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Notes

New Low-Pressure Synthesis of Phosphine-Containing Cobalt Carbonyl Complexes: $Co_2(CO)_6(PR_3)_2$

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Summary: A low-pressure, direct synthesis of phosphine-containing cobalt carbonyl complexes of the type $Co_2(CO)_6(PR_3)_2$ has been developed. A Co(II) precursor and PR_3 are allowed to react in a suitable solvent, such as toluene, under mild conditions (110 °C and 120 psi of CO/H_2) in the presence of a heterogeneous hydrogenation catalyst, e.g., Pd/C. Possible intermediate species have been independently synthesized and shown to be viable participants in the proposed catalytic cycle.

Introduction

Phosphine-containing cobalt carbonyl catalysts of the type $Co_2(CO)_6(PR_3)_2$ have been used extensively as hydroformylation catalysts[2] and have also been reported to be effective for the selective hydrogenation of polyenes to monoenes.[3] They can most easily be prepared by direct reaction of $Co_2(CO)_8$ with the appropriate phosphine.[4] However, the high cost of $Co_2(CO)_8$, due to the required high-pressure synthesis (500–15 000 psi),[5] and the precautions necessary to handle this thermally unstable, toxic complex are significant barriers when large quantities of the phosphine carbonyl catalyst are required.

A number of "wet" synthetic routes to $Co_2(CO)_8$ have been reported which could potentially be adapted for a direct $Co_2(CO)_6(PR_3)_2$ synthesis. Possibilities include reductive carbonylation of Co(II) species using CO/H_2,[6] reduction of Co(II) species with active metals in the presence of CO,[7] and carbonylation of highly active Co powders.[8]

Of these alternatives, reductive carbonylation using hydrogen is both economical and waste-free, since no metal halide byproducts are produced. A direct synthesis of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ based on this reasoning has recently been reported in the Chinese literature.[9] $CoCO_3$ was allowed to react under ca. 600 psi of H_2/CO (1.6:1) in the presence of $P(n\text{-}Bu)_3$ for 12 h at 170 °C. Raising the pressure to 1200 psi reduced the reaction time to 8 h. Once again, however, such pressures require access to a metal autoclave and significant safety precautions.

Interestingly, the temperature required for the reductive carbonylation of Co(II) carboxylate complexes to yield $Co_2(CO)_8$ can be lowered by addition of preformed dimer.[10] A thorough mechanistic study has shown the rate of cobalt 2-ethylhexanoate reductive carbonylation to be first order in both Co(II) carboxylate complex and $Co_2(CO)_8$, proportional to H_2/CO pressure, and autocatalytic.[11]

This study laid the groundwork for a report on the synthesis of $Co_2(CO)_8$ from cobalt(II) species in the presence of heterogeneous hydrogenation catalysts.[12] The reactions reported were optimized for high pressure/low temperature due to the thermal instability of the desired binary cobalt carbonyl species. Significantly, addition of triphenylphosphine was observed to have little effect on the initiation temperature of the reduction. Subsequent reaction of $Co_2(CO)_8$ with PPh_3 to yield $Co_2(CO)_6(PPh_3)_2$ was postulated, but no experimental data were reported.

We have used these leads to develop a low-pressure direct synthesis of $Co_2(CO)_6(PR_3)_2$ from soluble cobalt(II) complexes and trialkylphosphines, in the presence of a heterogeneous hydrogenation catalyst under a synthesis gas (CO/H_2) atmosphere.[13]

Results and Discussion

The conditions necessary to reduce cobalt(II) precursors with synthesis gas are changed considerably by addition of a trialkylphosphine and the presence of a heterogeneous catalyst (see eq 1). For example, the Pd/C-catalyzed

$$\text{“Co(II)”} + PR_3 + CO/H_2 \rightarrow {}^1/_2 Co_2(CO)_6(PR_3)_2 \tag{1}$$

synthesis of $Co_2(CO)_8$ from Co(II) precursors requires ca. 3000 psi of CO/H_2 between 50 and 80 °C for 12 h.[12] In the presence of PR_3, 120 psi of CO/H_2 at 80–110 °C for ca. 8 h is required, depending on the solubility of the precursor Co(II) complex. These mild conditions allow the reaction to be carried out in a glass Fischer–Porter bottle.

