Dicobaltbisnorbornadienetetracarbonyl [Co$_2$(nbd)$_2$(CO)$_4$] reacts with oxygen-containing alkynes and gives crossover products in the presence of other alkenes

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Dicobaltbisnorbornadienetetracarbonyl, [Co$_2$(nbd)$_2$(CO)$_4$] DDTC, (nbd = norbornadiene) which has previously been reported to be unreactive with alkynes is shown to react with oxygen-containing alkynes; in the presence of other alkenes crossover reaction is seen which has important implications for the mechanism of this, and possibly other, reactions.

In one of the earliest papers[1] describing the Pauson–Khand (PK) reaction, a by-product was observed which was shown to be dicobaltdinorbornabisenetetracarbonyl, DDTC **1** (Scheme 1). The solid state structure was shown to be the carbonyl bridged dimer **1**[2] although the solution structure is fluxional with bridged and non-bridged species in equilibrium.[3] This dimeric, carbonyl-bridged species was reported[1] to be inactive in the PK reaction and represented a dead-end in terms of wasting both metal and alkene. As, in recent years, both cost and environmental considerations have led to much investigation of catalytic variations on the PK reaction,[4,5] and in view of our interest in the fundamental organometallic chemistry of such systems[6] and the reactions of unsaturated bicyclics with cobalt carbonyl[7] an investigation was undertaken into the reported unreactivity of this species. Given that any species which could be formed by the displacement of either norbornadiene, **2** or carbonyls **3**, by an alkyne would be similar to the proposed intermediates **III** in the PK reaction[8] (Scheme 2) it might be expected that such a reaction would lead to cyclopentenone products. Pauson and Khand investigated the reactions of **1** with a series of purely hydrocarbon alkynes and reported that in no case were significant yields of the cyclopentenone observed.
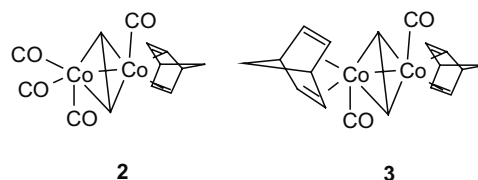

Fig. 1 Possible DDTC alkyne adducts.

Results and discussion

As benchmarks to ensure that our experimental procedures and findings were compatible with those previously reported this investigation repeated the earlier work with phenylacetylene, diphenylacetylene and hex-1-yne, recovering the cyclopentenone products in reasonable yields in the conventional reactions, and recovering no cyclopentenone at all from the reactions using **1** (Table 1). Having confirmed the earlier findings, which concerned only purely hydrocarbon alkynes, next a series of alkynols were introduced to the study. In dramatic contrast to the results obtained with hydrocarbon alkynes, prop-1-yn-3-ol, 3-methylbut-1-yn-3-ol, 1-butyn-4-ol and hex-1-yn-4-ol all gave substantial yields of cyclopentenones regardless of whether
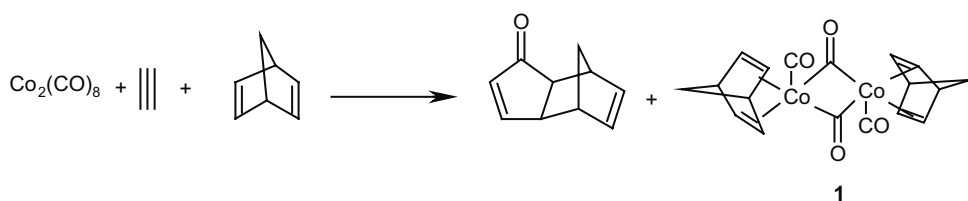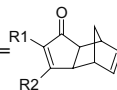

Scheme 1   Production of DDTC according to Khand *et al.*[1]
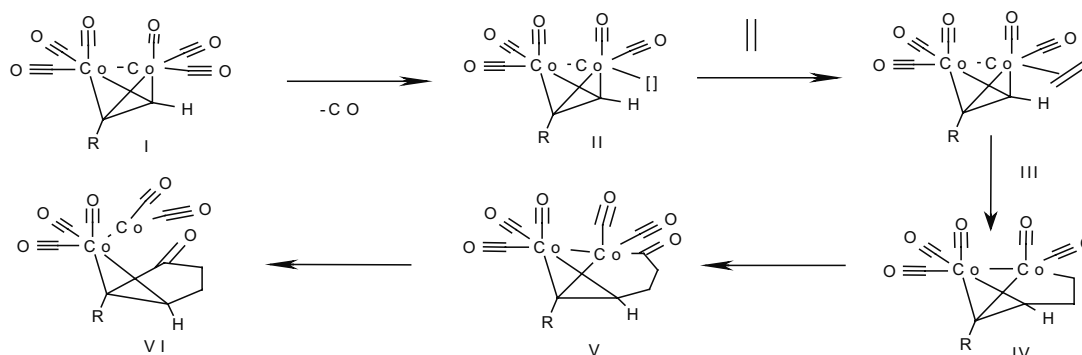
Scheme 2   Steps of the PK reaction.

