Formation of diaziridines by reaction of (CO)5W:C(OMe)Ph with electron-deficient azo compounds

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$[Fe_4(CO)_{12}(\mu_4\text{-}C)]^{2-}$, $[HFe_4(CO)_{12}(\mu_4\text{-}C)]$, $[Fe_4(CO)_{12}(\mu_4\text{-}CO)]$, $[HFe_4(CO)_{12}(\mu_4\text{-}CH)]$, and $[HFe_4(CO)_{12}(\mu_4\text{-}COCH_3)]$, the μ_4 carbon atom is semiencapsulated and almost collinear with the wingtip atoms (Fe–(μ_4-C)–Fe angles lie in the range 170–177°). These angles are somewhat larger than the corresponding Fe–C_α–C_β angles (150–165°) in the acetylides, but the latter lie closer to the Fe_4 carbides than the μ_3-η^2-⊥-acetylenes. The analogy can be taken a step further by recognizing that the formal attachment of a non-cluster-bound substitutent R^+ (R = COOMe) on the μ_4-carbide atom of $[Fe_4(CO)_{12}(\mu_4\text{-}C)]^{2-}$ gives $[Fe_4(CO)_{12}(\mu_4\text{-}COCOOMe)]^-$, an anion in which the wingtip–(μ_4-C)–wingtip angle is 148°.[31] In the Fe_3–acetylide M_4–carbide analogy this anion corresponds to the $Fe_3(\mu_3\text{-}\eta^2\text{-}RC{\equiv}CR)$ structures. It will be interesting to see whether these structural analogies translate into patterns of chemical reactivity for the $M_3(\mu_3\text{-}\eta^2$-acetylides) similar to those of the butterfly carbides.

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Supplementary Material Available: Positional coordinates and isotropic thermal parameters for the hydrogen atoms of 1 (Table SI) and anisotropic thermal parameters for the non-hydrogen atoms of 1 and 2 (Tables SII and SIII, respectively) (3 pages); observed and calculated structure factors from the final cycle of least-squares refinement for 1 and 2 (Tables SIV and SV, respectively) (47 pages). Ordering information is given on any current masthead page.

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Formation of Diaziridines by Reaction of $(CO)_5W{=}C(OMe)Ph$ with Electron-Deficient Azo Compounds

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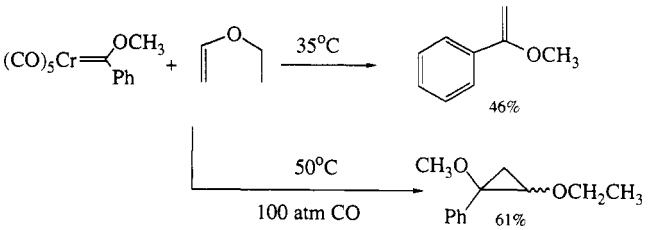
The reaction between $(CO)_5W{=}C(OMe)Ph$ (**7**) and 4-methyl-1,2,4-triazoline-3,5-dione in acetonitrile results in the formation of two isomeric diaziridines **8a** and **8b** in a 2:1 ratio. The related azo compound diethyl azodicarboxylate also reacts with **7** to produce a diaziridine product. This reactivity of electron-poor azo compounds is analogous to the cyclopropanation of olefins and contrasts with the previously reported metathesis reaction of tungsten carbenes with *cis*-azobenzene.

Introduction

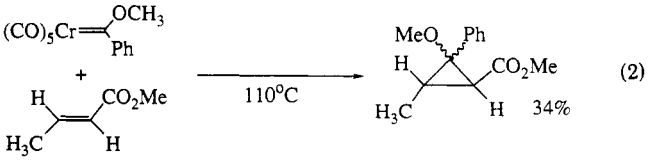
We previously reported the isolation of zwitterionic intermediate **4** in the azo metathesis reaction between $(CO)_5W{=}C(OCH_3)CH_3$ (**1**) and *cis*-azobenzene (**2**).[1] The proposed mechanism involves initial nucleophilic attack of *cis*-azobenzene on the carbene complex to give **3**, which then rearranges to give the observed zwitterionic species **4** (Scheme I). Cleavage of zwitterion **4** yields imino ether **5** and products derived from the low-valent nitrene complex **6**.

