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An Improved and One-Step Synthesis of Phosphido-Bridged Tetracobalt Carbonyl Cluster, $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$

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The use of transition metal cluster complexes has attracted a great deal of attention in recent years, especially with respect to their potential as homogeneous catalysts [1]. A key problem associated with the use of clusters in catalysis is their tendency to undergo metal–metal bond rupture under reaction conditions, so that fragmentation and/or aggregation to metal particles occurs [2–5]. One approach to avoid fragmentation is to use the clusters that are bound together both by metal–metal bonds and by stable, non-fluxional bridging ligands [2–4]. Pittman and co-workers [2] reported that the phosphido-bridged tetracobalt carbonyl cluster, $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$, was an active hydroformylation catalyst and the cluster could be recovered in high yield after completion of hydroformylation.

Ryan and Dahl [6] have synthesized $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ in 30 ~ 35% yield by a reduction of $Co_2(CO)_8$ with Zn powder under carbon monoxide atmosphere followed by an addition of $C_6H_5PCl_2$. We wish to report here an improved and one-step synthesis of the phosphido-bridged tetracobalt cluster.

The treatment of a toluene solution of $Co_2(CO)_8$ with an equimolar quantity of $C_6H_5PH_2$ results in an immediate evolution of a mixture of hydrogen and carbon monoxide and a color change of the solution from dark orange to deep red. The solution was then stirred at room temperature for 2 hr, heated at 110 ~ 125 °C for 3–6 hr, cooled, concentrated and purified on a silica gel column to give a dark red cluster complex, $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ in 28–59% yield. The tetracobalt cluster was characterized by its elemental analysis, IR, NMR and mass spectra. As can be seen from Table, I, reaction of $Co_2(CO)_8$ and $C_6H_5PH_2$ gave higher yield of tetracobalt cluster when the reaction was carried out under carbon monoxide atmosphere than under argon.

The phosphido-bridged tetracobalt cluster has been recently reported as homogeneous catalysts for the hydroformylation of olefins [2] and hydrogenation of carbon monoxide [7]. The cluster could be recovered unchanged from reaction mixtures after hydroformylation at 90–145 °C and 1200 psig. In our study, the cluster could also be recovered in good yield (~90%) after hydroformylation at 140 °C and 2100 psig for 6 hr. However, only 45% cluster was recovered after hydroformylation at 200 °C and 2500 psig for 6 hr. Hydrogenation of carbon monoxide with the cluster at 180 °C and 2600 psig ($CO/H_2 = 1/3$) for 7 hr gave methyl formate, methanol and ethanol with turnover numbers of 34.3, 6.1 and 2.4 respectively. The tetracobalt cluster-catalyzed homologation of methanol at 180 °C and 2600 psig /$CO/H_2 = 1/1$) for 7 hr gave mainly methyl formate and small amount of ethanol with turnover numbers of 53 and 7.2 respectively. In all cases, the phosphido-bridged tetracobalt cluster is much less reactive than dicobalt octacarbonyl.

An attempted synthesis of phosphido-bridged $MoCo_2$ cluster from reaction of $Mo(CO)_5(C_6H_5PH_2)$ and $Co_2(CO)_8$ was unsuccessful. At 110 °C, the reaction of $Co_2(CO)_8$ and $Mo(CO)_5(C_6H_5PH_2)$ in toluene gave $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ and $Mo(CO)_6$ instead. The isolation and characterization of other minor products from reactions of $Co_2(CO)_8$ with $C_6H_5PH_2$ and $Mo(CO)_5(C_6H_5PH_2)$ are under investigation.

TABLE I. Formation of $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ from Reaction of $Co_2(CO)_8$ and $C_6H_5PH_2$.

Ratio of $Co_2(CO)_8/C_6H_5PH_2$	Temp. (°C)	Time (hr)	Atmosphere (atm)	Yield (%)
2/1	110	21	Ar (1)	15
1/1	125	3	Ar (1)	28
1/1	110	6	Ar (1)	42
1/1	125	3	CO (1)	35
1/1	115	6	CO (3.5)	59
1/1	24	48	Ar (1)	<1

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Experimental

Manipulations involving air-sensitive materials were performed under argon in Schlenk-type vessels. Where necessary, transfers were made in an argon-filled glove box.

NMR spectra were obtained by use of a Bruker WP-200 spectrometer. IR spectra were recorded on a Beckman 4200 spectrometer. MS spectra were recorded on a high-resolution Kratos MS-30 spectrometer. Gas chromatography, GLC, analyses were performed by use of Hewlett-Packard model 5710A analytical gas chromatograph on a 32 ft × 1/8 in. 20% Carbowax 20 M/Chromosorb W column. Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

All solvents were A.C.S. reagent grade and were dried and freshly distilled before use. Dicobalt octacarbonyl, molybdenum hexacarbonyl and phenylphosphine were obtained from Strem Chemicals Inc. $Mo(CO)_5(C_6H_5PH_2)$ was prepared by the previously published procedures [8].

