Pergamon

Tetrahedron Letters 42 (2001) 1183–1185

TETRAHEDRON
LETTERS

New stable catalysts of the Pauson–Khand annelation

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Received 5 October 2000; accepted 29 November 2000

Abstract—A range of phosphine- and phosphite-substituted carbonylcobalt(0) complexes have been synthesised and screened as catalysts of the Pauson–Khand annelation. The readily prepared stable solid, heptacarbonyl(triphenylphosphine)dicobalt(0) **1**, performed well (78% yield) in a benchmark annelation reaction. © 2001 Elsevier Science Ltd. All rights reserved.

Some of the most significant contributions to organic synthesis during the past years have been made by transition metal-mediated reactions. A prime example is the Pauson–Khand annelation (PKA), first described in 1971,[1] which involves the synthesis of cyclopentenone derivatives via the carbonylcobalt(0)-mediated cyclisation of an alkyne, an alkene and carbon monoxide. During its development and application, the PKA has mainly been applied using a stoichiometric amount of the transition metal complex, usually by prior formation of a stable (alkyne)hexacarbonyldicobalt(0) complex. Although the catalytic Pauson–Khand annelation (CPKA) was reported as early as 1973,[2] it was confined to the strained reactive alkenes norbornene and norbornadiene and required an excess of the alkyne component. The 1990s saw a surge of interest in the CPKA and the current state-of-the-art can be attributed to Livinghouse who in 1996 reported a photochemically driven process requiring only mild temperatures (50–55°C) and one atmosphere of carbon monoxide.[3] A more recent report from the same group relates that careful control of temperature to within a narrow window (60–70°C) dispenses with the need for photolytic promotion.[4] Rigorous purification of $Co_2(CO)_8$ is essential for the success of these systems, however, and Livinghouse recommends recrystallisation or sublimation immediately prior to use or opening a fresh commercial sample in a glove-box. Such cumbersome techniques and purification steps can be obviated, reports Krafft, by prior base washing of the glassware and introduction of cyclohexylamine.[5] Persistent problems associated with the very labile $Co_2(CO)_8$ have spurred the development of stable cobalt–alkyne complexes as catalyst precursors. Livinghouse makes use of the hexacarbonyldicobalt(0) complex of 2-methyl-3-butyn-2-ol which is reduced in situ to an active source of a carbonyldicobalt(0) with triethylsilane.[6] Krafft uses either the hexacarbonyldicobalt(0) complex of the substrate as the catalyst precursor, or a complex of a polar enyne, the cyclopentenone product from which is readily removed from the reaction mixture by acid/base wash or silica plug filtration.[7]

As a result of our interest in the use of carbonylcobalt(0) complexes immobilised on 'polymer-bound triphenylphosphine' in the CPKA,[8] we initiated an 'off-polymer' study of phosphorus derivatives of carbonylcobalt(0) species. Despite (a) the significant use of phosphine and phosphite substituted alkyne complexes in the stoichiometric PKA, where co-ordination leads to a reduction in the rate and overall efficiency of the reaction,[9] and (b) the observation that the use of triphenylphosphite as an additive in the $Co_2(CO)_8$ mediated CPKA leads to an improvement in reaction efficiency,[10] the performance of preformed complexes of phosphines and phosphites in the CPKA has not been assessed. We report here that such complexes do catalyse the CPKA and that some of the systems studied provide an attractive practical alternative to the catalysts currently available.

A representative range of readily available phosphines and phosphites was selected for conversion into carbonylcobalt(0) complexes and testing as PKA catalyst precursors. Synthesis of the mono- and bis-phosphine complexes **1**–**9** was straightforward and generally achieved by reacting one or two equivalents respectively of the appropriate phosphine or phosphite with $Co_2(CO)_8$. Work-up gave the required complexes in satisfactory yield (58–96%).

