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Pauson–Khand Reaction of Allenic Hydrocarbons: Synthesis of 4-Alkylidenecyclopentenones

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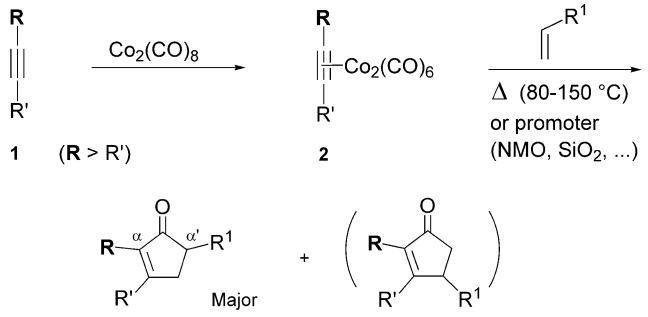
Keywords: Allenes / Cycloaddition / Enones / Configuration determination / Density functional calculations

The carbonyldicobalt-mediated alkyne/allene/CO cocyclization gives 4-alkylidenecyclopentenones as the major [2+2+1] cycloadducts. The regio- and stereoselectivities depend mainly on the substitution pattern of both the alkyne and the allenic moieties, which can be rationalized using the Magnus mechanism. However, contrary to this model, and in agreement with more recent mechanistic studies, our results provide evidence that both initial pseudo-equatorial and pseudo-axial coordination modes of the allenic hydrocarbons onto one of the cobalt atoms of the primary alkyne–dicobalt complex are involved. DFT calculations supporting both these coordination modes are given.

Introduction

The Pauson–Khand Reaction (PKR), a formal [2+2+1] cycloaddition, first described and used over three decades ago, is a carbonyldicobalt-mediated carbonylative cocyclization of an alkyne with an alkene giving cyclopentenones (Scheme 1).[1,2] The main feature of this cycloaddition is its high sensitivity to steric hindrance, so that the major regioisomeric cyclopentenone obtained is the one with the more bulky R and R^1 groups of both unsaturated partners at the α- and α′-positions of the cyclopentenone keto group (Scheme 1). However, the PKR with linear and cyclic alkenes was shown to be a low-yielding cycloaddition.[3] Consequently, the intermolecular PKR was initially limited to strained olefins such as norbornene,[1,4] norbornadiene,[4a] and 7-oxanorbornene derivatives.[5] It was later extended to a few other classes of unsaturated compounds, such as: cyclobutenes,[6] allenes,[7] methylenecyclopropanes,[8] or cyclopropenes,[9] and to some heteroatom-substituted[10] or activated alkenes.[11] On the other hand, the carbonylative cycloaddition of ene-ynes turned out to be far more efficient and synthetically useful.[12,2] Thus, intramolecular PKR has emerged as one of the most powerful routes to five-membered ring systems and has become the key step in numerous syntheses of complex polycyclic cyclopentenones[13] and natural products.[14]



Scheme 1. Pauson–Khand reaction (PKR).

Major improvements in the PKR came from finding new energetically activated procedures[15] or by using milder conditions with various promoters such as silica,[16] amines,[17] dimethylsulfoxide (DMSO),[18] sulfides[19] and molecular sieves.[20] Particularly, the use of tertiary amine *N*-oxides allowed the reaction to be carried out at room temperature.[21] Recent other developments in this powerful methodology includes the possibility of performing the cycloaddition under catalytic conditions[22] or enantioselectively.[23] It is noteworthy that similar intramolecular [2+2+1] cycloadditions have been recently described as being catalyzed by several other transition-metal complexes (Ti, Mo, Fe, Ru, Rh, Ir, and Pd).[24] However, the $Co_2(CO)_8$-mediated PKR remains very useful because of its specific stereochemical features and because of its high chemical compatibility with numerous functionalities.

A mechanistic rationalization for the PKR was first proposed in 1985 by Magnus.[25] This was later revisited by Laschat who shed new light on the coordination step in which the alkene coordinates to one of the cobalt atoms of the initial alkyne–dicobalt complex **2**.[26] Moreover, theoret-

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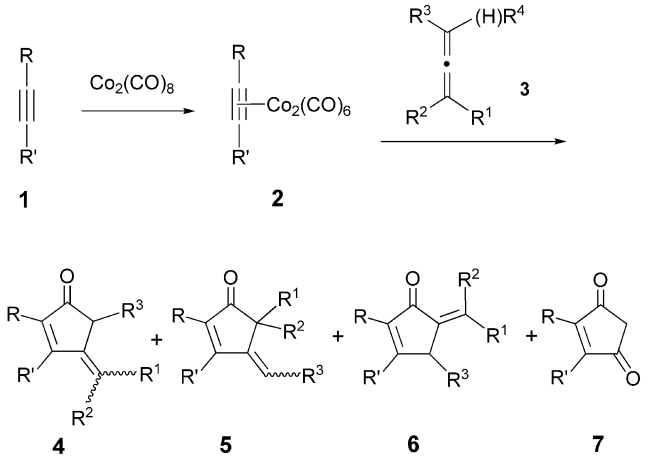
ical studies[27] (DFT calculations of the acetylene or propyne/ethylene/CO cocyclizations) and ESI tandem MS experiments,[28] confirmed the successive steps of the overall reaction. However, the $Co_2(CO)_8$-mediated reaction of 1,*n*-enynes has sometimes led to unexpected unsaturated (keto) compounds or other by-products, which also brought some light to the different steps of the PKR mechanism.[29]

At the outset of our work,[7a] additional data on the reactivity of allenic structures within PKR-like reactions were available. Octacarbonyldicobalt was shown to polymerize allene,[30] and Pauson's group was unable to characterize any cycloadduct from the reaction of cyclonona-1,2-diene under thermal conditions.[2k] Aumann realized the first intermolecular $Fe_2(CO)_9$-mediated alkyne/allene/CO cocyclization, but 4-alkylidenecyclopentenones were obtained with poor selectivities along with cyclopentadienones and cyclopentadienone–iron complexes.[31] Likewise, the first iron-mediated intramolecular cycloaddition of 1,6-yne-allenes was described.[32] Since then, the intramolecular PKR of 1,*n*-yne-allenes giving bicyclic cyclopentenones has also been described as being mediated by $Co_2(CO)_8$[33] or $Mo_5(CO)_6$,[34] and was further developed using rhodium catalysis.[35,36]

In this context, we became interested in the reactivity of allenic compounds **3** under mild conditions within the intermolecular Pauson–Khand reaction (Scheme 2).[7] Indeed, because of the two orthogonal double bonds of the allenic unit, the study of the alkyne/allene/CO cocyclization was expected to bring up interesting results in several directions: (1) the possibility of achieving a short route to the well-known 5-alkylidenecyclopentenones **6**,[37] or to the otherwise difficult to prepare, 4-alkylidenecyclopentenones **4** and **5**;[38] (2) the opportunity to gain new insights into the PKR mechanistic pathway by observing the selectivity of the reaction leading to cyclopentenones **4**–**6** (Scheme 2). Thus, we report herein a full account of our investigations into the PKR with allene **3a** and allenic hydrocarbons **3**, which gave 4-alkylidenecyclopentenones **4** with high selectivity in most cases.



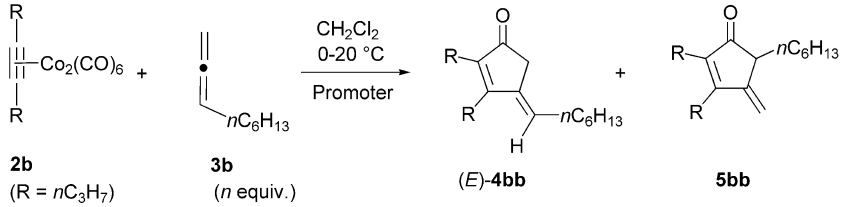
Scheme 2. Pauson–Khand reaction of allenic hydrocarbons **3**.

Results and Discussion

Model PKR of Alkynes with Allenes

Exploratory experiments with the acetylene–dicobalt complex **2a** (R = R′ = H) appeared to be complicated. So, as a starting point, the reaction of a symmetrically disubstituted alkyne–dicobalt complex such as 4-octyne–dicobalt complex **2b** with a monoalkylallene (e.g., 1,2-nonadiene **3b**) was taken to be an appropriate PKR model that could be used to check the feasibility of the cycloaddition and to find optimum reaction conditions. Indeed, the carbonyl–dicobalt complex **2b**, generated from 4-octyne (**1b**) in almost quantitative yield, reacted easily with one equivalent of 1,2-

Table 1. Model Pauson–Khand reaction with allenic hydrocarbons **3b**.



Entry	Allene **3b** [*n* equiv.]	Promoter	Yield [%][a] **4bb** + **5bb**	Ratio[b] **4bb**/**5bb**
1	1	NMO (6 equiv.)	59	96:4
2	1 + 0.5	NMO (6 equiv.)	(61)	96:4
3	1.2	NMO (6 equiv.)	(63)	96:4
4	1.5	NMO (6 equiv.)	71	96:4
5	1.5	TMANO (6 equiv.)	(68)	95:5
6	1.5	TMANO·H_2O	(32)	95:5
7	1.5	CAN (6 equiv.)	(15)	94:6

[a] Yields of isolated product after flash chromatography. Those in brackets were GC yields (internal standard: octadecane). [b] Ratio **4bb**/**5bb** was determined by GC analysis of the crude product.

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nonadiene (**3b**) under Schreiber's conditions[21] in dichloromethane at 0–20 °C, in the presence of six equivalents of *N*-methylmorpholine oxide (NMO; Table 1). 4-Heptylidenecyclopentenone [(*E*)-**4bb**] was obtained with high regioselectivity, along with traces of the regioisomeric cyclopentenone **5bb**, in a combined yield of 59% (**4/5** ratio 96:4, Table 1, entry 1). The yield of **4bb** and **5bb** was increased when a slight excess of 1,2-nonadiene (**3b**) was used (entries 2–4). This study resulted in an initial optimized procedure (Procedure A), where dichloromethane was used as solvent with 1.5 equiv. of allene **3b** (entry 4); under these conditions, cyclopentenones **4bb** and **5bb** were obtained in 71% overall yield.[7a] Other promoters were also tested: Trimethylamine oxide (TMANO) gave similar results (entry 5), whereas its hydrate TMANO·H_2O (entry 6), and cerium ammonium nitrate (CAN; entry 7) were less efficient in promoting the cycloaddition.

The possibility of using gaseous allene **3a** (b.p. –33 °C) as an unsaturated partner prompted us to carry out the reaction at low temperature. Another parameter was the nature of the solvent(s) since it has been previously demonstrated that the use of tetrahydrofuran (THF) as a cosolvent increases both the reaction rate and the yield of PKRs.[39] Thus, the effects of these parameters on the yield and selectivities of our model PKR (**2b** + **3b**) were investigated. When the cycloaddition was carried out in CH_2Cl_2/THF (1:1) at –78 °C, the reaction did occur but was very slow, as shown by GLC analysis of the reaction mixture (analysis performed every two hours); after 8 h, cyclopentenone (*E*)-**4bb** was then isolated in 20% yield, with most of the 1,2-nonadiene (**3b**) being recovered unchanged. Warming up the reaction mixture from –78 °C to room temperature resulted in a set of further experimental conditions (Procedures B–C), which are summarized in Table 2.

Table 2. Procedures A–D.

Entry	[a]	Solvent (ratio)	*T* [°C]	Time [h]	Yield [%][c] **4bb** + **5bb**	Ratio[d,e] **4bb/5bb**
1	A	CH_2Cl_2	0–20	15–18	71	96:4
2	B	CH_2Cl_2/THF (1:1)	–78 to r.t.[f] then r.t.	1 3	81	95:5
3	C	CH_2Cl_2/THF (1:1)	–78 to r.t.[g] then r.t	4 2	77	97:3
4	D[b]	CH_2Cl_2/THF (1:1)	–40 to r.t. then r.t	1	50	94:6

[a] Procedures A–C were performed on a 1–10 mmol scale (**2b/3b/**NMO, 1:1.5:6). [b] Procedure D was performed on a 20 mmol scale. [c] Yield of isolated products analyzed by flash chromatography. [d] Obtained by GC analysis of the crude reaction product. [e] If necessary, the less polar cyclopentenone **5bb** can be easily separated from **4bb** by flash chromatography. [f] –78 °C to r.t. over 1 h. [g] Stirring 2 h at –78 °C, then warming to r.t. over 2 h and stirring for a further 2 h at r.t.

In Procedure B, the NMO promoter was added as a solid at –78 °C over a few minutes. The reaction mixture was then warmed to room temperature over 1 h and stirred for 3 h at room temperature before workup; under these conditions, cyclopentenones **4bb** and **5bb** were obtained in 81% combined yield (Table 2, entry 2). Procedure C was similar to Procedure B, but the reaction mixture was stirred for 2 h at –78 °C before warming up slowly from –78 °C to room temperature over 2 h, and stirring for a further 2 h at this temperature. Cyclopentenones **4bb** and **5bb** were then obtained in 77% combined yield with a similar 97:3 regioselectivity (entry 3). Procedures A–C were all performed on a 1–5 millimolar scale and the study culminated in 81% yield for Procedure B. However, all these procedures were less efficient (25–35% yields) when carried out on a preparative 20–50 mmol scale, presumably because of the necessary decrease in the relative volume of solvent used.

For this purpose, a further set of conditions was established (Procedure D) that resulted in an optimized 50% yield (entry 4). This method involved the slow addition at –40 °C of the promoter NMO, which was diluted in dichloromethane, then allowing the reaction to come to room temperature over 1 h, then stirring again for 2–5 h. With experimental procedures A–D in hand, we then looked at the scope and limitations of the PKR with allenic hydrocarbons **3**. We were particularly interested in the relationship between the selectivities obtained in the formation of cyclopentenones **4**–**6** and the substitution patterns of both the acetylenic and allenic partners.

PKRs of Disubstituted Alkynes with Allenes

The reactivities of symmetrical dialkylalkyne–dicobalt complexes **2b**–**d** with allene **3a** and a range of monosubstituted allenes **3b**–**d** were first studied. The results are summarized in Table 3. All reactions gave cyclopentenone (*E*)-**4** with high regio- and stereoselectivities under procedures A, B and D. Procedure B, when carried out in a CH_2Cl_2/THF mixture, gave higher yields (compare entries 1/2, 4/5, 8/9, and 11/12), and up to 91% yield of cyclopentenones **4db** and **5db** (entry 7). Variation of the solvent and temperature had no effect on these selectivities, which seemed to depend only on the steric hindrance of the alkyne substituent R. Indeed, for the reactions of complexes **2b**–**d** with allene **3b**, both the regioselectivity (**4/5**) and the stereoselectivity [(*E*/*Z*)-**4**] were higher when the R group was more bulky (compare entries 4–6 with entry 7). Allenic hydrocarbons **3c** and **3d** with a larger R^1 group (R^1 = Ph or $SiMe_3$) gave cyclopentenones (*E*)-**4bc** and (*E*)-**4bd** as single products (entries 8–12). As mentioned above, procedure B was less efficient on a preparative scale (20–50 mmol) and furnished cyclopentenones **4da** and **4bc** in modest 25% and 36% yields, respectively (entries 3 and 10). Cyclopentenone **4cb** can be obtained by Procedure D in 53% yield on a 40 mmol scale (entry 6). It should also be noted that, on such preparative 30–40 mmol scales, it was possible to isolate small amounts (ca. 1–3%) of cyclopentene-1,3-dione **7**, resulting from the cobalt-catalyzed oxidative cleavage of the exocyclic double bond of the cyclopentenone **4** [1,3-diones **7d** (Table 3, entry 3) and **7c** (Table 4, entry 2)].[40]

We then examined the PKRs of a symmetrical dialkylalkyne such as 4-octyne (**1b**; R = nC_3H_7) with several polysubstituted allenes **3e**–**j** under experimental procedures A, B or

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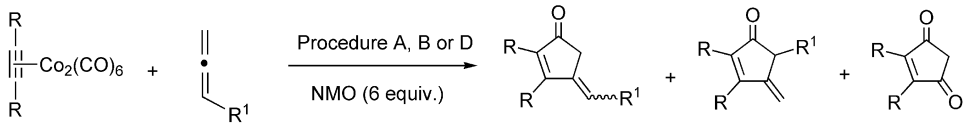
Table 3. Pauson–Khand reaction of symmetrical dialkylalkynes with monosubstituted allenes.



2b-d **3a-d** (1.5 equiv). **4** **5** **7d** (R = CH_3)

Entry	**2b–d**		Allene **3a–d**		Procedure[a]	Cyclopentenones **4–5**	Yield [%][c] **4 + 5**	Ratio **4/5**[d]	**4** (*E*/*Z*)[e]	Yield [%][c] **7**
1	**2d**	R = CH_3	**3a**	R^1 = H	A	**4da**	59	–	–	
2	**2d**	R = CH_3	**3a**	R^1 = H	B	**4da**	62	–	–	
3	**2d**	R = CH_3	**3a**	R^1 = H	B[b]	**4da**	25	–	–	1.5
4	**2b**	R = nC_3H_7	**3b**	R^1 = nC_6H_{13}	A	**4bb + 5bb**	71	96:4	100:0	
5	**2b**	R = nC_3H_7	**3b**	R^1 = nC_6H_{13}	B	**4bb + 5bb**	81	95:5	100:0	
6	**2c**	R = nC_2H_5	**3b**	R^1 = nC_6H_{13}	D	**4cb + 5cb**	53	97:3	97:3	
7	**2d**	R = CH_3	**3b**	R^1 = nC_6H_{13}	B[f]	**4db + 5db**	91	89:11[f]	94:6[f]	
8	**2b**	R = nC_3H_7	**3c**	R^1 = Ph	A	**4bc**	33	> 99:1	100:0	
9	**2b**	R = nC_3H_7	**3c**	R^1 = Ph	B	**4bc**	70	> 99:1	100:0	
10	**2b**	R = nC_3H_7	**3c**	R^1 = Ph	B[b]	**4bc**	36	> 99:1	100:0	
11	**2b**	R = nC_3H_7	**3d**	R^1 = $SiMe_3$	A	**4bd**	40	> 99:1	100:0	
12	**2b**	R = nC_3H_7	**3d**	R^1 = $SiMe_3$	B	**4bd**	61	> 99:1	100:0	

[a] Procedure A: reaction carried out in CH_2Cl_2 at 0–20 °C. Procedure B: reaction carried out in CH_2Cl_2/THF (1:1), warming up from –78 °C to r.t. over 1 h, then stirring at r.t. for 1–3 h. Procedure D (20–40 mmol scale): reaction carried out in CH_2Cl_2/THF (1:1) with addition of a CH_2Cl_2 solution of NMO at –40 °C. [b] Reaction carried out on a 40 mmol scale. [c] Yield of isolated products after flash chromatography. The less polar cyclopentenone **5** is easily separated from cyclopentenone **4**. [d] Ratio of regioisomers **4/5** was obtained by GC analysis of the crude reaction product. [e] Ratios *E*/*Z* of **4** were obtained from GC analysis of the crude reaction product. [f] Reaction was carried out on a 11 mmol scale. Ratios **4/5** and *E*/*Z* (**4**) were obtained from isolated products.

D (Table 4) [one example was also studied with 3-hexyne **1c** (R = Et): Table 4, entry 2]. The 1,1-disubstituted allenes **3e** and **3f** gave the cyclopentenone **4be** as the major adduct and **4ce** and **4bf** as single adducts (Table 4, entries 1–4). A small amount (5%) of the regioisomeric cyclopentenone **5be** was also isolated in the cycloaddition of complex **2b** with **3e** (Table 4, entry 1). 1,3-Disubstituted allenes such as 6,7-tridecadiene (**3g**) and cyclonona-1,2-diene (**3h**) gave cyclopentenones (*E*)-**4bg** and **4bh**, respectively, in fair 66–81% yields (entries 5–7). 2-Methyl-2,3-decadiene (**3i**) was studied as an example of a trisubstituted allene (entry 8); in this case the reaction gave a 60:40 mixture of cyclopentenones **4bi** and (*E*)-**5bi** in a lower overall yield (41%). No reaction was observed with tetrasubstituted allenes such as tetramethylallene (**3j**) under procedures A or B (entry 9). These last reactions clearly show that the PKR of allenic compounds is also very sensitive to steric hindrance around the allenic unit. It is noteworthy to point out here that the reaction of vinylidenecyclohexane (**3f**) did not give any 5,5-disubstituted cyclopentenone **5bf**, whereas allenes **3e** and **3i**, which have a dimethyl-substituted terminal carbon, led to the 5,5-disubstituted cyclopentenones **5be** and **5bi**, respectively, as minor cycloadducts (compare entries 3 and 4 with entries 1 and 8). This might be a result of the more sterically demanding environment about the cyclohexane ring of vinylidenecyclohexane (**3f**), compared to that of 1,1-dimethylallene (**3e**).

We also studied the reactivities of a few disymmetrical alkynes, such as 2-alkynes **1i–k** (R′ = CH_3) with 1,2-nonadiene (**3b**) under procedure B (Table 5). All these reactions gave the cyclopentenone (*E*)-**4** as the major product along with the regioisomeric cyclopentenone **5**, both of which have the larger R group on the 2-position of the cyclopentenone (Table 5). However, the dicobalt complexes **2i** also afforded the alternative regioisomeric cyclopentenone (*E*)-**4′ib**, with the larger *n*-butyl group on the 3-position of the cyclopentenone (entry 1); complexes **2j** and **2k** did not give the corresponding cyclopentenones **4′jb** and **4′kb** (entries 2 and 3). Thus, the bulky phenyl and *tert*-butyl groups of the 2-alkyne–dicobalt complexes **2j–k** completely controlled the selectivity of the cycloaddition to cyclopentenones **4jb** and **4kb**. It is noteworthy that the regioselectivity is lower (**4kb/5kb** = 88–92:12–8) when a small group, such as methyl, is one of the alkyne substituents; this regioselectivity was also observed for the reaction with the 2-butyne–dicobalt complex **2d** (Table 3, entry 7: **4db/5db** = 89:11).

PKRs of Monosubstituted Alkynes with Allenes

The cycloaddition of monosubstituted alkynes (1-alkynes **2e–g**) with allenes **3a–d** were examined under procedure A or B (Table 6). First, the cycloaddition of 1-pentyne (**2e**) with allene (**3a**) gave cyclopentenone **4ea** in 60% yield (Table 6, entry 1). All other reactions tested gave cyclopentenone **4** (mixture of *E* and *Z* isomers) as the major cycloadducts, along with the regioisomeric cyclopentenone **5** (entries 2–8), except for the reactions with trimethylsilylallene **3d**, which did not give the corresponding cyclopentenones **5ed** and **5fd** (entries 9–10). The regioselectivities **4/5** (approximately 83–92:17–8) were lower than for the cycloaddition of dialkylalkynes **2b** and **2c** (Table 3, entries 4–6)

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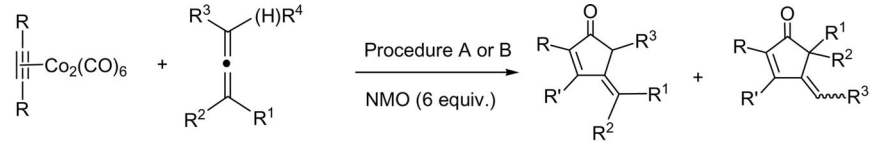
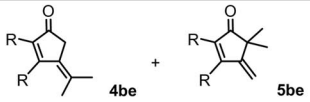
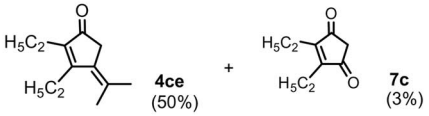
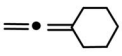
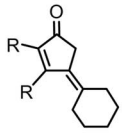
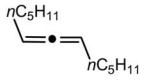
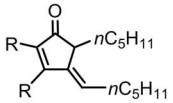
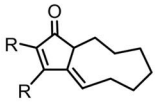
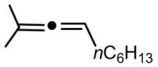
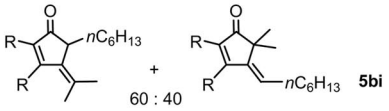
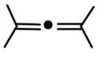
Table 4. PKR of symmetrical alkynes with polysubstituted allenes.

