Unusual [1,2]- and [1,3]-M(CO)$_5$ Shifts in Fischer Carbene Complexes: [4 + 3] and [3 + 3] Annulation Reactions of Furan and Pyrrole Rings

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Abstract: The cycloaddition reactions of various *C*-heteroarylimines with α,β-unsaturated Fischer carbene complexes have been studied. Either [3 + 3] carbocyclization or [3 + 3] and [4 + 3] heterocyclization reactions were accomplished, depending on the structure of the imine and on the type of unsaturation of the carbene complex. Imines derived from furan-, **4**, benzofuran-, **5**, and *N*-methylindole-2-carboxaldehyde, **7**, gave C3 + C3 cycloadducts **10**−**12** on reaction with alkynyl carbene complexes **2a** and **3**. The reaction of N-unsubstituted pyrrole imine **8a** with alkenyl carbene complexes **1** involved the ring nitrogen atom of the pyrrole unit leading to C2N + C3 heterocycloadducts **14** and **15**. Moreover, *N*-unsubstituted imines **8** and **9** underwent C2N2 + C3 heterocyclization to alkynyl carbene complexes **2** and **3** to furnish zwitterionic metalpentacarbonyl containing heterocycles **17** and **18**. We have studied the thermal behavior of heterocycles **17**, finding that they led to bispyrrole **21** or indolizine **20** when heated at 120 °C in the presence and in the absence of carbon monoxide, respectively. The results obtained show that the [3 + 3] cyclizations are promoted by a [1,2]-M(CO)$_5$ shift, while in the case of the [4 + 3] cyclization, a [1,3]-M(CO)$_5$ shift follows the ring-closure step. The X-ray analysis of compound **17b**, resulting from 1,3-pentacarbonyltungsten migration, is provided.

Introduction

Designing efficient routes for ring construction is currently one of the main challenges in synthetic organic chemistry. Much effort has been dedicated throughout the years to this purpose, and many efficient classical approaches have been perfectly established.[1] In this field, organotransition-metal compounds offer many interesting possibilities to build rings not readily accessible through conventional methods.[2] Among the organometallic compounds, group 6 heteroatom stabilized carbene complexes (Fischer carbene complexes) have in recent years opened up new pathways of carbo- and heterocyclization.[3] Apart from the reactions occurring on the organic moiety of the carbene ligand due to the activation by the M(CO)$_5$ fragment (for instance [4 + 2],[4] and [3 + 2][5] cycloadditions, formation of metalloenolate species,[6] Michael additions[7]), the most significant examples are those involving the carbon−metal double bond, particularly for α,β-unsaturated complexes. Thus, in addition to the intensive work done in cycloadditions such as [3 + 2 + 1] (Dötz benzannulation),[8] [2 + 1] (cyclopropanation reaction),[9] and [1 + 1 + 2] (Hegedus reaction),[10] there have been a limited number of reports on [3 + 2][11] and [4 + 3][12,13] carbocyclizations.

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(5) (a) Chan, K. S.; Wulff, W. D. *J. Am. Chem. Soc.* **1986**, *108*, 5229. (b) Chan, K. S.; Yeung, M. L.; Wang, R.; Mak, T. C. W. *J. Org. Chem.* **1995**, *60*, 1741. (c) Baldoli, C.; Del Buttero, P.; Licandro, E.; Maiorana, S.; Papagni, A.; Zanotti-Gerosa, A. *J. Organomet. Chem.* **1994**, *476*, C27. (d) Barluenga, J.; Fernández-Marí, F.; Viado, A. L.; Aguilar, E.; Olano, B. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2267.

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(8) a) Wulff, W. D.; Bax, B. M.; Brandvold, T. A.; Chan, K. S.; Gilbert, A. M.; Hsung, R. P.; Mitchell, J.; Clardy, J. *Organometallics* **1994**, *13*, 102. (b) Hsung, R. P.; Quinn, J. F.; Weisenberg, B. A.; Wulff, W. D.; Yap, G. P. A.; Rheingold, A. L. *Chem. Commun.* **1997**, 615 and references therein. (c) Barluenga, J.; Aznar, F.; Martín, A.; García-Granda, S.; Pérez-Carreño, E. *J. Am. Chem. Soc.* **1994**, *116*, 11191. (d) Dötz, K. H.; Stinner, C.; Nieger, M. *J. Chem. Soc., Chem. Commun.* **1995**, 2535.

Scheme 1

(ref 14 15)

(ref 16)

Scheme 2

(ref 17, 18)

(ref 19)

$[W] = (CO)_5W$

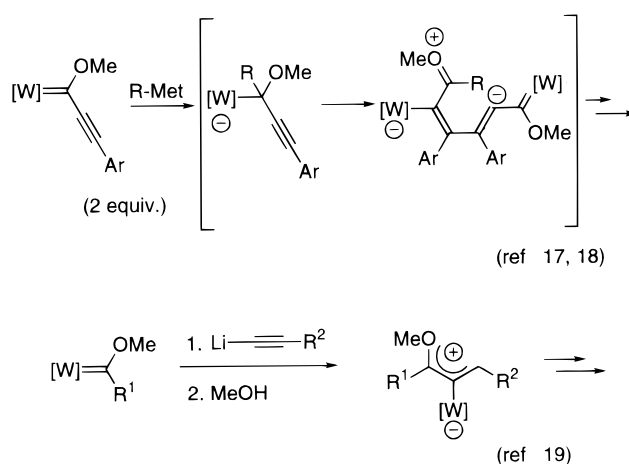**Scheme 3**


I

II

III

(ref 21)

IV
(X-ray)

$[M] = (CO)_5M$

Metal migrations are rare in the case of Fischer carbene complexes. Almost 10 years ago, the first $[1,3]$-$M(CO)_5$ shift in Fischer carbene complexes was observed independently by Hegedus[14] (for M = Cr) and McElwee-White[15] (for M = W) in the reaction with azo benzene. Later, Fischer[16] found an analogous behavior in the reaction of pentacarbonyl (phenyl-carbene)tungsten(0) with ketenimines. In all cases, the resulting anionic metal species were spectroscopically characterized (Scheme 1).

