Stereochemical Control of N,N-Disubstitution in Alkynylaminocarbene Complexes of Chromium(0) and Tungsten(0)

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Stereocontrol in the introduction of substituents on the nitrogen of alkynylaminocarbene complexes can be achieved by a proper sequential aminolysis of the starting alkoxy carbene analogs followed by treatment of the resulting (*E*-alkylamino)carbene complex with Cs_2CO_3 in the presence of the desired electrophile. The use of Cs_2CO_3 as a base affords good yields of N,N-disubstituted alkynylcarbene complexes. The isomerization described for other systems was avoided in this case. The reaction is also applicable to bulky electrophiles like (−)-myrtenyl or (−)-perillyl bromides and also to arylcarbene complexes.

Introduction

Our interest in the synthesis of N,N-disubstituted aminoalkynylcarbene complexes **2** lies in the fact that an intramolecular Pauson−Khand reaction[1] is facilitated by the lack of rotation around the C−N bond in (*E*-allylamino) alkynylcarbene complexes of Cr and W.[2]

The importance of stereochemical control in the introduction of both substitutents on the nitrogen atom arises from the requirement of complexes bearing a determined functional group specifically in the *E* or *Z* position (with respect to the metal moiety) to further unequivocally interact with the triple bond or the metal as is shown in Scheme 1.

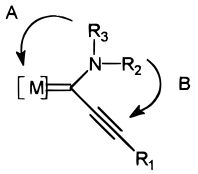
The procedures reported in the literature for the synthesis of these complexes consisting of the direct aminolysis with secondary amines at the carbene center[3] were not applicable in our case due to the competing conjugate addition to the triple bond even at very low temperatures.[4]

This fact prompted us to look for an alternative sequential way to obtain N,N-disubstitued amino complexes with two purposes in mind: first, to gain enough versatility to be applicable to a large variety of N-substituents and, second, to permit complete control of the arrangement of the amine on the final complex.

Thus, the general procedure to achieve this is described in Scheme 2. After initial aminolysis with a primary amine, the second substituent would be introduced by base deprotonation and subsequent reaction with an electrophile, in analogy to the acid−base chemistry of carboxylic acid amides.

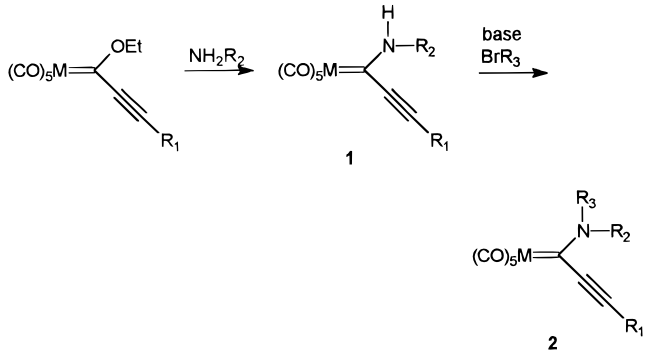
As previously reported,[5] the aminolysis of (alkynyl)-(alkoxy)carbenes with primary amines at −78 °C (kinetic control conditions) afforded mostly the corresponding *E*-allyl isomer. Therefore, the requirement to be attained was to avoid the isomerization often caused by the presence of base[6] in the introduction of the second substituent on the nitrogen.

Scheme 1



A: Interaction with the M=C system. Coordination,cyclopropanation..
B: Interaction with the triple bond. Addition, cycloaddition...

Scheme 2



Results and Discussion

When we applied the described literature procedures using bases like LDA or NaH[7] to our substrates, the

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(1) (a) Camps, F.; Moretó, J. M.; Ricart, S.; Viñas, J. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1470−1472. (b) Jordi, L.; Jordi, L.; Moretó, J. M.; Ricart, S.; Viñas, J. M.; Mejias, M.; Molins, E. *Organometallics* **1992**, *11*, 3507−3510.

(2) Connor, J. A.; Fischer, E. O. *J. Chem. Soc. A* **1969**, 578.

(3) (a) Klabunde, U.; Fischer, E. O. *J. Am. Chem. Soc.* **1967**, *89*, 7141. (b) Baikie, P. E.; Fischer, E. O.; Mills, O. S. *J. Chem. Soc., Chem. Commun.* **1967**, 1199.

(4) (a) Duetsch, M.; Stein, F.; Lackmann, R.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Chem. Ber.* **1992**, *125*, 2051−2065. (b) Stein, F.; Duetsch, M.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Organometallics* **1993**, *12*, 2556−2564.

(5) Aumann, R.; Hinterding, P. *Chem. Ber.* **1993**, *126*, 421−427. Also, nonpublished results from our laboratory.

(6) Moser, E.; Fischer, E. O. *J. Organomet. Chem.* **1968**, *15*, 147−155.

(7) (a) Casey, C. P.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 3754−3764. (b) Grotjahn, D. B.; Dötz, K. H. *Synlett* **1991**, 381. (c) Hegedus, L. S.; Schwindt, M. A.; De Lombaert, S.; Imwinkelried, R. *J. Am. Chem. Soc.* **1990**, *112*, 2264. (d) Rahm, A.; Wulff, W. D. *J. Am. Chem. Soc.* **1996**, *118*, 1807.

