Cobalt(I)-Mediated Cycloisomerization of Enynes: Mechanistic Insights

Olivier Buisine, Corinne Aubert,* and Max Malacria*[a]

Dedicated to Professor Jean Normant on the occasion of his 65th birthday

Abstract: [$CpCo(CO)_2$] catalyzes the cycloisomerization of 1,*n*-enynes to afford selectively five- and six-membered ring systems in high yields. The factors governing the cyclization have been explored and we have discovered that the reaction associates two different, but complementary, reactivities of the cobalt(I) complexes. By a judicious choice of the substitution of the enyne, it was also possible to isolate a cyclobutene that arises from a cobaltcyclopentene

Keywords: allyl ligands · cobalt · cobaltacyclopentene · cyclization · enynes

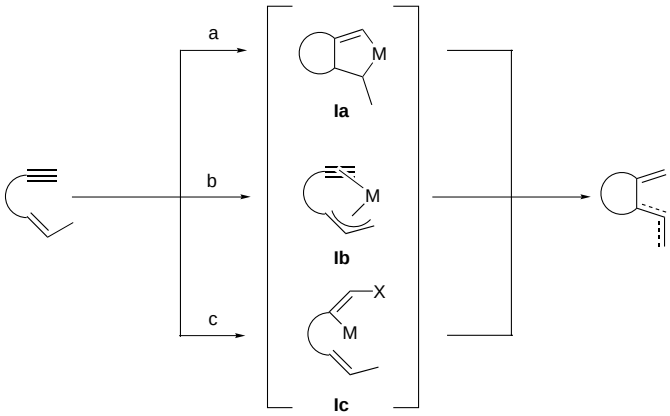
Introduction

Transition-metal-induced cycloisomerizations of 1,*n*-enynes have emerged as extremely attractive and unique tools for the synthesis of various type of cyclic compounds in a very easy one-pot process. Indeed, the rate accelerations provided by catalysis expand the scope of reactions such as the Alder ene reactions that normally require harsh conditions.[1] On the other hand, these cyclizations which generate 1,3- or 1,4-dienes provide clean chemical processes without any wasteful by-products. Cyclization of 1,*n*-enynes has been achieved with a wide range of transition metal complexes either in a catalytic or stoichiometric manner[2–6] and represent a versatile approach to a variety of products by a simple manipulation of the catalyst. Excellent reviews which have compiled differents aspects of the advances in these cyclization reactions have been published.[7]

Considering the mechanistic rationales of the transition-metal-catalyzed cycloisomerization of enynes, different pathways can be considered depending on the reaction conditions and on the choice of the precatalyst. Generally, the complexation of the metal to an alkene or alkyne allows the activation either of one or both moities. Depending on which unsaturated bond will react first, three main mechanisms can be proposed (Scheme 1).

The simultaneous complexation of both unsaturation bonds (path a) leads preferentially to the metallacycle **Ia**. Almost all the transition metal complexes could react to generate such intermediates; however, their reactivity can be quite different.

[a] Prof. Dr. M. Malacria, Dr. C. Aubert, Dr. O. Buisine
Université Pierre et Marie Curie (Paris 6)
Laboratoire de Chmie Organique de Synthèse associé au CNRS
Tour 44-54, Case 229, 4 place Jussieu
75252 Paris cedex 05 (France)
Fax: (+33) 1-44-27-73-60
E-mail: malacria@ccr.jussieu.fr, aubert@ccr.jussieu.fr



Scheme 1. Possible pathways for the cycloisomerization of 1,*n*-enynes.

The presence of a functional group in the allylic position allows the formation of a π-allyl complex **Ib** (path b), which could further react with the triple bond. Finally, hydridometallation of the alkyne leads to the corresponding vinylmetal **Ic** (path c), which is reactive enough to allow the carbometallation of the olefin.

Cobalt catalyst species are particularly useful mediators for effecting [2+2+2] cycloadditions,[8] Pauson–Khand reactions,[9] homo Diels–Alder, and [4+2+2] cyclizations.[10] More recently, it has been shown that the cobalt catalysts are also efficient in ene type reactions of ω-acetylenic-β-ketoesters[11] and reductive carbocyclization of enedienes.[12] To our knowledge, few examples of the cobalt-mediated cycloisomerizations of 1,*n*-enynes have been reported. Indeed, monocyclic 1,3-dienes were obtained by thermolysis of the hexacarbonyldicobalt complex of 1,6- and 1,7-enynes[13] and it was also found that dicobalt octacarbonyl could catalyze a new cycloisomerization reaction of 3-sila-1,7-enynes to eight-membered cyclic dienylsilanes.[14] In connection with our studies on cobalt-mediated [2+2+2] cycloaddition of allenediynes,[15] we

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have disclosed a new cobalt-mediated formal Alder ene reaction of allenynes.[16] While we focused on this reaction, we have found that (η^5-cyclopentadienyl)cobalt dicarbonyl [$CpCo(CO)_2$] is able to induce the cyclization of 1,*n*-enynes as well.[17] A mechanism involving selective cobalt allylic C–H activation was suggested.

Here, we present the full details of the scope and the limitations of such a new cobalt(I)-mediated cycloisomerization and particularly the investigations into the mechanism.

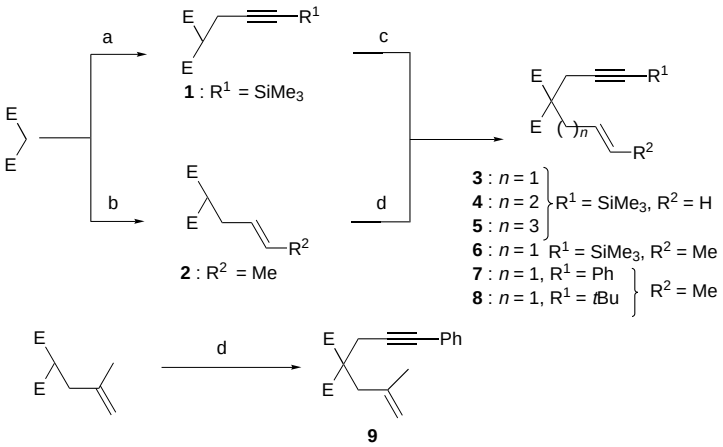
Results and Discussion

In order to gain a better understanding of the factors (steric, electronic, etc.) that govern cyclization, we checked the influence of several important features: the length of the carbon chain between the two unsaturated bonds, the nature of the substituent ($SiMe_3$, Ph, *t*Bu) at the triple bond, the degree of the substitution at the allylic position, and the substitution of the double bond. Thus, series of 1,*n*-enynes which fulfil these criteria were prepared as described in the following section.

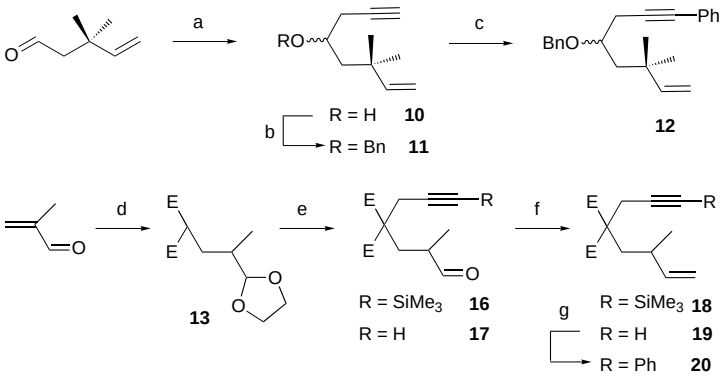
Preparation of the 1,*n*-enynes: Almost all 1,*n*-enynes were obtained by malonic synthesis. Double alkylation of the sodium derivative of the dimethylmalonate with silylpropargyl bromide to give compound **1** and then with allyl bromide, 4-bromobut-1-ene, 5-bromopent-1-ene, and *trans*-crotyl bromide furnished the enynes **3**–**6** in 86%, 98%, 90%, and 93% yields, respectively. Enynes **7**–**9** were obtained by the same procedure of double alkylations: first, with the *trans*-crotyl bromide (to give **2**) or methallylchloride[18] and then, with the mesylates derived from 3-phenylprop-2-yn-1-ol and 4,4-dimethylpent-2-yn-1-ol, generated from the alkylation of the lithium acetylide derived from the phenyl- and *tert*-butylacetylene with *para*-formaldehyde in 83% and 96% yields, respectively (Scheme 2).

The preparation of the enynes **12**, and **18**–**20**, which bear one or two substituents at the allylic position, is outlined on Scheme 3.

Condensation of the 3,3-dimethylpent-4-enal[19] with propargylic Grignard led to the alcohol **10** in quantitative yield. After protection[20] of **10**, the Pd–Cu coupling reaction[21] between **11** and iodobenzene led to the formation of the enyne **12**. Alkylation of the dimethylmalonate with 3-iodo-2-methylpropanal ethylene acetal[22] provided compound **13** in 80% yield. A second alkylation with silylpropargyl or propargyl bromide followed by a formic acid hydrolysis[23] gave the aldehydes **16** and **17**. Wittig olefination furnished the



Scheme 2. Preparation of 1,*n*-enynes **3**–**9**. a) NaH (0.6 equiv), $BrCH_2C{\equiv}CSiMe_3$, THF, RT, 70%. b) NaH (0.66 equiv), THF, 0 °C, $BrCH_2CH{=}CHCH_3$, 76%. c) NaH (1.1 equiv), THF, 0 °C, $BrCH_2CH{=}CH_2$, **3**: 86% or $Br(CH_2)_2CH{=}CH_2$, **4**: 98% or $Br(CH_2)_3CH{=}CH_2$, **5**: 90% or $BrCH_2CH{=}CHCH_3$, **6**: 93%. d) NaH (1.1 equiv), THF, $MsOCH_2C{\equiv}CPh$ or $MsOCH_2C{\equiv}Ct$Bu, **7**: 66%; **8**: 70%; **9**: 81%.



