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A simple method for the preparation of heterobimetallic alkyne complexes

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Abstract—A new, faster and cleaner method for the synthesis of heterobimetallic alkyne complexes is reported. Higher yields than previously obtained are achieved and in some cases moderate stereoselectivity has also been observed.

The use of bimetallic alkyne complexes has been prevalent in the literature for more than 30 years. Initially investigated for their structural attributes, they are now more commonly exploited for their unique reactivity. In this respect, the Pauson–Khand[1] and Nicholas[2] reactions are the most familiar reactions that employ these complexes. Bis-cobalt complexes continue to be the most accessible structures, however, in recent years other metals have seen some use. In this regard, we introduced the heterobimetallic cobalt–molybdenum species as Pauson–Khand substrates, and showed they are capable of producing a stereospecific reaction.[3] Further work has increased the scope of the reaction and highlighted some interesting regio and stereochemical issues.[4a] Very recently, the corresponding cobalt–tungsten complexes have also been subjected to the reaction, and produced similar reactivity.[4b] This paper also suggests that the tungsten analogues offer advantages over the molybdenum complexes since they can be prepared in higher yields and shorter reaction times. This paper will show an improved method for the production of the Co–Mo alkyne complexes, which circumvents these problems.

When we began work in this area, we utilised existing methodology[5] whereby the $CpMo(CO)_3$ anion is generated in situ, and then allowed to react with the bis-cobalt alkyne of choice. A nucleophilic substitution takes place to produce the product. A similar reaction also gives the tungsten analogue. Although this is a relatively simple process, it is very time consuming. The cyclopentadiene must be cracked from its dimer, then deprotonated with sodium hydride. Reaction with $Mo(CO)_6$ or $W(CO)_6$ requires overnight reflux for formation of the cyclopentadienyl metal carbonyl anion. When this is formed, reaction with the cobalt complex takes a further 1–2 h. Overall, including purification, the whole process can take 24 h. We wanted a much quicker and simpler route to these valuable complexes. In this regard, we were keen to adapt the Gladysz methodology[6] for the production of the $CpMo(CO)_3$ anion. Here, the corresponding, and commercially available, dimer $[CpMo(CO)_3]_2$ is reacted with L-Selectride to give the monomeric anion. Gladysz has shown a number of metal carbonyl dimers reacting with various electrophiles to produce the alkylated or acylated metals. We reasoned that reaction with a bis-cobalt alkyne would give the desired complexes.

Addition of L-Selectride to a solution of the dimer produced the monomeric anion in a virtually instantaneous reaction. The reaction can be followed visually since the dimer is purple and the anion is orange. We attempted to isolate the anion, but it proved too air and moisture sensitive. However, addition of a bis-cobalt alkyne produced the heterobimetallic complexes as expected (Scheme 1, Table 1).[7] In all cases, the new complex is more polar than the starting material, and the reaction can easily be monitored by TLC.

We were delighted to find that yields were comparable or higher than those already obtained for complexes we had prepared previously. However, extension of the

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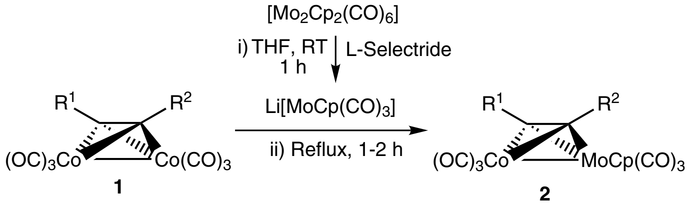


Scheme 1.

Table 1. Isolobal displacement with CpMo(CO)$_3$

R^1	R^2	Co/Mo–alkyne complex	Yield (%)
H	CH_2OH	**2a**	68 (65)[a]
H	Ph	**2b**	61 (58)[a]
H	$(CH_2)_3CH_3$	**2c**	62 (61)[a]
CH_3	CH_3	**2d**	92 (66)[a]
Ph	Ph	**2e**	89 (65)[a]
H	CH_2CH_2OH	**2f**	48
H	CH_2OMenthyl	**2g**	85 (78)[a]
H	$CH_2CH(OH)CH_2OBn$	**2h**	56
CH_3	CHO	**2i**	72
CH_3	$CH(OEt)_2$	**2i**[b]	77[b]
CH_3	$C(CH_3)CH_2$	**2j**	70
CH_3	$CH{=}CHCO_2Me$	**2k**	76
Et	$C(O)CH_3$	**2l**	54
Ph	$CH(OEt)_2$	**2m**	81
Ph	$Si(CH_3)_3$	**2n**	69
CO_2Me	CO_2Me	**2o**	51

Conditions: L-Selectride, THF, then addition of alkyne–$Co_2(CO)_6$ complex, THF, reflux, 1–2 h.

