Table I. Frequency Changes of Lipid LB Films (30 layers) at the Phase Transition Temperature (T_c) on the QCM in a Water Phase[a]

LB films	T_c^b/°C	$\Delta\Delta F$/Hz
$2C_{18}OH$	53	1800 ± 150
$2C_{18}COOH$	50	1500 ± 100
$2C_{18}$-glu-NH_3^+	52	1200 ± 100
$C_{18}OH$	55	1500 ± 100
$C_{17}COOEt$	33	1700 ± 100
$2C_{18}Si^c$	44^e	0
$2C_{18}$-glu-N^+3C_1/PSS^{-d}	45^e	0

[a] Temperatures were raised at a rate of 1.5 °C min^{-1}. [b] The temperature where the frequency increased abruptly, which was consistent with T_c obtained from DSC measurements. [c] $2C_{18}Si$ monolayers were polymerized on the acidic subphase, and the polymeric monolayers were transferred on the QCM substrate. [d] $2C_{18}$-glu-N^+3C_1 monolayer was spread on the subphase containing PSS^- polyanions and transferred as the polyion complex LB films of $2C_{18}$-glu-N^+3C_1/PSS^-. [e] Obtained from DSC measurements.

$2C_{18}COOH$, and $2C_{18}$-glu-NH_3^+ and of monoalkyl type $C_{17}COOEt$ and $C_{18}OH$ showed the clear frequency increase at the respective T_c in the water phase ($\Delta\Delta F$ = 1200–1800 Hz). Thus, the swelling and slipping behaviors of LB films in the water phase due to the phase transition are general phenomena which can be detected from the frequency change of the QCM. However, when the cationic $2C_{18}$-glu-N^+3C_1 monolayer was spread on the subphase containing poly(styrenesulfonate) (PSS^-) polyanions and transferred as a polyion complex LB films of $2C_{18}$-glu-N^+3C_1/PSS^- on the QCM,[22] the frequency change was not observed at the respective T_c (45 °C obtained from DSC measurements). When γ-(*N*,*N*-dioctadecylsuccinylamino)propyltriethoxysilane ($2C_{18}Si$) is spread on the acidic aqueous solution, the $2C_{18}Si$ monolayer can be easily polymerized on the subphase with a Si–O–Si linkage and can be transferred as polymeric Y-type LB films covalently crosslinked between interlayers.[17] In the case of the polymeric $2C_{18}Si$ LB films deposited on the QCM, the frequency enhancement was not observed at T_c although a sharp endothermic peak was observed at 44 °C by DSC measurements of aqueous dispersion of polymeric $2C_{18}Si$ LB films. Since these LB films are polymerized with polymeric counter ions or Si–O–Si linkages between interlayers near the hydrophilic head groups, the slipping behavior (the frequency increase at T_c) is difficult to occur at the fluid state, although the melting of alkyl chains occurs at the respective T_c.

Summary

Although characterizations of LB films in aqueous solutions are difficult to study because of the limitations of measurement methods, the quartz-crystal microbalance (QCM) can detect directly that LB films do not peel from the substrate in the water phase and that the swelling and the slipping behaviors between interlayers occur in the fluid liquid crystalline state above T_c of LB films. The QCM is a useful tool to characterize the LB films in air and water phases. This is the first example to show that QCM can detect the fluidity change of coating well-oriented layered materials such as LB films in addition to the frequency change due to the mass increase on the electrode.

Registry No. $C_{17}COOEt$, 111-61-5; $C_{18}OH$, 112-92-5; $2C_{18}OH$, 18794-74-6; $2C_{18}COOH$, 37519-63-4; $2C_{18}$-glu-NH_3^+, 123726-22-7; $2C_{18}$-glu-N^+3C_1, 123726-24-9; $2C_{18}Si$, 105442-22-6.

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[22] Higashi, N.; Kunitake, T. *Chem. Lett.* **1986**, 105.

The Course of the Reaction of Azobenzene with Chromium Carbene Complexes

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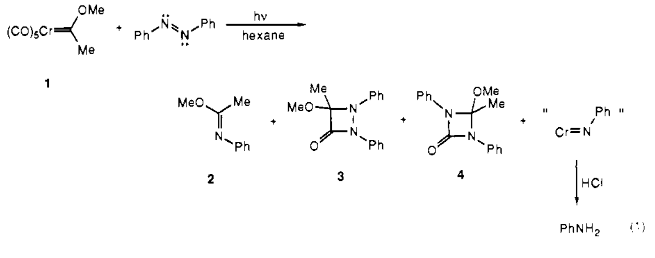
Abstract: The dark reaction between *cis*-azobenzene and pentacarbonyl[(methoxy)(methyl)carbene]chromium(0) was followed by ^1H NMR spectroscopy. The intervention of two discrete intermediates—thought to be a zwitterion and a metallacycle—was detected. Carrying out the reaction in hexane under a carbon monoxide atmosphere caused the reaction to stop at the metallacycle stage. Photolytic decomposition of this produced 1,3-diazetidinone and imidate products, as well as small amounts of azobenzene. 1,2-Diazetidinone products were thought to result from a primary photoreaction between *cis*-azobenzene and a photogenerated (methoxy)(methyl)ketene chromium complex.

