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PREPARATION AND PROPERTIES OF *cis*-DIALKYLCOBALT COMPLEXES, $CoR_2(acac)(PR'_3)_2$

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Summary

Treatment of $Co(acac)_3$ and tertiary phosphine with $AlR_2(OEt)$ in ether under nitrogen gives remarkably stable trivalent cobalt complexes, $CoR_2(acac)(PR'_3)_2$ (R = Me, Et, n-Pr, iso-Bu, PR'_3 = PEt_3, $P(n\text{-}Bu)_3$, $PPhMe_2$, PPh_2Me; acac = acetylacetonato). ^1H, ^{31}P and ^{13}C NMR spectra of these complexes show that they have an octahedral configuration with two tertiary phosphine ligands in axial positions. Pyridine replaces one of the phosphine ligands to give a pyridine-coordinated complex, $Co(CH_3)_2(acac)(PEt_3)(py)$, whereas a bidentate ligand 2,2'-bipyridine replaces both tertiary phosphines to yield the bipyridine-coordinated complexes, $CoR_2(acac)(bipy)$. The isolated complexes readily react with carbon monoxide to yield the dialkyl ketone and a univalent carbonyl complex with an acetylacetonato ligand, $Co(acac)(CO)_2(PR'_3)$.

Introduction

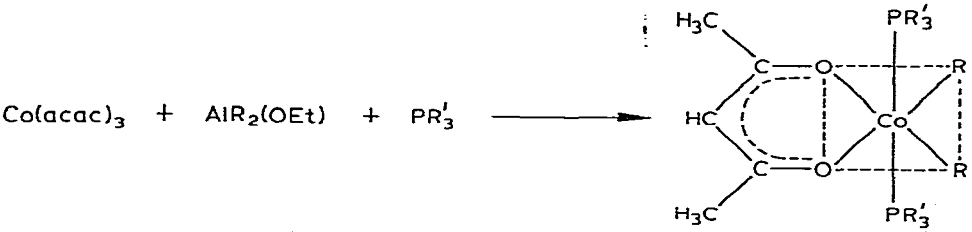
Much effort has been devoted to preparation and study of organocobalt complexes containing a macrocyclic ligand, partly because of the importance of this class of compounds in relation to the naturally occurring organocobalt complex, coenzyme B_{12}, and partly because of the belief that the macrocyclic ring contributes to stabilization of the cobalt—carbon σ-bond. The number of organocobalt(III) compounds of this type so far prepared now exceeds 1000 [1]. In contrast, only a little is known of other types of σ-organocobalt complexes [2—7,17].

As part of our project to study the properties of transition metal alkyls and hydrides we have previously studied the reaction systems consisting of cobalt acetylacetonate, alkylaluminum compounds and triphenylphosphine [6,7] or 1,2-bis(diphenylphosphino)ethane (DPE) [8] and have obtained some univalent cobalt hydride and methyl complexes. This type of reaction is considered to proceed through exchange of the acetylacetonato ligands in the cobalt acetylacetonate with the alkyl groups of the alkylaluminum compounds with formation of an intermediate alkylcobalt complex having the acetylacetonato ligand. Such intermediate alkylation products have been in fact isolated in the reactions of nickel [9] and iron [7] acetylacetonates with alkylaluminum compounds in the presence of suitable tertiary phosphine ligands. Examination of similar reaction systems containing cobalt acetylacetonate, dialkylaluminum monoethoxide and tertiary phosphines other than triphenylphosphine and DPE has led to isolation of a variety of new dialkylcobalt(III) complexes containing an acetylacetonato and two tertiary phosphine ligands. These trivalent dialkylcobalt complexes proved to be remarkably insensitive to air, thermally considerably stable and quite amenable to NMR study. We have previously reported the preparation and properties of $CoR_2(acac)(PR'_3)_2$ in a preliminary form [10]. In this and following papers we describe in detail the preparation and properties of these dialkylcobalt complexes. A similar dimethylcobalt complex with trimethylphosphines and an acetylacetonato ligand has been prepared recently by the reaction of trimethyltris(trimethylphosphine)cobalt(III) with acetylacetone, but isolation of the complex in pure form has failed due to the "instability" of the complex [5].

Insertion of carbon monoxide into the Co—C bond constitutes one of the key steps in the hydroformylation reaction of olefins catalyzed by cobalt carbonyl but very few model studies using an isolated alkylcobalt complex have been made. No example of CO insertion into alkylcobalt complexes with macrocyclic ligands has been reported [1,11]. The present complexes readily undergo the CO insertion reaction and provide some information concerning the reaction path of CO insertion into an alkylcobalt complex.