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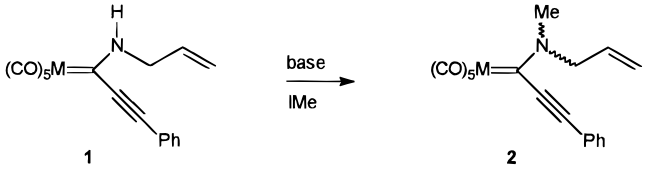
Table 1



2a M= Cr
2b M= W

entry	M	base	time (h)	solvent	product (yield (%))	*E*/*Z* (allyl)
1	Cr	NaH[a]	3	THF	**2a** (67)	85/15
2	W	NaH	3	THF	**2b** (85)	100/0
3	Cr	*t*-BuOK[b]	2.5	THF	**2a** (45)	85/15
4	W	*t*-BuOK	2.5	THF	**2b** (82)	100/0
5	Cr	K_2CO_3[c]	48	acetone	**2a** (59)	75/25
6	Cr	Cs_2CO_3[c]	1	acetone	**2a** (84)	100/0
7	W	Cs_2CO_3	1	acetone	**2b** (87)	100/0

[a] NaH (2 equiv), dry THF, −78 °C, IMe, −78 °C to room temperature. [b] *t*-BuOK (2 equiv), dry THF, −78 °C to room temperature. [c] K_2CO_3 or Cs_2CO_3 (2 equiv), wet acetone,[9] room temperature.

reaction proceeded fairly well, but some isomerization was observed and yields, especially for chromium complexes, were erratic and rather low.

In our search for alternative and more efficient bases to be used in this reaction, we turned our sight to those used in the related processes with carboxylic amides.[8] The results obtained are shown in Table 1.

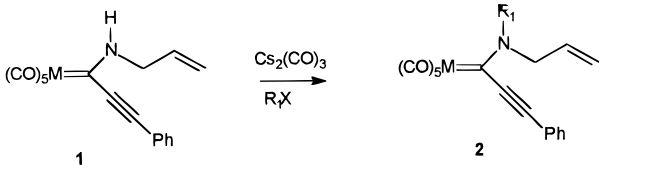
The use of Cs_2CO_3 (entries 6 and 7, Table 1) instead of NaH and *t*-BuOK improved not only the yields but also the stereoselectivity since only one of the two possible stereoisomers was obtained. In addition, the reaction times were reduced and Cs_2CO_3 was an easier base to handle than the bases used so far for identical purposes.

The extension of this reaction to different electrophiles was also studied, and the results are reflected in Table 2.

From this table we concluded that Cs_2CO_3 is an efficient base for the stereospecific introduction of a second functionality on the nitrogen of alkynylaminocarbene complexes under very mild conditions. The low yields obtained for chromium compounds using other bases were also improved (entries, 1, 4, and 6, Table 2).

Also remarkable is the successful use of bulky electrophiles such as (−)-myrtenyl or (−)-perillyl bromides (entries 1 and 3, Table 3) and also secondary allyl bromides[12] (entry 5, Table 3). In these cases addition of an additional 1 equiv of Cs_2CO_3 produced an improvement in final yields with complete retention of the *E* geometry of the allyl group (entries 2, 4, and 6, Table 3).

Table 2

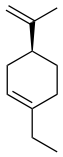
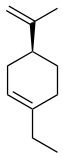
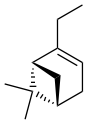
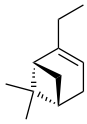


2c M= Cr R_1 = 
2d M= W R_1 = 
2e M= Cr R_1 = CH_2Ph
2f M= W R_1 = CH_2Ph
2g M= Cr R_1 = $CH_2C{\equiv}CCH_3$
2h M= W R_1 = $CH_2C{\equiv}CCH_3$

entry	M	R_1X	time (h)	product (yield (%))	*E*/*Z*
1	Cr	$BrCH_2CHCH_2$	1.75	**2c** (88)	
2	W	$BrCH_2CHCH_2$	1.75	**2d** (87)	
3	W	$ClCH_2CHCH_2$	3	**2d** (90)[a]	
4	Cr	$BrCH_2Ph$	1.75	**2e** (82)	100/0
5	W	$BrCH_2Ph$	1.75	**2f** (87)	100/0
6	Cr	$BrCH_2CCCH_3$	2	**2g** (53)	81/19[b]
7	W	$BrCH_2CCCH_3$	2	**2h** (30)	100/0[b]

[a] Addition of a 10% equiv of KI[10] in the reaction mixture. [b] A new compound identified as the corresponding (3-methylallenyl)amino complex[11] was obtained in both cases and separated form the mixture by flash chromatography (10% for Cr complexes) (8% for W complexes).

Table 3

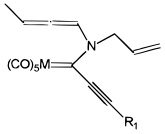
entry	M	R_1	base (equiv)	time (h)	product (yield (%))	*E*/*Z*
1	Cr		2	4	**2i** (24)	100/0
2	Cr		3	4	**2i** (89)	100/0
3	Cr		2	4	**2j** (28)	100/0
4	Cr		3	6	**2j** (66)	100/0
5	Cr		2	3	**2k** (traces)	
6	Cr		3	3	**2k** (38)	100/0

(8) (a) Park, J. D.; Englert, R. D.; Meek, J. S. *J. Am. Chem. Soc.* **1952**, *74*, 1010. (b) Luh, T.-L.; Fung, S. H. *Synth. Commun.* **1979**, *9*, 757. (c) Slocum, D. W.; Stonermark, F. E. *J. Org. Chem.* **1973**, *38*, 1677.

