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PREPARATION OF OLEFIN-COORDINATED COMPLEXES BY THE REACTIONS OF COBALT–METHYL AND HYDRIDE COMPLEXES WITH SUBSTITUTED OLEFINS

YOICHIRO KUBO, AKIO YAMAMOTO and SAKUJI IKEDA

The Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Meguro, Tokyo (Japan)

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SUMMARY

Reactions of $CoH(N_2)(PPh_3)_3$ (I) and $CoCH_3(PPh_3)_3$ (II) with various substituted olefins have been studied. Olefins having alkoxy, amide, and ester groups, such as isobutyl vinyl ether, acrylamide, methacrylamide and vinyl acetate, displaced all the triphenylphosphine ligands and gave complexes of the formula $CoH(\text{olefin})_n$ and $Co(\text{olefin})_n$ ($n=2, 3$); tetracyanoethylene and styrene displaced part of the triphenylphosphine ligands whereas acrylonitrile, methacrylonitrile and methyl methacrylate were polymerized by (I) and (II). The styrene complex obtained from (I) was characterized as $Co(\text{Styrene})[P(C_6H_4)Ph_2](PPh_3)_2$ where cobalt is bonded to an *ortho* carbon of one of the triphenylphosphine ligands.

INTRODUCTION

Transition metal alkyls and hydrides are considered as active intermediates in a variety of catalytic processes such as isomerization, hydrogenation and polymerization of olefins[1]. A key step in these reactions is the interaction of olefins with transition metal alkyls or hydrides leading to activation of the metal–carbon or metal–hydrogen bonds. The paucity of isolable transition metal alkyls or hydrides displaying reactivity toward olefins has so far hindered detailed investigation of the activation processes whereby transition metal alkyls and hydrides interact with olefins, and relatively limited results have been reported. Recent developments in the preparation of some stable transition metal alkyls and hydrides facilitated the investigation of the interaction of olefins with isolated alkyls and hydrides[2,3a]. As an extension of our previous work[3] on the mechanism of activation of transition metal–carbon and metal–hydrogen bonds we have studied the reactions of hydridodinitrogentris(triphenylphosphine)cobalt(I) (I)[4] and methyltris(triphenylphosphine)-cobalt(I) (II)[4] with various substituted olefins. In this paper we characterize products in these reactions, and in subsequent papers the kinetics of the activation of metal–alkyl and metal–hydrogen bonds by interaction with olefins and the polymerization of olefins with these cobalt complexes will be described.

RESULTS AND DISCUSSION

Table 1 summarizes analytical data and properties of the products isolated in the reactions of $CoH(N_2)(PPh_3)_3$ (I) and $CoCH_3(PPh_3)_3$ (II) with the olefins, and Schemes 1 and 2 illustrate the courses of the reactions starting from (I) and (II), yielding the olefin-coordinated complexes. Reactions of the methyl and hydride complexes with the same olefin yielded mutually similar complexes and their differentiation often presented difficult problems. The difference of one hydrogen in these olefin coordinated complexes is not discernible by analysis; the IR spectra were similar to each other and the presence of ν(Co–H) band was not observed in complexes derived from the hydride complex (I) which itself shows no ν(Co–H) band. Therefore structural assignments for the complexes are mostly based on chemical evidence. In cases where triphenylphosphine ligands are still present in the olefin-coordinated products a further complication exists because the phenyl group of the triphenylphosphine ligand participates in internal oxidative addition reactions. In this case mass spectrometric analysis combined with the deuteriolysis of the complexes permits differentiation between the products.

TABLE 1

ANALYSIS AND PHYSICAL CONSTANTS OF OLEFIN-COORDINATED COBALT COMPLEXES OBTAINED FROM (I) AND (II)

Starting complex	*Isolated complexes*[a]	*Analysis found (calcd.) (%)*			*Decomp. temp. (°C)*	*Magnetic moment (BM)*
		C	*H*	*N*		
(I)	$Co(St)\{P(C_6H_4)(C_6H_5)_2\}(PPh_3)_2$(III)	77.7 (78.5)	5.0 (5.5)		78–80	2.90
	$CoH(TCNE)_2(PPh_3)_2$(IV)	68.4 (68.7)	3.2 (3.6)	13.6 (13.4)	185–188	2.80
	$CoH(AcAm)_3$(V)	40.1 (39.5)	5.9 (5.9)	15.4 (15.7)	119–121	2.73
	$CoH(MeAcAm)_3$(VI)	46.1 (45.7)	6.8 (7.0)	12.9 (13.3)	171–174	2.95
	$CoH(VAc)_2$(VII)	40.9 (41.4)	5.1 (5.6)		173–174	3.00
	$CoH(IBVE)_2$(VIII)	54.0 (54.5)	8.9 (9.5)			
(II)	$Co(St)(PPh_3)_3$(IX)	77.3 (78.4)	5.0 (5.6)		79–80	2.89
	$Co(TCNE)_2(PPh_3)_2$(X)	67.9 (68.7)	3.7 (3.6)	13.0 (13.3)	205–209	2.62
	$Co(AcAm)_3$(XI)	40.0 (39.5)	5.9 (5.9)	15.9 (15.7)	73–75	2.81
	$Co(MeAcAm)_3$(XII)	46.3 (45.9)	6.8 (6.7)	14.0 (13.4)	72–74	2.90
	$Co(VAc)_2$(XIII)	40.5 (41.6)	4.2 (5.2)		184–185	3.03
	$Co(IBVE)_2$(XIV)	53.9 (54.4)	9.1 (9.7)			

[a] For abbreviations see Scheme 1.

