Reaction of Alkynyl Alkoxy Metal Carbene Complexes with 1,2-Diamines

Josep M. Moretó,[†] Susagna Ricart,*[,†] Karl Heinz Dötz,[‡] and Elies Molins[§]

Departament de Química Orgànica i Biològica, IIQAB (CSIC), C/J Girona 18-26, S-08034, Barcelona, Spain, Kekulé-Institut für Organische Chemie und Biochemie der Rheinischen Friedrich Wilhelms Universität, Gerhard-Domagk-Strasse 1, D-53121 Bonn, Germany, and Institut de Ciències de Materials de Barcelona, Campus Universitari de Bellaterra, 08193-Cerdanyola, Barcelona, Spain

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The reaction of alkynyl alkoxy metal carbene complexes with 1,2-primary and -secondary diamines is described. New mono- and biscarbene amino complexes are described and fully characterized, and the influence of the reaction conditions and esteric and electronic factors on the product distribution is studied.

Introduction

The activation of C═C and C≡C bonds in unsaturated Fischer-type carbene complexes due to the pentacarbonyl metal electron acceptor moiety has been widely applied in organic synthesis.[1] Typical examples of this activation are the facilitation of Diels−Alder[2] and intramolecular Pauson−Khand reactions in vinyl and alkynyl carbene complexes described some time ago.[3]

Our current interest in polar acetylenic systems has focused on alkynyl alkoxy carbene complexes, and thus, we have studied their reactivity toward different nucleophiles.[4] The presence of the metal carbonyl moiety enhances the inherent reactivity of the triple bond, and therefore, the addition of nucleophiles occurs under very mild reaction conditions.

The early work of E. O. Fischer on the reaction of primary and secondary amines with alkynyl alkoxy metal carbenes[5] revealed the importance of the kinetic versus thermodynamic control in this reaction and the influence brought about by the steric and electronic effects in the regiochemistry (1-substitution versus 3-addition) and stereochemistry in the resulting product mixture.[6] In this way, different studies aimed to control the stereochemistry of the products obtained either in the addition of amines onto the triple bond (3-addition) or in the substitution at the carbene carbon atom (1-substitution). Reactions of other nucleophiles such as carbanions,[7] alcohols, phenols, thiols,[8] and phosphines[9] have also been studied. As a general rule, when the reaction takes place at room temperature, the only product obtained corresponds to that from 3-addition, giving, usually, the *E* isomer. Softer and stabilized nucleophiles such as phenols and thiols exhibit a lower stereoselectivity, probably due to some extent to a retro-Michael reaction.[10] A special case is that of catechol, which gives a single product arising from double conjugate addition.[8]

In his studies on the reactivity of alkynyl alkoxy carbene complexes with hydrazines, Aumann observed at room temperature the exclusive formation of five-membered heterocycles.[11] However, at −78 °C a competition of aminolysis and [3+2] cycloaddition to give five-membered heterocycles was observed. Six-membered heterocycles were obtained exclusively in the reaction of alkynyl alkoxy carbene complexes with amidines, aminopyridines, ureas, and thioureas.[12] Recently Barluenga et al.[13] reported a [4+3] annulation of alkynyl alkoxy carbene complexes and pyrrol imines affording pyrrolodiazepine derivatives. We now report on the addition of 1,2-diamines to alkoxy alkynyl carbene complexes.

* Corresponding author. E-mail: srmqob@cid.csic.es.
[†] IIQAB.
[‡] Kekulé-Institut für Organische Chemie und Biochemie.
[§] ICMB.

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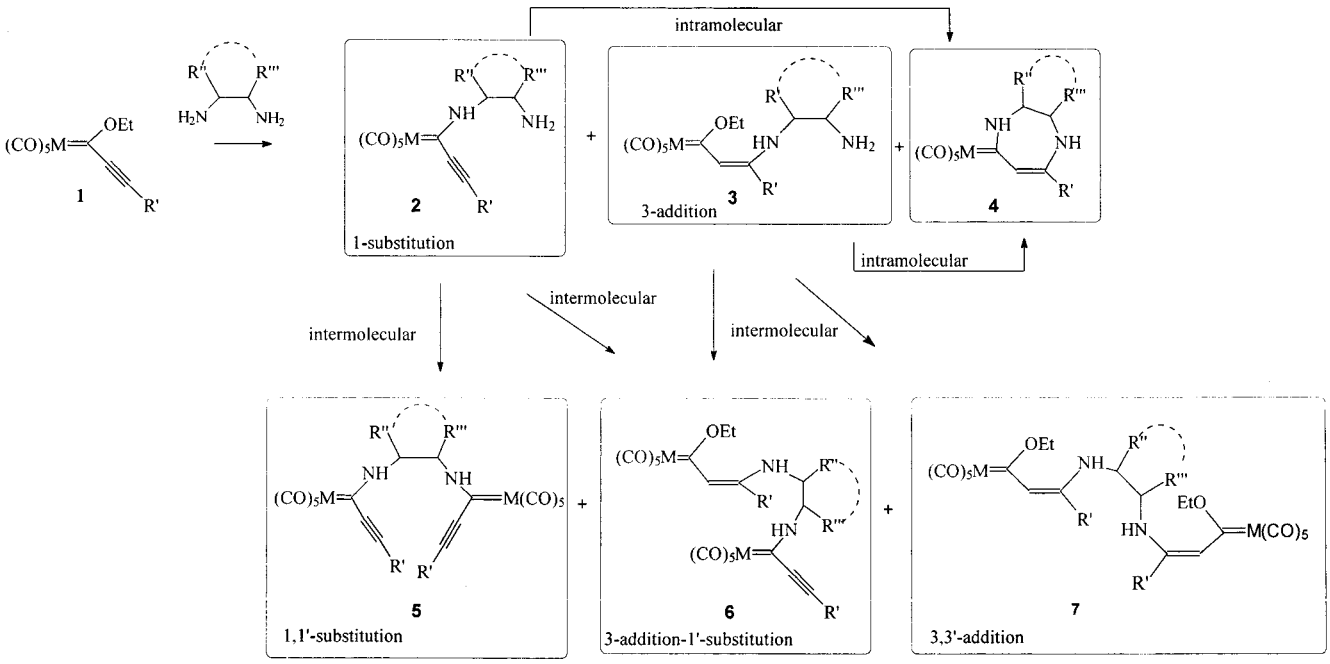
Scheme 1



Results and Discussion

Reaction with Primary 1,2-Diamines. Taking into account those precedents, the reaction of 1,2-primary diamines with alkynyl alkoxy metal carbene complexes at low temperatures in THF was expected to give the aminolysis (1-substitution) product **2** (Scheme 1). On the other hand, the presence of a second primary amino group nearby would likewise lead to the formation of the intramolecular 3-addition product **4**. However, the formation of a seven-membered ring product such as **4** in this case appeared rather unfavorable due to geometric factors. Alternatively, the reaction at room temperature could give the 3-addition product **3** as the major reaction product. In this case, the presence of a second amino group could afford, also, the seven-membered ring compound **4** in an intramolecular way.

If the reaction takes place in an intermolecular way, biscarbenes **5**, **6**, and **7** could be obtained.

The competition of intermolecular versus intramolecular pathways markedly depends on the reaction conditions and the electronic and steric properties of the diamine used. As shown in Figure 1 we have studied the reaction of alkynyl carbene complexes **1** with 1,2-primary and secondary diamines **8a**−**i**.

