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Catalysis by cobalt compounds of aldol and retroaldol reactions

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Abstract

Aldol condensation of acetone, butanone, and 2-pentanone, and retroaldol reaction of neat diacetone alcohol and 3-methyl-3-hydroxyheptan-5-one are catalyzed by $(Ph_3P)_3CoCH_3$ and $(Ph_3P)_3CoSi(CH_3)_3$. The condensations are reversible and the retroaldol reaction is favoured. Several hindered or cyclic ketones, such as higher homologues, 3-pentanone, methyl isopropyl ketone or cyclohexanone do not condense. By comparison, aliphatic aldehydes react fast and irreversibly to yield products comprised of three aldehyde units. $(Ph_3P)_3CoCH_3$ also catalyzes protium/deuterium scrambling between ketones and acetone-d_6. This exchange takes place preferably at the C3 carbon whereas condensation takes place at the C1 carbon. The reactions take place at 20 ° C or below, and of the several organometallic compounds tested only the two mentioned above were found to be active.

Introduction

Some years ago it was observed that $(Ph_3P)_3CoCH_3$ induces the self-condensation of acetone or butanone to give the corresponding aldols [1]. At that time and since, other examples of catalyzed condensation have emerged showing that the interaction of ketones and aldehydes with transition metal compounds has considerable scope [2–4]. Attention has focused on ketones as ligands and on condensation. We note here that $(Ph_3P)_3CoCH_3$ promotes both the ketone–aldol condensation, and the retroaldol reaction. Such reactions are relevant to the ubiquitous use of cobalt catalysts and phosphine substituted cobalt complexes in industrial hydroformulations (the Oxo reaction) since aldol condensation is one of the more important undesirable side reactions [5]. Undesirable aldol condensation was also encountered in ruthenium-catalysed heterocyclizations of aldehydes [3]. Catalytic reversal of the condensation is an important objective.

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Aprotic conditions and the absence of acid or base restrict further dehydration of the aldol to unsaturated carbonyl compounds, a process which is acid or base catalyzed [6], and so the aldol is easily isolated. As in aqueous media [6], catalyzed aldol condensation of the neat ketone is reversible, with the equilibrium lying far over toward the ketone. Clearly $(Ph_3P)_3CoCH_3$ is too sensitive to be used on an industrial scale, but its low temperature activity is unusual and is the focus of the present work. Other cobalt compounds are reactive at elevated temperature, and we have made comparisons with such catalysts. We obtained further insight into the scope of this reaction, the role of this and other cobalt compounds and whether a retroaldol reaction takes place under these conditions. It is suggested that $(Ph_3P)_3CoCH_3$ acts as a nucleophile but that the nucleophilicity alone does not provide sufficient explanation of its reactivity. Steric factors are also important, and certain bulky ketones do not react. $(Ph_3P)_3CoPCH_3$ causes hydrogen transfer between different ketones including those that do not condense. The selectivity and the effects of steric factors in this exchange have been studied.

Results

Aldol and retroaldol reaction

$(Ph_3P)_3CoCH_3$, isolated as a dry powder [7] and dissolved in acetone, catalyzes the aldol condensation. It reacts similarly with a limited number of straight-chain methyl ketones and with several aldehydes. The retroaldol condensation is also catalyzed and diacetone alcohol is decomposed to acetone. Dilution of the neat ketone with solvents significantly slows the reaction. So far reaction in the range −20 to 20 °C has been found only for $(Ph_3P)_3CoCH_3$ and its trimethylsilyl analogue $(Ph_3P)_3CoSi(CH_3)_3$.

The reaction of $(Ph_3P)_3CoCH_3$ with acetone yields a mixture of diacetone alcohol and mesityl oxide. When the reaction mixture is treated with 8% aqueous hydrochloric acid and the organic phase separated and distilled, mesityl oxide is the sole condensation product. If the mixture is distilled without hydrolysis the predominant product is diacetone alcohol (a typical ratio of diacetone alcohol to mesityl oxide is 12 : 1). When $(Ph_3P)_3CoCH_3$ and acetone are used in a 1/15 molar ratio the combined yield of diacetone alcohol and mesityl oxide after 24 h is 6% based on the acetone initially present, a turn-over number of 0.9–1.0 for the cobalt complex; this value is a lower limit since only part of $(Ph_3P)_3CoCH_3$ dissolves in this volume of acetone. When $(Ph_3P)_3CoCH_3$ and acetone are used in a 1 : 80 ratio distillation without hydrolysis after 24 h yields diacetone alcohol 3% (based on initial acetone), a turn-over number of 2.4 for cobalt.

