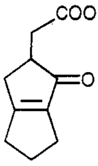
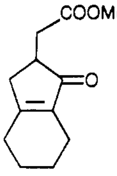
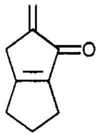
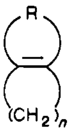

11 (82%)


12 (85%)


13 (75%)


14–17

	R	n	yield, %
14	$(CH_2)_3$	3	90
15	$(CH_2)_3$	4	87
16	$(CH_2)_2CHMe$	3	82
17	$CH_2CHMeCH_2$	4	70

In converting 5-iodo-1-pentyne into **11** via **3**, we added n-BuLi (2.4 M, 12.5 mL, 30 mmol) in hexane at −90 °C to a solution of 5-iodo-1-pentyne (5.82 g, 30 mmol) in 30 mL of hexane. After the mixture was stirred at −78 °C for 1 h, EtZnCl (1.0 M, 33 mL, 33 mmol) in CH_2Cl_2, prepared from 16.5 mmol each of Et_2Zn and dry $ZnCl_2$, was added at −78 °C, and the mixture was warmed to room temperature over 1–3 h. The solvents were removed under diminished pressure at or below room temperature. To the residue were added sequentially 60 mL of THF and a solution of allylzinc bromide prepared from allyl bromide (5.44 g, 45 mmol) and Zn (2.94 g, 45 mmol) in 30 mL of THF. The reaction mixture was stirred for 12 h at room temperature, quenched at −78 °C with iodine (25.4 g, 100 mmol) in 30 mL of THF, warmed to room temperature, and treated sequentially with pentane, aqueous NH_4Cl, and $Na_2S_2O_3$. The organic phase was washed with $NaHCO_3$ and brine, dried over $MgSO_4$, concentrated, and distilled to provide 6.25 g (86%, 93% by GLC) of **3**: bp 71–74 °C (5 mm); IR (neat) 3040 (w), 1630 (w), 900 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.8–2.1 (m, 2 H), 2.1–2.5 (m, 2 H), 2.5–2.8 (m, 2 H), 2.8–3.0 (m, 2 H), 4.9–5.2 (m, 2 H), 5.5–6.0 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.36, 33.83, 37.68, 44.17, 91.54, 116.10, 134.12, 145.69. Anal. Calcd for $C_8H_{11}I$: C, 41.05; H, 4.74. Found: C, 41.27; H, 5.01. To a glass vial containing a magnetic bar were sequentially added **3** (0.71 g, 3.0 mmol) in 3 mL each of benzene and CH_3CN, methanol (0.38 g, 12 mmol), triethylamine (0.45 g, 4.5 mmol), and $Cl_2Pd(PPh_3)_2$ (0.11 g, 0.15 mmol). The vial was placed in an autoclave, which was then charged with carbon monoxide (40 atm) and heated to 100 °C for 24 h in a stirred oil bath. The usual workup and distillation gave 0.48 g (82%) of **11**: bp 100–105 °C (0.15 mmHg, Kugelrohr); IR (neat) 1735 (s), 1695 (s), 1633 (m), 1215 (s), 1168 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 2.2–3.1 (m with peaks at 2.40, 2.47, 2.57, 2.77, 2.81, 2.99, and 3.13, 11 H), 3.70 (s, 3 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 24.70, 27.61, 32.00, 32.66, 35.30, 48.50, 51.53, 147.65, 172.39, 185.14, 202.72; high-resolution mass spectrum calcd for $C_{11}H_{14}O_3$ 194.0943, found 194.0937.

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Registry No. **3**, 112505-80-3; **4**, 40648-08-6; **5**, 112505-81-4; **6**, 112505-82-5; **7**, 112505-83-6; **8**, 112505-84-7; **9**, 112505-85-8; **10**, 112505-86-9; **11**, 112505-87-0; **12**, 112505-88-1; **13**, 112505-89-2; **14**, 6491-93-6; **15**, 695-90-9; **16**, 112505-90-5; **17**, 112505-91-6; $CH{\equiv}C(CH_2)_3I$, 2468-55-5; EtZnCl, 2633-75-2; Me_2AlCl, 1184-58-3; Et_2Zn, 557-20-0; Me_3Al, 75-24-1; $CH_2{=}CHCH_2ZnBr$, 18925-10-5; I_2ZrCp_2, 1298-41-5; Cl_2ZrCp_2, 1291-32-3; $Cl_2Pd(PPh_3)_2$, 13965-03-2; $Pd(PPh_3)_4$, 14221-01-3; i-Bu_3Al, 100-99-2; $(Me_2CHMeCH)_2BH$, 1069-54-1; 1-ethyl-2-iodo-1-cyclopentene, 112505-78-9; 1-methyl-2-iodo-1-cyclopentene, 112505-79-0.

