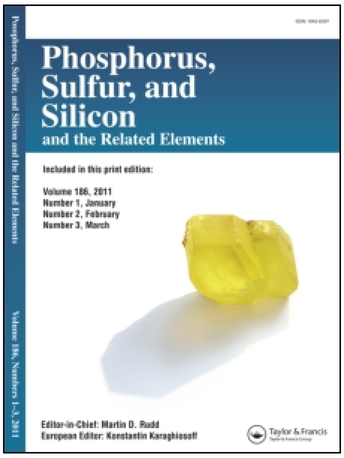

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Steric Versus Electronic Effects in the Ligation Behavior of Trivalent Phosphorus Compounds: ^{59}Co AND ^{31}P NMR Spectroscopic Studies

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STERIC VERSUS ELECTRONIC EFFECTS IN THE LIGATION BEHAVIOR OF TRIVALENT PHOSPHORUS COMPOUNDS: ^{59}Co AND ^{31}P NMR SPECTROSCOPIC STUDIES

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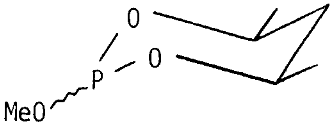
Abstract Using NMR techniques, the role of electronic and steric influences in phosphorus(III) ester complexes of the type CoL_6^{3+} and AgL_n^+ (where n = 1-4) are assessed.

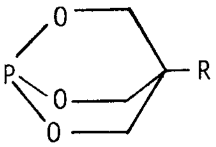
INTRODUCTION

$P(OMe)_3$

1



2a (MeO axial)
2b (MeO equatorial)



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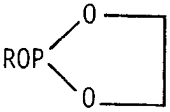


4 Me
5 Et
6 *n*-Pr
7 *i*-Pr
8 *n*-Bu
9 *i*-Bu
10 *t*-Bu

Homoleptic Co(III) complexes of monodentate phosphite ligands reported in the literature are restricted to 1 - 4[1] and are synthesized by reaction (1). The great sensitivity of δ^{59}Co to

$$2\ Co(II) + 11\ L \rightarrow CoL_5^{+} + CoL_6^{3+} \qquad (1)$$

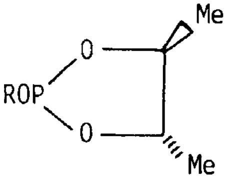
the ligand field in octahedral complexes permits study of the scope of reaction (1) and hence an analysis of the steric and electronic factors which stabilize CoL_6^{3+}. The interesting catalytic reaction (2) discovered in our current studies is also informative on these points. The Ag^+ ion is an excellent probe

$$2\,Co^{2+} + ROP\langle + MeOH \rightarrow [Co(MeOP\langle)_{x-n}(ROP\langle)_n]^{y+} \quad \begin{matrix} y=1, & x=5 \\ y=3, & x=6 \end{matrix} \qquad (2)$$

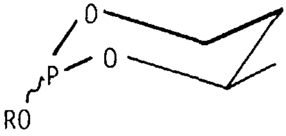
of the steric and electronic character of phosphorus(III) compounds because of its capability to coordinate one to four ligands and the relative ease with which such complexes can be detected by ^{31}P NMR spectroscopy.[2,3]

HEXACOORDINATE COBALT(III) COMPLEXES

The range of ligands which drive the disproportionation reaction (1) has now been extended to include *inter alia* 5 - 9, 11 - 13, 14a, 14b, 15 and the chelate 16. The chelates 17 and 18 were also shown earlier to drive reaction (1).[4]



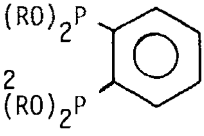
R
11 Me
12 Et
13 *n*-Pr



14a RO=MeO(ax)
14b RO=MeO(eq)
15 RO=*n*-PrO(ax)

$[CH_2P(OMe)_2]_2$

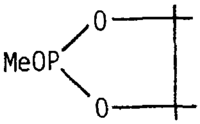
16



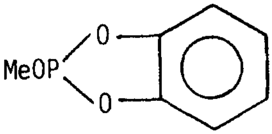
17 Me
18 Et

Steric Effects

Among acyclic phosphites, only the smallest member, 1, drives reaction (1). The aforementioned cyclic systems also do so but further enlargement of the exocyclic R substituent in 4 - 9 (e.g., 10) inhibits reaction (1) as do the sterically demanding ring substituents in 19 and 20. A more subtle steric "fit" effect is seen in the formation of CoL_6^{3+} with L = 2a,b but not with 21.



19



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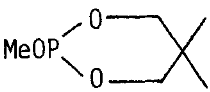

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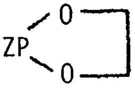
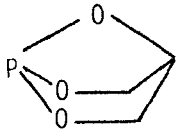


	Z
22	F
23	PhO
24	CF_3CH_2O

Electronic Effects

Although CoL_6^{3+} forms in reaction (1) with 7 (which possesses a bulky exocyclic substituent) the failure of this reaction with 22 - 24 is attributed to insufficient basicity for this type of ligand. The same can be concluded concerning the success of reaction (1) with 3 but not with the smaller 25 which has been shown to be considerably less basic than 3[5]. The most basic monodentate phosphorus ligand which drives reaction (1) appears to be 1, since $PPhH_2$ (which has a comparable cone angle[7]) does not facilitate this reaction. In addition to the expected linear correlation of $\delta^{59}Co$ with λ_{dd}, linear correlations of $\delta^{59}Co$ with $\delta^{31}P$ and with $^1J^{59}Co^{31}P$ have also been observed.



25

$P(OR)_3$

	R		R		R
26	Et	29	CH_2CH_2Cl	32	o-tolyl
27	i-Pr	30	CH_2CCl_3	33	$2,6\text{-}Me_2C_6H_3$
28	t-Bu	31	Ph		

Catalytic Transesterification of Specific Esters

Ligands 6 and 7 are catalytically transesterified to 4 in the presence of MeOH and Co^{2+}, and 13 is converted to 11 under these conditions. Moreover, both the starting ligand and the transesterified product is found to ligate in varying ratios to the Co(I) and Co(III) products of disproportionation.

ONE TO FOUR-COORDINATE SILVER(I)

In the process of examining the ligation properties of the phosphite esters 1 and 26 - 33 toward Ag(I) by a study of the $^{1}J^{107}Ag^{31}P$ values observed at low temperature, several new complexes were isolated such as $[Ag(\underline{27})_3]BPh_4$, $[Ag(\underline{31})_3]BF_4$, $[Ag(\underline{28})_2NO_3]$, $[Ag(\underline{28})_2]BF_4$ and $[Ag(\underline{33})BF_4]$.

Electronic Effects

In contrast to Ni(0) complexes wherein steric effects have been concluded to dominate,[6] Ag^+ should be more sensitive to electronic factors owing to its positive charge and slightly smaller size. The detection at -95°C of only $Ag(\underline{25})BF_4$ in the presence of excess ligand suggests that the exceedingly poor basicity[5] of this sterically small and strained ligand is responsible for the failure of more than one molecule to coordinate.

Steric Effects

The maximum coordination numbers observed in AgL_n^+ are n = 4, 3 and 2 for 31, 32 and 33, respectively. In ligand competition reactions involving AgL_4^+ the displacement orders 1 > PPh_3, monocyclic phosphites > 1 and 3 > 31 also strongly suggest the importance of steric effects.

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