The course of these reductive carbonylations can be followed quite easily using infrared and ^{31}P NMR spectroscopy. For example, the preformed cobalt carboxylate complex $Co[O_2C(CH_2)_3CH_3][P(n\text{-}Bu)_3]$ can be reduced under synthesis gas in the presence of Pd/C. The initial complex (ν(C═O) 1630 and 1730 cm^{-1}) rapidly converts

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to ^{31}P silent intermediate(s) ($\nu(C{\equiv}O)$ 1910 and 1975 cm^{-1}), which react further to give $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ ($\nu(C{\equiv}O)$ 1955 cm^{-1}, $\delta(^{31}P)$ 52.7 ppm).

Variation of the heterogeneous hydrogenation catalyst indicates that the rate of reaction follows the order 5% Pd/C > Raney Co ≫ autocatalysis. The nature and efficacy of the heterogeneous hydrogenation catalyst used in the $Co_2(CO)_8$ synthesis were investigated by Usami et al.[12] and shown to be dependent on the type of metal and the extent of its dispersion. Highly disperse palladium was found to be most active, consistent with our results. No heterogeneous catalyst-induced effect on yield or selectivity of subsequent $Co_2(CO)_6(PR_3)_2$-catalyzed olefin hydrogenations was observed, suggesting that the leaching had not occurred.

The rate of cobalt dimer formation in the presence of different phosphine ligands is observed to be $P(n\text{-}Bu)_3 > P(i\text{-}Bu)_3$, $P(s\text{-}Bu)_3$, with the less sterically hindered phosphine significantly faster. As the parent $Co_2(CO)_8$ synthesis is known to be promoted by Lewis bases, this rate effect is probably due to steric interaction in the initial complexation of the phosphine to the Co(II) complex. This complexation is observed to be very fast in the case of soluble species, such as the cobaltous naphthenoate and 2-ethylhexanoate species.

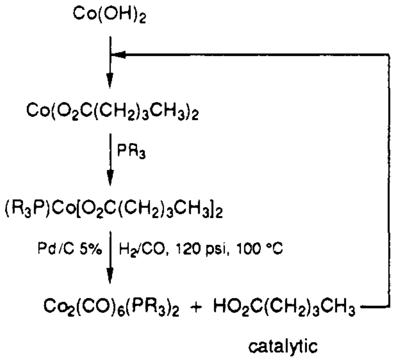
Only the desired cobalt dimer products, as monitored by ^{31}P NMR and IR spectroscopy, are observed during the slower reactions with $P(i\text{-}Bu)_3$ and $P(s\text{-}Bu)_3$. Intermediate complexes can be spectroscopically detected, as discussed above, during the course of reactions with $P(n\text{-}Bu)_3$. However, only $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ is present at the end of the reaction. No direct oxidation of the phosphine by the cobalt complexes is observed.

Reduction of Co(II) species in the presence of phosphines is dependent on both the H_2 and CO pressures. As expected when heterogeneous hydrogenation catalysts are used, the rate is increased by increasing H_2 pressure and is also sensitive to the amount of agitation during the reaction; i.e., mass transfer is important. However, the rate is decreased by increasing CO pressure. This could be due to poisoning of the hydrogenation catalysts, as well as to an inhibition of the autocatalytic pathway. An inverse CO dependence has been observed in the synthesis of $Co_2(CO)_8$ and attributed to a suppression of autocatalysis.[11]

A number of Co(II) species can be used in the synthesis. The reactivity parallels the solubility of the complex: carboxylates > hydroxide ≫ carbonate ≫ oxide. However, the synthesis can be optimized for the less expensive, and therefore more desirable, cobaltous hydroxide precursor, as outlined below.