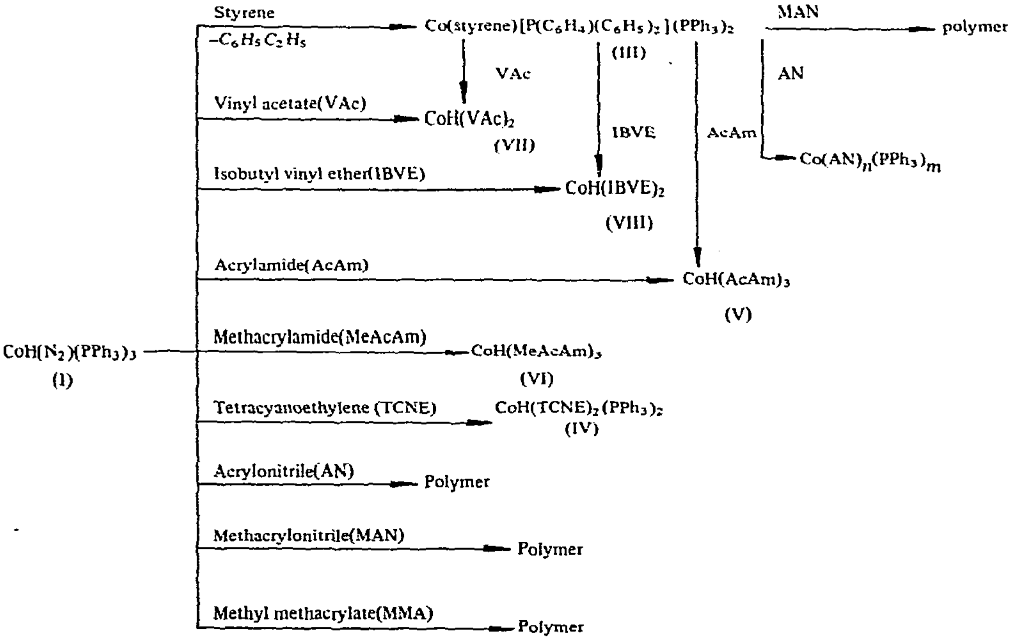
1. *Reactions of* $CoH(N_2)(PPh_3)_3$ *(I) with olefins*

a. Styrene. The reaction of (I) with styrene gave a brown complex of a composition $Co(C_6H_5C_2H_3)[P(C_6H_4)(C_6H_5)_2](PPh_3)_2$ (III) which can be recrystallized from undiluted styrene but decomposes in other solvents. The reaction proceeds according to the following equation releasing 1 mol each of N_2 and ethylbenzene as confirmed by gas chromatography. No hydrogen evolution was observed.

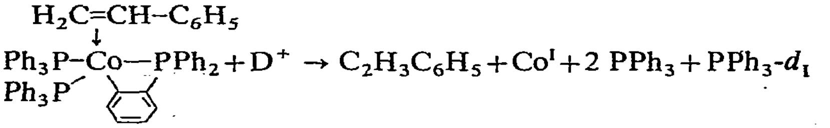
$$\underset{\text{(I)}}{CoH(N_2)(PPh_3)_3} + 2\,C_6H_5C_2H_3 \rightarrow \underset{\text{(III)}}{Co(C_6H_5C_2H_3)[P(C_6H_4)(C_6H_5)_2](PPh_3)_2} + N_2 + C_6H_5C_2H_5 \quad (1)$$

Treatment of (III) with dry hydrogen chloride gave $CoCl_2(PPh_3)_2$ and PPh_3, and released styrene and ethylbenzene in a molar ratio of 4/1. The molar ratio of the sum of styrene and ethylbenzene to cobalt complex (III) was 0.85. The reaction of complex (III) with acrylonitrile released 0.83 mol of styrene per complex giving an extremely air-sensitive acrylonitrile-coordinated complex, which could not be fully characterized, whereas the original hydride complex (I) initiated the polymerization of acrylonitrile. The infrared spectrum of (III) shows, in addition to the absorptions due to the triphenylphosphine ligands, a ν(C=C) band attributable to styrene coordinated to cobalt at 1630 cm^{-1} which is shifted by 20 cm^{-1} to lower frequency compared with free styrene, but no ν(Co–H) band was observed in the region between 1700–2500 cm^{-1}. Magnetic susceptibility measurements indicated the presence of two unpaired electrons in complex (III) in agreement with a spin-free univalent structure for (III). Hydrolysis of 1 mol of (III) with D_2SO_4 released 3 mol of triphenylphosphine which contained 2.3% deuterium as proved by mass spectrometric examination of the water

SCHEME 1



produced by combustion of the triphenylphosphine. The deuterium content agrees with the calculated value of 2.22% which corresponds to the presence of one deuterium atom per three triphenylphosphine residues as expected for the reaction product of D_2SO_4 with $Co(St)[P(C_6H_4)(C_6H_5)_2](PPh_3)_2$ which contains a Co–C bond between the cobalt and an *ortho* carbon of a triphenylphosphine ligand as shown below:



$$\overset{H_2C{=}CH{-}C_6H_5}{\downarrow}\ Ph_3P{-}Co{-}PPh_2 + D^+ \rightarrow C_2H_3C_6H_5 + Co^I + 2\,PPh_3 + PPh_3\text{-}d_1 \quad (2)$$

