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PREPARATION AND PROPERTIES OF METHYLBIS[1,2-BIS-(DIPHENYLPHOSPHINO)ETHANE]COBALT(I)

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Summary

Reaction of cobalt(III) acetylacetonate with dimethylaluminum monoethoxide in the presence of 1,2-bis(diphenylphosphino)ethane (dpe) gives methylbis-[1,2-bis(diphenylphosphino)ethane]cobalt(I), $\text{CoCH}_3(\text{dpe})_2$ (I), which was characterized by elemental analysis, chemical reactions, IR and NMR spectra. The cobalt-carbon bond in I is cleaved by a protic acid with liberation of methane. The reaction of I with D_2 liberated CH_3D as a sole gaseous product and afforded $\text{CoD}(\text{dpe})_2$. Insertion of carbon monoxide into the cobalt-carbon bond under mild conditions gave an acetylcobalt complex, $\text{Co}(\text{COCH}_3)(\text{CO})_2(\text{dpe}) \cdot \frac{1}{2}\text{Et}_2\text{O}$. Cobalt(I) acetylides, $\text{RC}\equiv\text{CCo}(\text{dpe})_2$ (R = Me, Ph) were obtained by the reaction of I with $\text{RC}\equiv\text{CH}$.

Introduction

A great number of trivalent alkylcobalt complexes with macrocyclic ligands have been synthesized and extensively studied [1], but only a few univalent alkylcobalt complexes are known [2]. In relation to the industrially important hydroformylation of olefins using a cobalt complex, more knowledge about the properties of univalent alkylcobalt complexes is required for understanding the carbonylation mechanism and designing new catalytic processes. We have previously studied the reaction of cobalt tris(acetylacetonate), diethylaluminum monoethoxide and 1,2-bis(diphenylphosphino)ethane (dpe) and obtained $\text{CoH}(\text{dpe})_2$ and $\text{Co}(\text{dpe})_2$ [3]. Since the dpe ligand is known as a useful stabilizing ligand for nickel [4] and iron alkyls [5], we have reexamined the alkylation of cobalt(III) acetylacetonate in the presence of dpe using dimethylaluminum monoethoxide as the reducing agent and obtained a new thermally stable methylcobalt complex, $\text{CoCH}_3(\text{dpe})_2$ (I). This complex reacts readily with carbon monoxide, molecular hydrogen and active hydrogen compounds. We report here the preparation and properties of the new methylcobalt(I) complex.

Results and discussion

The reaction of $\text{Co}(\text{acac})_3$, $\text{Al}(\text{CH}_3)_2(\text{OEt})$ and dpe in diethyl ether at room temperature gives $\text{CoCH}_3(\text{dpe})_2$ (I) as red prisms. Attempts to prepare similar alkylcobalt complexes using AlEt_3 , $\text{AlEt}_2(\text{OEt})$, $\text{Al}(\text{n-Pr})_3$ and $\text{Al}(\text{i-Bu})_3$ resulted in recovery of the known cobalt hydride complex, $\text{CoH}(\text{dpe})_2$. Being prompted by isolation of intermediate dialkylcobalt(III) complexes having both acetylacetonato and tertiary phosphine ligands with a composition of $\text{CoR}_2(\text{acac})(\text{PR}_3')_2$ [6] from the reaction mixture of $\text{Co}(\text{acac})_3$, $\text{AlR}_2(\text{OEt})$ and PR_3' , we tried to isolate a similar methylcobalt complex with the acetylacetonato and dpe ligands but the attempts have been so far unsuccessful.

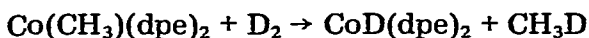
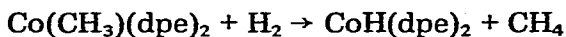
I is soluble in ether, toluene, benzene and pyridine, and can be recrystallized from ether. Although sensitive to oxygen and moisture, I is thermally very stable and decomposed at $194\text{--}195^\circ\text{C}$ in the solid state with liberation of methane and a trace of ethane.