In recent years, we and others have discovered a new reactivity pattern for Fischer carbene complexes which is promoted by $[1,2]$-metalpentacarbonyl migrations. Thus, $[1,2]$-migrations were initially proposed by Dötz[17] and Fischer[18] to explain the diethylzinc or aryllithium, respectively, induced cyclodimerization of Fischer alkynylcarbene complexes (Scheme 2). Recently, Iwasawa has shown this type of migration in the
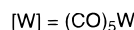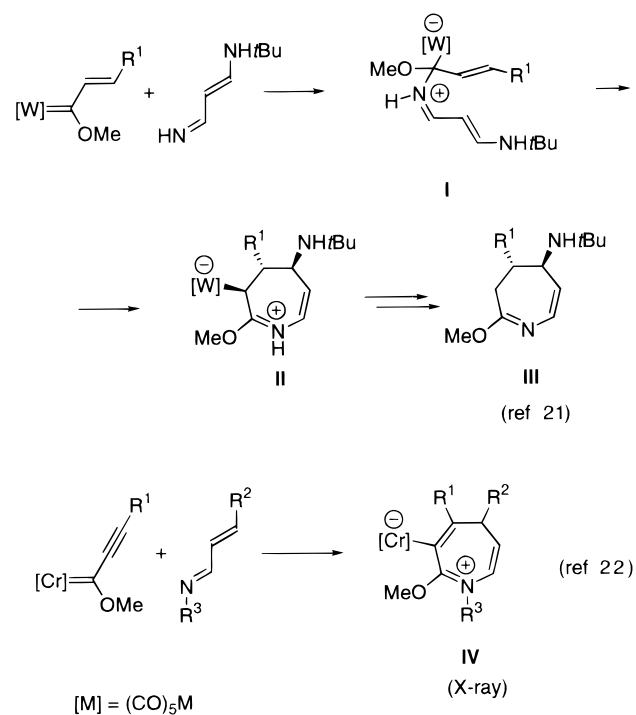
reverse process upon addition of alkynyllithium derivatives to alkyl Fischer carbene compounds. The intermediate resulting from 1,2-addition followed by $[1,2]$-$W(CO)_5$ shift and proton-ation with methanol was reported to be stable up to 0 °C, allowing it to be spectroscopically identified and its structure proven by reaction with electrophiles (Scheme 2).[19,20]

Moreover, we have demonstrated that both alkenyl and alkynyl Fischer carbene complexes are capable of undergoing $[1,2]$-migration of metalpentacarbonyl when reacted with aza-diene derivatives (Scheme 3). First, the NMR study performed on the reaction of alkenylcarbene complexes with 4-amino-1-

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(10) (a) Hegedus, L. S. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 12, p 549. (b) Reed, A. D.; Hegedus, L. S. *Organometallics* **1997**, *16*, 2313.

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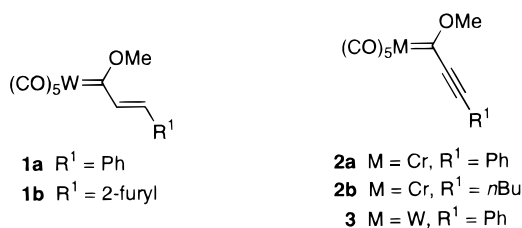
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(20) We have recently found that the 1,2-addition of alkynyllithium reagents to Fischer aryl carbenes derived from menthol is followed by [1,3]-migration of the pentacarbonyltungsten fragment: Barluenga, J.; Trabanco, A. A.; Flórez, J.; García-Granda, S.; Llorca, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 12129.
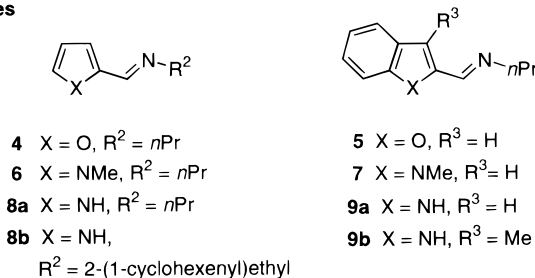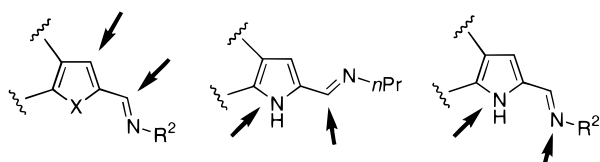
Fischer carbene complexes

1a R^1 = Ph
1b R^1 = 2-furyl

2a M = Cr, R^1 = Ph
2b M = Cr, R^1 = nBu
3 M = W, R^1 = Ph

Imines

4 X = O, R^2 = nPr
6 X = NMe, R^2 = nPr
8a X = NH, R^2 = nPr
8b X = NH,
   R^2 = 2-(1-cyclohexenyl)ethyl

5 X = O, R^3 = H
7 X = NMe, R^3= H
9a X = NH, R^3 = H
9b X = NH, R^3 = Me

Figure 1.

(X = O, NMe)

[3+3] carbocyclization   [3+3] heterocyclization   [4+3] heterocyclization

Figure 2.

azadienes, leading to dihydroazepines, **III**, permitted characterization of both the 1,2-addition, **I**, and the [1,2]-W(CO)$_5$, **II**, intermediates and thus enabled us to delineate a likely reaction pathway for this [4 + 3] cycloaddition.[21] Interestingly, we were also able to fully characterize by X-ray analysis the target species **IV** obtained from simple 1-azadienes and Fischer alkynyl complexes.[22]

Taking advantage of these precedents we have carried out further investigations using activated azadienes which are, in addition, intrinsically interesting substrates to be annulated. Therefore, we report herein [3 + 3] and [4 + 3] carbo- and/or heterocyclizations of alkenyl and alkynyl (methoxy)carbene complexes **1**−**3** to imines derived from furan-, benzofuran-, pyrrole-, and indole-2-carboxaldehydes **4**−**9** (Figure 1). All these processes are either promoted by [1,2]- or accompanied by [1,3]-metalpentacarbonyl migrations, the cyclization pattern being dependent on both the nature of the imine and the type of unsaturation of the carbene complex.

