Metathesis and Diaziridination Reactions of $(CO)_5W{=}C(OMe)$-*p*-XC_6H_4 with *cis*-Azobenzene. Electronic and Solvent Effects

Claudia Tata Maxey, Hanadi F. Sleiman, Scott T. Massey, and Lisa McElwee-White*

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305.
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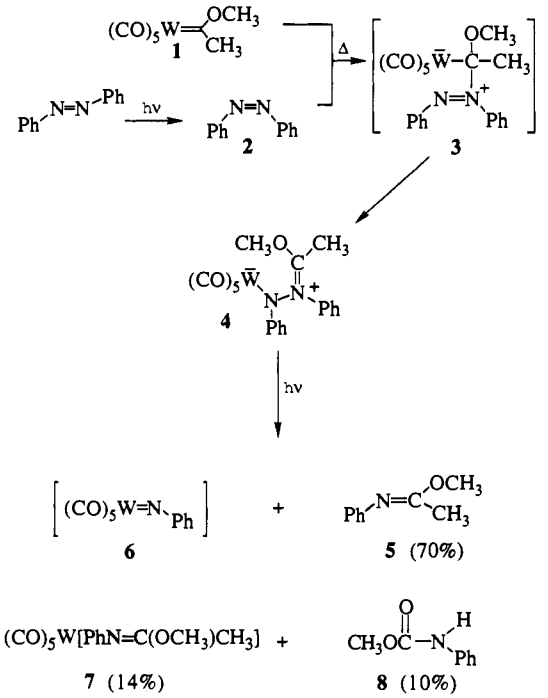
Abstract: The reaction of *cis*-azobenzene with a series of para substituted phenyl carbenes $(CO)_5W{=}C(OMe)p$-XC_6H_4 (X = H, OMe, CF_3) was carried out in both noncoordinating and coordinating solvents. The stability and reactivity of the initially formed zwitterionic species $(CO)_5WNPhNPhC(OMe)(p$-$XC_6H_4)$ depended on the substituent X. In noncoordinating solvents, the unsubstituted zwitterionic species $(CO)_5WNPhNPhC(OMe)C_6H_5$ was converted into an isomeric zwitterionic intermediate and a 2,4-diazametallacycle. Both isomeric zwitterions and the 2,4-diazametallacycle ultimately decomposed to yield the metathesis product PhN=C(OMe)Ph. The mechanism of 2,4-diazametallacycle formation was shown to involve the intermediacy of a coordinated diaziridine in which the metal subsequently inserts into the N-N bond. When the unsubstituted zwitterion was decomposed in CH_3CN, the coordinated diaziridine was displaced by solvent, inhibiting formation of the 2,4-diazametallacycle.

Introduction

The chemistry of Fischer carbenes with olefins has been extensively studied.[1] Metathesis and/or cyclopropanation products can be obtained depending on the reaction conditions and the nature of the substrates involved.[2] For example, the chromium carbene $(CO)_5Cr{=}C(OCH_3)Ph$ undergoes metathesis with electron-rich ethyl vinyl ether under mild conditions, but under a high pressure of CO, metathesis is suppressed and only cyclopropanation occurs.[3] When electron-poor methyl crotonate is the olefin substrate, the reaction pathway is cyclopropanation.[4] Solvent effects on the relative ratios of cyclopropanation and metathesis have also been examined. Casey[2] has shown that the product distribution can be altered in coordinating solvents. In acetonitrile, decomposition of the tungsten complex $(CO)_5W{=}C(OCH_2CH_2CH{=}CHOCH_3)p$-$CH_3C_6H_4$ results only in intramolecular cyclopropanation. In noncoordinating solvents, the same carbene complex gives a mixture of cyclopropane and metathesis products.

In contrast to olefins, the reactions of Fischer carbenes with heteroatom-containing double bonds are less well explored. The metathesis reaction is known for azo compounds[5-7] and nitroso compounds.[8] In addition, insertions of heteroatom-containing double bonds into the metal-carbene bond have been reported for azo compounds,[5-7,9] nitriles,[10a,b] isocyanides,[10c] cyanates,[10d] cyanamides,[10e] and ketenimines.[10f]

Scheme I



Azo compounds provide a particularly useful model system for comparing the reactivity of Fischer carbenes with heteroatom-containing double bonds to the reactivity of the carbenes with olefins because the products of both olefin reaction pathways, metathesis[5-7] and diaziridine formation[11] ("cyclopropanation"), have now been observed for azo compounds. The reaction mechanisms, however, turn out to be different for azo compounds than for their olefin counterparts, so that formally analogous products are obtained via different pathways.

We previously reported the isolation and characterization of the zwitterionic intermediate **4** in the metathesis reaction of the relatively electron-rich *cis*-azobenzene **2** with $(CO)_5W{=}C(OMe)Me$ (**1**).[5a,6] The proposed mechanism for this reaction is shown in Scheme I and involves initial nucleophilic attack of *cis*-azobenzene on the carbene to give **3**, which rearranges to give the isolable zwitterion **4**. Cleavage of **4** either photochemically or thermally yields the imidate **5**, its $(CO)_5W$ complex **7**, and carbamate **8**. On the basis of trapping experiments,[5b,6] the initial

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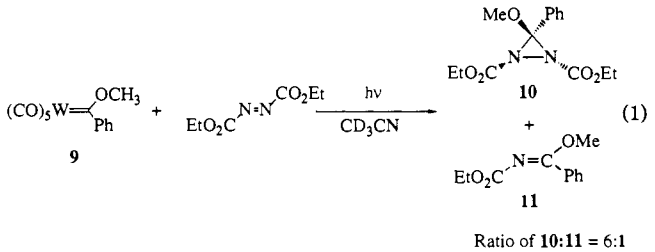
metal-containing product is postulated to be the transient low-valent nitrene complex **6**.

The first observation of the "cyclopropanation" pathway for substrates with a heteroatom-containing double bond involved a study of the reactions of Fischer carbenes with electron-deficient azo compounds.[11] For the reaction of diethyl azodicarboxylate with carbene complex **9**, diaziridine formation is favored over metathesis (eq 1). This electronic effect on the product distri-

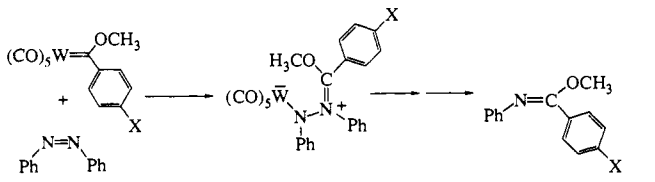


(1)

Ratio of **10**:**11** = 6:1

bution also extends to the electron-poor azo compound 4-methyl-1,2,4-triazoline-3,5-dione from which diaziridines are also formed.

This work addresses how electronic changes in the metal carbene affect the mechanism of the azo metathesis reaction and how the reaction manifold is altered in a coordinating solvent. Investigations of the electronic effects involved aryl carbenes **9**, **12**, and **13**. Substitution in the para position of the phenyl ring in these complexes provides the electronic variations while maintaining similar steric requirements. In noncoordinating solvents, the zwitterions **14–16** that formed when *cis*-azobenzene reacted with carbenes **9**, **12**, and **13** (eq 2) showed different relative stabilities, which were dependent on the substituent X. Also, zwitterions

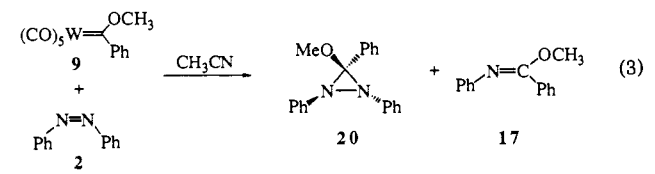


9. X=H	14. X=H	17. X=H
12. X=CF_3	15. X=CF_3	18. X=CF_3
13. X=OMe	16. X=OMe	19. X=OMe

(2)

14–16 exhibited new modes of decomposition, which resulted in the detection of additional intermediates and allowed the mechanism to be elaborated beyond the information obtained for the methyl derivative **4** (Scheme I).

In noncoordinating solvents, the final major products from the decompositions of zwitterions **14–16** were imidates **17–19**, which arose from azo metathesis. Observation of the diaziridination ("cyclopropanation") product in this system required a coordinating solvent. Upon reaction of **9** with *cis*-azobenzene in acetonitrile (eq 3), diaziridine **20** was formed in addition to imidate **17**. Although the solvent effects on product selectivity in the



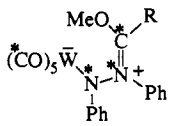
(3)

azobenzene–carbene system appear to parallel Casey's olefin–carbene system,[2] the mechanistic interpretations are different.