(9) Addition of 15 μL (approximately 2 drops) of water into the reaction mixture.

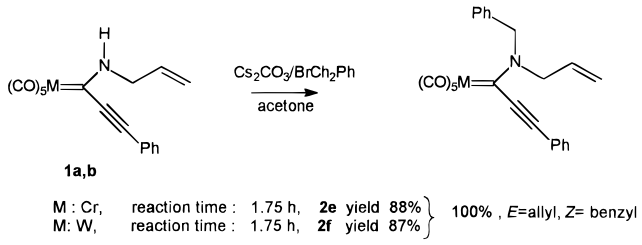
(10) Alami, M.; Ferri, F.; Gaslain, Y. *Tetrahedron Lett.* **1996**, *37*, 57−58.

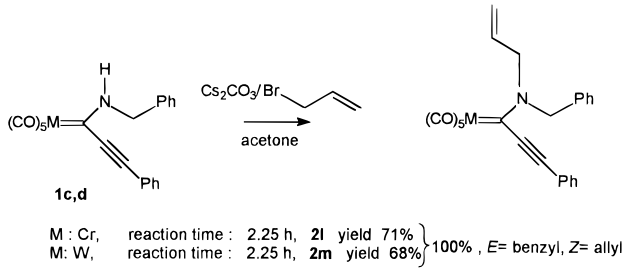
(11) The acidity of the protons of the methylenic group linked to the nitrogen may account for the rearrangement of the propargilic group to an allenic one. The structure proposed for these compounds is as follows:



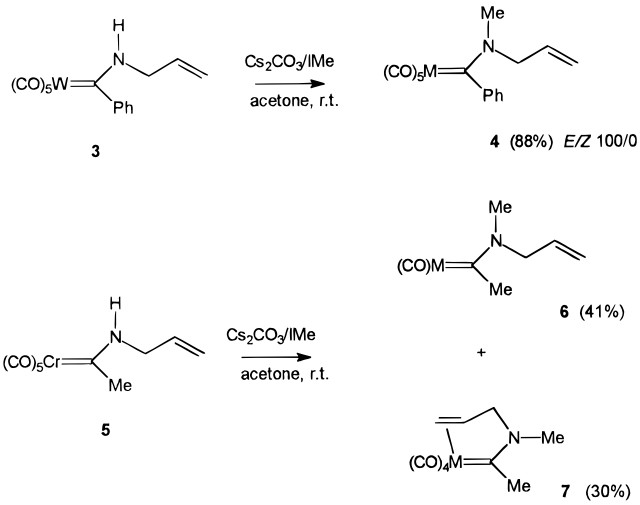
(12) Secondary allyl bromide gave only 10% yield of the expected product **2k** when NaH (2 or 3 equiv) was used.

Scheme 3





Scheme 4

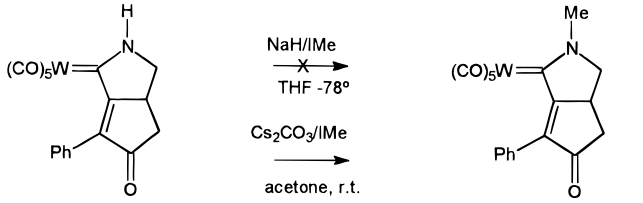


As an example of the stereochemical control displayed in the present procedure, we were able to stereospecifically prepare compounds **2e**,**f**,**l**,**m** as shown in Scheme 3.

The extension of the Cs_2CO_3 reaction to other carbene complexes with a different substituent on the carbenic carbon atom was also attempted affording good yields of the corresponding disubstituted amino complexes for the arene complex **3** (Scheme 4). In contrast, for the methyl analog **5** considerable *E*,*Z* isomerization was observed.

Despite that, the use of Cs_2CO_3 allowed us to work at room temperature avoiding completely the formation of the complex corresponding to the isomerization of the double bond *via* a dipole−stabilized carbanion.[13] As expected from an alkyl-substituted carbene complex, isomerization around the C−N bond was easier than for alkynyl or phenyl analogs and also coordination of the double bond to the metal moiety[14] ensued from the *Z* isomer (the acidity of the methyl hydrogens did not significatively interfere with the process).

Scheme 5



The synthesis of complex **9** illustrates the extension of this procedure to a carbene complex like **8** (Scheme 5). These complexes do not react with the corresponding bromides or halides in the presence of NaH or LDA.[15]

A possible explanation for the stereochemical control brought about by the Cs_2CO_3 system may arise from the reaction conditions. Since base and electrophile are present in the medium from the very beginning, generation and quenching of the anionic center on nitrogen are almost simultaneous, thus reducing the possible isomerization due to the presence of a base.

In conclusion, we present here a versatile, efficient, and easy way for the preparation of stereodefined disubstituted alkynylaminocarbene complexes. This procedure provides an alternative to that previously described especially for chromium complexes and bulky substituents.