The present study shows that these transformations are initiated by a 1,2- or 1,4-addition to the electrophilic carbene complex and that the different cyclizations observed involve the substrate centers marked in Figure 2. In all cases, the carbene complex ligand participates as a C$_3$ unit.
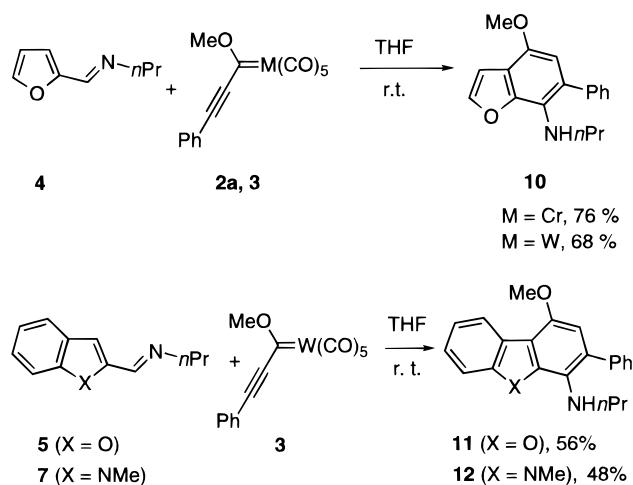
Results and Discussion

Reaction of Imines 4, 5, and 7 with Alkynyl Complexes 2a and 3: [3 + 3] Carbocyclization through [1,2]-Metal

Scheme 4

4   **2a, 3**   **10**

M = Cr, 76 %
M = W, 68 %

5 (X = O)   **3**   **11** (X = O), 56%
7 (X = NMe)   **12** (X = NMe), 48%

Migration. We started our work by testing the behavior of furan and benzofuran imines **4** and **5** with a,β-unsaturated carbene complexes. In line with previous work dealing with simple 1-azadienes, we observed first that alkenyl complexes **1** were not suitable reagents toward **4** or **5**, as, in all instances, either recovery of starting materials or oxidation of the carbene complex took place. We then turned our attention to alkynyl complexes, finding that, interestingly, a new and regioselective [3 + 3] carbocyclization took place. Thus, the reaction of carbene complexes **2a** and **3** with imine **4** (molar ratio 1:1) at room temperature in THF led to complete disappearance of the reagents in 4 h. Further purification of the reaction crude through column chromatography furnished a single benzofuran cycloadduct, **10**, in good yield. A slightly higher yield was observed on shifting from tungsten to chromium complexes (Scheme 4).[23]

The reaction also worked acceptably for the corresponding benzofuran imine **5** as well as for the indole imine **7**. Thus, the [C$_3$ + C$_3$] annulation products **11** (X = O, 56%) and **12** (X = NMe, 48%) were obtained by treatment of the tungsten complex **3** with imines **5** and **7**, respectively, under the same reaction conditions as above.[24]

This [3 + 3] carbocyclization process leading to the observed regioisomer can be explained by assuming a [1,2]-migration of the pentacarbonylmetal fragment as the key step. The proposed pathway is exemplified in Scheme 5 for the formation of adduct **10**. Thus, 1,2-addition of the ring C-3 carbon of **4** would generate intermediate **V**. Further [1,2]-M(CO)$_5$ shift would promote cyclization to **VI**, which would undergo hydrogen transfer and reductive elimination of the metal. On no occasion did these heterocyclic imines furnish fused azepines **13** as would be expected in light of the reaction pattern of simple alkenyl imines with alkynyl carbene complexes (see Scheme 3). Probably the formation of species **VII** is a reversible reaction, and the process becomes controlled primarily by thermodynamic factors.

It should be pointed out that, while [3 + 3] carbocyclizations are not frequent in general,[2,25] the process remained unknown in the case of Fischer carbene complexes.

Reaction of Imine 8a with Alkenyl Complexes (1): [3 + 3] Heterocyclization through [1,2]-Metal Migration. Then we

(21) Barluenga, J.; Tomás, M.; Ballesteros, A.; Santamaría, J.; López-Ortiz, F.; Carbajo, R. J.; García-Granda, S.; Pertierra, P. *Chem.−Eur. J.* **1996**, *2*, 88.

(22) Barluenga, J.; Tomás, M.; Rubio, E.; López-Pelegrín, J. A.; García-Granda, S.; Pertierra, P. *J. Am. Chem. Soc.* **1996**, *118*, 695.

(23) A complex mixture was formed from pyrrole imine **6**.

(24) The *N*-methyl carbazole structure has been recently described to possess a high agonist and antagonist activity as a melatonin receptor: Davies, D. J.; Garratt, P. J.; Tocher, D. A.; Vonhoff, S.; Davies, J.; Teh, M.-T.; Sugden, D. *J. Med. Chem.* **1998**, *41*, 451.

(25) Seebach, D.; Missbach, M.; Calderari, G.; Eberle, M. *J. Am. Chem. Soc.* **1990**, *112*, 7625.

Scheme 5

Scheme 6

14a, R^1 = Ph
14b, R^1 = 2-furyl

**15a**, R^1 = Ph, 58%
15b, R^1 = 2-furyl, 52%
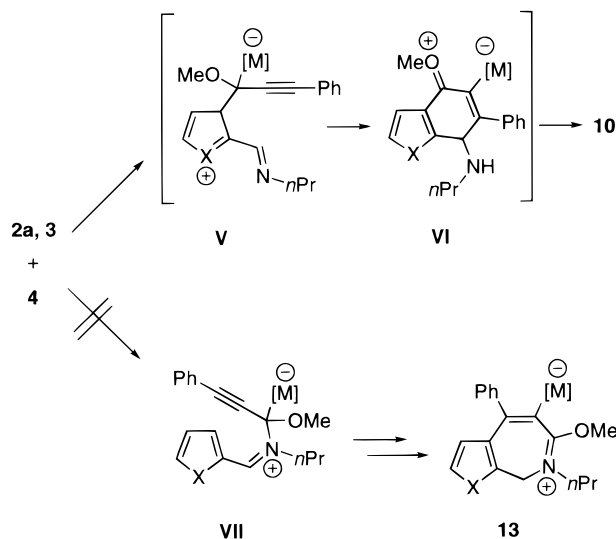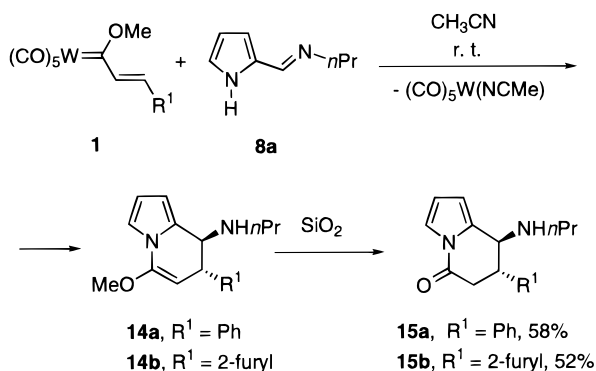
decided to investigate the behavior of N-unsubstituted pyrrole imines of the type of **8** toward Fischer carbene complexes in order to learn whether the amino function plays a role in the process, which would eventually result in a different cyclization mode. First, the reaction of the pyrrole-2-carboxaldehyde imine **8a** with alkenylcarbene complexes **1** was attempted (Scheme 6). Although unidentified complex mixtures were found when the reaction was carried out in hexane or THF under different reaction conditions, cycloadducts **15a,b** were formed in fair yields when the reaction of **8a** and complexes **1a,b** (molar ratio 1:1) was run in acetonitrile at room temperature for 8 h followed by silica-gel chromatography. The primary indolizidine cyclo-adducts **14a,b** could be spectroscopically characterized from the reaction crude. The coordinating ability of acetonitrile probably drives the cyclization forward and allows recovery of the metal carbonyl as pentacarbonyl(acetonitrile)tungsten (0).

