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The utility of vinyl ethers and vinyl esters in the Khand reaction. The value of vinyl esters as ethylene equivalents and a modified synthesis of (+)-taylorione as an example

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We dedicate this and the following paper to Myron Rosenblum on the occasion of his 75th birthday in friendship and admiration of his elegant contributions to organo-transition metal chemistry

Abstract

The behaviour of various oxygenated alkenes in the Khand cyclisation reaction has been studied. Although several vinyl ethers reacted to give the expected oxygenated cyclopentenone products, usually with good levels of regioselectivity, the use of vinyl esters was found to afford, as the major products, reduced cyclopentenones in which the carbon–oxygen bond had been cleaved. This unexpected reaction was developed into an alternative procedure to using ethylene gas in the Khand reaction and was found to be applicable with a variety of alkyne substrates. The method was then extended to form the key step in the synthesis of the natural product (+)-*taylorione* (and (+)-*nortaylorione*). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Khand reaction; Vinyl ethers; Vinyl esters; Ethylene equivalent; Taylorione; Nortaylorione

1. Introduction

Croudace and Schore first used vinyl ethers and esters in the Khand reaction in l981 [1]. Despite the fact that they obtained mixtures of regioisomers in rather low yields, we were interested in utilising such reactions towards the synthesis of natural products and specifically of the pentenomycins. Initially we failed to isolate the 4-alkoxycyclopentenones from reactions of vinyl ethers [2], but we suspected that the greater ease of elimination of alcohols from these compounds compared to the 5-isomers might be responsible. Having now repeated the reactions under considerably milder reaction conditions, we conclude that 5-alkoxycyclopent-2-en-1-ones are always the major products and that the 4-isomers are only isolable in some cases. Even under very mild reaction conditions, however, the behaviour of vinyl esters is more complex than initially suspected. As previously reported in preliminary form [3], under most conditions tried, the expected formation of 4- and 5-acyloxycyclopentenones is accompanied or replaced by reductive loss of the ester group. Similar cleavage had accompanied the reactions of vinyl bromide [4] so that both this and the vinyl esters can serve as substitutes for ethylene. As we were able to obtain moderate yields by these procedures, the greater convenience of using liquid alkenes in place of ethylene, which requires autoclave conditions for best results [5,6], prompted us to study the optimum choice of reactants and conditions.

Our results are outlined below, together with attempts to apply the new vinyl ester–ethylene equivalent method as an alternative procedure in the previously described synthesis of the natural product, taylorione [6] (and the preparation of the related natural material, (+)-nortaylorione).

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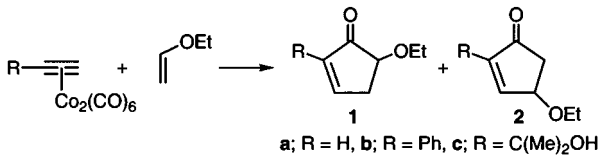


Scheme 1. Khand reaction of alkynehexacarbonyldicobalt complexes with ethyl vinyl ether.

2. Results and discussion

The introduction of amine *N*-oxides to promote Khand annulation reactions has allowed the use of very mild reaction conditions and has frequently led to substantially enhanced yields [5–8]. At the outset, it seemed worthwhile to determine whether these or other improved reaction conditions would also lead to significantly greater yields of alkoxy- and, in turn, hydroxycyclopentenones when applied to previously studied examples of vinyl ethers and esters [1,2].

2.1. Reactions of vinyl ethers

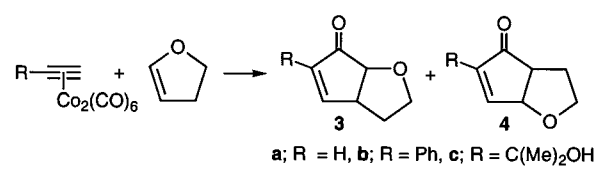
The reactions of ethyl vinyl ether with, in particular, the hexacarbonyldicobalt complexes of ethyne and of phenylethyne were examined under various conditions in an attempt to maximise the formation of the ethoxycyclopentenones **1** and **2** (Scheme 1). Simple thermal reaction of the ethyne complex in toluene at 65 °C had given only low yields of 5-ethoxycyclopent-2-en-1-one (**1a**). Its isomer **2a** was not detected. Under the milder conditions available with *N*-oxide or sulfide promotion [9] improved efficiency was observed; a 32% yield of **1a** was reached using either *n*-butyl methyl sulfide or the recently reported combination of ultrasound and trimethylamine *N*-oxide dihydrate (TMANO·$2H_2O$) [10]. Compound **2a** was again not detected.

With the phenylethyne complex the 4-substituted cyclopentenone was also isolated. Under thermal conditions (toluene, 70 °C) a 20% yield of ethoxyketones **1b** and **2b** (ca. 7:2) was obtained. Using anhydrous *N*-methylmorpholine *N*-oxide (NMO) with ultrasound the yield of this mixture rose to 31%. With NMO·H_2O in dichloromethane and excess ethyl vinyl ether as co-solvent, a 43% yield of only isomer **1b** was produced.

In similar fashion to ethyne, the hexacarbonyldicobalt complex of 2-methylbut-3-yn-2-ol gave only the product **1c** with ethyl vinyl ether. The yield reached an optimum of 35% when TMANO·$2H_2O$ was employed with sonication in a solvent mixture of methanol and toluene.

Use of 2,3-dihydrofuran as the alkene led to a single isomer **3** with each of the alkyne complexes tried; isomer **4** was not detected (Scheme 2). More specifically, with the ethyne complex under promotion by NMO·H_2O, a 48% yield of the bicyclic product **3a** was obtained. Similar procedures with the phenylethyne complex gave an optimum yield of 52% for compound **3b**. Furthermore, ketone **3c** was isolated in 49% yield from reaction of the corresponding dimethylpropargyl alcohol complex in toluene–methanol using the alkene as co-solvent, TMANO·$2H_2O$ as promoter, and sonication for 30 min.

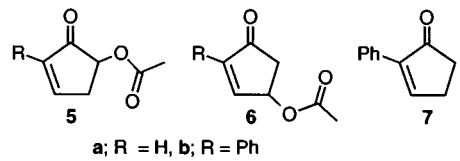
From these results it can be seen that, by the application of more recently developed milder and more efficient Khand reaction promotion methods, oxygenated cyclopentenone products from reactions of enol ethers can be obtained in moderate to good yields and with, at least, good levels of regioselectivity; in most instances, only one regioisomer is isolated.



Scheme 2. Khand reaction of alkynehexacarbonyldicobalt complexes with 2,3-dihydrofuran.

2.2. Reactions of vinyl esters and halides

We next investigated the behaviour of vinyl acetate within the Khand annulation process. Early results seemed similar to those with ethyl vinyl ether: without promoter reactions required prolonged heating and gave poor yields of one isomer **5** only [2]. However, when the phenylethyne complex was treated with vinyl acetate using amine *N*-oxide promoted conditions, the situation was seen to be more complex. With TMANO·$2H_2O$ in methanol and an excess of vinyl acetate as co-solvent in toluene at 45 °C or again with the same *N*-oxide promoter with sonication (35 min) the product, obtained in 53 and 51% yield, respectively, was 2-phenylcyclopent-2-en-1-one (**7**) (entries 1 and 2, Table 1). None of the expected acetoxy-substituted products **5b** and **6b** were observed. This behaviour was reminiscent of the formation of the same product, albeit in only 19% yield, noted previously by Khand [4] when using vinyl bromide as the alkene. Indeed, this yield could also be raised to 54% when vinyl bromide was used with NMO·H_2O (entry 3, Table 1).

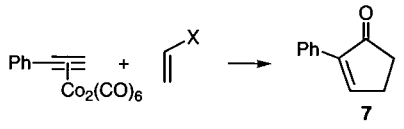


These results suggested that vinyl esters or halides could find general use to replace ethylene in the Khand reaction and avoid the need to employ autoclaves for

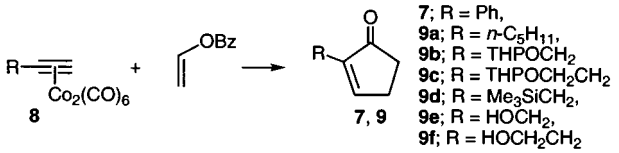
Table 1
Khand reactions of $(PhC{\equiv}CH)Co_2(CO)_6$ with vinyl esters and vinyl bromide

Entry	Complex		Vinyl-X	Amine *N*-oxide				Solvent		Conditions [a]		Yield	
	(mg)	(mmol)		Type	(g)	(mmol)	Addition time	Type	(ml)	Temp. (°C)	Time	(mg)	(%)
1	150	0.39	X = OAc, 4 ml	$TMANO{\cdot}2H_2O$	0.39	3.51	30 s	Tol., MeOH	10.5, 1	45	1 h	30	53
2	190	0.49	X = OAc, 4 ml	$TMANO{\cdot}2H_2O$	0.49	4.41	30 s	Tol., MeOH	12, 1.5	)))	35 min	40	51
3	540	1.39	X = Br, 14 ml [b]	$NMO{\cdot}H_2O$	1.63	12.07	10 min	DCM	20	25	16 h	120	54
4	560	1.44	X = OPiv, 1.8 g	$NMO{\cdot}H_2O$	1.69	12.52	10 min	DCM	20	25	16 h	70	31
5	350	0.90	$X = OCOCF_3$, 1.3 g	$NMO{\cdot}H_2O$	1.00	7.41	10 min	DCM	20	25	48 h	70	50
6	670	1.73	X = OBz, 2.6 g	$NMO{\cdot}H_2O$	2.00	14.81	10 min	DCM	30	25	16 h	160	58
7	380	0.98	X = OBz, 3.0 g	$NMO{\cdot}H_2O$	1.32	9.78	3 h	DCM	30	25	16 h	120	80

[a] The symbol))) refers to ultrasonication conditions.
[b] 1 M solution in THF.



