Low-Energy Pathway for Pauson−Khand Reactions: Synthesis and Reactivity of Dicobalt Hexacarbonyl Complexes of Chiral Ynamines

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A family of dicobalt hexacarbonyl complexes of 1-(dialkylamino)-2-(trimethysilyl)acetylenes (**3a**−**f**) derived both from achiral and chiral amines [**a**, morpholine; **b**, (*S*)-2-methoxymethylpyrrolidine; **c**, (2*R*,5*R*)-2,5-bis(methoxymethyl)pyrrolidine; **d**, (±)-*trans*-2,5-bis(benzyloxymethyl)pyrrolidine; **e**, (2*R*,5*R*)-2,5-dimethylpyrrolidine; **f**, (*S*)-(α-methylbenzyl)benzylamine] has been prepared by a one-stage process from dichloroacetylene. The methanolysis at room temperature of these complexes ($MeOH/K_2CO_3$) induces the selective cleavage of the carbon−silicon bond, leading to the thermally unstable terminal ynamine complexes **12a**−**f**. The Pauson−Khand reaction of **12a**−**f** with strained olefins (norbornadiene and norbornene) takes place at unprecedentedly low temperatures (−35 °C) in the absence of chemical promoters. Diastereoselectivities of up to 94:6 are recorded in these reactions with the ynamine complexes derived from C_2 symmetrical chiral auxiliaries (**12c,d**). The high reactivity depicted by terminal ynamines in the Pauson−Khand reaction has been analyzed by theoretical semiempirical procedures [PM3(tm)] and with density functional theory (VWN/B88), and appears to reflect an easy CO loss from the ynamine−dicobalt hexacarbonyl complexes.

Introduction

Since its introduction in 1973, the Pauson−Khand reaction (Scheme 1) has progressively gained importance as a synthetic method for cyclopentenone synthesis.[1] Depending on the substitution of the reacting olefin, up to two chiral centers are created in this annulation, and methods for controlling their absolute stereochemistry have been explored from different perspectives.[2,3]

Up to now, the most successful approaches to enantiocontrolled Pauson−Khand reactions have relied on the use of chiral auxiliaries covalently bonded to either the alkyne[4] or the alkene reagents,[5] and in fact, these enantioselective versions of the process have been applied in total synthesis.[5a,6] In this context, we have systematically explored the use of acetylenic ethers[4a−e] and thioethers[4k−m] as substrates for the reaction.

As a continuation of these efforts, we decided to test the use of amines directly bonded to the unsaturated system as chiral controllers for the Pauson−Khand reaction. To this end, the almost unknown[7] chiral ynamines (**1**; see Chart 1) were selected as starting materials. It is worth noting that, in addition to usual protocols involving auxiliary recovery, adducts **2** arising from these reactions could be, in principle, elaborated to

Scheme 1

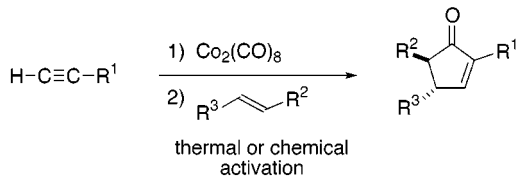

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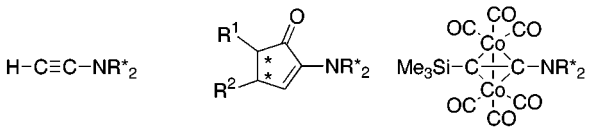
Chart 1



1 **2** **3**

enantiomerically pure α-aminocyclopentanones and α-aminocyclopentanols.[8]

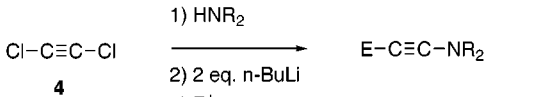
We wish to disclose here our results in this area, which cover the development of a high-yield one-pot procedure for the preparation of dicobalt hexacarbonyl complexes of chiral 1-amino-2-(trimethysilyl)acetylenes (**3**) from the corresponding chiral amines and the evaluation of a family of such chiral amines belonging to the C_1 and C_2 symmetry point groups as sterocontrollers in the Pauson−Khand reaction of ynamines. It has been established from these studies that ynamines represent a new paradigm of reactivity in Pauson−Khand reactions. An explanation of this behavior has been provided on the basis of theoretical studies.

Results and Discussion

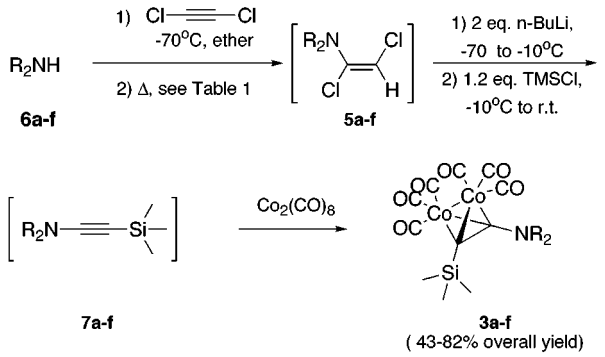
Preparation of Dicobalt Hexacarbonyl Complexes of Chiral Trimethylsilylynamines. A first target in the development of this project was the establishment of experimental conditions suitable for the high-yield synthesis of ynamines[9] derived from chiral secondary amines. The main restriction introduced by these substances is economical: the high value of the enantiomerically pure secondary amines makes advisable the preparation of the corresponding ynamines on small scale, whereas most reported syntheses of these compounds are carried out on large scale, to mitigate problems due to extremely easy hydrolysis during manipulation. Enhanced hydrolytic tendency and limited thermal stability of terminal ynamines derived from bulky, α-branched amines were other conceivable problems to be considered at the synthesis stage.

According to that, we planned to prepare the target ynamines starting from dichloroacetylene (**4**) and use a one-pot procedure similar to those previously developed for alkoxyacetylenes,[10] (alkylthio)acetylenes,[11] and bis(alkylthio)acetylenes.[4k,12] In the present instance, such methodology would bridge previous work by Brandsma, who reported on the preparation of dichloroenamines (**5**) from dichloroacetylene,[13] and by Ficini, who converted dichloroenamines into ynamines by treatment with base[14] (Scheme 2).

Scheme 2



Scheme 3



Trapping of the acetylide resulting from *β*-elimination would then be done with trimethylsilyl chloride; besides the known protecting effect of the triple bond exerted by silyl substituents,[15] we have previously shown that yields of formation of dicobalt hexacarbonyl complexes of electron-rich terminal alkynes, which are necessary intermediates for Pauson−Khand reactions, are highly increased on silylation of the triple bond.[4a] Once this beneficial effect has been exerted, desilylation can be readily achieved by methanolysis in the presence of potassium carbonate.[16]

Dichloroacetylene was prepared in ethereal solution according to a previously reported procedure.[17] Then, to a cold (−70 °C) solution of **4**, the secondary amines **6a**−**f** were added (Scheme 3), and interaction of these reagents was maintained until complete addition, as indicated in Table 1. The very unstable dichloroenamines **5a**−**f**, which were formed in essentially quantitative yield, were not isolated. After vacuum removal at low temperature of solvent and excess **4**, the crude dichloroenamines were converted to the silylynamines **7a**−**f** by treatment with 2 equiv of *n*-BuLi (−70 to −10 °C) followed by quenching with trimethylsilyl chloride (−10 °C to room temperature).

Crude silylynamines **7a**−**f** were obtained in high yield and were notably pure (^{1}H and ^{13}C NMR). According to our expectations, they showed an enhanced hydrolytic and thermal stability with respect to their terminal counterparts; however, their manipulation is still almost unavoidably accompanied by significant decomposition. Bearing in mind our ultimate target, the crude silylynamines **7a**−**f** were treated with octacarbonyldicobalt to produce in high yield complexes **3a**−**f**. These are green solids or oils (not red, as normally observed for alkyne−dicobalt hexacarbonyl complexes), stable for months at

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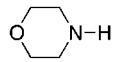
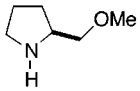
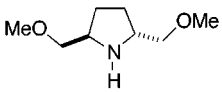
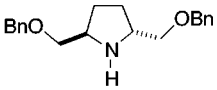
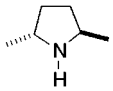
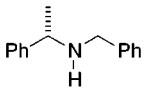
(17) Kende, A. S.; Fludzinski, P. *Synthesis* **1982**, 455−456.

Table 1. One-Pot Synthesis of Trimethylsilylynamines (7a-f) and of the Corresponding Dicobalt Hexacarbonyl Complexes (3a−f)

Entry	Amine **6**	Conditions for addition to **4**	Crude **7** Yield (%)	Complex **3** Yield (%)
a		30 min, 33 °C	88	90
b		90 min, 0 °C	87	94
c		90 min, 33 °C	96	45
d		120 min, 33 °C	85	50
e		90 min, -10 °C	86	80
f		24h, 33 °C	70	80

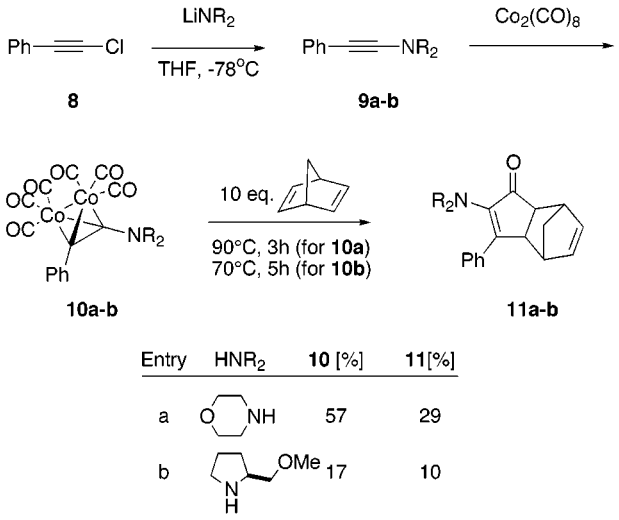
room temperature provided that they are kept under CO atmosphere, and can be easily purified by standard chromatography. Overall yields for the preparation of silylynamines (**7a**−**f**) and complexes (**3a**−**f**) are uniformly high and have been summarized in Table 1.

It is to be mentioned that Himbert and co-workers have explored a related approach to ynamines where the base employed for the generation of dichloroacetylene is the lithium amide of the secondary amine which has to be subsequently added to the generated triple bond.[18] When this elegant, atom-economical approach was applied to the bulky amines in the present study, the yields of ynamine **7** were ca. 30% lower than generating dichloroacetylene in a separate step.[19]

Pauson−Khand Reactions of Ynamines. The Pauson−Khand chemistry of ynamines has remained unexplored. The only related reports describe the cycloadditions of *N*-(1-alkynyl)sulfonamides or *N*-(1-alkynyl)-carboxamides, in which the electron-donating nature of the nitrogen atom has been deeply modified.[20] For simple ynamines, possessing electronically richer triple bonds, substantial differences in reactivity toward olefins could be anticipated.

