# Notes

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## Staudinger Reaction of $P_2(NCH_3)_6$

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In a recent publication we described[2] the action of phenyl azide on $P_4O_6$ and $P_4(NCH_3)_6$. It seemed valuable to extend this reaction to another type of birdcage molecule, namely, $P[N(CH_3)N(CH_3)]_3P$. This compound, I, which may be named tris(1,2-dimethylhydrazino)diphosphine or 2,3,5,6,7,8-hexamethyl-2,3,5,6,7,8-hexaaza-1,4-diphosphabicyclo[2.2.2]-octane, was first prepared[3a] in 1965 and a recent X-ray structure determination is available.[4] Oxidations of the tervalent phosphorus atoms with conservation of the cage structure have been carried out using oxygen, sulfur, diborane, $Mo(CO)_6$,[3] or $Al_2(CH_3)_6$.[5] Opening of the cage structure occurs upon reaction with phosphorus trichloride.[6] We wish to report herein the reaction of I with two azides, namely, phenyl azide and diphenylphosphinyl azide (Staudinger reaction.[7]).

## Experimental Section

**Materials.** All solvents used were Spectrograde quality and showed no evidence of containing water. Prior to use they were saturated with dry nitrogen. Handling of I was carried out under dry nitrogen due to the extreme sensitivity to moisture and oxygen. The general procedure as in an earlier paper[2] was followed. Compound 1 was prepared as described in the literature[3a] in 88.7% yield [$\delta_P$ − 107.5 ppm (benzene), $J_{PNCH_3}$ = 7.8 Hz], as was phenyl azide.[8] Diphenylphosphinyl azide, $(C_6H_5)_2P(O)N_3$, was purchased from Pfaltz and Bauer, Inc., and used as received.

**Analyses.** Elemental analyses were carried out by Chemalytics, Inc., Tempe, Ariz. Melting points were obtained on a Mel-Temp melting point block and are uncorrected.

**Spectra.** Infrared (ir) spectra were recorded on KBr pellets (0.5%) with a Beckman IR-10 spectrometer. $^1H$ nuclear magnetic resonance (nmr) spectra were obtained with a Varian A-60 spectrometer in $CDCl_3$ solutions with TMS as internal standard. Most of the $^{31}P$ nmr spectra were run with a Varian XL-100-15 spectrometer, operating at a frequency of 40.55 MHz and locked onto the deuterium resonance of $D_2O$. The samples were contained in 12-mm o.d. tubes into which was concentrically inserted, using Teflon spacers, a 5-mm o.d. tube containing the $D_2O$. Some $^{31}P$ nmr spectra were recorded on a JEOL C-60 HL instrument at 24.3 MHz. $^{31}P$ spectra were decoupled from the protons and chemical shifts are reported *vs.* external 85% $H_3PO_4$.

**Reaction of I with Phenyl Azide.** An amount of 3.30 g of I was dissolved in 10 ml of benzene (nitrogen atmosphere) and 3.33 g of phenyl azide in 10 ml of benzene (corresponding to a ratio $P_2(NCH_3)_6 : C_6H_5N_3$ = 1:2) was added with a syringe through a serum stopper. Upon slightly heating to *ca.* 40° (water bath) a vigorous reaction occurred and a white precipitate was formed. Stirring was continued for 15 min and the precipitate was filtered in a glove box and dried *in vacuo*, giving white crystals, yield 4.45 g (76.2% of theory); mp 243–244° dec.

*Anal.* Calcd for $C_{18}H_{28}N_8P_2$: C, 51.67; H, 6.74; N, 26.78; P, 14.80. Found: C, 51.97; H, 6.57; N, 26.62; P, 14.64.

Ir: 3060 (m), 2930 (m), 2890 (m), 1590 (vs), 1500 (vs), 1480 (s), 1440 (s), 1390–1360 (vs, b), 1270 (m), 1225 (w), 1200 (vs), 1170 (s), 1135 (w), 1095 (vs), 1070 (m, sh), 1050 (vs), 970 (vs), 890 (m), 790 (vs), 750 (vs), 710 (s), 690 (vs), 675 (s), 660 (vs), 625 (w), 570 (s), 500 (s), 490 (s) $cm^{-1}$.

Nmr: proton spectrum, $\tau_{C_6H_5}$ 3.07 (complex multiplet, 10 H), $\tau_{CH_3}$ 7.02 (triplet, 18 H), $J_{PNCH_3}$ = 5.5 Hz; phosphorus spectrum, $\delta_P$ +6.6 ppm ($CHCl_3$).