Several years ago, an unusual photoreaction between azobenzene and chromium carbene complexes to produce metathesis products and cyclocarbonylation products (eq 1) was reported from these laboratories.[1] At that time, a mechanism involving a 2 + 2 photocycloaddition of the azobenzene to the carbene to give a diazachromacyclobutane, followed by fragmentation and/or CO insertion, was advanced. Subsequent studies have shown that photolysis of carbene complexes such as **1** promotes a reversible CO insertion into the chromium–carbene bond to produce a metal-bound ketene,[2] a process that cannot account for the products observed in eq 1. This prompted a careful investigation of this reaction, the results of which are reported below.



(1)

Results and Discussion

A mechanistic scheme for the reaction in eq 1 must accommodate the following observations. (1) The reaction between *trans*-azobenzene and the carbene complex **1** does *not* occur in

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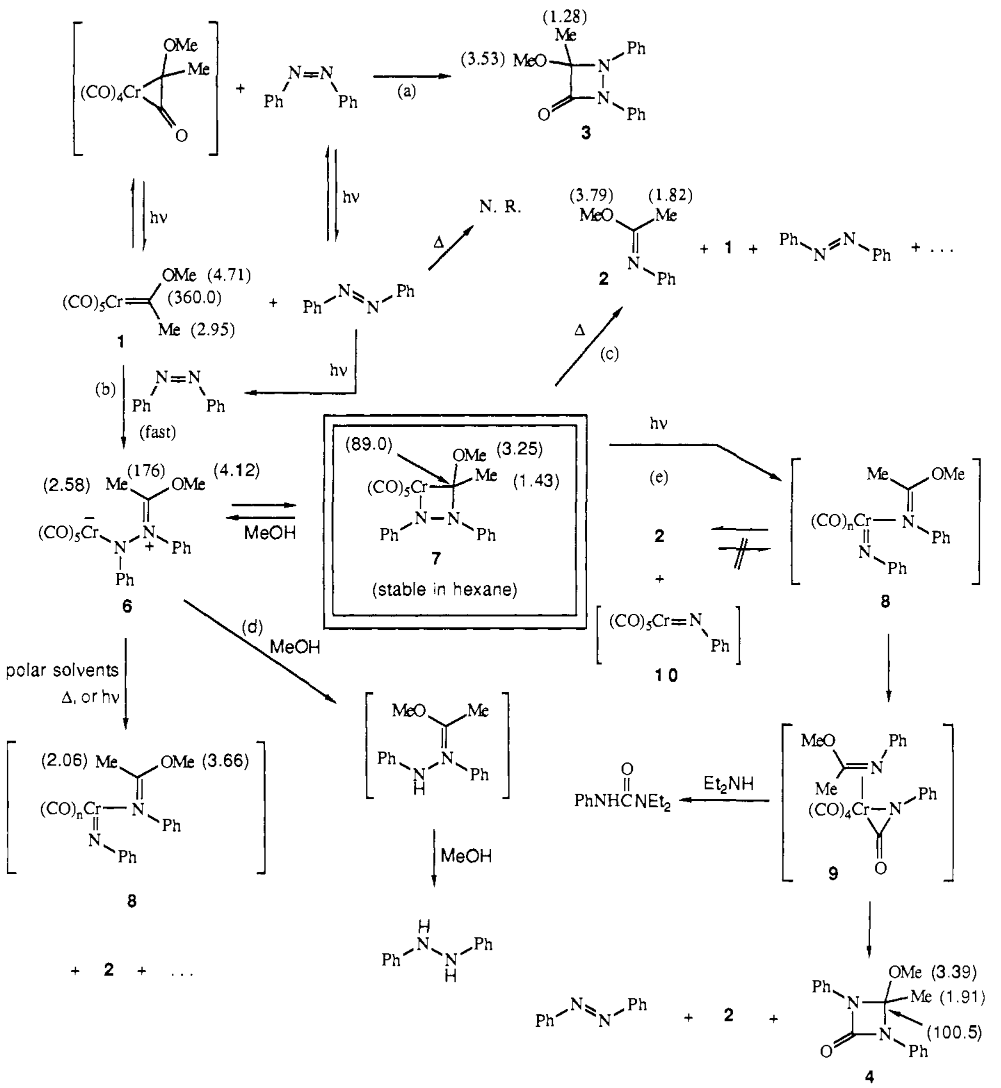
[1] Hegedus, L. S.; Kramer, A. *Organometallics* **1984**, *3*, 1263.

[2] Hegedus, L. S.; deWeck, G.; D'Andrea, S. *J. Am. Chem. Soc.* **1988**, *110*, 2122.

Scheme I



the absence of visible light irradiation. (2) The product distribution is strongly dependent on the solvent polarity, the temperature, and the intensity of the light. Metathesis products (imidate **2**) predominate at higher temperatures and light intensities, and 1,3-diazetidinone (**4**) predominates at lower temperatures and light intensities. (3) Azobenzenes bearing electron-donating substituents such as *p*-methoxy- or *p*-dimethylamino groups are more reactive than azobenzene itself, and *p*-nitroazobenzene does not react at all. (4) With 4-methoxyazobenzene, the imidate formed contained *only* the *unsubstituted* portion of the azobenzene (PhN, not *p*-MeOPhN) and the only cyclic product was 1,3-diazetidinone (**4**). (5) With azobenzene-d_5, no scrambling was observed.

Initially it was assumed that the reaction in eq 1 involved a *primary* photoreaction between azobenzene and carbene **1**, much as the related photoreactions of imines with chromium carbenes to produce β-lactams.[2] However, azobenzene undergoes a facile trans to cis isomerization when irradiated in the same wavelength range as that used for the reaction in eq 1.[3] Hence, the reactivity of *cis*-azobenzene with carbene **1** in the dark was first examined.

