Cobalt Carbonyl-Mediated Carbocyclizations of Enynes: Generation of Bicyclooctanones or Monocyclic Alkenes

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Depending on the thermolytic conditions, dicobalthexacarbonyl-complexed enynes underwent cyclizations to provide different carbocyclic frameworks. Bicyclopentanones were formed from enyne−$Co_2(CO)_6$ complexes, or from enynes that were treated with $Co_2(CO)_8$, or more effectively, with $Co_4(CO)_{12}$ in an alcoholic solvent under a H_2 or N_2 atmosphere. This transformation proceeded via a sequential cyclocarbonylation and 1,4-reduction and is the first account using the cobalt carbonyl cluster. Under these conditions a cobalt hydride was presumably generated, which mediated reduction of the enone to the saturated ketone. In contrast, thermolysis of dicobalthexacarbonyl-complexed enynes under a hydrogen atmosphere in toluene resulted in their reductive cyclization to form monocyclic alkenes in moderate yields, in addition to the bicyclopentenone product. In some cases, addition of a hydrosilane to the reaction induced a complete suppression of the bicyclopentenone formation. While the former results demonstrate a reaction that occurs after the cycloaddition, the latter depicts another example of an interruption of the normal route in the Pauson−Khand reaction pathway.

Introduction

Highly complex structural motifs have frequently been assembled via an organometallic approach using a transition metal as a template for preorganizing typically simple reactive groups. Not surprisingly, this extremely successful approach continues to be a focus of many research groups.[1] In the quest to understand more fully the mechanism of these reactions new and more elaborate transformations have been discovered.

Cobalt-based organic processes is one of the widely explored arenas in the vast array of reactions based on transition metals.[1g] Specifically, cobalt complexes are instrumental in promoting different reactivity patterns of alkynes with other unsaturated moieties.[1h] As a class of low-valent organometallic compounds, dicobalthexacarbonyl complexed alkynes, are commonly used as (a) a component in the Pauson−Khand reaction (PKR) to give 2-cyclopenten-1-ones upon reaction with alkenes,[2] (b) a protective group for alkynyl functionality,[3] and (c) a stabilizing moiety for propargylic cations in nucleophilic substitution reactions (Nicholas reaction).[4] Alkyne−$Co_2(CO)_6$ complexes that were derived from 1-(1-alkynyl)-cyclopropanols have been also reported to rearrange to 2-cyclopenten-1-ones.[5a] And most recently, an appropriately substituted (phenylthio)acetylene−cobalt carbonyl complex was shown to undergo an oxidative intramolecular [4 + 2] cycloaddition.[5b]

In the same vein, it was also shown in our laboratories that under the appropriate reaction conditions, other carbocyclic frameworks could likewise be generated from reactions of dicobalthexacarbonyl-complexed enynes. For instance, 1,3-dienes were formed in good yields from the thermolysis of dicobalthexacarbonyl complexes of unactivated 1,6- and 1,7-enynes (Scheme 1).[6] Interestingly, instead of the anticipated bicyclic enones, monocyclic enones were, in most cases, formed exclusively from the thermolyses of these complexes under an oxygenated atmosphere (air, 5% oxygen in nitrogen, or pure oxygen) (Scheme 1).[7] Meanwhile, thermolysis of the dicobalthexacarbonyl complex of 1-trimethylsilyl-6-hepten-1-ynes under an argon atmosphere was most recently noted by Gleason to generate vinyl cyclopentenes.[8] Formation of

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(2) For leading references on the Pauson−Khand reaction, see (a) Brummond, K. M.; Kent, J. L. *Tetrahedron* **2000**, *56*, 3263. (b) Schore, N. E. In *Comprehensive Organometallic Chemistry II*, Vol. 12; Abel, E. W., Stone, F. A., Wilkinson, G., Eds.; Elsevier: New York, 1995; p 703.

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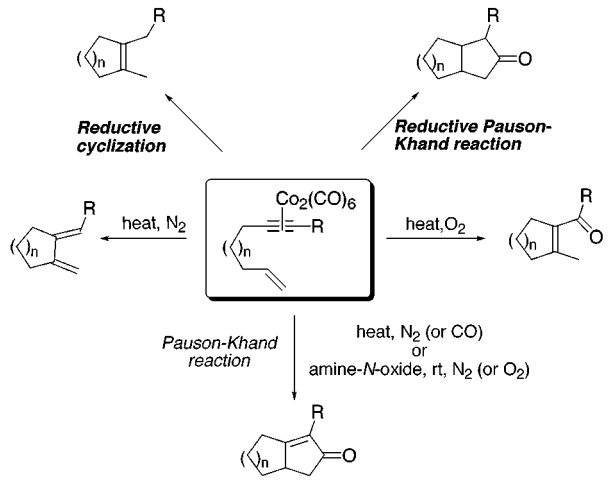
Scheme 1



other products, such as arenes, cyclopropyl ketones, and other ketonic products has also been known but has received less attention.[9] These *interrupted Pauson−Khand reactions* have resulted from a modification of reaction conditions, which has changed the normal Pauson−Khand reaction pathway, and have led to the formation of other carbocyclic frameworks. Herein, we disclose findings from our most recent studies on the carbocyclizations of enynes, via their dicobalthexacarbonyl-complexed alkyne complexes, that result in the generation of bicyclo[3.3.0]octanones (*reductive Pauson−Khand reaction*) or monocyclic alkenes (*reductive cyclization*) (Scheme 1).

Results and Discussion

A. Bicyclo[3.3.0]octanone Formation: Reductive Pauson−Khand Reaction of Enynes. Unlike the PKR, the analogous formation of cyclopentanones from alkenes and alkynes, the reductive PKR, has been studied less frequently. With the exception of a handful of detailed studies, only sporadic reports are available which describe cyclopentanone formation as a side reaction in several modified Pauson−Khand reaction procedures.[10] Unless the enone moiety formed from the PKR is needed for further elaboration, this protocol is a very straightforward approach to the bicyclo[3.3.0]octanone framework from enynes. This structure appears as a core skeleton in many natural products, such as the linearly and angularly fused triquinane sesquiterpenes.[11] Key steps in several synthetic studies and total syntheses have been based on a stepwise PK cyclization and subsequent 1,4-reduction.[12]

Isolation and identification of cyclopentanones under the PKR conditions at unusually high temperatures were first accounted by Serratosa.[13] Pauson later reported that cyclopentanones had been frequently encountered as trace byproducts in their earlier cyclization studies.[14] To date only three studies that exploited the exclusive formation of saturated ketones are available (Table 1). In a detailed study on PK cyclizations of *N*-acyl allyl propargylamines, exclusive formation of cyclopentanones was achieved by Pauson using several protocols (entry 1).[14] In these studies, related complexes of 1,7-enynes underwent the normal Pauson−Khand cyclization regardless of the reaction conditions. A systematic study was also conducted by Becker that demonstrated the exclusive formation of azabicyclic saturated ketones from enynes.[15] Pauson−Khand reactions under the Smit-Caple DSAC (dry state adsorption conditions) protocol in an inert atmosphere provided excellent yields of azabicyclo[3.3.0]octanones from *N*-protected allyl propargylamines. Standard cyclizations in air gave mixtures of ketones and enones (entry 2). The reversal of the reaction course is noteworthy in cyclizations of benzylated substrates under a N_2 atmosphere and air. This protocol was subsequently applied to the construction of the key *meso*-azabicyclo[3.3.0] intermediate for the syntheses of the antagonists SC-52490 and SC-52491 via the enantiomeric azanoadamantane.[15c] It was also reported by Periasamy that in the presence of trifluoroacetic acid, cyclopentanones were formed from the Pauson−Khand reactions of cobalt alkyne complexes with norbornene under a CO atmosphere although minor amounts of cyclopentenones were still observed (entry 3).[16] Under these reaction conditions, a cobalt carbonyl complex was generated in situ from the reduction of $CoBr_2$ by Zn metal, which then underwent reaction with the alkyne.

During our studies to explore the reactivity of $Co_4(CO)_{12}$,[17] in particular with enynes, we discovered that reaction of enyne **1** with a stoichiometric amount of $Co_4(CO)_{12}$ in 2-propanol under a H_2 atmosphere provided a good yield of a cyclopentanone **2** (eq 1). A *reductive Pauson−Khand cyclization* of enynes had presumably occurred under these conditions. It is in fact documented that $Co_4(CO)_{12}$ could be transformed into $Co_2(CO)_8$ in 2-propanol under a CO atmosphere at room temperature (eq 2).[18,19] Dicobaltoctacarbonyl is widely used as the source of cobalt carbonyl to form dicobalthexacarbonyl

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(15) (a) Becker, D. P.; Flynn, D. L. *Tetrahedron Lett.* **1993**, *34*, 2087. (b) Becker, D. P.; Flynn, D. L. *Tetrahedron* **1993**, *49*, 5047. (c) Becker, D. P.; Nosal, R.; Zabrowski, D. L.; Flynn, D. L. *Tetrahedron* **1997**, *53*, 1.

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(17) Krafft, M. E.; Boñaga, L. V. R. *Angew. Chem., Int. Ed.* **2000**, *39*, 3676.

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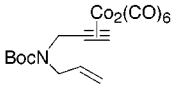
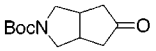
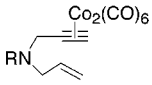
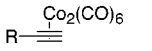
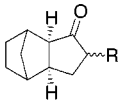
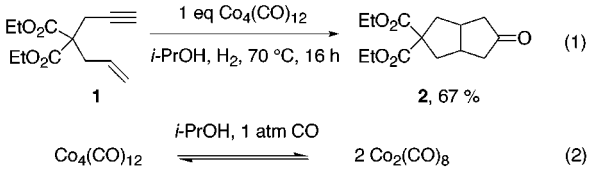
Table 1. Accounts of the Systematic Studies on the Reductive Pauson–Khand Reaction

Entry	Substrate(s)	Conditions	Products (% Yield)
1		SiO_2, 70 °C, 1.5 h	 67 %
		ultrasound, *i*-octane, 60 °C, 5 h	36 %
		uv, *i*-octane, 50 °C, 20 h (300 nm/ 85 w)	33 %
2		Merck silica gel 60, rotary evaporator, 70 °C	
			R = Boc: N_2 94 % (0:1); air 79 % (1:5)
			R = Bz: N_2 87 % (0:1); air <53 % (1:0)
3		a. 2 eq $CoBr_2$, 2.2 equiv Zn THF, CO, 25 °C, 3 h b. 2 eq. norbornene, 8 equiv TFA, 60-70 °C, 16 h	
			R = *n*-$C_{10}H_{21}$ 60 %; R = Ph 40 %

complexes with alkynes under stoichiometric and catalytic conditions.[2,20] Unless the enone moiety is needed for elaboration, this transformation should be potentially synthetically useful. Thus, we set out to investigate the scope and mechanism of this interesting reaction.



Preliminary Studies. We initiated our studies by generating ketone **2** independently. Catalytic hydrogenation of enone **3**, the Pauson–Khand cycloadduct of enyne **1**, provided an 89% yield of the saturated ketone **2** (0.03 M EtOH, catalytic Pd/C, H_2). We further investigated the origin of these unprecedented observations using $Co_4(CO)_{12}$, which subsequently led us to finding optimal conditions for the reaction (Table 2). To determine whether the observed transformation was a consequence of high dilution, reactions were carried out using different concentrations. The results indicated no significant change as a function of dilution (entries 1–3). Complete conversion of enyne **1** to bicyclopentanone **2** could be effected using a stoichiometric amount of $Co_4(CO)_{12}$ under a H_2 atmosphere (entry 1) although a slightly better yield of **2** was observed when using only 50 mol % of $Co_4(CO)_{12}$ (entry 7). Using 25 or 35 mol % of $Co_4(CO)_{12}$ led to the isolation of mixtures of enone **3** and ketone **2** (entries 5 and 6).

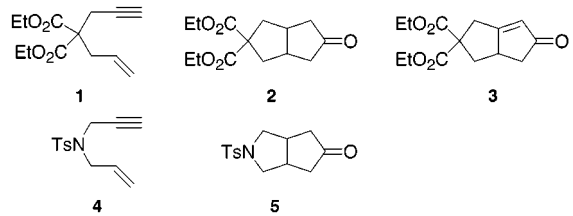
In our attempts to improve the yield using less than 1 equiv of $Co_4(CO)_{12}$, a mixture of H_2 and CO was used with the hope of regenerating and/or preserving the cobalt carbonyl complexes, which promote the desired transformations.[19] Unfortunately, no improvement was observed as is evident by the result in entry 6. Furthermore, reaction of enyne **1** furnished the bicyclopentanone in good yield under a N_2 atmosphere, albeit in slightly lower yield than the reaction under a H_2 atmosphere (entry 1 vs 4). Contrary to our initial assumption that H_2 was the reducing agent, this result suggests that the transformation does not require a H_2 atmosphere.