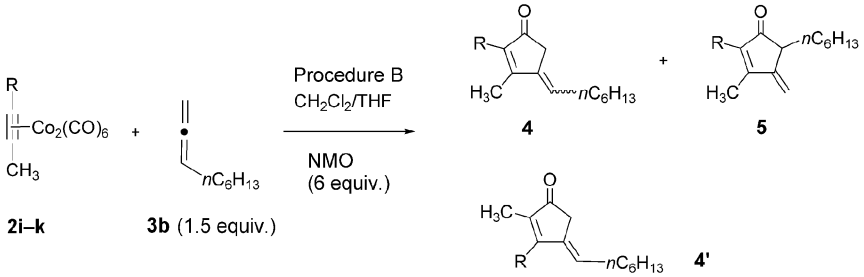


2b (R = nC_3H_7) **3e–j** (1.5 equiv.) **4** **5**

Entry		Allene **3e–j**	Procedure[a]	Cyclopentenone **4–5**		Yield [%][b] **4** (+ **5**)
1	**3e**		A	**4be** + **5be**	 **4be** + **5be**	62 (**4be**) 5 (**5be**)
2[d]	**3e**		D	**4ce**	 **4ce** (50%) + **7c** (3%)	50
3	**3f**		A	**4bf**		61
4			B			75
5	**3g**		A	(*E*)-**4bg**		66
6			B			81
7	**3h**		A	**4bh**		66
8	**3i**		B	**4bi** + (*E*)-**5bi**[c]	**4bi**  **5bi** 60 : 40	41
9	**3j**		A or B	–	n.r.[e]	–

[a] Procedure A: reaction carried out in CH_2Cl_2 at 0–20 °C. Procedure B: reaction carried out in CH_2Cl_2/THF (1:1), warming up from –78 °C to r.t. over 1 h, then stirring at r.t. for 1–3 h. [b] Yields of isolated product after flash chromatography. [c] Cyclopentenones **4bi** and **5bi** were separated as individual regioisomers by flash chromatography. [d] Reaction carried out with the 3-hexyne dicobalt complex **2c** (R = Et). [e] n.r.: no reaction.

Table 5. PKR of disymmetrical alkynes.



2i–k **3b** (1.5 equiv.) **4** **5** **4'**

Entry	Alkyne–[Co] **2i–k**[a]	Product **4**, **4′** and **5**	Yield **4** + **5** (+ **4′**)[b]	Ratio **4/5**[c]	Ratio *E*/*Z*-**4**[c]
1	**2i** R = nC_3H_7	**4ib** + **5ib**	70	88:12	> 99:1
		+ **4′ib**	14		> 99:1
2	**2j** R = Ph	**4jb** + **5jb**	85	85:15	93:7
3	**2k** R = *t*Bu	**4kb** + **5kb**	61	92:8	> 99:1

[a] [Co] = $Co_2(CO)_6$. [b] Yields of isolated product by flash chromatography. [c] Ratios **4/5** were obtained from GC analysis of the crude reaction product.

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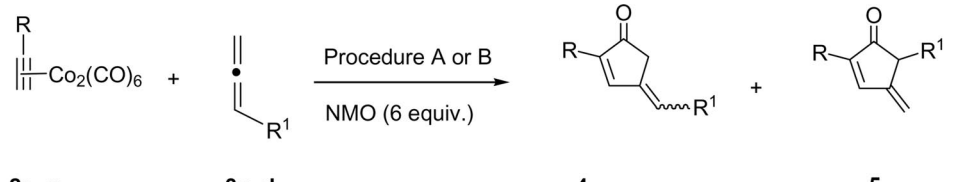
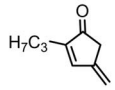
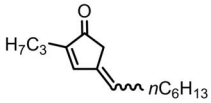
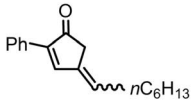
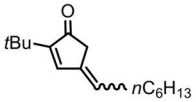
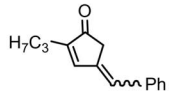
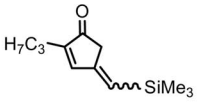
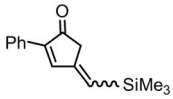
Table 6. PKR of monosubstituted alkynes with allenes **3a–d**.



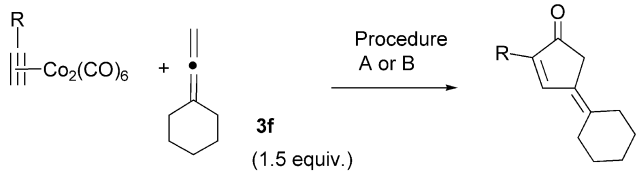
2e–g **3a–d** **4** **5**

Entry	2	R	Allene 3a–d	Procedure	4 + 5	Cyclopentenones 4	Yield [%][a] 4 + 5	Ratio[b] 4/5	4[c] (*E*/*Z*)
1	**2e**	nC_3H_7	**3a**	B	**4ea**		60	–	–
2	**2e**	nC_3H_7	**3b**	A	**4eb + 5eb**		86	88:12	70:30
3				B			80	85:15	71:29
4	**2f**	Ph	**3b**	A	**4fb + 5fb**		52	90:10	75:25
5				B			69	90:10	70:30
6	**2g**	*t*Bu	**3b**	A	**4gb + 5gb**		58	91:9	75:25
7				B			70	92:8	70:30
8	**2e**	nC_3H_7	**3c**	B	**4ec + 5ec**		83	83:17	75:25
9	**2e**	nC_3H_7	**3d**	B	**4ed**		54	100:0	92:8
10	**2f**	Ph	**3d**	A	**4fd**		46	100:0	91:9

[a] Yield of isolated products after flash chromatography. [b] Ratio **4/5** was obtained from GC analysis of the crude reaction product. [c] Ratios *E*/*Z* for cyclopentenones **4** were obtained from GC analysis and/or from ^{1}H NMR spectra.

and similar to those obtained with 2-alkynes **2d** (Table 3, entry 7) and **2i–k** (Table 5). These cycloadditions were less stereoselective because cyclopentenones (*Z*)-**4** were obtained in larger amounts (*E*/*Z* = 70–75:30–25; entries 2–8). Here again, it is worth mentioning the different behavior of trimethylsilylallene (**3d**), the cycloadditions of which were more stereoselective (compare entries 9 and 10 with entries 2–8). This demonstrates the importance of the steric effect of the allenic substituent on both the regio- and stereoselectivities of the cycloaddition.

The reactivity of vinylidenecyclohexane (**3f**), a 1,1-disubstituted allene, was also studied (Scheme 3). Both procedures A and B gave 4-alkylidenecyclopentenones **4hf** (R = nC_5H_{11}) and **4ff** (R = Ph), from **2h** and **2f**, respectively, with complete regioselectivity. Here again, procedure B, where the reaction is performed in CH_2Cl_2/THF, was more efficient. It is also worth mentioning that, similar to the reaction of vinylidenecyclohexane (**3f**) with complex **2b**



2h	(R = nC_5H_{11})	Procedure A	**4hf**	62%
	"	" B		74%
2f	(R = Ph)	Procedure A	**4ff**	66%
	"	" B		67%

Scheme 3. PKR of 1-alkynes **2h** and **2f** with vinylidenecyclohexane (**3f**).

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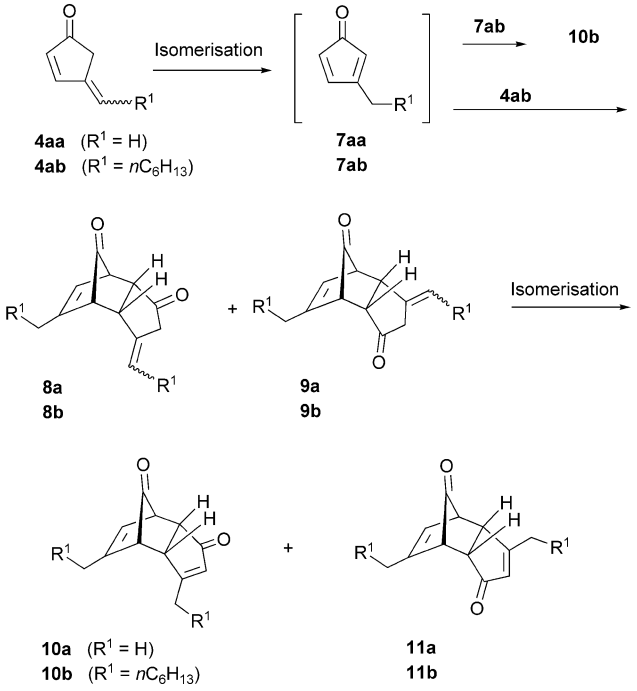
(Table 4, entries 3 and 4), no 5,5-disubstituted cyclopentenone (**5hf** or **5ff**) was isolated.

PKRs of Acetylene with Allenes

The reaction of acetylene hexacarbonyldicobalt complex **2a** with 1,2-nonadiene (**3b**) appeared to be more complex than the cycloadditions of mono- and disubstituted alkynes **2b**–**k**. When the conditions described for procedure B were applied for 15 h, the reaction gave a complex mixture of four cyclopentenones: the 4-alkylidenecyclopentenones **4ab** (*E*+*Z*), **5ab**, and the 5-alkylidenecyclopentenone (*E*)-**6ab** in a 73:7:20 ratio, together with a tricyclic diketone **10b**, which was isolated in 11% yield (Table 7, entry 1).

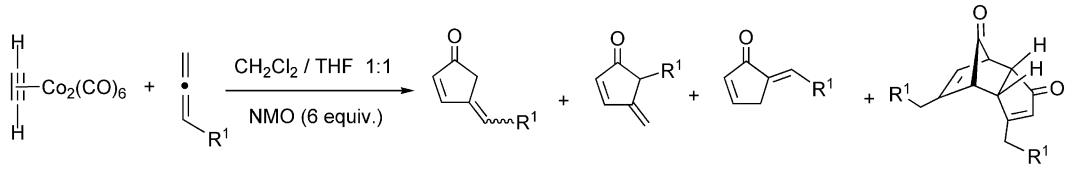
The structure of the latter diketone **10b** was determined by analysis of 2D NMR analysis (COSY experiments). This by-product **10b** might arise from the unstable isomeric cyclopentadienone **7ab**, which would be slowly generated in situ by the *N*-methylmorpholine-catalyzed isomerization of the primary cyclopentenones **4ab**. The [4+2] dimerization of cyclopentadienone **7ab** would then give the diketone **10b**.[41] A plausible alternative pathway might involve the three-step sequence: (1) the isomerization of cyclopentenone **4ab** to cyclopentadienone **7ab**, (2) the Diels–Alder reaction of this intermediate cyclopentadienone **7ab** with cyclopentenone **4ab**, leading to the bicyclic diketone **8b**,[42] and (3) the isomerization of this cycloadduct **8b** to cyclopentenone **10b** (Scheme 4). It is noteworthy that the isomeric cyclopentenone-dimer **11b** could not be detected.



Scheme 4. Plausible pathways to [4+2] dimers **10** and **11**.

The reaction times of further cycloadditions were then shortened in an attempt to avoid the isomerization of **4ab** to cyclopentadienone **7ab**; as hoped, this prevented the formation of the cyclopentenone **10b** (Table 7, entries 2–4). The selectivities of the formation of the isomeric cyclopentenones **4**–**6ab** were found to depend upon the temperature. Particularly, under procedure C when the reaction was allowed to slowly warm from –78 °C to room temperature over 4 h, the amount of regioisomer **5ab** formed decreased, while the amount of 5-alkylidenecyclopentenone (*E*)-**6ab** increased (compare entries 3 and 4). The *E*/*Z* selectivities for cyclopentenones **4ab** appeared to remain relatively unchanged. Reaction of dicobalt complex **2a** with phenylallene **3c** under procedure B also gave three isomeric cyclopentenones **4**–**6ac** (entry 5). Thus, the formation of the 5-alkylidenecyclopentenone **6** seems to be specific to the reactivity of the acetylene–dicobalt complex (**2a**).

Table 7. Pauson–Khand reaction of acetylene.



2a **3b** (R1 = nC_6H_{13}) **3c** (R1 = Ph) **4ab** **4ac** **5ab** **5ac** **6ab** **6ac** **10b** (R1 = nC_6H_{13})

Entry	Allene 3b–c		Procedure[a]	*T* [°C]	Time [h]	Cyclopentenones 4–6	Yield [%][d] 4 + 5 + 6	Ratio[e] 4/5/6	*E*/*Z* Ratio[f] 4	Yield [%][d] 10b
1	**3b**	$R^1 = nC_6H_{13}$	B[b]	–78 to r.t. (1 h)	2 + 15 (r.t.)	**4ab + 5ab + 6ab**	71	73:7:20	78:22	11
2	**3b**	"	A	0–20	2	**4ab + 5ab + 6ab**	78	85:8:7	70:30	–
3	**3b**	"	B	–78 to r.t. (1 h)	1 + 2 (r.t.)	**4ab + 5ab + 6ab**	79	90:3:7	73:27	–
4	**3b**	"	C	–78 to r.t. (4 h)	4 + 2 (r.t.)	**4ab + 5ab + 6ab**	82	85:2:13	75:25	–
5	**3c**	R^1 = Ph	B[c]	–78 to r.t. (2 h)	2 + 2 (r.t.)	**4ac + 5ac + 6ac**	28	77:5:18	86:14	–

[a] Procedure A: reaction carried out in CH_2Cl_2 at 0–20 °C. Procedure B: reaction carried out in CH_2Cl_2/THF (1:1), warming up from –78 °C to r.t. over 1 h, then stirring at r.t. for 1–3 h. Procedure C: warming up from –78 °C to r.t. over 4 h, then stirring at r.t. for 2 h. [b] Procedure B, but stirring at r.t. overnight (15 h). [c] Reaction performed on a 17 mmol scale. [d] Yield of isolated product after flash chromatography. [e] Ratios of regioisomers **4/5/6** were obtained from GC analysis of the crude reaction product. [f] Ratios *E*/*Z* of cyclopentenones **4** were obtained from GC analysis of the crude reaction product.

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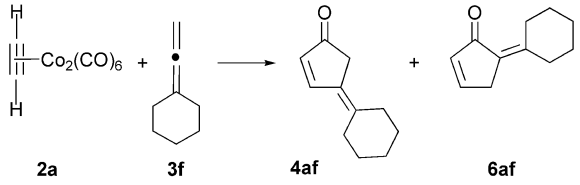
Results for the cycloadditions of **2a** with vinylidenecyclohexane (**3f**) are summarized in Table 8. All the reactions gave mixtures of cyclopentenone **4af** and 5-cyclohexylidenecyclopentenone (**6af**) regardless of which procedure was used (entries 1–3). Formation of the 5,5-disubstituted cyclopentenone **5af** was not observed, whereas the amount of cyclopentenone **6af** increased up to 28 molar% when the reaction was carried out at lower temperature (entry 3).

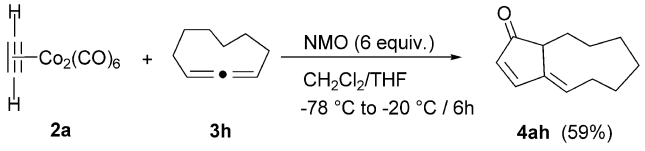
Table 8. Pauson–Khand reaction of acetylene **1a** with **3f**.



Entry	Reaction conditions	Yields[%][a] **4af** + **6af**	Ratio **4/6**[b]
1	20 °C	51	96:4
2	Procedure B (–78 °C to r.t. over 1 h)	52	80:20
3	Procedure C (–78 °C to r.t. over 4 h)	64	72:28

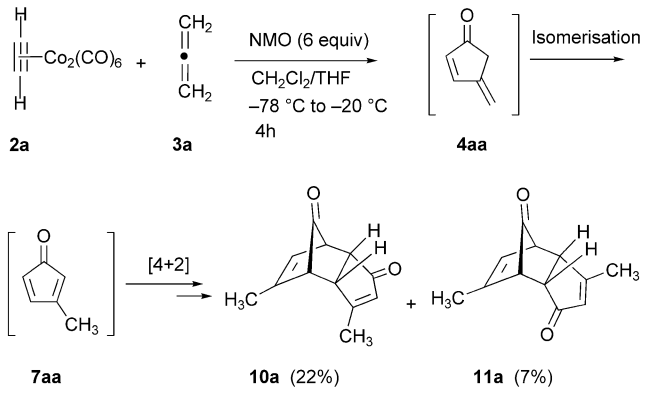
[a] Yields (**4af** + **6af**) of isolated products after flash chromatography. [b] Ratios **4af/6af** were obtained from GC analysis of the crude reaction product.

When the reactivity of cyclonona-1,2-diene (**3h**), as an example of a 1,3-disubstituted allene was examined under the conditions described for procedure C, the bicyclic cyclopentenone **4ah** was obtained as a single adduct in 59% yield (Scheme 5); no isomeric 5-alkylidenecyclopentenone-type product **6ah** was detected.



Scheme 5. Pauson–Khand reaction of acetylene (**2a**) with cyclonona-1,2-diene (**3h**).

Finally, attention was directed towards the cycloaddition of acetylene (**1a**) with allene (**3a**). Whereas no 4-methylenecyclopentenone (**4aa**) was obtained, instead, two regioisomeric [4+2] dimers of 3-methylcyclopentadienone **7aa**, namely **10a** and **11a**, were obtained in 22% and 7% yields, respectively (Scheme 6). All attempts to isolate 4-methylenecyclopentenone (**4aa**) by carrying out the reaction at –78 °C without warming, failed, and the reaction gave only mixtures of dimers **10a** and **11a**. The formation of these dimers might be rationalized as for the formation of adduct **10b** (Scheme 4).



Scheme 6. Pauson–Khand reaction of acetylene with allene.

Structure and Stereochemistry Assignments of 4- and 5-Alkylidenecyclopentenones

The structure and stereochemistry of alkylidenecyclopentenones **4**–**6** were assigned by means of their ^{1}H and ^{13}C NMR spectra. Thus, an 4-alkylidenecyclopentenone structure such as the cyclopentenone (*E*)-**4bb** was easily distinguished from the possible 5-alkylidenecyclopentenone structure **6bb**.[38] Indeed, the α-keto methylene group (C-5) H_2 of the former gave rise to an upfield ^{1}H NMR signal at δ = 2.86 ppm, whereas the signal from the (C-4)H_2 group of a typical 5-alkylidenecyclopentenone structure, such as (*E*)-**6bm** (R^1 = nC_5H_{11}), was found downfield at δ = 3.02 ppm [δ = 3.00 ppm for (*Z*)-**6bm**],[43] or at δ = 3.19 ppm for cyclopentenone (*E*)-**6ab** (Figure 1). The chemical shifts of their exocyclic vinylic protons are also very distinctive. These proton NMR signals are shifted upfield at δ = 5.5–5.9 ppm for 4-alkylidenecyclopentenones **4** [δ = 5.75 ppm for (*E*)-**4bb**] and downfield (≥6 ppm) for the 5-alkylidenecyclopentenone structure [δ = 6.57 ppm and 5.96 ppm for cyclopentenones (*E*)- and (*Z*)-**6bm** (R^1 = nC_5H_{11}), respectively].[43]

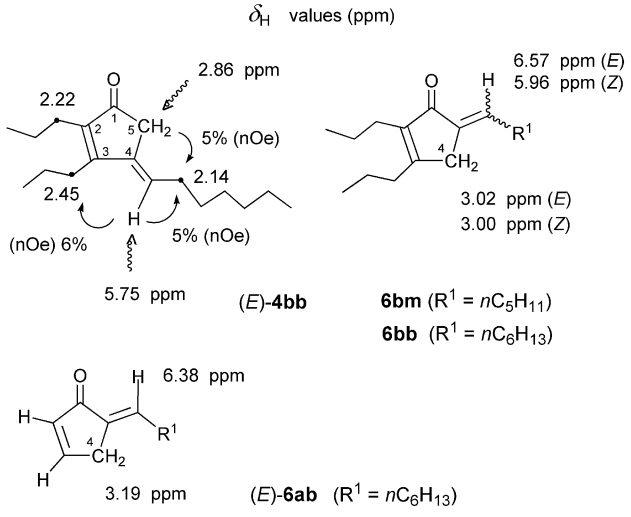


Figure 1. Structure assignment of alkylidenecyclopentenones **4** and **6**.

The E/Z configurational assignment of the exocyclic double bond of stereoisomers (*E*)-**4** and (*Z*)-**4** can be determined by using nuclear Overhauser effect (NOE) NMR spectroscopy.[44,45] As an example, the (*E*)-configuration of cyclopentenone **4bb** was proved by irradiating the exocyclic vinylic proton at δ = 5.75 ppm; this resulted in the enhancements (5–6% NOE) of both allylic methylene groups at δ

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= 2.14 and 2.45 ppm. Likewise, irradiation of the α′-keto methylene group at δ = 2.86 ppm gave an effect (5% NOE) only on the allylic protons at δ = 2.14 ppm (Figure 1).

However, the easiest and least ambiguous way to assign the (*E*) or (*Z*)-configuration of these 4-alkylidenecyclopentenones **4** relies on comparisons between the chemical shifts of both C-3 and C-5 carbons of each isomer (Figure 2). Thus, the C-5 carbon nucleus of cyclopentenone (*E*)-**4** resonates at high-field (δ = 37–39 ppm) compared to the analogous carbon of the (*Z*)-**4** isomer (δ = 40–43 ppm) because of the shielding due to a positive *cis*-γ-effect (γ-compression effect) from the allylic carbon (C-4)=C–*C*H_2 at δ = 30–31 ppm [δ = 37.3 ppm for (*E*)-**4cb** and 42.8 ppm for (*Z*)-**4cb**].[45,46] A similar shielding effect is observed for the C-3 carbon in cyclopentenone (*Z*)-**4**, which resonates at higher field [δ =167.7 ppm for (*Z*)-**4cb**], whereas it is further downfield for the isomer (*E*)-**4** [δ =168.2 ppm for (*E*)-**4cb**]. This last shielding effect is stronger (by approximately 5 ppm) for the C-3 carbon of 3-unsubstituted cyclopentenones (*Z*)-**4** (R′ = H). Thus, the C-3 carbon resonates further upfield at δ = 149.3 ppm for (*Z*)-**4eb**, whereas it is shifted more downfield (δ = 154.3 ppm) for the (*E*)-**4eb** isomer (Figure 2).

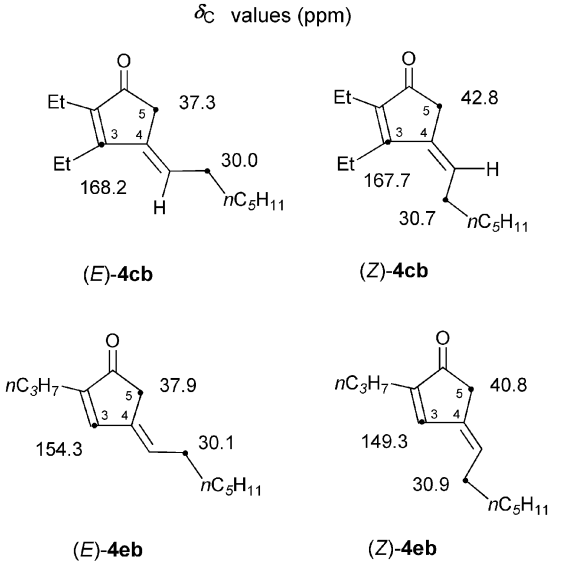

Figure 2. Configurational assignment of the exocyclic double bond of 4-alkylidenecyclopentenones (*E*)- and (*Z*)-**4** using ^{13}C NMR spectroscopy.