Results and Discussion

Formation and Characterization of Zwitterions 4, 14, and 15. When a solution of $(CO)_5W{=}C(OMe)Me$ (**1**) is mixed with 1 equiv of *cis*-azobenzene in benzene, there is a rapid color change. Removal of the solvent yields a dark red oil, which can be further purified by washing with hexane to remove traces of unreacted starting materials. This oil has been characterized by IR and multinuclear NMR techniques as having the zwitterionic structure **4**.[5a] Formation of the zwitterion **4** can be viewed as a formal insertion of *cis*-azobenzene into the metal–carbene bond. This reaction appears to be quite general[12] since the analogous zwitterions **14–16** are also formed when the phenylcarbenes $(CO)_5W{=}C(OMe)Ph$ (**9**), $(CO)_5W{=}C(OMe)p\text{-}CF_3C_6H_4$ (**12**), and $(CO)_5W{=}C(OMe)p\text{-}MeOC_6H_4$ (**13**) are reacted with *cis*-azobenzene (eq 2).

The phenyl zwitterions **14** and **15** have been spectroscopically characterized in the same manner as **4** by synthesizing the ^{13}C and ^{15}N labeled compounds **14a–d** and **15a–d** from the isotopically enriched substrates **9**, **12**, and **2**.[13,17] Although zwitterion **16** has



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

4. R=Me
14. R=Ph
15. R=p-$CF_3C_6H_4$

not been prepared isotopically labeled, spectral data obtained from unlabeled material support its structural assignment (see Experimental Section). The ^1H, ^{13}C, and ^{15}N NMR and IR data for compounds **4**, **14**, and **15** are summarized in Table I and support the zwitterionic structure for these intermediates. The ^{13}C NMR signals in the 170–177 ppm region for the labeled carbons in **4b,d**; **14b,d**; and **15b,d**, suggest that the original carbene fragment is doubly bonded to nitrogen, a feature confirmed by the large ^{13}C–^{15}N coupling of 25–28 Hz.[18] Observation of a 13–14-Hz ^{15}N–^{15}N coupling constant in **4c**, **14c**, **15c** establishes that the N–N bond is intact.[19] IR data for **4**, **14**, and **15** are also consistent with the structural assignment. The metal carbonyl region exhibits the characteristic pattern for $(CO)_5ML$ complexes,[20] in agreement with the observation of two W–CO signals in the ^{13}C NMR. The C=N stretch occurs in the 1590-cm^{-1} region and shows the expected shift to 1568 cm^{-1} upon substitution by ^{15}N in **4c**.

While isolated methyl zwitterion **4** is a red oil, both aryl zwitterions **14** and **15** are solids. Zwitterion **14** has been isolated in a 70% yield as a fine black powder with a bluish hue. The p-CF_3 phenyl zwitterion **15** must be generated at lower temperatures (−40 °C), and, although formed in essentially quantitative yield as determined by ^1H NMR, it could only be isolated as a black solid in 28% yield. While both compounds were stable if stored

(12) Subsequent to the report of zwitterion **4**, there have been two other reports of similar species. Brookhart and Templeton have reported the reaction of $(\eta^5\text{-}C_5H_5)(CO)_2Fe{=}CH(p\text{-}C_6H_4OMe)^+$ with azobenzene to produce the intermediate $(\eta^5\text{-}C_5H_5)(CO)_2FeNPhNPhCH(p\text{-}C_6H_4OMe)^+$.[9] Likewise, Hegedus has reexamined the previously reported[7a] reaction of $(CO)_5Cr{=}C(OCH_3)CH_3$ with azobenzene and has detected the chromium congener of zwitterion 4 by ^1H NMR.[7b]

(13) The carbenes **1**, **9**, and **10** were 16% enriched in ^{13}C at both the carbene carbon and metal carbonyl sites. The synthetic routes involved the reaction of $(CO)_5W(THF)$ with ^{13}CO to give $W(CO)_5(^{13}CO)$.[14] The carbenes were then prepared according to the usual fashion.[15,16]

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

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(17) Synthesis of ^{15}N-labeled zwitterions utilized azobenzene-$^{15}N_2$ prepared by reductive coupling of nitrobenzene-^{15}N. Coupling reaction: Bigelow, H. E.; Robinson, D. R. In *Organic Syntheses*, Wiley: New York, 1955; Collect. Vol. III, p 103.

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(19) The ^{15}N NMR shifts for **4c** in C_6D_6 at room temperature in our original communication[5a] are very different from those obtained at −40 °C in $CDCl_3$. Since the ^{15}N shifts of **4c** in toluene-d_8 are, however, similar to those observed in $CDCl_3$, dramatic solvent effects can be discounted. Our inability to reproduce the reported ^{15}N shifts for **4c** in C_6D_6 at this time leads us to conclude that the values in ref 5a are incorrect.

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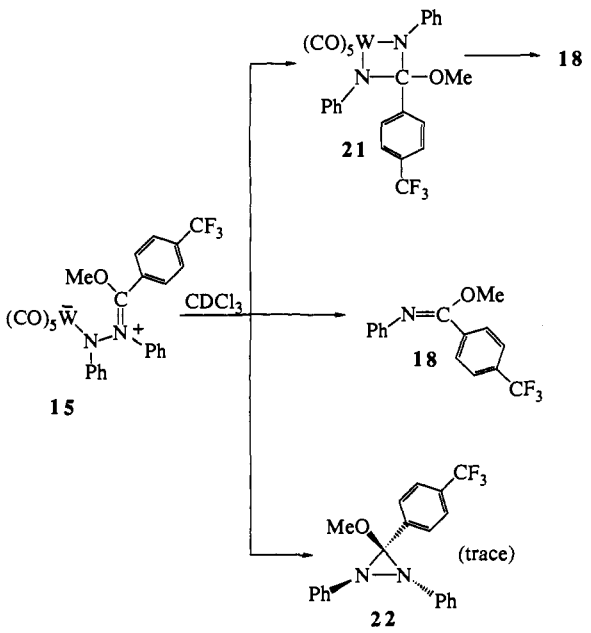
Table I. Spectroscopic Data for Zwitterions **4**, **14**, **15**, and **24**

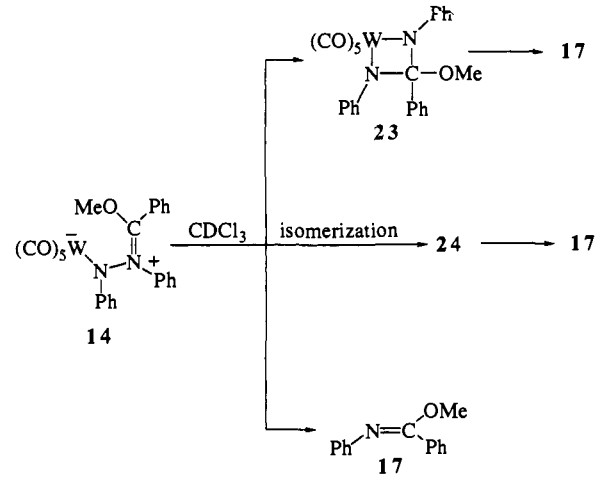
complex	^{13}C NMR,[a] δ	^{15}N NMR,[b] δ	IR,[c] cm^{-1}
4	200.0, 199.2, 176.1 (d, $^1J_{CN}$ = 28 Hz)	−249.5 (d, $^1J_{NN}$ = 13 Hz), −167.3 (d, $^1J_{NN}$ = 13 Hz)	ν_{WCO}: 2061, 1913, 1860 $\nu_{C=N}$: 1590[d]
14	203.2, 198.5, 172.0 (d, $^1J_{CN}$ = 25.1 Hz)	−248.7 (d, $^1J_{NN}$ = 14 Hz), −160.5 (d, $^1J_{NN}$ = 14 Hz)	ν_{WCO}: 2059, 1959, 1908, 1861 $\nu_{C=N}$: 1591
15	203.0, 198.2, 170.0 (d, $^1J_{CN}$ = 26.3 Hz)	−248.3 (d, $^1J_{NN}$ = 14 Hz), −157.3 (d, $^1J_{NN}$ = 14 Hz)	ν_{WCO}: 2062, 1972, 1908, 1871, 1848 $\nu_{C=N}$: 1590
24	203.2, 199.2, 172.5 (d, $^1J_{CN}$ = 24.7 Hz)	−244.9 (d, $^1J_{NN}$ = 14 Hz), −162.0 (d, $^1J_{NN}$ = 14 Hz)	ν_{WCO}: 2063, 1964, 1924, 1860 $\nu_{C=N}$: 1595

[a] Values obtained using compounds **4b,d**, **14b,d**, **15b,d**, and **24b,d**. Solvent used for complex **4d**: toluene-d_8. For complex **14d** spectra were taken at −20 °C in $CDCl_3$. For **15d** spectra were taken at −40 °C in $CDCl_3$. [b] Data taken from compounds **4c**, **14c**, **15c**, and **24c** in $CDCl_3$ at −40 °C. [c] Taken in KBr using compounds **4a**, **14a**, **15a**, and **24a**. [d] For **4d** $\nu_{C=N}$ = 1568 cm^{-1}.

