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The Preparation and Properties of Cobalt(III) Phosphine Complexes Containing Nitrite and Acetylacetonate Ions

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Synopsis. Two complexes, $[Co(NO_2)(acac)_2(P)]$ (acac=acetylacetonate ion, P=PBu_3, PBu_2Ph, PMe_2Ph, and $PMePh_2$) and $[Co(NO_2)_2(acac)(PMe_2Ph)_2]$, were prepared by a reaction between $Na[Co(NO_2)_2(acac)_2]$ and phosphines. The geometrical structures were determined on the basis of the ^1H NMR, electronic, and IR spectra. A *cis*(NO_2, P) configuration was assigned to $[Co(NO_2)(acac)_2(P)]$, and a *trans*(P,P) configuration, to $[Co(NO_2)_2(acac)(P)_2]$.

There have been a few cobalt(III) phosphine complexes among the so-called Werner-type complexes.[1)] The coordination of phosphine groups to a cobalt(III) ion may be affected by the kinds of other ligands coexisting in the complex. The unidentate phosphine complexes of cobalt(III) thus far prepared have been those with dimethylglyoximate,[2)] acetylacetonate,[3)] cyanide,[4,5)] and halide[6)] ions. Other types are, however, required to extend the study of the chemistry of cobalt(III) phosphine complexes. This note will be concerned with the preparation and properties of cobalt(III) phosphine complexes containing nitrite and acetylacetonate ions.

Experimental

The phosphines were prepared according to the procedures described previously,[7)] and handled under a nitrogen atmosphere until they formed cobalt(III) complexes. The electronic spectra were measured with a Hitachi 139 spectrophotometer, the ^1H NMR spectra, with a JEOL C-60 H spectrometer in $CDCl_3$, using tetramethylsilane as the internal reference, and the IR spectra, with a JASCO DS-301 spectrometer.

Preparation. *Nitrobis(acetylacetonato)tributylphosphinecobalt(III)*: Tributylphosphine(PBu_3) (4 cm^3, 12 mmol) was added to $Na[Co(NO_2)_2(acac)_2]$[8)] (4 g, 10 mmol) in a mixture (200 cm^3) of benzene and ethanol (4:1), after which the solution was stirred at 50 °C for 5 h. The resulting red-brown solution was evaporated under reduced pressure to dryness. The residue was extracted with a small amount of benzene, which was then chromatographed with a column ($\phi 1.5\times30$ cm) of alumina, using a mixture of benzene and acetone (6:1) as the eluent. Red-brown crystals were obtained by concentrating the first main, red-brown eluate and by adding a proper amount of hexane. Found: C, 52.10; H, 8.54; N, 3.05%. Calcd for $[Co(NO_2)(acac)_2(PBu_3)]$: C, 52.31; H, 8.12; N, 2.77%. The materials remaining at the top of the column were not characterized.

Nitrobis(acetylacetonato)dibutylphenylphosphinecobalt(III): This complex was prepared by means of a reaction between $Na[Co(NO_2)_2(acac)_2]$ and dibutylphenylphosphine(PBu_2Ph) in a mixture of benzene and ethanol (4:1) by a method similar to that used for the PBu_3 complex. Found: C, 54.64; H, 7.15; N, 2.66%. Calcd for $[Co(NO_2)(acac)_2(PBu_2Ph)]$: C, 54.86; H, 7.10; N, 2.67%.

Nitrobis(acetylacetonato)dimethylphenylphosphinecobalt(III): A mixture of $Na[Co(NO_2)_2(acac)_2]$ (3 g, 9 mmol) and dimethylphenylphosphine(PMe_2Ph) (1 cm^3, 9 mmol) in benzene (150 cm^3) was stirred at room temperature for 48 h. The resulting solution was then subjected to procedures similar to those used for the PBu_3 complex except for the use of a mixture of benzene and acetone (15:1) as the eluent. Found: C, 48.37; H, 5.71; N, 2.96%. Calcd for $[Co(NO_2)(acac)_2(PMe_2Ph)]$: C, 48.99; H, 5.71; N, 3.17%.

