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The effect of ultrasound and of phosphine and phosphine-oxides on the Khand reaction

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Abstract

Ultrasonic irradiation allows the Khand reaction to be conducted rapidly at low temperatures. Addition of phosphine oxides to the reaction mixture significantly increases yields in most cases.

Introduction

The formation of cyclopentenones from alkynehexacarbonyldicobalt complexes plus alkenes (Khand reaction) is finding increasing use as a general synthetic method [1,2] but still suffers from modest yields in all but the most favourable cases. As part of our continuing endeavours to improve this reaction we investigated both the effect of ultrasonic irradiation and that of modifying the complex by replacing one or two carbonyl ligands by a phosphine. Experiments were conducted both with isolated phosphine-substituted complexes and by simply adding phosphines to the reaction mixture. Neither method proved advantageous, but adventitious addition of tributylphosphine-oxide significantly enhanced the yield. This reagent has therefore been studied more extensively and one example of its use was included in a review [1]. The full results of this work are presented below.

Discussion

The Khand reaction is clearly a multi-step process but no intermediate has ever been isolated and no definitive mechanistic evidence is available. Observations of the regio- and stereoselectivity of the reaction have led to some speculation about

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the later stages of the mechanism including the type of complex formed when the alkene moiety has inserted into a cobalt–carbon (alkyne) bond [3–5]. It is assumed that carbon monoxide insertion and ring closure follow as subsequent steps. It appears likely that before insertion the alkene becomes coordinated to a cobalt atom. It is not know whether this occurs by a dissociative mechanism involving substitution of a CO ligand or by an additive mechanism which could involve detachment of the alkyne from one cobalt atom or more probably [6] its rearrangement to form a dicobaltacyclobutene. Although replacement of one CO in the original complex by a phosphine or phosphite ligand might be expected to reduce any tendency for CO dissociation, it could nevertheless promote the overall process by assisting a later stage. Moreover we considered that such substitution might stabilise an intermediate and hence allow its detection or isolation. We therefore employed the complexes **1a–g** and **2a–c** in model Khand reactions using 2,5-dihydrofuran as a typically reactive alkene. Some of the complexes are new (**1d**, **2a**, **2b**) and their preparation and properties are recorded in the experimental section together with previously unreported ^{1}H and ^{13}C NMR data for known complexes. Appreciable coupling is observed between the phosphorus atoms and the terminal hydrogen of the acetylenic ligand.

In every case, replacement of carbonyl by phosphine or phosphite ligands either reduced the final yield or at least reduced the rate of reaction (Table 1). No new complexes were detected. Addition of ligand to the alkyne-hexacarbonyl-dicobalt complex without isolation of the ligand-substituted complex had the same effect. The use of a sample of tributylphosphine which had become oxidised to the phosphine oxide however led to the recognition that the latter can have a beneficial effect. Table 2 summarises our experience with four typical alkyne complexes and four different alkenes and with some variations of reaction conditions. While some of these cases show no significant effect of adding the phosphine oxide, the general trend is of enhanced yield with a 50% enhancement not uncommon.

Precise comparison of the "catalyzed" and "uncatalysed" runs is not justified in view of the large variations in yields which we have experienced under apparently identical conditions. Attempts to trace the source of these variations have been inconclusive. Thus replacement of a nitrogen atmosphere by carbon monoxide did not consistently alter the yield while in a set of three simultaneous experiments (using 1-heptyne complex and 2,5-dihydrofuran) a static nitrogen atmosphere led to an exceptionally low yield, but a faster than "normal" nitrogen flow rate also diminished the yield. In the same system a dark reaction gave one of the lower yields, but irradiation did not significantly increase the yield above the average value.

