Versatile Reactivity of Alkynyl Fischer Carbene Complexes toward Pentafulvenes: Carbocyclization and C−H Insertion Reactions

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Akynylcarbene complexes of tungsten **1** and chromium **2** undergo a formal [4+3] cycloaddition to pentafulvenes **3** when heating under CO atmosphere to give bicyclo[3.2.1]octen-2-ones **4**. When the reaction of carbenes **1** and **2** and pentafulvenes **3** is carried out in hexane at room temperature, the [4+2] cycloadducts **5** (M = W) and **6** (M = Cr) are obtained. These new carbene complexes smoothly undergo, depending on the metal, ring expansion at 60 °C, affording the [4+3] cycloadducts **4** (for M = W) or rearrangement to new 1-alkyl-6-methoxy-6-alkynylfulvenes **9** (for M = Cr).

Introduction

Since their discovery by E. O. Fischer in 1964,[1] heteroatom-stabilized carbene complexes have been demonstrated to be useful organometallic reagents for carbo- and heterocyclization reactions.[2] In this way a number of cyclization reactions of alkenyl and alkynyl alkoxy carbene complexes have been described, allowing the construction of a plethora of three- to eight-membered carbocyclic rings.[3] Thus, apart from the [2+2][4] and [4+2][5] cyclization reactions involving the activated C=C and C≡C bond of α,β-unsaturated carbene complexes, the most characteristic and valuable reactions are those wherein the metal−carbon bond is involved. Thus, a number of carbocyclization reactions based on two components, e.g., [2+1],[6] [3+1],[7] [3+2],[8] [3+3],[7,9] [4+1],[8i,10] [4+3],[8d,10b,c,11] [5+1],[12] and [5+2],[13] as well as on various components, e.g., [2+2+1],[14] [3+2+1],[15] [3+2+2],[16] [4+2+1],[17] [5+2+1],[18] [2+2+1+1],[14d,19] and [2+2+2+1],[16a] have been reported in the recent past.

More recently, new models of reactivity for Fischer carbenes have been discovered when particular unsaturated substrates such as pentafulvenes[20] are used (see Figure 1 for 6,6-dimethylfulvene).[21] Thus, using simple carbene complexes

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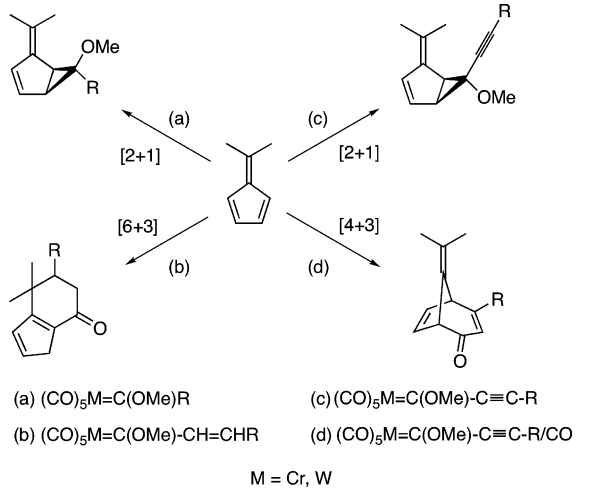


Figure 1. Reactivity of 6,6-dimethylfulvene and Fischer carbene complexes.

results in the cyclopropanation of the endocyclic carbon−carbon double bond (path a), while a [6+3] cyclization involving the whole π-framework of the fulvene structure takes place with alkenyl carbene complexes (path b). Interestingly, the preliminary work with alkynyl carbene complexes revealed a dual behavior. On one hand, the cyclopropanation reaction—a rather unusual process with alkynyl carbenes[22]—is exclusively observed on heating in MeCN (path c). On the other hand, the cyclopropanation reaction is completely inhibited in the presence of CO and the process evolves through the [4+3] cyclization (path d). Continuing the study of the reaction of pentafulvenes and Fischer alkynyl carbene complexes we report herein (i) further examples that broaden the scope of the discovered [4+3] cyclization reaction, (ii) the kinetic formation of [4+2] cycloadducts, (iii) the easy evolution of the latter to the [4+3] cycloadducts and to carbene-fulvene insertion adducts. The alkynyl(methoxy)carbene metal complexes **1** (M = W) and **2** (M = Cr) and the pentafulvenes **3** employed in the present work are displayed in Figure 2.

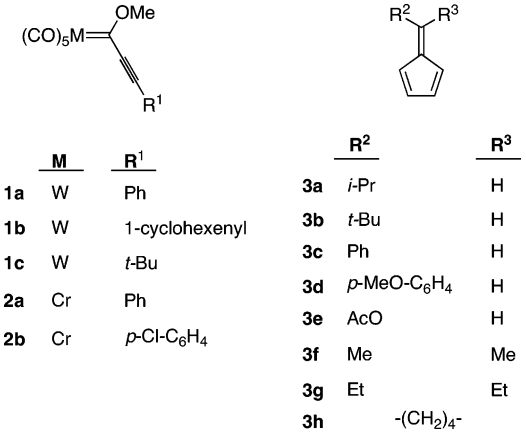
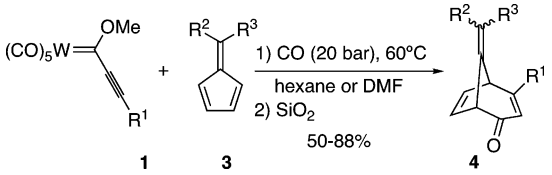


Figure 2. Carbene complexes **1** and **2** and fulvenes **3**.

Scheme 1. [4+3] Cyclization of Alkynylcarbene Complexes 1 and Fulvenes 3



Results and Discussion

[4+3] Cycloaddition of Alkynyl Carbene Complexes and Pentafulvenes. It was found that the reaction of alkynyl carbene complexes of tungsten and pentafulvenes can be efficiently driven to the [4+3] cyclization pathway by running the reaction under CO (20 bar) (Scheme 1).[21b,23] Moreover, after screening a diversity of solvents, hexane and DMF were chosen for the reaction with 6-substituted **3a**−**e** and 6,6-disubstituted pentafulvenes **3f**−**h**, respectively. Thus, phenylethynyl(methoxy)carbene complex **1a** was reacted, under a CO atmosphere (20 bar), with monosubstituted fulvenes **3a**−**e** in hexane at 60 °C. Solvent removal and column chromatography purification of the residue (SiO_2; hexanes/EtOAc, 5:1) afforded the bicyclo[3.2.1]octadien-2-ones **4a**−**e** in good yields (65−75%) as *E*/*Z* diastereomeric mixtures (Table 1, entries 1−5). The *E*/*Z* ratio was determined by ^{1}H NMR (NOE experiments) of the reaction crude. The cyclization reaction was found to work well for alkyl-, aryl-, and acetoxy-substituted fulvenes. In a similar way, the cycloaddition of disubstituted fulvenes **3f**−**h** with phenyl and cyclohexenylcarbene complexes **1a**,**b** was best accomplished in DMF [CO (20 bar), 60 °C] to provide the corresponding cycloadducts **4f**−**i** in 50−88% yield after column chromatography purification (Table 1, entries 6−9). The role of CO is noteworthy in the sense that not only is it crucial for controlling the cyclization, but it also allows one to quantitatively recover and to reuse the metal as $W(CO)_6$.