Interestingly, reaction of enone **3** with 1 equiv of $Co_4(CO)_{12}$ under an atmosphere of either H_2 or N_2 yielded ketone **2** in good yields (entries 9 vs 10 and 11). In addition, reactions of a mixture of enone **3** and enyne **4** with $Co_4(CO)_{12}$ under a N_2 or H_2 atmosphere gave similar yields of bicyclopentanone **5** (entries 12 and 13). Formation of the corresponding bicyclopentanones in good yields

Table 2. Preliminary Studies on the Reductive Pauson–Khand Reaction of Enynes[a]

entry	substrate	$Co_4(CO)_{12}$ (no. of equiv)	reaction atmosphere	% yield **3**	% yield **2**
1	**1**	1	H_2	–	67
2[b]	**1**	1	H_2	–	65
3[c]	**1**	1	H_2	–	56
4	**1**	1	N_2	–	56
5	**1**	0.35	H_2	42	17
6	**1**	0.25	H_2/CO	65	8
7	**1**	0.50	H_2	7	81
8	**1**	0.50	N_2	11	44
9	**3**	0.20	H_2	41	40
10	**3**	1	H_2	–	74
11	**3**	1	N_2	–	71
12	**3** + **4**	1	H_2	–	81[d]
13	**3** + **4**	1	N_2	–	91[e]

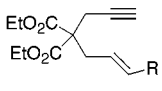
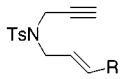
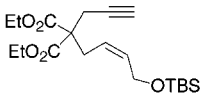
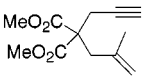
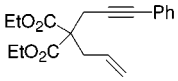
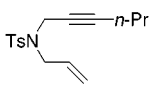
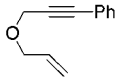
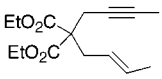
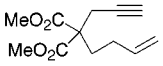
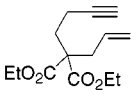
[a] Reactions were carried out at a substrate concentration of 0.005 M, unless specified otherwise, in *i*-PrOH at 70 °C. [b] 0.05 M. [c] 0.10 M. [d] 73% **5**. [e] 78% **5**.



(19) Catalytic Pauson–Khand reactions are carried out under a CO atmosphere to regenerate the active cobalt carbonyl complex. See ref 2.

(20) For references on cyclizations of these enynes using catalytic amounts of $Co_2(CO)_8$, see Krafft, M. E.; Boñaga, L. V. R.; Hirosawa, C. *J. Org. Chem.* **2001**, *66*, 3004.

Table 3. Reductive Pauson–Khand Reactions of Enynes Using $Co_4(CO)_{12}$ in *i*-PrOH[a]

Entry	Substrate	Product(s), % Yield
1 2 3		**1** R = H **2** 67 **6** Me **17** 61 **7** Ph **18** 45
4 5		**4** R = H **5** 62 **8** Me **19** 53
6		**9** → **17** + **20** (1.2 : 1) 50
7[b]		**10** → **21**, R = *i*-Pr, 9; **22**, R = Me, 43; **23**, 7
8		**11** → **24** 36
9		**12** → **25** 33
10		**13** → **26** 32
11		**14** → **27**, 39; **28**, 27
12[b]		**15** → **29**, 38; **30**, 21
13[b]		**16** → **31**, 20; **32**, 25

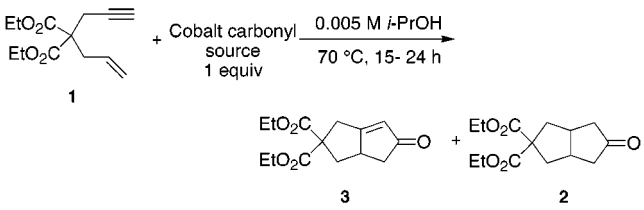
[a] Reactions were carried out at substrate concentrations of 0.005 M in 2-propanol using 1 equiv of $Co_4(CO)_{12}$, unless specified otherwise, under a H_2 atmosphere at 70 °C. Reactions were typically complete in 15–18 h. [b] 0.5 equiv of $Co_4(CO)_{12}$.

from a mixture of enyne **4** and bicyclopentenone **3** (entries 12 and 13) or from enone **3** (entry 10) alone suggested that the cobalt carbonyl species generated under these reaction conditions promoted both enyne cyclocarbonylation and enone reduction processes under a N_2 atmosphere. Thus, our preliminary studies indicated that reductive PK reactions could be best achieved using stoichiometric or substoichiometric amounts of $Co_4(CO)_{12}$ in 2-propanol at 70 °C under a H_2 atmosphere.

Scope of the Reaction. The scope and limitations of these observations are evident in the examples depicted in Table 3. As shown, good yields of the saturated carbocyclic and heterocyclic ketones were obtained from 1,6-enynes bearing a terminal alkyne (entries 1–7). Use of less than 1 equiv of $Co_4(CO)_{12}$ led to the formation of minor amounts of enone **23** from enyne **10** (entry 7) due to the incomplete conversion of the enone to the saturated ketone. Unlike substitution on the alkyne moiety (vide infra), disubstitution in the alkene did not affect the fate of the reaction. Disubstitution on the alkyne component of the 1,6-enynes provided solely the Pauson–Khand cycloadducts albeit in moderate yields (entries 8–10). This failure of the tetrasubstituted enones to undergo further 1,4-reduction has been independently reported in the early studies by several research groups.[14–16] It should be noted however, that only under the DSAC procedure developed by Becker were saturated ketones formed in significant amounts.[15] No saturated ketones were observed under our conditions as in the procedures reported by Pauson[14] and Periasamy[16] when internal alkynes were used as substrates. Disubstitution, however, in both the reactive unsaturated groups in a 1,6-enyne furnished a monocyclic alkene along with the usual bicyclic enone (entry 11).

On the contrary, reactions of 1,7-enynes yielded no saturated ketones (entries 12 and 13). In this case, monocyclic alkenes, in addition to the corresponding Pauson–Khand cycloadducts, were formed. In the studies

Table 4. Cyclizations in 2-Propanol with Different Cobalt Carbonyl Sources and Reaction Atmospheres



	% yield					
	nitrogen		hydrogen		carbon monoxide	
cobalt carbonyl source	**3**	**2**	**3**	**2**	**3**	**2**
$Co_4(CO)_{12}$	–	56	–	67	49	47
$Co_2(CO)_8$	7	48	58	21	41	17
enyne–$Co_2(CO)_6$[a]	38	60	7	67	15	52

[a] Isolated cobalt carbonyl complex of enyne **1**.

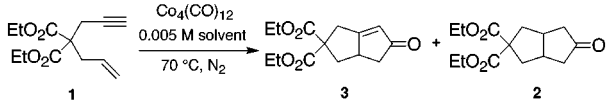
conducted by Pauson, reaction of *N*-acetyl-*N*-allyl-*N*-but-3-ynylamine provided only the corresponding bicyclopentenone under various reaction conditions (isooctane at 100 °C, 50 °C under UV light, or 60 °C under ultrasound, and the DSAC procedure).[14] Under the present reaction conditions we also noted significant formation of monocyclic alkenes, in addition to the normal Pauson–Khand reaction adduct, from reactions of 1,6-enynes bearing a disubstituted alkene and 1,7-enynes.

The hydrogenolysis observed in the cycloadducts derived from the substrates bearing a silylated allylic alcohol (entry 6) and a propargylated ether (entry 10) deserves comments. Silylated allylic alcohols are typically stable under the Pauson–Khand reaction conditions.[20,21] However, under the protic reaction conditions, elimination of the silyl ether β to the ketone (entry 6) should be a facile process, and subsequent reduction of the resulting enone would necessarily follow. Hydrogenolysis of ether linkages in bicyclopentenone adducts has been observed by Jeong[10a] and others[2] and was believed to occur as a result of formation of a hydrido cobalt complex. Finally, as shown in entry 7, transesterification might also occur as a minor reaction of ester-containing compounds under these conditions.

Mechanistic Studies. To verify whether the observed transformation is exclusive for $Co_4(CO)_{12}$, cyclizations using different sources of cobalt carbonyls under different atmospheres were likewise investigated (Table 4). The results in the table show that Pauson–Khand cycloaddition occurred in all cases in 2-propanol whether $Co_2(CO)_8$, $Co_4(CO)_{12}$, or an enyne–$Co_2(CO)_6$ complex was used, regardless of the reaction atmosphere. However, since enone reduction occurred to varying degrees when different metal carbonyl precursors were used, it is not clear whether the reducing agent corresponds to the same species in all cases. It further demonstrates that the desired transformation is best achieved using $Co_4(CO)_{12}$ under a H_2 atmosphere (cf. Table 2, entry 1 vs 4 and entry 7 vs 8). The results in Table 4 show that suppression of bicyclopentanone formation was generally observed under a CO atmosphere in reactions using all of the cobalt carbonyl sources.

We next investigated the nature of the reaction solvents and their effect on the efficacy of the reaction. Even

Table 5. Solvent Effect on $Co_4(CO)_{12}$-Mediated Cyclizations under a Nitrogen Atmosphere



			% yield	
entry	solvent	time (h)[a]	**3**	**2**
1	methanol	23.5	25	44
2	ethanol	16	33	38
3	2-propanol	15	–	56
4	*tert*-butyl alcohol	24	25	6
5	dimethyl sulfoxide[b]	13.5	–	–
6	acetonitrile	21.5	69	–
7[c]		21.5	53	–
8[d]		21.5	60	–
9	dichloroethane	16	17	–

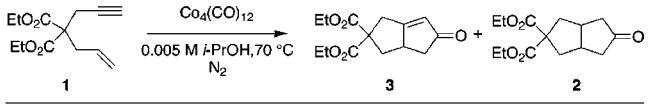
[a] In all cases the enyne was completely consumed within 1 h, as determined by TLC. [b] 72% recovered enyne. [c] H_2 atmosphere, [d] N_2 atmosphere, 5 equiv of *i*-PrOH.

though a H_2 atmosphere was apparently beneficial to these reactions, cyclizations of enyne **1** in different solvents were conducted under a N_2 atmosphere to ascertain the origin of the hydrogen atoms incorporated in the saturated ketone (Table 5). As shown, enone reduction was only observed in alcoholic solvents, where the highest efficiency was achieved in 2-propanol (entries 1–4 vs entries 5–9). A mixture of **3** and **2** was obtained from reactions conducted in primary and tertiary alcoholic solvents (entries 1, 2, and 4). Cyclizations in aprotic solvents did not provide the desired transformation but gave only the Pauson–Khand cycloadducts. Reaction in dimethyl sulfoxide (DMSO) only furnished the starting enyne **1** (entry 5). It had been observed in our studies on the catalytic Pauson–Khand reaction using $Co_4(CO)_{12}$ under a CO atmosphere that use of DMSO as the solvent is detrimental to the reaction,[17] and only the starting materials were isolated from the reaction. In contrast, the Pauson–Khand cycloadduct was the only isolated product from reactions in acetonitrile (MeCN) under a N_2 or H_2 atmosphere (entries 6 and 7, respectively), even in the presence of 5 equiv of 2-propanol (entry 8). These findings also indicate that a large excess of 2-propanol is necessary for these reactions. In 1,2-dichloroethane (DCE), a low yield of the bicyclopentenone was observed (entry 9).

At the outset of this study, we assumed the intermediacy of a bicyclopentenone in the transformation of enyne to bicyclopentanone where an in-situ 1,4-reduction of the Pauson–Khand reaction cycloadduct occurred. This is evident from the isolated bicyclopentenones and bicylopentanones (Tables 2 and 4) and independent reduction of the enone to the ketone (Table 2, entries 9–13). To further verify this assumption, a series of reactions was carried out in which the reactions were terminated at different reaction times and the products were evaluated. The results are summarized in Table 6 and indicate a direct relationship between bicyclopentanone formation and reaction time, although the yield was reduced after prolonged reaction times (entries 1, 4–7). It is noteworthy that in all cases, the enyne was completely consumed within an hour of reaction as determined by TLC, although no bicyclopentenone or dicobalthexacarbonyl complexed alkyne was isolated after workup. This result

(21) For cyclizations using catalytic amounts of $Co_4(CO)_{12}$, see ref 17 and references therein. See also (a) Belanger, D. B.; O'Mahony, D. J. R.; Livinghouse, T. *Tetrahedron Lett.* **1998**, *39*, 7637. (b) Belanger, D. B.; Livinghouse, T. *Tetrahedron Lett.* **1998**, *39*, 7641.

