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Demonstration of the facile reversibility of fulvene formation

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ABSTRACT

Cleavage of fulvenes under mild conditions and interchange between electron-deficient fulvenes and their constituent cyclopentadienes and imines is demonstrated for the first time. A series of cyclopentadienes and imines are investigated to probe the dependence of fulvene equilibration on structure. The exchange of one fulvene for another is demonstrated in the first reported example of transfulvenation. Finally, the metathesis of two fulvenes to generate all four possible cross products is shown.

1. Introduction

Alkylidene cyclopentadienes, commonly known as fulvenes,[1] are a class of 6π-electron cross-conjugated isomers of benzene first prepared by Thiele in 1900 (Fig. 1a).[2] In the ensuing 110 years, fulvenes have been the subject of extensive investigations into their physical properties, their potential as organometallic ligands, and their synthetic utility.[3] In light of this longstanding and intense interest in fulvene chemistry, we found it remarkable that the issue of fulvene cleavage (retrofulvenation) had never been examined. We became interested in the possibility of facile retrofulvenation because of its potential to serve as a novel mechanistic platform for applications ranging from catalysis to dynamic covalent chemistry. In this article we demonstrate for the first time the cleavage of fulvenes under mild conditions and the facile interconversion of fulvenes and their corresponding imines and cyclopentadienes.

Perhaps the most conspicuous feature of fulvenes is the relatively high polarization of the exocyclic olefin and the consequent electropositive character of the 6-carbon (Fig. 1b). This polarization is attributed to the fact that cyclopentadienyl anions, and hence the zwitterionic resonance form of fulvenes, possess aromatic character. Indeed, this polarization is such that the exocyclic fulvenic double bond displays many modes of reactivity analogous to that of aldehydes and ketones. For example, even simple fulvenes readily undergo nucleophilic substitution[4] at the 6-position and can be deprotonated to produce vinyl cyclopentadienyl anions (pK_a of 6,6-dimethylfulvene in DMSO=22.7).[5] The analogy between fulvenes

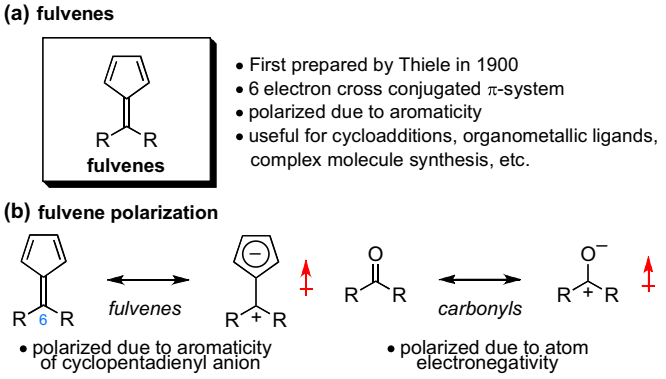

Fig. 1. Fulvenes.

and carbonyls is underscored by the fact that the most common synthetic approach to fulvenes is by condensation of a cyclopentadiene with an aldehyde or ketone, often via iminium ion activation. Indeed, base-promoted condensations have been the strategy of choice for fulvene synthesis ranging from Thiele's original work[2] (NaOMe) to the modern approaches of Little[6] and Erden[7] (pyrrolidine). As the dehydrative condensation of an acidic methylene compound with an aldehyde or ketone, this strategy of fulvene formation is of course an example of the Knoevenagel reaction. As such, we reasoned that it should, under appropriate circumstances, be a readily reversible process.

Surprisingly, however, this issue appears not to have been addressed in the literature. In fact, we know of only one reliable example of fulvene cleavage: a 1954 report by Taber describing the

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'retro-Mannich' reaction of 1,2,3,4-tetraphenylfulvene in refluxing piperidine (Fig. 2).[8] The dynamic interchange of fulvenes and carbonyls or imines is wholly unknown. Nevertheless, it seemed to us a reasonable assumption that sufficiently electron-deficient fulvenes should be prone to facile cleavage, particularly by nucleophilic amine bases. Because of the longstanding importance of fulvene chemistry and a significant opportunity to enable novel applications of this unique class of molecules, we decided to investigate the possibility of achieving facile fulvene reversibility.

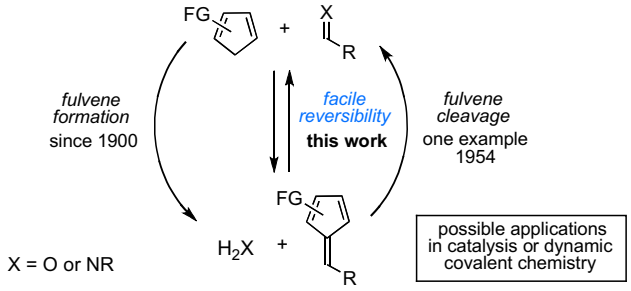
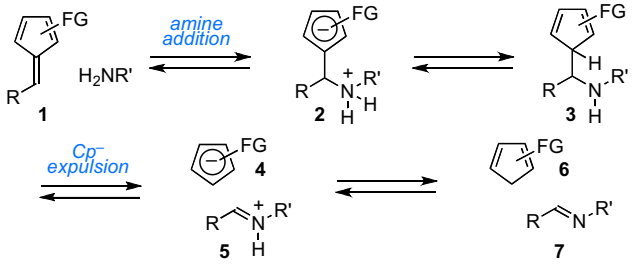


Fig. 2. Reversible fulvene formation.

2. Results and discussion

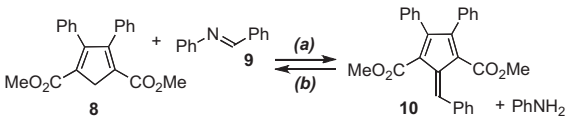
2.1. Demonstration of fulvene/imine interchange

The mechanism of the proposed fulvene aminolysis is essentially that of a retro-Knoevenagel condensation, and involves (1) addition of an amine to the exocyclic fulvenic olefin, and (2) subsequent expulsion of a cyclopentadienyl anion to form an iminium ion (Scheme 1). Based on this consideration we expected that those fulvenes prone to facile cleavage should possess relatively electron-deficient cyclopentadienyl moieties. Thus we decided to examine fulvenes prepared from carboxylate-bearing cyclopentadienes, which are relatively acidic[9] and straightforward to prepare (see Supplementary data).



Scheme 1. Mechanism of fulvene/imine equilibration.

