The Pauson−Khand Reaction on Enynes Bearing a Pentacarbonylmetal (Cr, W) Carbene Tether†

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Received January 28, 1997⊗

The study of the scope of the Pauson−Khand reaction on alkynyl(allylamino)carbene pentacarbonyl complexes of chromium and tungsten(0) is reported. This reaction affords good yields of the expected cycloadducts under very mild conditions and short reaction times. One of the features of this process is that the metal pentacarbonyl moiety remains in the final products. Substitution at different sites of the enyne chain shows a considerable influence of both steric and electronic effects in the overall reaction course. In this way, new cobalt carbene complexes are obtained and fully characterized. The effects of the presence of different heteroatoms in the enyne chain are also studied. A survey on the factors responsible for an easy intramolecular cycloaddition and a mechanistic proposal are also described. This study points to the geometry of the almost exclusive isomer formed in the aminolysis of the precursors **1** as the decisive (but not the only one) facilitation factor.

Since Fischer's early reports on heteroatom-stabilized carbene complexes with group VI transition metal carbonyls,[1] a special activation of the α site by the electron-withdrawing character of the metal−carbene unit has been recognized and widely used for synthetic purposes. Thus, on treating alkylalkoxycarbene complexes with bases, the hydrogen bonded to the α-carbon atom is easily removed and the remaining carbanion behaves similarly to typical organic enolates.[2] The effect of the electronic deficiency inherent to the carbene center is not limited to the α site, but in some cases, it can be transmitted further along the substituent chain, as for example, may be deduced from the atypical values of the ^{13}C-NMR chemical shift for the acetylenic carbon atoms in alkynylalkoxycarbene complexes.[3] This led us to conclude that these complexes could readily give reactions typical of propiolates under mild conditions such as the conjugate addition of nucleophiles on the triple bond.[4] This rational, brought to its limit, made us consider these complexes as propiolates with an internal Lewis acid,[5] and accordingly, they behave as Diels−Alder dienophiles with similar reactivity and selectivity.[6] In addition, the easy and stereospecific [2 + 2] cycloadditions with electron-rich olefins might well be the consequence of the vinyl cation-like character of these complexes as sketched in Chart 1.[7]

Chart 1

[M] = $(CO)_5W$, $(CO)_5Cr$

On the other hand, a great deal of effort has been recently devoted to activate the components of the Co-mediated carbonylative cycloaddition of alkynes and olefins (Pauson−Khand (P−K) reaction)[8]. Among different means of improving the yield in the expected P−K cycloadducts,[9] the linking of both components in a single

† Dedicated "in memoriam" to Prof. Felix Serratosa Palet.

⊗ Abstract published in *Advance ACS Abstracts,* May 15, 1997.

(1) For Fischer carbene complexes, see: (a) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1. (b) Dötz, K. H.; Fischer, H.; Hofman, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; VCH: Deerfield Beach, FL, 1983. (c) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (d) Wulff, W. D. In *Advances in Metal−Organic Chemistry*; Liebeskind, S. L., Ed.; JAI Press: Greenwich, CT, 1989; Vol. 1, pp 209−393. (e) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Emsford, NY, 1990; Vol. 5, pp 1065−1113.

(2) (a) Casey, C. P.; Anderson, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 1230. (b) Casey, C. P.; Brunswold, W. R. *J. Organomet. Chem.* **1976**, *118*, 309. (c) Wulff, W. D.; Gilbertson, S. R.; *J. Am. Chem. Soc.* **1984**, *107*, 503. (d) Anderson, B. A.; Wulff, W. D.; Rahm, A. *J. Am. Chem. Soc.* **1993**, *115*, 4602.

(3) Wang, S. L. B.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 4550.

(4) Camps, F.; Llebaria, A.; Moretó, J. M.; Ricart, S.; Viñas, J. M.; Ros, J.; Yañez, R. *J. Organomet. Chem.* **1991**, *401*, C-17−C-19.

(5) Llebaria, A.; Moretó, J. M.; Ricart, S.; Ros, J.; Viñas, J. M.; Yañez, R. *J. Organomet. Chem.* **1992**, *440*, 79−90.

(6) (a) Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642−3659. (b) Wulff, W. D.; Powers, T. S. *J. Org. Chem.* **1993**, *58*, 2381−2393.

(7) For [2 + 2] cycloadditions of (alkoxyalkynylcarbene) metal complexes, see: (a) Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1988**, *110*, 8727. (b) Camps, F.; Moretó, J. M.; Ricart, S.; Viñas, J. M.; Molins, E.; Miravitlles, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1560. (c) Camps, F.; Llebaria, A.; Moretó, J. M.; Ricart, S.; Viñas, J. M. *Tetrahedron Lett.* **1990**, *31*, 2479. (d) Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 6419. (e) Jordi, L.; Camps, F.; Ricart, S.; Viñas, J. M.; Moretó, J. M.; Mejias, M.; Molins, E. *J. Organomet. Chem.* **1995**, *494*, 53−64. (f) In agreement with the vinyl cation-like character of the (alkynylcarbene)metal complexes, the pressure dependence of the [2 + 2] cycloaddition reaction of different (alkoxyalkynylcarbene)-metal complexes with dihydropyrane supports the concertedness of the process; see: Pipoh, R.; van Eldik, R.; Wang, S. L. B.; Wulff, W. D. *Organometallics* **1992**, *11*, 490−492. (g) In addition, the most stable complexes of this class prepared so far correspond to the ones whose stability could be predicted on the reported data for organic vinyl cations; see: Hanack, M. *Acc. Chem. Res.* **1976**, *9*, 364−371.

(8) For reviews on the Pauson−Khand reaction, see: (a) Schore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, U.K., 1991; Vol. 5, p 1037. (b) Pauson, P. L. In *Organometallics in Organic Synthesis*; de Meijere, A., tom Dieck, H., Eds.; Springer-Verlag: Berlin, 1987; p 234. (c) Pauson, P. L. *Tetrahedron* **1985**, *41*, 5855. (d) Schore, N. E. *Org. React.* **1991**, *40*, 1.

(9) The use of SiO_2 (Simonian, S. O.; Smit, W. A.; Coybin, A. S.; Shaskov, A. S.; Mikaelian, G. S.; Torasov, V. A.; Ibragimov, I. J.; Caple, R.; Froen, D. E. *Tetrahedron Lett.* **1986**, *27*, 1245−1248) and amino *N*-oxides (Shambayati, S.; Crowe, W. E., Schreiber, S. L. *Tetrahedron Lett.* **1990**, *31*, 5289) allows the cycloaddition to occur at low temperatures with better yields.

S0276-7333(97)00062-9 CCC: $14.00

chain has been shown to give good results and applied to the synthesis of bioactive compounds.[10] However these enynes, in the presence of $Co_2(CO)_8$, had still to be heated or, alternatively, amine oxides added in order to obtain the corresponding cycloadducts.

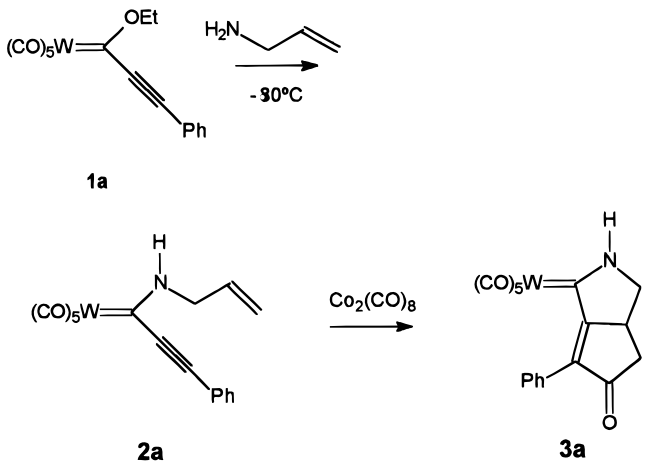
On the bases mentioned above, we reasoned that alkynylcarbene complexes with a distal double bond were potential candidates for an efficient carbonylative cycloaddition under milder conditions than those of the conventional Pauson−Khand protocol since, besides the effects of alkyne activation, a metal carbene tether would approach the enyne functionalities. In addition, the organometallic moiety, if kept unchanged during the process, might serve for subsequent benzannulation reactions.[11] Preliminary accounts on the results obtained from [(allylamino)alkynylcarbene]metal complexes have been reported.[12]

Results

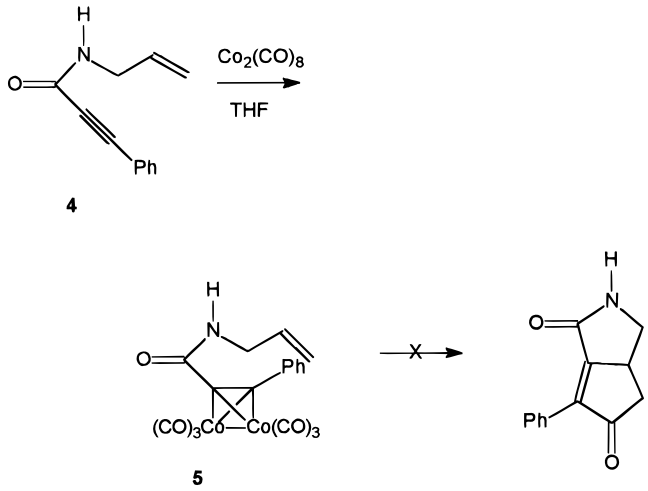
Scope of the Intramolecular Pauson-Khand Reaction on Fischer Carbene Metal Complexes. Reaction with Different [(Allylamino)ethynylcarbene]-metal (Cr, W) Complexes. As the preparation of [alkynyl(allyloxy)carbene]metal complexes in satisfactory yields was not trivial,[13] we decided to introduce a distal double bond by means of the easy nucleophilic displacement of the alkoxy group in an alkynyl ethoxy carbene metal complex by an allylamine. In this case, the ready conjugate addition on the triple bond was a drawback to be prevented.[14] Thus, complex **2a** was obtained by treatment of the corresponding ethoxy complex **1a** with allylamine at −80 °C under kinetic control. An important feature of this process is the practically exclusive production of the *E* isomer. Since the *E* and *Z* isomers of aminocarbene complexes are known not to interconvert below 100 °C,[15] we believe that this result arises from an orbital control involved in its formation.[16] When this complex was treated with $Co_2(CO)_8$ at *room temperature* in THF it readily transformed into the corresponding cycloadduct **3a** in good yield (75%) (Scheme 1).

The $Co_2(CO)_8$ proved very efficient in promoting this cycloaddition since no cobalt remained coordinated at any site of the final cycloadduct. The facilitation operated by the transition metal−aminocarbene unit

Scheme 1



Scheme 2



was further evidenced by the lack of cycloaddition from the corresponding propiolamide **4**, under the same conditions, in which only complex **5** could be obtained[17] (Scheme 2). The change of metal (Cr for W) led to similar results (Table 1, entries 1 and 2).

