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SYNTHESIS AND PROPERTIES OF DIALKYL(ACETYLACETONATO)BIS(TERTIARY PHOSPHINE)COBALT(III)

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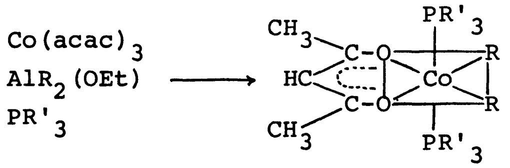
The complexes I-IV, $CoR_2(acac)(PR'_3)_2$ (R=Me, Et, n-Pr, iso-Bu; PR'_3=PEt_3,$P(n\text{-}Bu)_3$,$PPhMe_2$, PPh_2Me) have been prepared by the reactions of $Co(acac)_3$, $AlR_2(OEt)$ and tertiary phosphines in ether. These complexes were characterized by NMR, IR spectroscopy and the chemical reactions. H-D scrambling in ethyl groups of $Co(CH_2CD_3)_2(acac)(PPhMe_2)_2$ (V) has been observed.

In spite of the recent rapid increase in the number of isolated alkylcobalt complexes most of them have planar macrocyclic ligand, which are often believed essential in stabilizing the cobalt-carbon bond$^{1)}$, and examples of stable alkylcobalt complexes without the macrocycles are very limited.$^{2-5)}$

We report here the preparation and properties of novel, remarkably stable trivalent dialkylcobalt complexes with acetylacetonato and tertiary phosphine ligands and discuss the H-D scrambling reaction in deuterated ethyl groups of $Co(CH_2CD_3)_2(acac)(PPhMe_2)_2$.

The cis-dialkylcobalt(III) complexes, $CoR_2(acac)(PR'_3)_2$, have been prepared by the reaction of $Co(acac)_3$, $AlR_2(OEt)$ and tertiary phosphine in ether.



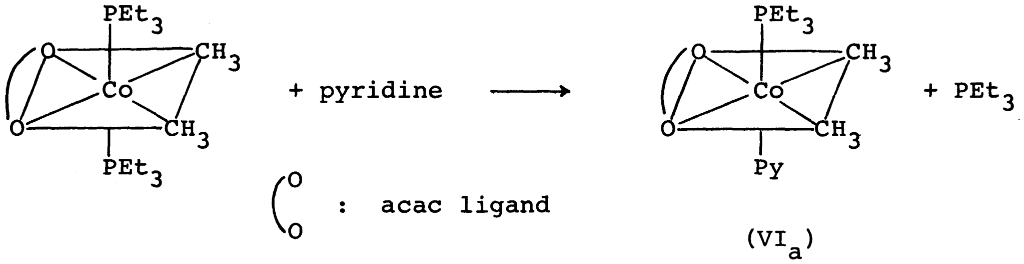
I	R=Me,	PR'_3=PEt_3
II$_a$	R=Me,	PR'_3=$PPhMe_2$
II$_b$	=Et	" = "
II$_c$	=n-Pr	" = "
II$_d$	=i-Bu	" = "
III	R=Me,	PR'_3=PPh_2Me
IV	R=Me,	PR'_3=$P(n\text{-}Bu)_3$
V	R=Et-d_3,	PR'_3=$PPhMe_2$

These complexes may be regarded as intermediate alkylation products of $Co(acac)_3$ by alkylaluminum compounds, which eventually give low valent alkyl- and hydridocobalt complexes.$^{6,7d)}$ Similar alkyl(acetylacetonato) complexes have been prepared in nickel and iron complexes.$^{7)}$

^1H, ^{31}P and ^{13}C NMR spectra of I-V show that these compounds have an octahedral configuration with two cobalt-bonded alkyl groups and an acetylacetonato ligand coplanar with cobalt which are coordinated with two tertiary phosphine ligands in axial positions. The protons in the methyl groups in the acac ligand of these complexes are magnetically equivalent in various solvents and appear as a singlet over a wide temperature range (-80 to +20°C). The methyl resonance in $PPhMe_2$ in II_a, II_b, II_c and V shows the characteristic triplet due to the virtual coupling with two phosphorus nuclei in mutually trans positions. The protons in the two methyl groups bonded to cobalt in I, II_a, III and IV are magnetically equivalent and appear as a triplet at low temperature in toluene by coupling with axial phosphine ligands ($^3J_{P-H}$=8 Hz). At higher temperatures the methyl protons are observed as a singlet because of the dissociation of the tertiary phosphine ligands. ^{31}P-{H}-NMR spectra of these complexes indicate that two phosphorus nuclei are magnetically equivalent and appear as a singlet at -70°C and that at higher temperatures the singlet becomes broader with a slight shift to higher field, suggesting the exchange of the tertiary phosphine ligands. IR spectra of these complexes show the characteristic aliphatic ν(C-H) bands of the metal-bonded alkyl groups at 2770-2870 cm^{-1} and ν(Co-C) bands at 570-585 cm^{-1}.