In one of our initial experiments to examine fulvene cleavage, we combined diester diphenylcyclopentadiene **8** with the aniline Schiff base of benzaldehyde (**9**) in $CDCl_3$ (Scheme 2). After 60 min, we observed by ^1H NMR an unchanging 2.2:1 mixture of fulvene **10** and imine **9**. To investigate whether this mixture was an equilibrium ratio, we subjected fulvene **10** to an equivalent of aniline under the same conditions.[10] Immediately, cyclopentadiene **8** and imine **9** were observed, and after 60 min. the ratio of fulvene to imine was a constant 2.5:1, suggesting that this is in fact the approximate thermodynamic ratio. Notably, in THF-d_8 the same reaction came to equilibrium within 10 min as a 6.5–7:1 ratio of fulvene to imine. To the best of our knowledge, these results represent the first example of fulvene cleavage under mild conditions and the first demonstration of a fulvene in equilibrium with its constituent imine and cyclopentadiene fragments.



solvent	(a) time (min) (b) time (min)	10:9 10:9
$CDCl_3$	60	2.2:1
	60	2.5:1
d_8-THF	10	6.5:1
	10	7.0:1

Scheme 2. Demonstration of fulvene/imine equilibration.

2.2. Effect of substrate structure on fulvene/imine interchange

Next, to probe the effect of fulvene structure and amine catalyst on this process, we prepared cyclopentadienes **11**–**13**, and, along with cyclopentadiene **8**, examined fulvene formation and cleavage with several imines (Table 1). For these experiments we again examined by ^1H NMR both the forward and reverse reactions in $CDCl_3$, noting, in each case, the ratio of fulvene to imine at a specified reaction time that for a number of the substrates (entries 1–6, 9, 10, 15, and 16) corresponded to the time to reach a steady state.

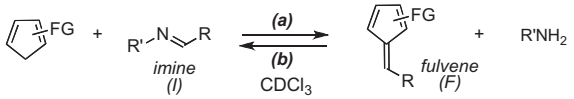
To begin, we examined the effect of imine structure on the formation and cleavage of fulvene **10** (Table 1). In comparison to the aniline derived imine (entry 1), *N*-cyclohexylamine (entry 2) and *N*-butylamine (entry 3) imines both resulted in decreased reaction time (20 min) and produced mixtures that slightly favored imine over fulvene. Interestingly, we found that in altering the electronic profile of the imine aryl substituent, both electron-withdrawing (entry 4) and electron-donating (entry 5) substituents increased reaction time substantially, although the effect was much greater in the latter case. Presumably the electron-donating methoxy substituent serves to hinder both the addition of cyclopentadienyl anion to iminium ion (forward) and the addition of amine to fulvene (reverse). An extended time period (12 h) was also required with cinnamaldehyde Schiff base; in this case fulvene was completely favored over imine (entry 6). This bias is likely the result of increased stabilization of the highly conjugated 6-vinylfulvene. However, an increased fulvene selectivity was observed with *N*-phenylcyclohexylimine as well, although in this case the forward and reverse reactions did not converge to the same fulvene/imine ratios (entry 7). Notably, fulvene formation with this aliphatic aldehyde occurred within 10 min, in sharp contrast to reactions with aryl imines.

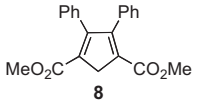
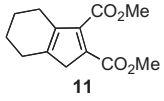
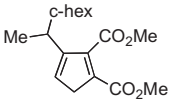
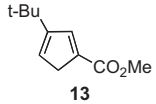
Fulvene/imine interchange was also observed with tetrahydroindene **11**, although aniline proved to be a poor participant in this case and did not result in convergence of the forward and backward reactions even after 48 h (entry 8). We rationalize this lower reactivity by the decreased acidity of the dialkyl-substituted cyclopentadiene **11** versus the diaryl-substituted **8**. On the other hand, *N*-cyclohexylamine and *N*-butylamine enabled rapid formation and cleavage, again favoring imine to a slight extent in both cases (entries 9 and 10).

In contrast to the above results, fulvenation dynamics using cyclopentadiene **12** were rather inconsistent. For instance, *N*-phenylbenzaldimine and **12** reacted to produce a 2:1 mixture of fulvene to imine over 48 h (entry 11). However, aniline was not productive at facilitating the corresponding retrograde reaction. As observed in entries 12 and 13, changing from *N*-aryl to *N*-alkyl substitution provided greatly increased reaction rate of both fulvene formation and cleavage, however neither the time to reach stasis nor the ratio of fulvene to imine was the same for the forward and reverse reactions (entries 12 and 13). Further experimentation will be required to determine the reason for this disparate behavior.

Finally, we examined the reaction profile of cyclopentadiene **13**, which bears only a single electron-withdrawing group and was thus expected to be less reactive than **8**, **11**, and **12**. Indeed, no

Table 1
Substrate scope studies for fulvene/imine exchange



Entry	Cyclopentadiene	Imine	(a) Time (b) Time	F:I[a,b] F:I
1		Ph–N=CH–Ph	60 min 60 min	2.2:1 2.5:1
2		*c*-hex–N=CH–Ph	20 min 20 min	1:1.6 1:1.9
3		*n*-Bu–N=CH–Ph	20 min 20 min	1:2.4 1:2.2
4	 **8**	Ph–N=CH–4-NO$_2$-Ph	120 min 150 min	3.1:1 2.4:1
5		Ph–N=CH–4-OMe-Ph	20 h 20 h	2.7:1 2.2:1
6		Ph–N=CH–CH=CH–Ph	12 h 12 h	>20:1 >20:1
7		Ph–N=CH–*c*-hex	10 min 10 min	13.1:1 6.3:1
8		Ph–N=CH–Ph	48 h 48 h	1.6:1 4.9:1
9	 **11**	*c*-hex–N=CH–Ph	20 min 20 min	1:1.8 1:1.3
10		*n*-Bu–N=CH–Ph	20 min 20 min	1:2.5 1:1.9
11		Ph–N=CH–Ph	48 h 48 h	1.8:1 >20:1
12	 **12**	*c*-hex–N=CH–Ph	45 min 120 min	1.6:1 5.6:1
13		*n*-Bu–N=CH–Ph	15 min 120 min	1.3:1 3.4:1
14		Ph–N=CH–Ph	8 days 8 days	<1:20 >20:1
15	 **13**	*c*-hex–N=CH–Ph	8 days 8 days	8.3:1 10.1:1
16		*n*-Bu–N=CH–Ph	8 days 8 days	5.1:1 5.7:1

[a] Fulvene and imine ratios were determined by ^{1}H NMR relative to Bn_2O as an internal standard.
[b] The reaction mixtures in entries 2, 3, and 8 contained intermediates in the amounts of 10, 25, and 7%, respectively, that we believe correspond to intermediate **3** in Scheme 1.

reaction was observed in either the forward (reaction of **13** with *N*-phenylbenzaldimine) or the reverse (reaction of fulvene with aniline) direction even after 8 days (entry 14). The alkyl amines/imines on the other hand provided observable albeit slow reaction in both directions (entries 15 and 16), with the butylamine case approaching similar ratios in either direction after 8 days (entry 16). Apparently, cyclopentadienes/fulvenes bearing a single electron-withdrawing group represent the lower boundary of reactivity for facile fulvene equilibration with imines.

