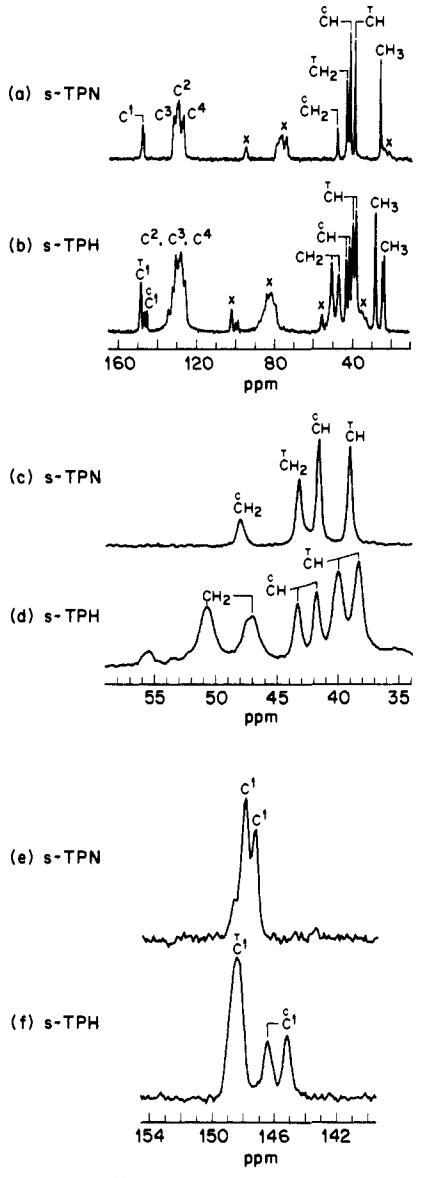

Figure 2. CPMAS/DD ^{13}C NMR spectra of crystalline s-TPH (b) and s-TPN (a) recorded at room temperature at 50.3 MHz on a Varian XL-200 spectrometer equipped with a Doty Scientific solids probe. Both samples were spun at the magic angle at a speed of ca. 2.5 kHz; a 40 kHz rf field strength was applied for 200 ms to achieve ^1H dipolar decoupling; and a 2.5-ms cross-polarization contact time was employed. Both spectra were referenced to external poly(oxymethylene) which resonates[15] at 89.1 ppm from TMS. Resonances marked with an X are the spinning sidebands of the aromatic carbon resonances. Expansions of the CH_2 and CH region of the s-TPN and s-TPH spectra are shown in parts c and d, while expansions of the C^1 region are shown in parts e and f.

observed in solid-state polymer ^{13}C NMR spectra to their solid-state conformations, we expect the pattern of ^{13}C resonances summarized in Table I. The central (C) methylene carbons in s-TPN and the methylene carbons in s-TPH should resonate downfield from the terminal (T) methylenes in s-TPN, because the T CH_2's (s-TPN) are shielded by the gauche arrangement of their γ-substituents [CH(C)'s] (see Figure 1), while the central CH_2's in s-TPN and the s-TPH methylenes are trans to their γ-CH(T)'s and are not shielded. The difference in methylene carbon chemical shifts should be ca. 5 ppm ($\gamma_{CH_2,CH}$), judging from previous experience.[13,14]

The methylene carbons in all-trans, planar-zigzag form I s-PS are not shielded by their γ-CH's, and they resonate at 48.4 ppm[10] very near the central CH_2's in s-TPN and the s-TPH methylenes. In form II s-PS the methylene carbons resonate at 49.1 and 38.1 ppm reflecting 0 and 2 gauche shielding arrangements with their γ-CH's, respectively, in the *...ttggttgg...* conformation proposed for this s-PS polymorph. The terminal CH_2 carbons in s-TPN resonate at 43.5 ppm (see Figure 2), or midway between the CH_2 carbons in form II s-PS, because these T CH_2's are gauche to a single γ-substituent, CH(C).