Reaction of 1a with Diamines 8a−**e.** We started our work by testing the behavior of three ethylenediamino compounds with **1a.** The diamines differed in the substitution pattern of the ethylene bridge in order to asses the effects of the steric hindrance on the course of the process. The treatment of carbene complex **1a** with diamines **8** (molar ratio 1:1) at −78 °C in THF led to complete disappearance of the starting complex after the addition of the diamine was completed. Noteworthy, in the case of ethylenediamine **8a**, the starting carbene complex completely disappeared (indicated by a titration-like change of the solution color from deep brown to bright yellow) even before completion of the addition. After evaporation of the solvent and flash chromatography of the crude, the biscarbene complex **5a** was

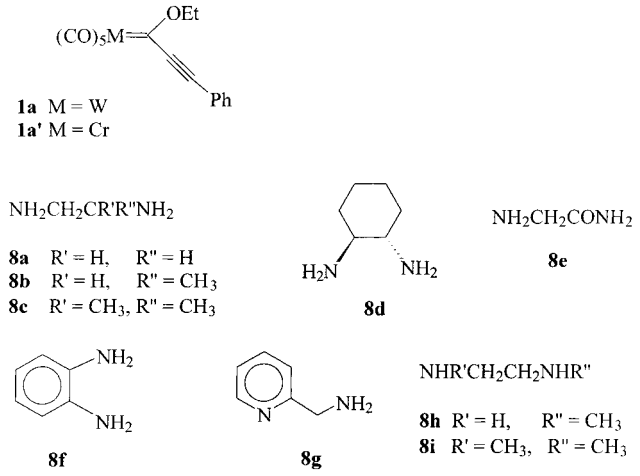
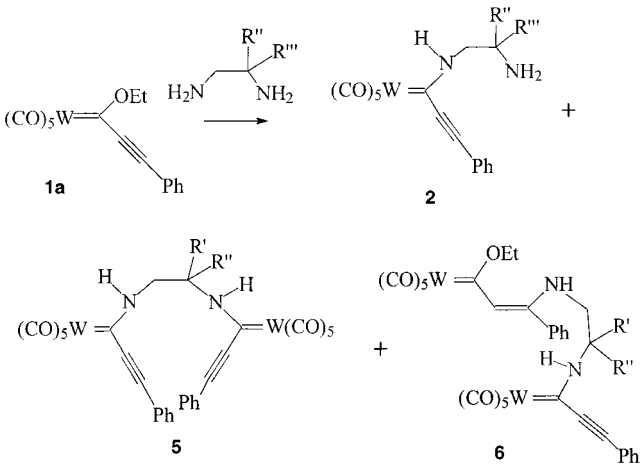


Figure 1.

obtained in good yield (60%). Under optimized conditions (increasing the carbene concentration and careful dropwise addition of diamine **8a)**, compound **5a** was isolated in nearly quantitative yield. On the contrary, more diluted solutions of the starting carbene complex after addition of an excess of the diamine **8a** decreased the yield of the biscarbene complex **5a**, while small amounts of the monoamino carbene complex **2a** could be isolated. When the reaction was performed at room temperature and with high carbene complex concentrations, biscarbene complex **6a** was obtained in 80% yield, indicating that, under these conditions an aminolysis and conjugate addition sequence is preferred. Using more diluted solutions of the starting carbene complexes, we obtained **6a** only with lower yields but the monoadduct carbene complex **3a** was never observed in the reaction mixture.

Similar results were obtained in the reaction of **1a** with the amines **8b** and **8c**, as shown in Table 1, although in these cases the aminolysis products **2b** and **2c** were obtained in higher yields depending on the reaction conditions.

Table 1



entry	amine	time	temp	products (yield)
1	**8a**	1 min	−78 °C	**5a** (60%), **2a** (tr)[a]
2	**8a**	1 min	−78 °C	**5a** (78%)[b]
3	**8a**	1 min	rt	**6a** (80%)[c]
4	**8b**	1 min	−78 °C	**2b** (70%)[a,d]
5	**8b**	1 min	−78 °C	**5b** (45%)[b]
6	**8b**	1 min	rt	**6b** (40%)[c], **9b** (12%), **10** (16%)[e]
7	**8c**	1 min	−78 °C	**2c** (90%)[a]
8	**8c**	24 h	−78 °C	**5c** (30%)[b], **6c** (17%)
9	**8c**	1 min	rt	**2c** (76%)[c]
10	**8c**	24 h	rt	**6c** (80%)[f]

[a] Reaction conditions: To a 0.02 M solution of **1** in dry THF at −78 °C under stirring was added 1 equiv of the diamine. [b] Reaction conditions: To a 0.2 M solution of **1** in dry THF at −78 °C under stirring was added dropwise 0.5 equiv of the diamine. [c] Reaction conditions: To a 0.2 M solution of **1** in dry THF at room temperature and under stirring was added dropwise a 0.2 M solution of the corresponding amine until color change. [d] Yield calculated from the NMR data. [e] A cyclic diamine **9b** and acetophenone **10** were obtained under these reaction conditions. [f] Reaction conditions: To a 0.2 M solution of **1** in dry THF at room temperature under stirring was added dropwise 0.5 equiv of the diamine.

Entries 4−10 demonstrate that the steric bulk of the ethylene bridge plays an important role in this type of reaction. Increasing alkylation hampers the formation of biscarbene complexes and, instead, favors the monoaminolysis. Under the standard low-temperature conditions complexes **2b** and **2c** were obtained in 70% and 90% yields, respectively. Only longer reaction times allowed the formation of significant amounts of dinuclear complexes (entries 8 and 10).

The reaction of diamine **8b** at room temperature deserves a special comment. In this case, a careful control of the reaction conditions was necessary to prevent the easy formation of byproducts such as acetophenone **10** and a cyclic diamino carbene complex **9** probably arising as described in Scheme 2. In the ^{1}H NMR spectrum of the crude mixture it was possible to observe a signal at 6.00 ppm, assignable to the intermediate **4**. This signal disappeared after some time in $CDCl_3$ solution.

This pathway suggests a pronounced basicity of amino compounds **4** imposed by the enamine moiety, which prevents their isolation by chromatography. This result contrasts with the recent report by Barluenga et al.[13] on the reaction of alkynyl alkoxy carbenes with imino pyrroles.

The reaction of **1a** with cyclohexyldiamine **8d** at −78 °C and under carefully controlled dropwise addition of the diamine afforded two main products, one (30%) corresponding to the 1-substitution product **2d** and the other (40%) to the biscarbene system **5d**. Working at room temperature, however, we always obtained complex mixtures of compounds containing small amounts of monoaminolysis (1-substitution) product **2d**, acetophenone **10**, and the product of the cross addition **6d**.

Table 2

	^{13}C δ CH_2 (ppm)	^{13}C δ CH (ppm)
8b	50.2	49.0
2b	58.9	45.9
5b	55.9	57.8
	^{13}C δ CH_2 (ppm)	^{13}C δ C (ppm)
8c	54.2	50.0
2c	62.4	49.7
5c	58.9	63.6

In the aminoacetamide **8e** the presence of the carbonyl functionality markedly reduces the nucleophilicity of the adjacent amino group. Thus, as expected, only the 1-substitution product **2e** was obtained in very good yield (94%) working at low temperature (−78 °C). Unexpectedly, complex **2e** was also the main product when working at room temperature (72%), and only minor amounts (12%) of the expected 3-addition product **3e** were obtained.

When the diamine **8a** was allowed to react with the chromium carbene complex **1a′**, the dinuclear products **5a′** and **6a′** were obtained in similar yields (80% and 90%, respectively) as described for the tungsten complexes.

Spectroscopy of 2b,c, 5a−c, and 6a−c. In all the cases studied, only one product from the monoaminolysis reaction of products **1** was obtained with the general structure **2**. The regiochemistry for **2b** and **2c** was established by means of ^{13}C NMR data by comparing the products obtained with the starting diamines (**8b** and **8c**) and with the product of the double aminolysis (**5b** and **5c**). The ^{13}C NMR shifts for the carbon atoms on the ethylene bridge are shown in the Table 2.

From the data shown in Table 2 we observe that there are significant changes in the ^{13}C chemical shift for the methylene and methyne (or quaternary) carbon atoms of the amines that can be of diagnostic value. Thus when observing the corresponding data, it can be concluded that for the methylene carbons there is a moderate change (∼7−9 ppm downfield) in the first aminolysis (products 2) and a small one (∼3 ppm upfield) after the second aminolysis (products **5**). The converse applies for the methyne (or quaternary) carbons. Taking into consideration that the carbene center is an electronically deshielded center, we can assume that the regiochemistry for compounds **2** is the one shown in the Figure 2.