Results and discussion

The reaction of cobalt acetylacetonate and dialkylaluminum monoethoxide in the presence of suitable tertiary phosphine ligands, when conducted with appropriate control of the reaction temperature (see Experimental Section), gives dialkylcobalt(III) complexes containing two tertiary phosphines and an acetylacetonato ligand.



I: PR'_3 = PEt_3 ; R = Me.

II: PR'_3 = $PPhMe_2$; IIa, R = Me; IIb, R = Et, IIc, R = n-Pr; IId, R = iso-Bu.

III: PR'_3 = PPh_2Me ; R = Me.

IV: PR'_3 = $P(n\text{-}Bu)_3$; R = Me.

These complexes are quite insensitive to air, soluble in almost all organic solvents and can be obtained as orange to yellow prisms. Table 1 summarizes the analytical data, yields and physical properties of the isolated complexes.

A series of dialkyl(acetylacetonato)cobalt(III) compounds with different alkyl

chain lengths was obtained when dimethylphenylphosphine was employed but attempts to obtain the other series of dialkylcobalt complexes have so far been unsuccessful. The melting point and thermal stability of a series of $CoR_2(acac)(PPhMe_2)_2$ decreased with an increase in the alkyl chain length and the thermally unstable isobutylcobalt complex IId was obtained only when the reaction was carried out under carefully controlled reaction conditions. When the reaction was carried out at room temperature, a hydridocobalt complex $CoH(PPhMe_2)_4$ was the sole isolable product. The similar reaction of $Co(acac)_3$ with $Al(n\text{-}Pr)_2(OEt)$ or $Al(iso\text{-}Bu)_2(OEt)$ using diphenylmethylphosphine gave the known hydridocobalt(I) complex, $CoH(PPh_2Me)_4$ [12].
Apparently, small differences in the electronic and steric factors in the tertiary phosphine ligand employed greatly influence the reactivity and stability of the alkylcobalt complex formed, as we observed in the preparation of tertiary phosphine-coordinated alkylnickel complexes [13]. When the complexes having various tertiary phosphine ligands are compared, the melting point (with decomposition) is observed to decrease as $PPhMe_2 > PPh_2Me > PEt_3 > P(n\text{-}Bu)_3$.

It may be expected that further alkylation of $CoR_2(acac)(PR'_3)_2$ with alkylaluminum compounds followed by reduction via splitting of alkyl—cobalt bonds may afford a univalent alkylcobalt complex, as we have previously obtained $CoCH_3(PPh_3)_3$ and $CoCH_3(PPh_3)_2$ from the reaction system of $Co(acac)_3$, $AlMe_2(OEt)$ and PPh_3 [7]. Attempts to isolate such a methylcobalt(I) complex with tertiary phosphines other than PPh_3 have so far been unsuccessful. We have previously obtained a dinitrogen-coordinated complex, $CoH(N_2)(PPh_3)_3$, from a similar reaction system by carrying out the reaction under dinitrogen. In none of the present reaction systems was formation of a dinitrogen-coordinated complex observed.

These dialkyl(acetylacetonato)cobalt complexes were characterized on the basis of elemental analysis, IR and NMR spectroscopy and chemical properties. ^1H and ^{31}P NMR spectra of I—IV support the formulation of the complexes having octahedral configurations with two cobalt-bonded alkyl groups and an acetylacetonato ligand coplanar with cobalt, which is coordinated with two tertiary phosphine ligands in the axial positions. Table 2 summarizes the ^1H NMR data for $CoR_2(acac)(PR'_3)_2$.

The two methyl groups in acac ligand in these complexes are magnetically equivalent in various solvents and appear as a singlet over a wide temperature range (—78— +20°C). The methyl resonance in $PPhMe_2$ in II shows the characteristic triplet due to the virtual coupling with two phosphorus nuclei in mutually *trans* positions. The two methyl groups bonded to cobalt in I, IIa, III and IV are magnetically equivalent and appear as a triplet at low temperatures by coupling with two phosphine ligands and as a singlet at higher temperatures, where the phosphine ligands are partly dissociated and exchanging rapidly with each other.

