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^{59}Co Quadrupole Effects on the ^{1}H, ^{31}P, and ^{59}Co NMR Spectra of $HFeCo_3(CO)_9[P(OCH_3)_3]_3$ and the ^{1}H NMR Spectra of Other Derivatives

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The ^{1}H NMR spectra of $HMCo_3(CO)_{12}$ (M=Fe or Ru) and $HFeCo_3(CO)_{12-x}[P(OR)_3]_x$ (x=1−3, R=CH_3; x=3, R=C_2H_5 or C_6H_5) showed very broad signals centered near δ=−21 at 27 °C. The band widths were generally smaller for the compounds of larger molecular volume, at lower temperatures and with higher viscosity of the solvent. These data were interpreted in terms of the quadrupole effects of ^{59}Co nuclei to which the hydride proton was μ_3-bonded. Supporting evidence was obtained from the ^{31}P and ^{59}Co NMR spectra and the relaxation time T_1 of $HFeCo_3(CO)_9[P(OCH_3)_3]_3$.

In a previous paper[1)] we reported the protonation of the coordinated dinitrogen by a highly acidic cluster hydride $HFeCo_3(CO)_{12}$ (**1**) (Fig. 1).[2)] There was a long controversy over the position of the hydride ligand in this cluster[3—7)] because ^{1}H NMR spectra did not show the signal for the proton[3,8)] and no X-ray data were published. The problem seems to have been settled when the X-ray[8)] and neutron[9)] diffraction studies of a trimethyl phosphite-substituted derivative $HFeCo_3(CO)_9[P(OCH_3)_3]_3$ indicated unequivocally that the hydride existed on the Co_3 face. Although it seemed probable that the hydride ligand in the unsubstituted cluster **1** was also located on the Co_3 face from the X-ray crystallographic study of $Ph_3PAuFeCo_3(CO)_{12}$,[10)] direct evidence was still not enough when the present study started.

During our study on the reaction of $Ni[P(OC_2H_5)_3]_4$ with **1**,[11)] we found an unexpected high-field signal in the ^{1}H NMR spectra of a product which was later proved to be due to the hydride in $HFeCo_3(CO)_{11}[P(OC_2H_5)_3]$. The detection of the hydride signals is significant because (i) face-bridged μ_3-hydride cluster compounds[8,12—16)] are interesting with respect to the dissociative adsorption of hydrogen molecules on metal surfaces.[9,17)] and (ii) the information will be useful for the cobalt hydride cluster compounds showing very broad NMR signals difficult to detect. Thus, we have measured the NMR spectra of **1** and its derivatives and interpreted them.

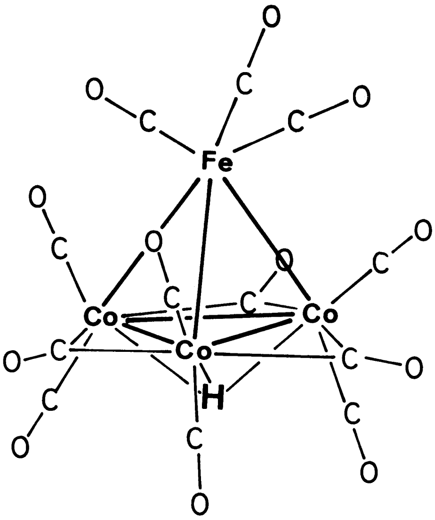

Fig. 1. Postulated structure of $HFeCo_3(CO)_{12}$.

Experimental

Hydridometalcarbonyl cluster compounds **1**—**7** (Table 1) were prepared by methods described in the literature with some modifications.[6,8,18)] The compounds obtained after chromatography gave satisfactory elemental analyses and the absence of paramagnetic impurities was checked by the sharpness of the phosphite bands in the ^{1}H NMR spectra.

