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Nuclear Magnetic Resonance Studies of Cobalt Complexes. Cobalt-59 Nuclear Magnetic Resonance Spectrum of the Hexakis(trimethyl phosphite)cobalt(III) Complex

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Synopsis. The well-resolved septet spectrum was recorded for cobalt-59 NMR of $[Co(P(OCH_3)_3)_6](BF_4)_3$ in an acetonitrile solution. The obtained NMR parameters are: σ(Co-59) = +304 ppm (upfield from $[Co(CN)_6]^{3-}$), ^1J(Co–P) = 414 Hz, and ΔH(Co) = 340 Hz.

The last member of the symmetric diamagnetic $Co^{III}L_6$-type complexes, the $Co^{III}P_6$-type hexakis(trimethyl phosphite)cobalt(III) complex, was examined by cobalt-59 nuclear magnetic resonance (NMR) spectroscopy. The coordination character of such a $Co^{III}P_6$-type complex seems very interesting because the relatively hard metal ion, Co(III), and the typically soft ligand, $P(OCH_3)_3$, form an octahedral complex which seems to have a very crowded configuration around the small central metal ion.[1] The result of the cobalt-59 NMR study is reported in this paper mainly because of the interest in the metal-ligand coordination bonding.

Experimental

Hexakis(trimethyl phosphite)cobalt(III) tetrafluoroborate was synthesized by a process similar to that of its perchlorate.[1] (Cobalt(II) tetrafluoroborate was used instead of cobalt(II) perchlorate.) The analyses of Co, P, and BF_4 were carried out gravimetrically. (Found: Co, 5.50; P, 17.89; BF_4, 25.03; Calcd for $C_{18}H_{54}O_{18}P_6CoB_3F_{12}$(=$[Co(P(OCH_3)_3)_6](BF_4)_3$): Co, 5.54; P, 17.47; BF_4, 24.48). The ultraviolet spectra and proton NMR spectra (100 MHz) were almost the same as those of the corresponding perchlorate in an acetonitrile solution: $\nu_{1\max}$=350 nm, log ε=2.3; $\delta(OCH_3)$=4.00 ppm (symmetric multiplet).

Cobalt-59 NMR spectral measurements were carried out with a Varian VF-16 NMR spectrometer operating at 7.9650 MHz (modulation of about 0.1 gauss). Potassium hexacyanocobaltate(III) was used as an external standard. The complex was dissolved in an acetonitrile, and poured into a 14 mmϕ sample tube for the spectral measurement.

Results and Discussion

The recorded cobalt-59 NMR spectrum is shown in Fig. 1. The well-resolved septet is clearly observed. The origin of this septet can be attributed to the scalar coupling of six equivalent phosphorus-31 nuclei (I=1/2) directly coordinated to the central cobalt-59 nucleus. The chemical shift was +304 ppm from the external standard $[Co(CN)_6]^{3-}$; this is the largest value for high-field resonance among the numerous tervalent cobalt complexes. The discussion of the chemical shifts will be published elsewhere. The line-shape simulation was carried out using the HITAC 8700/8800 computer of the Computer Centre, The University of Tokyo. The best-fitted parameters are: ^1J(Co–P) = 414 Hz, and ΔH(Co) = 340 Hz (assuming Gaussian curves). Simulation with the Lorentzian curves did not succeed in giving the approximate curves.

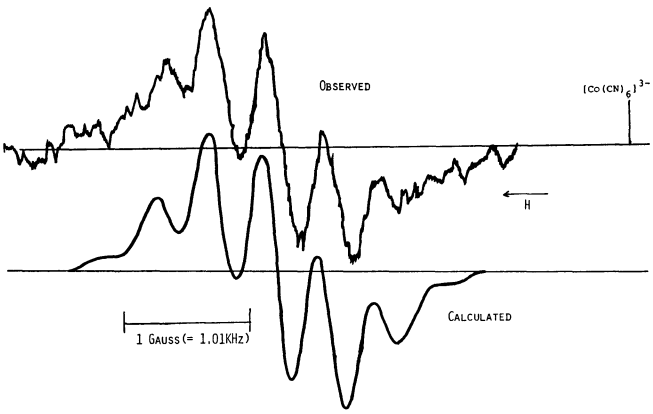

Fig. 1. Cobalt-59 nuclear magnetic resonance spectrum of $[Co(P(OCH_3)_3)_6](BF_4)_3$ in CH_3CN solution (7.9650 MHz), and its simulated spectrum with ^1J(Co–P) of 414 Hz, and ΔH=340 Hz (Gaussian curves).

