TABLE I

	PrN	NdN	GdN	TmN
Method of prepn of $LnHg_x$	A	A	B	B
x	1.26	2.09	20.0	10.0
N/Ln (±0.005)	0.995	0.970	0.998	0.990
a_0 (±0.001), Å	5.169	5.131	4.985	4.813

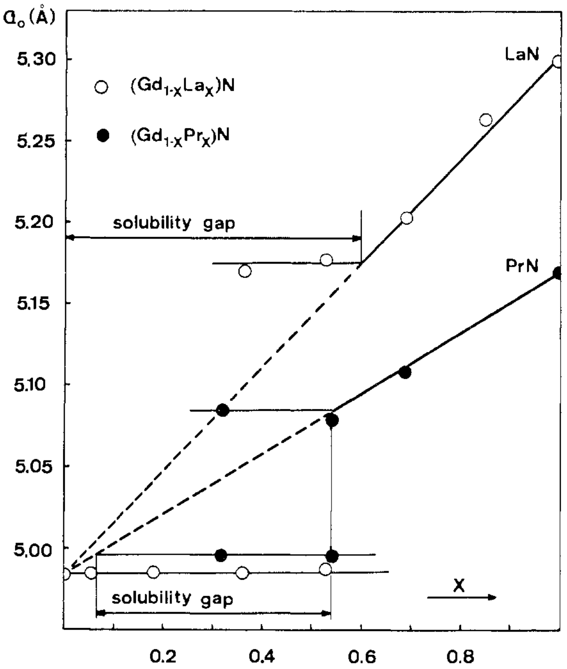


Figure 1.—Mutual solubility in the systems $Gd_{1-x}La_xN$ and $Gd_{1-x}Pr_xN$ at 1000°.

Experimental Section

All manipulations were carried out under nitrogen or argon.

(1) **Preparation of Amalgams. Method A.**—The dehydrated chloride was dissolved in methanol and electrolyzed with a graphite anode and a mercury cathode.[13] Electrolysis was carried out in a vessel provided with ground-glass joints to permit introduction of a graphite anode (diameter 12 mm), a stirrer, a combined inlet and outlet for nitrogen, a water jacket, and a tap on the bottom. A voltage of about 40 V was required to maintain a current of 1–2 A, depending upon the distance between the anode and cathode (10–20 mm), the concentration of the rare earth chloride (half-saturated), and the temperature (about 20°).

Owing to the large surface area of the cathode, a total current of 1 A corresponded to a density of 0.04 A/cm^2. The electrolysis was stopped after 20–40 hr, and the amalgam obtained was run off into a two-bulb vessel. Any electrolyte carried with the amalgam was washed out with methanol under nitrogen. This vessel was then evacuated and sealed. The excess of mercury was then distilled from bulb 1 into bulb 2 and finally the vessel was sealed between the two bulbs. The composition of the amalgam obtained in bulb 1 depended upon the temperature at which the mercury was distilled (200–300°).

Method B.—The amalgams of the rare earths were obtained by heating the metal (or metals for mixed nitrides) at 300–350° in a sealed glass tube with 20–30 times its weight of mercury. This at the same time achieved some purification of the metal, since the oxidation products were lighter than mercury and separated out at the surface of the amalgam. The amalgam was obtained as a thick pulpy solid and could be nitrided directly.

(2) **Nitridation.**—For the preparation of the nitride, the amalgam was placed in two molybdenum boats. The first of these, containing about one-fifth of the total amalgam, was used for further purification of the nitrogen, since the rare earth nitride formed from the amalgam was a very good absorbent for traces of oxygen. The boats were placed in a silica tube and heated in a stream of purified nitrogen in steps, as follows: 2–3 hr at 340°, 2–3 hr at 500°, 12–15 hr at 700°, and 1–5 hr at 1000°. The formation of the nitride is complete at 700°, but the final heating period is necessary to increase the particle size sufficiently in order to obtain sharp reflections in the X-ray powder diagrams. The use of rubber and plastic tubing for the nitrogen line was avoided because of their permeability to moisture. All connections were made from glass tubes, with spherical joints included at suitable positions to maintain flexibility.

(3) **Analyses.**—Analyses for the rare earths and nitrogen were carried out by complexometric and Kjeldahl assays, respectively, after dissolution of the nitride in 1 *M* hydrochloric acid. Owing to the violence of the reaction, especially with nitrides not annealed at high temperatures (1200°), the rate of dissolution in acid had to be carefully controlled to prevent loss of ammonia. This was conveniently accomplished by sealing a weighed amount of nitride in a glass bulb, fitted with a side arm drawn out into a capillary. For digestion, the capillary was broken, and when the dark nitride had become light in color owing to conversion into $LnCl_3 \cdot xH_2O$ and $Ln(OH)_3 \cdot xH_2O$, the bulb was broken completely, and the flask was closed until dissolution was complete.