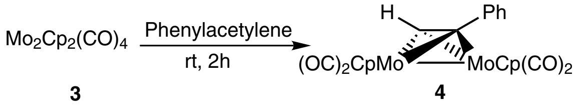
[a] Results in parentheses obtained from previous isolobal displacement methodology.[3,5]

[b] The aldehyde was isolated.

methodology has shown that functional group tolerance is also good, and we can use aldehydes, ketones, free alcohols and esters as shown in Table 1. The only problem case was using propargyl bromide, although it is unclear whether this is due to nucleophilic substitution of the bromide or to in situ Nicholas propargylic cation formation.

It is believed that the increases in yield are due to the more efficient conversion of the molybdenum cyclopentadienyltricarbonyl dimer to its corresponding salt, Li[MoCp(CO)$_3$], than when NaCp is reacted with Mo(CO)$_6$ under thermal conditions. Reactions also proceed more cleanly than before, with less degradation products being formed during the reaction. Therefore time consuming work-ups were not needed: the reaction mixture can simply be filtered through a pad of Celite and silica.

However, care needs to be taken upon scale up of the reaction due to the larger quantities of trialkyl boranes being produced. As noted by Gladysz, this can lead to a highly exothermic reaction upon filtering during the work-up of the reaction.



Scheme 2.

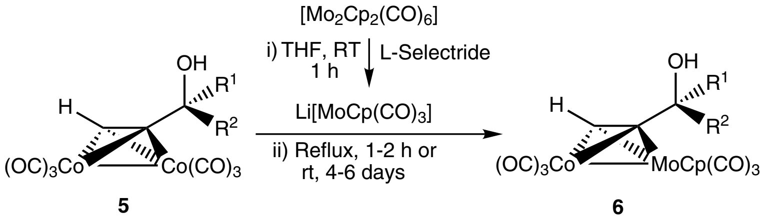
Attempts were also made at a reverse-type isolobal displacement reaction. The dimolybdenum alkyne complex **4** was formed from the triple bonded Mo–Mo species **3**.[8] Exposure of this to phenylacetylene at room temperature produced the required complex in 57% yield (Scheme 2).

Dicobalt octacarbonyl was exposed to L-Selectride, which gave a pale blue anion, compared to the yellow/orange colour seen with the corresponding Mo-dimer. Complex **4** was added to the cobalt anion and left for 1 h at ambient temperature. However, no reaction was observed even after refluxing for an extended period of time. This may be due to the relatively poor nucleophilicity of the $Co(CO_4)^-$ anion, or the increased thermodynamic stability of the Mo–Mo bond.

Our attention then turned towards investigating the applicability of this reaction in the preparation of diastereomerically enriched Co/Mo-complexes. McGlinchey and co-workers have shown[9] that camphor derived alkynols can produce a diastereoselective isolobal displacement. However, only a 2:1 ratio was obtained. Therefore the displacement was attempted on a range of simple substituted alkynols that were commercially available. Scheme 3 and Table 2 show the yield and diastereoselectivity of the reactions at room temperature and at reflux. Yields were comparable between the two sets of conditions. However, reaction times were much shorter with the higher temperature and stereoselectivities up to reasonable levels were obtained. The diastereoselectivities were easily obtained from the ^{1}H NMR spectra of the mixtures. At this point it is unclear why there is a difference in the diastereoselectivity at different temperatures, and between the substrates. However, the results have been reproduced.

We have not ruled out the possibility of epimerisation of the propargylic centre through intervention of a Nicholas carbocation during the course of the reaction.

We wondered whether the hydroxyl group was playing a key role in the displacement by directing the incoming nucleophile through prior coordination to the molybdenum anion. Substitution of the alcohol moiety for a methoxy group would inhibit any hydrogen bonding that may be influencing the stereochemistry. Scheme 4



Scheme 3.

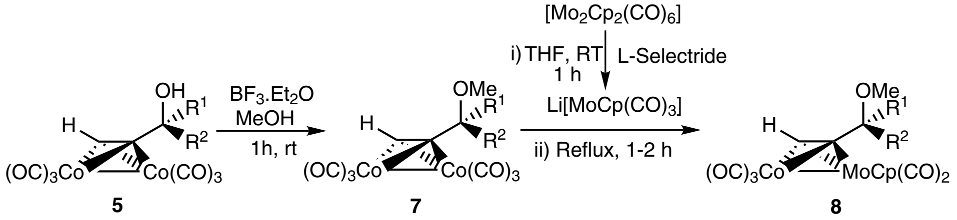
Table 2. Isolobal displacements of chiral alkynols

R^1	R^2	Conditions[a]	Co/Mo–alkyne complexes	Yield (%)	De (%)
H	Me	A	**6a**	41	33
		B	**6a**	48	36
H	^{i}Pr	A	**6b**	56[b]	74
		B	**6b**	55	6
H	Ph	A	**6c**	48[b]	30
		B	**6c**	50	71
—	Camphor[c]	B	**6d**	32	2

[a] Condition A: L-Selectride, THF, then addition of $Co_2(CO)_6$ complex, THF, rt, 4–6 d. Condition B: L-Selectride, THF, then addition of alkyne–$Co_2(CO)_6$ complex, THF, reflux, 1–2 h.

[b] Based on recovered starting material.

[c] Alkyne precursor to complex **6d** was prepared from the addition of lithium acetylide to (+)-camphor.



