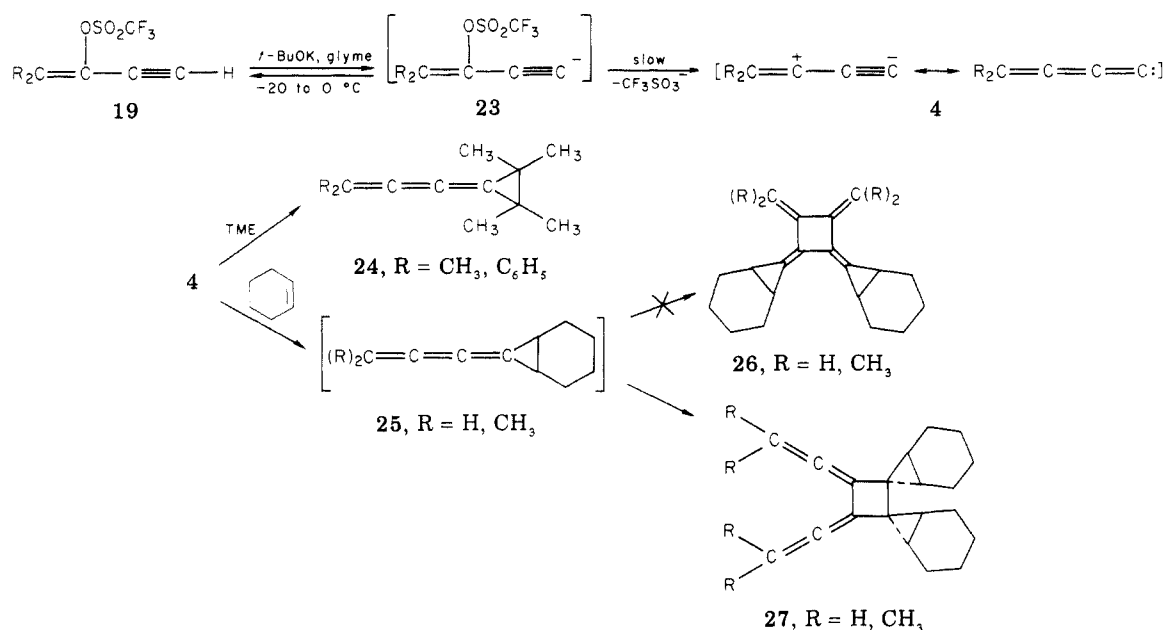
(28) Wolovsky, R.; Sondheimer, F. *J. Am. Chem. Soc.* **1965**, *87*, 5720.

(29) Santiago, C.; Houk, K. N.; DeCicco, G. J.; Scott, L. T. *J. Am. Chem. Soc.* **1978**, *100*, 692. Scott, L. T.; DeCicco, G. J. *Tetrahedron Lett.* **1976**, 2663.