Scheme 3. Preparation of the enynes **12**, **18**, and **20**. a) $BrMgCH_2C{\equiv}CH$ (1 equiv), Et_2O, 0 °C, quant. b) NaH (1.2 equiv), THF, cat. nBu_4NI, BnBr (1.1 equiv), quant. c) 10% [$Pd(PPh_3)_4$], 15% CuI, PhI, $BuNH_2$, RT, benzene, 50%. d) 1. NaI, TMSCl, CH_3CN, RT, $HO(CH_2)_2OH$, 81%; 2. NaH, $(MeO_2C)_2CH_2$, THF, 51%. e) 1. NaH, $BrCH_2C{\equiv}CSiMe_3$, THF, RT, **14**: 75% or $BrCH_2C{\equiv}CH$, **15**: 80%; 2. HCO_2H (15 equiv), petroleum ether, overnight, **16**: quant.; **17**: 60%. f) $Ph_3P(CH_3)Br$, *n*BuLi, THF, –78 °C to RT, **18**: 75%. g) 5% $Pd(OAc)_2$, 5% CuI, 10% NEt_3, PhI (1 equiv), DMF, **20**: 37% from **17**.

enynes **18** and **19**. The coupling[20] of the latter with iodobenzene gave enyne of **20**.

Cyclization of the enynes and discussion: When the enynes **3**–**6** were exposed to a stoichiometric amount of [$CpCo(CO)_2$] in boiling xylenes under irradiation, the starting materials were consumed after 3–5 h. This led to the formation of six compounds: the 1,2-dimethylenecyclopentanes **21** and **24**, their complexed forms **22** and **25**, and the (η^4-cyclopentadiene) cobalt complexes **23** and **26**.[24] In contrast to our preliminary communication,[17] we were able to isolate the cycloadducts **27** and **28** from **3** in 62% yield, but only if the crude product is directly submitted to an oxidative treatment[25] with copper(II) chloride (Scheme 4).

Control experiments showed that enynes **3**–**6** were totally recovered in the absence of [$CpCo(CO)_2$] in boiling xylenes with or without irradiation, indicating the crucial role of the

Abstract in French: *La cycloisomérisation d'énynes 1,n catalysée par $CpCo(CO)_2$ est très efficace pour la préparation régiosélective de systèmes cycliques à cinq et six chaînons. Les facteurs gouvernant la cyclisation ont été appréhendés et nous avons mis en évidence que cette réaction mettait en jeu des réactivités différentes, mais complémentaires des complexes du cobalt(I). Par un choix judicieux de la substitution de l'ényne, il a été possible d'isoler un cyclobutène résultant d'un cobaltacyclopentène intermédiaire.*

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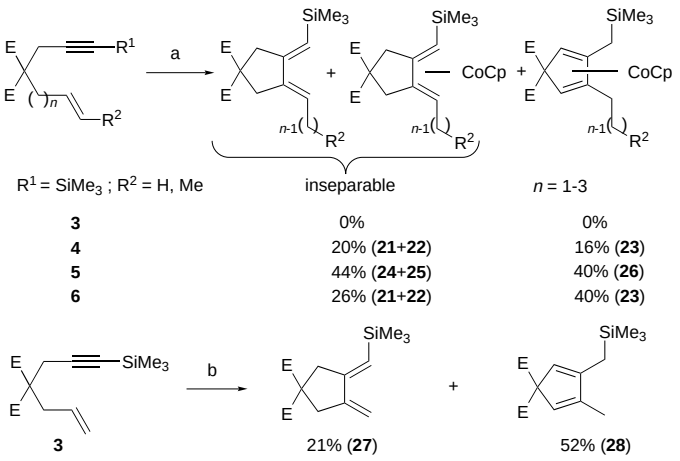
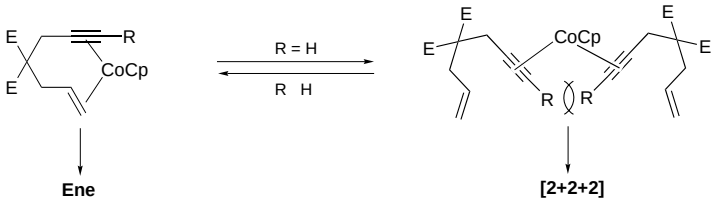


Scheme 4. Cyclization of the enynes **3**–**6**. a) $[CpCo(CO)_2]$, xylenes, *hv*, Δ. b) 1. $[CpCo(CO)_2]$, xylenes, *hv*, Δ; 2. $CuCl_2 \cdot 2\,H_2O$, MeCN.

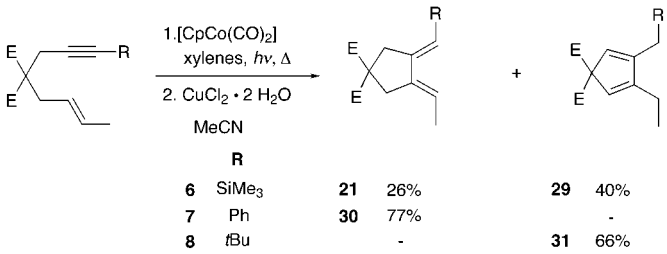
cobalt mediator. We noticed that decreasing the power and time of the irradiation, and the use of lower boiling solvents had negative effects. Thus, longer reaction times were required and, therefore, some decomposition was observed.

In addition, when the triple bond is monosubstituted ($R^1 = H$), the cyclization led to a complex mixture of cyclohexadienes and their metallated forms arising from an intermolecular [2+2+2] cyclization. Under the conditions of the reaction, the intermolecular complexation of two terminal alkynes occured in competition with the intramolecular complexation of the enyne (Scheme 5). However, by increasing the steric hindrance of the alkyne this competitive process can be completely suppressed. Thus, in harsh conditions (boiling xylenes) the use of disubstituted triple bonds allows this intramolecular complexation of the enyne and the unique course towards the ene reaction.



Scheme 5. Intra- versus intermolecular complexation of the enyne.

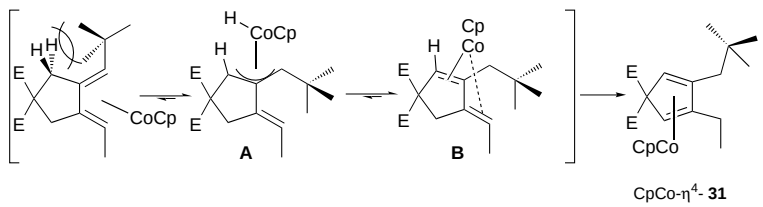
The assigned structure of **26** has been unambiguously confirmed by a single-crystal X-ray analysis.[17] Thus, whatever the length of the tether between the two unsaturated bonds, the cyclization leads only to five-membered ring compounds. The formation of these rings involves the isomerization of the terminal double bond of the starting enyne; this probably results from the oxidative formation of a cobalt η^3-allyl hydride through a C–H activation process. As far as we are aware, such intermediates with cobalt(I) are quite rare; however, they have been invoked to rationalize the migration of a dienic system.[26] Thus, we anticipated that the cyclization furnished first the *exo*-dienic complex and that the formation of the (η^4-cyclopentadiene) cobalt complexes **23** and **26** could be the result of an assisted migration of the double bonds of **22** and **25**. The cyclization of the enynes **7** and **8** contributes to the understanding of this proposal (Scheme 6).



Scheme 6. Cyclization of the enynes **6**–**8**.

Indeed, the cyclization of **7**, which bears a phenyl group on the triple bond, led exclusively to the corresponding 1,2-dimethylenecyclopentane **30** in 77% yield, whereas **8**, which has a *tert*-butyl substituent on the alkyne gave the *endo*-dienic system in 66% yield. These results showed that the migration of the double bonds is under steric control. Indeed, in all cases, the complexed cyclopentadiene *exo* is the compound resulting from the cyclization. However, when the triple bond is substituted by a bulky group such as *t*Bu, a strong allylic 1,3-strain is developed and, consequently, the formation of a cobalt η^3-allyl hydride complex **A** partially releases this strain (Scheme 7). The reductive elimination of the cobalt leads to the isomer in which one of the double bonds is in the *endo*-cyclic position. The resulting s-*trans* diene **B** was never isolated and the migration of the second double bond via a π-allyl cobalt intermediate furnished the complexed *endo*-cyclic diene CpCo-**31**. This isomerization is probably assisted by the metal and is a very fast process. Thus, the driving force of the reaction is the synergy of the release of the allylic strain and the complexation of the *endo*-cyclic s-*cis* diene with the cobalt.

In the case of the cyclization of **7**, as we already observed,[15b] the strong allylic strain of the styrene moiety evidently forces an out-of-plane rotation of the phenyl group. In addition, in the case of a metal-complexed dienic system, the influence of the conjugation of an aryl substituent is without efficiency. Therefore, the strain is minimized in the resulting system and allows the unique formation of the complexed *exo*-cyclic system, which after the oxidative treatment leads to the *exo*-diene **30** in 77% yield. Finally, the cycloadduct with a $SiMe_3$ group has an intermediate behavior.