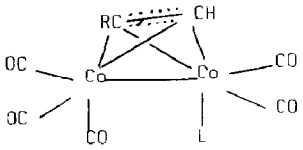
(*Continued on p. 238*)

Table 1

Reaction times and yields for the conversion of the complexes **1** into the bicyclic ketone **3a** [a]

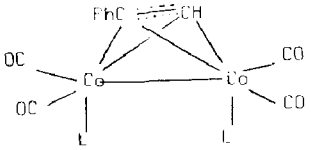
Complex:	**1a**	**1b**	**1c**	**1d**	**1e**	**2c**
Time (h)	24	5	36	8	16	40
Yield (%) [b]	36 [c]	8 [d]	45 *	14 *	6 *	5 *

[a] All reactions were conducted in refluxing toluene under nitrogen. [b] Based on unrecovered starting material (* indicates > 10% recovery). [c] cf. Table 2. [d] A 12% yield was obtained in refluxing benzene.



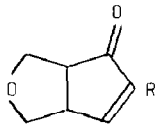
1

a) R = Ph, L = CO
b) R = Ph, L = PPh_3
c) R = Ph, L = PBu_3
d) R = Ph, L = $P(OPh)_3$
e) R = Ph, L = $P(OMe)_3$
f) R = n-C_5H_{11}, L = CO
g) R = n-C_5H_{11}, L = PBu_3
h) R = H, L = CO



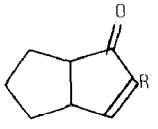
2

a) L = $P(OPh)_3$
b) L = $P(OMe)_3$
c) L_2 = $Ph_2PCH_2PPh_2$



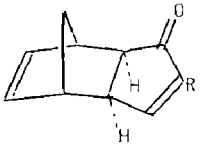
3

a) R = Ph
b) R = n-C_5H_{11}



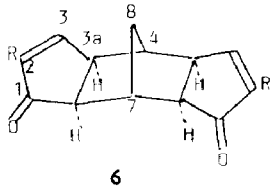
4

a) R = Ph
b) R = n-C_5H_{11}
c) R = H



5

a) R = H
b) R = C_5H_{11}



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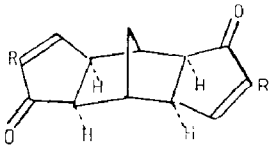

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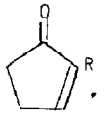


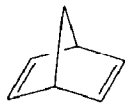
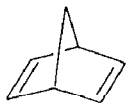
8

a) R = n-C_5H_{11}
b) R = *cis*-$CH_2CH{=}CHC_2H_5$
c) R = C_6H_5

Table 2

Effect of reaction conditions on yields in Khand reactions [a]

R in complex I (L = CO)	Alkene	Solvent	Temp. (° C)	Time (h)	Product	Yield "uncatalysed" (%)	Yield in Bu_3PO [b] promoted reaction (%)	Other yields (%)
C_6H_5		hexane	69	36	**3a**	37	69	
n-C_5H_{11}		hexane	69	36	**3b**	37		
n-C_5H_{11}		isooctane	60	36	**3b**			48 (Bu_3P)
n-C_5H_{11}		toluene	100	24	**3b**	47 (av.) [c]	64 [d]	54 (Ph_3PO), 34 [$(MeO)_2$-P(=O)Me], 56 [HMPT]
C_6H_5		hexane	69	36	**4a**	40	70	
C_6H_5		toluene	110	36	**4a**	42 [e] [49]	68	
C_6H_5		toluene	70	48	**4a**	12 [e] [25]		49 [e] [59] (US [f])
n-C_5H_{11}		hexane	69	24	**4b**	41	70	
H		toluene	110	36	**4c**	49, 45 [e]	53, 49 [e]	