Table 6. Time Dependence of Bicyclopentanone Formation: Intermediacy of Bicyclopentenone



entry	time (h)[a]	% yield 3	% yield 2
1	1.5	–	13
2[b]	1.5	17	28
3[c]	1.5	5	43
4	8	–	43
5	14.5	–	48
6	15	–	56
7	24	–	37

[a] In all cases the enyne was completely consumed within 1 h. [b] After 1.5 h, the reaction mixture was cooled to room temperature, added with 5 equiv of NMO in CH_2Cl_2 and stirred at room temperature overnight. [c] After 1.5 h, the reaction mixture was cooled to room temperature, added with 5 equiv of CAN in $CHCl_2$ and stirred at room temperature overnight.

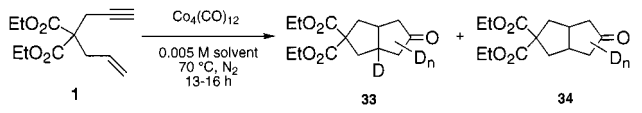
might suggest the formation of complexes or intermediates which were not isolable under standard workup conditions.

The very low yield of the bicyclopentanone isolated after 1.5 h prompted us to attempt intercepting any organocobalt species presumably still unconverted to the products (entry 1). Addition of oxidants common to the Pauson–Khand reaction, such as *N*-methylmorpholine *N*-oxide (NMO)[22] and ceric ammonium nitrate (CAN),[10a] at room temperature would presumably convert any organocobalt intermediates to organic products, possibly to the bicyclopentenone and/or bicyclopentanone. NMO has been used to remove metal species as oxidized clusters for easy workup after a typical thermal Pauson–Khand reaction,[7,23] and more extensively, to promote the Pauson–Khand reaction at ambient temperature.[22] As shown in entries 2 and 3, there was indeed a notable increase in the yields of the bicyclopentanone with the concomitant isolation of the bicyclopentenone. It was speculated that the increase in products resulted from conversion of intermediate organocobalt species to the bicyclopentenone by addition of the oxidant.

Moreover, the possibility of enyne reduction to diene prior to carbonylative cyclization was also addressed. Diethyl diallylmalonate showed no reaction when subjected to these reaction conditions, under either a H_2 or CO atmosphere, excluding the possibility of carbonylative cyclization of dienes. Over-reduction of bicyclopentanone to bicyclopentanol also did not occur, as evident from the recovery of the starting material when bicyclopentanone **2** was subjected to these reaction conditions. In addition, no bicyclopentanol has been isolated from any of these reactions.

The results obtained thus far show that an efficient enyne to saturated ketone conversion necessitates a hydroxylic solvent. Further demonstrated from these is the intermediacy of an enone that led us to speculate that its transformation to the saturated ketone proceeded via an in situ 1,4 reduction by a cobalt carbonyl hydride, "$HCo_x(CO)_y$".[24] We presumed that a cobalt carbonyl hydride, $HCo(CO)_4$, could be generated from the reaction

Table 7. Deuterium Labeling Experiments: Reactions in Deuterated Solvents



entry	solvent	% yield 3	% yield 33:34[c]
1	*i*-PrOD	64	27 (1:0)
2[a]	*i*-PrOD/HOAc	8	85 (1:7)
3[a]	*i*-PrOD/DOAc	–	83 (1:0)
4[b]	*i*-PrOH/HOAc	8	43 (1:4)
5[a]	*i*-PrOH/DOAc	–	76 (1:6)
6[a]	*i*-PrOD/*i*-PrOH	58	14 (1:3)
7[b]	*i*-PrOD/*i*-PrOH/HOAc	–	60 (1:5)
8	2(*d*)-*i*-PrOH	–[d]	–

[a] 1:1 volume ratio, [b] With 2 equiv of acetic acid, HOAc, [c] Determined from ^{1}H NMR spectroscopy, [d] 79% yield of **2**. D_n = deuterium substitution α to the carbonyl, $n = 1-4$.

of the solvent with $[Co(CO)_4]^-$ since reactions of cobalt carbonyls with alcohols have been known to generate the latter (eq 3):[25]

$$3Co_4(CO)_{12} + 24B \rightleftharpoons 4[CoB_6][Co(CO)_4]_2 + 4CO \quad (3)$$

where B = MeOH, EtOH, *i*-PrOH, *t*-BuOH.

Additionally, $HCo(CO)_4$ has long been reported by Orchin and others to promote 1,4-reductions of α,β-unsaturated ketones and aldehydes.[26] Under their conditions, $HCo(CO)_4$ was prepared independently from the dissociation of $Co_2(CO)_8$ with *N*,*N*-dimethylformamide, followed by acidification with HCl and an aqueous workup. Although the reactions in this present work proceeded under an atmosphere of either N_2 or H_2, it was found by Orchin that an atmosphere of CO was beneficial to the reaction presumably by retarding the decomposition of $HCo(CO)_4$.[26] Catalytic hydrogenations of α,β-unsaturated ketones and aldehydes have likewise been achieved using either $Co_2(CO)_8$ at 140 °C under a total pressure of 79 atm of CO and H_2[27] or $Co_2(CO)_6L_2$* (L* = chiral phosphine ligand) at 110 °C under 30 atm of H_2.[28] Our attempts, however, to independently generate $HCo(CO)_4$[29] and simulate our reaction conditions were not successful.

Thus, we proceeded to carry out a series of deuterium labeling experiments using 2-propan(ol-*d*) assuming that reaction of $Co_4(CO)_{12}$ with 2-propan(ol-*d*) could provide $DCo(CO)_4$ or a similar cobalt carbonyl deuteride complex (Table 7). We anticipated that deuterium would be eventually incorporated at the ring-fusion carbon in place

(22) Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Tetrahedron Lett.* **1990**, *31*, 5289.
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(24) (a) Periasamy, M.; Lakshmi, M.; Rao, N. Rajesh, T. *J. Organomet. Chem.* **1998**, *571*, 183. Orchin, M. *Acc. Chem. Res.* **1981**, *14*, 259. For an extensive review on $HCo(CO)_4$, see (b) Kemmitt, R. D. W.; Russell, D. R. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. A., Wilkinson, G., Eds.; Pergamon Press Ltd.: Oxford, 1982; Vol. 5, p 1.
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(27) Ucciani, E.; Lai, R.; Tanguy, L. *Compt. Rend. C.* **1975**, *281*, 877.
(28) Maux, P. L.; Massonneau, V.; Simonneaux, G. *J. Organomet. Chem.* **1985**, *285*, 101.
(29) Sternberg, H. W.; Wender, I.; Orchin, M. *Inorg. Syntheses* **1957**, *Vol. V*, 192.

of hydrogen. Cyclization of enyne **1** in 2-propan(ol-*d*) gave 64% of the Pauson−Khand adduct **3** and 27% of deuterated bicyclopentanone **33** (entry 1). This result is in marked contrast to the cyclization in 2-propanol as the solvent, in which the saturated ketone **2** was observed as the sole product of the reaction, and was obtained in higher yield (56%; Table 2, entry 4). As indicated in the ^{1}H NMR spectral data, deuterium had been incorporated α to the carbonyl and also at the ring-fusion carbon of the bicyclopentanone. Enolization at the α carbon has been observed to occur under the typical Pauson−Khand reaction conditions.[30] On the other hand, a much improved enyne to saturated ketone conversion (efficiency and yield) was noted when acetic acid (HOAc) was used as a cosolvent (*i*-PrOD: HOAc, 1:1 *v*/*v*) (entry 2 vs 1). The use of a more acidic hydrogen source in the reaction was thought to facilitate the formation of a cobalt carbonyl hydride, "$HCo_x(CO)_y$" or deuteride complex, "$DCo_x(CO)_y$". The utility of an acid under the reductive Pauson−Khand reaction conditions was first demonstrated by Periasamy.[16] It was observed that in the presence of trifluoroacetic acid, cyclopentanones were formed from the reactions of in situ generated cobalt carbonyl alkyne complexes with norbornene under a CO atmosphere.

As anticipated a 1:1 mixture of *i*-PrOD and deuterated acetic acid (DOAc) provided solely ketone **33** and in good yields (entry 3 vs 2). Yet when only 2 equiv of HOAc was used a lower yield of the saturated ketones was observed along with a small amount of the enone **3** (entry 4 vs 2). A 1:1 mixture of *i*-PrOH and DOAc, on the other hand, gave exclusively the saturated ketones in good yields (entry 5 vs 4). Interestingly, a 1:1 mixture of *i*-PrOD and *i*-PrOH furnished 58% of enone **3** and the deuterated ketones **33** and **34** (14%) (entry 6 vs 1 and Table 2, entry 4). The yields of the saturated ketones from the reactions carried out using the deuterated solvent is significantly lower than the corresponding reaction carried out in *i*-PrOH. We also observed that addition of 2 equiv of HOAc into the reaction mixture using a 1:1 mixture of *i*-PrOD and *i*-PrOH resulted in the sole formation of the saturated ketones and in higher yield (entry 7 vs 6).

Meanwhile, when (2-*d*)-2-propanol was used as the solvent, none of the Pauson−Khand cycloadduct **3** was observed, the reaction only provided saturated ketone **2** (entry 8). This further demonstrates that the hydroxylic hydrogen is the hydrogen that is being transferred to the enone and not the methinyl hydrogen of 2-propanol. This is likewise verified by the cyclization of enyne **1** using *i*-PrOTMS as the solvent, which only gave 18% yield of bicyclopentenone **3** as the sole product. The small amount of the cycloadduct obtained from this reaction possibly arose from the presence of small amounts of 2-propanol derived from the probable hydrolysis of *i*-PrOTMS. Conducting the reactions under a D_2 atmosphere further confirmed our hypothesis wherein no deuterium was detected in the saturated ketones. This result suggests that the hydrogen in the presumed cobalt carbonyl hydride complex originated from the hydroxylic solvent and not from the H_2 atmosphere under which these reactions were conducted.

The observed ratios of ketones **33** and **34** under the present reaction conditions indicate a large kinetic isotope effect in the reduction step, thus implying a highly symmetrical transition state. On the basis of the reaction conditions [$Co_4(CO)_{12}$ in hot 2-propanol, 70 °C], a hydrido cobalt carbonyl complex is the most plausible reducing agent. Mechanistic possibilities for the reduction include (a) an electron transfer that generates an enolate radical anion followed by proton abstraction from the solvent at the carbon β to the carbonyl; (b) a H atom transfer to the enone via homolytic cleavage of the M−H bond; or (c) a migratory insertion of a coordinated alkene into a Co−H bond. Hydrogen atom transfer from $HCo(CO)_4$ to alkenes[31,32] has been observed to demonstrate both inverse and normal deuterium isotope effects.[32−34] This reaction is thought to proceed by a H atom transfer from the metal to the alkene to generate a cage radical which, after cage escape, undergoes a subsequent H atom abstraction. Inverse isotope effects are observed when H atom transfer is reversible and generally result from a situation where normal kinetic isotope effects are observed for each individual reaction, but the isotope effect for the reverse reaction is larger than the forward reaction. Normal deuterium isotope effects are observed when the H atom transfer is irreversible, with the reverse reaction being slower than cage escape.[32−35] In the examples at hand, large normal deuterium isotope effects have been observed suggesting that, if H atom transfer from $HCo(CO)_4$ to the alkene is the operative mechanistic pathway, the addition must be irreversible, most likely due to the stability of the resulting radical. Conjugate reduction of enones, such as **24** (Table 3), via an electron transfer or hydrogen atom transfer should be facilitated by stabilization of the incipient radical. However, under the current conditions, the 2-phenyl-tetrasubstituted enone **24** was not reduced to any appreciable extent and only yielded small amounts of saturated ketone after prolonged reaction times. The slow reduction of the substituted enone and the large kinetic isotope effect suggest that neither electron transfer nor hydrogen atom transfer is the likely mechanistic processes.

Meanwhile, migratory insertions into metal−H bonds have also been shown to exhibit normal deuterium isotope effects.[35−37] In the current cases, reduction of the sterically hindered, tetrasubstituted alkenes did not proceed (Table 3, entries 8−11), suggesting that a migratory insertion via a symmetrical transition state, which becomes more sluggish as the alkene substitution increases, is the most plausible mechanistic route.

In conclusion, these deuterium labeling experiment studies suggest that a metal hydride species is involved in the product-determining step of the enone reduction, as indicated by the strong H/D selectivity differences. Our mechanistic studies further suggested that conversion of

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(35) Bullock, R. M. Isotope Effects in Reactions of Transition Metal Hydrides. In *Transition Metal Hydrides: Recent Advances in Theory and Experiment*; Dedieu, A., Ed.; VCH: New York, 1991.

