mixture of pyridine (4.55 g) and water (0.147 g). Then ethylenediamine (1.038 g) was added and stirred until the mixture became a clear solution. Finally boric acid (0.18 g) and 40% HF (0.062 g) were added to the obtained solution (pH 11.12), which was then heated at 170°C for 10 days in a 23 mL Teflon-lined Parr autoclave. The product (yield 0.206 g), consisting of a white powder and thin platelike single crystals, was collected, washed with deionized water and ethanol, and dried at room temperature. The Ge content was confirmed by energy-dispersive spectroscopy (EDS).

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[19] X-ray structure analysis: STOE IPDS system with image plate; graphite monochromator; $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å; $T = 293$ K; the structure was solved by using the direct-method routine of SIR-97[22] and refined by full-matrix least-squares methods using SHELXL-97;[23] numerical absorption correction by X-RED[24], $T_{\min} = 0.4281$, $T_{\max} = 0.8850$. Crystal data for $(C_2N_2H_{10})_2[(BO_{2.5})_2(GeO_2)_3]$: crystal dimensions $0.10 \times 0.10 \times 0.02$ mm, monoclinic, space group $P2_1/n$, $a = 6.9765(9)$, $b = 14.4103(12)$, $c = 11.6943(14)$ Å, $\beta = 91.093(15)°$, $V = 1175.46(23)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 2.69$ g cm^{-3}, $\mu(\mathrm{Mo_{K\alpha}}) = 76.833$ cm^{-1}, $2\theta_{\min} = 6.4°$, $2\theta_{\max} = 47°$, $R_1 = 0.034$ for 1525 reflections with $F_o > 4\sigma(F_o)$ and 0.039 for all 1729 reflections, $wR_2(F^2) = 0.095$, GOF = 1.136, 194 parameters were refined, max./min. residual electron density $-0.79/0.86$ e Å^{-3}. One of the $(H_3NCH_2CH_2NH_3)^{2+}$ ions was found to have two different conformations (Figure 1). This was refined as the N-population parameters of the N2 atom at two sites as 0.73 and 0.27. All other parameters are unexceptional. Most of the hydrogen atom positions could be located on the final difference Fourier maps, and they were introduced by the rigid-group riding mode, allowing refinement of their isotropic thermal parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-143794. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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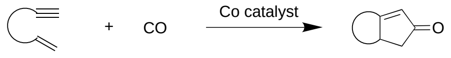
Dodecacarbonyltetracobalt Catalysis in the Thermal Pauson–Khand Reaction[**]

Marie E. Krafft[*] and Llorente V. R. Boñaga

Dicobaltoctacarbonyl, $[Co_2(CO)_8]$, has always been the metal complex of choice in the widely used Pauson–Khand reaction for the formation of bicyclo[3.3.0]octenones by the cyclocarbonylation of an alkene and an alkyne (Scheme 1).[1] Alternative sources of zero valent cobalt, namely [(indenyl)Co(cod)] and $[Co(acac)_2]/NaBH_4$, and cobalt carbonyl clusters, such as $[Co_4(CO)_{12}]$, $[Co_3(CO)_9(\mu_3\text{-}CH)]$, and $[Co_4(CO)_{11}P(OPh)_3]$, have also been developed but are less



Scheme 1. Cobalt catalysis in the Pauson–Khand reaction. Co catalyst: $[Co_2(CO)_8]$ with or without additive (phosphite, phosphane, cyclohexylamine ($CyNH_2$), phosphane sulfide, 1,2-dimethoxyethane (DME), water), $[Co_4(CO)_{12}]$, $[Co_4(CO)_{11}P(OPh)_3]$, $[Co_3(CO)_9(\mu_3\text{-}CH)]$, [(indenyl)Co(cod)], $[Co(acac)_2]/NaBH_4$. cod = cycloocta-1,4-diene; acac = acetylacetonate.

