Ferrocenylketene and Ferrocenyl-1,2-bisketenes: Direct Observation and Reactivity Measurements

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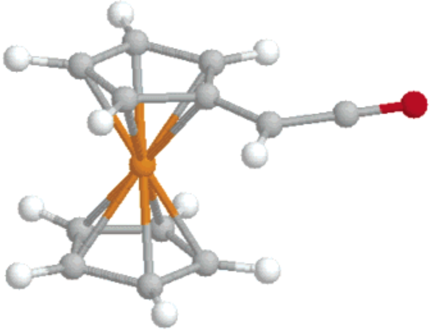

Ferrocenylketene (**1**) is calculated to be destabilized by 1.6 kcal/mol relative to phenylketene (**10**) by B3LYP isodesmic comparison to the corresponding alkenes. Ketene **1** generated by Wolff rearrangement in CH_3CN is identified by the IR band at 2119 cm^{-1} and has a rate constant for reaction with n-$BuNH_2$ less than that for **10** by a factor of 5. 1,2-Bisferrocenyl-1,2-bisketene **18** and 1-ferrocenyl-2-trimethylsilyl-1,2-bisketene **21** were prepared by photochemical ring opening of the corresponding cyclobutenediones, and **18** undergoes rapid ring closure 67 times faster than the corresponding 1,2-diphenyl-1,2-bisketene, while bisketene **21** is longer lived than **18** by a factor of 3.2×10^4.

Diphenylketene ($Ph_2C{=}C{=}O$) was prepared in 1905 as an isolable solid and was the first ketene to be characterized.[1a] Phenylketene was investigated soon after in 1911[1b] and is highly reactive, but may be observed in solution by infrared or ultraviolet spectroscopy.[2] Both of these ketenes have been extensively studied, including their kinetics of reaction with water,[2a−d] amines,[2e] and the stable free radical TEMPO.[3]

Despite the extensive investigations of ketenes[2−4] and bisketenes,[4] no direct observation of ferrocenylketene (**1**) or of any ferrocenyl-substituted ketene has been reported, although these species have received some attention.[5] The ketene **1** has been generated by treatment of the acid **2a** with the acid activator $PhOP(O)Cl_2$ and Et_3N or from the acyl chloride **2b** and Et_3N.[5a] In each case, the unobserved intermediate **1** was captured in [2 + 2] cycloaddition with imines such as $PhCH{=}NPh$ giving *cis*-β-lactam **3** (eq 1).[5a]

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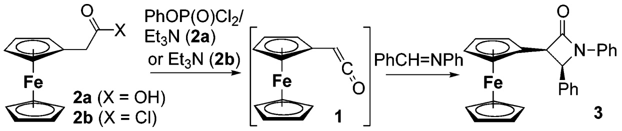
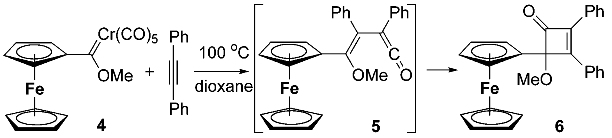


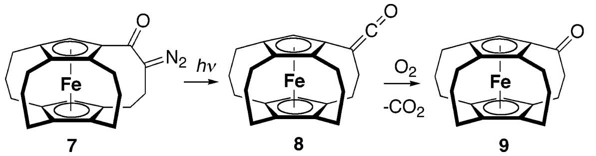
(1)

Thermolysis of the chromium carbene complex **4** in the presence of diphenylacetylene gave the cyclobutenone **6** in a reaction implicating addition of the alkyne to **4** forming the unobserved ferrocenylvinylketene **5**, which cyclized to **6** (eq 2).[5b]



(2)

Ring contraction of bridged ferrocenes has been achieved by Wolff rearrangement, as in the photolysis of **7** forming **9**, in a reaction evidently involving the unobserved ketene **8** that was oxidized by adventitious air to the ketone **9** (eq 3).[5c] Ring contraction by Wolff rearrangement was also demonstrated in ferrocenes with one, two, and three transannular bridges.[5c]



(3)

The study of ferrocenylketenes is of interest for theoretical reasons for the elucidation of the effect of the interactions of the ferrocenyl and ketenyl groups on each other and how these affect the structure and reactivity of the molecule. Ketenyl groups may also serve as linkers for incorporating ferrocenyl groups into novel structures.

