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The application of polymer-bound carbonylcobalt(0) species in linker chemistry and catalysis

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Carbonylcobalt(0) species have been used as linkers between alkynes and a polymer support for the first time. The alkynes may be loaded indirectly onto a phosphine functionalised polymer *via* their hexacarbonyldicobalt(0) complex, or directly onto a cobalt coated polymer. The alkynes have been released either as alkynes, thus providing a traceless method of immobilising alkynes, or by reaction with an alkene to generate a cyclopentenone *via* the Pauson–Khand reaction. The cobalt coated polymers produced during this study were shown to catalyse the Pauson–Khand reaction.

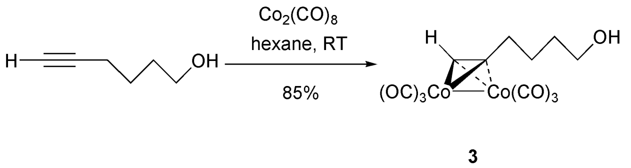
Multiple parallel synthesis and combinatorial chemistry are important methods of generating large numbers of compounds relatively quickly. Substrate molecules are generally attached to the polymer *via* a 'linker' molecule using covalent bonds.[1–3] Once attached, the immobilised substrate may be isolated simply by filtration of the polymer from the reaction mixture. Further organic transformations may then be carried out while the substrate is bound to the polymer before chemical cleavage of the final product from the solid support. We recently demonstrated the potential of π-bound ligands in linker chemistry by attaching substrates containing aromatic rings to polystyrene-diphenylphosphine (PSDP) using a chromium carbonyl linker, chemically manipulating the substrates, and then releasing the products from the polymer.[4,5]

The chemistry of carbonyldicobalt(0) alkyne complexes is well established in the solution phase and has been applied to great effect in organic synthesis: alkyne protection,[6] the Nicholas reaction,[7] and Pauson–Khand annelations,[8] for example, are amply documented. Given the ease of formation of these complexes and their tolerance to diverse reaction conditions it appeared that it may be possible to use these complexes to attach alkynes to solid supports. (At present, there are no methods available for attaching an alkyne to a solid support, manipulating its substituents and then releasing the alkyne.) To test this hypothesis, we proposed to immobilise an alkyne substrate onto PSDP using a carbonyldicobalt(0) species **1**, chemically manipulate a pendant functionality to give **2** and release the product from the resin to deliver a chemically-modified alkyne-bearing substrate. This paper describes how we achieved this goal, how the release strategy was subsequently modified to include a Pauson–Khand reaction, and how some of the carbonylcobalt(0) coated polymers generated during the course of this study were used as catalysts of the Pauson–Khand reaction. Some of the work on the linker chemistry and the catalyst discovery has been reported in communication form.[9,10]

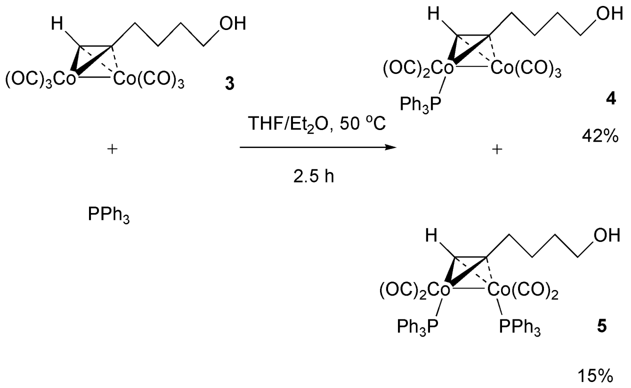
Results and discussion

The 'indirect' loading approach

The first approach to loading an alkyne onto a polymer support involved making a carbonylcobalt(0) derivative of the alkyne and then attaching the complex thus formed to the polymer. A commercially available alkyne with a pendant functional group, hex-5-yn-1-ol was thus treated with octacarbonyldicobalt(0) in hexane at ambient temperature to give the novel stable hexacarbonyldicobalt(0) complex **3** as a deep red oil in good yield.



Carbonyl exchange with an external ligand is a facile process for (η^2:η^2-alkyne)hexacarbonyldicobalt(0) complexes.[11] In order to confirm this literature precedent prior to attempting the chemistry on the solid support, and also to obtain readily-characterisable samples for the purpose of data comparison, complex **3** was treated with triphenylphosphine. Chromatographic purification gave novel monophosphine complex **4** as a deep red oil, and purple crystalline novel bisphosphine complex **5** in 42 and 15% yields respectively.



In order to attempt this chemistry on a solid support, PSDP was swollen in THF under constant nitrogen agitation in a glass frit-fitted vessel equipped with a condenser. Two equivalents of alkyne complex **3** were added and after four hours at 50 °C the mixture was filtered and washed with alternate aliquots of THF and Et_2O until the filtrate became colourless. The resulting deep purple beads **6**, significantly less swollen than the original PSDP beads, were dried *in vacuo*.

The nature of the two distinct complexes on the resin, **6a** and **6b**, was ascertained primarily by comparison of the ^{31}P NMR and IR spectra of the resin with data obtained in solution for mono- and bisphosphine complexes **4** and **5**. Analysis of the IR spectrum of the resin indicated the presence of the monophosphine **6a** as the major and the bisphosphine **6b** as the minor component in an approximate ratio of 6 : 4. Solution

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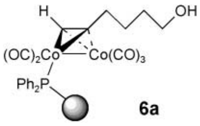
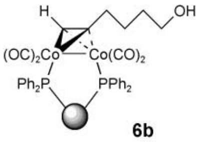
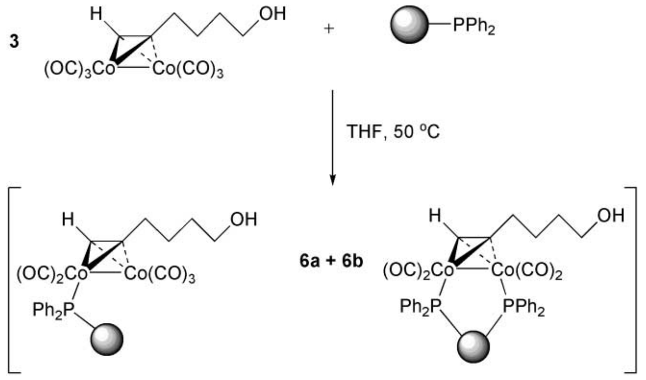
Table 1 Characterisation of carbonyldicobalt(0) by IR and ^{31}P NMR spectroscopy

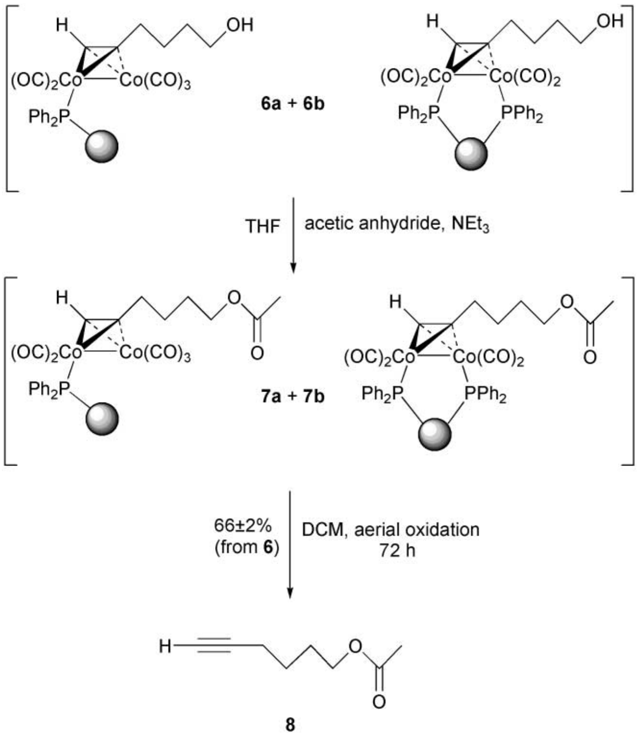
Polymer-bound complex	Data from resin	Data from solution-phase analogue (**4**, or **5**)
 **6a**	υ_{max}/cm^{-1}	υ_{max}/cm^{-1}
	2055s	2062s
		2028w
		2008ssh
	1998vs	2004s
	1979ssh	1990wsh
		1967w
	δ_P (ppm)	δ_P (ppm)
	55.5	55.2
 **6b**	υ_{max}/cm^{-1}	υ_{max}/cm^{-1}
	1998vs	2010s
	1979ssh	1962ssh
	1950s	1950s
		1930wsh
	δ_P (ppm)	δ_P (ppm)
	55.5	53.4

calibration studies with complexes **4** and **5** verified this estimate. ^{31}P NMR spectroscopy was extremely valuable in assessing the composition of the polymer. A relatively well-resolved resonance at 55 ppm integrated to an 80% complexation of phosphorus sites, the benign phosphine oxide, polymer-P(O)Ph$_2$, occupying the remaining 20%. Resolution in the polymer spectrum was insufficient to distinguish between **6a** and **6b**, however, solution-phase analogues **4** and **5** resonate at 55.2 and 53.4 ppm, respectively. In order to estimate the error margin when working with these resins generated by indirect loading, it was estimated that 5% inaccuracy accompanied analysis of IR and ^{31}P NMR spectra (Table 1). Consideration of both IR and ^{31}P NMR spectra and the assumed error margins for both techniques, therefore, allowed substrate loading to be calculated as 0.94 ± 0.02 mmol[hex-5-yn-1-ol]g^{-1}. The validity of the IR calibration study was established from microanalysis of **6**: both cobalt and phosphorus analyses were in excellent accord with values calculated on the basis of the loading calculation.

A polymer bearing a higher proportion of monophosphine complex **6a** would also be a less crosslinked one and one more able to swell effectively. Attempts to generate just one species on the resin by varying the stoichiometry of the reaction between hexacarbonyl complex **3** and PSDP, however, proved unsuccessful.