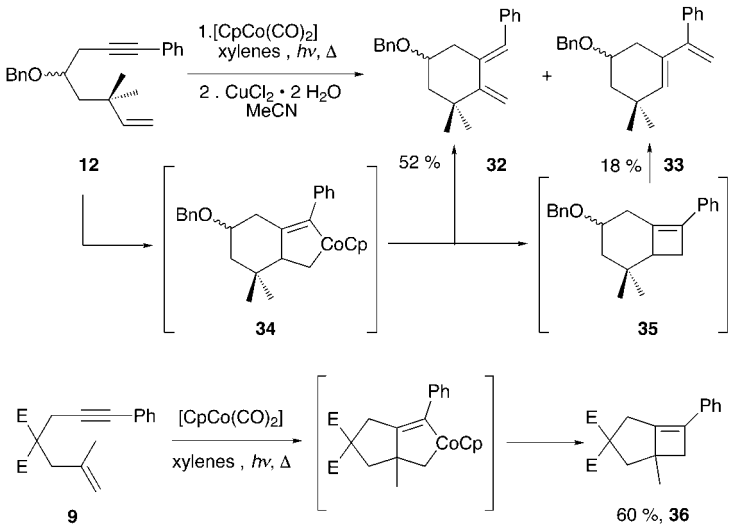


Scheme 7. Isomerization of exocyclic double bonds via a π-allyl hydride complex.

As the carbon–silicon bond is longer than a carbon–carbon bond,[27] the silylated substituent is less hindered than the *t*Bu group, the allylic strain is weaker, and the cyclization afforded a mixture of both *endo*- and *exo*-cyclic isomers.

Having speculated the existence of a π-allyl cobalt complex in the process of the cyclization, the question concerning the cyclizing moiety—π-allyl cobalt versus cobaltacyclopentene—was still open. Both pathways can be involved and be competitive. The cyclization of **3** is the only one which implicates a cobaltacyclopentene; actually, if one considers the initial formation of the π-allyl hydride intermediate with a *syn* configuration, a 6-*endo-trig* cyclization process is forbidden because it would lead to a *E*-cyclohexene derivative. The competitive 4-*exo-trig* process is totally disfavored in view of the formation of a highly constrained *exo*-methylenecyclobutane derivative.

To further probe the nature of the cobalt intermediates in this reaction, we carried out the cyclization with enyne **12** which has a disubstituted allylic position; this means that the formation of an η^3-allyl hydride is impossible. The reaction furnished, after oxidative decomplexation, two cyclohexadienes **32** and **33** (Scheme 8). The presence of the phenyl group avoids the migration of the double bond as in the case of **30**.

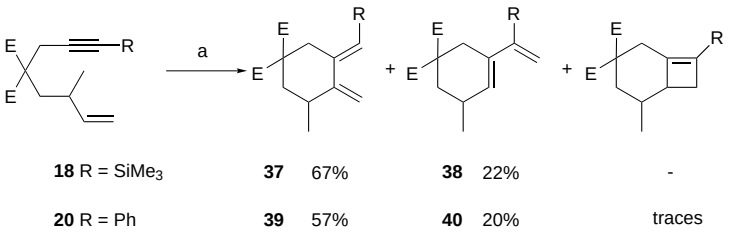


Scheme 8. Cyclization of the enynes **12** and **9**.

The cyclohexadienes **32** and **33** arose from the intermediate cobaltacyclopentene **34**. *β*-Elimination followed by a reductive elimination allowed the formation of **32**. For geometrical reasons, *β*-elimination slows down and, then, the reductive elimination is competitive affording the cyclobutene **35**, which in turn leads to **33** through an electrocyclic ring-opening reaction; nevertheless, this remains a minor process.

To probe the viability of such a pathway in presence of a cobalt(I) complex, we tried to cyclize the enyne **9**; this yielded only the cyclobutene **36**, as a very stable cycloadduct, in 60% yield. In this case, *β*-elimination is not possible and the reductive elimination becomes exclusive. Attempts to execute the reaction without cobalt mediator met with failure. No consumption of the starting material was observed even after 72 h in heating under reflux in xylenes. To our knowledge, the formation of such a cyclobutene from metallacyclopentene has never been reported with cobalt. They have been already involved, but not isolated, as intermediates in palladium-mediated cyclizations.[28]

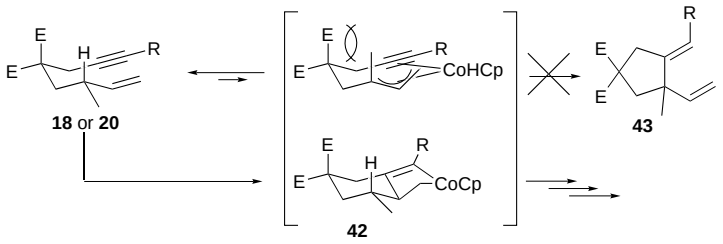
In order to more fully explore the competition of the different pathways, we checked the behavior of the enynes **18** and **20**. Similarly to **12**, two cyclohexadienes **37**/**38** and **39**/**40** were isolated in 89% and 77% yields respectively (Scheme 9). The proportion of the cyclohexadiene resulting from the opening of the cyclobutene is still around 20% in each case.



Scheme 9. Cyclization of the enynes **18** and **20**. a) 1. $[CpCo(CO)_2]$, xylenes, *hν*, Δ; 2. $CuCl_2 \cdot 2\,H_2O$, MeCN.

All these compounds are derived from the cobaltacyclopentene **42** which is the reactive intermediate of the cyclization (Scheme 10). No trace of the diene **43** was observed meaning that even the π-allyl hydride complex had been formed, it did not cyclize. Indeed, the metallo-ene reaction of an intermediate π-allyl cobalt complex would have led to a 1,4-diene bearing a tetrasubstituted diallylic position. Therefore, the latter could not undergo a *β*-elimination as the observation of **43** would have been a proof of a mechanism via a π-allyl cobalt complex. This result is in contrast to that obtained for the cyclization of **4**. The 1,7-enyne **4** is a poor ligand and its isomerization to the 1,6-enyne is faster than its cyclization. Furthermore, when the allylic position is monosubstituted, the behavior is inverted.

We anticipated that the formation of the π-allyl complex was prevented for steric reasons. The enyne **18** or **20** adopts a stable chairlike conformation, in which the methyl group is in a *pseudo*-equatorial position. The formation of the π-allyl complex would shift the methyl group to the axial position, which would in turn lead to 1,3-diaxial interactions with one of the ester groups. Therefore, the oxidative addition leads preferentially to the cobaltacyclopentene **42**, for which the



Scheme 10. Favored formation of a metallacycle versus a π-allyl complex for **18** or **20**.

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formation is more favored since the methyl stays in equatorial position.

Thus, in all cases, the cyclization proceeds via a cobaltacyclopentene, and we were unable to determine if an η^3-allyl hydride cobalt complex can undergo a metallo-ene reaction. However, for steric reasons its formation is not favored in intramolecular cyclization reactions.

Conclusion

In summary, we have shown that cobalt(I)-mediated cycloisomerization of 1,*n*-enynes is very efficient for the selective preparation of five- and six-membered ring systems in high yields. We have disclosed that this cyclization associates two different, but complementary, reactivities of the cobalt(I) complexes. One is the formation of the π-allyl cobalt hydrides which allow the isomerization of one double bond or more. Thus, several 1,*n*-enynes are in equilibrium with the 1,6-isomer which appears as the best ligand for the cobalt and which can react irreversively with the metal to give a cobaltacyclopentene. All the compounds that arise from this intermediate have been isolated. As the resulting dienes are very good ligands for cobalt(I) complexes, the reaction is stoichiometric with respect to the mediator.

Besides the reactivity of these two intermediate cobalt species, this study showed the crucial role of the complexation of the starting material. The course of the reaction is driven by the substitution of the triple bond and the degree of substitution at the allylic position. Finally, this new catalysis of the ene reaction is a further addition to the arsenal of transition metal cycloisomerization reactions.

Experimental Section

^{1}H NMR and ^{13}C NMR spectra were taken on 200 MHz Bruker AC200, 400 MHz Bruker ARX400 spectrometers. Chemical shifts are reported in ppm referenced to the residual proton resonances of the solvants. Infrared (IR) spectra were recorded by using a Perkin–Elmer 1420 spectrometer. Mass spectra (MS) were obtained on GC-MS Hewlett-Packard HP5971 apparatus. Thin-layer chromatography (TLC) was performed on Merck silica gel 60F254. Silica gel Merck Geduran SI (40–63 μm) was used for flash column chromatography by using the Still method.[29]

General procedure for the preparation of the enynes 1–8: a)A solution of dimethylmalonate (15.6 g, 118 mmol) in THF (150 mL) was added to a suspension of sodium hydride (60% in oil, 3.14 g, 78 mmol) in THF (50 mL) at 0 °C. After being stirred at room temperature for 1 h, silylpropargyl bromide (15 g, 78 mmol) or *trans*-crotyl bromide (10.53 g, 78 mmol) was added. After the solution was stirred for 1 h or overnight, the reaction mixture was quenched by a saturated solution of NH_4Cl and extracted with diethyl ether (300 mL). The organic layer was washed with brine, dried over $MgSO_4$, and concentrated. Purification by distillation or by flash chromatography (petroleum ether/ditehyl ether 80:20) led to **1** or **2** respectively.

b) The second alkylation followed the procedure given above for **1** and **2** but with the following quantities NaH (1.1 equiv); **1** or **2** (1 equiv); bromide or mesylate (1 equiv).

