agrees well with that predicted by Lipscomb's equations of balance for the 4120 styx structure of B_5H_9.[11] This value can be contrasted to a recent localized molecular orbital calculation in which $sp^{1.3}$ is obtained for the hybridization of the apex boron in B_5H_9.[12]

At present we are examining the ^{11}B and ^{13}C nmr of other organoboranes and carboranes to better characterize this important nmr parameter.

Acknowledgment. The XL-100-15 nmr spectrometer was purchased with funds from a National Science Foundation Department Development Grant. J. D. O. is grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and P. D. E. to the University of South Carolina Committee on Research and Productive Scholarship for support of this research.

---

(11) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, Chapter 2.

(12) E. Switkes, W. N. Lipscomb, and M. D. Newton, *J. Amer. Chem. Soc.*, **92**, 3847 (1970).

(13) National Science Foundation Undergraduate Research Participant, 1971.

Paul D. Ellis,* Jerome D. Odom,* Douglas W. Lowman
Alan D. Cardin[13]
Department of Chemistry, University of South Carolina
Columbia, South Carolina 29208

Received September 8, 1971

Univalent Palladium Complexes

Sir:

In industrial olefin catalysis by palladium(II) complexes it is known[1-3] that reduction of Pd(II) species takes place through decomposition of organopalladium(II) intermediates and that reoxidation of Pd(0) species can be effected with the aid of one-electron oxidant, cupric salt. Implication of Pd(I) species has been suggested[4,5] for these processes. However, no report has been made on univalent palladium complexes except the peculiar arene-sandwiched dimeric compound $[Pd\text{-}Al_2Cl_7(C_6H_6)]_2$[6,7] and the elusive complex of unknown molecular weight $[Pd(C_6H_6)(H_2O)ClO_4]_n$.[4] We wish to report here preparations and properties of novel diamagnetic, dimeric palladium(I) complexes.

These complexes are accessible through two routes from "$Pd(RNC)_2$."[8,9] One successful preparation uses $PdX_2(RNC)_2$ obtained by treating either palladium(II) halides (PdI_2 or $PdBr_2$) or the Kharash complex $PdCl_2(PhCN)_2$ with an excess of *tert*-BuNC in benzene. The palladium(II) complexes PdX_2(*tert*-BuNC)$_2$ (**1**, X = Cl; **2**, X = Br; **3**, X = I) are monomeric, thermally and air stable compounds[10] with spectroscopic features listed in Table I.

Table I. *tert*-Butyl Isocyanide–Palladium(II) and –Palladium(I) Complexes

Compound	^1H nmr, ppm	Ir,[a] cm^{-1} N≡C	Ir,[a] cm^{-1} Pd—X	λ_{max},[b] nm (ϵ)
cis-$PdCl_2$(*tert*-BuNC)$_2$[c]	8.43 (s)[d]	2251 2236	338 318	
trans-$PdBr_2$(*tert*-BuNC)$_2$[e]	8.47 (s)[d]	2224	269	
trans-PdI_2(*tert*-BuNC)$_2$[e]	8.46 (s)[d]	2216	231	
[PdCl(*tert*-BuNC)$_2$]$_2$-(C_6H_5Cl)	8.43 (s)[f] 2.65[g]	2166	259	307 (8000)
[PdBr(*tert*-BuNC)$_2$]$_2$	8.46 (s)[f]	2170	185	317 (6700)
[PdI(*tert*-BuNC)$_2$]$_2$	8.45 (s)[f]	2178	164	345 (8500)

[a] Nujol mull. [b] Measured in CH_2Cl_2: the extinction coefficients suggest that these absorption arise from charge transfer. [c] The cis configuration is deduced on the basis of the two ir NC and Pd–X stretching bands. [d] *tert*-Butyl proton resonances measured in chloroform at room temperature using TMS as a reference. [e] The ir data dictate the trans configuration. [f] Measured in acetone-d_6 using TMS as a reference. [g] Aromatic protons complex multiplets.