The ^1H NMR spectrum of the ethyl groups in IIb shows a singlet in toluene and acetone due to the accidental coincidence of the chemical shifts of the methyl and methylene groups [14,22]. The ^1H NMR spectrum of n-propyl groups in IIc shows a singlet due to β- and γ-protons of n-propyl groups at $\tau = 8.84$ and a broad multiplet due to α-methylene protons of these at $\tau = 9.64$. $^{31}P—\{^1H\}$ NMR spectra of these complexes show a singlet for I—IV at low temperatures, suggesting that two phosphorus nuclei are magnetically equivalent. At higher

TABLE 1

ANALYTICAL DATA FOR *cis*-DIALKYLCOBALT COMPLEXES

	Compound	Yield (%)	Color	M.p. (dec.) (°C)	Anal. found (calcd) (%)			IR (cm^{-1})	
					C	H	N	Co—C	CH$_3$
I	Co(CH$_3$)$_2$(acac)(PEt$_3$)$_2$	60	orange-yellow	78—81	54.1 (53.8)	11.0 (10.1)		573	2775 2840
IIa	Co(CH$_3$)$_2$(acac)(PPhMe$_2$)$_2$	70	orange-yellow	116—119	59.2 (59.5)	8.1 (7.5)		580	2770 2870
IIb	Co(C$_2$H$_5$)$_2$(acac)(PPhMe$_2$)$_2$	65	yellow	67—68	60.7 (60.9)	7.9 (7.9)		578	2820
IIc	Co(C$_3$H$_7$)$_2$(acac)(PPhMe$_2$)$_2$	35	yellow	49—50	61.9 (62.3)	8.5 (8.3)		570	2800
IId	Co(iso-Bu)$_2$(acac)(PPhMe$_2$)$_2$		yellow green	unstable [b]				574	2790 2845
III	Co(CH$_3$)$_2$(acac)(PPh$_2$Me)$_2$	90	orange-red	89—92	67.7 (67.4)	6.7 (6.6)		585	2775 2860
IV	Co(CH$_3$)$_2$(acac)[P(n-Bu)$_3$]$_2$	54	yellow	64—69	62.3 (62.2)	12.3 (12.2)		579	2865 2845
Va	Co(CH$_3$)$_2$(acac)(PEt$_3$)(py)	32	yellow	100—105	55.8 (56.1)	8.9 (8.6)	3.7 (3.6)	580	2775 2850
Vb	Co(CH$_3$)$_2$(acac)(PEt$_3$)(γ-pi)	40	yellow	100—101	57.3 (57.5)	8.7 (8.8)	3.6 (3.5)	580	2775 2850
VIa	Co(CH$_3$)$_2$(acac)(bipy)	35	red-purple	139—140 [a]	58.4 (59.3)	6.6 (6.1)	8.0 (8.1)	595	2770 2840
VIb	Co(C$_2$H$_5$)$_2$(acac)(bipy)	71	green	125—126 [a]	60.9 (61.3)	6.8 (6.7)	7.2 (7.5)	585	2840
VIc	Co(C$_3$H$_7$)$_2$(acac)(bipy)	41	green	45—47	63.6 (63.0)	7.0 (7.3)	6.1 (7.0)	550	2835

[a] At this temperature range the complex decomposes without melting. [b] Microanalysis of IId was not feasible due to its instability.

TABLE 2

^{1}H NMR DATA FOR $CoR_2(acac)(PR'_3)_2$

	R	PR_3'	Temp.	τ(Co—R)[a, b] (ppm)	τ(PR_3') (ppm)	acac	
						τ(CH_3) (ppm)	τ(CH) (ppm)
I	Me	PEt_3	—20	9.92(t, 6H)	8.9(qui, 18H) 8.4(m, 12 H)	8.21(s, 6H)	4.93(s, 1H)
			0	9.98(s, 6H)	8.9(t, 18H) 8.4(q, 12H)	8.23(s, 6H)	4.91(s, 1H)
IIa	Me	$PPhMe_2$	20	10.1(t, 6H)	8.68(t, 12H)	8.64(s, 6H)	5.16(s, 1H)
			50	10.1(br. s, 6H)	8.68(s, 12H)	8.64(s, 6H)	5.16(s, 1H)
IIb	Et	$PPhMe_2$	—20	9.44(s, 10H)	8.73(s, 12H)	8.44(s, 6H)	4.98(s, 1H)
IIc	n-Pr	$PPhMe_2$	—40	8.84(s, 10H) 9.64(m, 4H)	8.76(t, 12H)	8.40(s, 6H)	4.94(s, 1H)
III	Me	PPh_2Me	20	9.74(s, 6H)	9.15(s, 6H)	8.60(s, 6H)	5.12(s, 1H)
IV	Me	$P(n\text{-}Bu)_3$	—30	9.88(t, 6H)	8.3—9.1(m, 18H)	8.15(s, 6H)	4.88(s, 1H)
			20	10.1(s, 6H)	8.3—9.1(m, 18H)	8.20(s, 6H)	4.85(s, 1H)

[a] All the NMR spectra were observed in toluene-d_8. For avoiding the overlap of the TMS signal with that of cobalt bonded methyl group, no internal TMS was used. Instead, the ^{1}H toluene impurity in toluene-d_8 was used as the internal standard and the signals are referred to TMS based on the signal. [b] Abbreviation: s, singlet; d, doublet; t, triplet; q, quartet; qui, quintet; br. s, broad singlet; m, multiplet.

temperatures the partial dissociation and exchange of the tertiary phosphine ligands are observed.