^{1}H NMR spectra were measured using a JEOL FX-100 FT NMR spectrometer at 100 MHz in the temperature range of +70—−60 °C. Chloroform-*d* solutions were used for the phosphite-substituted cluster compounds, but because of the low solubilities of the unsubstituted clusters $HMCo_3(CO)_{12}$

TABLE 1. HYDRIDE CHEMICAL SHIFTS AND HALF-HEIGHT WIDTHS OF ^{1}H NMR SPECTRA OF $HFeCo_3(CO)_{12-x}[P(OR)_3]_x$ AND $HRuCo_3(CO)_{12}$

Compound		$\delta^{a)}$	$W_{h/2}$/Hz Temperature/°C 27	 0	 −20	 −40	 −60
$HFeCo_3(CO)_{12}{}^{b)}$	**1**	−21.1	487	472	201	93	$56^{c)}$
$HFeCo_3(CO)_{11}[P(OCH_3)_3]$	**2**	−21.4	366	217	133	85	62
$HFeCo_3(CO)_{10}[P(OCH_3)_3]_2$	**3**	−21.7	232	118	73	47	38
$HFeCo_3(CO)_9[P(OCH_3)_3]_3$	**4**	−22.1	137	78	49	29	28
$HFeCo_3(CO)_9[P(OC_2H_5)_3]_3$	**5**	−21.9	106	64	49	27	25
$HFeCo_3(CO)_9[P(OC_6H_5)_3]_3$	**6**	−21.0	91	61	45	39	51
$HRuCo_3(CO)_{12}$	**7**	−19.4	200	106	65	32	$27^{d)}$

a) Measured from a solvent peak and converted to δ values. b) Measured up to +70 °C and the line width was almost equal to that at 27 °C. c) −53 °C. d) −50 °C.

(M=Fe or Ru) in chloroform, they were dissolved in $Fe(CO)_5$ mixed with toluene-d_8 (5 vol%) for the measurements. $Fe(CO)_5$ did not affect the chemical shifts or line-widths of the spectra as compared with those recorded for saturated chloroform-*d* solutions which required many accumulations ($>10^4$ times) for the unsubstituted derivatives. Several hundred times accumulations were enough for the phosphite-substituted compounds. The relaxation times T_1 were obtained by the inversion recovery method. The effect of the sample viscosity on the line-width was tested for $HFeCo_3(CO)_9[P(OCH_3)_3]_3$ (**4**) in a chloroform-*d*/polyfluorinated hydrocarbon (Daifloil) (1:1) solvent which was about 3.5 times as viscous as pure chloroform-*d* indicated by a Ubbelohde viscosimeter at 27 °C.

^{31}P NMR spectra were recorded at 40.7 MHz with JEOL FX-100 FT NMR spectrometer. Chloroform-*d* solutions with external standard (3% aq H_3PO_4) were used for the measurements.

^{59}Co NMR spectra were recorded at 63.8 MHz with JEOL GX-270 FT NMR spectrometer at the laboratory of JEOL. The compouds **2**—**4** were dissolved in chloroform-*d* and **1** was dissolved in $Fe(CO)_5$ mixed with toluene-d_8 (5 vol%) and external standard ($[Co(NH_3)_6]Cl_3$ or $[Co(en)_3]Cl_3$) was used for the measurements. The relaxation times T_1 were obtained by the inversion recovery method.

Results

Figures 2—4 illustrate variable temperature ^1H NMR spectra of **1**, **7**, and **4**, respectively. The spectra of **2**, **3**, **5**, or **6** are similar to those of **4** except chemical shifts and line-widths and the values are listed in Table 1. Variable temperature ^{31}P and ^{59}Co NMR spectra of **4** are shown in Figs. 5 and 6, respectively.

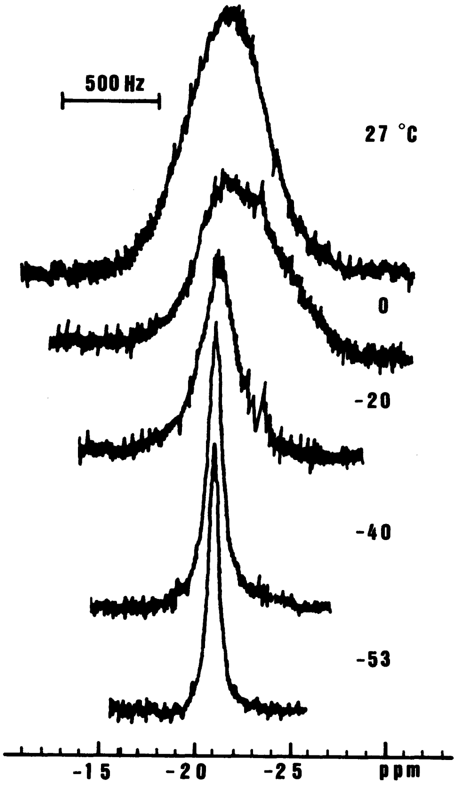

Fig. 2. Variable temperature ^1H NMR spectra of $HFeCO_3(CO)_{12}$ (**1**).