In the reaction of $(Ph_3P)_3CoCH_3$ with butanone, three products were obtained: the aldol 3-methyl-3-hydroxyheptan-5-one (**1**), and two corresponding dehydration products 3-methyl-3-hepten-5-one *cis* and *trans* isomers (**2**), (**3**). The turn-over number for the cobalt complex is 0.5. Distillation without hydrolysis at 80 °/3 mmHg yields a mixture of **2** and **3** (15% of the products), the NMR spectrum shows two vinylic bands at 5.95 and 6.05 in the ratio of 2 : 1. A second fraction is **1** (85% of the products). It is clear from the NMR spectrum of **1**, which shows the presence of two ethyl groups (A_3M_2- and A_3X_2-) in equal intensity, that the condensation of butanone takes place through the methyl rather than the methylene group of butanone [1]. The alternative aldol would include an acyl and a CH_3CH group adjacent to COH and a carbonyl, none of which is observed.

$$CH_3CH_2COCH_3 \rightarrow CH_3CH_2COCH_2C(OH)(CH_3)CH_2CH_3$$

(1)

$$+\ CH_3CH_2COCH{=}C(CH_3)CH_2CH_3$$

(2)(3)

From the reaction of $(Ph_3P)_3CoCH_3$ with 2-pentanone, chemical ionization GC-MS identified four products, two aldols and two dehydration products (denoted by I to IV in the Experimental section). The two aldols have different retention values and different CI-MS spectra. The aldol with longer retention time shows loss of H_2O whereas the more volatile one shows a McLafferty type rearrangement to pentanone (retroaldol). The two unsaturated ketones have very close GC retention values and identical MS. Assessment of the regioselectivity of condensation is best based on the analysis of product mixture.

$$CH_3CH_2CH_2COCH_3 \rightarrow CH_3CH_2CH_2COCH_2C(OH)(CH_3)CH_2CH_2CH_3$$

(4)

$$+\ CH_3COCH(CH_2CH_3)C(OH)(CH_3)CH_2CH_2CH_3$$

(5)

$$+\ CH_3COC(CH_2CH_3){=}C(CH_3)CH_2CH_2CH_3$$

6

$$+\ CH_3COCH(CH_2CH_3)C(CH_3){=}CHCH_2CH_3$$

(7)

$$+\ CH_3CH_2CH_2COCH{=}C(CH_3)CH_2CH_2CH_3$$

(8)

$$+\ CH_3CH_2CH_2COCH_2C(CH_3){=}CHCH_2CH_3$$

(9)

Non-conjugated products **7** and **9** are not excluded [8a]. Enone **6** should be the favoured product from **5**, and **8** the favoured product from **4**. The NMR spectrum of the distilled product mixture shows, when compared with that of 2-pentanone, additional triplets and a singlet at 2–2.4 ppm, the expected shift for hydrogen α to carbonyl. A singlet at 2–2.2 ppm from an acyl group is expected for **5**, **6** and **7**, whereas **4**, **8** and **9** will have triplet is this range. The singlet is indeed observed but constitutes at most 15% of the integrated spectrum. Enones **8**, **7** and **9** have a vinylic proton α to carbonyl to fit observed signals at 5.98 ppm. A set of signals at 3.8 disappears on addition of D_2O and is attributed to OH groups of the aldols. After subtracting 19 hydrogen atoms for each OH group (in the aldols), from the integrated intensity in the aliphatic range, the integral of the signals at 5.98 ppm accounts for at least 80% of the rest of the products and is about half that of the mentioned triplets around 2.1 ppm. Compound **8** would be the preferred product, and its *cis*- and *trans*-isomers would account for two peaks in the GC-MS analysis. The absence of fragments such as that with m/z 43 in the mass spectrum of the olefins supports this analysis. It is suggested that with 2-pentanone, condensation takes place preferably at the C1 methyl group and that steric control prevails over acidity factors. This is the regioselectivity generally observed [8].