IR spectra of these complexes show the characteristic aliphatic ν(C—H) bands due to the alkyl groups bonded to cobalt at 2770—2870 cm^{-1} in addition to bands due to tertiary phosphines and the acetylacetonato ligand and show ν(Co—C) bands at 570—585 cm^{-1}.

Reactions of $CoR_2(acac)(PR'_3)_2$

When the ethyl complex IIb was decomposed in the solid state ethane and ethylene were liberated in a 1 : 1 ratio with a trace amount of n-butane. The thermolysis at 30° C in solution liberated ethane and ethylene in 1 : 1.3 to 1 : 2 ratio. Acidolysis of IIb with concentrated H_2SO_4 liberated ethane and ethylene in a 3 : 1 ratio. IIb reacts with methyl iodide to produce methane, ethane and ethylene and a trace amount of propane.

Displacement of the tertiary phosphine ligands in $CoR_2(acac)(PR'_3)_2$ with pyridine bases

One of the two tertiary phosphine ligands in I can be readily displaced with pyridine to give a pyridine-coordinated complex, $Co(CH_3)_2(acac)(PEt_3)(py)$, which was isolated from this system. Similar replacement took place with γ-picoline, but not with α and β-picolines.

$$Co(CH_3)_2(acac)(PEt_3)_2 + py \rightarrow \underset{(Va)}{Co(CH_3)_2(acac)(PEt_3)(py)} + PEt_3$$

$$\underset{(\gamma\text{-pi} = \gamma\text{-picoline})}{Co(CH_3)_2(acac)(PEt_3)_2 + \gamma\text{-pi}} \rightarrow \underset{(Vb)}{Co(CH_3)_2(acac)(PEt_3)(\gamma\text{-pi})} + PEt_3$$

The replacement of the tertiary phosphine ligand in I with pyridine is also observed by NMR spectrscopy. The ^{1}H NMR spectrum of I in pyridine shows a doublet for the two cobalt-bonded methyl groups coupled with one phosphorus nucleus and a multiplet due to the free triethylphosphine ligand which is dissociated from complex I.

A bidentate ligand, 2,2'-bipyridine, replaces two tertiary phosphine ligands to yield 2,2'-bipyridine-coordinated complexes, $CoR_2(acac)$ (VIa—VId), which were isolated from the reaction of IIa—IId in ether with 2,2'-bipyridine. Complexes VIb, VIc and VId are green at a low temperature (—10° C) when prepared but turn to blue-violet irreversibly at room temperature. This color change from green to blue-violet might be due to a *cis-trans* configurational change between stereochemical isomers.

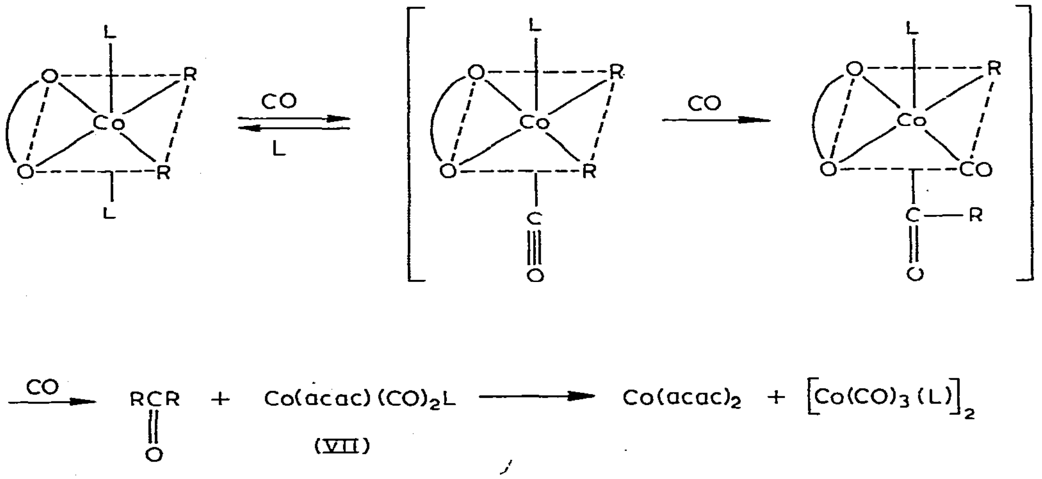
Although complex IId is too unstable to handle at room temperature, VId is fairly stable. Thus employment of organic nitrogen bases such as pyridine and 2,2'-bipyridine enhances the stabilities of these complexes and makes the isolation of unstable complexes such as isobutyl complex easier. Table 1 includes the analytical data of these base-coordinated complexes.

