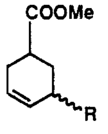
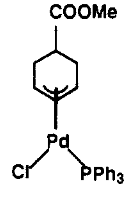
2814 J. Am. Chem. Soc. **1990**, *112*, 2814-2816

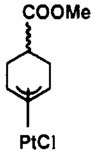
adduct **5**-cis[10] was isolated in almost quantitative yield from the reaction of **1** with $Pd(PPh_3)_4$ even in benzene, this observation being consistent with the stereochemical result in the catalytic reaction.[2b] Even a monophosphine coordinated Pd(0) species, $Pd(PPh_3)((E)\text{-}MeOOCCH{=}CHCOOMe)_n$,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



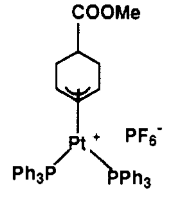
3 R= Ph
4 R= CH(COOMe)2
8 R= CH=CH2



5-cis



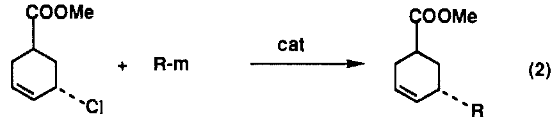
6



7-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.



(2)

R-m = Ph-BPh3‾ , Ph-SnBu3 , CH2=CH-SnBu3
cat = Olefin / Pd(C3H5)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.

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(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 $(E)\text{-}MeOOCCH{=}CHCOOMe$.[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).

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(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

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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

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(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.

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(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.

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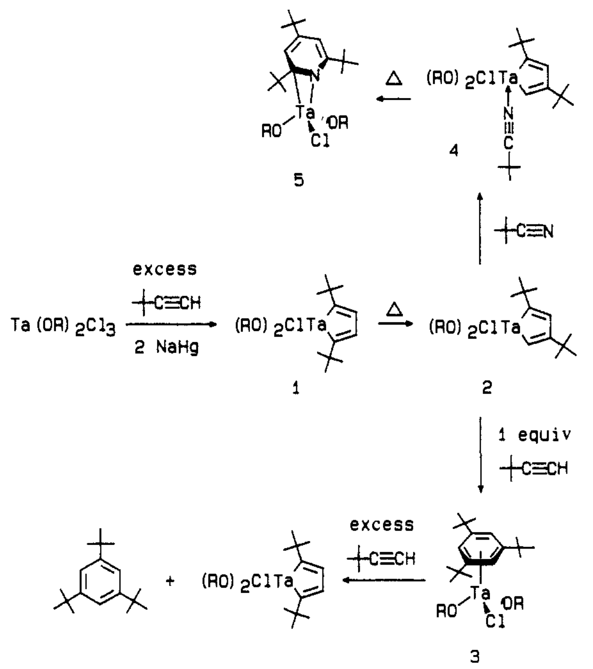
Scheme I

OR = 2, 6-diisopropylphenoxide



complexes featuring η^2-coordinated arenes have been characterized,[8] η^2-bound pyridines (also relevant to C–H bond activation) are elusive.[9,10] Herein we report the preparation and properties of a rare η^2-bound, substituted pyridine complex, (η^2(*N*,*C*)-2,4,6-$NC_5H_2{}^tBu_3$)Ta(DIPP)$_2$Cl (DIPP = 2,6-diisopropylphenoxide). Since the pyridine ligand has been assembled from two acetylenes and one nitrile, this complex may represent a heretofore unrecognized intermediate in metal-catalyzed [2 + 2 + 2] cycloaddition chemistry.[11,12]

The metallacyclopentadiene complex (DIPP)$_2$ClTa(CCMe$_3$=CHCH=CCMe$_3$) (**1**) can be isolated in 50% yield upon reacting Ta(DIPP)$_2$Cl$_3$·OEt$_2$,[13] at least 2 equiv of HC≡CCMe$_3$, and 2 equiv of NaHg in diethyl ether, Scheme I.[14] This α,α' metallacycle represents the kinetic product of this reaction since it can be thermolyzed (toluene, 70 °C, 3 days) to provide the α,β' isomer (DIPP)$_2$ClTa(CCMe$_3$=CHCCMe$_3$=CH) (**2**). Metallacycle **2** (but not **1**) reacts readily with 1 equiv of HC≡CCMe$_3$ to provide solutions from which blue crystals of (η^6-1,3,5-$C_6H_3{}^tBu_3$)Ta(DIPP)$_2$Cl (**3**) are obtained in ca. 30% yield, Scheme I. 1,3,5-$C_6H_3{}^tBu_3$ is formed quantitatively upon hydrolyzing **3** or upon reacting **3** with an excess of HC≡CCMe$_3$ (which also regenerates compound **1**).[15]