The current work addresses the question of how the reaction manifold is altered when less nucleophilic azo compounds are reacted with Fischer carbenes. Olefins react with carbene complexes to produce mixtures of metathesis and cyclopropanation products,[2] depending on the reaction conditions and the nature of the olefin substrate. For example, the chromium carbene $(CO)_5Cr{=}C(OCH_3)Ph$ undergoes metathesis with ethyl vinyl ether under mild conditions, but under a high pressure of CO, the metathesis pathway is shut down and only cyclopropanation occurs (eq 1).[3] When the electron-poor



(1)

methyl crotonate is used, the reaction pathway is cyclopropanation and no metathesis products are observed (eq 2).[4] The reaction between **1** and *cis*-azobenzene gives only



(2)

the azo metathesis product. We now have observed the equivalent of the cyclopropanation pathway for azo compounds. Reactions of $(CO)_5W{=}C(OMe)Ph$ (**7**) with the more electron-deficient azo substrates 4-methyl-1,2,4-tri-

(1) (a) Sleiman, H. F.; McElwee-White, L. *J. Am. Chem. Soc.* **1988**, *110*, 8700–8701. (b) Sleiman, H. F.; Mercer, S.; McElwee-White, L. *J. Am. Chem. Soc.* **1989**, *111*, 8007–8009.
(2) Casey, C. P.; Hornung, N. L.; Kosar, W. P. *J. Am. Chem. Soc.* **1987**, *109*, 4908–4916.
(3) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1972**, *105*, 3966–3973.
(4) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1972**, *105*, 1356–1367.

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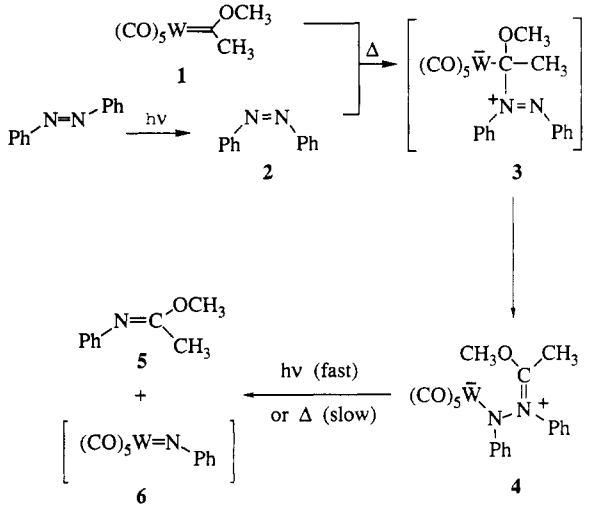
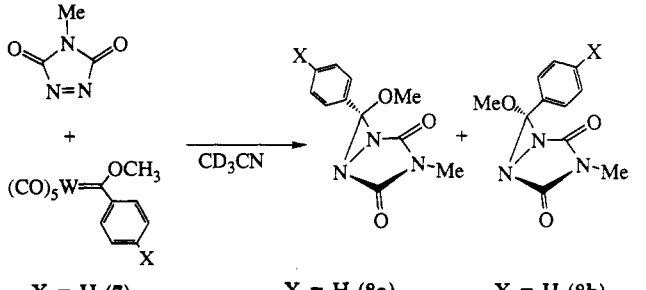
Scheme I



azoline-3,5-dione (MTAD) and diethyl azodicarboxylate (DEAD) give rise to diaziridines as their major non-oligomeric organic products.