The four quaternary, aromatic carbons of s-TPN [C^1(C) and C^1(T)] and the two terminal quaternary, aromatic carbons of s-TPH [C^1(T)] should resonate downfield from the central C^1 in s-TPH, because C^1(C) in s-TPH is shielded by two $\gamma_{C^1,CH}$, while the other C^1 carbons possess only a single $\gamma_{C^1,CH}$ interaction (see Figure 1). This additional shielding ($\gamma_{C^1,CH}$) should[13,14] move $\delta(C^1(C))$ in s-TPH ca. 2.5 ppm upfield from the remaining quaternary carbons in both s-PS model compounds.

The CPMAS/DD ^{13}C NMR spectra of crystalline s-TPH and s-TPN are presented in Figure 2. It is clear from their comparison[16] that the methylene and quaternary, aromatic carbon chemical shifts follow the pattern expected (Table I) from consideration of their crystalline conformations in terms of γ-gauche shielding effects. As a consequence, our previous analysis[10] of the ^{13}C chemical shifts observed in the high-resolution, solid-state ^{13}C NMR spectra of forms I and II s-PS is confirmed, and the conclusion that forms I and II s-PS adopt the *...ttttttt...* and *...ttggttgg...* conformations, respectively, receives further support.

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(15) Earl, W. L.; Vanderhart, D. L. *J. Magn. Reson.* **1822**, *48*, 35.

(16) Note the doubling of most resonances in the CPMAS/DD ^{13}C NMR spectrum of s-TPH shown in Figure 2b. This most likely reflects the fact that two s-TPH molecules form the asymmetric unit of its crystalline unit cell, and each experiences different intermolecular packing interactions. A single s-TPN molecule constitutes the asymmetric unit in its crystalline unit cell, and as expected we observe only single resonances for each carbon type (see Figure 2a).

Palladium-Catalyzed Carboannulation of 1,3-Dienes by Aryl Halides

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Received January 22, 1990

Carboannulation processes are among the most important reactions in organic synthesis, but few have proven very general in scope.[1,2] The addition of arylpalladium species to 1,3-dienes is known to afford π-allylpalladium compounds,[3] and extensive work

(1) (a) Jung, M. E. *Tetrahedron* **1976**, *32*, 3. (b) Trost, B. M. *Chem. Soc. Rev.* **1982**, *11*, 141. (c) Posner, G. H. *Chem. Rev.* **1986**, *86*, 831. (d) Piers, E. *Pure Appl. Chem.* **1988**, *60*, 107. (e) Yamago, S.; Nakamura, E. *J. Am. Chem. Soc.* **1989**, *111*, 7285. (f) Hudlicky, T.; Fleming, A.; Radesca, L. *J. Am. Chem. Soc.* **1989**, *111*, 6691.

(2) For recent palladium-promoted carboannulation processes, see: (a) Shimizu, I.; Ohashi, Y.; Tsuji, J. *Tetrahedron Lett.* **1985**, *26*, 3825. (b) Hayashi, T.; Yamamoto, A.; Ito, Y. *Tetrahedron Lett.* **1988**, *29*, 669. (c) Onoue, H.; Moritani, I.; Murahashi, S.-I. *Tetrahedron Lett.* **1973**, *121*. (d) Trost, B. M.; Vercauteren, J. *Tetrahedron Lett.* **1985**, *26*, 131. (e) Burgess, K. *Tetrahedron Lett.* **1985**, *26*, 3049. (f) Lu, X.; Huang, Y. *Tetrahedron Lett.* **1986**, *27*, 1615. (g) Huang, Y.; Lu, X. *Tetrahedron Lett.* **1988**, *29*, 5663. (h) Bäckvall, J.-E.; Vågberg, J.-O.; Granberg, K. L. *Tetrahedron Lett.* **1989**, *30*, 617. (i) Wu, G.; Rheingold, A. L.; Geib, S. J.; Heck, R. F. *Organometallics* **1987**, *6*, 1941. (j) Sakakibara, T.; Tanaka, Y.; Yamasaki, S. *Chem. Lett.* **1986**, 797. (k) Zhang, Y.; O'Connor, B.; Negishi, E. *J. Org. Chem.* **1988**, *53*, 5588. (l) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1. (m) Trost, B. M.; Scoane, P.; Mignani, S.; Acemoglu, M. *J. Am. Chem. Soc.* **1989**, *111*, 7487. (n) Binger, P.; Schäfer, B. *Tetrahedron Lett.* **1988**, *29*, 4539. (o) Shimizu, I.; Ohashi, Y.; Tsuji, J. *Tetrahedron Lett.* **1984**, *25*, 5183. (p) Binger, P; Büch, H. M. *Top. Curr. Chem.* **1987**, *135*, 77. (q) Binger, P.; Sternberg, E.; Wittig, U. *Chem. Ber.* **1987**, *120*, 1933. (r) van der Louw, J.; van der Baan, J. L; Bickelhaupt, F.; Klumpp, G. W. *Tetrahedron Lett.* **1987**, *28*, 2889.