(III)

These chemical properties and the IR spectrum of complex (III) support the coordination of styrene to cobalt through a π bond. Tyrlik and coworkers[5] have studied the reactions of (I) with styrenes by an ESR technique. Their results, however, contain some uncertainties since the reaction products were not isolated and, according to our experience, the styrene-coordinated cobalt complex gradually decomposes in solutions which do not contain enough styrene.

b. Tetracyanoethylene. Tetracyanoethylene (TCNE), having strongly electron-withdrawing cyano groups, is known to give many TCNE-coordinated transition metal complexes. The reaction of TCNE with (I) in toluene gave a dark brown complex of a composition $CoH(TCNE)_2(PPh_3)_2$ (IV) which was recrystallized from methanol. The formation of 0.9 mol of PPh_3 and 1 mol of nitrogen gas per mol of (I) was observed, but no hydrogen gas was evolved during the reaction. An infrared spectrum of complex (IV) shows $\nu(C{\equiv}N)$ of the TCNE cyano groups bonded to cobalt at 2190 and 2090 cm^{-1} and the presence of triphenylphosphine ligands, but no $\nu(Co{-}H)$ band. The C≡N stretching bands of the coordinated TCNE are shifted to lower frequencies (ca. 60–130 cm^{-1}) compared with those of free TCNE (at 2250 and 2220 cm^{-1}). Baddley[6] has classified the modes of bonding of TCNE with transition metals into three categories: in metal–N σ bonded complexes, $\nu(C{\equiv}N)$ is expected to be somewhat greater (ca. 50 cm^{-1}) than in the uncoordinated nitrile; somewhat lower (ca. 20–30 cm^{-1}) in π bonded olefinic complexes, and considerably lower (ca. 200 cm^{-1}) if the complex is π bonded through the C≡N bond. The shift of $\nu(C{\equiv}N)$ in the present complex may indicate π-bonding of TCNE with cobalt through the double bond.

c. Acrylamide, methacrylamide, vinyl acetate and isobutyl vinyl ether. Acrylamide (AcAm), methacrylamide (MeAcAm), vinyl acetate (VAc) and isobutyl vinyl ether (IBVE) reacted with (I) displacing dinitrogen (1 mol) and triphenylphosphine ligands (3 mol) and giving complexes of a general composition $CoH(olefin)_n$ ($n=2$ or 3). No hydrogen was released in any of the reactions and no vinyl acetate hydrogenation product was detected in the reaction of vinyl acetate with (I). The olefin-coordinated complexes were insoluble in most organic solvents and only slight blue coloring of the solvents was observed on suspending the acrylamide and methacrylamide complexes in benzene, toluene and tetrahydrofuran. On hydrolysis of $CoH(AcAm)_3$ (V) and $CoH(MeAcAm)_3$ (VI), 3 mol of acrylamide or methacrylamide coordinated to cobalt were released respectively.

The IR spectra of the olefin-coordinated complexes showed no band assignable to $\nu(C{=}C)$ indicating the profound change in double bond character of the olefins upon direct coordination to cobalt. These changes upon coordination are reflected indirectly in the shifts of the ν(NH), ν(C=O) and ν(COC) bands of substituents attached to the olefins. In complexes (V) and (VI), ν(N–H) and ν(C=O) bands of olefins are lowered by 20–50 cm^{-1} as compared with the free olefins, and in $CoH(VAc)_2$ (VII) and $CoH(IBVE)_2$ (VIII), ν(C=O) and ν(C–O–C) bands of olefins are lowered by 150–200 cm^{-1} as compared with those in the free olefins. Similar large shifts to lower frequencies were observed in a nickel–vinyl acetate complex[3a] and were attributed to coordination of the vinyl acetate through both the olefinic double bond and the carbonyl group.

Complexes (VII) and (VIII) (pink and light purple respectively) are quite different from amide complexes (V) and (VI) (deep blue and blue), and were all paramagnetic having magnetic moments of 2.7–3.0 BM corresponding to two unpaired electrons.

No reactions of (I) with saturated amide and carbonyl compounds took place, and compounds without double bond appear to be incapable of interaction with (I) giving rise to an isolable complex, whereas the methylcobalt complex (II) reacted with saturated amides as will be described later.

These olefin–cobalt complexes represent relatively rare examples of π complexes which contain only olefins as ligands. Furthermore, a comparison of the reactions of complex (I) with styrene and TCNE on one hand with those of acrylamide, methacrylamide, vinyl acetate and isobutyl vinyl ether on the other suggests that the coordination of the olefins through both the double bond and the substituted carbonyl or ether group leads to complete dissociation of the triphenylphosphine ligands from cobalt.