We studied, some time ago, the stereochemistry of the aminolysis reaction with primary amines in alkynyl alkoxy carbene systems[14] and established that, in all the cases studied, the stereochemistry *E* for the double bond between the nitrogen and the carbene carbon atom in the main reaction product (usually >95% of the overall yield) had resulted. As we stated before, only one product was obtained in the aminolysis reaction with primary diamines, and we assume then that

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Scheme 2

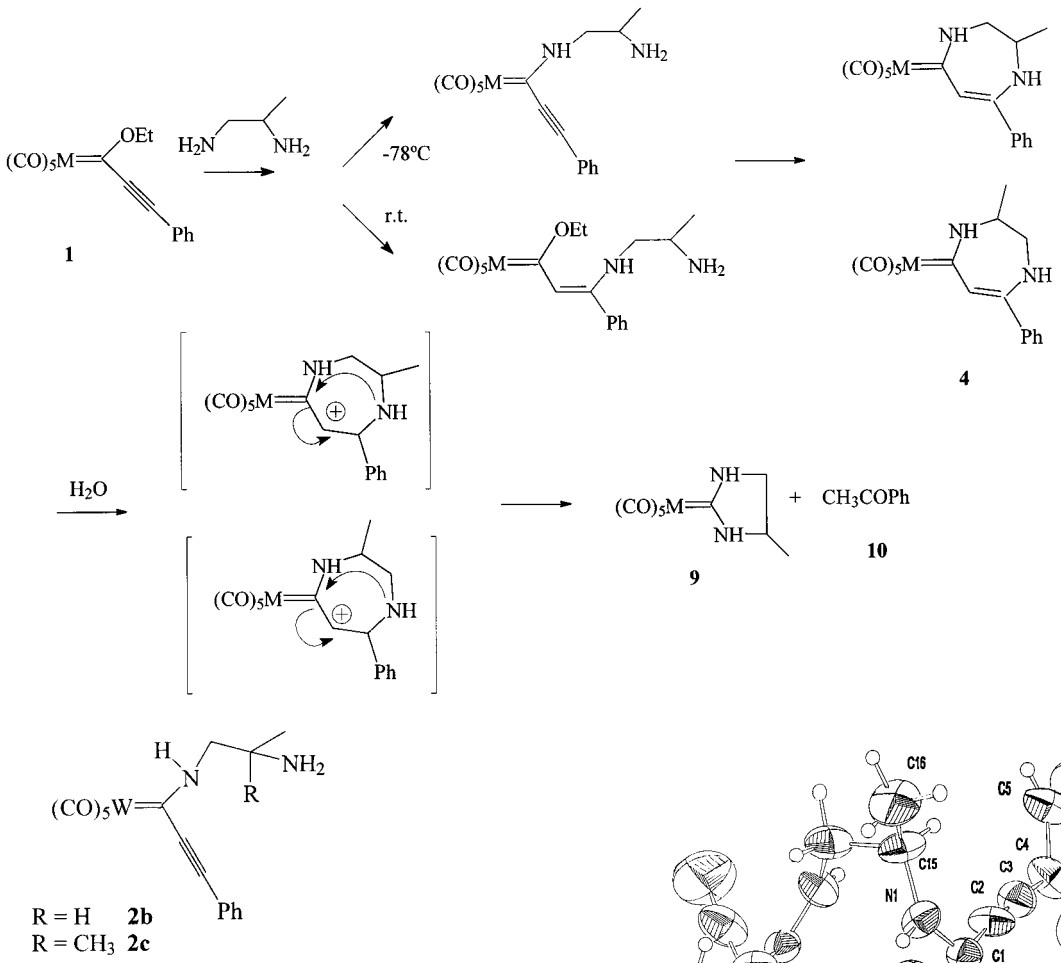


Figure 2.

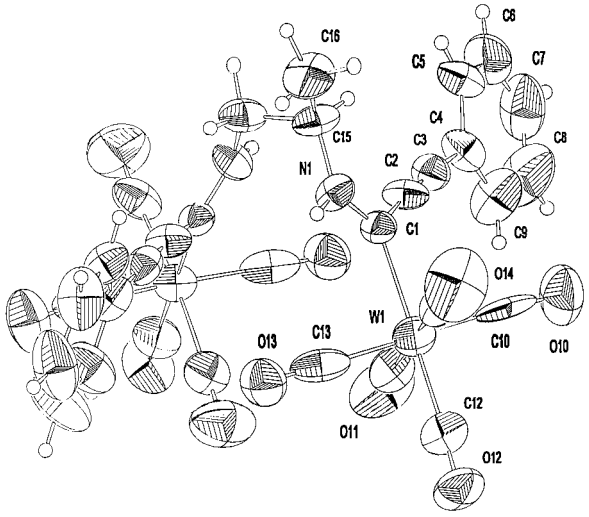


Figure 3. Molecular structure of biscarbene complex **5b**. Selected bond lengths (Å) and angles (deg): W (1)−C(1) = 2.246(13), C(1)−N(1) = 1.310(16), N(1)−C(15) = 1.459(16), C(1)−C(2) = 1.40(2), C(2)−C(3) = 1.19(2), C(3)−C(4) = 1.43(2); W(1)−C(1)−N(1) = 123.9(12) W(1)−C(1)−C(2) = 118.3(10), C(2)−C(1)−N(1) = 117.8(12), C(1)−N(1)−C(15) = 124.9(12).

product corresponded to the one with the former stereochemistry, which could be confirmed in the case of compounds **5b**, for which a X-ray diffraction structure could be carried out. Figure 3 shows the molecular structure of **5b**, confirming its dimeric character and the stereochemistry *E* for the nitrogen carbene carbon double bond.

Concerning products with the general structure **6**, we have established the regiochemistry in the case of **6b** and **6c** taking into account, as in the case of compounds **2**, the change in ^{13}C chemical shifts for the carbons in the ethylene bridge and also the fact that they could be obtained by further reaction of products **2** at room temperature with 1 equiv of the starting alkynyl alkoxy carbene **1a**. The *Z* stereochemistry for the C−C double bond was based on the work of Aumann[15] and confirmed by NOE experiments in the case of compounds **6a** and **6c**.

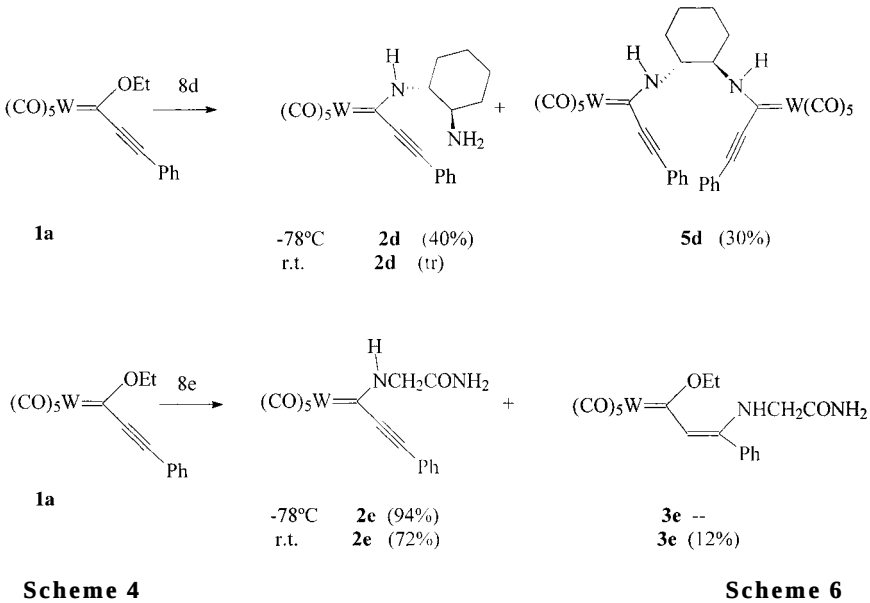
Reaction of 1a with Amines 8f and 8g. The reaction of aromatic diamine **8f** with carbene complex **1a** afforded the conjugate addition product **3f** independent of whether the reaction was run at −78 °C or at room temperature (see Scheme 5). The addition of another equivalent of carbene complex **1a** resulted in the formation of biscarbene complex **7f** in very good yield.

Picolylamine **8g** bears two N-functionalities, which significantly differ in their nucleophilicity. As expected, the amino group prefers addition at the "harder" electrophilic carbene center, giving a 90% yield of aminolysis product **2g** at −78 °C. At room temperature the regioselectivity is decreased, and the conjugate addition product **3g** is formed as a byproduct in significant amounts (Scheme 6).