2.3. Transfulvenation

We recognized that the facile reversibility of fulvene formation offers the possibility of achieving the heretofore unknown process of transfulvenation, whereby one fulvene would be mutated into another. To demonstrate this possibility, we examined the conversion of 6-phenylfulvene **10** (derived from benzaldehyde) to 6-styrenylfulvene **14** (derived from cinnamaldehyde) (Fig. 2). Interestingly, when fulvene **10** and the *N*-phenyl Schiff base of cinnamaldehyde **15** were simply combined in $CDCl_3$, we observed conversion to fulvene **14** with the proportion of fulvene **14** increasing to ~75% of the total fulvene content over the course of 5 days (Fig. 3a). This fulvene interconversion is particularly notable in that no amine was added, although we hypothesize that small

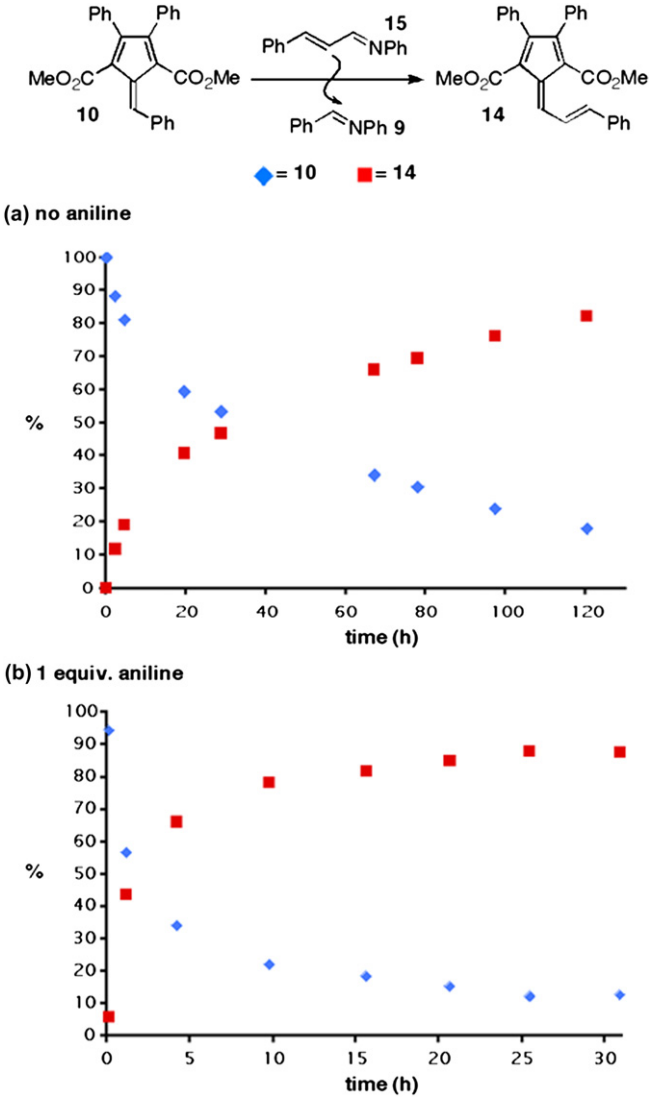
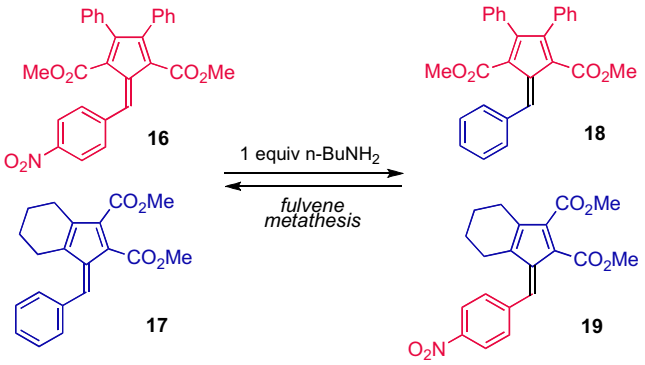


Fig. 3. Demonstration of transfulvenation.

amounts of aniline resulting from imine hydrolysis by adventitious water may have provided the means for the exchange. With this thought in mind, we conducted the same experiment with the addition of 1 equiv of aniline. As expected, the rate of conversion of **10** to **14** was dramatically increased, proceeding to >85% fulvene **14** in just over 1 day (Fig. 3b).

2.4. Demonstration of fulvene metathesis

As a further demonstration of fulvene exchange, we conducted the metathesis of two fulvenes composed of different cyclopentadienyl and exocyclic moieties (Scheme 3). Thus fulvenes **16** and **17** were combined with 1 equiv of butylamine in $CDCl_3$ at room temperature. After 19 h we observed by ^1H NMR a mixture of fulvenes **16**–**19**, representing all four possible fulvene products, in a 1.2:2.2:1.2:1.5 ratio, respectively, along with the *N*-butylimines **20** and **21**. This demonstration of facile fulvene exchange raises the possibility of developing dynamic covalent chemistry applications that capitalize on the unique properties of fulvene architectures.



compound	relative amount
16	1.2
17	2.2
18	1.2
19	1.5
20 4-NO_2-PhCH=NBu	1.6
21 PhCH=NBu	1.0

Scheme 3. Fulvene metathesis.

3. Conclusions

We have demonstrated for the first time (1) that suitably activated fulvenes undergo facile aminolysis under mild reaction conditions, (2) that such fulvenes may exist in observable equilibrium with their constituent cyclopentadienes and imines, and (3) that this equilibrium may be employed for the dynamic interchange of fulvenes. Given the broad interest fulvenes have long attracted from chemists of various disciplines, we expect these results may find useful application in a number of different contexts.

4. Experimental section

4.1. General information

All reactions were performed using oven-dried glassware under an atmosphere of dry argon. Non-aqueous reagents were transferred by syringe under argon. Organic solutions were concentrated using a Buchi rotary evaporator. Diethyl ether, tetrahydrofuran, and methylene chloride (CH_2Cl_2) were dried using a J.C. Meyer solvent purification system. Triethylamine (Et_3N), aniline, cyclohexylamine, and *n*-butylamine were freshly distilled over CaH_2 under argon. All other commercial reagents were used as provided. Flash column chromatography was performed employing 32–63 μm silica gel (Dynamic Adsorbents Inc). Thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} plates (EMD).