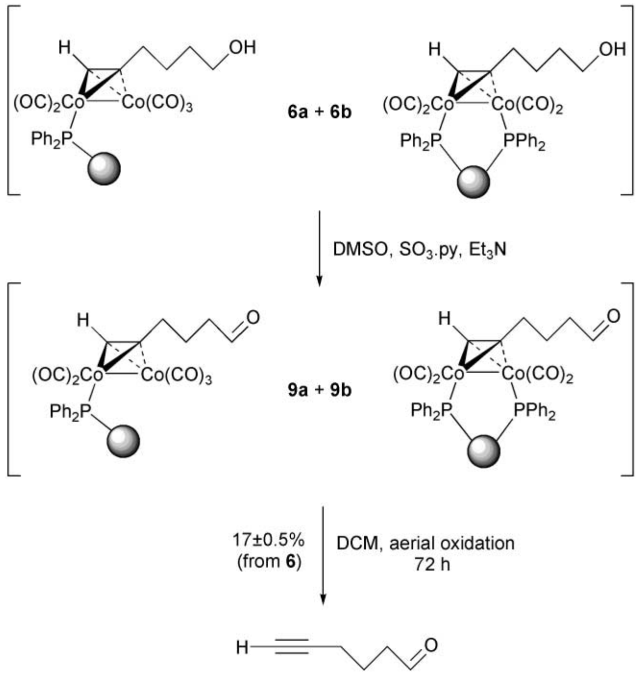
In order to start to probe the stability of the linker to chemical modification, the pendant alcohol of complexes **6** was acetylated. A suspension of **6** in THF was treated with triethylamine and acetic anhydride and the mixture was left at ambient temperature for 20 h under constant nitrogen agitation. Filtration, washing and drying *in vacuo* gave deep purple beads of acetate **7**. Analysis by IR spectroscopy revealed an additional absorption at 1734 cm^{-1} indicating successful acetate formation, and no apparent change in the linker: the mono- and bisphosphine composition was unchanged from that of **6**. Integration of the ^{31}P NMR spectrum of **7** indicated a reduction of phosphorus site occupancy to 75% (within the assumed error margin) and polymer loading was calculated as 0.87 ± 0.02 mmol[hex-5-yn-1-yl acetate]g^{-1}. The product hex-5-yn-1-yl acetate **8** was released by suspending a sample of resin **7**, ground to a fine brown powder, in DCM under white light for 72 h. Filtration of the resulting mixture and concentration of the colourless filtrate gave **8**[12] as the sole product in 66 ± 2% yield from **6**.



To explore further the stability of the linker to chemical modification, an oxidation reaction was examined. Of the many conditions available for oxidation of an alcohol, it was decided to apply those of a Swern reaction. However, on addition of an oxalyl chloride–DMSO mixture, cobalt(0) was instantly stripped from the brown beads to give a deep green solution indicating formation of liberated cobalt salts. It was suspected that the HCl evolved during the Swern oxidation might be responsible: indeed, addition of only a couple of drops of HCl to a DCM suspension of **6** resulted in the same colour change. A variety of "modified Swern" conditions exist.[13] One set of conditions that does not evolve HCl during the course of reaction uses a sulfur trioxide–pyridine complex.[14] Hence, alcohol **6** was suspended in DCM, and DMSO and triethylamine were added sequentially, followed by a solution of sulfur trioxide–pyridine complex. The resulting purple beads **9** were analysed in the usual way. The IR spectrum displayed a diagnostic aldehyde stretch at 1723 cm^{-1} and an unchanged mono-/bisphosphine complex composition from that of **6**. Furthermore, phosphorus site occupancy was reduced by only 10%, thus demonstrating an encouraging stability of the linker to these oxidising conditions. Hex-5-yn-1-al **10**[15] was isolated in 17 ± 0.5% yield after decomplexation as before, the low yield being attributed to the volatility of the aldehyde.

The 'direct' loading approach

'Direct' loading of a substrate onto a support is an attractive concept. The priming of the substrate by conventional solution chemistry prior to attaching it to a support for solid phase synthesis, often a multi-step process, can be laborious especially



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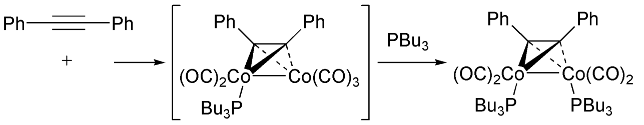
when the first degree of diversity in a combinatorial synthesis is introduced at the loading stage. Although only one preliminary step is required for the loading described in the previous section, and that it is a simple and high yielding complexation, it seemed that it might be possible to generate a suitably primed polymeric support that would enable us to by-pass this step. Literature precedent was encouraging: complexation of an alkyne to a phosphine-substituted carbonyldicobalt(0) complex, $[(Bu_3P)Co(CO)_3]_2$ **11**, has been reported.[16] At elevated temperature, one carbon monoxide and one phosphine are displaced resulting in monophosphine-substituted complex **12**. The phosphine released in this process then displaces a second carbon monoxide ligand to deliver the bisphosphine **13**.

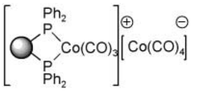
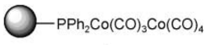
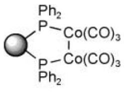


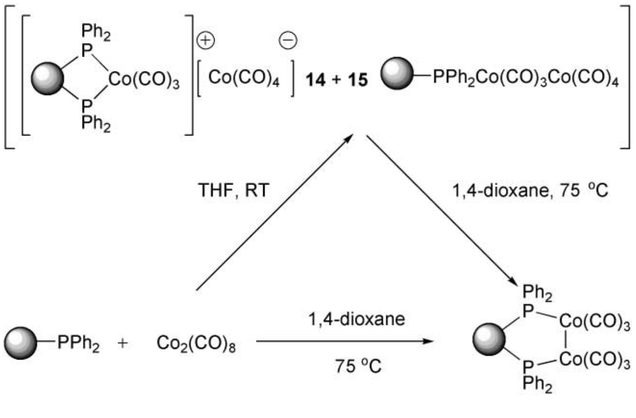
11 **12** **13**

A wide variety of transition metal carbonyl complexes have been immobilised onto a diverse array of supports,[17] both organic and inorganic, and octacarbonyldicobalt(0) is no exception. The reaction of PSDP with octacarbonyldicobalt(0) to give resin-bound complexes **14**,**15** and **16** has been reported.[18,19] Thus, treatment of a swollen suspension of PSDP in THF with octacarbonyldicobalt(0) at ambient temperature gave a resin-bound mixture of ionic **14** and monophosphine **15** as deep purple beads. Suspension of this material in 1,4-dioxane and heating to 75 °C gave the single resin-bound complex **16** bearing only a trace of monophosphine complex **15**, as determined by IR spectroscopy. Alternatively, **16** was accessed directly by treating PSDP with octacarbonyldicobalt(0) at elevated temperature.

The purple, stable resins [**14** + **15**] and **16** were characterised by comparison of their IR spectroscopy data in the carbonyl stretching region with those from the literature[18,19] and from ionic, monophosphine and bisphosphine complexes, **19**,[22] **18**[21] and **17**[20] prepared using literature procedures for that purpose, Table 2.

Table 2 Characterisation of cobalt coated resins by IR and ^{31}P NMR spectroscopy

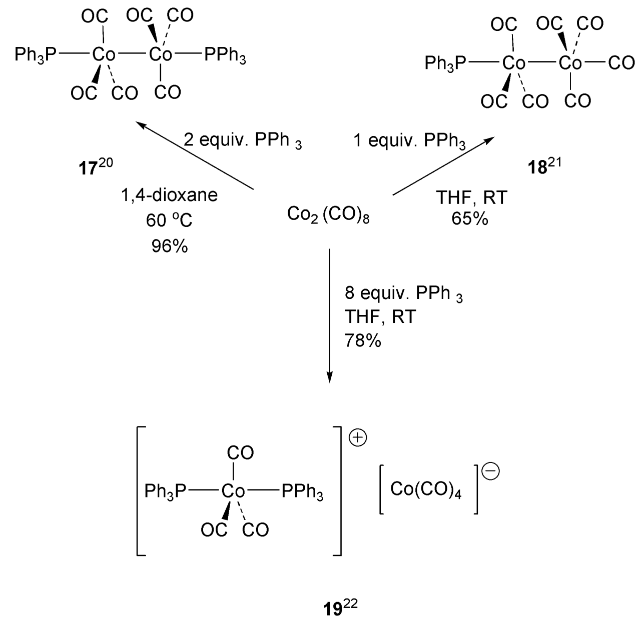
Polymer-bound complex	Data from resin	Data from solution-phase analogue (**19**, **18**, **17**)
 **14**	υ_{max}/cm^{-1} 1995s 1985msh 1880vs δ_P (ppm) 62	υ_{max}/cm^{-1} 1999s 1975msh 1888s δ_P (ppm) 55.5
 **15**	υ_{max}/cm^{-1} 2074w 2012msh 1995s 1955w δ_P (ppm) 62	υ_{max}/cm^{-1} 2077m 2023w 1988s 1958w δ_P (ppm) 65.3
 **16**	υ_{max}/cm^{-1} 1977msh 1949s 1025msh δ_P (ppm) 68	υ_{max}/cm^{-1} 1969msh 1943msh 1898msh 1810w