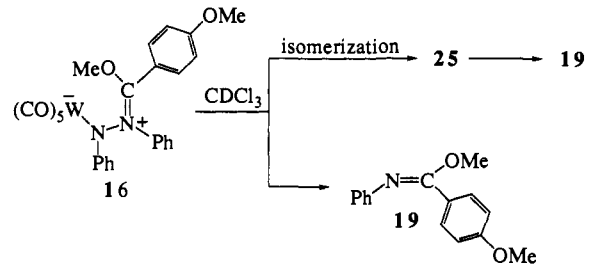
Scheme II



Scheme III



Scheme IV



as solids under N_2 at room temperature, their stability in solution was limited. Solutions of zwitterion **15** decomposed within 20 min, while **14** disappeared over a period of 2–3 h. The increased lability of **15** is presumably due to the electron-withdrawing *p*-CF_3 substituent on the phenyl ring, which would destabilize the positive charge on N_β of **15**.

Thermal Decomposition of Zwitterions 4 and 14–16. The zwitterion **4** decomposes over the course of 19 h to give a complex mixture containing imidate **5** (12%), the imidate complex $(CO)_5W$[PhN=C(OMe)Me] (<1%), the carbamate $PhNHCO_2Me$ (17%), and azobenzene (16%). No other organometallic intermediates can be observed. In contrast to **4**, decomposition of aryl zwitterions **14**, **15**, and **16** results in the formation of additional observable or isolable organometallic intermediates that eventually break down to imidates **17**, **18**, and **19**, respectively.

In chloroform, an NMR sample of the *p*-CF_3 zwitterion **15** at room temperature turns from blackish-green to dark red within 20 min. ^1H NMR reveals that the zwitterion is essentially gone and imidate **18** is formed in 24% yield together with 2,4-diazametallacycle **21** in 57.6% yield (Scheme II). Also detected in this stage of the decomposition are small amounts of the diaziridine **22**, formed in 3.8% yield. If the reaction mixture is left unperturbed, the metallacycle decomposes over a longer period of time (24–48 h) to produce more imidate **18** (overall yield 64% based on zwitterion **15**). Also present in the final reaction mixture is a 5% yield of carbamate **8**.

During decomposition of the phenyl zwitterion **14** in $CDCl_3$, the solution changes from blackish blue to dark red in 3 h, and three major species are detected by ^1H NMR. Imidate **17** forms in 27.6% yield, 2,4-diazametallacycle **23** in 30% yield, and an isomeric zwitterion **24** in 20.6% yield (Scheme III). If the reaction is worked up at this point, metallacycle **23** can be isolated in 5% yield, while zwitterion **24** is obtained in 11.6% isolated yield. If the solutions are instead left to react further, after 24 h, **23** and **24** have decomposed to give imidate **17** in 39% yield and the carbamate $PhNHCO_2Me$ in 24% yield based on the original amount of zwitterion **14**.

The reaction of *cis*-azobenzene with *p*-methoxyphenyl carbene **13** results in the quantitative formation of zwitterion **16** (Scheme IV).[21] After 5 min at room temperature, an NMR sample of zwitterion **25** gives a solution with the following composition: zwitterion **16** (45%), an isomeric zwitterion **25** (51%), and imidate **19** (3%). Since only a small amount of imidate has been formed at this stage, it suggests that the conversion of **16** to **25** is faster than the cleavage of **16** to imidate. In fact this rapid isomerization of **16** to **25** prevented our obtaining a sample of **16** that was uncontaminated by **25**. After further decomposition of the mixtures for 48 h, ^1H NMR shows imidate **19** to be formed in 57% yield and carbamate **8** in 15% yield.

We were puzzled to find the carbamate $PhNHCO_2Me$ among the products of zwitterion decomposition. While the mechanism for the formation of this product is unclear at this time, the carbamate is formally the methanol trapping product of phenyl isocyanate, a potential (but unobserved) decomposition product of low-valent nitrene complex **6**.[6] Addition of methanol to the

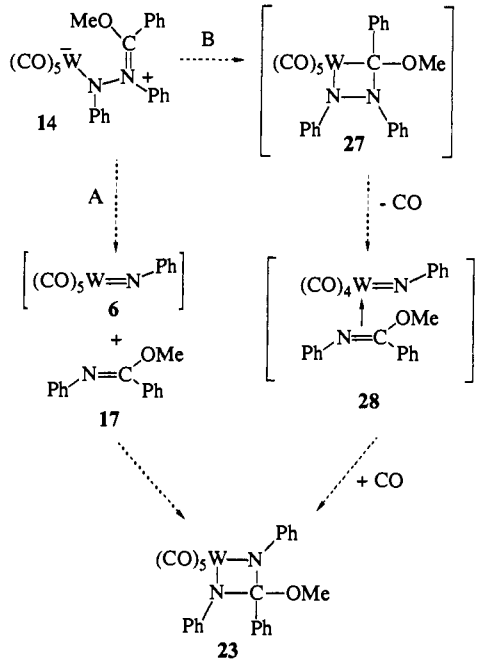
(21) Zwitterion **16** could not be isolated in pure form but could be obtained as a 50:50 mixture of **16**/**25**.

Table II. Spectroscopic Data for Metallacycles **21** and **23**

complex	^{1}H NMR,[a] δ	^{13}C NMR,[b] δ	^{15}N NMR,[c] δ	IR,[c] cm^{-1}
21	7.63 (d, 2 H, Ph), 7.44 (d, 2 H, Ph), 7.12 (t, 4 H, N-Ph), 6.93 (d, 4 H, N-Ph), 6.84 (t, 2 H, N-Ph), 3.20 (s, 3 H, OMe)	217.7, 120.7 (t, $^1J_{CN}$ = 5.7 Hz)	−190.5 (s, $^1J_{WN}$ = 50 Hz)	2074, 2000, 1965, 1920
23	7.50 (d, 2 H, Ph), 7.18 (d, 2 H, Ph), 7.12 (t, 1 H, Ph), 7.10 (t, 4 H, NPh), 6.96 (d, 4 H, NPh), 6.81 (t, 2 H, NPh), 3.17 (s, 3 H, OMe)	218.2, 121.2 (t, $^1J_{CN}$ = 5.7 Hz)	−188.7 (s, $^1J_{WN}$ = 50 Hz)	2076, 1985, 1969, 1915

[a] NMR taken in $CDCl_3$. [b] Values obtained in $CDCl_3$ using **21b,d** and **23b,d**. [c] Values taken at room temperature in $CDCl_3$ using **21c** and **23c**. [d] KBr pellet using **21a** and **23a**.

Scheme V



zwitterions does not lead to an increase in the amount of carbamate produced. The methanol does, however, increase the rate of decomposition of zwitterions **14** and **15**. Interestingly, neither the diazametallacycles **21**/**23** nor the isomerized zwitterion **24** is observed under these conditions, and the imidates **17**/**18** are formed in slightly higher yields.

Photochemical Decomposition of Zwitterions 4 and 14. Cleaner formation of the azo metathesis products can be achieved by decomposing the zwitterions under photochemical conditions. For example, photolysis of an NMR sample of zwitterion **4** in toluene-d_8 for 3 h results in complete disappearance of the zwitterion. The product composition consists of imidate **5** in 70% yield, the imidate complex $(CO)_5W[PhN{=}C(OMe)Me]$ in 14% yield, and the carbamate $PhNHCO_2Me$ in 10% NMR yield (Scheme I). Increased formation of imidate under photochemical conditions is also observed for phenyl zwitterion **14**. When an NMR sample of the zwitterion **14** is photolyzed at −50 °C in $CDCl_3$, imidate **17** is formed in 70% yield, as compared with 38% thermally. The imidate complex $(CO)_5W[PhN{=}C(OMe)Ph]$ **26** is also generated in 10% yield, giving a total yield of 80% for imidate products.