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. Elemental analyses were performed using a Carlo-Erba 1106 apparatus. MSHR were performed on an AutoSpec-Q mass spectrometer.

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

Unless otherwise indicated carbene complexes **1a-d**,[5] **3**,[16] **5**,[11b] and **8**[1] were prepared by literature procedures and yields of final products were not optimized.

Synthesis of Pentacarbonyl[(phenylethynyl)(*E*-allyl-*Z*-methylamino)carbene]chromium(0) (2a). Reaction of NaH with Complex 1a. Method A. Complex **1a** (0.1 g, 0.28 mmol) was added to a stirred suspension of NaH (0.022 g, 0.56 mmol, 60% in paraffin) in dry THF at −78 °C. The temperature of the suspension was allowed to rise to −40 °C and kept at this temperature for 2 h. Then the solution was again cooled to −70 °C and methyl iodide (0.035 mL, 0.56 mmol) injected. The solution was kept at room temperature for 1 h. Quenching of the reaction with ice water, extraction with pentane, and evaporation to dryness afforded a crude mixture, which after separation by flash chromatography (hexane/CH_2Cl_2, 4/1) gave 0.070 g (0.090 mmol) of the expected carbene complex **2a** as a red oil (67% yield, *E*/*Z* = 85/15).

Reaction of *t*-BuOK with 1a. Method B. Complex **1a** (0.1 g, 0.28 mmol) was added to a stirred solution of *t*-BuOK (0.062 g, 0.56 mmol) in dry THF at −78 °C. The temperature of the solution was allowed to rise to −40 °C and kept at this temperature for 2 h. Then the solution was again cooled to

(13) (a) Casey, C. P.; Hornung, N. L.; Vollendorf, N. W. *J. Organomet. Chem*. **1986**, *303*, 375−385. (b) Alvarez, C.; Parlier, A.; Rudler, H.; Yefsah, R.; Daran, J. C.; Knobler, C.; *Organometallics* **1989**, *8*, 2253.

(14) Denise, B.; Goumont, R.; Parlier, A.; Rudler, H.; Daran, J.-C.; Vaissermann, J.; *J. Organomet. Chem*. **1989**, *377*, 89−104.

(15) Unpublished results from our laboratory.

(16) Fischer, E. O. *Pure Appl. Chem*. **1970**, *24*, 407−423.

−70 °C and methyl iodide (0.035 mL, 0.56 mmol) injected. The solution was kept at room temperature for 1 h. After quenching, extraction, and separation by flash chromatography, 0.047 g of the carbene complex **2a** was obtained (45% yield, *E*/*Z* = 85/15).

Reaction of K_2CO_3 with Complex 1a. Method C. Complex **1a** (0.1 g, 0.28 mmol) was added to a stirred solution of K_2CO_3 (0.077 g, 0.56 mmol) in 10 mL of acetone. After 1 h at room temperature methyl iodide (0.035 mL, 0.56 mmol) was added. After 24 h at room temperature control by TLC showed the existence of some of the starting product and then 1 equiv of methyl iodide was added. After 48 h the reaction was stopped by quenching with ice water. Extraction, evaporation in vacuum, and separation afforded 0.008 g of the starting compound **1a** and 0.061 g of the expected product **2a** (59% yield, *E*/*Z* = 75/25).

Reaction of Cs_2CO_3 with Complex 1a. Method D. Methyl iodide (0.035 mL, 0.56 mmol) was added to a stirred solution of **1a** (0.1 g, 0.28 mmol) and Cs_2CO_3 (0.181 g, 0.554 mmol) in 10 mL of wet (15 μL of water was added) acetone. After 1 h at room temperature control by TLC showed the disappearance of the starting compound. Quenching, extraction, and separation by flash chromatography afforded 0.087 g of the expected product **2a** in 84% yield as an orange solid (*E*/*Z* = 100/0).

Data for 2a. IR ($CHCl_3$): 2169, 2061, 1974, 1932 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ): 3.84 (s, 3H, C*H*$_3$), 4.65 (d, *J* = 6 Hz, 2H, C*H*$_2$N), 5.30 (d, *J* = 17.1 Hz, 1H, C*H*$_2$), 5.38 (d, *J* = 10.2 Hz, 1H, C*H*$_2$), 5.88 (ddt, *J* = 17.1, 10.2, 6 Hz, 1H, C*H*), 7.39−7.53 (m, 5H, Ph). ^{13}C-NMR ($CDCl_3$) (δ): 47.0 (q), 63.2 (t), 90.6 (s), 120.0 (t), 122.2 (s), 128.7 (d), 129.3 (s), 130.3 (d), 130.5 (d), 131.6 (d), 217.4 (s), 224.1 (s), 250.2 (C═Cr). Anal. Calcd for $C_{18}H_{13}NO_5Cr$: C, 57.60; H, 3.47; N, 3.73. Found: C, 57.53; H, 3.45; N, 3.80.

Synthesis of Pentacarbonyl[(phenylethynyl)(*E*-allyl-*Z*-methylamino)carbene]tungsten(0) (2b). Reaction of NaH with Complex 1b. Method A. Using the same procedure described for complex **1a**, complex **2b** was obtained in 85% yield (*E*/*Z* = 100/0).