Scheme 3. Khand reaction of phenylethynehexacarbonyldicobalt with vinyl esters and vinyl bromide.



Scheme 4. Khand reaction of alkynehexacarbonyldicobalt complexes with vinyl benzoate.

optimum yields [5,6]. Systematic variation of the choice of vinyl ester and reaction conditions showed that the yield of 2-phenylcyclopent-2-en-1-one (**7**), could be raised up to 80% by employing vinyl benzoate as the alkene and co-solvent and adding the promoter, $NMO{\cdot}H_2O$, slowly by means of a syringe pump (Scheme 3, Table 1). The full range of modified conditions and results is collected in the tables contained within supplementary material that may be requested from the corresponding author.

Having selected vinyl benzoate as the alkene of choice, we compared its use with a series of alkyne complexes **8**, some of which had been previously studied with ethylene. The results, as summarised in Table 2, show that the majority of alkynes tested gave fair to excellent yields of the corresponding cyclopentenones **9** (and **7**) (Scheme 4). Indeed, in the cases where a comparison can be made, the vinyl benzoate technique provides yields that are, in almost every instance, greater than those achievable by using the practically less convenient optimum conditions with ethylene gas [5,6a]. It is worth noting that although the complex of propargyl alcohol gave only a 33% yield, to our knowledge, the Khand reaction with the same complex and ethylene gas has not been achieved. Furthermore, since the THP-protected form of this alkyne gave an 87% yield of the corresponding cyclopentenone **9b**, simple deprotection allows access to the free alcohol **9e**. Indeed, such deprotection of **9b** and of the homologous cyclopentenone **9c** gave the corresponding free hydroxy cyclopent-2-en-1-ones **9e** and **9f** in 99 and 95% yield, respectively. Internal alkynes are known to react less efficiently in intermolecular Khand cyclisations [11] and in the one example attempted with the new ethylene equivalent technique this is still the case. More specifically, when the hexacarbonyldicobalt complex of 2-butyne was subjected to the optimum developed conditions with vinyl benzoate, the expected 2,3-dimethylcyclopent-2-en-1-one was formed in only 5% yield.

With respect to the mode of reaction incorporating loss of the ester unit, it was further noted that, with the phenylethyne complex and vinyl acetate, the reductive cleavage of the alkene moiety, leading to ketone **7**, only occurred under an inert atmosphere, whereas reaction in air gave only the 5-acetoxyketone **5b**, albeit in poor 7% yield. When anhydrous NMO and dry reactants were employed with the same complex and vinyl acetate, the same product **5b** (admixed with the 4-acetoxyketone **6b**) formed in a combined yield of 4% (along with a 30% yield of ketone **7**). This indicates that the source of the hydrogen atom introduced in the cleavage process is water. In confirmation, we were able to form 5-deuterio-2-phenylcyclopent-2-en-1-one, in a good 62% yield, by using anhydrous NMO as promoter, with the phenylethyne complex and vinyl benzoate, and adding D_2O to the reaction mixture. If we accept that the mechanism of the Khand reaction involves complexation of alkene to cobalt followed by insertion into a cobalt to acetylene–carbon bond [11d], the latter insertion step must precede the C–O bond scission to account for the regioselective formation of the 5- (and not the 4-) deuterio compound. Furthermore, the C–O cleavage and subsequent replacement of the ester oxygen with H must involve a low oxidation

Table 2
Khand reactions of alkynehexacarbonyldicobalt complexes with vinyl benzoate

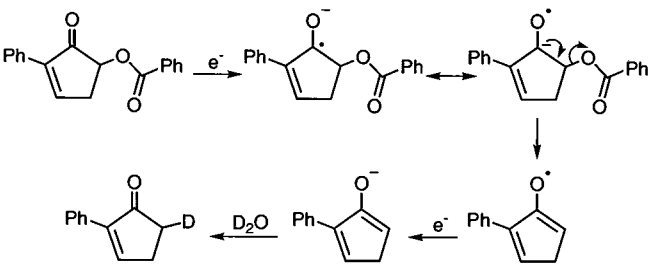
Entry	Complex	Product	Yield (%)	Literature yield with ethylene [5,6a]	
				Ambient conditions [a]	Autoclave conditions [b]
1	Ph–C≡C–H	**7**	80	52	71
2	**8a**	**9a**	77	58	73
3	**8b**	**9b**	87	33	22
4	**8c**	**9c**	80	–	–
5	**8d**	**9d**	45	35	48
6	**8e**	**9e**	33	–	–
7	**8f**	**9f**	61	–	–

[a] 1 atm, 25 °C.
[b] 25–30 atm, 40 °C.

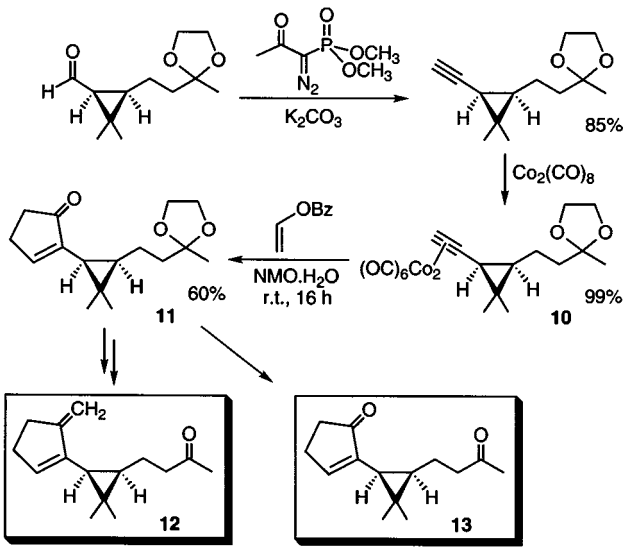
state cobalt species, as anticipated under the reaction conditions. Additionally, it seems likely that water causes partial disproportionation of the cobalt(0) precursor to yield $HCo(CO)_4$, which could also become the effective reducing agent. Scheme 5 depicts our tentative mechanistic reasoning for the formation of the reduced cyclopentenones following regioselective cyclisation with the vinyl ester; the phenylethyne complex, vinyl benzoate, and D_2O are used to illustrate the outcome of the labelling process as described above. The initially produced substituted cyclopentenone will be reduced to give the corresponding ketyl. Elimination of the benzoate unit, further reduction to the enolate, and subsequent quenching with D_2O will deliver the reduced (and, in this case, labelled) cyclopentenone.

2.3. Synthesis of (+)-taylorione (and (+)-nortaylorione)

Having established efficient and practically convenient conditions for the use of vinyl benzoate in place of ethylene, we wished to show the utility of this method when applied to a more complex example. In this regard, we chose one of the best and carefully optimised cases for which we had previously used ethylene: the conversion of the hexacarbonyl(alkyne)dicobalt complex **10** to the cyclopentenone **11**, a key step in the synthesis of (+)-taylorione **12**. This Khand reaction had been accomplished in 81% yield using ethylene under 25 atm. pressure at 40 °C with $TMANO{\cdot}2H_2O$ as the reaction promoter [6]. Alternatively, bubbling the gas through a benzene solution of the complex while slowly adding $TMANO{\cdot}2H_2O$ in methanol at room temperature had afforded a still acceptable 41% yield of **11** [6]. In a further modification of this synthesis the free alkyne required to obtain complex **10** was prepared in a single step from the corresponding aldehyde using the procedure of Ohira and Bestmann [12] and in an enhanced yield (85%) over the previously employed [6] two-step Ramirez–Corey method [13].



Scheme 5. Tentative mechanistic reasoning for formation of reduced cyclopentenones.



Scheme 6. Routes towards (+)-taylorione and (+)-nortaylorione using the ethylene equivalent technique in the key Khand annulation.

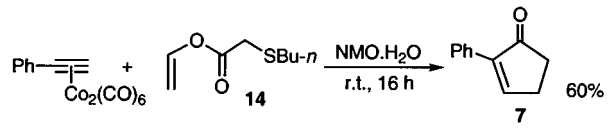
As can be seen from Scheme 6, in the key Khand annulation, when vinyl benzoate replaced ethylene in the reaction with complex **10**, the ketone **11** was obtained in 60% yield. Thus, whereas this method fails to match the result obtainable with ethylene under pressure, it is a significant advance on the use of the gas under ambient conditions. Additionally, the ethylene equivalent process shows how cheap, readily available, and easily handled vinyl esters can be employed under ambient conditions, and thus can be recommended for use without the requirement of suitable pressure vessels or a source of ethylene under pressure.

With respect to the Khand cyclisation reaction to form **11** (Scheme 6), it is also worth noting that this annulation provides the ketal protected form of the recently reported (+)-nortaylorione **13** [14]. Since we have prepared this natural product from **11** [6], by our novel PPh_3–CBr_4 ketal deprotection method [15], the strategy reported here also constitutes a formal total synthesis of (+)-nortaylorione **13**.