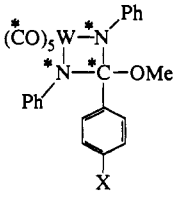
Characterization of Zwitterions 24 and 25. One of the two additional intermediates detected in the decomposition of zwitterion **14** can be isolated as a brown solid in 11.6% yield by precipitating it from $CHCl_3$ or CH_2Cl_2 with hexane. The new species (**24**) also decomposes to yield imidate **17** as its organic product (Scheme III). Its spectral properties bear a close resemblance to those of zwitterions **4**, **14**, and **15** (Table I), and we propose that intermediate **24** is a rotational isomer of zwitterion **14** in which the connectivity of the backbone is unchanged. There are three possible sites for this isomerism. Zwitterions **14** and **24** could be *E* and *Z* isomers about the N=C bond or they could be s-cis and s-trans isomers about either the N–N or C–O bonds. Presently we do not have sufficient information to assign conformations for zwitterions **14** and **24**, and, therefore, we are unable to determine the site of the isomerism.

In a similar fashion, decomposition of **16** yields the isomeric zwitterion **25** (Scheme IV). Although zwitterions **16** and **25** could not be separated from one another, NMR spectra of mixtures with varying ratios of **16**/**25** allowed the signals of each to be assigned. The similarities of the ^{13}C spectra of **16** to those of **14**/**15** and the similarity of the spectrum of **25** to that of **24** support the zwitterionic structure for both **16** and **25**.

No second zwitterion analogous to **24** and **25** is detected in the decomposition of the CF_3-substituted zwitterion **15**. This suggests that the electronic destabilization of the zwitterionic species by the electron-withdrawing *p*-CF_3 substituent results in decomposition that is too rapid for the isomerization to compete.

Although the methyl zwitterion **4** does not subsequently isomerize to give another zwitterion, when *cis*-azobenzene is added to carbene **1** in $CDCl_3$ two zwitterions are detected. These two zwitterions could not be separated, but their spectral data suggest that they are isomers in the same manner as **14** and **24** or **16** and **25**.

Characterization of Diazametallacycles 21 and 23. Decomposition of both zwitterions **14** and **15** produces an additional intermediate (**15** → **21**, **14** → **23**) that is relatively nonpolar and is fairly soluble in hexane. Intermediate **23** has been isolated



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

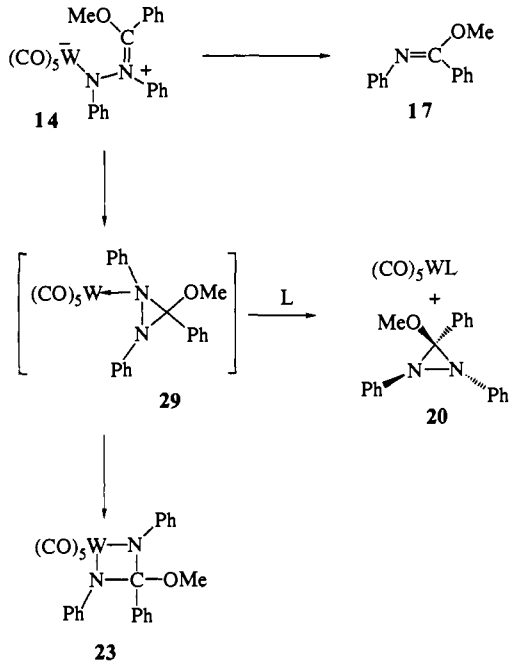
21. X=CF_3
23. X=H

in 5% yield by recrystallization from concentrated reaction mixtures. The spectral characteristics of **21** and **23** are similar as shown in Table II. On the basis of these data, 2,4-diazametallacycle structures have been assigned for intermediates **21** and **23**. The ^{1}H NMR spectra reveal that the two N–Ph groups on these molecules are equivalent. This is confirmed by the ^{15}N NMR spectra of **21c** and **23c** in which only one ^{15}N signal is detected. This signal exhibits coupling to tungsten ($^1J_{W\text{-}N}$ = 50 Hz), which establishes that the equivalent nitrogens are bonded to tungsten. The ^{13}C NMR spectra of the ^{13}C-enriched metallacycles **21b** and **23b** show that the signals at 121 ppm are enhanced. These signals appear as triplets ($^1J_{C\text{-}N}$ = 5.7 Hz) in the doubly labeled metallacycles **21d** and **23d**, which indicates that the original carbene carbon is now attached to both of the equivalent nitrogens.

The ^{13}C NMR spectra of compounds **21** and **23** contain only one signal in the carbonyl region. This is not consistent with formulation of **21** and **23** as octahedral $(CO)_4WL_2$ [L_2 = PhNC(OMe)ArNPh] complexes, since these would exhibit two carbonyl resonances. The result is instead consistent with assignment of the diazametallacycles as seven-coordinate complexes bearing five carbonyl ligands. Seven-coordinate complexes are known to be fluxional,[22] consistent with the equivalence of the carbonyl signals. In an attempt to freeze out this fluxionality,

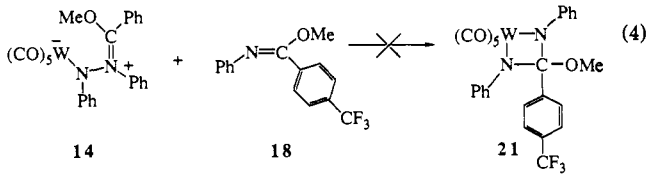
(22) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: Canada, 1988; pp 1321–1322.

Scheme VI

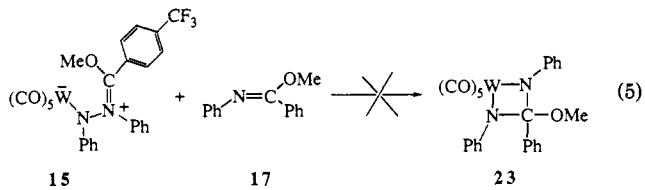


a series of low-temperature ^{13}C NMR spectra were taken of **21** in CD_2Cl_2. At −95 °C, the carbonyl signal at 218 ppm broadens significantly, while other signals show no line broadening. This result is consistent with slowing the motion that interchanges the carbonyls.[23]

Formation of Metallacycles 21 and 23. Possible mechanisms for the formation of 2,4-diazametallacycles during decomposition of **14** and **15** are shown in Schemes V and VI. In Scheme V, diazametallacycle **23** arises via an extension of the metathesis pathway. One possibility is cleavage to imidate **17** and nitrene complex **6**, followed by recombination to give **23** (path A). To test the viability of path A, crossover experiments were performed. The zwitterion **14** was allowed to decompose in the presence of the imidate **18** and the reaction mixtures examined for the presence of metallacycle **21**. The same experiment was repeated using zwitterion **15** and imidate **17**. Neither case showed any presence of the crossover product (eq 4 and 5).



(4)

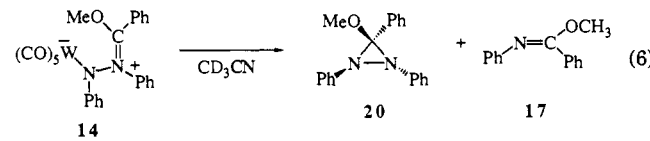


(5)

A second possibility involves intermediacy of the 2,3-diazametallacycle **27**.[25] In path B, subsequent ring opening would then yield the coordinated imidate–nitrene complex **28**, which could undergo ring formation in the opposite sense to give **23**. A coordinated nitrene–imidate intermediate has been invoked in a discussion of the analogous chromium system.[7b] However, arguments based on the spectral data above strongly suggest that metallacycles **21** and **23** each bear five CO ligands. Unless a 20-electron intermediate is invoked, intermediacy of an imidate–nitrene complex would require the loss of a CO ligand followed by recoordination of CO after ring closure. Path B would then predict that formation of metallacycle **23** should be inhibited under conditions in which free CO is lost from the solvent, since reassociation of the CO ligand could not occur. A sample of zwitterion **14** was thoroughly degassed and allowed to decompose in an evacuated vessel. Under these conditions, which facilitate CO loss from the solvent, there was no reduction in the yield of diazametallacycle **23**.

A mechanism that bypasses the metathesis pathway is illustrated in Scheme VI. In this mechanism, the critical intermediate is diaziridine complex **29**. This complex would arise via ring closure of the zwitterionic ligand of **14**. Insertion of the metal into the N–N bond of the diaziridine would then lead to **23**. A similar insertion of cobalt into the N–N bond of diaziridines has been invoked in the formation of 1,3-diazetidinones by using cobalt carbonyl.[26] If this mechanism were operative, it is possible that the decomposition of **14** in a coordinating solvent would lead to the displacement of diaziridine from **29** and observation of the free diaziridine in the reaction mixtures. These considerations led to a study of the decomposition of **14** in acetonitrile.