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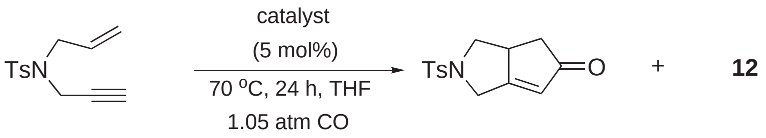
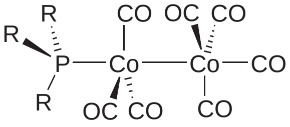
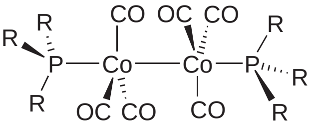
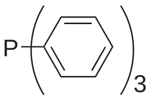
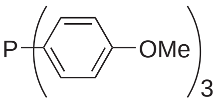
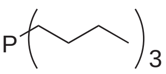
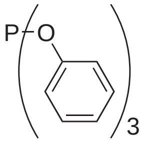
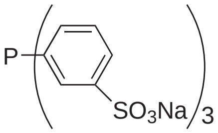
PII: S0040-4039(00)02204-8

The mono- and bis-phosphine complexes **1**–**9** were tested on one of the benchmark PKA reactions, i.e. the conversion of enyne **10** to cyclopentenone **11**. The conditions selected (5 mol% of catalyst, 70°C, 24 h, THF, 1.05 atm. CO) were those found to be the most successful using 'polymer-bound triphenylphosphine'.[8] Under these conditions, small amounts of a byproduct **12** are sometimes produced. After the reaction, the THF was removed from the product mixture and the resulting solid examined by ^{1}H NMR spectroscopy. The results of the screening are given in Table 1. These demonstrate that phosphine and phosphite derivatives of carbonylcobalt(0) complexes can indeed act as catalysts of the CPKA. The bisphosphine/bisphosphite complexes give poorer conversions to **11** than their monophosphine/monophosphite analogues, and this is tentatively attributed to their poorer solubility. The monophosphite complexes, **1**, **3**, **5** and **7**, however, all give very good conversions of **10** to **11**. Work-up of the product mixture obtained from the reaction performed with complex **1** [column chromatography (SiO_2; hexane–ethyl acetate, 6:4 to 1:1 gradient elution)] gave a crystalline sample of cyclopentenone **11** in 78% yield.

Table 1. Catalysts[a] and CPKA conversions (**11**:**12**:**10**)[b]



10 **11**

P–Co complex		
PR$_3$		
	**1**[11] 84:6:10	**2**[12] 61:8:31
	**3**[11] 91:6:3	**4**[13] 2:0:98
	**5**[11] 78:0:22	**6**[12] 14:0:86
	**7**[11] 84:3:13	**8**[12] 58:0:42
	Cobalt complex not isolable	**9**[14] 0:0:100

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[a] References for synthesis of catalysts provided.

[b] **11**:**12**:**10** as determined by ^{1}H NMR spectroscopy.

In conclusion we have demonstrated that a range of phosphorus substituted carbonylcobalt(0) complexes catalyse the PKA. The isolated yield of **11** obtained using **1** (78% using 5 mol% **1**, 70°C, 24 h, THF, 1.05 atm. CO) is comparable with the yields obtained by Livinghouse and by Krafft for the same cyclisation under similar conditions (86% using 7.5 mol% of rigorously purified $Co_2(CO)_8$, 60°C, 12 h, DME, 1 atm. CO;[4] 89% using 10 mol% $Co_2(CO)_8$ and 20 mol% cyclohexylamine in base washed glassware, 70°C, 14 h, DME, 1 atm. CO[5]). Complexes **1**, **3**, **5** and **7** are readily available and stable complexes. For example, complex **1** is a stable solid, easily prepared by stirring triphenylphosphine with $Co_2(CO)_8$ at room temperature for 1 h (65% yield).[11] It is considerably more stable than $Co_2(CO)_8$, which not only makes it easier to handle and measure, but also renders its reactions much more reliable.

Acknowledgements

The authors gratefully acknowledge AstraZeneca UK Ltd for studentships (for A.C.C. and A.S.).

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