To get a complete picture of the behavior of these alkynes in the reaction, we decided to study both unsubstituted ynamines **1** and their *C*-substituted congeners. Among these last substrates, we selected the 1-(dialkylamino)-2-phenylacetylenes **9a**,**b**, which are readily available from 1-chloro-2-phenylacetylene (**8**).[21] Both compounds were prepared uneventfully and readily converted to their dicobalt hexacarbonyl complexes **10a**,**b** (Scheme 4).

Scheme 4



Entry	HNR_2	**10** [%]	**11**[%]
a		57	29
b		17	10

The Pauson−Khand reactions of **10a**,**b** with norbornadiene took place with noticeable regioselectivity, exclusively leading to α-aminocyclopentenones **11a**,**b**. In the case of complex **10b**, moreover, the reaction was notably diastereoselective, the cyclopentenone adduct **11b** being obtained as a readily separable 4:1 mixture of diastereomers. On the negative side, the reactions required rather drastic conditions to proceed and, probably as a consequence, yields of **11a,b** were low.[22] The idea that steric effects by the bulky phenyl group could severely hinder cobaltacycle formation en route to cyclopentenones **11a**,**b** is fully confirmed by the results of attempted reactions of complexes **3a**,**b**, bearing an even bulkier trimethylsilyl group, with the same olefin. No cyclopentenone adduct could be detected in these cases.

In view of these results, we turned our attention to the unsubstituted ynamines **1**, which should be devoid of unfavorable steric effects. For reactivity studies, dicobalt hexacarbonyl complexes of unsubstituted ynamines **12a**−**f** were conveniently prepared through a one-pot process from crude trimethylsilylynamines **7a**−**f** as outlined in Scheme 5. Complexes **12a**−**f**, which are also green-colored solids or oils, are highly unstable, decomposing by CO loss with great ease. They could be stored under CO for limited periods of time but, in practice, were best prepared immediately prior to use.

The Pauson−Khand reactions of complexes **12a**−**f** with strained olefins [norbornadiene (NBD) and norbornene (NB)] were next studied under both thermal (A) and amine oxide promoted[23] (B) conditions, to afford the tricyclic adducts **13a**−**d** and **14b**−**d** as shown in Scheme 6. Relevant information for these reactions has been summarized in Table 2.

The most noticeable observation on these processes is the unprecedentedly high reactivity of the ynamine

(18) Himbert, G.; Nasshan, H.; Gerulat, O. *Synthesis* **1997**, 293−294.

(19) This is probably due to the coexistence in the reaction medium of dichloroenamine **5** and lithium amide. The formation of 1,1-bis-(dialkylamino)-2-chlorethenes has been reported by Brandsma under these conditions.[12]

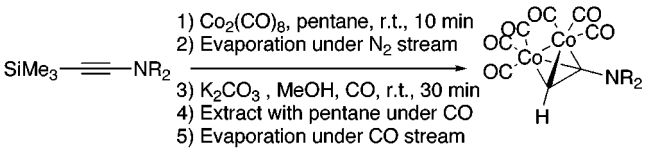
(20) Witulski, B.; Stengel, T. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 489−492. (b) Witulski, B.; Gössmann, M. *Chem. Commun.* **1999**, 1879. For the use of *N*-tosylynamines in a related 2 + 2 + 1 cobalt-mediated cycloaddition, see: Rainier, J. D.; Imbriglio, J. E. *Org. Lett.* **1999**, *1*, 2037−2039.

(21) Viehe, H. G.; Reinstein, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 506.

(22) Promotion of the reactions by NMO[23] led to diminished yields: 15% of **11a** and 0% of **11b**.

(23) Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Tetrahedron Lett.* **1990**, *31*, 5289−5292.

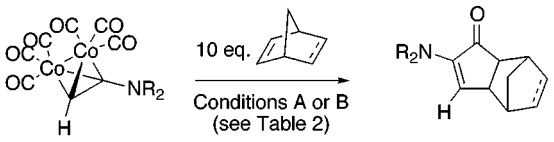
Scheme 5



7a-f **12a-f**

Entry	12 [%]
a	89
b	88
c	63
d	50
e	80
f	57

Scheme 6



12 **13** or **14**

Table 2. Pauson−Khand Reactions of Chiral Terminal Ynamines with Strained Alkenes

entry	starting complex	alkene[a]	reacn conditions[b] (temp (°C), time (h))	product (yield (%), dr[c])
1	**12a**	NBD	A (22, 0.03)	**13a** (78, -)
2	**12b**	NBD	A (22, 0.03)	**13b** (41, 1.6:1)
3		NBD	A (0, 1)	**13b** (44, 1.6:1)
4		NBD	A (−21, 24)	**13b** (77, 1.8:1)
5		NBD	B (−30, 12)	**13b** (68, 2.3:1)
6		NB	A (22, 0.5)	**14b** (22, 2.0:1)
7		NB	B (−21, 12)	**14b** (22. 2.4:1)
8	**12c**	NBD	A (22, 0.08)	**13c** (22, 4.5:1)
9		NBD	A (−21, 12)	**13c** (30, 7.3:1)
10		NBD	A (−35, 72)	**13c** (22, 8.0:1)
11		NBD	B (−20, 3)	**13c** (18, 4.9:1)
12		NBD	B (−30, 5)	**13c** (18, 15.6:1)
13		NB	A (22, 0.08)	**14c** (27, 5.3:1)
14		NB	A (−21, 144)	**14c** (20, 8.5:1)
15		NB	B (−20, 24)	**14c** (17, 7.4:1)
16		NB	B (−30, 72)	**14c** (17, 7.5:1)
17	**12d**	NBD	A (22, 0.17)	**13d** (24, 2.4:1)
18		NBD	A (0, 1.5)	**13d** (32, 4.6:1)
19		NBD	A (−21, 12)	**13d** (32, 7.0:1)
20		NBD	B (−21, 4)	**13d** (34, 7.7:1)
21		NB	A (22, 0.08)	**14d** (51, 5.9:1)
22		NB	A (0, 1.5)	**14d** (49, 6.4:1)
23		NB	A (−21, 168)	**14d** (49, 9.1:1)
24		NB	B (−21, 6)	**14d** (45, 6.8:1)

[a] NBD = norbornadiene; NB = norbornene. [b] A = The olefin (10 equiv) was added to a solution of complex **12** in toluene at the specified temperature. B = Anhydrous NMO (6 equiv) and the olefin (10 equiv) were added to a dichloromethane solution of complex **12** at the specified temperature. Reaction times are for complete conversion. [c] Determined by HPLC.

complexes **12a**−**d** toward strained olefins.[24] Thus, the reactions with NBD at room temperature are complete within 2−10 min (entries 1, 2, 8, and 17), while with the less reactive NB slightly longer (5−30 min) reaction times are needed for complete consumption of the starting complex. *The reactivity of these ynamine complexes is so high that, even at −20 °C, the purely thermal reactions with NBD (entries 4, 9, and 19) take place at reasonable rate, and in the case of complex* ***12c*** *it has been possible to conduct the reaction at −35 °C (entry 10).* These low-temperature, thermal reactions are also possible with NB, but require considerably longer periods of time for complete disappearance of the initial complexes (entries 14 and 23).

In general, for a certain complex/olefin pair, performing the reaction with chemical activation by NMO represents an important acceleration. Given the intrinsically high reactivity of the starting ynamine complexes, the most important practical application that can be drawn from this observation is from low-temperature reactions, which take place to completion in rather short periods of time (entries 5, 7, 12, 15, 20, and 24).

Although the yields of the Pauson−Khand cycloadditions of complexes **12** were only moderate, the reactions took place cleanly and adducts **13** or **14** were the only defined products arising from the ynamine complexes.

From the point of view of stereochemical outcome, complex **12b**, containing a singly α-substituted amine, reacts with strained olefins with poor diastereoselectivity. Moreover, the diastereoselectivity/temperature profile exhibited by the reactions of **12b** is essentially flat (compare entries 2 and 4). With complexes **12c,d**, containing a C_2 symmetrical amine, the situation is quite different. Thus, even at room temperature (entries 8, 13, 17, and 21) high diastereoselectivities are observed with the studied olefins and, for any of the C_2 auxiliaries, the observed diastereoselectivity sharply increases as the reaction temperature is lowered. Adduct **13c** can be obtained with a maximum 94:6 diastereoselectivity (dr 15.6:1; entry 12) by performing the reaction with NMO as a chemical promoter at −30 °C. Very interestingly, the reaction is complete in only 5 h at this very low temperature. On the other hand **14c**, which arises from the same ynamine reacting with norbornene, is obtained with a maximum 89.5:10.5 diastereoselectivity (dr 8.5:1; entry 14) by conducting the cycloaddition under purely thermal conditions at −21 °C.

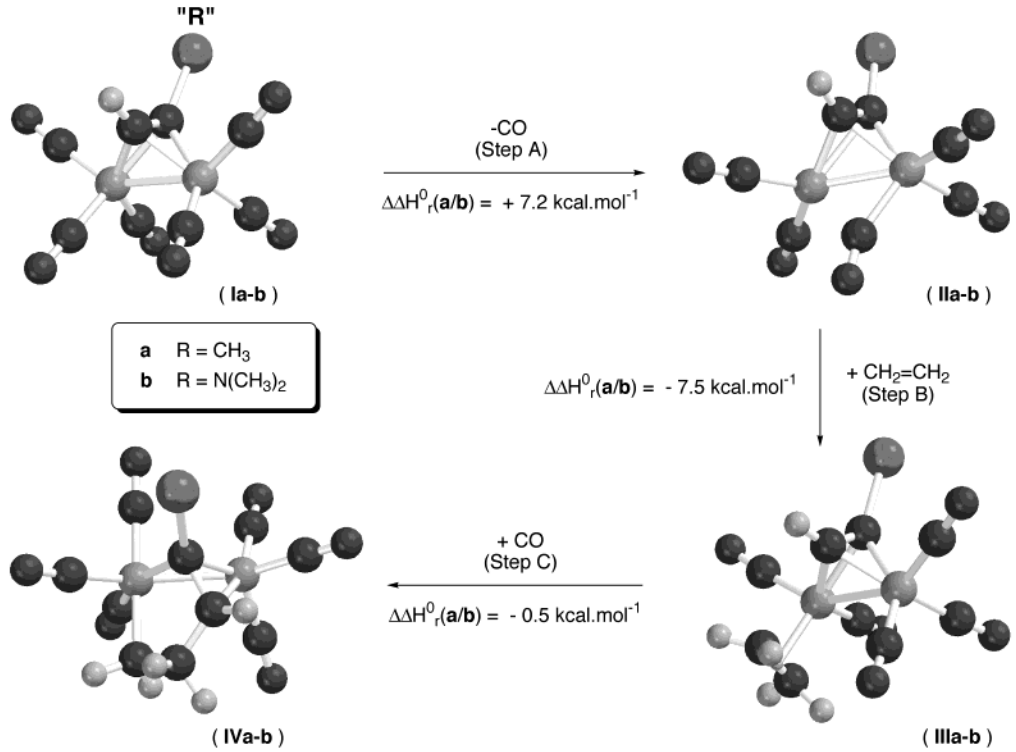
With the bulkier *trans*-2,5-bis(benzyloxymethyl)pyrrolidine as the chiral auxiliary, thermal reactions tend to be slightly slower but take place with considerably higher yields. Adduct **13d**, containing this auxiliary and arising from the reaction with NBD, can be obtained as an 88.5:11.5 mixture of diastereomers (dr 7.7:1, entry 20) by performing the process at −21 °C with chemical activation. Finally, adduct **14b** (involving the use of norbornene) is obtained in 49% yield as a 90:10 diastereomeric mixture (dr 9.1:1; entry 23) through a thermal reaction at −21 °C.