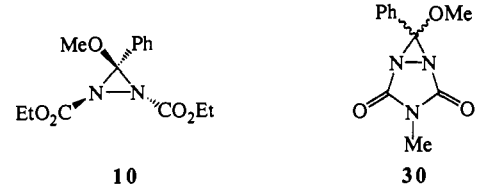
Decomposition of Zwitterions 14 and 15 in Acetonitrile. In contrast to the results obtained in $CHCl_3$, decomposition of zwitterion **14** in acetonitrile results in the formation of only a trace (<2% NMR yield) of 2,4-diazametallacycle **23** and a small amount (7% yield) of the isomeric zwitterion **24**. Instead, **14** decomposes to give a 39% yield of imidate **17** and a 45% yield of diaziridine **20** (eq 6). Similar results are obtained from the *p*-CF_3-substituted zwitterion **15**.



(6)

Ratio 20:17=1.2:1

Diaziridine **20** is extremely labile and eluded all attempts at isolation. It could, however, be partially purified to the point where the only contaminants were imidate **17** and a trace of $(CO)_5W(CH_3CN)$. Assignment of the structure for **20** rests on spectroscopic data. ^1H NMR analysis reveals that the N–Ph groups are inequivalent, and the phenyl group attached to C3 shows a splitting pattern similar to that seen for the previously isolated diaziridines **10** and **30**. The ^{15}N NMR shows two signals at −251.7 and



−256.0 ppm. By ^{13}C NMR, the diaziridine C3 appears at 90.7 ppm.[27] A high resolution electron impact mass spectrum gives an exact mass consistent with the diaziridine structure.

Reaction of Diaziridine 20 with $(CO)_5W(THF)$. Observation of diaziridine **20** during the decomposition of zwitterion **14** in acetonitrile is consistent with formation of diaziridine complex

(23) A referee has suggested that **23** could be a fluxional version of coordinated diaziridine **29** in which the metal is rapidly migrating between the nitrogens. Although we cannot strictly rule this out, we believe it to be highly unlikely. The acyclic hydrazine complexes $(CO)_5W(RNHNHR')$ show no evidence of exchange of the $(CO)_5W$ fragment between nitrogens.[24] This leaves insertion and deinsertion of the metal fragment (**29** → **23** → **29**) as the interconversion pathway. If that is the case, **23** must still live long enough for interconversion of the cis and trans carbonyls, a process that is highly unlikely for a $(CO)_5WL$ species such as **29**.

(24) Ackermann, M. N.; Hardy, L. C.; Xiao, Y. Z.; Dobmeyer, D. J.; Dunal, J. A.; Felz, K.; Sedman, S. A.; Alperovitz, K. F. *Organometallics* **1986**, *5*, 966–972.

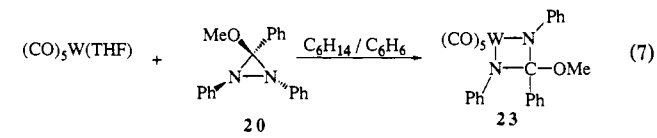
(25) The chromium analogue of this metallacycle has been isolated by Hegedus.[7b]

(26) Alper, H.; DelleDonne, D.; Kamayama, M.; Roberto, D. *Organometallics* **1990**, *9*, 762–765.

(27) This value is similar to the ^{13}C shifts observed for C3 in the diaziridines **10** and **31**, which appear at 115.6 and 102.0 ppm, respectively.[11]

29 during rearrangement of 14 to 2,4-diazametallacycle 23. Displacement of the ligand by CH_3CN would then result in the observed product. An independent synthesis of 29 was thus devised in order to test its viability as a precursor to 23.

A sample of $(CO)_5W(THF)$ in hexane was added to a benzene solution of diaziridine 20. The solution turned from yellow to dark red within several minutes. Removal of the solvent and analysis of the residue by ^1H NMR showed the presence of metallacycle 23 (eq 7). All of the imidate initially present in the sample of



20 23 (7)

20 (vide supra) could be accounted for as the imidate complex $(CO)_5W[PhN{=}C(OMe)Ph]$ (26). Formation of 23 in this experiment is consistent with the mechanism shown in Scheme VI for the formation of the 2,4-diazametallacycle via a diaziridine complex.

Decomposition of Zwitterion 14 in THF. If both 2,4-diazametallacycle 23 and free diaziridine 20 arise from the common intermediate 29, then the presence of a less strongly coordinating solvent than CH_3CN could result in competition between insertion of the metal into the N–N bond and displacement of the diaziridine by solvent. Over the course of 2 h in the more weakly coordinating THF, zwitterion 14 decomposes to give a reaction mixture that has the following composition as determined by ^1H NMR: diaziridine 20 (25%), 2,4-diazametallacycle 23 (16%), zwitterion 24 (20%), imidate 17 (20%), and zwitterion 14 (6%). A moderate amount of free diaziridine is produced in THF, but in contrast to the results in acetonitrile, substantial amounts of the metallacyclic intermediate 23 and the zwitterion 24 are also formed. These results are consistent with competition of all of the previously observed pathways under these conditions.

Conclusion

We have shown that reaction of *cis*-azobenzene with aryl carbene complexes yields zwitterions 14–16, which have stabilities and reactivities that are dependent on the para substituent. Subsequent decomposition of 14–16 in noncoordinating solvents gives rise to additional intermediates. Upon decomposition of the relatively electron-rich *p*-OMe-substituted zwitterion 16, the isomeric zwitterion 25 is detected. In contrast, the relatively electron-deficient *p*-CF_3-substituted zwitterion 15 yields the novel 2,4-diazametallacycle 21. Decomposition of the unsubstituted phenyl zwitterion 14 results in both a diazametallacycle (23) and an isomeric zwitterion (24). In noncoordinating solvents, all three intermediates also undergo cleavage to give imidate 17 as the major organic product.

We have presented evidence that the mechanism for formation of the 2,4-diazametallacycle involves the intermediacy of a metal-coordinated diaziridine. Decomposition of zwitterions 14 and 15 in acetonitrile does not result in formation of the 2,4-diazametallacycle. Displacement of the diaziridine by solvent prior to insertion yields free diaziridine instead.

Although these solvent effects on product selectivities parallel those in Casey's carbene–olefin system[2] (i.e., in acetonitrile the "cyclopropanation" product is obtained, while in noncoordinating solvents metathesis is the preferred mode of reactivity), the mechanistic interpretations are different. In the carbene–olefin system, metathesis is proposed to occur in noncoordinating solvents because CO loss leads eventually to a six-coordinate metallacycle that can convert to the carbene–olefin complex that yields metathesis products. In coordinating solvents, a seven-coordinate metallacycle undergoes reductive elimination to give the cyclopropane. For the azobenzene cases described in this work, the two pathways share common intermediates in zwitterions 14 and 15. The competition is between N–N cleavage to give the metathesis products and cyclization of the zwitterionic ligand to yield coordinated diaziridine. The nature of the solvent then determines the fate of the coordinated diaziridine. Coordinating solvents displace the diaziridine, while in noncoordinating solvents, insertion of the metal into the N–N bond leads to the 2,4-diazametallacycles.

Experimental Section

General. Standard inert atmosphere techniques were used in these experiments. Diethyl ether and toluene were distilled from sodium and benzophenone. Hexane, pentane, and methylene chloride were distilled from calcium hydride. Acetonitrile was distilled from phosphorus pentoxide. All NMR solvents were degassed by three freeze–pump–thaw cycles. Benzene-d_6 and toluene-d_8 were vacuum transferred from sodium and benzophenone. CD_3CN, $CDCl_3$, and CD_2Cl_2 were stored over 3-Å molecular sieves in an inert atmosphere box.

$(CO)_5W{=}C(OMe)Me$[28] and $(CO)_5W{=}C(OMe)Ph$[15] were prepared according to Fischer. $(CO)_5W{=}C(OMe)(p\text{-}CF_3C_6H_4)$ was prepared by the same method as its chromium congener.[16] *cis*-Azobenzene was prepared according to Cook.[29] An authentic sample of methyl *N*-phenylcarbamate was prepared from phenyl isocyanate and methanol. Authentic samples of imidate 5 and 19 were prepared from acetanilide and *p*-methoxybenzanilide by using the procedure of Fraser.[30] Authentic samples of imidates 17 and 18 were prepared from the imidoyl chloride[31] according to Lander.[32] *p*-(Trifluoromethyl)benzanilide and *p*-methoxybenzanilide were prepared from the reaction of aniline with *p*-(trifluoromethyl)benzoyl chloride and *p*-methoxybenzoyl chloride according to the procedure of Gutsche.[33] *p*-(Trifluoromethyl)benzanilimino chloride was prepared by using a modification[34] of the literature method.[31] The ^{13}C-enriched carbenes were prepared from $(CO)_5W(^{13}CO)$, which was labeled by the reaction of $(CO)_5W(THF)$ with ^{13}CO. ^{15}N-labeled azobenzene was prepared by reductive coupling of [^{15}N]nitrobenzene.[17]

^1H, ^{15}N, and ^{13}C NMR spectra were recorded on a Varian XL-400 spectrometer. IR spectra were recorded on an IBM IR/90 FTIR spectrometer. High-resolution mass spectra were performed at the Mass Spectrometry Facility, University of California, San Francisco.