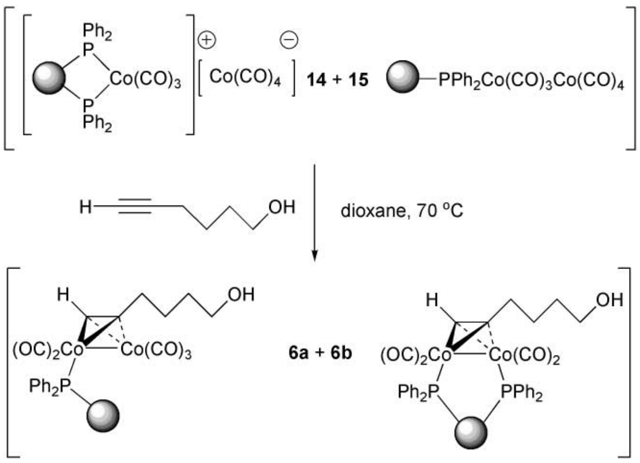
16

A very strong absorption at 1880 cm^{-1} ascribed to ionic **14**[18,22] was accompanied by weaker peaks at 2074, 2012 and 1955 cm^{-1} indicating a presence of the monophosphine-substituted complex **15** in a ratio estimated at 7 : 3.[21] This is largely consistent with literature precedent where one group observed only ionic species **14** on the resin:[19] that a proportion of the monophosphine **15** was also observed in these experiments possibly results from using a higher cobalt(0) : PSDP ratio in the resin synthesis. Attempts to isolate only the resin-bound ionic complex by decreasing this ratio to 1 : 2.5 failed, however, resulting in an identical complex composition as determined by IR spectroscopy. The neutral bisphosphine **16** gave a broad IR absorption at 1949 cm^{-1}.[20] The assignments are supported by ^{31}P NMR resonances at ~62 ppm for [**14** + **15**] and ~68 ppm for **16**; the broad signals for the latter were unsuitable for accurate quantitative analysis, however. In order to estimate the error margin when working with resins generated by direct loading, it was assumed that 5% inaccuracy accompanied analysis of IR spectra while a larger 10% margin needed to be used for ^{31}P NMR spectra of **16**. Hence, loadings of 0.96 ± 0.03 mmol$[Co_2(CO)_7]g^{-1}$ and 0.22 ± 0.05 mmol$[Co_2(CO)_6]g^{-1}$ were calculated for [**14** + **15**] and **16**, respectively.

Resins [**14** + **15**] and **16** are significantly more air-stable than $Co_2(CO)_8$: half-lives for the complexes have not been quantified but the resins can be left on the open bench for several days without apparent change in composition as determined by IR spectroscopy [the very labile $Co_2(CO)_8$ would exist for only minutes under these conditions]. Substantial cross linking of the polystyrene resin created by the bis-phosphine complexes is manifested by a greatly-reduced swelling ability of the resins.



'Direct' loading of an alkyne onto the carbonylcobalt(0) coated resin [**14** + **15**] was investigated next. Suspension of [**14** + **15**] in 1,4-dioxane and heating to 70 °C in the presence of hex-5-yn-1-ol generated the purple resin-bound alkyne complexes **6**, possibly *via* the intermediary carbonyl complex **16**. As before, overlapping sets of IR absorptions at 2055, 2009, 1967 cm^{-1} and 2009, 1948, 1930 cm^{-1} indicated the presence of both mono- and diphosphine substituted alkyne complexes, **6a** and **6b** respectively, Table 1. The strongest band at 1948 cm^{-1} suggested that the latter is the major component *via* this route in a composition estimated to be 3 : 7. Solution calibration studies with triphenylphosphine analogues **4** and **5** verified this estimate. The broad resonance in the ^{31}P NMR spectrum at 55 ppm supports alkyne complexation. Further inspection of the spectrum revealed a 20% phosphorus site occupancy leading to a loading of 0.30 ± 0.09 mmol[hex-5-yn-1-ol]g^{-1}.

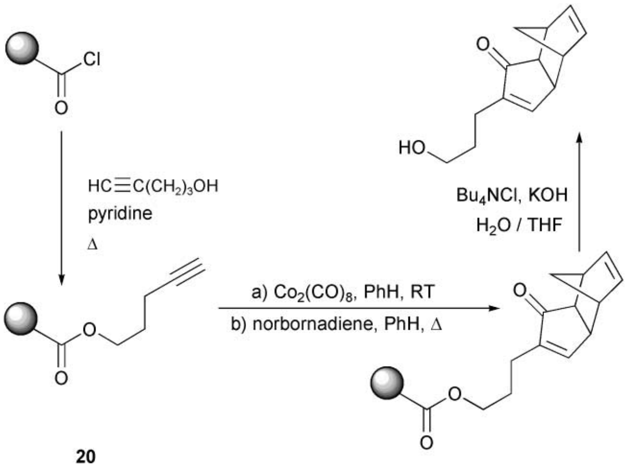


Using an acetylation procedure identical to that described above, hex-5-yn-1-yl acetate-bearing complexes **7** were generated from complexes **6** formed by direct loading of hex-5-yn-1-ol. Analysis of the linker by means of ^{31}P NMR and IR spectroscopy was consistent with no reduction in phosphorus site occupancy and with retention of monophosphine–bisphosphine complex composition. An additional acetate absorption at 1732 cm^{-1} indicated successful acetylation. Hex-5-yn-1-yl acetate **8** was released from the support by aerial oxidation as previously described. A yield of 70 ± 30% from resin **6** was recorded, a cleavage efficiency comparable to that obtained from 'indirect' loading.

A stoichiometric solid-phase Pauson–Khand annelation

Having established that carbonylcobalt(0) linkers could be used to immobilise alkynes, it occurred to us that a Pauson–Khand reaction might be used as an alternative approach to the release of the product alkyne.

Precedent for the solid phase PKA exists for substrates immobilised by means of a side-chain ester linkage. Schore describes the cyclisation of a tethered alkyne **20** with strained alkenes such as norbornadiene.[23] Cleavage of the linker in the presence of potassium hydroxide and a phase-transfer catalyst delivered the cyclopentenone bearing a pendant alcohol. In a solid phase intramolecular PKA reported by Bolton, cleavage of the product **21** with TFA afforded carboxylic acid-bearing products.[24] The use of carbonyldicobalt(0) complexes both as alkyne linkers *and* as a vehicle for PKA-induced cleavage from the polymer support would represent a new approach to solid phase Pauson–Khand annelations. Hence, it was decided to immobilise enyne **22**[25] onto PSDP *via* its carbonyldicobalt(0) complex.



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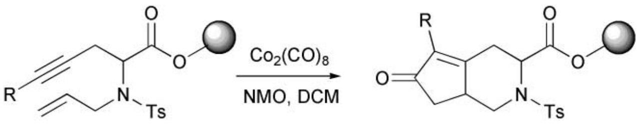

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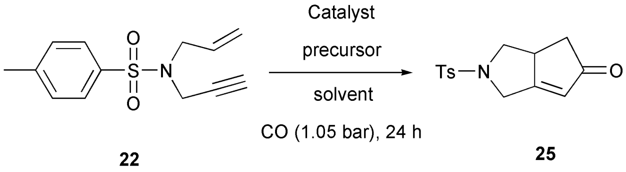
The hexacarbonyldicobalt(0) complex **23** was generated in 89% yield as red–purple crystals. Using the "indirect" approach described above, this material was reacted with THF-swollen PSDP at 50 °C to give resin **24** bearing a mixture of mono- and bisphosphine complexes, **24a** and **24b** respectively. Analysis of the IR spectrum of **24** revealed a predominance of **24b** accompanied by only a trace of monophosphine **24a**, an observation in contrast to the preparation of hex-5-yn-1-ol-loaded resin **6** where a 6 : 4 ratio of mono- to bisphosphine derivatives was obtained. Heating resin **24** at 70 °C under 1.05 bar CO in THF for 24 h was found to release the cyclopentenone product **25** in 26 ± 1% isolated yield after chromatographic purification.

Catalytic Pauson–Khand annelations

The stoichiometric version of the Pauson–Khand reaction is increasingly being replaced by catalytic versions of the reaction, many of which are based on octacarbonyldicobalt(0) or its derivatives.[26] In view of the increasing awareness of the environmental and handling advantages conferred by solid-phase reagents and catalysts, it was decided to determine whether or not the carbonylcobalt(0) containing polymers prepared in the studies described above could be used to catalyse the Pauson–Khand annelation.

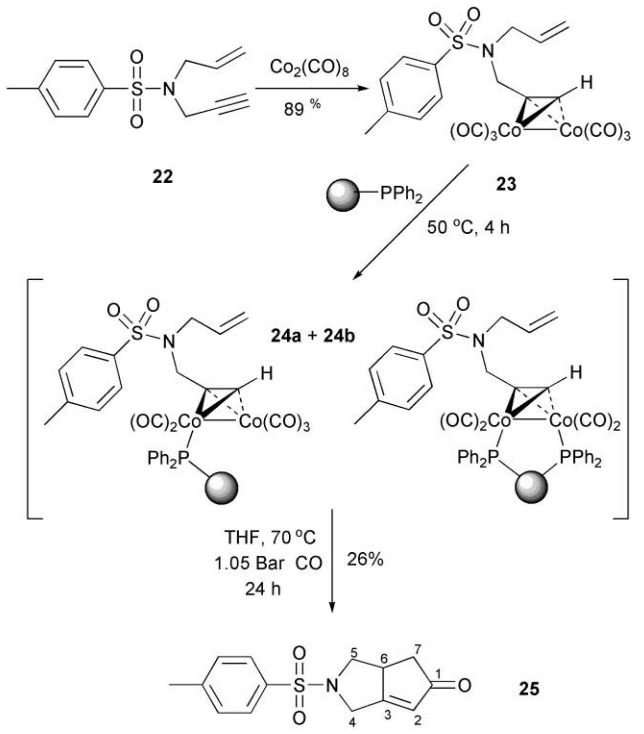
Initially new batches of resins [**14** + **15**] and **16** {[**14** + **15**]′ and **16**′} were prepared. The loading for **16**′ was calculated as

Table 3 CPKA conditions and version results using [**14** + **15**]′ and **16**′



Entry	Catalyst precursor	*T*/°C	Solvent	Conversion (%)[a]
1	[**14** + **15**]′	70	THF	37
2	**16**′	70	THF	(61)66
3	[**14** + **15**]′	65	THF	22
4	**16**′	65	THF	43
5	[**14** + **15**]′	75	THF	21
6	**16**′	75	THF	28
7	**16**′	70	1,4-Dioxane	51
8	**16**′	70	Toluene	45
9	**16**′ recycled	70	THF	28

[a] Conversion as determined by ^{1}H NMR spectroscopy (isolated yield following purification by flash column chromatography.)