Alternatively, the stereochemistry of the 3-unsubstituted cyclopentenones **4** obtained from the PKRs of 1-alkynes **1e**–**m** (R′ = H) could also be deduced from the chemical shifts of the vinylic protons H-3 and (C-4)=C*H*. Indeed, in agreement with the Cárdenas rule,[47] the H-3 proton resonates at high-field for the (*E*)-**4** isomer, whereas it is further downfield for the (*Z*)-**4** isomer because of a steric deshielding ($\Delta\delta \approx$ 0.3–0.4 ppm) effect from the *cis* group R^1 (Figure 3; the reference for the *cis*–*trans* description is the intracyclic double bond). For the exocyclic vinylic proton (C-4)=C*H*, the H-*cis* proton of the (*E*)-**4** isomer is deshielded compared with the H-*trans* proton of the (*Z*)-**4** isomer, because it experiences a low-field shift due to the magnetic anisotropy of the (C-2)=(C-3) double bond [H-*cis* appears at δ = 5.67 ppm in (*E*)-**4eb** and H-*trans* at δ = 5.55 ppm in (*Z*)-**4eb**].

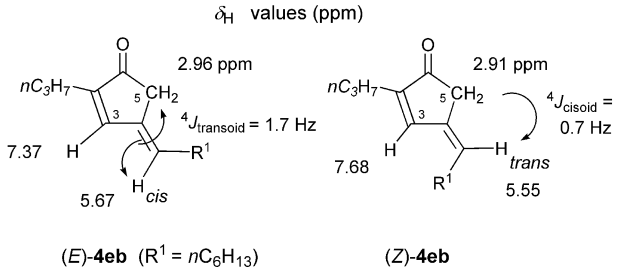

Figure 3. Configurational assignment of the exocyclic double bond of 4-alkylidenecyclopentenones (*E*)- and (*Z*)-**4eb** using ^{1}H NMR spectroscopy.

A further way to identify the stereoisomers of cyclopentenones **4** rests on the allylic coupling constant ^4J between the vinylic proton (C4)=C*H* and the (C-5)H_2 methylene group. This constant has previously been demonstrated to be higher for the vinylic proton H-*cis* that is *transoid* with respect to the methylene group than for the corresponding *cisoid* (H-*trans*): i.e., $|^4J_{transoid}| > |^4J_{cisoid}|$.[44,48] In the case of cyclopentenone **4eb**, the H-*cis* vinylic proton of (*E*)-**4eb** appears as an almost completely resolved triplet of triplets at δ = 5.67 ppm (^3J = 7.8 Hz and $|^4J_{transoid}|$ = 1.7 Hz) whereas the H-*trans* proton of the isomer (*Z*)-**4eb** resonates at δ = 5.55 ppm as a less well resolved triplet of triplets with ^3J = 7.5 Hz and $|^4J_{cisoid}| \approx$ 0.7 Hz (Figure 3). Simultaneously, the methylenic protons (C-5)H_2 of isomer (*E*)-**4eb** resonate upfield at δ = 2.96 ppm as a doublet ($|^4J_{transoid}|$ = 1.7 Hz), whereas they give a less well resolved doublet downfield at δ = 2.91 ppm ($|^4J_{cisoid}| \approx$ 0.7 Hz) for the isomer (*Z*)-**4eb**. However, these vinylic and methylenic protons often appear only as broad triplets and singlets because of several other long-range ^5J and ^6J couplings through the dienic structure. Consequently, these ^4J allylic coupling constants are not always available and their use as stereochemical proofs is thus restricted for cyclopentenones **4**; moreover, their erroneous use may lead to incorrect stereochemical assignments.[48,49]

Mechanism

A comprehensive view of the different pathways possible for the PKRs of allenic hydrocarbons should rationalize the various regio- and stereoselectivities observed in the formation of alkylidenecyclopentenones **4**–**6**; a reasonable explanation must surely take into account both the steric features of the allenic unit and the PKR Magnus mechanism depicted in Scheme 7.[25] This mechanistic model includes several steps from the tetrahedral alkyne–dicobalt cluster **2**, which is initially formed from alkyne **1** and $Co_2(CO)_8$ (step 1), and is the only isolable and well characterized intermediate along the overall cycloaddition process.[50] This first step is assumed to be followed by the loss of a CO ligand from

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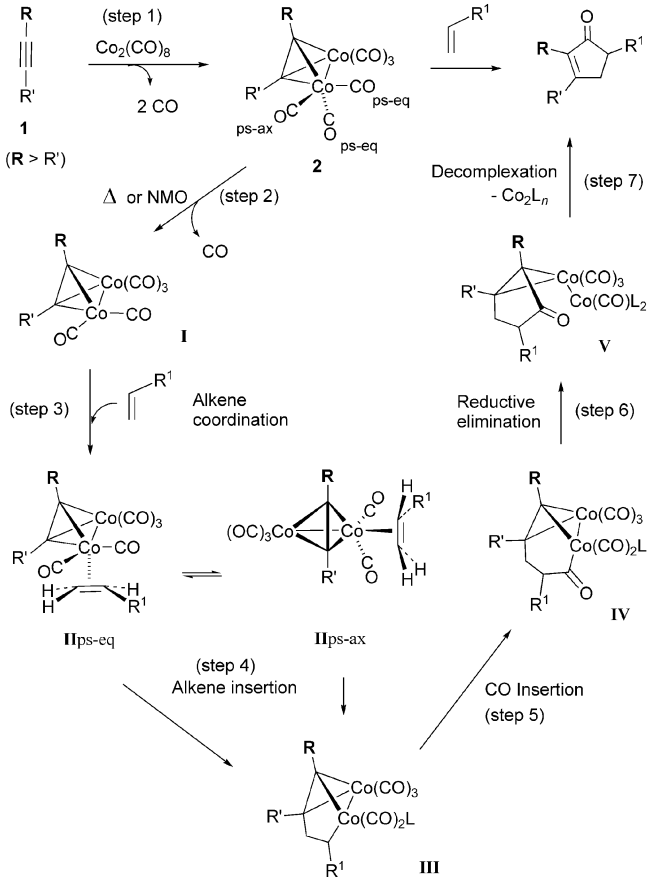
one of the cobalt atoms of cluster **2**, leading to the coordinatively unsaturated alkyne–pentacarbonyldicobalt intermediate **I** (step 2). For NMO-promoted PKRs, this CO decoordination is clearly executed through its oxidation to CO_2 with concomitant formation of *N*-methylmorpholine.[21] Further steps include: (1) olefin coordination to cobalt, which, for steric reasons, should preferentially take place *anti* to the larger substituent R of the alkyne in a pseudo-equatorial position (ps-eq) with respect to the Co–Co bond (step 3); (2) alkene insertion into the formal R′C–Co bond giving the cobaltacycle **III** (step 4); (3) CO insertion into the R^1C–Co bond giving the acylcobalt complex **IV** (step 5); (4) reductive elimination creating the RC–C(=O) bond of the intermediate **V** (step 6), and (5) decomplexation of the final cyclopentenone from the Co_2L_n cluster (step 7).



Scheme 7. PKR Magnus mechanism.

Evidence for the involvement of putative intermediates **I** and **II** has recently been obtained, and several refinements to this primary Magnus pathway, particularly about the olefin coordination and insertion steps (steps 3 and 4) have been made. Indeed, photochemically generated type-**I** intermediates have been identified by IR spectroscopy,[51] and intramolecularly chelated intermediates **I** have been characterized.[19a,52] A stable type-**II** alkene–pentacarbonyldicobalt cluster was also recently isolated and fully characterized.[53] For the PKR of norbornene derivatives, the coordination of the double bond to cobalt was recently discussed by Laschat who proposed a more realistic pseudo-axial coordination of the double bond because of the steric requirements of the methylene bridge of these compounds (step 3, giving the intermediate **II**-ps-ax).[26] Finally, DFT calculations on the propyne/ethylene PKR gave a more accurate description of the cycloaddition(s) pathway(s) and concluded that both olefin coordination modes were possible.[27c,27f] It is worth mentioning that electronic factors may play an important role in the regioselectivity of the PKRs when electron-poor alkynes are involved (e.g., R = CO_2Et).[54,27f] However, it was shown that when both steric and electronic factors were considered, steric factors superseded the latter.

Such electronic factors were also encountered in the PKRs of trimethylsilylalkynes with allenic hydrocarbons due to the β-effect of the silicon atom.[55] However, only alkynic and allenic hydrocarbons are addressed in detail within this paper. Consequently, only steric factors have to be considered. Thus, according to Magnus mechanism, complexation of the less substituted double bond of the allenic hydrocarbon **3** to the intermediate alkyne–pentacarbonyldicobalt complex **I** would preferentially occur *anti* to the R group (R >> R′) and also *anti* to the allenic substituent R^1 through the less hindered half-space defined by the allenic unit (Scheme 8). This coordination should result in the bending of the allenic ligand and would lead to the π complex **A**-*anti*.[56] Then, the insertion of the allenic unit into the adjacent R′C–Co bond would give the σ-allyl cobaltacycle **B**-*anti* (path a) from which the cyclopentenone (*E*)-**4** would be generated after further elementary steps of the PKR (CO insertion into the allylic C–Co bond giving the acylcobalt complex **C**, followed by a reductive elimination of cobalt to give complex **D** and decomplexation from Co_2L_n). Likewise, the π complex **A**-*syn* would give the minor cyclopentenone (*Z*)-**4** (path b). The high *E*-stereoselectivity (*E*/*Z* ≥ 95:5 when R′ ≠ H and *E*/*Z* ≈ 75:25 when R′ = H) would result from the large steric interaction between the R′ and R^1 groups within this last **A**-*syn* π complex. Formation of the minor regioisomeric cyclopentenone **5** could be explained from another, less favored (=CR^1R^2/Co–C≡O steric interactions) π complex **E** obtained by the coordination of the allenic unit through its more substituted double bond (path c). Insertion of the allene would lead to complex **F** and, finally, to cyclopentenone **5**. The isomer 5-alkylidenecyclopentenone (**6**) might emerge from the fourth π complex **G** (a rotamer of the **A**-*anti* π complex) through the insertion of the allene into the R′C–Co bond leading to the σ-vinyl cobalt complex **H**, followed by the three final steps (path d).

However, as qualitatively shown by using molecular models, the steric interactions of the R′ (alkyl or H) group of the alkyne unit with the R^1 or R^2 (alkyl or H) groups of the allenic hydrocarbon **3** should greatly influence the effective formation of these intermediate π complexes **A**, **E** and **G**. Particularly, it seems difficult to understand the formation, even in small amounts, of cyclopentenones (*Z*)-**4cb** (R = R′ = Et) and (*Z*)-**4db** (R = R′ = Me) from the **A**-*syn* π complex generated from complexes **2c** and **2d** and allene **3b**

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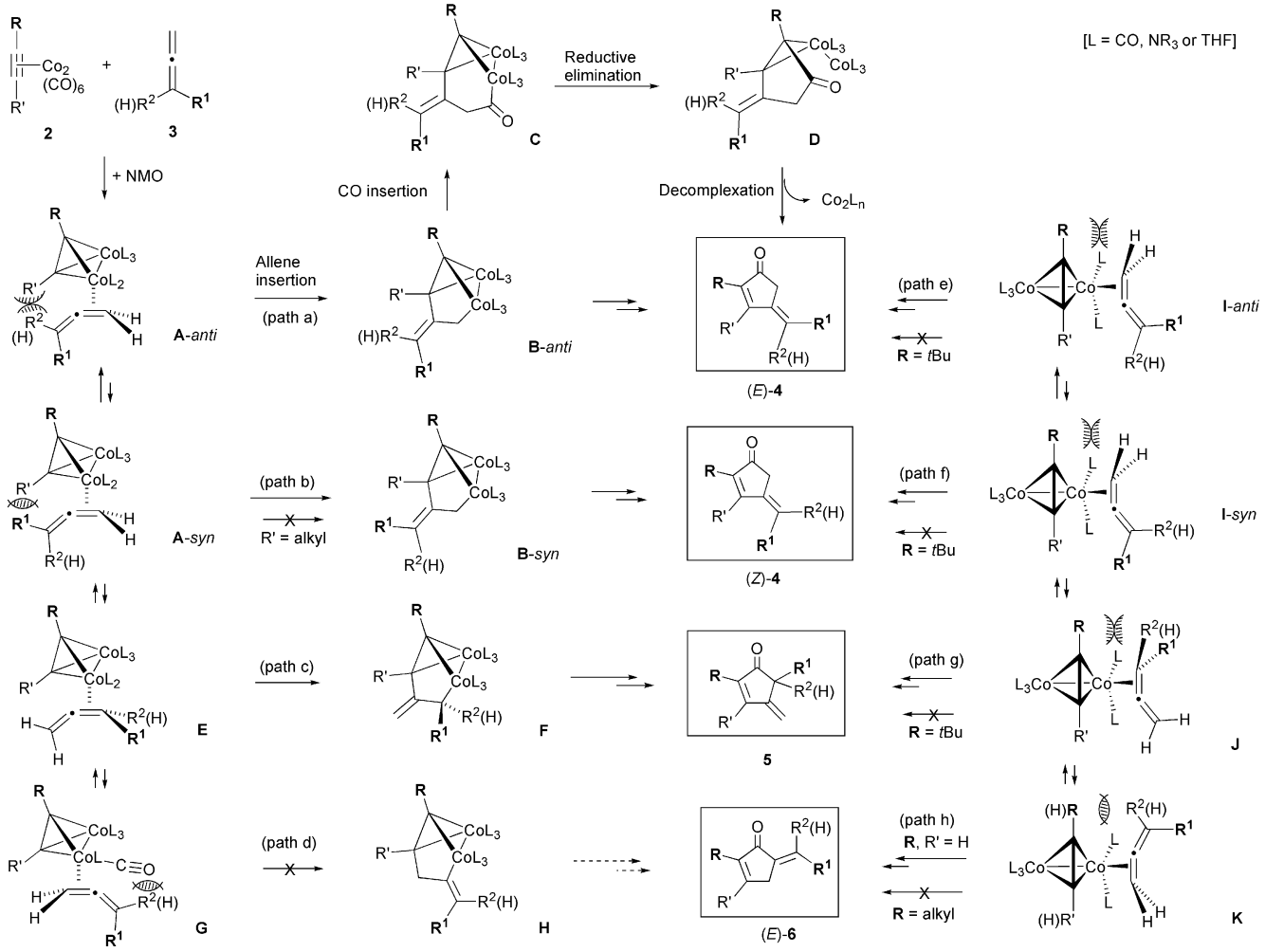

Scheme 8. Mechanistic pathways of the PKR of allenic hydrocarbons.

(R^1 = nC_6H_{13}) because of the large repulsion of the R′ (Et or Me) and R^1 (nC_6H_{13}) groups (Table 3, entries 6 and 7). On the other hand, the real reasons for the formation of the 5-alkylidenecyclopentenones (*E*)-**6ab**, (*E*)-**6ac** and (*E*)-**6af** (see Tables 7 and 8), which are obtained only in the reactions with the acetylene–dicobalt complex **2a**, are not totally clear within the Magnus mechanism. Indeed, understanding the difference in behavior between the dicobalt complexes of mono- or disubstituted alkynes **2b**–**k** (R = alkyl, R′ = alkyl or H) and complex **2a** (R = R′ = H) with allenes **3b**–**h** should involve some steric interaction between the alkyne group R (or H) and the allenic hydrocarbon **3** and its substituents R^1 or R^2. This is not the case if the initial coordination of the allenic unit takes place *anti* to the R group, and should rule out π complex **G** (and the associated path d) as a plausible intermediate π complex leading to cyclopentenone (*E*)-**6**. The steric interaction between the allenic group R^2 and the pseudo-equatorial CO ligand might inhibit the formation of this π complex **G**.

We envisioned that the coordination of allenes **3** to the alkyne–pentacarbonyldicobalt complex **I** may also occur on a pseudo-axial position (with respect to the Co–Co bond) of one of the cobalt atoms, as has already been suggested by Laschat.[26] Such a coordination would give rise to a set of π complexes **I**–**K** within dynamic equilibrium for which the allenyl ligands should be nearly parallel to the coordinated alkyne triple bond C_R–$C_{R'}$.[57] Among them, π complexes **I**-*anti* and **I**-*syn* can also explain the formation of cyclopentenones (*E*)-**4** and (*Z*)-**4**, respectively (paths e and f). As described for π complex **E**, the intermediate π complex **J** may also explain the formation of the regioisomeric cyclopentenone **5** (path g). However, for steric reasons, this pseudo-axial coordination does not seem as favored when R is a bulky group such as *tert*-butyl. Then, the formation of cyclopentenones (*E*)-**4kb** and **5kb** (Table 5, entry 3) and of cyclopentenones **4gb** (*E* and *Z*) and **5gb** (Table 6, entries 6 and 7) should stem from the intermediate π complexes **A** and **E**. To rationalize the possible formation of 5-alkylidenecyclopentenones **6**, we looked at the π complex **K**, which is a rotamer of the **I**-*anti* π complex and features an opposite spatial position of the C=CR^1R^2 group with respect to the alkyne C_R carbon. This π complex **K** seems to be the only one that presents: (1) a suitable coordination of the allenic double bond for the allene insertion (path h), and (2) steric interactions between the R and R^2(H) groups, which should explain the different reactivities of the dicobalt com-

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plexes **2a** (R = H) and **2b**–**f** (R ≠ H) as pointed out above.[7b] Indeed, when R is an alkyl group, these steric interactions disfavor coordination of the allenic unit and the subsequent production of cyclopentenone **6** (R ≠ H). Actually, in the PKRs with acetylene **1a** (R = R′ = H), the π complex **K** is identical to the **I**-*anti* π complex. In this case, path e is then favored over path h because the formation of the first C–C bond (step 4 of the PKR; Scheme 7) occurs preferentially between the alkyne (H)C carbon and the less bulky internal sp-carbon of the allenic unit (path e) rather than between this carbon and the allenic CH_2 terminus (path h) (Tables 7 and 8). Furthermore, the latter pathway h explains the *E*-configuration of the *exo*-cyclic double bond of cyclopentenone (*E*)-**6**, because the alkyne R (= H) and R^1 groups should adopt *anti* positions during the allene coordination in order to minimize the steric interactions between these two groups.

Modeling Study

To support the assumption that π complexes **I**–**K** are plausible alternative reaction intermediates, we investigated the stability of the most relevant species with respect to the more classical π complexes **A**–**G** through DFT calculations. Thus, we focused our attention on the two formal cycloadditions of methylallene (mimic of a monosubstituted allene **3**) with propyne (1-alkyne **1**) and with acetylene (**1a**), as model cycloaddition reactions that are under the steric influence of the substituent R of 1-alkyne **1**. For each of these reactions we calculated the optimized geometries of the π complexes **A**(MeH)-*anti*, **I**(MeH)-*anti* and **K**(MeH)-*anti*, and of **A**(HH)-*anti*, **G**(HH)-*anti*, and **K**(HH)-*anti*, respectively, which could be involved in the different pathways a–h.

DFT calculations were performed with the ADF 08 program developed by Baerends and co-workers.[58] The PBE gradient-corrected exchange-correlation functional,[59] and the TZP (Triple Zeta plus Polarisation) basis were retained for all the calculations. The frozen core approximation for the inner shells was retained (small core). Relativistic corrections were taken into account with the use of the relativistic scalar zero-order regular approximation (ZORA) method.[60] All the structures were characterized by vibrational analysis in the harmonic approximation. Furthermore, to allow comparison, post-SCF energy calculations were performed at the optimized geometries (using the METAGGA keyword), providing B3LYP and other GGA energies (Figure 4, Table 9). The rather small deviation of the relative energies with respect to popular excange-correlation functionals (less than 0.5 kcal mol^{-1}) underlines the reliability of the calculations within a chemical context.

We found localized minima for all six π complexes, and their optimized structures are shown in Figure 4. Their relative energies and most important structural features are given in Table 9. The axially allene-coordinated complexes **I**(RH)-*anti* and **K**(RH)-*anti* are energetically very close to the **A**(RH)-*anti* π complexes, which were the most stable in

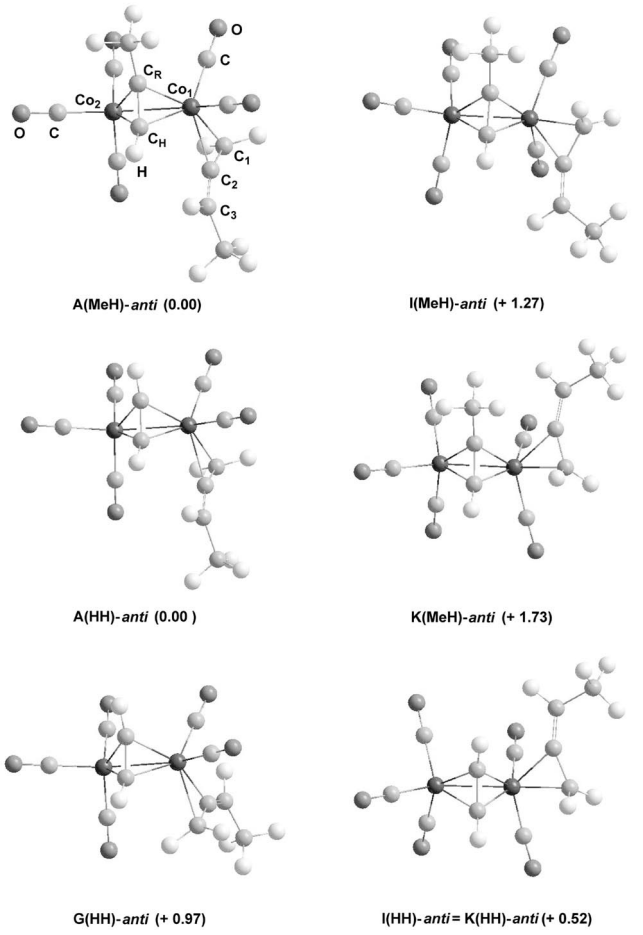

Figure 4. Optimized geometries of the methylallene-coordinated pentacarbonyldicobalt complexes **A**–**K**(RH) at the BPE level. The relative energies given in brackets (kcal mol^{-1}) for both series of π complexes (R = CH_3 or H) are relative to the more stable complexes **A**(MeH)-*anti* and **A**(HH)-*anti*, respectively.

both series (R = Me or H). The different calculated interatomic bonds of the $C_RC_HCo_2$ core of these complexes are very close to those calculated for the parent propyne and acetylene–dicobalt complexes **2** and **2a** (Table 9, entries 5–8).[27c,27f] The interatomic bonds or distances and the angles of the methylallene ligand are given in entries 9–16. For all complexes, the coordinated methylallene was planar and the allenic unit was bent (entry 13: angle C^1–C^2=C^3 = 150–153°). Particularly, the values (67–104°) of the dihedral angles C_H–Co^1–C^2–C^3 for the **I**(RH)-*anti* and **K**(RH)-*anti* π complexes show that the C^1–C^2 bond of the coordinated allene is nearly parallel to the alkyne bond C_R–C_H in these complexes, as anticipated qualitatively (entry 16), whereas it is nearly parallel to the C_H–Co^1 bond for the more classically postulated **A**(RH)-*anti* complexes (dihedral angle C_H–Co^1–C^2–C^3 was 33.5° for R = CH_3, and 34.5° for R = H). Consequently, the **I**(RH)-*anti* and **K**(RH)-*anti* π complexes should also be considered as plausible reaction intermediates in the Pauson–Khand cycloadditions of allenic compounds.

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Table 9. Relative energies and structural features of the **A**–**K**(RH)-*anti* π complexes.

Entry		**A**(MeH)-*anti*	**I**(MeH)-*anti*	**K**(MeH)-*anti*	**A**(HH)-*anti*	**K**(HH)-*anti*[i]	**G**(HH)-*anti*
1	ΔE(PBE)[a,b]	0.0	+1.27	+1.73	0.0	+0.52	+0.97
2	ΔE(PBE0)[a,c]	0.0	+1.40	+1.61	0.0	+0.28	+1.11
3	ΔE(B3LYP)[a,d]	0.0	+1.44	+2.19	0.0	+0.66	+0.95
4	ΔE(M06)[a,e]	0.0	+1.55	+1.91	0.0	+1.24	+0.96
5	Co_1–Co_2[f]	2.516	2.484	2.479	2.519	2.487	2.516
6	C_R–C_H	1.343	1.339	1.341	1.340	1.338	1.341
7	Co_1–C_R	1.984	1.990	2.012	1.966	1.982	1.966
8	Co_1–C_H	1.958	1.981	1.957	1.963	1.966	1.970
9	Co_1–C_1	2.121	2.078	2.083	2.054	2.083	2.123
10	Co_1–C_2	2.054	2.024	2.025	2.118	2.027	2.080
11	C_1–C_2	1.377	1.388	1.387	1.377	1.387	1.374
12	C_2=C_3	1.325	1.326	1.327	1.325	1.326	1.325
13	C_1–C_2=C_3[g]	152.4	150.9	150.4	152.5	151.1	152.8
14	C_H···C_1[h]	–	–	3.089	–	3.129	2.953
15	C_H···C_2[h]	2.869	2.650	–	2.863	–	–
16	C_H–Co_1–C_2–C_3[g]	33.5	67.2	104.7	34.5	97.0	134.3

[a] DFT relative energies are in kcal mol^{-1}. [b] PBE energy: ref.[59] [c] PBE0 energy: ref.[61] [d] B3LYP energy: ref.[62] [e] M06 energy: ref.[63] [f] Bond and distances are in Å. [g] Angles and dihedral angles are in degrees. [h] Interatomic distances between the future bonded atoms C_H and C_1 or C_2. [i] For R = H, complex **K**(HH)-*anti* is identical to complex **I**(HH)-*anti*.