Synthesis of $(CO)_5WNPhNPhC(OMe)Me$ (4). Zwitterion 4 was synthesized as described in ref 6. ^{13}C NMR (C_7D_8): δ 200.0, 199.2, 176.1, 59.3, 14.9. ^{15}N NMR ($CDCl_3$, −40 °C): δ −167.3 ($^1J_{N\text{-}N}$ = 13 Hz), −249.5 ($^1J_{N\text{-}N}$ = 13 Hz).[19] Other spectral data can be found in refs 5a and 6.

Synthesis of $(CO)_5WNPhNPhC(OMe)Ph$ (14). A −40 °C solution of *cis*-azobenzene (88 mg, 0.48 mmol) in 0.7 mL of toluene was added to a −40 °C solution of $(CO)_5W{=}C(OMe)Ph$ (210 mg, 0.47 mmol) in 0.7 mL of toluene. The solution turned dark greenish black immediately. After 1 h at −40 °C, hexane precooled to −40 °C (6 mL) was added to the solution. Zwitterion 14 precipitated out of solution as a fine black powder. The powder (220 mg, 77% isolated yield) was collected by filtration and rinsed with cold hexane. ^1H NMR ($CDCl_3$): δ 7.62 (m, 2 H), 7.55 (m, 3 H), 7.46 (m, 3 H), 7.38 (m, 2 H), 6.99 (t, 2 H), 6.61 (d, 2 H), 6.46 (t, 1 H), 3.81 (s, 3 H). ^{13}C NMR ($CDCl_3$, −20 °C): δ 203.16, 198.46, 171.97 (C=N, enhanced with use of ^{13}C-enriched carbene, upon ^{15}N enrichment: d, $^1J_{C\text{-}N}$ = 25.1 Hz), 160.34, 139.47, 132.73, 130.64, 129.71, 128.71, 128.65, 126.32, 125.50, 125.44, 115.48, 114.73, 61.78. ^{15}N NMR ($CDCl_3$, −40 °C): δ −248.7 (d, $^1J_{N\text{-}N}$ = 14 Hz), −160.5 (d, $^1J_{N\text{-}N}$ = 14 Hz). IR (KBr): ν_{WCO} 2059, 1959, 1908, 1861; $\nu_{C=N}$ = 1591 cm^{-1}. Anal. Calcd for $C_{25}H_{18}N_2O_6W$: C, 47.95; H, 2.90; N, 4.47. Found: C, 48.19; H, 2.81; N, 4.38.

Synthesis of $(CO)_5WNPhNPhC(OMe)(p\text{-}CF_3C_6H_4)$ (15). A −40 °C solution of *cis*-azobenzene (65 mg, 0.36 mmol) in 2 mL of toluene was added to a −40 °C solution of $(CO)_5W{=}C(OMe)p\text{-}CF_3C_6H_4$ (135 mg, 0.26 mmol) in 0.7 mL of CH_2Cl_2. The solution turned dark greenish black immediately. After 1 h at −40 °C, hexane precooled to −40 °C (20 mL) was added to the solution and the solution was left at −40 °C overnight. Zwitterion 15 precipitated out of solution as a fine black powder. The powder (52 mg, 28% isolated yield) was collected by filtration and rinsed with cold hexane. ^1H NMR ($CDCl_3$, −50 °C): δ 7.56 (m, 7 H), 7.53 (d, 2 H), 7.02 (t, 2 H), 6.55 (d, 2 H), 6.49 (t, 1 H), 3.84 (s, 3 H). ^{13}C NMR ($CDCl_3$, −40 °C): δ 203.00, 198.21, 170.03 (C=N, enhanced upon ^{13}C enrichment, upon ^{15}N enrichment: d, $^1J_{C\text{-}N}$ = 26.3 Hz), 160.36, 138.79, 133.53 (q, $^2J_{C\text{-}F}$ = 32.7 Hz), 131.02, 129.84, 129.03, 128.86, 126.48, 125.73, 125.51, 122.82 (q, $^1J_{C\text{-}F}$ = 275.1 Hz), 116.16, 114.86, 61.98 (OMe). ^{15}N NMR ($CDCl_3$, −40 °C): δ −248.3 (d, $^1J_{N\text{-}N}$

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(29) Cook, A. H. *J. Chem. Soc.* **1938**, 876–881.
(30) Fraser, R. R.; Swingle, R. B. *Can. J. Chem.* **1970**, *48*, 2067–2074.
(31) Spath, E.; Pailer, M. *Ber. Dtsch. Chem. Ges.* **1924**, 1212–1220.
(32) Lander, G. D. *J. Chem. Soc.* **1902**, 591–598.
(33) Gutsche, C. D.; Johnson, H. E. In Organic Syntheses; Wiley: New York, 1963; Collect. Vol. IV, pp 780–783.
(34) *p*-(Trifluoromethyl)benzanilide was refluxed with 4–5 equiv of neat thionyl chloride for 24 h. Removal of the excess thionyl chloride was achieved by vacuum distillation, to yield the crude imidoyl chloride.

= 14 Hz), −157.3 (d, $^1J_{N-N}$ = 14 Hz). IR (KBr): ν_{WCO} 2062, 1972, 1908, 1871, 1848; ν_{CN} 1590 cm^{-1}.

Thermal Decomposition of 14 in $CDCl_3$. An NMR sample was prepared containing **14** (20 mg, 0.03 mmol) in 0.7 mL of $CDCl_3$. After 3 h at room temperature, the solution turned from blackish blue to dark red. ^{1}H NMR showed that **14** had decomposed to give a complex mixture consisting of the following: metallacycle **23** (30% yield); zwitterion **24** (20.6%); imidate **17** (27.6%); carbamate **8** (7.9%); coordinated imidate **26** (4.8%). After an additional 19 h, the solution had turned light yellow and contained imidate **17** (39% yield), carbamate **8** (19.8% yield), and the coordinated imidate **26** (4.2% yield). **Metallacycle 23.** ^{1}H NMR ($CDCl_3$): δ 7.50 (d, 2 H), 7.18 (t, 2 H), 7.12 (t, 1 H), 7.10 (t, 1 H), 6.96 (d, 4 H), 6.81 (t, 2 H), 3.17 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 218.19 (CO, enhanced upon ^{13}C enrichment), 148.54, 139.00, 128.66, 127.96, 127.84, 126.40, 121.98, 121.19 (quaternary carbon enhanced upon ^{13}C enrichment, with ^{15}N label: t, $^1J_{C-N}$ = 5.7 Hz), 120.10, 47.99. ^{15}N NMR ($CDCl_3$): δ −188.7 ($^1J_{W-N}$ = 50 Hz). IR (KBr): ν_{WCO} 2076, 1985, 1969, 1915 cm^{-1}. **Zwitterion 24.** ^{1}H NMR ($CDCl_3$): δ 7.55 (t, 1 H), 7.46 (m, 4 H), 7.23 (m, 7 H), 6.95 (d, 2 H), 6.59 (t, 1 H), 3.98 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 203.27, 199.17, 172.53 (C=N, enhanced upon ^{13}C enrichment, with ^{15}N label: d, $^1J_{C-N}$ = 23.4 Hz), 157.26, 140.81, 133.08, 129.83, 129.65, 129.54, 129.24, 129.06, 128.65, 126.41, 115.59, 113.77, 61.95. ^{15}N NMR ($CDCl_3$, −40 °C): δ −244.9 (d, $^1J_{N-N}$ = 14 Hz), −162.0 (d, $^1J_{N-N}$ = 14 Hz). IR (KBr): ν_{WCO} 2063, 1964, 1924, 1860; $\nu_{C=N}$ 1595 cm^{-1}. **Imidate 17.** ^{1}H NMR: 7.27 (m, 3 H), 7.20 (d, 2 H), 7.16 (t, 2 H), 6.94 (t, 1 H), 6.71 (d, 2 H), 3.96 (s, 3 H).