It should be pointed out that this reaction represents one of the few examples of [4+3] cycloaddition with pentafulvenes described in the literature. For instance, the [4+3] cycloaddition of fulvenes with oxyallyl cations leading to a different regioi-

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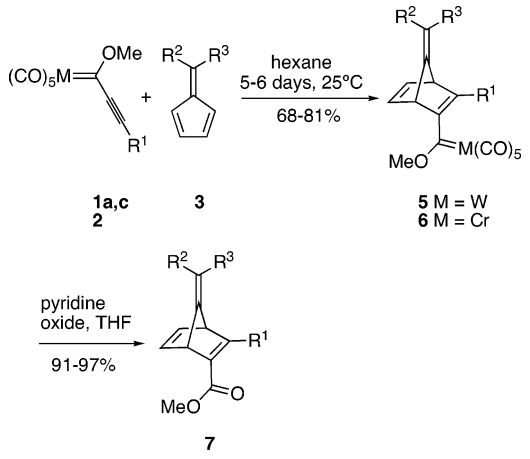
(23) Chromium carbene complexes are less efficient than the tungsten counterparts in terms of yield and selectivity (cyclopropanation vs [4+3] cyclization).

Table 1. Bicyclo[3.2.1]octadien-2-ones 4 from Carbene Complexes 1 and Fulvenes 3

entry	R^1	R^2	R^3	solvent	product (%)[a]	*E*/*Z*[b]
1	Ph	*i*-Pr	H	hexane	**4a** (70)	2:1
2	Ph	*t*-Bu	H	hexane	**4b** (65)	3:1
3	Ph	Ph	H	hexane	**4c** (65)[c]	2:1
4	Ph	*p*-$MeOC_6H_4$	H	hexane	**4d** (75)	2:1
5	Ph	AcO	H	hexane	**4e** (70)	2:1
6	Ph	Me	Me	DMF	**4f** (88)	
7	Ph	Et	Et	DMF	**4g** (84)	
8	Ph	$-(CH_2)_4-$		DMF	**4h** (80)	
9	1-cyclohexenyl	Me		DMF	**4i** (50)	

[a] Isolated yields. [b] *E*/*Z* ratio determined by ^{1}H NMR of the crude mixture. [c] Obtained along with a 25% mixture of the corresponding cyclopropane adduct.

Scheme 2. [4+2] Cyclization of Alkynylcarbene Complexes 1 and 2 and Fulvenes 3



somer adduct, specifically the bicyclo[3.2.1]octadien-3-one structure, has been reported and suffers from serious limitations in generating the three-carbon reagent.[24]

[4+2] Cyclization of Alkynyl Carbene Complexes and Pentafulvenes. The ease with which pentafulvenes cycloadd to activated alkenes/alkynes in a [4+2] fashion is well documented.[20,25] Therefore, we decided to check the reaction between alkyne carbenes and pentafulvenes under kinetic conditions (Scheme 2). It was found that alkynyl(methoxy)carbene complexes of tungsten (**1a**,**c**) and chromium (**2a**,**b**) slowly react with 6-isopropyl- (**3a**) and 6-*tert*-butylpentafulvene (**3b**) at room temperature in hexane.[26] After 5−6 days the reaction went to completion, as monitored by the disappearance of the starting carbene on TLC, and the resulting mixture was concentrated and chromatographed to furnish the 7-alkylidenenorbornadiene carbene complexes **5a**−**c** (M = W; 68−81%) and **6a**−**c** (M = Cr; 70−73%) as mixtures of diastereoisomers, except for **5c** (Table 2, entries 1−6). The metal-carbene function of these [4+2] cycloadducts was efficiently oxidized with pyridinium oxide to the corresponding ester derivatives **7a**−**c**. The *E*/*Z* ratio of compounds **5** and **7** was very similar to that encountered for

Table 2. [4+2] Cycloadducts 5−7 from Carbene Complexes 1 and 2 and Fulvenes 3

entry	M	R^1	R^2	R^3	**5** or **6** (%)[a]	**7** (%)	*E*/*Z*[b]
1	W	Ph	*i*-Pr	H	**5** (81)	**7a** (97)[c]	2:1
2	Cr	Ph	*i*-Pr	H	**6** (73)	**7a** (91)[c]	2:1
3	W	Ph	*t*-Bu	H	**5b** (81)	**7b** (95)[c]	3:1
4	Cr	Ph	*t*-Bu	H	**6b** (73)	**7b** (91)[c]	3:1
5	W	*t*-Bu	*t*-Bu	H	**5c** (68)		*E*
6	Cr	*p*-ClC_6H_4	*t*-Bu	H	**6c** (70)	**7c** (96)[c]	3:1
7	W	Ph	Me	Me	**5d** (−)	**7d** (79)[d]	
8	Cr	Ph	Me	Me	**6d** (−)	**7d** (82)[d]	

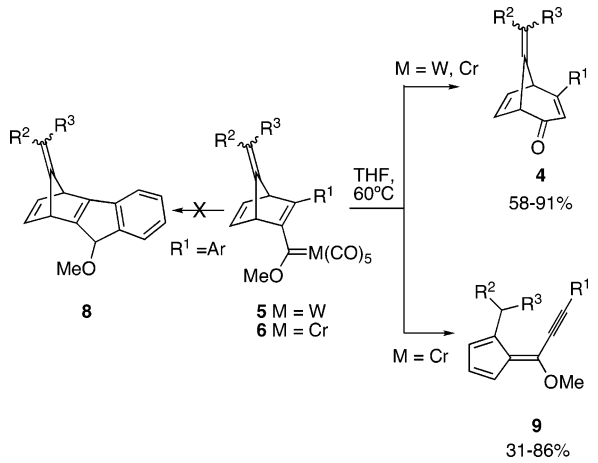
[a] Isolated yields from **1**, **2**, and **3**. [b] Determined for **5**, **6**, and **7** by ^{1}H NMR of the crude mixture. [c] Isolated yields from **5** and **6**. [d] Isolated yields from carbenes **1a** and **2a** and fulvene **3f**.