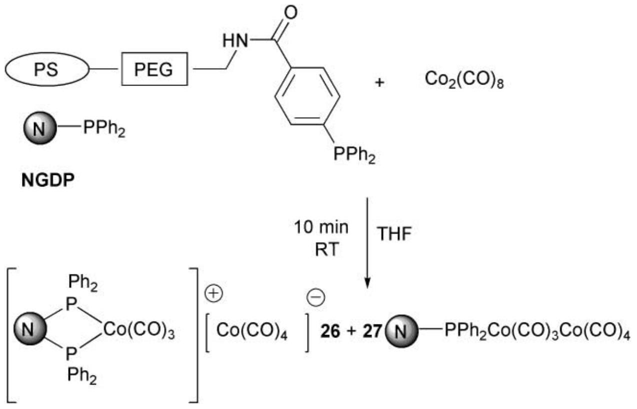


0.36 ± 0.04 mmol[Co$_2$]g^{-1} from a phosphorus site complexation of 50%, and the loading for [**14 + 15**]′ was calculated as 0.96 ± 0.03 mmol[Co$_2$]g^{-1} from a phosphorus site complexation of 75%. The resin loadings once again reflect the respective uncertainties in the ^{31}P NMR spectra and values of 0.4 mmol[Co$_2$]g^{-1} and 0.95 mmol[Co$_2$]g^{-1} were employed for **16**′ and [**14 + 15**]′ respectively.

The experiments to probe catalytic activity were carried out using 5 mol% of catalyst in THF, a solvent chosen for its ability to swell the PSDP, under 1.05 atmospheres of carbon monoxide, and with a reaction time of 24 hours. Preliminary experiments demonstrated that a static atmosphere of carbon monoxide was preferred over a continuous flow of carbon monoxide, which led to solvent evaporation and safety problems, and that no stirring retarded the degeneration of the beads into an amorphous gel. A temperature of 70 °C was selected, in keeping with Livinghouse's observation that there is a thermal window between 60 and 70 °C for the catalytic Pauson–Khand reaction.[27] Using resins [**14 + 15**]′ and **16**′, conversions of 37 and 66% were observed (Table 3, entries 1 and 2), and cyclopentenone **25** was isolated in 61% yield from the latter reaction. Thus both resins promoted a catalytic conversion of enyne **22** into cyclopentenone **25**.

To probe the effect of temperature, reactions were carried out at 65 and 75 °C with both catalyst precursors [**14 + 15**]′ and **16**′ (Table 3, entries 3 to 6). From these results it can be seen that maximum conversion is obtained at 70 °C and the consequence of a 5 °C increase or decrease in temperature leads to a drop in conversion for both forms of the catalyst. Two other solvents were applied to the system, both with moderate ability to swell the resins. Neither 1,4-dioxane (Table 3, entry 7) nor toluene (Table 3, entry 8), however, were as effective as THF. In one further experiment, the catalyst used in Table 3, entry 2 was recycled. Under identical conditions, a 28% conversion was observed (Table 3, entry 9).

The phosphines present in PSDP are held very close to its polystyrene backbone and thus site accessibility may be rather difficult for incoming substrates and reagents. It was thus decided to examine the Pauson–Khand reaction described above using Novageldiphenylphosphine (NGDP), a polystyrene polyethyleneglycol resin. Cobalt species bound to the phosphines present in this polymer should be sited further from the polymer backbone than cobalt species bound to the phosphines present in PSDP. NGDP was thus used instead of PSDP in the synthesis of resin [**26 + 27**], an analogue of [**14 + 15**]. The resulting resin was characterised by comparison of its IR and ^{31}P NMR spectra with those of [**14 + 15**]. The ^{31}P NMR spectrum proved to be much better resolved than that of [**14 + 15**] (error margin = ±1%) and thus the loading of resin [**26 + 27**] could be calculated more accurately.



Employing resin [**26 + 27**] in the Pauson–Khand reaction using substrate **22** gave a 68% conversion to cyclopentenone **25**. Thus the change in the environment around the cobalt centres appears to have had little effect on the catalysis of the Pauson–Khand reaction.

Conclusions

The utility of carbonyldicobalt(0) complexes as linkers for the immobilisation and subsequent release of alkyne substrates has been successfully demonstrated for the first time. The linker is readily characterisable by means of ^{31}P NMR and IR spectroscopy, techniques which allow substrate loading to be quantified. Alkyne substrates can be loaded onto the polymeric support both by 'indirect' and 'direct' means: it is not necessary to prime an alkyne prior to polymer-loading by cobalt(0) complexation. Substrate loading, however, is higher when the alkyne complex is pre-formed, but the immobilisation–chemical modification–release sequence proceeds with equal efficiency thereafter.

As an alternative to oxidative release of the alkyne, a Pauson–Khand reaction has been used to generate a cyclopentenone. Thus, in principle, an alkyne may be bound to a polymer, modified by solid-phase techniques and then converted to a cyclopentenone on release from the polymer.

It has also been demonstrated that resins bearing carbonylcobalt(0) species catalyse the Pauson–Khand reaction. Although it is as yet unclear whether catalysis is occurring on the polymer or whether the resin acts as a source of catalytically active carbonylcobalt(0) fragments (microanalysis of the resin after catalysis on one occasion revealed a 13% loss of cobalt) it is of note that from a practical viewpoint that the polymer-bound carbonylcobalt(0) is more stable and easier to handle than conventional solution catalysts of the Pauson–Khand reaction such as octacarbonyldicobalt(0).

Experimental

Reactions under nitrogen and carbon monoxide were performed using standard vacuum line and Schlenk tube techniques.[28] Diethyl ether, toluene and hexane were dried over sodium wire. THF was distilled from sodium benzophenone ketyl. DCM and 1,4-dioxane were distilled from calcium hydride. All solvents intended for use in chromatography were used as bought. SiO_2 refers to chromatography grade silica of particle size 40–63 µm. Enyne **22** was prepared using a literature procedure.[25]

Melting points, which are uncorrected, were determined using a Gallenkamp capillary melting point apparatus. IR spectra were obtained on a Perkin-Elmer 1710 FTIR spectrometer. NMR spectra were recorded at room temperature on Bruker AM360 (360.0 MHz ^1H, 90.6 MHz ^{13}C, 145.8 MHz ^{31}P), Bruker AMX400 (400.0 MHz ^1H, 100.6 MHz ^{13}C) (King's College) and Bruker DPX300 (300.0 MHz ^1H, 75.5 MHz ^{13}C) (AstraZeneca UK Ltd.). Mass spectra were recorded on a VG 70/250 SE spectrometer at AstraZeneca UK Ltd. and on Kratos MS890MS and JEOL AX505W instruments at King's College London. Microanalyses were conducted by Steven Boyer (S. A. C. S.) at the University of North London and by MEDAC Ltd., Analytical and Chemical consultancy services, Brunel Science Centre.

Hexacarbonyl-μ-(η^2:η^2-hex-5-yn-1-ol)dicobalt(0) 3

To a solution of octacarbonyldicobalt(0) (5.0 g, 14.6 mmol) in anhydrous, deoxygenated hexane (40 cm^3) at ambient temperature under nitrogen was added hex-5-yn-1-ol (1.61 cm^3, 14.6 mmol) and the solution was stirred for 24 h. Flash column chromatography (SiO_2, hexane–Et_2O 1 : 0 to 4 : 1 gradient elution) effected isolation of the *title complex* (4.78 g, 12.4 mmol, 85%) as a deep red oil (Found: C, 39.2; H, 2.8. $C_{12}H_{10}Co_2O_7$ requires C, 39.16; H, 2.62%); ν_{max}(hexane)/cm^{-1} 2092w, 2052s, 2029s and 2020m (C≡O); δ_H(360.0 MHz, $CDCl_3$) 1.50 (1 H, br s, OH), 1.72 (4 H, br m, $C\mathit{H}_2C\mathit{H}_2CH_2OH$), 2.90 (2 H, br m, $HCCC\mathit{H}_2$), 3.71 (2 H, br m, $C\mathit{H}_2OH$) and 6.03 (1 H, br m, CH); δ_C{^1H}(90.6 MHz, $CDCl_3$) 28.2 ($CCH_2\mathit{C}H_2$), 32.4 ($\mathit{C}H_2CH_2OH$), 34.2 ($C\mathit{C}H_2$), 62.5 (CH_2OH), 73.2 (H*C*≡C), 97.1 (HC≡*C*) and 200.1 [Co(CO)]; *m*/*z* (FAB positive) 365 (M^+ − H_2O − H, 11%), 356 (M − CO, 10), 351 (M − H_2O − CH_2 − H, 19), 328 (M − 2CO, 100), 300 (M − 3CO, 74), 272 (M − 4CO, 59), 244 (M − 5CO, 21) and 216 (M − 6CO, 11).