Scheme 4.

Table 3. Displacement of methoxy substituted complexes

R^1	R^2	Co/Co–alkyne complex	Yield (%)	Co/Mo–alkyne complex	Yield (%)	De (%)
H	Me	**7a**	88	**8a**	61	17
H	^{i}Pr	**7b**	88	**8b**	46	31
H	Ph	**7c**	89	**8c**	53	47

Conditions: L-Selectride, THF, then addition of alkyne–$Co_2(CO)_6$ complex, reflux, 1–2 h.

and Table 3 show the yields for methylation and the subsequent isolobal displacements, which were all carried out under reflux conditions.

The methoxy complexes were obtained in excellent yields via standard Nicholas reactions. In the case of the displacement reaction, yields were comparable to those obtained in the previous case, although the diastereoselectivity achieved was a little disappointing. For methyl and phenyl substituted alkynols, the diastereomeric ratio has decreased. However, for the ^{i}Pr alkynol the ratio has increased under the same conditions.

Other methods were also attempted to make stereoenriched heterobimetallic alkyne complexes. Gladysz et al.[6] proposed that there was no metal carbonyl–trialkyl borane interaction taking place, due to observed IR spectroscopy. However, when used for hydride transfer reactions, it has been noted that trialkyl borane interactions occur during the formation of anionic metal carbonyl formyl complexes.[10] It was thought that the use of a chiral borohydride reagent used during the splitting of the molybdenum dimer may help to induce chirality in the resulting bimetallic complex. For this purpose, commercially available (*R*)-alpine hydride was utilised in the same way as the Selectride reagents had been used previously. Starting with **1d**, complex **2d** was isolated in 40% yield, however, rather disappointingly, no stereoinduction was achieved.

In summary, we have illustrated a new approach to heterobimetallic alkyne complexes from commercially available starting materials in short reaction times. Generation of the anion is self-indicating, purification simple and yields good to excellent. Work is ongoing within the group to investigate the possibility of the same reaction utilising tungsten. In view of their increasing usage in Pauson–Khand reactions and as chiral auxiliaries, this method should be a valuable tool for the synthesis of these complexes.

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References and notes

1. For recent reviews of Pauson–Khand reaction, see: Brummond, K. M.; Kent, J. L. *Tetrahedron* **2000**, *56*, 3263; Fletcher, A. J.; Christie, S. D. R. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1657.
2. For a recent review of the Nicholas reaction, see: Teobold, B. *Tetrahedron* **2002**, *58*, 4133.
3. (a) Rutherford, D. T.; Christie, S. D. R. *Tetrahedron Lett.* **1998**, *39*, 9805; (b) Fletcher, A. J.; Rutherford, D. T.; Christie, S. D. R. *Synlett* **2000**, 1040.
4. (a) Rios, R.; Pericás, M. A.; Moyano, M.; Maestro, M. A.; Mahia, J. *Org. Lett.* **2002**, *4*, 1205; (b) Moyano, A.; Rios, R.; Pericás, M. A. *Tetrahedron Lett.* **2002**, *43*, 4903.
5. (a) Gruselle, M.; Malezieux, B.; Vaissermann, J.; Amouri, H. *Organometallics* **1998**, *17*, 2337; (b) Hong, F.; Lue, I.; Lo, S.; Yang, Y.; Lin, C. *Polyhedron* **1996**, 2793; (c) Manning, A.; Hacket, P.; Birdwinstell, R.; Soye, P. *Inorg. Synth.* **1990**, *28*, 148.
6. Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553.
7. Typical procedure: To a pre-dried flask was added $[CpMo(CO)_3)]_2$ (1.00 g, 2.0 mmol) and dry THF (70 mL). To this purple solution was added, dropwise, L-Selectride (5 mL, 5.0 mmol). The solution turned to an orange colour during the course of the addition. The reaction was left to stir briefly after completion of the addition. The bis-cobalt complex **1e** (1.97 g, 4.0 mmol) was added as a THF solution to the reaction mixture and the resulting solution was refluxed for 1–2 h, during which time it was monitored by TLC. Upon completion, the reaction mixture was filtered through a pad of Celite and silica and then purified further by flash silica column chromatography eluting with light petroleum–diethyl ether (10:1 v/v) to give the resulting bimetallic complex **2e** as an orange/red solid (1.94 g, 89%). IR (thin film)/cm^{-1} 3111, 3057, 3022, 2047, 2003, 1973, 1939. ^{1}H NMR (400 MHz, $CDCl_3$) 7.70–6.90 (10H, m, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) 225.4, 203.6, 142.2, 129.6, 128.6, 126.9, 91.7. Found: M$^+$, 539.9323 $C_{24}H_{15}O_5CoMo$ requires 539.9312.
8. Ginley, D. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1975**, *97*, 3535.
9. D'Agostino, M. F.; Frampton, C. S.; McGlinchey, M. J. *Organometallics* **1990**, *9*, 2972.
10. Gladysz, J. A.; Merrifield, J. H. *Inorg. Chim. Acta* **1978**, *30*, L317.