CD_3OD) indicate that the bound fluoride anion is labile on the ^{19}F NMR time scale, undergoing rapid exchange with free fluoride anion in solution. Currently, we are studying this exchange process and exploring the extent to which the protonated sapphyrins may serve as binding agents for other small anions and neutral molecules.

Acknowledgment. This work was supported by Grant No. 1581 from the Texas Advanced Research Program to J.L.S. and by NIH Grant HL 13157 to J.A.I. J.L.S. also thanks the NSF for a Presidential Young Investigator Award (1986), the Alfred P. Sloan Foundation for a Research Fellowship (1989-1991), and the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Award (1988-1992). J.L.S. and M.J.C. are grateful to Prof. David Dolphin for making available unpublished details of his sapphyrin-directed synthetic studies, to Prof. David Laude for laser desorption mass spectrometric analyses of compounds [**2**·$(2H^+)$·F^-][PF_6] and [**2**·$(2H^+)$·F^-]F, and to Kaori Furuta for synthetic assistance.

Supplementary Material Available: Preparative details and characterization data for compounds **2**, **3**, **4**, **5**, **10**, **11**, **12**, **14**, **15**, and **16** and a table of positional parameters for [**2**·$(2H^+)$·F^-][PF_6] (9 pages). Ordering information is given on any current masthead page.

Novel Dependency of Stereochemistry upon Metal, Ligand, and Solvent in Oxidative Addition of Allylic Chloride to Pd(0) and Pt(0) Complexes

Hideo Kurosawa,* Sensuke Ogoshi, Yoshikane Kawasaki, Shinji Murai, Masa-aki Miyoshi, and Isao Ikeda

Department of Applied Chemistry, Osaka University Suita, Osaka 565, Japan

Received November 2, 1989

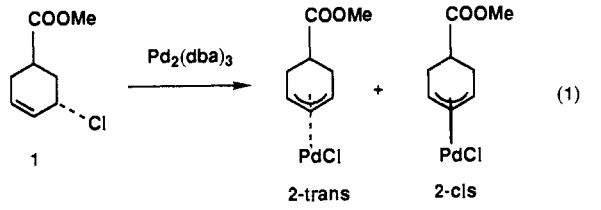
The reaction of allylic electrophiles with electron-rich metal complexes forming allylmetal intermediates is one of the most crucial steps in various metal-catalyzed organic transformations.[1] The stereochemistry of this reaction with regard to the relative disposition of the metal and the leaving groups is predominantly anti.[1a,2] The syn stereochemistry is limited to very few cases,[3,4] of which direct isolation of allylmetals has been achieved in only one example (a Mo complex and allylic acetate).[4] We describe here novel variation of the stereochemistry, ranging from almost pure anti to almost pure syn, in the synthesis of allylmetals from reactions of allylic chlorides with Pd(0) and Pt(0) nucleophiles depending on the nature of metal, ligands, and solvents. We also report a catalytic C-C coupling exhibiting a hitherto unknown stereochemical outcome based on the newly found syn stereochemistry of the stoichiometric process.

Table I. Reaction of **1** with $Pd_2(dba)_3$[a]

run	solvent	isomer ratio: **2**-trans/**2**-cis
1	benzene	100/0
2	dichloromethane	94/6
3	THF	95/5
4	acetone	75/25
5	DMF	29/71
6	acetonitrile	5/95
7	DMSO	3/97

[a] Reaction was run at room temperature for 5-10 h. Yields were almost quantitative in each case. Isomer ratio was determined by ^1H NMR.

Reactions of allylic chloride **1**[2b] with $Pd_2(dba)_3$[5] (dba = dibenzylideneacetone) at room temperature for several hours afforded good yields of a mixture of η^3-allyl complexes,[6] **2**-trans and **2**-cis, with the isomer ratio depending on the solvent used (eq 1 and Table I). In none of these reactions was trans to cis isomerization of **1** observed, nor did the interconversion between **2**-trans and **2**-cis occur under the reaction conditions. The structure of **2** could be assigned by converting these into **3** and **4**, of which both trans and cis configurations have been established before,[2b,e] via attack of phenyl anion[7a] (retention)[8] and dimethyl malonate anion[7b] (inversion).[8] Of particular interest is the almost exclusive formation of **2**-trans in the reaction carried out in benzene, CH_2Cl_2, and THF. To the best of our knowledge, this is the first example of the syn oxidative addition of allylic halides with metallic nucleophiles. Although the cis isomer of **1** did not react with $Pd_2(dba)_3$ under similar conditions so cleanly as to allow stereochemical examination, the results of catalytic reactions described later suggest that this isomer also undergoes dominant, albeit not exclusive, syn addition with Pd(0) olefin complexes in benzene. Contrary to these results, the anti addition dominated in acetonitrile and DMSO (Table I). It may well be that these solvents play a role in preventing Pd-Cl bond formation inherent in the syn addition[9] through coordination to Pd, and/or stabilizing the transition state of the anti addition in which charge separation would take place to a much greater extent than in the syn addition.