^1H and ^{13}C NMR were recorded in $CDCl_3$ on Bruker DRX-300, DRX-400, and DRX-500 spectrometers as noted. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s=singlet, br s=broad singlet, d=doublet, t=triplet, q=quartet, m=multiplet), coupling constant (Hz), integration, and assignment. Data for ^{13}C NMR are reported in terms of chemical shift. IR spectra were recorded on a Nicolet Avatar 370 DTGS (Thermo) using NaCl salt plates. High-resolution mass spectra were obtained from the Columbia University Mass Spectrometry Facility on JOEL JMS-HX110 HF mass spectrometer using the indicated ionization mode.

4.2. Synthesis of cyclopentadienes and fulvenes

4.2.1. Dimethyl 4,5-diphenylcyclopenta-3,5-diene-1,3-dicarboxylate ***8***. To 150 mL anhydrous ethanol was added dimethyl 2-oxo-4,5-diphenylcyclopenta-3,5-diene-1,3-dicarboxylate[11] (5.24 g, 15.0 mmol). The solution was then cooled to 0 °C and $NaBH_4$ was added portionwise over 10 min with stirring. The reaction was allowed to continue stirring at this temperature for 15 min and was then quenched by the addition of 100 mL of water. The mixture was extracted with EtOAc (250 mL). The organic layer was washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The crude alcohol was used in the following step without further purification.

The crude alcohol was dissolved in THF (200 mL). Acetic anhydride (2.13 mL, 22.5 mmol), triethylamine (3.14 mL, 22.5 mmol), and 4-(dimethylamino)pyridine (0.183 g, 1.50 mmol) were then added and the reaction was stirred at room temperature for 2 h. Water (150 mL) was added and the reaction was extracted with EtOAc (200 mL×3). The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The crude acetate was then used without further purification.

The crude acetate from the previous step was dissolved in dichloromethane (200 mL) and 1,8-Diazabicyclo[5.4.0]undec-7-ene (6.72 mL, 45 mmol) was added. The reaction mixture was stirred at room temperature for 2 h and then quenched by the addition of 1 M aqueous HCl (100 mL). This mixture was extracted with EtOAc (200 mL×3). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The crude oil was purified by flash chromatography (dichloromethane) and recrystallized twice from ether to yield the title compound (2.84 g, 8.49 mmol, 57% yield from ketone) as fine colorless crystals. ^1H NMR (300 MHz, $CDCl_3$) δ 7.20 (m, 6H, Ar*H*), 7.00 (m, 4H, Ar*H*), 3.95 (s, 2H, CH_2), 3.68 (s, 6H, CO_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) 164.2, 156.2, 134.0, 133.8, 129.1, 127.8, 127.3, 51.4, 43.1; IR (thin film) 1716, 1489, 1434, 1361, 1207, 1102, 1083, 1003, 741, 698 cm^{-1}; HRMS (FAB^+) *m*/*z*=334.1205 calcd for $C_{21}H_{19}O_4$ $[M]^+$, found 334.1202.

4.2.2. Dimethyl 4,5,6,7-tetrahydro-1H-indene-2,3-dicarboxylate ***11***. To sodium hydride (7 g, 60% in mineral oil, 175 mmol) that had been washed with pentanes (40 mL×3) was added 300 mL THF. The resulting suspension was cooled to 0 °C and freshly cracked cyclopentadiene (6.0 mL, 80.4 mmol) was added via syringe. The reaction flask was warmed to room temperature and stirred for 10 min before cooling back to 0 °C. After the addition of 1,4-dibromobutane (9.6 mL, 80.4 mmol), the solution was refluxed overnight. An additional equivalent of sodium hydride (3.08 g, 80.4 mmol) was added and the solution was further heated at reflux for 24 h. The reaction mixture was quenched with H_2O (250 mL) and extracted with EtOAc (200 mL×3). The organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo to give 10.7 g of pale yellow oil.

The crude oil was then used in the following step without further purification.

The crude product from the previous step (10.7 g) was added to 100 mL THF containing 5 g of activated 4 Å molecular sieves, and the resulting mixture was stirred at room temperature for 1 h. The dried solution was cannulated into a flask containing an additional 200 mL THF, which was then cooled to −78 °C. After the addition of *n*-butyllithium (35.4 mL of 2.5 M solution in hexanes, 88.5 mmol), the solution was warmed to room temperature and stirred for 30 min, then cooled back to −78 °C and treated with methyl chloroformate (6.8 mL, 88.5 mmol). The reaction solution turned purple as it was allowed to stir at room temperature for 36 h, after which H_2O (200 mL) was added. The resulting mixture was diluted with Et_2O before being extracted with 1 M NaOH (100 mL×3). The combined aqueous phase was acidified to pH 1 and extracted with EtOAc (150 mL×3). Concentration in vacuo yielded the title compound as a mixture of olefin isomers (600 mg, 2.54 mmol, 3% yield). NMR data are reported as the sodium salt of the title compound obtained by treatment with sodium hydride and extraction with water. ^{1}H NMR (300 MHz, D_2O) δ 6.42 (s, 1H, Cp*H*), 3.70 (s, 3H, CO_2CH_3), 3.68 (s, 3H, CO_2CH_3), 2.66 (m, 2H, $-CH_2-$), 2.45 (m, 2H, $-CH_2-$), 1.64 (m, 4H, 2× $-CH_2-$); ^{13}C NMR (75 MHz, D_2O) δ 169.5, 169.1, 133.0, 122.9, 119.2, 109.5, 106.9, 50.8, 50.6, 25.5, 24.2, 23.9, 23.7; IR (thin film) 2948, 1739, 1709, 1552, 1430, 1291, 1261, 1217, 1130 cm^{-1}; HRMS (EI$^+$) *m*/*z*=236.1049 calcd for $C_{13}H_{16}O_4$ [M]$^+$, found 236.1048.

4.2.3. Dimethyl 3-(1-cyclohexylethyl)cyclopenta-1,3-diene-1,2-dicarboxylate ***12***. To a mixture of sodium (5.31 g, 230.9 mmol) in 200 mL THF at 0 °C was added 30 mL cyclopentadiene (401.8 mmol). The resulting mixture was stirred at room temperature overnight, after which it was cooled to 0 °C, treated with methyl chloroformate (32.98 mL, 428.6 mmol), and then stirred for 2 h at room temperature. The reaction mixture was filtered through a Celite plug and concentrated in vacuo to furnish a brown oil. Addition of Et_2O (200 mL) resulted in precipitation of 6.50 g of a crude brown solid that contained 1,2-dicarboxymethylcyclopentadienyl anion as its sodium salt.