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**Table 1** Attempted reaction of DDTC with hydrocarbon alkynes product =

	Substrate		Reagents	a	Product	Yield/%
1	PhC≡CH	+	Co$_2$(CO)$_8$	→	R^1 = Ph, R^2 = H	45
			+ nbd	→	**4** [1]	
2	PhC≡CH	+	DDTC	→	None recovered	
3	PhC≡CPh	+	Co$_2$(CO)$_8$	→	R^1 = R^2 = Ph	30
			+ nbd	→	**5** [5]	
4	PhC≡CPh	+	DDTC	→	None recovered	
5	BuC≡CH	+	Co$_2$(CO)$_8$	→	R^1 = Bu, R^2 = H	32
			+ nbd	→	**6** [5]	
6	BuC≡CH	+	DDTC	→	None recovered	

[a] DCM reflux 12 h.

1 or dicobaltoctacarbonyl were used as the source of metal and carbon monoxide (Table 2). This reactivity is remarkable when contrasted with the complete failure of the hydrocarbon analogues to give the product. It seemed likely that the hydroxyl group was assisting the reaction by coordinating to cobalt and allowing the chelate effect to assist the formation of a cobalt–alkyne complex which is presumably required for cyclopentenone formation. Although cobalt carbonyls are generally thought of as preferring soft donors to hard, there is evidence[9] of Lewis bases such as ethers promoting the PK reaction and of alkenyl thiols and amines directing the regioselectivity of the PK[10] so such a proposal is not unreasonable. Indeed it is tempting to propose a correlation between proximity of the hydroxyl group to the alkyne and the reactivity, as the difference in yield of cylopentenone between the conventional reaction and the DDTC mediated analogue appears to correlate with the number of methylene units separating them:–n:($\Delta\%_{Co_2CO_8}$–$\%_{DDTC}$) 1:19; 2:34; 4:43. These comparisons are using recovered yield as a very approximate measure of reactivity and thus must be treated with some caution, but in the absence of a rigorous study of reactivity these data do seem to provide a *prima facie* case that oxygen substituents assist reactivity by interaction with cobalt centres.

This proposition implied that other oxo-alkynes could show reactivity with **1** and a small range of other such species were tested in the DDTC-modified PK reaction. Two methyl ethers, 3-methoxy-3-methylbut-1-yne and 3-methoxyprop-1-yne gave differing results, with the more sterically hindered alkyne failing to react, while the unhindered gave a reasonable yield of product **11**[14] (Scheme 3). An ester, ethyl propiolate, failed to give any product under the same conditions. To clarify if an electron rich alkyne were likely to be any more reactive in the absence of oxygenation, trimethysilylacetylene was screened under the same conditions, with no reaction being observed. (Scheme 4). These findings can be rationalised in terms of hemilabile coordination of oxygen: the alcohols and unhindered ethers thus showed reactivity as a result of assisted coordination of the alkyne by the chelate effect; the failure of the hindered ether to react can be rationalised in terms of failure of the hindered ether group to coordinate, and the conjugated ester may simply be too electron poor to provide a good donor.

Finally, and most informative in mechanistic terms, a reaction was undertaken in which a reactive alkyne, **1**, and another reactive alkene, norbornene, were heated together under the standard conditions. It was expected that the reaction of DDTC with an alkene would lead to very rapid formation

