Fluoride Ion in Group 6 Metal Carbonyl Chemistry: An Unexpected Promoter of Carbonylative Insertions in Organic and Organometallic Enynes

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Summary: Ready carbonylative cycloadditions were observed in the protodesilylation of (((trimethylsilyl)-alkynyl)(diallylamino)carbene)metal complexes mediated by fluoride ions. A study of the ability of this ion to activate the "$(CO)_5M$" fragments for an efficient carbonylative insertion process was carried out and extended to organic enynes.

Recently, we reported an intramolecular Pauson–Khand reaction involving alkynyl(allylamino)carbene complexes under very mild conditions.[1] Unexpectedly, this reaction failed to give the corresponding cycloadduct when Me₃Si was attached to the alkyne moiety,[2] in spite of the high yields of cycloadducts from (trimethylsilyl)acetylene derivatives in the conventional Pauson–Khand reaction reported by previous authors.[3] This case was of special interest for our study as an alternative to Fischer carbene complexes of terminal alkynes which have only been prepared very recently in some particular cases.[4] As depicted in Scheme I, we tried to circumvent that failure by protodesilylation of the original tungsten complex **1a** using the Magnus procedure[3b] to generate *in situ* the parent ethynyl(allylamino)carbene analog prior to the addition of Co₂(CO)₈. Surprisingly, under the reported reaction conditions, we obtained the desilylated complex **1e** (30%) together with cycloadduct **2a** (10%). To gain insight into the course of this reaction, the carbonylative cycloaddition was disassembled from desilylation by changing the fluoride concentration (0.5 equiv of KF·2H₂O/BzEt₃NCl) and lowering the reaction temperature (rt). Thus, complex **1e** could be obtained in almost quantitative yield (93%). This product proved to be stable under these reaction conditions and was *only transformed* into a 2/1 mixture of **2a** and **3a**[5] after refluxing in THF (22% conversion in 24 h).[6] When, in a separate experiment, the aforementioned fluoride system was added to the complex **1e** in refluxing THF, a remarkable improvement in the yield of these compounds (**2a** and **3a**) was observed (41% after only 30 min).

Scheme I
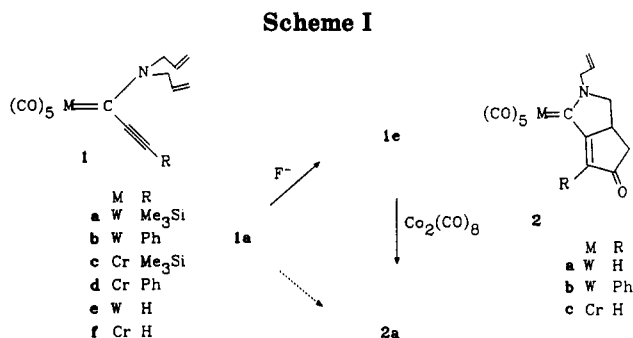
Since this yield could not be improved after many changes and the original complex had disappeared in all cases, we concluded that the cycloaddition should have been promoted by [(CO)₅WF]⁻ formed from breakage of the starting carbene complex by the added fluoride, in analogy with similar halide-promoted reactions on carbene complexes already reported by Fischer *et al.*[7] This species should promote the enyne carbonylation and insertion required to give the corresponding cycloadducts **2a** and **3a**.[5] The slower process (in the absence of fluoride) was thought to be triggered by thermal generation of (CO)₅-W·THF, as confirmed recently by Hoye et al. in a related cycloaddition with organic enynes.[8]
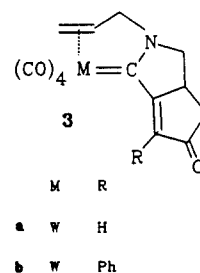
The extension of this reaction to the phenyl analog **1b** gave similar results. However, due to the higher stability of this complex, reflux of its THF solution for 24 h led only to the recovery of unchanged starting material, while in the presence of KF·2H₂O/BzEt₃NCl it gave a 30% yield of the cycloadducts **2b** and **3b** (1/3) after 15 h. As expected, other halides were also active in the present reaction: LiBr afforded a 23% yield of cycloadducts after 11 h while LiCl gave only a 9% yield after 2 days.

The role played by the fluoride ion in promoting enyne carbonylation is not only confined to tungsten derivatives, as revealed by the transformation of chromium complex

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(1) Camps, F.; Moretó, J. M.; Ricart, S.; Viñas, J. M. *Angew. Chem., Int. Ed. Engl.* 1991, *30*, 1470.