n-C_5H_{11}	C_2H_4/50 atm.	toluene	110	36	**8a**	36	70	26 (Bu_3P)
n-C_5H_{11}	C_2H_4/50 atm.	toluene	85	36	**8a**	44, 39		
n-C_5H_{11}	C_2H_4/50 atm.	toluene	80	36	**8a**	31	47	
n-C_5H_{11}	C_2H_4/50 atm.	toluene	15–20	330	**8a**	47	35, 49 [h]	
$CH_2CH{=}CHC_2H_5$ (*cis*) [i]	C_2H_4/35 atm.	toluene	110	36	**8b**	25	33	
$CH_2CH{=}CHC_2H_5$ (*cis*) [i]	C_2H_4/50 atm.	toluene	100	36	**8b**	32		
C_6H_5	C_2H_4/50 atm.	toluene	110	36	**8c**	31	45	
H		toluene	70	4	**5a**	44 *exo* 10 *endo*		
H		toluene	100	24	**5a**		34 *exo* 6.5 *endo*	
H		toluene	100	24	**5a**	33	54	
n-C_5H_{11}		toluene	100	48	**5b**	46 [e] [52]	62	
n-C_5H_{11}		toluene	70	48	**5b**	13 [e] [29]	–	56 [e] [65] (US [f])

[a] Reactions were conducted under a slow stream of nitrogen unless otherwise specified. [b] One mole per mole of complex **1**. [c] Average of 12 results: 5 under 'standard' conditions (36, 56, 34, 78, 53%) one in the dark (34%) two under irradiation (52, 52%), two under CO atmosphere (44, 63%), one under a fast N_2 stream (44%) and one under a static N_2 atmosphere (20%). [d] Average of 4 results (64, 63, 65, 65%). [e] Incomplete reaction, yield based on unrecovered complex I in brackets. [f] Under ultrasonic irradiation/3 h reaction time. [g] Under CO. [h] 16 days. [i] Details of this reaction will be reported elsewhere.

Even more erratic results have been obtained when testing trimethylamine-*N*-oxide as a potential promoter of the reaction; we defer an account until further study has clarified the effect of this substance.

The high reactivity of ethylene as the alkene component is revealed by its ability (Table 2) to react even at room temperature, albeit slowly (~ 14 d to give the cyclopentenone in comparable yield to reaction for 36 h at 85 °C). Two liquid alkenes were also tried under these conditions (room temp., 14 d with Bu_3PO), 2,5-dihydrofuran giving a very low yield (~ 7%) and cyclopentene giving none of the corresponding cyclopentenone. The single experiment using ethylene at 120 atm. (initial pressure) suggests that higher pressure might significantly enhance yields.

In contrast to the results in Table 2 we have not, to date, observed a significant yield enhancement by a phosphine oxide in any intramolecular Khand reaction. Moreover it has been reported [5] that its use in one such reaction led to reductive cleavage of a propargyl silyl ether grouping. Table 2 includes its use in the reaction of ethynehexacarbonyldicobalt with norbornadiene. This reaction had previously been observed [7] to be much less stereoselective than many closely related examples, yielding the corresponding *endo* isomer in addition to the expected product (**5a**). Neither the addition of the phosphine oxide nor the use of rather severe reaction conditions resulted in a stereoisomer ratio significantly different from that previously reported (~ 1/4) [7]. This conflicted with the earlier conclusion that the *endo*-compound results from isomerisation of the *exo* form. Indeed when a sample of pure *exo*-ketone (**5a**) was kept at 70 °C in the presence of octacarbonyldicobalt for 24 h no such isomerisation occurred but less than 50% of the ketone was recovered. We conclude that the previously noted change in isomer ratio of a mixed sample must have resulted from differential rate of loss of the two stereoisomers and not from isomerisation.

Cobalt complexes (**1**) of substituted alkynes react much more stereoselectively with norbornadiene; thus in conformity with our earlier work [7] the heptyne complex (**1f**) gave predominantly the *exo*-product (**5b**). Careful chromatographic separation permitted the isolation of the corresponding *endo*-ketone in an amount corresponding to approx. 2.5% of the total ketone yield and also provided small amounts of the diketones (**6** and **7**) expected [7] from further reaction at the isolated double bond ($\Delta - 5$) of the monoketones (**5**).