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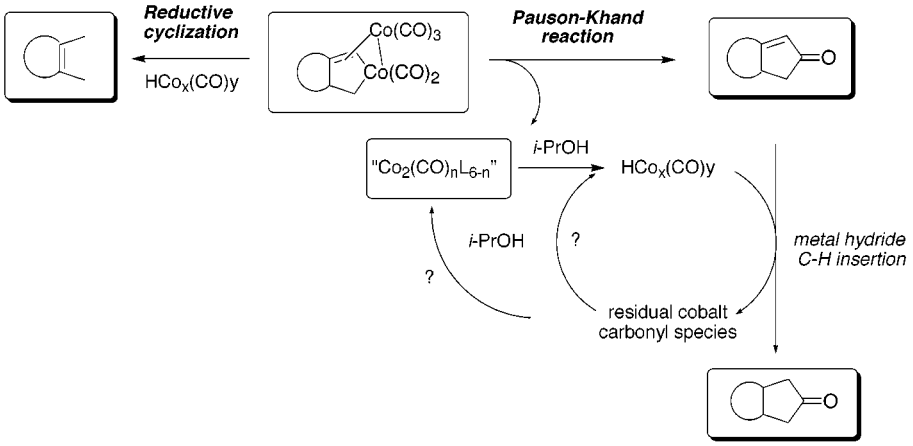
Scheme 2



the enyne to the saturated ketone proceeded via the cyclopentenone, i.e., a sequential Pauson−Khand reaction and 1,4-reduction. Mechanistic speculations on the cobalt carbonyl-mediated tandem Pauson−Khand reaction and 1,4-reduction of enynes is outlined in Scheme 2. A $Co_2(CO)_nL_{6-n}$ species could be derived from either $Co_2(CO)_8$ or $Co_4(CO)_{12}$, or from the residual cobalt carbonyl species liberated from the Pauson−Khand reaction of an enyne−$Co_2(CO)_6$ complex. Using $Co_4(CO)_{12}$, active cobalt carbonyl species were formed, possibly $Co_2(CO)_8$ or similar cobalt species, e.g., "$Co_2(CO)_nL_{6-n}$",[38] which mediate the Pauson−Khand cyclization of the enyne to the cyclopentenone.[2,39,40] Any unreacted or residual cobalt carbonyl species could further undergo dissociation in the presence of an excess of 2-propanol[25] to presumably form a cobalt carbonyl hydride, which has been known to reduce α,β-unsaturated aldehydes and ketones to saturated aldehydes and ketones.[27,28] Moreover, the cobalt carbonyl hydride is also invoked to induce reduction of the alkyl cobalt complex and account for the observed cycloalkenes (reductive cyclization, vide infra).

In comparison to previous protocols on the reductive Pauson−Khand cyclization of enynes, the present procedure is more advantageous primarily due to its simplicity and ease of operation. The evaluation is based on the (a) in-situ generation of the enyne cobalt carbonyl complex, (b) mildness of reaction conditions, (c) ease of workup, and (d) availability of the cobalt carbonyl sources ($Co_2(CO)_8$, or $Co_4(CO)_{12}$). This work has further demonstrated the utility of $Co_4(CO)_{12}$, which has been of more limited utility in organic synthesis compared to the corresponding $Co_2(CO)_8$ complex.[18]

B. Monocyclic Alkene Formation: Reductive Cyclization of Enynes. The novel transformation of enynes, as cobalt carbonyl complexes, to monocyclic alkenes described in Scheme 1 and exemplified briefly by the results in Table 3 suggest a disruption of the standard Pauson−Khand reaction pathway. A reduction of the alkyl cobalt intermediate has occurred presumably due to the presence of $HCo_x(CO)_y$ (Scheme 2). This observation is reminiscent of our previous reports that dicobalthexacarbonyl-complexed enynes could be transformed into different carbocycles when heated in toluene under different reaction conditions. Under a nitrogen atmosphere, 1,3 dienes were formed[6] whereas in an oxygenated atmosphere monocylic enones were obtained.[7] In the former case, an allylic C−H insertion was proposed to occur in the metallacyclic intermediate. Interception by molecular oxygen, presumably at the metal center, in this intermediate was proposed in the latter. Most recently, Gleason also reported the formation of vinyl cyclopentenes from the thermolysis of highly substituted enynes under an argon atmosphere.[8] Under these conditions, the alkyl cobalt carbonyl intermediate was proposed to undergo an allylic C−H activation followed by a formal *5-endo-dig* cyclization and generate vinyl cyclopentenes. These accounts show that with a careful manipulation of the reaction conditions the reactivity of the dicobalthexacarbonyl-complexed enyne could be diverted from the typical Pauson−Khand reaction pathway to generate other carbocyclic and heterocyclic frameworks.

Typically dicobalthexacarbonyl complexes of 1,6- and 1,7-enynes (or alkynes for intermolecular cyclizations with alkenes) undergo Pauson−Khand reaction to give bicyclic enones upon heating in aprotic solvents, such as isooctane,[41] 1,2-dichloroethane (DCE),[42] acetonitrile,[43] benzene,[10c,44] 1,2-dimethoxyethane (DME),[20,44] and toluene,[45] under either a CO or an inert atmosphere (N_2 or Ar). Air[10c] or an oxygenated[46] atmosphere has also been used in the Pauson−Khand cyclization of enynes. We became interested in examining the effect of a H_2 atmosphere on the thermal reaction of enynes complexed with cobalt carbonyls in toluene as the solvent, as the precedents above suggest the possibility of new reactivity patterns for this class of compounds. In fact, hydroformyl-

(38) It was reported that under 1 atm of CO at 53 °C, a hexane solution of $Co_4(CO)_{12}$ would be converted to a solution in which 50% of the cobalt content is present as $Co_2(CO)_8$ ($t_{1/2}$ = 160 days). Bor, G.; Dietler, U. K.; Pino, P. *J. Organomet. Chem.* **1978**, *154*, 301.

(39) $Co_4(CO)_{12}$ has been reported to react with alkynes to yield alkyne-$Co_4(CO)_{10}$ complexes. Under typical Pauson−Khand reaction conditions, they might be expected to decompose to alkyne−$Co_2(CO)_6$ complexes, which are requisite initial complexes for the Pauson−Khand reaction, and cobalt carbonyl complexes. Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323. See also ref 17.

(40) Thommen, M.; Verentenov, A. L.; Guideti-Grept, R.; Keese, R. *Helv. Chim. Acta* **1996**, *79*, 461.

(41) Schore, N. E.; Croudace, M. C. *J. Org. Chem.* **1981**, *46*, 5436.

(42) (a) Sugihara, T.; Yamada, M.; Ban, H.; Yamaguchi, M.; Kaneko, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2801. (b) Sugihara, T.; Yamada, M.; Yamaguchi, M.; Nishizawa, M. *Synlett* **1999**, 771.

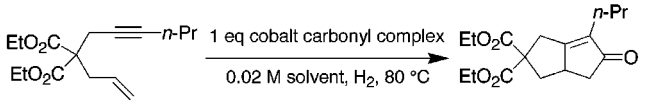
(43) Krafft, M. E.; Scott, I. L.; Romero, R. H.; Feibelmann, S.; Van Pelt, C. E. *J. Am. Chem. Soc.* **1993**, *115*, 7199.

(44) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. I. *J. Chem. Soc., Perkin Trans. 1* **1973**, 977.

(45) Billington, D. C.; Helps, I. M.; Pauson, P. L.; Thomson, W.; Willison, D. *J. Organomet. Chem.* **1988**, *354*, 233. Gordon, A.; Johnstone, C.; Kerr, W. J. *Synlett* **1995**, 1083.

(46) Stumpf, A.; Jeong, N.; Sunghee, H. *Synlett* **1997**, 205.

Table 8. Survey of Cobalt Carbonyl-Mediated Thermal Cyclizations of Enynes under a H_2 Atmosphere



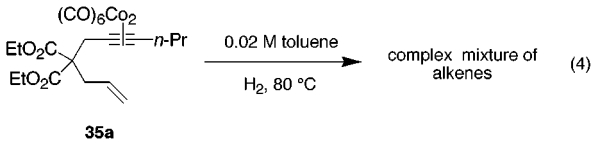
35 36

entry	cobalt carbonyl complex[a]	$CyNH_2$ (no. of equiv)	solvent	**36** (% yield)
1	"$Co_2(CO)_6$"[c]	0	toluene	—[b]
2	$Co_2(CO)_8$	0	toluene	29
3	$Co_2(CO)_8$	3	toluene	70
4	$Co_2(CO)_8$	3	DME	74
5	$Co_4(CO)_{12}$	0	toluene	—[b]
6	$Co_4(CO)_{12}$	1.5	toluene	77
7	$Co_4(CO)_{12}$	3	DME	78, 85[d]
8	$Co_4(CO)_{12}$	0	DME	16
9	$Co_4(CO)_{12}$	6	DME	82

[a] Entries 5−7: 50 mol % $Co_4(CO)_{12}$, [b] Mixture of alkene isomers, no bicyclopentenone **36**. [c] Isolated enyne−$Co_2(CO)_6$ complex. [d] 70 °C.

ations of alkenes using cobalt carbonyl complexes are generally performed under a mixture of H_2 and CO gases (synthesis gas), although at elevated pressures.[47]

Preliminary Studies. In a preliminary study, a toluene solution of the dicobalthexacarbonyl complex of enyne **35** was heated at 80 °C under a H_2 atmosphere (eq 4). The crude mixture of products seemingly showed no Pauson−Khand cycloadduct, but rather a mixture of monocyclic alkenes. The normal route to the Pauson−Khand cycloadduct had apparently been interrupted under the H_2 atmosphere. Thermolysis of an enyne−$Co_2(CO)_6$ complex in the presence of H_2 proceeded to give rise to a *reductive cyclization* to furnish monocyclic alkenes.[48] We explored these interesting and novel observations, and herein we describe the development of another interruption of the normal Pauson−Khand reaction pathway.[6−9]



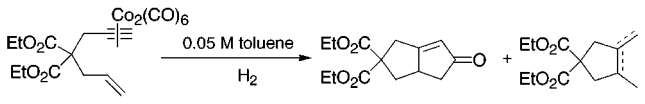
35a (4)

We initially set out to determine whether a disruption of the normal Pauson−Khand reaction pathway was general under a one atmosphere of H_2. Our preliminary results are summarized in Table 8. Interestingly, thermolysis of the dicobalthexacarbonyl complex of enyne **35** in toluene under a H_2 atmosphere yielded no Pauson−Khand cycloadduct but gave a complex mixture of alkene products (entry 1). Similar observations were noted using $Co_2(CO)_8$, although the bicyclopentenone was also obtained in low yield (entry 2). The presence of cyclohexylamine ($CyNH_2$) in the reaction significantly improved the yield of the cyclopentenone and suppressed the formation of the alkene products in toluene (entry 3) and DME (entry 4). It has been shown that cyclohexylamine is beneficial in enhancing the efficiency of thermal Pauson−Khand reactions.[20] No cyclopentenone was observed when

(47) For recent review on hydroformylations, see Ojima, I.; Tsai, C.-H.; Tzamarioudaki, M.; Bonafoux, D. *Org. React.* **2000**, *56*, 1.

(48) Enynes have also been known to undergo cycloisomerizations in the presence of other transition metal complexes. For a recent leading reference, see Cao, P.; Zhang, X. *Angew. Chem., Int. Ed.* **2000**, *39*, 4104.

Table 9. Temperature Effect on Reductive Cyclizations of Enyne−$Co_2(CO)_6$ Complexes



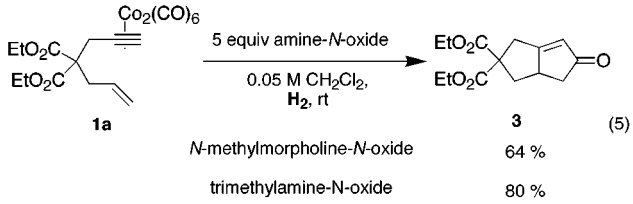
1a 3 37

temp (°C)	time (h)	% yield **3**	% yield **37** (*endo*/*exo*)[a]
60	5	16	52 (1:1)
70	5	14	34 (2:1)
80	5	16	59 (3:1)
90	2	21	6 (4:1)

[a] Ratio of *endo* and *exo* alkenes.

$Co_4(CO)_{12}$ was used in the cyclizations in toluene (entry 5) albeit it was obtained in low yield in DME in the absence of $CyNH_2$ (entry 8). Thermolysis of enyne **35** in toluene using $Co_4(CO)_{12}$ gave a mixture of alkenes instead of the bicyclopentenone (entry 5).[17] Once again, addition of cyclohexylamine resulted in good yields of cyclopentenones from reactions carried out in toluene (entry 6) and DME (entry 9). It is apparent from these results that the desired transformation could be best achieved thermally in a noncoordinating solvent, e.g., toluene, or in the absence of coordinating ligands, such as DME or cyclohexylamine. These results are encouraging because suppression of the normal Pauson−Khand reaction route is evident, albeit optimization studies needed to be pursued further.