Fig. 3. Variable temperature ^1H NMR spectra of $HRuCo_3(CO)_{12}$ (**7**).

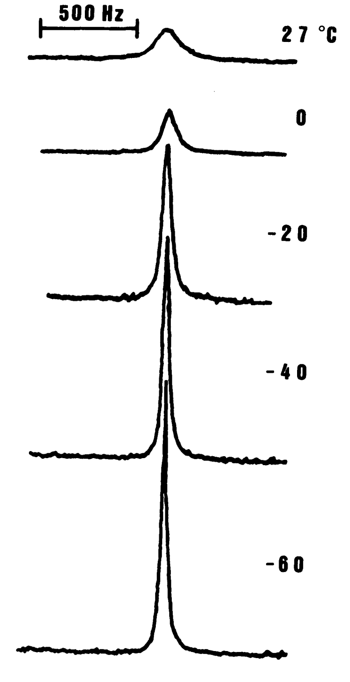

Fig. 4. Variable temperature ^1H NMR spectra of $HFeCo_3(CO)_9[P(OCH_3)_3]_3$ (**4**).

The ^1H NMR spectra indicated that the line-widths at half-signal height ($w_{h/2}$) were very broad and no couplings with ^{59}Co or ^{31}P nuclei were observed. The line-widths became narrower as the temperatures were lowered but the chemical shifts were invariable and no splittings of the major peaks resulted. A much sharper band of minor intensity ($<1/20$) appeared overlapped

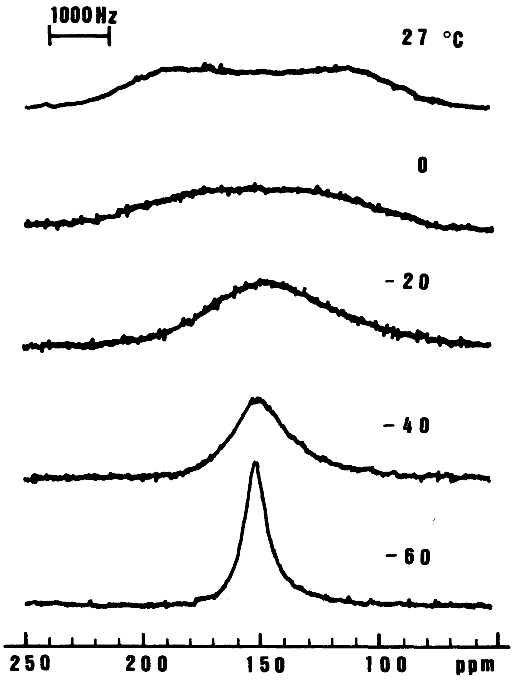

Fig. 5. Variable temperature ^{31}P NMR spectra of $HFeCo_3(CO)_9[P(OCH_3)_3]_3$ (**4**).

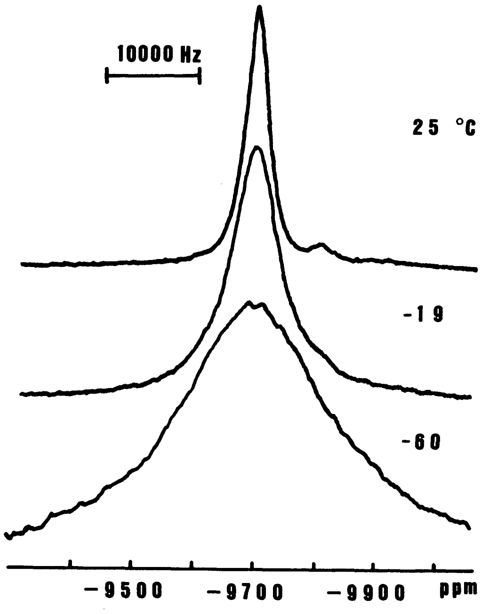

Fig. 6. Variable temperature ^{59}Co NMR spectra of $HFeCo_3(CO)_9[P(OCH_3)_3]_3$ (**4**). Chemical shifts were measured from $[Co(en)_3]Cl_3$ external standard.

on the major broad band and the signal intensities were temperature dependent.