Similar displacement of tertiary phosphines in complex I with a bidentate tertiary phosphine, 1,2-bis(diphenylphosphino)ethane, failed.

CO insertion into alkylcobalt bonds

In contrast to the reluctance of alkylcobalt complexes having macrocyclic ligands toward CO insertion into Co—C bond [11], the isolated dialkylcobalt(III) complexes I—IV undergo very facile CO insertion. Contact of toluene or ether solutions of I—IV with carbon monoxide at normal pressure causes a very facile reaction even at —50° C and gives 1 mol equiv. of dialkyl ketone per cobalt and an isolable acetylacetonatocobalt(I) complex with a composition of Co(acac)-$(CO)_2(PPh_2Me)$ (VII). Attemps to recrystallize the acetylacetonatocobalt(I) complex VII from acetone caused disproportionation and recovery of a mixture of $Co(acac)_2$ and a binuclear cobalt complex having CO and PPh_2Me ligands without the acetylacetonato ligand, $[Co(CO)_3(PPh_2Me)]_2$. Similar binuclear cobalt carbonyl complexes $[Co(CO)_3P(n\text{-}Bu)_3]_2$ [15] and $[Co(CO)_3(PPh_3)]_2$ [16] have been prepared and the former was characterized by X-ray analysis.

Under similar reaction conditions the bipy-coordinated dimethylcobalt complex VIa or $CoCH_3(bipy)_2$ * did not react with carbon monoxide. These results together with the NMR information [8] that the coordinated tertiary phosphine ligands are exchanging rapidly even at low temperatures suggest that a dissociation of a ligand at a *cis* position from the alkyl group may be required to accommodate a CO ligand which may be inserted into a Co—C bond (or mechanistically speaking the alkyl group may migrate to the CO ligand) to form an acyl—alkylcobalt complex, which gives the ketone and cobalt(I) complex VII on reductive elimination of the alkyl and acyl groups:



In order to test the validity of this mechanism carbon monoxide was allowed to contact a mixture of the ethyl complex IIb and the propyl complex IIc in toluene at —50° C in a closed system and the ketone formed was examined. Gas chromatographic analysis indicated that only diethyl ketone was formed and neither di-n-propyl ketone nor ethyl n-propyl ketone was detected. The result suggests that the ethylcobalt complex IIb is much more susceptible than the propyl complex to CO insertion to afford a propionyl ethyl complex which

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* This compound was initially identified as $Co(CH_3)_2(bipy)_2$ [17], but subsequent study revealed that it is in fact $CoCH_3(bipy)_2$.

liberates diethyl ketone by reductive elimination and that no intermolecular reaction is taking place.

For further examination of the reactivity of the possible intermediate, acylcobalt complex, the methylcobalt complex IIa was treated with carbon monoxide in the presence of ethyl iodide. Acetone was formed as the sole ketone and no methyl ethyl ketone was detected. The result suggests that the reductive elimination of the acetyl and methyl groups is taking place rapidly prior to the attack of ethyl iodide on the acetyl group. Attempts to isolate the intermediate product containing the alkyl and acyl groups have been so far unsuccessful. We have recently observed a facile CO insertion into a methylcobalt(I) complex with 1,2-bis(diphenylphosphino)ethane (dpe) ligands to give acetylcobalt complex with the dpe ligands [8]. Klein [5] has observed the formation of acetone and an acetylcobalt(I) complex in the reaction of trimethyltris(trimethylphosphine)cobalt with carbon monoxide.

Reaction with Hg^{2+}

Methyl cobalamin has been shown to methylate Hg(II) ions in a simple acid—base reaction which may be one of the ways in which methylmercury is produced in living systems [1].

Complex IIa also reacted with $Hg(OAc)_2$ to produce dimethylmercury(II), which was detected by NMR spectroscopy. The ^1H NMR spectrum of the reaction mixture of IIa and $Hg(OAc)_2$ in toluene-d_8 shows the two mercury-bonded methyl groups as a singlet with satellites ($^2J(Hg—C—H) = 102$ Hz) at $\tau = 9.90$ [18]

$$Co(CH_3)_2(acac)(PPhMe_2)_2 + Hg(OAc)_2 \rightarrow (CH_3)_2Hg$$

A similar methyl transfer reaction took place in the reaction of $CuI(PPh_3)_3$ and $Co(CH_3)_2(acac)(PEt_3)_2$ (I) in ether. When the ether solution of $CuI(PPh_3)_3$ and I was warmed to 30—35°C, methane and ethane were evolved with deposition of metallic copper. This result suggests that the following reaction took place [19]:

$$Co(CH_3)_2(acac)(PEt_3)_2 + 2CuI(PPh_3)_2 \rightarrow [2CuCH_3(PPh_3)_3]$$

$$\rightarrow Cu^0 + CH_4 + C_2H_6$$

Experimental

Materials and general procedures

All preparations and recrystallizations were carried out under deoxygenated nitrogen, argon, or in vacuo. Solvents were dried by the usual methods, distilled and stored under nitrogen or argon. Cobalt tris(acetylacetonate) and dialkylaluminum monoethoxides were prepared by the usual methods.