The anti addition dominated in the reaction of Pd(0) nucleophiles coordinated with much stronger donors. Thus, the anti

(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 19. (b) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1987**, *109*, 1469-1478 and references therein. (c) Trost, B. M.; Tometzki, G. B.; Hung, M. H. *Ibid.* **1987**, *109*, 2176-2177. (d) Xu, Y.; Zhou, B. *J. Org. Chem.* **1987**, *52*, 974-977. (e) Minami, I.; Shimizu, I.; Tsuji, J. *J. Organomet. Chem.* **1985**, *296*, 269-280.

(2) (a) Tseng, C. C.; Yen, S. J.; Goering, H. L. *J. Org. Chem.* **1986**, *51*, 2892-2895 and references therein. (b) Sheffy, F. K.; Godschalx, J. P.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4833-4840. (c) Corey, E. J.; Boag, N. W. *Tetrahedron Lett.* **1984**, *25*, 3063-3066. (d) Hayashi, T.; Hagihara, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1983**, *105*, 7767-7768. (e) Trost, B. M.; Verhoeven, T. R. *Ibid.* **1980**, *102*, 4730-4743.

(3) (a) Stary, I.; Kocovsky, P. *J. Am. Chem. Soc.* **1989**, *111*, 4981-4982. (b) Goering, H. L.; Kantner, S. S.; Tseng, C. C. *J. Org. Chem.* **1983**, *48*, 715-721.

(4) Faller, J. W.; Linebarrier, D. *Organometallics* **1988**, *7*, 1670-1672.

(5) (a) Moseley, K.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1974**, 169-175. (b) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253-266.

(6) Satisfactory analytical results were obtained. **2**-trans: ^1H NMR ($CDCl_3$) δ 1.74 (ddd, J = 3.6, 7.5, 17.0 Hz, 2 H), 2.22 (ddd, J = 3.0, 6.4, 17.0, Hz, 2 H), 3.41 (tt, J = 6.4, 7.5 Hz, 1 H), 3.66 (s, 3 H), 5.08 (ddd, J = 3.0, 3.6, 6.5 Hz, 2 H), 5.49 (t, J = 6.5 Hz, 1 H). **2**-cis: ^1H NMR ($CDCl_3$) δ 2.00-2.06 (m, 3 H), 2.26 (br m, 2 H), 3.67 (s, 3 H), 5.21 (t, J = 6.3 Hz, 2 H), 5.55 (t, J = 6.3 Hz, 1 H).

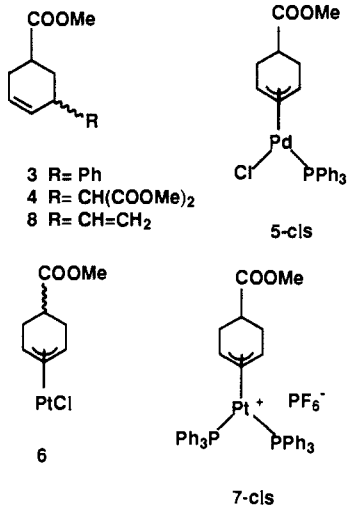
(7) (a) One equivalent of $NaBPh_4$ and 4 equiv of maleic anhydride in CH_2Cl_2 at room temperature for 24 h (yield 95%, stereospecificity almost 100%). (b) Addition of 2 equiv of PPh_3 in CH_2Cl_2 at 0 °C, followed by 1.5 equiv of $NaCH(COOMe)_2$ in THF for 2 h (yield and specificity almost 100%).

(8) Hayashi, T.; Konishi, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1984**, 107-108.

(9) (a) Syn addition would be related to reductive elimination of η^3-allyl(chloro)palladium by the microscopic reversibility principle where this step for η^3-allyl(organo)palladiums has been shown to be energetically feasible.[9b] Alternatively, an S_N2' mechanism may be consistent with syn addition,[9c] even though anti selectivity has often been encountered in this pathway,[9c] particularly in reactions involving organotransition-metal nucleophiles.[2c] (b) Kurosawa, H.; Emoto, M.; Ohnishi, H.; Miki, K.; Kasai, N.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1987**, *109*, 6333-6340. (c) Magid, R. M. *Tetrahedron* **1980**, *36*, 1901-1930.