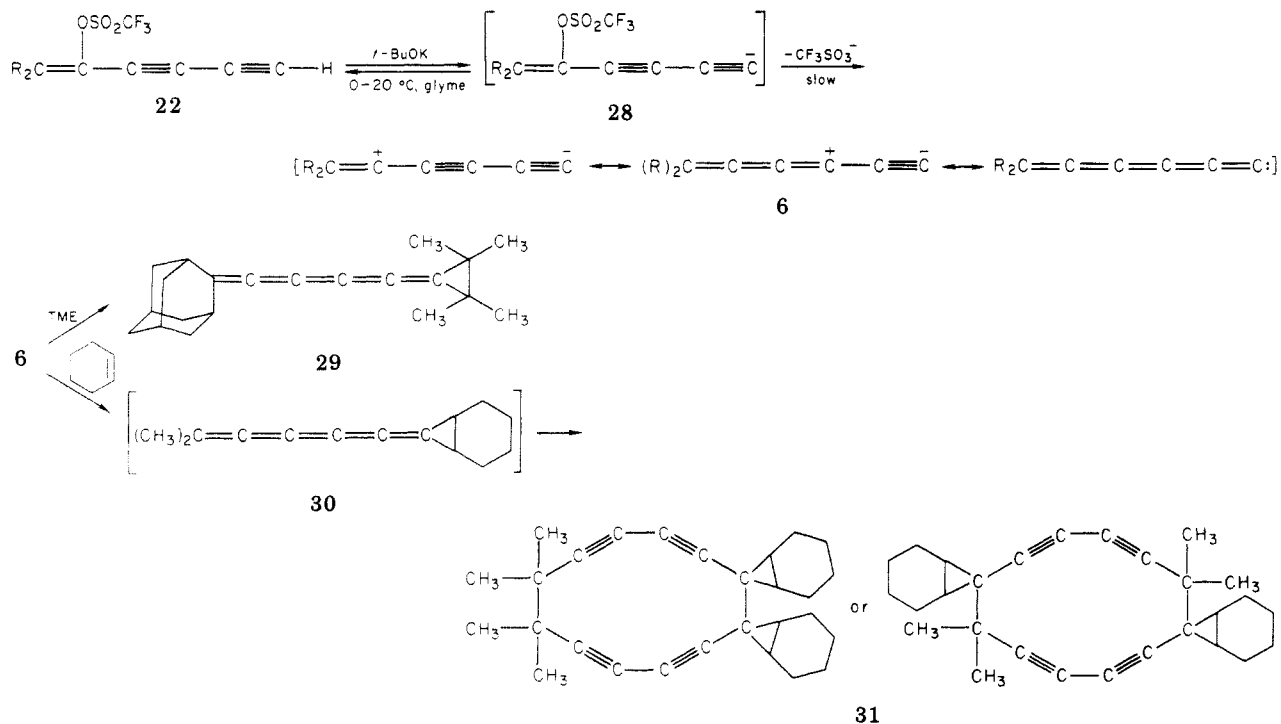
(30) Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58 and references therein.

(31) Kenney, J. W.; Simons, J.; Purvis, G. D.; Bartlett, R. J. *J. Am. Chem. Soc.* **1978**, *100*, 6930.

Scheme III



Scheme IV



removed from the reactive carbenic center, little or no steric problems exist in the interaction of these carbenes with substrates.

Recently, le Noble and co-workers<sup>32</sup> were able to generate the odd-member alkatrienylidencarbenes **5** as shown in Scheme V. Interestingly, extensive internal return to isomer **33** was observed<sup>33</sup> in this system upon reaction of progenitor **32** with *t*-BuOK. Similar to carbenes **4** and **6**, the initial adduct **34** was not observed, but a cyclodimer with either structure **35** or **36** was isolated. It will be interesting to see if odd members of the homologous series (1, *n* = 1, 3, 5, etc.) will have

(32) le Noble, W. J.; Basak, S.; Srivastava, S. *J. Am. Chem. Soc.* 1981, 103, 4638.

(33) le Noble, W. J., private communication.

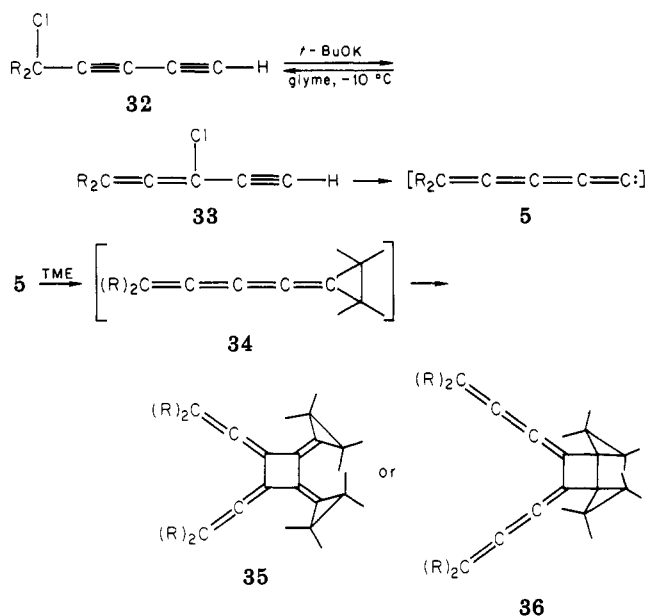
similar properties and behavior as the even members (1, *n* = 0, 2, 4, etc.). Initial indications are that they are comparable.