To a freshly prepared, cold (−30°) chlorobenzene solution of "Pd(*tert*-BuNC)$_2$" was added under nitrogen an equimolar amount of analytically pure **1**. The mixture was stirred for 4 hr maintaining the temperature around −30°. After 4 hr, the temperature was allowed to reach 0° within ~1 hr. Upon chilling at −20°, the palladium(I) complex [PdCl(*tert*-BuNC)$_2$]$_2$(C_6H_5Cl) (**4**) precipitates as yellow needles[11] (70%). This is fairly air and thermally stable; the decomposition (under nitrogen) starts slowly around 150° and was rapid above 200°. An equimolar mixture of Pd(*tert*-BuNC)$_2$ and **2**, dissolved in cold (−30°) ether, was stirred for 5 hr, allowing the temperature to rise in a similar fashion as above. The solvent being removed *in vacuo*, the residue was recrystallized from a *n*-hexane–tetrahydrofuran mixture to give [PdBr(*tert*-BuNC)$_2$]$_2$ (**5**) as orange prisms[10] (88%), dec 138–152°. Similarly, [PdI(*tert*-BuNC)$_2$]$_2$ (**6**) was obtained as orange needles[10] (90%), dec 125°, slightly soluble in benzene.

The oxidative addition of organic halides, *e.g.*, $PhCH_2I$ or XCH_2COOCH_3 (X = Cl, Br), to Pd(*tert*-BuNC)$_2$ led to **6** *via* the σ-alkyl isocyanide complex **7** (*cf.* Scheme I). Attempted preparations of phosphine-palladium(I) complexes from $Pd(PPh_3)_4$ and $PdI_2(PPh_3)_2$ have been unsuccessful. The capability of alkyl isocyanide ligands for stabilization of the odd valence state is noteworthy.

The three complexes **4**–**6** have bridging halogen atoms, as inferred from their ir spectra, which lack absorptions in the 1600–1800-cm^{-1} region, suggesting the absence of a bridging isocyanide group (>C=NR), but show low-frequency Pd–X stretching bands (Table I) assigned to bridging halogen–metal stretching vibrations.[12] The structure predicts two NC stretching

---

(1) E. W. Stern, *Catal. Rev.*, 1, 73 (1968).

(2) C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press Inc., New York, N. Y., 1967, p 88.

(3) A. Aguilo, *Advan. Organometal. Chem.*, **5**, 321 (1967).

(4) J. M. Davidson and C. Triggs, *J. Chem. Soc. A*, 1324 (1968).

(5) J. M. Davidson and C. Triggs, *ibid.*, *A*, 1331 (1968).

(6) G. Allegra, A. Immirzi, and L. Porri, *J. Amer. Chem. Soc.*, **87**, 1394 (1965).

(7) G. Allegra, G. Tettamanti Casagrande, A. Immirzi, L. Porri, and G. Vitulli, *ibid.*, **92**, 289 (1970).

(8) E. O. Fischer and H. Werner, *Chem. Ber.*, **95**, 703 (1962).

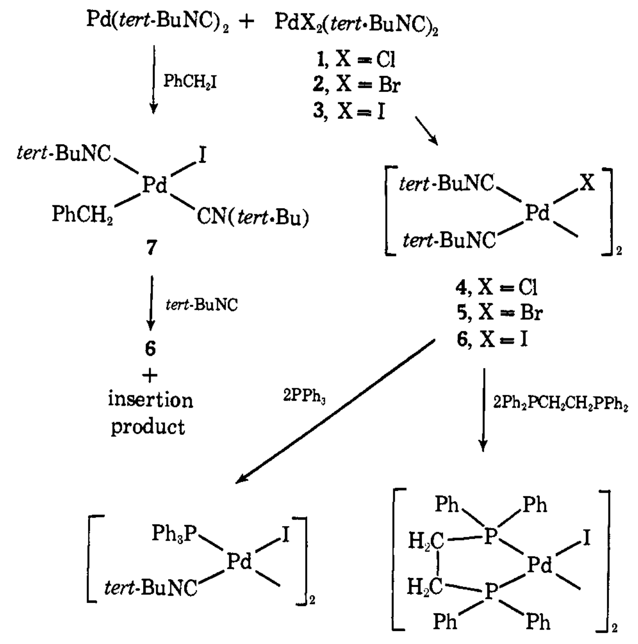
(9) S. Otsuka, A. Nakamura, and Y. Tatsuno, *J. Amer. Chem. Soc.*, **91**, 6994 (1969).

