

tion may be through methoxy bridges¹ or through acetylacetonate oxygens³ or both types may be involved.

Mg(CH₃O)(CH₃OH).—Since the transition metal complexes are paramagnetic, the magnesium complex was prepared for studies of the nuclear magnetic resonance spectrum.⁴ The two methyl groups of the acetylacetonate group appeared as a singlet at 1.90, methyl groups of the methoxide and methanol appeared at 3.06 and 3.32, and the two protons O–H and C–H appeared at 5.08 and 5.20 p.p.m.

The position of the C–H is shifted considerably from the position found by Holm and Cotton⁵ for various divalent metal acetylacetonates.

Other Studies.—The other methoxy complexes prepared were similar in properties to the examples discussed. The cobalt complex with 2'-hydroxyacetophenone was prepared in good yield without using base; in general, the 2'-hydroxyacetophenone and salicylaldehyde complexes seem more stable with respect to hydrolysis than the acetylacetonate complexes. The cobalt complex of 2'-hydroxyacetophenone reacted with pyridine to give a solid adduct which has not been completely characterized.

Analytical data for representative compounds are presented in Table I.

TABLE I
ANALYTICAL DATA FOR COMPOUNDS ML(CH₃O)(CH₃OH)

M	L	Calcd.		Found	
		C	H	C	H
Co	Acetylacetonate	38.0	6.3	38.0	5.7
Ni	Acetylacetonate	38.0	6.3	38.8	5.8
Mg	Acetylacetonate	45.2	7.5	45.5	7.8
Co	Salicylaldehyde	44.4	4.9	44.4	4.9
Co	2'-Hydroxyacetophenone	46.7	5.5	46.6	5.5

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(3) F. A. Cotton and R. H. Soderberg, *Inorg. Chem.*, **3**, 1 (1964).

(4) The n.m.r. spectrum was run in carbon tetrachloride using tetramethylsilane as an internal standard.

(5) R. H. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 5658 (1958).

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A Stereospecific Route to *trans*- and *cis*-1,2-Vinylenebis(diphenylphosphine)

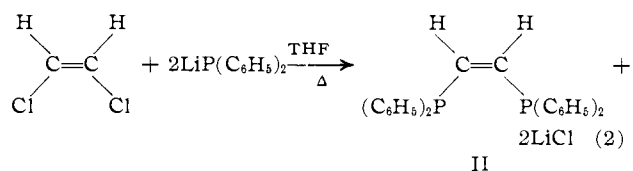
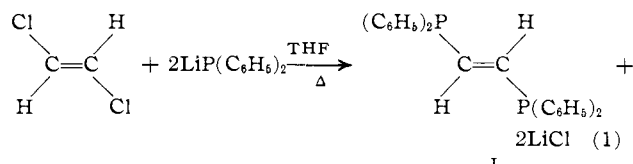
Sir:

Recent work on the nonaryne displacement of aryl halides by lithium diphenylphosphide has suggested the possibility of similar substitution of vinyl halides.¹

In this communication we report the stereospecific reaction of *trans*- and *cis*-1,2-dichloroethene with lithium diphenylphosphide to produce *trans*- and *cis*-1,2-vinylenebis(diphenylphosphine), respectively (eq. 1 and 2).

Addition of *trans*-1,2-dichloroethene to a hot solution of lithium diphenylphosphide in tetrahydrofuran, produced by the cleavage of triphenylphosphine with

(1) A. M. Aguiar, H. J. Greenberg, and K. E. Rubenstein, *J. Org. Chem.*, **28**, 2091 (1963).



lithium metal,² led to the isolation of compound I (m.p. 125–126), in 80% yield. *Anal.* Calcd. for C₂₆H₂₂P₂: C, 78.79; H, 5.56; P, 15.66; mol. wt., 396. Found: C, 78.47; H, 5.66; P, 15.45; mol. wt., 422 (by the ebullioscopic method). N.m.r. spectra of a deuteriochloroform solution of I at 60 Mc. exhibited the following bands relative to an internal standard of tetramethylsilane: a triplet centered at δ 6.78 p.p.m. with a coupling constant of 15 c.p.s. and a complex centered at δ 7.3 p.p.m. in the ratio of 1:10, respectively. These were assigned to vinyl hydrogens and phenyl hydrogens, respectively. Ethylenebis(diphenylphosphine) exhibits a triplet centered at δ 2.13 p.p.m. with a coupling constant of 4.25 c.p.s. which has been assigned to the methylene hydrogens.³ The infrared spectrum of a KBr pellet of I showed bands at 3.28 (w), 6.3 (w), 6.75 (m), 7.0 (m), 7.65 (w), 8.5 (m), 9.15 (w), 9.38 (w), 9.72 (w), 10.0 (w), 10.2 (m), 13.5 (s), and 14.4 μ (s). Essentially the same infrared spectrum was obtained from ethylenebis(diphenylphosphine) except for the presence of a small peak at 3.43 μ (w), the absence of the narrow peaks at 8.5 (m) and 10.2 μ (m), and a considerable difference in the region between 13 and 15 μ. Hydrogenation of I with Raney nickel at 2000 p.s.i. of pressure in hot ethanol produced 1,2-ethylenebis(diphenylphosphine).^{3–6} On the basis of the information described above, I was assigned the vinylenebis(diphenylphosphine) structure with a tentative assignment of a *trans* configuration.