Isolation of Metallacycle 23 and Zwitterion 24. Zwitterion **14** (400 mg, 0.639 mmol) was allowed to decompose in 5 mL of $CHCl_3$ under N_2 for 3 h at room temperature. The solvent was then removed under vacuum and the residue was dissolved in a minimum amount of $CHCl_3$ (about 1 mL). Cold hexane (about 10 mL at −40 °C) was added to the $CHCl_3$, causing a brown solid to precipitate. After 5 h in a freezer at −40 °C, the solution was filtered through a frit and the precipitate collected. The brown solid was washed twice with cold hexane to give pure zwitterion **24** in 11.6% yield (46.3 mg). The solvent was removed from the filtrate under vacuum and the residue was dissolved in a minimum amount of ether (about 0.5 mL). Another 0.5 mL of hexane was added to this solution, and the solution was placed in a freezer (−40 °C) overnight. The solvent was then carefully removed by using a pipet and the remaining solid material was dried under vacuum for 30 min to give 81 mg of dark red crystals, which were identified by NMR as impure metallacycle **23**. A second recrystallization gave 20 mg (5.0% yield) of pure **23**.

Generation of Imidate Complex 26 for Spectroscopic Characterization. A solution of $W(CO)_6$ (130 mg, 0.37 mmol) and imidate **17** (60 mg, 0.28 mmol) in 10 mL of THF was photolyzed under a static vacuum for 36 h. The CO was periodically removed every 6–12 h by using two freeze–pump–thaw cycles. After photolysis, 1 mL of the solution was set aside. The solvent was removed by evaporation and the residue dissolved in CH_2Cl_2 for IR analysis. NMR samples were prepared by removing the solvent from the rest of the mixture to give a yellow solid. The solid began to turn brown after an additional 10 min under vacuum and then turned black after addition of $CDCl_3$. The samples of **26** contained residual THF and $W(CO)_6$. **Imidate Complex 26.** ^{1}H NMR ($CDCl_3$): δ 7.27 (m, 3 H), 7.10 (t, 2 H), 7.05 (m, 2 H), 6.90 (t, 1 H), 6.75 (d, 2 H), 3.75 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 204.79, 198.97, 173.42, 151.15, 130.47, 128.65, 128.44, 128.01, 125.38, 123.09, 121.35, 59.14. IR (CH_2Cl_2): ν_{CO} 2069.2 (w, sh), 1926.5 (s, br), 1881.3 (m, br), $\nu_{C=N}$ 1663.5 cm^{-1} (w, br).

Formation and Thermal Decomposition of Zwitterion 15 in $CDCl_3$. *cis*-Azobenzene (0.9 mg, 0.0045 mmol) was dissolved in 0.5 mL of $CDCl_3$ and placed in an NMR tube capped with a septum. The solution was cooled to −40 °C and an excess of $(CO)_5W$=C(OMe)(*p*-$CF_3C_6H_4$) (4 mg, 0.0078 mmol) in 0.2 mL of $CDCl_3$ was syringed into the NMR tube. After the tube was inverted to mix the solution, the mixture immediately turned very dark with a green tinge. ^{1}H NMR revealed that zwitterion **15** had formed in quantitative yield. After 20 min at room temperature, the solution had turned dark red, and ^{1}H NMR revealed the mixture consisted of the following compounds: metallacycle **21** (58.6% yield), diaziridine **22** (3.8%), and imidate **18** (24%). After 24 h **21** and **22** had decomposed and the solution contained imidate **18** in 64% yield and carbamate **8** in 5% yield. (Yields based on the initial amount of zwitterion **15**.) **Metallacycle 21.** ^{1}H NMR ($CDCl_3$): δ 7.63 (d, 2 H), 7.44 (d, 2 H), 7.12 (t, 4 H), 6.93 (d, 4 H), 6.84 (t, 2 H), 3.20 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 217.71 (CO, enhanced with ^{13}C enrichment), 148.22, 143.27, 128.92 (q, $^2J_{CF}$ = 32.2 Hz), 128.84, 126.78, 125.10 (br), 124.00 (q, $^1J_{CF}$ = 271.9 Hz), 122.35, 120.70 (quaternary carbon, enhanced upon ^{13}C enrichment, with ^{15}N label: t, $^1J_{C-N}$ = 5.7 Hz), 120.01, 48.10. ^{15}N NMR ($CDCl_3$): δ −190.5 ($^1J_{W-N}$ = 50 Hz). IR (KBr): ν_{CO} 2074, 2000, 1965, 1920 cm^{-1}. **Imidate 18.** ^{1}H NMR ($CDCl_3$): δ 7.47 (d, 2 H), 7.40 (d, 2 H), 7.18 (t, 2 H), 6.97 (t, 1 H), 6.70 (d, 2 H), 3.98 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 157.58, 147.74, 134.69, 131.51 (q, $^2J_{C-F}$ = 32.5 Hz), 129.66, 129.03, 124.98 (br), 123.63 (q, $^2J_{C-F}$ = 272.5 Hz), 122.98, 121.42, 54.09. IR (thin film): $\nu_{C=N}$ 1663 cm^{-1}. Anal. Calcd for $C_9H_{12}F_3NO$: C, 64.51; H, 4.33; F, 20.41; N, 5.01. Found: C, 64.45; H, 4.29; F, 20.01; N, 4.86.

Formation and Thermal Decomposition of Zwitterion 16 in $CDCl_3$. *cis*-Azobenzene (12 mg, 0.066 mmol) was dissolved in 0.6 mL of $CDCl_3$ and placed in an NMR tube with a septum. The tube was cooled to −78 °C, and $(CO)_5W$=C(OMe)*p*-$MeOC_6H_4$ (36 mg, 0.076 mmol) was added with a syringe. After the NMR tube was inverted several times to mix the solution, the mixture turned very dark. ^{1}H NMR at room temperature showed that zwitterion **16** was formed in 92% yield and zwitterion **25** was formed in 7% yield. (In a similar experiment where the spectrum was taken at −40 °C without ever warming the sample to room temperature, the zwitterion **16** was formed exclusively in quantitative NMR yield.) After 5 min at room temperature, the ^{1}H NMR revealed the solution contained zwitterion **16**, zwitterion **25**, and imidate **19** in a 10:11:1 ratio. After 48 h, both zwitterions had decomposed to give imidate **19** in 57% yield and carbamate **8** in 15% yield. **Zwitterion 16.** ^{1}H NMR ($CDCl_3$, −20 °C): δ 7.63 (d, 2 H), 7.56 (m, 5 H), 7.02 (t, 2 H), 6.90 (d, 2 H), 6.66 (d, 2 H), 6.46 (t, 1 H), 3.89 (s, 3 H), 3.82 (s, 3 H). ^{13}C NMR ($CDCl_3$, −20 °C): δ 203.47, 198.82, 171.59 (C=N), 163.13, 159.47, 140.21, 130.32, 129.86, 129.65, 128.55, 125.16, 116.94, 115.14, 114.77, 114.22, 62.27, 55.70. IR (KBr) performed on a 50:50 mixture of **16**/**25**): ν_{WCO} 2061, 1963, 1909, 1869; $\nu_{C=N}$ 1605 cm^{-1}. **Zwitterion 25.** ^{1}H NMR ($CDCl_3$): δ 7.40 (d, 2 H), 7.27 (m, 5 H), 7.18 (t, 2 H), 6.93 (m, 4 H), 6.58 (t, 1 H), 4.02 (s, 3 H), 3.86 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 203.10, 198.10, 172.27 (C=N), 157.00, 141.02, 132.05, 129.37, 129.19, 128.83, 126.13, 118.02, 115.32, 114.90, 113.99, 61.92, 55.53. **Imidate 19.** ^{1}H NMR ($CDCl_3$): δ 7.27 (d, 2 H), 7.19 (t, 2 H), 6.96 (t, 1 H), 6.72 (m, 4 H), 3.94 (s, 3 H), 3.74 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 160.59, 158.52, 148.78, 131.10, 128.94, 123.38, 122.39, 121.53, 113.20, 55.18, 53.82. IR (thin film): $\nu_{C=N}$ 1656 cm^{-1}. HRMS (EI), *m/e* calcd for M^+ ($C_{15}H_{15}NO$): 241.1103. Found: 241.1107.

Photochemical Decomposition of Zwitterion 14 in $CDCl_3$. An NMR sample containing **14** (6 mg, 0.009 mmol) was prepared in $CDCl_3$ with solvent cooled to −40 °C. The sample was photolyzed for 1 h at −50 °C, after which 5.6% of the zwitterion remained unreacted. Imidate **17** was formed in 70% and coordinated imidate **26** was formed in 10% yield based on the amount of zwitterion consumed.

Reaction of Zwitterion 14 in $CDCl_3$ in the Presence of Methanol. An NMR sample of **14** (40 mg, 0.064 mmol) was prepared in a solution of 0.7 mL of $CDCl_3$ containing a drop of methanol-d_4. After 80 min, the solution was light brown and the zwitterion had decomposed to give imidate **17** in 53% yield and coordinated imidate **26** in 7.6% yield.