In parallel with the effects of addends we have studied the effect of ultrasonic irradiation of the reaction mixture. Results included in Table 2 show that this allows reactions to proceed considerably faster at lower temperatures but has little effect on the yields. Addition of tributylphosphine oxide did not enhance yields in reactions carried out under ultrasonic irradiation.

Experimental

All reactions were conducted under dinitrogen unless otherwise specified. Solvents were removed on a rotary evaporator. Alumina for chromatography was Spence's grade UG1 (100 mesh) which had been neutralised by treatment with ethyl acetate, washing with ethanol and water and dried at 150 °C for 12 h. Light petroleum refers to the fraction, b.p. 40–60 °C.

Complexes ***1*** *(L = CO)*

These were prepared [8,9] in 80–85% yield by stirring octacarbonyldicobalt (34.2

g, 0.10 mol) with an equimolar quantity or slight excess of the alkyne in dry, olefin-free light petroleum (150–200 ml) for 3–4 h and purified by alumina column chromatography (**1a**) or distillation (**1f**, **1h**):

*Phenylethene complex (**1a**).* Red oil which crystallises below 0 °C; ν(CO) (film) 2045, 2025, 2010 cm^{-1}; ^1H NMR: $\delta(CDCl_3)$ 7.4 (5H, m, C_6H_5), 6.35 ppm (1H, s, ≡CH; ^{13}C NMR: $\delta(CDCl_3)$ 137.4 (C(1) of C_6H_5), 130.2, 128.8, 128.1 (C_6H_5), 90.2 (C≡CH), 72.6 ppm (≡CH).

*1-Heptyne complex (**1f**) [1,10].* Dark red oil, b.p. 120 °C/0.1 torr; ν(CO) (film) 2042, 2025, 2005 cm^{-1}; $\delta(CDCl_3)$ 6.0 (1H, s, ≡CH), 2.9 (2H, t, J 7 Hz, CH_2C≡), 1.55 (6H, m, CH_2), 0.9 ppm (3H, t, J 6 Hz, CH_3). Anal. Found: C, 41.8; H, 3.5. $C_{13}H_{12}Co_2O_6$ calc: C, 40.9; H, 3.2%.

*Phosphine and phosphite substituted complexes (**1**)*

These were prepared by refluxing hexane solutions of the hexacarbonyl complex (**1a** or **1f**) with the appropriate ligand in 10% excess until TLC indicated disappearance of the initial complex (2–4 h). The resultant solutions were filtered through Kieselguhr, concentrated under reduced pressure and chromatographed on alumina columns. Traces of unreacted hexacarbonyls were eluted with light petroleum and the phosphine or phosphite substituted complexes were eluted with 1/1 ether/light petroleum.

*Pentacarbonyl [μ-[(η^2:η^2-ethynyl)benzene]]triphenylphosphinedicobalt-(Co–Co) (**1b**) [11–13]* (45% yield; lit. [14]: 70%) had m.p. 107 °C (lit. [13]: m.p. 104–107 °C), ν(CO) (Nujol) 2028, 2010, 1996 cm^{-1}; ^1H NMR: $\delta(CDCl_3)$ 7.2 (2OH, m, C_6H_5), 5.45 ppm (1H, d, J(H–P) 3.8 Hz, ≡CH); ^{13}C NMR: $\delta(CDCl_3)$ 138.9, 134.1 (d, J(C–P) 41 Hz), 133.0 132.9, 130.6, 130.0, 128.3, 128.22, 128.16, 126.7 (C_6H_5), 86.1 (C≡CH), 71.2 ppm (≡CH).