While the nature of the α-ferrocenyl carbocation $C_{10}H_9FeCH_2^+$ has been the subject of intense investigation for almost 50 years,[6a−c] much less is known of the corresponding radical[6d] and carbanion. Additions of radicals and of nucleophiles to the carbonyl carbon of the monoketene **1** should generate these respective intermediates. Because of our continuing interest in radical reactions of ketenes,[3] and in bisketene formation and reactivity,[4] the study of the generation, direct observation, and reactivity of ferrocenylketenes and bisketenes was undertaken.

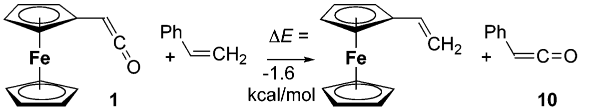
Results and Discussion

To evaluate the properties of ferrocenylketene (**1**), its structure and energy as well as those of phenylketene (**10**) and the corresponding alkenes were calculated at the B3LYP/6-311G(d,p)//B3LYP/6-311G(d,p) level, using Gaussian 03.[8a] This methodology has previously been successfully employed in studies of ferrocene derivatives.[8b] The calculated energy results are summarized in the isodesmic correlation of eq 4, which indicates that ferrocenylketene is destabilized in comparison to phenylketene by 1.6 kcal/mol. We have used such comparisons for the analysis of substituent effects on ketenes, which are found to be stabilized by electropositive substituents and by π-acceptor groups.[7a,b] Ketene substituent stabilization parameters (SE) were defined relative to CH_3,[7a,b] and thus the value for ferrocenyl is −0.7, meaning ferrocenylketene is less stable by isodesmic comparison to methylketene by 0.7 kcal/mol.

TABLE 1. Calculated Bond Distances and Bond Angles

	1	**10**	$FcCH{=}CH_2$	$PhCH{=}CH_2$
C(1)=O	1.1629	1.1613		
$CH{=}CH_2$			1.3352	1.3354
CH=C(1)	1.3162	1.3177		
Ar−C(1)	1.4655	1.4682	1.4624	1.4719
Ar−C(2)=C(1)	124.5	125.3	126.2	127.7
Ar−C(2)=C(1) (d)[a]	10.7	0.0	14.7	0.0

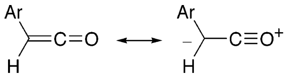
[a] Dihedral angle between the substituent and the aryl plane.



(4)

To determine if there is any solvent effect on the energy comparison of eq 4, a single-point energy calculation was carried out for a continuum of the highly polar acetonitrile, and this changed the energy difference by only −0.11 kcal/mol. This result is not unanticipated, as the net change in the calculated dipole moments in eq 4 is only 0.0072 D.

Selected calculated bond distances and bond angles for **1** and **10**, and for the corresponding vinyl derivatives, are summarized in Table 1, and computational details are given in the Supporting Information. These show a longer C=O bond and a shorter C=C bond for ferrocenylketene (**1**) compared to that of **10**, consistent with smaller C−O triple bond character in **1** due to reduced π-donation from oxygen to C(1). This is expected because of a smaller contribution from the normal ketene resonance structure **1a** due to the strong electron-donating character of ferrocenyl.[6a−c]



1a (Ar = $C_{10}H_9Fe$)