Comparing the relative energies of the different π complexes of both series (R = Me or H) supports our rationalization of the observed selectivities in the PKRs of allenic hydrocarbons. The small relative energy (+0.52 kcal mol^{-1}) of complex **K**(HH)-*anti* compared to complex **A**(HH)-*anti* allows an understanding of how it may also lead to cyclopentenones (*E*)-**4**, as the **A**(HH)-*anti* π complex, and to cyclopentenone (*E*)-**6** (R = R′ = H) (paths e and h, respectively), whereas the higher energy of the **G**(HH)-*anti* π complex (+0.97) seems to exclude this as a plausible intermediate in the formation of cyclopentenone (*E*)-**6**. The energy difference between complex **I**(MeH)-*anti* and **A**(MeH)-*anti* is larger, due to the presence of the alkyne methyl group, which makes a pseudo-axial coordination of an allenic unit less likely. However, it does not seem large enough to exclude **I**(MeH)-*anti* as an intermediate (path e). Within this series of (MeH)-intermediates, complex **K**(MeH)-*anti* has a higher energy (+1.73 kcal mol^{-1}), which may be relevant to the fact that the regioisomeric cyclopentenone **6** is never formed in the PKRs of substituted alkynes.

To sum up, the cyclopentenones (*E*)-**4** can arise from both **A**-*anti* and **I**-*anti* π complexes, and the minor cycloadducts (*Z*)-**4** should form preferentially from the **I**-*syn* π complex, and exclusively from the latter when R′ is an alkyl group. In contrast, when R is a large *tert*-butyl group and R′ is hydrogen, the **A**-*syn* π complex might be involved because the *tert*-butyl group disfavors pseudo-axial coordination of the allenic unit. The regioisomeric cyclopentenones **5** should come from both π complexes **E** and **J**, and only from the **E** π complex when R is *tert*-butyl. Finally, the 5-alkylidenecyclopentenones **6** (R and R′ = H) may only be produced from π complex **K** (identical to **I**-*anti* when R = R′ = H).

Thus, according to the steric hindrance of the R, R′, R^1, and R^2 groups of both partners **1** and **3**, all pathways a–h, except path b (when R′ is an alkyl group), path d and paths e–g [when R is a bulky group (*t*Bu)], might be involved as competitive pathways leading to cyclopentenones **4**–**6**, because both pseudo-equatorial and pseudo-axial coordination of allene **3** to the intermediate pentacarbonyldicobalt complex **I** appear to be plausible.

Conclusions

In summary, this work demonstrates that the PKR of allenic hydrocarbons **3** gives 4-alkylidenecyclopentenones **4** with high regio- and stereoselectivities (*E*/*Z* ≥ 70:30), with the formation of minor amounts of the regioisomeric cyclopentenones **5** and **6**.[64] By studying the relationship between the selectivity changes to these isomeric cyclopentenones **4**–**6** and the substitution patterns of both the acetylenic and the allenic partners, competitive mechanistic pathways could be established from several allene–dicobalt π complexes **A**–**K**, the involvement of which was supported by DFT calculations on the most relevant species of these intermediate π complexes. Thus, as far as we are aware, our experimental results provides evidence for the first time that the Pauson–Khand reaction may involve both a pseudo-equatorial and a pseudo-axial coordination of a double bond to one of the cobalt atoms, leading to two isomeric cyclopentenones. In particular, the formation of 5-alkylidenecyclopentenones **6**, which are only obtained from the acetylene–dicobalt complex **2a**, might be rationalized by an initial pseudo-axial coordination of the allenic unit to cobalt. This methodology constitutes a general approach to the synthesis of 4-alkylidenecyclopentenones **4**, which has been fruitfully used for the preparation of functionalized 4-alkylidenecyclopentenones.[65] Meanwhile, studies on their reactivity and synthetic applications are being developed in our group.[66]

Experimental Section

General: All reactions were carried out under nitrogen in oven-dried glassware using standard syringe, cannula and septa tech-

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niques. Tetrahydrofuran was distilled from deep-purple sodium-benzophenone dianion and stored under nitrogen. Dichloromethane was distilled from calcium hydride and stored under nitrogen. Thin-layer chromatography (TLC) was performed using precoated Kieselgel 60 F_{254} plates (Merck). Detection was achieved by UV irradiation (254 nm) followed by charring with 4% *p*-anisaldehyde, 5% acetic acid and 5% sulfuric acid in 86% ethanol. Flash chromatography was performed with silica gel 60 (40–63 μm, Merck) and refers to the procedure of W. C. Still.[67] UV spectra were recorded with a UV-160A spectrophotometer (Shimadzu). Absorption bands were measured in ethanol; positions of maximum absorption bands (λ_{max}) are reported in nm and intensities of absorption bands are characterized by absorption coefficients (ε) reported in $dm^3 mol^{-1} cm^{-1}$. IR spectra were recorded with a Perkin–Elmer 298 spectrophotometer from thin films on NaCl plates for oils or from KBr disc for solids. ^1H and ^{13}C NMR spectra were recorded at 300 or 200 MHz and 75 or 50 MHz, respectively, with a Bruker DRX 300 or an AC 200 instrument. ^1H NMR chemical shifts were obtained in $CDCl_3$ and are reported in ppm relative to the solvent shift of residual chloroform at δ = 7.26 ppm. Multiplicities are described as: s (singlet), d (doublet), dd, ddd, etc. (doublet of doublets, doublet of doublets of doublets, etc.), t (triplet), q (quartet), m (multiplet), and further qualified as br (broad), app (apparent); coupling constants (*J*) are reported in Hz. ^{13}C NMR chemical shifts were obtained in $CDCl_3$ and are reported in ppm relative to $CHCl_3$ at δ = 77.16 ppm. All the carbons were assigned with the aid of Dept 135 experiments. Low and high-resolution mass spectra were obtained with a Thermoquest Finnigan MAT 95 XL spectrometer in the Electron Impact (EI, ionization potential of 70 eV) mode or the Chemical Ionization (CI, isobutane as the reagent gas) mode. Low-resolution mass spectra were also performed with the ElectroSpray Ionization (ESI) mode. GC/MS was carried out with a Delsi-DI 700 gas chromatograph fitted with a DB5 capillary column (30 m), coupled to a Nermag R10–10S quadrupole mass spectrometer (EI mode at an ionization potential of 70 eV). Microanalyses were carried out by the "Service Central d'analyse du CNRS", Solaize, France. PE refers to petroleum ether (b.p. 40–60 °C).

Starting Materials: Octacarbonyldicobalt was purchased from Strem Chemicals, Inc. as a solid, stabilized with 1–5% hexane, and was used as received and stored under nitrogen at 0 °C. Acetylene (**1a**; dissolved) was purchased from Air Liquide, and alkynes **1b**–**k** were all commercially available. Allene (1,2-propadiene; **3a**) was purchased from Union Carbide. Nona-1,2-diene (**3b**),[68] phenylallene (**3c**),[68] trimethylsilylallene (**3d**),[69] 3-methyl-1,2-butadiene (**3e**),[70] vinylidenecyclohexane (**3f**),[71] trideca-6,7-diene (**3g**),[72] 2-methyldeca-2,3-diene (**3i**),[72] cyclonona-1,2-diene (**3h**),[73] and tetramethylallene (**3i**)[72] were prepared as reported in the literature.

General Procedure for the Preparation of the Alkyne–Hexacarbonyldicobalt Complexes 2a–k: To a solution of $Co_2(CO)_8$ (1 equiv.) in CH_2Cl_2 [2.5 mL per mmol of $Co_2(CO)_8$] at 0 °C, was added alkyne **1a**–**k** (1.2 equiv.), and the mixture was stirred at this temperature for 30 min. In the case of complex **2a**, acetylene gas (after condensation of acetone in a cooled trap) was bubbled through the solution of $Co_2(CO)_8$ for 1 h. The mixture was warmed to r.t. and stirred until all $Co_2(CO)_8$ was consumed (ca. 2–3 h). From an experimental point of view, the reaction was complete when emission of carbon monoxide stopped. The mixture was filtered through a short plug of Celite. Washing with dichloromethane and evaporation of solvent under vacuum with a rotary evaporator (without heating), gave the crude dicobalt complex **2** as a purple viscous precipitate. Yields ranged from 95 to 100%.

General Procedures for the Pauson–Khand Cycloadditions

Procedure A: To a stirred solution of the alkyne–hexacarbonyldicobalt complex **2** (1 mmol) in CH_2Cl_2 (8 mL) at –10 °C, was added a CH_2Cl_2 solution (2 mL) of the allenic compound **3** (1.5 mmol). Solid NMO (6 mmol) was added in fractions over 5 min and the mixture was warmed to r.t. and stirred overnight (ca. 15 h), during which a purple precipitate was formed. The mixture was filtered through a small amount of silica gel (diethyl ether as eluent). The organic layer was concentrated to dryness under reduced pressure and the black crude residue obtained was purified by flash chromatography eluting with PE/Et_2O mixtures to afford the alkylidenecyclopentenones **4**–**6**.

Procedure B: To a stirred solution of the alkyne–hexacarbonyldicobalt complex **2** (1 mmol) in CH_2Cl_2/THF (1:1, 10 mL) at –78 °C, was added a CH_2Cl_2 solution (1 mL) of the allenic hydrocarbon **3** (1.5 mmol). Solid NMO (6 mmol) was then added over 5 min. After 15 min at this temperature, the mixture was warmed to r.t. by removing the cold bath (1 h) and stirring was continued until the starting complex disappeared (1–3 h). The suspension was filtered through a small plug of silica gel (washing of the precipitate with diethyl ether) and concentrated under vacuum. The crude mixture was diluted with diethyl ether (5–10 mL) and stirred overnight in order to facilitate the precipitation of cobalt clusters. After filtration and evaporation of ether, the crude product was purified by flash chromatography (PE/Et_2O mixtures as eluent) to afford the alkylidenecyclopentenones **4**–**6**.

Procedure C: To a stirred solution of the alkyne–hexacarbonyldicobalt complex **2** (1 mmol) in CH_2Cl_2/THF (1:1, 10 mL) at –78 °C, was added a CH_2Cl_2 solution (1 mL) of the allenic hydrocarbon **3** (1.5 mmol). Solid NMO (6 mmol) was then added over 5 min. After stirring 2 h at –78 °C, the reaction mixture was slowly warmed to r.t. over 2 h and then stirred at r.t. for 2 h. Workup and flash chromatography as described in procedure B afforded alkylidenecyclopentenones **4**–**6**.

Procedure D: Performed on 20–40 mmol scale: To a stirred solution of the alkyne–hexacarbonyldicobalt complex **2** (32 mmol) in a mixture of CH_2Cl_2 (85 mL) and THF (145 mL) at –40 °C, was added allene **3** (48 mmol, 1.5 equiv.). A CH_2Cl_2 (60 mL) solution of NMO (192 mmol, 6 equiv.) was added dropwise over 40 min while the inside temperature was kept at –40 °C. After 30 min at this temperature, the mixture was warmed to r.t. by removing the cold bath (about 1 h) and stirring was continued until the starting complex disappeared (2–4 h). The solution was filtered through silica gel (washing of the precipitate with diethyl ether) and concentrated under vacuum. This operation was repeated several times if necessary to eliminate most of the cobalt residue. The crude product was purified by flash chromatography eluting with PE/Et_2O mixtures to give the corresponding alkylidenecyclopentenones **4**–**6**.

Remarks on Procedures A–D: (1) Compositions (% molar ratio) of the crude cyclopentenone mixtures **4**–**5** (and **6** when R = R′ = H) were analyzed by GC (DB5 capillary column). The retention times of **4**–**6** were as follows: t_R (**5**) << t_R [(*Z*)-**4**] < t_R [(*E*)-**4**] < t_R (**6**); (2) TLC: the retention factors R_f of cyclopentenones **4**–**6** were in the decreasing order: R_f (**5**) >> R_f [(*E*)-**4**] > R_f [(*Z*)-**4**] > R_f (**6**), except for the cyclopentenones (*E*)- and (*Z*)-**4** (R = R′ = H) produced in the PKRs with acetylene **1a**, which showed the same polarity. Consequently, the less polar cyclopentenones **5** were always very easily isolated from the cyclopentenones (*E*)- and (*Z*)-**4** by flash chromatography. These last stereoisomers could also be isolated, but sometimes needed a second chromatographic column to be completely separated. In contrast, the (*E*)- and (*Z*)-**4** (R = R′ =

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H) cyclopentenones, which stemmed from the PKRs of acetylene **1a**, could not be separated and were obtained as mixtures.

(*E*)-4-Heptylidene-2,3-dipropylcyclopent-2-enone (4bb): (Table 2, entry 2) Following procedure B, cycloaddition of (oct-4-yne)hexacarbonyldicobalt complex (**2b**; 198 mg, 0.5 mmol) with nona-1,2-diene (**3b**; 93 mg, 0.75 mmol) promoted by NMO (351 mg, 3 mmol) in CH_2Cl_2/THF (1:1, 14 mL) gave, after flash chromatography (PE/Et_2O, 90:10), the cyclopentenones (*E*)-**4bb** (98 mg, 75%) and **5bb** (8 mg, 6%).

(*E*)-4bb: Yellow oil; R_f = 0.35 (PE/Et_2O, 90:10). UV/Vis (EtOH): λ_{max} (ε, L mol^{-1} cm^{-1}) = 289 (13254) nm. IR (neat): $\tilde{\nu}$ = 2960, 2920, 2870, 2850, 1700 (C=O), 1600, 1470, 1380, 1270, 1100, 1080 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.72 [t, ^3J = 7.5 Hz, 1 H, (C-4)=C*H*], 2.87 (s, 2 H, 5-H), 2.47 [t, ^3J = 7.6 Hz, 2 H, (C-3)CH_2], 2.22 [t, ^3J = 7.4 Hz, 2 H, (C-2)CH_2], 2.18 [q, $^3J \approx$ 7.5 Hz, 2 H, (C-4)=CH-CH_2], 1.63–1.40 (m, 6 H, 3× CH_2), 1.35–1.20 (m, 6 H, 3× CH_2), 0.99 (t, ^3J = 7.0 Hz, 3 H, CH_3), 0.95 (t, ^3J = 7.5 Hz, 3 H, CH_3), 0.90 (t, ^3J = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 205.2 (C-1, *C*=O), 167.2 (C-3), 142.6 (C-2), 136.2 (C-4), 125.0 [(C-4)=*C*H], 37.5 (C-5), 31.7, 30.1, 29.3, 29.1 (4× *C*H_2), 28.3 [(C-3)*C*H_2], 25.7 [(C-2)*C*H_2], 22.8, 22.7 and 22.0 (3× *C*H_2CH$_3$), 14.5, 14.3 and 14.1 (3× *C*H_3) ppm. MS (EI): *m*/*z* (%) = 262 (23) [M]$^+$, 233 (22) [M$^+$ – C_2H_5], 178 (100), 149 (55), 121 (20), 107 (19), 91 (24), 79 (16), 55 (33), 43 (58), 41 (74), 29 (45), 27 (21). $C_{18}H_{30}O$ (262.44): calcd. C 82.38, H 11.52; found C 82.53, H 11.47.

5bb: Yellow oil; R_f = 0.48 (PE/Et_2O, 90:10). IR (neat): $\tilde{\nu}$ = 2960, 2920, 2850, 1700 (C=O), 1460, 1380, 885 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.31 [d, ^4J = 1.8 Hz, 1 H, (C-4)=CH_{cis}], 5.13 [d, ^4J = 0.7 Hz, 1 H, (C-4)=CH_{trans}], 2.78 (t, ^3J = 5.5 Hz, 1 H, 5-H), 2.49 [t, ^3J = 7.7 Hz, 2 H, (C-3)CH_2], 2.28–2.19 [m, 2 H, (C-2)CH_2], 1.63–1.20 (m, 14 H, 7× CH_2), 0.99 (t, ^3J = 7.4 Hz, 3 H, CH_3), 0.91 (t, ^3J = 7.4 Hz, 3 H, CH_3), 0.88 (t, ^3J = 6.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 208.1 (C-1, *C*=O), 165.6 (C-3), 148.8 (C-2), 143.6 (C-4, *C*=CH$_2$), 106.5 [(C-4)=*C*H$_2$], 48.0 (C-5), 31.6, 30.3 and 29.5 (3× *C*H_2), 28.0 [(C-3)*C*H_2], 25.7 and 25.0 (2× *C*H_2), 22.6, 22.5 and 21.8 (3× CH$_3$*C*H_2), 14.4, 14.2 and 14.1 (3× *C*H_3) ppm.

2,3-Dimethyl-4-methylenecyclopent-2-enone (4da):[44] (Table 3, entry 1) Following procedure B, a solution of (but-2-yne)hexacarbonyldicobalt complex (**2d**; 2 g, 5.88 mmol) in a 1:1 mixture of CH_2Cl_2 and THF (30 mL) was stirred at –78 °C in an autoclave. At the same time, propa-1,2-diene (**3a**; 0.8 mL, 13.6 mmol) was condensed at –78 °C, then transferred rapidly through a cannula into the autoclave. Solid NMO (4.13 g, 35.28 mmol) was added in one portion and the autoclave closed. The mixture was stirred at –78 °C for 2 h, then warmed to r.t. and stirred overnight. The mixture was filtered through a small plug of silica gel (washing the precipitate with diethyl ether) and the filtrate was concentrated under vacuum. Purification of the crude residue by flash chromatography eluting with a PE/Et_2O, 80:20 mixture afforded cyclopentenone **4da** (423 mg, 59%).

Reaction on a preparative scale (35 mmol): (Table 3, entry 3) Following procedure B as described above, a solution of complex **2d** (11.89 g, 35 mmol) in a 1:4 CH_2Cl_2/THF mixture (100 mL) was stirred at –78 °C in an autoclave closed with a septum. Propa-1,2-diene (**3a**; 4.5 mL, 77.6 mmol) and a solution of NMO (25.4 g, 210 mmol) in CH_2Cl_2 (60 mL) were successively added through a cannula into the autoclave at –78 °C. The autoclave was then closed and the mixture was warmed to r.t. and stirred overnight. After workup as described above, the purification of the crude residue by two successive flash chromatographic columns (PE/Et_2O, 80:20) afforded cyclopentenone **4da** (1.07 g, 25%) and the cyclopentene-1,3-dione **7d** (60 mg, 1.4%).

4da: Brown oil; R_f = 0.28 (PE/Et_2O, 70:30). IR (thin film): $\tilde{\nu}$ = 3060, 2960, 2910, 1700 (C=O), 1640, 1610, 1430, 1390, 1380, 1320, 1290, 1070, 930, 890 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.26 [br. s, 1 H, (C-4)=CH_{cis}], 5.08 [br. s, 1 H, (C-4)=CH_{trans}], 2.91 (s, 2 H, 5-H), 2.03 [s, 3 H, (C-3)CH_3], 1.77 [s, 3 H, (C-2)CH_3] ppm. The ^{1}H NMR spectroscopic data were in full agreement with those reported in the literature.[44] ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.0 (C-1, *C*=O), 162.3 (C-3), 144.6 (C-4), 141.0 (C-2), 107.4 [(C-4)=*C*H$_2$], 39.4 (C-5), 11.6 [(C-3)*C*H$_3$], 8.6 [(C-2)*C*H$_3$] ppm.

4,5-Dimethyl-4-cyclopentene-1,3-dione (7d): Brown oil; R_f = 0.20 (PE/Et_2O, 70:30). IR (thin film): $\tilde{\nu}$ = 2970, 2920, 2870, 1740, 1700 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.84 [s, 2 H, (C-2)CH_2], 2.01 (s, 6 H, 2× CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.9 (2× *C*=O, C-1 and C-4), 156.8 (2× C, C-4 and C-5), 41.2 (C-2), 9.7 (2× *C*H$_3$) ppm. HRMS (CI): calcd. for $C_7H_9O_2$ [M + H]$^+$ 125.06025; found 125.06049.

2,3-Diethyl-4-heptylidenecyclopent-2-enone (4cb): (Table 3, entry 6) Following procedure D, cycloaddition of (hex-3-yne)hexacarbonyldicobalt complex (**2c**; 8.75 g, 23.8 mmol) with nona-1,2-diene (**3b**; 3.73 g, 30.3 mmol) promoted by NMO (16.70 g, 143 mmol) in 1:1 CH_2Cl_2/THF (220 mL) gave, after flash chromatography (PE/Et_2O, 90:10), the cyclopentenones (*E*)-**4cb** (2.6 g, 47%), (*Z*)-**4cb** (88 mg, 2%), and **5cb** (71 mg, 1%).

(*E*)-4cb: Colorless oil; R_f = 0.39 (PE/Et_2O, 70:30). UV/Vis (EtOH): λ_{max} (ε, L mol^{-1} cm^{-1}): 289 (16815) nm. IR (neat): $\tilde{\nu}$ = 2960, 2920, 2880, 2860, 1690 (C=O), 1600, 1460, 1385, 1275, 1255, 1235, 1100, 1065, 1055, 1040, 1005, 940, 925, 720 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.74 [t, ^3J = 7.5 Hz, 1 H, (C-4)=C*H*], 2.87 (s, 2 H, 5-H), 2.51 [q, ^3J = 7.5 Hz, 2 H, (C-3)CH_2], 2.27 [q, ^3J = 7.5 Hz, 2 H, (C-2)CH_2], 2.15 [q, $^3J \approx$ 7.4 Hz, 2 H, (C-4)=CHCH_2], 1.49–1.23 (m, 8 H, 4× CH_2), 1.14 [t, ^3J = 7.5 Hz, 3 H, (C-3)CH$_2$CH_3], 1.03 [t, ^3J = 7.5 Hz, 3 H, (C-2)CH$_2$CH_3], 0.88 (t, ^3J = 6.7 Hz, 3 H, CH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.8 (C-1, *C*=O), 168.2 (C-3), 143.4 (C-2), 135.6 (C-4), 124.7 [(C-4)=*C*H], 37.3 (C-5), 31.7 (CH_2), 30.0 [(C-4)=CH*C*H$_2$], 29.2, 29.0 and 22.5 (3× CH_2), 19.2 [(C-3)*C*H$_2$], 16.6 [(C-2)*C*H$_2$], 14.0, 13.8 and 13.3 (3× CH$_2$*C*H$_3$) ppm. MS (CI): *m*/*z* = 235 [M + H]$^+$. HRMS (CI): calcd. for $C_{16}H_{27}O$ [M + H]$^+$ 235.2062; found 235.2069.