The crude solid containing this cyclopentadienyl salt (3.00 g) was dissolved in 200 mL THF and cooled to −30 °C. Cyclohexanecarboxaldehyde (1.62 mL, 13.4 mmol) and cyclohexylamine (1.50 mL, 13.4 mmol) were added and the reaction mixture was allowed to stir for 2 h. Acetic acid (10 mL) was added, and the resulting mixture was stirred for 30 min before warming to room temperature and stirring for an additional 15 min. The mixture was diluted with H_2O (200 mL) and extracted with EtOAc (200 mL×3). The combined organic extracts were washed with brine, dried (Na_2SO_4), concentrated in vacuo, and purified directly by flash chromatography (19:1 hexanes/EtOAc) to yield dimethyl 5-(cyclohexylmethylene)cyclopenta-1,3-diene-1,2-dicarboxylate (978 mg, 3.5 mmol, 3% yield from cyclopentadiene). ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.04 (d, *J*=10.2 Hz, 1H, Cp=C*H*Cy), 6.88 (d, *J*=5.4 Hz, 1H, Cp*H*), 6.66 (d of d, *J*=1.3, 5.4 Hz, 1H, Cp*H*), 3.75 (s, 3H, CO_2CH_3), 3.74 (s, 3H, CO_2CH_3), 2.85 (m, 1H, Cp=CH−Cy*H*), 1.69−1.10 (m, 10H, Cy*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9, 164.8, 157.3, 140.8, 137.9, 129.6, 129.2, 122.3, 51.8, 40.9, 32.5, 25.6, 25.1.

Methyllithium (8.8 mL, 14.4 mmol) was added via a syringe to a slurry of copper(I) iodide (1.337 g, 7.02 mmol) in 100 mL Et_2O at −10 °C. The reaction mixture was stirred for 1 h before being cooled to −30 °C. A 5 mL solution of 5-(cyclohexylmethylene)cyclopenta-1,3-diene-1,2-dicarboxylate (978 mg, 3.5 mmol) in Et_2O was added dropwise over 15 min, and the reaction mixture was immediately quenched with satd NH_4Cl (100 mL), acidified to pH 1 with 1 M HCl, and extracted with EtOAc (100 mL×3). The combined organic extracts were washed with H_2O, brine, and dried over Na_2SO_4. Concentration in vacuo and purification by column chromatography (19:1 hexanes/EtOAc) furnished the title compound as a mixture of olefin isomers (573 mg, 1.96 mmol, 56% yield). NMR data are reported as the sodium salt of the title compound obtained by treatment with sodium hydride and extraction with dimethylsulfoxide. ^{1}H NMR (300 MHz, DMSO) δ 6.16 (d, *J*=3.5 Hz, 1H, Cp*H*), 5.37 (d, *J*=3.5 Hz, 1H, Cp*H*), 3.50 (s, 3H, CO_2CH_3), 3.46 (s, 3H, CO_2CH_3), 2.95 (quintet, *J*=6.9 Hz, 1H, CpC(Me)(Cy)*H*), 1.70−1.50 (m, 5H, Cy*H*), 1.25−0.82 (m, 6H, Cy*H*), 1.01 (d, *J*=6.9 Hz, 3H, CpC(CH_3)CyH); ^{13}C NMR (75 MHz, DMSO) δ 168.3, 166.0, 137.5, 116.6, 110.3, 109.4, 106.7, 49.2, 49.0, 44.6, 36.6, 31.33, 29.5, 26.5, 26.4, 18.7; IR (thin film) 2926, 2848, 1739, 1709, 1539, 1435, 1257 cm^{-1}; HRMS (EI$^+$) *m*/*z*=292.1675 calcd for $C_{17}H_{24}O_4$ [M]$^+$, found 292.1661.

4.2.4. Methyl 3-tert-butylcyclopenta-1,3-dienecarboxylate ***13***. A solution of 6,6-dimethylfulvene[6] (22.61 g, 213.0 mmol) in 500 mL Et_2O was cooled to 0 °C and slowly treated with methyllithium (139.8 mL, 1.6 M in Et_2O, 223.0 mmol). The solution was warmed to room temperature and stirred for 1 h. After cooling back to 0 °C, methyl chloroformate (32.91 mL, 425 mmol) was added and the solution was stirred for 1 h. The reaction was then quenched with 500 mL H_2O and extracted with Et_2O (250 mL×3). The combined organic extracts were washed with brine, dried ($MgSO_4$), concentrated in vacuo, and purified by flash chromatography (10:1 hexanes/Et_2O) to yield the title compound as a yellow oil (6.43 g, 35.67 mmol, 19% yield) as a mixture of two olefin isomers (3:2 ratio). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (q, *J*=1.7 Hz, 1H, Cp*H*, minor), 7.31 (q, *J*=2.2 Hz, 1H, Cp*H*, major), 6.23 (m, 1H, Cp*H*, major and minor), 3.80 (s, 3H, CO_2CH_3, minor), 3.77 (s, 3H, CO_2CH_3, major), 3.31 (m, 2H $-CH_2-$, major), 3.28 (t, *J*=1.6 Hz, 2H, $-CH_2-$, minor), 1.20 (s, 9H, C(CH_3)$_3$, major), 1.18 (s, 9H, C(CH_3)$_3$, minor); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4, 164.7, 156.9, 143.1, 142.9, 137.6, 134.3, 129.1, 124.0, 51.1, 51.0, 40.4, 40.0, 33.8, 32.1, 30.6, 29.6; IR (thin film) 2961, 1713, 1530, 1435, 1357, 1239, 1104 cm^{-1}; HRMS (FAB$^+$) *m*/*z*=180.1150 calcd for $C_{11}H_{16}O_2$ [M]$^+$, found 180.1159.

4.2.5. Dimethyl 2-benzylidene-4,5-diphenylcyclopenta-3,5-diene-1,3-dicarboxylate. Dimethyl 4,5-diphenylcyclopenta-3,5-diene-1,3-dicarboxylate (50 mg, 0.15 mmol) was dissolved in 1 mL THF. Benzaldehyde (15 μL, 0.15 mmol) and cyclohexylamine (1.7 μL, 0.015 mmol) were added and the reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuo and the resulting residue was purified by flash chromatography (4:1 hexanes/EtOAc) to yield the title compound (52 mg, 0.12 mmol, 80% yield) as bright yellow crystals. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (s, 1H, Cp=C*H*−Ar), 7.40−7.50 (m, 5H, Ar*H*), 7.20 (m, 6H, Ar*H*), 7.06 (m, 4H, Ar*H*), 3.64 (s, 3H, CO_2CH_3), 3.02 (s, 3H, CO_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 165.2, 150.7, 150.6, 145.1, 139.3, 137.0, 134.4, 133.1, 130.3, 129.6, 129.4, 129.2, 128.3, 127.8, 127.6, 127.3, 126.7, 124.5, 51.3, 51.1; IR (thin film) 2948, 1721, 1595, 1571, 1434, 1384, 1355, 1257, 1214, 1193, 1166, 1126, 1075, 1028, 997, 759, 698 cm^{-1}; HRMS (FAB$^+$) *m*/*z*=422.1518 calcd for $C_{28}H_{23}O_4$ [M]$^+$, found 422.1524.

