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EUROPIUM-INDUCED SHIFTS IN THE ^{1}H AND ^{31}P NMR OF "MIXED" NITROGEN-PHOSPHORUS BIDENTATE LIGANDS: EVIDENCE FOR A $Eu(DPM)_3$-P(III) INTERACTION

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Since Hinckley's initial report that large chemical shifts are induced in the proton nmr spectrum of cholesterol by the addition of the dipyridine adduct of tris-(dipivalomethanato) europium (III), $Eu(dpm)_3 \cdot 2py$, numerous papers have appeared in the literature[2] describing the use of this reagent, as well as similar tris chelate rare earth complexes, for the elucidation of the proton nmr spectra of various complex organic molecules. Invariably, these reports have been concerned with the induced shifts in organic substrates possessing "hard" base sites (e.g. the N atom in amines and nitriles and the O atom in ethers, alcohols, esters, aldehydes, and ketones). Only brief mention has been made of the fact that certain "soft" bases (e.g. tertiary phosphines and arsines) interact, albeit weakly, with these shift reagents.[3,4]

During the course of some investigations in this laboratory into the coordination chemistry of "mixed" nitrogen-phosphorus bidentate ligands (I)[5,6] it was necessary to examine their proton nmr spectra. In particular, the proton nmr of Ib showed the NCH_2 and PCH_2 protons exhibited nearly identical chemical shifts making assignments and the determination of coupling constants virtually impossible. It was anticipated that upon addition of $Eu(dpm)_3$ interaction with the amine would occur and cause the two methylene resonances to shift by different amounts, thereby facilitating the assignment of the coupling constants. We wish to report here the somewhat unexpected results of these studies.

$R_2NC_2H_4P(C_6H_5)_2$ Ia, R=H
I Ib, $R=CH_3$

^{1}H nmr. The proton chemical shifts for Ia and Ib versus the mole ratio, $Eu(dpm)_3$/ substrate, are plotted in Figures 1 and 2, respectively. Surprisingly, the results are totally different for the two ligands. In the case of Ib, the methyl groups show the largest downfield shift: this is expected assuming the interaction with the shift reagent occurs via the N atom. However, the NH_2 resonance in Ia shifts by less that 0.2 p.p.m. whereas the ortho, meta, and para protons are clearly separated and exhibit downfield shifts in the range of 3.6 (ortho)-1.5 (para) p.p.m. at the highest Eu $(dpm)_3$/substrate ratio studied. This data strongly suggests the Eu $(dpm)_3$-Ia interaction occurs via the "soft" phosphorus atom rather than via the amine. The methylene resonances, which are separately by ~0.6 ppm in the free diamagnetic ligand (Ia) shift by as much as 13.5p.p.m.

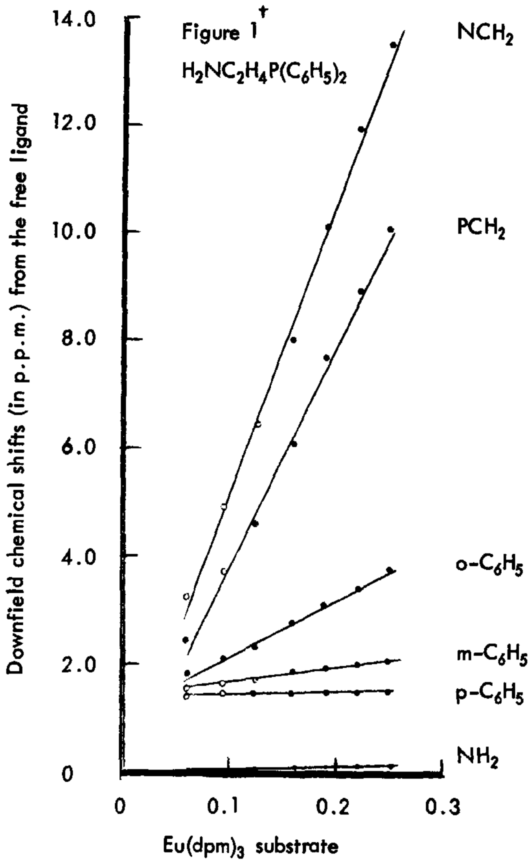

Figure 1[†]

$H_2NC_2H_4P(C_6H_5)_2$

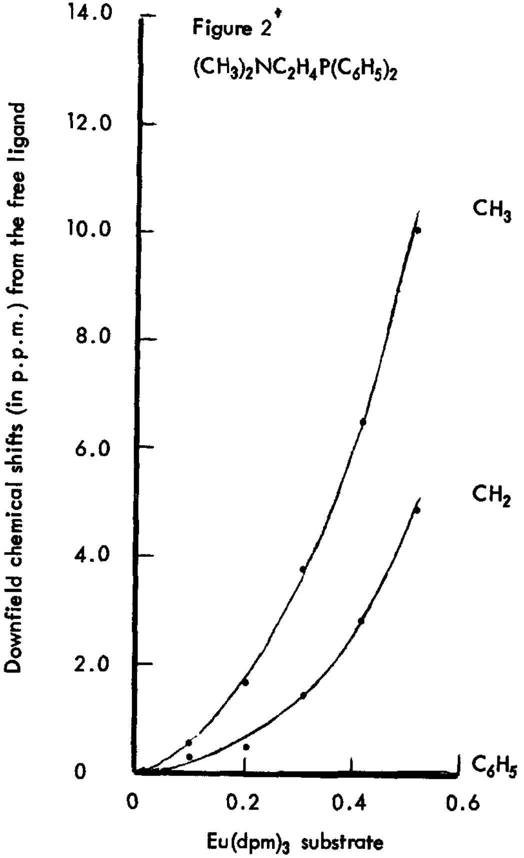

Figure 2[†]