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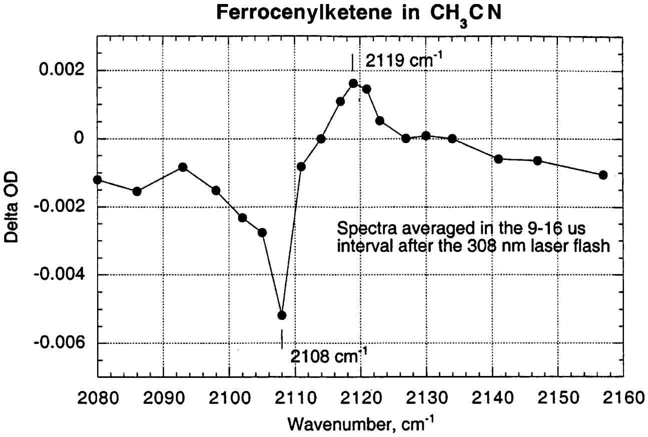
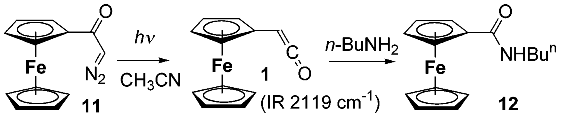


FIGURE 1. Time-resolved IR scan of photolysis of diazoacetylferrocene (**11**) showing bleaching of the IR absorption of **11** at 2108 cm^{-1} and the formation of the IR absorption of ferrocenylketene (**1**) at 2119 cm^{-1}.

Phenylketene and styrene are planar, but the ketenyl and vinyl groups of ferrocenylketene and vinylferrocene, respectively, are twisted above the ring plane, with 10.7 and 14.7° Ar−C=C dihedral angles, respectively. The two faces of the cyclopentadienyl ring bonded to the substituent are dissymmetric, and therefore this lack of coplanarity is not unexpected.

Laser flash photolysis with 308-nm light of diazoacetylferrocene (**11**)[9a] in CH_3CN gave ferrocenylketene (**1**) as detected by the disappearance of the diazo ketone absorption of **11** at 2108 cm^{-1} and the appearance of the characteristic ketenyl IR absorption of **1** at 2119 cm^{-1} using time-resolved IR spectroscopy (Figure 1), a technique we have used for the detection of other transient ketenes.[7c] Calculated ketenyl infrared bands (not scaled) were found at 2122 cm^{-1} for ferrocenylketene (**1**) and 2120 cm^{-1} for phenylketene (**10**), in good agreement with the measured values of 2119 and 2117 cm^{-1},[3b] respectively.

The identification of **1** was confirmed by reaction with n-$BuNH_2$ forming the amide **12**[9b] in 83% yield (eq 5). The kinetics of the reaction of **1** with n-$BuNH_2$ in CH_3CN at ambient temperature (22 °C) were measured by following the change in the IR absorption at 2119 cm^{-1} as a function of excess [n-$BuNH_2$]. A sample kinetic trace is shown in Figure 2, and a second-order rate constant dependent on the [n-$BuNH_2$] was determined, with $k_2 = (1.08 \pm 0.11) \times 10^8$ M^{-1} s^{-1}. This is smaller by a factor of 5 compared to the rate constant for the reaction of PhCH=C=O (**10**) with n-$BuNH_2$ ($k_2 = 5.2 \times 10^8$ M^{-1} s^{-1}).[7c]



(5)

The lower reactivity of ferrocenylketene (**1**) compared to that of phenylketene (**10**) by a factor of 5 is understandable, as reactivity in nucleophilic attack on arylketenes is enhanced by the electron-withdrawing effect of the aryl group. Thus, for arylketenes 4-RC_6H_4CH=C=O the dependence of the rate constants on the aryl substituents for hydration is correlated with σ-constants with $\rho = 1.2$,[2d] and because the ferrocenyl group is strongly electron-donating compared to phenyl,[6] lower reactivity is expected in nucleophilic addition for **1** compared to **10**.

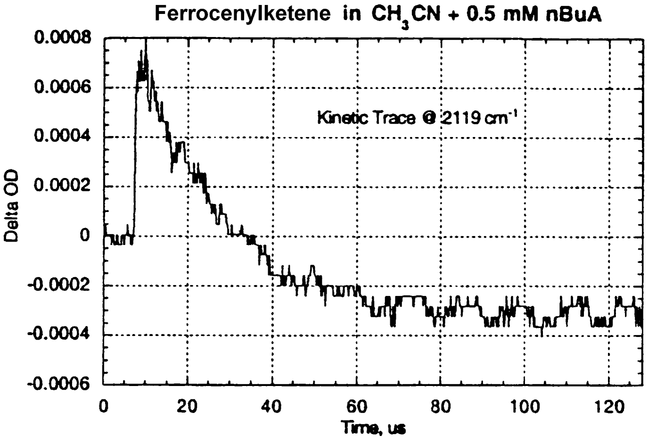
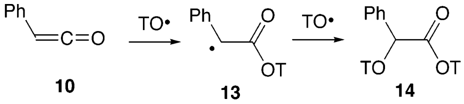