Results and Discussion

Reaction of 7 and 9 with MTAD. When an acetonitrile solution of $(CO)_5W{=}C(OCH_3)Ph$ (**7**) is mixed with 1 equiv of MTAD at room temperature, the solution changes from red to dark reddish black within 10 min. Monitoring the reaction by ^1H NMR spectroscopy shows that MTAD is consumed within 24 h and two isomeric products are formed in a 2:1 ratio. However, some carbene is still observed and, if more MTAD is added, the combined NMR yield of the products is 13% (based on the amount of carbene consumed; 4% remains unreacted). Also present in the ^1H NMR spectrum of the reaction mixture are broad peaks in both the phenyl and *N*-methyl regions, which are ascribed to the formation of oligomeric material. The two isomeric products have been isolated by column chromatography on silica and characterized as the diaziridines **8a** and **8b** (eq 3). Attempts to assign the stereochemistry of each isomer by nuclear Overhauser effect (NOE) difference spectroscopy have been unsuccessful.



X = H (**7**) X = CF_3 (**9**)

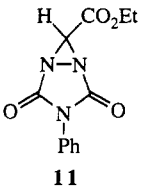
X = H (**8a**) X = CF_3 (**10a**)

X = H (**8b**) X = CF_3 (**10b**)

ratio of isomers 2:1

(3)

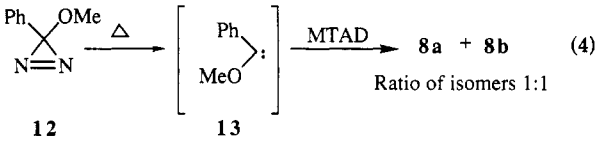
An interesting feature of the ^{13}C NMR spectra of **8a** and **8b** is the position of the quaternary carbon signals, which appear at 102.0 and 101.5 ppm, considerably downfield from the analogous signal at 64.7 ppm in the structurally similar diaziridine **11**.[5] Assignment of the peaks at 102.0 and 101.5 ppm in **8a** and **8b** has been verified by using **7**



11

that was partially enriched in ^{13}C at the carbene carbon,[6] which led to the enhancement of these signals in **8a** and **8b**. The difference in chemical shifts between **8a**, **8b**, and **11** can be explained by considering the substituent effects of the differing groups on ^{13}C shifts.[9]

In order to verify the assigned structure of the diaziridines, authentic samples of **8a** and **8b** were synthesized from phenylmethoxydiazirine (**12**)[10a] and MTAD (eq 4),



Ratio of isomers 1:1

(4)

a process that involves the intermediacy of free carbene **13**. When the diazirine **12** was allowed to decompose thermally in the presence of MTAD, the same diaziridines **8a** and **8b** were detected in the reaction mixture. However, synthesis from the free carbene resulted in a 1:1 ratio of **8a** and **8b** by ^1H NMR analysis.

Various modifications of the carbene complex and reaction conditions were then tested in an attempt to optimize the yield of diaziridines. The most promising results were obtained when the *p*-CF_3-substituted phenylcarbene **9** was used. A 1:1 ratio of carbene complex **9** to MTAD led to a reaction mixture containing 30% unreacted **9** and diaziridines **10a** and **10b** in a combined NMR yield of 50% based on consumed carbene. The two diaziridine isomers were formed in the same ratio (2:1) as in the unsubstituted phenylcarbene case (eq 3).

The mechanism shown in Scheme II is consistent with the product selectivity observed for the metal carbenes. The carbene complex reacts with MTAD to form the two diazametallacycles **14a** and **14b**, which subsequently reductively eliminate the respective isomers of the diaziridine. The exo or endo position of the substituents in the metallacycles is then reflected in the product diaziridines **8a** and **8b**.

Reaction of 7 with DEAD. In light of these results, it was expected that *cis*-$EtO_2CN{=}NCO_2Et$ (DEAD) would react in a similar manner to produce the diaziridine **15**. *cis*-DEAD can be generated photochemically,[11] and when an NMR sample of **7** and DEAD in CD_3CN is photolyzed, the solution darkens from red to black. Monitoring the reaction by ^1H NMR spectroscopy shows that, after 10 h of photolysis, all the DEAD is consumed and one major product (in 18% NMR yield based on consumed carbene) is observed, together with unreacted phenyl carbene (35%

(5) Izydore, R. A.; McLean, S. *J. Am. Chem. Soc.* **1975**, *97*, 5611-5612.

