$C_{\alpha,\beta,\gamma}C_6H_5$), 3.76 (spt, 6 H, C*H*Me$_2$), 1.22 (d, 18 H, CH*Me*$_2$), 1.15 (d, 18 H, CH*Me*$_2$), 0.40 (t, 3 H, C*H*$_3$CH$_2$CN). The resonances for the CH$_3$C*H*$_2$CN protons are partially obscured by the CH*Me*$_2$ doublets. ^{13}C NMR (C_6D_6): 202.7 (C_α), 165.1 (C_β), 157.0 (C_{ipso}, DIPP), 146.8, 142.3, 139.2 (C_{ipso}, $C_{\alpha,\beta,\gamma}C_6H_5$), 138.6 ($C_o$, DIPP), 129.2, 128.3, 128.2, 127.9, 127.7, 127.5, 126.9, 124.9 (C_o, C_m, C_p; $C_{\alpha,\beta,\gamma}C_6H_5$), 123.7 ($C_p$), 123.6 ($C_m$, DIPP), 95.9 ($C_\gamma$), 27.5 (*C*HMe$_2$), 24.3, 24.2 (CH*Me*$_2$), 10.3 (CH$_3CH_2$CN), 10.0 (*C*H$_3CH_2$CN). One resonance (for C_o, C_m, C_p; $C_{\alpha,\beta,\gamma}C_6H_5$) and the EtCN signal have not been observed. IR: 2275 w, 1580 br w, 1429 s, 1322 s, 1245 s, 1182 s, 1105 m, 1093 m, 1061 m, 1038 m, 1008 m, 914 sh, 897 s, 888 sh, 870 m, 831 w, 800 w, 788 m, 772 w, 742 s, 690 s, 643 m. Anal. Calcd for $C_{60}H_{72}NO_4Ta$: C, 68.49; H, 6.90; N, 1.33. Found: C, 68.75; H, 7.51; N, 1.15.

X-ray Structural Determination of (DIPP)$_3$(PhCH$_2$O)Ta(η^2-CPh=CPhCPh=O) (6). A red irregular block crystal of **6**, grown from a toluene/pentane solution at 5 °C, was mounted in air on a glass fiber in a random orientation and examined on a Syntex-Nicolet P2$_1$ diffractometer using Mo Kα radiation monochromatized with graphite (λ = 0.710 37 Å). Table I summarizes the crystal data and structure refinement results. Two check reflections were measured every 98 data reflections; the intensities of these standards remained constant within experimental error throughout the data collection. No decay correction was applied. Lorentz and polarization corrections were applied. An empirical absorption correction based on a series of ψ scans was applied to the data. Relative transmission coefficients ranged from 0.777 to 0.999 with an average value of 0.904. The structure was solved by using the Patterson heavy-atom method and refined in full-matrix least squares. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The largest peak in the final difference Fourier map was 0.58 (5) e/Å^3. All calculations were performed on a VAX computer using SDP/VAX.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also acknowledge partial support from the U.S. Army Research Office (Short Term Innovative Research Program).

Supplementary Material Available: Full details of the structure solution, tables of bond distances and angles, atomic positional and thermal parameters, and least-squares planes and dihedral angles, and a figure showing an additional ORTEP view of (DIPP)$_3$(PhCH$_2$O)Ta(η^2-CPh=CPhCPh=O) (**6**) (19 pages); a listing of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

Communications

Stereoselective Formation of (C_s-Symmetrical π-allyl)palladium Complexes

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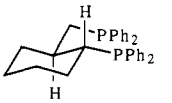
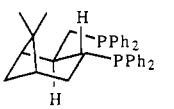
Summary: The complexation of C_s-symmetrical allyl moieties derived from 1-acetoxy-2-propene, 1-acetoxy-1,3-diphenyl-2-propene, and 1-acetoxy-2-cyclohexene to chiral (diphosphine)palladium species containing either of the two new chiral diphosphine ligands **1** and **2** proceeds in up to 88:12 stereoselectivity. Palladium complexes of diphosphine ligands **1** and **2** are unique in that they form *trans*-decalin-like structures possessing C_s symmetry local to the metal.

Interest in the enantioselective metal-catalyzed nucleophilic substitution of allylic acetates has grown in response to the need for new efficient methods for asymmetric carbon–carbon and carbon–heteroatom bond formation.[1] Although good procedures have been developed for the catalytic enantioselective alkylation of unsymmetrical allylic acetates,[2] the situation for C_s-symmetrical substrates is less developed.[3] A promising approach for these latter cases has been developed by Faller for (π-allyl)molybdenum complexes, yet it suffers from low catalytic activity.[4] This unique method relies on the selective formation of one (π-allyl)metal complex followed by the electronic, through-bond activation of one end of the coordinated allyl toward nucleophilic addition.[5] We have undertaken the development of conceptually similar, but potentially catalytically more active, chiral (diphosphine)palladium catalysts. We communicate here our efforts at meeting the first requirement for successful application of these catalysts, the ability to induce the stereoselective coordination of C_s-symmetrical π-allyls to chiral (diphosphine)palladium species. Utilizing the two new chiral diphosphine ligands 1 and 2 to enforce a local



1



2

C_s-symmetrical environment near the palladium leads to the formation of complexes with selectivities up to 88:12. These (π-allyl)palladium complexes are the first reported examples of isolated stereoisomers of C_s-symmetrical allyls. This ability to control C_s-symmetrical π-allyl complexation enables further studies concerning the asymmetric alkyl-

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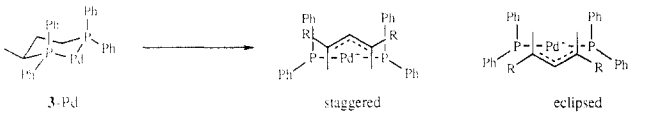
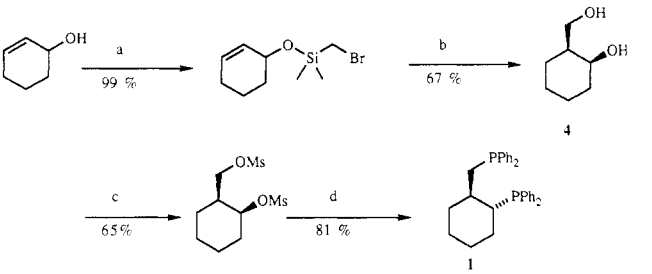
ation of an important class of synthetic substrates.