Methyl 2-(3-trimethylsilylprop-2-ynyl)propanedioate (1): Yield: 13.3 g, 70%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.72$ (s, 6H; OCH_3), 3.57 (t, $J =$ 7.8 Hz, 1H; $HC(CO_2Me)$), 2.77 (d, $J = 7.8$ Hz, 2H; $CH_2C{\equiv}CTMS$), 0.09 (s, 9H; $Si(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 168.4$ (2C; CO_2Me), 102.0 (C=CTMS), 87.2 (C≡CTMS), 52.7 (2C; OMe), 51.2 ($CHCO_2Me$), 19.2 (CH_2), −0.05 (3C; TMS); IR (neat): $\tilde{\nu} = 2950, 2170, 1750, 1735, 1430, 1250, 840\ cm^{-1}$.

Methyl 2-allyl-2-(3-trimethylsilylprop-2-ynyl)propanedioate (3): Yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.60$ (tdd, $J = 18.7$, 10.1, 9.1 Hz, 1H; $HC{=}CH_2$), 5.15 (d, $J = 18.7$ Hz, 1H; $=CH_2$ *cis*), 5.10 (d, $J = 10.1$ Hz, 1H; $=CH_2$ *trans*), 3.71 (s, 6H; OCH_3), 2.79 (s, 2H; $CH_2C{\equiv}C$), 2.77 (d, $J =$ 9.1 Hz, 2H; $CH_2CH{=}CH_2$), 0.11 (s, 9H; TMS); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 170.2$ (2C; CO_2Me), 131.9 ($CH{=}CH_2$), 119.8 ($=CH_2$), 101.3 (C≡C), 88.3 (C≡C), 57.2 ($C(CO_2Me)_2$), 52.7 (2C; OMe), 36.6 ($CH_2CH{=}CH_2$), 24.1 ($CH_2C{\equiv}C$), 0.0 (3C; TMS); IR (neat): $\tilde{\nu} = 2170$, 1740, 1640, 1430, 840 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{22}O_4Si$: C 59.54, H 7.85; found C 59.65, H 7.88.

Methyl 2-(but-3-enyl)-2-(3-trimethylsilylprop-2-ynyl)propanedioate (4):[18b] Yield: 98%; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.83–5.73$ (m, 1H; $HC{=}CH_2$), 5.12–4.96 (m, 2H; $=CH_2$), 3.72 (s, 6H; CO_2CH_3), 2.85 (s, 2H; $CH_2C{\equiv}C$), 2.16–2.12 (m, 2H; $CH_2CH{=}CH_2$), 1.97–1.95 (m, 2H; CH_2CH_2), 0.12 (s, 9H; TMS); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 170.6$ (2C; CO_2Me), 137.4 ($HC{=}CH_2$), 115.3 ($C{=}CH_2$), 110.2 ($C{=}CSi$), 88.3 ($C{\equiv}CSi$), 56.9 ($C(CO_2Me)_2$), 52.7 (2C; 2 OCH_3), 31.4 (CH_2), 28.4 (CH_2), 24.3 ($CH_2C{\equiv}C$), 0.01 (3C; TMS); IR (neat): $\tilde{\nu} = 2180$, 1760, 1640 cm^{-1}.

Methyl 2-(Pent-4-enyl)-2-(3-trimethylsilylprop-2-ynyl)propanedioate (5): Yield: 90%; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.83–5.59$ (m, 1H; $HC{=}CH_2$), 5.04–4.91 (m, 2H; $HC{=}CH_2$), 3.70 (s, 6H; OMe), 2.80 (s, 2H; $CH_2C{\equiv}C$), 2.10–2.04 (m, 4H; CH_2CH_2), 1.71–1.20 (m, 2H; $CH_2CH{=}CH_2$), 0.12 (s, 9H; TMS); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 170.8$ (2C; CO_2Me), 138.0 ($HC{=}CH_2$), 115.1 ($HC{=}CH_2$), 110.3 ($C{\equiv}CSi$), 89.0 ($C{\equiv}CSi$), 57.1 ($C(CO_2Me)_2$), 52.7 (2C; OMe), 33.7 (CH_2), 31.6 (CH_2), 24.2 ($CH_2CH{=}CH_2$), 23.2 ($CH_2C{\equiv}C$), 0.02 (3C; TMS); IR (neat): $\tilde{\nu} = 2180$, 1760, 1640 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{26}O_4Si$: C 61.90, H 8.44; found C 61.73, H 8.35; MS (70 eV, EI): *m*/*z* (%): 311 (55) $[M+H]^+$, 295 (60), 251 (97) $[M - C_2H_3O_2]^+$, 176 (80), 147 (80), 119 (100).

Methyl 2-[(*E*)-but-2-enyl]-2-(3-trimethylsilylprop-2-ynyl)-propanedioate (6): Yield: 93%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.57–5.39$ (m, 1H; $HC{=}CHMe$), 5.19–5.03 (m, 1H; $HC{=}CHMe$), 3.61 (s, 6H; OMe), 2.66 (s, 2H; $CH_2C{\equiv}C$), 2.61 (d, $J = 4.0$ Hz, 2H; $CH_2CH{=}CHMe$), 1.54 (d, $J =$ 6.5 Hz, 3H, $=CHMe$), 0.04 (s, 9H; TMS); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 170.4$ (2C; CO_2Me), 130.5 ($CH_2CH{=}CHMe$), 124.1 ($CH_2CH{=}CHMe$), 101.5 ($C{\equiv}CSi$), 88.1 ($C{\equiv}CSi$), 57.3 ($C(CO_2Me)_2$), 52.6 (2C; OMe), 35.4 ($CH_2CH{=}CH$), 23.9 ($CH_2C{\equiv}C$), 18.1 (CH_3), 0.0 (3C; TMS); IR (CH_2Cl_2): $\tilde{\nu} = 3040$, 2170, 1730, 1430, 1240, 960, 840 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{24}O_4Si$: C 60.78, H 8.16; found: C 60.84, H 8.17; MS (70 eV, EI): *m*/*z* (%): 296 (5) $[M]^+$, 237 (40) $[M - C_2H_3O_2]^+$, 161 (25), 133 (100), 105 (70), 89 (35), 73 (45), 50 (50).

Methyl 2-(3-phenylprop-2-ynyl)-2-[(*E*)-but-2-enyl]propanedioate (7): Yield: 66%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.40–7.37$ (m, 2H; Ph), 7.31–7.29 (m, 3H; Ph), 5.65 (dq, $J = 15.3$, 6.4 Hz, 1H; $=CHMe$), 5.31 (dtq, $J = 15.3$, 7.6, 1.5 Hz, 1H; $CH_2CH{=}CHMe$), 3.77 (s, 6H; OMe), 3.02 (s, 2H; $CH_2C{\equiv}C$), 2.81 (d, $J = 7.6$ Hz, 2H; $CH_2CH{=}CHMe$), 1.69 (dd, $J = 6.4$, 1.5 Hz, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 170.6$ (2C; CO_2Me), 131.7 (2C; Ph), 130.7 (Ph), 128.3 (2C; Ph), 128.0 (HC=CH), 124.1 (HC=CH), 123.3 (Ph), 84.5 ($C{\equiv}CPh$), 83.6 ($C{\equiv}CPh$), 57.6 ($C(CO_2Me)_2$), 52.8 (2C; OMe), 35.6 ($CH_2CH{=}CH$), 23.6 ($CH_2C{\equiv}C$), 18.2 (CH_3); IR (neat): $\tilde{\nu} = 2240$, 1730, 1595, 1570, 1480, 755, 690 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{20}O_4$: C 71.98, H 6.71; found C 71.65, H 6.37; MS (70 eV, EI): *m*/*z* (%): 301 (5) $[M+H]^+$, 241 (35) $[M - C_2H_3O_2]^+$, 225 (20), 213 (25), 181 (100), 165 (25), 145 (35), 115 (50), 77 (10).

Methyl 2-(4,4-dimethylpent-2-ynyl)-2-[(*E*)-but-2-enyl]propanedioate (8): Yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.5–5.6$ (m, 1H; $=CHMe$), 5.2–5.3 (m, 1H; $CH_2CH{=}CHMe$), 3.70 (s, 6H; OMe), 2.70 (d, $J = 2.0$ Hz, 2H; $CH_2C{\equiv}C$), 2.69 (s, 2H; $CH_2CH{=}CHMe$), 1.65 (d, $J = 5.1$ Hz, 3H; Me), 1.16 (s, 9H; *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 170.7$ (2C), 130.3 ($CH_2CH{=}CHMe$), 124.4 ($CH_2CH{=}CHMe$), 92.3 ($C{\equiv}CtBu$), 73.1 ($C{\equiv}CtBu$), 57.7 ($C(CO_2Me)_2$), 52.6 (2C; OMe), 35.4 (CH_2), 31.2 (3C; CMe_3), 27.4 (CMe_3), 22.7 (CH_2), 18.4 ($=CHMe$); IR (neat): $\tilde{\nu} = 2220$, 1730, 1430, 1350, 1200, 970, 910 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{24}O_4$: C 68.54, H 8.63; found C 68.65, H 8.36; MS (70 eV, EI): *m*/*z* (%): 281 (12) $[M+H]^+$, 220 (60), 205 (90), 161 (80), 145 (100), 133 (40), 119 (50), 105 (60), 91 (40).