The IR spectrum of I shows the aliphatic $\nu(\text{C-H})$ bands of the methyl group bonded to cobalt at 2870 and 2800 cm^{-1} and the presence of dpe ligands. The ^1H NMR spectrum of I in toluene at 20°C shows a quintet due to the methyl group bonded to cobalt at τ 10.3 ppm (3H, $^3J(\text{P-H})$ 9 Hz) and a broad peak due to the methylene groups in the dpe ligands at τ 7.6 ppm (8H) and a complex multiplet due to the phenyl groups in the dpe ligands at τ 2.6 to 3 ppm (40H). The proton-decoupled ^{31}P NMR spectrum of I in toluene shows a singlet due to the four phosphorus nuclei in the dpe ligands at 65.9 ppm downfield from external triphenylphosphine reference. These NMR data suggest that complex I has a square pyramidal geometry in solution at room temperature with a cobalt-bonded methyl group, or that the complex is fluxional. Similar NMR data of a methylcobalt complex were observed with $\text{CoCH}_3[\text{P}(\text{OCH}_3)_3]_4$ and an analogous hydridocobalt complex [2b], which showed fluxional behaviour in solution. Acidolysis of I with H_2SO_4 liberated one equivalent of methane for the calculated value.

In contrast to triphenylphosphine [2c], the bidentate ligand, dpe, has a large stabilizing effect on the thermal stability of the methylcobalt complex. A similar enhancement of stability of an alkyltransition metal complex due to the presence of a chelate ligand has been observed in 2,2'-bipyridine-coordinated complexes [7].

Reactions of I

Reactions with D_2 or H_2 . The reaction of I with molecular hydrogen in toluene solution at room temperature under atmospheric pressure quantitatively produced a deep red complex, $\text{CoH}(\text{dpe})_2$ (II) and liberated methane. A similar reaction of I with D_2 released CH_3D as the sole gaseous product and produced a deep red complex, $\text{CoD}(\text{dpe})_2$ (III).

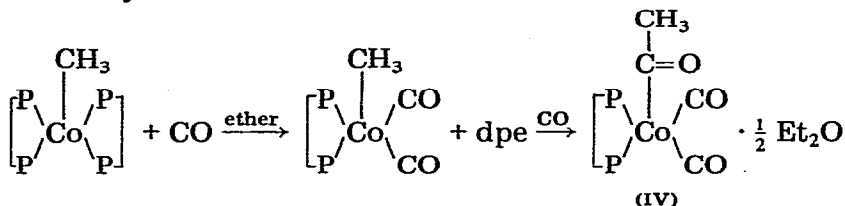


The IR spectrum of III showed a $\nu(\text{Co-D})$ band at 1355 cm^{-1} , in comparison with the $\nu(\text{Co-H})$ band of II at 1884 , the $\nu(\text{Co-H})/\nu(\text{Co-D})$ ratio being 1.4.

The hydrogenation reaction of alkyltransition metal complexes is of interest in relation to the catalytic olefin hydrogenation or hydroformylation reaction. The facile hydrogenation observed here is one of a few examples of hydrogenolysis of isolated alkyltransition metal complexes so far reported [5,8,9].

Reaction with carbon monoxide. Reports of the isolation of an acylcobalt complex from the reaction of an isolated alkylcobalt complex with carbon monoxide are still scarce [2e], although reports of reactions of cobalt carbonyls with alkyl halides to give acylcobalt complexes have been made [10–12]. Carbon monoxide is readily inserted into the cobalt–carbon bond in I under mild conditions. Contact of I with carbon monoxide under atmospheric pressure at room temperature in toluene solution followed by recrystallization from ether gives a CO-coordinated acetylcobalt complex with a dpe ligand, $\text{Co}(\text{COCH}_3)(\text{CO})_2(\text{dpe}) \cdot \frac{1}{2}\text{Et}_2\text{O}$ (IV). A part of the dpe ligands was recovered from the solution. The IR spectrum of IV shows $\nu(\text{C}\equiv\text{O})$ bands due to terminal carbonyl ligands bonded to cobalt at 1970, 1960(sh) and 1910 cm^{-1} and a $\nu(\text{C}=\text{O})$ band due to an acetyl group at 1640 cm^{-1} along with the aliphatic $\nu(\text{C}-\text{H})$ band of the methyl group in the acetyl group at 2840 cm^{-1} . The ^1H NMR spectrum of IV shows a singlet due to the methyl protons of the acetyl group at τ 7.62 ppm (s, 3H) and a doublet due to the methylene protons in the dpe ligand at τ 7.66 ppm (d, 4H, $J(\text{P}-\text{H})$ 16 Hz) and a complex multiplet due to the phenyl groups of dpe at τ 2.2 ~ 2.7 ppm (20H) in addition to a quartet (2H, $^3J(\text{H}-\text{H})$ 7 Hz), and a triplet (3H, 3J 7 Hz) due to the ethyl groups in ether at τ 6.46 and 8.54 ppm. No acetone was detected in the resultant solution. In relation to the hydroformylation reaction, attempts to induce IV to react with hydrogen at atmospheric pressure or high pressures were unsuccessful. IV reacted with methyl iodide to give acetone, which was detected by gas chromatography.