Treatment of *cis*-azobenzene with an equivalent amount of complex **1** in hexane produced *trans*-azobenzene as the major product. Even catalytic amounts (~5%) of complex **1** isomerized *cis*-azobenzene rapidly. Thus, it seemed likely that this isomerization resulted from conversion of small amounts of **1** to an unsaturated species and isomerization of *cis*-azobenzene by that unsaturated species. Indeed, isomerization was almost completely suppressed by saturation of solutions of **1** with carbon monoxide, to trap any unsaturated species produced, prior to addition of *cis*-azobenzene. Under these conditions, another reaction ensued. Within 3–5 h at 25 °C, at 100 psi CO, and in the dark, the azobenzene was consumed. Examination of the crude reaction after solvent removal by ^{1}H NMR spectroscopy showed a *single* major compound (**7**) whose NMR spectrum was different from any starting material or product observed in eq 1. Only minor amounts of carbene **1** and a corresponding amount of *trans*-azobenzene remained. Infrared spectroscopy indicated the presence of a chromium carbonyl fragment (ν_{CO}, 2063, 1939 cm^{-1}).

This compound was somewhat unstable and decomposed upon all attempts at purification. Gentle thermal decomposition (40 °C) of the hexane solution of **7** produced imidate **2**, regenerated carbene **1**, and azobenzene and produced a number of unidentified organic compounds as evidenced by a series of multiplets in the ^{1}H NMR spectrum ranging from 0.8 to 4.5 ppm. Photolysis of the hexane solution produced *trans*-azobenzene and a 1:1 mixture of imidate **2** and 1,3-diazetidinone (**4**). Reaction of this complex with methanol or using methanol as the solvent for the reaction between *cis*-azobenzene and complex **1** resulted in the production of hydrazobenzene. 1,2-Diazetidinone (**3**) was never observed in any of these reactions. To gain insight into this process, the reaction between *cis*-azobenzene and complex **1** was run in $CDCl_3$ and followed by ^{1}H NMR spectroscopy and by ^{13}C NMR spectroscopy using carbene complex **1** prepared from ^{13}C-enriched $Cr(CO)_6$, to permit unequivocal tracking of the carbene carbon throughout this process. Scheme I summarizes the observations from this experiment and provides a coherent explanation consistent with both the spectroscopic studies and the synthetic studies.

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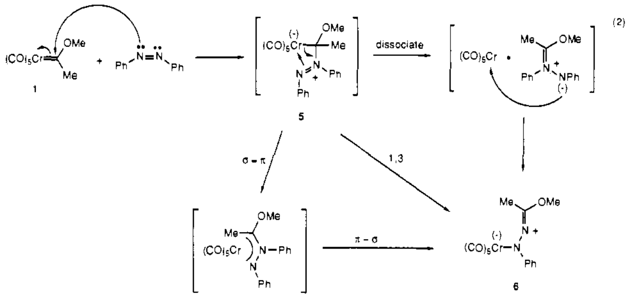
(3) Cook, A. H. *J. Chem. Soc.* **1938**, 876.

Recall that 1,2-diazetidinone *only* results from the photolytic reaction starting with *trans*-azobenzene and carbene complex **1** and that photolysis of **1** drives a reversible CO insertion to produce a metal-bound ketene.[2] Ketenes react with cis azo compounds to give 1,2-diazetidinones,[4] and thus 1,2-diazetidinone (**3**) results from the reaction of photogenerated *cis*-azobenzene with a photochemically generated chromium ketene complex (path a). The reaction with *preformed cis*-azobenzene takes a quite different course, as evidenced from the NMR study.

Addition of *cis*-azobenzene to carbene complex **1** (δ 2.95, 4.71) led to the immediate appearance of a new set of singlets (δ 2.58, 4.12) considerably upfield from the starting complex. The ^{13}C signal for the carbene carbon moved from δ 360 to δ 176. These peaks were originally assigned to zwitterion **5** (eq 2), resulting from nucleophilic attack of *cis*-azobenzene on the electrophilic carbene carbon of complex **1**. There is extensive precedent for this type of nucleophilic attack at the carbene carbon of **1**,[5] with the recently reported insertion of nitriles into complex **1** being the closest parallel.[6] However, recent, careful studies of the related [(methoxy)(methyl)carbene]tungsten/*cis*-azobenzene reaction[7] using ^{13}C-labeled carbene *and* ^{15}N-labeled azobenzene indicate that the first-detected intermediate is zwitterion **6** not zwitterion **5**. In the tungsten case, zwitterion **6** (M = W, not Cr) was stable and was fully characterized by multinuclear NMR studies. Its NMR spectra (CDCl$_3$, ^{1}H δ 2.50 and 4.12 vs 2.58 and 4.12 for Cr; ^{13}C δ 14.9, 59.3, and 176.1 vs 15.3, 60.3, and 176.0 for Cr—similar correspondence is seen in benzene-d_6) and virtually identical with those observed for **6** (M = Cr), and the connectivity must be the same. The mode of formation of **6** is unknown. Three paths involving either dissociation/recombination, 1,3-allyl transposition, or σ–π–σ rearrangement are presented in eq 2. In the tungsten case,[7] a pathway involving a metallacyclic intermediate such as **7** was proposed but is unlikely in the chromium system.