Triethylphosphine and tri-n-butylphosphine were used as purchased, dimethylphenylphosphine [20] and diphenylmethylphosphine [21] were prepared as described in the literature. For each complex isolated, the absence of aluminum component was confirmed by the Aluminon method after decomposition of the complexes. Analytical data of the alkyl complexes are summarized in Table 1. IR spectra of the complexes were recorded on a Hitachi Model EPI-3G as KBr discs and NMR spectra were recorded with a Japan Electron Optics Lab. JNM-PS-100 spectrometer. The microanalysis of carbon, hydrogen and nitrogen was performed by Mr. T. Saito of our laboratory with a Yanagimoto CHN Autocorder Type MT-2.

1. *Preparation of* $CoR_2(acac)(PR'_3)_2$

(a) $Co(CH_3)_2(acac)(PEt_3)_2$ *(I).* To a mixture of $Co(acac)_3$ (1.00 g, 0.0028 mol) and triethylphosphine (1.5 ml, 0.01 mol) in ether (10 ml), dimethylaluminum monoethoxide (3 ml) was added at room temperature. The reaction mixture was warmed to 40—45° C for a few minutes. At that temperature the reaction mixture suddenly changed from a green to a deep yellow solution with reflux of the solvent. As soon as the change to deep yellow set in the system was rapidly cooled to 0° C and stirred at that temperature until the reaction was complete. Then it was cooled to —78° C to precipitate the yellow to greenish yellow crystals, which were filtered and washed with ether and n-hexane three or four times. The yellow crystals thus obtained were recrystallized from ether to give yellow prisms (yield, 60%) (I). Complex I is insensitive to air and moisture, thermally stable at room temperature, and decomposes at 78—81° C, liberating methane and ethane. I is soluble in almost all organic solvents such as alcohol, hexane, toluene, benzene, acetone and ether. Acidolysis of I evolved methane. On iodinolysis in benzene, ethane (73%) and methane (5%) were liberated. Attempts to isolate higher homologues of $CoR_2(acac)(PEt_3)_2$ or a univalent methylcobalt complex failed.

(b) $CoR_2(acac)(PPhMe_2)_2$ *(IIa—IId) (R = Me, Et, n-Pr, iso-Bu).* $Co(CH_3)_2(acac)(PPhMe_2)_2$ (IIa) and $Co(C_2H_5)_2(acac)(PPhMe_2)_2$ (IIb) were prepared similarly to I as described in (a).

The n-propyl complex IIc was obtained by the reaction of $Co(acac)_3$ (1.00 g, 0.0028 mol), $PPhMe_2$ (1.5 ml, 0.01 mol) and $AlPr_2(OEt)$ in ether (10 ml) at room temperature. The reaction mixture was stirred at room temperature for 20 min. When it changed to a deep yellow solution, it was cooled to 0° C and stirred until reaction was complete. After evaporation of the solvent to a fourth of its volume followed by addition of acetone (2.5 ml), the mixture was stirred at —78° C until a yellow crystalline powder was deposited. The yellow precipitate was filtered and washed several times with ether, acetone and hexane and recrystallized from ether at low temperature (yield, 35%).

The isobutyl complex IId was prepared similarly to IIc. However, isolation of the pure complex was difficult, and care must be taken to avoid decomposition of the complex by carefully controlling the reaction temperature and time. IId was obtained as yellow to green crystals, sensitive to air and thermally unstable. It decomposed in ether solution turning from green to deep red even at 0° C.

(c) $CoH(PPhMe_2)_4$. When the reaction mixture of $Co(acac)_3$, $PPhMe_2$ and $Al(iso\text{-}Bu)_2(OEt)$ was stirred for ca. 1 h at room temperature, a deep red solution was obtained. On cooling the red solution to —78° C red crystals were deposited. The complex thus obtained is sensitive to air but thermally stable at room temperature under nitrogen. Its IR spectrum shows a characteristic ν(Co—H) at 1880 cm^{-1} and other bands due to the coordinated $PPhMe_2$ ligands, suggesting it to be the cobalt hydride complex, $CoH(PPhMe_2)_4$ (yield, 40%) (Anal. Found: C, 62.7; H, 7.9. $CoH(PPhMe_2)_4$ calcd.: C, 62.8; H, 7.4%.)