Supplementary Material Available: Spectral and analytical data for all compounds except **5**, **11**, and **15** (3 pages). Ordering information is given on any current masthead page.

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(9) Tour, J. M.; Negishi, E. *J. Am. Chem. Soc.* **1985**, *107*, 8289.

Umpolung of π-Allylpalladium Intermediates. A Chemoselective Reductive Elimination of Diols

Summary: The dicarbonates of enediols undergo reductive elimination to form conjugated dienes by using a catalytic amount of a Pd(0) complex wherein either the alkoxide liberated from the carbonate or triisopropyl phosphite serves as a stoichiometric reducing agent.

Sir: Due to the importance of carbonyl additions for C–C bond-forming reactions and the abundance of carbohydrates as starting materials, methods for deoxygenation have become powerful tools for synthesis.[1,2] Palladium-based methods for simple deoxygenation have normally required a hydride source,[3] electrolysis, or a low-valent metal reductant.[4] We wish to report that Pd(0) complexes can catalyze the reductive cleavage of enedicarbonates under very mild conditions either in the absence of any exogenous reducing agent or in the presence of a phosphite.[5] The reactions appear to involve the π-allyl-

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(1) For a few recent references, see: Watanabe, Y.; Araki, T.; Ueno, Y.; Endo, T. *Tetrahedron Lett.* **1986**, *27*, 5385. Barton, D. H. R.; Crich, D. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1603, 1613. Kimura, J.; Nishikubo, Y.; Mitsunobu, O. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2017. Robins, M. J.; Wilson, J. S.; Haneske *J. Am. Chem. Soc.* **1983**, *105*, 4059. Ueno, Y.; Tanaka, C.; Okawara, M. *Chem. Lett.* **1983**, 795. Barton, D. H. R.; Motherwell, W. B.; Stange, A. *Synthesis* **1981**, 743. Barton, D. H. R.; Subramaniam, R. *J. Chem. Soc. Perkin Trans. 1* **1977**, 1718.

(2) Ando, M.; Ohara, H.; Takase, K. *Chem. Lett.* **1986**, 879. Barua, N. C.; Sarma, J. C.; Sharma, R. P.; Barna, J. N. *Chem. Ind. (London)* **1982**, 956. Camps, P.; Cardellach, J.; Font, J.; Ortuno, R. M.; Pousatis, O. *Tetrahedron* **1982**, *38*, 2395. Corey, E. J.; Hopkins, P. B. *Tetrahedron Lett.* **1982**, *23*, 1979. Barua, N. C.; Sharma, R. P. *Tetrahedron Lett.* **1982**, *23*, 1365. Radatus, B. K.; Clarke, I. S. *Synthesis* **1980**, 47. Garegg, P. J.; Samuelsson, B. *Synthesis* **1979**, 813. Barrett, A. G. M.; Barton, D. H. R.; Bielski, R. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2378. Bessodes, M.; Abushanab, E.; Pangira, R. P. *J. Chem. Soc., Chem. Commun.* **1981**, 26. Hanessian, S.; Bargiotti, A.; LaRue, M. *Tetrahedron Lett.* **1978**, 737. Lauwers, M.; Magnane, R.; Krief, A. *Actual. Chim.* **1978**, *65*, Abstract 38; Hanfusa, T.; Imai, S.; Ohkata, K.; Suzuki, H.; Suzuki, Y. *J. Chem. Soc., Chem. Commun.* **1974**, 73. Trost, B. M.; Bright, G. M.; Frihart, C.; Brittelli, D. *J. Am. Chem. Soc.* **1971**, *93*, 737. Inhoffen, H. H.; Radscheit, K.; Stoche, V.; Kappe, V. *Ann.* **1965**, *684*, 24. Fleming, I.; Taddei, M. *Synthesis* **1985**, *898*, 899.