(6) The carbene **8** was 16% enriched in ^{13}C at both the carbene carbon and metal carbonyl sites. The synthetic route involved the reaction of $(CO)_5W(THF)$ with ^{13}CO to give $W(CO)_5(^{13}CO)$.[7] The carbene was then prepared according to the usual fashion.[8]

(7) Strohmeier, W.; Mueller, F.-J. *Chem. Ber.* **1969**, *102*, 3608-3612.

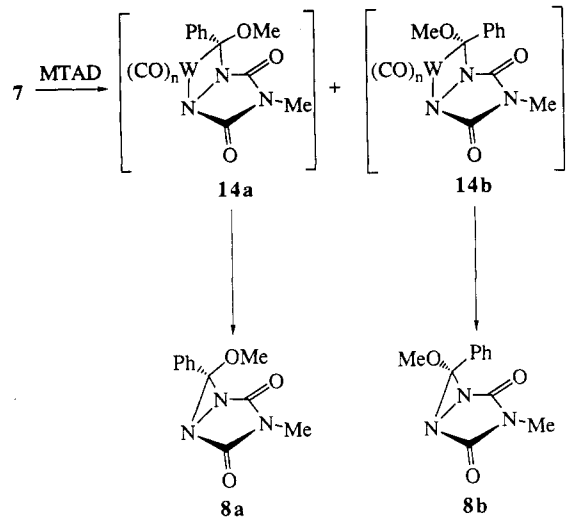
(8) Fischer, E. O.; Schubert, U.; Kleine, W.; Fischer, H. In *Inorganic Syntheses*; Wiley-Interscience: New York, 1979; Vol. XIX, pp 164-167.

(9) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 3rd ed.; John Wiley & Sons, Inc.: Canada, 1981; p 261.

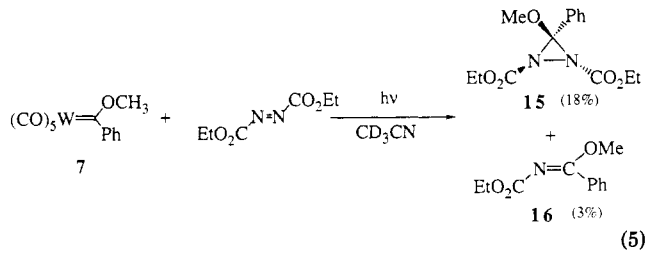
(10) (a) Wlostowska, J.; Moss, R. A.; Guo, W.; Chang, M. J. *J. Chem. Soc., Chem. Commun.* **1982**, 432-433. (b) Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396-4397.

(11) Schenck, G. O.; Kopp, H.-R.; Kim, B.; Koerner von Gustorf, E. *Z. Naturforsch. B* **1965**, *20B*, 637-639.

Scheme II



yield) and oligomeric material. The product has been characterized as the diaziridine **15** (eq 5). Diaziridine **15**

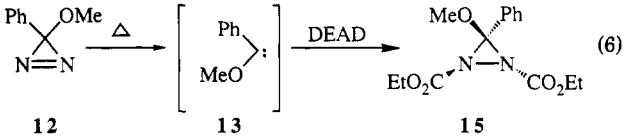


(5)

is extremely labile and easily hydrolyzes to methyl benzoate and the hydrazine $EtO_2CNHNHCO_2Et$.[12] Although the diaziridine **15** is the major nonoligomeric product in the reaction between **7** and DEAD, traces (3% NMR yield) of the metathesis product $EtO_2CN{=}C(OMe)Ph$ (**16**)[13] are also present.