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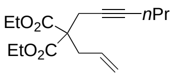
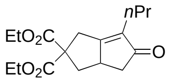
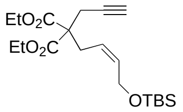
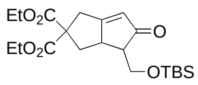
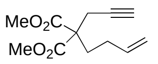
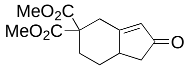
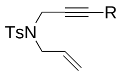
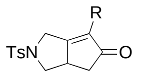
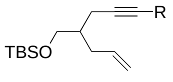
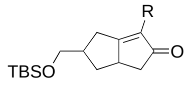
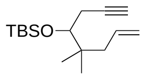
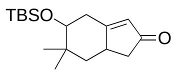
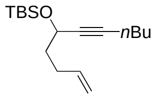
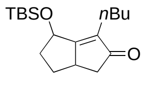
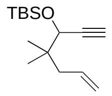
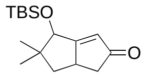
frequently employed. Of particular interest is the congeneric tetranuclear carbonyl cluster $[Co_4(CO)_{12}]$, which has seen very limited practical utility in this cyclization under one atmosphere of CO at moderate temperatures (such as 70 °C).[2, 7a, 8b] In fact, the advent of many protocols in the cobalt-catalyzed reactions stems from the common belief that $[Co_4(CO)_{12}]$ formation deters $[Co_2(CO)_8]$ catalysis and is generally regarded as a dead end route in this reaction.[1i, 3] Presumably derived from dimerization of "$[Co_2(CO)_n]$" upon release of the cyclopentenone product, $[Co_4(CO)_{12}]$ was suggested to be one of the cobalt species or clusters, which were believed to be nonviable for the reaction.[1i, 4] Consequently, development of methods involving $[Co_2(CO)_8]$ catalysis was based on preserving the catalytic species and preventing the formation of inactive cobalt species. Successful catalytic cyclizations using $[Co_2(CO)_8]$ were carried out with additives[5] or ultraviolet light,[6] under high operating temperatures and CO pressures,[7] or in supercritical fluids.[8] In addition to providing low valent cobalt species, the role of $NaBH_4$ in the $[Co(acac)_2]/NaBH_4$ catalyst system for the Pauson–Khand reaction was also based on these premises.[9]

The formation of $[Co_4(CO)_{12}]$ from the thermal decomposition of $[Co_2(CO)_8]$ in hexane, heptane, or toluene was extensively studied by several groups.[10] Isolation of this cobalt cluster was also reported by Pauson and co-workers in their seminal studies on the thermal cyclizations of $[(HC{\equiv}CH)Co_2(CO)_6]$ complexes with norbornene and its derivatives under a nitrogen atmosphere.[11a] Generation of $[Co_4(CO)_{12}]$ under these cyclization conditions in aromatic solvents, such as toluene and benzene, was also indicated by the isolation of $[(arene)Co_4(CO)_9]$ complexes.[11b,c]

In our continuing studies on the Pauson–Khand reaction, we observed that cyclizations can be effected using catalytic quantities of commercially available $[Co_2(CO)_8]$ under one atmosphere of CO. The efficiency of this process was further enhanced by the addition of cyclohexylamine ($CyNH_2$).[5b] It was later discovered that, in the presence of added cyclohexylamine, substoichiometric amounts of $[Co_2(CO)_8]$ were sufficient to catalyze the Pauson–Khand reaction under an N_2 atmosphere.[12] In these studies, we speculated an additive-derived stabilization of reaction intermediates originating from its coordination, by virtue of its Lewis basicity,[13] to coordinatively unsaturated organocobalt species. We also proposed that cyclohexylamine preserved the active cobalt species under the catalytic conditions and an iterative disproportionation of residual cobalt species, "$[Co_2(CO)_nL_{8-n}]$", where L = CO, $CyNH_2$, or DME, to provide active species under the substoichiometric conditions. Kinetic studies on the disproportionation of $[Co_2(CO)_8]$ by nitrogen-containing bases, such as cyclohexylamine, have been reported.[14c] Lewis bases, such as ammonia, pyridine, methanol, and ethanol are also well documented to induce disproportionation of $[Co_4(CO)_{12}]$.[14]

