atom in II through the vinyl group, and the interaction causes the "weakening" of the ethyl-nickel bonds. The weakening may lead to the fission of the ethylnickel bonds and the initiation of the polymerization by a coordinated mechanism. No reaction of I with acetonitrile was observed.

In explanation of the mechanism of polymerization with Ziegler-type catalysts, coordination of a monomer with an alkyl transition metal complex has often been postulated,⁴ but the isolation of such a complex has not been reported to our knowledge.⁵ Our orange complex II seems to provide the first example of the isolation of an alkyl transition metal complex which is coordinated with a monomer and is itself an active polymerization catalyst of the monomer.

Acknowledgment. The authors are grateful for the experimental assistance of Mr. N. Togashi and Mr. M. Nakai. The financial support of the Ministry of Education is gratefully acknowledged.

(4) For example, P. Cossee, J. Catalysis, 3, 80 (1964). (5) R. Cramer obtained nmr evidence of such a complex in the dimerization of ethylene: J. Am. Chem. Soc., 87, 4717 (1965).

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The Cleavage of $(CF_3P)_4$ by Primary and Secondary Phosphines and a Novel Insertion Reaction

Sir:

The chemical similarity of cyclopolyphosphines and cyclooctasulfur is exemplified by the interesting parallel between the reactions^{1,2}

$$(C_6H_5)_3P + \frac{1}{8}S_8 = (C_6H_5)_3P \rightarrow S$$
 (1)

$$(CH_3)_3P + \frac{1}{4}(CF_3P)_4 = (CH_3)_3P \rightarrow PCF_3$$
(2)

The observation³ that the S₈ ring is cleaved by primary phosphines suggested that cyclopolyphosphines might undergo a similar type of reaction. We now report that the reaction of CH_3PH_2 with $(CF_3P)_4$ (3 days at room temperature) proceeds virtually quantitatively according to the equation⁴

$${}^{1}/_{4}(CF_{3}P)_{4} + CH_{3}PH_{2} = CF_{3}PH_{2} + {}^{1}/_{5}(CH_{3}P)_{5}$$
 (3)

The extent of the above reaction appears to depend on the basicity of the phosphine. Thus, in a comparable reaction with $C_6H_5PH_2$ only 82.2% of the theo-

(1) P. D. Bartlett and G. Meguerian, J. Am. Chem. Soc., 78, 3710 (1956).

(2) A. B. Burg and W. Mahler, ibid., 83, 2388 (1961).

(3) L. Maier, *Helv. Chim. Acta*, 46, 1812 (1963). For a review, see L. Maier, "Topics in Phosphorus Chemistry," Vol. 2, Interscience

2. Match, Topics in Thispitols' formula (7), which is the science Publishers Inc., New York, N. Y., 1965, p 43. (4) Identification of CF_3PH_2 was made on the basis of its vapor tension of 45 mm at -78.5° [W. Mahler and A. B. Burg, J. Am. Chem. Soc., 80, 6161 (1958)] and proton nmr spectrum. The latter (neat liquid) consists of a pair of quartets centered at τ 6.48 with $J_{PH} = 10000$ sectors and τ 0.49 m topics. 199.99 cps and $J_{FCPH} = 11.90$ cps (S. L. Manatt, D. D. Elleman, A. H. Cowley, and A. B. Burg, to be published). The oily nonvolatile residue was identified as (CH₃P)5 by its complex proton nmr spectrum (A. H. Cowley, unpublished observation). For neat samples the spectrum consists of 15 clearly resolved peaks in the τ 8.21–8.82 region. Some of the resolution is lost in CDCl₃ solution.

retical yield of CF₃PH₂ was realized, and excess PH₃ failed to react with $(CF_3P)_4$ after 31 days at room temperature. In the $C_6H_5PH_2$ experiment the nonvolatile residue was identified as $(C_{\delta}H_{\delta}P)_{\delta}$ on the basis of its proton nmr spectrum⁵ (CS_2 solution).