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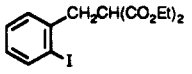
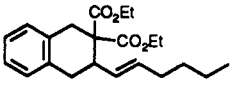
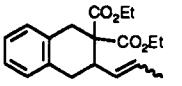
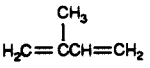
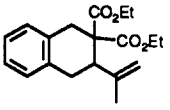
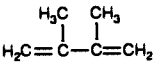
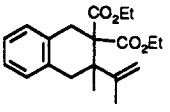
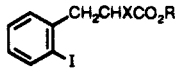
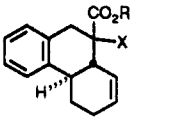
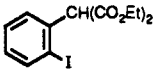
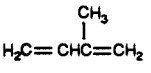
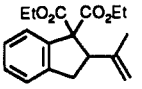
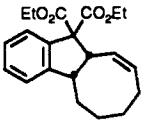
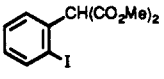
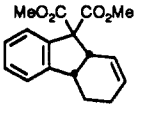
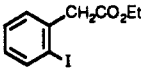
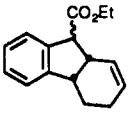
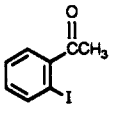
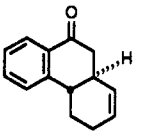
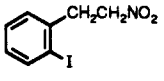
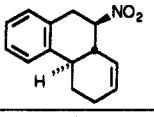
Table I. Palladium-Catalyzed Carboannulation of 1,3-Dienes[a]

entry	aryl halide	1,3-diene	base	PPh_3	reactn conditns	product[b]	% isolated yield
1		*n*-$C_4H_9CH{=}CHCH{=}CH_2$	Na_2CO_3	+	60 °C, 1 day		87
2		(*Z*)-$CH_3CH{=}CHCH{=}CH_2$	Na_2CO_3	+	60 °C, 2 days		95[c]
3			Na_2CO_3	+	60 °C, 12 days		92
4			Na_2CO_3	+	60 °C, 17 days		84
							
						R X	
5			NaOAc	−	80 °C, 1 day	Et CO_2Et	85
6			Na_2CO_3	+	80 °C, 3 days	Et CN	73[d,e]
7			NaOAc	−	80 °C, 4 days	Me SPh	96[e]
8			Na_2CO_3	+	60 °C, 8 days		82
9			Na_2CO_3	+	60 °C, 10 days		86
10			Na_2CO_3	−	60 °C, 1 day		87
11			KOAc	−	80 °C, 2 days		85[e]
12			KOAc	+	80 °C, 1 day		56
13			Li_2CO_3	+	80 °C, 7 days		73

[a] All reactions were run by heating 5% palladium acetate, 1 equiv of aryl iodide, 5 equiv of 1,3-diene, 1 equiv of *n*-Bu_4NCl, 5 equiv of base, DMF (4 mL/mmol of aryl halide) and where appropriate 5% of PPh_3 or $P(OPh)_3$. [b] All products gave appropriate ^1H and ^{13}C NMR, IR, and mass spectral or elemental analysis data. [c] *E*:*Z* ratio is 8:1. [d] Eleven percent of *o*-$IC_6H_4CH_2CH_2CN$ was also formed. [e] A mixture of diastereomers about the ester group is present.

on the inter- and intramolecular displacement of palladium from π-allylpalladium compounds by carbon nucleophiles has also been reported.[4] We report that the coupling of these two processes affords a convenient, versatile, new route for the carboannulation of 1,3-dienes as indicated by the examples reported in Table I.