(10) The elemental analysis as well as the vapor pressure osmometric molecular weight measurement in benzene conformed to the calculated values.

(11) It gave a good elemental analysis. The molecular weight in benzene was found as 603, 620 (calcd 729), indicating its slight dissociation of chlorobenzene. A question raised by a referee concerns the dissociation asking if some special mode of bonding to the aromatic ring is involved. The oxidative addition (cleavage of the C–Cl bond) can be excluded from the absence of terminal Cl–Pd stretching vibration. Solvated aromatics are found in some rhodium(I) complexes [R. Ugo, F. Bonati, and S. Cenini, *Inorg. Chim. Acta*, 3, 220 (1969)]. When the chloropalladium(I) complex was prepared by the alternative route using alkyl halide in benzene (see Scheme I), it was obtained as a benzene adduct, [PdCl(*tert*-BuNC)$_2$]$_2$(C_6H_6), dec 155°, which also gave a good elemental analysis.

(12) M. S. Lupin, J. Powell, and B. L. Shaw, *J. Chem. Soc.*, 1410 (1966).

Scheme I



bands. The appearance of one NC band could be a fortuitous consequence derived from a combination of two force constants, *i.e.*, the NC stretching and the interaction force constant. The ir spectrum measured in benzene shows a slight broadening of the NC stretching absorption. In view of the valence of the metal, the NC stretching frequency (Table I) is reasonably low compared to that of the corresponding halogenopalladium(II) complex (Table I).

Unexpectedly, the Pd–X bond was inert to attack by tertiary phosphines. Thus, **6** was treated with 1 mol of PPh$_3$ in toluene at room temperature for 2 hr to give, upon chilling at −78°, orange crystals[10] of formula [PdI(PPh$_3$)(*tert*-BuNC)]$_2$, dec 115–117°, ir (Nujol) 2165 cm^{-1} (N≡C). Similarly, treatment with an excess of a chelating diphosphine, Ph$_2$PCH$_2$CH$_2$PPh$_2$, in toluene yielded an extremely stable (no decomposition below 300°) dimer complex, [PdI(Ph$_2$PCH$_2$CH$_2$PPh$_2$)]$_2$, as orange crystals[10] (recrystallized from benzene–*n*-hexane). The remarkable stability of the dimer structure contrasts the facile bridge cleavage observed for bis(halogeno-π-allylpalladium) [π-C$_3$H$_5$–PdCl]$_2$.[13]

Attempts were made to find chemical behavior characteristic of a d^9 ion. No reaction took place between **6** and hexaphenylethane (hence, trityl radical) in boiling ether. The reaction of **6** with bis(decanoyl) peroxide, [CH$_3$(CH$_2$)$_8$COO]$_2$, produced 1-nonene. Since 1-nonene was also obtained in the reaction with **3**, the reaction does not necessarily provide a diagnosis for one-electron oxidation of alkyl radical.[14] Complexes **4** and **5** failed to show the catalytic activity that Pd(*tert*-BuNC)$_2$ displays for air oxidation of *tert*-BuNC.[15]

A characteristic reaction was observed when **5** was treated with nitric oxide in ether. A very facile reaction takes place at room temperature, producing a monomeric, diamagnetic complex, *trans*-PdBr(NO$_2$)(*tert*-BuNC)$_2$, as pale yellow crystals:[10] dec 86–88°; ir (Nujol) 2235 (N≡C), 1321, and 820 cm^{-1} (NO$_2$). From **4** was obtained the chloro analog, *cis*-PdCl(NO$_2$)(*tert*-BuNC)$_2$, as yellow needles:[10] dec 180°; ir (Nujol) 2235 and 2250 (sh) cm^{-1} (N≡C). Since these reactions were carried out under careful exclusion of air, the results imply a disproportionation of NO facilitated by the Pd(I) species. The disproportionation has been observed for reaction with complexes of Rh(I)[16] and Ni(0),[17] but not for reaction with Pd(II) complexes.[18,19] Attempted preparation of a Pd(III) complex by oxidation of **6** with iodine merely yields **3** in a high yield.