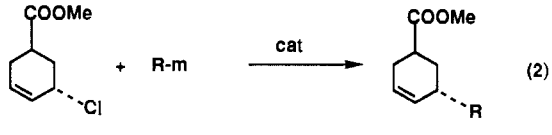
0002-7863/90/1512-2813$02.50/0

adduct **5**-cis[10] was isolated in almost quantitative yield from the reaction of **1** with $Pd(PPh_3)_4$ even in benzene, this observation being consistent with the stereochemical result in the catalytic reaction.[2b] Even a monophosphine coordinated Pd(0) species, $Pd(PPh_3)((E)\text{-}MeOOCCH{=}CHCOOMe)_n$, which was generated in situ in benzene,[11] also reacted with **1** in a predominantly anti fashion to give **5**-cis.



Unlike the syn addition of the dba-Pd complex in CH_2Cl_2, the anti addition was found dominant in the analogous, though somewhat slower, reaction of Pt complex $Pt(dba)_2$[5a] with **1** in the same solvent at room temperature, to give a moderate yield of **6** (**6**-trans/**6**-cis, 23/77).[12] The reaction of $Pt(C_2H_4)(PPh_3)_2$ with **1** in CH_2Cl_2, followed by treatment with NH_4PF_6, afforded a good yield of **7**-cis[13] exclusively.

Increasing attention has been paid to unique roles of Pd catalysts bearing activated olefins but not bearing ordinary phosphine ligands in accomplishing some selective couplings of organic electrophiles with nonstabilized carbanions.[14] Following the above-mentioned observation of syn addition under certain conditions, we carried out catalytic coupling of **1** with some organometallics using a catalyst, olefin/$Pd(\eta^3\text{-}CH_2CHCH_2)Cl$ (olefin = maleic anhydride, dimethyl fumarate), to find high-yield formation of net retention products (eq 2)[15] as the result of occurrence of two consecutive syn transformations (oxidative addition and reductive elimination).[16] The cis isomer of **1** also gave a higher amount of the net retention products than of the inversion products.[15] Further studies are in progress to elucidate electronic and/or steric factors for affecting the stereochemical course of the attack of metallic nucleophiles at allylic systems and to develop application of this key step.



R-m = Ph-BPh_3^-, Ph-$SnBu_3$, CH_2=CH-$SnBu_3$
cat = Olefin / $Pd(C_3H_5)Cl$

Acknowledgment. Partial support of this work by Grants-in-Aid from Ministry of Education, Science, and Culture (01550649, 01649511) is acknowledged. Thanks are also due to the Analytical Center, Faculty of Engineering, Osaka University, for the use of JEOL GSX-400 and Bruker AM600 spectrometers.

(10) Authentic samples of **5**-trans and **5**-cis were prepared from both of **2**-cis **2**-trans and with 1 equiv of PPh_3 and well characterized spectrally. The most diagnostic aspect was that the proton α to COOMe in the trans isomer resonated at much lower field with two moderate J_H values [δ 3.21 (tt, J = 6.8, 8.3 Hz)] than that in the cis isomer showing one moderate J_H value and one large J_H value [δ 1.99 (tt, J = 5.5, 10.8 Hz)].

(11) Via reductive elimination of $Pd(\eta^3\text{-}CH_2CHCH_2)(C_6H_3Cl_2\text{-}2,5)(PPh_3)$ in the presence of 4 equiv of (E)-MeOOCCH=CHCOOMe.[9b]

(12) **6**-trans: ^1H NMR ($CDCl_3$) δ 1.54 (br m, 2 H), 2.12 (ddd, J = 3.5, 6.2, 15.2 Hz, 2 H), 3.27 (br, 1 H), 3.66 (s, 3 H), 4.72 (v br, 2 H), 4.84 (t, J = 5.2 Hz, 1 H). **6**-cis: ^1H NMR ($CDCl_3$) δ 1.87-1.99 (m, 3 H), 2.25 (dt, J = 16.5, 5.5 Hz, 2 H), 3.69 (s, 3 H), 4.94 (br, 3 H).

(13) Compared spectrally with samples prepared from **6**, 2 equiv of PPh_3, and NH_4PF_6. In particular, **7**-cis showed a triplet of triplets at δ 1.90 (J = 5.5, 11.2 Hz), while **7**-trans showed one at δ 2.71 (J = 6.2, 9.4 Hz).

(14) (a) Sustmann, R.; Lau, J.; Zipp, M. *Tetrahedron Lett.* **1986**, *27*, 5207-5210. (b) Goliaszewski, A.; Schwartz, J. *Tetrahedron* **1985**, *41*, 5779-5789 and references therein. (c) Temple, J. S.; Riediker, M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 1310-1315. (d) Hayasi, Y.; Riediker, M.; Temple, J. S.; Schwartz, J. *Tetrahedron Lett.* **1981**, *22*, 2629-2632.