These preliminary observations encouraged us to pursue our studies with the aim to determine how the carbene moiety was exerting its activating role. To accomplish this purpose, the two branches of the starting carbene complex were systematically modified with substituents having different electronic character and/or introducing variable steric demands. The resulting complexes were treated with $Co_2(CO)_8$, in anhydrous THF, at room temperature without the presence of any external activator. The results obtained were then related to the modification introduced in the original enyne.

(1) Effects of Variations in the Heteroatom Branch. (a) Substitution at the Allyl Group. We first analyzed the effect of different groups by substituting the allyl moiety at its three unequivalent sites. The results are collected in Table 1. They showed us that the reaction was indeed sensitive to the steric requirements displayed by the substituents in the allyl moiety of the starting enyne **2**. Thus, the reaction of the

(10) (a) Schore, N. E.; Knudsen, M. J. *J. Org. Chem.* **1987**, *52*, 569−580. (b) Schore, N. E.; MacWhorter, S. E. *J. Org. Chem.* **1991**, *56*, 338−346. (c) Rowley, E. G.; Schore, N. E. *J. Org. Chem.* **1992**, *57*, 6853−6861. (d) Billington, D. C.; Willison, D. *Tetrahedron Lett.* **1984**, *25*, 4141−4144. (e) Magnus, P.; Exon, C.; Albaugh-Robertson, P. *Tetrahedron* **1985**, *41*, 5861−5869. (f) Magnus, P.; Becker, D. P. *J. Am. Chem. Soc.* **1987**, *109*, 7495−7498. (g) Magnus, P.; Principe, L. M.; Slater, M. J. *J. Org. Chem.* **1987**, *52*, 1483−1486. (h) Magnus, P.; Slater, M. J.; Principe, L. M. *J. Org. Chem.* **1989**, *54*, 5148−5153.

(11) For benzannulation examples, see: Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.

(12) (a) Camps, F.; Moretó, J. M.; Ricart, S.; Viñas, J. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1470−1472. (b) Dötz, K. H.; Christoffers, J. *J. Organomet. Chem.* **1992**, *426*, C58−C61.

(13) (a) Dötz, K. H.; Noack, R.; Harms, K.; Muller, G. *Tetrahedron* **1990**, *46*, 1235−1252. (b) Christoffers, J.; Dötz, K. H. *Organometallics* **1994**, *13*, 4189−4193.

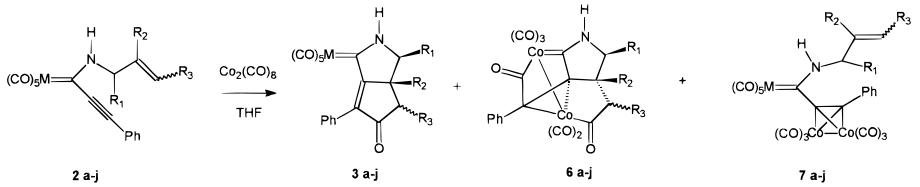
(14) Fischer, E. O.; Kalder, H. J. *J. Organomet. Chem.* **1977**, *131*, 57.

(15) The rotation barrier about C_{carb}−N bond in a typical aminocarbene complex is >25 kcal/mol, and this can be attributed to the high degree of delocalization from nitrogen to carbon. Anderson, B. A.; Wulff, W. D.; Powers, T. S.; Tribbitt, S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 10784−10798.

(16) A theoretical study to support the present observation is in progress.

(17) Complex **5** can be smoothly converted into the corresponding P−K cycloadduct in good yield by the addition of a *N*-amine oxide: Krafft, M. E.; Romero, R. H.; Scott, I. L. *J. Org. Chem.* **1992**, *57*, 5277−5278.

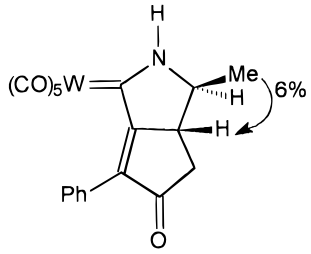
Table 1



entry		M	R_1	R_2	R_3	time (h)	products (yield %)		
1	**2a**	W	H	H	H	3	**3a** (75)		
2	**2b**	Cr	H	H	H	3	**3b** (72)		
3	**2c**	W	Me	H	H	3	**3c** (62)	**6c** (17)	
4	**2d**	W	H	Me	H	12	**3d** (28)	**6d** (20)	**7d** (38)
5	**2e**	W	H	H	Me (*E*)	3	**3e**[a] (72)		
6	**2f**	W	H	H	Me (*Z*)	3	**3e** + **3f**[b] (70)		
7	**2g**	W	*c*	H	*c*	12	**3g** (35)		
8	**2h**	W	H	H	CO_2Me				**7h**[d] (tr)
9	**2i**	W	H	2-furyl					**7i**[d] (2)
10	**2j**	W	H	H	Ph				**7j**[d] (tr)

[a] Only the product with *exo* R_3 was detected. [b] Obtained as a 30/70 mixture of the two possible stereoisomers (**3e**/**3f**). [c] R_1, R_3 = $-CH_2CH_2CH_2-$. [d] The low yield is most probably due to the low stability of this compound under the reaction conditions.

α-aminomethyl analog (entry 3) rendered a single stereoisomer **3c** as the major product in 62% yield. Its relative structure was determined by NOE signal enhancement experiments.



3c

In entries 3 and 4 we observed the presence of a second reaction product, **6** (postulated as that arising from an early internal quenching of a reaction intermediate[18]). The trans crotylamino complex (entry 5) gave a ready cycloaddition to afford complex **3e** in 72% yield as a single stereoisomer (exo R_3). The structural assignment for this adduct was made by considering the chemical shift and the coupling constants of the relevant signals related to those reported for purely organic diquinane structures and considered of diagnostic value by Schore and Knudsen.[10a] In fact, although all the signals in the present bicyclic complexes are shifted 0.2−0.4 ppm downfield from the corresponding ones in the organic analogs, they appear in the same relative order.

Although allylamino complexes with a *Z* double bond in the allyl group were not previously reported, we were able to synthesize complex **2f** with this geometry (entry 6). Under the reaction conditions, it afforded the corresponding cyclopentenone adduct in a fairly good yield but as a 30/70 mixture of the two possible stereoisomers (**3e** and **3f**, respectively). The presence of these two compounds in the mixture was established by ^{1}H-NMR spectroscopy after a sample of pure **3f** could be separated by flash chromatography and fully characterized. The remaining signals in the ^{1}H-NMR spectra of the original mixture were found to correspond to those of the stereoisomer **3e** previously characterized.

The next (allylamino)carbene complex to be tried in this reaction was **2g** with a double bond included in a six-membered ring. The reaction proceeded much slower and only after 12 h all the starting complex had disappeared (TLC) and the reaction was stopped. After the usual workup, a single adduct was obtained corresponding to the expected cyclopentenone adduct **3g** (entry 7) in only 35% yield. The product was sparingly soluble in most solvents, and suitable crystals for X-ray diffractometry structure resolution could not be grown. However, from its ^{1}H-NMR data, the structure of this complex could be established since the apical proton appears as a triplet with a rather high coupling constant (J = 7.3 Hz) with the other bridgehead protons. Such values have been reported for similar organic structures.[19] Moreover, the alternative structures would result in unbearable strain.

The next concern was to evaluate the effect of the change in the electronic character of the functionality attached to the allyl moiety. Reactions of allylamines containing electron-withdrawing (methyl 4-aminocrotonate) or conjugated systems (furfurylamine, cynnamylamine) were unsuccessful, leading only to the corresponding $Co_2(CO)_6$-alkynyl complexes **7** in minor yields (Table 1, entries 8−10).

(b) Change of the Heteroatom of the Allyl Branch. The effect of the heteroatom was also analyzed: Initial attempts addressed to the preparation of the (allyloxy)carbene complex **1c** met failure since the conventional methods gave low yields of the desired complex or failed completely. However, the addition of *in situ*-generated allyl triflate[13b,20] to the recently prepared acylate gave satisfactory results (65% M = W; 80%, M = Cr) (Scheme 3).

(18) Jordi, L.; Moretó, J. M.; Ricart, S.; Viñas, J. M.; Mejias, M.; Molins, E. *Organometallics* **1992**, *11*, 3507−3510.

(19) We thank Prof. Miwako Mori from Hokkaido University, Sapporo, Japan, for providing us with the coupling constant for the apical proton with the nearby bridgehead proton (J = 7−8Hz) in a structurally related model compound (having also an apical proton) in a total synthesis of dendroine: Mori, M.; Vesaka, N.; Shibasaki, M. *J. Org. Chem*. **1992**, *57*, 3519−3521.

(20) Beard, C. D.; Baum, K.; Grakauskas, V. *J. Org. Chem*. **1973**, *38*, 3673−3677.

Scheme 3

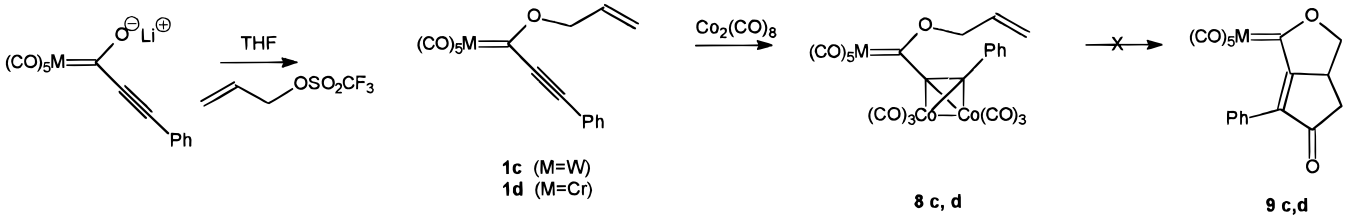
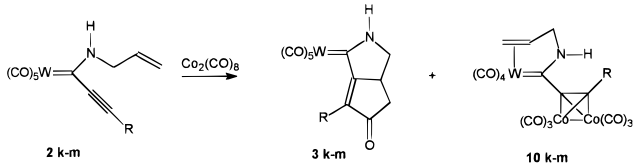
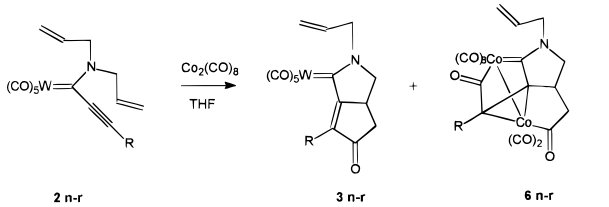


Table 2



entry		R	time (h)	products (yield %)	
1	**2k**	Et	1	**3k** (70)	
2	**21**	Me_3Si	8		**10l** (84)
3	**2m**	t-Bu	12		**10m** (40)

Table 3



entry		R	time (h)	products (yield %)		
1	**2n**	$SiMe_3$	48		**6n** (60)	
2	**2o**	Ph	2	**3o** (80)		
3	**2p**	Et	2	**3p** (70)		
4	**2q**	t-Bu	6 days		**6q** (11)	**12** (20)
5	**2r**	H	10 min	**3r** (60)		

This complex, **1c**, was reacted with $Co_2(CO)_8$ in THF at room temperature, and to our surprise, only the $Co_2(CO)_6$ complex **8c** was obtained. This compound, in THF or CH_3CN, evolved readily to many other minor complexes of difficult characterization. In contrast, in nonoxygenated solvents (isooctane, toluene) complex **8c** was isolated in 85% yield and showed no tendency to decomposition. Similar results were obtained for the chromium analog[21] (80% yield in **8d**). When complex **8c** was heated in isooctane to 50 °C under a CO atmosphere, it evolved to afford uncharacterizable products.