The reaction of $(CF_3P)_4$ with $(CH_3)_2PH$ also proved interesting because one of the products resulted from insertion of a CF₃P group into a P-P bond. Fractionation of the volatiles resulting from the reaction of 0.5565 mmole of $(CF_3P)_4$ and 4.705 mmoles of $(CH_3)_2PH$ (1 day at room temperature) resulted in 1.586 mmoles of recovered (CH₃)₂PH, 1.706 mmoles of CF₃PH₂, 1.181 mmoles of $(CH_3)_4P_2$ (recognized by its vapor tension⁶ and characteristic "deceptively simple" proton nmr spectrum⁷), and 38.0 mg of a substance with a vapor tension of 1 mm at 24°. Elemental analysis of this material suggested that it was the new triphosphine $CF_{3}P[P(CH_{3})_{2}]_{2}$ (I). Anal. Calcd for $C_{5}H_{12}$ -F₃P₃: C, 27.02; H, 5.41. Found: C, 27.34; H, 5.51. The hypothesis that I arose from the reaction of $(CF_{3}P)_{4}$ with $(CH_{3})_{4}P_{2}$ was confirmed by a separate experiment in which a mixture of 1.175 mmoles of $(CF_3P)_4$ and 4.863 mmoles of $(CH_3)_4P_2$ was allowed to stand 13 days at room temperature. Fractionation of the volatiles resulted in a 69.6% yield of I. Anal. Calcd for C₅H₁₂F₃P₃: C, 27.02; H, 5.41. Found: C, 27.19; H, 5.17. Strong support for the triphosphine formulation came from the ¹⁹F nmr spectrum of I (neat liquid) which consisted of a pair of triplets assignable as $J_{PCF} = 40.2$ cps and $J_{PPCF} = 6.4$ cps.⁸ The molecular weight determination of I was made difficult by absorption into vacuum greases and waxes. However, the value 219.0 (calculated 222.1) is probably reliable. The ultraviolet spectrum of I consisted of a broad maximum at 2400 A and a shallow minimum at 2275 A. Ultraviolet absorption in this range is characteristic of polyphosphines9 and is presumably due to delocalization of lone-pair electrons across P-P bonds. The infrared spectrum of I also displayed the expected features: namely, C-H stretching at 2820, 2905, and 2965 cm⁻¹, C-F stretching at 1108 and 1133 cm⁻¹ (with shoulders at 1112, 1150, and 1170 cm⁻¹), and CH₃ deformations at 1290 and 1435 cm⁻¹. A broad band at 701 \mbox{cm}^{-1} is probably due to $\mbox{P-CH}_3$ stretching. Vapor tension data for I in the range 24-68° determine the equation $\log p = 7.3510 - 2176/T$, giving an estimated boiling point of approximately 220° and a Trouton constant of 20.3 eu.

The CF₃P insertion reaction, which in some respects resembles a carbene insertion, might prove to be a source of other compounds with nonmetal-nonmetal bonds. This possibility is under investigation.

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(9) A. H. Cowley, Chem. Rev., 65, 617 (1965), and references therein.

⁽⁵⁾ W. A. Henderson, M. Epstein, and F. S. Seichter, J. Am. Chem. Soc., 85, 2462 (1963). These authors called this cyclopolyphosphine form A of $(C_6H_5P)_3$. However, since that time this compound has been shown to be (C6H5P)5 in the solid state by J. J. Daly and L. Maier, Mature, 203, 1167 (1964); and J. J. Daly, J. Chem. Soc., 6147 (1964).
 (6) A. B. Burg, J. Am. Chem. Soc., 83, 2226 (1961).

⁽⁷⁾ R. K. Harris and R. G. Hayter, Can. J. Chem., 42, 2282 (1964).