Table 3. Rearrangement of Carbene Complexes 5 and 6 to Compounds 4 and 9

entry	M	R^1	R^2	R^3	**5**, **6**	**4** (%)[a]	**9** (%)[a]
1	W	Ph	*i*-Pr	H	5a	**4a** (91)	
2	W	Ph	*t*-Bu	H	5b	**4b** (96)	
3	W	Ph	Me	Me	5d	**4f** (86)[b]	
4	Cr	Ph	*i*-Pr	H	6a	**4a** (58)	**9a** (31)
5	Cr	Ph	*t*-Bu	H	6b		**9b** (86)
6	Cr	*p*-ClC_6H_4	*t*-Bu	H	6c		**9c** (78)

[a] Isolated yields. [b] Isolated yield from carbene **1a** and fulvene **3f**.

Scheme 3. Thermal Rearrangement of [4+2] Cycloadducts 5 and 6



the direct [4+3] cyclization (Scheme 1; Table 1). In the case of the reaction between 6,6-dimethylfulvene (**3f**) and carbene complexes **1a** and **2a** the [4+2] cycloadducts formed could not be isolated by column chromatography because of partial oxidation, but they were spectroscopically characterized and in situ oxidized to the expected ester derivative **7d** (79−82% yield; Table 2, entries 7, 8).

Next, the thermal stability of this particular carbene structure was investigated (Scheme 3, Table 3). Thus, tungsten cycloadducts **5a**,**b**,**d** were heated at 60 °C in THF until consumption of the starting carbene complex (12−24 h) (Scheme 3). Unexpectedly, the well-known cyclopentannulation reaction through the 1-metalla-1,3,5-hexatriene unit[27] to form benzo derivatives of type **8** was not observed at all, but the ring expansion from the bicyclo[2.2.1]heptadiene structure to the metal-free bicyclo[3.2.1]octadienone structure cleanly took place to produce the [4+3] cycloadducts **4a**,**b**,**f** in yields higher than 86% and without affecting the stereochemistry of the exocyclic carbon−carbon double bond (Table 3, entries 1−3). A cross

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experiment consisting in heating carbene cycloadduct **5b**, derived from carbene **1a** and fulvene **3b**, in the presence of 5 equiv of fulvene **3f** led only to the [4+3] cycloadduct **4b**, the cross-cycloadduct **4f** not being observed at all. This evidence rules out a retro Diels−Alder process of **5** being involved in the ring expansion process.

However, another surprise came to us when the norbornadiene chromium carbenes **6a**−**c** were subjected to heating at 60 °C in THF. Thus, the chromium carbene **6a** did afford the expected ring expansion compound **4a** (58% yield) along with the novel fulvene-carbene coupling structure **9a** (31% yield) (Table 3, entry 4). The process could be entirely directed toward the new fulvene derivatives **9b**,**c** by using the 7-*tert*-butylmethylenenorbornadiene chromium carbenes **6b**,**c** (78−86% yield; Table 3, entries 5, 6). It is remarkable that compounds **9**, which contain a tetrasubstituted olefin, have been generated as a single isomer. The structure of these new fulvene derivatives was established on the basis of NMR spectroscopy (NOE, HMBC, and HMQC experiments). The structure **9** deserves some attention since extension of the fulvene conjugation through a carbon−carbon triple bond−6-alkynylfulvene derivatives−is very rare[28] and appears to be a matter of particular interest as σ,π-cyclopentadiene ligands in the important field of early transition metal catalyzed polymerization.[29]

Concerning the ring expansion process of tungsten cycloadducts (**5** → **4**), it should be noted that related metal-free norbornene cycloadducts suffer rearrangement under appropriate reaction conditions. Thus, the Lewis acid rearrangement of the norbornene [4+2] cycloadducts of cyclopentadiene and acroleins into the [4+3] cycloadducts has been reported recently as a powerful methodology to access bicyclo[3.2.1]octen-2-ones.[30] However, to the best of our knowledge, there are no examples of this type of rearrangement on the norbornadiene systems derived from acetylene dienophiles.

From a mechanistic point of view it is not a simple matter to disclose a feasible reaction pathway for the transformations of the [4+2] cycloadducts **5** and **6** into either the [4+3] cycloadducts **4** or the formal insertion product **9**, particularly if the retro-Diels−Alder reaction is excluded (see above). On the basis of the above-described rearrangement,[30] we tentatively propose at the present stage a common intermediate **II** to account for both rearrangements (Figure 3). First, the [1,2]-alkyl shift would produce the zwitterion intermediate **I**, which in turn would evolve into the species **II** by a subsequent [1,2]-M(CO)$_5$ migration. Both rearrangements may occur simultaneously if a synergic effect operates. The fate of such an intermediate **II** depends primarily on the nature of the metal. Thus, tungsten derivatives are stable under the reaction conditions leading to the [4+3] cycloadducts **4** after silica gel treatment. Conversely, chromium complexes **II** would suffer metal-assisted C4−C5 bond cleavage to form the chromium-coordinate intermediate **III**, which would transform into **9** by proton transfer, formation of the enol ether function, and metal decoordination.[31,32]

In conclusion, the [4+3] cyclization of diverse pentafulvenes to Fischer (alkynyl)carbene complexes takes place very efficiently, providing the bicyclo[3.2.1]octen-2-one framework. Moreover, the first [4+2] cycloaddition of fulvenes to such metal systems is reported to yield metal carbene complexes of remarkable structural complexity. These cycloadducts are prone to undergo, depending primarily on the metal, ring expansion (for M = tungsten) affording the known [4+3] cycloadducts or rearrangement to a new fulvene (M = chromium) that formally results from insertion of the (alkynyl)carbene ligand into the C1−H bond of the starting fulvene. Mechanistically, a proposal is outlined based on successive [1,2]-carbon and [1,2]-metal rearrangements. Therefore, the manifold reactivity of Fischer carbene complexes is again evidenced in the particular reaction of alkynyl(methoxy)carbene complexes with fulvenes, as four reaction pathways ([2+1], [4+3], and [4+2] cyclizations and insertion into a fulvene C−H bond) are displayed in the present work. It is noteworthy that each one can be controlled by selecting appropriately the reaction conditions or the structure of the reagents.

