Correspondence

Geometrical Isomerism in the Trimeric Phosphonitrilic Series

Sir:

Although the essentially planar arrangement of atoms in the N_3P_3 ring with substituents on the phosphorus atoms lying in planes perpendicular to the ring clearly suggests the possibility of both geometrical and optical isomerism in compounds of the type $N_3P_3A_3B_3$,[1] the only reported example is the substance $N_3P_3Cl_3[N(C_2H_5)_2]_3$, which was isolated in liquid and solid forms.[2] Geometrical isomers now have been identified for the compounds $N_3P_3(C_6H_5)_3(NH\textit{n}\text{-}C_3H_7)$ and $N_3P_3(C_6H_5)_3(NH\textit{n}\text{-}C_4H_9)_3$.

An extension of the procedure used in the successful syntheses of trimeric and tetrameric phosphonitrilic bromides[3,4] to the reaction between phenylphosphorus(III) dibromide, bromine, and ammonium bromide in *sym*-tetrachloroethane for a period of 12 days at 140–145° yielded a crystalline product (m.p. 135–145°, yield *ca.* 70%). That this material contained the N_3P_3 ring and not the N_4P_4 ring was indicated by well defined P–N stretching frequencies[4] at 1175 and 1124 cm.$^{-1}$ and none in the 1272-cm.$^{-1}$ region. Recrystallization from *n*-heptane gave fractions melting at 155–159° and 190–195° and characterized, respectively, by P–N stretching frequencies at 1180 and 1120 cm.$^{-1}$ and 1180 and 1130 cm.$^{-1}$ and by P–C_6H_5 frequencies at 1443 and 1445 cm.$^{-1}$.

Anal. Calcd. for $N_3P_3(C_6H_5)_3Br_3$: C, 35.67; H, 2.49; N, 6.93; P, 15.33; for $N_3P_3(C_6H_5)_3Br_2Cl$: C, 38.49; H, 2.69; N, 7.48; P, 16.55. Found (155–159° fraction): C, 37.94; H, 2.67; N, 7.19; P, 16.81; (190–195° fraction): C, 37.51; H, 2.59; N, 7.21; P, 16.48.

It is probable that the two fractions result from geometrical isomerism, but the facts that they both give qualitative tests for chlorine, agree better microanalytically with values calculated for chlorobromo species, and melt over ranges all suggest that they must be mixtures of the possible chlorobromo isomers. The source of chlorine is obscure. Although the initial phenylphosphorus dibromide was obtained by exchange between the dichloride and hydrogen bromide in boiling phosphorus(III) bromide,[5] its microanalysis indicated the absence of chlorine. It may be that exchange with the *sym*-tetrachloroethane solvent occurs. Attempts to eliminate this possibility by use of *sym*-tetrabromoethane have not yet resulted in satisfactory yields.

More definitive information on isomerism was obtained from the *n*-propylamino and *n*-butylamino compounds prepared by refluxing the initial $N_3P_3(C_6H_5)_3Br_2Cl$ mixture with the amine in benzene solution, removing the amine hydrohalides by filtration, and evaporating the clear benzene solution.[6] Purification by recrystallization (from *n*-heptane for the propyl compound and from 40–60° petroleum ether for the butyl compound) gave products in 70–80% yields but melting over ranges. However, fractional crystallization from the same solvents gave, in each instance, two fractions with different but sharply defined melting points. Numerical data for these substances are summarized in Table I.

It is apparent that each amino derivative exists in two forms that differ substantially from each other only in melting point. Inasmuch as molecular weight and infrared data indicate that these are all trimeric and inasmuch as the P–C_6H_5 bonds are retained in each, it is most logical to conclude that geometrically isomeric forms have been prepared. Preliminary proton magnetic resonance spectra for the two forms of each amino derivative are substantially identical except in the CH_2 region. Here the spectrum for the low-melting form is somewhat more complex and noticeably broader. A reasonable interpretation is that this difference is due to isomerism and that the low-melting materials have the *trans* configuration.