These results suggest that the insertion reaction of carbon monoxide into the cobalt–carbon bond is preceded by partial displacement of the dpe ligand from I by carbon monoxide.



In contrast to the reaction of the methylcobalt complex with carbon monoxide, which afforded the insertion product, the hydridocobalt complex II reacted with carbon monoxide to give the hydridocarbonyl complex, $\text{CoH}(\text{CO})_2(\text{dpe})$ (V), as yellow crystals, which was characterized by elemental analysis and IR spectrum.

Reactions with olefins. Complex I initiates the polymerization of acrylonitrile at low temperature. When the reaction of I with acrylonitrile was carried out under carefully controlled conditions, a yellow complex was obtained accompanied by some polymer of acrylonitrile and the liberated dpe ligand. The yellow complex VI thus obtained has a methyl group and coordinated-acrylonitrile. The IR spectrum of VI shows characteristic $\nu(\text{C}=\text{N})$ bands due to the coordinated acrylonitrile at 2175 and 2170 cm^{-1} and aliphatic $\nu(\text{C}-\text{H})$ bands

TABLE I

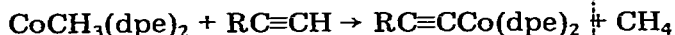
ANALYTICAL DATA FOR dpe-COORDINATED COBALT(I) COMPLEXES

| Complex | Color | Yield (%) | M.p. (d.p.) (°C) | Analysis found (calcd.) (%) | |
|--|--------------|-----------|------------------|-----------------------------|----------|
| | | | | C | H |
| Co(CH ₃)(dpe) ₂ | (I) Deep red | 82 | 194—195 | 72.5(73.1) | 6.0(5.9) |
| CoD(dpe) ₂ | (III) Red | 90 | 265—270 | 72.6(72.9) | 5.8(5.6) |
| Co(COCH ₃)(CO) ₂ (dpe) · ½Et ₂ O | (IV) Yellow | 62 | 120—121 | 64.8(65.4) | 5.4(5.9) |
| CoH(CO) ₂ (dpe) | (V) Yellow | 67 | 73—74 | 65.9(65.4) | 5.0(4.9) |
| Co(C≡CH ₃)(dpe) ₂ | (VIIa) Red | 70 | 205—207 | 74.0(73.8) | 6.2(5.7) |
| Co(C≡CPh)(dpe) ₂ | (VIIb) Brown | 80 | 238—239 | 74.7(75.3) | 5.8(5.6) |

at 2880, 2875 and 2830 cm⁻¹, in addition to the very weak band due to the polymer of acrylonitrile.

Acidolysis and thermolysis of VI liberated small amounts of methane and free acrylonitrile. Formation of a similar olefin-coordinated transition metal alkyl to VI was observed in the reaction of NiEt₂(bipy) with acrylonitrile at -78°C [13]. These olefin-coordinated alkyl complexes may be regarded as models of active intermediates in the coordination polymerization by transition metal catalysts. Complex I also initiates the polymerization of styrene, whereas hydrido complex II did not react with such vinyl compounds.

Reactions with RC≡CH and other active hydrogen compounds. Corresponding to the hydrolysis of I with H₂SO₄ and HCl, which quantitatively released methane, cleavage of the cobalt-carbon bond occurred by the reaction of I with active hydrogen compounds such as RC≡CH (R = Me, Ph), producing cobalt(I) acetylides, RC≡CCo(dpe)₂ (VII) and liberating methane quantitatively.



(VIIa) R = Me

(VIIb) R = Ph

VIIa and VIIb are stable in air, soluble in common organic solvents and can be recrystallized from toluene as red and brown crystalline complexes. The IR spectra of VIIa and VIIb show characteristic ν(C≡C) bands at 2100 and 2070 cm⁻¹. Table I shows the analytical data for the isolated dpe-coordinated cobalt(I) complexes.

The reactions of I with other types of active hydrogen compounds such as acetaldehyde and nitromethane also liberated methane. I reacted with acetaldehyde in toluene over a period of a few days, releasing methane and carbon monoxide. From the resulting solution a yellow complex was obtained. Its IR spectrum shows the ν(C=O) bands at 1965 and 1910 cm⁻¹. These results suggest that the reaction proceeds through oxidative addition of acetaldehyde to cobalt followed by decarbonylation. Since the carbonyl complex thus obtained is very sensitive to air and is contaminated with some polymers of acetaldehyde, its composition could not be determined.