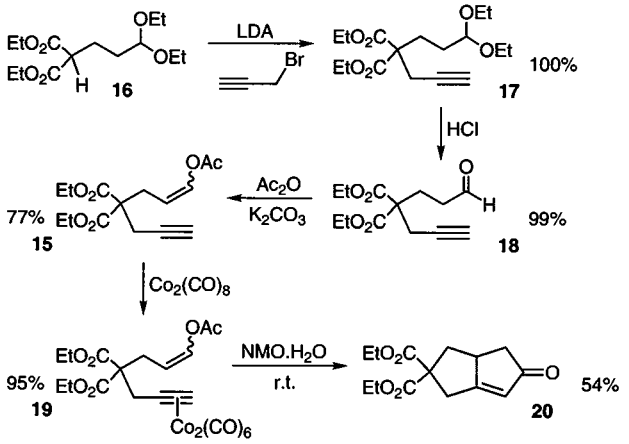
2.4. Miscellaneous aspects

Another vinyl ester tested under the developed Khand techniques was the sulfur-containing compound $BuSCH_2COOCH{=}CH_2$ (**14**). This was chosen since Krafft had shown that sulfur in the bis-homoallylic position (as well as the in the allylic and homoallylic positions) could, by coordination to cobalt, improve regioselectivity and yields in Khand processes [16]. From our result with the phenylethyne complex, it seems that such coordination, if it occurs in the present case, does not cause this vinyl ester to behave differently from other vinyl esters and leads to a 60% yield of the reduced cyclopentenone **7** (Scheme 7).

We also wished to ascertain whether the reductive elimination of an ester group would occur in an intramolecular Khand reaction. To this end ester **15** (as an E/Z mixture) was prepared from diethyl malonate.



Scheme 7. Khand reaction of phenylethynehexacarbonyldicobalt with vinyl *n*-butylthioacetate.



Scheme 8. Enyne substrate preparation and intramolecular Khand reaction.

The initial alkylation was performed with 3-chloropropanal diethyl acetal to yield $(EtO_2C)_2CHCH_2CH_2CH(OEt)_2$ (**16**) [17] followed by a second alkylation with propargyl bromide to give **17** (100%). Hydrolysis with aqueous hydrochloric acid solution liberated the free aldehyde **18** (99%) and treatment with acetic anhydride and a catalytic quantity of K_2CO_3 gave the enyne **15** (77%). The resultant hexacarbonyldicobalt complex **19** underwent the Khand reaction, promoted by $NMO{\cdot}H_2O$, with loss of acetate to give the bicyclic keto-diester **20** as the only isolable product in 54% yield (Scheme 8).

3. Conclusions

In summary, we have examined the use of several vinyl ethers and esters in the Khand cyclisation reaction. Using amine *N*-oxide promotion by itself, or in conjunction with ultrasonication or gentle heating, both ethyl vinyl ether and 2,3-dihydrofuran underwent the Khand reaction and afforded the anticipated oxygenated cyclopentenones in reasonable yields and with good to excellent levels of regioselectivity. In addition, it was found that vinyl esters behaved in an unexpected fashion when subjected to amine *N*-oxide promoted Khand reaction conditions. The pathway of such reactions featured a carbon–oxygen bond cleavage which resulted in the formation of the reduced cyclopentenones more normally accessed when ethylene gas is the alkene component used in the cyclisation. This process was optimised and now constitutes a novel method by which vinyl esters can be utilised as non-gaseous ethylene equivalents in the Khand annulation. The mild conditions and simple techniques employed provide significant advantages, both in terms of practical convenience and, in the majority of cases explored, reaction yield, over the corresponding gaseous alkene procedures. Furthermore, the developed method was applied as the key step in two independent natural product syntheses: the variant of our taylorione (and nortaylorione) synthesis described above and an efficient construction of a useful radiolabelled derivative of *cis*-methyl jasmonate as reported in the following paper.

4. Experimental

4.1. General remarks

Dry THF and Et_2O were obtained by distilling commercial solvents from sodium benzophenone ketyl and CH_2Cl_2 was distilled from calcium hydride. Light petroleum refers to the fraction of b.p. 30–40 °C and was distilled prior to use.

N-Methylmorpholine *N*-oxide (NMO) was obtained in anhydrous form by heating at 90 °C at 0.1 mmHg or as $NMO{\cdot}H_2O$ by recrystallisation from moist acetone. Trimethylamine-*N*-oxide as $TMANO{\cdot}2H_2O$, was used as supplied, or converted to the anhydrous form by the literature method [18]. Brucine *N*-oxide was prepared as described [19]. Except as stated, all other reagents were used as supplied.

Known hexacarbonyl(alkyne)dicobalt complexes $[(C_2H_2)Co_2(CO)_6$ [20], $(PhC_2H)Co_2(CO)_6$ [6a], $(HO(CH_3)_2C_2H)Co_2(CO)_6$ [21], **8a** [6a], **8b** [6a], **8d** [6a], **8e** [22], and $(CH_3C_2CH_3)Co_2(CO)_6$ [23]] were prepared by standard methods from free alkyne and commercial $Co_2(CO)_8$ at room temperature (r.t.) in light petroleum or CH_2Cl_2 and were purified by column chromatography on silica. All organometallic complexes were stored under nitrogen at, or below, −20 °C and all reactions were performed under a nitrogen atmosphere unless otherwise stated.

Khand reactions were carried out at various temperatures with or without promoter and/or ultrasonication (using a Vibracell VL 50 titanium horn operating at 50 W/20 kHz). Speed of addition of the promoter, if used, was found to have a considerable effect on the yields obtained; very slow addition was controlled by use of a syringe pump. Anhydrous *N*-oxides were used in tolu-

ene or CH_2Cl_2 solution, the hydrates more commonly in MeOH, which is itself a weak promoter [24]. Typical procedures are outlined below and further details are given in Tables 1 and 3.

^{1}H- and ^{13}C-NMR were run on a Bruker WM 250 and a Bruker WM 400 in $CDCl_3$ solutions. Chemical shifts are reported in parts per million downfield relative to Me_4Si (δ 0.00); coupling constants are reported in Hz. Infrared spectra were obtained on a Mattson 1000 or Nicolet Impact 400D FTIR spectrometer in CH_2Cl_2 solutions or as films. High resolution mass spectrometry was performed on a JEOL Instruments JMS-AX505HA mass spectrometer system or a Finnigan MAT 900XLT high resolution double focussing mass spectrometer. Mass spectral data is reported as m/z (relative intensity).

4.2. Reaction of ethyl vinyl ether with hexacarbonyl[μ-[(1,2-η:1,2-η)ethyne]]dicobalt-(Co–Co)

4.2.1. n-Butyl methyl sulfide promoted reaction

A mixture of hexacarbonyl[μ-[(1,2-η:1,2-η)ethyne]]-dicobalt-(Co–Co) (0.21 g, 0.67 mmol), ethyl vinyl ether (10 ml) and *n*-butyl methyl sulfide (0.25 g, 2.40 mmol) in 1,2-dichloroethane (10 ml) was heated under reflux for 30 min. The mixture was filtered through a pad of silica using Et_2O as the eluent. The filtrate was evaporated under reduced pressure to leave a residue, which was purified by column chromatography on silica using a 10–50% Et_2O in light petroleum gradient as the eluent to give 5-ethoxycyclopent-2-en-1-one (**1a**) [25] as a pale yellow oil (27.0 mg, 32%). ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 1.23$ (3H, t, $J = 7.0$ Hz, CH_3), 2.53–2.59 (1H, dq, $J = 18.6$, 2.5 Hz, H-4), 2.95–3.03 (1H, m, H-4), 3.60–3.67 (1H, m, CH_2CH_3), 3.84–3.95 (2H, overlapping m, CH_2CH_3, H-5), 6.15–6.17 (1H, m, H-2), 7.54–7.62 (1H, m, H-3). ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta = 15.4$, 35.9, 66.1, 77.2, 132.7, 161.5, 207.5. IR (cm^{-1}, CH_2Cl_2): ν_{max} 2966, 2883, 1721, 1594.

4.2.2. Ultrasound and $TMANO{\cdot}2H_2O$ promoted reaction

A mixture of hexacarbonyl[μ-[(1,2-η:1,2-η)ethyne]]-dicobalt-(Co–Co) (0.38 g, 1.23 mmol), ethyl vinyl ether (10 ml) and $TMANO{\cdot}2H_2O$ (1.36 g, 12.3 mmol) in toluene (20 ml) was sonicated for 2 h. The mixture was then filtered through a pad of silica using Et_2O as the eluent. The filtrate was evaporated under reduced pressure to leave a crude residue, which was purified by column chromatography on silica using a 10–50% Et_2O in light petroleum gradient as the eluent to give the product **1a** as a pale yellow oil (50.0 mg, 32%). Analytical data were as above.