All of the Pauson−Khand adducts reported in Table 2 are oily materials that could be easily purified by column chromatography and exhibited good chemical stability. Diastereomeric separation, however, proved to be much more difficult than in the case of adduct **11b** and could not be performed.

Rationalization of the Reactivity Behavior of Ynamines in the Pauson−Khand Cycloaddition. The very high reactivity depicted by ynamines in the purely thermal intermolecular Pauson−Khand reaction, which greatly exceeds that observed for closely related alkyne derivatives also containing an electron-rich triple bond,[25] was a striking observation. The existence of some correlation between reactivity and electronic nature of the triple bond was strongly indicated by the fact that

(24) It is to be mentioned that complexes **12e** and **12f**, which have not been included in Table 2, appear to react with NBD and NB in a much similar manner that of **12a**−**d**. However, any attempted isolation of the corresponding adducts involving chromatographic purification unavoidably leads to complete decomposition.

Scheme 7



the structurally related *N*-(1-alkynyl)sulfonamides, possessing an electronically poorer triple bond, require much higher temperatures to react. However, if one considers the geometric and electronic modifications suffered by the acetylenic bond upon complexation, the transmission (and even the nature) of the effects exerted by the alkyne substituents was much less clear.[27]

To shed some light on this behavior we decided to comparatively analyze by theoretical means[28] the thermochemistry of the steps which are believed to be kinetically relevant in the Pauson−Khand reactions of propyne (taken as an example of alkyne with *normal* reactivity) and of *N*,*N*-(dimethylamino)acetylene (a simple terminal ynamine) with ethylene. These steps (Scheme 7) are the initial dissociative loss of a CO ligand, which generates a free coordination site for the entrance of the reacting olefin, and the evolution of the so-generated olefin complex into a cobaltacycle.

For an initial screening, we examined these processes by the semiempirical PM3(tm) procedure,[29] as implemented in the Spartan suite of programs.[30] For the dissociative step A, the loss of each of the three distinct CO ligands in each starting complex (**Ia,b**) was considered. Moreover, the possible conformers generated by rotation around the C−N bond were considered in the case of **Ib**. In each case, the most stable pentacarbonyl complex presented a CO-bridged structure and was generated by the loss of a distal (with respect to R) equatorial CO ligand. Since it is known that cobalt carbonyl complexes of alkynes present fluxional character, all possible olefin-substituted complexes **III** were also examined. Again, it was found in both cases that complexes containing the olefin ligand at a distal equatorial site were considerably more stable (6−7 kcal·mol^{-1}) than any other stereoisomer. We finally considered the energetics of cobaltacycles **IV** arising from complexes **III**, with the restriction of considering only those able to lead to an α-substituted cyclopentenone, as experimentally observed.

When the energetics of the overall CO/CH_2═CH_2 substitution process (step **I** → **III**: **a,** −5.5 kcal·mol^{-1}; **b**, −5.2 kcal·mol^{-1}) and cobaltacycle formation (step **III** → **IV**: **a**, −37.6 kcal·mol^{-1}; **b**, −37.1 kcal·mol^{-1}) are considered, the two systems appear to be completely equivalent. However, if the dissociative step A is considered, the loss of carbon monoxide is predicted to be up to 7.9 kcal·mol^{-1} easier in the case of the (dimethylamino)acetylene complex **Ia**. Interestingly enough, this is in complete agreement with the experimental observation of the poor thermal stability of ynamine complexes **3a**−**f** and **12a**−**f**, which have to be stored under a CO atmosphere to prevent decarbonylation.

To examine this phenomenon more closely, the structures of the dicobalt hexacarbonyl complexes **Ia,b** were

(25) The reaction of the dicobalt hexacarbonyl complexes of acetylenic ethers with norbornene at 65 °C in isooctane requires 18 h for completion,[4c] while the reaction of the corresponding complex of (phenylthio)acetylene with norbornadiene in toluene is complete after 5 h at 60−70 °C.[26]

(26) Daalman, L.; Newton, R. F.; Pauson, P. L.; Wadsworth, A. *J. Chem. Res., Miniprint* **1984**, 3150−3164.

(27) For a discussion of changes in the reactivity of alkynes upon coordination to cobalt, see: Happ, B.; Bartik, T.; Zucchi, C.; Rossi, M. C.; Ghelfi, F.; Pályi, G.; Váradi, G.; Szalontai, G.; Horvath, I. T.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1995**, *14*, 809−819.

(28) For previous theoretical descriptions of bonding in dicobalt hexacarbonyl complexes of acetylenes with the extended Hückel formalism, see: (a) Thorn, D. L.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 126−140. (b) Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858−3875. (c) Pepermans, H.; Hoogzand, C.; Geerlings, P. *J. Organomet. Chem.* **1986**, *306*, 395−405. (d) Halet, J. F.; Saillard, J. Y. *J. Organomet. Chem.* **1987**, *327*, 365−77.

(29) PM3(tm) is a modification of the original PM3 procedure (Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209−220) including a parametrization for transition metals.

(30) SPARTAN, version 5.0, Wavefunction, Inc., 18401 Von Karman Ave., Suite 370, Irvine, CA 92612.

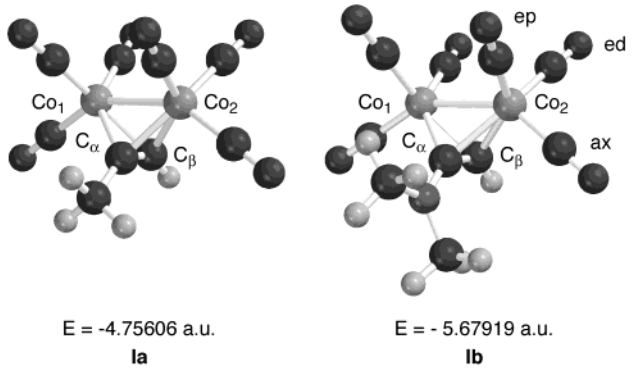


Figure 1. DFT-Optimized geometries and electronic energies (VWN/B88) of the dicobalt hexacarbonyl complexes **Ia,b**. (ax = axial; ep = equatorial proximal; ed = equatorial distal).

Table 3. Relevant Distances (Å) in the DFT (VWN/B88) Optimized Geometry of the Dicobalt Hexacarbonyl Complexes of Propyne (Ia) and (Dimethylamino)acetylene (Ib)

param[a]	Ia	Ib
$C_\alpha-CH_3$	1.513	
$C_\alpha-N(CH_3)_2$		1.355
$C_\alpha-C_\beta$	1.345	1.369
$C_\alpha-Co_1$	2.059	2.014
$C\alpha-Co_2$	2.058	2.166
$C_\beta-Co_1$	2.037	2.016
$C_\beta-Co_2$	2.038	1.995
Co_1-Co_2	2.576	2.618
Co_1-CO_{ep}	1.875	1.850
Co_1-CO_{ax}	1.835	1.825
Co_1-CO_{ed}	1.882	1.861
Co_2-CO_{ep}	1.875	1.847
Co_2-CO_{ax}	1.836	1.809
Co_2-Co_{ed}	1.882	1.871

[a] As defined in Figure 1.

submitted to full geometry optimization using ab initio DFT theory (VWN/B88),[31] as implemented in the ADF code, and using the ADF II(DZ)-SC basis set.[34] The results of this study have been summarized in Figure 1 and Table 3.

An analysis of the geometric parameters in these molecules helps in understanding the mechanism by which the dimethylamino substituent facilitates the dissociative loss of CO. In a comparison of the hexacarbonyl complexes **Ia**,**b**, it is interesting to observe that, whereas **Ia** is perfectly symmetrical, in **Ib** the $C_\alpha-Co_1$ and $C_\alpha-Co_2$ bonds show important differences in length, the later being longer by 0.150 Å. An inspection of the structure of **Ib** in Figure 1 provides an explanation for this behavior: The nitrogen atom in the dimethylamino substituent is essentially planar, and the conformation of this unit is such that the nitrogen lone pair can partially be delocalized into the $C_\alpha-Co_2$ σ^* orbital giving rise to a (negative or anionic) hyperconjugative interaction.[35] In other words, *an anomeric effect appears to exist in the N−C_α−Co_2 fragment, as dictated by the conformation of the amino substituent*.[36] In complete agreement with this interpretation, when the dimethylamino group in **Ib** was rotated by 90° to disrupt the hyperconjugation with the $C_\alpha-Co_2$ bond and the molecular geometry was reoptimized with this restriction, some important geometric changes took place: (i) The nitrogen atom became pyramidal. (ii) The $N-C_\alpha$ distance increased from 1.356 to 1.392 Å. (iii) The difference in length between the $C_\alpha-Co_1$ and $C_\alpha-Co_2$ bonds was greatly reduced, passing from 0.150 to 0.033 Å. From the energetic point of view, the electronic energy of this rotationally perturbed structure was 13.6 kcal·mol^{-1} higher than that of **Ib**. It is thus clear that hyperconjugation plays an important role in dictating the conformational preferences of **Ib** and in determining its geometric characteristics.

It is interesting to realize that the structural phenomena in **Ib** bear some analogy with the well-documented stabilization of propargyl cations by dicobalt hexacarbonyl complexes.[37] In these cases, it is assumed that the direction of the electron density flow is from the cluster toward the propargyl carbon,[38] and the phenomenon can be described as an example of (positive or cationic) hyperconjugation.