Integration of the ^1H NMR spectrum of **15** at ambient temperature reveals that the characteristic signals for the ethyl group [δ in CD_3CN: 1.37 (t), 4.34 (q)] account for only one of the two ester functionalities in the diaziridine. Under these conditions, the signals for the other ester group (δ 1.05 and 4.0) are broadened due to hindered rotation. Variable-temperature NMR studies show that these peaks sharpen at elevated temperatures. At 58 °C, the peak at 4.0 ppm resolves into a quartet, and at 75 °C the peak at 1.05 ppm resolves into a triplet. The ^{13}C NMR shift for the quaternary carbon for **15** appears at 115.6 ppm, which is consistent with the values obtained for the diaziridines **8a, 8b, 10a, and 10b.**

Diaziridine **15** is also formed in low yield from the reaction of diazirine **12** and *trans*-DEAD (eq 6). This contrasts with previous unsuccessful attempts to synthesize



(6)

diaziridines from the reaction of free carbenes with acyclic azodicarbonyl compounds, in which the carbene sources N_2CHCO_2Et and $PhHgCCl_2Br$ yielded rearranged products only.[14]

All of these reactions of **7** and **9** with electron-poor azo compounds produce large amounts of intractable material. In addition to the diaziridines and intractable material, the reaction mixtures also contain traces of methyl benzoate (or from **9**, p-$CF_3C_6H_4CO_2CH_3$), the product of oxidation of the carbene complex,[15] and either 4-methylurazole or $EtO_2CNHNHCO_2Et$, the reduction products of MTAD and DEAD, respectively.[16] Since the reaction is cleaner and the yields of diaziridines are higher from the CF_3-substituted carbene **9**, it is possible that formation of the intractable material is related to oxidation of the carbene by MTAD. An electron-withdrawing substituent on the carbene would then disfavor this process, resulting in an increased yield of diaziridines.

In conclusion, we have demonstrated that electron-poor azo compounds can display a very different reactivity with Fischer carbenes than their electron-rich azobenzene counterparts, forming diaziridines instead of metathesis products.

Experimental Section

General Considerations. Standard inert-atmosphere techniques were used in the experiments. Diethyl ether was distilled from sodium and benzophenone. Hexane was distilled from calcium hydride. Acetonitrile was distilled from phosphorus pentoxide. All NMR solvents were degassed by three freeze–pump–thaw cycles. CD_3CN and $CDCl_3$ were stored over 3-Å molecular sieves in an inert-atmosphere box.

$(CO)_5W{=}C(OMe)Ph$ was prepared according to Fischer.[8] $(CO)_5W{=}C(OMe)(p\text{-}CF_3C_6H_4)$ was prepared by the same method as its chromium congener.[17] Phenylbromodiazirine was prepared according to a procedure by Graham,[10b] and phenylmethoxydiazirine was prepared by a modification of Moss' procedure.[10a] 4-Methyl-1,2,4-triazoline-3,5-dione and diethyl azodicarboxylate were purchased from Aldrich.

^1H and ^{13}C NMR spectra were recorded on a Varian XL-400 spectrometer. NOE difference spectra were recorded on a Varian 300 Gemini spectrometer. IR spectra were recorded on an IBM IR/90 FTIR spectrometer. FAB high-resolution mass spectra for **8a** were performed at the University of California, Berkeley. FAB high-resolution mass spectra for **8b, 10a,** and **10b** were performed at the Midwest Center for Mass Spectrometry, an NSF Regional Instrumentation Facility at the University of Nebraska. High-resolution EI spectra for **15** were performed by the Mass Spectrometry Facility, University of California, San Francisco.

Photolyses were performed at room temperature in 5-mm NMR tubes or a 100-mL Pyrex photochemical reactor with a Hanovia medium-pressure mercury-vapor lamp in a Pyrex immersion well.