We were completely unable to obtain the sulfur analog, since any attempted nucleophilic substitution at the carbene center led to preferential conjugate addition, even at −30 °C, while below this temperature no changes were recorded.

(2) Effects of Changing the Substituent at the Triple Bond. For this purpose, the phenyl group present in the experiments, reported so far as the alkyne substituent, was replaced by an alkyl group. This caused an acceleration of the P−K cycloaddition although we recorded a similar yield (70%) in the corresponding cycloadduct[12] **3k** (Table 2, entry 1). In contrast, the Me_3Si and *tert*-butyl analogs led to the $Co_2(CO)_6$ complexes of the tetracarbonyl derivatives **10l** and **10m** in good yield (84%) for $SiMe_3$ but lower (40%) for *tert*-butyl.

We attributed these last results (entries 2 and 3) to steric encumbrance brought about by the alkyne substituent rather than to the change of electronic character as could be deduced from the similar products obtained in both cases. Treatment of **10l** with CO (10 psi), PPh_3, heat, or UV irradiation failed to reconduct the complex along the remaining steps of the carbonylative cycloaddition.

(3) Effects of Further Allyl Substitution at the Nitrogen. Due to the versatile role played by the trimethylsilyl group in organic synthesis,[22] we directed our efforts to circumvent the difficulties encountered with the trimethylsilyl derivative **2l**. The most trivial solution to this problem was to place two allyl substituents on the nitrogen atom of **2l** (complex **2n**). Thus, although coordination of the triple bond to $Co_2(CO)_8$ would force one of the allyl groups to chelate the metal, the remaining one might still interact with the Co-coordinated alkyne leading to the desired cycloaddition.

As reported in a previous publication,[18] the reaction of this synthesized (diallylamino)[(trimethylsilyl)ethynyl]-carbene complex **2n** with $Co_2(CO)_8$ led to an unexpected cobalt carbene complex **6n** in 60% yield (Table 3, entry 1). Similar complexes were already obtained as byproducts in the P−K reaction with complexes **2c** and **2d** (Table 1, entries 3 and 4). In view of these surprising results, we thought it interesting to extend the study of the P−K reaction to some other (diallylamino)-alkynylcarbene complexes differently substituted at the triple bond with the purpose to gain insight into the causes for the changes of the reaction course.

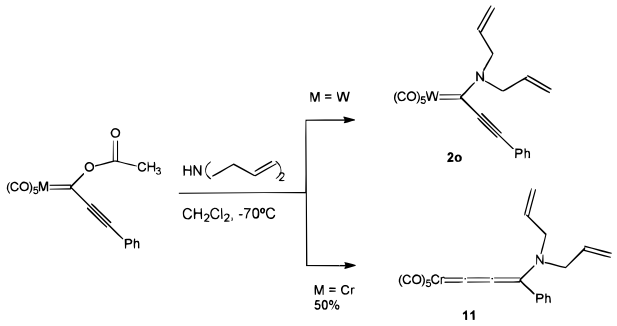
In this way, four new (diallylamino)carbenes (**2o**−**r**) with different substituents at the triple bond were synthesized. Although these (diallylamino)alkynylcarbene complexes are usually not available by aminolysis of the corresponding alkoxy complexes because of the preferred conjugated addition,[23] we were able to prepare complex **2n** and **2q** by this method.[24] However, the

(21) The results with allyloxycarbene complexes were surprising, *a priori*, because aminocarbene complexes are described as less reactive than the corresponding oxy counterparts. This higher stability of aminocarbene complexes is due to the higher electron donation capacity from the heteroatom to the carbene center: In this aspect, see: (a) Anderson, B. A.; Wulff, W. D.; Powers, T. S.; Tribbitt, S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 10784−10798. (b) Dötz, K. H.; Noack, R.; Harms, K.; Müller, C. *Tetrahedron* **1990**, *46*, 1235−1252. (c) Casey, C. P.; Wollendorf, N. W.; Haller, K. I. *J. Am. Chem. Soc.* **1984**, *106*, 3754−3764. (d) Casey, C. P.; Cesa, M. C. *Organometallics* **1982**, *1*, 87. (e) Conner, J. A. *Top. Curr. Chem.* **1977**, *71*, 71.

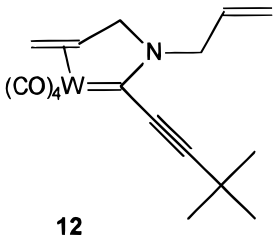
(22) For use of silicon in organic synthesis, see: (a) Calvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London 1981. (b) Reich, H. *Tetrahedron* **1983**, *39*, 839−1009. (c) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer Verlag: Berlin, 1983. (d) Chau, T. H.; Fleming, I. *Synthesis* **1979**, 761.

(23) (a) Klabunde, U.; Fischer, E. O. *J. Chem. Soc.* **1967**, *89*, 7141. (b) Connor, J. A.; Fischer, E. O. *J. Chem. Soc. A* **1969**, 578.

Scheme 4



preparation of (diallylamino)carbene complexes with a smaller alkyne substituent such as Ph (**2o**) or Et (**2p**) by aminolysis failed. The alternative way described in Scheme 4 afforded the corresponding tungsten complex (**2o**, 80%), but with the chromium complex we only obtained, after purification of the crude mixture, one single product identified as the allenylidene complex **11**. These allenylidene complexes have been described by de Meijere *et al.*[25] but only for bulky substituents either in the amine group or in R_1. Complex **2p** was prepared as **2o** in 40% yield. Reaction of $Co_2(CO)_8$ with **2o** and **2p** was brought up to completion following the usual pathway to the corresponding P−K cycloadducts (Table 3, entries 2 and 3), while the *tert*-butyl analog reacted sluggishly to give **6q** in 11% yield. In this case, the corresponding tetracarbonyl allyl alkynyl complex **12**



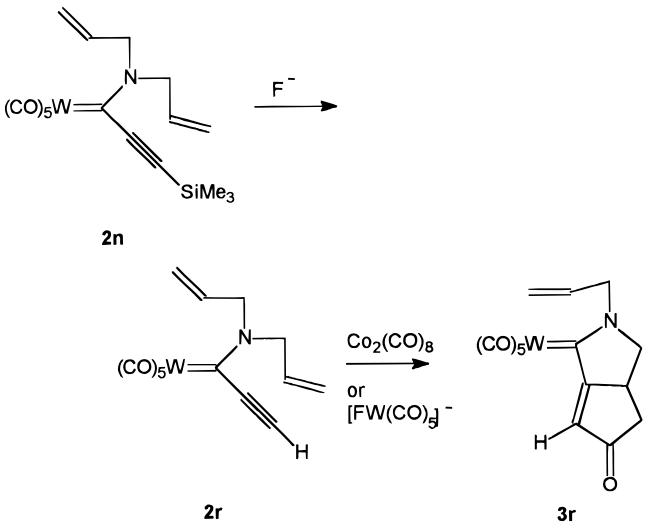
12

was also obtained in 20% yield. The results of entries 1 and 4 compared with the others displayed in Table 3 pointed out the difficulty in the coordination of $Co_2(CO)_8$ to a triple bond flanked by two bulky substituents.

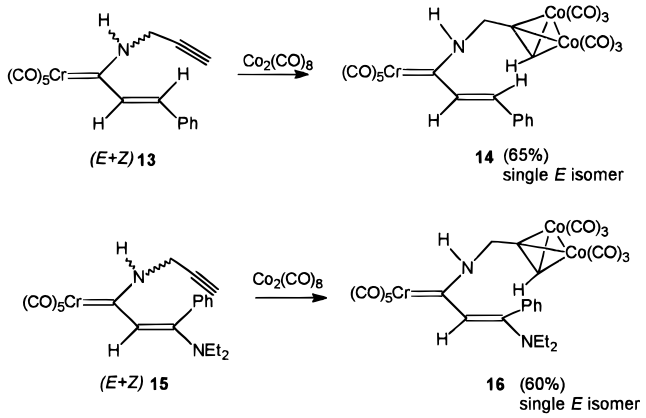
We decided to undertake the synthesis of the terminal alkynecarbene complex **2r** by protodesilylation of complex **2n** using benzyltriethylammonium fluoride under the Magnus conditions.[10e] Surprisingly, under these conditions, besides the expected desilylated complex **2r** (30%), cycloadduct **3r** (10%) was also obtained. As we already explained in a previous communication,[26] the concurrent generation of $[W(CO)_5F]^-$ in the desilylation process accounted for the present result (Scheme 5).

By lowering the temperature in the desilylation step, an excellent yield of complex **2r** could be obtained (93%). After its treatment with $Co_2(CO)_8$ following the general protocol, the complex **3r** was obtained in 60% yield (Table 3, entry 5).

Scheme 5



Scheme 6



(4) Change of the Mutual Disposition of the Double and Triple Bonds. Going on in the study of the scope of this intramolecular P−K reaction with metal carbene complexes, we decided to change the relative arrangement of the double and triple bonds related to the carbene center in the enynecarbene complex to assess to what extent the electronic interaction carbene triple bond was responsible for the P−K cycloaddition activation versus that brought about by the mutual geometry of the double and triple bonds.

