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Simple, Convenient Methods for the Preparation of Alkyne-$Co_2(CO)_6$ Complexes from $CoBr_2$ for Application in Pauson-Khand Cyclopentenone Synthesis†

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Abstract: Alkyne-dicobalthexacarbonyl complexes are readily prepared by the reduction of cobalt bromide by Zn in the presence of alkynes in THF while bubbling carbon monoxide under ambient conditions. The complexes prepared in this way react with olefins to give the corresponding Pauson-Khand cyclopentenones in moderate to good yields. The alkyne-dicobalthexacarbonyl complexes can be also prepared *in situ* by the reduction of cobalt bromide with sodium naphthalene under CO atmosphere followed by CuBr treatment in the presence of alkynes. The complexes prepared in this way also give cyclopentenones on heating with norbornene, but the former method utilizing zinc gives better results.

Introduction

In recent years, the transition metal carbonyl reagents have found several applications in organic synthesis, especially in carbon-carbon bond forming carbonylations and cyclizations.[1-4] The metal carbonyls have been found to be useful in quickly assembling cyclized skeletons. For example, the trust worthy Pauson-Khand cyclization to construct cyclopentenone derivatives can be readily achieved by heating an alkyne and alkene with $Co_2(CO)_8$.[1,5] However, the synthetic methods utilizing metal carbonyls are not widely utilized and there is some reluctance to apply this chemistry for synthesis. One of the reasons for this is the fact that these reagents are not readily accessible. Moreover, there is a notion that it is difficult to handle these reagents. Some of these difficulties can be alleviated if these reagents could be prepared *in situ* utilizing more readily accessible starting materials and the metal carbonyl intermediates could be destroyed before isolating the organic products.

Several metal carbonyl species can be readily synthesized by reducing transition metal complexes in the presence of carbon monoxide. The first serious efforts in the synthesis and utilization of such species have been made by Caubere and co-workers.

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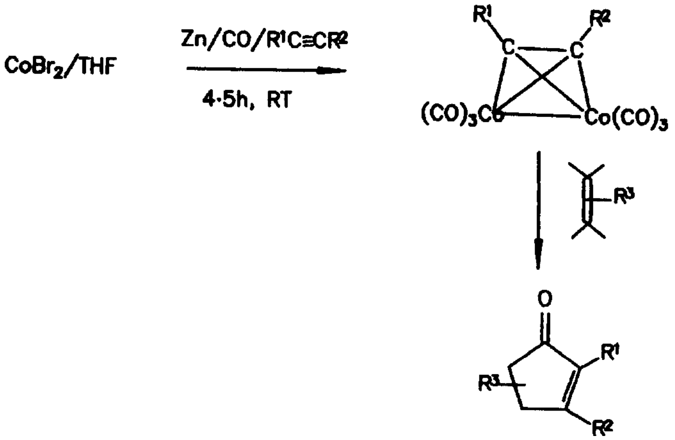
† Dedicated to Professor M.Vivekananda Bhatt on the occasion of his 70th birth day.

In a series of reports, these authors described the reduction of CoX_2 and FeX_3 reagents by NaH and sodium t-amyloxide in the presence of CO.[6] The CRA (complex redcing agent)-CO combinations have been utilized for several synthetic applications.[6] We have undertaken the synthesis and utilization of $^{-}Co(CO)_4$,[7] $^{-2}Fe(CO)_4$[8] and the $RC{\equiv}CR{-}Co_2(CO)_6$[9] complexes from readily accessible starting materials. We describe here the results of a detailed investigation of the preparation of alkyne-$Co_2(CO)_6$ complexes *in situ* in THF for utilization in the Pauson-Khand cyclopentenone synthesis.