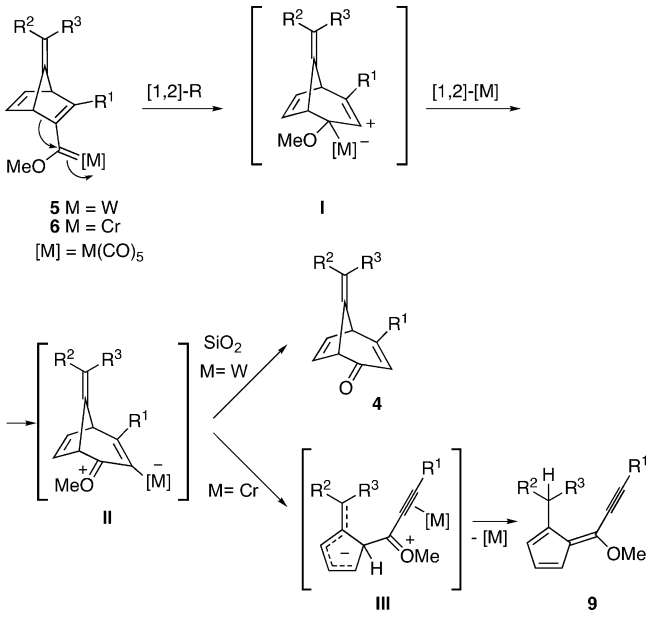

Figure 3. Proposed mechanism for the rearrangement of carbenes **5** and **6**.

Experimental Section

General Procedures. All reactions involving air-sensitive compounds were carried out under a N_2 atmosphere (99.99%). All glassware was oven-dried (120 °C), evacuated, and purged with nitrogen. All common reagents and solvents were obtained from commercial suppliers and used without any further purification unless otherwise indicated. Fischer carbene complexes **1** and **2**[1,33] and fulvenes **3**[34] were prepared following described procedures. Solvents were dried by standard methods and distilled prior to use. Flash column chromatography was carried out on silica gel 60, 230−240 mesh. All compounds were isolated as oils. NMR experiments were recorded on Bruker AC-200, AC-300, or DPX-300 spectrometers. ^{1}H NMR spectra were recorded in $CDCl_3$ (unless otherwise noted) at 300.08 MHz at 20 °C with tetramethylsilane

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($\delta = 0.0$) as the internal standard. ^{13}C NMR spectra were recorded in $CDCl_3$ at 75.46 MHz at 20 °C. ^{1}H NMR splitting pattern abbreviations are as follows: s, singlet; d, doublet; m, multiplet. ^{13}C NMR multiplicities were determined by DEPT, abbreviations are as follows: q, CH_3; t, CH_2; d, CH; s, quaternary carbons; some ^{13}C NMR signals overlap. COSY, HMSQC, HMBC, and NOESY experiments were carried out on a Bruker AMX-400 spectrometer. Standard pulse sequences were employed for the DEPT experiments. In some cases the spectral data are given for the mixture of unseparable diastereoisomers (several signals are coincidental). High-resolution mass spectra (HRMS) were obtained with a Finnigan Mat95 mass spectrometer, and electron impact techniques (70 eV) were employed. Elemental analyses were carried out with a Perkin-Elmer 240 B microanalyzer.

Synthesis of Bicyclo[3.2.1]octadien-2-ones 4. General Procedure. Alkynyl carbenes **1** and **2** (1 mmol) were dissolved in 20 mL of hexane (for **4a**−**e**) or DMF (for **4f**−**i**), and then the corresponding fulvene **3** (1.2 mmol) was added. The mixture was then transferred via cannula to an autoclave, and CO (20 bar) was introduced. The solution was heated at 60 °C for 6 h, and the solvent was removed under reduced pressure. The resulting crude was purified by column chromatography (SiO_2, hexanes/EtOAc, 5:1).

8-[(*E*/*Z*)-Isobutylidene)]-4-phenyl-3,6-bicyclo[3.2.1]octadien-2-one (4a): obtained as a 2:1 mixture of *E*/*Z* isomers; yield = 70%; ^{1}H NMR δ 0.85 (d, J = 6.6 Hz, 3H), 0.92 (d, J = 6.8 Hz, 3H), 0.94 (d, J = 6.8 Hz, 3H), 1.0 (d, J = 6.6 Hz, 3H), 2.5 (m, 2H), 3.7 (m, 1H), 4.0 (m, 1H), 4.1 (m, 1H), 4.3 (m, 1H), 5.0 (d, J = 9.5 Hz, 2H), 5.8 (s, 2H), 6.35 (dd, J = 5.6 and 3.4 Hz, 1H), 6.4 (dd, J = 5.4 and 3.4 Hz, 1H), 6.8 (dd, J = 5.4 y 3.1 Hz, 1H), 6.85 (dd, J = 5.6 and 3.1 Hz, 1H), 7.4−7.6 (m, 10H); ^{13}C NMR δ 23.0 (q), 23.1 (q), 23.1 (q), 26.5 (d), 27.0 (d), 47.3 (d), 52.3 (d), 59.5 (d), 63.8 (d), 118.9 (d), 119.9 (d), 121.6 (d), 122.1 (d), 125.8 (d), 125.9 (d), 128.8 (d), 128.9 (d), 130.0 (d), 130.2 (d), 133.1 (d), 133.3 (d), 136.7 (s), 137.0 (s), 142.0 (d), 142.3 (d), 149.2 (s), 149.4 (s), 164.7 (s), 165.1 (s), 197.0 (s), 197.1 (s); HRMS calcd for $C_{18}H_{18}O$ (M^+) 250.1357, found 250.1355. Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.74; H 7.50.

8-[(*E*/*Z*)-2,2-Dimethylpropylidene)]-4-phenyl-3,6-bicyclo[3.2.1]-octadien-2-one (4b): obtained as a 3:1 mixture of *E*/*Z* isomers; yield = 65%; ^{1}H NMR δ 1.05 (s, 9H), 1.1 (s, 9H), 3.7 (m, 1H), 3.9 (m, 1H), 4.4 (m, 1H), 4.6 (m, 1H), 5.1 (s, 1H), 5.15 (s, 1H), 5.8 (s, 1H), 5.85 (s, 1H), 6.3 (dd, J = 5.6, 3.3 Hz, 1H), 6.4 (m, 1H), 6.8 (m, 1H), 6.85 (m, 1H), 7.4−7.6 (m, 10H); ^{13}C NMR δ 31.0 (q), 31.1 (q), 32.5 (s), 32.9 (s), 47.6 (d), 54.2 (d), 60.2 (d), 65.8 (d), 118.5 (d), 119.8 (d), 125.0 (d), 125.8 (d), 126.0 (d), 128.3 (d), 128.4 (d), 128.8 (d), 128.9 (d), 130.1 (d), 133.2 (d), 133.3 (d), 136.7 (s), 141.9 (d), 142.0 (d), 149.6 (s), 149.7 (s), 164.5 (s), 165.3 (s), 197.0 (s), 197.4 (s); HRMS calcd for $C_{19}H_{20}O$ (M^+) 264.1514; found 264.1508. Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.11; H, 7.57.