FIGURE 2. Kinetic trace of the disappearance of the IR absorption of ferrocenylketene at 2119 cm^{-1} upon reaction with 0.5×10^{-3} M n-$BuNH_2$ in CH_3CN at 22 °C.

Arylketenes such as **10** react with the stable free radical TEMPO (TO•) by initial attack of the radical on the carbonyl carbon of the ketene forming intermediate enolic radical **13**, followed by addition of a second TEMPO giving the 1,2-diaddition product **14** (eq 6).[3] Photolysis of diazo ketone **11** in pentane with 300 and 350-nm light to generate the ketene **1** in the presence of TEMPO led to the formation of the diaddition product **16** in 73% yield through the intermediacy of the radical **15** (eq 7).



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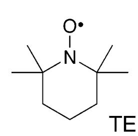
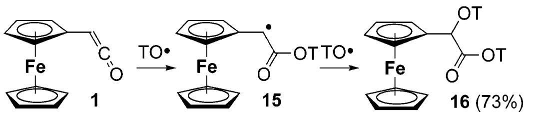


TEMPO (TO•)



(7)

We have studied the formation of 1,2-bisketenes from photolysis or thermolysis of cyclobutenediones,[4b,10] and with our recent efficient synthesis of 1,2-diferrocenylcyclobutenedione (**17**)[11] we have undertaken the study of this compound (eq 8). An X-ray structure of **17** has now

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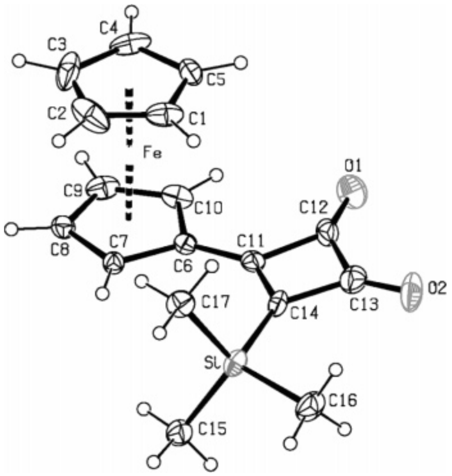
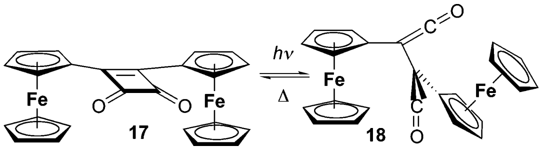


FIGURE 3. X-ray structure of ferrocenyl(trimethylsilyl)-cyclobutenedione (**20**).

been obtained (Supporting Information) and shows two similar structures in the crystal with the ferrocene rings on the same side of the cyclobutenedione ring, presumably because of better crystal packing, with little steric interference between the two ferrocenyl groups. Dihedral angles between the cyclobutenedione ring and the attached cyclopentadienyl ring of 8.1 to 27.1° were observed. Conventional broadband flash photolysis of **17** in isooctane resulted in the appearance of a new UV spectrum assigned to the bisketene **18**, and this rapidly changed back to **17** with a rate constant of 2.59 s^{-1} at 25 °C, as monitored by the increase at 320 nm (eq 8). This is 67 times faster than the value of 3.89×10^{-2} s^{-1} for the analogous diphenyl-1,2-bisketene.[4b] Bisketene **18** is too short-lived for structure determination, but is presumably twisted (eq 8), as found for other 1,2-bisketenes.[4a]



(8)