Table 2 Reaction of DDTC with oxy-alkynes product =
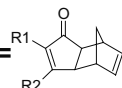
	Substrate	+	Reagents	a	Product	Yield/%
1	HC≡CH$_2$OH	+	Co$_2$(CO)$_8$ + nbd	→	R^1 =CH$_2$OH, R^2 = H **7**[11]	65
2	HC≡CH$_2$OH	+	DDTC	→	R^1 =CH$_2$OH, R^2 = H **7** [11]	46
3	HC≡CMe$_2$OH	+	Co$_2$(CO)$_8$ + nbd		R^1 =C(Me)$_2$OH, R^2 = H **8** [12]	60
4	HC≡CMe$_2$OH	+	DDTC		R^1 =C(Me)$_2$OH, R^2 = H **8**[12]	52
5	HC≡C(CH$_2$)$_2$OH	+	Co$_2$(CO)$_8$ + nbd	→	R^1 = (CH$_2$)$_2$OH, R2 = H **9** [9]	59
6	HC≡C(CH$_2$)$_2$OH	+	DDTC		R^1 = (CH$_2$)$_2$OH, R^2 = H **9** [13]	25
7	HC≡C(CH$_2$)$_4$OH	+	Co$_2$(CO)$_8$ + nbd	→	R^1 = (CH$_2$)$_4$OH, R^2 = H **10** [13]	63
8	HC≡C(CH$_2$)$_4$OH	+	DDTC	→	R^1 = (CH$_2$)$_4$OH, R^2 = H **10** [13]	20

[a] DCM reflux 12 h.

R=H, 11, 49%
R=Me no reaction
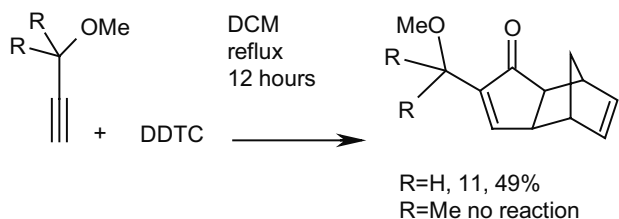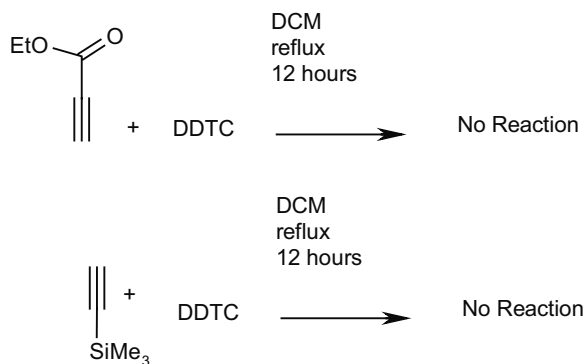
Scheme 3

Scheme 4

of PK products with as either of the species in Fig. 1 would be expected to follow the pathway of Scheme 2 and rapidly give cyclised products as direct observation of PK intermediates is rare and they are thought of as transient. Unexpectedly this gave a mixture of the products from norbornadiene incorporation into the cyclopentenone and incorporation of norbornene in a 2.3:1 ratio (Scheme 5). This indicates that a simple mechanistic explanation in which following oxygen coordination the alkyne displaces the bridging carbonyls, and then the dicobaltbisnorbornadiene carbonyl species follows the putative steps of the PK reaction[8] is either not occurring, or accounts for only one mechanistic path. Simple ligand exchange in the cobalt carbonyl alkene complex *prior* to reaction with the alkyne is unlikely to explain the formation of the crossover product for three reasons:

(1) Although an excess of norbornene is used, norbornadiene is a chelating ligand, thus at equilibrium a 2.3:1 ratio of alkenes is highly unlikely.

(2) No evidence was observed of mixed norbornadiene–norbornene complexes. Although the failure to observe a species is no evidence of its non-intermediacy it is difficult to explain why such an intermediate should so rapidly undergo the PK reaction that it is consumed preferentially to DDTC which is observed in incomplete reaction mixtures.

(3) The reaction of norbornene with cobalt carbonyl species which are not coordinated to other organic fragments leads not to stable alkene complexes but to a carbonylative dimerisation,[7] which was not observed in this reaction.

It is also possible that coordination of the hydroxyalkyne is leading to loss of a norbornadiene ligand, and that the insertion of alkene into a cobalt–carbon bond involves

a monocoordinated alkene, under which (weak) binding mode it is likely that norbornadiene and norbornene would exchange. Finally, it has been postulated[15] that in the case of the catalyst [(BINAP)Co$_2$(CO)$_6$], (BINAP = Bisdiphenylphosphinobinaphthylene) which shows asymmetric cobalt centres, the BINAP-coordinated cobalt is not involved in reaction, and that all the bond-forming steps take place on the other cobalt centre: if this suggestion is accepted then it could be postulated that a similar pathway is operating in the present system. This would involve an inert norbornadiene–Co(CO)$_2$ fragment acting as an observer to a series of displacements and insertions on the second metal centre which would necessarily involve non-chelated alkene ligands and thus promote exchange of the competitive alkenes (Fig. 2).