The cyclization showed complete chemo-, regio-, and dia-stereoselectivity, as only the isomer **14** was detected in the reaction crude. The trans stereochemistry was readily inferred from an NOESY experiment performed on compound **15b**.

This formal [3 + 3] heterocyclization[26] resembles the precedent [3 + 3] carbocyclization of imines **4**, **5**, and **7** except

(26) For previous [3 + 3] heterocyclizations of Fischer carbene complexes, see: (a) Polo, R.; Moretó, J. M.; Schick, U.; Ricart, S. *Organometallics* **1998**, *17*, 2135. (b) Bambal, R. B.; Kemmitt, D. W. *J. Organomet. Chem.* **1989**, *362*, C18. (c) Huang, Y.; Lu, X. *Tetrahedron Lett.* **1987**, *28*, 6219. (d) Wang, S. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 4550. (e) Merlic, C. A.; Xu, D. *J. Am. Chem. Soc.* **1991**, *113*, 9855. (f) Merlic, C. A.; Xu, D.; Nguyen, M. C.; Truong, V. *Tetrahedron Lett.* **1993**, *34*, 227. (g) Aumann, R.; Roths, K.; Jasper, B.; Frölich, R. *Organometallics* **1996**, *15*, 1257. (h) Aumann, R.; Meyer, A. G.; Frölich, R. *J. Am. Chem. Soc.* **1996**, *118*, 10853.

Scheme 7
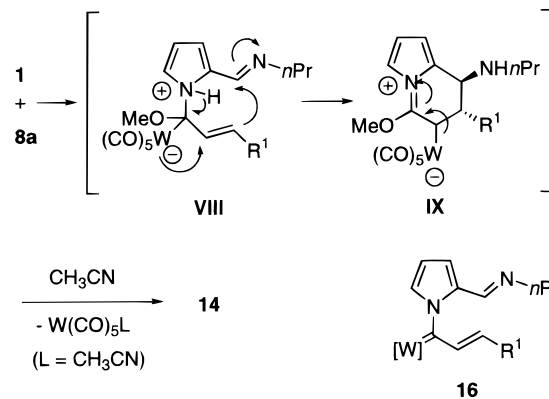
Scheme 8
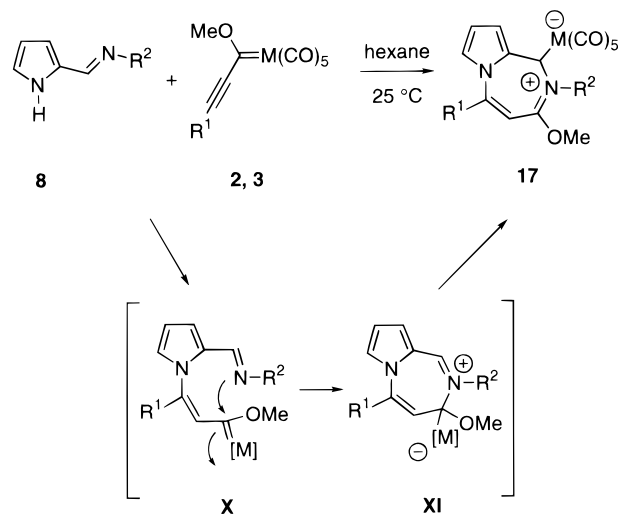
that the unsubstituted ring nitrogen is now involved rather than the ring C-3 atom. Thus, a reaction sequence involving two major steps can be envisaged, (i) 1,2-addition of the NH of **8a** to the carbene carbon of **1** to form **VIII** and (ii) cyclization to **IX** induced by [1,2]-migration of the metalpentacarbonyl group (Scheme 7). It was somewhat surprising and delightful to find that the [1,2]-M(CO)$_5$ shift took place in preference over the methoxy displacement by the amine function (compound **16**, not observed), a process which is well-known not only in the case of alkylamines but also for pyrrole itself.[27]

Reaction of Imines 8 and 9 with Alkynyl Complexes 2 and 3: [4 + 3] Heterocyclization and [1,3]-Metal Migration. We have finally studied the reaction of imines **8** and **9** from N-unsubstituted pyrrole- and indole-2-carboxaldehyde with alkynyl carbene complexes **2** and **3**. Again, the flexibility and/ or capriciousness of many transition-metal complexes toward organic substrates becomes more than apparent in this case since a different reaction pattern was observed in relation to the reaction courses outlined up to this point. Thus, when complexes **2** and **3** and imines **8** were mixed (molar ratio 1:1) in hexane at room temperature a brown solid precipitated from the reaction medium. The solid was filtered and washed with hexane to afford the zwitterionic pyrrolodiazepine derivatives **17** in good to excellent yields (Scheme 8, Table 1). Now, the following three-step reaction pathway apparently accounts well for the formation of **17**: (i) NH Michael type addition to form **X**, (ii) intramolecular 1,2-addition of the imine nitrogen leading to **XI**, and (iii) [1,3]-migration of M(CO)$_5$.

(27) Hegedus, L.; Merino, I. *Organometallics* **1995**, *14*, 2522.