These complexes are remarkably insensitive to air and moisture, thermally stable at room temperature and are very soluble in many organic solvents and can be readily recrystallized from these solvents.

One of the two tertiary phosphine ligands in I can be readily displaced with pyridine (Py) and γ-picoline (γ-Pi) to give base-coordinated complexes, $Co(CH_3)_2$-(acac)(PEt_3)(Py) (VI_a) and $Co(CH_3)_2$(acac)(PEt_3)(γ-Pi) (VI_b), respectively.

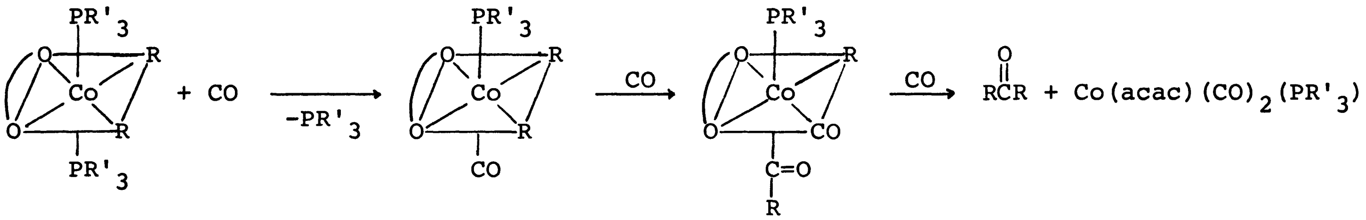


(VI_a)

2,2'-Bipyridine (bipy) displaces the two tertiary phosphines to give a bipyridine-coordinated complex, CoR_2(acac)(bipy) (VII). Satisfactory elemental analysis has been obtained for each dialkylcobalt complex.

The ethyl cobalt complex II_b is stable at room temperature in the solid state but decomposes by heating at 70°C liberating ethylene and ethane in a 1:1 molar ratio.

The isolated complexes I, II, III, IV and V readily react with carbon monoxide to yield dialkyl ketones and a univalent carbonyl complex, Co(acac)$(CO)_2(PR'_3)$.[8] The reaction may proceed by CO insertion into one of the alkylcobalt bonds to give an alkyl-acylcobalt complex which on reductive elimination gives the ketone and the univalent cobalt carbonyl complex.



The methyl groups bonded to cobalt in II_a can be transferred to mercury to give dimethylmercury (II), which was detected by NMR spectroscopy. ^{1}H-NMR spectrum of the reaction mixture of II_a and Hg(OAc) in toluene-d_8 shows the mercury-bonded two methyl groups as a singlet ($^2J_{Hg-C-H}$=102 Hz) at δ=0.10[9].

A specifically deuterated ethyl complex, $Co(CH_2CD_3)_2(acac)(PPhMe_2)_2$ (V) has been prepared by the reaction of $Co(acac)_3$, $PPhMe_2$ and $Al(CH_2CD_3)_2(OEt)$ (isotopic purity 99 %) in ether.

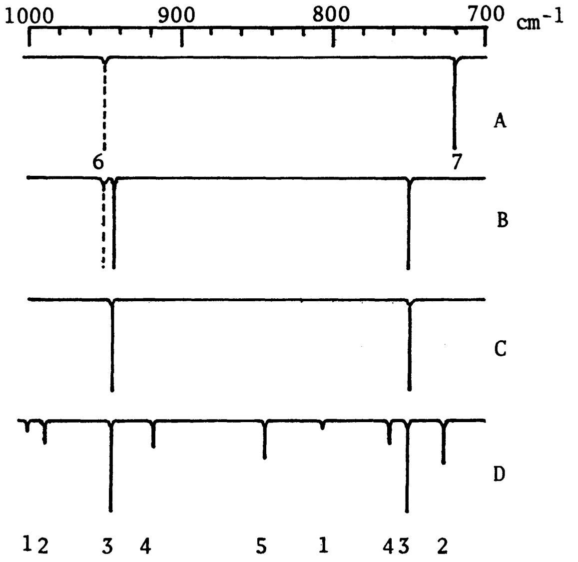


Fig 1 IR spectra of C_2H_4-d_n produced from $Co(CH_2CD_3)_2(acac)(PPhMe_2)_2$(V)