Results and Discussion

Synthesis of $RC{\equiv}CR{-}Co_2(CO)_6$ complex through reduction of $CoBr_2$. with Zn:

It has been known for a long time that metallic zinc reduces CoI in t-butanol/toluene mixture under carbon monoxide atmosphere to give $Co_2(CO)_8$ in 38% yield.[10] We have observed that anhydrous $CoBr_2$ does not undergo reduction under these conditions. However, when the reduction of $CoBr_2$ was carried out in anhydrous THF in the presence of alkynes while bubbling CO, the corresponding alkyne complexes are obtained. In the case of diphenylacetylene, the corresponding complex, $(Ph{-}C{\equiv}C{-}Ph)Co_2(CO)_6$ was isolated in 85% yield. We have also observed that the alkyne complexes prepared *in situ* in this way undergo the Pauson-Khand cyclization with representative alkenes (Table 1).



The yields of the cyclopentenones are comparable to the yields obtained following the original procedure.[1,5] The only side products are the hydrocarbon products resulting from trimerization of alkynes. The desired cyclopentenones can be readily separated from these hydrocarbon products by column chromatography on silica gel.

Table 1: Reaction of (alkyne)$Co_2(CO)_6$ complexes prepared using $CoBr_2$/Zn/CO in THF with olefins.[a]

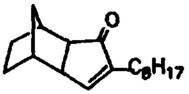
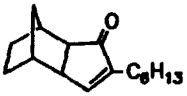
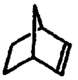
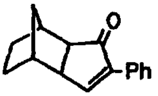
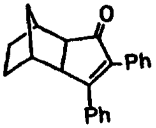
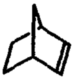
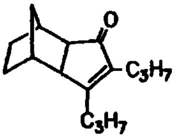
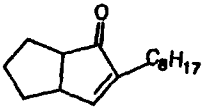
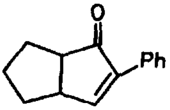
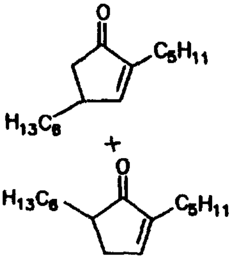
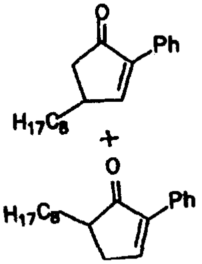
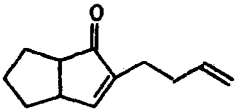
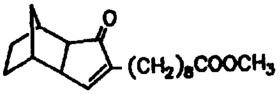
S.No	Alkyne	Alkene	Time	Product[b]	Yield(%)[c]
1	$n{-}C_8H_{17}C{\equiv}CH$		4h		92
2	$n{-}C_6H_{13}C{\equiv}CH$		4h		88
3	$PhC{\equiv}CH$		4h		80
4	$PhC{\equiv}CPH$		12h		38
5	$n{-}C_3H_7C{\equiv}C^nC_3H_7$		12h		78
6	$n{-}C_8H_{17}C{\equiv}CH$		12h		58
7	$PhC{\equiv}CH$		12h		47
8	$n{-}C_5H_{11}C{\equiv}CH$	$n{-}C_6H_{13}CH{=}CH_2$	24h		30

Table 1 contd..

9	PhC≡CH	n-$C_8H_{17}CH{=}CH_2$	24h		28
10	$HC{\equiv}C(CH_2)_2CH{=}CH_2$		12h		55
11	$HC{\equiv}C(CH_2)_8COOCH_3$		12h		91

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a) All reactions were carried out using $CoBr_2$(10mmol), Zn(11mmol), alkyne(5mmol) and alkene(10mmol) at refluxing THF temperature.