None of the following ketones underwent detectable condensation: methyl isopropyl ketone, 2-hexanone, 2-heptanone, mesityl oxide, diacetone alcohol, acetophenone, methyl benzyl ketone, cyclohexanone, cyclopentanone, 3-pentanone and 4-pentanone. Hence no self-condensation takes place with long-chain methyl ketones or in the absence of a terminal acetyl group as with the pentanone series, or with methyl isopropyl ketone, possibly because of its bulky alkyl group. Such limitation is not observed for cross-condensation with aldehydes. Reaction of $(Ph_3P)_3CoCH_3$ with an equimolar mixture of methyl isopropyl ketone and benzaldehyde gave a single product, 1-phenyl(4-methyl)1-pentenone-3, $PhCH{=}CHC({=}O)CH(CH_3)_2$, which is formed even in the neat aprotic medium. The yield corresponds to a turn-over number of 2.24 for cobalt. With a mixture of acetophenone and benzaldehyde phenyl-(2-phenylethylene)ketone $PhCH{=}CH(C{=}O))Ph$ is the only product. The turnover number for cobalt is 1.93. $(Ph_3P)_3CoCH_3$ also catalyzes the condensation of aldehydes, which takes place in high yield, is irreversible, and yields products of condensation of three molecules, as shown by GC-MS analysis. The product mixtures are difficult to separate.

When $(Ph_3P)_3CoCH_3$ is added to an excess of an equimolar mixture of acetone and diacetone alcohol the retroaldol reaction is observed. The ratio of acetone to diacetone alcohol was monitored by NMR spectroscopy, which revealed 3.4% decomposition of the aldol after 20 h, a turn-over number of 0.78 for cobalt. With neat diacetone alcohol, 38% decomposition of the aldol was observed after 20 h, and the turn-over number for cobalt was 6.5. 3-Methyl-3-hydroxyheptan-5-one (**1**) and $(Ph_3P)_3CoCH_3$ (1 : 1 molar ratio) yielded butanone 26% after 20 h, a turn-over number for cobalt of 4.5.

The reaction of $(Ph_3P)_3CoSi(CH_3)_3$ with acetone yielded a mixture of diacetone alcohol and mesityl oxide in 15/1 ratio. The turn-over number for cobalt determined for product recovered by distillation was 2.4. The complex $(Ph_2PGe(CH_3)_3)_3CoCH_3$ showed no reactivity, although the two complexes are very soluble in acetone.

Hydrogen exchange

Isotope tracing shows that $(Ph_3P)_3CoCH_3$ catalyzes the exchange of α hydrogen atoms between ketones. Mixtures of acetone-d_6 with several non-deuterated ketones were kept with $(Ph_3P)_3CoCH_3$ for predetermined times and analyzed. Mass spectrometry was carried out with very soft field-ionization on carbon whiskers [9] which allowed observation of molecular ions in high intensity and without fragmentation. This provides a straightforward analysis of isotopic clusters of labeled compounds which have been deuterated to varying degrees (Fig. 1). NMR spectroscopy provides complementary information on the location of carbon positions at which exchange takes place.

Addition of $(Ph_3P)_3CoCH_3$ to a mixture of acetone-d_6 and acetone, with rigid exclusion of water, caused intermolecular deuterium scrambling in the ketone. The pattern of deuterium distribution as the reaction time is increased implies that the change is stepwise (Fig. 1); the composition at several reaction times is shown in Table 1. By comparison, in water and acetone-d_6 or in a mixture of D_2O with acetone, no scrambling occurred under acidic conditions even after 7 days, but