Besides addition reactions to  $\pi$  systems, carbenes are known to undergo insertion reactions. Hence, we also examined the insertion of extended unsaturated carbenes into group 4 hydrides,<sup>25,34</sup> as shown in Scheme VI. These reactions yield previously unknown,<sup>35</sup> silyl-, germyl-, and stannyl-functionalized tetratrienes **37**, **39**, **41**, and hexapentaenes **38** and **40**. These cumulenylyl

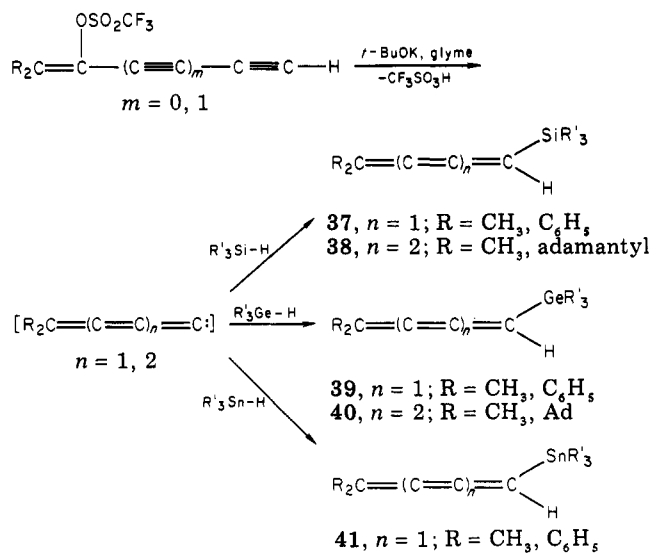
(34) Stang, P. J.; White, M. R. *J. Am. Chem. Soc.* 1981, 103, 5429.

(35) For reviews on cumulenes see: Hopf, H. "The Chemistry of Ketenes, Allenes and Related Compounds", Part 2; Patai, S., Ed.; Wiley-Interscience: Chichester, 1980; Chapter 20, pp 779-901. Murray, M. *Methoden Org. Chem. (Houben-Weyl)* 1977, 5/2a, 973-1076.

Scheme V

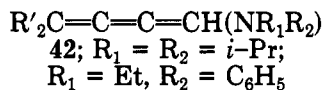
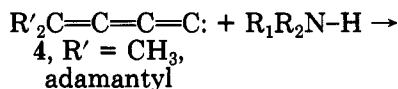


Scheme VI



silanes, germanes and stannanes have a characteristic, intense, absorption between 2015 and 2050  $\text{cm}^{-1}$  in the infrared and the expected chemical shifts in the  $^{13}\text{C}$  NMR.<sup>34</sup> They are somewhat oxygen-sensitive, but thermally stable, isolable, pale yellow liquids.

Likewise, alkadienylicidencarbenes **4** insert into the N-H of secondary amines, yielding N-functionalized tetratrienes, **42**, a type of unusual polyenamine.<sup>36</sup>



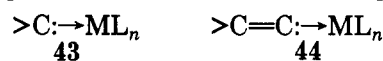
Unlike the group 4 metal functionalized tetratrienes, the nitrogen functionalized cumulenes **42** are unstable and can only be handled in solution.

These results indicate that extended unsaturated carbenes should also insert into various P-H, RO-H,

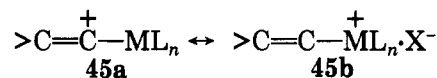
RS-H bonds, yielding other interesting, little-known or unknown, functionalized cumulenes.