Commercially available cobaltous hydroxide and valeric acid react in a solvent such as toluene to yield a red-purple, soluble complex, with the empirical formula $Co[O_2C(CH_2)_3CH_3]_2$.[14] This complex can be slurried at low temperature (ca. −40 °C) and reacts with trialkylphosphines to yield a deep blue, extremely soluble complex.[15] Examination of the carboxylate infrared stretches shows that formation of this species is dependent on the steric bulk of the phosphine ($P(n\text{-}Bu)_3 > P(s\text{-}Bu)_3 > P(t\text{-}Bu)_3$) and on the presence of phosphine aryl groups, which significantly lower the amount of complex formed. Attempts to completely characterize the blue species have been frustrated due to their extreme solubility and the lability of the phosphine ligands. More importantly, the blue phosphine adducts react readily under CO/H_2 in the presence of Pd/C to yield $Co_2(CO)_6(PR_3)_2$.

Scheme I. Cobalt Catalyst Synthesis with Proposed Intermediates



Addition of catalytic quantities (ca. 5–10%) of carboxylic acids to $Co_2(CO)_6(PR_3)_2$-catalyzed olefin hydrogenations does not appreciably affect the rate of selectivity of these reactions. This was tested by spiking isolated catalysts with valeric acid. This allowed the development of the process outlined in Scheme I, where a catalytic amount of valeric acid is used to solubilize $Co(OH)_2$ and reductive carbonylation occurs under synthesis gas to yield the desired dimeric product and regenerate valeric acid. This product can be used as prepared or isolated in high yield (ca. 85%, from toluene).

The new preparative method reported here allows the direct preparation of large quantities of $Co_2(CO)_6(PR_3)_2$ and can be carried out in an extremely economical fashion under conditions much milder than those previously possible. The use of heterogeneous catalysts is a concept which should be widely applicable and one which we are investigating further.

Experimental Section

All reactions at above ambient pressure were conducted in Fischer–Porter tubes or bottles. Gas mixtures were made by pressurizing with a given quantity of CO and then going to the appropriate total pressure with H_2. $Co(OH)_2$ was obtained from Mooney Chemicals and $P(n\text{-}Bu)_3$ from Strem; all other reagents were obtained from Aldrich. ^{31}P NMR spectra (C_6D_6 vs H_3PO_4 external standard) were obtained on a QE-300. IR spectra were obtained as Nujol mulls or as thin films of crude reaction solutions between KBr plates. Spiking experiments were done, and spectral data were compared with an authentic sample of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ prepared by the literature method from $Co_2(CO)_8$.[4] GC analyses of hydrogenation products were done on a 60 m, 0.32 mm i.d. Carbowax 20 M capillary column using a ramped temperature program (110 °C 15 min, 25 °C/min ramp, 200 °C 10 min). GC samples were prepared by taking 10 μL of sample in 1 mL of acetone with dodecane as an internal standard.

Preparation of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$. $Co(OH)_2$ (2.5 g, 27 mmol), $P(n\text{-}Bu)_3$ (6 mL, 24 mmol), valeric acid (0.5 mL, 2 mmol), and Pd/C (0.5 g, 5% loading, 2.5% Pd/Co) were taken up in 75 mL of toluene in a Fischer–Porter bottle with a mechanical stirrer. The mixture was pressurized to 110 psi with a 1:1 mixture of CO/H_2 and heated to 100 °C with vigorous stirring. The solution turned dark red-brown within 3 h. An infrared spectrum of the solution showed one major carbonyl band at 1955 cm^{-1}; however, some starting material was still observable and gas uptake continued. The solution was repressurized with 1:1 CO/H_2 and the reaction continued. After 7–8 h, the gas uptake ceased. The

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[14] This complex is presumably a higher order aggregate, as indicated by its moderate solubility in the absence of a coordinating ligand such as $P(n\text{-}Bu)_3$.