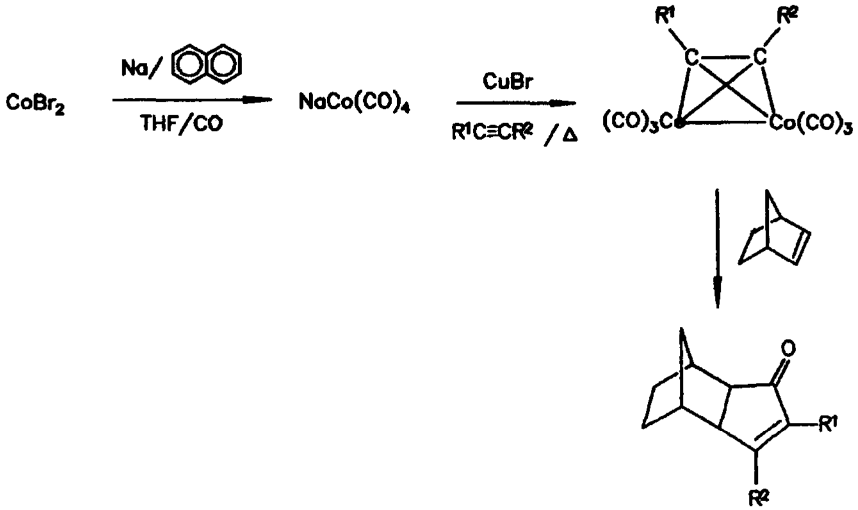
b) All products were identified by spectral data (IR, ^1H NMR and ^{13}C NMR), and comparison with the data reported in literature. Mass spectral data consistent with the assigned structures were obtained for the products in entries 1, 2, 3, 5, 6, 8, 9 and 11.

c) Yields are of isolated products, calculated on the basis of alkynes used.

It may be of interest to note that the hex-1-en-5-yne complex of $Co_2(CO)_6$ on reaction with cyclopentene gives the bicyclic product in which the 1-alkenyl group is intact (entry 10). Also, the reaction conditions permit the presence of an ester group in the alkyne (entry 11).

Synthesis of $RC{\equiv}CR{-}Co_2(CO)_6$ through reduction of $CoBr_2$ using Na/naphthalene followed by CuBr treatment.

The $NaCo(CO)_4$ reagent can be readily prepared by the reduction of CoX_2 (X = Cl, Br) by Na/naphthalene combination in the presence of CO.[7] It has been reported that the $NaCo(CO)_4$ reagent gives $[CuCo(CO)_4]_n$ complex on treatment with CuCl under certain conditions.[11] It was of interest to us to examine the reactivity of the $NaCo(CO)_4$ - CuBr system in THF. It was found that heating of a mixture of $NaCo(CO)_4$ and CuBr with an alkyne and norbornene gives the corresponding cyclopentenone in moderate to good yields (Table 2).

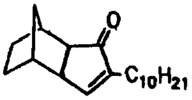
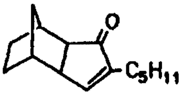
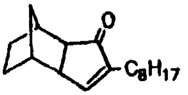
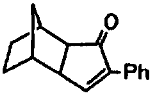
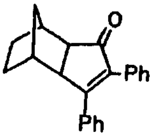


The yields are somewhat less compared to those obtained in the previous method utilizing metallic zinc for reduction in some cases. It was also found that this reagent system is more complicated. For example, whereas the methyl undecylenoate gave the cyclized product with norbornene in 91% yield, following the zinc method (Table 1), the $CoBr_2$/Na/naphthalene/CuBr combination gave a complex mixture of products. Similar complication was also observed when the reaction was carried out in the case of 1-heptyne in the presence of methyl butyrate. Clearly, the latter combination gives other reactive species in addition to the alkyne-$Co_2(CO)_6$ species, responsible for the Pauson-Khand cyclization.

Conclusions

Convenient procedures have been developed for the synthesis of alkyne-$Co_2(CO)_6$ complexes for application in Pauson-Khand cyclopentenone synthesis. The procedure utilizing metallic zinc for the reduction of $CoBr_2$ has been found to give cleaner reaction than the method utilizing the Na/naphthalene/CuBr combination. In addition to use in Pauson-Khand cyclopentenone synthesis, the alkyne complexes are also useful in masking the reactivity of alkynes and also in other useful transformations (e.g., Nicholas reaction).[12] Accordingly, the synthesis of these complexes, utilizing readily accessible reagents, following the procedures described here, should make these metal carbonyls more attractive for synthetic applications.