### Transition-Metal Complexes of Unsaturated Carbenes

A large number and variety of carbene transition-metal complexes (**43**) are known with important im-

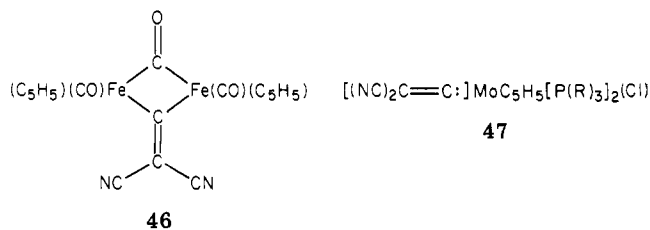


plications in catalysis, olefin metathesis, and related reactions.<sup>37,38</sup> In recent years, an increasing number of unsaturated carbene transition-metal complexes (**44**) have appeared. These complexes generally fall in two classes, neutral molecules of type **44** and cationic complexes **45**. In the latter case, the complex is a resonance

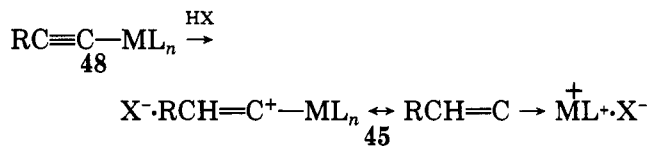


hybrid of two forms: **45a** with the charge on the  $\alpha$ -carbon or **45b** with the charge predominantly on the metal. Hence, such compounds are hybrids of a vinyl cation or an alkylidencarbene complexed to a transition metal.<sup>19</sup>

Early, pioneering work by King<sup>39</sup> and co-workers led to the first known neutral alkylidencarbene complexes with a bridging **46** as well as a terminal (**47**) dicyano-



carbene ligand. Subsequent work generally involved photo or base-initiated acetylene  $\pi$ -complex isomerizations, with a number of neutral complexes with terminal as well as bridging alkylidencarbenes as ligand reported.<sup>40</sup> Cationic complexes **45** are generally prepared by protonation of  $\alpha$ -alkynyl complexes **48**, and



a variety of such complexes are known with Pt,<sup>41</sup> Ru,<sup>42</sup> and Fe<sup>43</sup> as metals.

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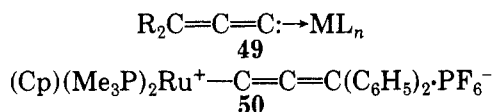
(40) Inter alia: Dawkins, G. M.; Green, M.; Jeffery, J. C.; Stone, F. G. *J. Chem. Soc., Chem. Commun.* 1980, 1120. Foltling, K.; Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* 1979, 18, 3483. Antonova, A. B.; Kolobova, N. E.; Petrovsky, P. V.; Lokshin, B. V.; Obezyuk, N. S. *J. Organomet. Chem.* 1977, 137, 55, 69. Mansuy, D.; Lange, M.; Chottard, J. C. *J. Am. Chem. Soc.* 1979, 101, 6437.

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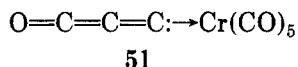
(42) Bruce, M. I.; Swincer, A. G. *Aust. J. Chem.* 1980, 33, 1471. Bruce, M. I.; Wallis, R. C. *Ibid.* 1979, 32, 1471.

(36) White, M. R.; Stang, P. J., unpublished results.

Neutral complexes of alkenylidene-carbenes with Cr, W, or Mn as metals (49) have also been reported,<sup>44</sup>



along with a recent example<sup>45</sup> of a cationic alkenylidene-carbene complex 50. The only known more-extended unsaturated carbene complex is the unusual compound 51.<sup>46</sup> However, no reports have appeared that would



suggest that any of the above metal complexes of unsaturated carbenes might serve as a progenitor of the carbene itself or that they might serve as carbene transfer agents to olefins or other substrates.

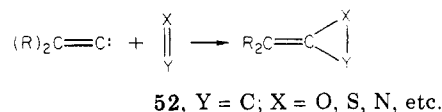
### Conclusion and Prognostication

It is evident from the foregoing that a great deal of progress has been made in a rather short interval in the area of unsaturated carbenes. A better understanding has been gained of the alkylidene-carbene-acetylene rearrangement as well as the intricate approaches and pathways of alkylidene-carbene-olefin interactions.<sup>15</sup> Extended carbenes through six carbons have become routinely available and have been used to prepare unusual functionalized cumulenes. Similarly, transition-metal complexes of unsaturated carbenes have been prepared and their structures have been examined by spectral means and, in many cases, by X-ray data.

