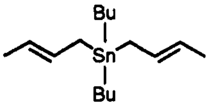
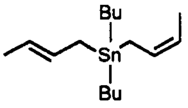
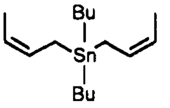
positions is related to the isomeric composition of the starting allyl bromide, which is trans:cis:α-methylallyl = 76:9:15.

The compound $Bu_2Sn(C_4H_7)_2$ (6) is obtained as an isomeric mixture in which the organic group C_4H_7 having the α-methylallyl configuration is completely absent. A mixture[18] of the isomers


trans,trans


trans,cis


cis,cis

is obtained with the following isomeric compositions: trans,trans:trans,cis:cis,cis = 6:42:52 (entry 6) and 20:51:29 (entry 7).

In the coupling reaction of Bu_3SnCl with propargyl bromide (entry 8) only the allenyl isomer 7 is obtained. This new route to allenylstannanes 7 has some advantages over the Grignard procedure, which requires a further step to isomerize the initial product mixture containing both isomers $Bu_3SnCH{=}C{=}CH_2$ and $Bu_3SnCH_2C{\equiv}CH$.[7b]

The present approach is analogous to the formation of Si—C and Ge—C bonds in organic solvents through coupling of organosilyl[19] and organogermyl chlorides[20] with α-bromo esters in the presence of zinc powder. These reactions presumably proceed via the intermediate formation of organozinc compounds. In our case, it is difficult to establish if organozinc or radical species are involved in the process. Zinc-mediated C–C bond-forming reactions in H_2O/THF medium are thought to follow a radical mechanistic pathway.[15]

These preliminary results clearly illustrate the potential of this Wurtz-type coupling reaction to form, in aqueous medium, simple allylstannanes. Further studies are now under way to apply this methodology to the preparation of more complex allyltin substrates.

Acknowledgment. We thank the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST), Rome, Italy, and the Consiglio Nazionale delle Ricerche, Rome, Italy, for financial support.

OM920316I

---

(19) Fessenden, R. J.; Fessenden, J. S. *J. Org. Chem.* 1967, *32*, 3535.

(20) Jean, A.; Lequan, M. C. R. *Seances Acad. Sci., Ser. C* 1971, *273*, 1662.

Reactions of Palladium Amide Complexes with Dimethyl Acetylenedicarboxylate. Palladium-Mediated C–N Bond Formation

Lawrence A. Villanueva, Khalil A. Abboud, and James M. Boncella*

Department of Chemistry, University of Florida, Gainesville, Florida 32611-2046

Received June 17, 1992

Summary: Reaction of the complexes *trans*-$Pd(C_6H_4C(H){=}NPh)(NHPh)(PMe_3)_2$ (1) and *trans*-$Pd(C_6H_5)(NHPh)(PMe_3)_2$ (3) with dimethyl acetylenedicarboxylate (DMAD) results in the insertion of the acetylene into the Pd–N bond, forming *cis*- and *trans*-$Pd[(MeOOC)C{=}C(COOMe)(NHPh)](C_6H_4C(H){=}NPh)(PMe_3)_2$ (2) and *trans*-$Pd[(MeOOC)C{=}C(COOMe)(NHPh)](C_6H_5)(PMe_3)_2$ (4). Thermolysis of 2 at 110 °C gives a high yield (76%) of *N*-phenyl-1-anilino-3,4-bis(methylcarboxy)-1,2-dihydroisoquinoline (5).

The synthesis of late-transition-metal amide complexes (groups 8–10) continues to attract considerable interest from inorganic and organometallic chemists.[1-6] One reason for this interest is the potential use of these complexes to facilitate the formation of carbon–nitrogen bonds through the insertion of unsaturated organic molecules into the metal–nitrogen bond. Although examples of insertion reactions do exist for these complexes, relatively little is known about the factors which control these reactions.[2,3a,c,d,4,5a,b,6b,g,i] We now report that the reaction of two palladium–amido complexes with dimethyl acetylenedicarboxylate (DMAD) results in carbon–nitrogen bond formation.