4.3. Reaction of ethyl vinyl ether with hexacarbonyl[μ-[(1,2-η:1,2-η)phenylethyne]]-dicobalt-(Co–Co)

4.3.1. Thermal reaction

A solution of ethyl vinyl ether (0.29 ml, 220 mg, 3.0 mmol) in toluene (4 ml) was added to a solution of hexacarbonyl[μ-[(1,2-η:1,2-η)phenylethyne]]dicobalt-(Co–Co) (195 mg, 0.50 mmol) in toluene (12 ml) and the mixture heated to 70 °C for 22 h. The mixture was then filtered through a pad of silica which retained the product. The product was extracted into Et_2O and the extract evaporated under reduced pressure. The crude residue was purified by column chromatography on silica using 50% Et_2O in light petroleum as the eluent ($R_f = 0.60$) to give the product as a pale yellow oil containing a mixture of the isomers **1b** and **2b** (7:2) (20 mg, 20%). *5-Ethoxy-2-phenylcyclopent-2-en-1-one* (**1b**): ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 1.29$ (3H, t, $J = 7.0$ Hz, CH_3), 2.60 (1H, dt, $J = 18.9$, 2.9 Hz, H-4), 3.06 (1H, ddd, $J =$ 18.9, 6.6, 3.4 Hz, H-4), 3.71 (1H, dq, $J = 9.1$, 7.0 Hz, CH_2CH_3), 3.98 (1H, dq, $J = 9.1$, 7.0 Hz, CH_2CH_3), 4.13 (1H, dd, $J = 6.6$, 3.0 Hz, H-5), 7.27–7.48 (3H, m, Ph), 7.69–7.72 (3H, m, Ph + H-3). ^{13}C-NMR (62.5 MHz, $CDCl_3$): $\delta = 15.5$, 38.8, 66.2, 78.9, 127.0, 128.7, 128.9, 131.5, 141.6, 154.7, 205.0. IR (cm^{-1}, CH_2Cl_2): ν_{max} 1710. *4-Ethoxy-2-phenylcyclopent-2-en-1-one* (**2b**): ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 1.20$ (3H, t, $J = 6.9$ Hz, CH_3), 2.03 (1H, ddd, $J = 14.4$, 7.4, 1.4 Hz, H-5), 2.88–2.95 (1H, m, H-5), 3.58 (1H, dq, $J =$ 9.1, 7.0 Hz, CH_2CH_3), 3.98 (1H, dq, $J = 9.1$, 7.0 Hz, CH_2CH_3), 4.25–4.35 (1H, m, H-4), 7.27–7.48 (3H, m, Ph), 7.69–7.72 (3H, m, Ph + H-3).

4.3.2. Ultrasound and anhydrous NMO promoted reaction

A mixture of ethyl vinyl ether (73 μl, 55.4 mg, 0.77 mmol), hexacarbonyl[μ - [(1,2 - η:1,2 - η)phenylethyne]]-dicobalt-(Co–Co) (1.00 g, 0.26 mmol), NMO (273 mg, 2.32 mmol) and toluene (10 ml) was subjected to ultrasonication for 25 min. The same product mixture (16 mg, 31%) was isolated as before.

4.3.3. $NMO{\cdot}H_2O$ promoted reaction

A solution of *N*-methylmorpholine *N*-oxide monohydrate (1.25 g, 9.30 mmol) in CH_2Cl_2 (20 ml) was added over a 30 min period to a stirred mixture of hexacarbonyl[μ - [(1,2 - η:1,2 - η)phenylethyne]]dicobalt-(Co–Co) (0.36 g, 0.93 mmol) and ethyl vinyl ether (5 ml) at 25 °C. The mixture was stirred for 60 h before it was filtered through a pad of silica using CH_2Cl_2 as the eluent. The filtrate was evaporated under reduced pressure to leave a crude residue, which was purified by column chromatography on silica using a 0–40% Et_2O in light petroleum gradient as the eluent to give *5-ethoxy-2-phenylcyclopent-2-en-1-one* (**1b**) (0.08 g, 43%) as a pale yellow oil.

4.4. Reaction of ethyl vinyl ether with hexacarbonyl[μ-[(3,4-η:3,4-η)-2-methylbut-3-yn-2-ol]]-dicobalt-(Co–Co)

4.4.1. Ultrasound and TMANO·2H$_2$O promoted reaction

A mixture of ethyl vinyl ether (2.5 ml), hexacarbonyl[μ-[(3,4-η:3,4-η)-2-methylbut-3-yn-2-ol]]-dicobalt-(Co–Co) (105 mg, 0.28 mmol), toluene (7.5 ml) and TMANO·2H$_2$O (200 mg, 2.52 mmol) in MeOH (2 ml) was sonicated for 85 min. The mixture was then filtered through a pad of kieselguhr, which was washed with CH_2Cl_2. The combined filtrate and washings were evaporated under reduced pressure to leave a brown oil, which was purified by column chromatography on silica using 20% light petroleum in Et_2O as the eluent (R_f (Et_2O) = 0.45) to give *5-ethoxy-2-(1-hydroxy-1-methylethyl)cyclopent-2-en-1-one* (**1c**) (18 mg, 35%) as a pale yellow oil. ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 1.30$ (3H, t, $J = 7.0$ Hz, CH_3CH$_2$), 1.46 (6H, s, C(CH$_3$)$_2$), 2.45 (1H, dt, $J = 18.4$, 2.8 Hz, H-4), 2.85 (1H, ddd, $J = 18.4$, 6.6, 3.2 Hz, H-4), 3.30 (1H, br s, OH), 3.66 (1H, dq, $J = 9.0$, 7.0 Hz, CH_2CH$_3$), 3.86 (1H, dq, $J = 9.0$, 7.0 Hz, CH_2CH$_3$), 3.99 (1H, dd, $J = 6.4$, 2.8 Hz, H-5), 7.30 (1H, t, $J = 2.6$ Hz, H-3). ^{13}C-NMR (62.5 MHz, $CDCl_3$): $\delta = 15.5$, 28.7, 28.8, 33.6, 66.3, 69.9, 78.6, 149.7, 152.5, 207.3. IR (cm^{-1}, CH_2Cl_2): ν_{max} 1709.

4.5. Reaction of 2,3-dihydrofuran with hexacarbonyl[μ-[(1,2-η:1,2-η)ethyne]]dicobalt-(Co–Co)

4.5.1. NMO·H$_2$O promoted reaction

A solution of NMO·H$_2$O (1.00 g, 7.41 mmol) in CH_2Cl_2 (20 ml) was added, over a 1 h period, to a solution of hexacarbonyl[μ - [(1,2 - η:1,2 - η)ethyne]]-dicobalt-(Co–Co) (0.22 g, 0.70 mmol) in a mixture of CH_2Cl_2 (10 ml) and 2,3-dihydrofuran (20 ml) at 25 °C. The mixture was stirred for 16 h before it was filtered through a pad of silica using Et_2O as the eluent. The filtrate was evaporated under reduced pressure to leave a crude residue, which was purified by column chromatography on silica using a 10–80% Et_2O in light petroleum gradient as the eluent to give *2,3,3a,6a-tetrahydro-6H-cyclopenta[b]furan-6-one* (**3a**) as a pale yellow oil (41.0 mg, 48%). ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 1.77$–1.82 (1H, m), 2.00–2.13 (1H, m), 3.47–3.55 (2H, m), 3.94–3.98 (1H, m), 4.26 (1H, d, $J = 5.6$ Hz), 6.23 (1H, dd, $J = 5.9$, 1.7 Hz), 7.58 (1H, dd, $J = 5.9$, 2.8 Hz). ^{13}C-NMR (62.5 MHz, $CDCl_3$): $\delta = 30.1$, 44.9, 67.5, 79.6, 134.7, 164.6, 207.2. IR (cm^{-1}, CH_2Cl_2): ν_{max} 2966, 2883, 1721, 1593, 1357, 1191, 1089. HRMS: m/z: Found: 124.05292 (100). Calc. for $C_7H_8O_2$ [M$^+$]: 124.05243.

4.6. Reaction of 2,3-dihydrofuran with hexacarbonyl[μ-[(1,2-η:1,2-η)phenylethyne]]-dicobalt-(Co–Co)

4.6.1. TMANO·2H$_2$O promoted reaction

A solution of TMANO·2H$_2$O (260 mg, 2.11 mmol) in MeOH (1 ml) was added over a 25 min period to a solution of 2,3-dihydrofuran (58 μl, 55 mg, 0.77 mmol) and hexacarbonyl[μ - [(1,2 - η:1,2 - η)phenylethyne]]-dicobalt-(Co–Co) (100 mg, 0.26 mmol) in toluene (10 ml) at 25 °C. The mixture was then warmed to 40 °C for 2 h. Work-up was the same as in the preceding experiments. Chromatographic purification used 20% light petroleum in Et_2O as the eluent ($R_f = 0.40$) to give *2,3,3a,6a-tetrahydro-5-phenyl-6H-cyclopenta[b]furan-6-one* (**3b**) (26 mg, 52%) as a yellow oil. ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 1.90$ (1H, ddt, $J = 12.5$, 5.3, 1.9 Hz, H-3), 2.18 (1H, dddd, $J = 12.5$, 10.8, 9.8, 7.5 Hz, H-3), 3.54 (1H, dddd, $J = 11.0$, 9.7, 5.5, 2.0 Hz, H-3a), 3.58 (1H, ddd, $J = 11.0$, 9.2, 5.5 Hz, H-2), 4.03 (1H, ddd, $J = 11.0$, 7.5, 2.0 Hz, H-2), 4.49 (1H, d, $J = 5.7$ Hz, H-6a), 7.27–7.41 (3H, m, Ar–H), 7.71–7.74 (3H, m, Ar–H + H-4). ^{13}C-NMR (62.5 MHz, $CDCl_3$): $\delta = 30.6$, 42.3, 67.6, 81.4, 127.1, 128.7, 129.9, 130.8, 143.6, 158.2, 204.9. IR (cm^{-1}, CH_2Cl_2): ν_{max} 1720.