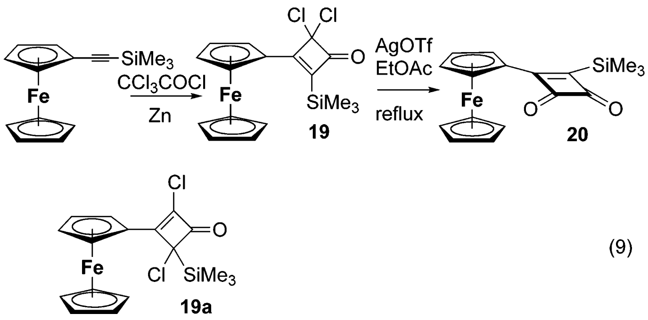
The greater reactivity of **18** to reform the cyclobutenedione compared to the diphenyl analogue is consistent with the known acceleration of ring closure of aryl-substituted 1,2-bisketenes by electron-donating aryl groups, with a dependence on σ^+ of substituents R for RC_6H_4, which stabilize the electron-deficient cyclobutenediones with ρ^+ of −1.10.[10a] The lower stability of ferrocenylketene (**1**) compared to that of phenylketene (**10**) as found in the isodesmic energy comparison (eq 4) is also consistent with this result.

For the study of a longer-lived ferrocenyl-substituted bisketene, the dichlorocyclobutene **19** (containing a small amount of the rearranged product **19a**) was prepared from ferrocenyltrimethylsilylacetylene[11c] by the addition of dichloroketene, and AgOTf-promoted hydrolysis gave the ferrocenyltrimethylsilylcyclobutenedione (**20**) (eq 9). The stucture of **20** was confirmed by an X-ray determination (Figure 3) and shows an essentially coplanar conformation of the cyclopentadienyl ring of the ferrocenyl group with the cyclobutenedione ring, with dihedral angles of 7.7 and 8.7°, permitting conjugative electron delocalization.

TABLE 2. Rate Constants for Ring Closure of 1,2-Bisketenes O=C=CRCR^1=C=O at 25 °C

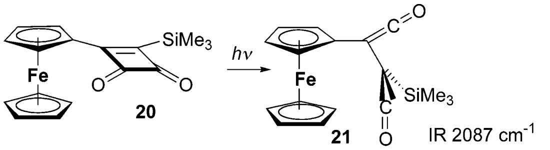
bisketene	R	R^1	solvent	k_1 s^{-1}	ref
18	$C_{10}H_9Fe$	$C_{10}H_9Fe$	hexanes	2.59	*a*
21	$C_{10}H_9Fe$	Me_3Si	C_6D_6	8.2×10^{-5}	*a*
	Ph	Ph	isooctane	3.89×10^{-2}	4b
	Ph	Me_3Si	isooctane	2.03×10^{-6}	4b

[a] This work.



(9)

Photolysis of **20** in C_6D_6 gave bisketene **21** as a rather long-lived transient, as identified by the IR band at 2087 cm^{-1}, and by ^1H, ^{13}C, and ^{29}Si NMR (eq 10). Particularly revealing were the characteristic ketenyl ^{13}C NMR signals at δ 9.4 (*C*SiMe$_3$), 28.6 (*C*Fc), 181.0 ($Me_3SiC{=}$*C*$=O$), and 205.2 (FcC=*C*=O), which correspond to those of other aryl(trimethylsilyl)-1,2-bisketenes.[10,12] Ring closure of **21** to **20** was monitored by ^1H NMR with a rate constant of 8.2×10^{-5} s^{-1}, which is less than that for **18** forming **17** by a factor of 3.2×10^4 (Table 2).