Reaction of *t*-BuOK with Complex 1b. Method B. Using the same procedure described for complex **1a**, complex **2b** was obtained in 82% yield (*E*/*Z* = 100/0).

Reaction of Cs_2CO_3 with Complex 1b. Method D. Using the same procedure described for complex **1a**, complex **2b** was obtained in 87% yield as an orange solid (*E*/*Z* = 100/0).

Data for 2b. IR ($CHCl_3$): 2169, 2061, 1974, 1932 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ): 3.73 (s, 3H, C*H*$_3$), 4.62 (d, *J* = 5.7 Hz, 2H, C*H*$_2$N), 5.31 (d, *J* = 17.1 Hz, 1H, C*H*$_2$), 5.39 (d, *J* = 10 Hz, 1H, C*H*$_2$), 5.90 (ddt, *J* = 17.1, 10, 5.7 Hz, 1H, C*H*), 7.39−7.53 (m, 5H, Ph). ^{13}C-NMR ($CDCl_3$) (δ): 49.2 (q), 62.0 (t), 92.4 (s), 120.3 (t), 121.9 (s), 126.0 (s), 128.8 (d), 130.3 (d), 130.4 (d), 131.8 (d), 198.5 (s), 204.2 (s), 229.8 (s).

Synthesis of Pentacarbonyl[(phenylethynyl)(diallylamino)carbene]chromium(0) (2c). Compound **2c** was obtained in 88% yield as an orange-red solid using method D.

Data for 2c. IR ($CHCl_3$): 2167, 2054, 1978, 1936 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ): 4.62 (d, *J* = 5.2 Hz, 2H, *E*-NC*H*$_2$), 4.85 (d, *J* = 5.2 Hz, 3H, *Z*-C*H*$_2$), 5.25−5.46 (m, 4H, C*H*$_2$ *(E) (Z)*), 5.80−6.04 (m, 2H, C*H (E) (Z)*), 7.40−7.54 (m, 5H, Ph). ^{13}C-NMR ($CDCl_3$) (δ): 58.9 (t), 61.5 (t), 90.9 (s), 119.6 (t), 120.7 (t), 122.1 (s), 128.7 (d), 130.4 (d), 130.0 (s), 130.6 (d), 131.6 (d), 131.7 (d), 217.1 (s), 224.1 (s), 251.0 (C═Cr). Anal. Calcd for $C_{20}H_{15}NO_5Cr$: C, 59.85; H, 3.74; N, 3.47. Found: C, 59.90; H, 3.76; N, 3.55.

Synthesis of Pentacarbonyl[(phenylethynyl)(diallylamino)carbene]tungsten(0) (2d). Compound **2d** was obtained in 87% yield as an orange solid using method D.

Data for 2d. IR ($CHCl_3$): 2167, 2061, 1947, 1939 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ): 4.58 (d, *J* = 5.7 Hz, 2H, (*E*)-NC*H*$_2$), 4.74 (d, *J* = 5.7 Hz, 2H, (*Z*)-NC*H*$_2$), 5.25−5.45 (m, 4H, C*H*$_2$ (*E*) (*Z*)), 5.81−5.99 (m, 2H, C*H* (*E*) (*Z*)), 7.40-7.53 (m, 5H, Ph). ^{13}C-NMR ($CDCl_3$) (δ): 57.8 (t), 63.4 (t), 92.8 (s), 119.8 (t), 120.6 (t), 121.8 (s), 126.6 (s), 128.6 (d), 131.7 (d), 130.3 (d), 130.4 (d), 131.3 (d), 198.2 (s), 203.8 (s), 230.4 (C═W). MS (FAB$^+$): *m*/*e* 533 (M^+).

Synthesis of Pentacarbonyl[(phenylethynyl)(*E*-allyl-*Z*-benzylamino)carbene]chromium(0) (2e). Compound **2e** was obtained in 82% yield as a red solid using method D.

Data for 2e. IR ($CHCl_3$): 2167, 2054, 1976, 1936 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ): 4.50 (d, *J* = 5.8 Hz, 2H, *E*-NC*H*$_2$), 5.16 (d, *J* = 17 Hz, 1H, C*H*$_2$), 5.31 (d, *J* = 10.2 Hz, 1H, C*H*$_2$), 5.48 (s, 2H, *Z*-NC*H*$_2$), 5.82 (ddt, *J* = 17, 10.2, 5.8 Hz, 1H, C*H*), 7.20−7.35 (m, 10H, Ph). ^{13}C-NMR ($CDCl_3$) (δ): 58.9 (t), 62.4 (t), 90.9 (s), 119.6 (t), 121.9 (s), 127.6 (d), 128.5 (d), 128.6 (d), 129.1 (d), 130.3 (d), 130.5 (d), 131.5 (d), 134.3 (s), 216.9 (s), 223.9 (s), 251.4 (C═Cr). Anal. Calcd for $C_{24}H_{17}NO_5Cr$: C, 63.86; H, 3.77; N, 3.10. Found: C, 64.06; H, 3.88; N, 3.13.