Methyl 2-(2-methallyl)-2-(3-phenylprop-2-ynyl)propanedioate (9): Yield: 81%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.40–7.28$ (m, 5H; Ph), 4.96 (d, $J =$ 1.5 Hz, 1H; $=CH_2$), 4.91 (d, $J = 1.5$ Hz, 1H; $=CH_2$), 3.78 (s, 6H; OMe), 3.08

(s, 2H; CH_2C≡C), 2.93 (s, 2H; CH_2CMe=), 1.71 (s, 3H; Me); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 170.8$ (2C; CO_2Me), 140.0 (Ph), 131.7 (2C; Ph), 128.3 (2C; Ph), 128.1 (Ph), 116.5 (=CH_2), 110.7 (*C*Me=CH_2), 84.7 (*C*≡CPh), 83.9 (C≡*C*Ph), 56.9 (*C*(CO_2Me)$_2$), 52.9 (2C; OMe), 39.9 (CH_2), 23.7 (CH_2), 23.3 (Me); IR (neat): $\tilde{\nu} = 2230$, 1730, 1640, 1570, 900, 750 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{20}O_4$: C 71.98, H 6.71; found C 71.85, H 6.74; MS (70 eV, EI): *m*/*z* (%): 300 (2) $[M]^+$, 240 (17), 209 (15), 181 (100), 165 (25), 115 (35), 91 (17), 77 (5).

Preparation of the enyne 12:

6,6-Dimethyloct-1-yn-7-en-4-ol (10): 3,3-Dimethylpent-4-enal (2.24 g, 20 mmol) was added dropwise to a cooled solution (0 °C) of propargylmagnesium bromide (25 mmol) in diethyl ether (10 mL). After stirring for 45 min, the reaction mixture was hydrolyzed with a saturated solution of NH_4Cl and extracted with diethyl ether (20 mL). The organic layer was washed with brine, dried ($MgSO_4$), and concentrated. The crude residue was purified by flash chromatography (petroleum ether/AcOEt 8:2) to afford the alcohol **10** (3.21 g, quantitaive). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.85$ (dd, $J = 17.4$, 10.5 Hz, 1H; *H*C=CH_2), 4.96 (d, $J = 17.5$ Hz, 1H; HC=CH_2 *trans*), 4.93 (d, $J = 10.5$ Hz, 1H; HC=CH_2 *cis*), 3.80 (quint, $J =$ 5.6 Hz, 1H; C*H*(OH)), 2.28 (dd, $J = 5.6$, 2.6 Hz, 2H; CH_2C≡), 2.00 (t, $J =$ 2.6 Hz, 1H; ≡CH), 1.53 (d, $J = 5.6$ Hz, 2H; CH(OH)CH_2), 1.03 (s, 6H; Me); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 148.5$ (*C*H=CH_2), 111.2 (=CH_2), 81.2 (*C*≡CH), 70.6 (C≡*C*H), 67.7 (CH(OH)), 48.7 (*C*H_2C≡C), 36.1 (*C*Me_2), 28.5 (Me), 27.9 (Me), 26.6 (*C*H_2CMe_2); IR (neat): $\tilde{\nu} = 3400$, 3300, 3070, 2110, 1630, 1610, 1190, 900 cm^{-1}.

5-Benzyloxy-3,3-dimethyloct-7-yn-1-ene (11): A solution of **10** (1.46 g, 10 mmol) in THF (10 mL) followed by benzyl bromide (1.31 mL, 11 mmol) was added dropwise at room temperature to a suspension of NaH (60% in oil, 0.48 g, 12 mmol) and ammonium tetrabutyl iodide (0.37 g, 1 mmol) in THF (10 mL). After stirring for 10 h, the reaction mixture was hydrolyzed with saturated solution of NH_4Cl and extracted with diethyl ether (30 mL). The organic layer was washed with brine until pH 7 was reached, dried ($MgSO_4$), and concentrated. Purification by flash chromatography (petroleum ether/diethyl ether 9:1) gave the ether **11** (2.46 g, quantitative). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.55$–7.32 (m, 5H; Ph), 5.91 (dd, $J = 17.1$, 10.7 Hz, 1H; *H*C=CH_2), 5.05 (d, $J = 17.1$ Hz, 1H; HC=CH_2 *trans*) 4.94 (d, $J = 10.7$ Hz, 1H; HC=CH_2 *cis*), 4.6–4.4 (AB, 2H; CH_2Ph), 3.60 (quint, $J =$ 3.3 Hz, 1H; C*H*(OBn)), 2.51–2.43 (m, 2H; CH_2C≡), 2.06 (t, $J = 2.5$ Hz, 1H; ≡C*H*), 1.8–1.7 (m, 2H; CH(OBn)CH_2), 1.12 (s, 3H; Me), 1.10 (s, 3H; Me); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 148.8$ (*C*H=CH_2), 129.2 (Ph), 128.8 (2C; Ph), 128.3 (2C; Ph), 128.0 (Ph), 110.7 (=CH_2), 81.8 (*C*≡CH), 75.8 (*C*H(OBn)), 71.5 (Ph*C*H_2O), 70.4 (C≡*C*H), 47.5 (*C*H_2C≡C), 36.6 (*C*Me_2), 28.3 (Me), 27.3 (Me), 25.1 (*C*H_2CMe_2); IR (neat): $\tilde{\nu} = 3300$, 2100, 1940, 1730, 1630, 1200, 910, 730 cm^{-1}.

5-Benzyloxy-3,3-dimethyl-7-phenyloct-7-yn-1-ene (12): At room temperature, under argon, copper(I) iodide (0.016 g, 0.08 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.063 g, 0.05 mmol) were added in one go to a solution of **11** (0.133 g, 0.55 mmol) in benzene (3 mL) in the presence of *n*-butylamine (0.27 mL, 2.7 mmol) and iodobenzene (0.23 g, 1.1 mmol). After stirring overnight, the reaction mixture was diluted with diethyl ether (10 mL) and hydrolyzed with saturated solution of NH_4Cl (8 mL). The organic layer was washed with a saturated solution of $CuSO_4$ (10 mL) and brine (2×10 mL), dried ($MgSO_4$), and concentrated. Purification of the residue by flash chromatography (petroleum ether/CH_2Cl_2 70:30) afforded **12** (0.87 g, 50%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.6$–7.25 (m, 10H; Ph), 6.00 (dd, $J = 17.4$, 10.7 Hz, 1H; *H*C=CH_2), 5.05 (d, $J = 17.1$ Hz, 1H; HC=CH_2 *trans*) 4.94 (d, $J = 10.7$ Hz, 1H; HC=CH_2 *cis*), 4.86–4.51 (AB, 2H; CH_2Ph), 3.75 (tdd, $J = 7.3$, 5.1, 4.7 Hz, 1H; C*H*(OBn)), 2.84 (dd, $J =$ 16.7, 5.1 Hz, 1H; CH_2C≡), 2.66 (dd, $J = 16.7$, 7.3 Hz, 1H; CH_2C≡), 1.88 (d, $J = 5.1$ Hz, 2H; CH(OBn)CH_2), 1.21 (s, 3H; Me), 1.99 (s, 3H; Me); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 148.6$, 138.6, 131.7, 128.5, 128.4 (2C), 128.2 (2C), 128.1 (2C), 127.7 (2C), 124.0 (2C), 110.5, 87.4, 82.3, 76.2, 71.4, 36.5, 28.1, 27.1, 26.0; IR (neat): $\tilde{\nu} = 2220$, 1940, 1740, 1630, 1590, 1090, 900, 750 cm^{-1}; elemental analysis calcd (%) for $C_{23}H_{26}O$: C 86.75, H 8.23; found C 85.40, H 8.06; MS (70 eV, EI): *m*/*z* (%): 318 (2) $[M]^+$, 235 (5), 206 (10), 159 (25), 115 (30), 91 (100), 65 (10).

Preparation of the enynes 18 and 20:

Methyl 2-(2-[1,3]dioxolan-2-ylpropyl)propanedioate (13): The preparation followed the procedure described above for **1** with dimethylmalonate (2 g, 15 mmol), sodium hydride (60% in oil, 0.4 g, 10 mmol), and freshly prepared 2-(2-iodo-1-methylethyl)[1,3]dioxolane[22] (1.94 g, 8 mmol), and furnished **13** (1.27 g, 51%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.7$ (d, $J =$ 4.1 Hz, 1H; OC*H*O), 4.0–3.9 (m, 2H; CH_2O), 3.9–3.8 (m, 2H; CH_2O), 3.74 (s, 6H; OMe), 3.64 (q, $J = 6.6$ Hz, 1H; ($MeO_2C)_2$C*H*), 2.2–2.1 (m, 1H; C*H*Me), 1.86–1.7 (m, 2H;CH_2), 0.97 (d, $J = 6.6$ Hz, 3H, Me); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 170.0$ (*C*O_2Me), 169.8 (*C*O_2Me), 107.0 (O*C*O), 65.0 (*C*H_2O), 64.9 (*C*H_2O), 52.4 (2C; OMe), 49.6 (*C*H($CO_2Me)_2$), 34.7 (CH_2), 30.5, 14.3 (Me); IR ($CDCl_3$): $\tilde{\nu} = 1730$, 1430, 1160, 1110 cm^{-1}.

Preparation of aldehydes 16 and 17:

*a) Alkylation of **13**:* Dialkylated compounds **14** and **15** were prepared by using the procedure described above for compounds **3**–**6**.