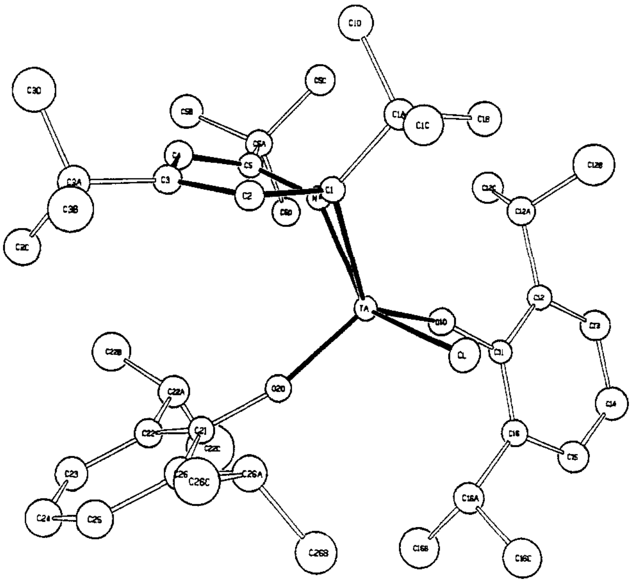


Figure 1. Drawing of (η^2(*N*,*C*)-2,4,6-$NC_5H_2{}^tBu_3$)Ta(DIPP)$_2$Cl (**5**, DIPP = 2,6-diisopropylphenoxide).

Although **2** has not been induced to crystallize, its reaction with *tert*-butylcyanide (pentane, −40 °C) provides solid samples of the yellow orange adduct (DIPP)$_2$Cl(Me$_3$CC≡N)Ta(CCMe$_3$=CHCCMe$_3$=CH) (**4**) ($\nu_{C\equiv N}$ = 2278 cm^{-1}). Within minutes at room temperature, **4** begins to rearrange to maroon complex **5**, Scheme I. The NMR spectra of **5** reveal that *all three tert*-butyl groups are inequivalent, even to 90 °C,[16] which contrasts sharply with the room-temperature equivalence of the *tert*-butyl groups in (η^6-1,3,5-$C_6H_3{}^tBu_3$)Ta(DIPP)$_2$Cl (**3**). Samples of **5** can be sublimed at 110 °C with little decomposition (2 × 10^{-5} Torr) while **3** releases its arene slowly at room temperature. The He I valence photoelectron spectrum of **5** reveals a broad ionization at ca. 6.75 eV, with a band shape reminiscent of the lowest energy ionization from tantalum olefin complexes which show a metallacyclopropane electronic structure.[17] The cyclic voltammogram of **5** displays an irreversible oxidation at $E_{p,a}$ = +0.63 V vs Ag/AgCl, which is ca. *0.5 V more positive* than the oxidation of the related arene complex (η^6-C_6Me_6)Ta(DIPP)$_2$Cl.[18] Accordingly, the chemical oxidation of **5** (e.g., with pyridine *N*-oxide) provides free 2,4,6-$NC_5H_2{}^tBu_3$. All of the above data require the formulation of **5** as the pyridine complex (2,4,6-$NC_5H_2{}^tBu_3$)Ta(DIPP)$_2$Cl; however, the striking differences between **3** and **5** implicate a structural formulation other than an η^6 complex.[19]

An X-ray crystallographic study of **5** established the η^2 coordination of the pyridine ligand, Figure 1.[20,21] The tantalum–

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[8] See, for example: (a) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883. (b) Harman, W. D.; Sekine, M.; Taube, H. *Ibid.* **1988**, *110*, 5725. (c) Harman, W. D.; Taube, H. *Ibid.* **1988**, *110*, 7555. (d) Sweet, J. R.; Graham, W. A. G. *Ibid.* **1983**, *105*, 305. (e) Belt, S. T.; Duckett, S. B.; Helliwell, M.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1989**, 928.

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[10] (a) Cordone, R.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 8101. (b) For related η^2-pyridinium complexes, see: Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 2896.