(d) $Co(CH_3)_2(acac)(PPh_2Me)_2$ (III). Complex III was prepared similarly to I or IIa as described above. III is soluble in toluene and CH_2Cl_2 but much less soluble in ether and hexane.

(e) $CoH(PPh_2Me)_4$. Using $AlPr_2(OEt)$ the reaction of $Co(acac)_3$ and PPh_2Me in ether at room temperature was carried out. The reaction mixture changed from a green suspension to a deep yellow solution at 40° C. After concentration of the solvent by evaporation and addition of acetone to the residue with stirring at —78° C red crystals were deposited, which were filtered and washed with ether and dried in vacuo (yield, 15%). The red complex thus obtained is thermally stable and insensitive to air. Its IR spectrum shows the characteristic ν(Co—H) band at 1955 cm^{-1}, and other bands due to the coordinated PPh_2Me ligands but no band assignable to the acac ligand, suggesting it to be the known complex, $CoH(PPh_2Me)_4$ [12].

(f) $Co(CH_3)_2(acac)[P(n\text{-}Bu)_3]_2$ (IV). Complex IV was prepared similarly to I or IIa or III as described above (yield, 54%).

2. Reaction of $CoR_2(acac)(PR'_3)_2$

(a) Ligand exchange reaction with pyridine. Pyridine (2 ml) was added to complex I (0.1 g) by a trap-to-trap distillation using a vacuum line and the reaction mixture was stirred at room temperature for 1 h. After concentration of the pyridine solution hexane was added to the residue to give a pyridine-coordinated complex as yellow crystals on cooling the mixture. The complex was recrystallized from hexane (yield, 32%). The IR spectrum of the yellow complex Va shows peaks due to the coordinated pyridine in addition to the coordinated triethylphosphine and acetylacetonato ligands. The ligand exchange reaction of I with γ-picoline was carried out similarly to yield a yellow crystalline complex, ($Co(CH_3)_2(acac)(PEt_3)(\gamma$-picoline). The corresponding α- and β-picoline-coordinated complexes were not obtained.

(b-i) Reaction of I with 2,2'-bipyridine. Ether was added to a solid mixture of complex I (0.1 g) and 2,2'-bipyridine (0.033 g) at —5° C. The temperature was gradually raised to 0° C and the solution was stirred for 2 h. After color change of the solution to dark yellow the solution was further stirred at room temperature until a red to purple micro-crystalline powder was deposited. The complex was filtered, washed repeatedly at low temperature with ether and hexane and dried in vacuum (yield, 40%).

(b-ii) Reaction of $CoR_2(acac)(PPhMe_2)_2$ (R = Me, Et, n-Pr, iso-Bu) with 2,2'-bipyridine. These reactions were carried out similarly to the reaction of I with 2,2'-bipyridine described above (b-i) except that the reactions of the ethyl, n-propyl and iso-butyl complexes were carried out at lower temperature (—10° C). On addition of ether to the solid mixture of II and bipyridine the color of the reaction system changed from yellow to deep green and a microcrystalline precipitate was deposited. When there was no precipitate deposited, concentration of the solution by evaporation and addition of hexane were necessary to induce the deposition of the green precipitate. The precipitate was washed with hexane and dried in vacuo. IR spectra of these green complexes were similar to that of $Co(CH_3)_2(acac)(bipy)$. The analytical values of the methyl, ethyl and n-propyl complexes (VIa—VIc) are given in Table I. The characterization of the

isobutyl complex was made on the basis of its IR spectrum which is similar to that of VIc.

(c) Reaction of $CoR_2(acac)(PR'_3)_2$ with carbon monoxide. The reactions were carried out similarly for all the complexes with a composition of $CoR_2(acac)(PR'_3)_2$. The dialkyl(acetylacetonato)complex was dissolved in 2 ml of toluene and brought in contact at —70° C with carbon monoxide at atmospheric pressure in a closed system. With the rise in temperature the color of the solution changed from yellow to red. The amounts of ketones formed in the reaction solutions were determined by GLC. The following are the yields of the ketones; acetone from I, 83%; from IIa, 84%; from III, 91%; diethyl ketone from IIb, 78%; di-n-propyl ketone from IIc, 70%. The cobalt carbonyl compounds with a formula of $Co(acac)(CO)_2(PR'_3)$ may be recovered from the reaction system. As an illustrative example we describe the reaction of III with carbon monoxide. The reaction was carried out at room temperature in ether, in which the product was less soluble and deposited as a red microcrystalline powder. The powder was filtered off, washed with ether and acetone, cooled to —10° C and dried in vacuo (yield, 65%); (Anal. Found; C, 57.0; H, 4.8. $Co(acac)(CO)_2(PPh_3Me)$ (VII) calcd.; C, 57.9; H, 4.8%). IR(KBr): $\nu(C{\equiv}O)$, 1965, 1955 and 1940 cm^{-1}, $\nu(acac)$, 1584, 1510, 1400, 1265, and 765 cm^{-1}.