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

(3) (a) Magnus, P.; Principe, L. M.; Slater, M. J. *J. Org. Chem.* 1987, *52*, 1483–1486. (b) Magnus, P.; Exon, C.; Albaugh-Robertson, P. *Tetrahedron* 1985, *41*, 5861–5869. (c) Magnus, P.; Becker, D. P. *J. Am. Chem. Soc.* 1987, *109*, 7495–7498. (d) Kraff, M. E.; Juliano, C. A.; Scott, I. L.; Wright, C.; McEachin, M. D. *J. Am. Chem. Soc.* 1991, *113*, 1693–1703.

(4) Rahm, A.; Wulff, W. D.; Rheingold, A. L. *Organometallics* 1993, *12*, 597.

(5) The spectroscopic data for this type of tetracarbonyl adducts reveal the presence of two stereoisomers. The origin of this phenomenon is under study.

(6) Desilylated complex **1e** gave the Co₂(CO)₈-induced carbonylative cycloaddition, *under mild conditions*, to **2a** in 73% yield.[1]

(7) Fischer, E. O.; Schmid, K. R.; Kalfbus, W.; Kreiter, C. G. *Chem. Ber.* 1973, *106*, 3893.

(8) (a) Hoye, T. R.; Suriano, J. A. *Organometallics* 1992, *11*, 2044. (b) Hoye, T. R.; Suriano, J. A. *J. Am. Chem. Soc.* 1993, *115*, 1154.

1c under the mentioned protodesilylation conditions: among a variety of products, the major one was the cycloadduct 2c (20%). However, in this case, although the desilylated intermediate complex 1f was spectroscopically detected, it could not be isolated due to its high instability. Surprisingly, the more stable phenyl analog 1d did not give any cycloadduct but a 90% yield of the complex 4a. Apparently, the recognized higher ability of
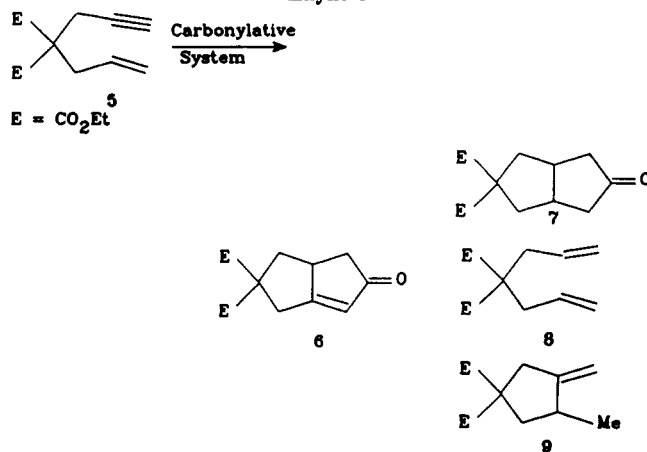

M	R
a	Cr	Ph
b	W	Ph
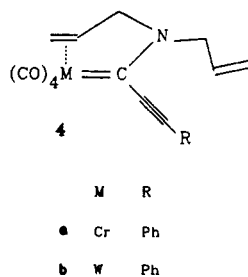
chromium to dissociate a cis carbonyl[9] precluded further carbonylative cycloaddition by the formation of this chelated species which, presumably, is unable to be cleaved by the presence of halide ions to give the required [(CO)₅CrX]⁻ fragments (or thermally to release "(CO)₅Cr" units).

In accord with our assumption, both types of fragments, independently generated, succeeded in performing the carbonylative cycloaddition: (CO)₅W·THF[10] and [(CO)₅WF]⁻Bu₄N⁺ generated from (CO)₆W[11] accomplished the original cycloaddition when applied to complex 1b in refluxing THF, giving 35% of 3b after 12 h and 40% of 2b + 3b (3/1) after 1 h, respectively. There may be an objection that the present yields are low when considering the optimum conditions imposed for the reaction. We give two reasons for these results: the high temperatures required by the reaction, which may cause complex degradation, and, in addition, the transformation of the original promoters into unreactive (CO)₆M by substraction of a CO from the starting carbene complex. A parallel experiment without the presence of these carbonylating agents did not produce any cycloadduct, and instead, almost all the starting complex could be recovered as a 8/2 mixture of 1b and 4b.