The line-widths of a viscous solution of **4** in chloroform-*d*/Daifloil was 74 Hz as compared with 137 Hz of the pure chloroform-*d* solution at 27 °C.

The ^{31}P NMR spectrum of **4** was a very broad saddle shaped doublet at 27 °C and became broad singlets at lower temperatures. The chemical shift (135.2 ppm) from the external H_3PO_4 standard did not change upon cooling the sample.

The chemical shifts and the line-widths of the ^{59}Co NMR spectra of **1**, **2**, **3**, and **4** at 27 °C are given in Table 2. The spectra of **1** and **4** are singlets and those of **2** and **3** are doublets, the higher field bands being assigned to the cobalt atoms coordinated with trimethyl phosphite.

Table 2. Chemical shifts and half-height widths of ^{59}Co NMR spectra of $HFeCo_3(CO)_{12-x}[P(OCH_3)_3]_x$

Compound		/ppm$^{a)}$	$W_{h/2}$/Hz
$HFeCo_3(CO)_{12}$	**1**	−3856	674
$HFeCo_3(CO)_{11}[P(OCH_3)_3]$	**2**	−3849 (1)$^{c)}$	1304
		−3913 (2)$^{c)}$	2065
$HFeCo_3(CO)_{10}[P(OCH_3)_3]_2$	**3**	−3836	b)
		−3863	
$HFeCo_3(CO)_9[P(OCH_3)_3]_3$	**4**	−3901	2609

a) Measured from $[Co(NH_3)_6]Cl_3$ external standard at 27 °C. b) Not resolved. c) Intensity ratio.

The relaxation times T_1 of the ^1H resonance of **4** were 207, 72, and 25 ms at 27, −20, and −60 °C, respectively. The T_1 for the ^{59}Co resonance of the same compound were 0.140, and 0.053 ms at 25, and −19 °C, respectively.

Discussion

The broad high-field signals in the ^1H NMR spectra of $HFeCo_3(CO)_{12-x}[P(OR)_3]_x$ show the calculated intensities relative to the phosphite protons and can be assigned to a single hydride proton. The signals for the unsubstituted $HMCo_3(CO)_{12}$(M=Fe or Ru) are also assignable to the hydride proton judging from the similarity of the chemical shifts and line shapes. The chemical shift values around $\delta=-21$ indicate that the hydrogens are bonded to transition metals and not to an oxygen atom of carbonyl groups.[19-21] Up-field shifts of about 0.3 ppm was observed by exchange of each carbonyl group on cobalt by a trimethyl phosphite, showing electron-donating influence of the latter ligand on the hydride proton. The proton chemical shift of the Co_3 face-bridged hydrides in $(\eta\text{-}C_5H_5)_4Co_4H_4$ was reported to be at $\delta=-23.06$[24] which is near the values of the present cluster hydrides. Thus it seems more likely that the hydride proton is bound to cobalt rather than to iron or ruthenium. The failure to detect the signals in the past[3,8] may be ascribable to the very broad nature of the resonance line due to the effect of the ^{59}Co quadrupole.[22,23]

The hydride spectra of cobalt hydride complexes generally do not show splittings due to scalar couplings of the proton with cobalt. For example, $HCo(CO)_2[P(OC_6H_5)_3]_2$[25] or $HCo[P(OC_2H_5)_3]_4$[26] show sharp resonance lines having splittings due to the coupling only with ^{31}P nuclei and $HCo(PF_3)_4$[22] shows a broad singlet with the width of about 180 Hz at room temperature. These spectral features are caused by the quadrupole of cobalt nuclei ($I=7/2$) which have the very short relaxation time T_1 except for the complexes with cubic symmetry around cobalt.[27]

The relaxation time T_1 of cobalt is expressed as follows:

$$\frac{1}{T_1}=\frac{3}{40}\frac{(2I+3)}{I^2(2I-1)}\left(\frac{e^2qQ}{\hbar}\right)^2\tau_c \quad (I=7/2), \tag{1}$$

$$\tau_c = \frac{4\pi\eta' a^3}{3kT}, \tag{2}$$

where e^2qQ/h is electric quadrupole coupling constant, τ_c correlation time of molecular reorientation, η' viscosity, a molecular radius, k Boltzman's constant and T absolute temperature.[28,29] The spectral shapes of NMR spectra of the nuclei (I=1/2) coupled with quadrupolar nuclei have been analyzed by Pople[30] and Suzuki and Kubo.[31] Yamasaki[32] has extended it to ^{59}Co (I=7/2) and calculated the simulation spectra which are dependent on a parameter $\eta=2\pi JT_1$ where T_1 is relaxation time of cobalt and J is scalar coupling constant. Where η is small, the splittings due to the scalar couplings are not observed and the spectra broaden. However, when η is much smaller, the resonance of the nuclei (I=1/2) is out of the influence of cobalt and becomes sharper.