4.7. Reaction of 2,3-dihydrofuran with hexacarbonyl[μ-[(3,4-η:3,4-η)-2-methylbut-3-yn-2-ol]]-dicobalt-(Co–Co)

4.7.1. Ultrasound and TMANO·2H$_2$O promoted reaction

A mixture of 2,3-dihydrofuran (4.0 ml), hexacarbonyl[μ-[(3,4-η:3,4-η)-2-methylbut-3-yn-2-ol]]dicobalt-(Co–Co) (200 mg, 0.54 mmol), TMANO·2H$_2$O (540 mg, 4.86 mmol) in MeOH (1.5 ml) and toluene (12 ml) was sonicated for 30 min and worked up as in the previous experiments. The product, *2,3,3a,6a-tetrahydro-5-(1-hydroxy-1-methylethyl)-6H-cyclopenta[b]furan-6-one* (**3c**) (49 mg, 49%), was eluted with Et_2O ($R_f = 0.30$). ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 1.44$ (6H, s, C(CH$_3$)$_2$), 1.83 (1H, ddt, $J = 12.5$, 9.5, 5.1 Hz, H-3), 2.09 (1H, dddd, $J = 12.5$, 10.8, 9.8, 7.5 Hz, H-3), 3.42 (1H, dddd, $J = 10.4$, 9.5, 5.4, 1.8 Hz, H-3a), 3.52 (1H, ddd, $J = 10.9$, 9.5, 5.4 Hz, H-2), 4.00 (1H, ddd, $J = 10.9$, 7.5, 1.8 Hz, H-2), 4.35 (1H, d, $J = 5.6$ Hz, H-6a), 7.27 (1H, d, $J = 2.8$ Hz, H-4). ^{13}C-NMR (62.5 MHz, $CDCl_3$): $\delta = 28.7$, 28.8, 30.3, 42.2, 67.6, 69.8, 81.1, 152.2, 156.0, 206.7. IR (cm^{-1}, CH_2Cl_2): ν_{max} 1709. HRMS: m/z: Found: 182.0957 (100). Calc. for $C_{10}H_{14}O_3$ [M$^+$]: 182.0943.

4.8. Reactions of vinyl esters and vinyl bromide

4.8.1. Reactions with hexacarbonyl[μ-[(1,2-η:1,2-η)phenylethyne]]-dicobalt-(Co–Co)

General: reactions proceeding with reductive cleavage of the halo- or ester group are collected in Table 1. The best procedure follows.

A solution of $NMO{\cdot}H_2O$ (1.32 g, 9.78 mmol) in CH_2Cl_2 (30 ml) was added over 3 h (syringe pump) to a stirred solution of hexacarbonyl[μ-[(1,2-η:1,2-η)phenylethyne]]dicobalt-(Co–Co) (380 mg, 0.98 mmol) in vinyl benzoate (3.00 g, 20 mmol) at 25 °C. The mixture was stirred for a further 16 h. Cobalt salts were removed from the resultant purple mixture by filtration through a 1 cm pad of silica using CH_2Cl_2 as the eluent. The yellow–brown filtrate was evaporated under reduced pressure to leave a crude residue which was purified by column chromatography on silica using a 0–40% Et_2O in light petroleum gradient as the eluent. Concentration of the first fraction, followed by distillation led to recovery of vinyl benzoate (2.50 g). 2-Phenylcyclopent-2-en-1-one (**7**) was eluted next as a pale yellow oil which solidified on standing (120 mg, 80%), m.p. 68–69 °C [lit. [4,6,26] 71–72 °C]. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 2.52$ (2H, m, H-5), 2.63 (2H, m, H-4), 7.27–7.44 (3H, m, Ar–H), 7.68 (2H, d, $J = 7.3$ Hz, Ar–H), 7.76 (1H, m, H-3). ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta = 26.4$, 36.0, 127.2, 128.5, 128.6, 131.9, 159.1, 207.0. IR (cm^{-1}, film): ν_{max} 3038, 1707.

4.8.2. Reactions of vinyl esters with selected hexacarbonyl(alkyne)dicobalt complexes

The general method outlined above for the phenylethyne complex was applied to a series of other complexes as detailed here and in Table 3.

*4.8.2.1. Hexacarbonyl[μ-[(1,2-η:1,2-η)-4-(tetrahydropyran-2-yloxy)but-1-yne]]dicobalt-(Co–Co) (**8c**).* A solution of 2-(but-3-ynyloxy)tetrahydro-2*H*-pyran [27] (1.10 g, 7.14 mmol) in CH_2Cl_2 (20 ml) was added over a 10 min period to a stirred solution of $Co_2(CO)_8$ (2.35 g, 6.87 mmol) in CH_2Cl_2 (30 ml) at 25 °C. The mixture was stirred for 2 h before it was filtered through a pad of silica using CH_2Cl_2 as the eluent. The filtrate was evaporated under reduced pressure to leave a crude residue, which was purified by filtration through a second pad of silica using 10% Et_2O in light petroleum as the eluent to give *hexacarbonyl[μ-[(1,2-η:1,2-η)-4-(tetrahydropyran-2-yloxy)but-1-yne]]dicobalt-(Co–Co)* (**8c**) (3.02 g, 96%) as a red oil. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 1.52$–1.65 (4H, m), 1.75 (1H, m) 1.84 (1H, m), 3.16 (2H, m), 3.53 (1H, m, $CH_2CH_2CH_2O$), 3.61 (1H, m, $CH_2CH_2CH_2O$), 3.88 (1H, m, CCH_2CH_2O), 4.00 (1H, m, CCH_2CH_2O), 4.63 (1H, t, $J = 2.9$ Hz, OCHO), 6.04 (1H, s, ≡CH). ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta = 19.7$, 25.6, 30.7, 34.3, 62.6, 67.5, 73.8 ($CH_2C{\equiv}CH$), 85.2 ($CH_2C{\equiv}CH$), 99.0 (OCHO), 200.0 (CO). IR (cm^{-1}, film) ν_{max} 2097, 2059, 2010. HRMS: *m*/*z*: Found: 383.94615. Calc. for $C_{13}H_{14}Co_2O_6$ [$M^+ - 2CO$]: 383.94543.

*4.8.2.2. Hexacarbonyl[μ-[(3,4-η:3,4-η)but-3-yn-1-ol]]-dicobalt-(Co–Co) (**8f**).* But-3-yn-1-ol (2.20 g, 31.4 mmol) in CH_2Cl_2 (10 ml) was added over a 10 min period to a stirred solution of octacarbonyldicobalt (10.9 g, 31.9 mmol) in CH_2Cl_2 (40 ml) at 25 °C. The mixture was stirred for 5 h before it was filtered through a pad of silica using 50% Et_2O in light petroleum as the eluent. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on silica using: 50% Et_2O in light petroleum as eluent to give *hexacarbonyl[μ-[(3,4-η:3,4-η)but-3-yn-1-ol]]dicobalt-(Co–Co)* (**8f**) (5.00 g, 99%) as a red oil. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta =$ 1.67 (1H, t, $J = 5.0$ Hz, HO), 3.12 (2H, dt, $J = 6.5$, 1.1 Hz, CH_2CH_2OH), 3.90 (2H, app q, $J = 6.5$ Hz, CH_2CH_2OH), 6.07 (1H, t, $J = 1.1$ Hz, ≡CH). ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta = 36.8$ (CH_2CH_2OH), 63.5 (CH_2CH_2OH), 73.7 ($CH_2C{\equiv}CH$), 91.3 ($CH_2C{\equiv}CH$), 202.4 (CO). IR (cm^{-1}, film): ν_{max} 3407, 2094, 2068, 2027. HRMS: *m*/*z*: Found: 327.88227. Calc. for $C_9H_6Co_2O_6$ [$M^+ - CO$]: 327.88283.

*4.8.2.3. 2-(2-(Tetrahydropyran-2-yloxy)ethyl)cyclopent-2-en-1-one (**9c**).* A solution of $NMO{\cdot}H_2O$ (1.50 g, 11.1 mmol) in CH_2Cl_2 (20 ml) was added over a 1 h period (syringe pump) to a stirred solution of hexacarbonyl[μ-

Table 3
Additional Khand reactions of alkynehexacarbonyldicobalt complexes with vinyl benzoate [a]

Entry	Complexed alkyne			Vinyl benzoate (g)	$NMO{\cdot}2H_2O$		DCM	Yield		References
	Identity	(mg)	(mmol)		(g)	(mmol)	(ml)	(mg)	(%)	
1	**8a**	520	1.36	3.00	1.84	13.6	30	160	77	[6a]
2	**8b**	440	1.04	3.00	1.40	10.37	30	180	87	[6a]
3	**8d**	340	0.85	3.00	1.20	8.89	20	64	45	[6a]
4	2-Butyne·$Co_2(CO)_6$	770	1.98	3.00	3.00	22.22	40	10.9	5	[29]
5	**10**	300	0.61	5.00	0.82	6.07	30	100	60	[6a]

[a] All reactions were performed at room temperature over 16 h.

[(1,2-η:1,2-η)-4-(tetrahydropyran-2-yloxy)but-1-yne]]-dicobalt-(Co–Co) (**8c**) (0.58 g, 1.32 mmol) in vinyl benzoate (10 ml) at 25 °C. The mixture was stirred for 16 h before it was filtered through a pad of silica using Et_2O as the eluent. The filtrate was evaporated under reduced pressure to leave a crude residue which was purified by column chromatography on silica using a 10–50% Et_2O in light petroleum gradient as the eluent to give *2-(2-(tetrahydropyran-2-yloxy)ethyl)cyclopent-2-en-1-one* (**9c**) (0.22 g, 80%) as a pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 1.47$ (4H, m), 1.63 (1H, m), 1.75 (1H, m), 2.33 (2H, m), 2.42 (2H, m), 2.54 (2H, m), 3.46 (2H, m), 3.78 (2H, m), 4.54 (1H, t, $J = 2.9$ Hz, OCHO), 7.42 (1H, s, H-3). ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta = 19.8$, 25.4, 25.6, 26.8, 30.8, 34.4, 62.6, 65.4, 99.0, 143.5, 159.1, 209.8. IR (cm^{-1}, film): ν_{max} 1702, 1625. HRMS: *m/z*: Found: 210.12722. Calc. for $C_{12}H_{18}O_3$ [M^+]: 210.12559.