In marked contrast to the tungsten case, this initially formed zwitterion **6** was short-lived, and within ~20 min, it was completely gone, to be replaced by a new complex, (^{1}H δ 1.43, 3.25) assigned to be metallacycle **7** on the basis of both its spectra and its reactivity. (Since **6** rapidly converts to metallacycle **7**, it is not reasonable to propose **7** as a *precursor* to **6**.) The chemical shift of the (former) carbene carbon is most informative, appearing at δ 89.0, considerably upfield from that expected for any sp^2-hybridized carbon but well within the range for an sp^3-hybridized carbon having three heteroatoms attached to it (see diazetidinone **4**, for example). Complexes of the type [(CO)$_5$MC(OMe)(R)(Z)] (M = Cr, W; R = Me, Ph; Z = Me, Ph, PMe$_3$) contain similarly substituted sp^3 carbon atoms, and these all appear between δ 82 and 95.[8] This complex persisted in nonpolar solvents such as hexane, which do not stabilize charge-separated species. Although **7** has resisted purification, it is sufficiently stable to assess its reactivity. Thermal decomposition in a variety of solvents produced imidate **2**, azobenzene, carbene **1**, and many other unidentified compounds (path c). Imidate **2** is the expected product of a metathesis reaction. Addition of methanol to **7** or running the reaction of *cis*-azobenzene with **1** in methanol produced hydrazobenzene as the major organic product (path d). Polar solvents should promote reopening of metallacycle **7** to zwitterion **6**. Protonolysis of the chromium–nitrogen bond and solvolysis of the imidate terminus would produce hydrazobenzene.

Photolysis of **7** produced some azobenzene and a 1:1 mixture of imidate **2** and 1,3-diazetidinone (**4**) (path e). Photolytically driven metathesis can produce either azobenzene and the starting carbene or, alternatively, the imidate–nitrene complex **8**. Photodriven insertion of CO into the chromium–nitrene bond would produce a coordinated isocyanate. Reaction of coordinated imidate with coordinated isocyanate within complex **9** would produce the observed 1,3-diazetidinone but *not* 1,2-diazetidinone; hence, its absence from this product manifold. This reaction is thought to occur in the coordination sphere of the metal from **8**, since free imidate does not react with free phenyl isocyanate. Ejection of imidate before CO insertion would produce the observed free imidate **2** and a "chromium nitrene" residue, which produces aniline upon protonation.[1] Once lost from coordination, free imidate *cannot* reenter the reaction manifold, hence the observed lack of scrambling when labeled azobenzene was used.[1] Evidence for the production of metal-bound isocyanate in the photolytic decomposition of **6** was obtained by addition of excess diethylamine to **7** prior to photolysis. This resulted in the production of substantial amounts of diethylphenylurea, from trapping of the isocyanate by diethylamine.

In polar solvents, (including deuteriochloroform), **7** continued to react. Over the course of ~4 h, compound **7** disappeared to be replaced mainly by imidate **2**. In addition, a small amount of a new species (δ 2.06, 3.66) appeared and persisted. This species, tentatively assigned as complex **8**, also converted to imidate **2** and other unidentified organic products upon standing or heating.

Scheme I accommodates all of the NMR spectroscopic data as well as all of the chemical observations made in the initial synthetic studies.[1] Hexane was the best solvent for the production of 1,3-diazetidinone **4** because metallacycle **7**, the precursor to **4**, was most stable in that solvent. More polar solvents promoted conversion of **7** to imidate **2** perhaps via complex **8**. The lack of reactivity of more nucleophilic carbenes (e.g., (CO)$_5$Cr=C(H)(NMe$_2$)) and less nucleophilic azobenzenes (e.g., *p*-nitroazobenzene) is consistent with the key first step involving *nucleophilic* attack of the azobenzene on the carbene complex to ultimately produce zwitterion **6**. The formation of *N*-phenylimidate **2** from the reaction of carbene **1** with mono-*p*-methoxyazobenzene as the only imidate (i.e., no *p*-methoxyphenyl imidate was found) is also consistent with formation of zwitterion **6** as a key intermediate, since attack of the *most* nucleophilic nitrogen[9] of this unsymmetrical azobenzene on the carbene complex will produce species that can *only* cleave to give the unsubstituted imidate (eq 3).

Chromium nitrene species (such as **10**, Scheme I) are obligate products of this azobenzene metathesis, but isolation and characterization of such a species has not been successful to date. Stable, mononuclear nitrene complexes of low-valent transition metals are unknown, although several triply bridging η^3-nitrene complexes have been characterized.[10] Isolation of substantial amounts of aniline by protolytic cleavage of the green chromium residue of the above reactions[1] indicates the presence of coordinated, reduced nitrogen species in the product mixture. Production

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(4) (a) Cook, A. H.; Jones, D. G. *J. Chem. Soc.* **1941**, 184. (b) Schenk, G. O.; Englehard, N. *Angew. Chem.* **1956**, *68*, 71.

(5) Kreissl, F. R. In *Transition Metal Carbene Complexes*; Seyfert, D., Ed.; Verlage Chemie: Deer Beach, FL, 1983; pp 152–166.