Synthesis of Pentacarbonyl[(phenylethynyl)(*E*-allyl-*Z*-benzylamino)carbene]tungsten(0) (2f). Compound **2f** was obtained in 87% yield as an orange solid using method D.

Data for 2f. IR ($CHCl_3$): 2167, 2061, 1975, 1934 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ): 4.45 (d, *J* = 6 Hz, 2H, NC*H*$_2$), 5.15 (d, *J* = 16.8 Hz, 1H, C*H*$_2$), 5.30 (d, *J* = 10.2 Hz, 1H, C*H*$_2$), 5.34 (s, 2H, NC*H*$_2$), 5.81 (ddt, *J* = 16.8, 10.2, 6 Hz, 1H, C*H*), 7.27−7.53 (m, 10H, Ph). ^{13}C-NMR ($CDCl_3$) (δ): 57.8 (t), 64.3 (t), 92.9 (s), 120.0 (t), 121.8 (s), 126.9 (s), 127.7 (d), 128.6 (d), 128.7 (d), 129.2 (d), 130.4 (d), 130.5 (d), 131.8 (d), 134.1 (s), 198.1 (s), 203.8 (s), 231.0 (C═W). Anal. Calcd for $C_{24}H_{17}NO_5W$: C, 49.40; H, 2.92; N, 2.40. Found: C, 49.53; H, 3.02; N, 2.48.

Synthesis of Pentacarbonyl[(phenylethynyl)(allylpropargylamino)carbene]chromium(0) (*E*- and *Z*-2g). Compound **2g** was obtained in 70% yield as a dark red oil, which proved to be a mixture of two isomers not separable by chromatography (81 (*E*-allyl)/19 (*Z*-allyl) determined by NMR), using method D.

Data for 2g (*E*-Allyl). IR ($CHCl_3$): 2167, 2056, 1978, 1938 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ): 1.90 (t, *J* = 2.4 Hz, 3H, C*H*$_3$), 4.78 (d, *J* = 6.3 Hz, 2H, *E*-C*H*$_2$N), 4.94 (q, *J* = 2.4 Hz, 2H, *Z*-C*H*$_2$N), 5.29 (d, *J* = 16.8 Hz, 2H, C*H*$_2$) 5.36 (d, *J* = 10.4 Hz, 1H, C*H*$_2$), 5.90 (ddt, *J* = 16.8, 10.4, 6.3 Hz, 1H, C*H*), 7.40−7.52 (m, 5H, Ph). ^{13}C-NMR ($CDCl_3$) (δ): 3.7 (q), 49.1 (t), 59.2 (t), 61.0 (s), 71.9 (s), 90.7 (s), 120.1 (t), 122.0 (s), 128.7 (d), 130.3 (d), 130.5 (d), 131.2 (s), 131.6 (d), 216.7 (s), 224.1 (s), 251.5 (C═Cr). Anal. Calcd for $C_{21}H_{15}NO_5Cr$: C, 61.02; H, 3.63; N, 3.37. Found: C, 61.17; H, 3.90; N, 3.35.

Data for 2g (*Z*-Allyl). ^{1}H-NMR ($CDCl_3$) (δ): 1.88 (t, *J* = 2.4 Hz, 3H, C*H*$_3$), 4.70 (q, *J* = 2.4 Hz, 2H, *E*-C*H*$_2$N), 4.98 (d, *J* = 6.3 Hz, 2H, *Z*-C*H*$_2$N), 5.45−5.50 (m, 2H, C*H*$_2$), 5.90−6.03 (m, 1H, C*H*), 7.39−7.56 (m, 5H, Ph).

Synthesis of Pentacarbonyl[(phenylethynyl)(*E*-allyl-*Z*-propargylamino)carbene]tungsten(0) (2h). Compound **2h** was obtained in 30% yield as an orange solid using method D.

Data for 2h. IR ($CHCl_3$): 2169, 2063, 1975, 1934 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ): 1.85 (t, *J* = 2.4 Hz, 3H, C*H*$_3$), 4.74 (d, *J* = 6.1 Hz, 2H, *E*-C*H*$_2$N), 4.83 (q, *J* = 2.4 Hz, 2H, *Z*-C*H*$_2$N), 5.28−5.40 (m, 2H, C*H*$_2$), 5.82−5.96 (m, 1H, C*H*), 7.38−7.45 (m, 5H, Ph). Anal. Calcd for $C_{21}H_{15}NO_5W$: C, 46.24; H, 2.57; N, 2.57. Found: C, 46.21; H, 2.88; N, 2.52.

Synthesis of Pentacarbonyl[(phenylethynyl)(*E*-allyl-*Z*-perillylamino)carbene]chromium(0) (2i). Compound **2i** was obtained in 89% yield as an orange solid using method D (with 3 equiv of Cs_2CO_3).