*Tributylphosphinepentacarbonyl[μ-[(η^2:η^2-ethynyl)benzene]]dicobalt(Co–Co) (**1c**) [11]* (68%) had m.p. 44 °C (lit: [11]: m.p. 45–46 °C), ν(CO) (Nujol) 2030, 2006, 1955 cm^{-1}; ^1H NMR: $\delta(CDCl_3)$ 7.3 (5H, m, C_6H_5), 5.60 (1H, d, J 3 Hz, ≡CH), 1.30 (18H, m, CH_2), 0.85 ppm (9H, t, CH_3); ^{13}C NMR: $\delta(CDCl_3)$ 139.8, 130.5, 128.5, 126.9 (C_6H_5), 84.3 (C≡CH), 68.3 (≡CH), 27.8 (d, J(C–P) 24 Hz, CH_2P), 25.38 (d, J(C–P) 3 Hz, CH_2CH_2P), 24.15 (d, J(C–P) 12 Hz, $CH_2CH_2CH_2P$), 13.55 ppm (CH_3).

*Pentacarbonyl[μ-[(η^2:η^2-ethynyl)benzene]](triphenyl phosphite)dicobalt(Co–Co) (**1d**)* (51%), deep red crystals, m.p. 145 °C; ν(CO) (Nujol) 2034, 2012, 2003 cm^{-1}; ^1H NMR: $\delta(CDCl_3)$ 7.2(2OH, br.m, C_6H_5), 5.30 ppm (1H, d, J(H–P) 4 Hz, ≡CH); ^{13}C NMR: $\delta(CDCl_3)$: 151.0 (d, J(C–P) 7 Hz, C-O-P), 138.7, 130.9, 129.8, 128.4, 127.2, 125.2, 121.1 (C_6H_5), 86.8 (C≡CH), 70.7 ppm (≡CH). Anal. Found: C, 55.1; H, 3.0; P, 4.6. $C_{31}H_{21}Co_2O_8P$ calc: C, 55.5; H, 3.1; P 4.6%. This complex was accompanied by tetracarbonyl[μ-[(η^2:η^2-ethynyl)benzene]]-bis(triphenyl phosphite)-dicobalt(*Co–Co*) (**2a**) (13%) which was not fully characterized, m.p. 139 °C (decomp.), ν(CO) (Nujol) 2060, 2015, 1978 cm^{-1}; $\delta(CDCl_3)$ 7.17 (35H, br.m, C_6H_5), 4.61 ppm (1H, t, J(H–P) 4 Hz, ≡CH).

*Pentacarbonyl[μ-[(η^2:η^2-ethynyl)benzene]](trimethyl phosphite)dicobalt(Co–Co) (**1e**) [13]* (49%) had m.p. 49–50 °C, ν(CO) (Nujol) 2058, 1995 cm^{-1}; $\delta(CDCl_3)$ 7.3 (5H, m, C_6H_5), 5.85 (1H, d, J(H–P) 3.5 Hz, ≡CH), 3.37 ppm (9H, d, J(H–P) 12 Hz, OCH_3). Anal. Found: C, 39.6; H, 2.9; P, 6.1. $C_{16}H_{15}Co_2O_8P$ calc: C, 39.7; H, 2.9; P, 6.4%. This was accompanied by tetracarbonyl[μ-[(η^2:η^2-ethynyl)ben-

zene]]bis(trimethyl phosphite)dicobalt(*Co–Co*) (**2b**) (26%), m.p. 53–54°C, ν(CO) (Nujol) 2015, 1925 cm^{-1}; $\delta(CDCl_3)$ 7.3 (5H, m, C_6H_5), 5.40 (1H, t, J(H–P) 3 Hz, ≡CH), 3.35 ppm (18H, t, J(H–P) 6 Hz, OCH_3). Anal. Found: C, 37.3; H, 4.1; P, 10.6. $C_{18}H_{24}Co_2O_{10}P_2$ calc: C, 37.2; H, 4.1; P, 10.6%.