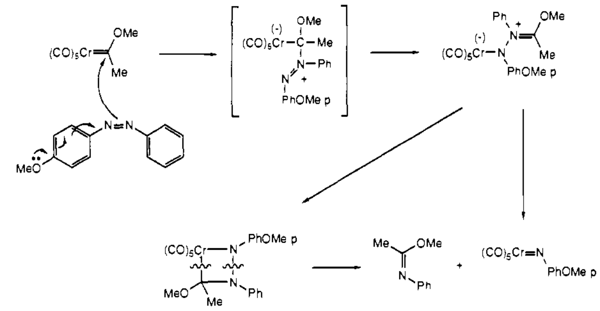
(6) Yang, D. C.; Dragisich, V.; Wulff, W. D.; Huffman, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 307. For other examples of insertions into carbene complexes involving zwitterionic intermediates, see: Kreiter, C. G.; Aumann, R. *Chem. Ber.* **1978**, *111*, 1223.

(7) Sleiman, H. F.; McElwee-White, L. *J. Am. Chem. Soc.* **1988**, *110*, 8700. We thank Professor McElwee-White for making this information available prior to publication and for suggesting the role of zwitterions in this process.

(8) (a) Fischer, E. O.; Held, W.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 3842. (b) Fischer, E. O.; Held, W.; Kreissl, F. R.; Frank, A.; Huttner, G. *Chem. Ber.* **1977**, *110*, 656.

(9) Rodgers, M. T.; Campbell, T. W.; Maatman, R. W. *J. Am. Chem. Soc.* **1951**, *73*, 5122.

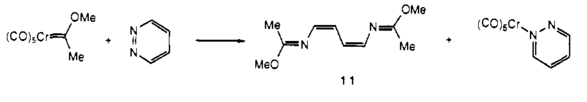
(10) For a review see: Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.



(3)

of ureas in path e, Scheme I, similarly argues for the production of chromium nitrene species in this metathesis process. Bridging nitrene complexes have been isolated and characterized in the reaction between azobenzene and $Nb_2Cl_6(Me_2S)_3$.[11] The triply bridging nitrene complex $Ru_3(ArN)(CO)_{10}$ underwent reaction with azoarenes to result in azometathesis along with the production of aryl isocyanates.[12] This same complex transferred its nitrene to alkynes and carbon monoxide to produce pyridones or maleimides.[13]

Carbene complex **1** is highly reactive to other cis azo compounds as well. Simply adding solid diazo[2.2.1]bicycloheptane to solid **1** resulted in ignition and fire. Addition of an ether solution of **1** to an ether solution of this diazo compound at −78 °C resulted in rapid (1 h) consumption of the carbene, but no identifiable organic compounds could be isolated from the reaction mixture. In contrast, pyridizine underwent smooth reaction with carbene **1** in THF in the dark to give a mixture of pyridazine–$Cr(CO)_5$ and bis-imidate **11** (eq 4). In this case, a different path must have been followed, since production of bis-imidate **11** from intermediates in Scheme I would require somewhat unorthodox species and reactions. Further, this reaction is *completely* suppressed by modest pressures of carbon monoxide, implying prior coordination of pyridizine.



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(4)

Efforts to control and direct in a synthetically useful manner the high reactivity of chromium carbene complexes toward azo compounds continue.

Experimental Section

General Procedures. Melting points were obtained with a Mel-Temp melting point apparatus and are uncorrected. Infrared spectra were recorded on a Beckman 4240 spectrophotometer. ^1H NMR spectra at 200 MHz were recorded on an IBM-Bruker WP 200 spectrometer. ^1H NMR spectra at 270 MHz were recorded on an IBM-Bruker WP 270 spectrometer. ^1H NMR spectra at 300 MHz were recorded on an IBM-Bruker ACE 300 spectrometer. All ^{13}C NMR (75-MHz) spectra were recorded on a IBM-Bruker ACE 300 spectrometer. All NMR spectra were obtained using $CDCl_3$ as solvent and Me_4Si as standard, unless otherwise noted. Mass spectra were recorded on a VG-Micromass 16F spectrometer.

Most chromatographic separations were accomplished by radial-layer chromatography with a Chromatotron Model 7924 and using silica gel 60 PF_{254} as adsorbent. All other chromatographic separations were performed on aluminum oxide (J. T. Baker, neutral Al_2O_3).

Materials. All solvents were freshly distilled, degassed, and saturated with argon immediately prior to use. Diethyl ether (ASP, analytical reagent) was predried over CaH_2, heated at reflux over benzophenone ketyl, and distilled from benzophenone ketyl under an N_2 atmosphere at atmospheric pressure. Diethylamine (Aldrich, reagent grade) was refluxed over and distilled from KOH at atmospheric pressure. Tetrahydrofuran (Fisher, reagent grade) was heated at reflux over benzophenone ketyl, and distilled from benzophenone ketyl under an N_2 atmosphere at atmospheric pressure. Hexane (technical grade) was distilled at atmospheric pressure. Ethyl acetate (technical grade) was heated at reflux over and distilled from CaH_2 under N_2 at atmospheric pressure. Methylene chloride was heated at reflux over and distilled from CaH_2 under N_2 at atmospheric pressure or filtered through aluminum oxide (5 g/100 mL).