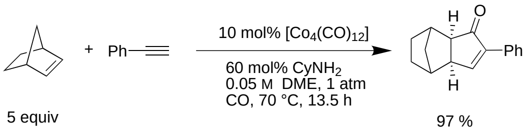
We conducted Pauson–Khand cyclization studies with the $[Co_4(CO)_{12}]$ cluster in an attempt to understand the efficiency enhancement provided by the amine ligand and to verify our hypothesis that cyclohexylamine preserves the active catalyst and induces its formation via disproportionation of $[Co_4(CO)_{12}]$, which may possibly be formed during catalytic reactions using $[Co_2(CO)_8]$. As anticipated, we observed that *catalytic* amounts of $[Co_4(CO)_{12}]$ could be used in conjunction with $CyNH_2$ to catalyze thermal Pauson–Khand reactions under practical reaction conditions. We then verified the extent of these observations in a series of catalytic cyclizations of a variety of substrates employing the $[Co_4(CO)_{12}]/CyNH_2$ system (Table 1).[15, 16] As was observed with the $[Co_2(CO)_8]$/

Table 1. $[Co_4(CO)_{12}]/CyNH_2$ as catalyst system for a practical thermal Pauson–Khand reaction.[a]

Entry	Substrate		Product[16] [diastereomeric ratio, dr]		Yield [%]
1		**1**		**11**	92, 94[b]
2		**2**		**12** [>20:1]	64
3		**3**		**13**	92, 70,[c] 89,[d] 55[e]
4		**4** (R = H)		**14**	88[b]
5		**5** (R = *n*Pr)		**15**	81
6		**6** (R = H)		**16**	85, 70,[d] 65[e]
7		**7** (R = *n*Pr)		**17** [1:1]	91
8		**8**		**18** [4:1]	80
9		**9**		**19** [1:1]	56,[f] 61[c]
10		**10**		**20** [1:1]	44,[f] 30[c]

[a] Reactions were carried out at substrate concentrations of 0.05 M in DME using 10 mol% $[Co_4(CO)_{12}]$ and 60 mol% $CyNH_2$ under a CO atmosphere at 70 °C. Reactions lasted typically 13–18 h. [b] 5 mol% $[Co_4(CO)_{12}]$, 30 mol% $CyNH_2$. [c] With pyridine. [d] In dichloroethane. [e] In isooctane. [f] 30 mol% $[Co_4(CO)_{12}]$, 60 mol% $CyNH_2$. TBS = *tert*-butyldimethylsilyl.

$CyNH_2$ system,[5b] good to excellent yields were obtained from enynes with significant Thorpe–Ingold properties (entries 1, 3–5, 8), although a lower yield was obtained from an enyne bearing a disubstituted olefin (entry 2). With the present catalyst system, a complete cyclization of enyne **7** was achieved using only a 10/60 ratio of $[Co_4(CO)_{12}]/CyNH_2$ whereas, with the $[Co_2(CO)_8]/CyNH_2$ system, a 30/60 ratio of $[Co_2(CO)_8]/CyNH_2$ was necessary. Similarly, enynes bearing internal alkynes and lacking significant Thorpe–Ingold assistance (entry 9) or which are sterically hindered (entry 10) needed higher catalyst loading (for example 30 mol%) for complete reactions, albeit still in modest yields. In our efforts to improve the cyclizations depicted in entries 9 and 10, pyridine was substituted for cyclohexylamine[12] but essentially identical results were obtained. Pyridine is one of the Lewis bases known to induce disproportionation of $[Co_2(CO)_8]$ and $[Co_4(CO)_{12}]$.[14] In contrast, cyclization of enyne **3** with pyridine as the additive was found to be inferior to cyclohexylamine (entry 3). An intermolecular version of this $[Co_4(CO)_{12}]/CyNH_2$-catalyzed cyclization was also demonstrated by the reaction of phenylacetylene and the reactive alkene norbornene to give the cycloadduct in 97% yield [Eq. (1)].