Tetracarbonyl[μ-[(η²:η²-ethynyl)benzene]][μ-[methylenebis(diphenylphosphine)-PP′]]dicobalt(Co–Co) (2c) [14] (67%) was obtained by stirring octacarbonyldicobalt (5.5 g, 16.1 mmol) and phenylethyne (1.65 g, 16.3 mmol) in hexane (100 ml) for 2 h and without isolation of the complex **1a** adding methylenebis(diphenylphosphine) [15] (6 g, 15.6 mmol) followed by heating to reflux for 4 h. It was purified by chromatography on alumina, eluting with 1/1 chloroform/light petroleum; purple crystals, m.p. 119°C; ν(CO) 2010, 1995, 1930 cm^{-1}; $\delta(CDCl_3)$ 7.25 (25H, br.m., C_6H_5), 5.8 (1H, t, J(H–P) 8 Hz, ≡CH), 3.62 an 3.16 ppm (ea. 1H, m, CH_2). Anal. Found: C, 62.6; H, 4.3; P, 8.2. $C_{37}H_{28}Co_2O_4P_2$ calc: C, 62.0; H, 3.9; P, 8.6%.

2-Pentylcyclopent-2-en-1-one [16]: A solution of 1-heptynehexacarbonyldicobalt (**1f**) (7.5 g) in toluene (200 ml) was placed in a 200 ml steel autoclave which was pressurised with ethylene (60 atm.). The autoclave was shaken and heated to 110°C for 36 h, then cooled and the contents filtered. After removal of toluene the residue was chromatographed on alumina. Light petroleum eluted unchanged complex **1f** (0.2 g) and ether/light petroleum (1/1) eluted the product which was further purified by flash chromatography [18] (same eluent) and distillation at 100°C (bath temp.)/0.4 torr (Lit. [16]; b.p. 60°C/0.2 torr) yielding a very pale yellow oil (1.06 g, 36%); $\nu_{max.}$ (film) 1700, 1633 cm^{-1}; $\delta(CDCl_3)$ 7.30 (1H, m, =CH), 2.57 (2H, m, H(4)), 2.40 (2H, m, H(5)), 2.16 (2H, br.t, J 7 Hz, H(1′), 1.48 (2H, quintet, H(2′)), 1.31 (4H, m, H(3′, 4′)), 0.90 ppm (3H, t, J 6 Hz, CH_3). The reaction in the presence of tributylphosphine oxide (4.1 g) was carried out in the same manner yielding 1.4 g (49%) of the ketone (cf. Table 2). Anal. Found: C, 78.9; H, 10.6. $C_{10}H_{16}O$ calc: C, 78.8; H, 10.6%.

1,3,3a,6a-Tetrahydro-5-phenyl-4H-cyclopenta[c]furan-4-one (3a).

(a) from complex 1a: A mixture of the complex **1a** (3.3 g, 8.5 mmol) and 2,5-dihydrofuran (3.9 g, 55 mmol) was heated in toluene (150 ml) under reflux for 24 h. The solution was filtered and evaporated under reduced pressure and the residue chromatographed on alumina. After elution of unreacted complex **1a** (0.42 g, 13%) with light petroleum, the product **3a** was eluted with chloroform. Removal of the solvent left a pale yellow solid (0.54 g, 32% [36% based on unrecovered complex]). Recrystallisation from 1/1 ether/light petroleum gave colourless crystals, m.p. 63°C, $\nu_{max.}$ (Nujol), 1700, 1598, 1490, 1445, 1325, 1130 cm^{-1}; $\delta(CDCl_3)$ 7.65 (3H, m, H(3) and 2H of C_6H_5), 7.32 (3H, m, C_6H_5), 3.3–4.3 (5H, m, H(4), H(6) and H(3a)), 3.1 ppm (1H, t, J 7 Hz, H(6a)). Anal. Found: C, 77.5; H, 5.9. $C_{13}H_{12}O_2$ calc: C, 78.0; H, 6.0%.

(b) from substituted complexes 1b–e and 2: The preceding procedure was employed with substitution of the appropriate complex and with the results summarised in Table 1. Complexes **2a** and **2b** failed to yield the cyclopentenone **3a** in isolable quantity.