(3) Cf.: Tsuji, J.; Sugiura, T.; Minami, I. *Synthesis* **1987**, 603 and earlier references cited therein. Rahman, M. A.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1985**, *107*, 5576. Sutherland, J. K.; Tometzki, G. B. *Tetrahedron Lett.* **1984**, 881. Hutchins, R. O.; Learn, K. *J. Org. Chem.* **1982**, *47*, 4380. Keinan, E.; Greenspoon, N. *J. org. Chem.* **1983**, *48*, 3345.

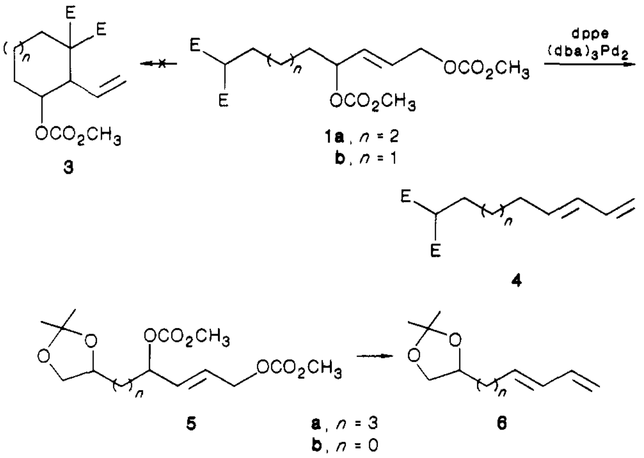
(4) Tabuchi, T.; Inanaga, J.; Yamaguchi, M. *Tetrahedron Lett.* **1986**, *27*, 601. Torii, S.; Tanaka, H.; Katoh, T.; Morisaki, K. *Tetrahedron Lett.* **1984**, *25*, 3207.

(5) A stoichiometric reductive cleavage of an acetoxy epoxide in the withanolide series has been reported: Kienan, E.; Sahai, M.; Kirson, I. *J. Org. Chem.* **1983**, *48*, 2550.

0022-3263/88/1953-0915$01.50/0

palladium intermediate serving as a nucleophile rather than its normal reactivity as an electrophile.[6]

Initially, the dicarbonate **1a** was subjected to $(dba)_3Pd_2 \cdot CHCl_3$ (**2**)[7a] in the presence of dppe[7b] at room temperature. None of the anticipated cyclization product **3a** formed. In its stead, the diene **4a**[8] formed in 73% isolated yield. The 16-Hz coupling constant for the protons on the disubstituted double bond indicates the *E* stereochemistry as depicted. The analogue **1b** behaved identically to give a 60% isolated yield of (*E*)-diene **4b**.



3

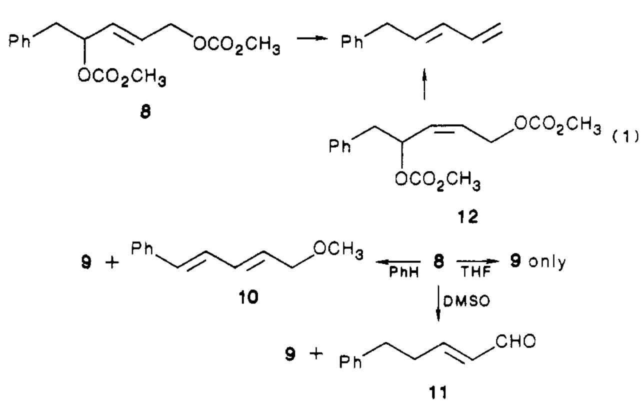
1a, *n* = 2
b, *n* = 1

4

5 **a**, *n* = 3 **6**
b, *n* = 0

In contrast to the above cases, subjecting the enedicarbonate **5a** to the same conditions showed incomplete consumption of starting material (60% recovered) and clean formation of the diene **6a**[8] (30%, 94% based upon recovered starting material). We attributed the low extent of reaction to the lack of an adequate stoichiometric reducing agent to convert Pd(II) to Pd(0). Earlier work in our laboratories suggested triisopropyl phosphite (**7**) was a satisfactory reducing agent for Pd(II) carboxylates.[9] Indeed, adding 80 mol % of phosphite **7** effected complete consumption of starting material and produced a 57% isolated yield of diene **6a**.