Preparation of $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$

Typically, to an 80 ml toluene solution of $Co_2(CO)_8$ (6.08 mmol), a toluene solution of $C_6H_5PH_2$ (6.08 mmol) was added slowly. An immediate reaction occurred with evolution of carbon monoxide and hydrogen and a color change of the solution from dark orange to deep red. The solution was stirred at ambient temperature for 2 hr and then treated at 110 °C for 6 hr, cooled, concentrated and purified on a silica gel column or preparative TLC (using silica gel $_{60}F_{254}$ as absorbent) by an elution with toluene to give a dark red crystalline product, isolated in 42% yield (based on $Co_2(CO)_8$).

An infrared spectrum of the above dark red crystal in CH_2Cl_2 exhibited carbonyl absorptions at 2040 (vs), 2030 (s), 2015 (s) and 1865 (w) cm^{-1}. A ^1H-NMR spectrum in C_6D_6 showed a multiplet at δ 7.00 ~ 7.27 (*vs.* internal TMS) characteristic of the phenyl protons. Its mass spectrum exhibitied peaks at m/e 732, 676, 592, 508, 480, 452, 154 and 78. The elemental analysis found: C, 35.74; H, 1.47; P, 8.67; Co, 31.99. $Co_4P_2C_{22}H_{10}O_{10}$ calcd. C, 36.10; H, 1.38; P, 8.46; Co, 32.20.

Reaction of $Mo(CO)_5(C_6H_5PH_2)$ *with* $Co_2(CO)_8$

To a toluene solution of $Co_2(CO)_8$ (7.31 mmol), a toluene solution of $Mo(CO)_5(C_6H_5PH_2)$ (7.31 mmol) was added slowly. The reaction mixture was stirred at ambient temperature for 2 hr, then was heated at 110 °C for 3 hr and a dark red solution resulted. The solution was cooled, concentrated and purified on a silica gel column by an elution with toluene to give a dark red crystalline product, $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$, (yield 1.72 mmol) and $Mo(CO)_6$ (yield 1.68 mmol).

Catalyic Reactions with $Co_4(CO)_{10}(C_6H_5P)_2$

Hydroformylation of 1-pentene

Typically, in a 300 ml autoclave, 0.447 g (0.61 mmol) $Co_4(CO)_{10}(C_6H_5P)_2$, 2 ml (18.3 mmol) 1-pentene and 60 ml anhydrous toluene were placed. The autoclave was sealed, flushed three times with carbon monoxide, pressurized with 1600 psig of an approximately equimolar mixture of carbon monoxide and hydrogen, and then heated to 140 °C with stirring. The reaction was allowed to proceed for 6 hr. The reactor was cooled and the reaction products were drawn out and analyzed with GC. It was found that 72% 1-pentene was converted into hexanal and 2-methylpentanal with n/i ratio of 2.1. The tetracobalt cluster, $Co_4(CO)_{10}(C_6H_5P)_2$, was recovered in 89% yield.

Similar reaction carried out at 2500 psig and 200 °C gave 91% conversion and a mixture of aldehydes with n/i ratio of 1.3. The tetracobalt cluster was only recovered in 45% yield and some unidentified precipitate was also obtained.

Hydrogenation of carbon monoxide

In a 300 ml Hastelloy C autoclave, 0.087 g (0.12 mmol) $Co_4(CO)_{10}(C_6H_5P)_2$ and 70 ml anhydrous dioxane were placed. The autoclave was sealed, flushed three times with CO, pressurized with 1900 psig of CO/H_2 (1/3), and then heated to 180 °C with stirring. The reaction was allowed to proceed for 7 hr. The reactor was cooled and the reaction products were analyzed with GC. The reaction solution was found to consist of 4.12 mmol methyl formate, 0.73 mmol methanol and 0.29 mmol ethanol.

Homologation of metahnol

In a 300 ml Hastelloy C autoclave, 0.098 g (0.13 mmol) $Co_4(CO)_{10}(C_6H_5P)_2$ 10 g (313 mmol) methanol and 70 ml anhydrous dioxane were placed. The autoclave was sealed, flushed three times with CO, pressurized with 1900 psig of CO/H_2 (1/1) and then heated to 180 °C for 7 hr. The reaction was cooled and the reaction solution was found to consist of 6.89 mmol methyl formate and 0.94 mmol ethanol.

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