Acknowledgment.—The author is indebted to Professor G. Busch, director of the Laboratory for Solid State Physics, for his continued interest and to the "Verein zur Forderung der Festkörperphysik an der E.T.H." for financial support of this work.

---

(13) H. S. Booth, *Inorg. Syn.*, **1**, 15 (1939).

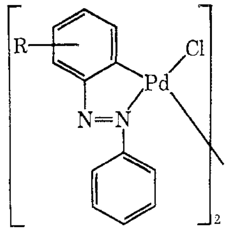
CONTRIBUTION FROM THE DEPARTMENT OF
CHEMICAL TECHNOLOGY, FACULTY OF ENGINEERING,
OSAKA UNIVERSITY, MIYAKOJIMA-KU, OSAKA, JAPAN

Chlorovinylation of Palladium

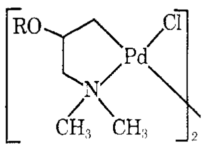
BY TOSHIHIDE YUKAWA AND SHIGERU TSUTSUMI

Received January 22, 1968

Recently some organopalladium compounds from the reactions of palladium(II) salts with unsaturated organics have been investigated by several workers.[1–5] For example, Anderson and Burreson have prepared acetoxy palladium(II) olefin adducts.[1] Cope and coworkers have found palladium(II) halides to react with azobenzenes to give I[2] and with allylic amines to give II.[3]



I



II

---

(1) C. B. Anderson and B. J. Burreson, *J. Organometal. Chem.* (Amsterdam), **7**, 181 (1967).

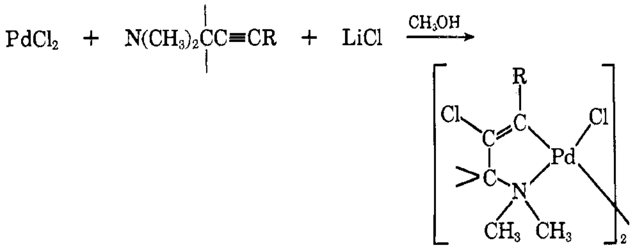
(2) A. C. Cope and R. W. Siekman, *J. Am. Chem. Soc.*, **87**, 3272 (1965).

(3) A. C. Cope, J. M. Klieman, and E. C. Friedrich, *ibid.*, **89**, 287 (1967).

(4) J. Tsuji and H. Takahashi, *ibid.*, **87**, 3275 (1965).

(5) J. K. Stille and R. A. Morgan, *ibid.*, **88**, 5135 (1966).

Here we wish to report propargyl amines which react with palladium chloride in the presence of lithium chloride to give chlorovinylated products



Experimental Section[6]

Materials.—The following compounds were prepared by literature methods: 3-N,N-dimethylamino-1-phenylprop-1-yne[7] and 3-N,N-dimethylamino-3-methylbut-1-yne.[8] The deuterated amine 3-N,N-dimethylamino-3-methylbut-1-yne-1-*d* was prepared as follows. To a solution of 3-N,N-dimethylamino-3-methylbut-1-yne in diethyl ether was added a slight excess of butyllithium solution. A large excess of deuterium oxide was slowly added to the resulting solution. The ether layer was separated and dried. Removal of ether gave 3-N,N-dimethylamino-3-methylbut-1-yne-1-*d*.

Di-μ-chloro-bis(2-chloro-3-N,N-dimethylamino-1-phenylpropenyl)dipalladium(II) (IV_a).—To a solution of 0.89 g (0.005 mol) of palladium chloride and 2 g (0.47 mol) of lithium chloride in 20 ml of methanol was added 0.8 g (0.005 mol) of 3-N,N-dimethylamino-1-phenylprop-1-yne. The yellow precipitate that formed was collected on a filter, washed with methanol, and dried. The yield was 1.05 g (95%). This was purified by passage over a silica gel column with benzene, mp 187–200° dec. *Anal.* Calcd for $C_{22}H_{26}N_2Cl_4Pd_2$: C, 39.21; H, 3.87; N, 4.17; Cl, 21.04; mol wt, 673.1. Found: C, 39.13; H, 4.00; N, 4.10; Cl, 21.22; mol wt,[6b] 675.6.

