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^1H Nuclear Magnetic Resonance Spectra of Trialkyl Phosphite Complexes with Transition-metal Ions

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Summary Decoupling of the n.m.r. signal of protons in phosphites normally split by phosphorus has been observed in the presence of transition-metal species.

THERE has been a recent interest in the spectra of transition-metal complexes with tervalent phosphorus esters.[1a–e] Solid complexes have been isolated in several instances[1d–e] although in the cases involving metal halides the complexes have resisted isolation and have been observed only in solution.[1a–c] We have observed the ^1H n.m.r. spectra of several of these complexes in organic solvents.

The *anhydrous* salts $NiCl_2$, $CoCl_2$, and $AgNO_3$ have been found to dissolve in organic solvents containing the trialkyl phosphites [$P(OR)_3$ where R is methyl or ethyl] with the spectroscopically observable formation of complexed species. With hydrocarbon solvents, decreasing the molar ratio of phosphite to transition-metal species below a value of 8:1, incomplete dissolution of salt is observed, indicative of an equilibrium between free and associated ligand. The presence of such an equilibrium is also indicated by the ^1H n.m.r. spectra.

The ^1H n.m.r. spectra of the $CoCl_2$–trimethyl phosphite system in benzene solution is shown in Figure 1.[†] With increasing concentration of metal, the proton signal collapses from the ordinary doublet (J_{PH} 11 Hz) to a singlet with a small change in chemical shift. In effect, the methyl protons have been decoupled from the phosphorus nuclei. The corresponding effect is noted with $NiCl_2$ complexes as shown in Figure 2. Here the methylene signal from triethyl phosphite has been decoupled from the phosphorus nuclei and the normal quartet (broadened) of an ethyl group is observed. There is no change in the signal of the methyl protons at these concentrations. With silver nitrate complexation, even at relatively high concentrations of salt, no such effect is observed, only the normal sharp signal.

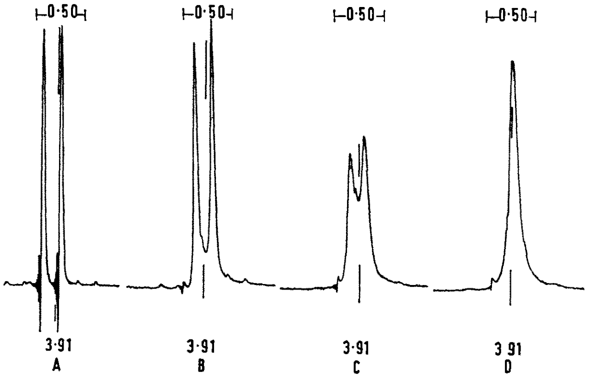

FIGURE 1

A—1·5 M-*trimethyl phosphite in benzene*; B—1·45 M-*trimethyl phosphite*: 5·15 × 10^{-3} M-$CoCl_2$ *in benzene*; C—1·48 M-*trimethyl phosphite*, 9·92 × 10^{-3} M-$CoCl_2$ *in benzene*; D—1·46 M-*trimethyl phosphite*, 5·45 × 10^{-2} M-$CoCl_2$ *in benzene. Positions given in p.p.m. upfield from benzene.*

The Co^{II}, and under these conditions the Ni^{II} as well, contain unpaired electrons, and are paramagnetic. Due to the intense localized magnetic field produced by the paramagnetic metal species the spin–lattice relaxation time for a nucleus in close proximity to it is expected to decrease greatly.[2,3] When the nucleus moves rapidly between its spin states in this manner, an average, or decoupled, signal is observed for nuclei normally coupled to it.[4] In the present

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[†] All spectra were measured on a Varian A-60A nuclear magnetic resonance spectrometer purchased under a grant from the National Science Foundation.

case where the phosphorus nuclei of the ligands are bound directly to the paramagnetic site the magnetic resonance signal for protons normally split by the phosphorus nuclei is decoupled.

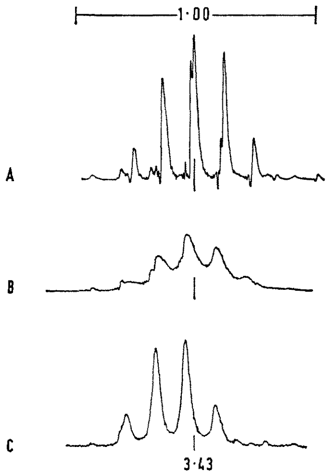

FIGURE 2

A—1·2 M*-triethyl phosphite in benzene; B—1·55* M*-triethyl phosphitte,* 1·91 10^{-2}M-$NiCl_2$ *in benzene; C—7·92* × 10^{-1} M*-triethyl phosphite,* 4·33 × 10^{-2} M-$NiCl_2$ *in benzene. Positions given in p.p.m. upfield from benzene.*

In the case of Ag^{I} complexation there exists a d^{10} diamagnetic system and only minor effects, if any, would be expected.[5]

There are several other points to note from the observations. First, as would be expected for the more paramagnetic substance, the decoupling effect is observed at lower concentrations for Co^{II}, a d^7 system, than for Ni^{II}, a d^8 system. Work with d^5 Fe^{III} complexing agents give the described result at even lower concentrations. Here, however, due to the magnitude of the paramagnetism the resolution of all signals in the system is decreased.

The existence of a rapid equilibrium of associated and free ligand can be established. Spectra at low concentrations of $CoCl_2$ with trimethyl phosphite indicate, by decoupling of the methylene protons, instantaneous incorporation into the co-ordination sphere of added triethyl phosphite.

In many complexes involving a paramagnetic species there can be observed a large change in chemical shift of nuclei in the ligand due to electron spin–nuclear spin interaction.[6] In the present systems such a large shift is absent, as presumably there is no efficient mode for transmission of unpaired electron density to the region of the protons.[7]

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