(c) tributylphosphine oxide catalysed reaction: This was carried out by heating the complex **1a** (7.5 g, 19.4 mmol), tri-n-butylphosphine oxide (3.1 g, 14.2 mmol) and 2,5-dihydrofuran (8 g, 114 mmol) in hexane (200 ml) under reflux. A control reaction was carried out omitting the phosphine oxide. Results are in Table 2.

1,3,3a,6a-Tetrahydro-5-pentyl-4H-cyclopenta[c]furan-4-one (3b). The preceding

procedures were used with the results summarised in Table 2. The ketone **3b** had b.p. 150 °C/0.3 torr; $\nu_{max.}$ (liquid film) 1700, 1630, 1460, 1375, 1075, 1036, 914, 892 cm^{-1}; $\delta(CDCl_3)$ 7.2 (1H, m, =CH), 3.3–4.2 (5H, m, H(4), H(6) and H(6a)), 2.9 (1H, m, H(3a)), 2.2. (2H, m, =C-CH_2), 1.2–1.7 (6H, m, CH_2 at 1′, 3′, 4′), 0.9 ppm (3H, t, CH_3). Anal. Found: C, 73.9; H, 9.7%; *m/z* 194.1303. $C_{12}H_{18}O_2$ calc: C, 74.2; H, 9.3%; *M*, 194.1307.

The experiment employing the tributylphosphine-substituted complex **1g** was conducted by warming the hexacarbonyl **1f** (5.7 g, 14.9 mmol) and tri-n-butylphosphine (3.0 g, 14.8 mmol) in iso-octane to 60 °C for 3 h. Although the complex **1g** was not isolated at this stage before addition of 2,5-dihydrofuran (5.0 g, 70 mmol), much (48%) was recovered from the incomplete reaction as a dark red oil, ν(CO) (liquid film) 2023, 1980, 1950 cm^{-1}, $\delta(CDCl_3)$, 5.25 (1H, d, *J*(H–P) 4 Hz, ≡CH), 2.7 (2H, br.t, ≡C-CH_2), 1.45 (24H, m, CH_2), 0.95 ppm (12H, t, CH_3). Anal. Found: C, 51.0; H, 7.0; P, 5.4. $C_{24}H_{39}Co_2O_5P$ calc.: C, 51.8; H, 7.0; P, 5.5%.

4,5,6,6a-Tetrahydro[3aH]pentalenones (4). The general methods follow those for compounds **3**. Formation of the 2-phenyl derivative **4a** by Khand reaction of cyclopentene has been reported previously [17]. In the present work it was purified by chromatography on alumina and had ν_{max} 1700, 1595, 1490, 1440, 760, 690 cm^{-1}; $\delta(CDCl_3)$ 7.5 (6H, br. m, C_6H_5 and =CH), 3.3 (1H, m, H(6a)), 2.9 (1H, m, H(3a)), 1.3–2.1 ppm (6H, m, CH_2). The n-pentyl derivative (**4b**) had b.p. 140 °C/0.3 torr, $\nu_{max.}$ 1700, 1628, 1460, 1445 cm^{-1}; $\delta(CDCl_3)$ 7.1 (1H, m, =CH), 3.25 (1H, m, H(6a)), 2.72 (1H, m, H(3a)), 2.2 (2H, m, =C-CH_2), 1.3-2.0 (12H, m, CH_2), 0.95 ppm (3H, t, *J* 5 Hz, CH_3). Anal. Found: C, 81.2; H, 10.4%; *m/z* = 192.1517. $C_{13}H_{20}O$ calc: C, 81.3; H, 10.4%; *M* = 192.1514.