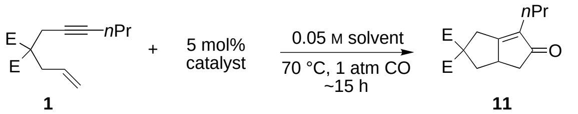


(1)

We have therefore shown that efficient cycloadditions of enynes could be attained using catalytic amounts of $[Co_4(CO)_{12}]$, with cyclohexylamine enhancing the reaction efficiency. These findings further exemplified the utility of additives, such as amines, in improving the catalytic efficiency of cobalt carbonyls in Pauson–Khand reactions. In the early studies on the thermal decomposition of $[Co_2(CO)_8]$ (in toluene), Ungvary and Marko showed that coordinatively unsaturated $[Co_2(CO)_6]$ fragments are necessary for the formation of $[Co_4(CO)_{12}]$.[10d] Hence, an atmosphere of CO or the presence of coordinating ligands, such as $CyNH_2$ would be expected to inhibit the formation of these fragments and, consequently, the dimerization to the tetranuclear cluster. On the contrary, it had been suggested that *only* at high CO pressures would formation of the dinuclear cobalt carbonyl be effectively favored from $[Co_4(CO)_{12}]$.[3b]

To further elucidate this observed reactivity, we examined the cyclizations of enyne **1** using $[Co_4(CO)_{12}]$ in the absence of additives in solvents commonly used in Pauson–Khand reactions (Table 2). Although we intended to confirm its lack of reactivity under our reaction conditions, we discovered otherwise that $[Co_4(CO)_{12}]$ catalyzes the cycloaddition in a number of solvents under normal laboratory conditions, in which the highest catalytic efficiency was observed in 1,2-dichloroethane (DCE) and isooctane. Interestingly, Pauson and co-workers isolated $[Co_4(CO)_{12}]$ from stoichiometric Pauson–Khand reactions in isooctane as the solvent.[11a] For comparison, cyclization efficiencies in DCE and DME under the reaction conditions described in Table 1 are comparable (see entries 3 and 6). However, under these catalytic conditions, no cyclization was evident in dimethyl sulfoxide (DMSO), presumably due to the formation of inactive DMSO–cobalt complexes.[17] Owing to its strong coordinating ability, DMSO possibly formed complexes with $[Co_4(CO)_{12}]$ or its degradation products which were inert toward catalysis in the Pauson–Khand reaction. On the contrary, DMSO has been widely used as an additive to promote Pauson–Khand reactions in benzene of $[(alkyne)Co_2(CO)_6]$ complexes (40 °C, air)[17c] and of $[(allylpropargylsulfide)Co_2(CO)_6]$ complexes (60 °C, O_2) in the presence of dimethylsulfide as a coligand.[17d] These suggest that DMSO is beneficial to $[(alkyne)Co_2(CO)_6]$ complexes, which renders them more reactive towards alkene coordination, but is detrimental to $[Co_2(CO)_8]$ and $[Co_4(CO)_{12}]$ complexes. As was already demonstrated by Kim and Chung, $[Co_4(CO)_{12}]$ did not exhibit any catalytic activity in dichloromethane under one atmosphere of CO and optimal catalysis was only achieved at 150 °C and 10 atm of CO.[7] In contrast, $[Co_2(CO)_8]$ exhibited its highest catalytic activity in DME.[18] A subsequent increase in yield was noted for cyclizations in DME when higher amounts of $[Co_2(CO)_8]$ were used (entries 8 versus 9), although less notably in dichloroethane (entries 4–6) and isooctane (entries 13–14).