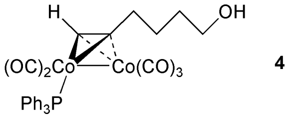
Pentacarbonyl-μ-(η^2:η^2-hex-5-yn-1-ol)(triphenylphosphine)-dicobalt(0) 4 and tetracarbonyl-μ-($\eta^2\eta^2$-hex-5-yn-1-ol)-di(triphenylphosphine)dicobalt(0) 5

To a solution of hexacarbonyl-μ-(η^2:η^2-hex-5-yn-1-ol)dicobalt(0) **3** (0.4 g, 1.04 mmol) in a solvent mixture of THF (30 cm^3) and Et_2O (10 cm^3) at 50 °C under nitrogen in the dark was added dropwise over 30 min a solution of triphenylphosphine (227 mg, 0.87 mmol) in THF (10 cm^3). After 2.5 h the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, hexane–Et_2O 4 : 1 to 0 : 1 gradient elution) to afford complexes **4** and **5**. Data for **4**: (hexane–Et_2O 2 : 1) deep red viscous oil (270 mg, 0.44 mmol, 42%) (Found: C, 56.7; H, 4.2. $C_{29}H_{25}Co_2O_6P$ requires C, 56.33; H, 4.08%); ν_{max}(hexane)/cm^{-1} 2062s, 2028w, 2008ssh, 2004s, 1990w, 1967w (C≡O); δ_H(360.0 MHz, $CDCl_3$) 1.29–1.56 (5 H, OH and $C\mathit{H}_2C\mathit{H}_2CH_2OH$), 1.98 (1 H, m, HCCC*H*H), 2.14 (1 H, m, HCCCH*H*), 3.50 (2 H, br t, *J* 5.7, $C\mathit{H}_2OH$), 5.17 (1 H, d, *J* 4.0, CH) and 7.44–7.52 (15 H, m, PPh_3); δ_C{^1H}(90.6 MHz, $CDCl_3$) 27.8 ($CCH_2\mathit{C}H_2$), 32.3 ($\mathit{C}H_2CH_2OH$), 32.5 ($C\mathit{C}H_2$), 62.7 (CH_2OH), 72.2 (H*C*≡C), 94.0 (HC≡*C*), 128.6 (d, $^3J_{CP}$ 10, Ar C-*m*), 130.4 (Ar C-*p*), 133.1 (d, $^2J_{CP}$ 11, Ar C-*o*), 134.9 (d, $^1J_{CP}$ 41, Ar C-*ipso*), 202.4 [PCoCo(CO)], 205.8 [d, $^2J_{PCoC}$ 101, PCo(CO)]; δ_P{^1H}(145.8 MHz, $CDCl_3$) 55.2 ($CoPPh_3$); *m*/*z* (FAB positive) 618 (M^+, 1%), 562 (M − 2CO, 3), 534 (M − 3CO, 26), 506 (M − 4CO, 8), 478 (M − 5CO, 100), 419 (M − 5CO − $CH_2CH_2CH_2OH$, 3) and 321 ($CoPPh_3$, 34). Data for **5**: (hexane–Et_2O 0 : 1) red–purple solid (130 mg, 0.15 mmol, 15%), mp 161–163 °C (Found: C, 64.8; H, 4.8. $C_{46}H_{40}Co_2O_5P_2$ requires C, 64.80; H, 4.73%); ν_{max}(DCM)/cm^{-1} 2010s, 1962ssh, 1950s and 1930wsh (C≡O); δ_H(360.0 MHz, $CDCl_3$) 0.70–0.95 (4 H, m, $C\mathit{H}_2C\mathit{H}_2CH_2OH$), 1.36 (1 H, s, OH), 1.40 (2 H, br m, $HCCC\mathit{H}_2$), 3.18 (2 H, br m, CH_2OH), 4.35 (1 H, br s, CH) and 7.27–7.37 (30 H, m, $2PPh_3$); δ_C{^1H}(90.6 MHz, $CDCl_3$) 27.0 ($CCH_2\mathit{C}H_2$), 31.3 ($C\mathit{C}H_2$), 32.6 ($\mathit{C}H_2CH_2OH$), 63.0 (CH_2OH), 71.9 (H*C*≡C), 89.8 (HC≡*C*), 128.3 (Ar C-*m*), 129.7 (Ar C-*p*), 133.1 (Ar C-*o*), 136.0 (m, Ar C-*ipso*), 207.4 [d, $^2J_{PCoC}$ 36, PCo(CO)]; δ_P{^1H}(145.8 MHz, $CDCl_3$) 53.4 ($CoPPh_3$); *m*/*z* (FAB positive) 796 (M^+ − 2CO, 4%), 768 (M − 3CO, 4), 740 (M − 4CO, 15), 642 [$Co_2(PPh_3)_2$, 12], 534 (M − 2CO − PPh_3, 6), 506 (M − 3CO − PPh_3, 3), 478 (M − 4CO − PPh_3, 100), 419 (M − 4CO − PPh_3 − $CH_2CH_2CH_2OH$, 5) and 321 ($CoPPh_3$, 55).

Pentacarbonyl-μ-($\eta^2\eta^2$-hex-5-yn-1-ol)(polystyrenediphenylphosphine)dicobalt(0) 6a and tetracarbonyl-μ-($\eta^2\eta^2$-hex-5-yn-1-ol)di(polystyrenediphenylphosphine)dicobalt(0) 6b

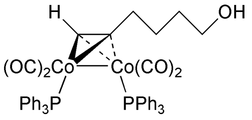
Polystyrenediphenylphosphine (1 g, 1.6 mmolP) was suspended at ambient temperature in anhydrous THF (5 cm^3) and, after 20 min under constant nitrogen agitation, a solution of hexacarbonyl-μ-(η^2:η^2-hex-5-yn-1-ol)dicobalt(0) **3** (1.2 g, 3.2 mmol) in THF (5 cm^3) was added. The mixture was heated to 50 °C under constant nitrogen agitation for 4 h. The resulting deep purple beads were filtered, washed with alternate aliquots (20 cm^3) of THF and diethyl ether until the filtrate became colourless, and dried *in vacuo* to afford the *title compound resin* (1.52 g, 0.94 ± 0.02 mmol[hex-5-yn-1-ol]g^{-1}) (Found: Co, 9.0; P, 3.6. Resin **6** requires Co, 8.90; P, 3.66%); ν_{max}(Nujol)/cm^{-1} 2055s (**6a**, C≡O), 1998vs, 1979ssh (**6a** and **6b**, C≡O) and 1950s (**6b**, C≡O) [**6a**–**6b** 6 : 4]; δ_P{^1H}(145.8 MHz)(D_2O capillary lock)

Table 4 IR spectroscopy calibration study for absorption intensities of mixtures of mono- and di(triphenylphosphine) substituted alkyne complexes **4** and **5**



4

5



Complex mixture composition **4** : **5**	**4** *a* mg, *b* mmol	**5** *c* mg, *d* mmol
6 : 4	6.4, 0.0104	5.9, 0.0069
5 : 5	6.4, 0.0104	8.8, 0.0104
4 : 6	6.4, 0.0104	13.2, 0.0155
3 : 7	3.2, 0.0052	10.3, 0.0121
2 : 8	1.6, 0.0026	8.8, 0.0104

25.6 [polystyrene-P(O)Ph_2, 20%] and 55.5 (polystyrene-PPh_2–Co, 80%).

Infra-red spectroscopy calibration study for mixtures of pentacarbonyl-μ-($\eta^2\eta^2$-hex-5-yn-1-ol)(triphenylphosphine)dicobalt(0) 4 and tetracarbonyl-μ-($\eta^2\eta^2$-hex-5-yn-1-ol)di(triphenylphosphine)dicobalt(0) 5

Complex **4** (*a* mg, *b* mmol) and complex **5** (*c* mg, *d* mmol) were dissolved in DCM (6 cm^3) and analysed by IR spectroscopy using a solution cell (Table 4). Qualitative comparison of absorption intensities with those from resin-bound mixtures provided an estimate of complex composition [**6a** + **6b**].

Pentacarbonyl-μ-(η^2:η^2-hex-5-yn-1-yl acetate)(polystyrenediphenylphosphine)dicobalt(0) 7a and tetracarbonyl-μ-(η^2:η^2-hex-5-yn-1-yl acetate)di(polystyrenediphenylphosphine)dicobalt(0) 7b

Carbonyl-μ-(η^2:η^2-hex-5-yn-1-ol)(polystyrenediphenylphosphine)dicobalt(0) [**6a** + **6b**] [300 mg, 0.28 mmol(hex-5-yn-1-ol)] was suspended at ambient temperature in anhydrous THF (10 cm^3) under constant nitrogen agitation and, after 20 min, triethylamine (2.5 cm^3) and acetic anhydride (1.5 cm^3) were added sequentially. After 20 h at ambient temperature, the resulting deep purple beads were filtered, washed thoroughly with alternate aliquots of THF and diethyl ether (20 cm^3) and dried *in vacuo* to afford the *title compound resin* (325 mg, 0.87 ± 0.02 mmol[hex-5-yn-1-yl acetate]g^{-1}); ν_{max}(Nujol)/cm^{-1} 2055s (**7a**, C≡O), 1994vs and 1981ssh (**7a** and **7b**, C≡O), 1950s (**7b**, C≡O) [**7a**–**7b** 6 : 4] and 1734m [O(C=O)CH_3]; $\delta_P\{^1H\}$(145.8 MHz)(D_2O capillary lock) 24.7 [polystyrene-P(O)Ph_2, 25%] and 54.3 (polystyrene-PPh_2-Co, 75%).

Hex-5-yn-1-yl acetate 8 [12]

Carbonyl-μ-(η^2:η^2-hex-5-yn-1-yl acetate)(polystyrenediphenylphosphine)dicobalt(0) [**7a** + **7b**] (150 mg, 0.132 mmol-[hex-5-yn-1-yl acetate]) was ground to a powder using a pestle and mortar and suspended in DCM (15 cm^3) in a 25 cm^3 round bottomed flask equipped with a condenser and $CaCl_2$ drying tube and stirred at ambient temperature in air under white light (100 W) for 72 h. The resulting brown suspension was filtered through Celite and the polymeric residue was washed with DCM. The combined filtrate and washings were concentrated *in vacuo* to afford the product as a colourless oil (12 mg, 0.09 mmol, 66 ± 2%); ν_{max}(neat)/cm^{-1} 3296w (C≡C) and 1732 (OC=O); δ_H(400.0 MHz, $CDCl_3$) 1.54 (2 H, m, $CH_2CH_2CH_2O$ or $CH_2CH_2CH_2O$), 1.68 (2 H, m, $CH_2CH_2CH_2O$ or CH_2CH_2-CH_2O), 1.90 (1 H, t, *J* 3, $HCCCH_2$), 1.98 (3 H, s, $COCH_3$), 2.17 (2H, td, *J* 7 and 3, $HCCCH_2$) and 4.02 (2 H, t, *J* 7, CH_2O) (lit.[12] 1.62, 1.77, 1.96, 2.1, 2.22 and 4.1); $\delta_C\{^1H\}$(90.6 MHz, $CDCl_3$) 18.1 ($CCCH_2$), 21.0 ($COCH_3$), 25.0 (CH_2CH_2O), 27.7 ($CCCH_2CH_2$), 64.0 (CH_2O), 68.8 (HC), 83.9 ($HCCCH_2$) and 171.2 (CO).