Experimental

General procedure for the PK reactions using dicobaltoctacarbonyl: To a flame dried (200 ml) Schlenk flask equipped with a reflux condenser was added dicobaltoctacarbonyl (3.0 g, 8.86 mmol), the relevant alkynol (8.05 mmol) and dry, degassed dichloromethane (20 ml) under an inert atmosphere. The mixture was stirred at room temperature until the dicobalthexacarbonyl alkyne complex was formed as indicated by a high running red TLC spot (*ca* 30 min). To the reaction mixture, norbornadiene (8.14 ml, 80.0 mmol) was added and the reaction mixture heated at reflux for 12 hours. The reaction mixture was then filtered and evaporated to dryness, dissolved in dichloromethane (DCM) (100 ml) treated with activated charcoal (0.5 g) silica (*ca* 0.5 g) and stirred under an atmosphere of air overnight then purified by column chromatography to give the results listed in Table 1.

General procedure for PK reactions of alkynols using [Co$_2$(nbd)$_2$(CO)$_4$]: To a flame dried (200 ml) Schlenk flask equipped with a reflux condenser was added DDTC (2.0 g, 4.72 mmol), the relevant alkynol (5.19 mmol) and dry, degassed dichloromethane (20 ml) under an inert atmosphere. The reaction mixture was heated at reflux for 12 hours then filtered over celite, evaporated to dryness dissolved in DCM (100 ml) treated with activated charcoal (0.5 g) silica (*ca* 0.5 g) and stirred under an atmosphere of air overnight. The product was then purified by column chromatography to give the products listed in table 2.

Compounds **4–10** (Tables 1 and 2) gave properties identical with those reported in the literature reference indicated in the tables.

2-(Methoxymethyl)-3a,4,7,7a-tetrahydro-4,7-methano-1H-inden-1-one (11): To a flame, dried (200 ml) Schlenk flask equipped with a reflux condenser was added DDTC (2.0 g, 4.72 mmol), methyl propargyl ether (0.44 ml, 5.19 mmol) and dry, degassed dichloromethane (20 ml) under an inert atmosphere. The reaction mixture was heated at reflux for 12 hours then filtered and evaporated to dryness (black/brown solid), dissolved in DCM (100 ml) treated with activated charcoal (0.5 g) silica (*ca* 0.5 g) and stirred under an atmosphere of air overnight. The product was then purified by column chromatography to give **11** as a yellow oil. (0.49 g, 2.6 mmol, 50%) properties as previously reported.[14]
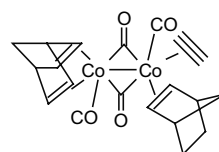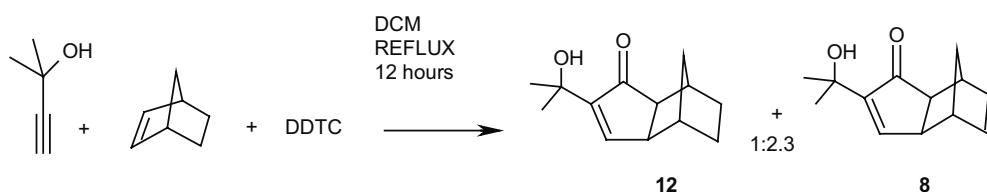

Fig.2 Non-bridging alkyne complexes see ref 15.

Scheme 5 Crossover reactions with DDTC and norbornene.

Crossover reaction of [Co₂(nbd)₂(CO)₄] with norbornene: To a flame, dried (200 ml) Schlenk flask equipped with a reflux condenser was added DDTC (2.0 g, 4.72 mmol), 2 methylbut-3-yn-2-ol (0.5 ml, 5.19 mmol) and norbornene (5 g, 0.053 mol). Dry, degassed dichloromethane (20 ml) was then added under an inert atmosphere. The reaction mixture was heated at reflux for 24 hours and the reaction mixture was then filtered over celite, evaporated to dryness to yield a black/brown solid, that was dissolved in DCM (100 ml) treated with activated charcoal (0.5 g) silica (*ca* 0.5 g) and stirred under an atmosphere of air overnight. Column chromatography gave a mixture of **8** and **12**[16] with care being taken not to artificially weight the ratio of these species by incomplete fraction collection. The ratio of **8** to **12** was estimated from the ratio of the H3 proton integrations (δ 7.20, 7.14 respectively), and also from the ratio of the combined integrations of both H3 protons to both of the norbornadiene derived alkene protons (δ 6.21 6.15) and both methods gave ratios of 2.3 : 1 in favour of **8**.

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