

## <sup>31</sup>P Chemical Shifts in Transition-metal Phosphite Complexes. The Effect of Metal Valency

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SIMPLE interpretation of the chemical shifts in the nuclear magnetic resonance of <sup>31</sup>P does not seem possible yet due to the complexity of the factors which cause the shifts.<sup>1-3</sup> Indeed, one should expect the interpretation of <sup>31</sup>P chemical shifts for transition-metal phosphite complexes to be even more difficult.<sup>3</sup> This is especially true because of the variability of the  $\pi$ - and  $\sigma$ -contributions to the metal-phosphorus bond. These contributions are dependent upon, for example, the substituents on phosphorus, the other ligands co-ordinated to the metal, the formal oxidation state of the metal, and the geometry of the complex. Thus we were quite pleased when we found what appears to be a correlation of the <sup>31</sup>P chemical shifts in transition-metal phosphite complexes with changes in the metal valency. The Table lists the chemical shifts of the complexes and free ligands.

Clearly in the uncomplexed ligands the oxygen substituents deshield the phosphorus atom.<sup>2</sup> However, for P<sub>4</sub>O<sub>6</sub>, the co-ordination of BH<sub>3</sub> causes a positive shift of 22.6 p.p.m.<sup>4</sup> Since it is reasonable to expect no significant amount of  $d\pi$ - $p\pi$ -bonding between phosphorus and boron, the shielding can be attributed to the inductive opposition of BH<sub>3</sub> to the oxygen groups. Previous work on the BH<sub>3</sub> adducts of 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane, 2,8,9-trioxa-1-phospha-adamantane, and trimethyl phosphite also shows this effect.<sup>5a</sup> The relative shifts are -5, +20, and +23 p.p.m., respectively. The "octane" compound has steric requirements which make it an unusual ligand, and the inconsistency of its BH<sub>3</sub> adduct may be connected with this factor.<sup>5b</sup>

If we assume the microsymmetry about the

TABLE  
L = ligand<sup>a</sup>

Compounds	P(OMe) <sub>3</sub>	P(OEt) <sub>3</sub>	P <sub>4</sub> O <sub>6</sub>
L .. ..	-141 <sup>b</sup>	-138 <sup>b</sup>	-113 <sup>c</sup>
Ni(CO) <sub>3</sub> L .. ..		-155 (-17) <sup>d</sup>	-126 (-13) <sup>c</sup>
NiL <sub>4</sub> .. ..		-157 (-19) <sup>d</sup>	
H <sub>3</sub> BL .. ..	-118 (+23) <sup>e</sup>		-90.4 (+22.6) <sup>c</sup>
(CuClL) <sub>4</sub> .. ..	-132 (+9)	-128 (+10)	
CuL <sub>4</sub> ClO <sub>4</sub> .. ..	-125 (+16) <sup>f</sup>	-121.5 (+16.5) <sup>f</sup>	
(AgClL) <sub>4</sub> .. ..	-135 (+6)		
AgL <sub>4</sub> ClO <sub>4</sub> .. ..	-130 (+11)	-128 (+10)	
AgL <sub>4</sub> NO <sub>3</sub> .. ..	-132 (+9)		
HgCl <sub>2</sub> L .. ..		-115 (+23)	
NiCl <sub>2</sub> L <sub>2</sub> .. ..		-118 (+20)	

<sup>a</sup> All values are reported in p.p.m. referenced to 85% H<sub>3</sub>PO<sub>4</sub>. In parentheses are the (complex - free ligand) values.

<sup>b</sup> see ref. 2.

<sup>c</sup> see ref. 4.

<sup>d</sup> see ref. 3.

<sup>e</sup> see ref. 5a.

<sup>f</sup> see ref. 5c.

complexed phosphorus atom is the same as in  $P_4O_6 \cdot BH_3$  this net shielding can be observed in  $Cu^I$ ,  $Ag^I$ ,  $Ni^{II}$ , and  $Hg^{II}$  phosphite complexes. Furthermore, in going from the +1 to the +2 state, the shielding becomes progressively greater, as would be expected for a charge effect. Comparison of the trimethyl and triethyl phosphite complexes of  $Cu^I$  and  $Ag^I$ , shows the same net shielding. The "anion effect", must wait for more data before it can be rationalized. However, for the trimethyl phosphite complexes of  $Cu^I$  and  $Ag^I$  the chloride-perchlorate difference is the same.

Finally, we must consider the  $Ni^0$  complexes. More data exist<sup>3,4</sup> for the  $Ni^0$  phosphite complexes. For the sake of brevity we include only a few compounds which are indicative of all those published. The  $^{31}P$  chemical shifts for the  $Ni^0$  phosphite complexes are more negative than for the free ligand. To be consistent with the charge

effect we might expect some or no net shielding, but not the observed net deshielding. Furthermore,  $Ni^0$ ,  $Cu^I$ ,  $Ag^I$  and  $Hg^{II}$  all have  $d^{10}$  configurations, and should utilize  $d\pi-d\pi$  back-bonding. Thus, the difference is that the lack of a formal positive charge for  $Ni^0$  allows  $d\pi-d\pi$  back-bonding to become important. Another way of viewing this is that the "temperature-independent paramagnetic" contribution has become more important and the total diamagnetic contribution is reduced resulting in a net shift to lower fields.<sup>3</sup>

The compounds synthesized for this work were made by known methods; <sup>5b,6</sup> analyses, stoichiometry (as compared to similar complexes) and conductivity measurements are consistent with the structures listed in the Table. All spectra were measured on an HA60 instrument.

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