Pentacarbonyl-μ-(η^2:η^2-hex-5-yn-1-al)(polystyrenediphenylphosphine)dicobalt(0) 9a and tetracarbonyl-μ-(η^2:η^2-hex-5-yn-1-al)di(polystyrenediphenylphosphine)dicobalt(0) 9b

Carbonyl-μ-(η^2:η^2-hex-5-yn-1-ol)(polystyrenediphenylphosphine)dicobalt(0) [**6a** + **6b**] (500 mg, 0.47 mmol[5-hexyn-1-ol]) was suspended at ambient temperature in anhydrous DCM (5 cm^3) under constant nitrogen agitation for 20 min. DMSO (3 cm^3) and triethylamine (515 mg, 0.71 cm^3, 5.1 mmol) were added sequentially, followed by a solution of sulfur trioxide pyridine complex (405 mg, 2.55 mmol) in DMSO (2 cm^3). After 7 h at ambient temperature, the resulting deep purple beads were filtered, washed thoroughly with alternate aliquots of DMSO, DCM and diethyl ether and dried *in vacuo* to afford the *title compound resin* (495 mg, 0.85 ± 0.03 mmol[hex-5-yn-1-al]g^{-1}); ν_{max}(Nujol)/cm^{-1} 2056s (**9a**, C≡O), 1996vs and 1980ssh (**9a** + **9b**, C≡O), 1951s (**9b**, C≡O) [**9a**–**9b** 6 : 4] and 1723m (CHO); $\delta_P\{^1H\}$(145.8 MHz)(D_2O capillary lock) 24.6 [polystyrene-P(O)Ph_2, 30%] and 54.1 (polystyrene-PPh_2–Co, 70%).

Hex-5-yn-1-al 10 [15]

Carbonyl-μ-(η^2:η^2-hex-5-yn-1-al)(polystyrenediphenylphosphine)dicobalt(0) [**9a** + **9b**] (420 mg, 0.36 mmol[hex-5-yn-1-yl acetate]) was ground to a powder using a pestle and mortar and suspended in DCM (15 cm^3) in a 25 cm^3 round bottomed flask equipped with a condenser and $CaCl_2$ drying tube and stirred at ambient temperature in air under white light (100 W) for 72 h. The resulting brown suspension was filtered through Celite and the polymeric residue was washed with DCM. Careful evaporation of the filtrate and washings afforded the colourless volatile product (5.7 mg, 0.06 mmol, 17 ± 0.5%); ν_{max}(neat)/cm^{-1} 3310m (CC–H stretch), 2145w (C≡C stretch), 1723s (HC=O) and 643m (CCH bend); δ_H (360.0 MHz, $CDCl_3$) 1.79 (2 H, qn, *J* 7, CH_2CH_2CHO), 1.92 (1 H, t, *J* 3, $HCCCH_2$), 2.21 (2 H, td, *J* 7 and 3, $HCCCH_2$), 2.55 (2 H, td, *J* 7 and 1, CH_2CHO) and 9.81 (1 H, t, *J* 1, CHO) (lit.[15] 1.85, 1.98, 2.27, 2.61 and 9.80); $\delta_C\{^1H\}$(90.6 MHz, $CDCl_3$) 17.8 ($CCCH_2$), 20.8 ($CCCH_2CH_2$), 42.6 (CH_2CHO), 69.4 ($HCCCH_2$), 79.8 ($HCCCH_2$) and 201.8 (CHO).

[Tricarbonyldi(polystyrenediphenylphosphine)cobalt(1+) tetracarbonylcobaltate(1−) 14 and heptacarbonyl(polystyrenediphenylphosphine)dicobalt(0)] 15 [19b]

Polystyrenediphenylphosphine (2 g, 3.2 mmol P) was suspended at ambient temperature in anhydrous THF (15 cm^3) and a solution of octacarbonyldicobalt(0) (2.2 g, 6.4 mmol) in THF (5 cm^3) was added *via* filter cannula. After 1.5 h under constant nitrogen agitation, the mixture was filtered and washed with alternate aliquots of THF and Et_2O until the filtrate became colourless. The resulting solid was dried *in vacuo* to afford the product complex (2.37 g, 0.96 ± 0.03 mmol[Co_2]g^{-1}) as purple–red beads; ν_{max}(Nujol)/cm^{-1} 2074w, 2012msh (**15**, C≡O), 1995s (**14** + **15**, C≡O), 1985msh (**15**, C≡O), 1955w (**14**, C≡O) and 1880vs (**15**, C≡O) [**14**–**15** 7 : 3] (lit.[19b] 2000s, 1955m, 1800s); $\delta_P\{^1H\}$(145.8 MHz)(D_2O capillary lock, THF-swollen resin) 32 [polystyrene-P(O)Ph_2, 25%] and 62 (polystyrene-PPh_2–Co, 75%).

Hexacarbonyldi(polystyrenediphenylphosphine)dicobalt(0)-(Co–Co) 16 [19b]

The resin-bound complex **16** was prepared both a) by thermal treatment of resin-bound complexes [**14** + **15**] and; b) by direct reaction between polystyrenediphenylphosphine and octacarbonyldicobalt(0) at elevated temperature.

a) Thermal treatment of resin-bound complexes [14 + 15]. Resin-bound complex mixture [**14** + **15**] (490 mg, 0.47 mmol-[Co_2]g^{-1}) was suspended in anhydrous 1,4-dioxane (10 cm^3) and was heated to 75 °C for 16 h in the dark. The black mixture was cooled, filtered and washed with alternate aliquots of THF and Et$_2$O until the filtrate became colourless. The resulting solid was dried *in vacuo* to afford the product complex (482 mg, 0.22 ± 0.05 mmol[Co$_2$]g^{-1}) as deep purple beads; ν_{max}(Nujol)/cm^{-1} 2032w, 1977msh, 1949s and 1925msh (C≡O) (lit.[19b] 2041vw, 1963sh, 1952vs and 1901vw); $\delta_P\{^1H\}$(145.8 MHz)(D$_2$O capillary lock, THF-swollen resin) 31 [polystyrene-P(O)Ph$_2$, 70%] and 68 (polystyrene-PPh$_2$–Co, 30%).

b) Direct reaction between polystyrenediphenylphosphine and octacarbonyldicobalt(0) at elevated temperature. Polystyrenediphenylphosphine (1 g, 1.6 mmol P) was suspended at ambient temperature in anhydrous 1,4-dioxane (15 cm^3) for 30 min, after which time a solution of octacarbonyldicobalt(0) (383 mg, 1.12 mmol) in 1,4-dioxane (5 cm^3) was added *via* filter cannula. After 30 min under constant nitrogen agitation at ambient temperature, the mixture was heated to 75 °C for 16 h in the dark. The black mixture was cooled, filtered and washed with alternate aliquots of THF and Et$_2$O until the filtrate became colourless. The resulting solid was dried *in vacuo* to afford the product complex (1.15 g, 0.42 ± 0.04 mmol[Co$_2$]g^{-1}) as deep purple beads (Found: Co, 7.7; P, 3.7. Resin **16** requires Co, 4.98; P, 3.61%); ν_{max}(Nujol)/cm^{-1} 2032w, 1977msh, 1949s and 1925msh (C≡O) (lit.[19b] 2041vw, 1963sh, 1952vs and 1901vw); $\delta_P\{^1H\}$(145.8 MHz, D$_2$O capillary lock, THF-swollen resin) 29 [polystyrene-P(O)Ph$_2$, 40%] and 69 (polystyrene-PPh$_2$–Co, 60%).

Hexacarbonyldi(triphenylphosphine)dicobalt(0) 17 [20]

Octacarbonyldicobalt(0) (1.1 g, 3.21 mmol), triphenylphosphine (1.69 g, 6.43 mmol) and 1,4-dioxane (20 cm^3) were combined under nitrogen and heated to 60 °C in the dark for 6 h. The red–brown precipitate was filtered, washed with THF (3 × 10 cm^3) and dried *in vacuo* to give the title complex (2.28 g, 2.81 mmol, 96%) as a brown powder, mp 125–130 °C (dec.) (lit.[20] 130 °C) (Found: C, 62.4; H, 3.8. $C_{42}H_{30}Co_2O_6P_2$ requires C, 62.24; H, 3.73%); ν_{max}(Nujol)/cm^{-1} 1969msh, 1943s, 1898msh and 1810w (C≡O); *m*/*z* (FAB positive) 321 (Ph$_3$PCo$^+$, 6%).