Experimental

General

All procedures were carried out under a nitrogen or argon atmosphere. Solvents were dried by usual methods, distilled and stored under nitrogen.

The isolated complexes were characterized by chemical reactions such as pyrolysis and hydrolysis, elemental analysis and IR and NMR spectroscopy. IR spectra were recorded on a Hitachi model EPI-3F spectrometer using KBr discs prepared under nitrogen and NMR spectra were recorded with a JEOL JNM-PS-100 spectrometer. Analysis of gases was carried out by mass spectrometry and gas chromatography after collecting gases using a Toepler pump. The micro-analysis of carbon, hydrogen and nitrogen was performed by Mr. T. Saito of our laboratory with a Yanagimoto CHN Autocorder Type MT-2. For the isolated complexes, the absence of aluminum compounds was confirmed by Aluminon test after decomposition of the complexes.

Preparation and properties of $\text{CoCH}_3(\text{dpe})_2$ (I)

Cobalt(III) acetylacetonate (2.0 g, 5.6 mmol) and dpe (4.5 g, 11.3 mmol) were suspended in 20 ml of diethyl ether and 8 ml of dimethylaluminum monoethoxide was added to the suspension at 20°C. Sometimes heating the reaction mixture to 30°C for a short period was effective to accelerate the reaction. The color of the reaction mixture changed from green to deep yellow and then a deep red solution was obtained. A red powder was deposited on cooling the latter solution. The precipitate was filtered, washed several times with ether and hexane and recrystallized from ether to give deep red prisms, which were dried in vacuo at room temperature. Yield 82%.

I is soluble in toluene, benzene, ether, and pyridine and thermally stable in the solid state but sensitive to air and moisture. Hydrolysis of I with H_2SO_4 released 92% of the theoretical amount of methane for I. I was decomposed by heating under vacuum at 194–195°C and melted at 200–203°C, releasing methane and a trace of ethane. IR(KBr): $\nu(\text{C-H})(\text{CH}_3\text{-Co})$, 2870 and 2800 cm^{-1} ; dpe(max), 1580, 1475, 1425, 1085, 735 and 695 cm^{-1} . ^1H NMR (τ , ppm) (20°C, toluene- d_8): 10.3 (quintet, 3H, $J(\text{P-H})$ 9 Hz), 7.6 (broad multiplet, 8H), 2.6–3 (complex multiplet, 20H); ^{31}P -{H} NMR (20°C, toluene): 65.9 ppm (s) (downfield from external triphenylphosphine).

Attempts to obtain the intermediate alkylation product containing the methyl, acetylacetonato and dpe ligands such as $\text{Co}(\text{CH}_3)_2(\text{acac})(\text{dpe})$ has been so far unsuccessful.

When AlEt_3 , $\text{AlEt}_2(\text{OEt})$, $\text{Al}(\text{n-Pr})_3$, or $\text{Al}(\text{i-Bu})_3$ was used instead of $\text{AlMe}_2(\text{OEt})$, the known complex $\text{CoH}(\text{dpe})_2$ (II) was obtained. The IR spectrum of II shows a characteristic $\nu(\text{Co-H})$ band at 1884 cm^{-1} in addition to the bands due to the dpe ligands.

Reaction of I

With H_2 or D_2 . Contact of I (0.25 g, 0.29 mmol) with D_2 in toluene at atmospheric pressure at room temperature caused a color change to give a red solution and then the red crystalline complex was deposited. At the same time CH_3D was evolved. The red complex thus obtained was washed with ether

and hexane, and dried in vacuo. Yield 90%. IR(KBr): $\nu(\text{Co-D})$, 1355 cm^{-1} , $\nu(\text{C-H})$, 3040, 1575, 1480, 1440, 1090, 740 and 695 cm^{-1} .

The reaction of I with H_2 was carried out similarly.

With CO. A solution of I (0.32 g, 0.37 mmol) in toluene was allowed to come in contact with CO at an atmospheric pressure at room temperature in a closed system. The reaction mixture was stirred for 2 h to give a yellow solution. Free dpe was recovered on cooling the resultant yellow solution. After evaporation of the solvent, the yellow residue was extracted with ether and the yellow prisms obtained from the extract were purified by repeated recrystallization with ether. In the reaction mixture neither acetone nor an α -diketone was detected. Yield 62%. IR(KBr): $\nu(\text{C=O})$, 1970, 1960(sh) and 1910 cm^{-1} ; $\nu(\text{C=O})$ of CH_3COCO , 1640 cm^{-1} ; $\nu(\text{C-H})$ of the acetyl group, 2840 cm^{-1} ; $\nu(\text{C-H})$, 3050, 1585, 1480, 1435, 1100, 1067, 750, and 698 cm^{-1} . $^1\text{H NMR}$ (τ , ppm) (CD_2Cl_2): 7.62 (s, 3H), 7.66 (d, 3H, $J(\text{P-H})$ 7 Hz), 2.2–3 (20H), 6.46 (quart, 2H, $J(\text{H-H})$ 7 Hz), 8.54 (t, 3H, $J(\text{H-H})$ 7 Hz).