In none of the complexes (IV) to (VIII) were ν(Co–H) bands observed and iodolysis of amide complexes (V) and (VI) released no hydrogen. Nevertheless the hydride structures for (IV)–(VIII) are favored on the following basis: (*i*) the reaction of (I) having a hydridic hydrogen with the olefins gave neither hydrogen gas nor the hydrogenated products of the olefins; (*ii*) pyrolysis of the vinyl acetate complex (VII) released 0.34 mol of H_2 per cobalt, whereas pyrolysis of the vinyl acetate complex (XIII), which was derived from the methylcobalt complex (II) and vinyl acetate, released no hydrogen; (*iii*) although pyrolysis of the acrylamide complex (V) liberated no hydrogen the pyrolysis residue showed a new IR band at 2180 cm^{-1} which may be assignable to ν(Co–H), whereas the pyrolysis product of the acrylamide complex (XI), which was derived from the methylcobalt complex (II), showed no IR band in the region from 1800 to 2300 cm^{-1}.

d. Acrylonitrile, methacrylonitrile and methyl methacrylate. Acrylonitrile, methacrylonitrile and methyl methacrylate were polymerized to materials of high molecular weights by (I). The mechanistic details of the polymerization will be reported separately.

2. *Reactions of* $Co(styrene)[P(C_6H_4)(C_6H_5)_2](PPh_3)_2$ *(III)*

The reactions of complex (III) are also included in Scheme 1 together with the reactions of complex (I).

The reactions of complex (III) with vinyl acetate, isobutyl vinyl ether and acrylamide released 1 mol of styrene and 3 mol of triphenylphosphine originally coordinated to cobalt in (III) yielding complexes of the type $CoH(olefin)_n$. The same complexes were obtained upon reaction of (I) with these olefins. The sources of hydrogen in the reactions of (III) with olefins giving the CoH(olefin)$_n$ type complexes were not established.

The reaction of acrylonitrile with complex (III) gives a light orange complex, the IR spectrum of which reveals the presence of triphenylphosphine ligands and $\nu(C\equiv N)$ of acrylonitrile coordinated to cobalt at 2180 cm^{-1}, a lowering of the frequency by 50 cm^{-1} compared with the free nitrile. The properties of the acrylonitrile complex were not investigated because of its extreme air sensitivity.

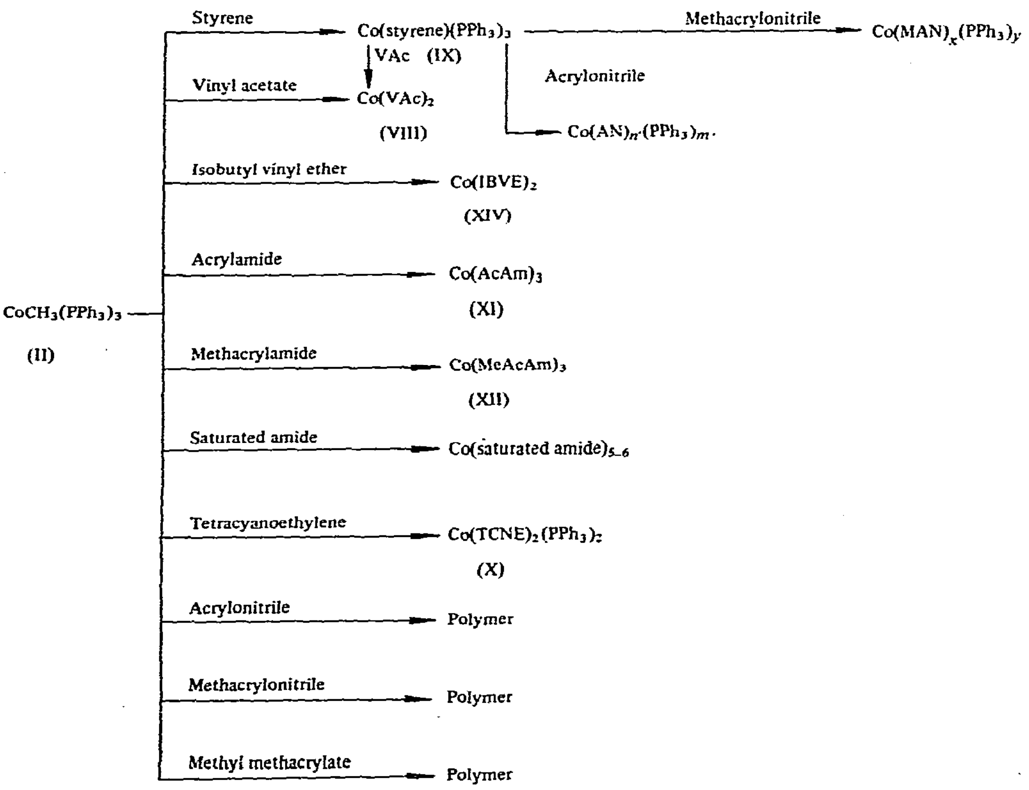
Complex (III) initiated the polymerization of methacrylonitrile to give a dimethylformamide-insoluble polymer indicating the formation of an isotactic product. The styrene complex (III) and hydride complex (I), are able to catalyze the hydrogenation of styrene at room temperature and atmospheric pressure.