Table 1. Fused Diazepines **17** and **18** Prepared

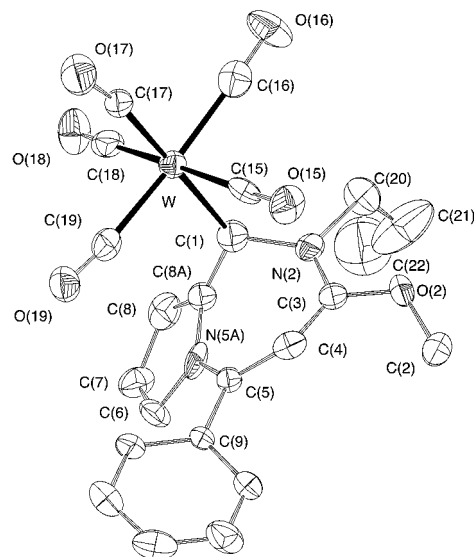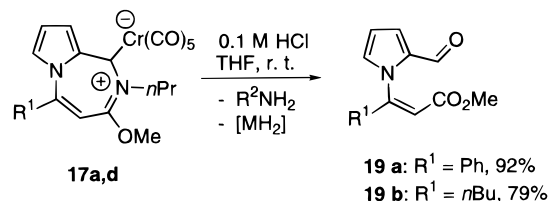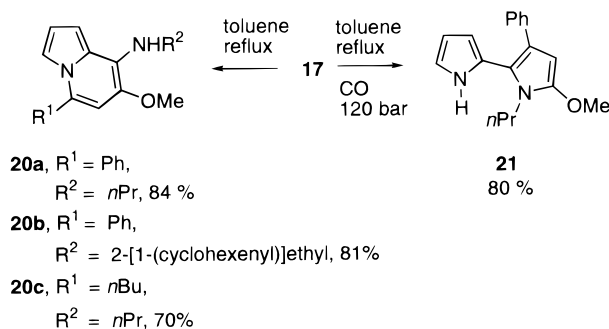| compound	metal	R^1	R^2	R^3	yield[a] (%)
17a	Cr	Ph	nPr		93
17b	W	Ph	nPr		89
17c	W	Ph	2-[1-(cyclohexenyl)]ethyl		95
17d	Cr	nBu	nPr		72
18a	Cr	Ph		H	33
18b	Cr	Ph		Me	28
18c	W	Ph		Me	30

[a] Yields not optimized.

Scheme 9
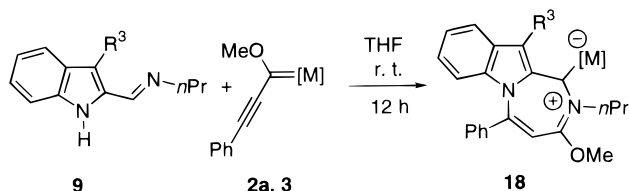
[M] = (CO)$_5$Cr, (CO)$_5$W

Significantly, this process could be extended to imines derived from indole-2-carboxaldehyde **9** since they followed the same reaction pathway (Scheme 9). Unlike pyrrole imines **8**, the reaction of indole imines **9** with carbene complexes **2a** and **3** did not work at all in hexane, but the corresponding indolodiazepines **18** were obtained by running the reaction in THF at room temperature for 12 h. These cycloadducts did not precipitate in the reaction medium and were isolated in rather low yields after column chromatography purification (Table 1).

The structural elucidation of compounds **17** and **18** was made, first, on the basis of their spectroscopic data. Thus, HMBC experiments on **17a** showed long-range connections between the aliphatic C(1) (δ = 50.8 ppm) and (i) the ligand carbonyl carbon atoms (δ = 220.8 ppm), (ii) the C(8) of the pyrrole unit, (iii) the imidate carbon atom C(3), and (iv) the C(20) directly bound to the iminium nitrogen (see Figure 3 for numbering of **17**). Finally, the structure of **17b** was confirmed by an X-ray analysis (Figure 3).[28]

In spite of the fact that the anionic metal is placed on an sp^3 carbon atom, compounds **17** display an unexpectedly high hydrolytic and thermal stability. They are air-stable and withstand silica-gel column-chromatography purification as well as water treatment (24 h, room temperature). The hydrolyses of **17a,d** required stirring with diluted hydrochloric acid (THF, 25 °C) to yield aldehydes **19a,b** (Scheme 10). The formation of these aldehydes seemingly implies hydrolysis of the imidate moiety along with an oxidative process at the metal-bound carbon center, probably through metal hydride β-elimination. The *Z*-configuration of the double bond in **19b** was ascertained through an NOE experiment.

A further task was to test the thermal behavior of compounds **17**. It has been recently described that complexes with the zwitterionic structure M$^-$−CH(R)−N$^+$R$_3$ act as masked, non-stabilized carbene complexes M = CH(R) which undergo in some occasions cyclopropanation reactions with electron-rich alkenes.[29] Heating of complexes **17** in toluene at reflux for 6 h resulted in the formation of indolizines **20** in good yields via

Figure 3. Crystal structure of **17b**.

Scheme 10

Scheme 11

20a, R^1 = Ph,
  R^2 = nPr, 84 %

20b, R^1 = Ph,
  R^2 = 2-[1-(cyclohexenyl)]ethyl, 81%

20c, R^1 = nBu,
 R^2 = nPr, 70%

21
80 %

azepine ring contraction (Scheme 11). However, neither intermolecular cyclopropanation (heating of **17** in the presence of an excess of activated olefin, e.g., 1,2-dihydrofuran, ethyl vinyl ether) nor intramolecular cyclopropanation (heating of **17c**) was observed. The structure of **20** was determined by 2D ^{1}H−^{13}C correlation experiments, such as HMQC and HMBC. In sharp contrast, refluxing **17b** in toluene under carbon monoxide (120 bar) afforded the unsymmetrical, substituted bispyrrole **21** in 80% yield. This result means that the unknown [3 + 2] cycloaddition of imines and alkynyl Fischer carbene complexes can be accomplished in two steps if an NH function is appropriately placed in the imine substrate, e.g., imines of type **8**.

Although an unambiguous reaction course is hard to delineate, it can be suggested that species of type **XII** and **XIII** might be involved in the formation of **20** and **21**, respectively (Scheme 12). In the first case, aziridine formation from **XII** and ring opening would lead to **20**.[30] Compound **21** would, in turn, result

(28) Crystal Data for structure **17b** 0.43 × 0.23 × 0.26 mm size, Monoclinic, space group P 2$_1$/c, a = 12.309(9) Å, b = 10.948(3) Å, c = 17.441(5) Å, γ = 103.00(6)°, V = 2290(2) Å^3, Z = 4, D$_x$ = 1.75 Mg/m^3, μ = 5.184 mm^{-1}, F(000) = 1176, T = 293(2) K. Final conventional R = 0.074 (ωR2 = 0.1753) for 2745 "observed" reflections and 265 variables, GOF = 1.033.