Table 2: Reaction of (alkyne)$Co_2(CO)_6$ complexes prepared in THF using $CoBr_2$/Na/naphthalene/CuBr with norbornene.[a]

S.No	Alkyne	Time	Product[b]	Yield(%)[c]
1	n-$C_{10}H_{21}C{\equiv}CH$	4h		76
2	n-$C_5H_{11}C{\equiv}CH$	4h		62
3	n-$C_8H_{17}C{\equiv}CH$	4h		65
4	$PhC{\equiv}CH$	4h		84
5	$PhC{\equiv}CPh$	12h		53

a) All reactions were carried out using $CoBr_2$(10mmol), Na(30mmol),naphthalene (10mmol), alkyne(5mmol), norbornene (10 mmol) and CuBr (10 mmol).

b) All products were identified by spectral data (IR, ^1H NMR and ^{13}C NMR) and comparison with the data reported in literature.

c) Yields are of isolated products, calculated based on the alkynes.

Experimental Section

General: Melting points reported in this manuscript are uncorrected and were determined using Buchi-510 capillary point apparatus. Infrared spectra were recorded on Perkin-Elmer model 1310 and JASCO FT-5300 with polystyrene as reference. ^1H NMR and ^{13}C NMR spectra were recorded on JEOL-FX-100 and Brucker-AC-200 spectrometers with chloroform-d as a solvent and TMS as reference (δ = 0 ppm). Elemental analysis were performed on a Perkin-Elmer elemental analyzer model-240C. Analytical thin layer chromatographic tests were carried out on glass plates (3×10 cm) coated with (250 mesh) Acme's silica gel G or G_{254} containing 13% calcium sulfate as binder. The spots were visualized by short exposure to iodine vapour or UV light. Column chromatography was carried out using Acme's silica gel (100–200 mesh). All yields reported are for isolated materials judged homogeneous by TLC, IR and NMR spectroscopy.

THF was freshly distilled over benzophenone–sodium. The alkenes, 1-heptyne and 4-octyne utilized were commercial samples, supplied by Fluka Switzerland. 1-Decyne, 1-octyne, phenylacetylene, diphenylacetylene and methyl undecylenoate were prepared following reported procedures.[13] Hex-1-en-yne was prepared from 1,6-dibromohexane following a reported procedure.[13–15] Activated zinc dust was prepared by treating commercial Zn dust with 1% H_2SO_4, washing with H_2O, acetone and drying at 150° C for 4h under vacuum. Anhydrous $CoBr_2$ was prepared from the hydrated complex. It was kept in the air oven at 150° C for 5–6h, further dried at 150°C for 4h under vacuum and was kept under nitrogen in a desiccator. CuBr (Fluka) was purified by treatment with a saturated solution of SO_2 in water. After decanting the water, it was washed with dry ether, ethanol and dried under vacuum at 100°c for 2–3h. Carbon monoxide was generated by dropwise addition of formic acid (98%) to conc. H_2SO_4 (96%) at 90°C using an apparatus recommended for utilization in the carbonylation of organoboranes.[16]

Preparation of the (Ph–C≡C–Ph)$Co_2(CO)_6$ complex:

A mixture of anhydrous $CoBr_2$ (2.18 g, 10 mmol) Zn dust (o.72 g, 11 mmol) and diphenylacetylene (0.89 g, 5 mmol) in THF (60 ml) was stirred for 3h while bubbling CO at 25°C. During this time the reaction mixture turned to reddish brown. The resulting mixture was taken in ether (60 ml), washed with H_2O (30 ml), brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatography on a silica gel column. The complex (Ph–C≡C–Ph)$Co_2(CO)_6$ was isolated in 85% (1.96 g) yield, using hexane as an eluent. M.P.: 105°C (lit[17] m.p. 109°C), IR(KBr): 680, 740, 2000, 2050, 2100, 3025 cm^{-1}

Preparation of (1-decyne)hexacarbonyldicobalt complex through reduction of $CoBr_2$ with Zn and it's reaction with norbornene.