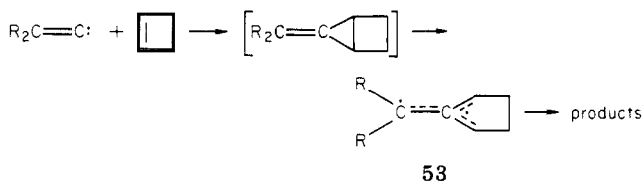
Yet much remains to be done. There is still no technique available for the photochemical or gas-phase generation of unsaturated carbenes.<sup>4</sup> Matrix isolation and detailed spectral observation await examination. Triplet unsaturated carbenes have not been observed, but the recent, elegant studies of Gilbert and co-workers,<sup>47</sup> using in situ diazoethenes as a means to alkylidene-carbenes, may be amenable to such investigations. May even more extended carbenes with seven, eight, and ten carbons or larger number of carbons be prepared? In principle the mode of generation illustrated in Scheme I and successfully used for the formation of the four-, five-, and six-carbon species may be applied for the generation of higher homologues. In practice, the technique is limited by the instability of the necessary polyacetylene precursors 9 and 10 and by the even greater instability and oxygen sensitivity of the resulting extended cumulene products.

There is also a great deal of derivative chemistry. Alkylidene-carbenes may, for example, be used as a

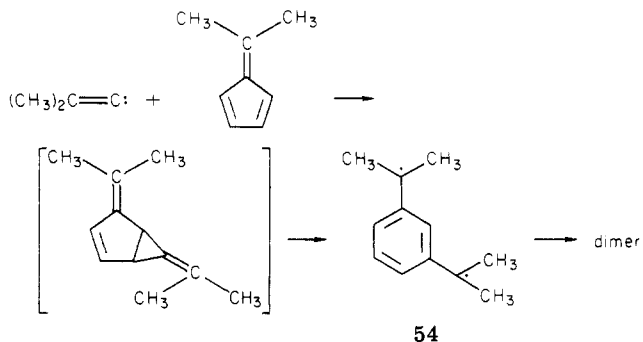
means of entry<sup>48</sup> to novel strained small-ring heterocycles 52 via addition across heteroatom  $\pi$  systems such



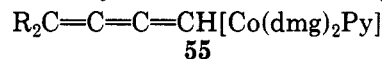
as  $R'_2C=S$  or  $R'N=O$  and others. They may be used as entries to interesting diradicals, such as trimethylenemethanes, 53, as demonstrated by Berson and co-workers:<sup>49</sup>



or *m*-xylylene,<sup>50</sup> 54:



These are but a few illustrative examples of the uses of unsaturated carbenes in the formation of molecules of unusual structural features and chemical properties. The main focus is now shifting to the nature and behavior of such unknown strained heterocycles as 52 and easily generated diradicals as 53 and 54. Likewise, alkylation, acylation, cycloadditions, etc., are potentially interesting reactions with carbene-derived functionalized cumulenes 37-42. Similarly, interest in unsaturated carbene transition-metal complexes has also led to the first known, and surprisingly stable,  $\sigma$ -bonded extended cumuleny transition-metal complexes 55.<sup>51</sup>



Hence, unsaturated carbenes have provided an additional dimension to the already fertile and fruitful area of carbene chemistry, with future advances dependent only upon the imagination of organic chemists.

*In am indebted to my able co-workers, as cited, for skillful and dedicated laboratory accomplishments in an experimentally often difficult area, as well as for stimulating discussions. Special thanks are due to Dr. Y. Apeloig of Israel for stimulating collaboration in the theoretical aspects of unsaturated carbenes. Financial support by the NSF (CHE81-07629) and in part by the Petroleum Research Fund, administered by the American Chemical Society, are gratefully acknowledged.*

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