⁽⁸⁾ These assignments compare with the values $J_{PCF} = 64.1$ cps and $J_{PPCF} = 7.9$ cps in the somewhat similar molecule (CH₃)₂P-P(CF₃)₂: S. L. Manatt, D. D. Elleman, A. H. Cowley, and A. B. Burg, to be published.

Pasadena, Calif., who recorded the nmr spectra of some of the reaction mixtures.

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1,3,7,9,13,15-Hexadehydro[18]annulene1

Sir:

1,5,9-Tridehydro[12]annulene (2), first discussed in 1948 by Sworski,² has been synthesized recently by two groups.^{3,4} This is a system containing 4n out-of-plane π electrons, formally derived from the (4n + 2) system benzene (1) by the insertion of three acetylene groupings at the places indicated. The nmr spectrum of 2 consists of a singlet at τ 5.58, and the comparatively high-field position appeared to provide experimental evidence for the existence of a paramagnetic ring current in $4n \pi$ electron systems.⁵ However, the possibility could not be excluded that the high-field position is due to the anisotropy of the triple bond.

We considered that information regarding this problem could be obtained by the preparation of



1,3,7,9,13,15-hexadehydro[18]annulene (3), formally derived from 1 by the insertion of three diacetylene groupings at the places indicated. The protons in this substance are in a similar environment to those in 2, but 3 contains (4n + 2) out-of-plane π electrons, and it should therefore possess a diamagnetic ring current.⁶ We now describe a synthesis of 3^7 , the nmr spectrum of which

(1) Part LIII in the series "Unsaturated Macrocyclic Compounds." For part LII, see R. H. Mitchell and F. Sondheimer, Tetrahedron, in press

(2) T. J. Sworski, J. Chem. Phys., 16, 550 (1948).

(3) R. Wolovsky and F. Sondheimer, J. Am. Chem. Soc., 87, 5720 (1965); F. Sondheimer, R. Wolovsky, P. J. Garratt, and I. C. Calder, ibid., 88, 2610 (1966).

(4) K. G. Untch and D. C. Wysocki, *ibid.*, 88, 2608 (1966).
(5) J. A. Pople and K. G. Untch, *ibid.*, 88, 4811 (1966); F. Baer,
H. Kuhn, and W. Regel, Z. Naturforsch., 22a, 103 (1967); H. C. Longuet-Higgins, Special Publication No. 21, The Chemical Society, London, p 109.

(6) See F. Sondheimer, Proc. Roy. Soc. (London), A297, 173 (1967); F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, Special Publication No. 21, The Chemical Society, London, p 75.

provides strong evidence that the high-field position of the resonance of 2 is indeed due to a paramagnetic ring current.

Reaction of hexa-1,5-divn-3-ol (4a)⁸ with p-toluenesulfonyl chloride (1.1 molar equiv) and pyridine (1.5 molar equiv) yielded 80% of the p-toluenesulfonate 4b, mp 74.5-75.0°. Treatment of 4b with excess 1,5diazabicyclo[4.3.0]non-5-ene⁹ in ether at room temperature for 1 hr¹⁰ gave rise to 70% of a mixture containing ca. 40% of cis-hex-3-ene-1,5-diyne (5) and ca. 60% of trans-hex-3-ene-1,5-diyne (6),¹¹ separated by preparative glpc. The cis isomer 5 (>99% pure by glpc) was a liquid showing λ_{max}^{MeOH} 250 m μ (ϵ 14,500) and 262 m μ (ϵ 12,500); ν_{max}^{film} (cm⁻¹) 3295 (s) (HC \equiv), 2105 (w), 2085 (w) (C=C), and 752 (m), 723 (m) (cis-C-H=CH), only very weak band (at 940) in 1000-900 region; nmr spectrum (CCl₄, 100 Mcps), 2 H singlet at τ 4.11 (olefinic protons) and 2 H singlet at τ 6.72 (acetylenic protons). The *trans* isomer 6 (>99%) pure by glpc) was a liquid showing $\lambda_{\max}^{\text{MeOH}}$ 251 m μ (ϵ 20,400) and 263 m μ (ϵ 18,100); ν_{\max}^{film} (cm⁻¹) 3300 (s) (HC \equiv), 2115 (w), 2090 (w) (C \equiv C), and 941 (m) (*trans*-CH=CH), no band in 800-700 region; nmr spectrum (CCl₄, 100 Mcps), 2 H singlet at τ 3.99 (olefinic protons) and 2 H singlet at τ 6.94 (acetylenic protons).