3. *Reactions of* $CoCH_3(PPh_3)_3$ *(II)*

The methylcobalt complex (II) reacted with olefins with splitting of the Co–C bond giving ethane or methane as the major gaseous product.

a. Styrene. The reaction between styrene and complex (II) gave 0.40 mol of ethane per cobalt atom, a trace of methane and a brown complex with composition

SCHEME 2



of $Co(Styrene)(PPh_3)_3$ (IX). In contrast to the reaction of $CoH(N_2)(PPh_3)_3$ with styrene, the reaction of the methylcobalt complex did not give any ethylbenzene but proceeded according to the following equation:

$$\underset{\text{(II)}}{CoCH_3(PPh_3)_3} + \underset{\text{(Styrene)}}{C_6H_5C_2H_3} \longrightarrow \underset{\text{(IX)}}{Co(St)(PPh_3)_3} + C_2H_6 \qquad (3)$$

Complex (IX) is more air sensitive than complex (III). The infrared spectrum of (IX) shows the presence of triphenylphosphine ligands, and the ν(C=C) band of the vinyl group of styrene coordinated with cobalt is lowered by ca. 20 cm^{-1} as compared with that of free styrene. The only significant difference in the IR spectrum of (IX) from that of (III) was the absence of a band at 540 cm^{-1}.

On reaction with acrylonitrile, 0.87 mol of styrene per mol of complex (IX) was released, but no ethylbenzene was formed. Dry hydrogen chloride reacted with (IX) to give $CoCl_2(PPh_3)_2$ and PPh_3, and released styrene and ethylbenzene in a molar ratio of 5/1. The molar ratio of the sum of styrene and ethylbenzene to cobalt was 0.85.

Hydrolysis with acidic deuterium oxide released 3 mol of triphenylphosphine coördinated to cobalt, but without deuterium incorporation on the basis of mass spectral data, suggesting the absence of a Co–C bond between the *ortho* carbon of the phenyl group and cobalt, unlike complex (III).

The chemical properties and IR spectrum of complex (IX) support its formulation as a zerovalent cobalt π complex coordinated to the olefinic bond of styrene.

b. Tetracyanoethylene. The reaction of TCNE with complex (II) released one mol of PPh_3 per cobalt atom and gave a dark brown complex of composition $Co(TCNE)_2(PPh_3)_2$ (X), purified by recrystallization from methanol. Ethane and methane in a molar ratio of 0.72/1 were formed in the reaction and the molar ratio of (2 ethane+methane) to complex (II) was 0.91.

An infrared spectrum of complex (X) shows the presence of triphenylphosphine ligands and ν(C≡N) of the cyano groups in tetracyanoethylene coordinated to cobalt at 2200 and 2100 cm^{-1}. These ν(C≡N) bands are shifted to lower frequencies (ca. 50–120 cm^{-1}) as compared with those of free TCNE (2250 and 2220 cm^{-1}) and the TCNE is considered to be bonded to the cobalt through its olefinic double bond.

c. Acrylamide, methacrylamide, vinyl acetate and isobutyl vinyl ether. The reactions of complex (II) with acrylamide, methacrylamide, vinyl acetate and isobutyl vinyl ether gave complexes of general composition $Co(olefin)_n$ ($n=2$ or 3). Each reaction released quantitatively 3 mol of triphenylphosphine and 1 mol of methane. These complexes are almost insoluble in common organic solvents; acrylamide and methacrylamide complexes are slightly soluble in toluene, benzene and tetrahydrofuran.

On hydrolysis of $Co(AcAm)_3$ (XI) and $Co(MeAcAm)_3$ (XII), each olefin coordinated to cobalt was released quantitatively. $Co(AcAm)_3$ was also obtained via an independent route by reaction of $Co(C_2H_5)Bipy_2$ with acrylamide[7].

The infrared spectra of the olefin-coordinated complexes showed no ν(C=C) bands where the ν(C=C) bands of the free olefins are observed. The ν(N–H) and ν(C=O) bands of complexes (XI) and (XII) are lowered by 20–50 cm^{-1} compared with those of the free olefins. The ν(C=O) and ν(C–O–C) bands of complex $Co(VAc)_2$ (XIII) and $Co(IBVE)_2$(XIV) are lowered by 150–200 cm^{-1}.

In contrast to the hydride complex (I) the reactions of the methyl complex (II) with saturated amides did occur, releasing methane, and gave complexes of a composition Co(amide)$_n$ ($n=5$ or 6). Presumably the methyl–cobalt bond in (II) is much weaker than the Co–H bond in (I) and is split by interaction with the saturated amide. The IR spectrum of Co(propionamide)$_n$ shows absorptions of the coordinated amide at 1590 and 1515 cm^{-1}. ν(CO) and δ(NH) are shifted by 70 and 115 cm^{-1} to lower frequency as compared with those of the free amide.

d. Acrylonitrile, methacrylonitrile and methyl methacrylate. Acrylonitrile, methacrylonitrile and methyl methacrylate were polymerized to high molecular weights products with (II).