Di-μ-acetato-bis(2-chloro-3-N,N-dimethylamino-1-phenylpropenyl)dipalladium(II) (IV_b).—In 20 ml of benzene, 0.2 g (0.0003 mol) of IV_a and 0.5 g (0.003 mol) of silver acetate were stirred for 1 hr. The solution was filtered and benzene was removed at reduced pressure. The residue was purified chromatographically on a silica gel column with ether as eluent. Ether was evaporated *in vacuo* and recrystallization of the residue from a benzene–heptane mixture gave 0.157 g (73%) of IV_b, mp 157–158°. *Anal.* Calcd for $C_{26}H_{32}O_4N_2Cl_2Pd_2$: C, 43.32; H, 4.45; N, 3.97; Cl, 9.85; mol wt, 720.2. Found: C, 43.32; H, 4.48; N, 3.94; Cl, 9.94; mol wt,[6b] 722.5. The nmr spectrum (3% in CH_2Cl_2) showed: a singlet (OCH_3, τ 8.83, wt 3), two singlets ($N(CH_3)_2$, τ 7.16 and 6.85, wt 6), two doublets (CH_2, J = 15 Hz, τ 4.18 and 3.41, wt 2), and multiplets (C_6H_5, τ 2.67–2.87, wt 5).

Chloro(2-chloro-3-N,N-dimethylamino-1-phenylpropenyl)(pyridine)palladium(II) (IV_c).—According to the direction of Cope for oxy adducts,[3] IV_c was prepared. To a solution of 0.2 g (0.0003 mol) of IV_a in benzene–heptane was added 0.05 g (0.0006 mol) of pyridine. After cooling, the light yellow crystals that formed were filtered to give 0.209 g (87%) of IV_c, which turned red at 145° and decomposed at 170°. *Anal.* Calcd for $C_{16}H_{18}N_2Cl_2Pd_2$: C, 46.18; H, 4.33; N, 6.74; Cl, 17.57; mol wt, 415.7. Found: C, 46.34; H, 4.38; N, 6.72; Cl, 17.31; mol wt,[6b] 418.2. The nmr spectrum (10% in $CDCl_3$) showed: a singlet ($N(CH_3)_2$, τ 7.05, wt 6), a singlet (CH_2, τ 6.36, wt 2), and multiplets (phenyl and pyridyl protons, τ 1.70–3.30, wt 10).

Di-μ-chloro-bis(2-chloro-3-N,N-dimethylamino-3-methylbutenyl)dipalladium(II) (VI_a).—To a solution of 0.89 g (0.005 mol) of palladium chloride and 2 g (0.47 mol) of lithium chloride in 10 ml of methanol was added 0.556 g (0.005 mol) of 3-N,N-dimethylamino-3-methylbut-1-yne in 5 ml of methanol with stirring for 10 min. Methanol was evaporated *in vacuo* at 40°, and the residue was extracted with benzene. Chromatography of the concentrated extract on a silica gel column with benzene as eluent gave 0.44 g (27%) of yellow crystals, mp 172–175° dec. *Anal.* Calcd for $C_{14}H_{26}N_2Cl_4Pd_2$: C, 29.10; H, 4.50; N, 4.85; Cl, 24.58; mol wt, 577.0. Found: C, 29.40; H, 4.68; N, 4.87; Cl, 24.49; mol wt,[6b] 584.0.

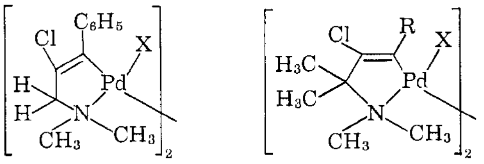
Di-μ-chloro-bis(2-chloro-3-N,N-dimethylamino-3-methyl-1-deuteriobutenyl)dipalladium(II) (VI_d).—The procedure for the preparation of VI_a was followed. From 0.096 g (0.00087 mol) of 3-N,N-dimethylamino-3-methylbut-1-yne-1-*d*, 0.153 g (0.00087 mol) of palladium chloride, and 0.5 g of lithium chloride in 5 ml of methanol was obtained 0.05 g (20%) of VI_d, mp 171–175° dec. The nmr spectrum (5% in $CDCl_3$) showed: a singlet ($C(CH_3)_2$, τ 8.57, wt 6) and a singlet ($N(CH_3)_2$, τ 7.38, wt 6). The infrared spectrum[6c] showed absorptions at 2250 cm^{-1} (=C—D stretching), 1555 cm^{-1} (C=C stretching), and 650 cm^{-1} (C—Cl stretching).