6-Phenyl-6-methoxy-3-methyl-1,3,5-triazabicyclo[3.1.0]hexane-2,4-dione (8a and 8b). $(CO)_5W{=}C(OMe)Ph$ (197 mg, 0.444 mmol) and 4-methyl-1,2,4-triazoline-3,5-dione (44 mg, 0.39 mmol) were dissolved in 4 mL of CH_3CN, and the solution was stirred for 24 h. The solution turned from red to reddish black within 10 min. Additional MTAD (33 mg, 0.292 mmol) was added and the solution stirred for an additional 12 h. The volume of solution was concentrated, and the crude diaziridines were purified by flash chromatography on freshly activated silica under nitrogen. A solvent gradient of 0% ether in hexane to 100% ether in hexane was used to afford partial separation of the desired isomeric diaziridines as white solids in a combined isolated yield of 10.6%, based on the initial amount of carbene used. Cleaner separation

(12) Diaziridines are known to cleave hydrolytically into carbonyl derivatives and substituted hydrazines. Heine, H. W. In *Small Ring Heterocycles: Azetidines, β-Lactams, Diazetidines, Diaziridines*, Hassner, A., Taylor, E. C., Eds.; Wiley: New York, 1983; pp 411–415.

(13) Imidate **16** was identified by comparison to an authentic sample. Allmann, R.; Krestel, M.; Kupfer, R.; Würthwein, E.-U. *Chem. Ber.* **1986**, *119*, 2444-2457.

(14) Reference 12, pp 555–557.

(15) Chan, K. S.; Wulff, W. D. *J. Am. Chem. Soc.* **1986**, *108*, 5229–5236.

(16) 4-Phenyl-1,2,4-triazoline-3,5-dione (PTAD) is known to oxidize alcohols to aldehydes and ketones. In this reaction PTAD is reduced to 4-phenylurazole. Cookson, R. C.; Stevens, I. D. R.; Watts, C. T. *J. Chem. Soc., Chem. Commun.* **1966**, 744.

(17) Fischer, E. O.; Kreiter, C. G.; Kollmeier, H. J.; Müller, J.; Fischer, K. D. *J. Organomet. Chem.* **1971**, *28*, 237–258.

of **8a** and **8b** can be achieved by further chromatography.

The NMR yield was determined from a CD_3CN solution containing $(CO)_5W{=}C(OMe)Ph$ (60 mg, 0.14 mmol) and 4-methyl-1,2,4-triazoline-3,5-dione (18 mg, 0.16 mmol). After 24 h, no MTAD remained. Additional MTAD (10 mg, 0.088 mmol) was added. After 12 h, only 4% of the carbene remained unreacted and the diaziridines **8a** and **8b** were formed in a combined yield of 13% based on the amount of carbene consumed.

Major isomer: ^1H NMR ($CDCl_3$) δ 2.91 (s, 3 H, CH_3), 3.88 (s, 3 H, OCH_3), 7.43 (m, 3 H, Ph), 7.83 (m, 2 H, Ph); ^{13}C NMR ($CDCl_3$) δ 150.39 (C=O), 134.18 (C_{ipso}), 130.56 (Ph), 128.58 (Ph), 126.55 (Ph), 102.03 (C6), 53.51 (OMe), 25.47 (Me); IR (CH_3CN) ν_{CO} 1742 cm^{-1}. HRMS (FAB) m/e Calcd for MH^+ ($C_{11}H_{12}N_3O_3$): 234.0879. Found: 234.0877.

Minor isomer: ^1H NMR ($CDCl_3$) δ 2.91 (s, 3 H, CH_3), 3.85 (s, 3 H, OCH_3), 7.43 (m, 3 H, Ph), 7.83 (m, 2 H, Ph); ^{13}C NMR ($CDCl_3$) δ 150.41 (C=O), 134.48 (C_{ipso}), 130.58 (br, Ph), 128.59 (br, Ph), 126.45 (br, Ph), 101.48 (C6), 53.20 (OMe), 25.48 (Me); IR (CH_3CN) ν_{CO} 1743 cm^{-1}. HRMS (FAB) m/e Calcd for MH^+ ($C_{11}H_{12}N_3O_3$): 234.0879. Found: 234.0888.