Identical treatment of *cis*-1,2-dichloroethene produced II having essentially identical melting point, composition, and molecular weight as I but differing in its n.m.r. and infrared spectra and exhibiting a depressed mixture melting point with I. A deuteriochloroform solution of II showed a complex at 7.25 p.p.m. which was assigned to the phenyl hydrogens and two small equal size peaks at δ 7.0 and 7.45 p.p.m. Perhaps the middle peak of a triplet falls at the same frequency at which the phenyl hydrogens resonate. If this is the case, the coupling constant of the triplet is about 14 c.p.s. The infrared spectrum of II was similar to that of I except for the absence of the bands at 8.5 and 10.2 μ and the presence of a small split peak at 7.73 μ, weak peaks at 10.3 and 10.4 μ, a large peak at 14.0 μ, and a weak band at 15.2 μ. If the band at 10.2 μ is considered to be a "trans band" and that at 14.0 μ a *cis* deformation band, I can be assigned the *trans* configuration and II the *cis* configuration. At-

(2) A. M. Aguiar, J. Beisler, and A. Mills, *ibid.*, **27**, 1001 (1962).

(3) A. M. Aguiar and J. Beisler, *ibid.*, in press.

(4) W. Hewertson and H. R. Watson, *J. Chem. Soc.*, **4**, 1490 (1962).

(5) P. T. Keough and M. Grayson, *J. Org. Chem.*, **27**, 1817 (1962).

(6) L. Horner, H. Hoffman, W. Klink, H. Ertel, and V. G. Toscano, *Chem. Ber.*, **95**, 581 (1962); *Chem. Abstr.*, **57**, 22383 (1962).

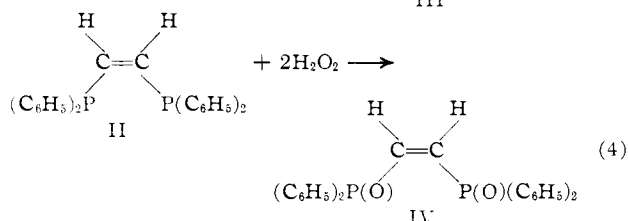
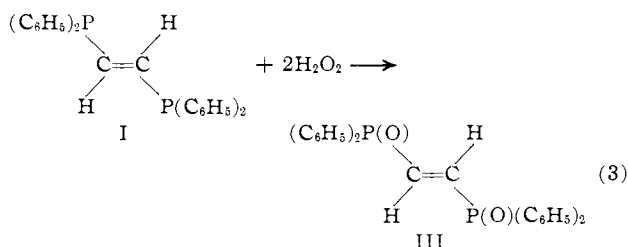
tempted hydrogenation of II under identical conditions resulted in quantitative recovery of II. This may be due to interaction between the Raney nickel and a *cis*-diphosphine.⁷

Oxidation of I and II by treatment with 3% hydrogen peroxide in hot acetone or ethanol gave III and IV, respectively.

Compound III (m.p. 310–311). *Anal.* Calcd. for $C_{26}H_{22}P_2O_2$: C, 72.89; H, 5.14; P, 14.48; mol. wt., 428. Found: C, 72.55; H, 5.23; P, 14.42; mol. wt., 458 (by osmometer method) gave an infrared spectrum which exhibited peaks at 3.28 (w), 3.35 (m), 6.3 (w), 6.7 (w), 6.95 (m), 8.4 (s), 8.55 (s), 8.9 (s), 9.1 (m), 9.3 (w), 9.8 (m), 10.0 μ (w), and four strong peaks at 13.0, 13.4, 13.85, and 14.5 μ . The n.m.r. of a glacial acetic acid solution of III showed a phenyl hydrogen complex centered at about δ 7.1 p.p.m. and two unequal-sized peaks at δ 7.5 and 7.9 p.p.m. The 7.9 peak was the smaller. Apparently the high-field peak of a triplet due to the vinyl hydrogens is hidden by the phenyl hydrogens. The coupling constant is 25 c.p.s. A trifluoroacetic acid solution of III displayed an n.m.r. spectrum showing the triplet more clearly.