(29) (a) Rudler, H.; Audouin, M.; Parlier, A.; Martin-Vaca, B.; Goumont, R.; Durand-Réville, T.; Vaissermann, J. *J. Am. Chem. Soc.* **1996**, *118*, 12045. (b) Martin-Vaca, B.; Durand-Réville, T.; Audouin, M.; Rudler, H. *Synthesis* **1998**, 1534.

Scheme 12

"Umpolung processes"

Figure 4.
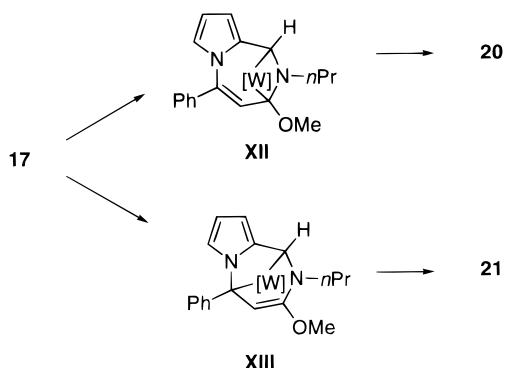
from **XIII** by nitrogen−carbon bond breaking via retro Michael type reaction followed by reductive elimination of the metal fragment.

Conclusions

We have shown that *C*-heteroarylimines, like those derived from furan-, benzofuran-, pyrrole-, and indole-2-carboxalde-hydes, smoothly undergo [3 + 3] and [4 + 3] cycloaddition reactions to alkenyl and alkynyl Fischer carbene complexes. These results are in sharp contrast with the observed failure of *C*-arylimines to react with Fischer carbene complexes.[31]

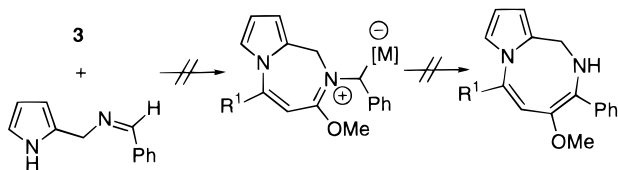For a wide generalization we can summarize the following:

(i) Imines derived from furan, benzofuran, and *N*-methyl indole aldehydes undergo [3 + 3] carbocyclization (C3 + C3) with alkynyl carbene complexes. The process involves nucleo-philic 1,2-addition of the ring C-3 carbon followed by [1,2]-M(CO)$_5$ promoted ring closure.

(ii) The reaction of N-unsubstituted pyrrole with alkenyl carbene complexes yields (C2N + C3) cycloadducts ([3 + 3] heterocyclization) in a similar manner as above except that the 1,2-addition occurs from the ring nitrogen atom.

In both cases, the [1,2]-migration of the metalpentacarbonyl moiety is responsible for the electrophilic-to-nucleophilic polar-ity change of the carbene ligand β-carbon (new "umpolung" reagent) (Figure 4). This finding allowed us to delineate new and unusual [3 + 3] carbo- and heterocyclizations which might be further extended to other types of substrates containing electrophilic/nucleophilic centers.

(iii) On the contrary, the Michael type addition takes place first when N-unsubstituted pyrrole and indole imines are reacted with alkynyl carbene complexes. The [4 + 3] heterocyclization (C2N2−C3) is completed by consecutive intramolecular attack of the imine nitrogen on the carbene carbon and [1,3]-M(CO)$_5$ migration. This new rearrangement probably is the result of a thermodynamic control, as a greater stabilization of the positive
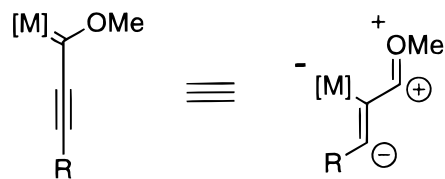
charge is achieved (species **XI** vs compound **17**; Scheme 8). In the context of Fischer carbene complexes, the X-ray analysis of the product resulting from a [1,3]-M(CO)$_5$ shift is provided for the first time.

In conclusion, we have presented new [4 + 3] and [3 + 3] cyclizations of alkynyl and alkenyl Fischer carbene complexes with various *C*-heteroaryl imines.[32] Significantly, the new patterns of reactivity disclosed for these versatile organometallic building blocks have been applied to annulations of pyrrole, furan, and indole rings. These results would complement sound achievements reached previously in the benzannulation of heteroaryl Fischer carbene complexes.[33]

Experimental Section

General Methods. IR spectra were recorded on an FT IR instrument. ^{1}H NMR spectra were recorded at 200 and 300 MHz using TMS as an internal standard. ^{13}C NMR spectra were recorded at 50, 75, and 100 MHz. ^{13}C NMR multiplicities were determined by DEPT experiments. 2D experiments were performed on a 400-MHz spectrometer. Unless otherwise noted, NMR experiments were run in CDCl$_3$. High-resolution mass spectra (HRMS) were determined at an ionizing voltage of 70 eV. Column chromatography was performed with silica gel (230−400 mesh) by standard flash chromatographic techniques. All reactions were carried out under nitrogen.

Materials. THF and hexane were treated with sodium and distilled over sodium. CH$_3$CN was distilled from CaH$_2$. The preparations of the starting Fischer carbene complexes **1**−**3** have been previously described.[21] Except for indole-2-carboxaldehyde,[34] all the aldehydes and amines necessary for preparing imines **4**−**8** are commercially available.

General Procedure for the Preparation of Imines 4−9. To a solution of the corresponding 2-carboxaldehyde heterocycle (20 mmol) in diethyl ether (40 mL) was slowly added a solution of the primary amine (30 mmol) in diethyl ether (40 mL). The reaction was stirred at room temperature for 4 h, anhydrous sodium sulfate (3 g) was added to the mixture, and the mixture allowed to stand for 30 min. The crude was then filtered off and the solvent removed under vacuum. The residue thus obtained consisted, almost quantitatively, of the imine derivatives which were used as such without further purification.

