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Polymer-supported cobalt carbonyl complexes as novel solid-phase catalysts of the Pauson–Khand reaction

Alex C. Comely,*[a] Susan E. Gibson (née Thomas)[a] and Neil J. Hales[b]

[a] *Department of Chemistry, King's College London, Strand, London, UK WC2R 2LS. E-mail: alex.comely@kcl.ac.uk*
[b] *AstraZeneca UK Ltd., Mereside, Alderley Park, Macclesfield, UK SK10 4TG*

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Cobalt carbonyl complexes immobilised onto a 'polymer-bound triphenylphosphine' solid support are effective and practical catalysts of the Pauson–Khand reaction.

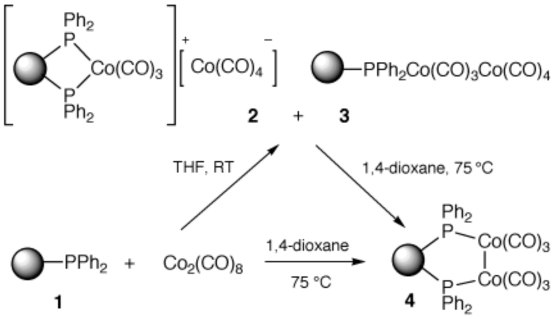
The synthesis of cyclopentenone derivatives *via* the cobalt carbonyl-mediated annulation of an alkyne, an alkene and carbon monoxide, the Pauson–Khand (P–K) reaction, was first described in 1971.[1] A synthetically very important process,[2] the P–K reaction is routinely applied using a stoichiometric amount of the transition metal complex. Although the catalytic process was reported as early as 1973,[1b] it was confined to the strained reactive alkenes norbornene and norbornadiene.

Ensuing years saw little development of the catalytic P–K reaction until a protocol developed by Rautenstrauch,[3] albeit one demanding extremely forcing conditions (310–360 bar ethene/CO, 150 °C) to realise only moderate yields, inspired several new approaches to catalysis. Promoters such as 1,2-dimethoxyethane or water have been investigated,[4] the addition of phosphites is shown to prevent inactive cluster formation[5] and the use of supercritical CO_2 as a reaction medium is described.[6] Alternative sources of zero valent cobalt [$Co(acac)_2/NaBH_4$[7] and (indenyl)Co(COD)[8]] and cobalt carbonyl clusters[9] have also been employed. Although yields and turnovers are excellent, these systems still suffer the requirement of high temperatures and pressures.

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 1 atm CO.[10] 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.[11] Rigorous purification of $Co_2(CO)_8$ in these systems can be obviated, reports Krafft, by prior base washing of the glassware.[12] Problems associated with the very labile $Co_2(CO)_8$, however, have also spurred the development of stable cobalt–alkyne catalyst precursors.[13]

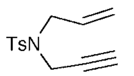
Given our current interest in polymer-supported cobalt complexes[14] and increasing awareness of the environmental and handling advantages conferred by such solid-phase methodologies,[15] we decided to determine the viability of the catalytic P–K reaction using immobilised cobalt carbonyls.† Our preliminary investigations, which reveal for the first time that polymer-supported cobalt complexes do indeed catalyse the P–K reaction, are reported herein.

The cobalt carbonyl resins to be tested as catalyst precursors were prepared as follows.[14] Reaction of 'polymer-bound triphenylphosphine' **1**‡ with $Co_2(CO)_8$ in THF at room temperature generated a resin-bound mixture of phosphine-substituted cobalt carbonyl complexes **2** and **3** (*ca.* 1:1) (Scheme 1). The purple resin, which is significantly more air-stable than $Co_2(CO)_8$, was characterised on the basis of its IR and ^{31}P NMR spectra.[14] Heating this resin at 75 °C in 1,4-dioxane cleanly converted it into a second form, assigned the structure of the neutral bisphosphine **4** on the basis of its IR and ^{31}P NMR spectra.[14] Resin **4**, however, can be more conveniently prepared directly from **1** and $Co_2(CO)_8$§ without prior isolation of **2** + **3**.