4.2.6. Dimethyl 2-(4-nitrobenzylidene)-4,5-diphenylcyclopenta-3,5-diene-1,3-dicarboxylate. N-(4-Nitrobenzylidene)aniline (68 mg, 0.30 mmol) was dissolved in THF (3 mL). Dimethyl 4,5-diphenylcyclopenta-3,5-diene-1,3-dicarboxylate (100 mg, 0.30 mmol) was then added and the resulting mixture was stirred at room temperature for 1 h. Solvent was removed in vacuo and the resulting residue was purified by flash chromatography (4:1 hexanes/EtOAc) to yield the title compound (83 mg, 0.18 mmol, 60% yield) as a bright orange solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.46 (s, 1H, Cp=C*H*−Ar), 8.29 (d, *J*=6.6 Hz, 2H, Ar*H*), 7.63 (d, *J*=6.3 Hz, 2H, Ar*H*), 7.24 (m, 6H, Ar*H*), 7.04 (d, *J*=5.1 Hz, 4H, Ar*H*), 3.65 (s, 3H, CO_2CH_3), 3.09 (s, 3H, CO_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 164.9, 152.4, 152.1, 147.7, 143.2, 141.5, 140.9, 133.9, 132.6, 130.7, 129.3, 129.1, 128.3, 128.1, 127.5, 126.1, 124.4, 123.3, 51.4, 51.4; IR (thin film)

1721, 1592, 1520, 1435, 1383, 1345, 1258, 1215, 1193, 1165, 995, 849, 756, 699 cm^{-1}; HRMS (FAB^+) m/z=467.1369 calcd for $C_{28}H_{22}NO_6$ $[M]^+$, found 467.1381.

4.2.7. Dimethyl 2-(4-methoxybenzylidene)-4,5-diphenylcyclopent-3,5-diene-1,3-dicarboxylate. Dimethyl 4,5-diphenylcyclopenta-3,5-diene-1,3-dicarboxylate (50 mg, 0.15 mmol) was dissolved in 1 mL THF. Anisaldehyde (27 μL, 0.23 mmol) and cyclohexylamine (1.7 μL, 0.015 mmol) were added and the reaction mixture was allowed to stir overnight at room temperature. Solvent was removed in vacuo and the resulting residue was purified by flash chromatography (4:1 hexanes/EtOAc) to furnish the title compound (40 mg, 0.088 mmol, 59% yield) as bright orange crystals. ^1H NMR (300 MHz, $CDCl_3$) δ 8.43 (s, 1H, Cp=C*H*–Ar), 7.49 (d, J=8.7 Hz, 2H, Ar*H*), 7.21 (m, 6H, Ar*H*), 7.07 (m, 4H, Ar*H*), 6.97 (d, J=8.7 Hz, 2H, Ar*H*), 3.87 (s, 3H, CO_2CH_3), 3.64 (s, 3H, CO_2CH_3), 3.16 (s, 3H, $ArOCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 165.5, 161.3, 150.2, 149.7, 145.4, 137.6, 134.8, 133.5, 133.0, 132.8, 129.9, 129.7, 129.3, 129.1, 127.3, 126.5, 124.7, 114.4, 114.0, 113.7, 51.3; IR (thin film) 1719, 1590, 1509, 1433, 1356, 1306, 1255, 1165, 1085, 1027 cm^{-1}; HRMS (FAB^+) m/z=452.1624 calcd for $C_{29}H_{25}O_5$ $[M]^+$, found 452.1600.

4.2.8. (E)-Dimethyl 4,5-diphenyl-2-(3-phenylallylidene) cyclopenta-3,5-diene-1,3-dicarboxylate. Dimethyl 4,5-diphenylcyclopenta-3,5-diene-1,3-dicarboxylate (50 mg, 0.15 mmol) was dissolved in 1 mL THF. *trans*-Cinnamaldehyde (21 μL, 0.17 mmol) and cyclohexylamine (1.7 μL, 0.015 mmol) were added and the reaction was allowed to stir overnight at room temperature. Solvent was removed in vacuo and the resulting residue was purified by flash chromatography (4:1 hexanes/EtOAc) to yield the title compound (44 mg, 0.098 mmol, 65% yield) as bright orange crystals. ^1H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, J=12.0 Hz, 1H, Cp=C*H*–CH=CHPh), 7.68 (dd, J=12.3, 15.0 Hz, 1H, Cp=CH–C*H*=CHPh), 7.56 (m, 2H, Ar*H*), 7.41 (m, 3H, Ar*H*), 7.23 (m, 7H, Cp=CH–CH=C*H*Ph+Ar*H*), 7.05 (m, 4H, Ar*H*), 3.75 (s, 3H, CO_2CH_3), 3.64 (s, 3H, CO_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 165.6, 149.4, 148.2, 146.4, 144.0, 137.4, 136.4, 135.0, 134.2, 130.1, 129.5, 129.2, 129.1, 128.1, 127.8, 127.7, 127.6, 127.5, 125.7, 125.4, 124.5, 52.2, 51.4; IR (thin film) 1702, 1598, 1578, 1434, 1361, 1263, 1220, 1193, 1163, 1086 cm^{-1}; HRMS (FAB^+) m/z=448.1675 calcd for $C_{30}H_{25}O_4$ $[M]^+$, found 448.1693.

4.2.9. Dimethyl 2-(cyclohexylmethylene)-4,5-diphenylcyclopenta-3,5-diene-1,3-dicarboxylate. Dimethyl 4,5-diphenylcyclopenta-3,5-diene-1,3-dicarboxylate (50 mg, 0.15 mmol) was dissolved in 1 mL THF. Cyclohexanecarboxaldehyde (27 μL, 0.23 mmol) and cyclohexylamine (3.4 μL, 0.030 mmol) were added and the reaction mixture was allowed to stir overnight at room temperature. Solvent was removed in vacuo and the resulting residue was purified by flash chromatography (4:1 hexanes/EtOAc) to yield the title compound (49 mg, 0.11 mmol, 73% yield) as bright yellow crystals. ^1H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, J=10.8 Hz, 1H, Cp=C*H*–Cy), 7.16 (m, 6H, Ar*H*), 6.99 (m, 4H, Ar*H*), 3.69 (s, 3H, CO_2CH_3), 3.57 (s, 3H, CO_2CH_3), 2.63 (m, 1H, Cp=CH–C*H*R_2), 1.82 (m, 5H, CH_2), 1.30 (m, 5H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 165.5, 155.5, 149.4, 147.1, 137.0, 134.8, 133.7, 129.3, 129.2, 127.9, 127.8, 127.6, 127.5, 126.6, 124.2, 52.2, 51.3, 40.4, 32.7, 25.8, 25.5; IR (thin film) 2929, 2851, 1724, 1704, 1623, 1434, 1391, 1365, 1258, 1234, 1220, 1194, 1171, 1144, 1128, 994, 699 cm^{-1}; HRMS (FAB^+) m/z=428.1988 calcd for $C_{28}H_{29}O_4$ $[M]^+$, found 428.1980.