(*Z*)-4cb: Colorless oil; R_f = 0.33 (PE/Et_2O, 70:30). IR (thin film): $\tilde{\nu}$ = 2960, 2920, 2880, 2860, 1690 (C=O), 1600, 1460, 1385, 1275, 1255, 1235, 1100, 1065, 1055, 1040, 1005, 940, 925, 720 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.33 [t, ^3J = 7.8 Hz, 1 H, (C-4)=C*H*], 2.93 (s, 2 H, 5-H), 2.64 [q, ^3J = 7.6 Hz, 2 H, (C-3)CH_2], 2.37 [q, ^3J = 7.4 Hz, 2 H, (C-2)CH_2], 2.26 [m, 2 H, (C-4)=CHCH_2], 1.49–1.23 [m, 8 H, 4× CH_2], 1.15 [t, ^3J = 7.6 Hz, 3 H, (C-3)CH$_2$CH_3], 1.02 [t, ^3J = 7.4 Hz, 3 H, (C-2)CH$_2$CH_3], 0.88 (t, ^3J = 6.7 Hz, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.4 (C-1, *C*=O), 167.7 (C-3), 143.8 (C-2), 133.8 (C-4), 128.4 [(C-4)=*C*H], 42.8 (C-5), 32.1, 30.7, 29.5 and 29.1 (4× *C*H_2), 23.0 [(C-3)*C*H$_2$], 22.3 (*C*H$_2$), 16.7 [(C-2)*C*H$_2$], 14.5, 14.1 and 13.9 (3× CH$_2$*C*H$_3$) ppm.

5cb: Yellow oil; R_f = 0.30 (PE/Et_2O, 90:10). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.32 [br. s, 1 H, (C-4)=CH_{cis}], 5.13 [br. s, 1 H, (C-4)=CH_{trans}], 2.76 [t, ^3J = 5.6 Hz, 1 H, (C-5)*H*], 2.46 [q, ^3J = 7.7 Hz, 2 H, (C-3)CH_2], 2.30 [q, ^3J = 7.6 Hz, 2 H, (C-2)CH_2], 1.67 [m, 2 H, (C-5)CH_2], 1.49–1.23 (m, 8 H, 4× CH_2), 1.15 [t, ^3J = 7.7 Hz, 3 H, (C-3)CH$_2$CH_3], 1.02 [t, ^3J = 7.6 Hz, 3 H, (C-2)CH$_2$CH_3], 0.85 (t, ^3J = 6.7 Hz, 3 H, CH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.4 (C-1, *C*=O), 167.0 (C-3), 148.6 (C-4), 144.8 (C-2), 106.7 [(C-4)=*C*H$_2$], 48.4 (C-5), 32.0, 30.6, 30.0, 25.3 and 23.0 (5× CH_2),

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19.4 [(C-3)CH_2], 17.1 [(C-2)CH_2], 14.4, 14.2 and 13.6 (3× CH_2CH_3) ppm.

4-Heptylidene-2,3-dimethylcyclopent-2-enone (4db): (Table 3, entry 7) Following procedure B, cycloaddition of (but-2-yne)dicobalthexacarbonyl complex (**2d**; 3.91 g, 11.5 mmol) with nona-1,2-diene (**3b**; 2.15 g, 17.25 mmol) promoted by NMO (8.08 g, 69 mmol) in 1:1 CH_2Cl_2/THF (65 mL) gave, after flash chromatography (PE/Et_2O, 90:10), the cyclopentenones (*E*)-**4db** (1.86 g, 78%), (*Z*)-**4db** (77 mg, 3%), and **5db** (232 mg, 10%).

(*E*)-4db: Yellow oil; R_f = 0.31 (PE/Et_2O, 90:10). IR (neat): $\tilde{\nu}$ = 2960, 2920, 2860, 1700 (C=O), 1620, 1470, 1400, 1380, 1270, 1080 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.71 [t, ^3J = 7.3 Hz, 1 H, (C-4)=C*H*], 2.87 (s, 2 H, 5-H), 2.14 [q, $^3J \approx 7.2$ Hz, 2 H, (C-4)=CHCH_2], 2.05 [s, 3 H, (C-3)CH_3], 1.79 [s, 3 H, (C-2)CH_3], 1.42 (m, 2 H, CH_2), 1.15–1.30 (m, 6 H, 3× CH_2), 0.88 (t, ^3J = 6.6 Hz, 3 H, CH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.1 (C-1, *C*=O), 163.3 (C-3), 138.7 and 137.2 (C-2 and/or C-4), 124.8 [(C-4)=*C*H], 37.1 (C-5), 31.7, 29.9, 29.3, 29.0 and 22.6 (5× *C*H_2), 14.0 (*C*H_3), 11.8 [(C-3)*C*H_3], 8.3 [(C-2)*C*H_3] ppm. MS (EI): *m*/*z* (%) = 206 (27) $[M]^+$, 135 (17) $[M^+ - C_5H_{11}]$, 122 (100), 91 (13), 79 (12), 41 (15), 29 (10), 27 (10). HRMS (EI): calcd. for $C_{14}H_{22}O$ $[M]^+$ 206.1671; found 206.1670.

(*Z*)-4db: Yellow oil; R_f = 0.22 (PE/Et_2O, 90:10). IR (thin film): $\tilde{\nu}$ = 2960, 2920, 2860, 1700 (C=O), 1620, 1470, 1400, 1380, 1270, 1080 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 5.52 [t, ^3J = 7.2 Hz, 1 H, (C-4)=C*H*], 2.95 (s, 2 H, 5-H), 2.43 [q, $^3J \approx 7.2$ Hz, 2 H, (C-4)=CHCH_2], 2.27 [s, 3 H, (C-3)CH_3], 1.69 [s, 3 H, (C-2)CH_3], 1.43–1.15 (m, 8 H, 4× CH_2), 0.90 (t, ^3J = 7.0 Hz, 3 H, CH_2CH_3) ppm. MS (EI): *m*/*z* (%) = 206 (15) $[M]^+$, 122 (100), 107 (25), 91 (15), 79 (11), 77 (10), 27 (11).

5db: Yellow oil; R_f = 0.40 (PE/Et_2O, 90:10). IR (neat): $\tilde{\nu}$ = 2960, 2920, 2860, 1700 (C=O), 1620, 1470, 1400, 1380, 1270, 1080 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 5.31 [br. s, 1 H, (C-4)=CH_{cis}], 5.12 [br. s, 1 H, (C-4)=CH_{trans}], 2.81 (t, ^3J = 5.5 Hz, 1 H, 5-H), 2.08 [s, 3 H, (C-3)CH_3], 1.82 [s, 3 H, (C-2)CH_3], 1.82–1.24 (m, 10 H, 5× CH_2), 0.87 (t, ^3J = 7.0 Hz, 3 H, CH_2CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 208.0 (C-1, *C*=O), 161.7 (C-3), 149.6 (C-2), 139.6 (C-4), 106.3 [(C-4)=*C*H_2], 47.8 (C-5), 30.1, 29.7, 29.6, 25.2 and 22.6 (5× *C*H_2), 14.1 (*C*H_3), 11.6 [(C-3)*C*H_3], 8.5 [(C-2)*C*H_3] ppm. MS (EI): *m*/*z* (%) = 206 (20) $[M]^+$, 122 (100), 107 (13), 91 (13), 41 (11).

(*E*)-4-Benzylidene-2,3-dipropylcyclopent-2-enone (4bc): (Table 3, entry 9) Following procedure B, cycloaddition of (oct-4-yne)hexacarbonyldicobalt complex (**2b**; 777 mg, 2 mmol) with phenylallene (**3c**; 343 mg, 2.95 mmol) promoted by NMO (1.380 g, 11.82 mmol) gave, after flash chromatography (PE/Et_2O, 80:20), cyclopentenone (*E*)-**4bc** (349 mg, 70%).

(*E*)-4bc: Yellow solid; m.p. 44 °C; R_f = 0.33 (PE/Et_2O, 80:20). UV/Vis (EtOH): λ_{max} (ε, L mol^{-1} cm^{-1}) = 294 (18324) nm. IR (thin film): $\tilde{\nu}$ = 3060, 3020, 2960, 2930, 2870, 1690 (C=O), 1600, 1490, 1465, 1450, 1380, 1360, 1260, 910, 755, 730, 690 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.22 (m, 5 H, 5× ArH), 6.64 [s, 1 H, (C-4)=C*H*-Ph], 3.24 (s, 2 H, 5-H), 2.61 [t, ^3J = 7.8 Hz, 2 H, (C-3)CH_2], 2.30 [t, ^3J = 7.7 Hz, 2 H, (C-2)CH_2], 1.64 (sextet, $^3J \approx 7.7$ Hz, 2 H, $CH_3CH_2CH_2$), 1.49 (sextet, $^3J \approx 7.5$ Hz, 2 H, $CH_3CH_2CH_2$), 1.06 (t, ^3J = 7.3 Hz, 3 H, CH_3), 0.95 (t, ^3J = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.4 (C-1, *C*=O), 168.6 (C-3), 143.3 (C-2), 137.2 and 137.0 [2× C_{quart}, C-4 and/or *C*(Ph)$_i$], 129.4 and 129.1 [2× *C*H(Ph)$_m$ and 2× *C*H(Ph)$_o$], 128.0 [*C*H(Ph)$_p$], 123.3 [(C-4)=*C*H], 39.8 (C-5), 28.6 [(C-3)CH_2], 26.2 [(C-2)CH_2], 23.1 and 22.4 (2× $CH_3CH_2CH_2$), 14.9 and 14.7 (2× *C*H_3) ppm. MS (EI): *m*/*z* (%) = 254 (100) $[M]^+$, 239 (24) $[M^+ - CH_3]$, 225 (64) $[M^+ - C_2H_5]$, 211 (22) $[M^+ - C_3H_7]$, 135 (35), 91 (50), 77 (15), 41 (18).

(*E*)-2,3-Dipropyl-4-[(trimethylsilyl)methylene]cyclopent-2-enone (4bd): (Table 3, entry 12) Following procedure B, cycloaddition of (oct-4-yne)dicobalthexacarbonyl complex (**2b**; 770 mg, 1.94 mmol) with trimethylsilylallene (**3d**; 327 mg, 2.91 mmol) promoted by NMO (1.36 g, 11.64 mmol) gave, after flash chromatography (PE/Et_2O, 92:8), the cyclopentenone (*E*)-**4bd** (290 mg, 61%).

(*E*)-4bd: Colorless oil; R_f = 0.38 (PE/Et_2O, 90:10). UV (EtOH): λ_{max} (ε, L mol^{-1} cm^{-1}) = 204 (34776), 284 (25752) nm. IR (thin film): $\tilde{\nu}$ = 2960, 2920, 2870, 1700 (C=O), 1600, 1460, 1370, 1310, 1250, 1190, 1100, 860, 840, 690 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.87 [t, ^4J = 1.4 Hz, 1 H, (C-4)=C*H*-$SiMe_3$], 2.94 (d, ^3J = 1.4 Hz, 2 H, 5-H), 2.47 [t, ^3J = 7.6 Hz, 2 H, (C-3)CH_2], 2.24 [t, ^3J = 7.4 Hz, 2 H, (C-2)CH_2], 1.24–1.60 (m, 4 H, 2× $CH_3CH_2CH_2$), 1.01 (t, ^3J = 7.3 Hz, 3 H, CH_3), 0.92 (t, ^3J = 7.3 Hz, 3 H, CH_3), 0.17 [s, 9 H, Si(CH_3)$_3$] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.6 (C-1, *C*=O), 167.1 (C-3), 150.4 (C-2), 149.3 (C-4), 123.1 [(C-4)=*C*H], 39.9 (C-5), 27.7 [(C-3)*C*H_2], 25.9 [(C-2)*C*H_2], 22.6 and 21.8 (2× $CH_3CH_2CH_2$), 14.5 and 14.3 (2× *C*H_3), –0.4 [3× *C*, Si(*C*H_3)$_3$] ppm. MS (EI): *m*/*z* (%) = 250 (100) $[M]^+$, 235 (29) $[M^+ - CH_3]$, 221 (58) $[M^+ - C_2H_5]$, 75 (28), 73 (100), 59 (26), 45 (19). $C_{15}H_{26}OSi$ (250.46): calcd. C 71.93, H 10.46; found C 71.27, H 10.78. HRMS (EI): calcd. for $C_{15}H_{26}OSi$ $[M]^+$ 250.1753; found 250.1751.

4-Isopropylidene-2,3-dipropylcyclopent-2-enone (4be): (Table 4, entry 1) Following procedure A, cycloaddition of (oct-4-yne)hexacarbonyldicobalt complex (**2b**; 396 mg, 1 mmol) with 1,1-dimethylallene (**3e**; 136 mg, 2 mmol) promoted by NMO (702 mg, 6 mmol) gave, after flash chromatography (PE/Et_2O, 90:10), the cyclopentenones **4be** (127 mg, 62%) and **5be** (10 mg, 5%).

4be: Colorless oil; R_f = 0.23 (PE/Et_2O, 85:15). IR (thin film): $\tilde{\nu}$ = 2960, 2920, 2870, 1690 (C=O), 1640, 1570, 1460, 1370, 1280, 1230, 1180, 1120, 1090, 1000 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.91 (s, 2 H, 5-H), 2.62 [t, ^3J = 8.1 Hz, 2 H, (C-3)CH_2], 2.21 [t, ^3J = 7.7 Hz, 2 H, (C-2)CH_2], 2.02 [s, 3 H, C=C(CH_3)$_{syn}$], 1.84 [s, 3 H, C=C(CH_3)$_{anti}$], 1.71–1.33 (m, 4 H, 2× $CH_3CH_2CH_2$), 1.02 (t, ^3J = 7.4 Hz, 3 H, CH_3), 0.92 (t, ^3J = 7.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 205.1 (C-1, *C*=O), 167.6 (C-3), 144.0 (C-2), 130.2 and 130.0 [C-4 and C=*C*$(CH_3)_2$], 41.4 (C-5), 31.3 [(C-3)*C*H_2], 25.6 [(C-2)*C*H_2], 25.4 [C=C(*C*H_3)$_{cis}$], 22.8 and 22.4 (2× $CH_3CH_2CH_2$), 21.1 [C=C(*C*H_3)$_{trans}$], 14.5 and 14.4 (2× *C*H_3) ppm. MS (EI): *m*/*z* (%) = 206 (53) $[M^+]$, 191 (100) $[M^+ - CH_3]$, 177 (13) $[M^+ - C_2H_5]$, 163 (34) $[M^+ - C_3H_7]$, 135 (15), 107 (17), 91 (28), 77 (18), 55 (13), 41 (26).

5be: Colorless oil; R_f = 0.52 (PE/Et_2O, 85:15). ^1H NMR (200 MHz, $CDCl_3$): δ = 5.26 [s, 1 H, (C-4)=CH_{cis}], 5.09 [s, 1 H, (C-4)=CH_{trans}], 2.49 [m, 2 H, (C-3)CH_2], 2.15–2.35 [m, 2 H, (C-2)CH_2], 1.25–1.70 (m, 8 H, 4× CH_2), 1.12 [s, 6 H, C(CH_3)$_2$], 0.91 (t, ^3J = 7.3 Hz, 3 H, CH_3), 0.88 (t, ^3J = 7.0 Hz, 3 H, CH_3) ppm. GC–MS (EI): *m*/*z* (%) = 206 (53) $[M]^+$, 191 (100) $[M^+ - CH_3]$, 177 (12) $[M^+ - C_2H_5]$, 163 (34) $[M^+ - C_3H_7]$, 149 (15), 135 (20), 107 (14), 91 (24), 77 (19), 55 (19), 41 (35).

2,3-Diethyl-4-isopropylidenecyclopent-2-enone (4ce): (Table 4, entry 2) Following procedure D, cycloaddition of (hex-3-yne)hexacarbonyldicobalt complex (**2c**; 12.28 g, 33.3 mmol) with 1,1-dimethylallene (**3e**; 3.4 g, 50 mmol) promoted by NMO (24.15 g, 200 mmol) in CH_2Cl_2/THF (1:1, 320 mL) gave, after two flash chromatographic columns (PE/Et_2O, 80:20), the cyclopentenones **4ce** (2.96 g, 50%) and the cyclopentene-1,3-dione **7c** (166 mg, 3%).

4ce: Yellow oil; R_f = 0.27 (PE/Et_2O, 70:30). IR (thin film): $\tilde{\nu}$ = 2980, 2940, 2880, 1695 (C=O), 1640, 1590, 1465, 1385, 1290, 1270,

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1190, 1090, 1120, 1055, 1010, 940, 830, 785 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.88 (s, 2 H, 5-H), 2.66 [t, ^3J = 7.5 Hz, 2 H, (C-3)CH_2], 2.23 [q, ^3J = 7.5 Hz, 2 H, (C-2)CH_2], 2.03 [s, 3 H, C=C(CH_3)$_{syn}$], 1.81 [s, 3 H, C=C(CH_3)$_{anti}$], 1.14 (t, ^3J = 7.5 Hz, 3 H, CH_3), 0.99 (t, ^3J = 7.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 205.2 (C-1, *C*=O), 168.9 (C-3), 145.2 (C-2), 130.5 and 129.9 [C-4 and C=*C*(CH_3)$_2$], 41.6 (C-5), 22.4 [(C-3)*C*H_2], 16.7 [(C-2)*C*H_2], 25.1 [C=C(*C*H_3)$_{cis}$], 21.3 [C=C(*C*H_3)$_{trans}$], 14.1 and 14.0 (2× *C*H_3) ppm. HRMS (CI): calcd. for $C_{12}H_{19}O$ $[M + H]^+$ 179.14359; found 179.14362.

4,5-Diethyl-4-cyclopentene-1,3-dione (7c): Brown oil; R_f = 0.30 (PE/Et_2O, 70:30). IR (thin film): $\tilde{\nu}$ = 2970, 2920, 2870, 1740 (C=O), 1700, 1630, 1455, 1375, 1350, 12380, 1240, 1120, 1055, 925, 755, 700, 660, 650 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.83 [s, 2 H, (C-2)CH_2], 2.47 (q, ^3J = 7.5 Hz, 4 H, 2× CH_2CH$_3$), 1.13 (t, ^3J = 7.5 Hz, 6 H, 2× CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.1 (2× *C*=O, C-1 and C-3), 161.1 (2× C, C-4 and C-5), 41.6 (C-2), 17.7 (2× *C*H_2CH$_3$), 13.1 (2× *C*H_3) ppm. HRMS (IC): calcd. for $C_9H_{13}O_2$ $[M + H]^+$ 153.0916; found 153.0921.

4-Cyclohexylidene-2,3-dipropylcyclopent-2-enone (4bf): (Table 4, entry 4) Following procedure B, cycloaddition of (oct-4-yne)dicobalthexacarbonyl complex (**2b**; 396 mg, 1 mmol) with vinylidenecyclohexane (**3f**; 162 mg, 1.5 mmol) promoted by NMO (702 mg, 6 mmol) gave, after flash chromatography (PE/Et_2O, 80:20), the cyclopentenone **4bf** as a yellow oil (185 mg, 75%): R_f = 0.15 (PE/Et_2O, 85:15). IR (thin film): $\tilde{\nu}$ = 2960, 2920, 2870, 1690 (C=O), 1640, 1570, 1460, 1370, 1280, 1230, 1180, 1120, 1090, 1000 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.92 (s, 2 H, 5-H), 2.61 [t, ^3J = 7.7 Hz, 2 H, (C-3)CH_2], 2.48 [m, 2 H, (C-4)=C(CH_2)$_{cis}$], 2.26–2.18 [m, 4 H, (C-4)=C(CH_2)$_{trans}$ and (C-2)CH_2], 1.62 (m, 6 H, 3× CH_2), 1.54 (sextet, ^3J = 7.3 Hz, 2 H, CH_3CH_2CH$_2$), 1.46 (sextet, ^3J = 7.3 Hz, 2 H, CH_3CH_2CH$_2$), 1.00 [t, ^3J = 7.3 Hz, 3 H, (C-3)CH_2CH_3], 0.92 [t, ^3J = 7.3 Hz, 3 H, (C-2)CH_2CH_3] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 204.9 (C-1, *C*=O), 167.3 (C-3), 144.8 (C-2), 139.1 [(C-4)=*C*(CH_2)$_5$], 126.4 [C-4, *C*=C(CH_2)$_5$], 40.7 (C-5), 34.9, 31.7, 31.0, 28.5, 28.1, 26.5 and 25.4 (7× *C*H_2), 22.4 and 22.2 (2× CH_3*C*H_2CH$_2$), 14.3 (2× *C*H_3) ppm.

(*E*)-4-Hexylidene-5-pentyl-2,3-dipropylcyclopent-2-enone (4bg): (Table 4, entry 6) Following procedure B, cycloaddition of (oct-4-yne)hexacarbonyldicobalt complex (**2b**; 88 mg, 0.22 mmol) with trideca-6,7-diene (**3g**; 60 mg, 0.32 mmol) promoted by NMO (154 mg, 1.32 mmol) in CH_2Cl_2/THF (1:1, 6 mL) gave, after flash chromatography (PE/Et_2O, 95:5), the cyclopentenone (*E*)-**4bg** as a yellow oil (57 mg, 81%): R_f = 0.43 (PE/Et_2O, 95:5). IR (neat): $\tilde{\nu}$ = 2960, 2920, 2870, 1700 (C=O), 1610, 1470, 1380, 1260, 730 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.67 [t, ^3J = 7.5 Hz, 1 H, (C-4)=C*H*], 2.87 (app t, $^3J \approx$ 5.1 Hz, 1 H, 5-H), 2.45 [t, ^3J = 7.6 Hz, 2 H, (C-3)CH_2], 2.21 [t, ^3J = 7.6 Hz, 2 H, (C-2)CH_2], 2.15 [q, $^3J \approx$ 7.5 Hz, 2 H, (C-4)=CHCH_2], 1.74–1.17 (m, 18 H, 9× CH_2), 0.97 (t, ^3J = 7.3 Hz, 3 H, CH_3), 0.90 (t, ^3J = 7.3 Hz, 6 H, 2× CH_3 of pentyl groups), 0.81 (t, ^3J = 7.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 208.2 (C-1, *C*=O), 166.9 (C-3), 141.3 (C-2), 140.1 (C-4), 124.6 [(C-4)=*C*H], 46.3 (C-5), 31.8, 31.5, 30.2, 29.6 and 29.1 (5× *C*H_2), 27.8 [(C-3)*C*H_2], 25.4 (*C*H_2), 23.7 [(C-2)*C*H_2], 22.4, 22.3, 22.2 and 21.7 (4× *C*H_2CH$_3$), 14.2, 14.1, 13.8 and 13.8 (4× *C*H_3) ppm. MS (EI): *m*/*z* (%) = 318 (9) $[M]^+$, 248 (68), 247 (38), 192 (100), 91 (13), 43 (33), 41 (35), 29 (19).

2,3-Dipropyl-6,7,8,9,10,10a-hexahydro-1(5*H*)-cyclopentacyclononenone (4bh): (Table 4, entry 7) Following procedure A, cycloaddition of the (oct-4-yne)hexacarbonyldicobalt complex (**2b**; 396 mg, 1 mmol) with cyclonona-1,2-diene (**3h**; 183 mg, 1.5 mmol) promoted by NMO (702 mg, 6 mmol) gave, after flash chromatography (PE/Et_2O, 80:20), the cyclopentenone **4bh** as a yellow oil (172 mg, 66%): R_f = 0.28 (PE/Et_2O, 85:15). IR (thin film): $\tilde{\nu}$ = 2970, 2920, 2850, 1695 (C=O), 1590, 1455, 1375, 930, 720 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 5.74 (dd, ^3J = 11.3, ^3J = 6.4 Hz, 1 H, 4-H), 2.72 (br. dd, ^3J = 8.7, ^3J = 2.5 Hz, 1 H, 10a-H), 2.51 [t, ^3J = 7.8 Hz, 2 H, (C-3)CH_2], 2.30–2.50 [m, 1 H + 2 H, 5-H and (C-3a)=CHCH_2], 2.23 [t, ^3J = 7.7 Hz, 2 H, (C-2)CH_2], 1.70 (m, 1 H, 5′-H), 1.20–1.60 (m, 12 H, 6× CH_2), 1.00 (t, ^3J = 7.4 Hz, 3 H, CH_3), 0.91 (t, ^3J = 7.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 208.3 (C-1, *C*=O), 166.9 (C-3), 142.8 (C-2), 140.3 (C-3a), 124.3 [C-4, (C-3a)=*C*H], 49.3 (C-10a), 29.5, 29.3, 29.2, 28.1, 27.8, 26.7, 26.5, 22.6, 22.1 and 21.8 (10× *C*H_2), 14.3 and 14.1 (2× *C*H_3) ppm. MS (EI): *m*/*z* (%) = 260 (56) $[M]^+$, 245 (20) $[M^+ - CH_3]$, 231 (29) $[M^+ - C_2H_5]$, 178 (20), 133 (19), 107 (21), 105 (46), 93 (32), 91 (100), 79 (56), 77 (47), 55 (41), 43 (32), 41 (72), 29 (20). $C_{18}H_{28}O$ (260.44): calcd. C 83.02, H 10.84; found C 82.74, H 10.99.

