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Heterobimetallic (Co–W) intermolecular Pauson–Khand reactions: scope and selectivity

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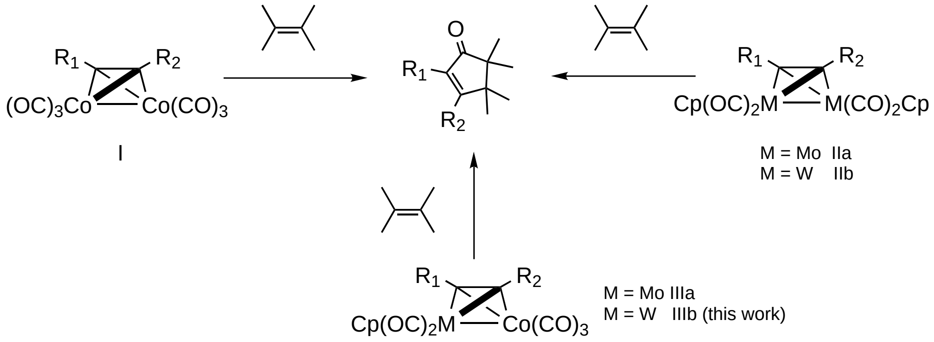
Abstract—Heterobimetallic μ-alkyne complexes [η^5-Cp(CO)$_2$W(μ-R^{1}C$_2$R^2)Co(CO)$_3$] are suitable substrates for the intermolecular Pauson–Khand reaction. They can be obtained in higher yields than the corresponding Mo–Co complexes, and the reaction with norbornadiene of those derived from several 2-butynoates offers a convenient way to the preparation of *endo*-fused, 1,3-dicarbonyl cyclopentenone adducts. © 2002 Elsevier Science Ltd. All rights reserved.

The cobalt-mediated cyclization between an alkyne, an alkene and carbon monoxide, known as the Pauson–Khand reaction, has become one of the preferred methods for the synthesis of cyclopentenones due to its convergent nature, to its broad applicability and to its high degree of regio- and stereoselectivity.[1] In addition to alkyne dicobalt(hexacarbonyl) complexes I, other stable dinuclear alkyne complexes[2] derived from Mo and W (IIa, IIb) have been shown to undergo the same type of reaction (Scheme 1).[3]

Work from the laboratory of Christie,[4] and more recently, from our own research group,[5] has demonstrated that heterobimetallic (Mo–Co) alkyne complexes IIIa are suitable substrates for the Pauson–Khand reaction, and that the chirality of these mixed metal alkyne complexes can be used to impart a high degree of stereoselectivity to the process. We have also found that in some instances the normal regio- and stereochemical course of the intermolecular Pauson–Khand reaction can be diverted by complexes IIIa.[5] On the other hand, heterobimetallic μ-alkyne cluster complexes IIIb of general formula [η^5-Cp(CO)$_2$W(μ-R^{1}C$_2$R^2)Co(CO)$_3$] have been known for some time,[6] but their reactivity has not been studied. We decided therefore to prepare a representative set of these compounds in order to explore their applicability to the intermolecular Pauson–Khand reaction. We report in this paper the results of this study, that has shown that the mixed W–Co present several advantages with respect to their Mo–Co counterparts.



Scheme 1. Use of different dinuclear alkyne complexes in the Pauson–Khand reaction.

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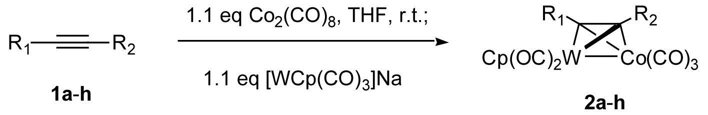
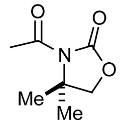
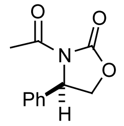
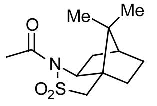
Table 1. Preparation of heterobimetallic (W–Co) complexes of alkynes



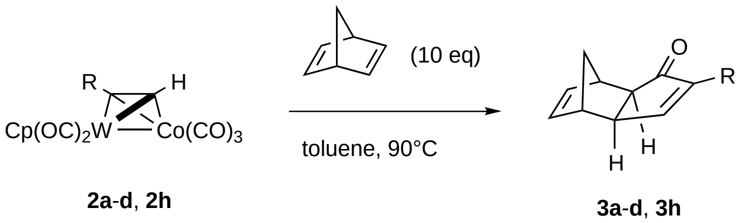
alkyne	R_1	R_2	temper ture; reaction time	complex; yield (%)[a]
1a	*n*-Bu	H	r.t.; 24 h	**2a**; 69 [61]
1b	$Me_2(OH)C$	H	reflux; 2.5 h	**2b**; 12
1c	Ph	H	reflux; 1.5 h	**2c**; 84 [58]
1d	Ph	Ph	reflux; 1.5 h	**2d**; 97 [65]
1e		Me	reflux; 15 min	**2e**; 54 [49]
1f		Me	reflux; 15 min	**2f**;[b] 60 [43]
1g		Me	reflux; 20 min	**2g**;[c] 62 [64]
1h	$-(CH_2)_4-$	H	reflux; 2.5	**2h**; 43

[a] Yields in brackets are those of the corresponding Mo–Co complexes (see refs. 4,5). b) Obtained as a 2.6:1 diastereomer mixture (a 2.3:1 d.r. was observed for the Mo–Co complex). c) Obtained as a 1.2:1 diastereomer mixture (same d.r. for the Mo–Co complex).