General Procedure for the Preparation of Benzofurans 10 and 11 and Carbazole 12. To a solution of carbenes **2a** and **3** (1 mmol) in THF (30 mL) the corresponding imine, **4**, **5**, or **7** (1 mmol), in THF (5 mL) was slowly added at room temperature. After being stirred for 4 h, the resulting mixture was filtered through Celite and the solvent was removed under vacuum. The crude thus obtained was purified by column chromatography (silica gel, 10:1 hexanes/ethyl acetate)) to afford the corresponding product **10**−**12**.

4-Methoxy-6-phenyl-7-propylaminobenzofuran (10). Yield: 76% from **2a**; 68% from **3**. ^{1}H NMR (300 MHz): δ = 0.84 (t, [3]*J*(H,H) =

(30) On the basis of this proposal, it was realized that ring expansion would occur if an imine derived from 2-aminomethylpyrrole were employed (see below):

Unfortunately, the reaction of the benzaldehyde imine with carbene **3** did not afford the corresponding pyrrolodiazepine, but only decomposition products were formed.

(31) (a) Murray, C. K.; Warner, B. P.; Dragisich, V.; Wulff, W. D.; Rogers, R. D. *Organometallics* **1990**, *9*, 3142. (b) Unpublished results from our laboratory.

(32) Regarding the metal there are only minor variations, all related to yields, when shifting from chromium to tungsten complexes. This is in sharp contrast with our previous results in the cyclization reactions of simple 1-azadienes with alkynyl Fischer carbene complexes (see refs 4e and 22).

(33) a) Yamashita, A. *J. Am. Chem. Soc.* **1985**, *107*, 5823. (b) Yamashita, A.; Scahill, T. A.; Toy, A. *Tetrahedron Lett.* **1985**, *26*, 2969. (c) Bauta, W. E.; Wulff, W. D.; Pavkovic, S. F.; Zaluzec, E. J. *J. Org. Chem.* **1989**, *54*, 3249 and references therein.

(34) Katritzky, A. R.; Akutagawa, K. *Tetrahedron Lett.* **1985**, *26*, 5935.

7.5 Hz, 3H); 1.46 (m, 2H); 3.30 (t, ^3J(H,H) = 7.2 Hz, 2H); 3.90 (s, 3H); 6.53 (s, 1H); 6.89 (d, ^3J(H,H) = 2.2 Hz, 1H); 7.3−7.5 (m, 5H); 7.62 (d, ^3J(H,H) = 2.2 Hz, 1H). ^{13}C NMR (75 MHz): δ = 147.3 (s), 146.3 (s), 143.6 (d), 140.0 (s), 129.5 (d), 128.6 (d), 127.1 (d), 126.2 (s), 126.0 (s), 118.4 (s), 106.0 (d), 104.1 (d), 55.7 (q), 49.4 (t), 23.7 (t), 11.3 (q). Anal. Calcd for C$_{18}$H$_{19}$NO$_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.91; H, 6.98; N, 4.77.

General Procedure for the Preparation of Indolizines 14 and Indolizinones 15. A solution of imine **8** (1 mmol) in acetonitrile (5 mL) was slowly added at room temperature to a solution of carbene **1** (1 mmol) in acetonitrile (40 mL). After being stirred for 8 h, the resulting mixture was filtered through Celite and the solvent removed under vacuum. The crude thus obtained was characterized by NMR to be the indolizine **14**. Column chromatography purification (silica gel, 4:1 hexanes/ethyl acetate) afforded the corresponding indolizinone **15**.

trans-**7-Phenyl-8-propylamino-7,8-dihydroindolizin-5-one 15a:** Yield: 58%. ^{1}H NMR: δ = 0.90 (t, ^3J(H,H) = 7.3 Hz, 3H); 1.42 (m, 2H); 1.7 (broad s, 1H); 2.65 (m, 2H); 2.94 (dd, ^2J(H,H) = 17.2 and ^3J(H,H) = 8.6 Hz, 1H); 3.23 (dd, ^2J(H,H) = 17.2 and ^3J(H,H) = 3.7 Hz, 1H); 3.48 (broad s, 1H); 4.17 (d, 1H, ^3J(H,H) = 7.2 Hz); 6.23 (m, 1H); 6.31 (m, 1H); 7.2−7.5 (m, 6H). ^{13}C NMR (75 MHz): δ = 167.3 (s), 140.0 (s), 133.9 (s), 128.8 (d), 127.2 (d), 127.1 (d), 116.5 (d), 112.9 (d), 110.6 (d), 56.9 (d), 48.0 (t), 44.9 (d), 37.6 (t), 23.3 (t), 11.5 (q). Anal. Calcd for C$_{17}$H$_{20}$N$_2$O: C, 76.09; H, 7.51; N, 10.44. Found: C, 75.87; H, 7.66; N, 10.55.

General Procedure for the Preparation of Pyrrolodiazepines 17. To a solution of carbenes **2** and **3** (1 mmol) in hexane (20 mL), imine **8** (1 mmol) in hexane (5 mL) was slowly added at room temperature. After 12 h the precipitate is filtered, washed with cold hexane (3 × 5 mL), and subjected to column-chromatography purification (silica gel, 4:1 hexanes/ethyl acetate) to afford the pyrrolodiazepines **17**.

Pyrrolo[1,2-a]-1,4-diazepine chromiumpentacarbonyl complex (17a): Yield: 93%. ^{1}H NMR: δ = 0.97 (t, ^3J(H,H) = 7.3 Hz, 3H); 1.8 (m, 2H); 3.2 (m, 1H); 4.0 (m, 1H); 4.16 (s, 3H); 4.67 (s, 1H); 5.6 (m, 2H); 6.2 (m, 2H); 7.4−7.8 (m, 5H). ^{13}C NMR (75 MHz): δ = 224.5 (s), 220.8 (s), 161.2 (s), 155.7 (s), 144.9 (s), 135.9 (s), 131.9 (d), 130.5 (d), 129.0 (d), 122.5 (d), 113.9 (d), 103.7 (d), 98.0 (d), 59.1 (q), 55.1 (t), 50.8 (d), 21.3 (t), 12.0 (q). IR (CDCl$_3$) v[cm^{-1}] = 1906, 2052. Anal. Calcd for C$_{23}$H$_{20}$CrN$_2$O$_6$: C, 58.48; H, 4.27; N, 5.93. Found: C, 58.10; H, 4.33; N, 6.13.