Compound IV (m.p. 244–245) had the same composition and molecular weight as III but gave an infrared spectrum displaying peaks at 3.0 (w), 3.4 (w), 6.35 (w), 6.8 (w), 7.0 μ (m), a complex set between 8.2 and 8.6 μ , with the strongest peak at 8.4 μ , 9.0 (s), 9.15 (w), 9.4 (w), 9.8 (w), 10.05 (w), 12.95 (w), 13.15 (w), 13.4 (m), 13.85 (s), 14.25 (m), 14.45 (s), 14.6 (m), and 15.2 μ (w). The n.m.r. of a glacial acetic acid solution of IV showed a phenyl hydrogen complex centered at δ 6.9 p.p.m. and two equal-size peaks at δ 6.38 and 7.4 p.p.m. Perhaps the vinyl hydrogens show up as a triplet with the middle peak falling at the same point as the phenyl hydrogens. If this is the case the coupling constant is about 32 c.p.s. Use of trifluoroacetic acid as solvent gave essentially the same results. Ethylenebis(diphenylphosphine) dioxide gave an infrared spectrum which also had a weak band at 3.0 μ but had two others at 3.42 and 3.47 μ . Unlike the vinyl dioxides the saturated dioxide in deuteriochloroform exhibits a doublet at δ 2.58 p.p.m. due to the methylene hydrogens.³

On the basis of the above data compounds III and IV were assigned the structures of *trans*- and *cis*-1,2-vinylenebis(diphenylphosphine) dioxide, respectively (eq. 3 and 4).



(7) J. Chatt, F. A. Hart, and D. T. Rosevear, *J. Chem. Soc.*, 5504 (1961).

Thiolate ions have been reported to react with *cis*-1,2-dichloroethene in the presence of sodium ethoxide to give a *cis*-vinyl bridged disulfide by an elimination-addition mechanism.⁸ The *trans*-dihalide was found unreactive under similar conditions.⁸ The elimination-addition path cannot be followed by both isomers in the reaction with lithium diphenylphosphide since the same vinylenebis(diphenylphosphine) would be produced in both cases from the common intermediate, chloroacetylene.

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(8) W. E. Truce, M. M. Boudakian, R. F. Heine, and R. J. McManis, *J. Am. Chem. Soc.*, **78**, 2743 (1956).

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Concerning the Role of Protonated Cyclopropane Intermediates in Solvolytic Reactions. II. The Deamination of 3,3,3- d_3 -1-Aminopropane

Sir:

Recently the suggestion was made¹ that a protonated cyclopropane might be the intermediate responsible for the rearranged 1-propanol obtained in the deamination of 1-aminopropane as well as for the cyclopropane obtained^{2,3} in such reactions. It was shown previously¹ that when D^+ is added to cyclopropane, extensive mixing of the added deuterium and the ring protons occurs during the lifetime of this protonated cyclopropane intermediate. If the cyclopropane formed in these deaminations is also formed *via* such an intermediate, then, by suitable choice of label, one should be able to demonstrate such mixing in the cyclopropane obtained.

A crucial test of this hypothesis is found in the deamination of 3,3,3- d_3 -1-aminopropane. In this case, formation of an intermediate such as I and subsequent mixing of H and D would lead to a mixture of cyclopropane- d_2 and cyclopropane- d_3 . The amount of cyclopropane- d_3 formed would give a measure of the extent of such mixing and of any isotope effect on deprotonation.⁴

The perchlorate of 3,3,3- d_3 -1-aminopropane was prepared from acetophenone *via* the sequence: exchange with D_2O , rearrangement,⁶ $LiAlH_4$ reduction, *p*-toluenesulfonate ester formation, $NaCN$ displacement, and reduction.⁷ The perchlorate (m.p. 167.5–

(1) R. L. Baird and A. A. Aboderin, *J. Am. Chem. Soc.*, **86**, 252 (1964).

(2) P. S. Skell and I. Starer, *ibid.*, **82**, 2971 (1960).

(3) M. S. Silver, *ibid.*, **82**, 2971 (1960).

(4) A small amount of mixing has been observed in the "deoxidation" of 1,1- d_2 -1-propanol.⁵ However, the combination of isotope effect, method of analysis, and short ion lifetimes obtained under these conditions tends to obscure the extent of such mixing.

(5) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **84**, 3962 (1962).

(6) M. F. Hawthorne, W. D. Emmons, and K. S. McCallum, *ibid.*, **80**, 6393 (1958).

(7) J. D. Roberts and M. Halmann, *ibid.*, **75**, 5759 (1953).