(a) Alkenyl(propargylamino)carbene Complexes. In our first attempt, we planned to exchange the double and triple bonds. In doing so, we were liable to profoundly alter the electronic influence of the metal carbene moiety on the triple bond while the relative geometry of the two interacting functionalities should be far less affected. Thus, complex **13** ($E + Z$)[27] was easily prepared from the corresponding ethoxy complex. None of the two isomers evolved to the wanted adduct by treatment with $Co_2(CO)_8$ in THF at room temperature, and instead, the triple bond had again coordinated the $Co_2(CO)_6$ unit, giving a single isomer **14** (Scheme 6). Since the electron deficiency of the olefin could be blamed for the lack of cycloaddition in **13**, we prepared complex **15** with a more electron rich double bond.[28]

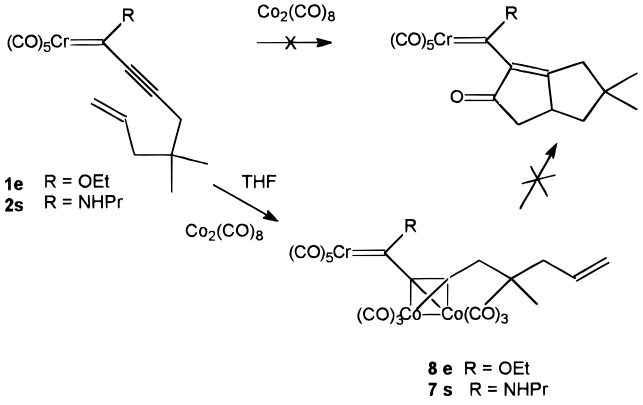
(24) Due probably to steric protection, (trimethylsilyl)ethynylcarbene complexes are reluctant to conjugate addition and therefore aminolysis at the carbene center is not disrupted.

(25) (a) Duetsch, M.; Strein, 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-Inner, R.; de Meijere, A. *Organometallics* **1993**, *12*, 2556−2564.

(26) Jordi, L.; Segundo, A.; Camps, F.; Ricart, S.; Moretó, J. M. *Organometallics* **1993**, *12*, 3795−3797.

(27) In this case, the aminolysis of the carbene center was performed at room temperature, given the absence of conjugate addition. Both amines resulted in a ratio E/Z = 9/1. The assignment was done following: Moser, E.; Fischer, E. O. *J. Organomet. Chem.* **1969**, *16*, 275−282.

Scheme 7



Again the reaction, at room-temperature conditions, stopped at the cobalt complex stage (**16**). These results showed us that this intramolecular P−K reaction fails when the olefin is conjugated to the carbene center. The electron deficiency of the olefin in one case and/or the steric crowding in the other (**15** has a trisubstituted olefin) could account for the lack of cycloaddition.

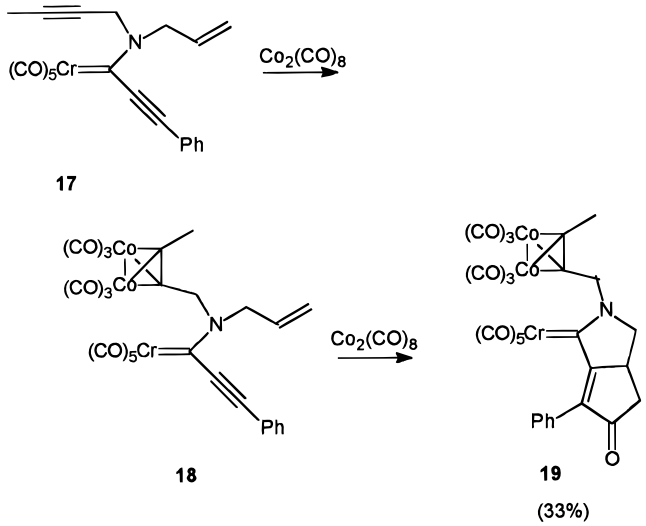
Particularly noteworthy is the low-temperature isomerization of *Z* isomers of **13** and **15** to the corresponding *E* of **14** and **16** entailed by complexation of the propargyl unit to the $Co_2(CO)_6$ moiety.

(b) Disassembly of the Mutual Arrangement of Triple and Double Bonds on the Aminocarbene Moiety. Next we tried to evaluate the effect of the electronic activation of the $(OC)_5M$ unit on the triple bond toward the facilitation of the Pauson−Khand reaction in the (allylamino)alkynylcarbene complexes. If this facilitation was due exclusively to electronic factors, the reaction could still proceed at low temperature provided we were binding the activating carbene center to the triple bond and keeping the double bond in a 1,5 relative distance. Chromium and alkoxycarbene were initially chosen to increase the reactivity and the *gem*-dimethyl substituents to favor cyclization.

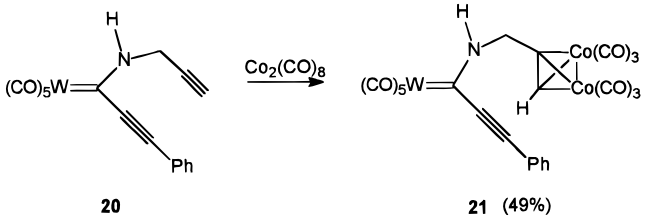
With this purpose in mind, we prepared complex **1e**, which was treated with $Co_2(CO)_8$ at room temperature (Scheme 7). Despite that, complex **8e** was the only product obtained (60%) after the reaction with $Co_2(CO)_8$ at room temperature in isooctane (in THF this compound, **8e**, evolves readily to many uncharacterizable complexes). Suspecting that the lone electron pair of the nitrogen could be required, we prepared **2s**, but it behaved similarly and only complex **7s** could be isolated, again in isooctane at room temperature. More forcing conditions (increase of the temperature up to 50 °C and CO atmosphere) led only to formation of an uncharacterizable cluster.[29]

Alternatively, in a further experiment, complex **17** (Scheme 8), having a further triple bond in *Z* disposition, was prepared. When this complex was treated with 1 equiv of $Co_2(CO)_8$, no cyclization was observed and only the alkynyl−$Co_2(CO)_6$ complex **18** was produced. This complex did not evolve, under mild conditions, to the

Scheme 8



Scheme 9



P−K cycloadduct although the double bond was at a reasonable distance for the P−K process.

However, when an additional equivalent of $Co_2(CO)_8$ was added, cyclization to **19** proceeded in the usual manner in a low but significant yield (33%).

To illustrate how electronically different a metal−carbene conjugated triple bond may be related to a conventional alkyne, complex **20** (Scheme 9) was prepared by kinetic controlled aminolysis with propargylamine. Again a single isomer (*E*) was obtained (91%), and after treatment with an excess of $Co_2(CO)_8$, a single alkyne complexed compound (**21**) was obtained in 49% yield. This fact was interpreted as the result of a preferential coordination of the cobalt to the electronically richer propargyl triple bond, with occupation of the region embraced by the two branches of the planar metal carbene unit, thus preventing the further coordination of the carbene conjugated triple bond to a second dicobalt unit.

From these last two experiments, we inferred that the cobalt was able to discriminate between the two electronically different alkynes, and therefore, its coordination to a triple bond conjugated with a metal carbene center requires a higher demand in terms of energy referred to that of an organic alkyne, that meaning some degree of activation.

Discussion

Scope of the Intramolecular Pauson−Khand Reaction with Fischer Carbene Complexes. Up to this point, we realized that the accomplishment of the intramolecular P−K reaction with Fischer carbene complexes was apparently restricted to (allylamino)-(alkynyl)carbene complexes (or diallylamino). Alternatively, the other enynecarbene complexes not leading to the corresponding cycloadducts at room temperature

(28) The stereochemistry of the double bond was ascertained by NOE enhancement experiments: irradiation of the two α-aminomethylene signals caused 23% of the effect on the vinyl proton signal while irradiation of the aromatic signals gave no effect. In the present case, both isomers, obtained in a ratio $E/Z = 8.5/1.5$, gave the same effect.

(29) Moldes, I.; Ros, J.; Torres, M. R.; Perales, A.; Mathieu, R. *J. Organomet. Chem.* **1994**, *464*, 219−223.

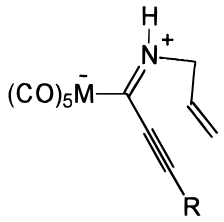


Figure 1.

could not be forced to cyclize by heating or addition of amine oxide. In the first case, prior to the cycloaddition there was a rearrangement of the $Co_2(CO)_6$-coordinated complex to other unstable products. In the second, the amine oxide releases the $(OC)_5M$ unit preferentially to any interaction with the $Co_2(CO)_6$ required for the P−K cycloaddition.

In our search for the origin of the activation, we also discarded the sole triple bond activation in the (allylamino)alkynylcarbene complexes after lack of further cycloaddition of complex **7s**. This complex had a triple bond with electronic characteristics similar to those of (allylamino)alkynylcarbene complexes and a double bond at a suitable distance but failed to provide the desired cycloadduct. In addition, we did not detect any change in a mixture of [(phenylethynyl)(propylamino)carbene]pentacarbonyltungsten and a strained olefin such as norbornene at reasonable temperatures[30] after the addition of $Co_2(CO)_8$. Therefore, we concluded that a favorable arrangement of the triple and double bonds in the starting (allylamino)alkynylcarbene complexes was required.

Thus, this favorable geometric arrangement would come from the partial double bond character inherent to the $C_{carbene}$−N bond[15] (Figure 1). In the preparation of the (allylamino)alkynylcarbene complexes (the only ones leading to P−K cycloadducts), we observed that only the *E* isomer was obtained. This *E* isomer points the allyl group toward the alkyne chain, in proper geometry for a further cycloaddition.[31] Furthermore, the coordination of $Co_2(CO)_8$ at the triple bond, as the first step of the P−K reaction, would even bring closer the two interacting functionalities. This approximation of the triple and double bonds after the $Co_2(CO)_8$ coordination is also supported by the fact that in complexes **2l** and **2m**, with larger substituents (TMS and *tert*-butyl) attached to the alkyne moiety, the reaction failed to attain the proper atom alignment to give the internal cycloadduct. Instead, the double bond is pushed away, isomerized, and finally chelated in the final products **10l** and **10m**, respectively.

As for (allyloxy)carbene complexes **1c** and **1d** likewise reported for other oxycarbene complexes, a rapid *E*−*Z* isomerization would proceed at room temperature.[32] Thus, for these complexes, the favorable geometry shown in the (allylamino)alkynylcarbene complexes (Figure 1) would rarely be attained.

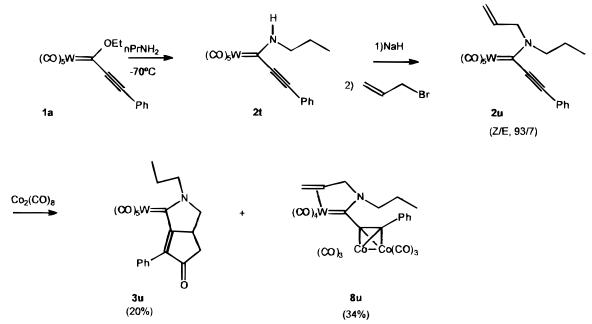
We then conclude that, while a carbene conjugated triple bond is required, the favorable mutual arrangement of the triple and double bonds in the organometallic enyne would be the most decisive factor for the accomplishment of an easy P−K cycloaddition in these complexes.