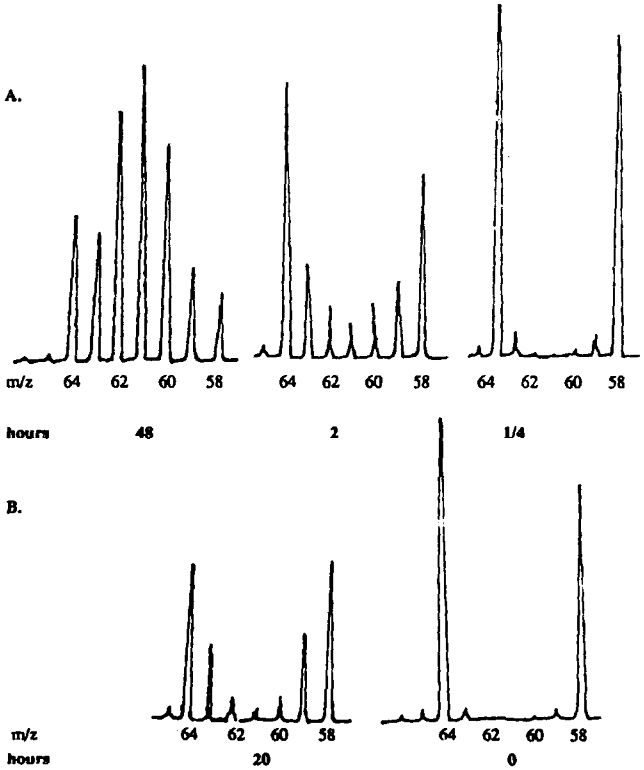

Fig. 1. Isotope cluster from field ionization MS in molecular ion of deuterated acetone from exchange between acetone and acetone-d_6. Catalyst: $(Ph_3P)_3CoCH_3$. Ratio of acetone/acetone-d_6/$(Ph_3P)_3CoCH_3$ in A 5/5/1, in B 15/15/1.

complete scrambling took place within 90 min in the presence of NaOH. Under aprotic conditions other bases such as pyridine caused no exchange, and there is no exchange between the two ketones alone. In Table 1 A, the ratio of acetone-d_6 and acetone to $(Ph_3P)_3CoCH_3$ is 5 : 5 : 1. In B it is 15 : 15 : 1, and the reaction is about ten times slower. There was no hydrogen exchange in the methyl group of

Table 1

Deuterium content of acetone from mixtures of acetone and acetone-d_6 kept with $(Ph_3P)_3CoCH_3$ in molar ratios of 5/5/1 (A) and 15/15/1 (B) respectively, for different reaction times

	A				B
	0 h	0.25 h	2 h	48 h	20 h
d_0	40.8	40.7	24	5.8	29
d_1	2.2	4	10	7.5	15
d_2	0.7	1.4	7.3	17.7	5
d_3	0	0.2	4.7	24.6	3.5
d_4	0.6	0.4	7	20.3	5
d_5	3.3	4	11.5	10.8	13.5
d_6	52.2	47	33.5	12.1	25.8

Table 2

Catalyzed exchange of deuterium between acetone-d_6 and other ketones. Ratio of acetone/ketone $(Ph_3P)_3CoCH_3$ 5/5/1 [a]

ketone	Time (h)	ketone-d_n						
		$n = 0$	1	2	3	4	5	6
acetone-d_6	2	–	–	–	–	–	8.9	87.4
MIK	2	82.9	12.4	4.6	–	–	–	–
acetone-d_6	4	8.8	4.0	2.8	7.2	16.8	26.0	31.8
2-butanone	4	31.4	28.9	25.9	7.7	2.8	1.15	2.3
2-butanone	30	5.9	15.7	38.4	22.6	11.3	2.4	2.4
acetone-d_6	16	4.3	1.8	5.0	10.3	18.8	30.1	26.2
2-pentanone		0	88.5	8.2	3.3	–	–	–
2-pentanone	11	81.0	12.4	6.6	–	–	–	–
2-pentanone	16	35.7	33.0	21.0	8.2	2.1	–	–

[a] MIK = methyl isopropyl ketone.

$(Ph_3P)_3CoCH_3$ as indicated by acid hydrolysis and collection and MS analysis of the evolved CH_4 and Ph_3P. Although $(Ph_3P)_3CoCH_3$ can decompose with loss of methane there is no release of methane during the reaction with acetone.

Some of the results of exchange between acetone-d_6 and other ketones are summarized in Table 2. The exchange is slower than that between acetone-d_6 and acetone. The deuterium distribution in deuterioacetone after 4 h with butanone is similar to that after 2 h with acetone. With 2-pentanone the extent of deuteration after 4 h is similar to that obtained with acetone after 15 min. With both 3-pentanone and methyl isopropyl ketone the reactions are very slow.