This multiplet confirms that the quadrupolar relaxation of the central cobalt-59 in this complex is not so effective as those of the other $Co^{III}L_6$-type complexes. The octahedral coordination of the six phosphorus ligands is also confirmed from the septet spectrum.

The magnitude of the spin-spin coupling constant, ^1J(Co–P) is noticeably smaller than that for the $[Co(PF_3)_4]^-$,[2] which was the only previously reported coupling constant between cobalt-59 and phosphorus-31. The coordinating characters of trifluorophosphine and trialkyl phosphite have been assumed to be quite similar, or almost the same.[3,4] Therefore, the difference in the ^1J(Co–P) values between $[Co(PF_3)_4]^-$ and $[Co(P(OCH_3)_3)_6]^{3+}$ can be attributed to the differences in the oxidation state or coordination number of the central cobalt ions. It has been noted that the s-characters of bonding atoms have a large influence on the spin-spin coupling constants.[3,5] For rhodium and platinum complexes, the metal-ligand coupling constants of tetracoordinated complexes (Rh(I), Pt(II)) are about 1.5 times those of the corresponding hexacoordinated complexes (Rh(III), Pt(IV))[3]: tetracoordinated complexes have an s-character of one fourth, while octahedral complexes have one sixth.

Although the contribution of the s-characters of the

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coordination bonds to the magnitude of the spin-spin coupling constants is quite attractive as an explanation of the differences among the many complexes, it is not sufficient to describe the quite small coupling constant ^1J(Co–P) in our $[Co(P(OCH_3)_3)_6]^{3+}$ complex. The ^1J(Co–P) in $[Co(PF_3)_4]^-$ is reported to be 1225 Hz,[2] and the corresponding coupling constant in our complex is only 414 Hz, which is much smaller than two thirds of the ^1J(Co–P) in $[Co(PF_3)_4]^-$. Therefore, further contributions should be taken into account.

Another possible factor which would decrease the coupling constants is the bond weakening due to steric or other repulsive interactions, such as so-called trans-effects. The geometric factors should be important in considering the complexes of bulky ligands such as phosphines and phosphites. Tolman[4] studied the steric hindrances by the ligand-cone angles, which is the apex angle of the minimum cones contered several angstroms (metal–phosphorus bond lengths) away from the center of the phosphorus atom along the threefold axis of phosphorus ligands which just touch the outermost extremities of a folded back ligand while maintaining C_3 symmetry. According to his study with CPK models, the cone angle of PF_3 (when coordinated to Ni(0)) is about 104°, and that of $P(OCH_3)_3$ is 107° (uncertainly of $\pm 2°$). He used the metal–phosphorus bond length of 2.28 Å, but he suggested that it was too long.

His cone angle estimation cannot be directly applied to our case, because the proton NMR showed that all fifty-four protons in $[Co(P(OCH_3)_3)_6]^{3+}$ are strictly equivalent. The equivalence of the six phosphorus-31 nuclei also confirms that there are no differences in the six phosphite groups. This means that the free rotation of each phosphite group occurs around the threefold axis, namely, the cobalt(III)–phosphorus bond. Therefore, the ligand-cone angles of phosphite esters in the $[Co(P(OCH_3)_3)_6]^{3+}$ should be smaller the 90°, and the bond length between the central cobalt(III) and the ligand phosphorus atom must be elongated to allow the free rotation of phosphite groups. Such bond stretching might cause a smaller spin-spin coupling constant than would occur in the case of no steric hindrances.

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