A I:$C_6H_5N_3$ ratio of 1:1 and/or adding compound I to phenyl azide resulted only in the isolation of the compound described above, excess compound I being recovered in the filtrate.

**Reaction of I with $(C_6H_5)_2P(O)N_3$ (1:2).** As previously, 3.25 g of I was dissolved in 10 ml of benzene and a solution of 6.42 g of diphenylphosphinyl azide in 10 ml benzene was added. Refluxing for 3 hr and cooling gave a white precipitate which was filtered in the absence of moisture and oxygen, washed two times with 10 ml of hexane, and dried *in vacuo*, giving white crystals, yield 6.35 g (69.2% of theory); mp 285–286° dec.

*Anal.* Calcd for $C_{30}H_{38}N_8O_2P_4$: C, 54.05; H, 5.75; N, 16.81; P, 18.58; O, 4.80. Found: C, 54.33; H, 5.89; N, 16.89; P, 18.51; O, 4.18 (by difference).

Ir: 3060 (m), 2970 (m), 2940 (s), 2900 (m), 1595 (m), 1490 (s, sh), 1440 (vs), 1400–1270 (vs, b), 1200 (vs), 1100 (vs), 1055 (vs), 1030 (s), 980–970 (vs, b), 845 (m), 780 (m), 760 (s), 745 (s), 720–680 (vs, b), 640 (w), 540–510 (vs, b), 495 (vs), 450 (vs) $cm^{-1}$.

Nmr: proton spectrum, $\tau_{C_6H_5}$ 2.17, 2.32, 2.65 (complex multiplet, 20 H), $\tau_{CH_3}$ 7.07 (triplet, 18 H), $J_{PNCH_3}$ = 6.0 Hz; phosphorus spectrum (proton decoupled, in $CH_2Cl_2$), $\delta_{P_A}$ −2.7 ppm (doublet), $\delta_{P_A'}$ = −2.5 ppm (doublet), $\delta_{P_B}$ −11.5 ppm (doublet), $\delta_{P_B'}$ −11.2 ppm (doublet), $J_{P_AP_B} = J_{P_A'P_B'} = 10.7 \pm 0.1$ Hz; $P_A:P_B = P_A':P_B'$ = 1:1 (theoretical 1:1).

## Results and Discussion

The formation of the compounds II and III according to eq 1 proceeds readily and, contrary to earlier work[2] with other birdcage molecules, monosubstitution with the phenylimino group was not observed. Evidence for II is given by the pmr spectra. The oxidation of the tervalent phosphorus in II is clearly seen by the large change in $^{31}P$ chemical shift (from $\delta_P$ −107.5 ppm in I to +6.6 ppm in II), while the $^1H$ nmr spectrum exhibits the correct shifts, splitting pattern, and areas for the phenyl and methyl groups. Furthermore, the infrared spectrum of II contains the $\nu_{P=N}$ at 1380–1360 $cm^{-1}$ and exhibits appropriate changes in the P-N region (850–690 $cm^{-1}$).

$$\begin{array}{lll} P[N(CH_3)N(CH_3)]_3P + 2RN_3 \rightarrow & RNP[N(CH_3)N(CH_3)]_3PNR + 2N_2 & \\ \qquad\qquad \text{I} & \text{II, } R = C_6H_5 & (1) \\ & \text{III, } R = (C_6H_5)_2P(O) & \end{array}$$

For compound III the relative areas of the methyl and phenyl groups in the $^1H$ nmr spectrum and of the endocyclic and exocyclic phosphorus atoms in the $^{31}P$ spectrum are in agreement with the elemental analysis in supporting the structure $(C_6H_5)_2(O)PNP[N(CH_3)N(CH_3)]_3PNP(O)(C_6H_5)_2$. However, the nmr patterns give additional information. Thus compound I exhibits a pseudo triplet in the methyl-group region of the $^1H$ spectrum; whereas compounds II and III show a simple 1:2:1 triplet. Furthermore, the $^{31}P$ spectrum of III exhibits eight peaks when there is broad-band decoupling

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[2] M. Bermann and J. R. Van Wazer, *Inorg. Chem.*, 12, 2186 (1973).

[3] (a) D. S. Payne, H. Noth, and G. Henniger, *Chem. Commun.*, 327 (1965); R. Goetze, H. Noth, and D. S. Payne, *Chem. Ber.*, 105, 2637 (1972); (b) J. W. Gilje and K. Seff, *Inorg. Chem.*, 11, 1643 (1972).