Except in the case of acetone, the predominance of products of the type ketone-d_1 and ketone-d_2 is noted. There are much smaller amounts of ketones having more than two deuterium atoms. Ketones which are more extensively deuterated become detectable only after long reaction times. Such a pattern is expected if deuterium exchange takes place preferentially at the α-methylene position C 3, rather than at the C 1-methyl group. This is independently shown by NMR analysis of exchange between acetone-d_6 and several ketones after 16 days with $(Ph_3P)_3CoCH_3$ in a 5 : 5 : 1 ratio (Table 3). At this point the exchange has essentially reached equilibrium and no further changes are discernible. The ketones were acetone, 2-butanone, 2-pentanone, 2-hexanone, 2-heptanone, methyl isopropyl ketone and diacetone alcohol. In diacetone alcohol, 40% of the hydroxyl hydrogen was exchanged. Mesityl oxide, 1,3-diketones and the aldehydes n-butanal and isobutanal which were similarly examined, showed no exchange at all. The results of NMR analysis of four straight-chain methyl ketones and of diacetone alcohol, at approximately the same level of deuteration of the α hydrogen positions, are shown in Table 3. There is a gradual change in the ratio of exchange at the methylene group to that at the methyl group, reflecting the increasing steric hindrance of the alkyl chains.

The complexes $(Ph_3P)_3CoCH_3$ and $(Ph_3P)_3CoSi(CH_3)_3$ are specific catalysts for the reaction. Samples of $(Ph_3P)_3CoCH_3$ which had been allowed to decompose prior to use were not reactive. Several cobalt salts, either alone or together with phos-

Table 3

Extent of hydrogen exchange after 16/h between acetone-d_6 and ketones: A denotes total deuterium incorporation (%) in the ketones: B denotes the ratio of methylene/methyl deuteration. Analysis by NMR

	A	B
acetone	50 [a]	-
2-butanone	34	1.49
2-pentanone	41	1.12
2-hexanone	38.6	0.85
2-heptanone	32.6	0.72
methyl isopropyl ketone	10	0.74
diacetone alcohol	37	1.28
1,3-diketones	0	
mesityl oxide	0	

[a] Maximum extent of exchange.

phines, and various other complexes and metal alkyls had no effect. Even a strong organometallic nucleophile such as $[CpFe(CO)_2]^-$ or organic bases such as pyridine had no effect. $Co(OAc)_2 \cdot 4H_2O$ and $CoCl_2 \cdot 6H_2O$ in the presence of one equivalent 2,2'-bipyridyl caused condensation of acetone with turnover numbers of 2.5 and 0.4 after 18 h at 80–90 °C.

Discussion

The obvious explanation is that both hydrogen exchange and the ketone-aldol equilibration take place by base catalyzed enolization, but mere basicity of e.g. pyridine, or the presence of a strong nucleophile such as $CpFe(CO)_2^-$ was not enough to bring about the reactions. $(Ph_3P)_3CoCH_3$ and $(Cp_3P)_3CoSi(CH_3)_3$ are unsaturated 16 electron compounds which easily undergo dissociation of triphenylphosphine in solution. Dissociation of phosphine ligands and association of a ketone or an enol can enhance the case of hydrogen exchange. Neither IR nor NMR (^1H and ^{31}P) analysis revealed any such complexation, so presumably, any contact between the cobalt compound and ketone is of very short duration. In the absence of direct proof, it is relevant to note that the rate of exchange is dependent on the cobalt concentration and the orientation on steric factors (Table 3). In addition, interference by coordination blocks the reaction with ketones. In the presence of an excess of diphenylacetylene, which is known to react with $(Ph_3P)_3CoCH_3$, hexaphenylbenzene is formed, and both hydrogen exchange and aldol reactions are completely suppressed. In the presence of an excess of acetone which competes with diphenylacetylene [10], reaction of the ketone predominates. Other cobalt compounds such as $(Ph_3P)_3CoCl$ which does not dissociate easily, $CoCl_2$ which is not nucleophilic the coordinatively saturated $Co(acac)_3$, or those which are very bulky, like $(Ph_2PGe(CH_3)_3)_3CoCH_3$, are ineffective.