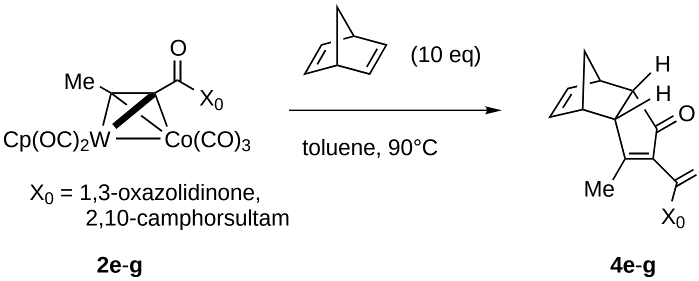
The heterobimetallic W–Co alkyne complexes **2a**–**h** were obtained from acetylenes **1a**–**h** by a one-pot procedure involving treatment of a THF solution of the alkyne with a slight excess of dicobalt(octacarbonyl) at room temperature followed by addition of a preformed solution of $[WCp(CO)_3]Na$, generated by heating to reflux a mixture of sodium cyclopentadienide and of $W(CO)_6$ in anhydrous THF. In this way, the W–Co complexes **2a**–**h** were isolated, after chromatographic purification, in yields that were in most instances substantially higher than those previously obtained for the corresponding Mo–Co complexes (Table 1). Reaction times for the formation of **2a**–**h** were also appreciably shorter than those required for the preparation of the Mo–Co complexes.[4,5] Complex **2b**, derived from 1,1-dimethyl-1-propynol was obtained in very low yield, probably for steric reasons. When the starting alkyne is chiral (as in the case of **1f** and **1g**), the two $Co(CO)_3$ groups of the homobimetallic Co–Co complex are diastereotopic, so that their substitution by a $WCp(CO)_2$ moiety can give rise to a pair of diastereomeric heterobimetallic complexes. Thus, **2f** was obtained as a 2.6:1 diastereomer mixture, that could be readily separated by standard column chromatography. On the other hand, **2g** was obtained as a 1.2:1 inseparable mixture of diastereomers. Finally, it is worth noting that starting from octadiyne **1h**, the double complex **2h** was isolated in 43% yield as a chromatographically homogeneous compound that showed a single set of signals in the ^{13}C NMR spectrum. All of the complexes were dark orange-colored solids or oils, stable for extended periods of time when kept under an inert atmosphere. Complexes **2e**–**g** were somewhat less stable and they decomposed readily in solution.[7]

We examined next the Pauson–Khand reactivity of these complexes by heating them in toluene in the presence of 10 molar equiv. of norbornadiene until no starting complex remained (TLC monitoring). The results obtained are summarized in Schemes 2 and 3 and in Table 2.[8]

The heterobimetallic W–Co complexes exhibited the dual behavior that we had previously observed for the corresponding Mo–Co complexes.[5] Those derived from alky-



Scheme 2. Intermolecular Pauson–Khand reactions of heterobimetallic W–Co complexes **2a–d** and **2h**, leading to *exo*-fused adducts.



Scheme 3. Intermolecular Pauson–Khand reactions of heterobimetallic W–Co complexes **2e–g**, leading to *endo*-fused adducts.

nes **1a–d** and **1h** gave rise to the expected *exo*-fused adducts **3**, while those derived from the 2-butynoates **1e–g**[9] led mainly to the formation of anomalous *endo*-fused, 1,3-dicarbonyl adducts **4** (see Schemes 2 and 3). It is thus clear that this reversal in the regio- and stereochemical course of the Pauson–Khand reaction is not limited to the heterobimetallic Mo–Co complexes. The *exo*-fused adducts **3** arising from monosubstituted alkynes **1a–c** and **1h** were obtained with complete regioselectivity and (with the exception of complex **2b**, that reacted sluggishly; see entry 2 of Table 2) in good yields. Complex **2d**, derived from diphenylacetylene (entry 4), also showed a decreased reactivity but afforded the expected *exo*-fused adduct **3d** with a remarkable 66% yield (a 60% yield has been reported[4] for the Mo–Co complex).