[4] W. VanDoorne, G. W. Hunt, R. W. Perry, and A. W. Cordes, *Inorg. Chem.*, 10, 2591 (1971).

[5] S. F. Spangenberg and H. H. Sisler, *Inorg. Chem.*, 8, 1004 (1969).

[6] T. T. Bopp, M. D. Havlicek, and J. W. Gilje, *J. Amer. Chem. Soc.*, 93, 3051 (1971); M. D. Havlicek and J. W. Gilje, *Inorg. Chem.*, 11, 1624 (1972).

[7] For a comprehensive review of this reaction up to 1966, see G. Singh and H. Zimmer, *Organometal. Chem. Rev., Sect. A*, 2, 279 (1967).

[8] R. O. Lindsay and C. F. H. Allen, "Organic Syntheses," Collect. Vol. 3, Wiley, New York, N. Y., 1955, p 710.

of the hydrogens, as compared to a singlet for compound II under the same conditions. Without this decoupling, the $^{31}P$ spectrum of III shows only two broad humps, one centered at $-2.6$ ppm and the other at $-11.3$ ppm. With broad-band hydrogen decoupling, each of these humps is resolved into four lines apparently of equal areas assignable to a pair of doublets due to P-P splitting. In order to determine the coupling constant, the $^{31}P$ spectrum of III was run at 24.3 MHz as well as at the usual frequency of 40.55 MHz. This showed that for the upfield as well as the downfield set of four lines, the coupling constant equals 10.7 ± 0.1 Hz at both magnetic field strengths.

Since the phosphorus chemical shift of compound II is +6.6 ppm and the chemical shift for diphenylphosphinyl azide, $(C_6H_5)_2P(O)N_3$, is $-28.7$ ppm, we assign the hump observed without hydrogen decoupling at $-2.6$ ppm to the endocyclic phosphorus of compound III and the hump at $-11.3$ ppm to the exocyclic phosphorus. The broad-band hydrogen decoupling shows that in III there are two kinds of endocyclic phosphorus, $\delta_{P_A}$ $-2.7$ ppm and $\delta_{P_{A'}}$ $-2.5$ ppm, and two kinds of exocyclic phosphorus, $\delta_{P_B}$ $-11.5$ ppm and $\delta_{P_{B'}} = -11.2$ ppm, with $J_{P_AP_B}$ and $J_{P_{A'}P_{B'}} = 10.7$ Hz.

The presence of A and A$'$ as well as B and B$'$ species may be indicative of geometrical isomerism of III. Two factors act to support the concept of an effective geometrical isomerism and simultaneously to complicate its interpretation. First of all, the two perpendicular $\pi$ orbitals in the phosphorimide bond (usually written $\rightarrow$>P=N–) are filled to sufficiently equal amounts[9] so that some rotation about this bond may well occur. Secondly, the cage structure will probably allow[10] electronic short-circuiting across it (*i.e.*, by a through-bond mechanism[11]), thereby enabling the rotational configuration of a diphenylphosphoryl group at one end of the molecule to have an influence on the similar group at the other end. However, we find it difficult to rationalize the essentially equal peak areas of the nmr multiplicity when ascribed to rotational isomerism.

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**Registry No.** I, 3478-74-8; $C_6H_5N_3$, 622-37-7; $(C_6H_5)_2P(O)N_3$, 4129-17-3; II, 42975-97-3; III, 42975-98-4.

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[9] For a somewhat similar situation see I. Absar and J. R. Van Wazer, *J. Amer. Chem. Soc.*, 94, 2382 (1972).

[10] P. J. Krusic, T. A. Rettig, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 94, 995 (1972).

[11] R. Hoffmann, *Accounts Chem. Res.*, 4, 1 (1971).

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## Kinetics of the Reactions of Tetrahalo Complexes of Palladium(II) and Platinum(II) with 1,10-Phenanthroline