6-[(*p*-Trifluoromethyl)phenyl]-6-methoxy-3-methyl-1,3,5-triazabicyclo[3.1.0]hexane-2,4-dione (10a and 10b). $(CO)_5W{=}C(OMe)(p\text{-}CF_3C_6H_4)$ (65 mg, 0.13 mmol) and 4-methyl-1,2,4-triazoline-3,5-dione (14.3 mg, 0.127 mmol) were dissolved in 1 mL of CH_3CN. The solution turned from dark red to dark reddish black within minutes. The solution was left for 12 h. No further MTAD was added. Flash chromatography (0% ether in hexanes to 100% ether to 20% CH_3CN in ether) afforded separation of the isomeric diaziridines. After chromatography, the major isomer was contaminated with $(CO)_5W(CH_3CN)$. Photolysis of the mixture in $CHCl_3$ for 1 h converted the metal complex into a blue precipitate. Filtration to remove the blue solid and evaporation of the filtrate yielded the clean diaziridine. The combined isolated yield for the white solids **10a** and **10b** was 22% based on the initial amount of carbene used.

The NMR yields were determined on a CD_3CN sample containing $(CO)_5W{=}C(OMe)(p\text{-}CF_3C_6H_4)$ (49 mg, 0.095 mmol) and 4-methyl-1,2,4-triazoline-3,5-dione (11.3 mg, 0.10 mmol). After 5.5 h, 30% of the carbene remained unreacted and no MTAD remained. The diaziridines **10a** and **10b** were formed in a 50% yield (based on consumed carbene).

Major isomer: ^1H NMR ($CDCl_3$) δ 2.93 (s, 3 H, CH_3), 3.88 (s, 3 H, OCH_3), 7.70 (d, 2 H, Ph) 7.96 (d, 2 H, Ph); ^{13}C NMR ($CDCl_3$) δ 150.14 (C=O), 137.48 (C_{ipso}), 132.59 (q, *p*-Ph, $^2J_{CF}$ = 32.8 Hz), 127.14 (br, Ph), 125.71 (br, Ph), 123.58 (q, CF_3, $^1J_{CF}$ = 272.5 Hz), 101.30 (C6), 53.62 (OMe), 25.63 (Me); IR (CH_3CN) ν_{CO} 1745 cm^{-1}. HRMS (FAB) m/e Calcd for MLi^+ ($C_{12}H_{10}N_3O_3F_3Li$): 308.0834. Found: 308.0838.

Minor isomer: ^1H NMR ($CDCl_3$) δ 2.94 (s, 3 H, CH_3), 3.87 (s, 3 H, OCH_3), 7.72 (d, 2 H, Ph), 7.96 (d, 2 H, Ph); ^{13}C NMR ($CDCl_3$) δ 150.18 (C=O), 137.90 (C_{ipso}), 132.63 (q, *p*-Ph, $^2J_{CF}$ = 32.5 Hz), 127.13 (br, Ph), 125.77 (br, Ph), 123.57 (q, CF_3, $^1J_{CF}$ = 272.7 Hz), 100.88 (C6), 53.38 (OMe), 25.65 (Me); IR (CH_3CN) ν_{CO} 1745 cm^{-1}. HRMS (FAB) m/e Calcd for MH^+ ($C_{12}H_{11}N_3O_3F_3$): 302.0753. Found: 302.0749.