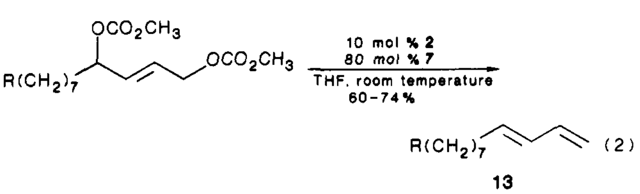
Other reducing agents were examined in the conversion of dicarbonate **8** to 5-phenylpenta-1,3-diene (**9**).[8] Use of complex **2** as the Pd(0) source and dppe gave poor results with chromous chloride. Clean formation of diene occurred with 1-hexene as reductant, but reaction only proceeded to partial completion. The volatile diene formed in 56% isolated yield by using 5 mol % **2** and 80 mol % phosphite **7** in THF at room temperature, a set of conditions that became our standard. Dramatic solvent effects were observed. As depicted in eq 1, whereas only diene **9** was observed in THF, switching to benzene or DMSO, but keeping all reagents constant, gave substantial byproducts **10** (15%)[10] and **11** (45%),[10] respectively.



8 **12** **10** **11** (1)

The geometry of the product is not related to the geometry of the starting material. Thus, the (*Z*)-olefin **12**[11] also produced only the (*E*)-diene **9** in 60% isolated yield. Monitoring the reaction reveals that (*Z*)- to (*E*)-olefin isomerization of the starting material (i.e., **12** to **9**) proceeded faster than elimination—a fact that suggests the methyl carbonate anion remains intact for some period of time.

Using our standard conditions, the chemoselectivity was examined as shown in eq 2 to form only the (*E*)-dienes **13**.[8]



13 (2)

R: **a**, $HOCH_2$ (60%); **b**, $AcOCH_2$ (64%); **c**, OCH (67%); **d**, $BrCH_2$ (69%); **e**, $CH_2{=}CHCO$ (74%)

Remarkably, the reaction showed little sensitivity to functional groups ranging from free hydroxyl groups to a very reactive terminal vinyl ketone. The acetate **13b** is the sex pheromone of the red bollworm moth, *Disparopsis castanea*,[12,13] a major pest of the African cotton crops, which previous workers had difficulty obtaining as a pure *E*-isomer.[14]

The stereochemistry of the bis elimination, as well as its application to the synthesis of a theoretically interesting hydrocarbon[15] was pursued by studying the reductive

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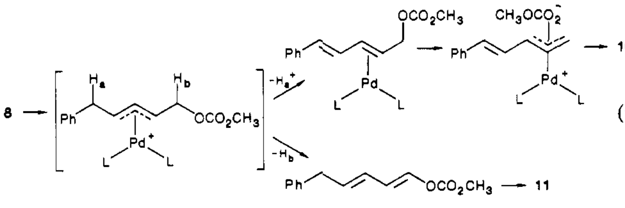
[6] For umpolung of π-allylpalladium intermediates, see: Trost, B. M.; Herndon, J. W. *J. Am. Chem. Soc.* **1984**, *106*, 6835. Matsubara, S.; Oshima, K.; Wakamatsu, K.; Morizawa, Y.; Tsubonwa, N.; Oshima, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1196. Sasaoka, S.; Yamamoto, T.; Kinoshita, H.; Inomata, K.; Kotake, H. *Chem. Lett.* **1985**, 315. Tabuchi, T.; Inanaga, J.; Yamaguchi, M. *Tetrahedron Lett.* **1986**, *27*, 601. Masuyama, Y.; Kinugawa, N.; Kurusu, Y. *J. Org. Chem.* **1987**, *52*, 3703.

[7] (a) dba = dibenzylideneacetone; Ukai, T.; Kawazura, H. Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253. (b) dppe = 1,2-bis(diphenylphosphino)ethane.

