Table I. X-Ray Powder Diffraction Data for PuN

Lattice planes (*hkl*)	PuN[a] d(Å)	Annealed reaction product[b] d(Å)
(111)	2.83	2.83
(200)	2.45	2.45
(220)	1.73	1.73
(311)	1.48	1.48
(222)	1.42	1.42
(400)	1.23	1.23
(331)	1.12	1.13
(420)	1.10	1.10
(422)	1.00	1.00
(511)	0.943	0.944
(440)	0.867	0.868
(531)	0.829	0.830
(600)	0.818	0.818

Calculated lattice parameters: [a] PuN sample (prepared by conventional techniques at Oak Ridge National Laboratory), a_0 = 4.905 ± 0.001 Å. [b] Annealed reaction product: a_0 = 4.909 ± 0.001 Å; PuN a_0 = 4.903–4.908 Å (J. M. Cleveland, "The Chemistry of Plutonium," Gordon and Breach, New York, N. Y., 1970, p 413).

shown in Table I, was that of PuN and thus confirmed the identity of the product and the absence of an appreciable amount of metallic plutonium. Since the samples were heated *in vacuo* and since their nitrogen content did not increase during heating, the possibility that the nitride was formed during annealing must be ruled out.

The relatively complete reaction to form plutonium nitride contrasts with the behavior of the transition metals cited above, which generally form mixtures of the metal, the amide, and the nitride. We believe that this difference is caused primarily by the greater reactivity of plutonium. A possible mechanism involves reduction of plutonium(III) to plutonium(0), which then reacts with ammonia to form the nitride. Although metallic plutonium and plutonium hydride do not react with ammonia at an appreciable rate at low temperatures, the reaction is rapid at 600° and in fact is a common method for the preparation of PuN. In the present case, individual atoms of plutonium could react with ammonia as soon as they are formed, before they have an opportunity to aggregate into larger—and hence less reactive—particles. Under these conditions, it is reasonable to expect that reaction with ammonia could occur at low temperatures. Support for this postulated mechanism was also obtained from an experiment in which an ammonia solution of PuI_3 was electrolyzed to produce a cathode deposit containing 3.4% nitrogen, suggesting partial conversion of the metal deposit to the nitride. (This experiment was not repeated because of the formation of explosive NI_3 on the anode.) The reaction would not occur as readily with transition metals, however, because of their lower reactivity.

Another possible mechanism involves the formation of small quantities of plutonium(0), which catalyzes the reaction of sodium with ammonia to form amide; the latter reacts with plutonium(III) to produce plutonium amide which is then deammoniated to form the nitride. This possibility was investigated by treating a $NaNH_2$ solution in ammonia with a solution of PuI_3 in the same solvent; a red-brown gelatinous precipitate was obtained which, after washing and vacuum drying, was found to contain less than 2% nitrogen—far too low for either PuN or $Pu(NH_2)_3$. (Also, the infrared spectrum of the product indicated the absence of N–H bonds.) Hence, the mechanism involving formation of plutonium amide appears unlikely.

In addition, the potassium solutions used in the earlier work are known to have a greater tendency than sodium toward ammonolysis to form the amide,[14] and this can react competitively with metal ions to precipitate the respective amide, thus yielding a mixed product. Use of sodium in the present experiments would therefore lead to a purer precipitate.

Reactions of uranium and thorium have also been investigated. Results of these experiments, as well as a more complete description of the plutonium studies and their possible practical significance will be published elsewhere.

Acknowledgment. The authors thank R. S. Cichorz and H. L. Bramlett for the infrared and X-ray analyses. This work was performed for the U.S. Atomic Energy Commission under Contract AT(29-1)-1106.

---

(14) J. Kleinberg, W. J. Argersinger, Jr., and G. Griswold, "Inorganic Chemistry," D. C. Heath, Boston, Mass. 1960, pp 306–307.