Data for 2i. IR ($CHCl_3$): 2171, 2060, 1968, 1916 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ): 1.40−2.30 (m, 6H, C*H*$_2$), 1.74 (d, *J* = 3.4 Hz, C*H*$_3$), 4.40−4.80 (m, 6H, C*H*$_2$), 5.20 (d, *J* = 16 Hz, 1H,

CH_2), 5.31 (d, J = 10.2 Hz, 1H, CH_2), 5.68 (bs, 1H, CH), 5.93 (ddt, J = 17, 10.2, 5.4 Hz, 1H, CH), 7.40−7.60 (m, 5H, Ph). ^{13}C-NMR ($CDCl_3$) (δ): 20.8 (q), 26.9 (t), 27.4 (t), 30.9 (t), 40.6 (d), 59.1 (t), 64.5 (t), 91.2 (s), 109.1 (t), 119.3 (t), 122.2 (s), 125.8 (d), 128.8 (d), 129.6 (s), 130.4 (d), 130.9 (d), 131.4 (s), 131.7 (d), 134.5 (s), 217.3 (s), 224.2 (s), 250.8 (C═Cr). MS (EI): *m/e* 495, 439, 411, 383, 355, 303, 221, 135, 93. Anal. Calcd for $C_{27}H_{25}NO_5Cr$: C, 65.45; H, 5.09; N, 2.83. Found: C, 65.36; H, 5.19; N, 2.84.

Synthesis of Pentacarbonyl[(phenylethynyl)(*E*-allyl-*Z*-myrthenylamino)carbene]chromium(0) (2i). Compound **2j** was obtained in 66% yield as an orange solid using method D (with 3 equiv of Cs_2CO_3).

Data for 2j. IR ($CHCl_3$): 2167, 2053, 1976, 1934 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ): 0.83 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 2.10−2.50 (m, 6H, CH, CH_2), 4.29 (dd, J = 14.7, 6.3 Hz, 1H, CH_2N), 4.50 (d, J = 15.3 Hz, 1H, CH_2N), 4.86 (dd, J = 14.7, 4.2 Hz, 1H, CH_2N), 5.02 (d, J = 15.3 Hz, 1H, CH_2N), 5.20 (d, J = 16.8 Hz, 1H, CH_2), 5.31 (d, J = 10.2 Hz, 1H, CH_2), 5.58 (bs, 1H, CH), 5.83 (ddt, J = 16.8, 10.2, 6.3 Hz, 1H, CH), 7.35−7.56 (m, 5H, Ph). ^{13}C-NMR ($CDCl_3$) (δ): 20.8 (q), 25.8 (q), 31.5 (d), 31.7 (s), 38.3 (d), 40.6 (d), 42.9 (t), 58.5 (t), 63.6 (t), 92.0 (s), 119.3 (d), 122.2 (s), 122.8 (t), 126.6 (s), 128.6 (d), 130.2 (d), 130.7 (d), 131.5 (d), 217.1 (s), 224.0 (s), 250.1 (C═Cr). HRMS (EI): Calcd for $C_{27}H_{25}O_5NCr$, *m/e* 495.115 239; found, *m/e* 495.113 783.

Synthesis of Pentacarbonyl[(phenylethynyl)(*E*-allyl-*Z*-cyclohexenylamino)carbene]chromium(0) (2k). Compound **2k** was obtained as an orange solid in 38% yield using method D (with 3 equiv of Cs_2CO_3).

Data for 2k. IR ($CHCl_3$): 2167, 2051, 1924 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ): 1.60−2.40 (m, 6H, CH_2), 4.35 (dd, J = 15.3, 5.1 Hz, 1H, CH_2N), 4.76 (bs, 1H, CHN), 5.17 (d, J = 17.1 Hz, 1H, CH_2), 5.26 (d, J = 10.5 Hz, 1H, CH_2), 5.60−5.90 (m, 2H, CH), 7.30−7.50 (m, 5H, Ph). ^{13}C-NMR ($CDCl_3$) (δ): 20.9 (t), 24.6 (t), 28.5 (t), 55.8 (d), 68.8 (t), 118.2 (t), 122.4 (s), 126.0 (d), 128.7 (d), 130.3 (d), 131.5 (d), 131.6 (d), 133.5 (d), 217.2 (s), 224.4 (s), 249.3 (C═Cr). HRMS (EI): Calcd for $C_{23}H_{19}O_5NCr$, *m/e* 441.067 308; found, *m/e* 441.066 833.

Synthesis of Pentacarbonyl[(phenylethynyl)(*E*-benzyl-*Z*-allylamino)carbene]chromium(0) (21). Compound **21** was obtained in 71% yield as a dark red solid using method D.

Data for **2l.** IR ($CHCl_3$): 2165, 2054, 1976, 1936 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ): 4.77 (d, J = 6 Hz, 2H, *Z*-CH_2N), 5.29 (s, 2H, *E*-CH_2N), 5.38 (d, J = 17 Hz, 1H, CH_2), 5.49 (d, J = 10.2 Hz, 1H, CH_2), 6.00 (ddt, J = 17, 10.2, 6 Hz, 1H, CH), 7.24−7.51 (m, 10H, Ph). ^{13}C-NMR ($CDCl_3$) (δ): 59.8 (t), 60.8 (t), 91.3 (s), 120.9 (t), 121.9 (s), 127.5 (d), 128.4 (d), 128.6 (d), 129.2 (d), 129.7 (s), 130.3 (d), 131.6 (d), 131.7 (d), 134.2 (s), 217.0 (s), 224.0 (s), 251.6 (C═Cr).

Synthesis of Pentacarbonyl[(phenylethynyl)(*E*-benzyl-*Z*-allylamino)carbene]tungsten(0) (2m). Compound **2m** was obtained in 68% yield as a red orange solid using method D.