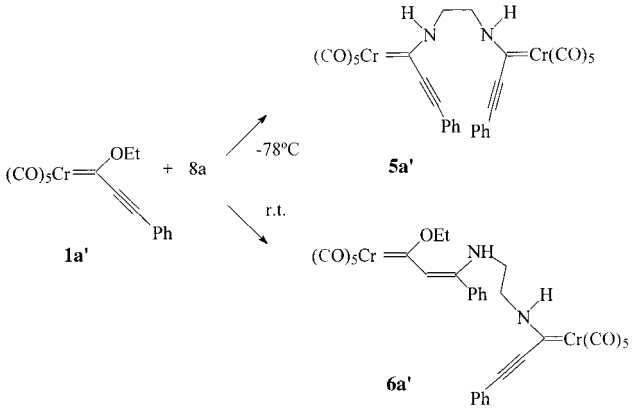
Reaction of 1a with Secondary Diamines 8h,i. The reaction of complex **1a** with diamines **8h**,**i** was less selective and afforded very complex mixtures. A carefully controlled addition of the amine to the stirred solution of the carbene complex was required to allow

(15) Aumann, R.; Roths, K. B.; Kössmeier, M.; Frölich, R. *J. Organomet. Chem.* **1998**, *556*, 119−127.

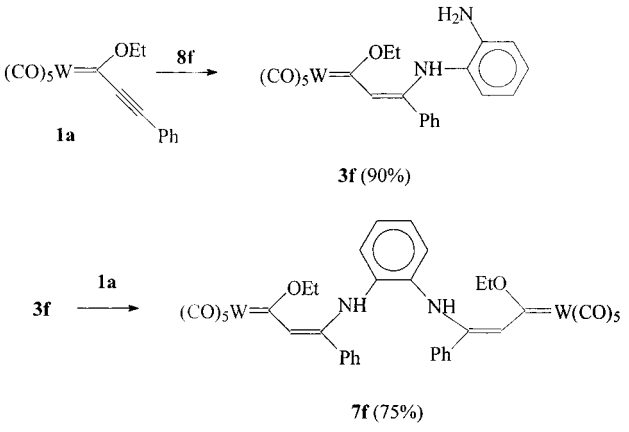
Scheme 3



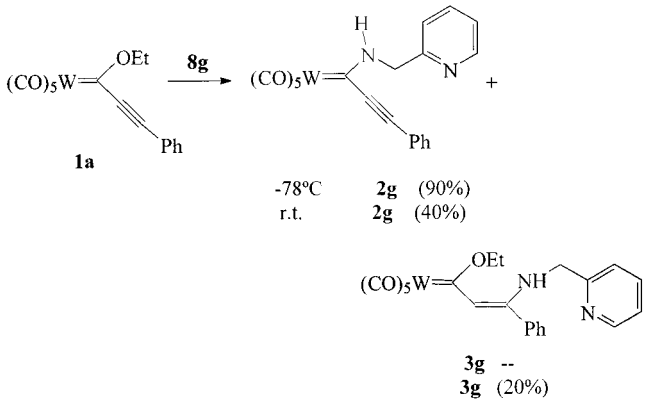
Scheme 4



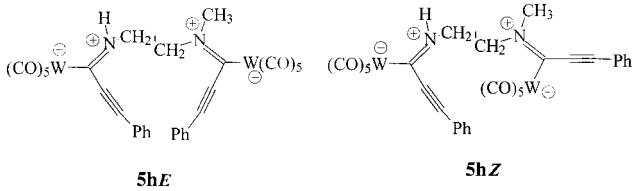
Scheme 5



Scheme 6



Scheme 7



isolation and identification of some of the compounds formed. The results are shown in Table 3.

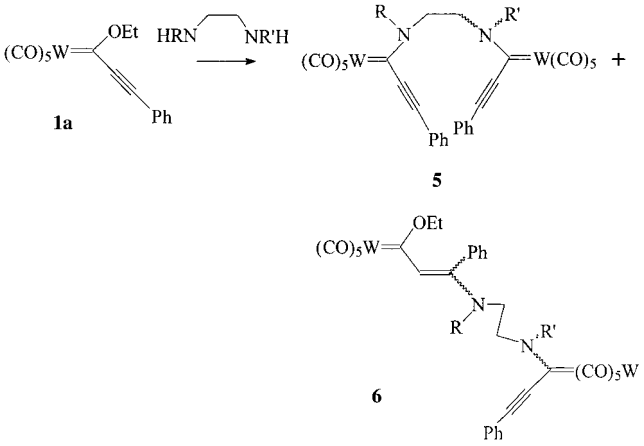
It is known that the aminolysis reaction of carbene complexes with secondary amines[16] affords a mixture of isomers due to the double bond character of the nitrogen−carbene carbon bond. In our case, spectroscopic data[11,14] established the existence of a 70/30 mixture of isomers *E*,*E*-**5h** and *E*,*Z*-**5h** (Scheme 7), which could be separated by chromatography. However, from diamine **8i**, although we obtained two products with the molecular weight corresponding to the cross addition complex **6i** (entries 4, 5, and 6, Table 3), we were not able, from the spectroscopic data, to make an univocal assignment in this case. The possible existence of a dynamic process between *E* and *Z* isomers might produce a global broadening of the signals in both the ^{1}H and ^{13}C spectra, as is observed. Studies directed to explain this abnormal behavior are currently in progress in our laboratory.

Discussion

Taking into account all our results, it is evident that the 1-substitution product arising from aminolysis is generally preferred for the diamines studied here. The only exception is the aromatic diamine **8f**, a possible explanation for this behavior being based on the soft/

(16) (a) Fischer, E. O.; Leupold, M. *Chem. Ber.* **1972**, *105*, 599. (b) Moser, E.; Fischer, E. O. *J. Organomet. Chem.* **1969**, *16*, 275−282.
(17) Dötz, K. H.; Kuhn, W. *J. Organomet. Chem.* **1985**, *286*, C23−C26.

Table 3



entry	amine	temp	products (yield)
1	**8h**	−78 °C	**5h** (9%),[a] **14h** (30%)
2	**8h**	−78 °C	**5h** (70%)[b,c]
3	**8h**	rt	**6h** (56%)[d]
4	**8i**	−78 °C	**6i** (50%)[a,c]
5	**8i**	−78 °C	**6i** (50%)[b,c]
6	**8i**	rt	**6i** (70%)[c,d]

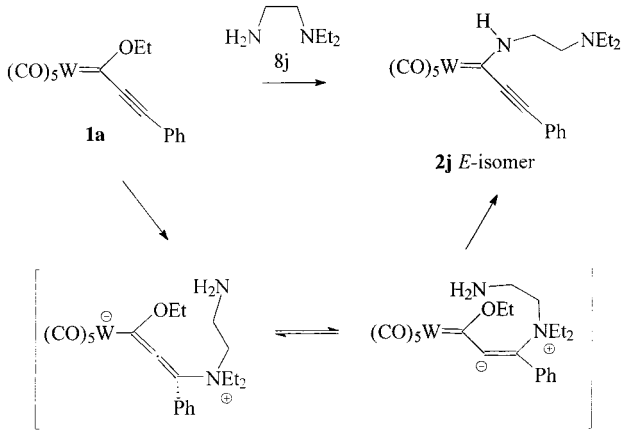
[a] Reaction conditions: To a 0.02 M solution of **1** in dry THF at −78 °C under stirring was added 1 equiv of the diamine. [b] Reaction conditions: To a 0.2 M solution of **1** in dry THF at −78 °C under stirring was added dropwise 0.5 equiv of the diamine. [c] In this case a mixture of isomers was obtained. [d] Reaction conditions: To a 0.2 M solution of **1** in dry THF at room temperature and under stirring was added dropwise a 0.2 M solution of the corresponding amine until color change.