J. M. Cleveland,* G. H. Bryan
C. R. Heiple, R. J. Sironen
The Dow Chemical Company, Rocky Flats Division
Golden, Colorado 80401
Received January 7, 1974

Synthesis and Characterization of Di-μ-thiocyanato-bis[hydrogen bis(diphenylphosphinato)]dipalladium(II). A Complex Containing a Novel Symmetrically Hydrogen-Bonded Anion

Sir:

The reactions of coordinated ligands have provided synthetic routes to many novel compounds, such as metal carbene complexes or macrocyclic chelates. The reactivity of coordinated phosphorus ligands,[1] however, has not been studied extensively in spite of the importance of phosphines in coordination chemistry. The tertiary alkyl- or arylphosphine complexes were reported to be resistant to attack by water although the chlorophosphine complexes of Pt(II) and Pd(II) can be readily hydrolyzed.[2] In contrast, we have found that the acetylenic phosphine complexes $MCl_2(Ph_2PCCF_3)_2$, M = Pd or Pt and Ph is phenyl, undergo hydrolysis with cleavage of the alkynyl groups and the formation of chloro-bridged dimers. The analogous bromo and thiocyanato complexes were prepared by metathetical reactions. The unusual nature of these complexes prompted an X-ray crystal structure study of the thiocyanato-bridged species $Pd_2(SCN)_2[(Ph_2PO)_2H]_2$ which has revealed the existence of the unusual hydrogen bis(diphenylphosphinate) anion. This anion contains a rare symmetrical hydrogen bond between the Ph_2PO moieties. Furthermore, our results may be of more

---

(1) Recent studies which illustrate the potential synthetic utility of such reactions include the following: (a) the deprotonation and subsequent alkylation of primary and secondary phosphine complexes reported by P. M. Treichel, W. M. Douglas, and W. K. Dean, *Inorg. Chem.*, **11**, 1615 (1972), and references therein; (b) the debromination of PF_2Br complexes reported by W. M. Douglas and J. K. Ruff, *ibid.*, **11**, 901 (1972) and D. P. Bauer, W. M. Douglas, and J. K. Ruff, *J. Organometal. Chem.*, **57**, C19 (1973); and (c) addition reactions of coordinated phosphines studied by M. A. Bennett, K. Hoskins, W. R. Kneen, R. S. Nyholm, P. B. Hitchcock, R. Mason, G. B. Robertson, and A. D. C. Towl, *J. Amer. Chem. Soc.*, **93**, 4592 (1971), and references therein.

(2) J. Chatt and B. T. Heaton, *J. Chem. Soc. A*, 2745 (1968).

general significance in that complexes previously formulated as $\{PdCl[(RO)_2PO][(RO)_2POH]\}$ (R = Et, Ph)[3,4] or $(Et_3As)PtCl[(RO)_2PO][(RO)_2POH]$ (R = Me, Ph)[4] may be best reformulated with hydrogen bis{dialkyl(aryl)-phosphonate} anions.

The complex $PdCl_2(Ph_2PC{\equiv}CCF_3)_2$ in aqueous ethanol at room temperature (5 hr) is easily converted into $\{PdCl[(Ph_2PO)_2H]\}_2$. Hydrolysis of the analogous platinum complex requires several hours under reflux. The yellow crystals of $\{PdCl[Ph_2PO]_2H\}_2$ show no infrared absorptions due to either $\nu(C{\equiv}C)$ or $\nu(C{-}F)$ but have strong bands near 1100 cm^{-1} which are typical of $\nu(P{-}O)$ for coordinated Ph_2PO groups. The ^{19}F nmr spectra confirmed the absence of fluorine and the ^1H spectra at 100 MHz in CD_2Cl_2 exhibited multiplet resonances from the phenyl protons (20 protons at δ 7.45) and a broad unresolved signal (one proton at δ 4.75) due to the hydrogen on the anion. In the far-infrared spectrum only one frequency was found for $\nu(M{-}Cl)$ (273 cm^{-1}).