Acknowledgment.—This investigation was supported by the Materials Laboratory of Wright Air Development Command, Wright-Patterson Air Force Base, Ohio, under Contract AF-33 (616)-5486. Reproduction of this communication

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TABLE I

PROPERTIES OF COMPOUNDS $N_3P_3(C_6H_5)_3(NHR)_3$

Compound	M.p., °C.	Mol. wt. Calcd.	Mol. wt. Found[a]	P–N freq., cm.$^{-1}$	P–C_6H_5 freq., cm.$^{-1}$	Analysis, %[b] C	H	N	P
$N_3P_3(C_6H_5)_3(NH\mathit{n}\text{-}C_3H_7)_3$						59.98	7.27	15.54	17.19
	92–93	540	519	1190, 1120	1440	60.15	7.19	15.34	17.20
	128–129	540	530	1190, 1128	1442	60.01	7.22	15.26	17.34
$N_3P_3(C_6H_5)_3(NH\mathit{n}\text{-}C_4H_9)_3$						61.83	7.78	14.42	15.95
	78–79	582	595	1185, 1123	1440	62.14	7.71	14.66	16.13
	97–98	582	595	1185, 1125	1440	61.47	7.78	14.35	15.85

[a] Ebullioscopic ($CHCl_3$ for propyl compound; C_6H_6 for butyl). [b] First line for each substance calculated; others found.

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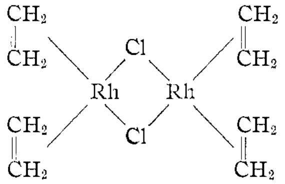
NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
T. MOELLER
P. NANNELLI

RECEIVED MAY 22, 1962

μ-Dichlorotetraethylenedirhodium(I)

Sir:

We wish to report the first synthesis of a coordination compound of monovalent rhodium and a monoölefin. μ-Dichlorotetraethylenedirhodium(I) is obtained with remarkable ease from



(I)

ethylene and hydrated rhodium(III) chloride in aqueous methanol. In this reaction (see eq. 1) rhodium(III) is reduced to rhodium(I), and an equivalent amount of ethylene is oxidized to acetaldehyde in a manner reminiscent of Smidt's[1] palladium-catalyzed aldehyde synthesis. The sparingly soluble orange-red complex (I) crystallizes from the reaction mixture. The stability of I is rather surprising in view of the lability of dichlorodiethyleneplatinum(II)[2] but may be ascribed to the high lattice energy of the solid as indicated by its low solubility.

$$2RhCl_3 + 2H_2O + 6C_2H_4 \longrightarrow \underset{(I)}{(C_2H_4)_4Rh_2Cl_2} + 2CH_3CHO + 4HCl \quad (1)$$

In a typical preparation, a solution of 20 g. of "rhodium trichloride trihydrate" (obtained from Engelhard Industries, actual composition $RhCl_{3.33}(H_2O)_{2.30}$) in 30 ml. of water was added to 500 ml. of methanol, and a slow stream of ethylene was bubbled through the stirred solution. After about 1 hr. the product began to crystallize, and, after 7 hr., 9.65 g. of I was collected by filtration, washed with methanol and ether, and dried in air. Further similar treatment of the filtrate with ethylene yielded 1.27 g. more of I. Since recrystallization of I is difficult, larger crystals suitable for X-ray diffraction measurements were obtained by a slower reaction at 0° with ethylene partial pressures of less than an atmosphere.

Elemental analyses correspond to the postulated composition. Calcd. for C_4H_8RhCl: C, 24.70; H, 4.15; Rh, 52.90; Cl, 18.23. Found C, 24.81; H, 4.17; Rh, 51.23; Cl, 18.26. Infrared absorption (KBr wafer) at 3.20 and 3.33 μ is attributed to the coördinated ethylene –C–H stretching vibration, while absorption at 6.58 μ is assigned to C═C stretching vibration.[3] Preliminary X-ray diffraction studies indicated that the crystals have a tetragonal structure and that the unit cell, which contains eight formula weights of the chlorine-bridged complex, has the dimensions A_0 = 10.07 Å., C_0 = 23.50 Å. Structures have been assigned to two related compounds on the basis of X-ray diffraction. Dahl, Martell, and Wampler[4] have reported that in red $(CO)_4Rh_2Cl_2$, the rhodium and bridging chloride ions lie in two planes which form an angle of 124°. Furthermore, $(CO)_4Rh_2Cl_2$ units appear to be connected by Rh–Rh bonds. On the other hand, Ibers and Snyder[5] ascribe a planar monomer structure to yellow $(C_8H_{14})Rh_2Cl_2$. On the basis of color and low solubility we are inclined to

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