Centering now our attention on the origin of the easy loss of CO from **Ib**, it is important to realize that, as a consequence of hyperconjugation, the Co_2 cobalt atom in **Ib** should become more electronically rich (as it is the case), and this should be reflected in shorter Co_2-CO distances as a consequence of increased back-bonding capacity in the metal.[39] When the Co_1-CO and Co_2-CO distances in **Ib** are compared, it can be seen that this is in fact the case except for the Co_2-CO_{ed} bond in **Ib**, which is elongated. Since this bond is *trans* to the $C_\alpha-Co_2$ one in the distorted octahedral coordination sphere of the Co_2 atom, *it seems that the dimethylamino substituent is assisting and directing the dissociative loss of CO through a trans effect*,[40] as pictorially represented by the resonance structures in Figure 2.

(31) Calculations performed using the VWN local functional[32] with Becke's 1988 (B88) nonlocal exchange correction.[33]

(32) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200−1211.

(33) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100.

(34) Baerends, E. J.; Ellis, D. E.; Ros, P. E. *Chem. Phys.* **1973**, *2*, 41−51. (b) Baerends, E. J.; Ellis, D. E.; Ros, P. E. *Chem. Phys.* **1973**, *2*, 52−59. (c) te Velde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84−98.

(35) Negative hyperconjugation occurs in X−C−Y systems where X is an atom bearing one or more nonbonding electron pairs and the C−Y bond is characterized by a low-lying LUMO, when a electron pair on X is oriented antiperiplanar to the C−Y bond. The geometrical consequences of hyperconjugation are the shortening of the C−X bond and the lengthening of the C−Y bond. The stabilization arising from such phenomenon can be rationalized in terms of double bond−no bond resonance: X−C−Y ⇔ (+)X=C Y(−). For a discussion on the importance of negative hyperconjugation, see: Schleyer, P. v. R.; Kos, A. J. *Tetrahedron* **1983**, *39*, 1141−1150.

(36) The term *anomeric effect* is normally used to jointly designate the preference for conformational arrangements allowing the existence of negative hyperconjugation and the consequences (enthalpic, geometric, and kinetic) of this phenomenon. For recent, general references on this topic, see: (a) *The Anomeric Effect and Associated Stereoelectronic Effects*; ACS Symposium Series 539; Thatcher, G. R. J., Ed.; American Chemical Society: Washington, DC, 1993. (b) Juaristi, E. *The Anomeric Effect*; CRC Press: Boca Raton, FL, 1994. For an example of anomeric interaction involving a $Mn(CO)_5$ fragment as a C-2 substituent on a tetrahydropyranyl ring, see: DeShong, P.; Lessen, T. A.; Le, T. X.; Anderson, G.; Sidler, D. R.; Slough, G. A.; von Philipsborn, W.; Vöhler, M.; Zerbe, O. In *The Anomeric Effect and Associated Stereoelectronic Effects*; ACS Symposium Series 539; Thatcher, G. R. J., Ed.; American Chemical Society: Washington, DC, 1993; pp 227−239.

(37) For leading references, see: (a) Caffyn, A. J. M.; Nicholas, K. M. In *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Ed.; Elsevier: Oxford, U.K., 1995; Vol. 12, pp 685−702. (b) Nicholas, K. M. *Acc. Chem. Res.* **1987**, *20*, 207−214.

(38) Schreiber, S. L.; Klimas, M. T.; Sammakia, T. *J. Am. Chem. Soc.* **1987**, *109*, 5749.

(39) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Organic Chemistry*, 6th ed.; Wiley-Interscience: New York, 1999; pp 636−639.

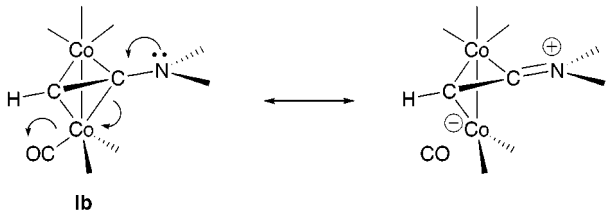


Figure 2. Anomeric (N−C−Co) and trans (C−Co−CO) effects in **Ib** facilitating the dissociative loss of CO. Some CO ligands have been omitted for clarity.

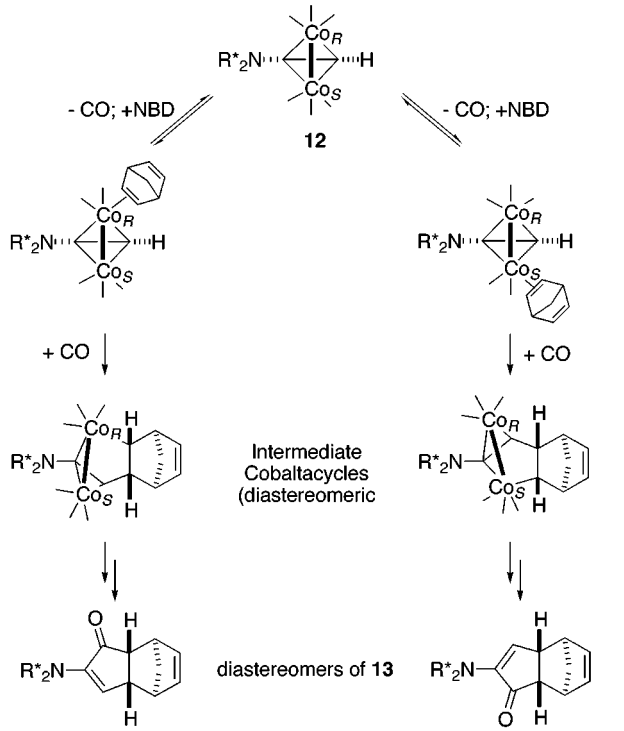
Rationalization of the Observed Diastereoselectivity in the Pauson−Khand Cycloadditions of Ynamines. Regarding diastereoselectivity, the Pauson−Khand reaction has normally been analyzed by comparing, on the basis of either qualitative[41] or quantitative arguments,[4e,42] the relative stabilities of the diastereomeric cobaltacycles which are assumed to intermediates in the commonly accepted mechanism of the process.[1] According to this mechanism, cobaltacycle formation is the product-determining step, i.e., where the regio- and the stereochemistry of the cyclopentenone products is fixed.

In the case of ynamines the great facility of the initial dissociative loss of CO we have just discussed tells in favor of cobaltacycle formation being kinetically important, so that the assumption of the existence of a parallelism between the relative energies of these cobaltacycles and those of the transition states leading to them (Hammond postulate) seems fully justified. According to this, the greater the energy difference between the diastereomeric cobaltacycle intermediates in a given reaction, the higher the diastereoselectivity of the process should be.

To analyze the differences in the diastereoselectivity of the Pauson−Khand reactions of ynamines derived from amines structurally similar but belonging to the C_1 and the C_2 point groups (like **6b**,**c**), we decided to perform a PM3(tm) study of the cobaltacycle intermediates in the reactions of ynamine complexes **12b,c** with norbornadiene. For comparison purposes, we selected the chiral auxiliaries as belonging to the same enantiomeric series: (*R*)-**6b** and (*R*,*R*)-**6c**. Since it is well-known that NBD exclusively reacts through its *exo* face,[1] and it has been established that only cobaltacycles with the $Co(CO)_3$ and CH_2 (bridge) moieties in a distal arrangement are energetically viable,[4e] the only source of stereochemical diversity in these processes is the nature [Co_R (pro-*R*) or Co_S (pro-*S*)] of the cobalt atom of the starting complex involved in the formation of the cobaltacycle (Scheme 8).

The classical view in comparing the efficiency as a chiral auxiliary of 2-(methoxymethyl)pyrrolidine (**6b**) and *trans*-2,5-bis(methoxymethyl)pyrrolidine (**6c**) is based on the consideration that the system containing the C_2 symmetrical amine has many less available conformations, since neither the rotation around the substrate−nitrogen bond nor the inversion at nitrogen generates a new conformer.[43] In a parallel manner, less competing conformationally isomeric transition states should exist in the reactions of the system containing the C_2 symmetrical amine, and an efficient transmission of the stereochemical information of the chiral auxiliary toward the newly created stereocenters should be possible in all of them. In agreement with this view, up to 8 conformational minima were located for any of the two diastereomeric cobaltacycles arising from **12b**, which contain **6b** as the chiral auxiliary. We have represented in Figure 3 (top) the most stable conformers of the cobaltacycles involving each of the diastereotopic cobalt atoms in **12b**. As it can be seen, the one involving the Co_S cobalt atom is predicted to be 1.5 kcal·mol^{-1} more stable than the one involving the Co_R cobalt atom.

Scheme 8



For each of the cobaltacycles arising from **12c**, which contain the C_2 symmetrical amine **6c** as the chiral auxiliary, only two conformational minima could be located. The most stable ones have been represented in Figure 3 (bottom). Also in this case the cobaltacycle involving the Co_S cobalt atom is predicted to be the most stable one, and the energy difference with the one involving the Co_R cobalt atom is now 2.3 kcal·mol^{-1}.

Thus, the present theoretical calculations provide an explanation for the observation of diastereoselectivity in the Pauson−Khand reactions of the ynamine complexes, since they predict the existence of significant energy differences between the cobaltacycles leading to the two possible diastereomers of the reaction products. Moreover, the calculations succeed in predicting that the use of C_2 symmetrical amines as chiral auxiliaries will lead to increased diastereoselectivities.

(40) Although *trans* influences (structural) and effects (kinetic) are most common in square planar complexes, they are not rare in octahedral ones. An illustrative example is provided by $[Co(NH_3)_5(CH_3)]$-S_2O_6, in which the Co−N bonds cis to the strong σ-donor methyl group exhibit distances in the range 1.957−1.969 Å, whereas the trans Co−N bond is much longer (2.127 Å). See: Kofod, P.; Harris, P.; Larsen, S. *Inorg. Chem.* **1997**, *36*, 2258−2266.

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(42) Castro, J.; Moyano, A.; Pericàs, M. A.; Riera, A. *Tetrahedron* **1995**, *51*, 6541−6556.

(43) For some reviews, see: (a) Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581−1590. (b) Rosini, C.; Franzini, L.; Raffaelli, A.; Salvadori, P. *Synthesis* **1992**, 503−517.