The diamagnetism, as exhibited by the sharp ^{1}H nmr resonances, suggests strong magnetic exchange intereactions between the two d^9 nuclei, possibly through the bridging halogen ligands and through space. The latter mechanism, however, must be confirmed by an X-ray structural analysis.

---

(13) M. L. H. Green in "Organometallic Compounds," Vol. 2, G. E. Coates *et al.*, Ed., Methuen, London, 1968, p 52.

(14) J. K. Kochi, *J. Amer. Chem. Soc.*, **85**, 1958 (1963).

(15) S. Otsuka, A. Nakamura, and Y. Tatsuno, *Chem. Commun.*, 836 (1967).

(16) W. B. Hughes, *ibid.*, 1126 (1969).

(17) F. A. Snavely, W. S. Trahanovsky, and F. H. Suydam, *Inorg. Chem.*, 3, 123 (1964).

(18) W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 1775 (1959).

(19) W. Manchot and H. Waldmuller, *Ber.*, **59**, 2363 (1926).

Sei Otsuka,* Y. Tatsuno, K. Ataka
Department of Chemistry, Faculty of Engineering Science
Osaka University, Toyonaka, Osaka, Japan

Received August 5, 1971

Total Synthesis of *dl*-Y Base from Yeast Phenylalanine Transfer Ribonucleic Acid and Determination of Its Absolute Configuration

Sir:

Structure **1** was recently proposed[1] for the fluorescent Y base which is obtained from baker's yeast phenylalanine tRNA upon submitting the latter to mild acid treatment.[2] In view of the scarcity of material available (300 μg), structural studies were based on interpretation of spectroscopic data, syntheses of model compounds[3] having fully substituted aromatic nuclei, and a separate synthesis of the side chain. The proposed structure has since been supported by independent physical data and results of microchemical and enzymatic reactions.[4] Recently, we have assigned to the fluorescent bases isolated from various liver tRNA$^{\text{Phe}}$'s the peroxy-Y base structure **2**,[5] which also appears to account for results published by Yoshikami and Keller.[6] On the other hand, structure **3** without the side chain has been established for the Y-like base isolated from brewer's yeast tRNA$^{\text{Phe}}$.[7] In the following we report the total synthesis of *dl*-Y base, thus con-

---

(1) K. Nakanishi, N. Furutachi, M. Funamizu, D. Grunberger, and I. B. Weinstein, *J. Amer. Chem. Soc.*, **92**, 7617 (1970); *cf. Nature (London), New Biol.*, **230**, 196 (1971).

(2) R. Thiebe and H. G. Zachau, *Eur. J. Biochem.*, **5**, 546 (1968).

(3) A. Feinberg, M. Funamizu, N. Furutachi, A. Terahara, and K. Nakanishi, manuscript in preparation.

(4) R. Thiebe, H. G. Zachau, L. Baczynsky, K. Biemann, and J. Sonnenbichler, *Biochem. Biophys. Acta*, **240**, 163 (1971).

(5) K. Nakanishi, S. Blobstein, M. Funamizu, N. Furutachi, G. Van Lear, D. Grunberger, K. W. Lanks, and I. B. Weinstein, *Nature (London)*, in press.

(6) D. Yoshikami and E. B. Keller, *Biochemistry*, 10, 2969 (1971).

(7) H. Kasai, M. Goto, S. Takemura, T. Goto, and S. Matsuura, *Tetrahedron Lett.*, 2725 (1971).