The crude mixture of 5 and 6 (from 1 part 4b) was oxidized with cupric acetate monohydrate (15 parts) in pyridine (100 parts) at room temperature for 2 hr. This reaction led to a mixture of products, from which the cyclic "trimer" $\mathbf{3}$ could be separated in 3.1% yield (based on 4b) by chromatography on alumina.¹² Substance 3 formed amber prisms (yellow in concentrated solution), which turned black at $ca. 75^{\circ}$ and then exploded at ca. 85° on attempted melting point determination (capillary); $\lambda_{\max}^{\text{cyclohexane}}$ 227 m μ (ϵ 25,500), 236 (21,500), 260 (5900), 315 sh (41,000), 317 (41,500), 333 (75,800), 357 (13,000), 366 (7400), 378 (15,500), 388 (17,600) and 405 sh (790); ν_{max}^{KBr} 2180 (w) cm⁻¹ and 2110 (w) cm⁻¹ (C=C); mass spectrum, molecular ion m/e222.047 (base peak) (calculated for ¹²C₁₈H₆, 222.047). Anal. Calcd for C₁₈H₆: C, 97.28, H, 2.72. Found: C, 97.29; H, 2.76. The crystalline substance decomposed within a few hours at room temperature but was relatively stable in dilute ether solution. The monocyclic nature of 3 was confirmed by catalytic hydrogenation in ethanol over platinum oxide, which led to cyclo-

(8) F. Sondheimer, Y. Amiel, and Y. Gaoni, ibid., 84, 270 (1962).

(9) H. Oediger, H. J. Kabbe, F. Möller, and K. Eiter, Chem. Ber., 99, 2012 (1966).

(10) For the base elimination of p-toluenesulfonates of β -hydroxyacetylenes to a mixture of conjugated cis- and trans-vinylacetylenes, see G. Eglinton and M. C. Whiting, J. Chem. Soc., 3650 (1950); J. L. H. Allan and M. C. Whiting, *ibid.*, 3314 (1953).

(11) See A. Roedig and K. Kiepert, Ann., 593, 55, 71 (1955); G. Peiffer, Bull. Soc. Chim. France, 537 (1963); T. Böhm-Gössl, W. Hunsmann, L. Rohrschneider, W. M. Schneider, and W. Ziegenbein, Chem. Ber., 96, 2504 (1963).

(12) In separate cupric acetate oxidation experiments, trans-hex-3ene-1,5-diyne (6) was found to give no 3, while the cis isomer 5 produced 3 in ca. 20% yield. Similarly, hexa-1,5-diyne on oxidation with cupric acetate in pyridine has been shown to yield the corresponding cyclic trimer, in addition to higher cyclic oligomers.7 By contrast, the ring compounds o-diethynylbenzene and 1,2-diethynylcyclohexene under these conditions gave the corresponding cyclic dimers, but none of the cyclic trimers: O. M. Behr, G. Eglinton, A. R. Galbraith, and R. A. Raphael, J. Chem. Soc., 3614 (1960); G. M. Pilling and F. Sondheimer, unpublished experiments.

⁽⁷⁾ A previous attempt to prepare 3 was unsuccessful.⁸ For the synthesis of other dehydro[18]annulenes, see F. Sondheimer and R. Wolovsky, J. Am. Chem. Soc., 84, 260 (1962); R. Wolovsky, ibid., 87, 3638 (1965).