Methyl 2-(2-[1,3]dioxolan-2-ylpropyl)-2-(3-trimethylsilylprop-2-ynyl)propanedioate (14): Yield: 1.32 g, 75%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 4.55 (d, $J = 3.5$ Hz, 1H; OC*H*O), 3.90–3.75 (m, 2H; CH_2O), 3.75–3.65 (m, 2H; CH_2O), 3.59 (s, 6H; OMe), 2.82–2.68 (AB, 2H; CH_2C≡C), 2.25 (dd, $J = 14.7$, 3.0 Hz, 1H; CH_2CHMe), 1.82 (dd, $J = 14.7$, 7.1 Hz, 1H; CH_2CHMe), 1.65 (m, 1H; C*H*Me), 0.82 (d, $J = 7.1$ Hz, 3H, Me), 0.0 (s, 9H; TMS); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 171.1$ (*C*O_2Me), 170.8 (*C*O_2Me), 107.3 (OCO), 101.5 (*C*≡CSi), 88.3 (C≡*C*Si), 65.2 (CH_2O), 65.1 (CH_2O), 56.7 (*C*($CO_2Me)_2$), 52.7 (2C; OMe), 33.2 (CH_2), 32.5 (*C*HMe), 24.5 (*C*H_2C≡C), 15.5 (Me), 0.0 (3C; TMS); IR ($CDCl_3$): $\tilde{\nu} = 2170$, 1730, 1260, 840 cm^{-1}.

Methyl 2-(2-[1,3]dioxolan-2-ylpropyl)-2-(prop-2-ynyl)propanedioate (15): Yield: 2.54 g, 80%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.63$ (m, 1H; OCHO), 3.91–3.89 (m, 2H; CH_2O), 3.88–3.79 (m, 2H; CH_2O), 3.68 (s, 6H; OMe), 2.79 (d, $J = 2.6$ Hz, 2H; CH_2C≡C), 2.30 (dt, $J = 14.7$, 3.2 Hz, 1H; CH_2CHMe), 1.98 (t, $J = 2.6$ Hz, 1H; C≡CH), 1.88 (ddd, $J = 14.7$, 7.3, 3.2 Hz, 1H; CH_2CHMe), 1.76–1.70 (m, 1H; C*H*Me), 0.89 (d, $J = 7.3$ Hz, 3H; Me); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 171.0$ (*C*O_2Me), 170.7 (*C*O_2Me), 107.2 (OCO), 79.0 (*C*≡CH), 71.6 (C≡*C*H), 65.2 (CH_2O), 65.1 (CH_2O), 56.4 (*C*($CO_2Me)_2$), 52.7 (OMe), 52.5 (OMe), 33.2 (CH_2), 32.5 (CHMe), 23.2 (*C*H_2C≡C), 15.4 (Me); IR ($CDCl_3$): $\tilde{\nu} = 3280$, 2120, 1730, 1200, 1110 cm^{-1}.

*b) Hydrolysis of **14** and **15**:* A solution of **14** (0.85 g, 2.3 mmol) or **15** (3.44 g, 12 mmol) and formic acid (2.5 or 6 mL, 92 or 600 mmol, 40 equiv) in petroleum ether (10 or 60 mL) was stirred at room temperature for 2 h or overnight. The reaction mixture was diluted with diethyl ether and neutralized by the addition of anhydrous K_2CO_3. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated. Purification by flash chromatography (petroleum ether/AcOEt 90:10) afforded **16** (0.765 g, quantitative) or **17** (1.7 g, 60%).

Methyl 2-(2-methyl-3-oxo-propanyl)-2-(3-trimethylsilylprop-2-ynyl)propanedioate (16): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 9.46$ (d, $J = 1.8$ Hz, 1H; C*H*O), 3.66 (s, 6H; OMe), 2.93 (s, 2H; CH_2C≡C), 2.80–2.40 (m, 2H; CH_2CHMe + C*H*Me), 1.95 (dd, $J = 14.0$, 3.2 Hz, 1H; CH_2CHMe), 1.06 (d, $J = 7.5$ Hz, 3H; Me), 0.07 (s, 9H; TMS); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 203.2 (*C*HO), 170.2 (2C; *C*O_2Me), 101.5 (*C*≡CSi), 89.5 (C≡*C*Si), 52.9 (2C; OMe), 42.4 (*C*($CO_2Me)_2$), 42.1 (CHMe) 33.1 (CH_2), 25.2 (*C*H_2C≡C), 15.5 (Me), 0.0 (3C; TMS); IR ($CDCl_3$): $\tilde{\nu} = 2830$, 2225, 1730, 1430, 1250, 840 cm^{-1}.

Methyl 2-(2-methyl-3-oxopropanyl)-2-(prop-2-ynyl)propanedioate (17): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 9.49$ (d, $J = 1.5$ Hz, 1H; CHO), 3.70 (s, 3H; OMe), 3.69 (s, 3H; OMe), 2.79–2.85 (ABX, $J = 1.5$ Hz, 2H; CH_2C≡C), 2.55–2.65 (ABX, 2H; CH_2CHMe), 2.45–2.55 (m, 1H; C*H*Me), 1.95–2.05 (m, 1H; C≡CH), 1.10 (d, $J = 7.12$ Hz, 3H; Me); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 202.8$ (CHO), 170.1 (*C*O_2Me), 170.0 (*C*O_2Me), 78.1 (*C*≡CH), 71.9 (C≡*C*H), 55.6 (*C*($CO_2Me)_2$), 52.6 (2C, OMe), 42.1 (CHMe), 32.6 (CH_2), 20.7 (*C*H_2C≡C), 15.1 (Me); IR (neat): $\tilde{\nu} = 3280$, 2250, 1730, 1430, 1280, 1200, 910, 730 cm^{-1}.

Methyl 2-(2-methylbut-3-enyl)-2-(3-trimethylsilylprop-2-ynyl)propanedioate (18): A solution of *n*-BuLi (2.1M, 1.2 mL, 2.5 mmol) in hexanes was added dropwise to a cooled (−78 °C) solution of methylphosphonium bromide (0.893 g, 2.5 mmol) in THF (10 mL) and the mixture was allowed to warm to room temperature. After being cooled again to −78 °C, a solution of aldehyde **16** (0.72 g, 2.3 mmol) in THF (20 mL) was added. The reaction mixture was stirred for 30 min at −78 °C and at room temperature overnight. The reaction mixture was partitioned between CH_2Cl_2 and saturated solution of NH_4Cl. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated. The crude residue was filtered on Celite, washed with diethyl ether, and then purified by flash chromatography (petroleum ether/diethyl ether 70:30) to afford **18** (0.534 g, 75%).

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^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 4.84$ (dd, $J = 16.5$, 1.2 Hz, 1H; $=CH_2$ *cis*), 4.76 (dd, $J = 9.9$, 1.2 Hz, 1H; $=CH_2$ *trans*), 4.48 (ddd, $J = 16.5$, 9.9, 1.9 Hz, 1H; *HC*$=CH_2$), 3.62 (s, 3H; OMe), 3.56 (s, 3H; OMe), 3.00–2.62 (AB, 2H; $CH_2C\equiv C$), 2.11–1.90 (m, 3H; CH_2CH), 0.92 (d, $J = 6.2$ Hz, 3H; Me), 0.04 (s, 9H; TMS); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 170.8$ (*C*O_2Me), 170.5 (*C*O_2Me), 143.4 (*C*H$=CH_2$), 113.5 ($=CH_2$), 101.6 (*C*$\equiv$CSi), 88.3 (C$\equiv$*C*Si), 56.4 (*C*(CO_2Me)$_2$), 52.7 (OMe), 52.4 (OMe), 38.0 (CH_2), 34.4 (CHMe), 24.2 (CH_2C$\equiv$C), 22.6 (Me), 0.0 (3C; TMS); IR ($CDCl_3$): $\tilde{\nu} = 2230$, 1730, 1640, 1235, 840 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{26}O_4Si$: C 61.90, H 8.44; found C 62.15, H 8.39; MS (70 eV, EI): *m*/*z* (%): 311 (2) $[M+H]^+$, 251 (20)$[M - C_2H_3O_2]^+$, 227 (40), 147 (100), 119 (60), 89 (42), 73 (150), 60 (30).

Methyl 2-(2-methylbut-3-enyl)-2-(3-phenylprop-2-ynyl)propanedioate (20): NEt_3 (5 mL, 38 mmol), copper(I) iodide (38 mg, 0.2 mmol), and iodobenzene were successively added to a solution of the alkyne **19** (0.915 g, 3.8 mmol) [prepared following the procedure described for **18** and engaged directly in the next step] in DMF (15 mL). Then, $Pd(OAc)_2$ (42 mg, 0.2 mmol) and PPh_3 (0.105 g, 0.4 mmol) were simultenously added. The resulting red solution was stirred for 5 h at room temperature. The mixture was diluted with diethyl ether, washed with saturated solution of NH_4Cl and brine, dried, and concentrated. Purification by flash chromatography (petroleum ether/diethyl ether 90:10) furnished **20** (0.445 g, 37%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.2-7.4$ (m, 5H; Ph), 5.58 (m, 1H; *H*C$=CH_2$), 4.94 (d, $J = 17.1$ Hz, 1H; $=CH_2$ *cis*), 4.85 (dd, $J = 10.8$, 2.8 Hz, 1H; $=CH_2$ *trans*), 3.72 (s, 3H; OMe), 3.67 (s, 3H; OMe), 2.9–3.2 (AB, 2H; $CH_2C\equiv C$), 2.1–2.4 (m, 1H; CHMe), 2.20 (s, 2H; CH_2CH), 1.02 (d, $J = 6.2$ Hz, 3H; Me); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 170.9$ (*C*O_2Me), 170.7 (*C*O_2Me), 143.4 (*C*H$=CH_2$), 131.7 (Ph), 128.2 (2C; Ph), 128.0 (2C; Ph), 123.3 (Ph), 113.6 ($=CH_2$), 84.5 (*C*$\equiv$CPh), 83.6 (C$\equiv$*C*Ph), 56.6 (*C*(CO_2Me)$_2$), 52.8 (OMe), 52.2 (OMe), 38.2 (CH_2), 34.5 (CHMe), 23.8 (CH_2C$\equiv$*C*), 22.7 (Me); IR (neat): $\tilde{\nu} = 2220$, 1740, 1640, 1690, 1480, 1430, 1280, 1200, 910, 740 cm^{-1}; elemental analysis calcd (%) for $C_{19}H_{22}O_4$: C 72.59, H 7.05; found C 72.88, H 6.74.