*4.8.2.4. 2-(2-Hydroxymethyl)cyclopent-2-en-1-one (**9e**) [28].* (a) A solution of *N*-methylmorpholine *N*-oxide monohydrate (1.38 g, 10.2 mmol) in CH_2Cl_2 (20 ml) was added over a 2 h period to a stirred solution of hexacarbonyl[μ - [(2,3 - η:2,3 - η)prop - 2 - yn - 1 - ol]dicobalt-(Co–Co) (**8e**) (0.35 g, 1.02 mmol) in vinyl benzoate (3.00 g, 20.3 mmol) at 25 °C. The mixture was stirred for a further 16 h before it was filtered through a pad of silica using Et_2O as the eluent. The filtrate was evaporated under reduced pressure to leave a crude residue, which was purified by column chromatography on silica using a 20–100% Et_2O in light petroleum gradient as the eluent to give 2-hydroxymethylcyclopent-2-en-1-one (**9e**) (37.0 mg, 33%) as a colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 2.45$ (2H, m, H-5), 2.52 (1H, s, OH), 2.64 (2H, m, H-4), 4.37 (2H, s, CH_2OH), 7.54 (1H, app t, $J = 1.2$ Hz, H-3). IR (cm^{-1}, film): ν_{max} 3450, 3025, 2930, 1700, 1645.

(b) Pyridinium *para*-toluenesulfonate (0.12 g, 0.48 mmol) was added to a solution of 2-((tetrahydro-2*H*-pyran-2-yloxy)methyl)cyclopent-2-en-1-one (**9b**) (0.95 g, 4.8 mmol) in MeOH (50 ml) and the mixture was heated under reflux for 1 h. The solvent was then evaporated under reduced pressure to leave a crude residue, which was purified by filtration through a pad of silica using Et_2O as the eluent to give 2-hydroxymethylcyclopent-2-en-1-one (**9e**) (0.54 g, 99%) as a white crystalline solid. Analytical data were identical with the above sample.

*4.8.2.5. 2-(2-Hydroxyethyl)cyclopent-2-en-1-one (**9f**).* (a) A solution of *N*-methylmorpholine *N*-oxide monohydrate (20.0 g, 0.15 mol) in CH_2Cl_2 (300 ml) was added over a 30 min period (dropping funnel) to a stirred solution of hexacarbonyl[μ-[(3,4-η:3,4-η)but-3-yn-1-ol]]dicobalt-(Co–Co) (**8f**) (4.00 g, 16.8 mmol) in vinyl benzoate (70 ml) at 25 °C. The mixture was stirred for a further 16 h before it was filtered through a pad of silica using Et_2O as the eluent. The filtrate was evaporated under reduced pressure to leave a crude residue, which was purified by column chromatography on silica using a 10–100% Et_2O in light petroleum gradient as the eluent to give *2-(2-hydroxyethyl)cyclopent-2-en-1-one* (**9f**) (1.30 g, 61%) as a pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 2.42$ (2H, m, H-5), 2.47 (2H, t, $J = 5.8$ Hz, CH_2CH$_2$OH), 2.60 (2H, m, H-4), 2.83 (1H, s, OH), 3.71 (2H, t, $J = 5.8$ Hz, CH$_2$CH_2OH), 7.50 (1H, s, H-3). ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta = 27.0$, 29.2, 34.7, 61.2 (*C*H$_2$OH), 143.9 (C-2), 160.6 (C-3), 211.3 (C-1). IR (cm^{-1}, film): ν_{max} 3400, 1664. HRMS: *m/z*: Found: 126.06816. Calc. for $C_7H_{10}O_2$ [M^+]: 126.06808.

(b) Pyridinium *p*-toluenesulfonate (0.21 g, 0.86 mmol) was added to a solution of 2-(2-(tetrahydropyran-2-yloxy)ethyl)cyclopent-2-en-1-one (**9c**) (1.80 g, 8.57 mmol) in MeOH (60 ml) and the mixture heated under reflux for 1 h. The solvent was then evaporated under reduced pressure to leave a crude residue, which was purified by column chromatography on silica using Et_2O as the eluent to give *2-(2-hydroxyethyl)cyclopent-2-en-1-one* (**9f**) (1.02 g, 95%) as a pale yellow oil. Analytical data were identical with the above sample.

2,3-Dimethylcyclopent-2-en-1-one [29] was obtained as a colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta =$ 1.70 (3H, s, CH_3), 2.05 (3H, s, CH_3), 2.37 (2H, m, H-5), 2.49 (2H, m, H-4). IR (cm^{-1}, film): ν_{max} 2971, 2914, 1698, 1650.

4.9. Reaction of vinyl acetate with hexacarbonyl[μ-[(1,2-η:1,2-η)phenylethyne]]-dicobalt-(Co–Co) in air

A solution of TMANO·2H_2O (0.84 g, 7.57 mmol) in MeOH (30 ml) was added over a 15 min period to a stirred solution of hexacarbonyl[μ-[(1,2-η:1,2-η)-phenylethyne]]dicobalt-(Co–Co) (500 mg, 1.46 mmol) in vinyl acetate (10 ml) at 25 °C, under an air atmosphere. The mixture was stirred for 16 h before it was filtered through a pad of silica using Et_2O as the eluent. The filtrate was evaporated under reduced pressure to leave a crude residue, which was purified by column chromatography on silica using a 0–50% Et_2O in light petroleum gradient as the eluent to give *5-acetoxy-2-phenylcyclopent-2-en-1-one* (**5b**) (20.3 mg, 7%) as a pale yellow oil; no *2-phenylcyclopent-2-en-1-one* was obtained. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 2.19$ (3H, s, CH_3CO), 2.67 (1H, m, H-4), 3.23 (1H, ddd, $J = 19$, 7.0, 3.4 Hz, H-4), 5.33 (1H, dd, $J = 7.0$, 3.3 Hz, H-5), 7.38 (3H, m, Ar–H), 7.74 (3H, m, Ar–H + H-3). ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta = 21.0$ (C-4), 33.6 (*C*H$_3$CO), 73.2 (C-5), 127.1 (Ar–C), 128.8 (Ar–C), 129.1 (Ar–C), 130.9 (Ar–C), 143.0 (C-2), 154.6 (C-3). 169.5 (CH$_3$*C*O), 201.2 (C-1). IR (cm^{-1}, film): ν_{max} 1715, 1651. HRMS: *m/z*: Found: 200.08551. Calc. for $C_{13}H_{12}O_2$ [$M^+ - O$]: 200.08373.

4.10. Reaction of vinyl acetate with hexacarbonyl[μ-[(1,2-η:1,2-η)phenylethyne]]-dicobalt-(Co–Co) under 'dry' conditions

Anhydrous NMO (1.50 g, 12.9 mmol) was dissolved in CH_2Cl_2 (20 ml) and added over 1 h to a stirred solution of hexacarbonyl[μ-[(1,2-η:1,2-η)-phenylethyne]]dicobalt-(Co–Co) (500 mg, 1.29 mmol) in vinyl acetate (5 ml) at 25 °C. The mixture was stirred for 5 h, then filtered through a pad of silica using Et_2O as the eluent. The filtrate was evaporated under reduced pressure to leave a crude residue, which was purified by column chromatography on silica using a 0–50% Et_2O in light petroleum gradient as the eluent to give *2-phenylcyclopent-2-en-1-one* (**7**) (61.1 mg, 30%) followed by *5-acetoxy-2-phenylcyclopent-2-en-1-one* (**5b**), admixed with *4-acetoxy-2-phenylcyclopent-2-en-1-one* (**6b**) [30] (~ 1:1) (10 mg, 4%) which failed to separate adequately on this scale; only the faster moving isomer **5b** could be obtained in pure form. Analytical data for **5b** were as given above.

4.11. Reaction of vinyl benzoate with hexacarbonyl[μ-[(1,2-η:1,2-η)phenylethyne]]-dicobalt-(Co–Co) in the presence of D_2O

A solution of anhydrous *N*-methylmorpholine *N*-oxide (0.95 g, 8.15 mmol) in dry CH_2Cl_2 (20 ml) was added over 1 h to a mixture of hexacarbonyl[μ-[(1,2-η:1,2-η)phenylethyne]]dicobalt-(Co–Co) (310 mg, 0.80 mmol), vinyl benzoate (1.30 g, 8.00 mmol) and D_2O (1 ml) at 25 °C. The mixture was stirred for 16 h, then filtered through a pad of silica using CH_2Cl_2 as the eluent. The filtrate was evaporated under reduced pressure to leave a crude residue, which was purified by column chromatography on silica 0–40% Et_2O in light petroleum gradient as the eluent to give *2-phenyl-5-deuteriocyclopent-2-en-1-one* (80 mg, 62%) as a pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 2.59$ (1H, m, H-5), 2.72 (2H, m, H-4), 7.40 (3H, m, Ar–H), 7.71 (2H, m, Ar–H), 7.89 (1H, m, H-3). ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta = 26.3$ (C-4), 35.7 (t due to D-splitting, C-5), 127.3 (Ar–C), 128.5 (Ar–C), 128.6 (Ar–C), 131.9 (Ar–C), 143.8 (C-2), 159.1 (C-3), 208.0 (C-1). IR (cm^{-1}, film): ν_{max} 3049, 1706. HRMS: *m*/*z*: Found: 159.07878. Calc. for $C_{11}H_9DO$ [M^+]: 159.07944.