8-[(*E*/*Z*)-Benzylidene]-4-phenyl-3,6-bicyclo[3.2.1]octadien-2-one (4c): obtained as a 2:1 *E*/*Z* mixture of isomers, yield = 65%; ^{1}H NMR δ 4.0 (m, 1H); 4.2 (m, 1H), 4.4 (m, 1H), 4.6 (m, 1H), 5.85 (m, 1H), 5.9 (m, 1H), 6.2 (m, 2H), 6.4 (dd, J = 5.60 and 3.12 Hz, 1H), 6.5 (dd, J = 5.75 and 2.93 Hz, 1H), 6.8 (dd, J = 5.75 and 2.93 Hz, 1H), 6.9 (dd, J = 5.60 and 3.12 Hz, 1H), 7.1 (m, 1H), 7.2−7.6 (m, 19H); ^{13}C NMR δ 47.31 (d), 53.45 (d), 60.30 (d), 64.83 (d), 114.56 (d), 115.52 (d), 119.68 (d), 120.35 (d), 126.08 (d), 126.05 (d), 126.83 (d), 126.90 (d), 128.21 (d), 128.44 (d), 128.96 (d), 129.01 (d), 130.34 (d), 130.58 (d), 132.69 (d), 133.99 (d), 135.51 (s), 135.55 (s), 135.96 (s), 136.57 (s), 141.56 (s), 142.52 (s), 152.91 (s), 163.36 (s), 164.98 (s), 196.43 (s); HRMS calcd for $C_{21}H_{16}O$ (M^+) 284.1201, found 284.1202. Anal. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.54; H, 5.90.

8-[(*E*/*Z*)-4-Methoxybenzylidene]-4-phenyl-3,6-bicyclo[3.2.1]-octadien-2-one (4d): obtained as a 2:1 mixture of *E*/*Z* isomers; yield = 75%; ^{1}H NMR δ 3.75 (s, 3H), 3.8 (s, 3H), 4.0 (m, 1H), 4.2 (m, 1H), 4.4 (m, 1H), 4.6 (m, 1H), 5.9 (s, 1H), 6.0 (s, 1H), 6.15 (s, 1H), 6.2 (s, 1H), 6.35 (dd, J = 5.3, 3.2 Hz, 1H), 6.4 (dd, J = 5.4, 3.2 Hz, 1H), 6.75 (d, J = 9.0 Hz, 2H), 6.8 (dd, J = 5.4, 3.0 Hz, 1H), 6.9 (d, J = 8.7 Hz, 2H), 6.95 (m, 1H), 7.0 (d, J = 9.0 Hz, 2H), 7.2 (d, J = 8.7 Hz, 2H), 7.4−7.6 (m, 10H); ^{13}C NMR δ 47.2 (d), 53.4 (d), 55.1 (d), 60.2 (d), 64.8 (q), 113.6 (d), 113.8 (d), 113.9 (d), 114.9 (d), 119.5 (d), 120.2 (d), 125.9 (d), 126.0 (d), 128.0 (s), 128.8 (d), 129.0 (d), 129.3 (d), 129.6 (d), 130.2 (d), 130.4 (d), 132.6 (d), 133.9 (d), 135.9 (s), 136.5 (s), 141.6 (d), 142.5 (d), 151.4 (s), 151.6 (s), 158.3 (s), 158.4 (s), 163.3 (s), 165.0 (s), 196.45 (s), 196.5 (s); HRMS calcd for $C_{22}H_{18}O_2$ (M^+) 314.1307, found 314.1304. Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.20; H, 5.71.

8-[(*E*/*Z*)-Acetoxymethylene)]-2-phenyl-3,6-bicyclo[3.2.1]-octadien-2-one (4e): obtained as a 2:1 mixture of *E*/*Z* isomers; yield = 70%; ^{1}H NMR δ 2.1 (s, 6H), 3.8 (m, 1H), 4.1 (m, 1H), 4.3 (m, 1H), 4.5 (m, 1H), 5.8 (m, 2H), 6.35 (dd, J = 5.7, 3.2 Hz, 1H), 6.4 (dd, J = 5.4, 3.1 Hz, 1H); 6.8 (dd, J = 5.4, 3.1 Hz, 1H), 6.9 (dd, J = 5.7, 3.0 Hz, 1H), 7.0 (s, 1H), 7.05 (s, 1H), 7.4−7.6 (m, 10H); ^{13}C NMR δ 20.55 (q), 20.6 (q), 45.5 (d), 47.8 (d), 57.4 (d), 59.0 (d), 119.2 (d), 119.8 (d), 121.2 (d), 121.9 (d), 125.9 (d), 125.95 (d), 128.9 (d), 130.3 (d), 130.4 (d), 132.8 (d), 133.5 (d), 136.9 (s), 137.0 (s), 141.9 (d), 142.5 (d), 163.2 (s), 164.3 (s), 167.6 (s), 167.9 (s), 195.3 (s), 195.8 (s); HRMS calcd for $C_{17}H_{14}O_3$ (M^+) 266.0943, found 266.0948. Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.74; H, 5.23.

8-Isopropylidene-4-phenyl-3,6-bicyclo[3.2.1]octadien-2-one (4f): yield = 88%; ^{1}H NMR δ 1.65 (s, 3H), 1.7 (s, 3H), 4.1 (m, 1H), 4.3 (m, 1H), 5.7 (s, 1H), 6.4 (dd, J = 5.4, 3.3 Hz, 1H), 6.8 (dd, J = 5.4, 3.1 Hz, 1H), 7.4−7.6 (m, 5H); ^{13}C NMR δ 18.9 (q), 19.2 (q), 48.4 (d), 60.6 (d), 116.1 (s), 119.6 (d), 125.9 (d), 128.9 (d), 130.0 (d), 133.4 (d), 137.0 (s), 142.3 (d), 145.2 (s), 165.0 (s), 197.2 (s); HRMS calcd for $C_{17}H_{16}O$ (M^+) 236.1201, found 236.1196. Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.54; H, 6.85.

8-(1-Ethylpropilidene)-4-phenyl-3,6-bicyclo[3.2.1]octadien-2-one (4g): yield = 84%; ^{1}H NMR δ 0.9 (t, J = 7.70 Hz, 3H); 0.95 (t, J = 7.70 Hz, 3H), 2.0 (m, 4H), 4.1 (m, 1H), 4.3 (m, 1H), 5.7 (s, 1H), 6.3 (m, 1H), 6.8 (m, 1H), 7.4−7.5 (m, 5H); ^{13}C NMR δ 13.2 (q), 23.8 (t), 48.2 (d), 60.4 (d), 119.7 (d), 125.9 (d), 127.5 (s), 128.8 (d), 130.0 (d), 133.3 (d), 137.0 (s), 142.2 (d), 145.4 (s), 165.4 (s), 197.4 (s); HRMS calcd for $C_{19}H_{20}O$ (M^+) 264.1514, found 264.1512. Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.54; H, 7.43.