Di-μ-acetato-bis(2-chloro-3-N,N-dimethylamino-3-methylbutenyl)dipalladium(II) (VI_b).—The procedure for the preparation of IV_b was followed. From 0.2 g (0.00035 mol) of VI_a and 0.5 g (0.003 mol) of silver acetate was obtained 0.102 g (47%) of yellow crystals, mp 139–140° dec. *Anal.* Calcd for $C_{18}H_{32}N_2O_4Cl_2Pd_2$: C, 34.61; H, 5.13; N, 4.48; Cl, 11.36; mol wt, 624.2. Found: C, 34.83; H, 5.20: N, 4.59; Cl, 11.54; mol wt,[6b] 628.0. The nmr spectrum (10% in $CDCl_3$) showed: a singlet ($C(CH_3)_2$, τ 8.50, wt 6), a singlet (OCH_3, τ 8.06, wt 3), a singlet ($N(CH_3)_2$, τ 7.22, wt 6), and a singlet (=C—H, τ 3.87, wt 1).

Chloro(2-chloro-3-N,N-dimethylamino-3-methylbutenyl)(pyridine)palladium(II) (VI_c).—The procedure for the preparation of IV_c was followed. From 0.1 g (0.00018 mol) of VI_a and 0.03 g (0.00038 mol) of pyridine was obtained 0.122 g (95%) of white crystals, mp 189–190° dec. *Anal.* Calcd for $C_{13}H_{16}N_2Cl_2Pd$: C, 39.17; H, 4.90; N, 7.61; Cl, 19.29; mol wt, 367.6. Found: C, 39.22; H, 5.05; N, 7.63; Cl, 19.28; mol wt,[6b] 374.2. The nmr spectrum (3% in $CDCl_3$) showed: a singlet ($C(CH_3)_2$, τ 8.55, wt 6), a singlet ($N(CH_3)_2$, τ 7.15, wt 6), a singlet (=C—H, τ 4.21, wt 1), and multiplets (pyridyl protons, τ 1.15–2.85, wt 5).

Results and Discussion

Palladium chloride and 1 mol of 3-N,N-dimethylamino-1-phenylprop-1-yne (III) in methanol saturated with lithium chloride react immediately to give a yellow precipitate which on filtration gives IV_a in 95% yield. Similarly palladium chloride and 3-N,N-dimethylamino-3-methylbut-1-yne (V) react to give VI_a in 27% yield. The proposed structures of IV_a and VI_a are shown in Figure 1.



IV_a, X = Cl
IV_b, X = OAc

VI_a, X = Cl, R = H
VI_b, X = OAc, R = H
VI_d, X = Cl, R = D

Figure 1.

Elemental analyses are satisfactory and molecular weight measurements agree with the dimeric structures. The infrared spectrum of IV_a shows new bands at 1626 and 670 cm^{-1} assigned to the C=C and C—Cl stretch-

---

(6) (a) Melting Points are uncorrected; (b) molecular weight measurements were determined with an osmometer (benzene; at 45°); (c) infrared spectra were recorded with a Hitachi EPI-2G spectrometer.

(7) C. Mannich and F. T. Chang, *Ber.*, **66**, 418 (1933).

(8) G. F. Hennion and K. W. Nelson, *J. Am. Chem. Soc.*, **79**, 2142 (1957).

ing modes, respectively. With the disappearance of bands at 3310 and 2080 cm^{-1} of the free base V, compound VI_a shows a band at 3010 cm^{-1} assigned to the =C—H stretching mode. This assignment is confirmed by the comparison with the corresponding band (2250 cm^{-1}) of the deuterated complex VI_d. Compound VI_a also shows other bands at 1575 and 675 cm^{-1} assigned to the C=C and C—Cl stretching modes, respectively. The nmr spectra of IV_a and VI_a are also consistent with the structures. The ethynyl proton of the free base V appears at τ 7.85 (in CCl_4) besides other peaks at τ 8.65 (singlet, $(CH_3)_2C$) and τ 7.80 (singlet, $(CH_3)_2N$), whereas VI_a (in $CDCl_3$) shows three singlet signals at τ 8.57, 7.28, and 4.18 in the ratio 6:6:1. They are assigned to C-methyl protons, N-methyl protons, and the C_1-vinyl proton, respectively. The spectrum of IV_a (in CH_2Cl_2) consists of singlets at τ 7.26 and 7.16 (N-methyl protons, wt 6), a singlet at τ 6.41 (methylene protons, wt 2), and multiplets at τ 2.80–3.12 (phenyl protons, wt 5).