There are few examples of mixed aldol condensations which are catalysed by $[HFe(CO)_4]^-$ [11] or bivalent transition-metal salts [12,13]; the scope of the later is limited in condensation of methyl ketones with benzaldehyde to form chalcones. Elevated temperatures (60–80 °C) are needed, and dehydrated products are obtained. No self condensation of ketones was reported in these cases. We found these metal-amine catalysts to be inactive at 25 °C. Coordination of ketones to metals has been observed but is not common. One condensation of two acetone molecules to diacetone alcohol involves ketone complexes of the type $M[(CH_3)_2CO]_2[TPyEA]$-$[BPh_4]_2$ (M = Ni, Co), which have been isolated [4]. Heating acetone with certain Ru^{3+} and Ir^{3+} compounds yields the corresponding $CpM[(CH_3)_2CO]_3(PF_6)_2$ (M = Ru or Ir) and a complex bearing mesityl oxide bonded as enolate [14]. Heating benzyl methyl ketone with $CH_3Mn(CO)_5$ yields an enolate complex with loss of the manganese bonded methyl group [15]. Diacetone alcohol is formed as a result of coordination of acetone to $Ru_2(arene)_2Cl_4$ [16]. The isotopic distribution in the hydrogen exchange revealed in this work is reminiscent of enolization. It is possible that coordination to cobalt may somewhat stabilise the enol form. Metal complexes have been shown to stabilise enol conformations, but very few enol complexes have been isolated from keto-enol equilibrium; this topic has recently been reviewed [17]. Bonding of acetone to pentammineosmium at the oxygen as η^2 and η^1 complexes has been described in detail. It is noteworthy that isotopic exchange of such complexes with methanol-d_4 takes place in presence of traces of sodium methoxide but slowly compared to that of free acetone [18]. Thus slow exchange may also be some evidence for complexation.

In summary, $(Ph_3P)_3CoCH_3$ catalyzes the establishment of equilibrium between ketone and the diketone alcohol rather than promoting reaction in only one direction. The equilibrium position reflects the dominance of the retro aldol reaction, whereas with aldehydes only the condensation is observed. All of this is in accord with the behaviour generally observed [6,8]. Of the ketones tested, condensation is limited to methyl ketones and takes place at the methyl group α to the carbonyl implying steric control. Ketones which themselves do not self-condense can undergo cross condensation with aldehydes. The exchange of hydrogen, on the other hand, is related to keto-enol conversions, and shows preference for the α methylene (C3) position. The C–H acidity is the governing factor, as in α-halogenation, with which analogy has often been drawn [19,20]. The relative stability of the enol form is probably very important, but since keto-enol equilibrium is solvent dependent it is not possible to discuss the relative activity of the various ketones on the basis of data from aqueous solutions [20]. For example enolization of cyclohexanone in water is more favourable than that of acetone, so the inactivity of the former in the present case must be due to other factors. Some of the ketones do not condense even though they readily exchange hydrogen.

The special catalytic ability of $(Ph_3P)_3CoCH_3$ and $(Ph_3P)_3CoSi(CH_3)_3$ may be attributed to a dual effect: the enhancement of enolization through their nucleophilicity and stabilization of the enol form through weak complexation or complexation with the keto form.

Experimental

General

All procedures and solvent purification were carried out under dry argon. Solvents: Diethyl ether and THF were dried over $CaCl_2$ then filtered, and finally distilled over a sodium dispersion. Analytical grade CH_2Cl_2 and $CHCl_3$ were used as supplied. Aldehydes and ketones were all analyzed by GC and NMR spectroscopy and distilled when necessary. They were stored over molecular sieve 4A and argon was bubbled through each sample for at least 5 min before use. Cobalt acetylacetonate $(Ph_3P)_2CoCl_2$ [21] and $(Ph_3P)_3CoCH_3$ [7] were prepared by known procedures. IR spectra were recorded on a Perkin Elmer 337 spectrophotometer, linked GC-MS was carried out on a Varian MAT 311 spectrometer for both electron ionization (EI) and chemical ionization (CI). NMR spectra were recorded on Varian T-60, Bruker WH 300 and Bruker WP 200 SY instruments. Isotope analysis was carried out with a Varian MAT SM 1-B mass spectrometer, which was specially fitted with a source for soft field ionization on carbon whiskers [9*].

Reaction of $(Ph_3P)_3CoCH_3$ with ketones

The ketone was added to dry powdery $(Ph_3P)_3CoCH_3$ (typically about 5 g) or an equivalent amount of another cobalt compound at −10 °C in a molar ratio of 15–20/1. The slurry was stirred for 24 h at 20–25 °C. CH_2Cl_2 (30 g) and 8% aqueous hydrochloric acid was added and the mixture stirred for 4 h. The organic layer was separated, dried over $MgSO_4$, and distilled. Termination of reactions without hydrolysis was by distillation of the slurry under reduced pressure (1 mmHg) on a Büchi GKR-50 apparatus. $(Ph_3P)_3CoCH_3$ is only partially soluble in the specified amounts of acetone whereas $(Ph_3P)_3CoSi(CH_3)_3$ and $(Ph_2PGe(CH_3)_3)_3CoCH_3$ [22] are completely soluble.