Insight into the Stereochemistry of the Reaction. Cobalt Carbene Complex Formation. The major features of the process here reported indicate that a Pauson−Khand-like mechanism should be operating on the enyne after addition of $Co_2(CO)_8$. The reaction shows a high degree of stereoselectivity, which probably emerges from the strict requirements imposed in the coordination of the distal double bond to one of the cobalt atoms placed in a considerably crowded surrounding. We will follow the Magnus rationale[10a,e] to explain the main facts concerning the stereochemistry of the process. However, we will consider in the present case the two possible coordination modes in intermediate **I**, since probably they are closer in energy than in the process on organic enynes (Scheme 10). We will call *syn* and *anti* **I** these intermediates referring to the mutual disposition of the internal olefinic substituent C (meant to be the one of the bridgehead carbon in the cycloadduct) and the Co_2 unit related to the plane defined by the original alkyne and the internal olefin carbon. For the α-aminomethyl derivative **2c** the methyl group would preferentially be arranged as B in its *syn* **I** intermediate (in other words, *cis* to the substituent C) as it is actually found in **3c**, the main reaction product. However, the presence of **6c** in the reaction mixture with a bridgehead proton anti to the cobalt carbonyl moiety seems contradictory with Magnus assumptions to consider the *syn* **I** conformation as the only relevant intermediate species.

A careful inspection of intermediates *syn* **I** and *anti* **I** reveals that the most congested region should be that where R and the carbonyls of $(CO)_5W$ may interfere. The seemingly important steric hindrance between these groups and the substituents at the saturated allyl methylene in *syn* **I** would lead to a relatively important presence of *anti* **I**. Rather probable is also a slight bending of the $(CO)_5W$ moiety toward the substituent R in intermediate *syn* **I** caused by the action of the bulky adjacent group $Co_2(CO)_6$. This effect is also liable to add steric congestion in the region around R favoring formation of *anti* **I**. Since *anti* **I** is not well provided for acquiring the planar conformation required by the original triple and double bonds to afford the final cyclopentenone ring, its intramolecular insertion should

(30) Preliminary results obtained in our laboratory.

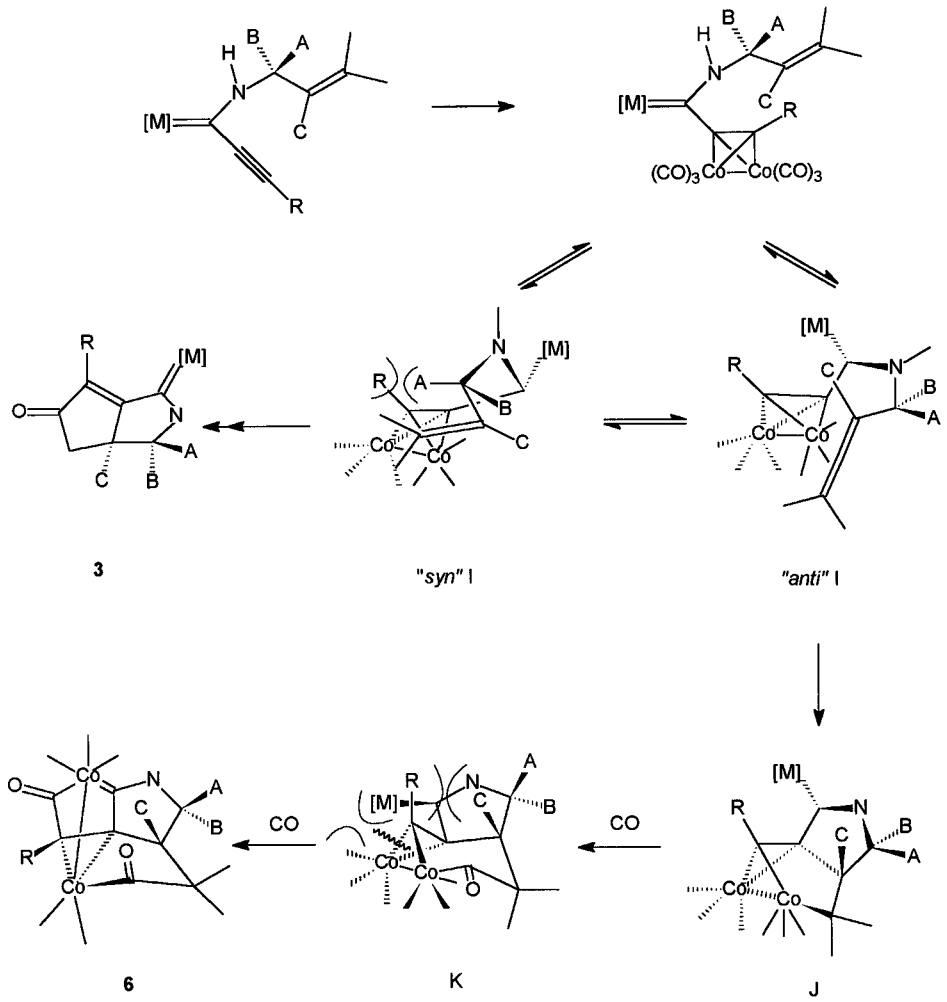
(31) An additional experiment consisted of the obtaining and further reaction with $Co_2(CO)_8$ of complex **2u** having a double bond anti to the triple one. Since it could not be obtained by the usual aminolysis path, an alternative method was designed. After treating **2u** with $Co_2(CO)_8$, the reaction proceeded very sluggishly. After 24 h, 40% of the starting complex **2u** was still present.



The major product (34%) consisted of the tetracarbonyl complex **8u**. However, some P−K cycloadduct **3u** was obtained but in a yield (20%) far inferior to that obtained from the diallyl complex **2o** (Table 3, entry 2) in only 2 h. Getting the cycloadduct **3u** was interpreted as the result of a slow $Co_2(CO)_8$ induced isomerization of *E* and *Z* isomers.

(32) Fischer, E. O.; Kreiter, C. G.; Kollmeier, H. J.; Müller, J.; Fischer, R. D. *J. Organomet. Chem.* **1971**, *28*, 237−258.

Scheme 10



only lead to acylcobalt complexes like **K**. The replacement of the $(CO)_5W$ moiety by the nearby $Co(CO)_3$ group after a further acylation would relieve strain in intermediate **K** and also steric hindrance, to give the stable complex **6**. The substituent C can also contribute to this effect since, to avoid any pseudoaxial interaction with R and with the carbonyls of $(CO)_5W$, it may tilt far from R and A, that causing a decrease in the dihedral angle of the bicyclic structure and therefore an approximation of one of the Co atoms to the carbene center.

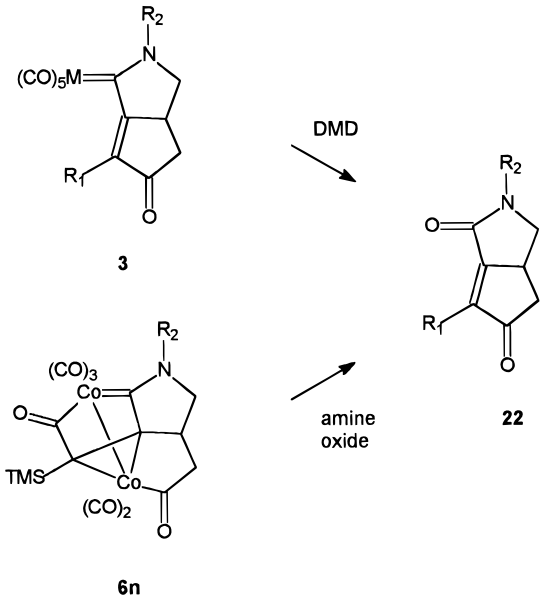
The reaction is considerably stereospecific: from the trans olefin starting complex, **2e**, only the trans cycloadduct, **3e**, was recorded in the product. However, for the cis isomer, **2f**, the results were not as that sharp since both diastereoisomers were obtained. While partial isomerization of the olefin prior to $Co_2(CO)_8$ coordination or epimerization of the final cycloadduct at its α-keto carbon by concurrent organometallic species seems most probable[33] (among others, pentacarbonyl metal fragments easily generated from carbene complexes[34] or tetracarbonyl cobalt hydride[35] have been described as olefin isomerizing species), conformational changes in the course of the P−K process cannot be excluded.

Removal of the Metal Moiety from Pauson−Khand Adducts. As initially reported, one of the features of the P−K reaction with alkynyl(allylamino)carbene complexes is the presence of the metal−carbene unit in the final cycloadduct. However, for synthetic purposes, an easy and efficient method to release the organic ligand is necessary. A very mild oxidation procedure consisting of the use of dimethyldioxirane (DMD)[36] has been successfully applied on the P−K cycloadducts **3**, otherwise difficult to oxidize by common systems such as DMSO, amine oxides, or Ce(IV).[37] Getting the cobalt carbene complexes **6** prompted us to also investigate the use of different agents to accomplish the closure of the cyclopentenone skeleton. The use of CO (to coordinatively saturate the Co, therefore, forcing the reductive elimination) or desilylation (to generate an anion capable of nucleophilic attack to the carbonyl) did not afford the expected result.

Finally, the treatment of **6n** (Scheme 11) with 5 equiv of $Me_3NO{\cdot}2H_2O$ in CH_2Cl_2 at room temperature gave the expected organic cyclopentenone **22** (R_1 = H, R_2 = allyl) in moderate yield (40%). The availability of both systems (DMD and amine oxides) merging to a single organic cycloadduct represents a potential enhancement of the practical yields.

(33) Krafft, M. E.; Juliano, C. A.; Scott, I. L.; Wright, C.; McEachin, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 1693−1703.
(34) Hoye, T. R.; Suriano, J. A. *Organometallics* **1992**, *11*, 2044−2050.
(35) Heck, R. F. In *Organotransition Metal Chemistry*; Maitlis, P. M., Stone, F. G. A., West, R. Eds., Academic Press: New York, 1974; pp 76−111.
(36) Lluch, A. M.; Jordi, L.; Sanchez-Baeza, F.; Ricart, S.; Camps, F.; Messeger, A.; Moretó, J. M. *Tetrahedron Lett.* **1992**, *33*, 3021−3022.
(37) Davies, S. G. *Organotransition Metal Chemistry. Applications to Organic Synthesis*; Pergamon Press: Oxford, U.K., 1984; pp 19−82.

Scheme 11



Conclusion

We have studied the easy $Co_2(CO)_8$-mediated carbonylative cycloaddition of (allylamino)alkynylcarbene complexes of W and Cr and found that the facilitation of this reaction related to those reported on organic enynes is due to the electronic influence of the metal carbene center on the nearby triple bond and the geometries inherent to the almost exclusive *E* isomer formed in the aminolysis process of the precursors under kinetic-controlled conditions. The reasons for the preference of the *E* isomer in such a process are currently being studied in our laboratories.

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 NMR) or a Varian XL-300 apparatus (300 MHz for ^{1}H NMR and 75.4 MHz for ^{13}C NMR). 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 reactions were performed under Ar atmosphere. Carbene complexes **1a,b**[38] and **2a**−**s**[14] were prepared by literature procedures and yields of final products were not optimized.

