presence of $SnCl_4$, provides the corresponding *C*-glycosyl compounds in one step and highly stereoselectively. Since the starting furanosides are readily available in the ribo,[13] xylo,[14] and arabino[14] series, this process constitutes a simple, highly useful methodology for the synthesis of *C*-furanosides of well-defined stereochemistry.

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Supplementary Material Available: Physical constants and spectroscopic data for the new compounds (or their acetates) (10 pages). Ordering information is given on any current masthead page.

"Photochemical" Azo Metathesis by $(CO)_5W{=}C(OCH_3)CH_3$. Isolation of a Zwitterionic Intermediate

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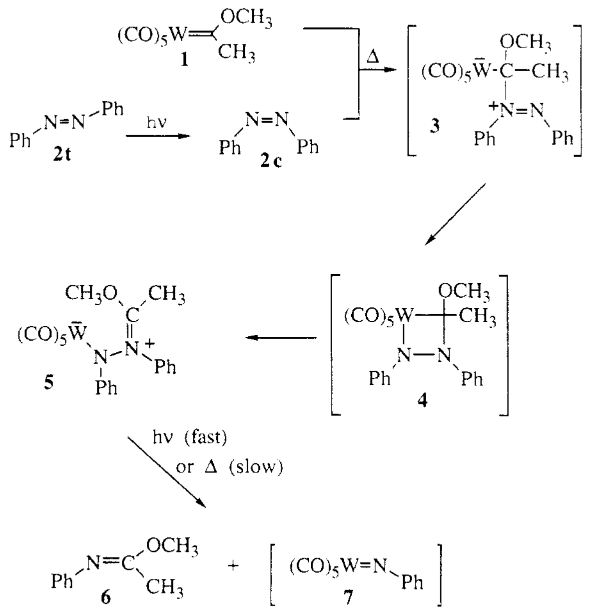
The photolysis of $(CO)_5Cr{=}C(OCH_3)CH_3$ and azobenzene has recently been reported to give mixtures of heterocycles (1,2- and 1,3-diazetidinones) and the azo metathesis product $PhN{=}C(OCH_3)CH_3$ (**6**).[1] The three products were suggested to arise from a common intermediate, a diazametallacycle arising from [2 + 2] cycloaddition of azobenzene to the carbene complex. We have examined the photochemical reaction of the related tungsten carbene $(CO)_5W{=}C(OCH_3)CH_3$ (**1**)[2] with azobenzene in benzene solution. In contrast to the chromium chemistry, the tungsten system does not give heterocycles. Only products of azo metathesis are observed. The primary photoprocess is trans–cis isomerization of azobenzene (**2t** → **2c**),[3] with the cis isomer undergoing thermal reaction with **1** to yield **5**, the first zwitterionic intermediate to be isolated from a metathesis system. Photolysis or thermolysis of **5** gives imidate **6**[4] (Scheme I) and products apparently deriving from low-valent tungsten nitrene **7**.

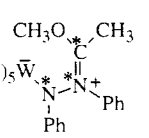
The UV–vis spectra of carbene **1**[5] and azobenzene[3] are quite similar, and irradiation of the reaction mixtures at wavelengths where one absorbs will also result in excitation of the other. *trans*-Azobenzene is known to undergo photoisomerization to the cis isomer, producing a photostationary state that is 37% cis, 63% trans.[6] Pure *cis*-azobenzene, isolated by the method of Cook,[7] undergoes a room temperature *thermal* reaction with carbene **1** which gives the same intermediate (**5**) and product (**6**) as photolysis of the reaction mixtures. It is thus not necessary to invoke photochemistry of the carbene in the metathesis process.

Upon mixing **2c** with a slight excess of **1** in benzene at room temperature, quantitative formation of zwitterion **5** can be observed by NMR. Under these conditions, **5** is stable for several hours in the dark. Evaporation of the solvent and washing with pentane to remove unreacted starting material gives **5** as a red oil in 55% yield. For spectroscopic characterization of **5** we have prepared the ^{15}N and ^{13}C labeled compounds **5b–d** from isotopically enriched **1**[8] and **2**.[11]

Scheme I



The ^1H, ^{13}C, and ^{15}N NMR data[12] from compounds **5a–d**



5a $*N = {}^{14}N$ $*C = {}^{12}C$
5b $*N = {}^{14}N$ $*C = {}^{13}C$
5c $*N = {}^{15}N$ $*C = {}^{12}C$
5d $*N = {}^{15}N$ $*C = {}^{13}C$

support the zwitterionic structure for the intermediate. The ^{13}C chemical shift of 176.1 for the labeled carbon in **5b,d** suggests double bonding of nitrogen to the original carbene fragment, a feature confirmed by the 28 Hz ^{13}C–^{15}N coupling.[13] Observation of a 14 Hz coupling between the ^{15}N's in **5c,d** establishes that the N-N bond is intact.[14] IR data for **5**[15] are also consistent. The metal carbonyl region exhibits the characteristic pattern for $(CO)_5ML$, in agreement with the observation of two W–CO signals in the ^{13}C NMR. The C=N stretch is found at 1590 cm^{-1} and shifts to 1568 upon substitution with ^{15}N. The alternative structure **3** can be ruled out by comparison of the spectral data for the intermediate with that of the known phosphorus ylide **8** (vide infra). Also, no IR stretch between 1260 and 1500 cm^{-1} shifts upon ^{15}N substitution as would be expected for the N=N double bond of **3**. A saturated system such as metallacycle **4** is

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[8] **5b** and **5d** are 16% enriched in ^{13}C at the starred positions. The synthetic route to the enriched carbene began with reaction of $(CO)_5W(THF)$[9] with ^{13}CO to give $W(CO)_5(^{13}CO)$. The carbene was then prepared in the usual fashion.[10]

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[11] Synthesis of **5c** and **5d** utilized $[^{15}N_2]$azobenzene prepared by reductive coupling of $[^{15}N]$nitrobenzene. Coupling reaction: Bigelow, H. E.; Robinson, D. R. In *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 103.

