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The Phosphorus-31 Nuclear Magnetic Resonance Spectra of Bis(acetylacetonato)cobalt(III) Complexes Containing Bidentate Diphosphines

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Synopsis. The phosphorus-31 nuclear magnetic resonance spectra of $[Co(acac)_2(P\text{-}P)]^+$(P-P=diphosphine ligand) of the Werner type were measured, and the coordination chemical shifts were compared with those of complexes studied before. The coordination chemical shifts of the five-membered chelate ring were twice as much as those of the six-membered ring.

The nuclear magnetic resonance spectoroscopy of phosphines in coordination compounds is an area of considerable potential interest and a great deal of ^{31}P NMR data of transition metal phosphine complexes have been reported. However, all the metals dealt with thus far have been soft, such as the Pt, Rh, Hg, and Ag atoms and Ni, Mn, Co, Cr, Mo, and W in their lower-valence states.[1,2] Though recently several cobalt(III) phosphine complexes of the Werner type have been prepared, no ^{31}P-NMR data of these complexes have been reported.[3] The paper deals with the ^{31}P NMR spectra of bis(acetylacetonato)cobalt(III) complexes with a bidentate diphosphine. Some complexes were newly prepared.

Experimental

The diphosphine ligands and their abbreviations are as follows;

(a) $Ph_2PCH_2CH_2PPh_2$ (dppe)
(b) $Ph_2PCH(CH_3)CH_2PPh_2$ (mdppe)
(c) $Ph_2PCH_2CH_2CH_2PPh_2$ (dppp)
(d) $Ph_2PCH(CH_3)CH_2CH_2PPh_2$ (mdppp)
(e) $Ph_2PCH{=}CHPPh_2$ (dpp)

The dppe, dppp, and dpp ligands were prepared by the method of Hewertson and Watson,[4] while the mdppe and mdppp ligands were prepared by the method of Fryzuk.[5] All the complexes were prepared by a method similar to that of Kashiwabara *et al.*[3] from tris(acetylacetonato)cobalt(III) and the corresponding diphosphine. The analytical data of the new complexes are as follows; Calcd for $[Co(acac)_2mdppe]BF_4\cdot H_2O$ C, 57.39; H, 5.47; N, 0.00%. Found: C, 57.21; H, 5.08; N, 0.02%. The ^{31}P NMR spectra were obtained in the Fourier transform mode with a Varian FT-80A spectrometer. The chemical shifts at 32.206 MHz were determined by the use of a 4 kHz range and a 16 K memory and were measured with respect to an external 85% H_3PO_4. The pulse width was 15μs, and the pulse delay, 4s. About 200 mg of the complex was dissolved in 1.5 cm^3 of $CDCl_3$ in a 10 mm tube, and the spectra were accumulated 1000 times for free ligands and 15000 times for the complexes at 37 °C.

Results and Discussion

The ^{31}P NMR spectra of the ligands are shown in Fig. 1 (upper). Symmetrical ligands have one peak (ligands (a), (c), (e)), while unsymmetrical ones have more than one peak (ligands (b), (d)). The chemical shifts of the ligands can reasonably be predicted from the group contributions in terms of the α, β, and γ substituent effects at the α, β, and γ positions (P_α–C_β–C_γ–C_δ; P=phosphorus, C=carbon). The effect of substituting a methyl group for a hydrogen atom at C_β is deshielding, while an upfield shift is observed when a methyl group replaces a hydrogen atom at C_γ. The splitting of the two peeks for Ligand (b) is due to the ^{31}P-^{31}P coupling (24.6 Hz).

The ^{31}P NMR spectra of bis(acetylacetonato)cobalt(III) complexes with a bidentate diphosphine are shown in Fig. 1 (lower). The chemical shift data are listed in Table 1. When the saturated 5-membered chelate ligands (a) and (b) coordinate to the cobalt(III) ion, the coordination chemical shifts, $\Delta(=\delta(\text{coordinated})-\delta(\text{free}))$, are about 56—62 ppm for Ligands (a) and (b), whereas the values for the saturated 6-membered chelate ligands (c) and (d) are 26—28 ppm, much smaller than those for Ligands (a), (b). Several authors have found a trend of ^{31}P NMR chemical shifts in relation to the chelate effect of diphosphins in organometallic complexes. The coordination chemical shifts always show a low-field shift for four-, five-, and six-membered