4.2.10. Dimethyl 1-benzylidene-4,5,6,7-tetrahydro-1H-indene-2,3-dicarboxylate. Dimethyl 4,5,6,7-tetrahydro-1*H*-indene-2,3-dicarboxylate (100 mg, 0.42 mmol) was dissolved in 3 mL THF. Benzaldehyde (0.13 mL, 1.26 mmol) was added, followed by cyclohexylamine (10 μL, 0.08 mmol) and the reaction mixture was allowed to stir for 48 h at room temperature. Solvent was removed in vacuo and the resulting residue was purified by flash chromatography (9:1 hexanes/EtOAc) to yield the title compound as a red oil (100 mg, 74% yield, 2:1 *E*/*Z*). ^1H NMR (300 MHz, $CDCl_3$) δ 8.23 (s, 1H, Cp=C*H*–Ar *E* isomer), 7.52 (s, 1H, Cp=C*H*–Ar *Z* isomer), 7.4–7.3 (m, 5H, Ar*H*, *E*/*Z* isomers), 3.88 (s, 3H, CO_2CH_3, *E* isomer), 3.83 (s, 3H, CO_2CH_3, *E* isomer), 3.79 (s, 3H, CO_2CH_3, *Z* isomer), 3.27 (s, 3H, CO_2CH_3 *Z* isomer), 2.51 (m, 2H, $-CH_2-$ *E* isomer), 2.42 (m, 4H, 2× $-CH_2-$ *Z* isomer), 2.05 (m, 2H, $-CH_2-$ *E* isomer), 1.77 (m, 4H, 2× $-CH_2-$ *Z* isomer), 1.69 (m, 2H, $-CH_2-$ *E* isomer), 1.49 (m, 2H, $-CH_2-$ *E* isomer). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5 *Z*, 166.4 *E*, 164.7 *Z*, 164.3 *E*, 143.7, 141.8, 141.4, 141.0, 140.0, 139.3, 137.0, 136.1, 135.9, 133.6, 133.4, 130.0, 129.4, 129.1, 128.9, 128.1, 128.0, 125.2, 51.9 *E*, 51.6 *E*/*Z*, 51.3 *Z*, 26.4 *E*, 23.8 *Z*, 23.5 *E*, 23.0 *Z*, 22.9 *E*, 22.3 *Z*, 22.0 *E*, 21.7 *Z*; IR (thin film) 2939, 2857, 1730, 1713, 1609, 1535, 1435, 1270, 1222, 1122 cm^{-1}; HRMS (EI^+) m/z=324.1362 calcd for $C_{20}H_{20}O_4$ $[M]^+$, found 324.1353. The substitution patterns on the fulvenes were confirmed by NOESY.

4.2.11. (E)-Dimethyl 5-benzylidene-3-(1-cyclohexylethyl) cyclopenta-1,3-diene-1,2-dicarboxylate. Dimethyl 3-(1-cyclohexylethyl)cyclopenta-1,3-diene-1,2-dicarboxylate (100 mg, 0.34 mmol) was dissolved in 4 mL THF. Benzaldehyde (105 μL, 1.03 mmol) and cyclohexylamine (8 μL, 0.07 mmol) were added and the reaction mixture was stirred at room temperature overnight. Solvent was removed in vacuo and the resulting residue was purified by flash chromatography (19:1 hexanes/EtOAc) to yield the title compound as a deep red oil (130 mg, 0.34 mmol, 100% yield). ^1H NMR (300 MHz, $CDCl_3$) δ 8.22 (s, 1H, Cp=C*H*–Ar), 7.60–7.56 (m, 2H, Ar*H*), 7.48–7.40 (m, 3H, Ar*H*), 6.56 (s, 1H, Cp*H*), 3.88 (s, 3H, CO_2CH_3), 3.83 (s, 3H, CO_2CH_3), 2.51 (quint, J=6.9 Hz, 1H, CpC*H*(CH_3)(Cy)), 1.73–1.67 (m, 5H, Cy*H*), 1.39–0.88 (m, 6H, Cy*H*), 1.15 (d, J=7.0 Hz, 3H, CpCH(CH_3)(Cy)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 163.8, 151.5, 144.2, 143.6, 139.9, 136.5, 131.2, 129.9, 128.7, 124.9, 120.6, 52.0, 51.6, 42.6, 38.3, 31.7, 29.1, 26.6, 26.4, 16.6; IR (thin film) 2926, 2848, 1735, 1709, 1613, 1513, 1430, 1287, 1239, 1222, 1057 cm^{-1}; HRMS (FAB^+) m/z=380.1988 calcd for $C_{24}H_{28}O_4$ $[M]^+$, found 380.2000. The substitution pattern on the fulvene was confirmed by NOESY.

4.2.12. (E)-Methyl 5-benzylidene-3-tert-butylcyclopenta-1,3-dienecarboxylate. Methyl 3-*tert*-butylcyclopenta-1,3-dienecarboxylate (100 mg, 0.56 mmol) was dissolved in 4 mL THF. Benzaldehyde (0.12 mL, 1.20 mmol) and triethylamine (0.80 mL, 0.60 mmol) were added and the reaction mixture was stirred at room temperature for 48 . Solvent was removed in vacuo and the resulting residue was purified by flash chromatography (19:1 hexanes/EtOAc) to yield the title compound (130 mg, 0.48 mmol, 86% yield). ^1H NMR (300 MHz, $CDCl_3$) δ 8.32 (s, 1H, Cp=C*H*Ar), 7.60–7.57 (m, 2H, Ar*H*), 7.50 (d, J=1.6 Hz, 1H, Cp*H*), 7.44–7.40 (m, 3H, Ar*H*), 6.57 (d, J=1.5 Hz, 1H, Cp*H*), 3.84 (s, 3H, CO_2CH_3), 1.22 (s, 9H, CpC(CH_3)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 157.4, 141.5, 141.3, 140.9, 137.0, 130.8, 129.1, 128.6, 126.1, 118.9, 50.9, 32.2, 29.6; IR (thin film) 3061, 2952, 2861, 1700, 1613, 1565, 1504, 1343, 1148, 1052 cm^{-1}; HRMS (FAB^+) m/z=268.1463 calcd for $C_{18}H_{20}O_2$ $[M]^+$, found 268.1448. The substitution pattern on the fulvene was confirmed by NOESY.