The T_1 of ^{59}Co is reciprocally proportional to τ_c and becomes smaller when the viscosity and molecular volume increase and the temperature decreases. As the viscosity of the solvent increases at lower temperatures, the effect of lowering the temperature on the T_1 is most pronounced. A typical example of the temperature effect was illustrated in the variable temperature ^{1}H, ^{31}P, and ^{59}Co NMR spectra of **4**. The T_1 of ^{59}Co decreased when the temperature was lowered and the spectra broadened (Fig. 6). On the other hand, ^{1}H and ^{31}P spectra became sharper at lower temperatures (Figs. 4 and 5). The line shapes of ^{31}P (I=1/2) spectra correspond to those of the simulation curves[32] at *ca.* η=0.5 for the spectrum at 27 °C and *ca.* 0.2 for that at −20 °C. The ^{1}H spectra are already singlets at 27 °C and the line widths decrease at lower temperatures. Since the trimethyl phosphite ligands are bound to cobalt,[8,9] the line broadening mechanism for the ^{31}P nuclei is likely the same as that for the hydride. Namely, both the ^{1}H and ^{31}P spectra broaden because of the quadrupolar effect of ^{59}Co nuclei and sharpen at lower temperatures where the T_1 of ^{59}Co becomes much smaller.

The influence of viscosity upon the T_1 was evident from the comparison of the spectra in chloroform and in Daifloil. The increase of molecular volume by the phosphite exchange was also reflected in the decrease of line-widths (Table 1). For instance, by the approximation of regarding the cluster compounds as spheres, the molecular volume of **6** is calculated to be about twice that of **4**, and corresponding decrease of the line-widths was observed (Table 1).

The scrambling of carbonyl groups in $HFeCo_3(CO)_{12}$ and its derivatives was studied by ^{13}C and ^{17}O NMR spectroscopies.[33,34] It was shown that the scrambling was rather slow at lower temperatures, especially for the phosphite-substituted hydrides which have larger energy barrier for the fluxionality. As most of the ^{1}H NMR spectra of the present study were recorded below 27 °C, the chemical shifts and line-widths are probably not influenced significantly by the carbonyl scrambling. The possibility that the sharpening of the spectra at lower temperatures may have been caused by hydride fluxionality can be ruled out because there were no chemical shifts and splittings of the signals which must have been shown in the temperature dependent spectra of the fluxional hydride. However a minor fraction of the hydride may be bound to iron or ruthenium,[7] since we observed a weak and sharp line overlapped on the broad main peak.

Conclusion

The present study has shown that the ^{1}H NMR spectra of the mixed carbonyl hydride complexes $HMCo_3(CO)_{12-x}[P(OR)_3]_x$ (M=Fe or Ru, x=0—3) have resonances in the normal region as transition metal hydrides but the line widths are murh broader than ordinary hydride complexes. We consider that the line broadening is caused by intermediate length of the relaxation time T_1 of cobalt, namely the T_1 is too short to show the ^{1}H-^{59}Co scalar couplings but too long to decouple the interaction completely. The T_1 could be remarkably reduced by lowering the temperature of the measurements, by raising the viscosity of the solvents or by increasing the molecular volume. When the T_1 became short enough in these ways, the hydride resonance was effectively "decoupled" and showed much narrower lines. As the spectral changes of the hydride resonance upon lowering temperature are similar to the behavior of ^{31}P NMR spectra of **4** in which trimethyl phosphites are coordinated to each cobalt,[8,9] the hydride proton must be bonded also to cobalt. It is reasonable to assume that the hydride is bonded to the Co_3 face in solution just as in the solid state.[8,9] The similarity of the ^{1}H NMR spectra of other derivatives including **1** or **7** suggests that the hydride ligands in these complexes are bonded also to the Co_3 face.

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