While (CO)₅Cr·THF was already reported by Aumann et al. to promote the catalytic carbonylative cyclodimerization of allenes,[12] and as indicated above, the tungsten analog was applied to the carbonylative cycloaddition of organic enynes,[8] to our knowledge, there is no precedent for our [(CO)₅MX]⁻ systems in such a class of reactions. Consequently, we decided to apply this anionic system to organic enynes with the hope that the higher thermal stability of these substrates would avoid its decomposition and, therefore, a higher yield of the corresponding cycloadducts might be obtained.

According to our expectations, treatment of enyne 5, in refluxing THF, with in situ generated Bu₄N[(CO)₅WF]

(9) (a) Casey, C. P.; Cesa, M. C. *Organometallics* 1982, *1*, 87. (b) Connor, J. A. *Top. Curr. Chem.* 1977, *71*, 71.

(10) (CO)₅Cr·THF was also shown to be active in this reaction (12% of cycloadduct with a substantial portion of the starting product being recovered). The inherent high instability of the "(CO)₅Cr" fragment was considered to be responsible for this lower yield (see also Table I, entry 5).

(11) (CO)₅W·THF: Wrighton, M. *Chem. Rev.* 1974, *74*, 401. Bu₄N[(CO)₅WF]: Abel, E. W.; Butler, I. S.; Reid, J. G. *J. Chem. Soc.* 1963, 2068.

(12) Aumann, R.; Uphoff, J. *Angew. Chem., Int. Ed. Engl.* 1987, *99*, 361.

Table I. Reactions of Different Carbonylative Systems with Enyne 5

entry no.	carbonylative syst[a]	time (h)	yield of 6 (%)	other products (yield, %)
1	Bu₄N[(CO)₅WF]	1	56	7 (8), 8 (10) 9 (7)
2	Bu₄N[(CO)₅CrF]	3	10	8 (36)
3	K(DB18C6)[(CO)₅CrF]	4	59	traces
4	K(DB18C6)[(CO)₅WF]	7	52	traces
5	(CO)₅Cr·THF	12	22[b]	not detected

[a] The present carbonylative systems have been generated *in situ* by following known procedures.[11,15] [b] 66% of the starting enyne was recovered.

gave 56% of the expected diquinane derivative 6 together with three minor reduction products (see Table I, entry 1).

The corresponding chromium system gave predominantly reduction of the substrate (entry 2). We attributed this result to a higher reducing activity of the chromium complex in relation to that of the tungsten analog[13] (insertion into the triple bond and further hydride transfer caused by the presence of water from the salt[14]). To circumvent this difficulty, we prepared an equivalent anhydrous system[15] which was able to accomplish the carbonylative cycloaddition of the starting enyne with minimal reduction (entry 3). Conversely, the tungsten system, although it behaved similarly, required longer reaction times (entry 4). In view of the remarkable activity exhibited by these chromium complexes we decided to check the assumed absence of carbonylative cycloaddition from the enyne 6 and the (CO)₅Cr·THF system.[8] Unexpectedly, we obtained a 22% yield of carbonylated adduct but the reaction did not go to completion (entry 5), since most of the starting enyne remained unchanged even after extended reaction times. Therefore, it seems that the lower performance of chromium in this type of reaction might only arise from the higher instability of the "(CO)₅Cr" that would readily decompose to a considerable extent before being able to coordinate the substrate.

At this point, a clear conclusion with respect to the role played by fluoride ion (either as stabilizing agent of the active "(CO)₅M" fragments or carbonylation and/or insertion promoter) cannot be advanced. However, from comparative results shown in Table I (entries 3 and 5) and those obtained by Hoye et al., the fluoride system, apart from its higher stability and easier generation, leads to a

(13) Herndon, J. W.; Turner, S. U. *Tetrahedron Lett.* 1989, *30*, 295.

(14) In a parallel experiment enyne 5 was treated with (CO)₆Cr and 3 equiv of H₂O in refluxing THF. After a long period (24 h) no products from reduction could be observed. We think that, in that case, the reported reduction was due to the presence of the "(CO)₅Cr" fragment.

(15) Cihonski, J. L.; Levenson, R. A. *Inorg. Chem.* 1975, *14*, 1717.

better control of the reaction product (cycloaddition *vs* reduction) by modulation of the metal and counterion in shorter reaction times. Further studies along these lines are currently under way in our laboratories.

Supplementary Material Available: Text giving spectral and analytical data for compounds 1d,e, 2a,c, 3a,b, and 4a (3 pages). Ordering information is given on any current masthead page.

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