8-Cyclohexylidene-4-phenyl-3,6-bicyclo[3.2.1]octadien-2-one (4h): yield = 80%; ^{1}H NMR δ 1.4−1.6 (m, 6H), 2.1 (m, 4H), 4.1 (m, 1H), 4.4 (m, 1H), 5.7 (s, 1H), 6.4 (dd, J = 5.5 and 3.3 Hz, 1H), 6.8 (dd, J = 5.5 and 3.1 Hz, 1H), 7.4−7.6 (m, 5H); ^{13}C NMR δ 26.54 (t), 27.41 (t), 27.46 (t), 29.43 (t), 29.86 (t), 48.03 (d), 60.13 (d), 119.54 (d), 124.24 (s), 125.85 (d), 128.84 (d), 129.92 (d), 133.38 (d), 137.05 (s), 142.32 (d), 142.57 (s), 165.43 (s), 197.24 (s); HRMS calcd for $C_{20}H_{20}O$ (M^+) 276.1514, found 276.1516. Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.74; H, 7.50.

4-(1-Cyclohexenyl)-8-isopropylidene-3,6-bicyclo[3.2.1]octadien-2-one (4i): yield = 50%; ^{1}H NMR δ 1.6 (s, 6H), 1.5−1.7 (m 4H), 2.1 (m, 2H), 2.3 (m, 2H), 4.0 (m, 1H), 4.2 (m, 1H), 5.4 (s, 1H), 6.3 (dd, J = 5.4, 3.4 Hz, 1H), 6.5 (m, 1H), 6.6 (dd, J = 5.4, 3.1 Hz, 1H); ^{13}C NMR δ 19.0 (q), 19.1 (q), 21.6 (t), 22.3 (t), 25.0 (t), 26.7 (t), 45.4 (d), 60.6 (d), 115.6 (s), 116.6 (d), 132.3 (d), 133.4 (d), 134.3 (s), 142.1 (d), 145.1 (s), 164.6 (s), 198.0 (s); HRMS calcd for $C_{17}H_{20}O$ (M^+) 240.1514, found 240.1516. Anal. Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 84.68; H, 8.45.

Synthesis of [4+2] Carbene Cycloadducts 5 and 6. General Procedure. Alkynylcarbene **1** or **2** (1.0 mmol) was dissolved in hexane (10 mL), and the corresponding alkylfulvene **3** (2.0 mmol) was added. The reaction mixture was stirred at room temperature

for 5−6 days. Solvent was then removed and the [4+2] carbene cycloadducts were purified by flash chromatography (hexane/AcOEt, 5:1).

Carbene 5a: obtained as a 2:1 mixture of *E*/*Z* isomers; yield = 81%; ^{1}H NMR δ 0.8−1.0 (m, 12H), 2.2−2.3 (m, 2H), 3.9 (s, 3H), 4.0 (s, 3H), 4.2 (m, 1H), 4.3 (m, 1H), 4.35 (m, 1H), 4.5 (m, 1H), 4.6 (m, 2H), 6.8−7.0 (m, 4H), 7.2−7.7 (m, 10H); ^{13}C NMR δ 25.48 (q), 25.68 (q), 29.34 (d), 29.4 (d), 55.3 (d), 56.35 (d), 59.4 (d), 60.7 (d), 68.5 (q), 68.5 (q), 106.8 (d), 106.9 (d), 126.9 (d), 127.2 (d), 127.6 (d), 128.0 (d), 128.9 (d), 129.1 (d), 136.5 (s), 136.7 (s), 137.4 (s), 137.8 (s), 144.0 (d), 145.0 (d), 145.5 (d), 146.0 (d), 161.4 (s), 162.9 (s), 163.9 (s) 165.2 (s), 199.6 (s), 206.8 (s), 324.5 (s), 325.5 (s); HRMS calcd for $C_{24}H_{20}O_6W$ (M^+) 588.0769, found 588.0765. Anal. Calcd for $C_{24}H_{20}O_6W$: C, 49.00; H, 3.43. Found: C, 49.21; H, 3.51.

Carbene 5b: obtained as a 3:1 mixture of *E*/*Z* isomers; yield = 81%; ^{1}H NMR δ 0.9 (s, 9H), 1.0 (s, 9H), 3.8 (m, 1H), 4.0 (s, 3H), 4.1 (s, 3H), 4.15 (m, 1H), 4.2 (m, 1H), 4.3 (m, 1H), 4.6 (s, 1H), 4.65 (s, 1H), 7.0−7.1 (m, 4H), 7.1−7.3 (m, 10H); ^{13}C NMR δ 30.4 (q), 30.9 (q), 31.9 (s), 32.1 (s), 53.3 (d), 54.6 (d), 59.3 (d), 60.2 (d), 66.8 (q), 67.6 (q), 108.6 (d), 109.4 (d), 127.2 (d), 127.3 (d), 127.9 (d), 128.6 (d), 134.1 (s), 140.0 (s), 141.2 (d), 141.4 (d), 141.7 (d), 142.1 (d), 143.5 (s), 159.6 (s), 160.6 (s), 196.8 (s), 204.3 (s), 322.0 (s), 322.2 (s); HRMS calcd for $C_{25}H_{22}O_6W$ (M^+) 602.0926, found 602.0926. Anal. Calcd for $C_{25}H_{22}O_6W$: C, 49.86; H, 3.68. Found: C, 50.02; H, 3.75.

Carbene 5c: only the *E* isomer obtained; yield = 68%; ^{1}H NMR δ 0.9 (s, 9H), 1.1 (s, 9H), 4.1 (s, 3H), 4.2 (m, 1H), 4.3 (m, 1H), 4.6 (s, 1H), 7.0 (m, 1H), 7.1 (m, 1H); ^{13}C NMR δ 30.8 (q), 30.9 (q), 31.8 (s), 34.1 (s), 54.5 (d), 58.50 (q), 60.3 (d), 106.6 (d), 141.1 (d), 141.5 (s), 142.0 (d), 150.3 (s), 159.9 (s), 197.3 (s), 205.1 (s), 326.5 (s); HRMS calcd for $C_{23}H_{26}O_6W$ (M^+) 582.1239, found 582.1243. Anal. Calcd for $C_{23}H_{26}O_6W$: C, 47.44; H, 4.50. Found: C, 47.50; H, 5.82.