1, C_2H_3D; 2, trans-$C_2H_2D_2$; 3, asym-$C_2H_2D_2$; 4, C_2HD_3; 5, cis-$C_2H_2D_2$; 6, C_2H_4; 7, C_2D_4

A) II_b+ C_2D_4 at 28°C, 1 day

B) II_b+ asym-$C_2H_2D_2$ at 28°C, 1 day

C) V at 5°C for a few days

D) V at 32°C 1 day

Thermolysis of V in the solid state liberates mainly CH_2=CD_2 and CH_2DCD_3 in a 1:1 molar ratio and a trace amount of cis and trans $C_2H_2D_2$. Complex V reacts with carbon monoxide at -40 to -50°C to yield CD_3CH_2CO-CH_2CD_3 (isotopic purity of $CD_3CH_2COCH_2CD_3$, 95 %) as determined by NMR spectroscopy. These results indicate that no scrambling occurred during and after the preparation of V. In toluene at low temperature (below +5°C) V decomposed slowly evolving CH_2=CD_2 and CH_2DCD_3, suggesting that the decomposition of the ethyl complex proceeds through a typical β-elimination process at low temperature. At higher temperatures in benzene more extensive H-D scrambling takes place. Fig 1 shows the IR spectra of deuterated ethylenes evolved on allowing V to stand in solutions. Evolved gaseous products were analysed and identified by vpc, IR and mass spectroscopy.

Following observations are made concerning the scrambling and thermolysis experiments. a) The main decomposition pathway of the ethylcobalt complexes is via β-elimination as revealed by liberation of CH_2=CD_2 and CH_2DCD_3 from V on thermolysis[10-12] b) Contact of non-deuterated ethyl complex II_b with deuterated ethylenes C_2D_4 and CH_2=CD_2 at 28°C causes no H-D exchange. c) H-D scrambling of V occurred at 28-42°C as is indicated by appearance of <u>trans</u>- and <u>cis</u>-$C_2H_2D_2$, C_2HD_3 and C_2H_3D in the gas pase. d) Heating the benzene solution of V at 50°C effectively

Table 1 Composition of gaseous products produced from $Co(CH_2CD_3)_2(acac)(PPhMe_2)_2$(V)

Run	C_2HD_3	$C_2H_2D_2$*	C_2H_3D %	$C_2H_2D_4$	$C_2H_3D_3$ %
1	12	79	9	75	25
2	13	76	11	73	27

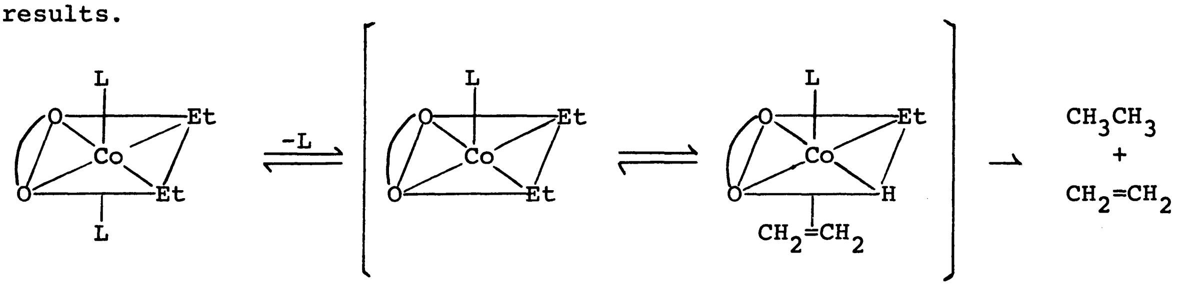
1 Treatment of V at 28°C for 1 day in benzene

2 Treatment of V at 42°C for 2 days in benzene

* $C_2H_2D_2$ = asym-$C_2H_2D_2$ + cis-$C_2H_2D_2$ + trans-$C_2H_2D_2$

induces the scrambling. Table 1 shows the representative ratio of gaseous products determined by mass spectroscopy.

Variable temperature NMR investigation[8)] of the solution behavior of these complexes suggests that the β-elimination and H-D scrambling processes are preceded by partial dissociation of the tertiary phosphine ligands from the ethylcobalt complex to accomodate coordination position for the β-elimination process. Weakening of the cobalt-ethyl bonds by heating may lead to β-elimination and reductive elimination of a hydrido-ethyl complex liberating ethylene and ethane. If the β-elimination and its reverse process, ethylene-insertion, should take place rapid enough prior to the eventual decomposition of the ethylcobalt complex, the scrambling would result. The following scheme is compatible with the experimental results.



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