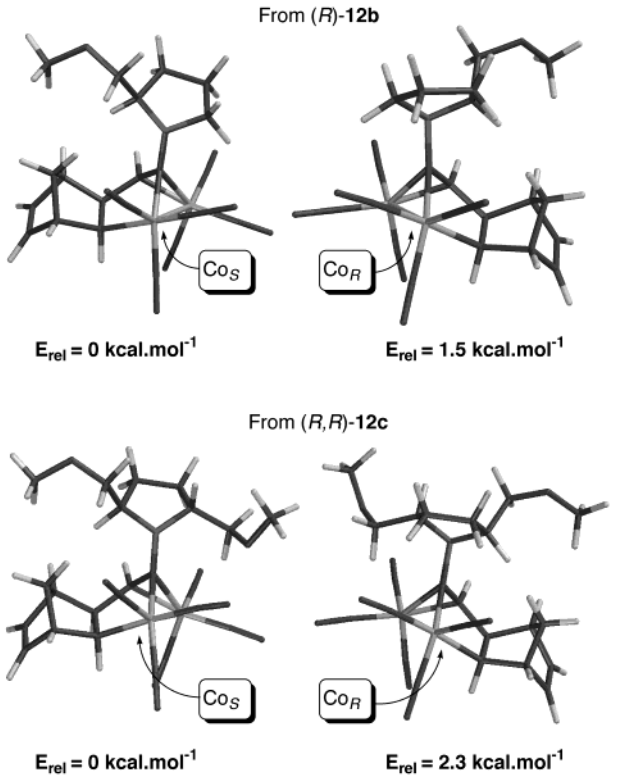

Figure 3. PM3(tm)-optimized geometries of the most stable conformers of the putative cobaltacycles leading to **13b**,**c**.

Conclusions

In summary, we have developed an efficient one-stage method for the conversion of chiral secondary amines into the hexacarbonyldicobalt complexes of the corresponding trimethylsilylynamines. We have also shown that the desilylation of these species is a convenient method for the preparation of the very unstable dicobalt hexacarbonyl complexes of terminal ynamines.

The reactivity of these last complexes toward strained olefins for cyclopentenone building (the Pauson−Khand reaction) is the highest ever recorded under purely *thermal* conditions, the process taking place even at −35 °C. With complexes containing C_2 symmetrical amines, the possibility of performing Pauson−Khand reactions at such low temperatures allows the achievement of high levels of diastereoselectivity.

According to semiempirical and density functional theory calculations, the increased reactivity of ynamine complexes has its origin in the unusually easy dissociative loss of CO in the derived dicobalt hexacarbonyl complexes. This behavior, in turn, seems to arise from an anomerically assisted and directed dissociative loss of CO. Such stabilization should be absent (or present to a much lesser extent) in *N*-(1-alkynyl)amides which, as we have already commented, only undergo intermolecular Pauson−Khand reaction at much higher temperatures.

The operation of anomeric effects in the dicobalt hexacarbonyl complexes of ynamines is being currently investigated in our laboratories by accurate DFT theory and will be reported separately.

Experimental Section

General Methods. General experimental aspects have been published elsewhere.[4e] High-resolution mass spectra were performed by the "Servicio de Espectrometría de Masas, Universidad de Córdoba". Solutions of dichloroacetylene in diethyl ether were prepared by the method of Kende.[17] (***Warning!*** *Dichloroacetylene is toxic and explosive. Although this procedure appears to be completely safe, it is strongly recommended that all work with dichloroacetylene be conducted in a hood and behind appropriate shielding.*) (*S*)-2-(Methoxymethyl)pyrrolidine,[44] (2*R*,5*R*)-2,5-bis(methoxymethyl)pyrrolidine,[45] and (2*R*,5*R*)-2,5-dimethylpyrrolidine[46] were prepared according to reported procedures. (±)-*trans*-2,5-Bis(benzyloxymethyl)pyrrolidine[47] was prepared by alkylation of (±)-*trans*-2,5-bis(hydroxymethyl)pyrrolidine.[45]

General Procedure for the Synthesis of Dicobalt Hexacarbonyl Complexes of Trimethylsilylynamines. Hexacarbonyl(*μ*-(*η*-1-morpholino-2-(trimethysilyl)acetylene))dicobalt(*Co*−*Co*), 3a. Freshly distilled morpholine (**6a**) (522 mg, 6.0 mmol) was added to a solution of 8.0 mmol of dichloroacetylene (**4**) in 5 mL of diethyl ether cooled to −70 °C. The mixture was then allowed to warm to room temperature, heated to 33 °C for 30 min, and cooled again to −70 °C. Solvent and excess dichloroacetylene were eliminated at reduced pressure at that temperature. The crude dichloroenamine (**5a**) was dissolved in 15 mL of diethyl ether, cooled to −70 °C, and *n*-BuLi (8.25 mL, 13.2 mmol, 1.6 M in hexanes) was added via syringe. The temperature was slowly raised to −10 °C, and 0.91 mL (7.2 mmol) of chlorotrimethylsilane was added via syringe. The mixture was then allowed to warm to room temperature, 10 mL of anhydrous hexane was added, and after 15 min, the mixture was filtered through a pad of Celite under nitrogen. Solvent evaporation at reduced pressure afforded 980 mg of the crude trimethylsilylynamine **7a** as a colorless oil.

A small sample of this oil (98 mg) was dissolved in 2 mL of anhydrous pentane, and the resulting solution was transferred to another flask containing a solution of 185 mg (0.54 mmol) of $Co_2(CO)_8$ in 4 mL of pentane. Gas evolution was observed, as the solution became green in color. After 15 min of stirring at room temperature, the mixture was concentrated to 1/3 of its initial volume under a mild CO stream and directly introduced in a chromatographic column (2.5% v/v triethylamine pretreated SiO_2), and elution with hexane/dichloromethane mixtures of increasing polarity was started. Complex **3a** (226 mg) could be isolated from the eluate as a green solid (80% yield, based on initial morpholine): IR (film) ν_{max} 2090, 2050, 2010, 1600 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.32 (s, 9H), 2.93 (br, 4H), 3.75 (br, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 1.1 ($3CH_3$), 53.9 ($2CH_2$), 66.2 ($2CH_2$), 68.0 (Cq), 133.2 (Cq), 200.0 (CO); MS (FAB-NBA) *m*/*z* (relative intensity) 469 (M^+, 14), 441 (M^+ − CO, 100), 413 (M^+ − 2CO, 100).

Hexacarbonyl-*μ*-(*η* -1-[(*S*)-2-methoxymethylpyrrolidino]-2-(trimethysilyl)acetylene)-dicobalt (*Co*−*Co*), 3b. The above procedure was followed starting from a solution of 10.0 mmol of **4** in 6 mL of diethyl ether and 690 mg (6.0 mmol) of (*S*)−(−)-2-methoxymethylpyrrolidine (**6b**). The reaction leading to the dichloroenamine **5b** was carried out for 2 h at 0 °C. After that time, 8.25 mL (13.2 mmol, 1.6 M in hexanes) of *n*-BuLi were used for the elimination/transmetalation step, and 0.91 mL (7.2 mmol) of chlorotrimethylsilane were used to trap the lithium acetylide. After filtration and solvent removal, 1.10 g of the crude trimethylsilylynamine **7b** was obtained as a brown oil.

A portion of this oil (110 mg) was dissolved in 3 mL of pentane and the resulting mixture added to a solution of 178 mg (0.52 mmol) of $Co_2(CO)_8$ in 5 mL of pentane. After 15 min stirring at room temperature and column chromatography, **3b** (243 mg) was isolated as a green oil (81% yield based on the starting amine **6b**): IR (film) ν_{max} 2080, 2040, 2010, 1600 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 0.32 (s, 9H), 0.85 (br, 2H), 1.24

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(br, 2H), 1.90 (br, 2H), 2.80−3.00 (m, 1H), 3.33 (s, 3H), 3.20−3.60 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 1.4 ($3CH_3$), 24.0 (CH_2), 28.8 (CH_2), 55.3 (CH_2), 59.0 (CH_3), 64.8 (CH), 70.0 (Cq), 72.9 (CH_2), 129.5 (Cq), 200.9 (CO). MS (FAB-NBA) *m/z* (relative intensity) 469 (M^+ − CO, 24), 441 (M^+ − 2CO, 97), 413 (M^+ − 3CO, 51), 385 (M^+ − 4CO, 100).

Hexacarbonyl(*μ*-(*η* -1-[(*R,R*)-2,5-bis(methoxymethyl)-pyrrolidino]-2-(trimethysilyl)acetylene))dicobalt(*Co*−*Co*), 3c. The general procedure was followed starting from a solution of 8.0 mmol of **4** in 5 mL of diethyl ether and 636 mg (4.0 mmol) of (*R,R*)-2,5-bis(methoxymethyl)pyrrolidine (**6c**). The reaction leading to the dichloroenamine **5c** was carried out for 2 h at 20 °C. After that time, 5.5 mL (8.8 mmol, 1.6 M in hexanes) of *n*-BuLi was used for the elimination/transmetalation step, and 0.60 mL (4.8 mmol) of chlorotrimethylsilane was used to trap the lithium acetylide. After filtration and solvent removal, 985 mg of the crude trimethylsilylynamine **7c** was obtained as a brown oil.

A portion of this oil (110 mg) was dissolved in 3 mL of pentane and the resulting mixture added to a solution of 148 mg (0.43 mmol) of $Co_2(CO)_8$ in 5 mL of pentane. After 15 min of stirring at room temperature and column chromatography, **3c** (87 mg) was isolated as a green oil (36% yield, based on the starting amine **6c**): IR (film) ν_{max} 2100, 2060, 2020, 1600 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.41 (s, 9H), 1.80−2.30 (m, 4H), 3.37 (br, 6H), 3.30−3.80 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 1.7 ($3CH_3$), 27.0 ($2CH_2$), 58.8 (2CH), 63.6 ($2CH_3$), 70.7 ($2CH_2$), 200.9 (CO). Absorptions due to the triple bond carbons were not observed. MS (FAB-NBA) [*m/z* (relative intensity)]: 513 (M^+ − CO, 10%), 485 (M^+ − 2CO, 37%), 457 (M^+ − 3CO, 30%), 429 (M^+ − 4CO, 89%), 401 (M^+ − 5CO, 100%).

Hexacarbonyl(*μ*-(*η*-1-[(±)-*trans*-2,5-bis(benzyloxymethyl)pyrrolidino]-2-(trimethysilyl)acetylene))dicobalt(*Co*−*Co*), 3d. The general procedure was followed starting from a solution of 5.0 mmol of **4** in 3 mL of diethyl ether and 933 mg (3.0 mmol) of (±)-*trans*-2,5-bis(benzyloxymethyl)pyrrolidine (**6d**). The reaction leading to the dichloroenamine **5d** was carried out for 2 h at 33 °C. After that time, 4.12 mL (6.6 mmol, 1.6 M in hexanes) of *n*-BuLi was used for the elimination/transmetalation step, and 0.45 mL (3.6 mmol) of chlorotrimethylsilane was used to trap the lithium acetylide. After filtration and solvent removal, 854 mg of the crude silylynamine **7d** was isolated as a brown oil.