[15] Note: $Co(OH)_2$ does not directly react with $P(n\text{-}Bu)_3$.

solution was repressurized with H_2, and the reaction continued for 10 h total. The solution was filtered (reactor and frit were washed with toluene) and the volatiles removed under vacuum. The dark red-brown oil was slurried in petroleum ether and allowed to sit at −40 °C overnight. The mother liquor was decanted and the product dried to yield dark red-brown blocks: 6.86 g first crop, 1.42 g second crop; total isolated yield 89%. Infrared of the product shows one major carbonyl band at 1955 cm^{-1} and the ^{31}P NMR one peak at 52.8 ppm. Anal. Calcd for $C_{30}H_{54}O_6P_2Co_2$: C, 52.2; H, 7.8. Found: C, 51.8; H, 7.7.

$Co(OH)_2 + CH_3(CH_2)_3CO_2H$. $Co(OH)_2$ (1 g, 10 mmol) and valeric acid (2.46 mL, 22 mmol) were slurried in 20 mL of toluene and heated to reflux. The solution turned purple and the solid dissolved after ca. 15 min. The hot solution was filtered (frit washed with toluene) and the solution cooled to room temperature. Pentane was added to the solution until solid began to precipitate. The solution was cooled to yield red-purple crystals. The mother liquor was dried under vacuum to yield a thick oil. A red powder formed upon slurrying with petroleum ether, which was then filtered and dried. A broad carboxyl peak was observed in both samples at 1570 cm^{-1}. The combined yield was quantitative. Anal. Calcd for $C_{10}H_{18}O_4Co$: C, 46.0; H, 6.9. Found: C, 45.5; H, 6.9.

$Co[O_2C(CH_2)_3CH_3]_2 + PR_3$. $Co[O_2C(CH_2)_3CH_3]_2$ (0.5 g, 1.9 mmol) was dissolved in 20 mL of CH_2Cl_2 and the solution cooled to −40 °C (note that this compound is not very soluble. $P(n\text{-}Bu)_3$ (0.47 mL, 1.9 mmol) was added, causing an immediate color change to dark blue and giving a homogeneous solution. The solution was warmed to room temperature, the volatiles were removed under vacuum, and the oily blue residue was extracted with petroleum ether. After filtration, the volatiles were removed under vacuum, yielding a dark blue oil. Carboxylate bands at 1630 and 1730 cm^{-1} (neat, KBr plates) were observed in the IR spectrum. Crystals could not be obtained from petroleum ether at low temperature. TLC on silica gel and reverse-phase plates led to smearing and formation of a red spot (presumably starting material). An analogous reaction with PMe_2Ph led to a mixture of starting material and a new complex with IR stretches at 1610 and 1730 cm^{-1}, and reaction with PPh_3 yielded only starting material.

$Co[O_2C(CH_2)_3CH_3]_2(PR_3) + CO/H_2$. $Co[O_2C(CH_2)_3CH_3]_2$-$[P(n\text{-}Bu)_3]$ (0.5 g, 1 mmol, dark blue oil as prepared above) and 100 mg of Pd/C (5% loading) were taken up in 5 mL of *trans,trans,cis*-1,5,9-cyclododecatriene (CDDT) in a Fischer–Porter tube. The reaction mixture was pressurized up to 120 psi of CO/H_2 (1:1) and heated to 110 °C. An IR spectrum was taken every 2 h. After 2 h, multiple carbonyl bands were observed with the major band at 1960 cm^{-1}. After 4 h, only one carbonyl IR band at 1960 cm^{-1} was observed. The major peak in the ^{31}P NMR spectrum was at 52.7 ppm (ca. 90%), with a smaller peak at 48.9 ppm and a trace of free phosphine.

Representative Olefin Hydrogenations. Samples of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ (0.1 g, 0.14 mmol) in 7 mL of CDDT (38.4 mmol) were taken up in 10-cm^3 shaker tubes and hydrogenated under 500 psi of H_2 for 2 h at 140 °C. By capillary GC, a sample of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$, as prepared above from $Co(OH)_2$, achieved an 80% conversion to *cis*- and *trans*-cyclododecene and cyclododecane, with 74% selectivity (*cis*- + *trans*-cyclododecene + cyclodecane). A sample of the same batch of $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ spiked with 10 mol % $CH_3(CH_2)CO_2H$ (with respect to cobalt catalyst) achieved an 84% conversion, with 75% selectivity.

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