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 ethyl–nickel 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.

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(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]

$$(C_6H_5)_3P + {}^1/_8S_8 = (C_6H_5)_3P{\rightarrow}S \qquad (1)$$

$$(CH_3)_3P + {}^1/_4(CF_3P)_4 = (CH_3)_3P{\rightarrow}PCF_3 \qquad (2)$$

The observation[3] that the S_8 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 equation[4]

$$^1/_4(CF_3P)_4 + CH_3PH_2 = CF_3PH_2 + {}^1/_5(CH_3P)_5 \qquad (3)$$

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 theoretical yield of CF_3PH_2 was realized, and excess PH_3 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 $(C_6H_5P)_5$ on the basis of its proton nmr spectrum[5] (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 CF_3P 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 $(CH_3)_2PH$, 1.706 mmoles of CF_3PH_2, 1.181 mmoles of $(CH_3)_4P_2$ (recognized by its vapor tension[6] and characteristic "deceptively simple" proton nmr spectrum[7]), 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 $CF_3P[P(CH_3)_2]_2$ (I). *Anal.* Calcd for $C_5H_{12}F_3P_3$: C, 27.02; H, 5.41. Found: C, 27.34; H, 5.51. The hypothesis that I arose from the reaction of $(CF_3P)_4$ with $(CH_3)_4P_2$ 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 $C_5H_{12}F_3P_3$: C, 27.02; H, 5.41. Found: C, 27.19; H, 5.17. Strong support for the triphosphine formulation came from the ^{19}F 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 polyphosphines[9] 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 CH_3 deformations at 1290 and 1435 cm^{-1}. A broad band at 701 cm^{-1} is probably due to 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 CF_3P 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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(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 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} = 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 $(CH_3P)_5$ 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 $CDCl_3$ solution.
(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 $(C_6H_5P)_4$. However, since that time this compound has been shown to be $(C_6H_5P)_5$ in the solid state by J. J. Daly and L. Maier, *Nature*, 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 $(CH_3)_2P$–$P(CF_3)_2$: S. L. Manatt, D. D. Elleman, A. H. Cowley, and A. B. Burg, to be published.
(9) A. H. Cowley, *Chem. Rev.*, 65, 617 (1965), and references therein.

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

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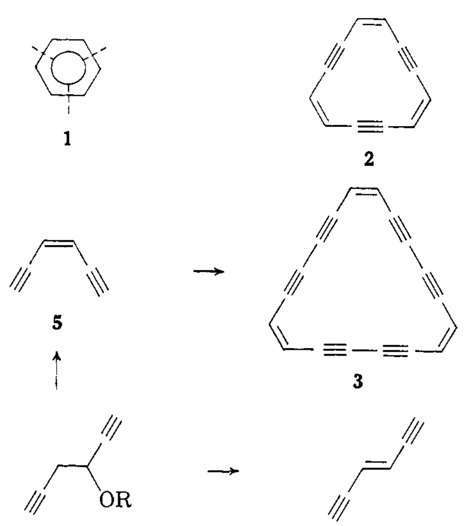
1,3,7,9,13,15-Hexadehydro[18]annulene[1]

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 4*n* out-of-plane π electrons, formally derived from the (4*n* + 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 4*n* π-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 **2** **5** **3** **4a**, R = H **b**, R = Ts **6**

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 (4*n* + 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 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-diyn-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 1,5-diazabicyclo[4.3.0]non-5-ene[9] in ether at room temperature for 1 hr[10] 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 mμ (ε 14,500) and 262 mμ (ε 12,500); ν_{max}^{film} (cm^{-1}) 3295 (s) (HC≡), 2105 (w), 2085 (w) (C≡C), and 752 (m), 723 (m) (*cis*-CH=CH), only very weak band (at 940) in 1000–900 region; nmr spectrum (CCl_4, 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 λ_{max}^{MeOH} 251 mμ (ε 20,400) and 263 mμ (ε 18,100); ν_{max}^{film} (cm^{-1}) 3300 (s) (HC≡), 2115 (w), 2090 (w) (C≡C), and 941 (m) (*trans*-CH=CH), no band in 800–700 region; nmr spectrum (CCl_4, 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" **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° and then exploded at *ca.* 85° on attempted melting point determination (capillary); $\lambda_{max}^{cyclohexane}$ 227 mμ (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/e* 222.047 (base peak) (calculated for $^{12}C_{18}H_6$, 222.047). *Anal.* Calcd for $C_{18}H_6$: 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-

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(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.

(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).

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(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-3-ene-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.