Nitrobis(acetylacetonato)methyldiphenylphosphinecobalt(III): A mixture of $Na[Co(NO_2)_2(acac)_2]$ (3 g, 9 mmol) and methyldiphenylphosphine($PMePh_2$) (3 cm^3, 15 mmol) in benzene (150 cm^3) was stirred at room temperature for 48 h. The subsequent procedures were similar to those used for the PBu_3 complex. Found: C, 54.62; H, 5.57; N, 2.69%. Calcd for $[Co(NO_2)(acac)_2(PMePh_2)]$: C, 54.88; H, 5.41; N, 2.78%.

Dinitroacetylacetonatobis(dimethylphenylphosphine)cobalt(III): A mixture of $Na[Co(NO_2)_2(acac)_2]$ (3 g, 9 mmol) and PMe_2Ph (1.3 cm^3, 12 mmol) in ethanol (100 cm^3) was stirred at 50 °C for 2 h. The resulting red-brown solution was evaporated under reduced pressure to dryness. The residue was extracted with benzene, which was then chromatographed in a way similar to that used for the PBu_3 complex. The eluate was concentrated under reduced pressure to a small volume and then allowed to stand in a refrigerator to yield red-brown crystals. The presence of $[Co(NO_2)(acac)_2(PMe_2Ph)]$ in the solution was confirmed by the ^1H NMR spectrum. Found: C, 48.16; H, 5.64; N, 4.87%. Calcd for $[Co(NO_2)_2(acac)(PMe_2Ph)_2]$: C, 47.92; H, 5.55; N, 5.32%.

The yields for the above-mentioned complexes were 10—20%.

Results and Discussion

The facile substitution or solvolysis of a nitrite ion in $Na[Co(NO_2)_2(acac)_2]$ has been known and utilized for preparing other bis(acetylacetonato)cobalt(III) derivatives, such as $[Co(NO_2)(acac)_2L]$.[8,9)] Tertiary monophosphines can also be expected to react with the dinitro complex in a similar manner. Trialkyl- or alkylarylphosphines react readily with the dinitro complex and yield complexes of the $[Co(NO_2)(acac)_2(P)]$ type, but triphenylphosphine does not yield the corresponding complex.

$[Co(NO_2)_2(acac)(PMe_2Ph)_2]$ was obtained from a reaction mixture of PMe_2Ph and $Na[Co(NO_2)_2(acac)_2]$ in ethanol, $[Co(NO_2)(acac)_2(PMe_2Ph)]$ also being involved in the solution. Free PMe_2Ph and the liberated NO_2^- might attack the $[Co(NO_2)(acac)_2(PMe_2Ph)]$ first formed, thus yielding $[Co(NO_2)_2(acac)(PMe_2Ph)_2]$.

A nitrite ion can coordinate to a metal ion through a nitrogen or oxygen atom. None of the complexes prepared in this study show the N–O stretching in the region of 1000—1100 cm^{-1}, indicating the coordination through the nitrogen atom.

There are two geometrical isomers for the [Co-

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Table 1. Electronic (AB) and NMR spectral data

	AB	NMR, δ (J/Hz)[a]		
	$\tilde{\nu}/10^3$ cm^{-1}(log ε)	-CH$_3$(acac)	-CH	P-CH$_3$
$[Co(NO_2)(acac)_2(PBu_2Ph)]$	19.8(2.54)	1.66 1.77 1.97 2.18	5.00 5.44	
$[Co(NO_2)(acac)_2(PBu_3)]$	20.6(2.50)	1.94[b] 2.02 2.25	5.40 5.52	
$[Co(NO_2)(acac)_2(PMePh_2)]$	19.2(2.56)	1.61 1.86 2.04 2.24	5.03 5.57	2.00(d, 13)
$[Co(NO_2)(acac)_2(PMe_2Ph)]$	19.7(2.50)	1.51 1.86 2.01 2.25	5.02 5.46	1.76(d, 13)
$[Co(NO_2)_2(acac)(PMe_2Ph)_2]$	20.8(3.34)	1.26	4.67	1.90(t, 8)
cis-Na$[Co(NO_2)_2(acac)_2]$[9]	19.2(2.25)	2.10 2.20	5.75	
trans-Na$[Co(NO_2)_2(acac)_2]$[8,9]	19.3(2.24)	2.18	5.79	