[8] All new compounds have been fully characterized.

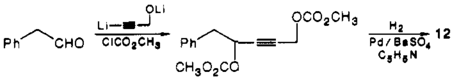
[9] Lynch, J., unpublished observations in these laboratories. Trost, B. M.; Nanninga, T. N. *J. Am. Chem. Soc.* **1985**, *107*, 1293. Trost, B. M.; Renaut, P. *J. Am. Chem. Soc.* **1982**, *104*, 6668.

[10] The formation of **10** and **11** can be rationalized as depicted in eq i.



(i)

[11] The (*Z*)-olefin **12** was produced as outlined in eq ii.



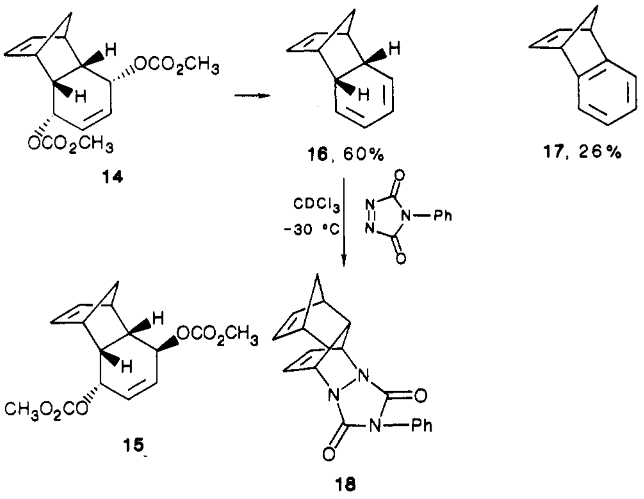
(ii)

[12] For reviews, see: Hendrick, C. A. *Tetrahedron* **1977**, 1845. Brand, J. M.; Young, J. C.; Silverstein, R. M. *Fortschr. Chem. Org. Naturst.* **1975**, *37*, 1.

[13] Nesbitt, B. F.; Beevor, P. S.; Cole, R. A.; Lester, R.; Poppi, R. G. *Nature (London), New Biol.* **1973**, *244*, 208.

[14] Nesbitt, B. F.; Beevor, P. S.; Cole, R. A.; Lester, R.; Poppi, R. G. *Tetrahedron Lett.* **1973**, 4669. Mori, K. *Tetrahedron* **1974**, *30*, 3807. For a stereoselective synthesis, see: Tanaka, S.; Yasuda, A.; Yamamoto, H.; Nazaki, H. *J. Am. Chem. Soc.* **1975**, *97*, 3252.

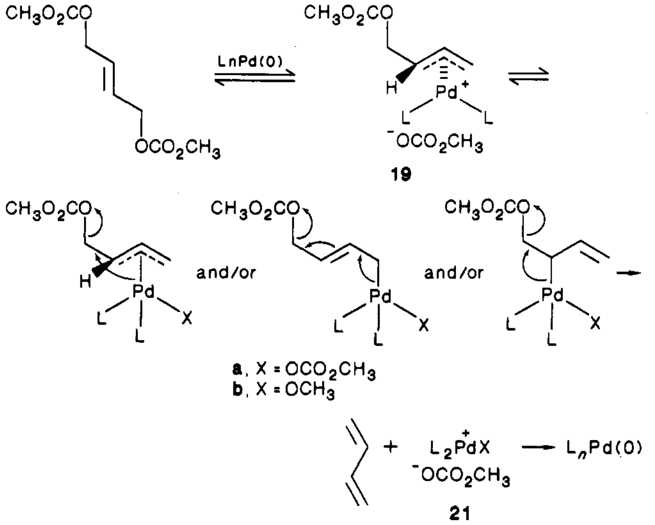
eliminations of 14[16] and 15,[17] both available from the Diels–Alder adduct of cyclopentadiene and benzoquinone.