Best results have been obtained by using 5% $Pd(OAc)_2$, 1 equiv of *n*-Bu_4NCl, and carbonate or acetate bases in DMF at 60–80 °C.[5,6] While catalytic amounts of PPh_3 are not necessary, the yield, regioselectivity, and amount of 1-aryl 1,3-diene side product are frequently improved by its presence.

Unlike intermolecular π-allylpalladium carbanion displacement processes, which usually require carbanions stabilized by at least two strong electron-withdrawing groups,[7] our intramolecular

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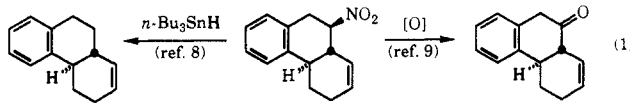
(4) (a) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615. (b) Tsuji, J. *Organic Synthesis With Palladium Compounds*; Springer-Verlag: New York, 1980. (c) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985.

(5) For early work on this type of catalyst system, see: (a) Jeffery, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1287. (b) Jeffery, T. *Tetrahedron Lett.* **1985**, *26*, 2667. (c) Jeffery, T. *Synthesis* **1987**, *70*.

(6) For recent applications of this catalyst system in our own work, see: (a) Larock, R. C.; Babu, S. *Tetrahedron Lett.* **1987**, *28*, 5291. (b) Larock, R. C.; Baker, B. E. *Tetrahedron Lett.* **1988**, *29*, 905. (c) Larock, R. C.; Song, H.; Baker, B. E.; Gong, W. H. *Tetrahedron Lett.* **1988**, *29*, 2919. (d) Larock, R. C.; Stinn, D. E. *Tetrahedron Lett.* **1988**, *29*, 4687. (e) Larock, R. C.; Gong, W. H. *J. Org. Chem.* **1989**, *54*, 2047. (f) Larock, R. C.; Gong, W. H.; Baker, B. E. *Tetrahedron Lett.* **1989**, *30*, 2603.

displacement process is quite successful when a single such group is present (entries 11-13). The ability to generate in a single step highly functionalized carbocycles amenable to further functional-group manipulation, such as that shown in eq 1, is one of the most important features of this process.



(1)

A wide variety of 1,3-dienes undergo facile, regioselective carboannulation. While we have generally employed 5 equiv of the readily available diene, only slightly reduced yields of carbocycle are obtained when 2 or even 1 equiv of diene is used (Table I, entry 5: 5 equiv, 85%; 2 equiv, 77%; 1 equiv, 76%), but the reaction time is increased substantially (1 day, 6 days, and 7 days, respectively). Simple linear *trans*-dienes afford exclusively the trans olefinic product, but *cis*-1,3-pentadiene affords approximately an 8:1 ratio of *E*:*Z* olefinic products (entry 2).

This carboannulation process most likely proceeds by (1) reduction of $Pd(OAc)_2$ to the actual catalyst Pd(0), (2) oxidative addition of the aryl halide to Pd(0), (3) arylpalladation of the 1,3-diene to form a π-allylpalladium intermediate, and (4) formation of the neighboring carbanion and subsequent front- or backside displacement of palladium, which regenerates the Pd(0) catalyst. The predominant formation of the trans product from *cis*-1,3-pentadiene (entry 2) is best explained by isomerization of an initially formed anti π-allylpalladium intermediate to the more thermodynamically stable syn intermediate.[10] The presence of some cis product, however, suggests that palladium displacement either can occur through a σ-allylpalladium intermediate or is sufficiently rapid to occur via the initially formed anti π-allylpalladium intermediate prior to isomerization. Since all five-membered-ring products contain exclusively cis ring fusion as determined by ^1H NMR spectroscopy,[11] they are most likely arising by halide displacement from the initially formed π-allylpalladium intermediate by the tethered nucleophile and subsequent reductive elimination with retention, an unusual path for palladium displacement by stabilized carbanions.[4] All six-membered-ring products contain exclusively a trans ring fusion as determined by ^1H NMR spectroscopy,[12] most likely formed by backside palladium displacement.