(10)

The longer lifetime for **21** compared to that of **18** is expected, as trimethylsilyl has a strong stabilizing effect on ketenes and bisketenes.[4,7a,b] Replacement of one phenyl in 1,2-diphenyl-1,2-bisketene by trimethylsilyl decreases the rate constant for ring closure by a very similar factor of 1.9×10^4 (Table 2).[4b]

The rate constants for the ring closure of **18** and **21** fit on the previous correlation[4b] with the sum of the substituent stabilization energies (ΣSE) ketene using the value of −0.7 derived for ferrocenyl relative to CH_3 (Figure 4). As can be seen, these fit within the precision of the previous correlation and give the new correlation of eq 11.

$$\log k = -0.28\Sigma\text{SE} - 1.94 \; (r = 0.95) \tag{11}$$

In conclusion, ferrocenylketene **1** and ferrocenyl-substituted bisketenes **18** and **21** have been generated and directly observed in solution, and their reactivity has been studied. The stability of **1** relative to other ketenes

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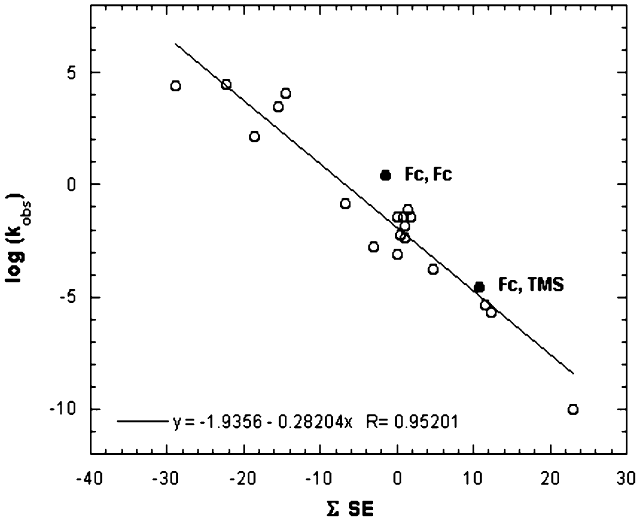

FIGURE 4. Correlation of log *k* for bisketene ring closure with the sum of the ketene substituent stabilization energies (ΣSE).

has been determined by computational methods, and the reactivities of **1**, **18**, and **21** compared to those of other ketenes and bisketenes have been analyzed based on their stability and electronic properties.

Experimental Section

Ferrocenylcarbonyl Chloride.[9a] Oxalyl chloride $(COCl)_2$ (0.05 mL, 5 mmol) was added dropwise to a stirred solution of ferrocenecarboxylic acid (0.05 g, 2 mmol) in CCl_4 (5 mL) and stirred at room temperature for 2 h. The solvent was removed in vacuo to give the known[9a] ferrocenylcarbonyl chloride as red crystals (0.051 g, 98%), used subsequently without further purification. ^1H NMR (400 MHz, $CDCl_3$) δ 4.92 (d, 2H, J = 1.8 Hz), 4.64 (d, 2H, J = 2.0 Hz), 4.34 (s, 5H).

Ferrocenyl Diazomethyl Ketone (11).[9a] Ferrocenylcarbonyl chloride (0.051 g, 0.2 mmol) in ether (2 mL) was added dropwise to a stirred cooled solution of diazomethane (0.8 mmol) and Et_3N (0.1 mL) in ether (40 mL), and the solution was stirred for an additional 2 h. Excess diazomethane was removed by evacuating with a water aspirator pump through an empty Erlenmeyer flask and quenched in acetic acid, and the remaining solution was concentrated. Chromatography (silica gel, $CHCl_3$) gave the known **11**[9a] (32 mg, 80%) as red crystals. ^1H NMR (400 MHz, $CDCl_3$) δ 5.50 (s, 1H), 4.67 (t, 2H, J = 1.8 Hz), 4.47 (t, 2H, J = 1.9 Hz), 4.23 (s, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.5, 79.5, 71.9, 70.2, 68.6, 53.5. IR ($CDCl_3$) 2104, 1614 cm^{-1}. EIMS (*m/z*) 255 (MH$^+$), 254, 226, 198, 172, 142, 121, 81, 56. HREIMS, *m/z* calcd for $C_{12}H_{10}FeN_2O$ 254.0140, found 254.0142.

Ferrocenylketene (1). Laser flash photolysis of **11** in CH_3CN using the time-resolved IR spectrometer previously described[7c] resulted in the disappearance of the diazo ketone absorption at 2108 cm^{-1} and the appearance of a new absorption at 2119 cm^{-1} assigned to **1** (Figure 1).