When complex VII was dissolved in acetone at room temperature disproportionation occurred to produce a red complex $[Co(CO)_3(PPh_2Me)]_2$ (VIII) and $Co(acac)_2$ which was characterized by the measurement of the IR spectrum. IR(KBr); $\nu_{max}(acac)$ 1605, 1520, 1400, 1025, 935, and 770 cm^{-1}. VIII was characterized on the basis of elemental analysis and its IR spectrum which indicates the presence of CO and the PPh_2Me ligand and the absence of the acac ligand. (Anal. Found: C, 55.6; H, 4.1. $[Co(CO)_3(PPh_2Me)]_2$ (VIII) calcd.; C, 56.0; H, 3.8%). IR(KBr): $\nu(C{\equiv}O)$, 1940 cm^{-1} vs; $\nu_{max}(PPh_2Me)$, 3045, 1470, 1435, 1000, 890, 885, 750, 735, and 695 cm^{-1}.

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References

1 (a) D. Dodd and M.D. Johnson, Organometal. Chem. Rev., 52 (1973) 1. (b) J.M. Pratt and P.J. Craig, in F.G.A. Stone and R. West, (Eds.) Advances in Organometallic Chemistry, Vol. 11, Academic Press, New York, 1973, p. 331.
2 G. Mestroni, A. Camus and E. Mestroni, J. Organometal. Chem., 24 (1970) 775.
3 R.B. King, Inorg. Chem., 5 (1966) 82.
4 J. Ellermann and W.H. Gruber, Angew. Chem. Int. Ed. Engl. 7 (1968) 129.
5 H.F. Klein and H.H. Karsch, Chem. Ber., 108 (1975) 944, 956.
6 A. Yamamoto, A. Kitazume, L.S. Pu, and S. Ikeda, J. Amer. Chem. Soc., 93 (1971) 371.
7 Y. Kubo, L.S. Pu, A. Yamamoto and S. Ikeda, J. Organometal. Chem., 84 (1975) 369.
8 T. Ikariya and A. Yamamoto, J. Organometal. Chem., 116 (1976) 231.
9 (a) P.W. Jolly, K. Jonas, C. Krüger and Y.H. Tsay, J. Organometal. Chem., 33 (1971) 109. (b) A. Yamamoto, T. Yamamoto, T. Saruyama and Y. Nakamura, J. Amer. Chem. Soc., 95 (1973) 4073.
10 T. Ikariya and A. Yamamoto, Chem. Lett. (1976) 85.
11 G. Costa, G. Mestroni and G. Pellizer, J. Organometal. Chem., 15 (1968) 187.
12 M. Rossi and A. Sacco, J. Chem. Soc. Chem. Commun., 471 (1969).

13 A. Yamamoto, T. Yamamoto, M. Takamatsu, T. Saruyama and Y. Nakamura, in Y. Ishii and M. Tsutsui (Eds.), Organotransition-Metal Chemistry, Plenum Press, New York, 1975.
14 F.A. Cotton, B.A. Frenz and D.L. Hunter, J. Amer. Chem. Soc., 96 (1974) 4820.
15 J. Ibers, J. Organometal. Chem., 14 (1968) 423.
16 W. Hieber and E. Lindner, Chem. Ber., 94 (1961) 1417.
17 T. Saito, Y. Uchida, A. Misono, A. Yamamoto, K. Morifuji and S. Ikeda, J. Organometal. Chem., 6 (1966) 572.
18 J.V. Hatton and W.G. Schneider, J. Chem. Phys., 39 (1963) 1330.
19 (a) A. Yamamoto, A. Miyashita, T. Yamamoto and S. Ikeda, Bull. Chem. Soc. Japan, 45 (1972) 1583. (b) T. Ikariya and A. Yamamoto, J. Organometal. Chem., 72 (1974) 145.
20 W. Hewertson and H.R. Watson, J. Chem. Soc., (1962) 1490.
21 J.A.C. Allison and F.G. Mann, J. Chem. Soc., (1949) 2915.
22 T. Yamamoto and A. Yamamoto, Bull. Chem. Soc. Japan, 49 (1976) 191; T. Yamamoto, T. Saruyama, Y. Nakamura and A. Yamamoto, ibid., 49 (1976) 589.