A mixture of anhydrous $CoBr_2$ (2.18 g, 10 mmol), Zn dust (0.72 g, 11 mmol) and 1-decyne (5 mmol) in THF (60 ml) was stirred for 3h while bubbling CO at 25°C. During this time the reaction mixture turned to reddish-brown. The CO atmosphere was replaced by N_2, norbornene (10 mmol) was added and the contents were stirred for 4h at 65°C (note the changes in time for less reactive olefins. Table 1). The reaction mixture was added to H_2O (60 ml). Hexane (40 ml) was added and the organic phase was separated. The aqueous phase was saturated with NaCl and extracted with ether (2x30 ml). The combined organic extract was washed with brine (20 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column. The cyclopentenone derivative was isolated using hexane/ethyl acetate (95:5) as eluent. Yield 92% (1.20 g)(entry 1, Table 1); IR(neat): 1040, 1180, 1440, 1630, 1700, 2950, 3025 cm^{-1}; ^{1}H NMR: δppm 0.8 (t, 3H), 1.0–1.6 (m, 20H), 2.1 (m, 2H), 2.3 (br s, 1H), 2.5 (br s, 1H), 7.0 (br s, 1H); ^{13}C NMR: δppm 13.6, 22.2, 24.3, 27.4, 28.0, 28.6, 28.8, 30.5, 31.4, 37.7, 38.5, 47.7, 53.4, 149.2, 158.1, 210.3. Mass(m/e): 260 (M$^+$, 50%), 232(10%), 163(100%).

The above procedure was followed for other substrates (Table 1, entries 2–11). The physical constants and spectral data obtained are summarized below.

(2). Yield 88% (1.02 g); IR(neat): 1040, 1180, 1440, 1630, 1700, 2950, 3025 cm^{-1}; ^{1}H NMR: δppm 0.7 (t, 3H), 0.8–1.5 (m, 16H), 1.9 (m, 2H), 2.2 (br s, 1H), 2.4 (br s, 1H), 6.9 (br s, 1H); ^{13}C NMR: δppm 13.4, 21.9, 24.1, 27.2, 27.8, 28.5, 30.4, 30.9, 37.5, 38.4, 47.5, 53.2, 149.0, 157.8, 209.0; Mass (m/e): 232 (M$^+$, 43%), 203(20%), 175(22%), 163(100%), 91(68%).

(3). Yield 80% (0.90 g); M.P.: 92°C (lit.^{5} m.p. 93–95°C); IR(KBr): 700, 765, 1300, 1320, 1600, 1610, 1695, 2950, 3025, 3040 cm^{-1}; ^{1}H NMR: δppm 0.9–1.1 (m, 2H), 1.1–1.8 (m, 4H), 2.3–2.5 (m, 3H), 2.6 (m, 1H), 7.2–7.5 (m, 5H), 7.6–7.8 (m, 1H); ^{13}C NMR: δppm 28.4, 29.1, 31.2, 38.3, 39.4, 47.7, 54.9, 127.1, 128.4, 131.6, 146.1, 160.3, 209.1; Mass (m/e): 224 (M$^+$, 100%), 196(10%), 158(75%), 156(60%). Analysis calcd for $C_{16}H_{16}O$ C% 85.60, H% 7.14; found C% 85.43, H% 7.17.