5-Hexyl-4-isopropylidene-2,3-dipropylcyclopent-2-enone (4bi) and (*E*)-4-Heptylidene-5,5-dimethyl-2,3-dipropylcyclopent-2-enone (5bi): (Table 4, entry 8) Following procedure B, cycloaddition of the (oct-4-yne)hexacarbonyldicobalt complex (**2b**; 748 mg, 1.88 mmol) with 2-methyldeca-2,3-diene (**3i**; 431 mg, 2.83 mmol) promoted by NMO (1.32 g, 11.3 mmol) in CH_2Cl_2 (10 mL) gave, after flash chromatography (PE/Et_2O, 95:5), a mixture of the cyclopentenones **4bi** and (*E*)-**5bi** (226 mg, 41%, **4bi/5bi** 60:40). These could be separated by a further chromatographic column.

4bi: Yellow oil; R_f = 0.18 (PE/Et_2O, 95:5). IR (thin film): $\tilde{\nu}$ = 2960, 2920, 2870, 1690 (C=O), 1590, 1470, 1380, 1190, 1090 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.80 (dd, ^3J = 7.1, ^3J = 3.7 Hz, 1 H, 5-H), 2.54 [t, ^3J = 7.7 Hz, 2 H, (C-3)CH_2], 2.14 [t, ^3J = 7.4 Hz, 2 H, (C-2)CH_2], 1.94 [s, 3 H, (C-4)=C(CH_3)$_{cis}$], 1.80 [s, 3 H, (C-4)=C(CH_3)$_{trans}$], 1.54–1.13 (m, 14 H, 7× CH_2), 0.88 (t, ^3J = 7.4 Hz, 3 H, CH_3), 0.84 (t, ^3J = 7.5 Hz, 3 H, CH_3), 0.81 (t, ^3J = 7.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 208.6 (C-1, *C*=O), 167.1 (C-3), 142.4 (C-2), 134.8 (C-4), 128.8 [(C-4)=*C*(CH_3)$_2$], 49.5 (C-5), 31.5, 31.4, 31.2, 29.4 and 25.2 (5× *C*H_2), 24.8 [C=C-(*C*H_3)$_{cis}$], 24.3 (*C*H_2), 22.5, 22.4 and 22.0 (3× CH_3*C*H_2), 21.1 [C=C(*C*H_3)$_{trans}$], 14.2, 14.1 and 13.9 (3× *C*H_3) ppm.

(*E*)-5bi: Yellow oil; R_f = 0.32 (PE/Et_2O, 95:5). IR (thin film): $\tilde{\nu}$ = 2960, 2920, 2870, 1690 (C=O), 1590, 1470, 1380, 1290, 1190 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.55 [t, ^3J = 7.6 Hz, 1 H, (C-4)=C*H*], 2.38 [t, ^3J = 7.6 Hz, 2 H, (C-3)CH_2], 2.25 [t, ^3J = 7.5 Hz, 2 H, (C-2)CH_2], 2.16 [q, $^3J \approx$ 7.6 Hz, 2 H, (C-4)=CHCH_2], 1.54–1.13 (m, 12 H, 6× CH_2), 1.11 [s, 6 H, 2× (CH_3)$_{gem}$], 0.90 (t, ^3J = 7.2 Hz, 3 H, CH_2CH_3), 0.82 (t, ^3J = 7.2 Hz, 6 H, 2× CH_3CH$_2$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 211.2 (C-1, *C*=O), 165.4 (C-3), 145.6 (C-2), 137.7 (C-4), 125.4 [(C-4)=*C*H], 44.7 (C-5), 31.6, 29.7, 29.0 and 28.5 (4× *C*H_2), 27.7 [(C-3)*C*H_2], 25.5 [(C-2)*C*H_2], 22.7 [2× (*C*H_3)$_{gem}$], 22.6, 22.4 and 21.7 (3× CH_3*C*H_2), 14.2, 14.0 and 13.8 (3× *C*H_3) ppm.

(*E*)-4-Heptylidene-3-methyl-2-propylcyclopent-2-enone (4ib): (Table 5, entry 1) Following the procedure B, cycloaddition of the (hex-2-yne)hexacarbonyldicobalt complex (**2i**; 392 mg, 1.05 mmol) with nona-1,2-diene (**3b**; 195 mg, 1.57 mmol) promoted by NMO (738 mg, 6.30 mmol) in CH_2Cl_2/THF (1:1, 8 mL) gave, after flash chromatography (PE/Et_2O, 90:10), the cyclopentenones (*E*)-**4ib** (141 mg, 57%), (*E*)-**4′ib** (35 mg, 14%) and **5ib** (30 mg, 12%).

(*E*)-4ib: Yellow oil; R_f = 0.26 (PE/Et_2O, 90:10). IR (thin film): $\tilde{\nu}$ = 2960, 2920, 2860, 1700 (C=O), 1610, 1470, 1390, 1090, 920, 730 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.69 [t, ^3J = 7.3 Hz, 1 H, (C-4)=C*H*], 2.84 (s, 2 H, 5-H), 2.19 [t, ^3J = 7.7 Hz, 2 H, (C-2)CH_2], 2.11 [q, $^3J \approx$ 7.3 Hz, 2 H, (C-4)=CHCH_2], 2.03 [s, 3 H, (C-3)CH_3], 1.40 [sextet, ^3J = 7.7 Hz, 2 H, (C-2)CH_2CH_2CH$_3$], 1.25 (m, 10 H,

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5× CH_2), 0.85 (t, ^3J = 7.7 Hz, 2×3 H, 2× CH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.8 (C-1, *C*=O), 163.3 (C-3), 142.9 (C-2), 137.2 (C-4), 125.0 [(C-4)=*C*H], 37.2 (C-5), 31.7, 30.0, 29.2, and 29.0 (4× CH_2), 25.3 [(C-2)CH_2], 22.6 and 21.7 (2× CH_2CH_3), 14.1 and 14.0 (2× CH_2CH_3), 11.8 [(C-3)CH_3] ppm. MS (EI): *m*/*z* (%) = 234 (24) $[M]^+$, 205 (19) $[M^+ - C_2H_5]$, 150 (100), 121 (18), 91 (27), 77 (21), 41 (34), 29 (18). HRMS (CI): calcd. for $C_{16}H_{26}O$ $[M + H]^+$ 235.2062; found 235.2058.

(*E*)-4′ib: Yellow oil; R_f = 0.18 (PE/Et_2O, 90:10). IR (thin film): $\tilde{\nu}$ = 2960, 2920, 2860, 1700 (C=O), 1610, 1470, 1390, 1090, 920, 730 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.49 [t, ^3J = 7.3 Hz, 1 H, (C-4)=C*H*], 2.89 (s, 2 H, 5-H), 2.44 [t, ^3J = 7.7 Hz, 2 H, (C-3)CH_2], 2.11 [q, $^3J \approx 7.3$, Hz, 2 H, (C-4)=CHCH_2], 1.76 [s, 3 H, (C-2)CH_3], 1.48 [sextet, ^3J = 7.7 Hz, 2 H, (C-3)$CH_2CH_2CH_3$], 1.23 (m, 10 H, 5× CH_2), 0.87 (t, ^3J = 7.7 Hz, 2×3 H, 2× CH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.4 (C-1, *C*=O), 167.5 (C-3), 138.6 (C-2), 136.2 (C-4), 124.9 [(C-4)=*C*H], 37.3 (C-5), 31.8, 30.1, 29.4, and 29.1 (4× CH_2), 28.3 [(C-3)CH_2], 22.7 and 22.2 (2× CH_2CH_3), 14.4 and 14.2 (2× CH_2CH_3), 8.5 [(C-2)CH_3] ppm. MS (EI): *m*/*z* (%) = 234 (13) $[M]^+$, 205 (21) $[M^+ - C_2H_5]$, 150 (100), 135 (21), 121 (44), 107 (43), 105 (25), 91 (80), 79 (39), 77 (48), 43 (50), 41 (89), 29 (82), 27 (40).

5ib: Yellow oil; R_f = 0.36 (PE/Et_2O, 90:10). IR (thin film): $\tilde{\nu}$ = 2960, 2920, 2860, 1700 (C=O), 1640, 1610, 1470, 1380, 890, 730 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.31 [br. s, 1 H, (C-4)=CH_{cis}], 5.12 [br. s, 1 H, (C-4)=CH_{trans}], 2.80 (t, ^3J = 5.5 Hz, 1 H, 5-H), 2.24 [t, ^3J = 7.3 Hz, 2 H, (C-2)CH_2], 2.08 [s, 3 H, (C-3)CH_3], 1.24 (m, 12 H, 6× CH_2), 0.87 (t, ^3J = 7.3 Hz, 2×3 H, 2× CH_2CH_3) ppm. MS (EI): *m*/*z* (%) = 205 (5) $[M^+ - C_2H_5]$, 150 (100), 135 (10), 121 (17), 107 (20), 105 (15), 91 (93), 79 (18), 77 (61), 43 (46), 41 (96), 29 (81), 27 (39).

(*E*)-4-Heptylidene-3-methyl-2-phenylcyclopent-2-enone (4jb): (Table 5, entry 2) Following procedure B, cycloaddition of the (1-phenylpropyne)hexacarbonyldicobalt complex (**2j**; 740 mg, 1.85 mmol) with nona-1,2-diene (**3b**; 343 mg, 2.77 mmol) promoted by NMO (1.293 g, 11.04 mmol) in CH_2Cl_2/THF (1:1, 12 mL) gave, after flash chromatography (PE/Et_2O, 90:10), the cyclopentenones (*E*)-**4jb** (322 mg, 65%), (*Z*)-**4jb** (29 mg, 6%) and **5jb** (70 mg, 14%).

(*E*)-4jb: Yellow oil; R_f = 0.33 (PE/Et_2O, 90:10). IR (thin film): $\tilde{\nu}$ = 3030, 3010, 2960, 2920, 2850, 1700 (C=O), 1590, 1490, 1440, 1390, 1280, 1170, 940, 910, 760, 730, 700 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.33 (m, 5 H, 5× ArH), 5.93 [t, ^3J = 7.4 Hz, 1 H, (C-4)=C*H*], 3.08 (s, 2 H, 5-H), 2.22 [m, 2 H, (C-4)=CHCH_2], 2.21 [s, 3 H, (C-3)CH_3], 1.50 (m, 2 H, CH_2), 1.20–1.40 (m, 6 H, 3× CH_2), 0.92 (t, ^3J = 7.0 Hz, 3 H, CH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.7 (C-1, *C*=O), 163.6 (C-3), 141.3 (C-2), 136.9 (C-4), 131.7 [*C*(Ph)$_i$], 129.3 [2× *C*H(Ph)$_o$], 128.2 [2× *C*H-(Ph)$_m$], 127.6 [*C*H(Ph)$_p$], 127.2 [(C-4)=*C*H], 37.7 (C-5), 31.6, 30.1, 29.1 and 29.0 (4× CH_2), 22.5 (CH_2CH_3), 14.0 (CH_2CH_3), 12.7 [(C-3)CH_3] ppm. MS (EI): *m*/*z* (%) = 268 (66) $[M]^+$, 197 (19) $[M^+ - C_5H_{11}]$, 184 (100), 183 (14) $[M^+ - C_6H_{13}]$, 154 (12), 141 (14).

(*Z*)-4jb: Yellow oil; R_f = 0.22 (PE/Et_2O, 90:10). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.30 (m, 5 H, 5× ArH), 5.71 [t, ^3J = 7.3 Hz, 1 H, (C-4)=C*H*], 3.14 (s, 2 H, 5-H), 2.50 [m, 2 H, (C-4)=CHCH_2], 2.39 [s, 3 H, (C-3)CH_3], 1.20–1.60 (m, 8 H, 4× CH_2), 0.89 (t, ^3J = 7.0 Hz, 3 H, CH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 203.5 (C-1, *C*=O), 163.2 (C-3), 143.9 (C-2), 134.8 (C-4), 132.0 [*C*(Ph)$_i$], 129.3 [2× *C*H(Ph)$_o$], 128.8 [2× *C*H(Ph)$_m$], 128.0 [*C*H(Ph)$_p$], 127.9 [(C-4)=*C*H], 42.6 (C-5), 30.7, 29.1, 29.0 and 26.6 (4× CH_2), 22.5 (CH_2CH_3), 14.0 (CH_2CH_3), 17.9 [(C-3)CH_3] ppm. MS (EI): *m*/*z* (%) = 268 (84) $[M]^+$, 197 (19) $[M^+ - C_5H_{11}]$, 184 (100), 183 (14) $[M^+ - C_6H_{13}]$, 154 (12), 153 (16), 141 (16).

5jb: Yellow oil; R_f = 0.45 (PE/Et_2O, 90:10). IR (thin film): $\tilde{\nu}$ = 3030, 2950, 2920, 2850, 1700 (C=O), 1445, 1390, 1270, 1180, 910, 89, 740, 700 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.36 (m, 5 H, 5× ArH), 5.50 [d, ^4J = 1.5 Hz, 1 H, (C-4)=CH_{cis}], 5.32 [br. s, 1 H, (C-4)=CH_{trans}], 3.00 (t, ^3J = 5.5 Hz, 1 H, 5-H), 2.25 [s, 3 H, (C-3)CH_3], 1.28 (m, 10 H, 5× CH_2), 0.88 (t, ^3J = 6.6 Hz, 3 H, CH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.8 (C-1, *C*=O), 161.9 (C-3), 149.5 (C-4), 141.8 (C-2), 131.5 [*C*(Ph)$_i$], 129.4 [2× *C*H(Ph)$_o$], 128.1 [2× *C*H(Ph)$_m$], 128.0 [*C*H(Ph)$_p$], 108.4 [(C-4)=*C*H_2], 48.3 (C-5), 31.6, 30.4, 29.5 and 25.2 (4× CH_2), 22.6 (CH_2CH_3), 14.0 (CH_2CH_3), 12.5 [(C-3)CH_3] ppm. MS (EI): *m*/*z* (%) = 268 (50) $[M]^+$, 197 (15) $[M^+ - C_5H_{11}]$, 185 (16), 184 (100), 183 (11) $[M^+ - C_6H_{13}]$, 153 (10), 141 (11).

(*E*)-2-*tert*-Butyl-4-heptylidene-3-methylcyclopent-2-enone (4kb): (Table 5, entry 3) Following procedure B, cycloaddition of the (4,4-dimethylpent-2-yne)hexacarbonyldicobalt complex (**2k**; 680 mg, 1.78 mmol) with nona-1,2-diene (**3b**; 332 mg, 2.67 mmol) promoted by NMO (1.251 g, 10.68 mmol) in CH_2Cl_2/THF (1:1, 10 mL) gave, after flash chromatography (PE/Et_2O, 97:3), the cyclopentenones (*E*)-**4kb** (244 mg, 55%) and **5kb** (29 mg, 6%).

(*E*)-4kb: Yellow oil; R_f = 0.50 (PE/Et_2O, 90:10). IR (thin film): $\tilde{\nu}$ = 2960, 2920, 2860, 1700 (C=O), 1640, 1470, 1460, 1380, 1280, 1050, 850 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.74 [tt, ^3J = 7.4, ^4J = 1.6 Hz, 1 H, (C-4)=C*H*], 2.81 (br. s, 2 H, H-5), 2.22 [s, 3 H, (C-3)CH_3], 2.11 [q, $^3J \approx 7.4$ Hz, 2 H, (C-4)=CHCH_2], 1.43–1.27 (m, 8 H, 4× CH_2), 1.32 (s, 9 H, 3× CH_3), 0.87 (t, ^3J = 6.8 Hz, 3 H, CH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.0 (C-1, *C*=O), 160.9 (C-3), 147.9 (C-2), 137.5 (C-4), 124.2 [(C-4)=*C*H], 38.3 (C-5), 34.1 (*C*Me_3), 31.8, 30.1, 29.3 and 29.1 (4× CH_2), 30.0 [3× *C*H_3, C(*C*H_3)$_3$], 22.6 (CH_2CH_3), 14.1 (CH_2CH_3), 13.5 [(C-3)CH_3] ppm. MS (EI): *m*/*z* (%) = 248 (38) $[M]^+$, 233 (32) $[M^+ - CH_3]$, 165 (15), 164 (100), 149 (32), 55 (22).

5kb: Yellow oil; R_f = 0.57 (PE/Et_2O, 90:10). IR (thin film): $\tilde{\nu}$ = 2960, 2920, 2860, 1700 (C=O), 1640, 1470, 1460, 1380, 1280, 1050, 850 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.32 [d, ^4J = 1.5 Hz, 1 H, (C-4)=CH_{cis}], 5.07 [d, ^4J = 1.1 Hz, 1 H, (C-4)=CH_{trans}], 2.69 (br. t, ^3J = 5.5 Hz, 1 H, 5-H), 2.24 [s, 3 H, (C-3)CH_3], 1.32 (s, 9 H, 3× CH_3), 1.30–1.15 (m, 10 H, 5× CH_2), 0.86 (t, ^3J = 6.6 Hz, 3 H, CH_2CH_3) ppm. MS (EI): *m*/*z* (%) = 248 (39) $[M]^+$, 233 (28) $[M^+ - CH_3]$, 164 (100), 149 (19), 55 (25).

4-Methylene-2-propylcyclopent-2-enone (4ea): (Table 6, entry 1) Following procedure B as for the preparation of the cyclopentenone **4da**, cycloaddition of the (pent-1-yne)hexacarbonyldicobalt complex (**2e**; 669 mg, 1.9 mmol) with propa-1,2-diene (**3a**; 1 mL, 17 mmol) promoted by NMO (1.32 g, 11.32 mmol) in CH_2Cl_2/THF (1:1, 20 mL) gave, after flash chromatography (PE/Et_2O, 90:10), the cyclopentenone **4ea** as a yellow oil (150 mg, 58%). R_f = 0.27 (PE/Et_2O, 90:10). IR (thin film): $\tilde{\nu}$ = 2960, 2920, 2860, 1710 (C=O), 1640, 1590, 1460, 1380, 1290, 1190, 1100, 940, 890 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.41 (br. s, 1 H, 3-H), 5.26 [br. s, 1 H, (C-4)=CH_{cis}], 5.14 [br. s, 1 H, (C-4)=CH_{trans}], 2.98 (s, 2 H, 5-H), 2.24 [t, ^3J = 7.4 Hz, 2 H, (C-2)CH_2], 1.54 [sextet, ^3J = 7.4 Hz, 2 H, (C-2)CH_2CH_2], 0.93 (t, ^3J = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.0 (C-1, *C*=O), 153.6 (C-3), 149.1 (C-2), 142.9 (C-4), 110.4 [(C-4)=*C*H_2], 39.7 (C-5), 26.7 [(C-2)CH_2], 20.8 [(C-2)CH_2CH_2], 13.8 (*C*H_3) ppm. MS (EI): *m*/*z* (%) = 136 (54) $[M]^+$, 121 (12) $[M^+ - CH_3]$, 108 (28), 107 (11) $[M^+ - C_2H_5]$, 93 (61) $[M^+ - C_3H_7]$, 91 (28), 79 (90), 77 (100), 66 (21), 65 (30), 63 (16), 55 (12).

4-Heptylidene-2-propylcyclopent-2-enone (4eb): (Table 6, entry 3) Following procedure B, cycloaddition of the (1-pentyne)hexacarbonyldicobalt complex (**2e**; 292 mg, 0.82 mmol) with nona-1,2-

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diene (**3b**; 153 mg, 1.23 mmol) promoted by NMO (574 mg, 4.9 mmol) in CH_2Cl_2/THF (1:1, 10 mL) gave, after flash chromatography (PE/Et_2O, 90:10), the cyclopentenones (*E*)-**4eb** (86 mg, 48%), (*Z*)-**4eb** (37 mg, 20%) and **5eb** (22 mg, 12%).

(*E*)-4eb: Yellow oil; R_f = 0.32 (PE/Et_2O, 90:10). IR (thin film): $\tilde{\nu}$ = 2960, 2920, 2870, 1700 (C=O), 1590, 1460, 1380, 1300, 1050, 930, 730 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.37 (s, 1 H, 3-H), 5.67 [tt, ^3J = 7.4, $^4J_{transoid}$ = 1.7 Hz, 1 H, (C-4)=C*H*CH_2], 2.91 (d, $^4J_{transoid}$ = 1.7 Hz, 2 H, 5-H), 2.25 [q, $^3J \approx$ 7.4 Hz, 2 H, (C-4, C=CHC*H*$_2$)], 2.12 [t, ^3J = 7.3 Hz, 2 H, (C-2)C*H*$_2$], 1.58–1.22 (m, 10 H, 5× C*H*$_2$), 0.89 (t, ^3J = 6.2 Hz, 6 H, 2× C*H*$_3$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 205.9 (C-1, *C*=O), 154.3 (C-3), 146.7 (C-2), 136.2 (C-4), 128.6 [(C-4)=*C*H], 37.9 (C-5), 31.8, 30.1, 29.3 and 29.1 (4× *C*H_2), 26.5 [(C-2)*C*H_2], 22.7 and 21.2 (2× CH_3*C*H_2), 14.3 and 14.1 (2× *C*H_3) ppm. MS (EI): *m*/*z* (%) = 220 (62) $[M]^+$, 191 (26) [$M^+ - C_3H_7$], 149 (21), 136 (100), 121 (22), 108 (46), 107 (23), 93 (34), 91 (35), 79 (53), 77 (38), 65 (20). HRMS (EI): calcd. for $C_{15}H_{26}O$ $[M]^+$ 220.1827; found 220.1822.

(*Z*)-4eb: Yellow oil; R_f = 0.26 (PE/Et_2O, 90:10). IR (thin film): $\tilde{\nu}$ = 2960, 2920, 2870, 1700 (C=O), 1590, 1460, 1380, 1300, 1050, 930, 730 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.68 (s, 1 H, 3-H), 5.55 [t, ^3J = 7.8, $^4J_{cisoid} \approx$ 0.7 Hz, 1 H, (C-4)=C*H*CH_2], 2.97 (d, $^4J_{cisoid} \approx$ 0.7 Hz, 2 H, 5-H), 2.30 [m, 2 H, (C-4)=CHC*H*$_2$], 2.12 [t, ^3J = 7.3 Hz, 2 H, (C-2)C*H*$_2$], 1.58–1.22 (m, 10 H, 5× C*H*$_2$), 0.89 (t, ^3J = 6.2 Hz, 6 H, 2× C*H*$_3$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 206.6 (C-1, *C*=O), 149.3 (C-3), 147.9 (C-2), 134.3 (C-4), 127.4 [(C-4)=*C*H], 40.8 (C-5), 31.7, 30.9, 28.4 and 27.6 (4× *C*H_2), 25.1 [(C-2)*C*H_2], 22.7 and 22.5 (2× CH_3*C*H_2), 14.1 and 14.0 (2× *C*H_3) ppm. MS (EI): *m*/*z* (%) = 220 (100) $[M]^+$, 191 (28) [$M^+ - C_3H_7$], 149 (23), 136 (83), 121 (19), 108 (44), 107 (16), 93 (22), 91 (28), 79 (47), 77 (43), 65 (25).