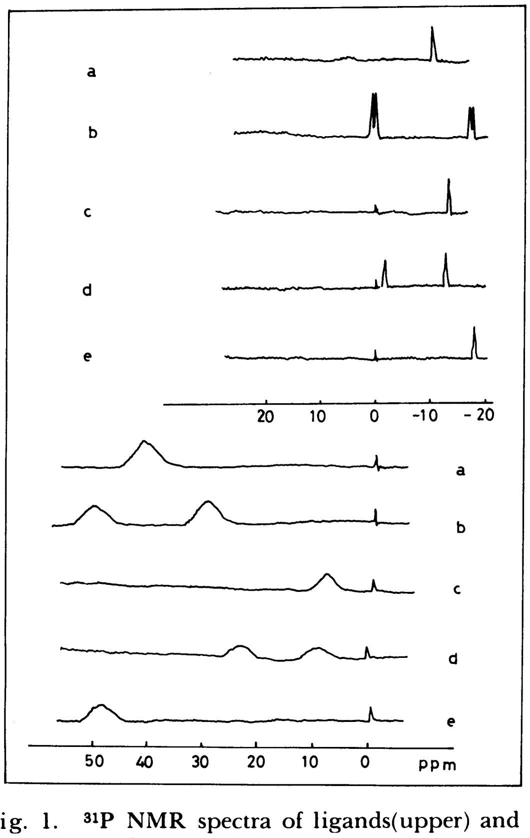

Fig. 1. ^{31}P NMR spectra of ligands(upper) and the complexes(lower).

TABLE 1. ^{31}P CHEMICAL SHIFTS OF THE FREE LIGANDS AND THEIR COMPLEXES

Ligand	Free	Complex	Δ
(a) $Ph_2PCH_2CH_2PPh_2$	−12.42	49.68	62.10
(b) $Ph_2PCH(CH_3)CH_2PPh_2$	−20.80	36.02	56.82
	0.93	60.24	59.31
(c) $Ph_2PCH_2CH_2CH_2PPh_2$	−17.17	9.32	26.49
(d) $Ph_2PCH(CH_3)CH_2CH_2PPh_2$	−16.77	9.33	26.10
	−2.64	24.84	27.48
(e) $Ph_2PCH{=}CHPPh_2$	−19.87	57.13	77.00

*δ ppm from H_3PO_4. $\Delta=\delta_{\text{complex}}-\delta_{\text{free}}$.

diphosphine chelate-ring complexes,[1,2] the Δ values of five-membered chelate rings are about two or three times as much as those of six-membered chelate rings. For example, the values of Δ for $[Pt(CH_3)_2dppe]$ and $[Pt(CH_3)_2dppp]$ are 67.7 and 20.5 ppm respectively. As is shown in Table 1, the coordination chemical shifts of the five-membered chelate rings obtained are twice as large as those of the six-membered chelate rings.

The coordination chemical shift of $[Co(acac)_2dpp]$ is 77 ppm, the largest of all the complexes studied here. It shoud be compared with the datum that the Δ value of +120 ppm for $[CpV(CO)_2(dpp)]$ (Cp=cyclopentadienyl) is slightly larger than that of +112 ppm for $[CpV(CO)_2(dppe)]$.[6]

Organometallic phosphine complexes have been reported to show relatively sharp signals, with couplings of the phosphorus atom to other nuclei of spin 1/2, while all the peaks studied here show broadening (half-width, *ca.* 100 Hz). Though the complexes containing the (b) and (d) ligands must have diastereomers, it is of no use to ascertain their geometries because the broad peaks were obtained. Several possible origins may be considered the broadening of the ^{31}P NMR peaks of cobalt(III) complexes: (a) a configurational change between Δ and Λ (b) a coupling between cobalt-59 and phosphorus atom, and (c) the paramagnetic effect. The (a) factor can easily be eliminated because $[Co(acac)_2$(S-mdppe)] could be resolved to Δ and Λ isomers with Sephadex A-25 chromatography. No datum has been reported concerning any coupling between the cobalt-59 and phosphorus-31 atoms. The paramagnetic effect may broaden the ^{31}P signals, this parhaps because of cobalt(II) ion yielded by the following redox reaction.

$$2Co^{3+} + \geqslant P + H_2O \longrightarrow 2Co^{2+} + \geqslant P{=}O + 2H^+$$

However the ^{1}H NMR spectra of these complexes show sharp signals for all complexes. We can not explain this broadening well.

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