Reaction of Ferrocenylketene (1) with TEMPO. A solution of **11** (20 mg, 0.079 mmol) and TEMPO (25 mg, 0.165 mmol) in pentane (25 mL) was degassed by bubbling in argon for 10 min, photolyzed for 10 min with 300- and 350-nm lamps, and stirred a further 2 h at room temperature. Chromatography (silica gel, $CHCl_3$) gave **16** (31 mg, 73%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.56 (s, 1H), 4.94 (t, 2H, J = 1.9 Hz), 4.48 (t, 2H, J = 1.8 Hz), 4.27 (s, 5H), 1.68−0.86 (m, 36 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.0, 80.2, 71.1, 69.8, 62.1, 61.2, 60.9, 41.1, 34.8, 34.3, 33.3, 31.8, 29.9, 26.844, 22.6, 19.1, 17.9, 17.3, 14.3. IR ($CDCl_3$) 1734 cm^{-1}. EIMS (*m/z*) 539 (MH$^+$), 538. HREIMS, *m/z* calcd for $C_{30}H_{46}FeN\ _2O_3$ 538.2847, found 538.2858.

Photolysis of Ferrocenylketene (1) with *n*-Butylamine. A solution of **11** (30 mg, 0.02 mmol) in pentane (25 mL) containing *n*-$BuNH_2$ (0.02 mL, 17 mg, 0.024 mmol) was degassed for 10 min, photolyzed for 15 min with 300- and 350-nm light, and stirred a further 2 h at room temperature. Chromatography (silica gel, 30/70 EtOAc/hexane) gave the known[9b] *N*-*n*-butyl ferrocenylacetamide (**12**, 29 mg, 83%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.56 (brs, 1H), 4.17 (t, 2H, J = 1.5 Hz), 4.16 (t, 2H, J = 1.6 Hz), 4.14 (s, 5H), 3.33 (s, 2H), 3.18 (q, 2H), 1.41−1.37 (m, 2H), 1.28−1.24 (m, 2H), 0.86−0.88 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 95.7, 69.4, 69.1, 68.7, 39.4, 38.2, 31.778, 20.2, 13.9. IR ($CDCl_3$) 1653 cm^{-1}. EIMS (*m/z*) 300 (MH$^+$), 299, 285, 234, 223, 199, 190, 167, 134, 83, 71, 57. HREIMS, *m/z* calcd for $C_{16}H_{21}FeNO$ 299.0972, found 299.0973.

Trimethylsilylethynylferrocene (22).[11c] To ethynylferrocene[11c] (930 mg, 4.43 mmol) in THF (30 mL) was added *n*-BuLi (3.5 mL, 1.6 M, 5.6 mmol, in hexane), and the solution was stirred for 2.5 h. A solution of Me_3SiCl (0.75 mL, 5.9 mmol) in THF (5 mL) was added, the mixture was heated for 1 h at 35 °C and then stirred at room-temperature overnight, and ice was added. The aqueous layer was extracted with ether, and the combined ether layers were washed with water, dried, and concentrated. Chromatography (alumina, ether) gave the known **22**,[11c] mp 79−81 °C (1.11 g, 89%). ^1H NMR ($CDCl_3$) δ 0.29 (s, 9), 3.82 (t, 2), 4.02 (s, 5), 4.39 (t, 2). ^{13}C NMR ($CDCl_3$) δ 0.5, 65.5, 69.1, 70.5, 72.1, 90.6, 105.1. IR (KBr) 2147 cm^{-1}. EIMS *m/z* (282, M$^+$, 100), 267 (44), 73 (8).