Table 4

	E,E-**5h**		*E,Z*-**5h**	
	^{1}H	^{13}C	^{1}H	^{13}C
CH_3	3.86	50.0	3.68	44.36
CH_2	4.40	57.1	4.55	61.5

hard relationship between the diamino systems and the two electrophilic centers present in the alkynyl carbene complex **1**. Additional support for this idea arises from the reaction with picolylamine, where the two N-functionalities significantly differ in their nucleophilicity. The soft aromatic nitrogen favors addition to the soft alkynyl carbon, while the harder alkyl amino group prefers the hard carbene center. In the case of two equivalent amino groups (ethylenediamines **8** or diaminocyclohexane **8d**) the products obtained under thermodynamic conditions (higher temperatures) are those that may be regarded arising from a kinetically controlled reaction (**2c**,**d**). However, since we are dealing here with diamines, we can explain the apparent change in trend by the existence of a distal N-assistance, with formation of a zwitterionic intermediate, due to the presence of the second nitrogen atom. To assess this pathway, we have performed the reaction of complex **1** with diamine **8j** at room temperature. Product **2j** is exclusively obtained in 90% yield. We can assume that the softer tertiary amine reacts preferentially with the triple bond, affording the quaternary ammonium salt in a reversible reaction which eventually would release back the diethylamino terminus. Distal N-assistance could be thought responsible for a very high yield of the kinetically favored product under thermodynamic control conditions (Scheme 8).

Scheme 8



Likewise, the formation of biscarbenes **6** could be explained by an intermolecular conjugate addition reaction after the initial intermolecular aminolysis. This assumption could be corroborated by the fact that compound **6c** is also obtained by reaction of **2c** with 1 equiv of **1a** in THF at room temperature. So, it can be concluded that products of type **6** for diamines are energetically more stable than **7** since they are exclusively formed from **1** and **2a**−**c** and **2h**,**i** at room temperature.

Conclusions

We have studied the reaction of alkynyl alkoxy carbenes **1** with 1,2-primary and -secondary diamines. Contrary to our initial expectations, we could not obtain seven-membered ring systems. Changes in the reaction conditions produced dramatic changes in the resulting reaction products. In this way, the aminolysis (1-substitution) products **2** or alternatively new biscarbene complexes **5**, **6**, and **7** were obtained. The influence of the steric hindrance and the nucleophilic character of the diamine system were considered relevant to account for the present results.

Experimental Section

Unless otherwise stated all common reagents and solvents were used as obtained from commercial suppliers without further purification.

NMR spectra were recorded on a Varian Gemini-200 (200 MHz for ^{1}H NMR and 50 MHz for ^{13}C) or a Varian XL-300 apparatus (300 MHz for ^{1}H NMR and 75.4 MHz for ^{13}C). All samples of carbene complexes were filtered through a pad of Celite and EDTA prior to recording the spectra. IR spectra were recorded on a Bomem FT-IR M-120 spectrophotometer. Mass spectra were obtained on an AutoSpec-Q mass spectrometer. Elemental analyses were performed using a Carlo Erba 1106 apparatus.

Flash column chromatography was performed with "flash grade" silica (SDS 230−400 mesh).

Unless otherwise indicated all the reactions were performed under Ar atmosphere. Carbene complexes **1a**,**a′**[17] were prepared according to literature procedures.

General Procedure. Method A. To a stirred 0.02 M solution of the carbene **1** in dry THF at −78 °C was added 1 equiv of the diamine. The reaction course was monitored by thin-layer chromatography. After the starting carbene complex had completely disappeared, the solvent was removed and the residue passed through a flash chromatography column.

Method B. To a stirred 0.2 M solution of the carbene **1** in dry THF at −78 °C, 0.5 equiv of the diamine was added dropwise. The reaction course was monitored by thin-layer chromatography. After the starting carbene complex had completely disappeared, the solvent was removed and the residue passed through a flash chromatography column.

Method C. To a stirred 0.2 M solution of the carbene **1** in dry THF at room temperature was added dropwise 1 equiv of the diamine. The reaction course was monitored by thin-layer chromatography. After the starting carbene complex had completely disappeared, the solvent was removed and the residue passed through a flash chromatography column.

Reaction of 1a with Diamine 8a. Method A. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.030 g (0.5 mmol) of diamine **8a** in 20 mL of dry THF. After purification by flash chromatography (5:2 hexanes/ethyl acetate) 0.140 g of complex **5a** was obtained as a red solid (60% yield).

Method B. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.015 g (0.25 mmol) of diamine **8a** in 2 mL of dry THF. A total of 0.180 g of complex **5a** was obtained as a red solid. (78% yield).

Method C. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.030 g (0.5 mmol) of diamine **8a** in 2 mL of dry THF. A total of 0.195 g of complex **6a** was obtained as an orange solid (80% yield).

5a. IR ($CHCl_3$): 2167, 2063, 1978, 1940 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.90 (bs, 2H, N*H*); 7.22−7.52 (m, 10H, Ph); 3.95−4.10 (bs, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ 237.9 (C═W); 203.4 (s); 198.1 (s); 132.6 (d); 131.3 (d); 130.1 (s); 128.9 (d); 121.0 (s); 91.7 (s); 50.7 (t). Anal. Calcd for $C_{30}H_{16}N_2O_{10}W_2$: C, 38.62; H, 1.72; N, 3.00. Found: C, 38.44; H, 1.70; N, 3.11.

6a. IR ($CHCl_3$): 2167, 2059, 1978, 1930 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.97 (bt, 1H, NH); 8.84 (bt, 1H, NH); 7.25−7.50 (m, 10H, Ph); 6.33 (s, 1H, *CH*); 4.65 (q, J = 7 Hz, 2H, CH_2); 3.72 (bs, 2H, CH_2); 3.51 (bs, 2H, CH_2); 1.48 (t, J = 7 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 276.5 (C═W); 237.2 (C═W); 204.3 (s); 203.7 (s); 199.2 (s); 198.3 (s); 156.8 (s); 133.8 (s); 132.4 (s); 132.0 (d); 131.1 (d); 130.5 (d); 129.0 (d); 128.8 (d); 127.5 (d); 123.0 (d); 120.9 (s); 91.3 (s); 76.9 (t); 52.1 (t); 44.2 (t); 15.8 (q). Anal. Calcd for $C_{32}H_{22}O_{11}N_2Cr_2$: C, 39.26; H, 2.25; N, 2.86. Found: C, 39.43; H, 2.25; N, 2.87.

Reaction of 1a′ with Diamine 8a. Method B. The reaction was performed using 0.350 g (1 mmol) of **1a′** and 0.030 g (0.5 mmol) of diamine **8a** in 2 mL of dry THF. A total of 0.530 g of complex **5a′** was obtained as a red solid (80% yield).

Method C. The reaction was performed using 0.350 g (1 mmol) of **1a′** and 0.030 g (1 mmol) of diamine **8a** in 2 mL of dry THF. A total of 0.643 g of complex **6a′** was obtained as an orange solid (90% yield).

5a′. IR ($CHCl_3$): 2160, 2056, 1986, 1957 cm^{-1}. ^1H NMR (CD_3COCD_3): δ 9.25 (bs, 2H, NH); 7.30−7.45 (m, 10H, Ph); 4.40−4.46 (bs, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ 253.9 (C═Cr); 224.2 (s); 217.5 (s); 132.5 (d); 131.3 (d); 131.0 (s); 129.2 (d); 122.0 (s); 89.5 (s); 52.3 (t). Anal. Calcd for $C_{30}H_{16}N_2O_{10}Cr_2$: C, 53.89; H, 2.39; N, 4.19. Found: C, 53.63; H, 2.66; N, 4.04.

6a′. IR ($CHCl_3$): 2167, 2056, 1951, 1907 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.87 (bt, 1H, NH); 8.79 (bt, 1H, NH); 7.25−7.55 (m, 10H, Ph); 6.36 (s, 1H, *CH*); 4.89 (q, J = 7 Hz, 2H, CH_2); 3.85 (bs, 2H, CH_2); 3.53 (bs, 2H, CH_2); 1.57 (t, J = 7 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 300.3 (C═Cr); 224.0 (C═Cr); 224.0 (s); 223.1 (s); 218.2 (s); 216.9 (s); 152.7 (s); 134.5 (s); 134.1 (s); 132.0 (d); 131.3 (d); 130.6 (d); 129.2 (d); 128.9 (d); 127.8 (d); 121.2 (d); 120.5 (s); 88.7 (s); 74.4 (t); 52.3 (t); 44.5 (t); 16.1 (q).

Reaction of 1a with Diamine 8b. Method A. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.037 g (0.5 mmol) of diamine **8b** in 20 mL of dry THF. Product **2b** was characterized from the crude reaction mixture. All attempts to purify it failed, leading to decomposition and formation of a mixture of compounds. Among them **9b** and **10** could be identified.

Method B. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.019 g (0.25 mmol) of diamine **8b** in 2 mL of dry THF. After purification by flash chromatography 0.111 g of complex **5b** was obtained as an orange solid (45% yield).