3a,4,7,7a-Tetrahydro-4,7-methanoinden-1-ones (5) were also made by the same general procedures. The unsubstituted ketone **5a** has previously been prepared by this route [9]. In the present work reaction of the ethyne complex **1h** (4 g, 12.8 mmol) and norbornadiene (2.4 g, 26 mmol) in toluene (~ 150 ml) at 70 °C for 4 h gave a mixture of *endo* and *exo* isomers which was freed from metal-containing products and from the diketones (~ 0.6 g) by chromatography on neutral alumina and eluted with ether. Separation of the isomers was then effected by flash chromatography [18] on MN-Kieselgel (230–400 mesh, Macherey-Nagel and Co) using 1/4 ethyl acetate/light petroleum as eluent. The *exo*-isomer **5a** (0.822 g, 44%) was eluted before its *endo*-isomer (0.192 g, 10.3%). Addition of tri-n-butylphosphine oxide to the reaction mixture did not significantly alter the yield or isomer ratio.

3a,4,7,7a-Tetrahydro-2-pentyl-4,7-methanoindan-1-one (5b) was obtained similarly (Table 2). Isomer separation was effected in one experiment in which the complex **1f** (7.64 g, 20 mmol) and norbornadiene (9.20 g, 100 mmol) were warmed to 55–60 °C in toluene (75 ml) under carbon monoxide for 3 h. Workup as in the preceding experiment and distillation (Kugelrohr, 150 °C/0.01 torr) yielded the *exo*-isomer **5b** (1.59 g, 37%), $\nu_{max.}$ ($CHCl_3$) 2900, 2850, 1665, 1640 cm^{-1} and its *endo*-isomer (37 mg, 0.9%). Anal. Found: C, 82.7; H, 9.1. $C_{15}H_{20}O$ calc: C, 83.3; H, 9.3%. Full identification was by ^1H NMR with the aid of decoupling and of "Eu(fod)$_3$" shift reagent ["H-8a" is *cis* to the cyclopentenone ring]:

Ketone **5b** (*exo*) showed: $\delta(CDCl_3)$ 7.16 (1H, m, H(3)), 6.29 (1H, dd, H(5)), 6.21 (1H, dd, H(6)), 2.91 (1H, br.s, H(7)), 2.71 (1H, m, H(3a)), 2.67 (1H, m, H(4)), 2.29 (1H, dd, H(7a)), 2.16 (2H, dt, H(1)), 1.37 (1H, dt, H(8b)), 1.24–1.36 (3H, m, H(2′, 3′, 4′)), 1.22 (1H, br. d, H(8a)), 0.89 ppm (3H, t, H(5′)).

The *endo*-isomer of ketone **5b** showed: $\delta(CDCl_3)$ 6.99 (1H, m, H(3)), 5.87 (1H, dd, H(6)), 5.76 (1H, dd, H(5)), 3.27 (1H, m, H(7)), 3.23 (1H, m, H(3a)), 2.92 (1H, m, H(4)), 2.82 (1H, t, H(7a)), 2.02 (2H, m, H(1′)), 1.73 (1H, dt, H(8b)), 1.60 (1H, dt, H(8a)), 1.37 (2H, quintet, H(2′)), 1.19–1.38 (4H, m, H(3′, 4′)), 0.87 ppm (3H, t, H(5′)).

From another experiment using equimolar amounts of complex **1f** and norbornadiene the diketones **6** and **7** were isolated in small amount (~ 0.1% each). Ketone **6** was pure enough to give good spectral data [numbering as shown for easy correlation with **5** (cf. [7])]: ν_{max}. ($CHCl_3$) 2890, 2850, 1695, 1600, 1450, 1180, 1020 cm^{-1}; $\delta(CDCl_3)$ 7.09 (2H, d, H(3)), 3.28 (2H, m, H(7)), 2.80 (2H, m, H(3a)), 2.72 (2H, br. s, H(4)), 2.45 (2H, m, H(7)), 2.35 (2H, m, H(7a)), 2.17 (4H, t, H(1′)), ~ 1.48 (4H, quintet, H(2′)), 1.30 (1OH, br. m, H(3′, 4′, 8)), 0.91 ppm (6H, t, H(5′)) (assignments are by analogy with the ketones **6** (R = H) [9] and **5**).

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