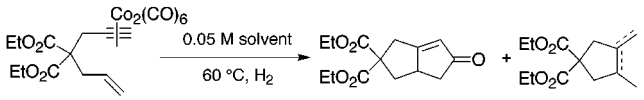
On the contrary, under the amine-*N*-oxide-promoted reaction conditions a H_2 atmosphere did not influence the fate of these reactions and cyclopentenones were obtained in good yields (eq 5). Amine-*N*-oxide promoted protocols are typically carried out under either a nitrogen, argon, or oxygen atmosphere (for Me_3NO only).[10a,22]



(5)

Optimization of Reaction Conditions. It had been demonstrated in our preliminary studies that a reductive cyclization of an enyne−$Co_2(CO)_6$ complex to generate monocyclic alkenes was favored in a noncoordinating solvent, e.g., toluene, although it appeared not to be optimal yet (Table 8). We then proceeded to determine the most appropriate temperature for these cyclizations (Table 9). In addition to incomplete suppression of cyclopentenone formation, the table shows variable yields of monocyclic alkenes from cyclizations carried out at different temperatures. The effect of different solvents on the fate of these cyclizations at 60 °C was also examined, and the results confirmed that the desired transformation could indeed be best achieved in toluene despite the formation of cyclopentenones (Table 10). The desired monoalkene products have not been observed from reactions conducted in DMSO and acetonitrile. These results evidently indicated that a mere change in the atmosphere from N_2 to H_2 at one atmosphere is insufficient to effect a complete disruption of the normal route in the Pauson−Khand reaction pathway. These

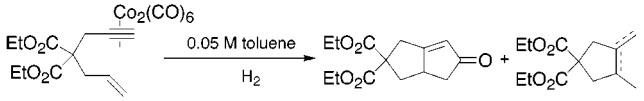
Table 10. Survey of Solvents for Reductive Cyclizations of Enyne−$Co_2(CO)_6$ Complexes



solvent	time (h)	% yield 3	% yield 37 (*endo*/*exo*)[a]
dimethyl sulfoxide	2	26[b]	–
acetonitrile	2	75	–
1,2-dimethoxyethane	2.5	36	10 (2:1)
dichloroethane	4	25	36 (1:1)
toluene	5	16	52 (1:1)
hexane	2	10	22 (2:1)

[a] Ratio of *endo* and *exo* alkenes. [b] 41% enyne **1**.

Table 11. Et_3SiH-Induced Reductive Cyclizations of Enyne−$Co_2(CO)_6$ Complexes



entry	Et_3SiH (mol %)	temp (°C)	time (h)	% yield 3	% yield 37 (*endo*/*exo*)[a]
1	10	60	1	14	30 (1:1)
2	10	60	2	27	40 (1:1)
3	**25**	**60**	**2**	–	**62 (3:1)**
4	25	60	15	–	29 (3:1)
5	50	60	2	21	6 (2:1)
6	10	80	15	–	27 (4:1)
7	25	80	15	–	41 (8:1)

[a] Ratio of *endo* to *exo* alkenes.

results further suggested that under these conditions insertion of CO into a cobalt−carbon bond in the metallacycle is presumably competitive with reduction.

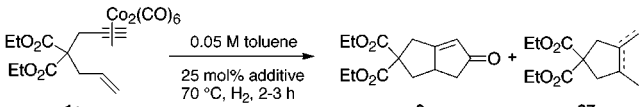
Meanwhile, the utility of triethylsilane under the thermally promoted Pauson−Khand reaction conditions has been demonstrated.[21b] It was used as an additive in PK reactions to generate, via a reductive decomplexation,[49] an active cobalt carbonyl species from an alkyne−$Co_2(CO)_6$ complex, which catalyzed efficient cyclizations of enynes under one atmosphere of CO. Encouraged by these findings, we pursued our studies using Et_3SiH as an additive with the hope that metallacycle reduction would occur at a faster rate than CO insertion, providing an interruption of the Pauson−Khand reaction pathway.[50]

The effect of triethylsilane on the thermolysis of an enyne−$Co_2(CO)_6$ complex under a H_2 atmosphere was then investigated. As shown in Table 11, a complete suppression of the Pauson−Khand reaction was indeed achieved in the thermolysis of enyne−$Co_2(CO)_6$ complex **1a** using 25 mol % of Et_3SiH at 60 °C (entry 3). A mixture of the *endo*- and *exo*-alkene isomers of **37** was obtained as the only products.

(49) Hokosawa, S.; Isobe, M. *Tetrahedron Lett.* **1998**, *39*, 2609.

(50) During these studies, it was reported by Widenhoefer that high-yielding and highly selective cycloisomerizations of functionalized 1,6-dienes to form 1,2-disubstituted cyclopentenes using catalytic amounts of cationic (π-allyl)palladium complex, $[\eta^3$-$(C_3H_5)Pd(OEt)_2PCy_3]BAr_4$] Ar=3,5-$C_6H_3(CF_3)_2$, could be achieved in the presence of Et_3SiH. Triethylsilane was presumed to facilitate the formation of the active palladium hydride species. Pei, T. Widenhoefer, R. A. *Tetrahedron Lett.* **2000**, *41*, 7597. Widenhoefer, R. A.; Perch, N. S. *Org. Lett.* **1999**, *1*, 1103.

Table 12. Survey of Additives for Reductive Cyclizations of Enyne−$Co_2(CO)_6$ Complexes



entry	additives	temp (°C)	% yield 3	% yield 37 (*endo*/*exo*)[a]
1	Et_3SiH	60	–	62 (3:1)
2	$(EtO)_3SiH$	60	–	40
3	Cl_3SiH	70	23	20
4	Ph_2MeSiH	60	–	60
5	$PhMe_2SiH$	60	–	66
6	Ph_2SiH_2	60	–	52
7	PMHS[b]	70	15	33 (2.5:1)
8	Bu_3SnH[c]	70	23	30 (1:1)
9		70	18	27 (1:1)
10	Ph_3SnH	70	10	33
11	catecholborane	70	22	26
12	9-BBN	70	21	27
13	BH_3·THF	70	15	29

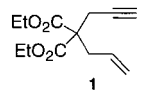
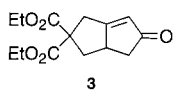
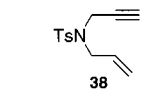
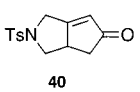
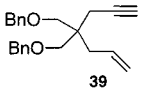
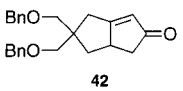
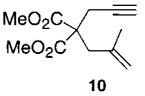
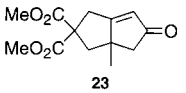
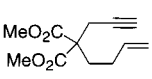
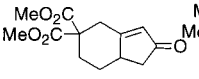
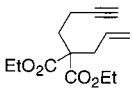
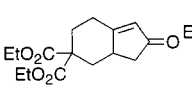
[a] The yields correspond to the isolated *endo* alkene only unless otherwise the ratio of the *endo* to *exo* alkenes is indicated. [b] PMHS = polymethyl hydrosiloxane, [c] 10 mol % Bu_3SnH.

It was further observed that the amount of the reducing agent is critical in the reaction. While a lower amount of the additive resulted in the formation of bicyclopentenone at 60 °C (entries 1 and 2), higher amounts led to a reversal of the product ratio, in addition to a decrease in yield (entry 5). The use of a stoichiometric amount of Et_3SiH effected incorporation of alkyl silane into the starting material. It was also observed that a prolonged reaction time led to reduction in yield although none of the cyclopentenone was isolated (entry 4). Furthermore, reactions conducted at 80 °C gave lower yields of the monocyclic alkenes (entries 6 and 7). It is also noteworthy that incremental addition of NMO (1 equiv × 5) to the reaction in eq 5, in the presence of 1.3 equiv of Et_3SiH, resulted in only 45% of enone **3**. Unfortunately, our attempts to carry out deuterium labeling experiments and understand the role of Et_3SiH in these reactions failed.

To further improve the efficiency in these cyclizations other hydride sources were also screened (Table 12). Among the alkylsilanes surveyed, Et_3SiH, Ph_2MeSiH, $PhMe_2SiH$, and Ph_2SiH_2 behaved equally well (entries 1, 4−6). It is noteworthy that addition of a less reactive silane, poly(methylhydrosiloxane) (PMHS) did not provide a significant difference in the reaction (entry 7 compared to Table 9, entry 2, without PHMS). Cyclization reactions with tin and boron hydrides as additives gave lower yields as did the corresponding reactions with hydrosilanes. A mixture of cyclopentenone and monocyclic alkene was observed in all of these cases (entries 3 and 7−13). In addition to Et_3SiH, PMHS, pinacolborane, $(EtO)_3SiH$, and Bu_3SnH had been used by Livinghouse in their studies on the generation of the active cobalt carbonyl species from an alkyne−$Co_2(CO)_6$ complex.[21b] Except for $(EtO)_3SiH$, which behaved as well as Et_3SiH, these additives proved less effective for catalyst generation in the studies by Livinghouse.

Scope and Limitations. The scope of these observations was then examined in the thermolyses of several 1,6- and 1,7-enyne−$Co_2(CO)_6$ complexes (Table 13). We observed modest yields in these reactions and were disappointed to discover that this observation is quite

Table 13. Reductive Cyclizations of Enyne−$Co_2(CO)_6$ Complexes

Entry	Substrate	Products	(% Yield)[b] without silane enone	without silane alkene	with silane enone	with silane alkene
1	 **1**	 **3** **37a**	16	52 (1:1)[c]	–	62 (3:1)[c]
2	 **38**	 **40** **41**	34	37	–	49
3	 **39**	 **42** **43**	–	–	11	37
4	 **10**	 **23**	50	–	–	–
5	 **15**	 **30** **29**	29	46	–	31[d]
6	 **16**	 **32** **31**	30	28	19 19 – –	23 25[d] 40[e] 37[f]

[a] Reactions were carried out at a substrate concentration of 0.05 M in toluene at 60 °C under a H_2 atmosphere, without or with 25 mol % of Et_3SiH. Enyne−$Co_2(CO_6)$ complexes were prepared from the corresponding enyne and $Co_2(CO)_8$ and were isolated prior to the reactions. Reactions were typically completed in 1−2 h. [b] Yield of *endo* alkene isomer except for entry 1 where a mixture of isomers was obtained. [c] Ratio of *endo* to *exo* alkene isomers. [d] Ph_2SiH_2. [e] Ph_2MeSiH. [f] $PhMe_2SiH$.

variable. Nevertheless, these studies demonstrated the formation of monocyclic alkenes from the reductive cyclization of enynes, via their cobalt carbonyl complexes. We speculated that the presence of Et_3SiH has induced a reduction of the alkyl cobalt complex demonstrating an interruption in the Pauson−Khand reaction pathway with the consequent formation of another carbocylic framework.

Summary and Conclusions

Thermolyses of dicobalthexacarbonyl-complexed enynes, under different reaction conditions, have resulted in the generation of different carbocyclic frameworks. Bicyclopentanones were formed from enyne−$Co_2(CO)_6$ complexes, or enynes that were treated with $Co_4(CO)_{12}$ or $Co_2(CO)_8$ in an alcoholic solvent under a H_2 or N_2 atmosphere. Although the present protocol necessitated a stoichiometric quantity of $Co_4(CO)_{12}$, this provided an extension of the utility of this tetranuclear cobalt cluster in organic transformations. We speculated that an in situ 1,4-reduction of the intermediate bicyclopentenone (from the Pauson−Khand reaction) by the metal hydride $HCo(CO)_4$, that is presumably generated from the reaction of residual cobalt carbonyl complexes with an excess of 2-propanol, is responsible for bicyclopentanone formation. It was also determined that the hydroxylic hydrogen is the hydrogen that is being transferred into the enone. In several cases monocyclic alkenes, which arise from the reduction of the alkyl cobalt carbonyl intermediate in the Pauson−Khand reaction mechanistic pathway, were also observed under these reaction conditions.

Furthermore, thermolyses of dicobalthexacarbonyl-complexed enynes under a hydrogen atmosphere led to reductive cyclizations to form monocyclic alkenes in moderate yields, in addition to the expected bicyclopentenone product. In most cases, addition of a hydrosilane in the reaction induced a complete suppression of the bicyclopentenone formation. These results demonstrate another example of an interruption of the normal route in the Pauson−Khand reaction pathway and are the first examples of such transformations using this class of complexes.