Whereas 14 reacted smoothly in 6 h to give the triene 16 in addition to some aromatic product 17 (the latter coming in part by oxidation of 16), the trans dicarbonate 15 failed to produce any triene 16. It should be noted that the triene 16 is obtained in three steps with a 43% overall yield from the benzoquinone–cyclopentadiene Diels–Alder adduct in contrast to the literature route of six steps and 12% overall yield from this same adduct.[15a]

The above results are consistent with the mechanism outlined in Scheme I. The initial step presumably is the normal Pd(0)-induced ionization with inversion of configuration to give the cationic complex 19.[18] Coordination of the carboxylate leaving group,[19] either intact as 20a or with extrusion with carbon dioxide as 20b, enhances the nucleophilic properties of the allylpalladium complex.[20] The fact that acetates are not and carbonates are good substrates suggests that the higher nucleophilicity associated with the palladium complex bearing the stronger donor methoxide ligand 20b rather than a carboxylate ligand as in 20a is necessary for the second ionization to give diene and a Pd(II) complex 21.[21] The known β-hydrogen insertion associated with the noble metal alkoxides which, in effect, reduces the metal provides a pathway for the reduction of 21 if X = OCH$_3$ to regenerate the requisite Pd(0) catalyst.[22] The inefficiency of this reduction mechanism limited the useful cases where only phosphines could be employed as ligands for palladium to only 5a and 5b. On the other hand, the ability of triisopropyl phosphite to reduce Pd(II) allows this compound to serve both as ligand and reducing agent (where it is converted to triisopropyl phosphate) to reform Pd(0) and maintains the catalytic cycle. The comparison of 14 and 15 reveals that the second ionization also occurs with inversion—an overall cis reductive elimination. In acyclic systems, it appears that isomerization of the initial π-allylpalladium complex 19 is faster than fragmentation to diene—thus the stereochemistry of the starting diol is irrelevant. On the other hand, the absence of an easy isomerization mechanism in cyclic systems requires a cis diol for elimination.

Scheme I. Mechanistic Rationale for Pd(0)-Catalyzed Reductive Elimination



The proposed inversion of the electronic sense of the electrophilic cationic complex 19 by coordination of an anionically charged ligand opens a new approach for use of such complexes in synthesis. The facile chemoselective deoxygenation of enediols via their dicarbonates appears to be a fruitful approach for diene synthesis.

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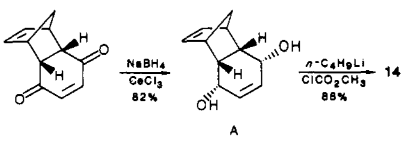
[15] (a) Rye, A. R.; Wege, D. *Aust. J. Chem.* **1974**, *27*, 4943. (b) Grimme, W.; Mauer, W.; Sarter, C. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 331.

[16] Equation iii outlines the synthesis of 14.



(iii)

[17] The trans-dicarbonate 15 was synthesized from diol A by performing a Mitsonubu alcohol inversion of the monosilyl ether of A followed by acylation to the dicarbonate.

[18] Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730. Hayashi, T.; Hagihara, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1983**, *105*, 7767.

[19] Cf.: Trost, B. M.; Verhoeven, T. R.; Fortunak, J. M. *Tetrahedron Lett.* **1979**, 2301. Yamamoto, T.; Saito, D.; Yamamoto, A. *J. Am. Chem. Soc.* **1981**, *103*, 5600. Baeckvall, J. E.; Nordberg, R. E.; Wilhelm, D. *J. Am. Chem. Soc.* **1985**, *107*, 6892.

[20] For the purposes of the present discussion, we do not attempt to distinguish between a π- and a σ-structure for 20.

[21] Nucleophilic properties have been observed for bis(π-allyl)palladium complexes. See: Hung, T.; Jolly, P. W.; Wilke, G. *J. Organomet. Chem.* **1980**, *190*, C5. Ito, T.; Kindaichi, Y.; Takami, Y. *Chem. Ind. (London)* **1980**, 82. Santi, R.; Marchi, M. *J. Organomet. Chem.* **1979**, *182*, 117. Theoretical calculations predict that the terminal carbon atoms in π-allylpalladium cationic complexes are, in fact, slightly negatively charged. Gordon, D. J.; Fenske, R. F.; Nanninga, T. N.; Trost, B. M., unpublished work in these laboratories. Sakaki, S.; Nishikawa, M.; Ohyoshi, A. *J. Am. Chem. Soc.* **1980**, *102*, 4062.

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