$(CH_3)_2NC_2H_4P(C_6H_5)_2$

[†] Determined at 100 MHz in $CDCl_3$ solutions, TMS as internal standard

(NCH_2) and 10.2 p.p.m. (PCH_2) at the highest Eu(dpm)$_3$/substrate ratio studied.[*]

The larger chemical shift for the NCH_2 protons, as compared to the PCH_2 protons, can be rationalized after consideration of the geometric factors which determine the magnitude of the dipolar interaction. An examination of a molecular model of Eu(dpm)$_3$-Ia (assuming a Eu(III)-P(III) interaction) indicates the NCH_2 protons are closer on the average to the paramagnetic center than are the PCH_2 protons.

^{31}P nmr. The conclusions drawn from the ^1H nmr are confirmed by examination of the ^{31}P nmr spectra of Ia and Ib in the presence of Eu(dpm)$_3$. These data are plotted in Figure 3. It is evident the ^{31}P shift for $H_2NC_2H_4P(C_6H_5)_2$ substantiates the conclusion drawn from the ^1H nmr. Even with a Eu(dpm)$_3$/ substrate ratio of only 0.2, the phosphorus resonance has been shifted by ~23.0 p.p.m. Higher ratios could not be examined because of excessive dipolar broadening of the signal. On the other hand, the extremely small ^{31}P shift for Ib (~ 1.5 p.p.m. at a ratio of 0.2) coupled with the proton nmr data supports a Eu(III)-N interaction.

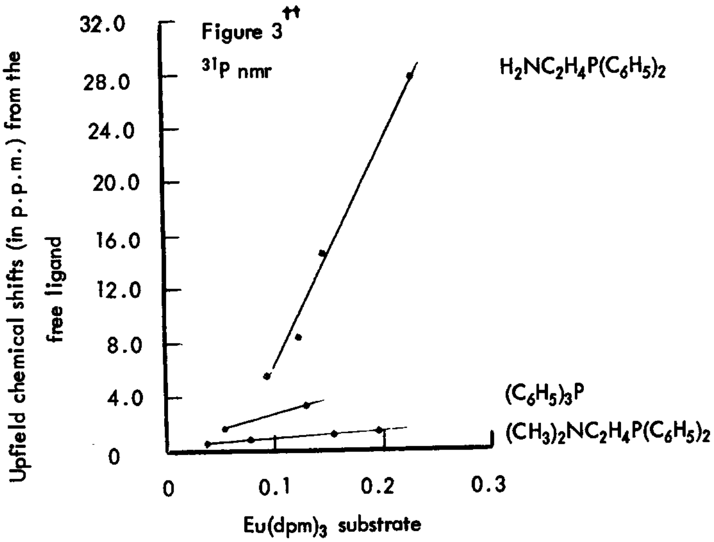
Figure 3[††]

[††] Determined at 40.5 MHz in $CDCl_3$ solutions, 85 H_3PO_4 as external standard

The factors which can account for this difference in the behavior of Ia and Ib are not presently understood. Obviously, subtle changes in steric requirements and changes in the relative basicities of the

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[*] The assignment of the chemical shifts for the NCH_2 and PCH_2 protons in the free ligand is based on electronegativity considerations and the relative magnitudes of the J_{PCH} and J_{PCCH} coupling constants. The NCH_2 resonance is expected to occur at lower applied fields because of the greater electronegativity of N as compared to P. The J_{PCCH} coupling constants are larger in magnitude than J_{PCH}.[7] Thus J_{PCCH} = 6.0-6.5 Hz and $J_{PCH} \geqslant 2.0$ Hz for $H_2NC_2H_4P(C_6H_5)_2$.

amine and phosphine dictate the interaction site as well as the strength of the interaction with the shift reagent.

Interestingly, $(C_6H_5)_3P$, which shows no detectable proton shift upon addition of Eu(dpm)$_3$, does exhibit a small but definite ^{31}P shift. This result points out the danger involved in drawing conclusions from an examination of the proton nmr of an organic substrate in the presence of a shift reagent. If the interaction between the paramagnetic center and the donor is weak, as it presumably is in $(C_6H_5)_3P$, examination of a magnetic nuclei 4 atoms removed from the paramagnetic center may show little or no shift.

Studies are presently being carried out with other "mixed" ligands and various tertiary phosphines in the presence of Eu(dpm)$_3$ and other lanthanide shift reagents.

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