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The rate law for substitution reactions of most platinum(II) and palladium(II) complexes is

$$\text{rate} = k_1[\text{M}] + k_2[\text{M}][\text{L}] \tag{1}$$

where M is the metal complex and L is the entering ligand.[1] The second-order term is attributed to direct attack by L (reaction 2), while the first-order term is the result of a rate-

$$\text{MA}_4 + \text{L} \rightarrow \text{MA}_3\text{L} + \text{A} \tag{2}$$

determining attack by the solvent, S (reaction 3). Recently,

$$\text{MA}_4{}^{2-} + \text{S} \rightarrow \text{MA}_3\text{S} + \text{A} \xrightarrow[+\text{L}]{} \text{MA}_3\text{L} + \text{S} \tag{3}$$

data were published[2-16] for some substitution reactions of tetrahalo complexes, $MX_4{}^{2-}$, mostly $PtCl_4{}^{2-}$. Few if any of these reactions were found to have rate laws with first-order terms, perhaps in some cases because aquation of $PtCl_4{}^{2-}$ is fairly rapid, and since water is not very different from chloride either as a leaving group or as a trans labilizing ligand, $Pt(H_2O)Cl_3{}^-$ is similar in reactivity to $PtCl_4{}^{2-}$. Although the product may be formed *via* a solvated intermediate, formation of the intermediate is not the rate-determining step, and the rate law contains two second-order terms[9]

$$\text{rate} = k_2[\text{MX}_4{}^{2-}][\text{L}] + k_2'[\text{MX}_3\text{S}^-][\text{L}] \tag{4}$$

The kinetics of reaction 5 has been examined for M = Pd

$$\text{MX}_4{}^{2-} + \text{AA} \xrightarrow{k_{\text{obsd}}} \text{M(AA)X}_2 + 2\text{X}^- \tag{5}$$

and Pt, AA = 1,10-phenanthroline (phen) and 2,2$'$-bipyridyl, and X = Cl.[9,14,16] This paper reports an extension of the research to systems M = Pd and Pt, AA = phen, and X = Br and I. The system M = Pt, AA = phen, and X = Cl was reexamined because the supporting electrolyte used in ref 9 was found to affect the rates of some of the reactions. New kinetics constants are reported for this system. The purpose of the research was to find how changing the halide affected the reaction rate and to determine whether other halides gave complexes that behaved like the chloro complexes in not having a first-order term in the rate law.

### Experimental Section

**Chemicals.** Potassium tetrabromopalladate(II) was obtained by twice evaporating a solution of $K_2PdCl_4$ (10 g) in 48% HBr (150 ml) to the point of crystallization on a steam bath. As the solution cooled, brown needlelike crystals formed, which were filtered out and dried under vacuum; yield 10.1 g (65%). *Anal.* Calcd for $K_2PdBr_4$: Pd, 21.1; Br, 63.4. Found: Pd, 21.0; Br, 63.3. Potassium tetrabromoplatinate(II) cannot be prepared by the method given above, because platinum(II) is oxidized to platinum(IV) by the bromine in

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[1] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 377.

[2] L. F. Grantham, T. S. Elleman, and D. S. Martin, *J. Amer. Chem. Soc.*, 77, 2956 (1955).

[3] M. A. Tucker, C. B. Colvin, and D. S. Martin, *Inorg. Chem.*, 3, 1373 (1964).

[4] L. Cattalini, A. Orio, and M. Nicolini, *J. Amer. Chem. Soc.*, 88, 5734 (1966).

[5] C. B. Colvin, R. G. Gunther, L. D. Hunter, J. A. McLean, M. A. Tucker, and D. S. Martin, *Inorg. Chim. Acta*, 2, 487 (1968).

[6] R. M. Milburn and L. M. Venanzi, *Inorg. Chim. Acta*, 2, 97 (1968).

[7] E. D. Smith, J. A. McLean, and J. E. Teggins, *Inorg. Chem.*, 8, 1872 (1969).

[8] R. Pietropaolo, M. Graziani, and U. Belluco, *Inorg. Chem.*, 8, 1506 (1969).

[9] F. A. Palocsay and J. V. Rund, *Inorg. Chem.*, 8, 524 (1969).

[10] J. V. Rund and F. A. Palocsay, *Inorg. Chem.*, 8, 2242 (1969).

[11] J. H. Cawley and J. V. Rund, *J. Inorg. Nucl. Chem.*, 32, 1406 (1970).

[12] G. Dolcetti, R. Pietropaola, and U. Belluco, *Inorg. Chem.*, 9, 553 (1970).

[13] R. A. Reinhardt and W. W. Monk, *Inorg. Chem.*, 9, 2026 (1970).

[14] J. V. Rund, *Inorg. Chem.*, 9, 1211 (1970).

[15] R. Pietropaolo, P. Uguagliati, T. Boschi, B. Crociani, and U. Belluco, *J. Catal.*, 11, 499 (1972).

[16] D. E. Schwab and J. V. Rund, *Inorg. Chem.*, 11, 499 (1972).