Heptacarbonyl(triphenylphosphine)dicobalt(0) 18 [21]

To a solution of octacarbonyldicobalt(0) (2 g, 5.85 mmol) in THF (15 cm^3) under nitrogen in the dark was added a solution of triphenylphosphine (1.38 g, 5.26 mmol) over 30 min. After a further 30 min the mixture was concentrated *in vacuo* and the brown residue was purified by flash column chromatography (SiO$_2$, hexane–Et$_2$O 1 : 0 to 9 : 1 gradient elution) and recrystallisation (hexane–Et$_2$O) to give the title complex (1.97 g, 3.42 mmol, 65%) as deep purple crystals, mp 120–125 °C (dec.) (Found: C, 52.1; H, 2.7. $C_{25}H_{15}Co_2O_7P$ requires C, 52.11; H, 2.62%); ν_{max}(THF)/cm^{-1} 2077m, 2023w, 1988s and 1958w (C≡O) (lit.[21] 2079, 2026, 2010sh, 1996, 1964); δ_H(360.0 MHz, CDCl$_3$) 7.48 (m, Ar–H); $\delta_C\{^1H\}$(90.6 MHz, CDCl$_3$) 129.5 (d, $^3J_{CP}$10, Ar C-*m*), 131.3 (s, Ar C-*p*), 132.6 (Ar C-*ipso*), 133.1 (d, $^2J_{CP}$10, Ar C-*o*) and 201.1 [br s, Co(CO)]; $\delta_P\{^1H\}$(145.8 MHz, CDCl$_3$) 65.3 (CoPPh$_3$); *m*/*z* (FAB positive) 548 (M$^+$ − CO, 2%), 492 (M − 3CO, 21), 405 (M − Co − 4CO, 7), 377 (M − Co − 5CO, 13), 349 (M − Co − 6CO, 17) and 321 (CoPPh$_3$, 100).

Tricarbonyldi(triphenylphosphine)cobalt(1+) tetracarbonylcobaltate(1−) 19 [22]

To a solution of octacarbonyldicobalt(0) (300 mg, 0.88 mmol) in THF (50 cm^3) under nitrogen at ambient temperature was added triphenylphosphine (1.84 g, 7.02 mmol) as one portion. After stirring for 20 min, the solution was cooled to 0 °C whereupon hexacarbonyldi(triphenylphosphine)dicobalt(0) **17** (104 mg, 0.13 mmol, 15%) precipitated. The mixture was filtered *via* filter cannula under nitrogen and to the filtrate was added hexane (50 cm^3). The resulting precipitate was collected by filtration, washed with hexane (3 × 10 cm^3) and dried *in vacuo* to afford the title complex (575 mg, 0.69 mmol, 78%) as a pale brown crystalline solid, mp 135–140 °C (dec.) (Found: C, 61.6; H, 3.8. $C_{43}H_{30}Co_2O_7P_2$ requires C, 61.59; H, 3.61%); ν_{max}(Nujol)/cm^{-1} 1999s, 1975msh and 1888sbr (C≡O) (lit.[22] 2002s, 1883vs); δ_H(360.0 MHz, CDCl$_3$) 7.44 (12 H, br m, Ar–H) and 7.63 (18 H, br m, Ar–H); $\delta_P\{^1H\}$(145.8 MHz, CDCl$_3$) 55.5 (CoPPh3); *m*/*z* (FAB positive) 667 [Co(CO)$_3$(PPh$_3$)$_2$$^+$, 50%], 611 [Co(CO)(PPh$_3$)$_2$, 16], 583 [Co(PPh$_3$)$_2$, 100] and 321 (CoPPh$_3$, 90).

Pentacarbonyl-μ-(η^2:η^2-hex-5-yn-1-ol)(polystyrenediphenylphosphine)dicobalt(0) 6a and tetracarbonyl-μ-(η^2:η^2-hex-5-yn-1-ol)di(polystyrenediphenylphosphine)dicobalt(0) 6b (direct method)

To a suspension of complex mixture [**14** + **15**] (400 mg, 0.38 mmol[Co$_2$]) in anhydrous dioxane (10 cm^3) was added hex-5-yn-1-ol (254 mg, 0.29 cm^3, 2.6 mmol). After 2 h constant nitrogen agitation at 70 °C, the deep purple beads were filtered, washed thoroughly with alternate aliquots of THF and diethyl ether and dried *in vacuo* to afford the product complex (408 mg, 0.30 ± 0.09 mmol[hex-5-yn-1-ol]g^{-1}); ν_{max}(Nujol)/cm^{-1} 2055w (**6a**, C≡O), 2009s (**6a** and **6b**, C≡O), 1967ssh (**6a**, C≡O) and 1948vs and 1930ssh (**6b**, C≡O) [**6a**–**6b** 3 : 7]; $\delta_P\{^1H\}$(145.8 MHz, D$_2$O capillary lock) −5 (polystyrene-PPh$_2$, 20%), 25 [polystyrene-P(O)Ph$_2$, 60%] and 55 (polystyrene-PPh$_2$–Co, 20%).

For acetylation and decomplexation of the product alkynyl ester the procedures were identical to those employed for the indirect loading method.

Pentacarbonyl-μ-(η^2:η^2-hex-5-yn-1-yl acetate)(polystyrenediphenylphosphine)dicobalt(0) 7a and tetracarbonyl-μ-(η^2:η^2-hex-5-yn-1-yl acetate)di(polystyrenediphenylphosphine)dicobalt(0) 7b

Carbonyl-μ-(η^2:η^2-hex-5-yn-1-ol)(polystyrenediphenylphosphine)dicobalt(0) [**6a** + **6b**] [300 mg, 0.09 mmol(hex-5-yn-1-ol)] was suspended at ambient temperature in anhydrous THF (10 cm^3) under constant nitrogen agitation and, after 20 min, triethylamine (2.5 cm^3) and acetic anhydride (1.5 cm^3) were added sequentially. After 20 h at ambient temperature, the resulting deep purple beads were filtered, washed thoroughly with alternate aliquots of THF and diethyl ether (20 cm^3) and dried *in vacuo* to afford the product resin (296 mg, 0.30 ± 0.09 mmol[hex-5-yn-1-yl acetate]g^{-1}); ν_{max}(Nujol)/cm^{-1} 2055w (**7a**, C≡O), 2010s (**7a** and **7b**, C≡O), 1967ssh (**7a**, C≡O), 1949vs and 1930ssh (**7b**, C≡O) [**7a**–**7b** 3 : 7] and 1732m [O(C=O)CH$_3$]; $\delta_P\{^1H\}$(145.8 MHz, D$_2$O capillary lock) −5.2 (polystyrene-PPh$_2$, 20%), 24.8 [polystyrene-P(O)Ph$_2$, 60%] and 53.4 (polystyrene-PPh$_2$–Co, 20%).

Hex-5-yn-1-yl acetate 8 [12]

Carbonyl-μ-(η^2:η^2-hex-5-yn-1-yl acetate)(polystyrenediphenylphosphine)dicobalt(0) [**7a** + **7b**] (280 mg, 0.08 mmol-[hex-5-yn-1-yl acetate]) was ground to a powder using a pestle and mortar and suspended in DCM (15 cm^3) in a 25 cm^3 round bottomed flask equipped with a condenser and CaCl$_2$ drying tube and stirred at ambient temperature in air under white light (100 W) for 72 h. The resulting brown suspension was filtered through Celite and the polymeric residue was washed with DCM. The combined filtrate and washings were concentrated *in vacuo* to afford the product as a colourless oil (8.5 mg, 0.06 mmol, 72 ± 30%).

Hexacarbonyl[*N*-(prop-2-enyl)-*N*-μ-(η^2:η^2-prop-2-ynyl)-*p*-toluenesulfonamide]dicobalt(0) 23

To a solution of *N*-(prop-2-enyl)-*N*-(prop-2-ynyl)-*p*-toluenesulfonamide **22** (1 g, 4.02 mmol) in DCM (20 cm^3) at ambient temperature under nitrogen was added octacarbonyldicobalt(0) (1.51 g, 4.42 mmol). After 2 h the mixture was concentrated

Table 5 Conditions and reagents for catalytic Pauson–Khand annelation

Entry	Catalyst precursor	Catalyst precursor (mg, mmol)	Solvent	*T* / °C (*z*)
3.1	[**14** + **15**]′	26, 0.025	THF	70
3.2	**16**′	63, 0.025	THF	70
3.3	[**14** + **15**]′	26, 0.025	THF	65
3.4	**16**′	63, 0.025	THF	65
3.5	[**14** + **15**]′	26, 0.025	THF	75
3.6	**16**′	63, 0.025	THF	75
3.7	**16**′	63, 0.025	1,4-Dioxane	70
3.8	**16**′	63, 0.025	Toluene	70

in vacuo and purified by flash column chromatography (SiO_2, hexane–Et_2O 1 : 0 to 19 : 1 gradient elution) to give the *title complex* (1.92 g, 3.59 mmol, 89%) as a deep red solid, mp 100–101 °C (Found: C, 42.6; H, 2.9; N, 2.6. $C_{19}H_{15}Co_2NO_8S$ requires C, 42.64; H, 2.82; N, 2.62%); ν_{max}(DCM)/cm^{-1} 2096w, 2058s, 2029s (C≡O) and 1159 [S(=O)$_2$]; δ_H(360.0 MHz, $CDCl_3$) 2.44 (3 H, s, CH_3), 3.97 (2 H, d, *J* 7, CH_2CH=CH$_2$), 4.49 (2 H, s, CH_2CCH), 5.16 [1 H, dd, *J* 11, 1, C=C*H*H], 5.20 [1 H, dd, *J* 7, 1, C=CH*H*], 5.54 (1 H, m, C*H*=CH$_2$), 6.01 (1 H, s, CH$_2$CC*H*) and 7.31 (2 H, d, *J* 8, Ar–H) and 7.72 (2 H, d, *J* 8, Ar–H); δ_C\{^{1}H\}(90.6 MHz, $CDCl_3$) 21.6 (CH_3), 48.8 (*C*H$_2$CCH), 50.5 (*C*H$_2$CH=CH$_2$), 73.7 (CH$_2$C*C*H), 89.7 (CH$_2$*C*CH), 120.1 (CH=*C*H$_2$), 127.3 (*o*-Ar), 129.9 (*m*-Ar), 132.1 (*C*H=CH$_2$), 137.4 (*p*-Ar), 143.7 (*ipso*-Ar) and 199.1 [Co(CO)]; *m*/*z* (FAB positive + NaI) 557 (MNa$^+$ − H, 22%), 501 (MNa − H − 2CO, 38), 473 (MNa − H − 3CO, 47), 417 (MNa − H − 5CO, 52), 366 (MH − 6CO, 40), 272 (MNa − 2Co − 6CO, 59), 143 [Co(CO)$_3$, 23] and 59 (Co, 100).