[11] For examples of pyridine syntheses via [2 + 2 + 2] cycloaddition chemistry, see: (a) Wakatsuki, Y.; Yamazaki, H. *Synthesis* **1976**, 26. (b) Wakatsuki, Y.; Yamazaki, H. *Tetrahedron Lett.* **1973**, 3383. (c) Bönnemann, H.; Brinkmann, R.; Schenkluhn, H. *Synthesis* **1974**, 575. (d) Bönnemann, H.; Brinkmann, R. *Ibid.* **1975**, 600. (e) Parnell, C. A.; Vollhardt, K. P. C. *Tetrahedron* **1985**, 5791.

[12] (a) A "metallanorcaradiene" (η^2-benzene) has been considered as a possible intermediate which forms from the collapse of a metallacycloheptatriene in the cycloaddition preparation of benzocyclobutanes. See refs 6b and 12b. (b) Vollhardt, K. P. C.; Bergman, R. G. *J. Am. Chem. Soc.* **1974**, *96*, 4996.

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[14] Analytical and spectroscopic data for compounds **1–4** are available as supplementary material.

[15] The hydrolysis of **3** produces 1,3,5-$C_6H_3{}^tBu_3$ and HDIPP as the only NMR-observable products, along with, presumably, hydrated Ta$_2$O$_5$. See: Neithamer, D. R.; LaPointe, R. E.; Wheeler, R. A.; Richeson, D. S.; Van Duyne, G. D.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1989**, *111*, 9056.

[16] (η^2(*N*,*C*)-2,4,6-$NC_5H_2{}^tBu_3$)Ta(DIPP)$_2$Cl (**5**). ^{1}H NMR (toluene-d_8, 90 °C): δ 7.02–6.84 (A$_2$B m, 6 H, H$_{aryl}$), 5.71 (br (FWHM = 40 Hz), 2 H, $NC_5H_2{}^tBu_3$), 3.57 (spt, 4 H, C*H*Me$_2$), 1.20 (d, 24 H, CH*Me*$_2$), 1.17, 1.14, 1.03 (s, 9 H each, $NC_5H_2{}^tBu_3$). Partial ^{1}H NMR (C$_6$D$_6$, probe temperature): δ 5.93 (br) and 5.55 (s) (1 H each, $NC_5H_2{}^tBu_3$), 1.36, 1.12, 1.05 (s, 9 H each, $NC_5H_2{}^tBu_3$). Partial ^{13}C NMR (CDCl$_3$, probe temperature): 2,4,6-$NC_5H_2{}^tBu_3$ ring carbon resonances at δ 171.7, 149.6, 117.4, 106 (br), 100.6. Anal. Calcd for $C_{41}H_{63}ClNO_2Ta$: C, 60.18; H, 7.76; N, 1.71. Found: C, 60.50; H, 8.01; N, 1.77.

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[18] (a) $E_{p,a}$ values reported at a Pt electrode vs Ag/AgCl for CH$_2$Cl$_2$ solution, 0.1 M in ^{n}Bu$_4$NPF$_6$. $E_{p,a}$ for (η^6-C_6Me_6)Ta(DIPP)$_2$Cl[18b] occurs at ca. +0.10 V vs Ag/AgCl. Unfortunately, (η^6-1,3,5-$C_6H_3{}^tBu_3$)Ta(DIPP)$_2$Cl (**3**) reacts with MeC≡N, CH$_2$Cl$_2$, and other electrochemical solvents so that a direct comparison between **3** and **5** is not yet possible. (b) Bruck, M. A.; Copenhaver, A. S.; Wigley, D. E. *J. Am. Chem. Soc.* **1987**, *109*, 6525.

[19] For examples of η^6-pyridines, see: (a) Davies, S. G.; Shipton, M. R. *J. Chem. Soc., Chem. Commun.* **1989**, 995. (b) Schmidt, R. E.; Massa, W. *Z. Naturforsch.* **1984**, *39B*, 213. (c) Simons, L. H.; Riley, P. E.; Davis, R. E.; Lagowski, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 1044. (d) Wucherer, E. J.; Muetterties, E. L. *Organometallics* **1987**, *6*, 1691.