General Procedure for the Preparation of Pyrrolodiazepines (18). To a solution of carbenes **2** and **3** (1 mmol) in THF (20 mL) imine **8** (1 mmol) in THF (5 mL) was slowly added at room temperature. After 12 h the crude was filtered through Celite and subjected to column-chromatography purification (silica gel, 4:1 hexanes/ethyl acetate) to afford the pyrrolodiazepines **18**.

Indolo[1,2-a]-1,4-diazepine Chromiumpentacarbonyl Complex (18a). Yield: 33%. ^{1}H NMR: δ = 0.94 (t, ^3J(H,H) = 7.2 Hz, 3H); 1.83 (m, 2H); 3.16 (m, 1H); 4.02 (m, 1H); 4.16 (s, 3H); 4.72 (broad s, 1H); 5.2 (m, 2H); 7.0−7.6 (m, 9H). ^{13}C NMR (75 MHz): δ = 223.7 (s), 219.8 (s), 160.9 (s), 155.2 (s), 153.3 (s), 136.6 (s), 135.8 (s), 132.5 (s), 131.5 (d), 128.7 (d), 128.6 (d), 122.1 (d), 120.9 (d), 120.2 (d), 113.8 (d), 99.7 (d), 98.7 (d), 58.6 (q), 54.8 (t), 50.8 (d), 20.6 (t), 11.4 (q). IR (CDCl$_3$) v[cm^{-1}] = 1907, 2048. Anal. Calcd for C$_{27}$H$_{22}$CrN$_2$O$_6$: C, 62.07; H, 4.24; N, 5.36. Found: C, 61.75; H, 4.34; N, 5.55.

Hydrolysis of Pyrrolodiazepine Complexes 17. Preparation of Pyrrole-2-carboxaldehydes 19. A solution of complex **17** (0.5 mmol) in 15 mL of a mixture of 01.M HCl−THF (1:1 v/v) was stirred at room temperature for 2 h and then extracted with ethyl acetate (3 × 20 mL). The organic layers were washed with brine and dried with anhydrous sodium sulfate, and the solvents were removed under vaccum. The crude thus obtained was purified by column chromatography (silica gel, 10:1 hexanes/ethyl acetate) affording the correponding pyrroles **19**.

Methyl-(Z)-3-(2-formylpyrrole-1-yl)-2-heptenoate (19b): Yield: 79%. ^{1}H NMR: δ = 0.8 (m, 3H); 1.2−1.4 (m, 4H); 3.0 (t, ^3J(H,H) = 7.0 Hz, 2H); 3.4 (s, 3H); 5.9 (s, 1H); 6.2 (m, 1H); 6.8 (m, 1H); 7.0 (m, 1H); 9.5 (s, 1H). ^{13}C NMR (75 MHz): δ = 178.0 (d); 156.0 (s); 146.0 (s); 131.6 (s); 131.1 (d); 124.4 (d); 114.6 (d); 110.0 (d); 52.1 (q); 36.1 (t); 24.4 (t); 21.9 (t); 13.6 (q). MS(70 eV) *m/z*: 235 (4) [M$^+$], 205 (100), 190 (26), 176 (38), 162 (51). Anal. Calcd for C$_{13}$H$_{17}$NO$_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.23; H, 7.45; N, 6.21.

Heating of Pyrrolodiazepine Complexes 17. Preparation of Indolizines 20. A solution of pyrrolodiazepine **17** (0.5 mmol) in toluene (15 mL) was refluxed for 6 h. The crude was filtered through Celite, the solvent removed under vacuum, and the residue subjected to column-chromatography purification (silica gel, 4:1 hexanes/ethyl acetate) to afford the indolizines **20**.

7-Methoxy-5-phenyl-8-propylaminoindolizine (20a). Yield: 84%. ^{1}H NMR: δ = 1.04 (t, ^3J(H,H) = 7.3 Hz, 3H); 1.67 (m, 2H); 3.46 (t, ^3J(H,H) = 7.4 Hz, 2H); 3.86 (s, 3H); 6.41 (s, 1H); 6.52 (m, 1H); 6.72 (m, 1H); 7.31 (m, 1H); 7.4−7.6 (m, 5H). ^{13}C NMR (75 MHz): δ = 137.3 (s), 135.7 (s), 129.9 (s), 129.8 (s), 128.8 (d), 128.6 (d), 128.5 (d), 126.1 (s), 112.8 (d), 110.2 (d), 104.4 (d), 96.7 (d), 58.2 (q), 48.3 (t), 24.1 (t), 11.4 (q). Anal. Calcd for C$_{18}$H$_{20}$N$_2$O: C, 77.11; H, 7.19; N, 9.99. Found: C, 77.34; H, 7.09; N, 10.12.

Heating of Pyrrolodiazepine Complexes 17 under CO. Preparation of Bispyrrole 21. A solution of pyrrolodiazepine **17** (0.5 mmol) in toluene (15 mL) was refluxed under CO pressure (120 bar) for 48 h. The residue was then filtered through Celite and the solvent removed under vacuum. Purification by column chromatography (silica gel, 8:1 hexanes/ethyl acetate) afforded the bispyrrole **21** in 68% yield. ^{1}H NMR: δ = 0.9 (t, ^3J(H,H) = 7.3 Hz, 3H); 1.67 (m, 2H); 3.76 (t, ^3J(H,H) = 7.5 Hz, 2H); 3.92 (s, 3H); 5.61 (s, 1H); 6.3 (m, 2H); 6.8 (m, 1H); 7.0−7.4 (m, 5H); 7.92 (broad s, 1H). ^{13}C NMR (75 MHz): δ = 148.9 (s); 136.2 (s); 128.1 (d); 126.8 (d); 124.9 (d); 122.3 (s); 120.1 (s); 117.8 (d); 114.0 (s); 109.7 (d); 108.9 (d); 82.7 (d); 57.3 (q); 43.9 (t); 23.9 (t); 11.1 (q). Anal. Calcd for C$_{18}$H$_{20}$N$_2$O: C, 77.11; H, 7.19; N, 9.99. Found: C, 77.14; H, 7.12; N, 10.11.

Supporting Information Available: Spectroscopic data and elemental analyses for compounds **11**, **12**, **14a,b**, **15b**, **17b**−**d**, **18b,c**, **19a**, **20b,c**. Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **17b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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