Experimental Section

Compounds **1**, **3**, **4**, **9**, **10**, **12**, **15**, **23**, **25**, **30**, **35**, **36**, **38**, and **40** have been previously synthesized and characterized.[20] All protons were assigned with the aid of ^1H NOE or decoupling experiments. Commercially available $Co_2(CO)_8$ and $Co_4(CO)_{12}$, purchased from Strem Chemicals, MA, were stored in the freezer and used without further purification.

A. Bicyclo[3.3.0]octanone Formation: Reductive Pauson−Khand Reaction of Enynes. 1. Representative Experimental Procedures. Preparation of Enyne−$Co_2(CO)_6$ Complexes. To a solution of enyne **1** (101 mg, 0.42 mmol) in petroleum ether (4.0 mL) was added $Co_2(CO)_8$ (160 mg, 0.47 mmol), and the mixture was stirred at room temperature for 1 h (or until complex formation was complete by TLC). Filtration through a short pad of Celite (eluent petroleum ether) followed by concentration under reduced pressure at room temperature gave a quantitative yield of enyne−$Co_2(CO)_6$

complex **1a**. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.98 (s, 1H, CH_2-CC*H*), 5.68 (dddd, J = 17.5, 10.1, 7.4, 7.4 Hz, 1H, C*H*=CH_2), 5.18 (dm, J = 10.1 Hz, 1H, CH=C*H*H), 5.13 (dm, J = 17.0 Hz, 1H, CH=CH*H*), 4.27 (dq, J = 14.8, 7.4 Hz, 2H, 2 CH_2O), 4.17 (dq, J = 14.1, 7.4 Hz, 2H, 2 CH_2O), 3.62 (2, 2H, CH_2CCH), 2.76 (d, J = 7.4 Hz, 2H, 2 CH_2CH=C), 1.26 (t, J = 7.4 Hz, 6H, 2 CH_3).

Typical Reductive Pauson−Khand Cyclization Protocol (for the reactions depicted in Table 3). In a round-bottom vessel equipped with a three-way stopper and a balloon of H_2, a mixture of enyne **1** (27 mg, 0.11 mmol) and $Co_4(CO)_{12}$ (65 mg, 0.11 mmol) was pumped briefly and purged three times with H_2. *i*-PrOH (23.0 mL) was then added, and the mixture was heated at 70 °C for 16 h. Upon completion of the reaction, the purple to pink mixture was cooled to room temperature, concentrated in vacuo, diluted with EtOAc, and plugged through a pad of silica gel. Subsequent removal of the solvent and purification by flash chromatography (SiO_2, 20% EtOAc in hexanes) afforded 20 mg of bicyclopentanone **2** (67% yield) as a colorless oil.

A similar general procedure was used for the reactions depicted in the following:

(a) Table 2, except for the reactions conducted under a N_2 or a CO atmosphere, which replaced the H_2 atmosphere, and the use of enyne **4**, which was mixed with enone **3** prior to evacuation and purging of the system.

(b) Table 4, where $Co_2(CO)_8$ and enyne−$Co_2(CO)_6$ complex **1a** were used as alternatives for $Co_4(CO)_{12}$ and the H_2 atmosphere was replaced with either a N_2 or a CO atmosphere.

(c) Table 5, where 2-propanol was replaced with the appropriate solvent. In entry 8, 5 equiv of 2-propanol was added as a solution in acetonitrile.

(d) Table 6, entries 1, 4−7, where the reactions were stopped at different reaction times. For entries 2 and 3, the reaction mixtures were heated at 70 °C for 1.5 h, cooled to room temperature, added with either NMO in CH_2Cl_2 (entry 2, 5 × 1 equiv) or CAN in CH_2Cl_2 (entry 2, 5 × 1 equiv), and stirred at room temperature overnight.

(e) Table 7, where 2-propanol was replaced with the appropriate premixed deuterated solvent systems and the H_2 atmosphere by N_2.

Synthesis of Bicyclopentanone 2 via Hydrogenation. To a 10 mL round-bottom flask equipped with a three-way stopper saturated with argon atmosphere were added ca. 10 mg of Pd/C and ethanol (2.5 mL). It was then pumped briefly and purged three times with a hydrogen gas. A solution of enone **3** (28 mg, 0.11 mmol) in ethanol (1.5 mL) was added, and the mixture was stirred at room temperature for 15.5 h. After concentration, the residue was washed with EtOAc (4 × 10 mL), where the combined organic layers were washed with brine, dried (Na_2SO_4), and filtered through a short plug of coarse silica gel. Concentration in vacuo and purification by flash chromatography (SiO_2, 50% EtOAc in hexanes) yielded 25 mg (89%) of bicyclopentanone **2**.

Preparation of Diethyl Diallylmalonate. To a cooled suspension (0 °C) of hexane-washed NaH (454 mg, 11.4 mmol, 60% dispersion in mineral oil) in THF (18.0 mL) was added dropwise a solution of diethyl allylmalonate (1.1 g, 5.6 mmol) in THF (7.0 mL). Ten minutes after addition was completed the bath was removed, and the reaction mixture was allowed to warm to room temperature. After being stirred for 30 min, it was cooled to 0 °C, and allyl bromide (2.0 mL, 23 mmol) was added dropwise. It was then stirred overnight with the bath warming to room temperature. After being quenched with 2 N HCl at 0 °C, the mixture was extracted with EtOAc (3 × 15 mL), and the combined organic layers were successively washed with 2 N HCl, saturated $NaHCO_3$, and brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by flash chromatography (SiO_2, 6% EtOAc in hexanes) provided 902 mg (67%) of diethyl diallylmalonate as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.65 (dddd, J = 16.8, 9.6, 7.4, 7.4 Hz, 2H, 2 C*H*C=CH_2), 5.13 (d, J = 16.1 Hz, 2H, 2 CH=C*H*H), 5.10 (d, J = 10.1 Hz, 2H, 2 CH=CH*H*), 4.19 (q, J = 7.4 Hz, 4H, 2 OCH_2), 2.64 (d, J = 7.4 Hz, 4H, 2 CH_2CH=C), 1.25 (t, J = 7.4 Hz, 6H, 2 CH_2CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.71, 132.28, 119.08, 61.14, 57.15, 36.65, 14.03. IR (cm^{-1}): 2983, 2363, 1732, 1642, 1445, 1368, 1286, 1217, 1144, 1036, 921. MS [EI, *m*/*z* (rel intensity)]: 93.1, 153.1 (100), 240.3 (M^+). Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 65.11; H, 8.35.

2. Enynes. Enyne 6:[51] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.60 (dqt, J = 15.9, 7.4, 1.7 Hz, 1H, CH_2CH=C*H*CH_3), 5.22 (dddq, J = 15.9, 7.4, 7.4, 1.7 Hz, 1H, CH_2C*H*=$CHCH_3$), 4.20 (q, J = 7.0 Hz, 4H, ($CH_3CH_2O_2C$) × 2), 2.77 (d, J = 2.9 Hz, 2H, CH_2-CCH), 2.72 (d, J = 7.4 Hz, 2H, CH_2CH=$CHCH_3$), 2.00 (t, J = 2.5 Hz, 1H, CH_2CC*H*), 1.64 (dm, J = 6.6 Hz, 3H, CH_2CH=CHCH_3), 1.24 (t, J = 7.0 Hz, 6H, ($CH_3CH_2O_2C$) × 2).

Enyne 7:[52] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.20−7.36 (m, 5H, aromatic H), 6.52 (d, J = 16.1 Hz, 1H, CH_2CH=C*H*C_6H_5), 6.02 (dt, J = 15.4, 7.4 Hz, 1H, CH_2C*H*=C_6H_5), 4.23 (q, J = 7.4 Hz, 4H, ($CH_3CH_2O_2C$) × 2), 2.96 (d, J = 6.7 Hz, 2H, CH_2CH=CHC_6H_5), 2.84 (d, J = 2.7 Hz, 2H, CH_2CCH), 2.06 (t, J = 2.7 Hz, 1H, CH_2CC*H*), 1.26 (t, J = 7.4 Hz, 6H, ($CH_3CH_2O_2C$) × 2).

Enyne 8. To a solution of *N*-allyl-4-methylbenzenesulfonamide (148 mg, 0.694 mmol) in THF/DMSO (5/2 mL) was slowly added sodium hydride (31 mg, 0.763 mmol, 60% dispersion in mineral oil). After stirring for 15 min at room temperature, propargyl bromide (0.08 mL, 0.763 mmol, 80% solution in toluene) was added dropwise. Next, the reaction mixture was heated at 70 °C and continued to stir under N_2 for 30 min. After quenching with water and removal of most of the solvent, the solution was diluted with ethyl acetate, washed twice with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification by flash column chromatography (SiO_2, 12% EtOAc in hexanes) provided 157 mg (90%) of enyne **8** as a colorless oil that later solidified upon cooling. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.72 (d, J = 8.7 Hz, 2H, aromatic H^{ortho}), 7.28 (d, J = 8.7 Hz, 2H, aromatic H^{meta}), 5.70 (dq, J = 15.4, 6.7, 1H, CH_2CH=C*H*CH_3), 5.35 (dtd, J = 14.8, 6.7, 2.0 Hz, 1H, CH_2C*H*=$CHCH_3$), 4.07 (d, J = 2.7 Hz, 2H, CH_2CCH), 3.74 (d, J = 6.7 Hz, 2H, CH_2CH=$CHCH_3$), 2.41 (s, 3H, C$H_3C_6H_4SO_2N$), 1.97 (t, J = 2.7 Hz, 1H, CH_2CC*H*), 1.68 (d, J = 6.0 Hz, 3H, CH_2CH=CHCH_3). Anal. Calcd for $C_{14}H_{17}NO_2S$: C, 63.85; H, 6.51; N, 5.32. Found: C, 63.73; H, 6.41; N, 5.37.

Enyne 11:[53] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.33−7.41 (m, 2H, aromatic H), 7.27−7.31 (m, 3H, aromatic H), 5.69 (ddt, J = 17.5, 10.1, 7.4 Hz, 1H, CH_2C*H*=CH_2), 5.21 (dm, J = 16.8 Hz, 1H, CH_2CH=CH*H*), 5.14 (dm, J = 10.1 Hz, 1H, CH_2CH=C*H*H), 4.22 (q, J = 7.4 Hz, 4H, ($CH_3CH_2O_2C$) × 2), 3.01 (s, 2H, CH_2CCC_6H_5), 2.86 (d, J = 7.4 Hz, 2H, CH_2CH=CH_2), 1.26 (t, J = 7.4 Hz, 6H, ($CH_3CH_2O_2C$) × 2).

Enyne 13:[53] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.42−7.48 (m, 2H, aromatic H), 7.28−7.34 (m, 3H, aromatic H), 5.95 (ddt, J = 17.5, 10.7, 5.4 Hz, 1H, CH_2C*H*=CH_2), 5.35 (ddt, J = 17.5, 2.0, 1.3 Hz, 1H, CH_2CH=CH*H*), 5.24 (dd, J = 10.1, 1.3 Hz, 1H, CH_2CH=C*H*H), 4.38 (s, 2H, CH_2CCC_6H_5), 4.14 (dm, J = 5.4 Hz, 2H, CH_2CH=CH_2).

Enyne 14:[54] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.57 (dqm, J = 15.4, 6.0 Hz, 1H, CH_2CH=C*H*CH_3), 5.22 (dtm, J = 14.8, 7.4, 7.4 Hz, 1H, CH_2C*H*=$CHCH_3$), 4.19 (q, J = 6.7 Hz, 4H, ($CH_3CH_2O_2C$) × 2), 2.66−2.75 (m, 4H, CH_2CCCH_3, CH_2CH=$CHCH_3$), 1.75 (t, J = 2.7 Hz, 3H, CH_2CCCH_3), 1.64 (d, J = 5.4 Hz, 3H, CH_2CH=CHCH_3), 1.23 (t, J = 6.7 Hz, 6H, (CH_3-CH_2O_2C) × 2).

Enyne 16. To a cooled solution (0 °C) of diethyl allylmalonate (4.045 g, 20.2 mmol) in THF (100 mL) was slowly added sodium hydride (877 mg, 36.6 mmol, 60% dispersion in mineral oil). Five minutes after the sodium hydride had been added, the ice bath was removed. After stirring for 30 min at room temperature, the mesylate of 3-butyn-1-ol (3.285 g, 22.2 mmol) was added dropwise. The reaction mixture was then

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(52) Chatani, N.; Morimoto, T.; Muto, T.; Murai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6049.

(53) Grossman, R. B.; Buchwald, S. L. *J. Org. Chem.* **1992**, *57*, 5803.