Pentacarbonyl(polystyrenediphenylphosphine)[*N*-(prop-2-enyl)-*N*-*μ*-(η^2:η^2-prop-2-ynyl)-*p*-toluenesulfonamide]dicobalt(0) 24a and tetracarbonyldi(polystyrenediphenylphosphine)[*N*-(prop-2-enyl)-*N*-*μ*-(η^2:η^2-prop-2-ynyl)-*p*-toluenesulfonamide]dicobalt(0) 24b

Polystyrenediphenylphosphine (1 g, 1.6 mmolP) was suspended at ambient temperature in THF (10 cm^3) under constant nitrogen agitation for 20 min. To the suspension was added a solution of hexacarbonyl[*N*-(prop-2-enyl)-*N*-*μ*-(η^2:η^2-prop-2-ynyl)-*p*-toluenesulfonamide]dicobalt(0) **23** (860 mg, 1.6 mmol) in THF (5 cm^3) *via* cannula under nitrogen and the mixture was heated to 50 °C for 4 h in the dark. The beads were filtered and washed with alternate aliquots of THF and Et_2O until the filtrate became colourless and dried *in vacuo* to give the *title compound resin* (1.61 g, 0.44 ± 0.03 mmol[*N*-(prop-2-enyl)-*N*-(prop-2-ynyl)-*p*-toluenesulfonamide]g^{-1}) as deep purple beads; ν_{max}(Nujol)/cm^{-1} 2075w and 2047w (**24a**, C≡O), 2031m, 2008m, 1976m, 1949s and 1926msh (**24b**, C≡O) and 1350w and 1157w [S(=O)$_2$]; δ_P\{^{1}H\}(145.8 MHz, D_2O capillary lock) 28 [polymer-P(O)Ph$_2$, 30%], 63 [polymer-PPh$_2$Co, 70%]; *m*/*z* (FAB positive) 437 (tetracarbonyl[*N*-(prop-2-enyl)-*N*-*μ*-(η^2:η^2-prop-2-ynyl)-*p*-toluenesulfonamide]dicobalt(0)$^+$ − CH$_2$CH=CH$_2$ − H, 1%), 410 (tricarbonyl[*N*-(prop-2-enyl)-*N*-*μ*-(η^2:η^2-prop-2-ynyl)-*p*-toluenesulfonamide]dicobalt(0) − CH$_2$CH=CH$_2$, 2%) and 394 (monocarbonyl[*N*-(prop-2-enyl)-*N*-*μ*-(η^2:η^2-prop-2-ynyl)-*p*-toluenesulfonamide]dicobalt(0)$^+$ − H, 1%).

Procedure for stoichiometric Pauson–Khand annelation of polymer-bound complexes [**24a** + **24b**]:

2,3,3a,4-Tetrahydro-2-[(4-methylphenyl)sulfonyl]cyclopenta[*c*]-pyrrol-5(1*H*)-one 25[27b]

Resin [**24a** + **24b**] (600 mg, 0.26 mmol[*N*-(prop-2-enyl)-*N*-(prop-2-ynyl)-*p*-toluenesulfonamide]) was suspended in THF (10 cm^3) under an atmosphere of CO (1.05 mbar) and was heated to 70 °C for 24 h in the dark. The resulting deep brown mixture was filtered, the purple beads were washed with alternate aliquots of THF and Et_2O (4 × 5 cm^3) and the combined filtrates were concentrated *in vacuo*. Purification of the resulting brown residue by flash column chromatography (SiO_2, hexane–EtOAc 4 : 1 to 3 : 2 gradient elution) gave the title compound **25** (19 mg, 0.069 mmol, 26 ± 1%) as a white solid. (See below for spectroscopic data.)

Characterisation of batches of resins [14 + 15]′ and 16′ used for catalysis experiments

Employing a method identical to that for [**14** + **15**] described above, the resin complex [**14** + **15**]′ was isolated as purple–red beads:

[**14** + **15**]′: (1.19 g, 0.96 ± 0.03 mmol[Co$_2$]g^{-1}) [0.95 mmol-[Co$_2$]g^{-1} applied to catalysis]; ν_{max}(Nujol)/cm^{-1} 2074w, 2014msh (**14**, C≡O), 1995s (**14**+**15**, C≡O), 1982msh (**1**, C≡O), 1955w (**14**, C≡O) and 1878vs (**14**, C≡O) [**14**–**15** 7 : 3] (lit.[19b] 2000s, 1955m, 1800s); δ_P\{^{1}H\}(145.8 MHz)(D_2O capillary lock, THF-swollen resin) 31 [polystyrene-P(O)Ph$_2$, 25%] and 68 (polystyrene-PPh$_2$–Co, 75%).

Employing a method identical to that for **16** described above, the resin complex **16**′ was isolated as deep purple beads (1.15 g, 0.36 ± 0.04 mmol[Co$_2$]g^{-1}) [0.4 mmol[Co$_2$]g^{-1} applied to catalysis]; ν_{max}(Nujol)/cm^{-1} 2032w, 1977msh, 1949s and 1925msh (C≡O) (lit.[19b] 2041vw, 1963sh, 1952vs and 1901vw); δ_P\{^{1}H\}(145.8 MHz)(D_2O capillary lock, THF-swollen resin) 29 [polystyrene-P(O)Ph$_2$, 50%] and 69 (polystyrene-PPh$_2$–Co, 50%).

2,3,3a,4-Tetrahydro-2-[(4-methylphenyl)sulfonyl]cyclopenta[*c*]-pyrrol-5(1*H*)-one 25 *via* catalysis[27b]

A mixture of Catalyst Precursor ([**14** + **15**]′, or **16**′) and *N*-(2-propenyl)-*N*-(2-propynyl)-4-methylphenylsulfonamide **22** (125 mg, 0.5 mmol) in anhydrous solvent (5 cm^3) under an atmosphere of CO (1.05 bar) was heated to *z* °C for 24 h in the dark without stirring (for details refer to Table 5). The mixture was filtered, the resin was washed with alternate aliquots of THF and Et_2O (4 × 1 cm^3) and the combined filtrates were concentrated *in vacuo*. The brown residue was redissolved in $CDCl_3$ and the extent of reaction was calculated from ^{1}H NMR spectroscopy.

For the experiment listed in Table 5, entry 2, purification of the residue by flash column chromatography (SiO_2, hexane–EtOAc 4 : 1 to 3 : 2 gradient elution) gave the title compound (85 mg, 0.31 mmol, 61%) as a white solid; mp 147–149 °C (lit.[27b] 145–148 °C); ν_{max}(DCM)/cm^{-1} 3058w [C–H(Ar)], 1716s (C=O) and 1350s and 1164 (NSO$_2$); δ_H(360.0 MHz, $CDCl_3$) 1.99 [1 H, dd, *J* 18, 4, C*H*H(7)], 2.32 (3 H, s, CH_3), 2.48–2.58 [2 H, m, CH*H*(7) and C*H*H(4)], 3.08 [1 H, m, CH(6)], 3.93–3.98 [2 H, m, CH*H*(4) and C*H*H(5)], 4.27 [1 H, d, *J* 17, CH*H*(5)], 5.92 (1 H, s, C=C*H*), 7.28 (2 H, d, *J* 8, *m*-Ar–*H*), 7.66 (2 H, d, *J* 8, *o*-Ar–*H*); δ_C\{^{1}H\}(90.6 MHz, $CDCl_3$) 21.6 (CH_3), 39.8 [CH$_2$(7)], 44.0 [CH(6)], 47.7 [CH$_2$(5)], 52.5 [CH$_2$(4)], 126.2 (C=*C*H), 127.5 (*o*-Ar-C), 130.1 (*m*-Ar-C), 144.2 (*ipso*-Ar–C), 178.6 (*C*=CH), 207.2 (C=O); *m*/*z* (FAB positive) 278 (MH$^+$, 38%), 154 (M − $C_7H_7O_2$, 100), 122 (M − $C_7H_7O_2S$, 100) and 91 (C_7H_7, 23).

On one occasion, the deep purple resin collected after catalysis was dried *in vacuo* and sent for microanalysis (Found: Co, 6.7; P, 3.48).

[Tricarbonyldi(Novageldiphenylphosphine)cobalt(1+) tetracarbonylcobaltate(1−) 26 and heptacarbonyl(Novageldiphenylphosphine)dicobalt(0)] 27

The resin 'Novageldiphenylphosphine' (NGDP) (250 mg, 0.53 mmol Pg^{-1}) was suspended in oxygen-free anhydrous THF (5 cm^3) and allowed to swell for 10 min under nitrogen agitation. A solution of commercial octacarbonyldicobalt(0) (226 mg, 0.66 mmol) in anhydrous, deoxygenated THF (5 cm^3) was added under nitrogen agitation and the dark mixture was left at RT for 10 min. 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; {100% P site complexation, 60% ionic complex (**26**), 40% mono complex (**27**), 0.47 mmol $[Co_2(CO)_7]$ g^{-1}}, ν_{max}(Nujol)/cm^{-1} 2074w, 2012msh, 1995s, 1955w and 1880vs (C≡O); δ_P(145 MHz; THF [D_2O capillary lock]) 66 (polymer-PPh_2–[Co], mono complex (**16**), 40%), 75 (polymer-PPh_2–[Co], ionic complex (**15**), 60%).

Application in the Pauson–Khand annelation

Resin [**26** + **27**] was subjected to identical reaction conditions to those used for entry 1 in Table 3 (see Protocol above and Table 4) and was found to produce a conversion to cyclopentenone **25** of 68%.

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