(15) To a CH_2Cl_2 solution (2 mL) of **1** (0.4 mmol), $Pd(\eta^3\text{-}CH_2CHCH_2)Cl$ (0.02 mmol), and dimethyl fumarate (0.07 mmol) was added drop by drop under argon a THF solution (1 mL) of $NaBPh_4$ (0.4 mmol). After the mixture was stirred for 24 h at room temperature, the solvents were evaporated under reduced pressure and crude products were analyzed by GLC and ^1H NMR spectroscopy (yield 95%, **3**-trans/**3**-cis, 90/10). Similarly, **1** and Bu_3SnPh or $Bu_3SnCH{=}CH_2$ in the presence of $Pd(\eta^3\text{-}CH_2CHCH_2)Cl$ (5 mol % based on **1**) and maleic anhydride (20 mol %) in benzene at room temperature for 48 h afforded **3** (80%, **3**-trans/**3**-cis, 98/2) and **8**[2b] (92%, **8**-trans/**8**-cis, 92/8), respectively. A trans/cis mixture (mole ratio 2/1) of **1** was also allowed to react with these tin reagents under the same conditions except for longer reaction periods employed for converting almost all of the allyl chlorides into the products. On the basis of the total isomer ratio of the products determined (**3**-trans/**3**-cis, 3.1/1; **8**-trans/**8**-cis, 2.75/1) and the reaction selectivity exhibited by the trans chloride described above, it was deduced that the cis isomer of **1** afforded a mixture of the products in the ratio **3**-trans/**3**-cis, 30/70, and **8**-trans/**8**-cis, 36/64.

(16) The stereochemistry of the attack of Pd(0) maleic anhydride complex at allylic acetates in THF has been deduced as anti from the result of the catalytic alkylation.[14d]

Synthesis and Characterization of a Substituted η^2-Pyridine Complex of Tantalum Prepared by [2 + 2 + 2] Cycloaddition Chemistry

Jamie R. Strickler, Michael A. Bruck, and David E. Wigley*

Carl S. Marvel Laboratories of Chemistry
Department of Chemistry, University of Arizona
Tucson, Arizona 85721

Received October 18, 1989

Understanding the interactions between aromatic hydrocarbons and metal surfaces,[1] atoms,[2] and coordination complexes[3] has proven essential for elucidating the mechanistic details of aromatic C-H bond activation,[4] arene hydrogenation,[5] and alkyne cyclotrimerization.[6] Interconversions between the various arene-metal structural forms (e.g., $\eta^6 \rightleftarrows \eta^4 \rightleftarrows \eta^2$) may be of considerable importance to such processes.[3b,7] While several transition-metal

(1) (a) Demuth, J. E.; Eastman, D. E. *Phys. Rev. B.* **1976**, *13*, 1523. (b) Moyes, R. B.; Wells, P. B. *Adv. Catal.* **1973**, *23*, 121 and references therein. (c) Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 773.

(2) (a) Klabunde, K. J. *Acc. Chem. Res.* **1975**, *8*, 393. (b) Green, M. L. H. *J. Organomet. Chem.* **1980**, *200*, 119. (c) Allison, J. *Prog. Inorg. Chem.* **1986**, *34*, 628. (d) Timms, P. L. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 273.

(3) (a) Silverthorn, W. E. *Adv. Organomet. Chem.* **1975**, *13*, 47. (b) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499.

(4) (a) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650. (b) Jones, W. D.; Feher, F. J. *Ibid.* **1982**, *104*, 4240.

(5) (a) Bleeke, J. R.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 556. (b) Muetterties, E. L.; Bleeke, J. R. *Acc. Chem. Res.* **1979**, *12*, 324 and references therein.

(6) (a) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (b) Vollhardt, K. P. C. In *Strategies and Tactics in Organic Synthesis*; Lindberg, T., Ed.; Academic Press: Orlando, 1984; pp 299-324. (c) McAlister, D. R.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1666 and references therein.

(7) For examples of η^4-arenes, see: (a) Boncella, J. M.; Green, M. L. H.; O'Hare, D. *J. Chem. Soc., Chem. Commun.* **1986**, 618. (b) Finke, R. G.; Voegeli, R. H.; Laganis, E. D.; Boekelheide, V. *Organometallics* **1983**, *2*, 347. (c) Bowyer, W. J.; Geiger, W. E. *J. Am. Chem. Soc.* **1985**, *107*, 5657.

0002-7863/90/1512-2814$02.50/0