Data for 2m. IR ($CHCl_3$): 2167, 2061, 1975, 1934 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ): 4.45 (d, J = 6 Hz, 2H, *Z*-CH_2N), 5.15 (d, J = 17 Hz, 1H, CH_2), 5.31 (d, J = 10.2 Hz, 1H, CH_2), 5.34 (s, 2H, *E*-CH_2N), 5.81 (ddt, J = 17, 10, 6 Hz, 1H, CH), 7.28−7.52 (m, 10H, Ph). ^{13}C-NMR ($CDCl_3$) (δ): 58.7 (t), 62.8 (t), 93.3 (s), 121.0 (t), 121.7 (s), 126.2 (s), 127.6 (d), 128.5 (d), 128.7 (d), 129.3 (d), 130.5 (d), 131.3 (d), 131.9 (d), 134.0 (s), 198.2 (s), 203.9 (s), 230.7 (C═W).

Synthesis of Pentacarbonyl[phenyl(*E*-allyl-*Z*-methylamino)carbene]tungsten(0) (4). Compound **4** was obtained in 88% yield as an orange solid using method D.

Data for 4. IR ($CHCl_3$): 2061, 1971, 1928 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ): 3.86 (s, 3H, CH_3), 3.96 (m, 2H, CH_2N), 5.15−5.35 (m, 2H, CH_2), 5.57−5.70 (m, 1H, CH), 6.76−6.80 (m, 2H, Ph), 7.12−7.18 (m, 1H, Ph), 7.35−7.41 (m, 2H, Ph). ^{13}C-NMR ($CDCl_3$) (δ): 51.0 (q), 59.3 (t), 119.3 (d), 120.1 (t), 126.3 (d), 128.3 (d), 130.8 (d), 152.7 (s), 198.5 (s), 204.3 (s), 259.1 (C═W). Anal. Calcd for $C_{16}H_{13}NO_5W$: C, 39.75; H, 2.69; N, 2.90. Found: C, 39.65; H, 2.64; N, 3.00.

Synthesis of Pentacarbonyl[methyl(*E*-allyl-*Z*-methylamino)carbene]chromium(0) (6). Compound **6** was obtained in 41% yield as a yellow solid using method D together with a 30% yield of compound **7** as a yellow orange solid. Separation of both products was attained by flash chromatography (2:1 hexane/CH_2Cl_2).

Data for 6. ^{1}H-NMR ($CDCl_3$) (δ): 2.72 (s, 3H, CH_3), 3.82 (s, 3H, CH_3N), 4.27 (ddd, J = 4.8, 1.8, 1.5 Hz, 2H, CH_2N), 5.09 (dt, J = 17.5, 1.8 Hz, 1H, CH_2), 5.33 (dt, J = 10.5, 1.5 Hz, 1H CH_2), 5.77 (ddt, J = 17.1, 10.5, 4.8 Hz, 1H, CH). ^{13}C-NMR ($CDCl_3$) (δ): 39.6 (q), 51.1 (q), 57.3 (t), 118.1 (t), 129.1 (d), 217.9 (s), 223.5 (s), 257.6 (C═Cr). Anal. Calcd for $C_{11}H_{11}NO_5Cr$: C, 45.76; H, 3.80; N, 4.84. Found: C, 45.56; H, 3.92; N, 4.82.

Data for 7. ^{1}H-NMR ($CDCl_3$) (δ): 2.33 (s, 3H, CH_3), 3.07 (s, 3H, CH_3N), 2.95−3.10 (m, 2H, CH_2), 4.05−4.12 (m, 1H, CH), 4.34−4.46 (m, 2H, CH_2N). ^{13}C-NMR ($CDCl_3$) (δ): 33.4 (q), 38.1 (q), 63.6 (t), 64.4 (t), 72.9 (d), 225.5 (s), 225.7 (s), 226.1 (s), 233.1 (s), 281.0 (C═Cr). Anal. Calcd for $C_{10}H_{11}NO_4Cr$: C, 45.97; H, 4.21; N, 5.36. Found: C, 46.15; H, 4.48; N, 5.21.

Synthesis of Compound 9. Compound **9** was obtained in 78% yield as a red solid using method D.

Data for 9. IR ($CHCl_3$): 2063, 1976, 1938, 1720 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ): 2.27 (dd, J = 18.5, 2.1 Hz, 1H, CH_2), 2.67 (dd, J = 18.5, 6 Hz, 1H, CH_2), 3.34−3.44 (m, 2H, CH, CH_2), 3.55 (s, 3H, CH_3), 3.76−3.87 (m, 1H, CH_2), 7.05−7.30 (m, 5H, Ph). ^{13}C-NMR ($CDCl_3$) (δ): 38.5 (t), 42.7 (q), 45.3 (d), 65.8 (t), 128.3 (d), 129.0 (d), 130.0 (d), 130.2 (s), 141.9 (s), 180.2 (s), 197.3 (s), 202.1 (s), 206.7 (s), 236.2 (C═W). Anal. Calcd for $C_{19}H_{13}NO_6W$: C, 42.64; H, 2.45; N, 2.62. Found: C, 42.06; H, 2.59; N, 2.57.

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