# Bis(cyclopentadienyl)tetracarbonyldimolybdenum-alkyne Complexes Mediated [2 + 2 + 1] Cycloaddition: the Formation of 3-Substituted Cyclopentenone Derivatives

**Chisato Mukai, Masahiko Uchiyama and Miyoji Hanaoka***

*Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920, Japan.*

On heating, bis(cyclopentadienyl)tetracarbonyldimolybdenum-alkyne complexes undergo a [2 + 2 + 1] cycloaddition with norbornadiene or norbornene to afford the corresponding 3-substituted cyclopentenone derivatives, which could hardly be obtained in the cobalt-complexed alkyne-mediated Pauson–Khand reaction.

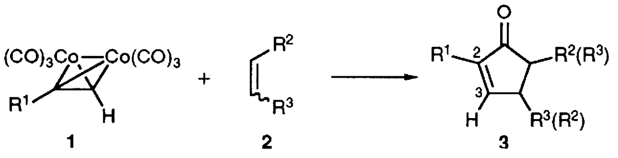
The Pauson–Khand reaction[1] is a formal [2 + 2 + 1] cycloaddition of alkynes, alkenes and carbon monoxide through hexacarbonyldicobalt-alkyne complexes **1**. This useful cyclopentenone formation reaction has been successfully applied to the synthesis of various natural products.[2]

In an intermolecular Pauson–Khand reaction,[1] the substituted terminals of the cobalt-complexed alkynes **1** are exclusively incorporated at the C-2 position of the resulting cyclopentenone derivatives **3**. However, no report† dealing with the extension of the method to the formation of 3-substituted cyclopentenone derivatives in a Pauson–Khand type reaction has so far been made. We describe a novel method for production of the 3-substituted cyclopentenone derivatives mediated by molybdenum-alkyne complexes.

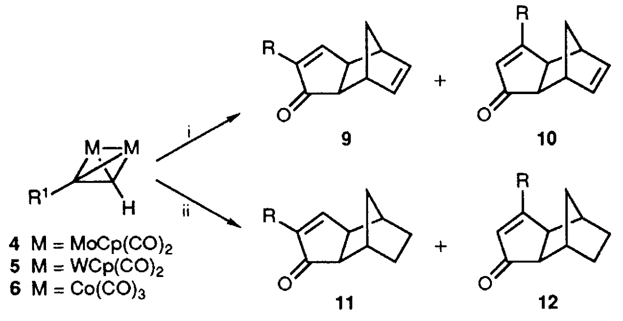
Bis(cyclopentadienyl)tetracarbonyldimolybdenum-alkyne complexes **4**, isoelectronic compounds of hexacarbonyldicobalt congeners **6**, were prepared according to the literature.[3] The molybdenum-alkyne complex **4a** was heated under reflux with norbornadiene **7** in toluene under a nitrogen atmosphere for 6 h to give, after chromatographic separation, the 2-phenylcyclopentenone derivative **9a** and the 3-phenyl derivative **10a** in 45 and 32% yields, respectively. The former was identified with an authentic sample[4] obtained from the reaction of **6** with norbornadiene. The 3-phenyl derivative **10a** showed a diagnostically higher field shifted vinylic proton at δ 6.61 in its $^1H$ NMR spectrum.‡ The *endo*-structure for **10a** could be easily ruled out by comparing its spectroscopic data with those of the corresponding *endo*-adduct[5] in the literature. *p*-Methylphenyl and n-butyl derivatives **4b** and **c** also afforded the 'abnormal' 3-substituted adducts **10b** and **c** along with the 'normal' Pauson–Khand products **9b** and **c**.§ However, the molybdenum complexed trimethylsilylacetylene **4d** produced only 'normal' Pauson–Khand product **9d**§ in 39% yield. The results are summarised in Table 1.

When an isoelectronic tungsten complex **5a**[6] was submitted to the [2 + 2 + 1] cycloaddition reaction with norbornadiene, cycloadducts **9a** and **10a** were obtained, but the ratio of **10a** to **9a** was significantly decreased. Although the desired 3-substituted cyclopentenones **12** were consistently formed in the reaction of **4** with norbornene **8**, the yields were rather lower compared with the case of norbornadiene.

The molybdenum-alkyne complex was found to be effective for intramolecular cyclisation as well. The complex **13** prepared from diethyl allylpropynylmalonate was heated under reflux in toluene for 8 h under nitrogen to give the bicyclo[3.3.0]octene derivative **14** in 50% yield.