4. *Reactions of Co(styrene)(PPh$_3$)$_3$ (IX)*

The reactions of the styrene complex (IX) are summarized in Scheme 2 together with the reactions of the methyl–cobalt complex (II). The reaction of complex (IX) with vinyl acetate quantitatively released styrene and triphenylphosphine coordinated with cobalt to form Co(VAc)$_2$ which is also given by the reaction of complex (II) with vinyl acetate. The reaction between complex (IX) and acrylonitrile gives a light orange complex whose IR spectrum shows the presence of triphenylphosphine ligands and ν(C≡N) of acrylonitrile at 2180 cm^{-1} which is lowered by 50 cm^{-1} as compared with the free olefin. The properties of the complex are similar to the reaction product of complex (III) with acrylonitrile. In contrast with complex (III), the reaction of complex (IX) with isobutyl vinyl ether did not give complex (XIV) and the reaction with methacrylonitrile did not yield the polymer but gave the complex of a composition Co(MAN)$_x$(PPh$_3$)$_y$ (MAN=methacrylonitrile). The IR spectrum of this orange complex shows the presence of triphenylphosphine ligands and the ν(C≡N) of methacrylonitrile at 2170 cm^{-1} which is shifted by 70 cm^{-1} to lower frequency compared with that of free methacrylonitrile probably by coordination through the olefinic double bond.

The magnetic moments of these olefin-coordinated cobalt complexes were in the range of 2.6–3.0 BM corresponding to two unpaired electrons. The results are incompatible with the formulation as zerovalent cobalt complexes if structures with extreme charge transfer from cobalt to the coordinated olefins are not to be taken into account. At the moment, with the lack of evidence to support other structures such as hydrides, the olefin-coordinated complexes are formulated as in Table 1 and Scheme 2.

EXPERIMENTAL SECTION

General

All preparations and recrystallizations were carried out under a nitrogen or argon atmosphere, or *in vacuo*. Solvents and liquid olefins were dehydrated, distilled and stored under nitrogen before use. Liquid olefins were introduced by a trap-to-trap distillation *in vacuo* into reaction vessels containing the alkyl– or hydrido–cobalt complexes. With a solid olefin such as TCNE or acrylamide, the solvent was introduced to a solid mixture of the cobalt complex and the olefin held in a vacuum by a trap-to-trap distillation.

Analysis of non-condensable and condensable gases at liquid nitrogen temperature was carried out by mass spectrometry and gas chromatography after collecting the non-condensable gas using a Toepler pump, by which the volume of the gas was measured.

Analysis of the hydrogenation products from reaction of liquid olefins with the cobalt complexes was carried out by gas chromatography after collecting the liquid by a trap-to-trap distillation. The amount of triphenylphosphine released from the complex was determined by a spectroscopic method after reaction and extraction of triphenylphosphine with hexane. The deuterium content of the triphenylphosphine in (III) and (IX) obtained by deuterolysis with acidic D_2O was determined by mass spectrometric examination of water formed in the combustion of triphenylphosphine with copper oxide *in vacuo*. Magnetic susceptibility was measured using a Shimazu magnetic balance MB-100 under nitrogen. The results are shown in Table 1. The complexes coordinated with isobutyl vinyl ether, (VIII) and (XIV), were too air-sensitive to determine the susceptibility.

Materials

$CoH(N_2)(PPh_3)_3$ and $CoCH_3(PPh_3)_3$ were prepared using the methods described in our previous paper[4].

1. *Reactions of $CoH(N_2)(PPh_3)_3$ with olefins*

a. With styrene. Styrene (2.00 ml; 15.4 mmol) was introduced to 772 mg (0.88 mmol) of $CoH(N_2)(PPh_3)_3$ by trap-to-trap distillation. The mixture was stirred for 3 h at room temperature, and a brown precipitate was formed. The evolved gas contained only nitrogen which corresponded to 0.84 mol per mol of complex (I). The excess of styrene, removed by trap-to-trap distillation, contained 0.99 mmol of ethylbenzene per (I) as determined by gas chromatography. The brown complex was washed several times with hexane, recrystallized from styrene and dried under vacuum. The brown complex was insoluble in almost all organic solvents except in styrene. Yield 70%; IR(KBr): ν(C=C) 1630 cm^{-1}.

b. With TCNE. A mixture of 500 mg (0.57 mmol) of complex (I) and 150 mg (1.20 mmol) of TCNE in 15 ml of toluene was allowed to react for 1 h at room temperature. The evolved gas contained only nitrogen (11.4 ml S.T.P., 0.51 mmol), and 130 mg (0.50 mmol) of the released triphenylphosphine was collected from the toluene solution. The dark brown complex was removed by filtration and washed several times with hexane, recrystallized from methanol and dried under vacuum. Yield 60%; IR(KBr): ν(C≡N) 2190 and 2090 cm^{-1}.

c. With acrylamide. A mixture of 1.80 g (2.06 mmol) of complex (I) and 700 mg (9.86 mmol) of acrylamide in 15 ml of toluene was stirred for 2 h at room temperature. The evolved gas contained 1.95 mmol of nitrogen, and the amount of triphenylphosphine collected was 5.40 mmol. The deep blue crystals were removed by filtration and washed repeatedly with diethylether and hexane, and dried under vacuum. Yield 45%; IR(KBr): ν(N–H) 3370, 3180; ν(C=O) 1650 cm^{-1}. The pyrolysis of the acrylamide complex (V) (58.7 mg, 0.22 mmol) at 200° for 2 h released a part of acrylamide and no hydrogen gas. The pyrolysis residue showed a new IR band at 2180 cm^{-1} which may be assignable to ν(Co–H).