Examples. The reaction of $(Ph_3P)_3CoCH_3$ (4.2 g, 4.9 mmol) with acetone (4 g, 70 mmol) yielded a distilled fraction (70 °C/1 mmHg) of diacetone alcohol and mesityl oxide (0.3 g, 2.77 mmol). Another sample of $(Ph_3P)_3CoCH_3$ (2.6 g, 3.0 mmol) yielded 0.3 g (2.6 mmol) of these products from the same amount of acetone. Reactions of $(Ph_3P)_3CoCH_3$ (3 g, 3.5 mmol) with 2-butanone (5 g, 70 mmol) yielded 0.2 g (1.4 mmol) of the combined condensation products, aldol and eneones. The NMR of the aldol was that of 3-methyl-3-hydroxyheptan-5-one (δ: 0.876 (*t*, 3H); 1.03 (*t*, 3H); 1.16 (s, 3H); 1.49 (q, 2H); 2.44 (q, 2H), 2.55 (d, 2H); 3.83 (s, 1H). Reactions of $(Ph_3P)_3CoCH_3$ (4 g, 4.7 mmol) with 2-pentanone (6 g, 70 mmol) yielded 0.48 g (3.1 mmol) of aldol and eneones. Similar reactions were carried out with $(Ph_3P)_3CoCH_3$ (2.5–4 g) and 70 mmol of one of the following: methyl isopropyl ketone, 2-hexanone, 2-heptanone, mesityl oxide, diacetone alcohol, acetophenone, methyl benzyl ketone, cyclohexanone, cyclopentanone, 3-pentanone and 4-pentanone. No condensation took place in any of these cases. Products from condensation of acetone and butanone were identified by comparison with products of condensation promoted by aqueous NaOH, and by NMR, IR spectroscopy and GC-MS analysis. Products from 2-pentanone were not separated except in the GC-MS analysis; the data were compared with those previously reported [8a].

Use of $(Ph_3P)_3CoCH_3$ (3.7 g, 4.317 mmol) with a mixture of benzaldehyde (5.3 g, 50 mmol) and methyl isopropyl ketone (4.3 g, 50 mmol) yielded a single product, distilled at 160 °C/1 mmHg, which was identified as 1-phenyl(4-methyl)1-pentenone-3 (1.7 g, 9.7 mmol). NMR: 1.13 (d, 6H); 2.88 (m, 1H); 6.76 (d, 1H); 7.56 (d, 1H); 7.3–7.5 (m, 5H). GC-MS (CI) $m/z = 175$.

Use of $(Ph_3P)_3CoCH_3$ (2 g, 1.714 mmol) with a mixture of benzaldehyde (5.3 g, 50 mmol) and acetophenone (4.3 g) yielded a single product, which was isolated by preparative TLC and identified by GLC, m.p., NMR spectroscopy, and comparison with an authentic sample, as phenyl-(2-phenylethylene)ketone (0.68 g, 3.3 mmol).

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* A reference number with an asterisk indicates a note in the list of references.

To $(Ph_3P)_3CoCH_3$ (0.49 g, 0.57 mmol) was added a mixture of acetone and diacetone alcohol 0.93 : 1 molar ratio, 1.6 g). The mixture was well stirred. The ratio of acetone to aldol (as determined by NMR spectroscopy) increased as the reaction progressed; e.g. 1.12 after 9 h and 1.17 after 32 h. The reaction was repeated using $(Ph_3P)_3CoCH_3$ (2.1 g, 2.45 mmol) and diacetone alcohol (4.55 g, 39 mmol).

Reactions of $(Ph_3P)_3CoSi(CH_3)_3$ and $(Ph_2PGe(CH_3)_3)_3CoH_3$ with acetone

A solution of $(Ph_3P)_3CoSi(CH_3)_3$ (1.02 g, 1.1 mmol) in acetone (4 g, 70 mmol) was kept for 48 h at 20 ° C and the solution distilled under vacuum. A mixture (0.31 g) of diacetone alcohol and mesityl oxide in a 12/1 ratio was collected. Under the same conditions no reaction took place when $(Ph_2PGe(CH_3)_3)_3CoCH_3$ was used.