Although the infrared bands at 670 cm^{-1} of IV_a and 675 cm^{-1} of VI_a are attributed to the C–Cl stretching mode, these assignments are not reliable. To clarify the presence of a chlorine atom bonded to a carbon atom, IV_a and VI_a are converted to acetato-bridged complexes. When IV_a and VI_a are treated with excess silver acetate in benzene, compounds IV_b and VI_b are obtained, respectively. The infrared spectra of both IV_b and VI_b show bands at 1555 and 1430 cm^{-1} which are ionic acetate carbon–oxygen stretching frequencies. The nmr spectra of IV_b and VI_b show singlets at τ 8.83 and 8.06, respectively, which integrate one acetate group per two N-methyl groups. Molecular weight measurements and elemental analyses also show these are dimeric and one chlorine atom is present per one palladium atom. Only one of the chlorines can be replaced by an acetate group with silver acetate, and this suggests the residual one is not bonded to palladium atom.

Although the direction of addition cannot be decided from the above data alone, we prefer the proposed one on the analogy of the oxy adducts by Cope.[2]

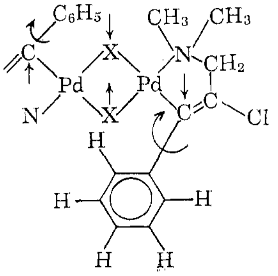


Figure 2.

Chloro-bridged dimers IV_a and VI_a are readily split by pyridine to give monomeric species IV_c and VI_c, respectively.

It will be noted that N-methyls of IV_a appear as two singlets in the nmr spectrum whereas that of VI_a appears as one signal. A possible explanation of this is the steric hindrance caused by the phenyl group. Because of the steric interference of the phenyl group with the μ-chlorine atom, the latter is lifted up (or let down) and the former is let down (or lifted up) with some rotation of the ring. Thus the σ symmetry of the molecule is broken, making the two methyls nonequivalent (Figure 2). This effect also appears in the case of the acetato complex IV_b, where N-methyl groups appear as two singlets (ν_{diff} = 0.25 ppm) and methylene protons as four-line AB pattern (ν_{diff} = 0.68 ppm, J = 15 Hz). Moreover, for the rotation of the phenyl ring, the acetate methyl is placed above the ring, and the signal appears at τ 8.83 which is 0.77 ppm higher than that of VI_b. Being monomeric, pyridine adduct IV_c is much released from the steric restriction, and N-methyls appear as one signal.

Contribution from the Istituto Chimica Generale,
II Sezione, The University, Padua, Italy

Five-Coordinated Low-Spin Complexes of Cobalt(II) with Tertiary and Ditertiary Phosphines

By P. Rigo, M. Bressan, and A. Turco

Received January 22, 1968

Cobalt(II) gives with tertiary phosphines a number of tetrahedral high-spin complexes $Co(PR_3)_2X_2$ but does not form low-spin five-coordinated complexes $Co(PR_3)_3X_2$ (X^- = Cl^-, Br^-, I^-, NCO^-).[1] However, such complexes can be easily formed when $X^- = NCS^-$.[2] The peculiar role of the NCS^- ion in determining the stability of the tris(phosphine) complexes has been attributed to ligand-field effects and it has been suggested that other strong anionic ligands should enhance the ability of cobalt(II) to give this type of five-coordination.

Nickel(II) can form $Ni(PR_3)_3X_2$ complexes when $X^- = CN^-$ (and not when X^- = Cl^-, Br^-, NCO^-, NCS^-),[3] and this suggested that the hitherto unknown corresponding complexes of cobalt(II) could also be prepared. To obtain such complexes may be difficult because the large affinity of cobalt(II) for CN^- may prevent binding of other ligands. Thus, mixed cyano complexes of cobalt(II) have not been reported to date (neglecting $[Co(CN)_5(H_2O)]^{3-}$). We report the preparation of five-coordinated complexes formed by $Co(CN)_2$ with tertiary and ditertiary phosphines and by $Co(CNS)_2$ with ditertiary phosphines. The new complexes with tertiary phosphines have the composition $Co(PR_3)_3(CN)_2$ (PR_3 = $P(C_2H_5)_2C_6H_5$, $PC_2H_5(C_6H_5)_2$).

---

[1] The only known exception is $Co(C_{14}H_{13}P)_3X_2$ ($C_{14}H_{13}$ = 2-phenylisophosphindoline), the stability of which is related to the peculiar stereochemistry of the phosphine.

[2] T. Boschi, M. Nicolini, and A. Turco, *Coord. Chem. Rev.*, **1**, 269 (1966).

[3] P. Rigo, C. Pecile, and A. Turco, *Inorg. Chem.*, **6**, 1636 (1967).