Chromium hexacarbonyl (Pressure Chemicals), trimethyloxonium tetrafluoroborate (Lancaster Synthesis Ltd.), azobenzene (Eastman Kodak), pyridazine (Aldrich), methanol (EM Science), Celite (J. T. Baker, 503), and chloroform-*d* (Cambridge Isotope Laboratories) were used as received. Pentacarbonyl[(methoxy)(methyl)carbene]chromium(0)[14] (**1**), *cis*-azobenzene,[15] methyl *N*-phenylacetimidate,[16] 2,3-diazabicyclo[2.2.1]hept-2-ene,[17] and 1,1-diethyl-3-phenylurea[18] were prepared by literature procedures. ^{13}C-Enriched pentacarbonyl[(methoxy)(methyl)carbene]chromium(0) was prepared from ^{13}C-enriched chromium hexacarbonyl.[19]

Reaction of 1 with *cis*-Azobenzene under an Inert Atmosphere. A 100-mL Airless-ware flask was equipped with a magnetic stirring bar and a rubber septum. The flask was flame-dried under vacuum and cooled under argon. When cool, the flask was charged with carbene complex **1** (0.12 g, 0.50 mmol) dissolved in 50 mL of distilled hexane, evacuated, filled with argon (three cycles), and covered with aluminum foil. Solid *cis*-azobenzene (0.09 g, 0.50 mmol) was then added to the stirring solution of the carbene complex. The reaction flask was again evacuated and filled with argon (two cycles). The reaction was allowed to proceed for 2 h at which time the solvent was removed from the reaction mixture under reduced pressure (water aspirator). The red/brown residue was further dried under vacuum. The reaction mixture was separated on a 2-mm SiO_2 Chromatotron plate (hexane/Et_2O 5:1) to give *trans*-azobenzene (56.1 mg, 0.31 mmol, 61.7%).

Reaction of a Catalytic Amount of 1 with *cis*-Azobenzene. A 25-mL round-bottom flask equipped with a magnetic stirring bar was flame-dried and cooled under argon. The flask was charged with *cis*-azobenzene (0.04 g, 0.21 mmol) dissolved in 15 mL of hexane. The flask was then evacuated and filled with argon (three cycles). A catalytic amount of the carbene complex **1** (3.7 mg, 0.01 mmol) was added to the stirring solution of the azobenzene. Analytical TLC (SiO_2, hexane/Et_2O 5:1) showed that within 15 min all of the azobenzene had isomerized from cis to trans. After the solvent was removed from the reaction mixture under vacuum, the ^1H NMR spectrum of the crude reaction mixture confirmed that only *trans*-azobenzene was present.

Reaction of 1 with *cis*-Azobenzene under CO Pressure: Generation of 7 (Scheme I). General Procedure. A 300-mL Fisher-Porter bottle was equipped with a magnetic stirring bar, and 200 mL of hexane was added. The hexane was saturated with CO by charging the flask to 100 psi, stirring for 10 min, and releasing the pressure (three cycles). The CO-saturated hexane was charged with carbene complex **1** (0.62 g, 2.45 mmol), and the solution was again charged with CO to 100 psi. The pressure was released, solid *cis*-azobenzene (0.37 g, 2.05 mmol) was added to the stirring solution of the carbene, and the flask was again charged to 100 psi with CO. After the solution stirred for 1 h at room temperature, a 2.0-mL aliquot was removed from the red homogeneous mixture and the solvent was removed under vacuum. ^1H NMR (270 MHz) δ: 1.43, 3.25 (s, s, CH_3, OCH_3, 6 H, **7**), 2.95, 4.71 (s, s, CH_3, OCH_3, 6 H, **1**), 7.52, 7.95 (m, m, ArH, 10 H, PhN=NPh) in a relative ratio of 2.89:1.08:1, respectively. IR (film) ν: 2063, 2007 (sh), 1938, 1669, 1596 cm^{-1}.

In each of the following reactions, the existence of **7** was confirmed by removing an aliquot from the reaction mixture and recording its ^1H NMR spectrum. In every case, the aliquot taken was identical with that described immediately above.

a. Thermolysis of 7. Carbene **1** (0.08 g, 0.33 mmol) and *cis*-azobenzene (0.05 g, 0.27 mmol) were combined in 50 mL of hexane in the manner described above. After the reaction mixture was stirred at room temperature for 5 h, the pressure was reduced to 75 psi and the vessel was immersed in an oil bath at 60 °C. The mixture was stirred at this temperature for a period of 24 h and filtered through a small pad of Celite to remove chromium residue, the solvent removed under reduced pressure (water aspirator), and the red/brown residue further dried under vacuum. The ^1H NMR spectrum (270 MHz) showed that the major

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(11) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *J. Am. Chem. Soc.* **1984**, *106*, 4749.

(12) Smieja, J. A.; Gozum, J. E.; Gladfelter, W. L. *Organometallics* **1986**, *5*, 2154.

(13) Han, S.-H; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1987**, *6*, 2380.

(14) (a) Aumann, R.; Fischer, E. O. *Chem. Ber.* **1968** *101*, 954. (b) Fischer, E. O.; Kreiter, C. G.; Fischer, R. D. *J. Organomet. Chem.* **1971**, *28*, 237.

(15) Cook, A. H. *J. Chem. Soc.* **1938**, 876.

(16) Pilotti, Å.; Reutherhäll, A.; Torssell, K. *Acta. Chim. Scand.* **1969**, *23*(3), 818.

(17) Singh, P. *J. Org. Chem.* **1975**, *40*(10), 1405.

(18) Papesch, V.; Schroeder, E. F. *J. Org. Chem.* **1951**, *16*(12), 1879.