*4.12. Synthesis of the (+)-taylorione (and (+)-nortaylorione) precursor **11** [6]*

4.12.1. (1R,3R)-cis-1-Ethynyl-2,2-dimethyl-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)cyclopropane [6]

Potassium carbonate (2.20 g, 15.9 mmol) was added to a stirred solution of (1*S*,3*R*)-*cis*-2,2-dimethyl-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)cyclopropanecarboxaldehyde [6] (1.00 g, 4.72 mmol) and dimethyl (1-diazo-2-oxopropyl)phosphonate [12] (1.50 g, 7.81 mmol) in MeOH (100 ml) at 25 °C. The mixture was stirred for 16 h before the solvent was evaporated under reduced pressure. The residue was partitioned between ether (100 ml) and saturated aqueous $NaHCO_3$ (100 ml). The organic phase was dried and evaporated under reduced pressure and the residue chromatographed on silica using a 0–50% ether in light petroleum gradient as the eluent to give (1*R*,3*R*)-*cis*-1-ethynyl-2,2-dimethyl-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)cyclopropane (0.84 g, 85%) as a pale yellow oil. 1H-NMR (250 MHz, $CDCl_3$): $\delta = 0.77$ (1H, dt, $J = 8.5$, 7.1 Hz, C*H*CH_2), 1.07 (3H, s, CH_3), 1.11 (3H, s, CH_3), 1.17 (3H, dd, $J = 8.6$ 2.3 Hz, CH–C≡), 1.35 (3H, s, CH_3COOCH_2), 1.56–1.70 (4H, m, CHCH_2CH_2), 1.89 (1H, d, $J = 2.2$ Hz, HC≡), 3.86–4.02 (4H, m, OCH_2CH_2O). IR (cm^{-1}, film): ν_{max} 3310, 2978, 2953, 2927, 2110, 1472.

*4.12.2. Hexacarbonyl[(1S,3R)-cis-1-[μ-[(1,2-η:1,2-η)-ethynyl]]-2,2-dimethyl-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)cyclopropane]dicobalt-(Co–Co) (**10**) [6]*

A solution of (1*R*,3*R*)-*cis*-1-ethynyl-2,2-dimethyl-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)cyclopropane (0.85 g, 4.09 mmol) in light petroleum (20 ml) was added to a stirred solution of octacarbonyldicobalt (1.40 g, 4.09 mmol) in the same solvent over 10 min at 25 °C. After being stirred for 2 h the mixture was filtered through a pad of silica, eluting with 50% ether–light petroleum. The solution was evaporated under reduced pressure and the residue purified by chromatography on silica using a 0–30% ether in light petroleum gradient to elute the complex hexacarbonyl[(1*S*,3*R*)-*cis*-1-[μ-[(1,2-η:1,2-η)ethynyl]]-2,2-dimethyl-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)cyclopropane]dicobalt-(Co–Co) (**10**) (2.00 g, 99%) as a red oil. ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 0.86$ (1H, m, C*H*CH_2), 1.07 (3H, s, CH_3), 1.18 (3H, s, CH_3), 1.33 (3H, s, CH_3COOCH_2), 1.59–1.72 (4H, overlapping m, CHCH_2CH_2), 2.08 (1H, dd, $J = 8.1$, 0.7 Hz, C*H*–C≡), 3.81–4.02 (4H, overlapping m, OCH_2CH_2O), 5.84 (1H, d, $J = 0.9$ Hz, HC≡). IR (cm^{-1}, film): ν_{max} 2989, 2951, 2884, 2095, 2057, 2019, 1588.

*4.12.3. (1S,3R)-cis-1-(Cyclopent-2-en-1-on-2-yl)-2,2-dimethyl-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-cyclopropane (**11**) [6]*

A solution of *N*-methylmorpholine *N*-oxide monohydrate (0.82 g, 6.07 mmol) in CH_2Cl_2 (30 ml) was added over a 2 h period to a stirred solution of hexacarbonyl[(1*S*,3*R*)-*cis*-1-[μ-[(1,2-η:1,2-η)ethynyl]]-2,2-dimethyl-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-cyclopropane]dicobalt-(Co–Co) (**10**) (0.30 g, 0.61 mmol) in vinyl benzoate (5.00 g, 33.8 mmol) at 25 °C. The mixture was stirred for a further 16 h and then filtered through a pad of silica using CH_2Cl_2 as eluent. The filtrate was evaporated under reduced pressure

and the residue subjected to chromatography on silica using a 0–40% ether in light petroleum gradient as eluent to give (1*S*,3*R*)-*cis*-1-(cyclopent-2-en-1-on-2-yl)-2,2-dimethyl-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-cyclopropane (**11**) as a colourless oil (0.10 g, 60%). ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 0.97$ (3H, s, CH_3), 1.16 (3H, s, CH_3), 1.27 (3H, s, CH_3COOCH_2), 1.10–1.46 (6H, overlapping m, CH–C= + $CHCH_2CH_2$), 2.35 (2H, m, CH_2C=O), 2.57 (2H, m, CH_2CH=C), 3.81–4.01 (4H, overlapping m, OCH_2CH_2O), 7.24 (1H, m, CH_2CH=C). IR (cm^{-1}, film): ν_{max} 2989, 2957, 2893, 1704, 1627, 1455.

4.13. n-Butylthioacetic acid [31]

A solution of sodium chloroacetate (208.0 g, 1.80 mol) in water (700 ml) was slowly added to a solution of 1-butanethiol (153.0 g, 1.70 mol) in aqueous NaOH solution (5.7 M, 300 ml) at 0 °C. After the addition was complete the mixture was heated under reflux for 1 h before it was allowed to cool and was acidified with aqueous HCl solution to pH 1. The *n*-butylthioacetic acid separated as an oily layer on top of the aqueous phase and was extracted using Et_2O (3 × 300 ml). The organic phase was dried and evaporated under reduced pressure to yield *n*-butylthioacetic acid (230 g, 90%) as a clear liquid. Analytical data were identical with those previously published. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 0.93$ (3H, t, $J = 7.4$ Hz, CH_3), 1.42 (2H, m, CH_2), 1.60 (2H, m, CH_2), 2.67 (2H, t, $J = 7.3$ Hz, CH_2S), 3.26 (2H, s, SCH_2CO_2). IR (cm^{-1}, film): ν_{max} 3661–2346 (br, O–H), 2685, 2563, 1695, 1427.

4.14. Vinyl n-butylthioacetate (**14**)

According to the method of Swern and Jordan [32]: mercuric acetate (1.60 g, 5.02 mmol) and 100% sulfuric acid (0.15 ml) were added to a solution of *n*-butylthioacetic acid (59.2 g, 0.40 mol) in vinyl acetate (206.0 g, 2.40 mol). The mixture was heated under reflux for 3 h before the reaction was quenched by the addition of AcONa (1.00 g, 0.01 mol). The mixture was then partitioned between aqueous potassium carbonate solution (300 ml) and CH_2Cl_2 (300 ml). The organic phase was dried and evaporated under reduced pressure to yield *vinyl n-butylthioacetate* **14** (33 g, 47%) as a clear liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 0.93$ (3H, t, $J = 7.7$ Hz, CH_3), 1.40 (2H, m, CH_2), 1.59 (2H, m, CH_2), 2.66 (2H, t, $J = 7.4$ Hz, CH_2S), 3.28 (2H, s, SCH_2CO_2), 4.64 (1H, dd, $J = 6.3$ 1.8 Hz, =CH_2), 4.95 (1H, dd, $J = 14.0$, 1.8 Hz, =CH_2), 7.29 (1H, dd, $J =$ 14.0, 6.3 Hz, CH=). ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta = 14.1$ (CH_3), 22.3 (CH_2), 31.5 (CH_2), 32.9 (CH_2S), 33.8 (SCH_2CO_2), 99.0 (=CH_2), 141.8 (CH=), 168.0 (CO_2). IR (cm^{-1}, film): ν_{max} 3093, 2059, 2882, 1759, 1644, 1465, 1407. HRMS: m/z: Found: 175.07986. Calc. for $C_8H_{15}O_2S$ [$M^+ + 1$]: 175.07928.

4.15. Reaction of vinyl n-butylthioacetate (**14**) with hexacarbonyl[μ-[(1,2-η:1,2-η)phenylethyne]]-dicobalt-(Co–Co)

A solution of *N*-methylmorpholine *N*-oxide monohydrate (0.97 g, 7.18 mmol) in CH_2Cl_2 (30 ml) was added over a 2 h period to a stirred mixture of hexacarbonyl[μ-[(1,2-η:1,2-η)phenylethyne]]dicobalt-(Co–Co) (0.28 g, 0.72 mmol) and vinyl *n*-butylthioacetate (**14**) (2.00 g, 11.5 mmol) at 25 °C. The mixture was stirred for a further 16 h before it was filtered through a pad of silica using CH_2Cl_2 as the eluent. The filtrate was evaporated under reduced pressure to leave a crude residue, which was purified by column chromatography on silica using a 0–40% Et_2O in light petroleum gradient as the eluent to give 2-phenylcyclopent-2-en-1-one (**7**) (68.0 mg, 60%) as a pale yellow oil. Analytical data were as given above.