(4). Yield 38% (0.57 g); M.P.: 129–130°C (lit.^{5} m.p. 130–131°C); IR(KBr): 700, 730, 800, 1300, 1340, 1600, 1610, 1685, 2950, 3025, cm^{-1}; ^{1}H NMR: δppm 0.9–1.7 (m, 6H), 2.3–2.6 (m, 3H), 3.2 (d, 1H), 7.1–7.3 (m, 10H); ^{13}C NMR: δppm 28.8, 29.0, 31.6, 38.4, 39.5, 50.8, 54.1, 127.9, 128.5, 128.7, 129.5, 129.6, 132.4, 135.3, 170.1, 208.8

(5). yield 78% (0.90 g); IR(neat): 1100, 1350, 1640, 1700, 2950 cm^{-1}; ^{1}H NMR: δppm 0.7–1.1 (m, 14H), 1.2–1.7 (m, 6H), 1.9–2.6 (m, 4H); ^{13}C NMR: δppm 13.8, 13.9, 20.6, 21.5, 24.8, 28.4, 28.8, 30.8, 31.1, 36.9, 28.4, 49.7, 53.1, 143.5, 174.1, 210.4; Mass (m/e): 232 (M$^+$, 40%), 217(100%), 204(10%), 189(30%).

(6). yield 58% (0.68 g); IR(neat): 1040, 1260, 1440, 1630, 1700, 2950, 3025 cm^{-1}; ^{1}H NMR: δppm 0.6–0.9 (t, 3H), 0.9–1.3 (m, 14H), 1.3–1.6, 1.6–1.8, 1.9–2.1 (m, 6H), 2.5–2.8, 3.0–3.2 (m, 2H), 7.0 (br s, 1H); ^{13}C NMR: δppm 13.9, 22.5, 23.4, 24.6, 27.8, 29.2, 29.6, 30.1, 31.5, 31.8, 43.8, 50.1, 147.0, 160.2, 212.9; Mass (m/e): 234 (M$^+$, 42%), 177(44%), 137(100%), 79(75%).

(7). yield 47% (0.47 g); M.P.: 40–42°C (lit.^{5} m.p. 40–44°C); IR(neat): 690, 755, 1290, 1310, 1600, 1620, 1695, 2950, 3025, 3040 cm^{-1}; ^{1}H NMR: δppm 1.1–2.0 (m, 6H), 2.9–3.0, 3.2–3.4 (m, 2H), 7.2–7.5, 7.6–7.8 (m, 6H); ^{13}C NMR: δppm 23.3, 29.4, 30.2, 42.2, 50.9, 126.9, 127.7, 128.1, 129.6, 143.2, 161.8, 210.7.

(8). Yield 30% (0.35 g); IR(neat): 1045, 1360, 1440, 1630, 1700, 2950, 3025 cm^{-1}; ^{1}H NMR: δppm 0.6–1.0 (m, 6H), 1.0–1.4 (m, 18H), 1.9–2.2, 2.3–2.7 (m, 3H), 7.1–7.4 (m, 1H); ^{13}C NMR: δppm 13.6, 22.2, 24.3, 24.6, 26.6, 26.9, 27.2, 27.3, 29.1, 31.4, 31.5, 31.9, 32.3, 33.2, 38.5, 41.4, 45.2, 52.2, 55.5, 61.6, 145.6, 145.8, 155.3, 160.8, 208.9, 211.4; Mass (m/e): 236 (M$^+$, 6%), 165(13%), 152(48%), 95(85%), 55(92%).

(9). Yield 26% (0.35 g); IR(neat): 700, 750, 1300, 1445, 1600, 1620, 1695, 2950, 3025, 3050 cm^{-1}; ^{1}H NMR: δppm 0.7–1.0 (t, 3H), 1.1–1.4 (m, 14H), 1.9–2.2, 2.2–2.7 (m, 3H), 7.1–7.8 (m, 6H); ^{13}C NMR: δppm 14.1, 22.7, 27.2, 27.6, 29.2, 29.5, 29.6, 30.0, 31.6, 31.8, 33.2, 35.1, 38.4, 41.8, 42.9, 60.4, 126.7, 127.2, 127.5, 128.0, 128.5, 129.0, 129.5, 130.0, 131.7, 140.9, 142.6, 157.5, 162.9, 207.3, 209.8; Mass (m/e): 270 (M$^+$ 13%), 158(60%), 129(45%), 105(100%).