The pale yellow crystals of the thiocyanate derivative are monoclinic with cell dimensions of a = 10.323 (2), b = 13.340 (2), c = 18.392 (2) Å, and β = 100.14 (1)°. The space group is $P2_1/c$ and with four molecules of $C_{25}H_{21}NO_2P_2SPd$, the calculated density is 1.513 g cm^{-3}, compared to an experimental value of 1.50 g cm^{-3}. The intensity data were measured using a Syntex P1 diffractometer with Cu Kα radiation. The structure was solved by the heavy atom method and refined by least-squares techniques. The locations of all the hydrogen atoms, including the hydrogen between the two P-O groups, were determined from a difference Fourier synthesis. Refinement of the nonhydrogen atoms with anisotropic thermal parameters and the hydrogen atoms with individual isotropic thermal parameters reduced R (the usual residual) to 0.053 for the 2486 observed reflections used in the analysis. For final atomic parameters and structure factors, see paragraph at end of paper regarding supplementary material.

The molecular structure, atomic numbering, and the thermal ellipsoids are illustrated in Figure 1. The structure consists of centrosymmetric thiocyanate bridged dimers. The palladium atom is coordinated in square planar fashion to a nitrogen and a sulfur atom from the bridging thiocyanates and the two phosphorus atoms of the unusual, symmetrically hydrogen-bonded anion. The Pd-N1 distance of 2.078 (7) Å and especially the Pd-S1 distance of 2.453 (2) Å are both longer than the distances reported in other related diphosphine-palladium-thiocyanate complexes.[5] The lengthening of the Pd-N and Pd-S bonds may indicate a greater trans influence for the $(PhO)_2PO$ ligand compared to R_3P, as has been suggested.[6,7]

Of great interest is the presence of the $[(PhO)_2PO]H$ anion which contains a symmetrical O···H···O hydrogen bond. The O1···O2 distance of 2.421 (7) Å is one of the shortest known for acid salts.[8] An O···O distance of less than 2.5 Å is generally regarded as definitive evidence for a symmetrical hydrogen bond.[9] The P-O distances (P1-O1 of 1.549 (6) and P2-O2 of 1.536 (6) Å) are equal within experimental error and provide additional evidence for the postulation of the symmetrical hydrogen bond. The unexpected discovery of this anion suggests that the compounds previously formulated as *cis*-$[(RO)_2PO][(RO)_2POH]$ complexes containing discrete diphenylphosphonato and diphenylphosphonous acid groups are most likely to contain the $[(RO)_2PO]_2H$ anion. The absence of the $\nu(O{-}H)$ frequency in the normal region of the infrared spectra, noted previously,[4] is now understandable since the frequencies for symmetrical hydrogen bonds are below 1800 cm^{-1} and are notoriously difficult to assign unambiguously.[9]

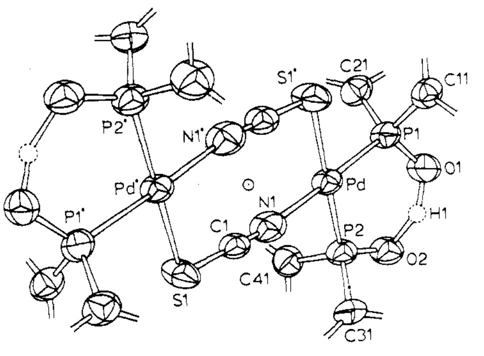


Figure 1. An ORTEP drawing of di-μ-thiocyanato-bis[hydrogen bis(diphenylphosphinato)]dipalladium(II), showing the thermal ellipsoids and atomic numbering. Only the first carbon atoms (C11, C21, C31, and C41) of the four phenyl groups attached to P1 and P2 are shown. The hydrogen atom H1 which is symmetrically placed between O1 and O2 is shown with a broken circle for emphasis.

The stabilization of the acid anion in $\{PdX[Ph_2PO]_2H\}_2$ is noteworthy in view of the fact that the tautomeric equilibrium $Ph_2POH \rightleftharpoons Ph_2P(O)H$ lies far to the right in aqueous solution; hence the diphenylphosphinous acid is present in negligibly small concentrations in the absence of complexation.[2]

In conclusion, we note that acetylenic phosphines are susceptible to nucleophilic attack at both the phosphorus atom and the alkyne group,[10] in sharp contrast to the stability of trialkyl- or arylphosphines. These observations suggest that an extensive derivative chemistry may be evolved from these reactive phosphino-acetylene complexes.

Acknowledgments. We are grateful for a grant of computing time from the Northeast Regional Data Center at the University of Florida (G. J. P.) and to the National Research Council of Canada (A. J. C.) for financial support.