When *trans*-$Pd(C_6H_4C(H){=}NPh)(NHPh)(PMe_3)_2$ (1)[7] was allowed to react with 1 equiv of DMAD in pentane at room temperature (eq 1), the immediate precipitation of an off-white solid was observed. The ^1H NMR spectrum

---

(1) For reviews see: (a) Bryndza, H. E.; Tam, W. *Chem. Rev.* 1988, *88*, 1163. (b) Fryzuk, M. D.; Montgomery, D. C. *Coord. Chem. Rev.* 1989, *95*, 1–40. (c) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastrava, R. C. *Metal and Metalloid Amides*; Halsted Press: Chatham, Kent, England, 1980; pp 488–533. More recent work on group 8–10 metal amide complexes can be found in ref 2.

(2) (a) Koelliker, R.; Milstein, D. *J. Am. Chem. Soc.* 1991, *113*, 8524. (b) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* 1988, *110*, 6738.

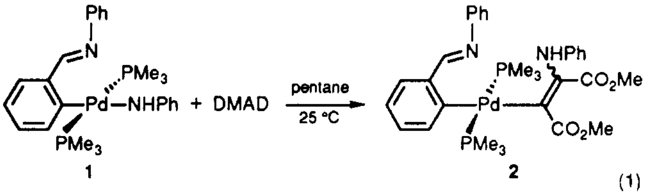
(3) (a) Bryndza, H. E.; Fultz, W. C.; Tam, W. *Organometallics* 1985, *4*, 939. (b) Park, S.; Roundhill, D. M.; Rheingold, A. L. *Inorg. Chem.* 1987, *26*, 3972. (c) Cowan, R. L.; Trogler, W. C. *Organometallics* 1987, *6*, 2451. (d) Cowan, R. L.; Trogler, W. C. *J. Am. Chem. Soc.* 1989, *111*, 4750. (e) Park, S.; Rheingold, A. L.; Roundhill, D. M. *Organometallics* 1991, *10*, 615.

(4) Seligson, A. L.; Cowan, R. L.; Trogler, W. C. *Inorg. Chem.* 1991, *30*, 3371.

(5) (a) Klein, D. P.; Hayes, J. C.; Bergman, R. G. *J. Am. Chem. Soc.* 1988, *110*, 3704. (b) Glueck, D. S.; Winslow, L. J.; Bergman, R. G. *Organometallics* 1991, *10*, 1462. (c) Glueck, D. S.; Bergman, R. G. *Organometallics* 1991, *10*, 1479.

(6) (a) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* 1987, *109*, 1444. (b) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* 1989, *111*, 2717. (c) Martin, G. C.; Boncella, J. M. *Organometallics* 1989, *8*, 2968. (d) Martin, G. C.; Palenik, G. J.; Boncella, J. M. *Inorg. Chem.* 1990, *29*, 2027. (e) Joslin, F. L.; Johnson, M. P.; Mague, J. T.; Roundhill, D. M. *Organometallics* 1991, *10*, 41. (f) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *Organometallics* 1991, *10*, 1875. (g) Joslin, F. L.; Johnson, M. P.; Mague, J. T.; Roundhill, D. M. *Organometallics* 1991, *10*, 2781. (h) Martin, G. C.; Boncella, J. M.; Wucherer, E. J. *Organometallics* 1991, *10*, 2804. (i) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* 1991, *113*, 6499.

(7) Villanueva, L. A.; Abboud, K.; Boncella, J. M. *Organometallics* 1991, *10*, 2969.



