

Fig. 1.—Ultraviolet absorption spectra of XeF_2 : —, aqueous solution at ca. 5° ; - - - - - , gas at 30° .⁶

From these results it seems clear that XeF_2 dissolves in water to the extent of about 0.15 M and is present in solution as undissociated molecules which do not form complex anions with F^- . From Fig. 1 we see that the ultraviolet absorption spectrum of these solutions is similar to that of gaseous XeF_2 .⁶ It appears that hydrolyzed Xe(II) cannot persist in aqueous solution, and reagents that remove the fluoride from XeF_2 bring about the rapid evolution of xenon and oxygen. We estimate the Xe-XeF_2 potential in acid to be about 2.2 v.

Kirschenbaum and Grosse reported that by hydrolyzing XeF_4 in water at 0° they obtained an unstable, volatile, and pungent-smelling xenon compound which they considered to be a compound of hexavalent xenon,⁷ although other workers have found Xe(VI) to be odorless, stable, and nonvolatile in aqueous solution.^{8,9} In a private communication Grosse has informed us that the XeF_4 he used was severely contaminated with XeF_2 and that he now feels his solutions contained a mixture of the stable, nonvolatile XeO_3 and another hitherto unknown compound. We believe that this new compound is aqueous XeF_2 .

The transient bright yellow color observed when a XeF_2 solution is made basic is interesting. Presumably it is the same as the yellow color formed on the surface of the solid when XeF_2 is hydrolyzed in base.² However, it also resembles the yellow color that appears on the surface of solid XeF_4 when it is hydrolyzed,⁷

(6) E. S. Pysh, J. Jortner, and S. A. Rice, *J. Chem. Phys.*, **40**, 2018 (1964).

(7) A. D. Kirschenbaum and A. V. Grosse, *Science*, **143**, 3592 (1963), and information presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(8) S. M. Williamson and C. W. Koch, *Science*, **139**, 1046 (1963).

(9) E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2141 (1964), and information presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

and it is similar to the flash of yellow that is seen when a strongly alkaline Xe(VI) solution is reduced with H_2O_2 . The hydrolysis of XeF_4 has been postulated to proceed through Xe(II) ,² and divalent xenon may also be produced during the peroxide reduction of Xe(VI) . The yellow color may thus possibly belong to an oxygen compound of divalent xenon.

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Preparation and Properties of Methoxy Complexes of Divalent Metal Ions

Sir:

A recent paper¹ reported the preparation of polymeric bis(3-nitropentane-2,4-diono)di- μ -methoxydi-beryllium from the corresponding diol complex. The diol complex was prepared by treating beryllium acetylacetonate with beryllium nitrate in acetic anhydride.

We have employed a more general method for the preparation of methoxy complexes of divalent metal ions with various chelating anions. The metal chelates ML_2 react with base in methanol to produce the insoluble methoxy compounds $[\text{ML}(\text{CH}_3\text{O})(\text{CH}_3\text{OH})_x]$. Divalent metal ions which have been employed include cobalt, nickel, copper, and magnesium; chelating agents employed have included acetylacetonone (hereafter abbreviated A), 3-ethylacetylacetonone, salicylaldehyde, and 2'-hydroxyacetophenone.

$\text{CoA}(\text{CH}_3\text{O})(\text{CH}_3\text{OH})$.—In the initial preparations of this complex, weak nitrogen bases were employed and poor yields were obtained; later studies showed that potassium hydroxide gave almost quantitative yields. Further investigation of the reaction showed that continued reflux of CoA_2 in methanol without added base produced a small amount of the methoxy compound. The ease of preparation of this and similar complexes is evidently a result of the extremely low solubility of these complexes in methanol.

Heating the complex to 100° *in vacuo* resulted in the removal of 1 mole of methanol; the color changed from deep red to violet.

The complex reacted with *p*-nitrobenzoyl chloride to give substitution at the 3-position of the chelate ring. Similar reaction of the bis(acetylacetonato)-metal(II) compounds has been reported.²

The infrared spectrum was similar to that of CoA_2 , but had additional absorptions indicative of methanol and methoxy groups; the carbonyl stretching band was much sharper than that of CoA_2 . The spectrum of the violet compound, $\text{CoA}(\text{OCH}_3)$, was identical except in the region of O-H absorptions.

The ultraviolet spectrum of the complex was identical, with respect to absorption position, with that of CoA_2 ; the extinction coefficient at the band maximum was only half as great as that of CoA_2 .

Similarity of the visible spectrum of the complex and CoA_2 indicates that the ligand field is essentially "octahedral," which would require some type of molecular association. The molecular weight obtained with a Mechrolab vapor pressure osmometer for a 0.05 F solution in chloroform was above 4000. The associa-

(1) R. M. Klein and J. C. Bailar, Jr., *Inorg. Chem.*, **2**, 1189 (1963).

(2) D. C. Nonhebel, *J. Chem. Soc.*, 4628 (1962).

tion may be through methoxo 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 methoxo 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

Acknowledgment.—The Cary spectrophotometer used in this study was purchased with funds from the National Science Foundation and the Charles F. Kettering Foundation. We thank Dr. W. J. Hart for the molecular weight determination of the cobalt compound.

(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)

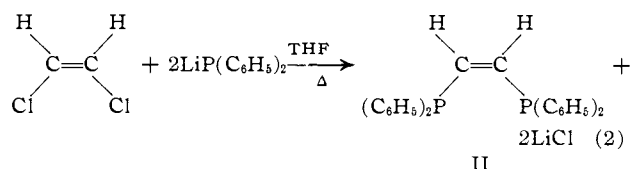
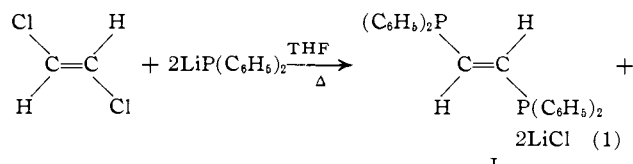
Sir:

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).