General Procedure. Reaction of Dicobalt Octacarbonyl with Complex 2a. $Co_2(CO)_8$ (1.1 mmol) was added to the (allylamino)carbene complex **2a** (1 mmol) in 25 mL of dry THF, and the reaction mixture was left, under Ar, at room temperature for 2−12 h. The reaction course was monitored by thin-layer chromatography (hexane/ethyl acetate 7/3). After the starting product had completely disappeared, the solvent was removed and the residue passed through a flash chromatography column using the mentioned eluent, affording the corresponding cyclopentenone complex **3a** as a red solid in 75% yield. **3a.** IR ($CHCl_3$): 2060, 1975, 1930, 1710 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.95 (br s, 1H, NH); 7.32 (br s, 5H, Ph), 4.00 (m, 1H, C*H*$_2$N); 3.42 (m, 2H, C*H*$_2$N, C*H*CH$_2$N), 2.92 (dd, J = 17.8, 5.8 Hz, 1H, C*H*$_2$CO), 2.52 (dd, J = 17.8, 3.4 Hz, 1H, C*H*$_2$CO). ^{13}C NMR ($CDCl_3$): δ 238.6 (C═W), 206.9 (s), 202.1 (s), 197.4 (s), 178.3 (s), 143.7 (s), 130.3 (d), 130.1 (s), 129.0 (d), 128.1 (d), 59.4 (t), 42.3 (d), 39.2 (t). Anal. Calcd for $C_{18}H_{11}O_6NW$: C, 41.48; H, 2.13; N, 2.69. Found: C, 41.51; H, 2.14; N, 2.65.

Reaction of Dicobalt Octacarbonyl with Complex 2b. According to the general procedure, complex **3b** was obtained in 72% yield as a red solid. **3b**. IR ($CHCl_3$): 2030, 1960, 1930, 1710 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.17 (br s, 1H, N*H*), 7.32−7.45 (m, 5H, Ph), 4.13 (m, 1H, C*H*$_2$N), 3.52 (m, 2H, C*H*$_2$N, C*H*CH$_2$N), 2.92 (dd, J = 17.8, 5.9 Hz, 1H, C*H*$_2$CO), 2.52 (dd, J = 17.8, 3.6 Hz, 1*H*, CH$_2$CO). ^{13}C NMR ($CDCl_3$): δ 265.0 (C═Cr), 222.3 (s), 216.4 (s), 206.8 (s), 176.2 (s), 144.1 (s), 130.0 (d), 129.8 (s), 129.3 (d), 128.3 (d), 59.1 (t), 42.6 (d), 39.0 (t). Anal. Calcd for $C_{18}H_{11}O_6NCr$: C, 55.53; H, 2.85; N, 3.60. Found: C, 55.60; H, 2.80; N, 3.62.

Reaction of Dicobalt Octacarbonyl with Complex 2c. Using the general procedure conditions and after separation by flash chromatography, two different complexes were obtained, **3c** in 62% yield as a red solid and **6c** in 17% yield as an orange solid. **3c.** IR ($CHCl_3$): 3230, 2063, 1976, 1909, 1704 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.90 (br s, 1H, N*H*), 7.25−7−44 (m, 5H, Ph), 3.74 (dq, J = 7.2, 6.4 Hz, 1H, C*H*CH$_3$), 3.05−3.15 (m, 1H, C*H*CH$_2$CO), 2.86 (dd, J = 18, 6.7 Hz, 1H, C*H*$_2$CO), 2.45 (dd, J = 18, 6.7 Hz, 1H, C*H*$_2$CO), 1.61 (d, J = 6.4 Hz, 3H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 239.1 (C═W), 206.5 (s), 201.8 (s), 197.2 (s), 178.4 (s), 143.0 (s), 130.1 (d), 129.3 (d), 128.3 (d), 128.2 (s), 68.1 (d), 50.2 (d), 38.1 (t), 18.9 (q). Anal. Calcd for $C_{19}H_{13}O_6NW$: C, 42.61; H, 2.43; N, 2.61. Found: C, 42.60; H, 2.49; N, 2.59.

6c. IR ($CHCl_3$): 2084, 2050, 2025, 2003, 1716 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.27−7.43 (m, 5H, Ph), 5.89 (br s, 1H, N*H*), 3.67−3.73 (m, 1H, C*H*CH$_3$), 2.86−2.92 (m, 1H, C*H*CH$_2$), 2.70 (dd, J = 16.2, 6.4 Hz, 2H, C*H*$_2$CO), 1.60 (d, J = 4.8 Hz, 3H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 243.8 (C═Co), 213.3 (s), 201.1 (s), 197.2 (s), 132.2 (s), 129.6 (d), 128.7 (d), 128.2 (d), 119.1 (s), 87.3 (s), 71.0 (d), 62.7 (t), 41.0 (d), 20.5 (q).

Reaction of Dicobalt Octacarbonyl with Complex 2d. After reaction under standard conditions, three complexes, separated by flash chromatography (hexane/ethyl acetate 1/1), were obtained from the reaction crude. Complex **3d** as a red solid (28%), complex **6d** as an orange solid (20%), and complex **7d** as a black solid (38%). **3d**. IR ($CHCl_3$): 2061, 1974, 1905, 1710, 1592 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.12 (br s, 1H, N*H*), 7.32−7.44 (m, 5H, Ph), 3.71 (dd, J = 11.6, 2 Hz, 1H, C*H*$_2$N), 3.59 (d, J = 11.6 Hz, 1H, C*H*$_2$N), 2.67 (d, J = 1.4 Hz, 2H, C*H*$_2$-CO), 1.38 (s, 3H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 239.9 (C═W), 206.5 (s), 201.8 (s), 197.2 (s), 181.6 (s), 142.3 (s), 130.1 (d), 129.3 (d), 128.3 (d), 125.2 (s), 65.7 (t), 48.4 (s), 47.8 (t), 26.0 (q). Anal. Calcd for $C_{19}H_{13}O_6NW$: C, 42.61; H, 2.43; N, 2.61. Found: C, 42.56; H, 2.51; N, 2.54.

6d. IR ($CHCl_3$): 2063, 2046, 2025, 2007, 1922, 1697 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.23−7.37 (m, 5H, Ph), 5.61 (br s, 1H, N*H*), 3.87 (d, J = 10.4 Hz, 1H, NC*H*$_2$), 3.82 (dd, J = 10.4, 2.2 Hz, 1H, NC*H*$_2$), 2.70 (d, J = 4.8 Hz, 2H, C*H*$_2$CO), 1.37 (s, 3H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 243.6 (C═Co) 215.2 (s), 199.2−203.0 (br s), 132.0 (s), 131.1 (d), 128.4 (d), 128.3 (d), 121.7 (s), 90.9 (s), 70.5 (t), 69.2 (t), 40.1 (s), 21.5 (q). Anal. Calcd for $C_{20}H_{13}O_7NCo_2$: C, 48.29; H, 2.61; N, 2.81. Found: C, 48.21; H, 2.75; N, 2.98.

7d. IR ($CHCl_3$): 2096, 2063, 2044, 2032, 2007, 1970, 1932 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.83 (br s, 1H, N*H*), 7.48−7.70 (m, 5H, Ph), 5.11 (s, 1H, ═C*H*$_2$), 5.03 (s, 1H, ═C*H*$_2$), 4.37 (d, J = 6.2 Hz, 2H, NC*H*$_2$), 1.94 (s, 3H, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 245.4 (C═W), 201.5 (s), 198.3 (s), 197−199 (br s), 164.7 (s), 139.1 (s), 137.0 (s), 129.5 (d), 129.1 (d), 128.9 (s), 128.7 (d), 114.1 (t), 60.2 (t), 20.5 (q). Anal. Calcd for $C_{24}H_8O_{11}NWCo_2$: C, 36.31; H, 1.76; N, 1.64. Found: C, 36.11; H, 1.73; N, 1.63.

(38) Dötz, K. H.; Kuhn, W. *J. Organomet. Chem*. **1985**, *286*, C23−C26.

Reaction of Dicobalt Octacarbonyl with Complex 2e. After reaction under standard conditions, complex **3e** was obtained in 72% yield as a red solid. **3e**. IR ($CHCl_3$): 2058, 1989, 1943, 1925, 1755 cm^{-1} ^1H NMR ($CDCl_3$): δ 7.25 (br s, 5H, Ph), 4.12 (ddd, J = 11.7, 8.4, 1.8 Hz, 1H, CH_2N), 3.50 (dd, J = 11.7, 8.4 Hz, 1H, CH_2N), 3.25 (dt, J = 8.4, 4.2 Hz, CHCH$_2$), 2.55 (dq, J = 7.2, 4.2 Hz, 1H, CHCO), 1.42 (d, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 232.9 (C═W), 209.7 (s), 202.9 (s), 198.3 (s), 178.1 (s), 143.0 (s), 131.9 (s), 131.0 (d), 129.3 (d), 128.5 (d), 59.6 (t), 51.4 (d), 47.6 (d), 13.7 (q). Anal. Calcd for $C_{19}H_{13}O_6NW$: C, 42.61; H, 2.43; N, 2.61. Found: C, 42.86; H, 2.54; N, 2.54.

Reaction of Dicobalt Octacarbonyl with Complex 2f. After reaction under standard conditions, a mixture of diastereomers **3e** and **3f** (30/70) was obtained in 70% yield. Separation under the usual chromatographic conditions (hexane/ethyl acetate 1/1) gives a pure sample of **3f**. IR ($CHCl_3$): 2063, 1976, 1940, 1915, 1720 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.15 (br s, 1H, NH), 7.40 (m, 5H, Ph), 3.87 (ddd, J = 11.1, 8.0, 2.1 Hz, 1H, CH_2N), 3.69 (dt, J = 8.0, 7.2 Hz, 2H, CHCH$_2$), 3.55 (dd, J = 11.1, 8.0 Hz, 1H, CH_2N), 2.95 (dq, J = 8.0, 7.2 Hz, 1H, CHCH$_3$), 1.23 (d, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 232.6 (C═W), 211.2 (s), 202.9 (s), 198.3 (s), 179.3 (s), 142.2 (s), 131.8 (s), 131.1 (d), 129.2 (d), 128.5 (d), 59.6 (t), 55.9 (t), 47.7 (d), 42.9 (d), 15.5 (q).

Reaction of Dicobalt Octacarbonyl with Complex 2g. After reaction under standard conditions, complex **3g** was obtained as the only single identifiable compound in 35% yield. **3g.** IR ($CHCl_3$): 2060, 1970, 1920, 1705 cm^{-1}. ^1H NMR (CD_3COCD_3): δ 7.45 (br s, 5H, Ph), 4.25 (m, 1H, CHN), 3.52 (dd, J = 7.4, 7.2 Hz, 1H, CHCH), 3.03 (m, 1H, CH_2), 2.75 (br s, 1H, CHCO), 2.20 (m, 1H, CH_2), 1.30 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ 236.3 (C═W), 210.8 (s), 201.9 (s), 197.4 (s), 174.9 (s), 145.0 (s), 130.2 (s), 130.1 (s), 129.4 (d), 128.4 (d), 63.8 (d), 45.7 (d), 43.0 (d), 31.2 (t), 25.7 (t), 19.9 (t). Anal. Calcd for $C_{21}H_{15}O_6NW$: C, 44.94; H, 2.69; N, 2.50. Found: C, 45.04; H, 2.70; N, 2.47.