[12] For **5a**: ^1H NMR (C_6D_6) δ 1.64 (s, 3 H), 2.45 (s, 3 H), 6.68 (t, 1 H), 6.82 (d, 2 H), 6.93 (m, 3 H), 7.20 (t, 2 H), 7.27 (d, 2 H); ^{13}C NMR (C_7D_8) δ 14.9, 59.3, 176.1, 199.2, 200.0. For **5c**: ^1H NMR (C_6D_6) 1.64 (d, $^1J_{NH} = 2.3$ Hz); ^{15}N NMR (chemical shifts upfield of CH_3NO_2) 53.9 (d, $^1J_{NN} = 14$ Hz), 58.0 (d). For **5d**: ^{13}C NMR δ 176.1 (d, $^1J_{CN} = 28$ Hz).

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[15] IR of **5a**: ν_{WCO} 2061 (m), 1913 (vs), 1860 (s); $\nu_{C=N}$ 1590 cm^{-1}. For **5c**: $\nu_{C=N}$ 1568 cm^{-1}.

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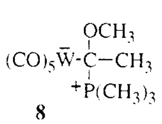
not consistent with the magnitudes of the ^{15}N chemical shifts, $^1J_{CN}$ and $^1J_{NN}$.[16]

Our results are consistent with the mechanism shown in Scheme I, in which nucleophilic attack of **2c** on the carbene gives the zwitterionic species **3**. Rearrangement of **3** through the transient metallacycle **4**[17] would then yield the observed zwitterion **5**. Cleavage of the N–N bond in **5** would then lead to the organic product **6**. The organometallic product of cleavage would be an unobserved low-valent tungsten nitrene species $(CO)_5W{=}NPh$ (**7**) which decomposes.

Fischer carbenes are well known to undergo nucleophilic attack at the carbene carbon.[18] Precedent for the formation of zwitterionic species **3** occurs in the reaction of **1** with $P(CH_3)_3$ to give ylide **8**.[19] In addition, zwitterionic or dipolar species have been



$$(CO)_5\bar{W}\text{-}\underset{^+P(CH_3)_3}{\overset{OCH_3}{C}}-CH_3$$

8

proposed in the cyclopropanation and olefin metathesis pathways of several electrophilic carbene complexes.[20] Conversion of dipolar intermediates to metallacycles has been observed[20b] and invoked[20a,c,e] in various systems. Formation of **5** is, in effect, insertion of azobenzene into the metal–carbene bond. Such insertions have previously been reported for nitriles,[21a,b] isocyanides,[21c] cyanates,[21d] cyanamides,[21e] and electron-rich acetylenes.[20e,21f]

Metallacyclobutane intermediates in metathesis and cyclopropanation are often formed from carbene–olefin complexes $(CO)_4(olefin)W{=}C(OR)R$.[22] Since reaction of **1** with **2c** occurs upon mixing while CO exchange in $(CO)_5W{=}C(OCH_3)C_6H_5$ is slow[23] and 1 atm of CO does not depress the reaction rate, CO loss and precoordination of **2c** cannot be involved. Conversion of **3** to **5** most likely occurs through an 18-electron seven-coordinate metallacycle[22a] (**4**) in which five CO ligands are retained.

Cleavage of **5** to give **6** should also produce the metal nitrene complex $(CO)_5W{=}NPh$ (**7**). Such low-valent nitrene complexes are unknown, and reactions that might be expected to generate them have produced phenyl isocyanide[24] and phenyl isocyanate[25] complexes instead. Neither these complexes nor the free ligands can be observed in IR spectra of the reaction mixtures. Alternatively, if **7** is a source of free phenylnitrene, the expected products in benzene solution would be low yields of aniline and azobenzene.[26] GC/MS of the reaction mixtures does indeed show the presence of aniline.[27,28] Further studies on the reactivity of the phenylnitrene fragment are in progress.

We have shown that photochemical azo metathesis by the tungsten carbene **1** is initiated by nucleophilic attack of *cis*-azobenzene on the carbene. A zwitterionic intermediate (**5**) has been isolated and spectroscopically characterized. It is believed to arise via an unprecedented zwitterion–metallacycle–zwitterion rearrangement. Although our current study only involves tungsten complexes, it is reasonable that the azo metathesis product found in the chromium carbene reaction[1] arises through a similar pathway.

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Note Added in Proof. Geoffroy has just reported evidence for the transient formation of **7** in the metathesis of $(CO)_5W{=}C(OMe)Ph$ with nitrosobenzene.[30]

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First-Principle Calculations of the Ionization Potentials and Electron Affinities of the Spheroidal Molecules C_{60} and LaC_{60}

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Shortly after the discovery of the remarkable stable C_{60} molecule,[1] experimental evidence has been presented for a new class of organometallic clusters of the type M_mC_n, where M = La, K, Cs ...[2-6] In the first experiment with La,[2] only LaC_n complexes were studied with a dominating abundance of LaC_{60} and with a similar stability as for the earlier studied C_{60} cluster. Further, the LaC_{60} complex was inert to react with different molecules[6] similar to the C_{60} molecule.[7] To explain the inertness and the stability of LaC_{60}, the metal atom was suggested to be located within the spheroidal carbon cage.[2] The idea has also gotten further support by observation of C_2 fragments from laser photodissociation studies of MC_n^+ similar to C_{60} for $n > 30$,[6] while

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