4.2.13. Dimethyl 1-(4-nitrobenzylidene)-4,5,6,7-tetrahydro-1H-indene-2,3-dicarboxylate. Dimethyl 4,5,6,7-tetrahydro-1*H*-indene-2,3-dicarboxylate (100 mg, 0.42 mmol) was dissolved in 3 mL THF. 4-Nitrobenzaldehyde (190 mg, 1.26 mmol) was then added, followed by cyclohexylamine (10 μL, 0.08 mmol) and the reaction mixture was allowed to stir for 48 h at room temperature. Solvent was removed in vacuo and the resulting residue was purified by flash chromatography (9:1 hexanes/EtOAc) to yield the title compound as a 3:2 *E*/*Z* mixture as a red oil (90 mg, 58% yield). ^1H NMR (300 MHz, $CDCl_3$) δ 8.24–8.18 (m, 5H, Ar*H*/Cp=C*H*Ar), 7.51–7.42 (m, 5H, Ar*H*/Cp=C*H*Ar), 3.86 (s, 3H, CO_2CH_3 *E*), 3.81 (s, 3H, CO_2CH_3

E), 3.78 (s, 3H, CO_2CH_3 *Z*), 3.30 (s, 3H, CO_2CH_3 *Z*), 2.47 (m, 4H, 2× $-CH_2-$ *Z*), 2.36 (m, 2H, $-CH_2-$ *E*), 1.90 (m, 2H, $-CH_2-$ *E*), 1.75 (m, 4H, 2× $-CH_2-$ *Z*), 1.65 (m, 2H, $-CH_2-$ *E*), 1.46 (m, 2H, $-CH_2-$ *E*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 165.9, 164.4, 163.7, 147.7, 143.8, 142.9, 142.3, 141.6, 141.3, 139.8, 138.7, 135.9, 133.8, 133.4, 130.6, 130.0, 128.2, 124.2, 123.3, 123.1, 52.1, 51.9, 51.8, 51.7, 26.4, 23.7, 23.4, 22.7, 22.2, 21.8, 21.7; IR (thin film) 2948, 2857, 1735, 1709, 1596, 1522, 1435, 1348, 1265, 1217, 1121 cm^{-1}; HRMS (FAB^+) *m*/*z*=369.1212 calcd for $C_{20}H_{19}NO_6$ $[M]^+$, found 369.1227.

4.3. pK_a Estimation of 8

Dimethyl 4,5-diphenylcyclopenta-3,5-diene-1,3-dicarboxylate (1.5 mg, 0.0045 mmol) was dissolved in 0.5 mL CD_3CN and 2-NH_2−benzimidazole (2.6 mg, 0.0195 mmol) was added. Using the ^{1}H NMR chemical shifts of fully protonated (3.613 ppm), fully deprotonated (3.499 ppm) and the observed chemical shift (3.537 ppm) of the cyclopentadiene methyl esters, the equilibrium ratio of cyclopentadiene and cyclopentadienyl anion was determined to be 33.3% protonated.[12] Thus, the amounts of neutral cyclopentadiene (0.0015 mmol), deprotonated cyclopentadiene (0.0030 mmol), neutral 2-NH_2−benzimidazole (0.0165 mmol) and protonated 2-NH_2−benzimidazole (0.0030 mmol) were obtained. Using the obtained amounts and the known pK_a of 2-NH_2−benzimidazole in acetonitrile,[13] the pK_a of dimethyl 4,5-diphenylcyclopenta-3,5-diene-1,3-dicarboxylate was calculated to be 16.52 in acetonitrile.

4.4. General procedure for fulvene/imine interchange experiments

4.4.1. Forward. Stock solutions (1−2 mL) of imine (0.30 M), cyclopentadiene (0.30 M), and benzyl ether (0.30 M) in $CDCl_3$ were prepared fresh. To an NMR tube, 0.20 mL of each solution was added and mixed. The fulvene/imine ratio was monitored by ^{1}H NMR until no change in the ratio was observed.

4.4.2. Reverse. Stock solutions (1−2 mL) of fulvene (0.30 M), amine (0.30 M), and benzyl ether (0.30 M) in $CDCl_3$ were prepared fresh. To an NMR tube, 0.20 mL of each solution was added and mixed. The fulvene/imine ratio was monitored by ^{1}H NMR and reported at the equilibrium time determined for the forward reaction.

4.5. Transfulvenation experiments

4.5.1. No additional aniline. A solution of dimethyl 2-benzylidene-4,5-diphenylcyclopenta-3,5-diene-1,3-dicarboxylate (25.3 mg, 0.06 mmol) in $CDCl_3$ 300 μL was added to a solution of *N*-(3-phenylallylidene)aniline (12.4 mg, 0.06 mmol) and benzyl ether (11.4 μL, 0.06 mmol) as internal standard in $CDCl_3$ (300 μL total volume). Reaction progress was followed by ^{1}H NMR over the course of 5 days.

4.5.2. Stoichiometric aniline. A solution of dimethyl 2-benzylidene-4,5-diphenylcyclopenta-3,5-diene-1,3-dicarboxylate (25.3 mg, 0.06 mmol) in $CDCl_3$ 300 μL was added to a solution of *N*-(3-phenylallylidene)aniline (12.4 mg, 0.06 mmol), aniline (5.5 μL, 0.06 mmol), and benzyl ether (11.4 μL, 0.06 mmol) as internal standard in $CDCl_3$ (300 μL total volume). Reaction progress was followed by ^{1}H NMR over the course of 30 h.

4.6. Fulvene metathesis

Dimethyl 1-benzylidene-4,5,6,7-tetrahydro-1*H*-indene-2,3-dicarboxylate (4.9 mg, 0.015 mmol, 1.7:1.0 *E*/*Z* ratio) and dimethyl 2-(4-nitrobenzylidene)-4,5-diphenylcyclopenta-3,5-diene-1,3-dicarboxylate (7.0 mg, 0.015 mmol) were dissolved in 0.30 mL $CDCl_3$ before benzyl ether (2.9 μL, 0.015 mmol in 0.15 mL $CDCl_3$) and *n*-butylamine (1.5 μL, 0.015 mmol in 0.15 mL in $CDCl_3$) were added as stock solutions. The solution was mixed in an NMR tube and the reaction progress was monitored by ^{1}H NMR. After 19 h, the relative fulvene and imine ratios were constant as shown in Scheme 3. The total amount of dimethyl 2-benzylidene-4,5-diphenylcyclopenta-3,5-diene-1,3-dicarboxylate and dimethyl 3-(4-nitrobenzylidene)octahydro-1*H*-indene-1,2-dicarboxylate were calculated by integrating the *Z* isomer and using the *E*/*Z* ratio previously determined in Table 1, entry 10. Chemical shifts used to determine the final ratios are shown on the spectrum in the provided Supplementary data.

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Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2011.03.094.

References and notes

1. Alkylidene cyclopentadienes are technically called 'pentafulvenes', which represent only one of a number of fulvene subclasses. However, in the absence of additional qualifiers, 'fulvene' and 'pentafulvene' are generally understood to be synonymous.
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