(19) Darensbourg, D. J.; Darensbourg, M. Y.; Walker, N. *Inorg. Chem.* **1981**, *20*, 1918.

product in the crude mixture was the imidate **2** and that the mixture contained a number of unidentified products as evidenced by a series of multiplets ranging from 0.8 to 4.5 ppm.

b. Photolysis of 7. Complex **7** was generated as described above. The aliquot removed for NMR was dried under vacuum, blanketed with argon, redissolved in Al_2O_3-filtered $CDCl_3$, and transferred into an argon-filled NMR tube fitted with a rubber septum. $Me_3SiOSiMe_3$ (2.0 μL, internal standard) was added to the NMR sample, and the ^1H NMR spectrum was recorded. The sample was then irradiated (450-W lamp) at room temperature for 10 h, and centrifuged to concentrate the chromium residue that had formed during photolysis, and the ^1H NMR spectrum was recorded again. ^1H NMR (270 MHz) δ: 1.82, 3.79 (s, s, CH_3, OCH_3, 6 H, **2**), 1.91, 3.39 (s, s, CH_3, OCH_3, 6 H, **4**) in a relative ratio of 1:1.15, respectively. In addition, unresolved aromatic protons are present in the appropriate region for both **2** and **4**, δ 6.8–7.6. As expected, the relative number of aromatic to aliphatic protons is exactly 10:6.

Detailed comparison of the two ^1H NMR spectra showed that the photolysis resulted in the total consumption of complex **7** and in the generation of imidate **2** and 1,3-diazetidinone (**4**) in a ratio of 1:1.

c. Treatment of 7 with Excess MeOH. Carbene **1** (0.20 g, 0.79 mmol) and *cis*-azobenzene (0.14 g, 0.79 mmol) were allowed to react in 50 mL of hexane as described above (generation of **7**). After 2.5 h, one-half (25 mL) of the reaction mixture was removed by syringe and put into a 100-mL round-bottom flask, which was equipped with a magnetic stirring bar and which was filled with argon. Argon-saturated methanol (30 mL) was rapidly added to the stirring solution of the reaction mixture, and the solution was allowed to stir at room temperature for 14 h. The solvent was removed by water aspirator, and the mixture was separated by chromatography (Chromatotron, 2 mm thick SiO_2, hexane/Et_2O). *trans*-Azobenzene (16.2 mg, 0.09 mmol, 22.5%) and (based on consumed azobenzene) hydrazobenzene (19.6 mg, 0.11 mmol, 34.8%) were recovered. Hydrazobenzene was obtained as a white solid, mp 125–128 °C (lit. 123–127 °C).[20] Its spectral data (^1H NMR and IR) were identical in all respects with those reported in the literature,[20,21] and the mass spectrum had a parent ion at *m/e* 184. ^{13}C NMR (75 MHz) δ: 112.34 (4 *o*-C), 119.91 (2 *p*-C), 129.35 (4 *m*-C), 148.85 (2 ipso-C).

d. Photolysis of 7 in the Presence of $HNEt_2$. Complex **7** was generated as described above in 50 mL of hexane from carbene complex **1** (0.18 g, 0.72 mmol) and *cis*-azobenzene (0.13 g, 0.72 mmol). After a period of 2 h, the pressure was released from the reaction mixture and the mixture was transferred via cannula to a 100-mL Pyrex test tube. Diethylamine (50 mL) was added to the reaction mixture, the solution blanketed with argon, and the tube irradiated (450-W lamp) for a period of 18 h. The reaction mixture was filtered over a pad of Celite and then chromatographed (Chromatotron, 2 mm thick SiO_2, hexane/Et_2O 5:1, then $MeCl_2$/*i*-PrOH 20:1) to yield (based on consumed azobenzene) 1,1-diethyl-3-phenylurea as a white crystalline solid (0.04 g, 0.18 mmol, 37.9%). Spectral data (^1H NMR, IR, mass spectrum) of the isolated urea are identical in all respects with that of the authentic sample.

Reaction of 1 with *cis*-Azobenzene, an ^1H NMR Experiment. A 5-mm NMR tube was evacuated and then filled with argon (three cycles). Carbene complex **1** (12.5 mg, 0.05 mmol) was transferred into the NMR tube with $CDCl_3$ (0.3 mL), and the tube was again evacuated and filled with argon. *cis*-Azobenzene was transferred into the tube using $CDCl_3$ (0.3 mL), the tube immediately dropped into the probe, and ^1H NMR (200 MHz) spectra were recorded at regular intervals over a period of 24 h. The data are described in the text and are available as supplementary information.

Reaction of ^{13}C-Enriched 1 with *cis*-Azobenzene. a. Generation and Characterization of ^{13}C-Enriched 6. A 5-mm NMR tube was evacuated and then filled with argon (three cycles). ^{13}C-Enriched (20%) carbene complex **1** (19.9 mg, 0.08 mmol) was placed into the NMR tube and dissolved in Al_2O_3-filtered $CDCl_3$ (0.7 mL), and the tube was again evacuated and filled with argon. The tube was lowered into the NMR probe and both ^1H and ^{13}C NMR spectra were recorded at −20 °C. ^{13}C NMR (75 MHz) δ: 50.0 (CH_3), 67.7 (OCH_3), 216.3 (cis CO, enriched), 223.3 (trans CO, enriched), 360.0 (carbene C, enriched).