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heated at reflux under N_2 for 24 h. After being quenched with water, most of the solvent was removed under vacuo. The reaction mixture was then diluted with diethyl ether, washed twice with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification by flash column chromatography (SiO_2, 5% EtOAc in hexanes) followed by distillation under vacuo (to remove remainder of diethyl allylmalonate) and a second chromatography afforded 1.734 g (34%) of enyne **16** as a colorless oil. ^{1}H NMR (C_6D_6, 500 MHz): δ 5.66 (ddt, J = 17.1, 10.3, 7.3 Hz, 1H, CH_2CH=CH_2), 4.96 (obscured ddt, J = 17.1, 2.0, 1.5 Hz, 1H, CH_2CH=CHH), 4.93 (obscured dm, J = 9.8 Hz, 1H, CH_2CH=CHH), 3.90 (ABq, J_{AB} = 16.6, J = 7.0 Hz, 2H, $CH_3CH_2O_2C$), 3.88 (ABq, J_{AB} = 16.6, J = 7.0 Hz, 2H, $CH_3CH_2O_2C$), 2.75 (d, J = 7.3 Hz, 2H, CH_2CH=CH_2), 2.34−2.40 (m, 2H, CH_2CH_2CCH), 2.22 (td, J = 8.8, 2.4 Hz, 2H, CH_2CH_2CCH), 1.73 (t, J = 2.4 Hz, 1H, CH_2CH_2CCH), 0.86 (t, J = 7.3 Hz, 6H, ($CH_3CH_2O_2C$) × 2). Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.61; H, 8.08.

3. Cycloadducts. Bicyclopentanone 2: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.21 (q, J = 7.1 Hz, 2H, OCH_2), 4.18 (q, J = 7.1 Hz, 2H, OCH_2), 2.83 (br m, 2H, 2 CH_2CHCH_2), 2.67 (ABd, J_{AB} = 14.1, J = 8.1 Hz, 2H, 2 $CHCHHC(CO_2Et)_2$), 2.48 (ABd, J_{AB} = 19.5, J = 9.4 Hz, 2H, 2 $CHHC$=O), 2.12 (ABd, J_{AB} = 19.5, J = 4.0 Hz, 2H, 2 $CHHC$=O), 2.00 (ABd, J_{AB} = 14.5, J = 7.1 Hz, 2H, 2 $CHCHHC(CO_2Et)_2$), 1.26 (t, J = 7.1 Hz, 3H, CH_2CH_3), 1.24 (t, J = 7.1 Hz, 3H, CH_2CH_3). Anal. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.42; H, 7.46.

Bicyclopentanone 5: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.71 (d, J = 8.1 Hz, 2H, 2 aromatic H), 7.35 (d, J = 8.1 Hz, 2H, 2 aromatic H), 3.46 (dd, J = 10.1, 7.4 Hz, 2H, 2 $CHHC$=O), 3.08 (dd, J = 10.7, 4.3 Hz, 2H, 2 $CHHC$=O), 2.88 (br m, 2H, 2 CH_2CHCH_2), 2.45 (s, 3H, CH_3), 2.43 (obscured dd, J = 19.5, 8.7 Hz, 2H, 2 $NCHH$), 2.01 (dd, J = 19.5, 4.8 Hz, 2H, 2 $NCHH$). MS [CI, m/z (rel intensity)]: 280.2 (M^+ + 1, 100). Anal. Calcd for $C_{14}H_{17}O_3NS$: C, 60.19; H, 6.13. Found: C, 60.03; H, 6.23.

Bicyclopentanone 17: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.20 (q, J = 7.1 Hz, 2H, $CH_3CH_2O_2C$), 4.17 (q, J = 7.1 Hz, 2H, $CH_3CH_2O_2C$), 2.74 (obscured m, 1H, CH_2CHCH_2C=O), 2.70 (obscured dd, J = 14.2, 8.0 Hz, 1H, $CHHCHCHCH_3C$=O), 2.66 (obscured dd, J = 13.6, 7.7 Hz, 1H, $CHHCHCH_2C$=O), 2.44 (dd, J = 19.1, 8.9 Hz, 1H, $CH_2CHCHHC$=O), 2.32 (dddd, J = 8.0, 7.4, 4.9, 2.8 Hz, 1H, $CH_2CHCHCH_3C$=O), 2.23 (dd, J = 19.4, 3.1 Hz, 1H, $CH_2CHCHHC$=O), 2.16 (dd, J = 14.2, 4.9 Hz, 1H, $CHHCHCHCH_3C$=O), 2.02 (dq, J = 7.4, 7.4 Hz, 1H, $CH_2CHCHCH_3C$=O), 1.95 (dd, J = 13.2, 9.9 Hz, 1H, $CHHCH-CH_2C$=O), 1.26 (t, J = 7.1 Hz, 3H, $CH_3CH_2O_2C$), 1.24 (t, J = 7.1 Hz, 3H, $CH_3CH_2O_2C$), 1.08 (d, J = 7.1 Hz, 3H, $CH_2-CHCHCH_3C$=O). Anal. Calcd for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85. Found: C, 63.93; H, 7.87.

Bicyclopentanone 18: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.33 (dd, J = 7.8, 7.1 Hz, 2H, aromatic H^{meta}), 7.25 (t, J = 7.1 Hz, 1H, aromatic H^{para}), 7.14 (d, J = 7.8 Hz, 2H, aromatic H^{ortho}), 4.21 (q, J = 7.0 Hz, 4H, 2 $CH_3CH_2O_2C$), 3.26 (d, J = 7.3 Hz, 1H, $CH_2CHCHC_6H_5C$=O), 2.88−2.92 (m, 2H, CH_2CHCH_2C=O, $CH_2CHCHC_6H_5C$=O), 2.79 (dd, J = 13.7, 6.8 Hz, 1H, $CH_2-CHCHHC$=O), 2.67 (dd, J = 15.1, 6.8 Hz, 1H, $CHHCHCH_2C$=O), 2.63 (dd, J = 18.6, 7.8 Hz, 1H, $CHHCHCHC_6H_5C$=O), 2.39 (d, J = 18.6 Hz, 1H, $CHHCHCHC_6H_5C$=O), 2.32 (dd, J = 14.6, 3.4 Hz, 1H, $CHHCHCH_2C$=O), 2.06 (dd, J = 13.2, 8.3 Hz, 1H, $CH_2CHCHHC$=O), 1.26 (t, J = 7.0 Hz, 3H, $CH_3CH_2O_2C$), 1.25 (t, J = 7.0 Hz, 3H, $CH_3CH_2O_2C$). Anal. Calcd for $C_{20}H_{24}O_5$: C, 69.75; H, 7.02. Found: C, 69.55; H, 6.97.

Bicyclopentanone 19: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.71 (d, J = 8.0 Hz, 2H, aromatic H^{ortho}), 7.34 (d, J = 8.0 Hz, 2H, aromatic H^{meta}), 3.48 (dd, J = 10.1, 8.7 Hz, 1H, $NCHHCH-CH_2C$=O), 3.36 (dd, J = 10.3, 6.0 Hz, 1H, $NCHHCHCHCH_3C$=O), 3.33 (dd, J = 10.3, 2.7 Hz, 1H, $NCHHCHCHCH_3C$=O), 3.02 (dd, J = 10.1, 6.7 Hz, 1H, $NCHHCHCH_2C$=O), 2.81 (ddddd, J = 8.7, 8.7, 6.7, 3.9, 3.4 Hz 1H, NCH_2CHCH_2C=O), 2.44 (s, 3H, $CH_3C_6H_4SO_2N$), 2.40 (dd, J = 19.0, 8.7 Hz, 1H, $NCH_2CHCHHC$=O), 2.36 (dddd, J = 7.3, 6.0, 3.9, 2.7 Hz, 1H, $NCH_2CHCHCH_3C$=O), 2.20 (dd, J = 19.3, 3.4 Hz, 1H, $NCH_2CHCHHC$=O), 1.87 (dq, J = 7.3, 7.3 Hz, 1H, $NCH_2-CHCHCH_3C$=O), 1.04 (d, J = 7.1 Hz, 3H, $NCH_2CHCHCH_3C$=O). Anal. Calcd for $C_{15}H_{19}NO_3S$: C, 61.41; H, 6.53; N, 4.77. Found: C, 61.35; H, 6.56; N, 4.76.

Bicyclopentanone 21: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.02 (qq, J = 6.1, 6.1 Hz, 1H, $OCH(CH_3)_2$), 3.74 (s, 3H, OCH_3), 2.70 (dd, J = 14.1, 7.1 Hz, 1H, $CH_2CHCHHC$=O), 2.45 (m, 2H, CH_2CHCH_2C=O and $CHHCHCH_2C$=O), 2.44 (AB, J_{AB} = 14.4 Hz, 1H, CH_2CCH_3CHHC=O), 2.36 (AB, J_{AB} = 14.4 Hz, 1H, CH_2CCH_3CHHC=O), 2.34 (br AB, J_{AB} = 18.5 Hz, 1H, $CHHCCH_3CH_2C$=O), 2.24 (br dm, J = 18.5 Hz, 1H, $CHHCH-CH_2C$=O), 2.15 (br AB, J_{AB} = 18.8 Hz, 1H, $CHHCCH_3CH_2C$=O), 2.02 (dd, J = 13.8, 8.7 Hz, 1H, $CH_2CHCHHC$=O), 1.21 (d, J = 6.7 Hz, 6H, $OCH(CH_3)_2$), 1.19 (s, 3H, $CH_2CCH_3CH_2C$=O MS [EI, m/z (rel intensity)]: 109.0 (100), 282.2 (M^+).

Bicyclopentanone 22: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.75 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 2.72 (dd, J = 14.1, 7.4 Hz, 1H, $CH_2CHCHHC$=O), 2.39−2.52 (m, 4H), 2.33 (br AB, J_{AB} = 18.1 Hz, 1H, CH_2CCH_3CHHC=O), 2.20 (br dm, J = 14.8 Hz, 1H, $CHHCHCH_2C$=O), 2.15 (br AB, J_{AB} = 18.1 Hz, 1H, CH_2-CCH_3CHHC=O), 2.03 (dd, J = 14.1, 9.4 Hz, 1H, $CH_2-CHCHHC$=O), 1.18 (s, 3H, $CH_2CCH_3CH_2C$=O).

Enone 24:[55] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.28−7.60 (m, 5H, aromatic H), 4.28 (q, J = 6.7 Hz, 2H, $CH_3CH_2O_2C$), 4.10−4.22 (m, 2H, $CH_3CH_2O_2C$), 3.65 (AB, J_{AB} = 18.8 Hz, 1H, $CHHC$=CC_6H_5C=O), 3.29 (AB, J_{AB} = 18.8 Hz, 1H, $CHHC$=CC_6H_5C=O), 3.14 (m, 1H, CH_2CHCH_2C=O), 2.83 (obscured dd, J = 12.8, 7.7 Hz, 1H, $CHHCHCH_2C$=O), 2.82 (obscured dd, J = 17.7, 6.6 Hz, 1H, $CH_2CHCHHC$=O), 2.32 (dd, J = 17.8, 2.7 Hz, 1H, $CH_2CHCHHC$=O), 1.77 (dd, J = 12.8, 12.8 Hz, 1H, $CHHCHCH_2C$=O), 1.31 (t, J = 7.4 Hz, 3H, $CH_3CH_2O_2C$), 1.23 (t, J = 7.4 Hz, 3H, $CH_3CH_2O_2C$).

Enone 26: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.27−7.43 (m, 5H, aromatic H), 3.93 (ABd, J_{AB} = 10.7, J = 4.7 Hz, 1H, $HOCHHCHCH_2C$=O), 3.85 (ABd, J_{AB} = 10.7, J = 5.4 Hz, $HOCHHCHCH_2C$=O), 2.98−3.06 (m, 1H, $HOCH_2CHCH_2C$=O), 2.69 (dd, J = 18.1, 6.7 Hz, 1H, $HOCH_2CHCHHC$=O), 2.46 (dd, J = 18.8, 2.0 Hz, 1H, $HOCH_2CHCHHC$=O), 2.18 (s, 3H, CH_3C=CC_6H_5), 1.60 (br s, 1H, $HOCH_2CHCH_2C$=O). Anal. Calcd for $C_{13}H_{14}O_2$·0.2 H_2O: C, 75.85; H, 6.85. Found: C, 75.75; H, 6.59.

Alkene 27:[56] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.18 (q, J = 7.0 Hz, 4H, ($CH_3CH_2O_2C$) × 2), 2.94 (s, 4H, (CCH_2C) × 2), 2.03 (q, J = 7.4 Hz, 4H, (CCH_2CH_3) × 2), 1.24 (t, J = 7.0 Hz, 6H, ($CH_3CH_2O_2C$) × 2), 0.95 (t, J = 7.4 Hz, 6H, (CCH_2CH_3) × 2).