Scheme 1

In light of the mild and very attractive conditions reported by Livinghouse for the catalytic P–K reaction, and in particular the thermal window identified between 60 and 70 °C,[11] it was these conditions which were used as the basis for our initial experiments with the cobalt–carbonyl loaded resins.¶ At 65 °C we were very encouraged by the observation that 5 mol% of either precursor **2** + **3** or **4** effected a moderate conversion of enyne substrate **5**[17] to cyclopentenone **6**[10] after 24 h in THF under a 50 mbar overpressure of CO (Table 1, entries 1 and 2). In preliminary steps to optimise the methodology, the first parameter investigated was temperature. An increase to 70 °C (Table 1, entries 3 and 4) resulted in a significant increase in conversion for both catalyst precursors, the bisphosphine-substituted complex **4** again proving to be the most effective



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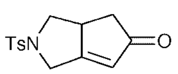

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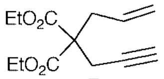

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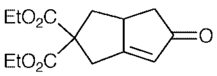

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Table 1 Conversion of substrates **5** and **7** into **6** and **8** respectively *via* the catalytic Pauson–Khand reaction using cobalt resins **2** + **3** and **4**¶

Entry	Catalyst precursor (5 mol%)	*T*/°C	Substrate	Product	Yield (%)[a] (isolated)
1	**2** + **3**	65	**5**	**6**	22
2	**4**	65	**5**	**6**	48
3	**2** + **3**	70	**5**	**6**	37
4	**4**	70	**5**	**6**	66 (61)
5	**2** + **3**	75	**5**	**6**	21
6	**4**	75	**5**	**6**	28
7	**2** + **3**	70	**7**	**8**	28
8	**4**	70	**7**	**8**	57 (49)

[a] Describes percentage conversion measured by ^1H NMR spectroscopy. Isolated yields are those obtained after flash column chromatography. Products were characterised by comparison of their ^1H, ^{13}C and IR spectra with the literature values (ref. 10).

producing 66% conversion and 61% isolated yield of **6**. The consequence of a further 5 °C increase in temperature, however, was a precipitous drop in conversion for both forms of the catalyst alike (Table 1, entries 5 and 6).

A further substrate was subjected to our preliminarily optimised conditions. Hence, enyne **7**[10,18] was cyclised to cyclopentenone **6**[10] in a respectable 49% isolated yield, catalyst precursor **4** again resulting in the highest conversion (Table 1, entries 7 and 8).

In conclusion, we have shown for the first time that solid-phase cobalt carbonyl complexes have significant potential as catalysts of the P–K reaction. As with all supported catalysts, a very simple work-up procedure is required: filtration of the polymer-bound catalyst and concentration of the filtrate. A further advantage conferred by the increased air-stability of the immobilised cobalt complexes is ease of handling using readily available laboratory equipment. Our results, together with the environmental advantages of immobilising metal carbonyls on a solid support, suggest that this new approach to the P–K reaction is worthy of considerable further investigation.

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Notes and references

† Polymer-bound P–K substrates have been cyclised in the presence of stoichiometric amounts of $Co_2(CO)_8$ (ref. 16).

‡ 'Polymer-bound triphenylphosphine' (commercially available from Fluka, ~1.6 mmol P g^{-1}) describes a diphenylphosphino polystyrene polymer crosslinked with 1% divinylbenzene.

§ The experimental procedure for the formation of **4** is as follows: commercial polymer-bound triphenylphosphine (1 g, ~1.6 mmol P) was suspended in oxygen-free anhydrous 1,4-dioxane (15 cm^3) and allowed to swell for 30 min under N_2 agitation. A solution of commercial $Co_2(CO)_8$ complex (383 mg, 1.12 mmol) in anhydrous, deoxygenated 1,4-dioxane (5 cm^3) was added under nitrogen agitation, the black mixture was left at room temperature for 30 min and subsequently heated to 75 °C for 16 h. After cooling, the resin beads were filtered, washed with alternate aliquots of THF and Et_2O until the filtrate became colourless, and dried *in vacuo* to afford deep purple beads of **4** {1.15 g, 50% P site complexation, 0.35 ± 0.05 mmol $[Co_2(CO)_6]\ g^{-1}$}.

¶ A general experimental for the catalytic P–K reaction is as follows: resin **4** {63 mg, 0.025 mmol $[Co_2(CO)_6]$} and substrate **5** (125 mg, 0.5 mmol) were combined in a 10 cm^3 round-bottomed flask fitted with a condenser. The apparatus was thoroughly purged with CO and sealed under 1.05 bar CO. CO-saturated THF (5 cm^3) was added and the mixture was heated to 70 °C for 24 h. Filtration of the pale brown mixture, thorough washing of the polymer beads with alternate aliquots of THF and Et_2O, and concentration of the combined filtrates *in vacuo* afforded cyclopentenone **6** [66% conversion by ^1H NMR spectroscopy; 85 mg, 61% isolated by flash chromatography (SiO_2, EtOAc–light petroleum, 2 : 8 to 4 : 6 gradient elution), 0.31 mmol].

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