Carbene 6a: obtained as a 2:1 mixture of *E*/*Z* isomers; yield = 73%; ^{1}H NMR δ 0.8−1.0 (m, 12H), 2.1−2.3 (m, 2H), 4.0 (s, 3H), 4.05 (s, 3H), 4.2 (m, 2H), 4.3 (m, 1H), 4.35 (m, 1H), 4.5 (m, 1H), 4.6 (m, 1H), 6.9−7.1 (m, 4H), 7.2−7.6 (m, 10H); ^{13}C NMR δ 23.6 (q), 24.1 (q), 27.8 (d), 27.9 (d), 28.0 (d), 55.0 (d), 57.3 (d), 59.2 (d), 66.1 (q), 66.5 (q), 105.2 (d), 105.3 (d), 127.2 (d), 127.4 (d), 127.7 (d), 128.5 (d), 128.8 (d), 129.1 (d), 134.4 (s), 134.6 (s), 137.9 (s), 138.5 (s), 140.9 (d), 141.5 (d), 142.5 (d), 143.1 (d), 162.6 (s), 163.9 (s), 164.9 (s), 165.4 (s), 216.4 (s), 224.9 (s), 351.6 (s), 352.1 (s); HRMS calcd for $C_{24}H_{20}CrO_6$ (M^+) 456.0665, found 456.0661. Anal. Calcd for $C_{24}H_{20}CrO_6$: C, 63.16; H, 4.42. Found: C, 63.41; H, 4.33.

Carbene 6b: obtained as a 3:1 mixture of *E*/*Z* isomers; yield = 73%; ^{1}H NMR δ 1.0 (s, 9H), 1.1 (s, 9H), 4.1 (m, 1H), 4.15 (m, 1H), 4.2 (s, 3H), 4.3 (m, 1H), 4.4 (s, 3H), 4.5 (m, 1H), 4.7 (s, 1H), 4.75 (s, 1H), 6.9−7.1 (m, 4H), 7.2−7.6 (m, 10H); ^{13}C NMR δ 30.9 (q), 31.0 (q), 31.9 (s), 32.3 (s), 52.7 (d), 54.9 (d), 59.0 (d), 60.5 (d); 66.0 (q), 66.8 (q), 108.5 (d), 108.7 (d), 127.3 (d), 127.5 (d), 127.6 (d), 127.7 (s), 127.9 (s), 129.1 (d), 129.3 (d), 129.6 (d), 133.9 (s), 133.9 (s), 141.0 (s), 141.9 (s), 142.0 (d), 142.4 (d), 156.6 (s), 158.8 (s), 215.9 (s), 224.3 (s), 350.7 (s), 351.7 (s); HRMS calcd for $C_{25}H_{22}CrO_6$ (M^+) 470.0821, found 470.0826. Anal. Calcd for $C_{25}H_{22}CrO_6$: C, 63.83; H, 4.71. Found: C, 63.50; H, 4.93.

Carbene 6c: obtained as a 3:1 mixture of *E*/*Z* isomers; yield = 70%; ^{1}H NMR δ 1.0 (s, 9H), 1.05 (s, 9H), 4.2 (s, 3H), 4.3 (s, 3H), 4.4 (m, 2H), 4.7 (m, 1H), 4.9 (m, 1H), 5.1 (s, 1H), 5.3 (s, 1H), 7.0 (m, 2H), 7.05 (m, 2H), 7.3 (m, 4H), 7.45 (m, 4H); ^{13}C NMR δ 30.2 (q), 31.3 (q), 32.4 (s), 32.8 (s), 52.9 (d), 53.3 (d), 55.5 (d), 59.5 (q), 61.2 (d), 66.5 (q), 109.3 (d), 109.4 (d), 128.4 (d), 128.8 (s), 128.9 (d), 129.1 (d), 129.3 (d), 133.0 (s), 133.4 (s), 134.4 (s), 140.3 (s), 141.5 (d), 142.2 (d), 142.6 (d), 142.8 (d), 159.3 (s) 160.5 (s), 216.3 (s), 224.6 (s), 350.9 (s), 351.9 (s); HRMS calcd for $C_{25}H_{21}ClCrO_6$ (M^+) 504.0432, found 504.0430. Anal. Calcd for $C_{25}H_{21}ClCrO_6$: C, 59.47; H, 4.19. Found: C, 59.63; H, 4.03.

Synthesis of [4+2] Esters 7. General Procedure. Pyridine *N*-oxide (190 mg, 2 mmol) was added to a solution of carbenes **5** and **6** (1 mmol) in 10 mL of THF. The reaction was stirred at room temperature for 5 h, H_2O (30 mL) was then added, and the mixture was extracted with Et_2O (2 × 20 mL). Solvent was then removed, and the crude mixture was purified by flash chromatography (SiO_2, hexane/AcOEt, 5:1).

7-[(*E*/*Z*)-Isobutylidene)-3-phenyl-2,5-bicyclo[2.2.1]heptadiene-2-carboxylic methyl ester (7a): 2:1 mixture of *E*/*Z* isomers; yield = 97% (from **5a**); ^{1}H NMR δ 0.8 (d, J = 6.8 Hz, 6H), 0.9 (d, J = 6.3 Hz, 6H), 2.2−2.4 (m, 2H), 3.7 (s, 3H), 3.75 (s, 3H), 4.1 (m, 2H), 4.15 (d, J = 9.1 Hz, 1H), 4.3 (m, 1H), 4.35 (m, 1H), 4.6 (m, 1H), 7.0−7.2 (m, 4H), 7.2−7.4 (m, 6H), 7.6 (m, 4H); ^{13}C NMR δ 23.1 (q), 23.5 (q), 26.8 (d), 27.5 (d), 51.3 (q), 51.9 (q), 55.9 (d), 57.5 (d), 61.4 (d), 62.0 (d), 104.9 (d), 104.9 (d), 127.7 (d), 127.7 (d), 127.8 (d),127.9 (d), 128.6 (d), 128.7 (d), 134.9 (s), 135.0 (s), 137.8 (s), 138.7 (s), 140.1 (d), 140.8 (d), 142.7 (d), 143.4 (d), 163.9 (s), 164.0 (s), 165.1 (s), 165.2 (s), 165.4 (s), 166.0 (s); HRMS calcd for $C_{19}H_{20}O_2$ (M^+) 280.1463, found 280.1467. Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.53; H, 7.36.