Table 2. Intermolecular Pauson–Khand reactions of heterobimetallic complexes **2a–h** with norbornadiene

Entry	Starting complex	Reaction time (h)	Adduct; yield (%)
1	**2a**	3	**3a**; 90
2	**2b**	24	**3b**; 40
3	**2c**	2	**3c**; 70
4	**2d**	48	**3d**; 66
5	**2e**	2	**4e**; 65[a]
6	**2f** (major isomer)	2	**4f**; 92 (4.8:1)[b]
7	**2g** (isomer mixture)	2	**4g**; 30 (>10:1)[b,c]
8	**2h**	2	**3h**; 70

[a] The *exo*-1,3-dicarbonyl and the *exo*-1,4-dicarbonyl adducts were also isolated in 8 and 7% yields, respectively.

[b] Diastereomer ratio calculated by ^{13}C NMR of the reaction mixture.

[c] A 13% of the *exo*-1,3-dicarbonyl adduct was also obtained.

Treatment of the 4,4-dimethyloxazolidinone-derived heterobimetallic complex **2e** with norbornadiene afforded as the main reaction product the *endo*-fused, 1,3-dicarbonyl adduct **4e** in an isolated 65% yield (entry 5). The unusual structure of this compound had been previously established by means of X-ray diffraction analysis.[5] The most relevant differences in reactivity with respect to the Mo–Co complexes were found in the case of **2f** (entry 6). The major isomer of **2f** reacted readily with norbornadiene, affording the *endo*-adduct **4f** as the sole isolated product in an excellent 92% yield, and with a 4.8:1 diastereomer ratio. Since the two diastereomers can be separated by column chromatography, stereoisomerically pure **4f** can be easily accessed by this procedure. The corresponding Mo–Co complex gave **4f** (4:1 diastereomer ratio) in a much lower yield (24%), together with the *exo*-adducts (regioisomer mixture, 18% yield).[5] On the other hand, attempted reaction of the minor isomer of **2f** resulted only in the total decomposition of the complex. Thus, **4f** can be obtained directly from the isomer mixture of **2f**, so that its preparation from **1f** is more convenient via the W–Co than via the Mo–Co complex. In a somewhat similar way, only one isomer of **2g** appeared to react with norbornadiene (entry 7) to give the *endo*-adduct **4g** as the major (but not exclusive) product with excellent diastereoselectivity, albeit in modest yield (30%). Essentially the same results were obtained in this case with the Mo–Co complex.[5]

In summary, we have shown for the first time that the readily accessible heterobimetallic [Cp(CO)$_2$WCo(CO)$_3$](μ-alkyne) complexes are useful substrates for the intermolecular Pauson–Khand reaction. Further studies and applications of these complexes are being pursued in our laboratory.

Acknowledgements

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7. General procedure for the preparation of heterobimetallic (W–Co) complexes: To a stirred solution of $W(CO)_6$ (14.2 mmol) in anhydrous THF (40 mL), under an Ar atmosphere, a 2.0 M THF solution of sodium cyclopentadienide (7.8 mL) was added dropwise, and the mixture was heated to reflux overnight. Once cooled, the resulting yellow solution was added dropwise to a stirred solution of the alkyne–dicobalt hexacarbonyl complex (10.9 mmol, 0.1 M in THF), prepared by reaction of the alkyne with a slight excess (12.0 mmol) of dicobalt octacarbonyl at room temperature for 1–2 h. The mixture was stirred at room temperature or heated to reflux until TLC showed that no dicobalt complex remained. After elimination of the solvent at reduced pressure, the crude product was purified by column chromatography on silica gel, eluting with hexane–ethyl acetate mixtures.
8. General procedure for the Pauson–Khand reaction of the heterobimetallic (W–Co) alkyne complexes: To a stirred solution of the complex (3.5 mmol) in anhydrous toluene (40 mL), under Ar atmosphere, norbornadiene (3.64 g, 34.6 mmol) was added in one portion, and the mixture was heated at 90°C until TLC showed the complete disappearance of the starting complex. After cooling, the reaction mixture was filtered through a short Celite® pad to remove the metallic residues. Elimination of the solvents at reduced pressure gave the crude product that was purified by column chromatography on silica gel, eluting with hexane–ethyl acetate mixtures. Spectral data of the adducts **4a**–**g** were coincident with those described in the literature.[5,10] Spectral data for **4h**: ^1H NMR (300 MHz, $CDCl_3$): $\delta=6.35$ (m, 2H), 6.30 (m, 2H), 6.00 (m, 2H), 2.80–2.60 (m, 4H), 2.40–2.20 (m, 6H), 1.80–1.20 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=209.7$ (C_q), 158.9 (CH), 150.4 (C_q), 138.4 (CH), 137.0 (CH), 52.5 (CH), 47.6 (CH), 43.6 (CH), 42.9 (CH), 41.1 (CH_2), 27.6 (CH_2), 24.7 (CH_2).
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