pyridine interaction features a Ta–C(1) bond of 2.126 (9) Å and Ta–N bond of 1.966 (6) Å, while C(2) and C(5) are clearly out of bonding range (2.99 (1) Å and 3.159 (8) Å from Ta, respectively). Unlike the related structure of $(\text{silox})_3\text{Ta}(\eta^2(N,C)\text{-NC}_5\text{H}_5)$[9] (silox = ${}^t\text{Bu}_3\text{SiO}$), a clear 1,3-diene π localization is not evident in **5**.[21] The pyridine is far from planar: the severe distortion (perhaps sterically enhanced) appears to be toward a twist-boat conformation. Ta–N–C(5) = 140.3 (5)° and Ta–C(1)–C(2) = 111.5 (6)° while the dihedral angle between the best pyridine plane and the Ta–(N,C) plane is 117.6 (5)°. A short Ta–N bond in conjunction with the NMR data[16] fully supports the η^2-(N,C) mode of bonding as in $(\text{silox})_3\text{Ta}(\eta^2(N,C)\text{-NC}_5\text{H}_5)$,[9] rather than an η^2-(C,C) mode reported in the lutidine complex $[(\eta^2\text{-lutidine})\text{Os}(\text{NH}_3)_5]^{2+}$.[10]

The structure of **5** suggests that a metal–ligand π interaction ($d\pi \rightarrow p\pi^*$) is preferred over the rather inefficient δ back-bonding ($d\delta \rightarrow$ arene δ^* (arene π^* LUMO) as in **3**)[13,22] to allow the metal to attain its highest oxidation state. No intermediates are observed (by ^{1}H NMR) in the rearrangement of **4** to **5**; thus, whether a transient η^6-pyridine or N-metallacycloimine ($\text{TaN=CCMe}_3\text{CH=CCMe}_3\text{CH=CCMe}_3$) is involved is unknown. Since the tri-*tert*-butylbenzene ligand coordinates η^6 in complex **3**, it is unlikely that *steric* constraints are inducing an incipient η^6-tri-*tert*-butylpyridine ligand to slip to the observed η^2 form in **5**. The η^2 coordination results in a disruption of the pyridine's aromaticity, severely distorts the ligand, and extracts a high energetic price,[23] but one that seems to be more than recovered in the tantalum–nitrogen interaction. Additionally, compounds related to **5** may be relevant to C–H bond activation: intermediate η^2-(N,C) pyridine species may be implicated prior to pyridyl $(\eta^2(N,C)\text{-NC}_5\text{H}_4)$ formation[24] and related pyridine C_α functionalizations.[25]

Acknowledgment. Support from the U.S. Army Research Office (Short Term Innovative Research Program) and the Department of Chemistry, University of Arizona, are gratefully acknowledged. We thank Dr. A. Rai-Chauduri for obtaining the PES spectrum of **5**.

Supplementary Material Available: Analytical and spectroscopic data for compounds **1**–**4** and tables of crystal data and data collection parameters, atomic positional and thermal parameters, bond distances, and bond angles for $(\eta^2(N,C)\text{-2,4,6-NC}_5\text{H}_2{}^t\text{Bu}_3)\text{Ta}(\text{O-2,6-C}_6\text{H}_3{}^i\text{Pr}_2)_2\text{Cl}$ (**5** pages). Ordering information is given on any current masthead page.

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(20) A dark red irregular crystal of $(\eta^2(N,C)\text{-2,4,6-NC}_5\text{H}_2{}^t\text{Bu}_3)\text{Ta}(\text{DIPP})_2\text{Cl}$ (approximate dimensions 0.30 × 0.30 × 0.30 mm) crystallized (pentane, −40 °C) in the orthorhombic space group $Pca2_1$ (No. 29) with a = 20.674 (2) Å, b = 10.087 (5) Å, c = 19.908 (5) Å, and V = 4151.6 Å^3 with $Z = 4$ (ρ_{calcd} = 1.31 g cm^{-3}) and μ = 27.1 cm^{-1}. Data were collected on a Syntex P2$_1$ diffractometer at 23 ± 1 °C with Mo Kα radiation (λ = 0.71073 Å). A total of 4153 reflections were collected in the h, k, $\pm l$ octants (3799 unique) in the range $2° \leq 2\theta \leq 50°$. Only the 2536 reflections having $I \geq 3\sigma(I)$ were used in the refinements. The structure was solved by direct methods and is at an intermediate stage of refinement (full-matrix least-squares techniques) for a current $R = 0.041$ and $R_w = 0.045$. The largest peak in the difference Fourier map has a height of 1.21 e/Å^3. No numerical absorption correction was made, but Lorentz and polarization corrections were applied. The final details will be provided in a full report.