(1)

of the solid revealed a mixture of two products, as determined by the presence of two distinct sets of imine proton and PMe_3 resonances, as well as new methoxy resonances at 3.73, 3.69, 3.63, and 3.50 ppm. The $^{31}P\{^1H\}$ NMR spectrum also revealed two singlets at −16.79 and −17.95 ppm. This NMR data suggested that two isomers, *E* and *Z* at the carbon–carbon double bond, had been generated by the insertion of DMAD into the Pd–C or Pd–N bond of **1**.[8] The disappearance of the Pd–N*H* singlet at 1.53 ppm and the appearance of two broad singlets at 5.89 and 5.76 ppm led us to believe the insertion had occurred between the Pd–N bond and not the Pd–C bond of **1** to produce compound **2** (eq 1). This proposed structure is consistent with ^{15}N-labeling experiments[9a] as well as with the single-crystal X-ray diffraction study of compound **4**.

The two isomers of **2** proved to be inseparable by column chromatography; thus, variable-temperature NMR experiments were undertaken in order to observe whether rapid cis–trans isomerization of the carbon–carbon double bond was responsible for their inseparability. At 60 °C in $CDCl_3$, significant peak broadening of the imine proton signals was observed. Magnetization transfer experiments were conducted at 45 °C and confirmed that the isomers of **2** were interconverting. The rate constant for the exchange was calculated[10] to be 0.312 s^{-1}, yielding a value for $\Delta G^{\ddagger}$ of 19.3 kcal mol^{-1} for the isomerization of **2**. The mechanism of the isomerization of **2** is currently under active investigation.

When *trans*-$Pd(C_6H_5)(NHPh)(PMe_3)_2$ (**3**)[8b] was allowed to react with DMAD under the same conditions as **1**, precipitation of a beige solid was observed. The ^1H NMR spectrum of this solid revealed the presence of only *one* broad singlet at 5.66 ppm and two singlets at 3.73 and 3.70 ppm, which are assigned to the amine and methoxy protons, respectively. These findings, as well as the presence of one singlet at −16.66 ppm in the $^{31}P\{^1H\}$ NMR spectrum, demonstrated that insertion had occurred between the Pd–N bond and that one isomer with trans PMe_3 groups was present (**4**). In the absence of the imine functionality, no isomerization of the C=C bond was observed, suggesting that the imine is assisting the interconversion of the isomers of **2**.[9b]

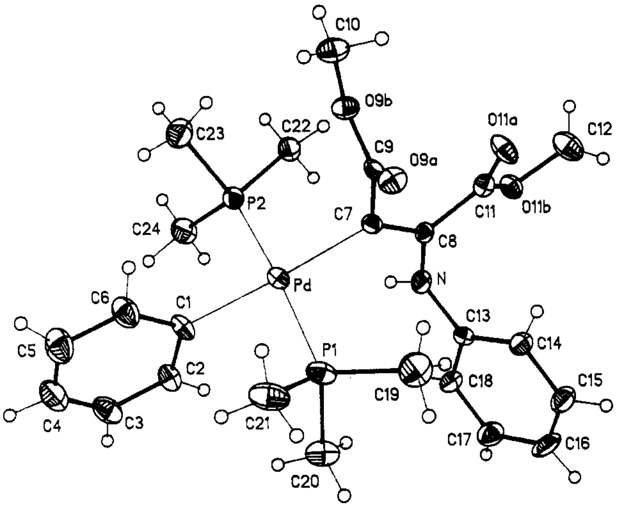
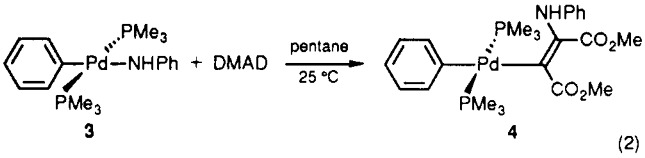