Supplementary Material Available. A listing of final atomic parameters and structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or

---

(3) G. A. Levshina, A. D. Troitskaya, and R. R. Shagidullin, *Russ. J. Inorg. Chem.*, **11**, 985 (1966).

(4) A. Pidcock and C. R. Waterhouse, *J. Chem. Soc. A*, 2080 (1970).

(5) G. J. Palenik, W. L. Steffen, M. Mathew, M. Li, and D. W. Meek, *Inorg. Nucl. Chem. Lett.*, **10**, 125 (1974).

(6) F. H. Allen, A. Pidcock, and C. R. Waterhouse, *J. Chem. Soc. A*, 2087 (1970).

(7) A lengthening of the Pd-S bond because the thiocyanate is bridging is effectively ruled out by the studies of W. A. Gregory, J. A. J. Jarvis, B. T. Kilbourn, and P. G. Owston, *J. Chem. Soc. A*, 2770 (1970).

(8) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968.

(9) (a) D. Hadzi, B. Orel, and A. Novak, *Spectrochim. Acta, Part A*, **29**, 1745 (1973); (b) P. J. Miller, R. A. Butler, and E. R. Lippincott, *J. Chem. Phys.*, **57**, 5451 (1972).

(10) R. T. Simpson, S. Jacobson, A. J. Carty, M. Mathew, and G. J. Palenik, *J. Chem. Soc., Chem. Commun.*, 388 (1973), and this work.

microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-2286.

Datta V. Naik, Gus J. Palenik*
Center for Molecular Structure, Department of Chemistry
University of Florida
Gainesville, Florida 32611

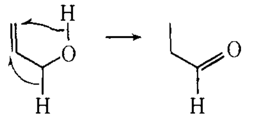
Stephen Jacobson, Arthur J. Carty
Department of Chemistry, University of Waterloo
Waterloo, Ontario, Canada

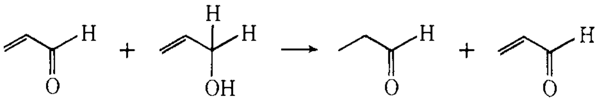
Received December 14, 1973

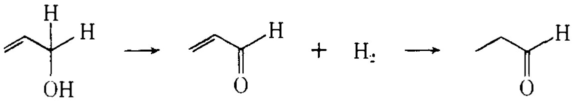
Copper Catalyzed Rearrangement of Allylic Alcohols to Saturated Aldehydes and Ketones

Sir:

The rearrangement of allylic alcohols to saturated aldehydes or ketones in the presence of metal and metal oxide catalysts and in the vapor phase is a reaction of demonstrated synthetic utility.[1] Despite the long history of the reaction,[2] its mechanism remains controversial. Constable proposed that the transformation over metallic copper involved an intramolecular tautomerization reaction (eq 1).[3] Weston and Adkins suggested that the conversion of allyl alcohol to propionaldehyde over zinc oxide involved propenal as an intermediate (eq 2),[4] although they favored an intramolecular mechanism for the transformation over aluminum oxide.[5] On the basis of kinetic evidence, both groups of workers excluded the possibility of a dehydrogenation–hydrogenation mechanism (eq 3). More recently, however, Flid and Prostakov have proposed a mechanism (eq 4 through 6) involving the formation of adsorbed H_2 on several metal and metal oxide catalysts, including metallic copper and zinc oxide.[6] In light of these ambiguities an investigation into the mechanism of this unusual transformation was begun, using principally the technique of deuterium labeling. The catalysts chosen for study were metallic copper[7a] and cupric oxide;[7b] the experimental results reported here were obtained using metallic copper as catalyst, although qualitatively similar results were obtained over cupric oxide. The procedure and apparatus used for these studies has already been described;[8] a 20-μl sample of the allylic alcohol was injected onto a 700-cm Teflon column packed with copper or cupric oxide and mounted in a gas chromatograph oven. Helium flow rate was maintained at 15 ml/min and oven temperatures utilized varied between 150 and 220°. The effluent (retention times were about 60 sec) was collected in a Dry Ice cooled trap and analyzed by reinjection onto a 7-m column packed with 10% UCW-98 on Chromosorb P (60/80). 1-Alken-3-ols of less than 11 carbons invariably gave 75–95% yields of saturated carbonyl compound, 5–20% α,β-unsaturated carbonyl compound (favored by higher reaction temperatures and lower alcohol concentrations), and traces of dehydration products. With these catalysts, increased alkyl substitution about the carbon–carbon double bond favors the dehydration and dehydrogenation reactions. The following observations are relevant to the mechanism of allylic alcohol-saturated ketone interconversion.