General procedure for the cyclization of the enynes: $[CpCo(CO)_2]$ (125 µL, 1 mmol) was added to a solution of the enyne (1 mmol) heated under reflux in xylenes (20 mL), which were first degassed by three freeze-pump-thaw cycles, and was irradiated (light from a projector lamp; ELW 300 W, 80% of its power). The reaction was monitored by TLC, and after completion the solvent was removed by vacuum transfer. The residue was purified by flash chromatography to afford the cycloadducts. In the majority cases, the *exo*cycloadducts were too unstable to run a ^{13}C NMR spectrum.

General procedure for the cyclization of the enynes followed by oxidative treatment: The cyclization was carried out following the preceeding description. The residue was diluted with acetonitrile (10 mL) and $CuCl_2 \cdot 2H_2O$ (1 equiv) was added. After being vigorously stirred for 30 min at room temperature, the mixture was purified by flash chromatography without concentration to afford the cycloadducts.

Methyl 3-ethylidene-4-trimethylsilylmethylenecyclopentan-1,1-dicarboxylate (21): Yield: 51 mg, 17% from **6**; ^{1}H NMR (400 MHz, C_6D_6): $\delta =$ 5.98 (s, 1H; $=$C*H*Si), 5.34 (q, $J = 6.9$Hz, 1H; $=$C*H*Me), 3.44 (s, 6H; OMe), 1.99 (s, 2H; CH_2), 1.64 (s, 2H; CH_2), 1.63 (d, $J = 6.9$ Hz, 3H; Me), 0.12 (s, 9H; TMS).

η^4-(Methyl 3-ethylidene-4-trimethylsilylethylenecyclopentan-1,1-dicarboxylate)-η^5-cyclopentadienyl cobalt(I) (22): Yield: 36 mg, 9% from **6**; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 4.63$ (s, 5H; Cp), 3.64 (s, 3H; OMe), 3.32 (s, 3H; OMe), 2.93–2.30 (m, 4H; CH_2 + HC$=$CC$=$CH), 1.60 (AB, 2H; CH_2), 0.55 (s, 3H; Me), 0.29 (s, 9H; TMS).

η^4-(Methyl 3-ethyl-4-trimethylsilylmethylcyclopenta-2,4-dien-1,1-dicarboxylate)-η^5-cyclopentadienyl cobalt(I) (23): Yield: 168 mg, 40% from **6**; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 4.52$ (s, 5H; Cp), 3.56 (s, 3H; OMe), 3.10 (s, 3H; OMe), 2.95 (d, $J = 2$ Hz, 1H; $=$C*H*), 2.92 (d, $J = 2$ Hz, 1H; $=$C*H*), 2.44 (m, 2H; CH_2Me), 2.14 (d, $J = 14.2$ Hz, 1H; CH_2Si), 1.22 (d, $J = 14.2$ Hz, 1H; CH_2Si), 0.93 (t, $J = 7.6$ Hz, 3H; Me), 0.08 (s, 9H; TMS); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 168.9$ (*C*O_2Me), 166.9 (*C*O_2Me), 97.2 (HC$=$*C*), 94.2 (HC$=$*C*), 80.6 (5C; Cp), 67.7 (*C*(CO_2Me)$_2$), 51.4 (OMe), 51.0 (OMe), 40.7 (HC$=$), 37.3 (HC$=$), 21.3 (CH_2), 19.5 (CH_2), 13.3 (Me), –1.6 (3C; TMS); IR (neat): $\tilde{\nu} = 3040$, 1725, 1430, 1240, 850 cm^{-1}.

Compound 24: Yield: 22%; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 5.87$ (s, 1H; $=$C*H*Si), 5.23 (m, 1H; $=$C*H*), 3.34 (s, 6H; OMe), 2.90–2.42 (m, 6H; 3 CH_2), 1.23 (t, $J = 7.2$ Hz, 3H; Me), 0.00 (s, 9H; TMS).

Compound 25: Yield: 22%; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 4.55$ (s, 5H; Cp), 3.55 (s, 3H; OMe), 3.20 (s, 3H; OMe), 2.90–2.42 (m, 6H; $=$C*H*Si, $=$C*H*, CH_2, CH_2), 1.43 (AB, 2H; CH_2), 0.98 (t, $J = 7.2$ Hz, 3H; Me), 0.19 (s, 9H; TMS).

Compound **26**: Yield: 40%; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 4.55$ (s, 5H; Cp), 3.57 (s, 3H; OMe), 3.13 (s, 3H; OMe), 3.01 (AB, 2H; HC$=$CC$=$CH), 2.64–2.28 (m, 2H; $=$CCH_2CH$_2$), 2.20 (d, $J = 14.1$ Hz, 1H; CH_2Si), 1.52–1.35 (m, 2H; $=$CCH$_2$CH_2), 1.28 (d, $J = 14.1$ Hz, 1H; CH_2Si), 0.95 (t, $J =$ 7.3 Hz, 3H; Me), 0.12 (s, 9H; TMS); ^{13}C NMR (50 MHz, C_6D_6): $\delta = 168.7$ (*C*O_2Me), 166.8 (*C*O_2Me), 95.5 (HC$=$*C*), 94.3 (HC$=$*C*), 80.7 (5C; Cp), 67.7 (*C*(CO_2Me)$_2$), 51.4 (OMe), 50.9 (OMe), 40.5 (HC$=$), 38.3 (HC$=$), 22.9 (CH_2), 19.3 (CH_2), 14.4 (Me), –1.6 (3C; TMS).

Methyl 3-ethylidene-4-trimethylsilylmethylenecyclopentan-1,1-dicarboxylate (27): The spectral data were in agreement with those described in the literature.[2e]

Methyl 3-methyl-4-trimethylsilylmethylcyclopenta-2,4-dien-1,1-dicarboxylate (28): Yield: 52%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.07$ (s, 1H; $=$CH), 5.86 (s, 1H), 3.72 (s, 6H; OMe), 1.90 (s, 3H; Me), 1.76 (s, 2H; CH_2Si), 0.04 (s, 9H; TMS); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 168.8$ (2C; *C*O_2Me), 148.4 (HC$=$*C*), 146.9 (HC$=$*C*), 127.4 ($=$*C*H), 124.0 ($=$*C*H), 52.7 (2C; OMe), 70.1 (*C*(CO_2Me)$_2$), 17.7 (CH_2Si), 14.1 (Me), –1.7 (3C; TMS); IR ($CDCl_3$): $\tilde{\nu} = 1720$, 1620, 1560, 1430, 840 cm^{-1}.

Methyl 3-ethyl-4-trimethylsilylmethylcyclopenta-2,4-dien-1,1-dicarboxylate (29): Yield: 40%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.01$ (d, $J =$ 2.0 Hz, 1H; *H*C$=$CCH$_2$Me), 5.85 (s, 1H; HC$=$), 3.69 (s, 6H; OMe), 2.17 (dq, $J = 7.6$ Hz, 2.0 Hz, 2H; CH_2Me), 1.72 (s, 2H; CH_2Si), 1.15 (t, $J = 7.6$ Hz, 3H; Me), 0.00 (s, 9H; TMS); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 170.6$ (2C; *C*O_2Me), 154.6 (HC$=$*C*), 149.8 (HC$=$*C*), 126.9 ($=$CH), 125.7 ($=$CH), 71.8 (*C*(CO_2Me)$_2$), 54.3 (2C; OMe), 22.9 (CH_2Me), 19.1 (CH_2Si), 13.4 (Me), 0.0 (3C; TMS); IR (neat): $\tilde{\nu} = 1725$, 1245, 1430, 850 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{24}O_4Si$: C 60.77, H 8.16; found C 60.71, H 7.95.

Methyl 4-ethylidene-3-phenylmethylidenecyclopentan-1,1-dicarboxylate (30): Yield: 231 mg, 77%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.5-7.2$ (m, 5H; Ph), 6.67 (d, $J = 2.0$ Hz, 1H; $=$C*H*Ph), 5.97 (dq, $J = 7.1$, 2.0 Hz, 1H; $=$C*H*Me), 3.26 (s, 2H; CH_2), 3.63 (s, 6H; OMe), 2.95 (s, 2H; CH_2), 1.71 (d, $J = 7.1$ Hz, 3H; Me); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 172.3$ (2C; *C*O_2Me), 139.2 (1C), 138.6 (1C), 138.0 (1C), 129.1 (2C; Ph), 128.9 (2C; Ph), 126.8 (Ph), 119.3 ($=$CH), 116.3 ($=$CH), 58.6 (*C*(CO_2Me)$_2$), 53.3 (2C; OMe), 40.1 (CH_2), 37.3 (CH_2), 15.4 (Me); IR (neat): $\tilde{\nu} = 1740$, 1590, 1490, 1060, 790, 730 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{20}O_4$: C 71.98, H 6.71; found C 71.74, H 6.45.