Table 2. $[Co_4(CO)_{12}]$ and $[Co_2(CO)_8]$ catalyses in different solvents.[a]



(2)

Entry	Solvent	$[Co_4(CO)_{12}]$ Yield [%] **1**	**11**	TON[b]	$[Co_2(CO)_8]$ Yield [%] **1**	**11**	TON[b]
1	dimethyl sulfoxide	93	–	0	94	–	0
2	acetonitrile	61	35	6.9	76	9	1.7
3	dichloromethane	47	–	0			
4	dichloroethane	–	68	14.3	29	26	5.0
5					–	37[c]	3.7
6					–	50[d]	2.4
7	tetrahydrofuran	–	21	4.4			
8	1,2-dimethoxyethane	–	23	4.4	9	41	7.8
9			59[c]	6.0	–	82[c]	8.3
10	toluene	86	9	1.9			
11	*n*-hexane	24	37	6.2			
12	*n*-heptane	30	41	8.7			
13	isooctane	–	59	12.5	31	19	3.3
14		–	61[c]	6.5	–	57[d]	2.6

[a] In [Eq. (2)], E = CO_2Et, catalyst = $[Co_4(CO)_{12}]$ or $[Co_2(CO)_8]$. [b] Turnover number (TON) is the mole ratio of product to catalyst. [c] 10 mol%. [d] 20 mol%.

The observed reactivity of $[Co_4(CO)_{12}]$ at 70 °C and one atmosphere of CO suggested that, under our conditions, it probably underwent disproportionation into $[Co_2(CO)_8]$ or a similar catalytically active cobalt species.[19] Although generation of $[Co_4(CO)_{12}]$ under the $[Co_2(CO)_8]$-catalyzed conditions has been only assumed, we have discounted the assumption that $[Co_4(CO)_{12}]$ is inactive toward the Pauson–Khand cyclizations under mild conditions, such as a normal pressure of CO and a lower temperature. Thus, $[Co_4(CO)_{12}]$ can now serve as an alternative for $[Co_2(CO)_8]$, which is more prone to air oxidation,[20] and possibly $[Co_3(CO)_9(\mu_3\text{-}CH)]$.[21] It is also noteworthy that commercially available samples of $[Co_4(CO)_{12}]$ were used without purification and found to be catalytically efficient.[22]

In conclusion, we demonstrated that, contrary to common belief, $[Co_4(CO)_{12}]$ catalyzes the Pauson–Khand reaction under very practical laboratory conditions (70 °C, 1 atm CO). Its catalytic efficiency was further enhanced by the utility of an additive, such as cyclohexylamine, which possibly facilitated its disproportionation into and promoted preservation of the catalytically active cobalt species. Finally, we have provided the first practical procedures using the commercially available and more stable $[Co_4(CO)_{12}]$ cluster as a catalyst precursor. Studies on reactions using this cluster are underway.

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[4] $[Co_4(CO)_{12}]$ was claimed to be inert toward enynes, thus, in the Pauson–Khand reaction. However, its reactivity with alkynes was previously documented. $[Co_4(CO)_{12}]$ react with alkynes to yield $[(alkyne)Co_4(CO)_{10}]$ complexes. Under the normal Pauson–Khand reaction conditions, this complex might be expected to decompose to an $[(alkyne)Co_2(CO)_6]$ complex, a requisite initial complex for the Pauson–Khand reaction, and cobalt carbonyl fragments: a) R. S. Dickson, G. R. Tailby, *Aust. J. Chem.* **1970**, *23*, 229; b) R. S. Dickson, P. J. Fraser, *Adv. Organomet. Chem.* **1974**, *12*, 323; c) For a review on alkyne cobalt complexes, see ref. [2b], p. 192; d) V. Cadierno, M. P. Gamasa, J. Gimeno, J. M. Moreto, S. Ricart, A. Roig, E. Molins, *Organometallics* **1998**, *17*, 697.