Reaction of Dicobalt Octacarbonyl with Complex 2k. After reaction under standard conditions, complex **3k** was obtained as a single compound in 70% yield. **3k.** IR ($CHCl_3$): 2060, 1970, 1925, 1705 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.10 (br s, 1H, NH), 4.05 (bt, J = 9.6 Hz, 1H, CH_2N), 3.42 (br s, 1H, CH_2N), 3.20−3.40 (m, J = 9 Hz, 1H, CH), 2.72−2.90 (m, 3H, CH_2CO, CH_2CH$_3$), 2.30 (dd, J = 18.3, 3.6 Hz, 1H, CH_2CO), 1.5 (t, J = 7.2 Hz, CH$_3$). ^{13}C NMR ($CDCl_3$): δ 238.2 (C═W), 209.2 (s), 202.1 (s), 197.6 (s), 175.9 (s), 148.0 (s), 58.9 (t), 41.9 (d), 39.5 (t), 18.4 (t), 13.0 (q). Anal. Calcd for $C_{14}H_{11}NO_6W$: C, 35.54; H, 2.34; N, 2.96. Found: C, 35.56; H, 2.37; N, 2.87.

Reaction of Dicobalt Octacarbonyl with Complex 2l. After reaction under standard conditions, only tetracarbonyl complex **10l** was obtained as a single compound in 84% yield. **10l.** IR ($CHCl_3$): 2195, 2060, 2030, 1930, 1882 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.60 (br s, 1H, NH), 4.65 (m, 1H, CHCH$_2$), 4.51 (dd, J = 4, 1.6 Hz, 2H, CH_2N), 3.41 (dd, J = 13.6, 8.8 Hz, 2H, CH_2CH), 0.41 (s, 9H, Si-CH_3). ^{13}C NMR ($CDCl_3$): δ 251.8 (C═W), 214.1 (s), 208.7 (s), 205.1 (s), 202.8 (s), 198.8 (br s), 112.2 (s), 89.8 (s), 69.9 (t), 57.2 (s), 53.6 (t), 1.5 (q). Anal. Calcd for $C_{19}H_{15}O_{10}SiCo_2W$: C, 30.54; H, 2.02; N, 1.88. Found: C, 30.41; H, 2.06; N, 1.91.

Reaction of Dicobalt Octacarbonyl with Complex 2m. After reaction under standard conditions, only tetracarbonyl complex **10m** was obtained as a single compound in 40% yield. **10m.** IR ($CHCl_3$): 2095, 2057, 2035, 2030, 2011, 1932, 1983 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.40 (br s, 1H, NH), 4.56 (m, 2H, CH_2N), 4.15 (m, 1H, ═CH), 3.30 (d, J = 14.1 Hz, 1H, ═CH_2), 2.91 (d, J = 18.0 Hz, 1H, ═CH_2), 1.37 (s, 9H, CH_3).

Reaction of Dicobalt Octacarbonyl with Complex 2n. When complex **2n** was treated with $Co_2(CO)_8$ (1.1 equiv) in dry THF, under Ar, at room temperature for 2 days, the new complex **6n** could be isolated after flash chromatography (hexane/*tert*-butyl methyl ether 3/2) in 48% yield. A second product was also isolated, although it was too unstable to be characterized. This product, after it stood in hexane solution for 1 day and was filtered and separated by flash chromatography afforded **6n**, corresponding to a 60% overall yield. **6n.** IR ($CHCl_3$): 2080, 2040, 2020, 1700, 1630 cm^{-1}. ^1H-NMR ($CDCl_3$): δ 5.93 (m, 1H, ═CH), 5.41 (m, 2H, ═CH_2), 4.59 (dd, J = 11.1, 7.2 Hz, 1H, NCH_2CH), 4.20 (d, J = 5.7 Hz, 2H, NCH_2-CH═), 3.66 (d, J = 11.1 Hz, 1H, NCH_2-CH), 3.45 (dd, J = 16.8, 8.0 Hz, 1H, CH_2CO), 3.12 (m, 1H, CH), 2.85 (dd, J = 16.8, 3.3 Hz, 1H, CH_2CO), 0.20 (s, 9H, CH_3). ^{13}C-NMR (CD_2Cl_2): δ 243.8 (C═Co), 218.0 (s), 200.0 (br s), 131.2 (d), 121.5 (s), 120.7 (t), 74.7 (s), 74.0 (t), 72.1 (t), 56.0 (t), 30.8 (d), 0.5 (q). MS (FAB+) (matrix NBA): *m/e* 520 (M^+, 28), 491 (15), 463 (30), 435 (85), 407 (100), 379 (45), 351 (25), 323 (35). Anal. Calcd for $C_{19}H_{19}O_7NCo_2Si$: C, 43.91; H, 3.70; N, 2.70. Found: C, 43.48; H, 3.70, N, 2.66%.

Reaction of Dicobalt Octacarbonyl with Complex 2o. After reaction under standard conditions, complex **3o** was obtained as a single compound in 80% yield. **3o.** IR (CCl_4) 2063, 1978, 1938, 1901, 1722 cm^{-1}. ^1H-NMR ($CDCl_3$): δ 7.26−7.44 (m, 5H, Ph), 5.92−6.01 (m, 1H, ═CH), 5.50 (d, J = 10.2 Hz, 1H, ═CH_2), 5.43 (d, J = 17.1 Hz, 1H, ═CH_2), 4.61−4.75 (dd, J = 14.7, 6.3 Hz, 2H, NCH_2CH═), 4.01 (dd, J = 10.2, 7.2 Hz, 1H, NCH_2CH), 3.42−3.61 (m, 2H, CH), 2.87 (dd, J = 18.6, 6.3 Hz, 1H, COCH_2), 2.46 (dd, J = 18.6, 2.8 Hz, 1H, COCH_2). ^{13}C NMR ($CDCl_3$): δ 237.7 (C═W), 206.3 (s), 201.7 (s), 197.2 (s), 180.1 (s), 141.9 (s), 130.2 (d), 129.9 (d), 129.0 (d), 128.5 (d), 121.0 (t), 62.9 (t), 59.8 (d), 42.6 (t), 38.2 (t). Anal. Calcd for $C_{21}H_{15}O_6NW$: C, 44.93; H, 2.67; N, 2.49. Found: C, 45.20; H, 2.79; N, 2.50.

Reaction of Dicobalt Octacarbonyl with Complex 2p. After reaction under standard conditions, complex **3p** was obtained as a single compound in 70% yield. **3p.** IR (CCl_4) 2061, 1971, 1930, 1718, 1475 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.83−6.02 (m, 1H, CH), 5.45 (d, J = 10.2 Hz, 1H, CH_2), 5.39 (d, J = 17.1 Hz, 1H, CH_2), 4.58−4.90 (dd, J = 14.9, 6.4 Hz, 2H, NCH_2), 3.90 (dd, 1H, J = 10.6, 7.5 Hz, CH), 3.29−3.49 (m, 2H, CH_2), 2.65−3.08 (dq, J = 13.3, 7.4 Hz, 2H, CH_2CH$_3$), 2.70 (dd, J = 18.2, 6.2 Hz, 1H, COCH_2), 2.25 (dd, J = 18.2, 3.4 Hz, 1H, COCH_2), 1.10 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 238.9 (C═W), 205.3 (s), 201.5 (s), 197.8 (s), 180.3 (s), 141.5 (s), 131.2 (d), 119.0 (t), 62.3 (t), 48.4 (d), 41.6 (t), 37.2 (t), 26.1 (t), 22.8 (q). EM (FAB$^+$) (matrix NBA): *m/e* 513 (M^+, 15), 457 (10), 429 (20), 399 (15). Anal. Calcd for $C_{17}H_{15}O_6NW$: C, 39.78; H, 2.92; N, 2.73. Found: C, 39.81; H, 2.98; N, 2.65.

Reaction of Dicobalt Octacarbonyl with Complex 2q. Complex **2q** was treated with $Co_2(CO)_8$ (1.1 equiv) in dry THF, under an Ar atmosphere, at room temperature for 6 days. After this period, the solvent was removed and the crude reaction chromatographed using hexane/*tert*-butyl methyl ether (6/4) as eluent. In that way we isolated the starting product **2q** (20%), the tetracarbonylallylaminoyl complex **12** (20%), and the cobalt carbene complex **6q** (11%). **6q.** IR (CCl_4) 2079, 2042, 2019, 1990, 1697, 1652 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 5.93−6.01 (m, 1H, ═CH), 5.31−5.51 (m, 2H, ═CH_2), 4.50 (dd, J = 11.1, 7.2 Hz, 1H, NCH_2CH), 4.29−4.31 (m, 2H, NCH_2CH═), 3.61−3.83 (m, 2H, NCH_2CH, CH_2CO) 3.38 (m, 1H, CH), 2.95 (d, J = 16.8 Hz, 1H, COCH_2), 1.25 (s, 9H, CH_3). ^{13}C NMR (CD_2Cl_2): δ 246.5 (C═Co), 217.0 (s), 200.0 (br s, s), 131.4 (d), 120.6 (t), 119.4 (s), 96.7 (s), 75.8 (t), 69.6 (t), 54.7 (t), 35.1 (d), 31.9 (s), 29.8 (q). EM (FAB$^+$) (matrix NBA): *m/e* 504 (M^+, 23), 476 (10), 448 (25), 419 (60), 391 (55), 363 (34), 335 (23), 307 (35).

12. IR (CCl_4): 2190, 2025, 1932, 1911, 1895 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.75 (ddt, J = 16.8, 10.2, 6 Hz, 1H, CH), 5.31 (dd, J = 10.2, 1.2 Hz, 1H, CH_2), 5.22 (dd, J = 16.8, 1.2 Hz, 1H, CH_2), 4.42−4.53 (m, 2H, NCH, CH), 4.27 (dt, J = 14.7, 6.0, 1.2 Hz, 2H, NCH_2), 3.80−3.90 (m, 1H, NCH), 3.28 (d, J = 8.4 Hz, 1H, CH_2), 3.20 (d, J = 12 Hz, 1H, CH_2), 1.30 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$): δ 237.6 (C═W), 211.7 (s), 210.1 (s), 203.3 (s), 202.9 (s), 135.8 (s), 130.5 (d), 119.8 (t), 82.7 (s), 68.9 (d), 60.9 (t), 57.8 (t), 56.9 (t), 30.3 (q), 29.5 (s). EM (FAB+) (matrix NBA): *m/e* 485 (M^+, 100), 457 (20), 429 (67), 400 (20), 389 (5),

372 (15). Anal. Calcd for $C_{17}H_{19}O_4NW$: C, 42.07; H, 39.5; N, 2.89. Found: C, 41.99; H, 3.93; N, 2.91.