4.16. Diethyl 7,7-diethoxyhept-1-yne-4,4-dicarboxylate (**17**)

A solution of *n*-BuLi in hexanes (8.00 ml, 2.5 M, 19.9 mmol) was added dropwise over a 10 min period to a stirred solution of *N*,*N*-diisopropylamine (2.01 g, 19.9 mmol) in THF (75 ml) at 0 °C. The solution of lithium *N*,*N*-diisopropylamide was then cooled to − 75 °C and a solution of diethyl 1,1-diethoxypropane-3,3-dicarboxylate [17] (5.24 g, 18.1 mmol) in THF (75 ml) was added over a 20 min period. The mixture was stirred for 30 min before propargyl bromide (80% in toluene, 3.00 g, 20.0 mmol) was added. The mixture was then stirred for a further 30 min before it was quenched by the addition of saturated aqueous ammonium chloride solution (10 ml) and allowed to warm to r.t. The solvent was evaporated under reduced pressure to leave a residue which was partitioned between Et_2O (150 ml) and saturated aqueous ammonium chloride solution (100 ml). The organic phase was dried and evaporated under reduced pressure to give *diethyl 7,7-diethoxyhept-1-yne-4,4-dicarboxylate* (**17**) (5.94 g, 100%) as a pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 1.20$ (6H, t, $J = 7.2$ Hz, 2 × CH_3), 1.26 (6H, t, $J = 7.2$ Hz, 2 × CH_3), 1.50 (2H, m, H-6), 1.98 (1H, t, $J = 2.7$ Hz, HC≡), 2.09 (2H, m, H-5), 2.77 (2H, t, $J = 2.7$ Hz, H-3), 3.46 (2H, m, OCH_2), 3.60 (2H, m, OCH_2), 4.18 (4H, m, 2 × OCH_2), 4.46 (1H, t, $J = 5.7$ Hz, O_2CH). ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta = 14.2$, 15.4, 23.0, 27.3, 28.4, 56.5, 61.0, 61.9, 71.5 (alkyne-C), 78.9 (alkyne-C), 102.6 (O_2CH), 170.2 (CO_2). IR (cm^{-1}, film): ν_{max} 2129, 1727. HRMS: m/z: Found: 351.1775. Calc. for $C_{17}H_{28}NaO_6$ [$M^+ + Na$]: 351.1784.

4.17. Diethyl hept-6-yn-1-al-4,4-dicarboxylate (18)

Diethyl 7,7-diethoxyhept-1-yne-4,4-dicarboxylate (**17**) (1.89 g, 5.76 mmol) was added to dilute aqueous HCl solution (1 M, 70 ml) and the mixture was heated on a steam bath for 30 min. The mixture was then extracted with Et_2O (3 × 50 ml) and the combined extracts were dried and evaporated under reduced pressure to give *diethyl hept-6-yn-1-al-4,4-dicarboxylate* (**18**) (1.44 g, 99%) as a pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 1.26$ (6H, t, $J = 7.2$ Hz, CH_3), 2.03 (1H, t, $J = 2.7$ Hz, HC≡), 2.38 (2H, m, H-3), 2.51 (2H, m, H-2), 2.81 (2H, d, $J = 2.7$ Hz, H-5), 4.20 (4H, m, 2 × OCH_2), 9.74 (1H, s, HCO). ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta = 14.2$, 23.7, 24.9, 39.2, 56.0, 62.1 (OCH_2), 72.0 (alkyne-C), 78.6 (alkyne-C), 169.9 (CO_2), 200.7 (HCO). IR (cm^{-1}, film): ν_{max} 2985, 2940, 2927, 2908, 1733. HRMS: m/z: Found: 255.1234. Calc. for $C_{13}H_{19}O_5$ [$M^+ + 1$]: 255.1232.

4.18. (E/Z)-Diethyl 1-acetoxyhept-1-en-6-yne-4,4-dicarboxylate (15)

Potassium carbonate (42.0 mg, 0.30 mmol) was added to a solution of diethyl hept-6-yn-1-al-4,4-dicarboxylate (**18**) (0.78 g, 3.07 mmol) in Ac_2O (30 ml) and the mixture was heated under reflux for 2 h. The mixture was then concentrated under reduced pressure and the residue was partitioned between Et_2O (50 ml) and saturated aqueous sodium hydrogen carbonate solution (50 ml). The organic phase was dried and evaporated under reduced pressure to leave a crude residue, which was purified by column chromatography on silica using 50% Et_2O in light petroleum as the eluent to give *diethyl 1-acetoxyhept-1-en-6-yne-4,4-dicarboxylate* (**15**) (0.70 g, 77%) as a colourless oil containing both *E*- and *Z*-isomers. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 1.34$ (6H, t, $J = 7.1$ Hz, 2 × CH_3CH_2), 2.09, 2.12 (1H, 2 × t, $J = 2.7$ Hz, HC≡), 2.18, 2.23 (3H, 2 × s, CH_3CO), 2.84, 3.01 (2H, 2 × dd, $J = 8.2$, 1.2, 7.8, 1.4 Hz, H-3), 2.87 (2H, d, $J = 2.7$ Hz, H-5), 4.30 (4H, m, 2 × OCH_2), 4.82, 5.34 (1H, 2 × m, 2-H), 7.21, 7.25 (1H, 2 × d, $J = 6.5$, 12.3 Hz, H-1). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (14.2 and 20.8), (22.8 and 23.0), (27.6 and 30.3), (56.7 and 57.0), (61.9 and 62.0 (OCH_2)), (71.3 and 71.9 (alkyne-C)), (78.8 and 79.2 (alkyne-C)), (107.2 and 108.0 (C-2)), (137.4 and 138.7 (C-1)), 167.0 (CO_2CH_2) and (169.7 and 169.8 (CH_3CO_2)). IR (cm^{-1}, film): ν_{max} 2104, 1753, 1734, 1676. HRMS: m/z: Found: 297.13186. Calc. for $C_{15}H_{21}O_6$ [$M^+ + 1$]: 297.13381.

4.19. Hexacarbonyl[μ-[(6,7-η:6,7-η)-(E/Z)-diethyl 1-acetoxyhept-1-en-6-yne-4,4-dicarboxylate]]-dicobalt-(Co–Co) (19)

A solution of (*E*/*Z*)-diethyl 1-acetoxyhept-1-en-6-yne-4,4-dicarboxylate (**15**) (1.16 g, 3.93 mmol) in CH_2Cl_2 (40 ml) was added to a stirred solution of octacarbonyldicobalt (1.34 g, 3.93 mmol) in CH_2Cl_2 (40 ml) at 25 °C. The mixture was stirred for 1 h before it was filtered through a pad of silica using a light petroleum eluent to remove less polar impurities, then 10% Et_2O in light petroleum to elute *hexacarbonyl[μ-[(6,7-η:6,7-η)-(E/Z)-diethyl 1-acetoxyhept-1-en-6-yne-4,4-dicarboxylate]]dicobalt-(Co–Co)* (**19**) (2.17 g, 95%) as a red oil. Anal. Found: C, 43.0; H, 3.4. Calc. for $C_{21}H_{20}Co_2O_{12}$ requires C, 43.3; H, 3.4%. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 1.29$ (6H, t, $J = 6.8$ Hz, 2 × CH_3CH_2), 2.10, 2.18 (3H, 2 × s, CH_3CO), 2.71, 2.90 (2H, 2 × d, $J = 8.1$, 7.3 Hz, H-3), 3.62, 3.64 (2H, 2 × s, H-5), 4.22 (4H, m, 2 × OCH_2), 4.79, 5.30 (1H, 2 × m, H-2), 5.98, 5.99 (1H, 2 × s, HC≡), 7.15 (1H, 2 × overlapping d, H-1). ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta =$ 14.2, 20.8, 20.9, 28.2, 30.8, 37.7, 38.0, 57.9, 58.7, 61.9, 62.0, 73.4, 87.3 (107.0 and 108.0 (C-2)), (137.0 and 138.5 (C-1)), 168.0 (CO_2CH_2), (170.0 and 170.3 (CH_3CO_2)), 199.7 (CO). IR (cm^{-1}, film): ν_{max} 2097, 2053, 2002, 1740, 1638.

4.20. Diethyl 3,3a,4,5-tetrahydro-5-oxo-(1H)-pentalene-2,2-dicarboxylate (20) [33]

A solution of *N*-methylmorpholine *N*-oxide monohydrate (1.00 g, 7.40 mmol) in CH_2Cl_2 (25 ml) was added over a 90 min period (syringe pump) to a stirred solution of hexacarbonyl[μ-[(6,7-η:6,7-η)-(*E*/*Z*)-diethyl 1-acetoxyhept-1-en-6-yne-4,4-dicarboxylate]]dicobalt-(Co–Co) (**19**) (0.43 g, 0.74 mmol) in CH_2Cl_2 (15 ml) at 25 °C. The mixture was stirred for 16 h before it was filtered through a pad of silica using Et_2O as the eluent. The filtrate was evaporated under reduced pressure to leave a crude residue which was purified by column chromatography on silica using a 20–50% Et_2O in light petroleum gradient as the eluent to give *diethyl 3,3a,4,5-tetrahydro-5-oxo-(1H)-pentalene-2,2-dicarboxylate* (**20**) (10 mg, 54%) as a colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 1.21$ (6H, apparent q, $J = 7.3$ Hz, CH_3), 1.70 (1H, app. t, $J = 12.7$ Hz), 2.09 (1H, dd, $J = 17.8$, 3.2 Hz), 2.59 (1H, dd, $J = 17.9$, 6.4 Hz), 2.76 (1H, dd, $J = 12.7$, 7.6 Hz), 3.07 (1H, m), 3.26 (2H, m), 4.19 (4H, m, 2 × OCH_2), 5.89 (1H, m, H-6). IR (cm^{-1}, film): ν_{max} 3080, 2939, 1731, 1709, 1636.

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