The sample was removed from the probe and further cooled to −78 °C. Solid *cis*-azobenzene (14.5 mg, 0.08 mmol) was added to the carbene solution at −78 °C, and the sample was immediately lowered into the probe. After the sample was allowed to equilibrate to the temperature of the probe, both ^1H and ^{13}C NMR spectra were recorded. ^1H NMR (300 MHz) δ: 2.58 (s, 3, CH_3), 4.15 (s, 3, OCH_3), 7.0–7.5 (m, 10, ArH). ^{13}C NMR (75 MHz) δ: 15.3 (CH_3), 60.3 (OCH_3), 176.0 ($\mathit{C}(CH_3)OCH_3$, enriched), 214.3 (cis CO, enriched), 221.4 (trans CO, enriched).

b. Generation and Characterization of 7. ^{13}C-Enriched (5%) carbene complex **1** (0.05 g, 0.19 mmol) was placed in a 25-mL Ace threaded pressure tube and dissolved in 20 mL of hexane. The solution was saturated with CO in the manner described above (generation of **7**). Solid *cis*-azobenzene was added, and the tube was pressurized to 100 psi with CO. After 1 h, the pressure was released, the solution transferred to a 50-mL round-bottom flask, and the solvent removed under reduced pressure (water aspirator). The red oily residue was dissolved in 0.7 mL of Al_2O_3-filtered $CDCl_3$ and was transferred to a 5-mm NMR tube. ^1H and ^{13}C NMR spectra were recorded at −20 °C. ^1H NMR (300 MHz) δ: 1.43 (s, 3, CH_3), 3.25 (s, 3, OCH_3), 7.0–7.6 (m, 10, ArH). ^{13}C NMR (75 MHz) δ: 17.8 (CH_3), 54.4 (OCH_3), 89.0 ($\mathit{C}(CH_3)OCH_3$, enriched), 211.3 (cis CO, enriched), 213.8 (trans CO, enriched).

NOTE: Warming the above sample to 40 °C for only 15 min results in complete decomposition of the intermediate **7** with simultaneous production of imidate **2**, *trans*-azobenzene, and carbene **1**.

Reaction of 1 with 2,3-Diazabicyclo[2.2.1]hept-2-ene. Solid carbene complex **1** (0.06 g, 0.25 mmol) was added to a 10-mL Pyrex test tube. The solid azo compound (0.02 g, 0.25 mmol) was added to the carbene complex, and upon contact, fire rapidly ensued.

Reaction of 1 with Pyridazine. A 200-mL Airless-ware flask equipped with a magnetic stirring bar was flame-dried and cooled under argon. Argon-saturated THF (100 mL) was added to the flask and the flask evacuated and filled with argon (three cycles). Carbene complex **1** (0.50 g, 2.02 mmol) was added, and the flask was again evacuated and filled with argon (two cycles). Pyridazine (0.15 mL, 2.00 mmol) was syringed into the stirring solution of the carbene. After 24 h, a 2.0-mL aliquot was removed from the yellow/orange solution, and the solvent was removed under vacuum. The ^1H NMR spectrum (270 MHz) of this aliquot showed that the only products are the bis-imidate **11** (2.71 mg, 34.5%) and the $(CO)_5Cr$–pyridazine complex (8.27 mg, 65.5%). The solvent was removed from the reaction mixture under reduced pressure (water aspirator), and the yellow/brown residue was filtered through a 2.5 × 4.0 cm plug of Al_2O_3 (hexane/Et_2O 1:1). The first band (light yellow) to elute primarily contains the bis-imidate **11** (0.02 g, 5.1%). Isolated yields of **11** are substantially lower than the crude yields as a result of its facile hydrolysis. ^1H NMR (270 MHz) δ: 1.97 (s, 6, CH_3), 3.76 (s, 6, OCH_3), 6.34 (dd, J = 1.8 and 5.0 Hz, 2, $\mathit{H}C{=}CHN$), 6.50 (dd, J = 1.8 and 5.0 Hz, 2, $HC{=}C\mathit{H}N$). ^{13}C NMR (75 MHz) δ: 15.3 (CH_3), 52.9 (OCH_3), 116.2 ($\mathit{C}{=}CN$), 131.3 ($C{=}\mathit{C}N$), $(CH_3O)(CH_3)\mathit{C}{=}N$ not observed. IR ($CDCl_3$): 1640 (C═N), 1265 cm^{-1} (C—O). Mass spectrum (NH_3 C.I.): *m/e* 197 (M^+).

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Registry No. **1**, 20540-69-6; **1** (^{13}C-enriched), 122821-64-1; **2**, 24433-81-6; **3**, 90742-54-4; **4**, 90742-55-5; **6**, 122821-62-9; **6** (^{13}C-enriched), 122821-65-2; **7**, 122821-63-0; **7** (^{13}C-enriched), 122821-66-3; **11**, 122821-61-8; PhNHNHPh, 122-66-7; Et_2NH, 109-89-7; *trans*-azobenzene, 17082-12-1; *cis*-azobenzene, 1080-16-6; 1,1-diethyl-3-phenylurea, 1014-72-8; 2,3-diazabicyclo[2.2.1]hept-2-ene, 2721-32-6; pyridazine, 289-80-5.

Supplementary Material Available: Stacked plot of the NMR experiment as well as the ^1H and enriched ^{13}C NMR spectra of **6** and **7** (6 pages). Ordering information is given on any current masthead page.

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[20] Pouchert, C. J. *The Aldrich Library of Infrared Spectra*, 2nd ed.; Aldrich Chemical Company: Milwaukee, WI, 1978; p 662.

[21] Pouchert, C. J. *The Aldrich Library of NMR Spectra*, 2nd ed.; Aldrich Chemical Company: Milwaukee, WI, 1983; Vol. 1, p 989.