Control experiments for condensation

The following compounds were unreactive when mixed with acetone alone or with acetone and dimethylformamide under the specified conditions or at 85 ° C: $Co(OAc)_2 \cdot 4H_2O$, $(Ph_3P)_3CoCl$, $CoCl_2 \cdot 6H_2O$, trimethylaluminum (in THF), methyllithium (in ether), and Ph_3P. Condensations of benzaldehyde and methyl isopropyl ketone were observed with methyllithium (3 equivalents) and 25 ° C (95% yield). Some side products were formed. No reaction was observed with any of the cobalt salts: $Co(OAc)_2 \cdot 4H_2O$, $(Ph_3P)_3CoCl$, $CoCl_2 \cdot 6H_2O$, even when one equivalent of 2,2′-bipyridyl was added by analogy with the reagents used by Irie and Watanabe [12,13]. The reactions were carried out for 1 week at 20 ° C in the presence of DMF and the molar ratio of carbonyl compounds to cobalt compound was 8 : 1. However at 85 ° C, after 18 h condensation was observed with $Co(OAc)_2 \cdot 4H_2O$ (250% by cobalt), or $CoCl_2 \cdot 6H_2O$ (40% by cobalt), provided one equivalent of 2,2′-bipyridyl was present. $(Ph_3P)_3CoCl$, Ph_3P and AcONa were unreactive in all these tests.

The anion η^5-$CpFe(CO)_2^-$ was prepared by adding 45% sodium dispersion (0.9 g, 15 mmol) to the dimer $[CpFe(CO)_2]_2$ (1.8 g, 5 mmol) in 120 ml THF and refluxing the mixture for 6 h with occasional monitoring of the IR bands at 1955–2000 cm^{-1} [23]. The mixture was cooled and filtered and acetone was added (5 g, ~ 70 mmol), at −18 ° C. After 24 h at 25 ° C the mixture was treated with 8% aqueous hydrochloric acid. No products of acetone condensation were detected.

The reaction of $(Ph_3P)_3CoCH_3$ (4.7 g, 5.5 mmol) with acetone (1.5 g, 26 mmol) was carried out at room temperature for 48 h in the presence of diphenylacetylene (3 g, 16.5 mmol). Analysis showed complete consumption of diphenylacetylene and no reaction of the acetone. The only product, which separated during 4 h as a colourless powder, was hexaphenylbenzene (2.7 g, 90%).

H–D exchange

A ketone was mixed with acetone-d_6 and $(Ph_3P)_3CoCH_3$ was added at −10 ° C in molar ratios of 5/5/1 or 15/15/1 respectively. The slurry was stirred and then kept at 20 ° C for selected times, and samples were filtered and analyzed. The MS background was checked before each analysis.

Control experiments. No H–D exchange occured when acetone-d_6 was kept with $(Ph_3P)_3CoCH_3$ in 5/1 ratio for 30 h. No H–D exchange was detected between acetone-d_6 and acetone during 30 h or between acetone-d_6 and n-butanal or isobutanal during 30 h.

Table 4

Mass spectral data (CI) (obtained by GC-MS) for products II and III from the aldol condensation of 2-pentanone

%	m/e	
100	155	[MH^+] of aldol-H_2O
2	127	
2	73	
1.5	71	

Table 5

Mass spectral data (CI) (obtained by GC-MS) for products I and IV from the aldol condensation of 2-pentanone

% I	% IV	m/e	
19	10	173	[MH^+] of aldol
	100	155	[MH^+]−18
	2	141	
	2	127	
	2	113	
	2	99	
100	53	87	[MH^+] 2-pentanone
3	6	73	
2	14	71	

No H–D exchange was detected in 48 h between acetone-d_6 and acetone, butanone, or 2-pentanone, in presence of pyridine (molar ratios 10/10/1).

No H–D exchange occurred in 48 h between acetone-d_6 and acetone or butanone with samples of $(Ph_3P)_3CoCH_3$ which had decomposed upon exposure to air before use.

Extensive H–D exchange took place between acetone or butanone or 2-pentanone and D_2O in 1/1 ratio in the presence of KOH. The maximum degree of exchange was reached within 90 min (50 out of 55%) for both types of α hydrogen.

No H–D exchange occurred in 48 h, between acetone-d_6 and butanone in the presence of H_2SO_4 (up to 4 M) during 7 days.

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