

Substituent Effects in Cyclopolyphosphines

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Summary For cyclopolyphosphines, $(RP)_n$, a linear relationship which is independent of the ring size, n , exists between the electrochemical reduction potential of the ring and the inductive effect of the pendant organic group.

RECENTLY Cowley *et al.*¹ reported the results of a photoelectron spectroscopic study of perfluoropolyphosphines indicating that $p\pi-d\pi$ bonding involving phosphorus lone

pairs and empty $3d$ orbitals was relatively unimportant in the cyclopolyphosphines $(CF_3P)_4$ and $(CF_3P)_5$. We report the results of an electrochemical investigation of alkyl- and aryl-cyclopolyphosphines which supports their conclusion and which indicates that intra-annular π bonding is not a determining factor in the ring size of a particular cyclopolyphosphine.

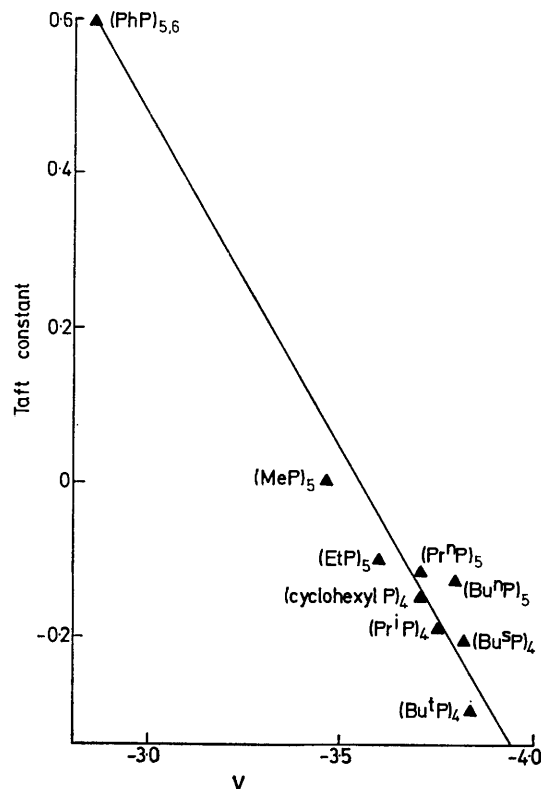
We recently found that four- and five-membered cyclopolyphosphine rings could be differentiated in solution by

use of ^1H -decoupled ^{31}P n.m.r. spectroscopy.² This method led to the reassignment of the ethyl, n-propyl, and n-butyl substituted rings to penta- rather than tetra-cyclopolyphosphines, and to the discovery that the ^{31}P chemical shift is a diagnostic criterion of ring size. We now report that the electrochemical reduction of several alkyl tetra- and penta-cyclopolyphosphines as well as the penta- and hexa-phenylcyclopolyphosphines³ yield $E_{p/2}$ reduction potentials which appear to be almost solely dependent on the inductive effect of the pendant organic group. No effect of ring size on the reduction potential was noted. Thus, as indicated in the Figure, a linear relationship exists between the inductive effect of the organic unit (in this case represented by the Taft⁴ constant) and the reduction potential $E_{p/2}$ of the cyclopolyphosphines, regardless of the ring size.

It is known that the electron transfer during electrochemical reduction occurs to an orbital formed as a consequence of the ring formation, inasmuch as the primary phosphines and biphosphines are electroinactive.³ The observation that the energy of this orbital appears to be a direct function of the inductive effect of the exocyclic organic group and is independent of the ring size of the cyclopolyphosphine strongly argues against any type of $p\pi-d\pi$ delocalization of phosphorus lone pairs around the ring into neighbouring empty phosphorus $3d$ orbitals; if such delocalization occurred, the orbital energy of the symmetric four-membered rings could be expected to be considerably different from that of the pentacyclopolyphosphines where a break in orbital symmetry must occur.⁵ It appears then, that π bonding is of negligible importance in cyclopolyphosphines in general. The determining factor in the ring size of cyclopolyphosphines appears to be steric crowding of the pendant organic group, not electronic bonding effects, with four-membered rings being favoured when the organic group is bulky, *e.g.* cyclohexyl, t-butyl or isopropyl.

Voltammograms were recorded at scan speeds of 250 mV/s at a platinum bead electrode in tetrahydrofuran solvent using $\text{Bu}^n_4\text{NClO}_4$ as the supporting electrolyte, and the previously described high-vacuum electrochemical cell and electrochemical instrumentation.³ Cyclopolyphosphine concentrations during voltammetry were generally 1–3 mM. Because the reductions were extremely irreversible (as

indicated by cyclic voltammetry), the $E_{p/2}$ values were sensitive to small variations in concentration; thus the $E_{p/2}$ values are accurate only to ± 0.05 V. In general the behaviour of the cyclopolyphosphine rings following



FIGURE

reduction was similar to that of the previously reported phenylcyclopolyphosphines.³

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¹ A. H. Cowley, M. J. S. Dewar, D. W. Goodman, and M. C. Padolina, *J. Amer. Chem. Soc.*, 1974, **96**, 3666.

² L. R. Smith and J. L. Mills, *J.C.S. Chem. Comm.*, 1974, 808.

³ T. J. DuPont and J. L. Mills, *Inorg. Chem.*, 1973, **12**, 2487.

⁴ R. W. Taft, 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, p. 619.

⁵ W. Mahler and A. B. Burg, *J. Amer. Chem. Soc.*, 1957, **79**, 251; 1958, **80**, 6161.