Figure 1. ORTEP drawing of *trans*-$(Me_3P)_2Pd(C_6H_5)$-$[(CH_3COO)C{=}C(COOCH_3)(NHPh)]$ (**4**). Selected bond lengths (Å): Pd-P(1), 2.298 (2); Pd-P(2), 2.309 (2); Pd-C(1), 2.070 (9); Pd-C(7), 2.075 (8); C(7)-C(8), 1.336 (10); N-C(8), 1.429 (12). Selected bond angles (deg): P(1)-Pd-C(1), 87.8 (2); P(2)-Pd-C(1), 87.9 (2); P(2)-Pd-C(7), 92.1 (2); P(1)-Pd-C(7), 92.5 (2); Pd-C(7)-C(8), 127.8 (6); N-C(8)-C(7), 121.0 (8); C(7)-C(8)-C(11), 122.1 (8).



(2)

The structure of **4** in the solid state has been determined by a single-crystal X-ray diffraction study.[11] An ORTEP drawing of **4** appears in Figure 1, along with selected bond lengths and angles. The structure reveals that compound **4** results from insertion of DMAD into the Pd–N bond of **3**. The metal center has the expected square-planar geometry with trans-PMe_3 groups, while the stereochemistry at the C=C double bond is cis. The two Pd–P bond lengths are the same within experimental error, as are the Pd–C bond lengths. The C7–C8 bond length of 1.33 (1) Å is consistent with that of a C=C double bond. Proton difference NOE experiments suggest that the solid state structure is maintained in solution.[12]

Thermolysis of **2** in refluxing toluene for 12 h afforded a black solid (assumed to be palladium metal) and the trisubstituted dihydroisoquinoline **5** in 76% yield (eq 3).

---

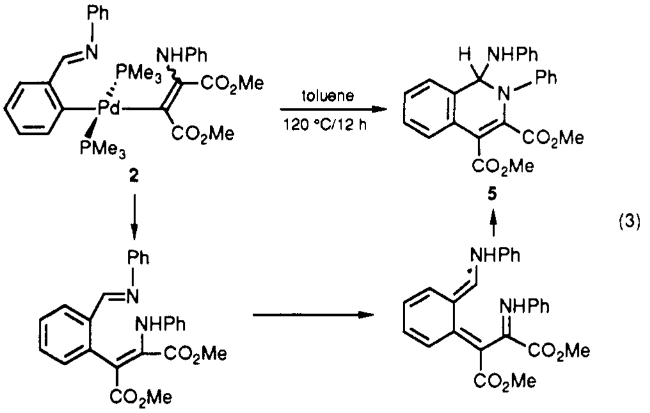
(8) (a) The ratio of the two isomers is 1.5:1, as determined from the $^{31}P\{^1H\}$ NMR spectrum of **2**. The compounds **1–6** have been prepared in 40–75% yields. Complete experimental details have been included as supplementary material, along with spectroscopic and analytical data. (b) General procedures for the synthesis of compounds **1–6** are described below. All procedures were carried out under an argon atmosphere. Compounds **1** and **3**: To a cold (−78 °C) solution of $[(C_6H_4C(H){=}NPh)Pd(PMe_3)_3][BF_4]$[7] or *trans*-$Pd(C_6H_5)I(PMe_3)_2$[8c] in THF was added 1 equiv of KNHPh in THF. The reaction mixture was warmed to room temperature and stirred for 12 h. Solvent removal under reduced pressure was followed by extraction of the residue with diethyl ether. Concentrating and cooling the diethyl ether extracts to −78 °C affords **1** or **3** in 50–60% yield as yellow crystalline solids. The insertion products **2** and **4** are formed by reaction between pentane solutions of **1** or **3** and 3 equiv of DMAD at room temperature. Compounds **2** and **4** precipitate from pentane upon formation. They can be purified by recrystallization from diethyl ether. Compound **5** (*N*-phenyl-1-anilino-3,4-bis(methylcarboxy)-1,2-dihydroisoquinoline) was prepared by refluxing a toluene solution of **2** for 12 h. Solvent removal under reduced pressure was followed by extraction with warm hexane. The hexane solution was filtered and the hexane removed under reduced pressure, giving **5** as a yellow powder in 76% yield. Compound **6** (1-anilino-(*Z*)-1,2-bis(methylcarboxy)-2-phenylethylene) was prepared from **4** in exactly the same manner as **5** and was isolated as a brown oil in 66% yield. (c) Milstein, D. *J. Chem. Soc., Chem. Commun.* **1986**, 817.