Reaction of Zwitterion 15 in $CDCl_3$ in the Presence of Methanol. An NMR sample of **15** (approximately 5 mg, 0.007 mmol) was prepared in a solution of 0.7 mL of $CDCl_3$ containing a drop of methanol-d_4. After 10 min, the solution had turned from black to yellow, and the zwitterion had decomposed to give imidate **18** in 75% yield.

Decomposition of Zwitterion 14 in Acetonitrile. An NMR sample containing **14** (19 mg, 0.03 mmol) was prepared in 0.7 mL of CD_3CN. After 2 h at room temperature the solution had turned from dark red to brown, and ^{1}H NMR revealed that zwitterion **14** had decomposed to give diaziridine **20** in 45% yield, imidate **17** in 39% yield, and zwitterion **24** in 7% yield. **Diaziridine 20.** ^{1}H NMR ($CDCl_3$): δ 7.50 (m, 2 H), 7.38 (m, 4 H), 7.23 (m, 3 H), 7.20 (m, 1 H), 7.09 (t, 2 H), 6.98 (m, 2 H), 6.92 (t, 1 H), 3.25 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 148.02, 147.63, 132.55, 128.63, 128.48, 128.15, 124.37, 123.76, 121.10, 120.08, 91.89 (C3), 55.10. ^{15}N NMR ($CDCl_3$, −40 °C): δ −251.7, −256.0. HRMS (EI), *m/e* calcd for M^+ ($C_{20}H_{18}N_2O$): 302.1419. Found: 302.1426.

Decomposition of Zwitterion 15 in Acetonitrile. An NMR sample containing zwitterion **15** was prepared in 0.7 mL of CD_3CN. After 2 h at room temperature, the solution had turned dark red and ^{1}H NMR showed that the zwitterion had decomposed to give diaziridine **22** in 50.8% yield and imidate **18** in 32.9% yield. **Diaziridine 22.** ^{1}H NMR ($CDCl_3$): δ 7.57 (d, 2 H), 7.46 (d, 2 H), 7.34 (m, 3 H), 7.19 (t, 2 H), 7.15 (t, 2 H), 6.95 (m, 3 H), 3.23 (s, 3 H). HRMS (EI), *m/e* calcd for M^+ ($C_{21}H_{17}N_2OF_3$): 370.1293. Found: 370.1306.

Decomposition of Zwitterion 14 in $CDCl_3$ under Vacuum. A solution of **14** (39.5 mg, 0.063 mmol) was dissolved in 2 mL of $CDCl_3$ precooled to (−40 °C). Half the solution was placed in an NMR tube as a control and the other half was placed in a 25-mL Teflon-stoppered flask. The solution was degassed by using three freeze–pump–thaw cycles. (Thaw cycles were performed at −40 °C to prevent thermal decomposition.) Both samples were allowed to decompose at room temperature for 3 h. ^{1}H NMR revealed that the amount of metallacycle **23** formed in each case was the same.

Crossover Experiment of Zwitterion 14 with 18. An NMR sample containing zwitterion **14** (22 mg, 0.035 mmol) and imidate **18** (10 mg, 0.036 mmol) in 0.7 mL of $CDCl_3$ was prepared. After 2.5 h at room temperature, no metallacycle **21** could be detected by ^1H NMR.

Crossover Experiment of Zwitterion 15 with 17. An NMR sample containing zwitterion **15** (12 mg, 0.017 mmol) and imidate **17** (6 mg, 0.028 mmol) in 0.7 mL of $CDCl_3$ was prepared. After 2.5 h at room temperature, no metallacycle **23** could be detected by ^1H NMR.

Reaction of $(CO)_5W(THF)$ with Diaziridine 20. The $(CO)_5W(THF)$ was prepared by photolyzing a degassed (by two freeze-pump-thaw cycles) solution containing $W(CO)_6$ (400 mg, 1.14 mmol) in 10 mL of THF. After 13 h of photolysis the solution was degassed again (by two freeze-pump-thaw cycles) and photolyzed for an additional 24 h. About one-fifth of the solution was used, and the solvent was removed in vacuo at 0 °C to yield a yellow solid, which was dissolved in hexane.

A mixture of diaziridine **20** and imidate **17** was prepared by dissolving zwitterion **14** (43 mg, 0.07 mmol) in 2 mL of CH_3CN. After 1 h the imidate and diaziridine mixture was extracted from the CH_3CN with 3 × 3 mL of hexane. The solvent was removed in vacuo and the residue was washed with hexane. The solvent from the washings was removed and the residue dissolved in C_6H_6. The hexane solution of $(CO)_5W$-(THF) was added dropwise to the mixture of the diaziridine and imidate in C_6H_6, and the solution turned from yellow to dark reddish brown. The solution was left to stir for 15 min. After the solvent was removed, ^1H NMR showed that all the imidate had been coordinated to $(CO)_5W$ and metallacycle **23** was formed in 11.5% yield.

Decomposition of Zwitterion 14 in THF. A sample of **14** (25 mg, 0.040 mmol) was dissolved in 1 mL of THF. After 2 h at room temperature, the solution had turned dark red and the removal of the solvent in vacuo yielded a dark red oil. Analysis of this oil by ^1H NMR revealed a complex mixture with the following composition: diaziridine **20** (25%), imidate **17** (20%), zwitterion **24** (20%), metallacycle **23** (16%), coordinated imidate **26** (11%), and unreacted zwitterion **14** (6%).

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Nickel-Catalyzed, Chlorotrialkylsilane-Assisted Conjugate Addition of Alkenyltributyltin Reagents to α,β-Unsaturated Aldehydes. Evidence for a [1-((Trialkylsilyl)oxy)allyl]nickel(II) Mechanism

Bryan A. Grisso, John R. Johnson, and Peter B. Mackenzie*

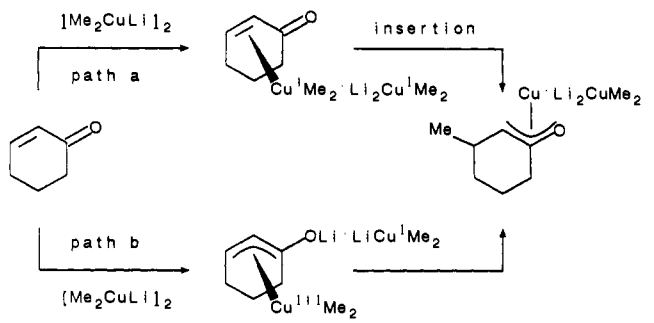
Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113. *Received October 8, 1991*

Abstract: α,β-Unsaturated aldehydes $R^1CH{=}CR^2CHO$ (R^1 = H, Me, *n*-Pr; R^2 = H, Me) react with ethenyl-, (1-ethoxyethenyl)-, (2-phenylethenyl)-, and 1-propenyltrialkyltin reagents and chlorotrialkylsilanes (Me_3SiCl or *t*-$BuMe_2SiCl$) in the presence of $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) or 1-((trialkylsilyl)oxy)allylnickel(II) chloride catalyst precursors to afford the corresponding trialkylsilyl (*E*)-enol ethers in 48-79% yield. High C(3)-regioselectivities (≥15:1 crude, ≥50:1 purified) are observed when R^1 = H; moderate C(3)-regioselectivities (2-12:1 crude, 2->50:1 purified) are observed when R^1 = Me or *n*-Pr. High (*E*)-enol ether selectivities (5->19:1 crude, 10->50:1 purified) are observed in all cases save the addition of (1-ethoxyethenyl)tributyltin to 2-propenal, for which case a 2:1 *E*/*Z* ratio is observed. Stoichiometric model reaction and kinetic studies strongly support a Ni(0)/Ni(II) mechanism involving 1-((trialkylsilyl)oxy)allylnickel(II) intermediates and turnover-limiting alkenyl group transmetalation.

Introduction

Although frequently employed in synthesis, transition-metal-catalyzed conjugate addition reactions are mechanistically ill-defined.[1] Important issues such as the extent of electron transfer from the metal to the α,β-unsaturated carbonyl compound[1b,e] and the oxidation state and coordination number of the metal remain to be resolved,[1g,h] so that it is unclear, for example, whether organocuprate conjugate addition reactions are best thought of as redox-neutral alkene insertion reactions (Scheme I, path a) or as oxidative addition/reductive elimination reactions involving [1-(metalloxy)allyl]copper(III)[1d] intermediates (Scheme I, path b). A similar dichotomy exists for Me_3SiCl-modified organocuprate conjugate addition reactions[1d,f] and for related nickel- and palladium-catalyzed conjugate additions of organoaluminum,[2,3] organozirconium,[4] and organozinc[5] reagents to enones, all of which

Scheme I



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