a) d; doublet, t; triplet, the J value refers to the interval of the two outer peaks. b) The peak intensity is twice that of the others because of accidental degeneracy.

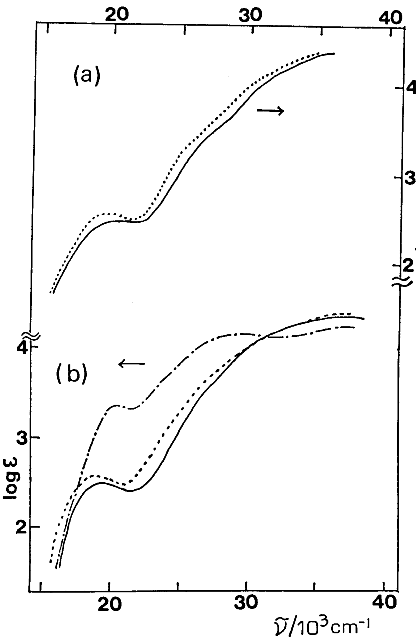

Fig. 1. Absorption spectra in dichloromethane.
(a): $[Co(NO_2)(acac)_2(PBu_2Ph)]$ (----), $[Co(NO_2)(acac)_2(PBu_3)]$ (——), (b): $[Co(NO_2)(acac)_2(PMePh_2)]$ (——), $[Co(NO_2)(acac)_2(PMePh)]$ (----), $[Co(NO_2)_2(acac)(PMe_2Ph)_2]$ (—·—·—).

$(NO_2)(acac)_2(P)]$ complex. The ^{1}H NMR spectra can distinguish a *cis* or *trans* configuration. The spectral data are summarized in the table, together with those of the related compounds. All complexes of this type can be assigned to a *cis* configuration on the basis of the number of methyl and methine signals of the coordinated acetylacetonate. One of the methine peaks in each PBu_2Ph, PMe_2Ph, and $PMePh_2$ complex is shielded by a phenyl group on the phosphorus atom and is observed at high magnetic fields, 5.00—5.03 ppm.[10] The absorption spectra exhibit a broad first-absorption band around 20000 cm^{-1} (see Fig. 1). The replacement of the alkyl groups on a phosphorus atom by a phenyl group causes the red shift and increases the intensity of the first absorption band. The ligand-field strength of these phosphines is nearly identical with that of a nitro ligand, or slightly stronger.

There are three geometrical isomers for $[Co(NO_2)_2(acac)(PMe_2Ph)_2]$. The ^{1}H NMR spectrum shows one kind of methyl signal for the acetylacetonato ligand, indicating a *trans*(P,P) or *trans*(N,N) configuration. The remarkable high-field shift of the methine signal strongly suggests a *trans*(P,P) configuration where a phenyl group of the PMe_2Ph molecule is located over the acetylacetonate ring and shields the methine proton, causing it to resonate at a higher magnetic field.[10] The electronic and IR spectra also suggest a *trans*(P,P) configuration. The first absorption band shows a strong intensity (log ε=3.34), which is characteristic of the *trans*(P,P) arrangement of two phosphorus donor atoms.[11] The IR spectrum shows sharp peaks at 821 and 825 cm^{-1} attributable to the NO_2^- bending mode, the presence of two bands suggesting a *cis* configuration of two nitrite ions.[12]

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