When a similar reaction of complex II, $\text{CoH}(\text{dpe})_2$ (0.09 g, 0.1 mmol), with carbon monoxide was carried out under the same conditions, the color of the reaction mixture changed from red to yellow. On cooling the solution, a yellow crystalline complex was deposited, which was purified by recrystallization from ether and characterized as V by elemental analysis and IR spectrum. Yield, 67%.

IR(KBr): $\nu(\text{Co-H})$, 1884 cm^{-1} ; $\nu(\text{C=O})$, 1978 and 1917 cm^{-1} ; $\nu(\text{C-H})$, 1585, 1482, 1438, 1092, 740, and 698 cm^{-1} .

With olefins. Acrylonitrile (1–2 ml) was transferred into a Schlenk tube containing complex I (0.1 g) by trap-to-trap distillation in vacuum. The reaction mixture was stirred for 2 h, at -15°C to -5°C , causing a change in color from deep red to yellow. Subsequently, the reaction system was cooled to -78°C to precipitate a yellow complex. The precipitate was freed from acrylonitrile by evaporation. If the yellow solution was stirred further, polymerization of acrylonitrile took place.

The yellow precipitate VI thus obtained was washed with ether and hexane and dried in vacuo. Its unequivocal characterization was not possible because of the contamination of the product with some polymers of acrylonitrile but the composition is close to $\text{Co}(\text{CH}_3)(\text{CH}_2=\text{CHCN})(\text{dpe})_2$ on the basis of elemental analysis, some chemical reactions and IR spectroscopy. Upon acidolysis of VI, methane and acrylonitrile were released. On pyrolysis at 130 – 135°C , the yellow solid changed to deep red and above 150°C it decomposed, releasing methane and acrylonitrile. VI reacted with methyl iodide to produce methane and a trace amount of ethane. The gaseous products evolved in these reactions were identified by gas chromatography. (Found: C, 74.8; H, 6.1; N, 3.4. $\text{C}_{56}\text{H}_{54}\text{CoN}$ calcd.: C, 72.7; H, 5.9; N, 1.5%.)

IR(KBr): $\nu(\text{C}\equiv\text{N})$, 2175 and 2170 cm^{-1} ; $\nu(\text{C-H})$, 2880, 2875, and 2830 cm^{-1} ; $\nu(\text{C-H})$, 1585, 1482, 1435, 1097, and 699 cm^{-1} . Complex II did not react with acrylonitrile even after a week's contact.

With $\text{RC}\equiv\text{CH}$. To a toluene solution of I (0.25 g, 0.25 mmol) $\text{PhC}\equiv\text{CH}$ (100 ml) was added by a trap-to-trap distillation and the reaction mixture was stirred for 5 h at room temperature. The color of the reaction mixture changed from deep red to brown, a quantitative amount of methane (100%) was evolved and a brown powder was obtained from the solution. Recrystallization from a

toluene/hexane mixture gave the brown crystals of VIIb. Yield 70%. IR(KBr): $\nu(\text{C}\equiv\text{C})$, 2095 cm^{-1} , $\nu(\text{C}-\text{H})$ 2875 and 2825 cm^{-1} ; dpe(max), 3045, 1585, 1480, 1430, 1095, 735, and 695 cm^{-1} .

A similar experiment with $\text{CH}_3\text{C}\equiv\text{CH}$ gave $\text{Co}(\text{C}\equiv\text{CCH}_3)(\text{dpe})_2$ (VIIa) in 80% yield.

The reaction of I with acetaldehyde at room temperature gave a pale red solution and evolved a gas consisting of 26% methane and 74% carbon monoxide as determined by mass spectrometry. Air sensitive yellow crystals were deposited, from the pale red solution which were purified by repeated recrystallization. The IR spectrum of the complex shows the characteristic $\nu(\text{C}=\text{O})$ bands at 1965 and 1910 cm^{-1} suggesting that it is the carbonyl complex with dpe ligands.

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