Method C. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.037 g (0.5 mmol) of diamine **8b** in 2 mL of dry THF. After separation by flash chromatography 0.050 g of complex **6b** was obtained as an orange solid (10% yield). Two other products were identified as **9b** (0.023 g, 12% yield) and **10** (0.010 g, 16% yield).

2b. IR ($CHCl_3$): 2160, 2065, 1975, 1953, 1924 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.50 (bs, 1H, N*H*); 7.40−7.60 (m, 5H, Ph); 3.60−3.80 (m, 1H, CH_2); 3.34−3.43 (m, 1H, C*H*); 3.20−3.30 (m, 1H, CH_2); 1.19 (d, J = 6.5 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 230.6 (C═W); 204.0 (s); 198.6 (s); 132.2 (d); 130.7 (d); 128.8 (d); 126.5 (s); 121.6 (s); 91.8 (s); 58.9 (t); 45.9 (d); 22.1 (q).

5b. IR ($CHCl_3$): 2167, 2063, 1978, 1936 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.82 (bt, 1H, N*H*); 8.50 (bd, J = 9 Hz, 1H, N*H*); 7.30−7.65 (m, 10H, Ph); 4.87 (m, 1H, *CH*); 3.88−4.04 (m, 2H, CH_2); 1.56 (d, J = 9 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 238.1 (C═W); 235.8 (C═W); 203.6 (s); 198.2 (s); 198.0 (s); 132.7 (d); 132.6 (d); 131.4 (d); 131.3 (d); 130.3 (s); 130.1 (s); 128.9 (d); 128.8 (d); 121.09 (s); 121.07 (s); 91.8 (s); 91.7 (s); 57.9 (d); 56.1 (t); 18.1 (q). Anal. Calcd for $C_{31}H_{18}O_{10}N_2W_2$: C, 39.30; H, 1.90; N, 2.95. Found: C, 39.29; H, 2.19; N, 2.87.

6b. IR ($CHCl_3$): 2156, 2059, 1953, 1928 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.90 (bd, 1H, N*H*); 7.30−7.65 (m, 10H, Ph); 6.39 (s, 1H, *CH*); 4.81 (q, J = 7 Hz, 2H, CH_2); 4.60−4.80 (m, 1H, C*H*); 3.66 (s, 1H, N*H*); 3.45−3.80 (m, 2H, CH_2); 1.68 (t, J = 7 Hz, 3H, CH_3); 1.36 (t, J = 6.7 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 278 (C═W); n.o.(C═W); 203.8 (s); 198.9 (s); 155.1 (s); 134.3 (s); 132.2 (d); 130.6 (d); 129.4 (d); 129.0 (d); 127.7 (s); 127.4 (d); 123.3 (s); 121.1 (s); 77.1 (t); 50.1 (t); 49.8 (d); 19.3 (q); 16.0 (q).

9b. IR ($CHCl_3$): 2167, 1063, 1955, 1928 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.01 (bs, 1H, N*H*); 5.91 (bs, 1H, N*H*); 3.98 (ddq, J = 10, 7.2, 6.4 Hz, 1H, C*H*); 3.70 (t, J = 10 Hz, 1H, CH_2); 3.15 (dd, J = 10, 7.2 Hz, 1H, CH_2); 1.22 (d, J = 6.4 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 202.8 (s); 201.8 (C═W); 198.1 (s); 53.3 (d); 52.3 (t); 21.4 (q).

10. IR ($CHCl_3$): 1691 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.88 (d, 2H, Ph); 7.40−7.60 (m, 3H, Ph); 2.54 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 198.5 (s);137.1 (s); 133.3 (d); 128.6 (d); 128.3 (d); 26.7 (q).

Reaction of 1a with Diamine 8c. Method A. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.045 g (0.5 mmol) of diamine **8c** in 20 mL of dry THF. After separation by flash chromatography 0.236 g of **2c** (90% yield) was isolated as a yellow solid.

Method B. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.022 g (0.25 mmol) of diamine **8c** in 2 mL of dry THF. After 24 h purification by flash chromatography, 0.072 g of complex **5c** as an orange solid (30% yield) and 0.045 g of complex **6c** were obtained as a red solid (17% yield).

Method C. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.022 g (0.5 mmol) of diamine **8c** in 2 mL of dry THF. After 24 h separation by flash chromatography, 0.212 g of complex **6c** was obtained as an orange solid (80% yield).

2c. IR ($CHCl_3$): 2171, 2061, 1973, 1934 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.55 (bs, 1H, N*H*); 7.40−7.60 (m, 5H, Ph); 3.49 (d, J =5.4 Hz, 2H, CH_2); 1.22 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 230.0 (C═W); 204.0 (s); 198.5 (s); 132.2 (d); 130.6 (d); 128.7 (d); 125.9 (s); 121.6 (s); 91.7 (s); 62.7 (t); 49.7 (s); 28.8 (q). MS (FAB$^+$, matrix NBA), *m/e* 524, 496, 440, 412, 384, 200.

5c. IR ($CHCl_3$): 2171, 2061, 1978, 1934 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.65 (bs, 1H, N*H*); 7.30−7.60 (m, 10H, Ph); 4.33 (d, J = 6 Hz, 2H, CH_2); 1.76 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 238.4 (C═W); 238.2 (C═W); 203.6 (s); 198.3(s); 198.2(s); 137.9 (s); 132.4 (d); 132.1 (d); 131.6 (d); 131.2 (d); 130.4 (s); 129.0 (d); 128.9 (d); 128.8 (d); 121.4 (s); 121.0 (s); 92.3 (s); 91.8 (s); 63.6 (s); 58.9 (t); 25.0 (q). Anal. Calcd for $C_{32}H_{20}N_2O_{10}W_2$: C, 40.00; H, 2.08; N, 2.92. Found: C, 39.22; H, 2.31; N, 2.99.

6c. IR ($CHCl_3$): 2167, 2061, 1978, 1930 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.15 (bs, 1H, N*H*); 8.60 (bs, 1H, N*H*);7.40−7.60 (m, 10H, Ph); 6.35 (s, 1H, *CH*); 4.79 (d, J = 7 Hz, 2H, CH_2); 3.56 (bd, J = 5 Hz, 2H, CH_2); 1.62 (t, J = 7 Hz, 3H, CH_3); 1.28 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 276.5 (C═W); 236.9 (C═W); 203.7 (s); 203.3 (s); 198.8 (s); 198.1 (s); 155.3 (s); 135.8 (s); 132.1 (d); 131.0 (d); 130.2 (s); 128.8 (d); 128.7 (d); 127.5 (d); 125.3 (d); 121.0 (s); 91.6 (s); 77.2 (t); 61.0 (t); 57.5 (s); 28.0 (q), 15.6 (q). Anal. Calcd for $C_{34}H_{26}N_2O_{11}W_2$: C, 40.55; H, 2.58; N, 2.78. Found: C, 40.41; H, 2.61; N, 2.86.

Reaction of 1a with Diamine 8d. Method A. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.060 g (0.5 mmol) of diamine **8d** in 20 mL of dry THF. After separation by flash chromatography 0.215 g of **2d** (78% yield) was isolated as a yellow solid.

Method B. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.040 g (0.25 mmol) of diamine **8d** in 2 mL of dry THF. Separation by flash chromatography gave 0.098 g of complex **5c** as an orange solid (40% yield) and 0.080 g of **2d** (30% yield).

Method C. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.060 g (0.5 mmol) of diamine **8d** in 2 mL of dry THF. After separation by flash chromatography only small amounts (<5%) of **2d**, **6d**, **9d**, and **10** were isolated from the crude mixture.

2d. IR ($CHCl_3$): cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.00 (bd, 1H, N*H*); 7.30−7.60 (m, 5H, Ph);3.70−3.90 (dt, J = 3.6, 13.2 Hz, 1H, C*H*); 2.74 (dt, J = 10.5, 4.2 Hz, 1H, C*H*); 2.17 (bd, J = 10 Hz, 2H, CH_2); 1.98 (bd, J = 13 Hz, 2H, CH_2); 1.20−1.70 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ 230.4 (C═W); 204.0 (s); 198.7 (s); 132.3 (d); 130.7 (d); 128.8 (d); 127.4 (s); 121.7 (s); 91.8 (s); 69.8 (d); 53.9 (d); 34.9 (t), 31.8(t); 24.5(t); 24.5(t).