5eb: Yellow oil; R_f = 0.45 (PE/Et_2O, 90:10). IR (thin film): $\tilde{\nu}$ = 2960, 2920, 2870, 1700 (C=O), 1590, 1460, 1380, 1300, 1050, 930, 730 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.34 (s, 1 H, 3-H), 5.20 [br. s, 1 H, (C-4)=CH_{trans}], 5.08 [br. s, 1 H, (C-4)=CH_{cis}], 2.76 (app t, $^3J \approx$ 5.3 Hz, 1 H, 5-H), 2.18 [t, ^3J = 7.4 Hz, 2 H, (C-2)CH_2], 1.48 [sextet, ^3J = 7.4 Hz, 2 H, CH_3CH_2*C*H_2CH$_2$(C-2)], 1.19 (m, 10 H, 5× C*H*$_2$), 0.87 (t, ^3J = 7.4 Hz, 3 H, C*H*$_3$), 0.80 (t, ^3J = 6.2 Hz, 3 H, C*H*$_3$ of hexyl) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 208.9 (C-1, *C*=O), 153.2 (C-3), 148.2 and 147.7 (C-2 and/or C-4), 109.4 [(C-4)=*C*H_2], 48.5 (C-5), 31.6, 29.8, 29.4, 26.8 and 25.2 (5× *C*H_2), 22.5 and 20.9 (2× *C*H_2CH$_3$), 14.0 and 13.8 (2× *C*H_3) ppm. MS (EI): *m*/*z* (%) = 220 (34) $[M]^+$, 191 (37) [$M^+ - C_3H_7$], 136 (35), 108 (15), 91 (16), 79 (33), 77 (31), 97 (15), 55 (100).

4-Heptylidene-2-phenylcyclopent-2-enone (4fb): (Table 6, entry 5) Following procedure B, cycloaddition of the phenylacetylene-hexacarbonyldicobalt complex (**2f**; 1.094 g, 2.82 mmol) with nona-1,2-diene (**3b**; 526 mg, 4.23 mmol) promoted by NMO (1.980 g, 16.91 mmol) in CH_2Cl_2/THF (1:1, 14 mL) gave, after flash chromatography (PE/Et_2O, 90:10), cyclopentenones (*E*)-**4fb** (306 mg, 43%), (*Z*)-**4fb** (136 mg, 19%) and **5fb** (50 mg, 7%).

(*E*)-4fb: Yellow oil; R_f = 0.38 (PE/Et_2O, 90:10). IR (thin film): $\tilde{\nu}$ = 3080, 3050, 3020, 2950, 2920, 2850, 1700 (C=O), 1600, 1490, 1120, 930, 760, 690 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.87 (s, 1 H, 3-H), 7.80 (dd, ^3J_o = 8.1, ^4J_m = 1.1 Hz, 2 H, 2× H_o), 7.36 (m, 3 H, 2× H_m and 1× H_p), 5.88 [t, ^3J = 7.4 Hz, 1 H, (C-4)=C*H*CH_2], 3.12 (s, 2 H, 5-H), 2.22 [q, $^3J \approx$ 7.4 Hz, 2 H, (C-4)=CHCH_2], 1.66–1.24 (m, 8 H, 4× CH_2), 0.90 (t, ^3J = 6.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 203.5 (C-1, *C*=O), 154.5 (C-3), 141.5 (C-2), 135.6 and 131.6 [C-4 and *C*(Ph)$_i$], 131.3 (C=*C*HCH$_2$), 128.4 [2× *C*H(Ph)$_m$ and *C*H(Ph)$_p$], 127.1 [2× *C*H(Ph)$_o$], 38.9 (C-5), 31.6, 30.3, 29.1 and 29.0 (4× *C*H_2), 22.6 (*C*H_2CH$_3$), 14.1 (*C*H_3) ppm. MS (EI): *m*/*z* (%) = 254 (64) $[M]^+$, 183 (60), 170 (100), 155 (36), 153 (33), 141 (32), 129 (20), 128 (32), 115 (34), 77 (28) $[Ph^+]$, 43 (20), 41 (34), 29 (31), 27 (24).

(*Z*)-4fb: Yellow oil; R_f = 0.33 (PE/Et_2O, 90:10). IR (thin film): $\tilde{\nu}$ = 3080, 3050, 3020, 2950, 2920, 2850, 1700 (C=O), 1600, 1490, 1120, 930, 760, 690 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.19 (s, 1 H, 3-H), 7.80 (dd, ^3J_o = 8.1, ^4J_m = 1.1 Hz, 2 H, 2× H_o), 7.36 (m, 3 H, 2× H_m and 1× H_p), 5.72 [t, ^3J = 7.4 Hz, 1 H, (C-4)=C*H*CH_2], 3.17 (s, 2 H, 5-H), 2.37 [q, $^3J \approx$ 7.4 Hz, 2 H, (C-4)=CHCH_2], 1.66–1.24 (m, 8 H, 4× CH_2), 0.90 (t, ^3J = 6.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 203.6 (C-1, *C*=O), 148.9 (C-3), 142.4 (C-2), 135.6 and 133.6 [C-4 and/or *C*(Ph)$_i$], 130.0 [(C-4)=*C*HCH$_2$], 128.4 [2× *C*H(Ph)$_m$ and *C*H(Ph)$_p$], 127.3 [2× *C*H(Ph)$_o$], 41.9 (C-5), 31.7, 29.7, 28.9, 28.6 and 22.5 (5× *C*H_2), 14.2 (*C*H_3) ppm. MS (EI): *m*/*z* (%) = 254 (60) $[M]^+$, 183 (70), 170 (100), 155 (36), 153 (54), 141 (40), 129 (38), 128 (29), 115 (41), 77 (28) $[Ph]^+$, 43 (30), 41 (56), 29 (40), 27 (25).

5fb: Yellow oil; R_f = 0.50 (PE/Et_2O, 90:10). IR (thin film): $\tilde{\nu}$ = 3080, 3050, 3020, 2950, 2920, 2850, 1700 (C=O), 1600, 1490, 1120, 930, 760, 690 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.90 (s, 1 H, 3-H), 7.84 (d, $^3J_{ortho}$ = 7.4 Hz, 2 H, 2× H_o), 7.42–7.35 (m, 3 H, 2× H_m and 1× H_p), 5.45 [br. s, 1 H, (C-4)=CH_{cis}], 5.30 [br. s, 1 H, (C-4)=CH_{trans}], 3.02 (t, ^3J = 5.4 Hz, 1 H, 5-H), 1.40–1.19 (m, 10 H, 5× CH_2), 0.86 (t, ^3J = 6.6 Hz, 3 H, CH_3) ppm. MS (EI): *m*/*z* (%) = 254 (60) $[M]^{+\cdot}$, 183 (18), 170 (100), 155 (8), 153 (9), 141 (5), 55 (7).

2-*tert*-Butyl-4-heptylidenecyclopent-2-enone (4gb): (Table 6, entry 7) Following procedure B, cycloaddition of the (3,3-dimethylbut-1-yne)hexacarbonyldicobalt complex (**2g**; 385 mg, 1.05 mmol) with nona-1,2-diene (**3b**; 196 mg, 1.57 mmol) promoted by NMO (738 mg, 6.3 mmol) in CH_2Cl_2/THF (1:1, 12 mL) gave, after flash chromatography (PE/Et_2O, 95:5), the cyclopentenones (*E*)-**4gb** (111 mg, 45%), (*Z*)-**4gb** (48 mg, 19%) and **5gb** (14 mg, 6%).

(*E*)-4gb: Yellow oil; R_f = 0.40 (PE/Et_2O, 95:5). IR (thin film): $\tilde{\nu}$ = 2960, 2920, 2850, 1700 (C=O), 1460, 1360, 1320, 980, 930 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.33 (s, 1 H, 3-H), 5.65 [t, ^3J = 7.4 Hz, 1 H, (C-4)=C*H*CH_2], 2.90 (s, 2 H, 5-H), 2.11 [q, $^3J \approx$ 7.4 Hz, 2 H, (C-4)=CHCH_2], 1.41–1.23 (m, 8 H, 4× CH_2), 1.21 (s, 9 H, 3× CH_3), 0.88 (t, ^3J = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.7 (C-1, *C*=O), 153.9 (C-3), 153.1 (C-2), 135.4 (C-4), 128.5 [(C-4)=*C*HCH$_2$], 39.0 (C-5), 31.9 [*C*(*t*Bu)], 31.7, 30.0, 29.2 and 29.0 (4× *C*H_2), 28.4 [3× *C*H_3(*t*Bu)], 22.6 (*C*H_2CH$_3$), 14.1 (CH$_2$*C*H_3) ppm. MS (EI): *m*/*z* (%) = 234 (60) $[M]^+$, 219 (32) [$M^+ - CH_3$], 163 (26), 150 (100), 149 (21), 135 (35), 107 (21), 91 (21), 79 (19), 77 (21), 57 (20) [*t*Bu]$^+$, 55 (52).

(*Z*)-4gb: Yellow oil; R_f = 0.32 (PE/Et_2O, 95:5). IR (thin film): $\tilde{\nu}$ = 2960, 2920, 2850, 1700 (C=O), 1460, 1360, 1320, 980, 930 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.63 (s, 1 H, 3-H), 5.52 [t, ^3J = 7.4 Hz, 1 H, (C-4)=C*H*CH_2], 2.94 (s, 2 H, C-5), 2.27 [q, $^3J \approx$ 7.4 Hz, 2 H, (C-4)=CHCH_2], 1.41–1.23 (m, 8 H, 4× CH_2), 1.23 (s, 9 H, 3× CH_3), 0.88 (t, ^3J = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.4 (C-1, *C*=O), 155.1 (C-2), 147.2 (C-3), 133.5 (C-4), 127.3 [(C-4)=*C*HCH$_2$], 42.0 (C-5), 33.6 (*C*H_2), 32.2 [*C*(*t*Bu)], 29.7, 29.5 and 28.9 (3× *C*H_2), 28.3 [3× *C*H_3(*t*Bu)], 22.6 (*C*H_2CH$_3$), 14.1 (CH$_2$*C*H_3) ppm. MS (EI): *m*/*z* (%) = 234 (100) $[M]^+$, 219 (43) [$M^+ - CH_3$], 191 (20), 107 (15), 149 (21), 135 (26), 107 (15), 77 (16), 57 (19) [*t*Bu]$^+$, 55 (46).

5gb: Yellow oil; R_f = 0.48 (PE/Et_2O, 95:5). IR (thin film): $\tilde{\nu}$ = 2960, 2920, 2850, 1700 (C=O), 1460, 1360, 1320, 980, 930 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.35 (s, 1 H, 3-H), 5.24 [br. s, 1 H, (C-4)=CH_{trans}], 5.11 [br. s, 1 H, (C-4)=CH_{cis}], 2.78 (t, ^3J = 5.5 Hz, 1

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H, 5-H), 1.30–1.16 (m, 10 H, 5× CH_2), 1.23 (s, 9 H, 3× CH_3), 0.86 (t, ^3J = 6.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.1 (C-1, *C*=O), 155.5 (C-2), 151.4 (C-3), 147.6 (C-4), 109.5 [(C-4)=*C*H_2], 49.5 (C-5), 32.1 [*C*(*t*Bu)], 31.7, 29.9 and 29.5 (3× *C*H_2), 28.3 [3× *C*H_3(*t*Bu)], 25.0 (*C*H_2), 22.6 (*C*H_2CH$_3$), 14.1 (CH$_2$*C*H_3) ppm. MS (EI): *m*/*z* (%) = 234 (71) $[M]^+$, 219 (18) $[M^+ - CH_3]$, 177 (83) $[M^+ - t\text{Bu}]$, 164 (100), 163 (23), 150 (39), 149 (30), 91 (16), 77 (14), 57 (55) $[t\text{Bu}]^+$, 55 (60).

4-Benzylidene-2-propylcyclopent-2-enone (4ec): (Table 6, entry 8) Following procedure B, cycloaddition of the (pent-1-yne)hexacarbonyldicobalt complex (**2e**; 347 mg, 0.98 mmol) with phenylallene (**3c**; 170 mg, 1.47 mmol) promoted by NMO (689 g, 5.88 mmol) in CH_2Cl_2/THF (1:1, 12 mL) gave, after flash chromatography (PE/Et_2O, 85:15), the cyclopentenones (*E*)-**4ec** (108 mg, 52%), (*Z*)-**4ec** (35 mg, 17%) and **5ec** (30 mg, 14%).

(*E*)-4ec: Yellow oil; R_f = 0.28 (PE/Et_2O, 85:15). IR (thin film): $\tilde{\nu}$ = 3060, 3020, 2960, 2920, 2860, 1700 (C=O), 1610, 1490, 1450, 1380, 1250, 1190, 1100, 930, 850, 760, 740, 690 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (s, 1 H, 3-H), 7.42–7.33 (m, 3 H, 2× H_m and 1× H_p), 7.27 (dd, ^3J_o = 5.9, ^4J_m = 1.5 Hz, 2 H, 2× H_o), 6.56 [s, 1 H, (C-4)=C*H*Ph], 3.27 (s, 2 H, 5-H), 2.29 [t, ^3J = 7.3 Hz, 2 H, (C-2)CH_2], 1.58 [sextet, ^3J = 7.3 Hz, 2 H, (C-2)CH$_2$CH_2], 0.96 (t, ^3J = 7.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.7 (C-1, *C*=O), 156.7 (C-3), 146.5 (C-2), 136.7 and 136.6 [C-4 and/or *C*(Ph)$_i$], 128.9 [2× *C*H(Ph)$_m$], 128.8 [2× *C*H(Ph)$_o$], 127.8 [*C*H(Ph)$_p$], 126.5 [(C-4)=*C*HPh], 39.8 (C-5), 26.9 [(C-2)*C*H_2], 21.2 (*C*H_2CH$_3$), 14.0 (*C*H_3) ppm. MS (EI): *m*/*z* (%) = 212 (100) $[M]^+$, 197 (22) $[M^+ - CH_3]$, 183 (30) $[M^+ - C_2H_5]$, 169 (35) $[M^+ - C_3H_7]$, 155 (42), 153 (30), 141 (24), 115 (45), 91 (20), 77 (20) $[Ph]^+$, 39 (27).

(*Z*)-4ec: Yellow oil; R_f = 0.23 (PE/Et_2O, 85:15). IR (thin film): $\tilde{\nu}$ = 3060, 3020, 2960, 2920, 2860, 1700 (C=O), 1600, 1490, 1450, 1380, 1350, 1120, 750, 730 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 (s, 1 H, 3-H), 7.55–7.29 (m, 5 H, 5× ArH), 6.57 [s, 1 H, (C-4)=C*H*Ph], 3.16 (s, 2 H, 5-H), 2.30 [t, ^3J = 7.3 Hz, 2 H, (C-2)CH_2], 1.57 [sextet, ^3J = 7.3 Hz, 2 H, (C-2)CH$_2$CH_2], 0.86 (t, ^3J = 7.3 Hz, 3 H, CH_3) ppm. MS (EI): *m*/*z* (%) = 212 (99) $[M]^+$, 197 (23) $[M^+ - CH_3]$, 183 (50) $[M^+ - C_2H_5]$, 169 (59) $[M^+ - C_3H_7]$, 155 (78), 153 (52), 141 (42), 129 (38), 128 (44), 115 (100), 91 (39), 77 (43) $[Ph^+]$, 69 (29), 63 (35), 51 (34), 41 (28), 39 (57), 27 (42).

5ec: Yellow oil; R_f = 0.37 (PE/Et_2O, 85:15). IR (thin film): $\tilde{\nu}$ = 3080, 3060, 3020, 2960, 2920, 2860, 1710 (C=O), 1640, 1600, 1500, 1450, 1380, 1190, 1060, 910, 740, 700 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60 (s, 1 H, 3-H), 7.34–7.24 (m, 3 H, 2× H_m and 1× H_p), 7.14 (dd, ^3J_o = 8.1, ^4J_m = 1.5 Hz, 2 H, 2× H_o), 5.39 [br. s, 1 H, (C-4)=CH_{trans}], 5.05 [br. s, 1 H, (C-4)=CH_{cis}], 4.01 (s, 1 H, 5-H), 2.31 [t, ^3J = 7.3 Hz, 2 H, (C-2)CH_2], 1.60 [sextet, ^3J = 7.3 Hz, 2 H, (C-2)CH$_2$CH_2], 0.97 (t, ^3J = 7.3 Hz, 3 H, CH_3) ppm. MS (EI): *m*/*z* (%) = 212 (99) $[M]^+$, 197 (19) $[M^+ - CH_3]$, 183 (42) $[M^+ - C_2H_5]$, 169 (53) $[M^+ - C_3H_7]$, 155 (84), 153 (47), 141 (40), 128 (44), 115 (100), 91 (43), 77 (33) $[Ph^+]$, 39 (39), 27 (33).

2-Propyl-4-[(trimethylsilyl)methylene]cyclopent-2-enone (4ed): (Table 6, entry 9) Following procedure B, cycloaddition of the (1-pentyne)hexacarbonyldicobalt complex (**2e**; 230 mg, 0.65 mmol) with trimethylsilylallene (**3d**; 109 mg, 0.97 mmol) promoted by NMO (457 mg, 3.9 mmol) in CH_2Cl_2/THF (1:1, 8 mL) gave, after flash chromatography (PE/Et_2O, 90:10), the cyclopentenones (*E*)-**4ed** (77 mg, 50%) and (*Z*)-**4ed** (7 mg, 4%).

(*E*)-4ed: Yellow oil; R_f = 0.35 (PE/Et_2O, 92:8). IR (neat): $\tilde{\nu}$ = 2960, 1710 (C=O), 1610, 1380, 1250, 1040, 930, 840, 690 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27 (s, 1 H, 3-H), 5.81 [s, 1 H, (C-4)=C*H*-SiMe$_3$], 2.95 (s, 2 H, 5-H), 2.21 [t, ^3J = 7.3 Hz, (C-2)CH_2], 1.50 (sextet, $^3J \approx$ 7.3 Hz, CH$_2$CH_2CH$_3$), 0.91 (t, ^3J = 7.3 Hz, CH$_2$CH_3), 0.12 [s, 9 H, Si(CH_3)$_3$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 206.6 (C-1, *C*=O), 156.3 (C-3), 150.2 (C-2), 148.1 (C-4), 128.2 [(C-4)=*C*H], 40.2 (C-5), 26.7 [(C-2)*C*H_2], 21.0 (*C*H_2CH$_3$), 13.9 (CH$_2$*C*H_3), –0.50 [3× Si(*C*H_3)$_3$] ppm.

(*Z*)-4ed: Yellow oil; R_f = 0.28 (PE/Et_2O, 92:8). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52 (s, 1 H, 3-H), 5.70 [s, 1 H, (C-4)=C*H*-SiMe$_3$], 2.87 (s, 2 H, 5-H), 2.42 [t, ^3J = 7.3 Hz, (C-2)CH_2], 1.50 (sextet, ^3J = 7.3 Hz, CH$_2$CH_2CH$_3$), 0.91 (t, ^3J = 7.3 Hz, CH$_2$CH_3), 0.18 [s, 9 H, Si(CH_3)$_3$] ppm.

2-Phenyl-4-[(trimethylsilyl)methylene]cyclopent-2-enone (4ef): (Table 6, entry 10) Following procedure B, cycloaddition of the (phenylacetylene)hexacarbonyldicobalt complex (**2f**; 388 mg, 1 mmol) with trimethylsilylallene (**3d**; 169 mg, 1.5 mmol) promoted by NMO (703 mg, 6 mmol) in CH_2Cl_2/THF (1:1, 12 mL) gave, after flash chromatography (PE/Et_2O, 90:10), cyclopentenones (*E*)-**4fd** (98 mg, 42%) and (*Z*)-**4fd** (11 mg, 4%).

(*E*)-4fd: Yellow oil; R_f = 0.40 (PE/Et_2O, 90:10). IR (neat): $\tilde{\nu}$ = 3030, 2860, 1700 (C=O), 1600, 1440, 1260, 1250, 1140, 1120, 910, 840, 730, 690 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (s, 1 H, 3-H), 7.78 (m, 2 H, 2× H_o), 7.38 (m, 3 H, 2× H_m and 1× H_p), 6.05 [s, 1 H, (C-4)=C*H*-SiMe$_3$], 3.18 (s, 2 H, 5-H), 0.20 [s, 9 H, Si(CH_3)$_3$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 204.5 (C-1, *C*=O), 155.6 (C-3), 149.4 (C-2), 131.3 (C-4), 128.9 [*C*(Ph)$_i$], 128.6 [2× *C*H(Ph)$_o$], 127.6 [2× *C*H(Ph)$_m$ and *C*H(Ph)$_p$], 127.5 [(C-4)=*C*H], 41.5 (C-5), –0.20 [3× Si(*C*H_3)$_3$] ppm.

(*Z*)-4fd: Yellow oil; R_f = 0.33 (PE/Et_2O, 90:10). IR (neat): $\tilde{\nu}$ = 3080, 3050, 3020, 2950, 2920, 2850, 1700 (C=O), 1600, 1490, 1120, 930, 760, 690 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (s, 1 H, 3-H), 7.80 (m, 2 H, 2× H_o), 7.38 (m, 3 H, 2× H_m and 1× H_p), 5.92 [s, 1 H, (C-4)=C*H*-SiMe$_3$], 3.32 (s, 2 H, 5-H), 0.27 [s, 9 H, Si(CH_3)$_3$] ppm.

4-Cyclohexylidene-2-pentylcyclopent-2-enone (4hf): (Scheme 3) Following procedure B, cycloaddition of the (hept-1-yne)hexacarbonyldicobalt complex (**2h**; 2.314 g, 6 mmol) with vinylidenecyclohexane (**3f**; 780 mg, 7.2 mmol) promoted by NMO (4.220 g, 36 mmol) in CH_2Cl_2/THF (1:1, 30 mL) gave, after flash chromatography (PE/Et_2O, 80:20), the cyclopentenone **4hf** as a yellow oil (1.03 g, 74%): R_f = 0.33 (PE/Et_2O, 80:20). IR (thin film): $\tilde{\nu}$ = 2960, 2920, 2860, 1700 (C=O), 1650, 1580, 1450, 1200, 990, 920, 880, 850 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72 (s, 1 H, 3-H), 2.92 (s, 2 H, 5-H), 2.38 (m, 2 H, C=CCH_2), 2.24 [t, ^3J = 7.7 Hz, 2 H, (C-2)CH_2], 2.19 (m, 2 H, C=CCH_2), 1.60 (m, 6 H, 3× CH_2), 1.55–1.45 (m, 2 H, CH_2), 1.33–1.27 (m, 4 H, 2× CH_2), 0.88 (t, ^3J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.4 (C-1, *C*=O), 150.5 (C-3), 146.1 (C-2), 138.9 [(C-4)=*C*(CH$_2$)$_5$], 127.0 (C-4), 39.0 (C-5), 32.9, 31.7, 30.4, 28.1, 27.8, 27.7, and 25.0 (7× *C*H$_2$), 26.5 (*C*H$_2$C-CO), 22.5 (CH$_3$*C*H$_2$), 14.0 (*C*H$_3$) ppm. MS (EI): *m*/*z* (%) = 232 (100) $[M]^+$, 203 (31) $[M^+ - C_2H_5]$, 189 (66) $[M^+ - C_3H_7]$, 176 (61), 175 (26) $[M^+ - C_4H_9]$, 133 (26), 108 (26), 90 (50), 79 (39), 77 (38), 67 (26), 41 (50). $C_{16}H_{24}O$ (232.37): calcd. C 80.70, H 10.41; found C 80.53, H 10.44.

4-Cyclohexylidene-2-phenylcyclopent-2-enone (4ff): (Scheme 3) Following procedure B, cycloaddition of the (phenylacetylene)hexacarbonyldicobalt complex (**2f**; 776 mg, 2 mmol) with vinylidenecyclohexane (**3f**; 260 mg, 2.4 mmol) promoted by NMO (1.405 g, 12 mmol) in CH_2Cl_2/THF (1:1, 12 mL) gave, after flash chromatography (PE/Et_2O, 80:20), the cyclopentenone **4ff** as a yellow oil (318 mg, 67%): R_f = 0.34 (PE/Et_2O, 80:20). IR (thin film): $\tilde{\nu}$ = 3030, 2960, 2920, 2860, 1690 (C=O), 1650, 1600, 1580, 1490, 1450, 1350, 1290, 1270, 1130, 920, 770, 730, 690 cm^{-1}. ^{1}H NMR

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(300 MHz, $CDCl_3$): δ = 8.23 (s, 1 H, 3-H), 7.82 (dd, ^3J_o = 8.3, ^4J_m = 1.3 Hz, 2 H, 2× H_o), 7.41–7.26 (m, 3 H, 2× H_m and 1× H_p), 3.12 (s, 2 H, 5-H), 2.48 [m, 2 H, (C-4)=CCH_2], 2.26 [m, 2 H, (C-4)=CCH_2], 1.65 (m, 6 H, 3× CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.3 (C-1, *C*=O), 150.3 (C-3), 142.5 (C-2), 141.0 [(C-4)=*C*(CH_2)$_5$], 132.2 [*C*(Ph)$_i$], 128.5 [2× *C*H(Ph)$_m$], 128.2 [*C*H-(Ph)$_p$], 127.1 [2× *C*H(Ph)$_o$], 126.8 (C-4), 40.3 (C-5), 33.2, 30.6, 28.3, 27.9 and 26.5 (5× *C*H_2) ppm. HRMS (EI): calcd. for $C_{17}H_{18}O$ $[M]^+$ 238.1358; found 238.1350.