(10). Yield 55% (0.48 g); IR(neat): 800, 1630, 1640, 1700, 2950, 3025, 3050 cm^{-1}; ^{1}H NMR: δppm 1.1–2.3 (m, 10H), 2.7–3.2 (m, 2H), 4.8–5.1 (m, 2H), 5.7 (m, 1H), 7.1 (br s, 1H); ^{13}C NMR: δppm 22.9, 23.5, 29.1, 29.6, 31.1, 43.5, 49.5, 114.7, 137.2, 145.3, 160.5, 212.1; Mass (m/e): 176 (M$^+$ 98%), 107(60%), 91(96%), 79(96%).

(11). Yield 91% (1.45 g); IR(neat): 1188, 1437, 1699, 1739, 2928 cm^{-1}; ^{1}H NMR: δppm 0.8–1.1, 1.1–1.6 (m, 22H), 2.0–2.3 (m, 3H), 2.5 (br s, 1H), 3.6 (s, 3H), 7.0 (br s, 1H); ^{13}C NMR: δppm 24.2, 24.4, 27.3, 27.9, 28.6, 28.8, 30.5, 33.4, 37.6, 38.5, 47.6, 50.7, 53.3, 148.9, 157.9, 173.4, 210.1.

Preparation of (1-dodecyne)hexacarbonyldicobalt complex using $NaCo(CO)_4$/CuBr and its reaction with norbornene.

CuBr (1.43 g, 10 mmol), 1-dodecyne (0.83 g, 5 mmol) was added to $NaCo(CO)_4$ [prepared using $CoBr_2$ (1.28 g, 10 mmol), Na (0.69 g, 30 mmol), naphthalene (1.28 g, 10 mmol)] in THF (60 ml) under N_2 atmosphere. The contents were stirred for 6h at 25°C. Norbornene (0.94 g, 10 mmol) was added and further stirred at 65°C for 4h. The resulting mixture was added to H_2O (60 ml). Hexane (40 ml) was added and the organic phase was separated. The aqueous phase was saturated with NaCl and extracted with ether (2x30 ml). The combined organic extract was washed with brine (30 ml); dried over anhydrous $MgSo_4$ and concentrated. The residue was chromatographed on a silica gel column and the cyclopentenone derivative was isolated in 76% (1.1 g) yield using 5% ethyl acetate in hexane as eluent.

IR(neat): 1040, 1180, 1440, 1620, 1700, 2950 cm^{-1}; ^{1}H NMR: δppm 0.8 (t, 3H), 1.2–1.7 (m, 24H), 2.1 (m, 2H), 2.4 (br s, 1H), 2.6 (br s, 1H), 7.1 (br s, 1H); ^{13}C

NMR: δppm 13.9, 22.5, 24.6. 27.8, 28.3, 29.0, 29.5, 30.9, 31.8, 38.0, 38.9, 48.0, 53.7, 149.4, 158.2, 210.6.

The above procedure was followed for other substrates (Table 2, entries 2-5). (2) Yield 62% (0.68g); IR(neat): 1053, 1186, 1456, 1699, 2872, 2957 cm^{-1}; ^{1}H NMR: δppm 0.9 (t, 3H), 1.1-1.7 (m, 14H), 2.1 (m, 2H), 2.3 (br s, 1H), 2.5 (br s, 1H), 7.1 (br s, 1H). ^{13}C NMR: δppm 13.2, 21.7, 24.0, 26.8, 27.8, 28.4, 30.2, 31.0, 37.4, 38.2, 47.4, 53.1, 148.9, 157.7, 209.8.

The physical constants and spectral data of the cyclopentenone derivatives obtained in these experiments (entries 3-5, Table 2) were identical to the data of the samples previously obtained using the $CoBr_2$/Zn/CO system.

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