In conclusion, the simple palladium-catalyzed arylannulation of 1,3-dienes by functionally substituted aryl halides utilizes readily available starting materials and proceeds under mild conditions in high yield, completely stereo- and regioselectively, to form a wide variety of functionally substituted carbocycles.

Acknowledgment. We gratefully acknowledge the National Institutes of Health for their generous financial support and Johnson Matthey, Inc., and Kawaken Fine Chemicals Co., Ltd., for the palladium acetate.

(7) For exceptions, see: (a) Trost, B. M.; Keinan, E. *Tetrahedron Lett.* **1980**, *21*, 2591. (b) Fiaud, J.-C.; Malleron, J.-L. *J. Chem. Soc., Chem. Commun.* **1981**, 159. (c) Negishi, E.; Matsushita, H.; Chatterjee, S.; John, R. A. *J. Org. Chem.* **1982**, *47*, 3188. (d) Negishi, E.; Luo, F.-T.; Pecora, A. J.; Silveira, A., Jr. *J. Org. Chem.* **1983**, *48*, 2427. (e) Negishi, E.; John, R. A. *J. Org. Chem.* **1983**, *48*, 4098.

(8) Larock, R. C. *Comprehensive Organic Transformations: A Guide to Functional Group Preparations*; VCH Publishers: New York, 1989; p 26.

(9) Larock, R. C. *Comprehensive Organic Transformations: A Guide to Functional Group Preparations*; VCH Publishers: New York, 1989; p 603.

(10) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. *Compr. Organomet. Chem.* **1982**, *6*, 385.

(11) The stereochemical assignment is based on the mechanistic argument that backside displacement of palladium by the tethered carbanion would be expected to be stereochemically quite difficult and the fact that the product reported in entry 10 of Table I exhibits $J = 6.9$ Hz coupling between the two hydrogens on the ring-fused carbons, coupling that is more consistent with cis ring fusion.

(12) Six-membered-ring products, such as the product reported in entry 13 in Table I, which exhibits $J = 11.7$ Hz coupling between the two hydrogens on the ring-fused carbons, exhibit coupling constants only consistent with an axial-axial arrangement of the two hydrogens.

Supplementary Material Available: General procedure for carboannulation reactions and experimental data (NMR, IR, elemental analysis) for **1-13** (6 pages). Ordering information is given on any current masthead page.

Stereochemical Studies of Coenzyme F430 Based on 2D NOESY Back-Calculations

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Coenzyme F430 is a nickel-containing tetrapyrrole from methanogenic bacteria that is utilized in the biocatalytic conversion of CO_2 to methane.[1-6] Although atomic-level structural data for F430 are lacking, elegant one-dimensional (1D) NMR experiments have led to the primary structure determination of the pentamethyl ester derivative (F430M), and 1D nuclear Overhauser effect (NOE) data in combination with chemical data provided a partial stereochemical assignment for the F430M corphin macrocycle.[7-10] The stereochemistry of the C17 carbon (Figure 1) could not be assigned due to severe signal overlap, and the relative stereochemical assignments for C18 and C19 were assigned on the basis of weaker NMR and chemical data and might be considered tentative.[8,11] The C17-C18-C19 stereochemical assignments were determined recently by 2D NMR to be either *R,R,S* (consistent with the *original* stereochemical assignments) or *S,S,R* (*reverse* assignment).[12] We describe here the results of a new approach for stereochemical analysis that employs 2D NOESY back-calculations for F430 model structures generated by distance geometry (DG) computations.

DG calculations were performed with DSPACE.[13-16] Covalency constraints dictated by the primary structures of the *original* and

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(1) Gunsalus, R. P.; Wolfe, R. S. *FEMS Microbiol. Lett.* **1978**, *3*, 191.
(2) Diekert, G.; Konheiser, U.; Piechulla, K.; Thauer, R. K. *J. Bacteriol.* **1981**, *148*, 459.
(3) Walsh, C. T.; Orme-Johnson, W. H. *Biochemistry* **1987**, *26*, 4901.
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