4-Heptylidenecyclopent-2-enone (4ab): (Table 7, entry 1) Following procedure B, after warming up the reaction mixture over 1 h and stirring at r.t. for 15 h, the cycloaddition of the acetylene-hexacarbonyldicobalt complex (**2a**; 468 mg, 1.5 mmol) with nona-1,2-diene (**3b**; 280 mg, 2.25 mmol) promoted by NMO (1.054 g, 9 mmol) in CH_2Cl_2/THF (1:1, 16 mL) afforded, after flash chromatography (PE/Et_2O, 75:25), the cyclopentenone **4ab** as an inseparable mixture of *E* and *Z* stereoisomers (139 mg, 52%, *E*/*Z* = 78:22), the cyclopentenone **5ab** (13 mg, 5%), the 5-alkylidenecyclopentenone (*E*)-**6ab** (37 mg, 14%), and the tricyclic diketone **10b** (30 mg, 11%).

Alternatively, following procedure B (Table 7, entry 3), after 4 h, the cycloaddition of the acetylene-hexacarbonyldicobalt complex (**2a**; 156 mg, 0.5 mmol) with nona-1,2-diene (**3b**; 93 mg, 0.75 mmol) promoted by NMO (351 mg, 3 mmol) in CH_2Cl_2/THF (1:1, 6 mL) gave, after flash chromatography (PE/Et_2O, 75:25), the cyclopentenones **4ab** (*E*/*Z* = 73:27), **5ab** and (*E*)-**6ab** (70 mg, 79%, with a 90:3:7 ratio determined by GC analysis).

4ab (*E* and *Z*): Yellow oil; R_f = 0.37 (PE/Et_2O, 70:30). UV/Vis (EtOH): λ_{max} (ε, L mol^{-1} cm^{-1}) (*E* + *Z*): 283 (17105) nm. IR (neat): $\tilde{\nu}$ (*E* + *Z*) = 2960, 2920, 2850, 1710 (C=O), 1610, 1540, 1460, 1180, 1160, 1070, 780 cm^{-1}.

(*E*)-4ab: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (d, ^3J = 5.5 Hz, 1 H, 3-H), 6.15 (d, ^3J = 5.5 Hz, 1 H, 2-H), 5.77 [t, ^3J = 7.7 Hz, 1 H, (C-4)=C*H*CH_2], 2.85 (s, 2 H, 5-H), 2.12 [q, $^3J \approx$ 7.4 Hz, 2 H, (C-4)=CHCH_2], 1.44–1.23 (m, 8 H, 4× CH_2), 0.84 (t, ^3J = 6.6 Hz, 3 H, CH_2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.3 (C-1, *C*=O), 160.5 (C-3), 137.5 (C-4), 132.7 and 131.7 [C-2 and/or (C-4)=*C*H], 37.2 (C-5), 31.6, 30.1, 28.9 and 28.8 (4× *C*H_2), 22.5 (*C*H_2CH$_3$), 14.0 (*C*H_3) ppm.

(*Z*)-4ab: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00 (d, ^3J = 5.5 Hz, 1 H, 3-H), 6.22 (dd, ^3J = 5.5, ^5J = 1.5 Hz, 1 H, 2-H), 5.66 [t, ^3J = 7.9 Hz, 1 H, (C-4)=C*H*CH_2], 2.91 (s, 2 H, 5-H), 2.27 [q, $^3J \approx$ 7.4 Hz, 2 H, (C-4)=CHCH_2], 1.44–1.23 (m, 8 H, 4× CH_2), 0.84 (t, ^3J = 6.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.9 (C-1, *C*=O), 154.7 (C-3), 135.7 (C-4), 133.8 (C-2), 130.4 [(C-4)=*C*H], 40.0 (C-5), 31.6, 29.5, 28.8 and 28.4 (4× *C*H_2), 22.5 (*C*H_2CH$_3$), 14.0 (*C*H_3) ppm. GC–MS (EI): *m*/*z* (%) (*E*)-**4ab** = 178 (27) $[M]^+$, 107 (15) $[M^+ - C_5H_{11}]$, 95 (26), 94 (100), 79 (17), 77 (24), 66 (17), 55 (11), 43 (14), 41 (16), 39 (11). GC–MS (EI): *m*/*z* (%) (*Z*)-**4ab** = 178 (25) $[M]^+$, 107 (14) $[M^+ - C_5H_{11}]$, 95 (27), 94 (100), 79 (23), 77 (25), 66 (20), 55 (13), 43 (14), 41 (16), 39 (10).

5ab: R_f = 0.46 (PE/Et_2O, 70:30). IR (neat): $\tilde{\nu}$ = 2960, 2920, 2850, 1710 (C=O), 1610, 1540, 1460, 1180, 1160, 1070, 780 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73 (d, ^3J = 5.5 Hz, 1 H, 3-H), 6.27 (dd, ^3J = 5.5, ^5J = 1.1 Hz, 1 H, 2-H), 5.40 [d, ^4J = 0.7 Hz, 1 H, (C-4)=CH_{cis}], 5.29 [br. s, 1 H, (C-4)=CH_{trans}], 2.81 (t, ^3J = 5.7 Hz, 1 H, 5-H), 1.61 [m, 2 H, (C-4)=CHCH_2], 1.48–1.25 (m, 8 H, 4× CH_2), 0.88 (t, ^3J = 6.8 Hz, 3 H, CH_3) ppm. MS (EI): *m*/*z* (%) = 178 (6) $[M]^+$, 95 (14), 94 (100), 77 (16), 41 (17).

(*E*)-6ab: R_f = 0.27 (PE/Et_2O, 70:30). IR (neat): $\tilde{\nu}$ = 2960, 2920, 2850, 1700 (C=O), 1460, 1380, 1260, 740 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (dt, ^3J = 5.9, ^3J = 2.9 Hz, 1 H, 3-H), 6.62 [t, ^3J = 7.4 Hz, 1 H, (C-5)=C*H*CH_2], 6.38 (dt, ^3J = 5.9, ^4J = 2.2 Hz, 1 H, 2-H), 3.19 [br. s, 1 H, (C-4)H_2], 2.21 [q, $^3J \approx$ 7.4 Hz, 2 H, (C-5)=CHCH_2], 1.53–1.21 (m, 8 H, 4× CH_2), 0.88 (t, ^3J = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.6 (C-1, *C*=O), 158.9 (C-3), 136.22 and 136.20 [C-2 and/or (C-5) C=*C*H], 134.0 (C-5), 32.1 (C-4), 31.7, 29.7, 29.0 and 28.4 (4× *C*H_2), 22.6 (*C*H_2CH$_3$), 14.0 (*C*H_3) ppm. MS (EI): *m*/*z* (%) = 178 (10) $[M]^+$, 121 (33), 95 (100), 91 (22), 82 (78), 79 (47), 77 (57), 55 (60), 53 (22), 43 (29), 40 (48), 39 (31).

3,5-Diheptyl-3a,4,7,7a-tetrahydro-4,7-methano-1*H*-indene-1,8-dione (10b): R_f = 0.20 (PE/Et_2O, 70:30). IR (thin film): $\tilde{\nu}$ = 2960, 2920, 2850, 1790 (C=O of bridge), 1700 (conjugated C=O), 1610, 1460, 1380, 1180 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.06 (dt, ^4J = 1.4, ^4J = 1.4 Hz, 1 H, 2-H), 5.96 (dt, ^3J = 3.4, ^4J = 1.5 Hz, 1 H, 6-H), 3.40 (ddd, ^3J = 6.2, ^3J = 4.5, ^4J = 1.4 Hz, 1 H, 3a-H), 3.32 (ddd, ^3J = 5.0, ^3J = 3.4, ^4J_w = 1.5 Hz, 1 H, 7-H), 3.10 (dd, ^3J = 4.5, ^4J_w = 1.5 Hz, 1 H, 4-H), 2.92 (dd, ^3J = 6.2, ^3J = 5.0 Hz, 1 H, 7a-H), 2.32 [dt, ^3J = 7.0, ^4J = 1.4 Hz, 2 H, (C-3)CH_2], 1.99 [m, 2 H, (C-5)CH_2], 1.52–1.20 (m, 20 H, 10× CH_2), 0.87 (t, ^3J = 7.0 Hz, 6 H, 2× CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.7 (*C*-8), 198.6 (*C*-1), 179.7 (*C*-3), 143.4 (*C*-5), 135.2 (*C*H-2), 121.7 (*C*H-6), 52.6, 49.6, 45.2 and 43.4 (4× *C*H), 32.6, 31.9, 31.8, 31.7, 31.6, 29.7, 29.3, 29.1, 29.0, 26.8, 26.1 and 22.6 (12× *C*H_2), 14.0 and 14.0 (2× *C*H_3) ppm.

4-Benzylidenecyclopent-2-enone (4ac):[31a] (Table 7, entry 5) Following procedure B, after 4 h, the cycloaddition of the acetylene-hexacarbonyldicobalt complex **2a** (5.39 g, 17.3 mmol) with phenylallene **3c** (2.72 g, 23.4 mmol) promoted by NMO (12.18 g, 104 mmol) in CH_2Cl_2/THF (1:1, 140 mL), gave a crude oil (GC analysis: **4ac**/**5ac**/**6ac** = 77:5:18). Purification by flash chromatography (PE/Et_2O, 60:40) gave the cyclopentenone (*E* + *Z*)-**4ac** (673 mg, 23%, *E*/*Z* = 86:14), the cyclopentenone **5ac** (41 mg, 1%), and the 5-alkylidenecyclopentenone (*E*)-**6ac** (yellow solid, 112 mg, 4%). Pure (*E*)-**4ac** was isolated after a second flash chromatographic column.

(*E* + *Z*)-4ac: Yellow solid; R_f = 0.23 (PE/Et_2O, 60:40). IR (KBr disc): $\tilde{\nu}$ = 3095, 3065, 3025, 2970, 2910, 1705 (C=O), 1670, 1535, 1495, 1445, 1395, 1355, 1235, 1195, 1155, 1080, 930, 915, 890, 835, 825, 790, 750, 700, 685, 645, 620 cm^{-1}.

(*E*)-4ac: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, ^3J = 5.5 Hz, 1 H, 3-H), 7.47–7.28 (m, 5 H, 5× ArH), 6.68 [s, 1 H, (C-4)=C*H*-Ph], 6.30 (d, ^3J = 5.5 Hz, 1 H, 2-H), 3.27 (s, 2 H, 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.3 (C-1, *C*=O), 162.4 (C-3), 137.7 and 136.2 [C-4 and/or *C*(Ph)$_i$], 132.7 (C-2), 129.3 [2× *C*H(Ph)$_o$], 129.2 [*C*H(Ph)$_p$], 128.9 [2× *C*H(Ph)$_m$], 128.5 [(C-4)=*C*HPh], 39.4 (C-5) ppm. MS (ESI): (*E* + *Z* **4ac**): *m*/*z* = 193 $[M + Na]^+$, 171 $[M + H]^+$, 153 $[(M + H)^+ - H_2O]$.

(*Z*)-4ac: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.24 (d, ^3J = 5.7 Hz, 1 H, 3-H), 7.47–7.28 (m, 5 H, 5× ArH), 6.72 [s, 1 H, (C-4)=C*H*Ph], 6.41 (dd, ^3J = 5.5, ^5J = 1.8 Hz, 1 H, 2-H), 3.17 (s, 2 H, 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.0 (C-1, *C*=O), 155.5 (C-3), 137.3 [C-4 or *C*(Ph)$_i$], 136.4 (C-2), 136.3 [C-4 or *C*(Ph)$_i$], 128.8, 128.5, 128.2 and 128.1 [5× *C*H(Ph) and (C-4)=*C*HPh], 41.5 (C-5) ppm. The ^{1}H and ^{13}C NMR spectroscopic data were in full agreement with those reported in the literature for (*E*)-**5ac** and (*Z*)-**5ac**.[31a]

5ac: Yellow oil; R_f = 0.30 (PE/Et_2O, 60:40). IR (neat): $\tilde{\nu}$ = 2940, 2900, 2840, 1700 (C=O), 1490, 1460, 1445, 1370 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 (d, ^3J = 5.6 Hz, 1 H, 3-H), 7.40–7.10 (m, 5 H, 5× ArH), 6.36 (d, ^3J = 5.6 Hz, 1 H, 2-H), 5.54 [s, 1 H, (C-4)=CH_{cis}], 5.20 [s, 1 H, (C-4)=CH_{trans}], 3.99 (s, 1 H, 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.5 (C-1, *C*=O), 159.8 (C-3),

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149.9 (C-4), 137.2 [*C*(Ph)$_i$], 133.9 (C-2), 129.2 [2× *C*H(Ph)$_o$], 128.9 [2× *C*H(Ph)$_m$], 127.6 [*C*H(Ph)$_p$], 115.6 [(C-4)=*C*H$_2$], 55.6 (C-5) ppm.

(*E*)-6ac: Yellow solid; R_f = 0.20 (PE/Et$_2$O, 60:40). IR (KBr disc): ṽ = 3060, 3030, 2925, 2855, 1690 (C=O), 1630, 1495, 1450, 1405, 1340, 1290, 1270, 1225, 1185, 1080, 1030, 945, 840, 790, 760, 740, 690, 635 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.71–7.66 (dtd, ^3J = 5.9, ^3J = 2.4, ^5J = 0.9 Hz, 1 H, 3-H), 7.59 (dd, ^3J_o = 7.8, ^4J_m = 1.4 Hz, 2 H, 2× H_o), 7.46–7.30 [m, 4 H, 2× H_m, H_p and (C-5)=CH*Ph*], 6.48 (dt, ^3J = 5.9, ^4J = 2.1 Hz, 1 H, 2-H), 3.58 (ddd, ^3J = 2.4, ^4J = 2.1, ^4J = 2.1 Hz, 2 H, 4-H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 197.9 (C-1, *C*=O), 157.5 (C-3), 135.9 [(C-5)=*C*HPh], 135.6 [*C*(Ph)$_i$], 132.7 (C-5), 132.4 (*C*H-2), 130.8 [2× *C*H(Ph)$_o$], 129.9 [*C*H(Ph)$_p$], 129.3 [2× *C*H(Ph)$_m$], 34.7 (*C*H$_2$-4) ppm.

4-Cyclohexylidenecyclopent-2-enone (4af): (Table 8, entry 3) Following procedure C, cycloaddition of the acetylene-hexacarbonyldicobalt complex **2a** (312 mg, 1.0 mmol) with vinylidenecyclohexane **3f** (162 mg, 1.5 mmol) promoted by NMO (703 mg, 6 mmol) in CH$_2$Cl$_2$/THF (1:1, 10 mL) gave, after flash chromatography (PE/Et$_2$O, 60:40), the cyclopentenone **4af** (83 mg, 46%) and 5-cyclohexylidenecyclopent-2-enone **6af** (21 mg, 18%).

4af: Yellow oil; R_f = 0.34 (PE/Et$_2$O, 60:40). IR (neat): ṽ = 2960, 2920, 2850, 1700 (C=O), 1670, 1600, 1530, 1450, 1390, 1190, 1170, 920, 860, 850, 800 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.05 (d, ^3J = 5.5 Hz, 1 H, 3-H), 6.15 (d, ^3J = 5.5 Hz, 1 H, 2-H), 2.87 (s, 2 H, 5-H), 2.37 [m, 2 H, (C-4)=CC*H*$_2$], 2.19 [m, 2 H, (C-4)=CC*H*$_2$], 1.59 (m, 6 H, 3× C*H*$_2$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 207.1 (C-1, *C*=O), 155.9 (C-3), 142.5 (C-4), 132.6 (C-2), 128.7 [(C-4)=*C*], 38.5 (C-5), 33.1, 30.5, 28.2, 27.7 and 26.4 (5× *C*H$_2$) ppm. HRMS (EI): calcd. for C$_{11}$H$_{14}$O [M]$^+$ 162.1045; found 162.1042.

6af: Yellow oil; R_f = 0.44 (PE/Et$_2$O, 60:40). IR (thin film): ṽ = 2960, 2920, 2850, 1700 (C=O), 1670, 1600, 1530, 1450, 1390, 1190, 1170, 920, 860, 850, 800 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.40 (dt, ^3J = 5.9, ^3J = 2.8 Hz, 1 H, 3-H), 6.31 (dt, ^3J = 5.9, ^4J = 2.0 Hz, 1 H, 2-H), 3.18 [dd, ^3J = 2.8, ^4J = 2.0 Hz, 2 H, H-4], 3.06 [app t, ^3J = 6.2 Hz, 2 H, (C-5)=C(C*H*$_2$)$_{cis}$], 2.23 [app t, ^3J = 6.2 Hz, 2 H, (C-5)=C(C*H*$_2$)$_{trans}$], 1.70–1.60 (m, 6 H, 3× C*H*$_2$) ppm.

6,7,8,9,10,10a-Hexahydro-1(5*H*)-cyclopentacyclononenone (4ah): (Scheme 5) Following procedure B, after 6 h, the cycloaddition of the acetylene-hexacarbonyldicobalt complex **2a** (1.21 g, 3.84 mmol) with cyclonona-1,2-diene **3h** (709 mg, 5.8 mmol) promoted by NMO (2.7 g, 23.04 mmol) in CH$_2$Cl$_2$/THF (1:1, 20 mL) gave, after flash chromatography (PE/Et$_2$O, 70:30), the cyclopentenone **4ah** (402 mg, 59%).

4ah: Yellow oil; R_f = 0.35 (PE/Et$_2$O, 70:30). IR (neat): ṽ = 2920, 2850, 1700 (C=O), 1550, 1470, 1440, 1350, 1240, 1160, 1080, 940, 870, 830, 820, 790 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.71 (d, ^3J = 5.5 Hz, 1 H, 3-H), 6.12 (d, ^3J = 5.5 Hz, 1 H, 2-H), 5.82 (dd, ^3J = 11.5, ^3J = 6.3 Hz, 1 H, 4-H), 2.72 (dd, ^3J = 9.1, ^3J = 3.4 Hz, 1 H, 10a-H), 2.46 (m, 1 H, 5-H), 2.38 (m, 1 H, 5′-H), 2.28 (m, 1 H, 10-H), 1.87 (m, 1 H, 10′-H), 1.60–1.70 (m, 4 H, 2× C*H*$_2$), 1.37–1.60 (m, 4 H, 2× C*H*$_2$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 209.8 (C-1, *C*=O), 160.9 (C-3), 144.6 (C-3a), 131.6 (C-2), 130.6 [C-4, (C-3a)=*C*H], 49.6 (C-10a), 30.1, 29.0, 28.2, 27.7, 26.7 and 22.2 (6× *C*H$_2$) ppm. MS (EI): *m*/*z* (%) = 176 (58) [M]$^+$, 133 (19), 107 (25), 105 (25), 95 (31), 94 (46), 91 (86), 81 (58), 79 (65), 77 (64), 67 (58), 65 (51), 55 (71), 53 (49), 51 (41), 41 (100), 39 (84), 27 (50).

Tricyclic Diketones 10a and **10b:** (Scheme 6) Following procedure B (as for cyclopentenone **4da**, Table 3, entry 2), cycloaddition of the acetylene-hexacarbonyldicobalt complex **2a** (1.25 g, 4 mmol) with propadiene (condensed at –78 °C, 1 mL, 17 mmol) promoted by NMO (2.8 mg, 24 mmol) in CH$_2$Cl$_2$/THF (50 mL) gave, after 4 h reaction time followed by purification by flash chromatography (PE/Et$_2$O, 20:80), the tricyclic diketones **10a** (85 mg, 22%) and **11a** (26 mg, 7%).

3,5-Dimethyl-3a,4,7,7a-tetrahydro-4,7-methano-1*H*-indene-1,8-dione (10a):[74] Yellow oil; R_f = 0.36 (PE/Et$_2$O, 20:80). IR (neat): ṽ = 2920, 1780 (C=O of bridge), 1690 (conjugated C=O), 1610, 1440, 1380, 1300, 1280, 1190, 1090, 910, 880, 820, 710 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 6.00 (q, ^4J = 2.5 Hz, 1 H, 2-H), 5.89 (dq, ^3J = 4.9, ^4J = 3.0 Hz, 1 H, 6-H), 3.29 (dd, ^3J = 5.3, ^3J = 5.0 Hz, 1 H, 7a-H), 3.20 (dd, ^3J = 5.0, ^3J = 4.9 Hz, 1 H, 7-H), 3.01 (d, ^3J = 4.4 Hz, 1 H, 4-H), 2.83 (dd, ^3J = 5.3, ^3J = 4.4 Hz, 1 H, 3a-H), 2.05 [d, ^4J = 2.5 Hz, 3 H, (C-3)C*H*$_3$], 1.69 [d, ^4J = 3.0 Hz, 3 H, (C-5)C*H*$_3$] ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 206.6 (*C*-8, *C*=O), 198.5 (*C*-1, *C*=O), 174.8 (*C*-3), 138.7 (*C*-5), 136.7 (*C*H-2), 122.9 (*C*H-6), 53.2, 50.0, 45.4 and 44.5 (4× *C*H), 18.4 and 18.1 (2× *C*H$_3$) ppm. MS (EI): *m*/*z* (%) = 160 (29) [M$^+$ – CO], 150 (100), 117 (26), 115 (28), 91 (36), 68 (20), 65 (18), 40 (31), 39 (27).

3,6-Dimethyl-3a,4,7,7a-tetrahydro-4,7-methano-1*H*-indene-1,8-dione (11a): Yellow oil; R_f = 0.42 (PE/Et$_2$O, 20:80). IR (neat): ṽ = 2920, 1780 (C=O of bridge), 1690 (conjugated C=O), 1610, 1440, 1380, 1300, 1280, 1190, 1090, 910, 880, 820, 710 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 6.06 (s, 1 H, 2-H), 5.73 (dd, ^3J = 4.4, ^4J = 1.1 Hz, 1 H, 5-H), 3.30 (dd, ^3J = 5.5, ^3J = 5.2 Hz, 1 H, 7a-H), 3.18 (dd, ^3J = 5.5, ^3J = 4.4 Hz, 1 H, 4-H), 3.14 (d, ^3J = 5.2 Hz, 1 H, 7-H), 2.93 (t, ^3J = 5.5 Hz, 1 H, 3a-H), 2.03 [s, 3 H, (C-3)C*H*$_3$], 1.79 [d, ^4J = 1.1 Hz, 3 H, (C-6)C*H*$_3$] ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 205.8 (*C*-8, C=O), 198.6 (*C*-1, C=O), 175.7 (*C*-3), 141.4 (*C*-6), 136.8 (*C*H-2), 120.4 (*C*H-5), 53.3, 49.9, 45.9 and 44.7 (4× *C*H), 18.2 and 18.1 (2× *C*H$_3$) ppm. MS (EI): *m*/*z* (%) = 160 (34) [M$^+$ – CO], 15 (100), 117 (26), 115 (32), 91 (38), 68 (15), 65 (15), 40 (21), 39 (19).

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[57] Whereas numerous rotamer π complexes may exist for π complexes such as **I**–**K** with a pseudo-axially coordinated allenic unit, minimization of the steric interactions of the allenic substituents R^1, R^2(H) and R^3(H) with the R and R′ groups and the CO ligands implies that the coordinated double bond should be approximately parallel with respect to the cluster-alkyne RC≡CR′ triple bond. From another source, DFT calculations have demonstrated that only one rotamer could be found for a pseudo-axial coordination of ethylene to the propyne-pentacarbonyldicobalt cluster; this rotamer involved a parallel coordination mode with respect to the alkyne MeC≡CH triple bond. See ref.[27c]

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