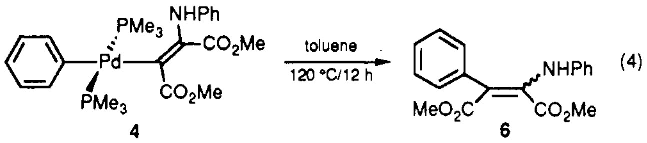
(9) (a) The ^1H NMR spectrum of **2**-^{15}N exhibited two doublets at 5.89 (J_{NH} = 83 Hz) and 5.76 ppm (J_{NH} = 86 Hz), indicating that the two broad singlets in **2** are indeed the amine protons of the *E* and *Z* isomers from the insertion of DMAD into the Pd–N bond of **1**. (b) The ^1H NMR spectrum of **4**-^{15}N has a doublet at 5.95 ppm (J_{NH} = 84 Hz), which is assigned to the N–H proton. Attempts at catalyzing the isomerization of **4** to a mixture of cis and trans isomers have been unsuccessful.

(10) Dahlquist, F. W.; Longmuir, K. J.; Du Vernet, R. B. *J. Magn. Reson.* **1975**, *17*, 404.

(11) (a) Crystal data: $C_{24}H_{35}NO_4P_2Pd$, monoclinic, $P2_1/c$, a = 9.679 (1) Å, b = 21.514 (4) Å, c = 14.005 (3) Å, β = 109.76 (1)°, V = 2744.6 (8) $Å^3$, Z = 4, D_{calc} = 1.379 g cm^{-3}, Mo Kα (λ = 0.71069 Å), T = 298 K. The structure was solved by the heavy-atom method in SHELXTL Plus,[11b] from which the location of the Pd atom was obtained. The rest of the non-hydrogen atoms were obtained from difference Fourier maps, and the structure was refined using full-matrix least squares. The refinement converged to R = 0.0432 and R_w = 0.0462 using 2323 reflections with $I > 3\sigma(I)$. (b) Sheldrick, G. M. SHELXTL Plus; Nicolet XRD Corp., Madison WI, 1990.

(12) Irradiation of the PMe_3 protons of **4** results in a 7% enhancement of the amine proton and a 4% enhancement of *one* of the methoxy signals.





Structure elucidation of **5** was assisted by 2D COSY ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. A mechanism that is consistent with the formation of **5** involves thermally induced reductive elimination of the two organic substituents followed by a formal [1,7]-sigmatropic shift and rearrangement to regain aromaticity. Although sigmatropic shifts of this nature involving heteroatoms are not common,[13] they are symmetry-allowed rearrangements.[14] Both isomers of **2** lead to the formation of **5**; however, it is not known if reductive elimination occurs first, followed by generation of the *Z* isomer of the styrene intermediate or if only the *Z* isomer of **2** reductively eliminates and cyclizes. Thermolysis of **4** under the same conditions as **2** afforded the substituted styrene **6** (eq 4).[15] A broad singlet at 11.07 ppm and two singlets at 3.31 and 2.91 ppm in the ^{1}H NMR spectrum of **6** are assigned to the amine and methoxy protons, respectively.