A portion of this oil (85 mg) was dissolved in 2 mL of pentane and the resulting mixture added to a solution of 103 mg (0.30 mmol) of $Co_2(CO)_8$ in 4 mL of pentane. After 15 min of stirring at room temperature and column chromatography, **3d** (88 mg) was isolated as a green solid (42% yield, based on the starting amine **6d**): IR (film) ν_{max} 2215, 2060, 2020, 1950, 1570 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.30 (s, 9H), 1.40−2.40 (m, 4H), 3.20−3.80 (m, 6H), 4.45 (s, 4H), 7.0−7.4 (br, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 1.8 ($3CH_3$), 27.2 ($2CH_2$), 63.8 (2CH), 68.4 ($2CH_2$), 73.4 ($2CH_2$), 127.7 (6CH), 128.4 (4CH), 138.0 (2Cq), 200.9 (CO). Absorptions due to the triple bond carbons were not observed. MS (FAB-NBA) [*m/z* (relative intensity)]: 609 (M^+ − 3CO, 42%), 525 (M^+ − 6CO, 100%).

Hexacarbonyl(*μ*-(*η* -1-[(*R,R*)-2,5-dimethylpyrrolidino]-2-(trimethysilyl)acetylene))dicobalt(*Co*−*Co*), 3e. The general procedure was followed starting from a solution of 8.0 mmol of **4** in 5 mL of diethyl ether and 252 mg (2.54 mmol) of (*R,R*)-2,5-dimethylpyrrolidine (**6e**). The reaction leading to the dichloroenamine **5e** was carried out for 1 h at −10 °C. After that time, 3.49 mL (5.58 mmol, 1.6 M in hexanes) of *n*-BuLi was used for the elimination/transmetalation step, and 0.38 mL (3.04 mmol) of chlorotrimethylsilane was used to trap the lithium acetylide. After filtration and solvent removal, 429 mg of the crude trimethylsilylynamine **7e** was isolated as a brown oil.

A portion of this oil (98 mg) was dissolved in 2 mL of pentane and the resulting mixture added to a solution of 171 mg (0.50 mmol) of $Co_2(CO)_8$ in 6 mL of pentane. After 15 min of stirring at room temperature and column chromatography, **3e** (192 mg) was isolated as a green solid (69% yield, based on the starting amine **6e**): IR (film) ν_{max} 2215, 2060, 2020, 1950, 1570 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.34 (s, 9H), 1.19 (d, J = 6.6 Hz, 6H), 1.50−1.60 (m, 2H), 2.05−2.25 (m, 2H), 3.5−3.7 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 1.9 ($3CH_3$), 18.4 ($2CH_3$), 30.7 ($2CH_2$), 59.7 (2CH), 201.5 (CO). Absorption for the triple bond carbon atoms was not observed. MS (FAB-NBA) [*m/z* (relative intensity)]: 481 (M^+, 5%), 453 (M^+ − CO, 100%).

Hexacarbonyl(*μ*-(*η*-1-[(*S*)-(α-methylbenzyl)benzylamino]-2-(trimethysilyl)acetylene))dicobalt(*Co*−*Co*), 3f. The general procedure was followed by starting from a solution of 8.0 mmol of **4** in 5 mL of diethyl ether and 1.266 g (6.0 mmol) of (*S*)-(α-methylbenzyl)benzylamine **(6f)**. The reaction leading to the dichloroenamine **5f** was carried out for 24 h at 33 °C. After that time, 8.25 mL (13.2 mmol, 1.6 M in hexanes) of *n*-BuLi was used for the elimination/transmetalation step, and 0.91 mL (7.2 mmol) of chlorotrimethylsilane was used to trap the lithium acetylide. After filtration and solvent removal, 1.307 g of the crude silylynamine **7f** was isolated as a brown oil.

A portion of this oil (109 mg) was dissolved in 3 mL of pentane and the resulting mixture added to a solution of 171 mg (0.50 mmol) of $Co_2(CO)_8$ in 6 mL of pentane. After 15 min of stirring at room temperature and column chromatography, **3f** (162 mg) was obtained as a green oil (55% yield, based on the starting amine **6f**): IR (film) ν_{max} 2060, 2010, 2000, 1570 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.21 (s, 9H), 1.51 (d, J = 6.6 Hz, 3H), 4.0 (d, J = 14 Hz, 1H), 4.35 (d, J = 14 Hz, 1H), 4.85−4.95 (m, 1H), 6.90−7.40 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 1.3 ($3CH_3$), 15.6 (CH_3), 55.4 (CH_2), 65.3 (CH), 70.1 (Cq), 127.1 (CH), 127.5 (2CH), 127.7 (2CH), 127.8 (CH), 128.2 (2CH), 128.5 (2CH), 132.6 (Cq), 137.6 (Cq), 140.4 (Cq), 200.9 (CO); MS (FAB-NBA) *m/z* (relative intensity) 565 (M^+ − CO, 15%), 509 (M^+ − 3CO, 55%), 481 (M^+ − 4CO, 100%).

Synthesis of Dicobalt Hexacarbonyl Complexes of 1-Amino-2-phenylacetylenes. Hexacarbonyl(*μ*-(*η*-1-morpholino-2-phenylacetylene))dicobalt(*Co*−*Co*), 10a. To a solution of 261 mg (3.0 mmol) of freshly distilled morpholine (**6a**) in 7 mL of THF, cooled to −78 °C, was added via syringe 1.87 mL (3.0 mmol, 1.6 M in hexanes) of *n*-BuLi. After 5 min, a solution of 409 mg (3.0 mmol) of 1-chloro-2-phenylacetylene (**8**) in 3 mL of THF was added to the mixture. The system was then allowed to warm to room temperature, 10 mL of anhydrous hexane was added, and the solution was filtered through Celite under nitrogen. Solvents were removed in vacuo, and the residual brown oil consisting of crude 1-morpholino-2-phenylacetylene (**9a**) (759 mg) was dissolved in 3 mL of anhydrous pentane. This solution was transferred to another flask containing a solution of 1.02 g (3.0 mmol) of $Co_2(CO)_8$ in 4 mL of pentane. After 30 min of stirring at room temperature, the mixture was filtered through a pad of Celite and purified by column chromatography, eluting with hexanes, to afford 810 mg (57% yield) of **10a** as a green solid: IR (film) ν_{max} 2100, 2060, 2010, 1710, 1620 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.93 (t, J = 4.8 Hz, 4H), 3.82 (t, J = 4.8 Hz, 4H), 7.20−7.40 (m, 3H), 7.45−7.50 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.4 ($2CH_2$), 66.2 ($2CH_2$), 127.3 (CH), 128.8 (4CH), 138.8 (Cq), 200.6 (CO). Absorptions due to the triple bond carbon atoms were not observed. MS (FAB-NBA) [*m/z* (relative intensity)]: 473 (M^+ , 20%), 445 (M^+ − CO, 100%), 417 (M^+ − 2CO, 100%).

Hexacarbonyl(*μ*-(*η* -1-[(*S*)-2-(methoxymethyl)pyrrolidino]-2-phenylacetylene))dicobalt(*Co*−*Co*), 10b. To a solution of 250 mg (2.17 mmol) of freshly distilled (*S*)-2-(methoxymethyl)pyrrolidine (**6b**) in 7 mL of THF, cooled to −78 °C, was added via syringe 1.35 mL (2.17 mmol, 1.6 M in hexanes) of *n*-BuLi. After 5 min, a solution of 273 mg (2.0 mmol) of **8** in 3 mL of THF was added to the mixture. The system was then allowed to warm to room temperature, 10 mL of anhydrous hexane was added, and the solution was filtered through Celite under nitrogen. Solvents were removed at reduced pressure, and the residual brown oil, consisting of 1-[(*S*)-2-(methoxymethyl)pyrrolidino]-2-phenylacetylene (**9b)** (385 mg) was dissolved in 3 mL of anhydrous pentane. This solution was transferred to another flask containing a solution of 684 mg (2.0 mmol) of $Co_2(CO)_8$ in 4 mL of pentane. After 30 min of stirring at room temperature, the mixture was filtered through a pad of Celite and purified by column chromatography, eluting with hexanes, to afford 185 mg (17% yield) of **10b**

as a green solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.01 (br, 4H), 3.00 (br, 2H), 3.20−3.80 (m, 3H), 3.32 (s, 3H), 7.20−7.70 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.1 (CH_2), 28.7 (CH_2), 54.6 (CH_2), 58.8 (CH_3), 64.0 (CH), 73.2 (CH_2), 86.3 (Cq), 119.3 (Cq), 126.9 (CH), 128.5 (2CH), 129.1 (2CH), 139.7 (Cq), 200.6 (CO); MS (FAB-NBA) *m/z* (relative intensity) 501 (M^+, 8%), 473 (M^+ − CO, 50%), 445 (M^+ − 2CO, 100%).

Pauson−Khand Reactions of 1-(Cycloalkylamino)-2-phenylacetylenes. (±)-(1*S,2*S**,6*R**,7*R**)-5-Phenyl-4-morpholinotricyclo[5.2.1.0^{2,6}]deca-4,8-dien -3-one, 11a. Thermal Reaction.** To a solution of 100 mg (0.211 mmol) of complex **10a** in 2 mL of toluene was added norbornadiene (195 mg, 2.11 mmol) dissolved in toluene (3 mL), and the mixture was heated at 95 °C for 3 h, allowed to cool to room temperature, filtered through Celite, and purified by column chromatography (2.5% v/v triethylamine pretreated SiO_2, eluting with hexanes/diethyl ether, 91/9), to give 19 mg (29% yield) of **11a** as a colorless oil.

***N*-Oxide-Promoted Reaction.** A solution of 71 mg (0.15 mmol) of the complex **10a** in 2 mL of dichloromethane was cooled to −20 °C, and 106 mg (0.9 mmol) of anhydrous NMO was added in one portion. After 10 min, 138 mg (1.5 mmol) of norbornadiene was added, and the mixture was then allowed to warm to 0 °C. After 3 h, the reaction mixture was filtered through Celite and purified by column chromatography to give 7 mg (15%) of **11a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 2H), 2.32 (d, J = 5.8 Hz, 1H), 2.51 (s, 1H), 2.80−2.90 (m, 2H), 2.95 (d, J = 5.0 Hz, 2H), 3.10−3.30 (m, 2H), 3.70 (quintuplet, J = 3 Hz, 4H), 6.24 (m, 2H), 7.30−7.45 (m, 3H), 7.45−7.55 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.5 (CH_2), 43.0 (CH), 43.6 (CH), 47.5 (CH), 49.6 ($2CH_2$), 51.2 (CH), 67.2 ($2CH_2$), 128.0 (2CH), 128.1 (2CH), 128.6 (CH), 136.2 (Cq), 137.3 (CH), 138.1 (CH), 148.4 (Cq), 152.0 (Cq), 206.5 (Cq); MS (CI-NH_3) *m/z* (relative intensity) 308 (M^+ + 1, 100%); HRMS (CI, butane) calcd for $C_{20}H_{22}NO_2$ [MH^+] 308.1651, found 308.1674.