(21) Selected interatomic distances (Å): Ta–O(10) = 1.876 (6), Ta–O(20) = 1.861 (6), Ta–Cl = 2.343 (3), N–C(1) = 1.48 (2), C(1)–C(2) = 1.46 (1), C(2)–C(3) = 1.43 (2), C(3)–C(4) = 1.46 (2), C(4)–C(5) = 1.35 (2), C(5)–N = 1.386 (9). Selected bond angles (deg, (N,C) = N–C(1) midpoint): Ta–O(10)–C(11) = 161.7 (7), Ta–O(20)–C(21) = 165.1 (6), (N,C)–Ta–O(10) = 116.3 (3), (N,C)–Ta–O(20) = 112.2 (2), (N,C)–Ta–Cl = 110.9 (1), O(10)–Ta–O(20) = 117.3 (4), O(10)–Ta–Cl = 95.2 (3), O(20)–Ta–Cl = 102.5 (2), Ta–C(1)–N = 63.1 (6), Ta–N–C(1) = 75.2 (7).

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Novel Allene–Acetylene Cross-Condensation Catalyzed by Palladium Complexes

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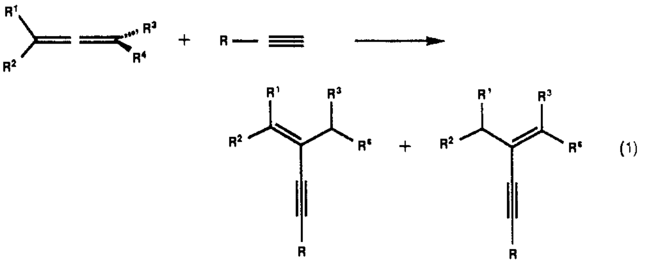
The high propensity for allenes to undergo oligomerization in the presence of Pd catalysts[1] has greatly limited their usefulness as substrates for C–C bond formation with such catalysts.[2] The increasing synthetic availability of allenes enhances their attractiveness as reactive building blocks. In our search for new condensation reactions to maximize synthetic efficiency in which the product is the simple sum of the reactants, we were attracted to the reaction of eq 1. In this paper, we report our preliminary results, in which we succeeded in achieving such a condensation with an unusual dependence of product regioselectivity on the choice of catalyst.[3]

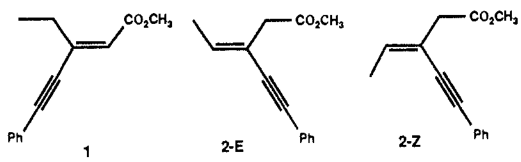


The sensitivity of the allenes toward oligomerization with palladium complexes was revealed by our earlier failures to effect cycloisomerizations of enallenes, a process that ultimately succeeded with a nickel–chromium catalyst.[4,5] In contrast to that study, exposing an equimolar mixture of phenylethyne and methyl 2,3-pentadienoate to various palladium(2+) catalysts in benzene at 65 °C gave cross-coupled products as summarized in Table I. The most striking feature of this table is the favoring of the conjugated enoate **1** with the more electron deficient catalyst systems (optimized at 81:19 of **1**:**2**) and the favoring of the nonconjugated enoates **2** with the more electron rich catalyst systems (optimized at 9:91 of **1**:**2**).

Table II and eq 2 illustrate the generality with respect to the acetylene and 1,2-disubstituted allenes. In all cases, catalyst A (see Table I entry 1) gave products of type **3**[7] predominantly, but catalyst B (see Table I, entry 5) gave predominantly enynes **4**.[7]

Allene substitution dramatically affects the regioselectivity. 1,1-Di- and 1,1,3-trisubstituted allenes **5** and **6** give the conjugated enoates **7**[7] and **8**[7] regardless of the catalyst. On the other hand,

Table I. Catalyst Dependence of Condensation of Phenylethyne and Methyl 2,3-Pentadienoate



entry	catalyst[a]	**1**, %	**2**-E, %	**2**-Z, %	yield[b,c]
1	4% Pd(OAc)_2, TDMPP (cat. A)	76	18	6	55
2	4% Pd(OAc)_2, TTMPP	66	29	5	(55)
3	4% Pd(OAc)_3, Ph_3P	81	19		(43)
4	4% TCPC, TDMPP	42	37	21	(62)
5	4% TCPC, TTMPP (cat. B)	9	47	44	(64)
6	4% TCPC, Ph_3P	83	17		(48)
7	4% $(\text{CH}_3\text{CN})_2\text{PdCl}_2$, TDMPP	58	21	21	38

[a] TDMPP = tris(2.6-dimethoxyphenyl)phosphine; TTMPP = tris(2,4,6-trimethoxyphenyl)phosphine; TCPC = tetrakis(carbomethoxy)palladacyclopentadiene.[6] [b] Yields either are for isolated product or are determined by NMR spectroscopy (in parentheses). [c] See ref 7.

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