The potential of these palladium–amido complexes to facilitate carbon–nitrogen bond formation has been demonstrated by the thermal generation of the trisubstituted dihydroisoquinoline **5** from compound **2**. Although the synthesis of dihydroisoquinolines can be achieved by conventional organic methods, they can be limited by reaction conditions and availability of starting materials.[16] The synthesis of *N*-alkylisoquinolinium salts via the reaction between *cationic* palladium complexes and acetylenes is known.[17] The formation of other heterocycles by the reaction of metallated palladium complexes with acetylenes is also known;[18] however, these reactions proceed by insertion of the acetylene into the metal–carbon bond rather than the metal–nitrogen bond. Research involving the reaction of **1** and **3** with other substituted acetylenes is currently in progress in order to determine whether less electrophilic substrates will undergo similar reactions.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Supplementary Material Available: Text giving experimental details of the synthesis of compounds **1**–**6**, tables of NMR data for **1**–**6**, and X-ray crystal structure details and tables of fractional coordinates, thermal parameters, and bond distances and angles for **4** (25 pages). Ordering information is given on any current masthead page.

OM9203587

---

[13] Schweizer, E. E.; Crouse, D. M.; Dalrymple, D. L. *J. Chem. Soc. D* **1969**, 354.

[14] Woodward, R. B.; Hoffmann, R. *Acc. Chem. Res.* **1968**, *1*, 17.

[15] The stereochemistry about the C–C double bond of **6** could not be assigned by using NMR techniques. However, from the ^{1}H NMR of **6** it is clear that only one isomer is present.

[16] *Organic Reactions*; Wiley: London, Sydney, 1951; Vol VI, Chapters 2–4.

[17] (a) Wu, G.; Geib, S. J.; Rheingold, A. L.; Heck, R. F. *J. Org. Chem.* **1988**, *53*, 3238. (b) Wu, G.; Geib, S. J.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1987**, *6*, 1941. (c) Tao, W.; Silverberg, L. J.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1989**, *8*, 2550.

[18] (a) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985. (b) Sakamoto, T.; Kondo, Y.; Hiroshi, Y. *Heterocycles* **1988**, *27*, 2225. (c) Cacchi, S. *Pure Appl. Chem.* **1990**, *62*, 713. (d) Pfeffer, M. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 567.

Synthesis and Structure of an Organotitanium Hydroxide Containing an O–H–O Bond

Feng-quan Liu, Herbert W. Roesky,* Hans-Georg Schmidt, and Mathias Noltemeyer

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, 3400 Göttingen, Germany

Received June 15, 1992

Summary: The preparation of the first binuclear titanium hydroxide containing an O–H–O bond is described. The X-ray structural analysis indicates that steric factors prevent the elimination of water.

Organotitanium compounds are the most widely used reagents for the synthesis of basic organic compounds and polymers.[1] To the best of our knowledge there are no reports on multinuclear Ti(IV) hydroxides.[2,3] Compounds of this type might play an important role in condensation and epoxidation reactions.

According to Parshall[4] Re, Cr, Mo, V, Zr, and Ti are active catalysts in this field. Our interest in model compounds for metal oxides on silica surfaces[5] prompted us

---

[1] *Gmelin Handbook of Inorganic Chemistry*; Springer-Verlag: Heidelberg, Germany, 1977–1990; Organotitanium Compounds 1–5. Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99. Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds. *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, U.K., 1982; Vol. 3.

[2] Röhl, H.; Lange, E.; Gössl, T.; Roth, G. *Angew. Chem.* **1962**, *74*, 155. Chem. Werke Hüls AG, Ger. Patent 1153365, 1961; *Chem. Abstr.* **1964**, *60*, 17941794. Bochmann, M.; Jaggar, A. J.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Polyhedron* **1989**, *8*, 1938. Bochmann, M.; Jaggar, A. J.; Hursthouse, M. B.; Mazid, M. *Polyhedron* **1990**, *9*, 2097.

[3] For a report on a Ti(III) hydroxide of composition [CpTi(OH)]$_2$C$_{10}$H$_8$, see: Guggenberger, L. J.; Tebbe, F. N. *J. Am. Chem. Soc.* **1976**, *98*, 4137.

[4] Parshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980.