Reaction of Dicobalt Octacarbonyl with Complex 2r. After reaction under standard conditions, complex **3r** was obtained as a single compound in 60% yield. **3r.** IR (CCl_4) 2063, 1973, 1932, 1724 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.75 (d, J = 2.4 Hz, 1H, C*H*), 5.93 (ddt, J = 16.8, 10.2, 6.3 Hz, 1H, =C*H*), 5.48 (d, J = 10.2 Hz, 1H, CH_2), 5.41 (d, J = 16.8 Hz, 1H, =CH_2), 4.62−4.76 (d_{ABsyst}, J_{AB} = 13.6, 6.3 Hz, 2H, NCH_2CH), 3.95 (dd, J = 10.5, 7.5 Hz, 1H, NCH_2-CH), 3.38−3.52 (m, 2H, NCH_2CH, C*H*), 2.85 (dd, J = 17.7, 6.3 Hz, 1H, COCH_2), 2.38 (dd, J = 17.7, 3.6 Hz, 1H, COCH_2). ^{13}C NMR ($CDCl_3$): δ 233.7 (C=W), 206.6 (s), 202.3 (s), 197.2 (s), 189.1 (s), 132.9 (d), 129.9 (d), 121.85 (t), 62.14 (t), 59.9 (t), 42.6 (d), 41.1 (CH_2, 6-C). Anal. Calcd for $C_{15}H_{11}O_6NW$: C, 37.12; H, 2.27; N, 2.89. Found: C, 37.09; H, 2.31; N, 2.87.

Preparation of Complex 1c. To a solution of 1.1 mL of phenylacetylene (10 mmol) in anhydrous THF stirred at −70 °C and under Ar atmosphere was added 6.7 mL of BuLi (10 mmol). The resulting solution was warmed to −30 °C, and 3.5 g of $W(CO)_6$ (10 mmol) was added. The resulting mixture was stirred for 2 hours at 0 °C.

At the same time the allyl triflate was prepared as follows: A mixture of 0.78 mL (11.5 mmol) of allyl alcohol and 0.93 mL of pyridine (11.5 mmol) in CCl_4 was added, dropwise, to a solution of 1.95 mL (11.5 mmol) of anhydrous trifluoromethanesulfonic acid in CCl_4, maintaining the temperature at 0 °C. This solution was filtered through a small Celite pad and the filtrate directly poured into the first solution (all these operations should be done under Ar). After the usual workup, the crude reaction mixture was purified by flash chromatography using hexane as eluent. Complex **1c** was obtained in 65% yield (3.2 g, 6.5 mmol). **1c.** IR (CCl_4): 2150, 2067, 1978, 1955, 1182, 1170, 1045 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.29−7.71 (m, 5H, Ph); 5.91−6.41 (m, 1H, CH=), 5.29−5.61 (m, 2H, =CH_2), 5.14 (dt, J = 4.8, 2 Hz, 2H, OCH_2). ^{13}C NMR ($CDCl_3$): δ 285.7 (C=W); 205.8 (s), 197.4 (s), 133.0 (d), 132.0 (d), 131.0 (s), 129.1 (d), 128.6 (d), 121.1 (s), 120.0 (t), 97.6 (s), 79.9 (t). EM (FAB+): *m/e* 494 (M^+, 50), 466 (15), 453 (42), 437 (22), 382 (100). Anal. Calcd for $C_{17}H_{10}O_6W$: C, 41.32; H, 2.04. Found: C, 41.54; H, 2.04.

Preparation of Complex 1d. Complex **1d** was prepared following the above procedure in 80% yield. **1d.** Mp: 62−64 °C. IR (KBr): 2138, 2050, 1933, 1489, 1445 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.44−7.60 (m, 5H, Ph), 5.22 6.12 (ddt, J = 17.1, 10.8, 5.1 Hz, 2H, CH=), (d, J = 5.1 Hz, 2H, OCH_2), 5.53 (d, J = 17.1 Hz, 1H, =CH*H*), 5.43 (d, J = 10.8 Hz, 1H, =C*H*H). ^{13}C NMR ($CDCl_3$): δ 313.7 (C=Cr), 225.8 (s), 216.3 (s), 136.3 (s), 132.7 (d), 131.8 (d), 131.8 (d), 131.2 (d), 129.0 (d), 121.0 (s), 119.9 (t), 92.1 (s), 79.9 (t). Anal. Calcd for $C_{17}H_{10}O_6Cr$: C, 56.36; H, 2.78. Found: C, 56.80; H, 2.81.

Reaction of Dicobalt Octacarbonyl with Complex 1c. A total of 1.1 molar equiv of $Co_2(CO)_8$ was added to a solution of **1c** in isooctane. This mixture was deoxygenated and stirred under argon at room temperature during 1 h. The solvent was removed and the crude mixture purified by flash chromatography using hexane/CH_2Cl_2 (9/1). Complex **8c** was obtained in a 85% yield. **8c.** Mp: 105−107 °C. IR (CCl_4): 2096, 2064, 2034, 1978, 1949, 1614, 1474 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.21−7.72 (m, 5H, Ph), 6.01−6.51 (m, 1H, =CH), 5.31−5.80 (m, 4H, OCH_2, =CH_2). ^{13}C NMR (CD_2Cl_2): δ 307.6 (C=W), 202.8 (s), 198.8 (br s), 197.6 (s), 138.4 (s), 131.0 (d), 129.9 (d), 129.1 (d), 128.6 (d), 121.4 (t), 118.9 (s), 102.3 (s), 84.4 (d). EM (FAB^+): *m/e* 724 (25), 696 (100), 668 (55), 640 (45), 612 (70), 599 (40), 556 (82). Anal. Calcd for $C_{23}H_{10}O_{12}Co_2W$: C, 35.39; H, 1.28. Found: C, 35.54; H, 1.35. No change, or any evolution of the complex **8c**, is observed (TLC) in the reaction mixture after 48 hours at room temperature under Ar.

Reaction of Dicobalt Octacarbonyl with Complex 1d. By the above procedure complex **8d** was obtained in a 85% yield. **8d.** Mp: 93−95 °C. IR (CCl_4): 2096, 2088, 2063, 2052, 2029, 1984, 1953 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.45−5.57 (m, 4H, OCH_2, =CH_2), 6.15−6.31 (m, 1H, =CH), 7.35−7.47 (m, 5H, Ph). ^{13}C NMR (CD_2Cl_2): δ 82.2 (t), 97.4 (s), 101.2 (s), 121.5 (t), 128.5 (d), 129.3 (d), 129.8 (d), 131.2 (d), 138.5 (s), 198.8 (br s), 216.5 (s), 223.4 (s), 332.9 (C=Cr). Anal. Calcd for $C_{23}H_{10}O_{12}Co_2Cr$: C, 42.62; H, 1.56. Found: C, 42.55; H, 1.60.

Reaction of Dicobalt Octacarbonyl with Complex 17. After reaction under standard conditions of complex **17** with 2 equiv of $Co_2(CO)_8$, one single product was isolated from the crude mixture and identified as **19** in 33% yield. **19.** IR ($CHCl_3$): 2094, 2057, 2030, 1984, 1946, 1938, 1917, 1724 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.44−7.19 (m, 5H, Ph), 6.24 (d, J = 15.5 Hz, 1H, Co-C-CH_2N), 5.15 (d, J = 15.5 Hz, 1H, CoCCH_2N), 4.13 (dd, J = 10.8, 8.1 Hz, 1H, CHCH_2N), 3.76 (dd, J = 10.8, 9.3 Hz, 1H, CHCH_2N), 3.66−3.57 (m, 1H, C*H*), 2.90 (dd, J = 18.6, 6.6 Hz, 1H, COCH_2), 2.77 (s, 3H, CH_3), 2.49 (dd, J = 18.6, 3.3 Hz, 1H, COCH_2). ^{13}C NMR ($CDCl_3$): δ 261.9 (C=Cr), 222.5 (s), 216.4 (s), 206.4 (s), 198.9 (br s), 178.0 (s), 142.4 (s), 130.3 (s), 129.9 (d), 129.1 (d), 128.4 (d), 94.5 (s), 87.6 (s), 65.0 (t), 58.2 (t), 42.8 (d), 38.5 (t), 20.7 (q). Anal. Calcd for $C_{28}H_{15}NO_{12}Co_2Cr$: C, 46.22; H, 2.06; N, 1.93. Found: C, 46.34; H, 2.20; N, 1.83.

Oxidation of Compound 6n with Amine Oxide. Compound **6n** (70 mg, 0.13 mmol) was dissolved in 10 mL of CH_2Cl_2 and trimethylamino oxide dihydrate (58 mg, 0.52 mmol) was added at room temperature. After 48 h of stirring at room temperature, complete disappearance of the starting complex was observed by TLC. Filtration, evaporation of the solvent on a rotary evaporator, and subsequent flash chromatography (hexane/ethyl acetate 7/3) afforded 10 mg (43% yield) of the 7-allyl-7-azabicyclo[3.3.0]oct-1-en-3,8-dione (**22n**). IR ($CHCl_3$): 1706, 1540, 1405 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.51−5.64 (m, 1H, =C*H*), 5.10 (br s, 1H, =C*H*), 5.00−5.06 (m, 2H, =CH_2), 3.90 (dd, J = 15.3, 6 Hz, 1H, NCH_2CH=), 3.70 (d, J = 15.3, 1H, NCH_2CH=), 3.48 (dd, J = 9.3, 8.1 Hz, 1H, NCH_2), 3.15−3.22 (m, 1H, C*H*), 2.99 (dd, J = 9.3, 7.5 Hz, NCH_2), 2.51 (dd, J = 17.1, 6.6 Hz, 1H, CH_2CO), 2.10 (dd, J = 17.1, 4.5 Hz, 1H, CH_2CO). ^{13}C NMR ($CDCl_3$): δ 211.9 (s), 178.5 (s), 164.4 (s), 143.7 (d), 131.6 (d), 118.7 (t), 51.5 (t), 45.9 (t), 42.7 (t), 41.6 (d).

Acknowledgment. The authors acknowledge the financial support from DGICYT (PB-94-0084); we thank Mr. Ramon Sabaté and Mr. Joan Parés for their cooperative assistance. L.J. thanks the Departament dÉnsenyament (Generalitat de Catalunya) and J.M.V. the CIRIT (Generalitat de Catalunya) for fellowships.

Supporting Information Available: Text of spectroscopic data for compounds **1e**, **2c**−**u**, **7s**, **8e**, **11**, **13**, **14**, **15**, **16**, **20**, **21**, **22** (7 pages). Ordering information is given on any current masthead page.

OM9700627