1-Ferrocenyl-2-trimethylsilyl-3-oxo-4,4-dichlorocyclobutene (19). To alkyne **22** (200 mg, 0.71 mmol) in Et_2O (10 mL) with zinc (288 mg, 4.4 mmol, activated by heating with a Bunsen flame) was added CCl_3COCl (465 mg, 2.56 mmol) in ether (5 mL) over 1 h. The mixture was stirred for 30 min, filtered through silica gel, washed with water, dried, and concentrated. Chromatography (silica gel, 9:1 hexanes/EtOAc) gave a mixture of **19** containing some product **19a** from chlorine migration as red crystals, mp 140−141 °C. ^1H NMR (C_6D_6) δ **19**: 0.14 (s, 9), 3.92 (s, 5), 4.19 (t, 2, J = 1.8 Hz) 4.62 (t, 2, J = 1.8 Hz). **19a**: 0.10 (s, 9), 3.94 (s, 5), 4.13 (m, 1), 4.17 (m, 1), 4.50 (m, 1), 4.88 (m 1). ^{13}C NMR (C_6D_6) δ **19**: −2.8, 69.4, 69.8, 71.4, 71.5, 73.0, 73.8, 74.0, 115.9, 175.5, 180.8. IR (KBr) 1785, 1771 cm^{-1}. EIMS (*m/z*) 392 (M$^+$, 100), 299 (27), 73 (45).

1-Ferrocenyl-2-trimethylsilyl-3,4-cyclobutenedione (20). A mixture of **19** and **19a** (25 mg, 0.064 mmol) in EtOAc (20 mL) was added to AgOTf (80 mg, 0.31 mmol) in refluxing degassed EtOAc (5 mL). The mixture was heated 12 min and cooled, and water was added. The aqueous layer was extracted with ether, and the combined organic layers were washed, dried, and chromatographed (silica gel, 5:95 EtOAc/hexanes) to give **20** (5 mg, 23%), which on recrystallization from hexanes gave red needles, mp 137−138 °C. ^1H NMR (C_6D_6) δ 0.20 (s, 9), 3.74 (s, 5), 4.18 (t, 2, J = 1.9 Hz), 4.77 (t, 2, J = 1.9 Hz). ^{13}C NMR (C_6D_6) δ −1.9, 70.0, 70.7, 71.1, 74.1, 194.3, 199.0, 199.9, 203.1. ^{29}Si NMR (C_6D_6) δ −10.6. IR (KBr) 1777, 1752 cm^{-1}. UV λ_{max} (CH_3CN) 238 (ϵ 5300), 296 (ϵ 5600), 504 (ϵ 1750). EIMS *mz* 338 (M$^+$, 48), 282 (100), 267 (25) 73 (15).

The structure of **20** was confirmed by X-ray (Figure 3).

2-Ferrocenyl-3-trimethylsilyl-1,3-butadiene-1,4-dione (21). Irradiation of **20** (5 mg, 0.015 mmol) in degassed C_6D_6 (0.5 mL) in an NMR tube with 300- and 350-nm light for 1 h gave signals corresponding to 90% conversion to **21**. ^1H NMR (C_6D_6) δ 0.03 (s, 9), 3.93 (t, 2, J = 1.8 Hz), 4.01 (t, 2, J = 1.9 Hz), 4.05 (s, 5). ^{13}C NMR (C_6D_6) δ −1.0, 9.4, 28.6, 65.8, 68.1, 69.3, 69.7, 181.0, 205.2. ^{29}Si NMR (C_6D_6) δ 2.3. IR (KBr) 2087 cm^{-1}.

Kinetic Measurements. Laser flash photolysis of the diazo ketone **11** at 308 nm was used to produce the ketene **1**. Kinetic measurements of the reaction of **1** with *n*-butylamine were carried out as described previously.[7c] A plot of k_{obs} versus [*n*-$BuNH_2$] used to derive k_2 is shown in the Supporting Information.

Photolysis of the cyclobutenedione **17** to produce the bisketene **18** was carried out using a Xenon M-73D-8 capillary broadband xenon lamp, and the kinetics of ring closure to reform the cyclobutenedione **17** were measured by observing the growth of the characteristic UV absorption of the bisketene. A representative kinetic plot is shown in the Supporting Information. Photolysis of **20** to form **21** was carried out on a C_6D_6 solution in an NMR tube as described above, and the reformation of **20** was monitored by ^{1}H NMR.

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Supporting Information Available: Experimental details, ^{1}H NMR spectra, and X-ray data. This material is available free of charge via the Internet at http://pubs.acs.org.

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