7-[(*E*/*Z*)-2,2-Dimethylpropylidene)-3-phenyl-2,5-bicyclo[2.2.1]-heptadiene-2-carboxylic methyl ester (7b): 3:1 mixture of *E*/*Z* isomers; yield = 95% (from **5b**); ^{1}H NMR δ 1.0 (s, 9H), 1.05 (s, 9H), 3.7 (s, 3H), 3.75 (s, 3H), 4.0 (m, 1H), 4.2 (m, 2H), 4.3 (m, 1H), 4.5 (s, 1H), 4.8 (s, 1H), 7.0−7.1 (m, 4H), 7.2−7.4 (m, 6H), 7.5−7.6 (m, 4H); ^{13}C NMR δ 30.8 (q), 30.9 (q), 31.6 (s), 31.9 (s), 51.3 (q), 52.5 (q), 57.7 (d), 58.1 (d), 62.0 (d), 63.3 (d), 108.6 (d), 108.7 (d), 127.7 (d), 128.0 (d), 128.6 (d), 128.7 (d), 134.9 (s), 135.1 (s), 137.6 (s), 138.7 (s), 140.0 (d), 140.8 (d), 142.7 (d), 143.5 (d), 164.1 (s), 165.2 (s), 165.4 (s); HRMS calcd for $C_{20}H_{22}O_2$ (M^+) 294.1620, found 294.1621. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.74; H, 7.23.

3-(4-Chlorophenyl)-7-[(*E*/*Z*)-2,2-dimethylpropylidene)-2,5-bicyclo[2.2.1]heptadiene-2-carboxylic methyl ester (7c): 3:1 mixture of *E*/*Z* isomers; yield = 96%; ^{1}H NMR δ 1.0 (s, 9H), 1.06 (s, 9H), 3.71 (s, 3H), 3.73 (m, 3H), 4.0 (m, 1H), 4.2 (m, 2H), 4.3 (m, 1H), 4.5 (s, 1H), 4.8 (s, 1H), 7.0−7.1 (m, 4H), 7.2−7.4 (m, 6H), 7.5−7.6 (m, 4H); ^{13}C NMR δ 32.2 (q), 32.3 (q), 33.4 (s), 34.2 (s), 53.84 (q), 55.0 (q), 60.2 (d), 60.4 (d), 62.0 (d), 66.0 (d), 111.5 (d), 112.0 (d), 128.2 (d), 128.5 (d), 130.5 (d), 131.0 (s), 131.3 (s), 131.6 (d), 131.8 (s), 132.8 (s), 141.9 (d), 142.3 (d), 145.2 (d), 145.7 (d), 145.9 (s), 146.0 (s), 166.5 (s), 166.7 (s); HRMS calcd for $C_{20}H_{21}ClO_2$ (M^+) 328.1230, found 328.1231. Anal. Calcd for $C_{20}H_{21}ClO_2$: C, 73.05; H, 6.44. Found: C, 73.34; H, 6.53.

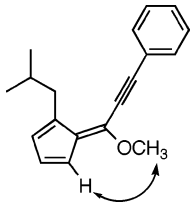
7-Isopropylidene-3-phenyl-2,5-biclyclo[2.2.1]heptadiene-2-carboxylic methyl ester (7d): yield = 82% (from **2a** and **3f**); ^{1}H NMR δ 1.5 (s, 3H), 1.5 (s, 3H), 3.7 (s, 3H), 4.3 (m, 1H), 4.5 (m, 1H), 7.1 (m, 2H), 7.2−7.4 (m, 3H), 7.6 (m, 2H); ^{13}C NMR δ 18.5 (q), 18.61 (q), 51.3 (q), 52.9 (d), 58.4 (d), 99.2 (s), 127.8 (d), 127.9 (d), 128.7 (d), 135.1 (s), 138.7 (s), 140.7 (d), 143.4 (d), 160.6 (s), 165.3 (s), 166.1 (s); HRMS calcd for $C_{18}H_{18}O_2$ (M^+) 266.1307, found 266.1303. Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.22; H, 6.69.

Thermal Rearrangement of Carbenes 5 and 6. General Procedure. Carbenes **5** and **6** (1 mmol) were dissolved in THF (10 mL) and heated at 60 °C for 12−24 h. Solvent was then removed and the product purified by flash chromatography (SiO_2, hexane/AcOEt, 10:1).

Fulvene 9a: yield = 31%; ^{1}H NMR δ 1.0 (d, J = 6.5 Hz, 6H), 2.1 (m, 1H), 2.7 (d, J = 7.4 Hz, 2H), 3.9 (s, 3H), 6.7 (d, J = 8.3 Hz, 1H), 6.8 (d, J = 7.8 Hz, 1H), 7.2 (dd, J = 7.8 and 8.3 Hz, 1H), 7.3 (m, 3H), 7.6 (m, 2H); ^{13}C NMR δ 22.5 (q), 29.5 (d), 44.0 (t), 55.8 (q), 84.6 (s), 97.4 (s), 107.8 (d), 112.1 (s), 122.1 (d), 123.9 (s), 127.9 (d), 128.2 (d), 128.6 (d), 131.4 (d), 146.0 (s), 160.1 (s);

HRMS calcd for $C_{19}H_{20}O$ (M^+) 264.1514, found 264.1516. Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.14; H, 7.82.

The geometry of the tetrasubstituted olefin in **9a** was determined by NOE experiments:



Fulvene 9b: yield = 86%; ^{1}H NMR δ 1.0 (s, 9H), 2.9 (s, 2H), 3.9 (s, 3H), 6.8 (d, J = 7.8 Hz, 1H), 6.85 (d, J = 7.9 Hz, 1H), 7.2 (dd, J = 7.8 and 7.9 Hz, 1H), 7.3 (m, 3H), 7.6 (m, 2H); ^{13}C NMR δ 29.7 (q), 33.1 (s), 47.1 (t), 55.8 (q), 85.8 (s), 97.0 (s), 107.7 (d), 113.3 (s), 123.3 (d), 123.9 (s), 127.8 (d), 120.0 (d), 128.2 (d), 131.3 (d) 144.0 (s), 160.1 (s); HRMS calcd for $C_{20}H_{22}O$ (M^+) 278.1670, found 278.1671. Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97. Found: C, 86.54; H, 7.75.

Fulvene 9c: yield = 78%; ^{1}H NMR δ 1.0 (s, 9H), 2.8 (s, 2H), 3.9 (s, 3H), 6.75 (d, J = 8.3 Hz, 1H), 6.8 (d, J = 7.7 Hz, 1H), 7.2 (dd, J = 7.7 and 8.3 Hz, 1H), 7.3 (m, 2H), 7.5 (m, 2H); ^{13}C NMR δ 29.9 (q), 33.3 (s), 47.3 (t), 56.0 (q), 87.0 (s), 96.0 (s), 107.9 (d), 113.5 (s), 123.5 (d), 126.3 (s), 128.2 (d), 129.0 (d), 132.6 (d), 135.6 (s), 144.2 (s); 160.2 (s); HRMS calcd for $C_{20}H_{21}ClO$ (M^+) 312.1281, found 312.1282. Anal. Calcd for $C_{20}H_{21}ClO$: C, 76.79; H, 6.77. Found: C, 76.54; H, 6.84.

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