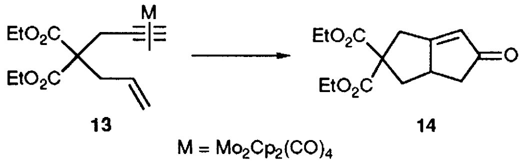


**Scheme 1** $R^1$, $R^2$, $R^3$ = alkyl, aryl, TMS, alkylthio etc.



**a** R = Ph, **b** R = *p*-Me–$C_6H_4$, **c** R = Bu, **d** R = $SiMe_3$

**Scheme 2** *Reagents:* i, norbornadiene **7**; ii, norbornene **8**



**Scheme 3**

**Table 1** [2 + 2 + 1] Cycloaddition of metal-complexed alkynes with alkenes

| Complexed alkyne | Cycloadduct (%) | |
|---|---|---|
| | 2-Substituted | 3-Substituted |
| **4a**[a,c] | **9a** (45) | **10a** (32) |
| **4b**[a,c] | **9b** (31) | **10b** (25) |
| **4c**[a,c] | **9c** (28) | **10c** (20) |
| **4d**[a,c] | **9d** (39) | — |
| **5a**[b,c] | **9a** (33) | **10a** (3) |
| **4a**[b,d] | **11a** (5) | **12a** (3) |
| **4c**[b,d] | **11c** (18) | **12c** (11) |

[a] Refluxed in toluene. [b] Heated in toluene at 160 °C in a sealed tube. [c] With norbornadiene. [d] With norbornene.

---

† Krafft[7] has recently isolated and characterised 3-methyl-[2-(phenylthio)ethyl]-2-cyclopentenone in 2–3% yield along with the 2-methyl congener (65%) in the reaction of the cobalt-complexed propyne with homoallylphenylsulfide. Pauson[1c] also reported the formation of trace amounts of the 3-substituted cyclopentenone derivatives without any characterisation of their structures.

‡ The vinylic proton of the 2-phenyl derivative **9a** appeared at δ 7.69 in its $^1H$ NMR spectrum which was shifted 1.08 ppm downfield from the vinylic proton of **10a**. This observation corroborates the 3-phenyl substituted structure for **10a**.

§ The 2-substituted cyclopentenone derivatives were identified with the authentic specimen prepared by using the cobalt-complexed alkynes. In all cobalt-complexed alkyne mediated experiments we examined, no 3-substituted products could be detected by thin-layer chromatography.

In summary, we describe the first practical example† of the formation of an 'abnormal' 3-substituted cyclopentenone derivative in a Pauson–Khand type reaction using bis(cyclopentadienyl)tetracarbonyldimolybdenum-alkyne complexes **4**, although their reactivity and regioselectivity are not satisfactory yet. Further studies on optimising the reaction conditions for exclusive production of the 3-substituted cyclopentenones as well as improvement of the reactivity are now in progress.

*Received, 21st April 1992; Com. 2/02024F*

## References

1 For reviews see: (*a*) N. E. Schore, *Org. React.*, NY, 1991, **40**, 1; (*b*) P. L. Pauson, *Organometallics in Organic Synthesis. Aspects of a Modern Interdisciplinary Field*, ed. A. de Meijere and H. tom Dieck, Springer, Berlin, 1988, p. 233; (*c*) P. L. Pauson, *Tetrahedron*, 1985, **41**, 5855; (*d*) P. L. Pauson and I. U. Khand, *Ann. NY Acad. Sci.*, 1977, **295**, 2.

2 For examples see: M. E. Krafft and C. Wright, *Tetrahedron Lett.*, 1992, **33**, 151; J. Castro, H. Sorensen, A. Riera, C. Morin, A. Moyano, M. A. Pericas and A. E. Greene, *J. Am. Chem. Soc.*, 1990, **112**, 9388; M. E. Price and N. E. Schore, *Tetrahedron Lett.*, 1989, **30**, 5865; *J. Org. Chem.*, 1989, **54**, 5662; N. E. Schore and E. G. Rowley, *J. Am. Chem. Soc.*, 1988, **110**, 5224; P. Magnus, L. M. Principe and M. J. Slater, *J. Org. Chem.*, 1987, **52**, 1483; P. Magnus, C. Exon and P. Albaugh-Robertson, *Tetrahedron*, 1985, **41**, 5861; C. Exon and P. Magnus, *J. Am. Chem. Soc.*, 1983, **105**, 2477.

3 J. A. Beck, S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 195.

4 I. U. Khand, G. R. Knox, P. L. Pauson and W. E. Watt, *J. Chem. Soc., Perkin Trans. 1*, 1973, 975; I. U. Khand, G. R. Knox, P. L. Pauson, W. E. Watt and M. I. Foreman, *J. Chem. Soc., Perkin Trans. 1*, 1973, 977.

5 T. Ogino, K. Awano and Y. Fukazawa, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1735.

6 D. S. Ginley, C. R. Bock and M. S. Wrighton, *Inorg. Chim. Acta*, 1977, **23**, 85.

7 M. E. Krafft, C. A. Juliano, I. L. Scott, C. Wright and M. D. McEachin, *J. Am. Chem. Soc.*, 1991, **113**, 1693.