5d. IR ($CHCl_3$): 2164, 2065, 1978, 1926 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.54 (bd, 1H, N*H*); 7.30−7.55 (m, 10H, Ph); 4.25−4.40 (m, 2H, C*H*N); 2.33 (bd, J = 13 Hz, 2H, CH_2); 1.97 (bd, J = 8 Hz, 2H, CH_2); 1.30−1.70 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ 235.3 (C═W); 203.3 (s); 197.9 (s); 132.3 (d); 131.1 (d); 128.9 (s); 128.8 (d); 121.0 (s); 91.6 (s); 65.2 (d); 31.8 (t), 23.9 (t). Anal. Calcd for $C_{34}H_{22}N_2O_{10}W_2$: C, 41.37; H, 2.23; N, 2.83. Found: C, 41.42; H, 2.41; N, 2.71.

6d. IR ($CHCl_3$): 2167, 2061, 1978, 1930 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.99 (d, J = 10.8 Hz, 1H, N*H*); 8.20 (d, J = 9.3 Hz, 1H, N*H*); 7.40−7.60 (m, 10H, Ph); 6.31 (s, 1H, *CH*); 4.63 (dq, J = 7.2, 10.2 Hz, 1H, CH_2); 4.37 (dq, J = 6.9, 10.2 Hz, 1H, CH_2); 4.04 (dq, J = 4.2, 10.2 Hz, 1H, C*H*); 3.34 (dq, J = 4.2, 10.9 Hz, 1H, C*H*); 1.04−2.30 (m, 8H, CH_2); 1.36 (t, J = 7.2. Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 275.3 (C═W); 234.5 (C═W); 203.8 (s); 203.1 (s); 198.8 (s); 198.0 (s); 155.8 (s); 134.3 (s); 132.3 (d); 132.1 (d); 131.2 (s); 129.4 (d); 128.9 (d); 128.8 (d); 127.2 (d); 120.9 (s); 91.6 (s); 76.6 (t); 67.0 (d); 57.5 (d); 34.2 (t); 31.8 (t); 31.8 (t); 23.9 (t), 15.6 (q).

Reaction of 1a with Aminoacetamide 8e. Method A. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.037 g (0.5 mmol) of **8e** in 20 mL of dry THF. After separation by flash chromatography 0.240 g of **2e** (94% yield) was isolated as a yellow solid.

Method B. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.019 g (0.25 mmol) of **8e** in 2 mL of dry THF. Separation by flash chromatography gave 0.110 g of complex **2e** (43% yield) and the recovery of 0.100 g of the starting complex **1a**.

Method C. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.037 g (0.5 mmol) of **8e** in 2 mL of dry THF. After purification by flash chromatography, an inseparable mixture (83:17) of **2e** and **3e** was obtained (0.218 g, 84% overall yield).

2e. IR ($CHCl_3$): 2169, 2063, 1976, 1932, 1701 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.59 (s, 1H, N*H*); 7.40−7.60 (m, 5H, Ph); 6.33 (s, 1H, N*H*); 5.83 (s, 1H, N*H*); 4.32 (d, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 234.2 (C═W); 203.8 (s); 198.4 (s); 168.8 (s); 132.7 (d); 130.9 (d); 128.8 (d); 127.0 (s); 121.5 (s); 92.2 (s); 52.8 (t).

3e. IR ($CHCl_3$): cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.49 (s, 1H, N*H*); 7.30−7.60 (m, 5H, Ph); 6.40 (s, 1H, C*H*); 6.05 (s, 1H, N*H*); 5.55 (bs, 1H, *NH*); 4.79 (q, J = 7.2 Hz, 2H, CH_2); 3.82 (d, J = 5 Hz, 2H, CH_2); 1.69 (t, J = 7.2 Hz, 3H, CH_3).

Reaction of 1a with Diamine 8f. Method A. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.054 g (0.5 mmol) of **8f** in 20 mL of dry THF. After separation by flash chromatography, 0.265 g of **3f** (90% yield) was isolated as a yellow solid.

Method B. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.030 g (0.25 mmol) of diamine **8f** in 2 mL of dry THF. Separation by flash chromatography gave 0.120 g of complex **3f** as a yellow solid (40% yield), and 0.100 g of the starting complex **1a** was recovered.

Method C. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.030 g (0.5 mmol) of diamine **8f** in 2 mL of dry THF. After 18 h the reaction was stopped, and after separation by flash chromatography 0.200 g of complex **7f** was obtained as a red solid (75% yield).

3f. IR ($CHCl_3$): 2157, 2056, 1973, 1928 cm^{-1}. ^1H NMR ($CDCl_3$): δ 10.28 (s, 1H, N*H*); 7.20−7.50 (m, 5H, Ph); 6.97 (dt, 1H, Ph); 6.74 (s, 1H, C*H*); 6.72−6.80 (m, 2H, Ph); 6.49 (ddt, 2H, Ph); 4.85 (q, J = 7 Hz, 2H, CH_2); 3.86 (bs, 1H, N*H*); 1.66 (t, J = 7 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 276.4 (C═W); 203.8 (s); 198.4 (s); 168.8 (s); 132.7 (d); 130.9 (d); 128.8 (d); 127.0 (s); 121.5 (s); 92.2 (s); 52.8 (t).

7f. IR ($CHCl_3$): 2059, 1973, 1936 cm^{-1}. ^1H NMR ($CDCl_3$): δ 10.38 (s, 2H, NH); 7.10−7.50 (m, 10H, Ph); 6.88 (s, 1H, C*H*); 6.84 (dd, J = 3.6, 9.6 Hz, 2H, Ph); 6.52 (dd, J = 2.4, 9.6 Hz, 2H, Ph); 4.90 (q, J = 7 Hz, 2H, CH_2); 1.61 (t, J = 7 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 282.9 (C═W); 203.7 (s); 198.6 (s); 149.3 (s); 134.3 (s); 131.1 (s); 130.7 (d); 129.0 (d); 128.2 (d); 126.3 (d); 125.7 (d); 125.1 (d); 77.9 (t); 15.5 (q). Anal. Calcd for $C_{38}H_{28}O_{12}N_2W_2$: C, 42.53; H, 2.61; N, 2.61. Found: C, 42.42; H, 2.61; N, 2.84.

Reaction of 1a with Diamine 8g. Method A. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.054 g (0.5 mmol) of **8g** in 20 mL of dry THF. After purification by flash chromatography (CH_2Cl_2/hexanes), 0.245 g of **2g** (90% yield) was isolated as a yellow solid.

Method B. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.030 g (0.25 mmol) of diamine **8g** in 2 mL of dry THF. Separation by flash chromatography gave 0.100 g of complex **2g** as a yellow solid (37% yield) and 0.120 g of the starting complex **1a**.

Method C. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.054 g (0.5 mmol) of diamine **8g** in 2 mL of dry THF. After separation by flash chromatography, 0.109 g of complex **2g** (40.% yield) and 0.060 g of complex **3g** (20% yield) as an orange solid were obtained.

2g. IR ($CHCl_3$): 2169, 2063, 1976, 1930 cm^{-1}. ^1H NMR ($CDCl_3$): δ 10.10 (s, 1H, N*H*); 8.67 (d, J = 5 Hz, 1H, Ph); 7.76 (dt, J = 7.2, 1.8, 1H Ph); 7.25−7.60 (m, 7H, Ph); 4.94 (d, J = 5 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 231.6 (C═W); 203.9 (s); 198.5 (s); 152.8 (s); 149.6 (d); 137.4 (d); 132.4 (d); 130.8 (d); 128.8 (d); 127.4 (s); 123.3. (d); 121.8 (d); 92.3 (s); 55.5 (t). Anal. Calcd for $C_{19}H_{10}N_2O_5W$: C, 43.18; H, 1.89; N, 5.30. Found: C, 43.10; H, 2.17; N, 5.00.