(1*S,2*S**,6*R**,7*R**)-5-Phenyl-4-[(*S*)-2-(methoxymethyl)-pyrrolidino]tricyclo[5. 2.1.0^{2,6}]deca-4,8-dien-3-one, 11b.** The procedure described for the preparation of **11a** was followed starting from 170 mg (0.339 mmol) of complex **10b** in 2.5 mL of toluene and 312 mg (3.4 mmol) of norbornadiene in toluene (2.5 mL) The reaction was conducted at 70 °C for 5 h and led to **11b** (11 mg) as a 4:1 mixture of diastereomers in 9% yield. The major one could be separated by column chromatography as an oil. **11b** (major diastereomer: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.20−2.10 (m, 9H), 2.23 (m, 1H), 2.70−3.40 (m, 5H), 3.24 (s, 3H), 6.10−6.30 (m, 2H), 7.20−7.40 (m, 3H), 7.50−7.60 (m, 2H).

General Procedure for the Pauson−Khand Reactions of Terminal Ynamines. (±)-(1*S,2*S**,6*S**,7*R**)-4-Morpholinotricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one, 13a.** To a solution of 410 mg (1.2 mmol) of $Co_2(CO)_8$ in 5 mL of pentane was added at room temperature 187 mg (1.0 mmol) of 1-morpholino-2-(trimethysilyl)acetylene (**7a**). Gas evolution and development of green color in the solution were observed. After 10 min, the solvent was removed by passing a CO stream over the solution, and 400 mg (2.9 mmol) of potassium carbonate and 5 mL of methanol were added to the system. After 30 min of vigorous stirring, 5 mL of pentane was added. Stirring was continued for 2 min, the phases were allowed to separate, and the pentane one was transferred, via cannula and under CO pressure, to another flask. This extraction operation was repeated 3−4 times, until the pentane phase was colorless. Pentane was removed by passing a nitrogen stream over the solution, and the resulting green oil (353 mg, 0.89 mmol, 89%), consisting of the desilylated dicobalt hexacarbonyl complex **12a**, was dissolved in 5 mL of toluene. Norbornadiene (920 mg, 10 mmol) was added dropwise at room temperature. When the addition was complete, the green color had disappeared and no **12a** could be detected by TLC. The mixture was filtered through a pad of Celite and purified by chromatography (2.5% v/v triethylamine pretreated SiO_2, eluting with hexanes/diethyl ether, 91/9) to afford 160 mg (78% yield) of **13a** as an oil: IR (film) ν_{max} 1705, 1610 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.20−1.40 (m, 2H), 2.22 (d, J = 7.5 Hz, 1H), 2.60 (br, 2H), 2.90 (br, 1H), 2.95−3.25 (m, 4H), 3.78 (t, J = 7.2 Hz, 4H), 6.15−6.20 (m, 1H), 6.20−6.30 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 41.0 (CH_2), 43.7 (CH), 43.6 (CH), 43.9 (CH), 48.3 ($2CH_2$), 52.2 (CH), 66.5 ($2CH_2$), 135.5 (CH), 136.5 (CH), 138.4 (CH), 154.2 (Cq), 206.9 (Cq); MS (CI-NH_3) *m/z* (relative intensity) 232 (M^+ + 1, 100%); HRMS (CI, butane) calcd for $C_{14}H_{18}NO_2$ [MH^+] 232.1337, found 232.1317.

(1*S,2*S**,6*S**,7*R**)-4-[(*S*)-2-(Methoxymethyl)pyrrolidino]-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one, 13b. Thermal Reaction at −22 °C.** The above procedure was followed by starting from 213 mg (0.57 mmol) of $Co_2(CO)_8$ in 5 mL of pentane and 110 mg (0.52 mmol) of 1-[(*S*)-2-(methoxymethyl)-pyrrolidino]-2-(trimethysilyl)acetylene (**7b**). After the desilylation, 225 mg (0.45 mmol, 87% yield) of complex **12b** was obtained as a green oil. This complex was dissolved in 5 mL of toluene, the solution was cooled to −22 °C, and 415 mg (4.5 mmol) of norbornadiene was added to the system. After 24 h of stirring at −22 °C, the mixture was filtered through Celite and purified by chromatography to give 90 mg (77%) of **13b** as an oil. HPLC analysis (Nucleosil 120 C-18, 20 cm, MeOH/H_2O, 70/30, 0.5 mL/min): 27.50 min (64.6%), 29.30 min (35.4%).

***N*-Oxide-Promoted Reaction at −30 °C.** Starting from 190 mg (0.55 mmol) of $Co_2(CO)_8$ in 5 mL of pentane and 98 mg (0.464 mmol) of **7b**, 172 mg (0.40 mmol, 87%) of the desilylated complex **12b** was obtained. This complex was dissolved in 5 mL of dichloromethane, the solution was cooled to −30 °C, and 284 mg (2.43 mmol) of anhydrous NMO and 378 mg (4.1 mmol) of norbornadiene were added to the system. After 12 h the reaction was complete. The mixture was filtered through Celite and purified by chromatography to give 71 mg (68%) of **13b** as an oil: HPLC analysis 27.50 min (69.4%), 29.30 min (30.6%); IR (film) ν_{max} 1700, 1600 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$, major diastereomer) δ 1.25−1.35 (m, 2H), 1.76 (br, 1H), 1.82−1.95 (m, 3H), 2.21 (m, 1H), 2.57 (br, 2H), 2.86 (s, 1H), 3.00−3.20 (m, 2H), 3.35 (s, 3H), 3.30−3.50 (m, 2H), 4.15−4.20 (m, 1H), 5.85−5.90 (m, 1H), 6.10−6.20 (m, 1H), 6.20−6.30 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$, major diastereomer) δ 22.9 (CH_2), 28.4 (CH_2), 41.1 (CH_2), 43.5 (CH), 43.9 (CH), 44.1 (CH), 49.3 (CH_2), 52.0 (CH), 57.2 (CH), 59.0 (CH_3), 74.2 (CH_2), 128.3 (CH), 136.3 (CH), 138.5 (CH), 150.2 (Cq), 205.7 (Cq); MS (CI-NH_3) *m/z* (relative intensity) 260 (M^+ + 1, 100%); HRMS (CI, butane) calcd for $C_{16}H_{22}NO_2$ [MH^+] 260.1650, found 260.1605.

(1*R,2*S**,6*S**,7*S**)-4-[(*S*)-2-(Methoxymethyl)pyrrolidino]tricyclo[5.2.1.0^{2,6}]-4-decen-3-one, 14b. Thermal Reaction at Room Temperature.** The general procedure was followed starting from 87 mg (0.26 mmol) of $Co_2(CO)_8$ in 5 mL of pentane and 45 mg (0.21 mmol) of **7b**. After the desilylation, 80 mg (0.19 mmol, 88%) of complex **12b** was obtained as a green oil. This complex was dissolved in 4 mL of toluene, and 188 mg (2.0 mmol) of norbornene was added to the system. After 30 min of stirring at room temperature, the mixture was filtered through Celite and purified by chromatography to give 11 mg (22%) of **14b** as an oil. HPLC analysis (Nucleosil 120 C-18, 20 cm. MeOH/H_2O, 70/30, 0.5 mL/min): 34.66 min (66.6%); 36.52 min (33.4%).

***N*-Oxide-Promoted Reaction at −22 °C.** If one starts from 183 mg (0.53 mmol) of $Co_2(CO)_8$ in 5 mL of pentane and 94 mg (0.445 mmol) of **7b**, 161 mg (0.378 mmol, 85%) of the desilylated complex **12b** was obtained. This complex was dissolved in 5 mL of dichloromethane, the solution was cooled to −22 °C, and 266 mg (2.26 mmol) of anhydrous NMO and 357 mg (3.8 mmol) of norbornene were added to the system. After 12 h at that temperature, the reaction was complete. The mixture was filtered through Celite and purified by column chromatography to give 22 mg (22%) of **14b** as a colorless oil. HPLC analysis: 34.66 min (70.7%); 36.52 min (29.3%). IR (film): ν_{max} 1700, 1610 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, major diastereomer): δ 0.85−0.95 (m, 1H), 1.05−1.35 (m, 3H), 1.40−1.70 (m, 3H), 1.75−2.00 (m, 3H), 2.05 (br, 1H), 2.12 (d, J = 5 Hz, 1H), 2.35 (br, 1H), 2.50 (br, 1H), 2.95−3.20 (m, 2H), 3.33 (s, 3H), 3.30−3.50 (m, 2H), 4.05−4.20 (m, 1H), 5.80 (d, J = 2.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, major diastereomer): δ 22.9 (CH_2), 28.4 (CH_2), 28.4 (CH_2), 28.9 (CH_2), 30.8 (CH_2), 39.0 (CH), 39.3 (CH), 45.3 (CH), 49.4 (CH_2), 54.0

(CH), 57.2 (CH), 58.8 (CH_3), 74.2 (CH_2), 128.3 (CH), 149.5 (Cq), 206.0 (Cq). MS (CI-NH_3) [*m*/*z* (relative intensity)]: 262 (M^+ + 1, 24%). HRMS (CI, butane): calcd for $C_{16}H_{24}NO_2$ [MH^+] 262.1807, found 262.1778.

(1*S,2*S**,6*S**,7*R**)-4-[(2*R*,5*R*)-2,5-Bis(methoxymethyl)-pyrrolidino]tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one, 13c. Thermal Reaction at −35 °C.** The general procedure was followed starting from 203 mg (0.596 mmol) of $Co_2(CO)_8$ in 6 mL of pentane and 152 mg (0.596 mmol) of 1-[(2*R*,5*R*)-2,5-bis-(methoxymethyl)pyrrolidino]-2-(trimethysilyl)acetylene (**7c**). After desilylation, 176 mg (0.375 mmol, 63%) of complex **12c** was obtained as a green oil. This complex was dissolved in 5 mL of toluene, the mixture was cooled to −35 °C, and 350 mg (3.8 mmol) of norbornadiene was added to the system. After 3 days of stirring at −35 °C, the mixture was filtered through Celite and purified by column chromatography to give 25 mg (22%) of **13c** as an oil. HPLC analysis (Nucleosil 120 C-18, 20 cm. MeOH/H_2O, 70/30, 0.5 mL/min): 22.74 min (88.8%); 24.47 min (11.2%).