Diethyl 3-Methoxy-3-phenyldiaziridine-1,2-dicarboxylate (15). In an inert-atmosphere box a 100-mL photochemical reactor was charged with 50 mL of CH_3CN solution containing $(CO)_5W{=}C(OMe)Ph$ (1.03 g, 2.3 mmol) and diethyl azodicarboxylate (0.422g, 2.4 mmol). After 10.75 h of photolysis at room temperature, the solution turned from red to black and all the DEAD was consumed. As the compound is extremely water-sensitive, both the workup and the column chromatography were performed in an inert-atmosphere box. The solvent was concentrated in vacuo to a volume of 3 mL. Addition of 40 mL of 1:1 ether:hexane precipitated out some of the oligomer as a black oil. The solution was filtered and the oil washed well with ether. The washings were combined with the filtrate, and the solvent was removed in vacuo. Flash chromatography on activated silica (5% ether in hexane to 100% ether) produced 106 mg of a dark oil, which contained the diaziridine in 50% purity by ^1H NMR spectroscopy. The dark oil was dissolved in CH_3CN and passed through a small frit containing alumina, and the alumina was rinsed well with ether. The filtrate and washings were combined and the solvent removed in vacuo. Further purification by repeated chromatography on silica afforded cleaner samples of the diaziridine **15** in much reduced yield. A pure sample (5.8 mg, 0.9% yield based on initial amount of carbene used) of **15** was isolated as a dark yellow oil. Another fraction containing 8.9 mg of **15** in a purity of 74% (determined by ^1H NMR analysis) was also obtained.

The NMR yields were determined on a sample containing $(CO)_5W{=}C(OMe)Ph$ (30 mg, 0.068 mmol) and diethyl azodicarboxylate (12 mg, 0.069 mmol) in CD_3CN. After 12 h of photolysis at room temperature, 35% of the carbene remained unreacted and the diaziridine **15** was formed in 18% yield (based on the amount of carbene consumed). The imidate **16** was formed in 3% yield.

^1H NMR (CD_3CN, 75.1 °C): δ 1.05 (t, 3 H, CH_3), 1.41 (t, 3 H, CH_3), 3.47 (s, 3 H, OMe), 4.02 (q, 2 H, CH_2), 4.37 (q, 2 H, CH_2), 7.42 (m, 3 H, Ph), 7.55 (m, 2 H, Ph). ^{13}C NMR ($CDCl_3$, 18 °C): δ 156.66 (C=O), 150.66 (C=O), 136.42 (br, C_{ipso}), 129.68 (Ph), 127.91 (Ph), 125.98 (Ph), 115.13 (C3), 67.64 (CH_2), 61.85 (br, CH_2), 50.13 (OMe), 14.13 (CH_3), 14.01 (br, CH_3). IR (CH_3CN) ν_{CO} 1674 cm^{-1}; HRMS(EI): m/e Calcd for M^+ ($C_{14}H_{18}N_2O_5$): 294.1216. Found 294.1203.

Reaction of Phenylmethoxydiazirine with Diethyl Azodicarboxylate. Phenylmethoxydiazirine was generated in solution from phenylbromodiazirine by using a modification of the literature procedure.[10a] Sodium methoxide was freshly prepared by mixing small pieces of sodium (0.14 g, 6 mmol) with dry absolute methanol (3–5 mL). The mixture was stirred at 0 °C until no more sodium remained and then the excess methanol was removed in vacuo. Dimethylacetamide (DMA, 3 mL) and hexamethylphosphoric triamide (HMPA, 3 mL) were added and the solution was cooled to −10 °C. Phenylbromodiazirine (0.40 g, 2.0 mmol) in 0.5 mL of DMA was added slowly. After the reaction mixture had stirred at −10 °C for 1 h, 15 mL of ice cold water and 10 mL of acetonitrile were added to quench the HMPA and the greenish yellow diaziridine was extracted three times with 10 mL of cooled petroleum ether. The combined extracts were washed with ice cold water and dried over anhydrous $MgSO_4$. The solvent was concentrated to a volume of 5 mL, while the temperature was kept at −10 °C. DEAD (0.122 g, 0.7 mmol) was added to the solution of phenylmethoxydiazirine, and the solution was stirred overnight at room temperature to yield the diaziridine **15** in 5% (by NMR analysis) overall yield from phenylbromodiazirine.

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