3g. IR ($CHCl_3$): 2059, 1969, 1928 cm^{-1}. ^1H NMR ($CDCl_3$): δ 10.21 (s, 1H, N*H*); 8.60 (d, J = 5 Hz, 1H, Ph); 7.67 (dt, J = 7.8, 1.8 Hz, 1H, Ph); 7.25−7.51 (m, 6H, Ph); 7.05 (d, J = 7.8 Hz, 1H, Ph); 6.37 (s, 1H, C*H*); 4.79 (q, J = 7 Hz, 2H, CH_2); 4.42 (d, J = 5.1, 2H, CH_2); 1.67 (t, J = 7 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 271.1 (C═W); 204.0 (s); 198.4 (s); 156.6 (s); 149.2 (d); 137.0 (d); 135.3 (s); 130.2 (d), 128.9 (d); 128.8 (s); 127.6 (d); 123.0 (d); 122.3 (d); 121.5 (d); 77.3 (t); 50.6 (t); 15.7 (q).

Reaction of 1a with Diamine 8h. Method A. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.037 g (0.5 mmol) of **8h** in 20 mL of dry THF. After purification by flash chromatography (CH_2Cl_2/petroleum ether),

0.022 g of **5h** (9% yield) as an orange solid and 0.074 g of **9h** (30% yield) were isolated as a yellow solid.

Method B. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.019 g (0.25 mmol) of diamine **8h** in 2 mL of dry THF. Separation by flash chromatography gave 0.165 g of complex **5h** as an orange solid (70% yield).

Method C. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.037 g (0.5 mmol) of diamine **8h** in 2 mL of dry THF. After separation by flash chromatography, 0.280 g of complex **6h** (56% yield) was obtained as an orange solid.

5h. IR ($CHCl_3$): 2167, 2063, 1978, 1932 cm^{-1}. *E* isomer ^1H NMR ($CDCl_3$): δ 8.80 (s, 1H, N*H*); 7.25−7.60 (m, 10H, Ph); 4.40 (t, $J = 6$ Hz, 2H, CH_2); 4.20 (q, $J = 6$ Hz, 2H, CH_2); 3.87 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 238.0 (C═W); 234.6 (C═W); 203.9 (s); 203.2 (s);198.0 (s); 197.8 (s); 132.6 (d); 132.3 (s); 132.1 (d); 131.4 (d); 130.9 (d); 130.7 (s); 128.9 (d); 128.8 (d); 121.3 (s); 120.9 (s); 92.4 (s); 91.5 (s); 57.1 (t); 50.0 (q); 49.7 (t). Anal. Calcd for $C_{31}H_{18}N_2O_{10}W_2$: C, 39.32; H, 1.90; N, 2.96. Found: C, 39.64; H, 2.20; N, 3.03. *Z* isomer δ ^1H NMR ($CDCl_3$): 8.90 (s, 1H, N*H*); 7.25−7.60 (m, 10H, Ph); 4.55 (t, $J = 6$ Hz, 2H, CH_2); 4.23 (q, $J = 6$ Hz, 2H, CH_2); 3.69 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ n.o. (C═W); n.o. (C═W); 203.9 (s); 203.2 (s); 198.2 (s); 197.9 (s); 132.2 (d); 131.7 (d); 131.2 (d); 130.7 (d); 130.9 (s); 128.9 (s); 128.9 (d); 128.7 (d); 121.3 (s); 120.9 (s); n.o. (s); n.o. (s); 61.5 (t); 50.5 (t); 44.3 (q).

6h. IR ($CHCl_3$): 2169, 2063, 1980, 1938 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.05 (s, 1H, N*H*); 7.25−7.60 (m, 10H, Ph); 6.43 (s, 1H, *CH*); 4.83 (q, $J = 7.2$ Hz, 2H, CH_2); 4.16 (m, 2H, CH_2); 3.58 (m, 2H, CH_2); 3.26 (s, 3H, CH_3); 1.63 (t, $J = 7.2$ Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 276.9 (C═W); 237.6 (C═W); 203.9 (s); 203.2 (s);198.9 (s); 198.1 (s); 156.4 (s); 134.0 (s); 132.2 (d); 131.3 (d); 130.7 (d); 130.5 (s); 129.3 (d); 129.0 (d); 127.6 (d); 123.3 (d); 121.0 (s); 91.4 (s); 77.0 (t); 52.1 (t); 44.3 (t); 15.9 (q).

9h. IR ($CHCl_3$): 2063, 1980, 1938 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.70 (bs, 1H, N*H*); 3.60 (m, 4H, CH_2); 3.22 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 205.6 (s); 201.6 (C═W); 198.2 (s); 50.8 (t); 45.2 (t); 38.8 (q).

Reaction of 1a with Diamine 8i. Method A. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.044 g (0.5 mmol) of **8i** in 20 mL of dry THF. After purification by flash chromatography (CH_2Cl_2/petroleum ether) 0.125 g of complex **6i** (mixture of 2 isomers) (50% yield) was isolated as an orange solid.

Method B. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.022 g (0.25 mmol) of diamine **8i** in 2 mL of dry THF. Separation by flash chromatography gave 0.125 g of complex **6i** (mixture of 2 isomers) as an orange solid (50% yield).

Method C. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.022 g (0.5 mmol) of diamine **8i** in 2 mL of dry THF. After separation by flash chromatography 0.132 g of complex **6i (**mixture of 2 isomers) (70% yield) was obtained.

6i. (Isomer 1) IR ($CHCl_3$): 2169, 2057, 1971, 1930 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.15−7.60 (m, 10H, Ph); 6.80 (s, 1H, *CH*); 4.83 (q, $J = 7.2$ Hz, 2H, CH_2); 3.10−4.00 (bm, 10H, CH_2, CH_3); 0.82 (t, $J = 7.2$ Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 280.8 (C═W); 231.9 (C═W); 203.8 (s); 202.9 (s);199.3 (s); 198.0 (s); 155.3 (s); 136.5 (s); 131.7 (d); 130.7 (d); 128.9 (d); 128.7 (d); 128.7 (d); 127.4 (d); 122.6 (d); 121.4 (s); 92.8 (s); 77.1 (t); 60.6 (t); 50.4 (t); 44.3 (q); 39.1 (q); 13.7 (q). MS (FAB$^+$ matrix NBA): 1006, 978, 922, 866, 838, 810, 782, 754, 726. Anal. Calcd for $C_{32}H_{20}N_2O_{10}W_2$: C, 40.55; H, 2.58; N, 2.78. Found: C, 41.16; H, 2.72; N, 2.97.

6i. (Isomer 2) ^1H NMR ($CDCl_3$): δ 7.15−7.60 (m, 10H, Ph); 6.74 (bs, 1H, *CH*); 2.60−4.60 (bm, 12H, CH_2, CH_3); 0.91 (t, $J = 7.2$ Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 280.8 (C═W); 232.0 (C═W); 203.8 (s); 203.0 (s);199.4 (s); 198.1 (s); 155.5 (s); 136.6 (s); 131.7 (d); 130.7 (d); 128.9 (d); 128.7 (d); 128.7 (d); 127.4 (d); 122.6 (d); 121.4 (s); 92.8 (s); 76.4 (t); 60.2 (t); 50.5 (t); 49.7 (q); 31.6 (q); 14.8 (q). MS (FAB$^+$ matrix NBA) 1006, 978, 922, 866, 838, 810, 782, 754, 726. Anal. Calcd for $C_{32}H_{20}N_2O_{10}W_2$: C, 40.55; H, 2.58; N, 2.78. Found: C, 41.59; H, 2.93; N, 2.93.

Reaction of 1a with Diamine 8j. Method C. The reaction was performed using 0.250 g (0.5 mmol) of **1a** and 0.058 g (0.5 mmol) of diamine **8j** in 2 mL of dry THF. Purification by flash chromatography gave 0.222 g of complex **2j** as an orange solid (90% yield).

2j. IR ($CHCl_3$): 2169, 2063, 1976, 1930 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.61 (bs, 1H, N*H*); 7.40−7.60 (m, 5H, Ph); 3.69 (dd, $J = 6$ Hz, 2H, CH_2); 2.72 (dd, $J = 6$ Hz, 2H, CH_2); 2.62 (t, $J = 7.2$ Hz, 2H, CH_2), 1.23 (t, $J = 7.2$ Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 228.6 (C═W); 203.9 (s); 198.5 (s); 132.2 (d); 130.5 (d); 128.6 (d); 125.5 (s); 121.6. (s); 91.9 (s); 50.2 (t); 48.9 (t), 46.8 (t); 12.2 (q).

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Supporting Information Available: Details of the X-ray crystal structure analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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