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[8] Under supercritical fluids, it was believed that the catalytic metals would be well dispersed and the chances of their aggregation would be substantially reduced: a) supercritical CO_2: N. Jeong, S. H. Hwang, Y. W. Lee, J. S. Lim, *J. Am. Chem. Soc.* **1997**, *119*, 10549; b) supercritical ethylene: N. Jeong, S. H. Hwang, *Angew. Chem.* **2000**, *112*, 650; *Angew. Chem. Int. Ed.* **2000**, *39*, 636.

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[12] M. E. Krafft, L. V. R. Boñaga, *Synlett* **2000**, 959.

[13] For a review on the utility of Lewis bases in the Pauson–Khand reaction, see: a) T. Sugihara, M. Yamaguchi, M. Nishizawa, *Rec. Res. Devel. Organomet. Chem.* **1999**, *2*, 13, and references therein; b) T. Sugihara, M. Yamaguchi, M. Nishizawa, *Rev. Heteroatom Chem.* **1999**, *21*, 179. The Lewis base character of amines is also believed to facilitate the decarbonylation step to generate a vacant site on the cobalt center and thereby speeding up the reaction. See ref. [5e].

[14] Both $[Co_2(CO)_8]$ and $[Co_4(CO)_{12}]$ are known to undergo disproportionation upon reaction with Lewis bases. $[Co_2(CO)_8]$: a) F. Calderazzo, R. Ercoli, G. Natta in *Organic Syntheses via Metal Carbonyls, Vol. 1* (Eds.: I. Wender, P. Pino), Interscience-Wiley, New York, **1968**, Chapter 1; b) I. Wender, H. W. Sternberg, M. Orchin, *J. Am. Chem. Soc.* **1952**, *74*, 1216; $[Co_4(CO)_{12}]$: ref. [2a], p. 56. Kinetic studies on the disproportionation of $[Co_2(CO)_8]$ induced by nitrogen-containing bases, such as cyclohexylamine, was also reported: c) E. Mentasti, E. Pelizzetti, R. Rossetti, P. L. Stanghellini, *Inorg. Chim. Acta.* **1977**, *25*, 7; for a review on Lewis-base–metal-carbonyl complexes see: d) T. Manuel, *Adv. Organomet. Chem.* **1965**, *3*, 181.

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[16] References for enynes and their corresponding cycloadducts: entry 1: T. Kondo, N. Suzuki, T. Okada, T. Mitsudo, *J. Am. Chem. Soc.* **1997**, *119*, 6187; entry 2: ref. [18a]; entries 3 and 4: ref. [6]; entries 5 and 7: M. E. Krafft, A. M. Wilson, O. A. Dasse, B. Shao, Y. Y. Cheung, Z. Fu, L. V. R. Boñaga, M. K. Mollman, *J. Am. Chem. Soc.* **1996**, *118*, 6080; entry 8: S. Shambayati, W. E. Crowe, S. L. Schreiber, *Tetrahedron Lett.* **1990**, *31*, 5289; entry 9: ref. [12]; entries 6 and 10: ref. [5b]; entry 10:

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[19] 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).[10b]

[20] Upon exposure to air, $[Co_4(CO)_{12}]$ oxidizes to a purple Co^{II} species but this proceeds at an appreciably slower rate than $[Co_2(CO)_8]$: a) ref. [2b]; b) R. B. King in *Organometallic Syntheses, Vol. 1* (Eds.: J. J. Eisch, R. B. King), Academic Press, New York, **1965**, p. 103.

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[22] Highly purified $[Co_2(CO)_8]$ and $[Co_4(CO)_{12}]$ were reported by Jeong et al. to undergo spontaneous ignition upon exposure to air; ref. [8b]. See also ref. [5b].