(1)


(2)

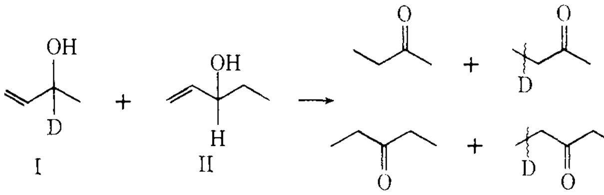

(3)

$$CH_2{=}CHCH_2OH + I \rightleftharpoons CH_2{=}CHCHO(ads) + I\text{-}H_2 \quad (4)$$

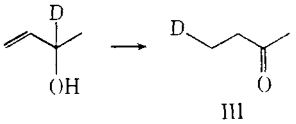
$$I\text{-}H_2 + CH_2{=}CHCHO(ads) \rightleftharpoons I + CH_3CH_2CHO(ads) \quad (5)$$

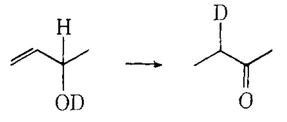
$$CH_3CHCHO(ads) \longrightarrow CH_3CH_2CHO(gas) \quad (6)$$

The reaction is intermolecular. Coinjection of 1-buten-3-ol-*3-d* (I) and 1-penten-3-ol (II) produced large amounts of labeled 3-pentanone and unlabeled 2-butanone (eq 7).[9] Control experiments ascertained that the unreacted allylic alcohols had not undergone H–D exchange and that 2-butanone-*4-d*, and 2-butanone-*1,1,1,3,3-d*$_5$ did not undergo extensive H–D exchange with 3-pentanone under these conditions. Thus, the observed exchange is intrinsic to the reaction and intramolecular mechanisms can be excluded as major pathways to product.


I II (7)

The hydroxyl hydrogen and the hydrogen atom at C-3 do not become equivalent during the rearrangement. Reaction of 1-buten-3-ol-*3-d*, produces 2-butanone-*4-d* (III) more than 80% specifically labeled (eq 8).[10] To


III (8)


IV V (9)

---

[1] M. Kraus, *Collect. Czech. Chem. Commun.*, 37, 460 (1972), and references cited therein.

[2] P. Sabatier and J. B. Senderens, *C. R. Acad. Sci.*, **136**, 983 (1902).

[3] F. H. Constable, *Proc. Roy. Soc., Ser. A*, **113**, 254 (1926).

[4] P. E. Weston and H. Adkins, *J. Amer. Chem. Soc.*, **50**, 1930 (1928).

[5] P. E. Weston and H. Adkins, *J. Amer. Chem. Soc.*, **51**, 2430 (1929).

[6] R. M. Flid and N. S. Prostakov, *Tr. Mosk. Inst. Tonkoi Khim. Tekhnol.*, No. 4, 19 (1953); M. Ya. Kagan, R. M. Flid, and N. S. Prostakov, *ibid.*, No. 5, 45 (1955).

[7] (a) Electrolytic dust obtained from Fischer Scientific Co. or wire obtained from Matheson Coleman and Bell. (b) Black powder obtained from Matheson Coleman and Bell or wire obtained from J. T. Baker Chemical Co.

[8] M. Y. Shiekh and G. Eadon, *Tetrahedron Lett.*, 257 (1972).

[9] Determined by mass spectral analysis of the pure ketones.

[10] Determined by integration of the nmr spectrum of the pure ketone. The nmr spectrum (CCl_4) consists of a triplet of triplets (J_{vic} = 7.6 Hz, J_{gem} = 2 Hz) at 1.00, a singlet at 2.05, and a broadened triplet (J_{vic} = 7.6 Hz) at 2.35 ppm.