d. With methacrylamide. A mixture of 1.30 g (1.49 mmol) of complex (I) and 420 mg (4.90 mmol) of methacrylamide in 40 ml of toluene was allowed to react for 6 h at room temperature. The evolved gas was 0.87 mol of nitrogen per cobalt, and the amount of triphenylphosphine collected was 3.90 mmol. The blue crystals were removed by filtration and washed with hexane and diethylether, and dried under vacuum. Yield 35%; IR(KBr): ν(N–H) 3330 cm^{-1}; ν(C=O) 1650 cm^{-1}.

e. With vinyl acetate. Vinyl acetate (3.0 ml; 28.1 mmol) was introduced to 701 mg (0.80 mmol) of complex (I) by trap-to-trap distillation. The mixture was stirred for 3 h at room temperature and a pink complex was precipitated. The evolved gas was nitrogen [0.93 mol per complex (I)], and the amount of triphenylphosphine released in the reaction was 580 mg (2.2 mmol). After the excess vinyl acetate was removed with a trap-to-trap distillation, the pink complex was removed by filtration and was washed repeatedly with diethyl ether and hexane, and dried under vacuum. The vinyl acetate collected did not contain any hydrogenation products of vinyl acetate. Yield 60%; IR(KBr): ν(C=O) 1570–1580 cm^{-1}. Pyrolysis of the vinyl acetate complex (VII) (57.3 mg; 0.24 mmol) (250° for 2 h) released 0.084 mmol of hydrogen.

f. With isobutyl vinyl ether. Isobutyl vinyl ether (5.0 ml, 40.0 mmol) was introduced to 920 mg (1.05 mmol) of complex (I) via trap-to-trap distillation. The mixture was stirred for 2 days at room temperature and a light purple precipitate was obtained. The evolved gas contained 0.85 mol of nitrogen per complex (I). The light purple complex was filtered and washed several times with hexane, and dried under vacuum. The excess of isobutyl vinyl ether collected after the reaction did not contain any hydrogenation products. Yield 20%; IR(KBr): ν(COC) 1070 cm^{-1}.

2. *Reactions of (III) with olefins*

a. With vinyl acetate. Vinyl acetate 4.0 ml (50.0 mmol) was introduced to 380 mg (0.40 mmol) of complex (III) by trap-to-trap distillation. After reaction for 2 h at room temperature, the pink precipitate was formed, and styrene and triphenylphosphine were released. The IR spectrum of the pink complex was identical with complex (VII) obtained from (I).

b. With isobutyl vinyl ether. Isobutyl vinyl ether 2.0 ml (16.0 mmol) was introduced to 230 mg (0.24 mmol) of complex (III) by trap-to-trap distillation. After the reaction for 6 h at room temperature, a light purple precipitate was formed, and triphenylphosphine and styrene were released. The IR spectrum of the light purple complex was similar to that of (VIII) obtained from the reaction of (I) with isobutyl vinyl ether.

c. With acrylamide. A mixture of 180 mg (0.19 mmol) of complex (III) and 59 mg (0.83 mmol) of acrylamide in 2.0 ml of styrene as solvent was stirred for 2 h at room temperature. Triphenylphosphine (140 mg; 0.53 mmol) was released and a deep blue complex was precipitated. The IR spectrum of the deep blue complex was similar to that of complex (V) obtained from (I).

d. With acrylonitrile. Acrylonitrile 2.5 ml (38.0 mmol) was introduced to 660 mg (0.70 mmol) of complex (III) by trap-to-trap distillation. After the reaction for 1 day at room temperature a light orange complex was formed. Excess of acrylonitrile, removed by trap-to-trap distillation, contained 0.57 mmol of styrene [0.83 mol per complex (III)] as determined by gas chromatography. The light orange complex burns in air and attempts at microanalysis failed. IR(KBr); ν(C≡N) 2180 cm^{-1}.

e. With methacrylonitrile. Methacrylonitrile (5.0 ml, 60 mmol) was introduced to 250 mg (0.26 mmol) of complex (III) by trap-to-trap distillation. After reaction for 2 days at room temperature a methacrylonitrile polymer was formed. Yield 80%.

f. Reaction of (III) with dry hydrogen chloride. Dry hydrogen chloride was introduced to a mixture of 575 mg (0.61 mmol) of complex (III) and 5.0 ml of benzene. After the reaction for 1 h at room temperature, a blue complex $CoCl_2(PPh_3)_2$ (360 mg; 0.55 mmol) and triphenylphosphine 155 mg (0.58 mmol) were formed, and styrene and ethylbenzene in a molar ratio of 4/1 were released from complex (III). The molar ratio of the sum of styrene and ethylbenzene to cobalt complex (III) was 0.85 as determined by gas chromatography. (Analysis of the blue complex: found: C, 65.4; H, 5.1; Cl, 10.1. $C_{36}H_{30}Cl_2P_2Co$ calcd.: C, 66.1; H, 4.6; Cl, 10.9%.)