Methyl 4-ethyl-3-(2,2-dimethylpropanyl)cyclopenta-2,4-dien-1,1-dicarboxylate (31): Yield: 194 mg, 66%; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 6.67$ (s, 6H; OMe), 6.04 (d, $J = 2.2$ Hz, 1H; $=$CH), 5.96 (dt, $J = 2.2$, 2.0 Hz, 1H; *H*C$=$CCH$_2$Me), 2.18 (dq, $J = 7.3$, 2.0 Hz, 2H; CH_2Me), 2.09 (s, 2H; CH_2*t*Bu), 1.08 (t, $J = 7.3$ Hz, 3H; Me), 0.86 (s, 9H; *t*Bu); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 168.7$ (2C; *C*O_2Me), 153.7 (HC$=$*C*), 148.2 (HC$=$*C*), 129.8 ($=$CH), 124.9 ($=$CH), 70.4 (*C*(CO_2Me)$_2$), 52.9 (2C; OMe), 40.1 (*C*H_2*t*Bu), 29.6 (3C;C*Me*$_3$), 31.9; (*C*Me$_3$), 21.5 (CH_2Me), 12.0 (Me); IR (CH_2Cl_2): $\tilde{\nu} = 3050$, 1730, 1670, 1220, 830 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{24}O_4$: C 68.54, H 8.63; found C 68.49, H 8.59; MS (70 eV, EI): *m*/*z* (%): 280 (10) $[M]^+$, 265 (20), 220 (40), 205 (100), 161 (55), 145 (75, 119 (25), 105 (25).

Compounds 32 and 33: Obtained as a mixture 224 mg, (**32**/**33** 75:25); Data for **32**: Yield: 52%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.3-7.1$ (m, 10H; Ph), 6.21 (s, 1H; $=$CHPh), 4.80 (d, $J = 1.0$ Hz, 1H; $=CH_2$), 4.73 (s, 1H; $=CH_2$), 4.5–4.4 (AB, 2H; OCH_2Ph), 3.75–3.65 (m, 1H; *H*COBn), 2.74 (ddd, $J =$ 12.2, 4.1, 2.0 Hz, 1H; CH_2C$=$CHPh *eq*), 2.18 (dd, $J = 12.2$, 10.1 Hz, 1H; CH_2C$=$CHPh ax), 1.89 (ddd, $J = 12.7$, 4.1, 2.0 Hz, 1H; CH_2CMe$_2$ eq), 1.49 (dd, $J = 12.7$, 11.1 Hz, 1H; CH_2CMe$_2$ ax), 1.17 (s, 3H; Me), 1.11 (s, 3H; Me); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 151.5$ (*C*$=CH_2$), 138.5, 137.8, 136.3, 131.4 (2C; Ph), 127.5 (2C; Ph), 127.3 (2C; Ph), 126.8 (2C; Ph), 126.5, 125.4, 125.2, 109.1 ($=CH_2$), 73.7 (*C*HOBn), 69.3 (O*C*H$_2$Ph), 46.2, 44.4, 36.5 (CMe$_2$), 27.4 (Me), 26.4 (Me); Data for **33**: Yield: 18%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.1-7.3$ (m, 10H; Ph), 6.49 (s, 1H; $=$C*H*), 4.95 (s, 1H; $=$CH_2), 4.73 (s, 1H; $=$CH_2), 4.3–4.4 (AB, 2H; CH_2Ph), 3.55–3.65 (m, 1H; *CH*OBn), 3.27 (ddd, $J = 10.2$, 6.6, 2.0 Hz, 1H; $CH_2C = eq.$), 2.06 (dd, $J = 10.7$, 10.2 Hz, 1H; $CH_2C=$ ax), 1.86 (ddd, $J = 12.7$, 4.1, 2.0 Hz, 1H; CH_2CMe_2eq), 1.40 (dd, $J =$ 12.7, 11.1 Hz, 1H; CH_2CMe_2 ax), 1.18 (s, 3H; Me), 1.16 (s, 3H; Me); IR

(**32** + **33**, $CDCl_3$): $\tilde{\nu}$ = 1950, 1880, 1800, 1700, 1620, 1590, 1250, 1200, 860, 800 cm^{-1}.

Methyl 5-methyl-7-phenylbicyclo[3.2.0]hept-1(7)-ene-3,3-dicarboxylate (36): Yield: 181 mg, 60%; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.31 (m, 5H; Ph), 3.83–3.28 (AB, 2H; =CCH_2C), 3.83 (s, 3H; OMe), 3.66 (s, 3H; OMe), 2.65 (s, 2H; CH_2), 2.66–2.28 (AB, 2H; CH_2), 1.22 (s, 3H; Me); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.0 (*C*=CPh), 172.4 (*C*O_2Me), 171.8 (*C*O_2Me), 134.3 (C=*C*Ph), 130.8 (Ph), 128.8 (2C; Ph), 128.5 (2C; Ph), 128.4 (Ph), 60.7 (CMe), 53.5 (OMe), 53.4 (OMe), 52.5 (=CCH_2CMe), 48.0 (*C*(CO_2Me)$_2$), 44.6 (CH_2), 34.8 (CH_2), 26.9 (Me); IR (CH_2Cl_2): $\tilde{\nu}$ = 1730, 1650, 1480, 1430, 1240, 1020, 860 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{20}O_4$: C 71.98, H 6.71; found C 72.14, H 6.92.

Compound 37: Yield: 67%; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.62 (d, *J* = 2.0 Hz, 1H), 5.05 (s, 1H), 4.68 (s, 1H), 3.75 (s, 3H; OMe), 3.74 (s, 3H; OMe), 3.22 (dd, *J* = 14.0, 2.0 Hz, 1H), 2.60 (dd, *J* = 14.0, 2.0 Hz, 1H), 2.5–2.3 (m, 2H;), 1.59 (m, 1H;), 1.11 (d, *J* = 6.0 Hz, 3H; Me), 0.15 (s, 9H; TMS); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.0 (*C*O_2Me), 171.1 (*C*O_2Me), 155.1, 153.0, 126.1, 107.4, 55.6, 52.8 (OMe), 52.5 (OMe), 39.4, 37.7, 33.0, 18.4, 0.0 (3C; TMS); IR (CH_2Cl_2): $\tilde{\nu}$ = 1730, 1650, 1480, 1430, 1240, 1020, 860 cm^{-1}; NOE experiments were used for the assignment of the 1,3-diene moiety and the configuration of the double bond (Figure 1).

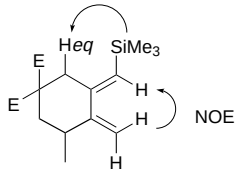

Figure 1. NOE contacts observed for **37**.

Compound 38: Yield: ^1H NMR (400 MHz, $CDCl_3$): δ = 5.57 (s, 1H), 5.07 (s, 1H), 5.00 (s, 1H), 3.73 (s, 6H), 2.54–2.37 (m, 2H), 1.72 (t, *J* = 14.0 Hz, 1H), 1.9–1.67 (AB, 2H), 1.16 (d, *J* = 6.0 Hz, 3H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.3 (2C), 138.9, 135.2, 119.5, 109.8, 55.4, 52.8, 52.7, 37.7, 31.6, 23.8,18.9, –1.0 (3C).

Compounds 39 and 40: Obtained as an inseparable mixture (**39**/**40** 74:26); Data for **39**: ^1H NMR (400 MHz, $CDCl_3$): δ = 6.27 (d, *J* = 1.0 Hz, 1H; =CHPh), 4.83 (s, 1H; =CH_2), 4.79 (d, *J* = 1.3 Hz, 1H; =CH_2), 3.76 (s, 3H; OMe), 3.74 (s, 3H; OMe), 2.90 (ABX, *J* = 13.1, 2.3 Hz, 2H), 2.20 (dd, *J* = 18.7, 2.2 Hz, 1H), 1.09 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.9 (*C*O_2Me), 171.0 (*C*O_2Me), 149.4 (C=), 139.0 (C=), 137.5 (C=), 129.1 (2C; Ph), 128.9 (2C; Ph), 126.5 (=CH), 126.0 (=CH), 109.7 (=CH_2), 57.0 (*C*(CO_2Me)$_2$), 52.7 (OMe), 52.4 (OMe), 43.5 (CH_2), 39.6 (CH_2), 35.0 (CHMe), 18.1 (Me). Data for **40**: ^1H NMR (400 MHz, $CDCl_3$): characteristic chemical shifts δ = 6.64 (d, *J* = 1.7 Hz, 1H), 5.12 (s, 1H), 4.79 (d, *J* = 1.3 Hz, 1H), 3.74 (s, 3H; OMe), 3.56 (s, 3H; OMe), 1.13 (d, *J* = 6.3 Hz, 3H; Me); IR (**39** + **40**, $CDCl_3$): $\tilde{\nu}$ = 1730, 1690, 1640, 1490, 1440, 1430, 1250, 1030 cm^{-1}.

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