***N*-Oxide-Promoted Reaction at −35 °C.** Starting from 227 mg (0.66 mmol) of $Co_2(CO)_8$ in 5 mL of pentane and 170 mg (0.66 mmol) of **7c**, 200 mg (0.42 mmol, 63%) of the desilylated complex **12c** was obtained. This complex was dissolved in 5 mL of dichloromethane, the solution was cooled to −35 °C, and 295 mg (2.52 mmol) of anhydrous NMO and 386 mg (4.2 mmol) of norbornadiene were added to the system. After 5 h of stirring at that temperature, the reaction was complete. The mixture was filtered through Celite and purified by column chromatography to give 23 mg (18%) of **13c** as an oil. HPLC analysis: 22.74 min (94.0%); 24.47 min (6.0%). IR (film): ν_{max} 1705, 1605 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, major diastereomer): δ 0.85−0.95 (m. 1H), 1.20−1.40 (m, 2H), 1.70−2.20 (m, 4H), 2.50−2.65 (m, 2H), 2.87−2.90 (m, 1H), 3.03 (dd, J = 9.6, 7.8 Hz, 2H), 3.20−3.40 (m, 2H), 3.28 (s, 6H), 4.18 (br, 2H), 6.00 (d, J = 3.0 Hz, 1H), 6.15−6.20 (m, 1H), 6.23−6.30 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, major diastereomer): δ 26.1 ($2CH_2$), 41.1 (CH_2), 43.7 (CH), 43.9 (CH), 44.5 (CH), 51.5 (CH), 57.4 (2CH), 59.0 ($2CH_3$), 73.1 ($2CH_2$), 130.4 (CH), 136.2 (CH), 138.4 (CH), 148.8 (Cq), 205.9 (Cq). MS (CI-NH_3) [*m*/*z* (relative intensity)]: 304 (M^+ + 1, 100%). HRMS (CI, butane): calcd for $C_{18}H_{26}NO_3$ [MH^+] 304.1912, found 304.1907.

(1*R,2*S**,6*S**,7*S**)-4-[(2*R*,5*R*)-2,5-Bis(methoxymethyl)-pyrrolidino]tricyclo[5.2.1.0^{2,6}]dec-4-en-3-one, 14c. Thermal Reaction at −21 °C.** The general procedure was followed starting from 201 mg (0.588 mmol) of $Co_2(CO)_8$ in 6 mL of pentane and 150 mg (0.588 mmol) of **7c**. After desilylation, 160 mg (0.34 mmol, 58%) of complex **12c** was obtained as a green oil. This complex was dissolved in 5 mL of toluene, the mixture was cooled to −21 °C, and 320 mg (3.4 mmol) of norbornene was added to the system. After 6 days of stirring at −21 °C, the mixture was filtered through Celite and purified by column chromatography to give 21 mg (20%) of **14c** as a colorless oil. HPLC analysis (Nucleosil 120 C-18, 20 cm, MeOH/H_2O, 70/30, 0.5 mL/min): 26.65 min (89.5%); 28.55 min (10.5%).

***N*-Oxide-Promoted Reaction at −30 °C.** If one starts from 218 mg (0.639 mmol) of $Co_2(CO)_8$ in 5 mL of pentane and 163 mg (0.639 mmol) of **7c**, 187 mg (0.39 mmol, 62%) of the desilylated complex **12c** was obtained. This complex was dissolved in 5 mL of dichloromethane, the solution was cooled to −30 °C, and 280 mg (2.39 mmol) of anhydrous NMO and 375 mg (4.0 mmol) of norbornene were added to the system. After 3 days at that temperature, the reaction was complete. The mixture was filtered through Celite and purified by chromatography to afford 21 mg (17%) of **14c**. HPLC analysis: 26.65 min (88.3%); 28.55 min (11.7%). IR (film): ν_{max} 1705, 1605 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, major diastereomer): δ 0.85−1.35 (m, 4H), 1.50−1.70 (m, 2H), 1.80−2.15 (m, 6H), 2.25−2.40 (m, 1H), 2.45−2.55 (m, 1H), 3.03 (dd, J = 9.3, 7.8 Hz, 2H), 3.20−3.40 (m, 2H), 3.29 (s, 6H), 4.1 (m, 2H), 5.95 (d, J = 4.0 Hz, 1H [major]). ^{13}C NMR (75 MHz, $CDCl_3$, major diastereomer): δ 26.1 ($2CH_2$), 28.3 (CH_2), 28.9 (CH_2), 30.9 (CH_2), 39.1 (CH), 39.4 (CH), 45.6 (CH), 53.6 (CH), 57.5 (2CH), 59.0 ($2CH_3$), 73.0 ($2CH_2$), 130.3 (CH), 148.0 (Cq), 206.2 (Cq). MS (CI-NH_3) [*m*/*z* (relative intensity)]: 306 (M^+ + 1, 100%). HRMS (CI, butane): calcd for $C_{18}H_{28}NO_3$ [MH^+] 306.2069, found 306.2022.

(±)-(1*S,2*S**,6*S**,7*R**)-4-[*trans*-2,5-Bis(benzyloxymethyl)pyrrolidino]tricycl o[5.2.1.0^{2,6}]deca-4,8-dien-3-one, 13d. Thermal reaction at −20 °C.** The general procedure was followed starting from 131 mg (0.384 mmol) of $Co_2(CO)_8$ in 5 mL of pentane and 130 mg (0.32 mmol) of (±)-1-[*trans*-2,5-bis(benzyloxymethyl)pyrrolidino]-2-(trimethysilyl)acetylene, **7d**. After desilylation, 100 mg (0.161 mmol, 50%) of complex **12d** was obtained as a green oil. This complex was dissolved in 5 mL of toluene, the mixture was cooled to −20 °C, and 160 mg (1.7 mmol) of norbornadiene was added to the system. After 12 h of stirring at −20 °C, the mixture was filtered through a short pad of Celite and purified by column chromatography to afford 24 mg (32%) of **13d** as an oil. HPLC analysis (Nucleosil 120 C-18, 20 cm, MeOH/H_2O, 70/30, 1.0 mL/min): 109.6 min (87.4%); 116.6 min (12.6%).

***N*-Oxide-Promoted Reaction at −20 °C.** If one starts from 131 mg (0.384 mmol) of $Co_2(CO)_8$ in 5 mL of pentane and 130 mg (0.32 mmol) of **7d**, 100 mg (0.161 mmol, 50%) of desilylated complex **12d** was obtained. This complex was dissolved in 5 mL of dichloromethane, the solution was cooled to −20 °C, and 115 mg (0.982 mmol) of anhydrous NMO and 160 mg (1.7 mmol) of norbornadiene were added to the system. After 4 h of stirring at that temperature, the reaction was complete. The mixture was filtered through Celite and purified by column chromatography to give 25 mg (34%) of **13d**. HPLC analysis: 109.6 min (88.6%); 116.6 min (11.4%). IR (film): ν_{max} 1680, 1580 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, major diastereomer): δ 0.80−0.95 (m, 1H), 1.05−1.15 (m, 1H), 1.20−1.30 (m, 1H), 1.80−2.10 (m, 4H), 2.47 (br, 2H), 2.82 (s, 1H), 3.15 (dd, J = 6.4, 5.0 Hz, 2H), 3.34 (dd, J = 6.4, 2.2 Hz, 2H), 4.20 (br, 2H), 4.40−4.50 (m, 4H), 5.88 (d, J = 3.3 Hz, 1H), 6.14−6.20 (m, 1H), 6.21−6.25 (m, 1H), 7.20−7.40 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$, major diastereomer): δ 26.5 ($2CH_2$), 41.1 (CH_2), 43.6 (CH), 44.2 (CH), 44. 5 (CH), 51.5 (CH), 57.7 (2CH), 70.7 ($2CH_2$), 73.1 ($2CH_2$), 127.5 (2CH), 127.6 (4CH), 128.3 (4CH), 130. 7 (CH), 136.2 (CH), 138.4 (CH), 138.4 (Cq), 148.9 (2Cq), 205.9 (Cq). MS (CI-NH_3) [*m*/*z* (relative intensity)]: 456 (M^+ + 1, 100%). HRMS (CI, butane): calcd for $C_{30}H_{34}NO_3$ [MH^+] 456.2539, found 456.2475.

(±)-(1*R,2*S**,6*S**,7*S**)-4-[*trans*-2,5-Bis(benzyloxymethyl)pyrrolidino]tricycl o[5.2.1.0^{2,6}]dec-4-en-3-one, 14d. Thermal Reaction at −21 °C.** The general procedure was followed by starting from 141 mg (0.41 mmol) of $Co_2(CO)_8$ in 5 mL of pentane and 170 mg (0.41 mmol) of **7d**. After desilylation, 130 mg (0.21 mmol, 51%) of complex **12d** was obtained as a green oil. This complex was dissolved in 5 mL of toluene, the mixture was cooled to −21 °C and 197 mg (2.1 mmol) of norbornene was added to the system. After 7 d of stirring at −21 °C, the mixture was filtered through a pad of Celite and purified by column chromatography to give 47 mg (49%) of **14d** as a colorless oil. HPLC analysis (Nucleosil 120 C-18, 20 cm, MeOH/H_2O, 70/30, 1.0 mL/min): 121.5 min (90.1%); 128.5 min (9.9%).

***N*-Oxide Promoted Reaction at −21 °C.** If one starts from 159 mg (0.466 mmol) of $Co_2(CO)_8$ in 5 mL of pentane and 190 mg (0.466 mmol) of **7d**, 143 mg (0.23 mmol, 49%) of the desilylated complex was obtained. This complex was dissolved in 6 mL of dichloromethane, the solution was cooled to −21 °C, and 161 mg (1.38 mmol) of anhydrous NMO and 216 mg (2.3 mmol) of norbornene were added to the system. After 6 h of stirring at that temperature, the reaction was complete. The mixture was filtered through a pad of Celite and purified by column chromatography to give 47 mg (45%) of **14d**. HPLC analysis: 121.5 min (87.2%); 128.5 (12.8%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.80−1.00 (m, 2H), 1.10−1.30 (m, 2H), 1.50−1.60 (m, 2H), 1.75−2.10 (m, 6H), 2.10−2.45 (m, 2H), 3.12 (dd, J = 9.3, 7.5 Hz, 2H), 3.35 (dd, J = 7.5, 3.6 Hz, 2H), 4.20 (br, 2H), 4.40−4.50 (m, 4H), 5.85 (d, J = 4.0, 1H [major]), 7.20−7.40 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$, major diastereomer): δ 26. 5 ($2CH_2$), 28.3 (CH_2), 28.9 (CH_2), 30.9 (CH_2), 39.1 (CH), 39.3 (CH), 45.7 (CH), 53.6 (CH), 57.7 (2CH), 70.3 ($2CH_2$), 73.1 ($2CH_2$), 127.5 (2CH), 127. 6 (4CH), 128.3 (4CH), 130.5 (CH), 138.5 (Cq), 148.0 (2Cq), 206.2 (Cq). MS (CI-NH_3) [*m*/*z*

(relative intensity)]: 458 ($M^+ + 1$, 100%). HRMS (CI, butane): calcd for $C_{30}H_{36}NO_3$ [MH^+] 458.2695, found 458.2714.

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Supporting Information Available: ^{13}C NMR spectra of compounds **3a**−**f**, **10a**,**b**, **11a**, **13a**−**d**, and **14b**−**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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