3. *Reactions of $CoCH_3(PPh_3)_3$ with olefins*

a. With styrene. Styrene (1.0 ml; 7.7 mmol) was introduced to 169 mg (0.20 mmol) of $CoCH_3(PPh_3)_3$ by trap-to-trap distillation. The mixture was stirred for 2 h at 0°, and a brown precipitate was formed. The evolved gas contained ethane (0.08 mmol) which corresponded to 0.40 mol per cobalt complex (II) and a trace of methane. The excess styrene removed by a trap-to-trap distillation contained no ethylbenzene. The brown complex was washed several times with hexane, recrystallized from styrene and dried under vacuum. The brown complex was insoluble in almost all organic solvents except in styrene. Yield 66%; IR(KBr): ν(C=C) 1630 cm^{-1}. The styrene complex catalyzes the hydrogenation of styrene at room temperature and normal pressure.

b. With TCNE. A mixture of 650 mg (0.75 mmol) of complex (II) and 200 mg (1.60 mmol) of TCNE in 10 ml of toluene was allowed to react for 3 h at −20°. The evolved gas contained ethane and methane in a molar ratio of 0.7/1, and triphenylphosphine was released. The dark brown complex was filtered off and washed several times with hexane, recrystallized from methanol and dried under vacuum. Yield 70%; IR(KBr): ν(C≡N) 2200, 2100 cm^{-1}.

c. With acrylamide. A mixture of 450 mg (0.52 mmol) of complex (II) and 200 mg (2.81 mmol) of acrylamide in 15 ml of toluene was stirred for 3 h at −15°. The evolved gas contained 0.49 mmol of methane, and 1.40 mmol of triphenylphosphine collected. The deep blue crystals were filtered off and washed repeatedly with hexane and dried under vacuum. Yield 41%; IR(KBr): ν(N–H) 3370, 3180 cm^{-1} ν(C=O) 1650 cm^{-1}. The pyrolysis of the acrylamide complex (XI) (54.1 mg; 0.19 mmol) at 220° for 2 h released a part of acrylamide coordinated to cobalt and no gas. The pyrolysis residue showed no new IR band in metal–hydride region in contrast with the acrylamide complex (V).

d. With methacrylamide. A mixture of 1.20 g (1.39 mmol) of complex (II) and 390 mg (4.6 mmol) of methacrylamide in 25 ml of toluene was stirred for 5 h at −15°. The evolved gas contained only methane which corresponded to 0.90 mol per cobalt complex (II). The amount of triphenylphosphine collected was 3.70 mmol. The blue crystals were filtered off and washed with hexane and diethylether, and dried under vacuum. Yield 39%; KBr: ν(N–H) 3380, 3180 cm^{-1}, ν(C=O) 1650 cm^{-1}.

e. With vinyl acetate. Vinyl acetate 1.5 ml (14 mmol) was introduced to 450 mg (0.52 mmol) of complex (II) by trap-to-trap distillation. The mixture was stirred for 4 h at −10° and a pink complex was precipitated. The evolved gas contained methane and ethylene in a molar ratio of 2/1, and 1.40 mmol of triphenylphosphine was released in the reaction. The pink complex was filtered off and washed repeatedly with diethylether and hexane, and dried under vacuum. Yield 53%; IR(KBr): ν(C=O) 1570–1580 cm^{-1}. Heating the complex at 250° for 2 h released no gas.

f. With isobutyl vinyl ether. Isobutyl vinyl ether 4.0 ml (32.0 mmol) was introduced to 1.00 g (1.16 mmol) of complex (II) by trap-to-trap distillation. The mixture was stirred for 2 days at 0° and a light purple precipitate was obtained. The evolved gas contained 0.89 mol of methane per complex (II), and the amount of triphenylphosphine released in the reaction was 3.1 mmol. The light purple complex was filtered off and washed with hexane, and dried under vacuum. Yield 25%; IR(KBr): ν(COC) 1070 cm^{-1}.

4. *Reactions of (IX) with olefins*

a. With vinyl acetate. Vinyl acetate (4.0 ml; 37 mmol) was introduced to 500 mg (0.53 mmol) of complex (IX) by trap-to-trap distillation. The mixture was stirred for 2 h at room temperature, and a pink complex was formed. Styrene and triphenylphosphine were released from complex (IX). The IR spectrum of the pink complex was identical with complex (XIII) obtained from complex (II) and vinyl acetate.

b. With acrylonitrile. Acrylonitrile (1.0 ml; 15.2 mmol) was introduced to 500 mg (0.53 mmol) of complex (IX) by trap-to-trap distillation. After the reaction for 1 day at room temperature, a light orange complex was formed. The excess of acrylonitrile removed by trap-to-trap distillation contained 0.46 mmol of styrene (0.87 mol per complex (IX)) as determined by gas chromatography. IR(KBr): ν(C≡N) 2180 cm^{-1}.

c. With methacrylonitrile. Methacrylonitrile (2.0 ml; 24 mmol) was introduced to 150 mg (0.16 mmol) of complex (IX) by trap-to-trap distillation. After reaction for 5 h at room temperature, an orange complex was precipitated, which was filtered off and washed with hexane, and dried under vacuum. IR(KBr): ν(C≡N) 2170 cm^{-1}.

d. Reaction of (IX) with dry hydrogen chloride. Dry hydrogen chloride was introduced to a mixture of 1.95 g (2.0 mmol) and 5 ml of benzene. After reaction for 2 h at room temperature, a blue complex $CoCl_2(PPh_3)_2$ (950 mg; 1.64 mmol) and triphenylphosphine (510 mg; 1.95 mmol) were formed, and styrene and ethylbenzene in a molar ratio of 5/1 were released from complex (IX). The molar ratio of the sum of styrene and ethylbenzene to cobalt complex (IX) was 0.80 as determined by gas chromatography.

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