Enone 28:[54] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.25 (q, J = 7.4 Hz, 2H, $CH_3CH_2O_2C$), 4.21 (q, J = 7.4 Hz, 2H, $CH_3CH_2O_2C$), 3.23 (AB, J_{AB} = 19.5 Hz, 1H, $CHHC$=CCH_3C=O), 3.14 (AB, J_{AB} = 19.8 Hz, 1H, $CHHC$=CCH_3C=O), 2.81 (dd, J = 12.8, 7.4 Hz, 1H, $CHHCHCHCH_3C$=O), 2.60 (m, 1H, $CH_2CHCH-CH_3C$=O), 2.09 (dq, J = 2.7, 7.4 Hz, 1H, $CH_2CHCHCH_3C$=O), 1.72 (obscured s, 3H, CH_2C=CCH_3C=O), 1.70 (obscured dd, J = 12.8, 12.8 Hz, 1H, $CHHCHCHCH_3C$=O), 1.29 (t, J = 7.4 Hz, 3H, $CH_3CH_2O_2C$), 1.26 (t, J = 7.4 Hz, 3H, $CH_3CH_2O_2C$), 1.21 (d, J = 7.4 Hz, 3H, $CH_2CHCHCH_3C$=O).

Alkene 29:[57] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.71 (s, 6H, (OCH_3) × 2), 2.45 (br s, 2H, CH_2CCH_3=CCH_3), 2.10 (t, J = 6.7 Hz, 2H, $CH_2CH_2CCH_3$=CCH_3), 1.97 (br m, 2H, $CH_2CH_2-CCH_3$=CCH_3), 1.63 (s, 3H, CCH_3=CCH_3), 1.57 (s, 3H, CCH_3=CCH_3). IR (cm^{-1}): 2956, 1736, 1437, 1259.

Alkene 31:[58] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.17 (q, J = 7.0 Hz, 4H, ($CH_3CH_2O_2C$) × 2), 2.44 (br s, 2H, CH_2CCH_3=CCH_3), 2.10 (t, J = 7.3 Hz, 2H, $CH_2CH_2CCH_3$=CCH_3), 1.98 (br m, 2H, $CH_2CH_2CCH_3$=CCH_3), 1.64 (s, 3H, CCH_3=CCH_3), 1.58 (s, 3H, CCH_3=CCH_3), 1.23 (t, J = 7.0 Hz, 6H, ($CH_3-CH_2O_2C$) × 2).

Enone 32: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.89 (s, 1H, CH_2-CH_2C=CHC=O), 4.30 (q, J = 7.3 Hz, 2H, $CH_3CH_2O_2C$), 4.20 (q, J = 7.3 Hz, 2H, $CH_3CH_2O_2C$), 2.84 (obscured dddd, J =

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12.7, 6.4, 2.4, 2.4 Hz, 1H, CH_2CHCH_2C=O), 2.80 (obscured dm, J = 14.2 Hz, 1H, CH_2CHHC=CHC=O), 2.76 (obscured ddd, J = 13.2, 5.4, 2.4 Hz, 1H, $CHHCHCH_2C$=O), 2.65 (obscured m, 1H, $CHHCH_2C$=CHC=O), 2.63 (obscured dd, J = 19.0, 6.4 Hz, 1H, $CH_2CHCHHC$=O), 2.51 (ddd, J = 14.2, 14.2, 5.4 Hz, 1H, CH_2CHHC=CHC=O), 2.01 (dd, J = 19.0, 2.4 Hz, 1H, $CH_2CHCHHC$=O), 1.82 (ddd, J = 13.7, 13.7, 4.9 Hz, 1H, $CHHCH_2C$=CHC=O), 1.56 (dd, J = 12.7, 12.7 Hz, 1H, $CHHCHCH_2C$=O), 1.30 (t, J = 7.3 Hz, 3H, $CH_3CH_2O_2C$), 1.24 (t, J = 7.3 Hz, 3H, $CH_3CH_2O_2C$). Anal. Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.02; H, 7.18.

B. Monocyclic Alkene Formation: Reductive Cyclization of Enynes. 1. Representative Experimental Procedures. Typical experimental procedure for reactions depicted in Table 8: In a round-bottom vessel equipped with a three-way stopper and a balloon of H_2, a mixture of enyne **35** (24 mg, 0.086 mmol) and $Co_2(CO)_8$ (31 mg, 0.091 mmol) was pumped briefly and purged three times with H_2. A solution of cyclohexylamine (31 μL, 0.27 mmol) in toluene (4.6 mL) was then added, and the mixture was heated at 80 °C for 2.5 h. Upon completion of the reaction, the brown mixture was cooled to room temperature and treated with a solution of NMO in chloroform until a clear solution was obtained. Filtration of the mixture through a short pad of coarse silica gel using a solution of 10% EtOAc in hexanes provided a colorless solution. Subsequent removal of the solvent and purification by flash chromatography (SiO_2, 20% EtOAc in hexanes) afforded 19 mg of enone **36** (70% yield) as a colorless oil. A similar general procedure was followed in the other reactions where the enyne−$Co_2(CO)_6$ complex or $Co_4(CO)_{12}$ was used as an alternative cobalt carbonyl source, or DME as an alternative solvent. The desired amount of cyclohexylamine was added as a solution in the appropriate solvent, otherwise only the solvent was added into the reaction mixture.

Typical experimental procedure for reactions depicted in eq 5: In a round-bottom vessel equipped with a three-way stopper and a balloon of H_2, enyne−$Co_2(CO)_6$ complex **1a** (49 mg, 0.093 mmol) was pumped briefly and purged three times with H_2. It was then dissolved in CH_2Cl_2 (1.9 mL), and a solution of Me_3NO in CH_2Cl_2 (0.47 mL, 0.094 mmol, 0.20 M) was then added thrice at 1 h intervals at room temperature. Additional quantities of Me_3NO in CH_2Cl_2 (0.90 mL, 0.18 mmol) was added, and the mixture was stirred overnight. Upon completion of the reaction, the mixture was filtered through a short pad of coarse silica gel using a solution of 10% EtOAc in hexanes. Subsequent removal of the solvent and purification by flash chromatography (SiO_2, 20% EtOAc in hexanes) afforded 20 mg of enone **3** (80% yield) as a colorless oil. A similar general procedure was followed in the reactions where NMO (as a solution in CH_2Cl_2) was used as an alternative oxidant. In the reaction using Et_3SiH, the silane was added into the reaction mixture as a solution in CH_2Cl_2 prior to the incremental addition of NMO (1 × 5 equiv) at 1 h intervals at room temperature.

Typical experimental procedure for reactions depicted in Table 9: In a round-bottom vessel equipped with a three-way stopper and a balloon of H_2, enyne−$Co_2(CO)_6$ complex **1a** (64 mg, 0.12 mmol) was pumped briefly and purged three times with H_2. Toluene (2.4 mL) was then added, and the mixture was heated at 60 °C for 5 h. Upon completion of the reaction, the brown mixture was cooled to room temperature and then treated with a solution of *N*-methylmorpholine *N*-oxide in chloroform. Filtration of the mixture through a short pad of coarse silica gel using a solution of 10% EtOAc in hexanes provided a colorless solution. Subsequent removal of the solvent and purification by flash chromatography (SiO_2, 3%, 20%, and then 50% EtOAc in hexanes) afforded 15 mg of the monocyclic alkenes **37** (52% yield, 1:1 ratio of *endo* to *exo* alkene isomers) and 5 mg of enone **3** (16% yield). A similar general procedure was used for the reactions carried out with different solvents (Table 10).

Typical experimental procedure for the silane-induced reductive cyclizations of enyne−$Co_2(CO)_6$ complexes. These are the reactions depicted in Tables 11−13: In a round-bottom vessel equipped with a three-way stopper and a balloon of H_2, enyne−$Co_2(CO)_6$ complex **1a** (31 mg, 0.059 mmol) was pumped briefly and purged three times with H_2. Et_3SiH (2.4 μL, 0.015 mmol) in toluene (1.3 mL) was then added, and the mixture was heated at 60 °C for 2 h. Upon completion of the reaction, the brown mixture was cooled to room temperature and then treated with a solution of *N*-methylmorpholine *N*-oxide in chloroform. Filtration of the mixture through a short pad of coarse silica gel using a solution of 10% EtOAc in hexanes provided a colorless solution. Subsequent removal of the solvent and purification by flash chromatography (SiO_2, 3% EtOAc in hexanes) afforded 9 mg of the monocyclic alkenes **37** (62% yield, 3:1 ratio of *endo* to *exo* alkene isomers). A similar general procedure was followed in the other reactions where alternative sources of hydrides were used (Table 12).

2. Alkene 37:[58] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.18 (q, J = 7.0 Hz, 4H, $(CH_3CH_2O_2C) \times 2$), 2.92 (br s, 4H, $(CCH_2C) \times 2$), 1.59 (s, 6H, CH_3C=CCH_3), 1.24 (t, J = 7.0 Hz, 6H, $(CH_3CH_2O_2C) \times 2$).

Enyne 39:[59] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.26−7.38 (m, 10H, aromatic H), 5.77 (ddt, J = 16.8, 9.4, 8.1 Hz, 1H, CH_2CH=CH_2), 5.08 (dm, J = 16.1 Hz, 1H, CH_2CH=CHH), 5.04 (dm, J = 8.1 Hz, 1H, CH_2CH=CHH), 4.49 (s, 4H, $(C_6H_5CH_2) \times 2$), 3.41 (AB, J_{AB} = 8.7 Hz, 1H, $C_6H_5CH_2OCHHC$), 3.37 (AB, J_{AB} = 8.7 Hz, 1H, $C_6H_5CH_2OCHHC$), 2.28 (d, J = 2.7 Hz, 2H, CH_2CCH), 2.24 (d, J = 7.4 Hz, 2H, CH_2CH=CH_2), 1.94 (t, J = 2.7 Hz, 1H, CH_2CCH).

Alkene 41:[57] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.72 (d, J = 7.8 Hz, 2H, aromatic H^{ortho}), 7.31 (d, J = 8.3 Hz, 2H, aromatic H^{meta}), 3.97 (s, 4H, $(NCH_2C) \times 2$), 2.42 (s, 3H, $CH_3C_6H_4SO_2N$), 1.54 (s, 6H, CH_3C=CCH_3).

Enone 42: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.27−7.36 (m, 10H, aromatic H, 5.83 (s, 1H, CH_2C=CHC=O), 4.55 (s, 2H, $C_6H_5CH_2O$), 4.49 (s, 2H, $C_6H_5CH_2O$), 3.53 (AB, J_{AB} = 8.8 Hz, 1H, $C_6H_5CH_2OCHHC$), 3.51 (AB, J_{AB} = 8.8 Hz, 1H, $C_6H_5CH_2OCHHC$), 3.37 (AB, J_{AB} = 8.8 Hz, 1H, AB, J_{AB} = 8.8 Hz, 1H, $C_6H_5CH_2OCHHC$), 3.31 (AB, J_{AB} = 8.8 Hz, 1H, AB, J_{AB} = 8.8 Hz, 1H, $C_6H_5CH_2OCHHC$), 3.09−3.14 (m, 1H, CH_2CHCH_2C=O), 2.59 (obscured dd, J = 17.6, 6.3 Hz, 1H, $CH_2CHCHHC$=O), 2.58 (obscured s, 2H, CH_2C=CHC=O), 2.17 (dd, J = 12.7, 8.8 Hz, 1H, $CHHCHCH_2C$=O), 2.03 (dd, J = 17.6, 2.9 Hz, 1H, $CH_2CHCHHC$=O), 1.12 (dd, J = 12.7, 12.7 Hz, 1H, $CHHCHCH_2C$=O). Anal. Calcd for $C_{24}H_{26}O_3$: C, 79.53; H, 7.23. Found: C, 79.46; H, 7.33.

Alkene 43: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.27−7.39 (m, 10H, aromatic H), 4.52 (s, 4H, $C_6H_5CH_2O) \times 2$), 3.41 (s, 4H, $(C_6H_5CH_2OCH_2C) \times 2$), 2.17 (s, 4H, $(CCH_2C) \times 2$), 1.55 (d, J = 1.3 Hz, 6H, CH_3C=CCH_3). Anal. Calcd for $C_{23}H_{28}O_2 \cdot 0.10$ H_2O: C, 81.67; H, 8.34. Found: C, 81.66; H, 8.30.

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Supporting Information Available: Copies of ^{1}H NMR spectra of compounds **21** and **22** and IR and ^{13}C NMR spectral data for compounds **2**, **5**, **8**, **16**−**19**, **21**, **26**, **32**, **42**, **43**. This material is available free of charge via the Internet at http://pubs.acs.org.

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