In analogy to the use of (diphosphine)palladium complexes possesing local C_2 symmetry at the metal to induce diastereoselective coordination of unsymmetrical allyls,[6] we have incorporated diphosphine ligands possessing local C_s symmetry near palladium to induce stereoselective coordination of C_s-symmetrical π-allyls. This approach is advantageous in the use of synthetically accessible ligands that contain nonstereogenic phosphorus atoms. Initially we examined the stereoselective formation of allylpalladium complexes of the known chairphos chiral diphosphine **3**.[7] These compounds could exist in two



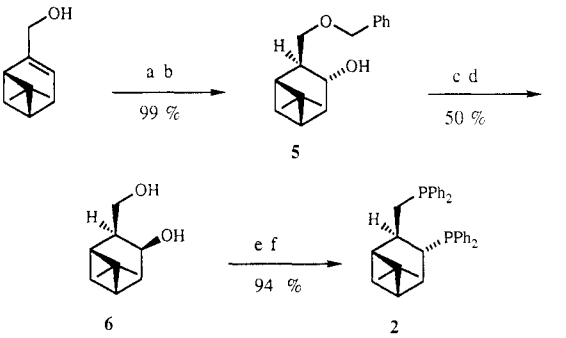
isomeric square-planar forms, one containing the allyl substituents eclipsing the phenyl groups on the phosphines and the other complex having the substituents staggered.[8] It has been established that π-allyls coordinated to (diphosphine)palladium do not rotate, preventing the direct interconversion of these isomers.[9] The parent allyl complex was formed by the addition of the chairphos diphosphine to the (π-allyl)palladium chloride dimer and was isolated as its perchlorate salt.[6a,10] The ratio of the diastereomers formed was 50:50. Since we were interested in establishing the stereoselectivity of the formation of allylpalladium complexes during potential catalytic alkylations, we exchanged the parent allyl under catalytic alkylation conditions[6a] (1.2 equiv of sodium malonate followed by 2 equiv of 1-acetoxy-2-propene, 1-acetoxy-1,3-diphenyl-2-propene, or 1-acetoxy-2-cyclohexene) and isolated after 30 min the allyl, 1,3-diphenylallyl, and cyclohexenyl complexes with stereoisomeric ratios of 50:50, 55:45, and 78:22, respectively. We rationalized these disappointingly low ratios by taking into consideration possible chair flipping of the (chairphos)palladium complexes, which would effectively negate the energy difference between the staggered and eclipsed forms. In order to prevent chair flipping, we synthesized two new diphosphine ligands that would form *trans*-decalin-like complexes which should be conformationally more rigid.

Scheme I[a]



[a] Conditions and reagents: (a) $Me_2Si(Cl)CH_2Br$ (1.2 equiv), Et_3N (1.5 equiv), CH_2Cl_2; (b) (i) *n*-Bu_3SnH (1.2 equiv), AiBN (0.015 equiv), C_6H_6, reflux, 4 h, (ii) 30% H_2O_2 (6 equiv), MeOH, THF, Na_2CO_3, reflux, 5 h; (c) MsCl (2.3 equiv, Ms = mesyl), Et_3N (2.3 equiv), CH_2Cl_2, −30 °C (20 min), 23 °C (5 min); (d) Ph_2PH (2.15 equiv), *n*-BuLi (2.10 equiv), THF, −78 °C (15 min), 23 °C (45 min).

Scheme II[a]



[a] Conditions and reagents: (a) $PhCH_2Br$ (1.2 equiv), NaH (1.2 equiv), DMF, 3 h; (b) (i) BH_3·THF (1.2 equiv), THF, 23 °C, 3 h, (ii) 30% H_2O_2 (1.4 equiv), HO^- (0.4 equiv), 1 h; (c) (i) DIAD (1.5 equiv), Ph_3P (1.1 equiv), $PhCO_2H$ (1.1 equiv), Et_2O, 23 °C, 5 h, (ii) NaOH (8 equiv), MeOH, reflux, 4 h; (d) 5% Pd/C, 30 psi H_2, EtOH, 23 °C, 24 h; (e) MsCl (2.3 equiv), Et_3N (2.3 equiv), CH_2Cl_2, −30 °C (20 min), 23 °C; (f) Ph_2PH (2.15 equiv), *n*-BuLi (2.10 equiv), THF, −78 °C (15 min), 23 °C (45 min).

The facile synthesis of racemic **1** is shown in Scheme I. We based our approach on the analogous synthesis of the chairphos ligand from 1,3-butanediol.[7] The needed *cis*-2-methanol-1-cyclohexanol **4** was prepared by a known radical cyclization procedure.[11] Activation of this diol as the bis(methanesulfonate) followed by displacement with lithium diphenylphosphide readily provided the desired diphosphine. The synthesis of enantiomerically pure **2** is shown in Scheme II. Hydroboration/oxidation of benzyl-protected (1*R*)-(−)-myrtenol gave the alcohol **5** with the incorrect stereochemistry of the secondary hydroxy group.[12] Inversion under Mitsunobo conditions[13] followed by removal of the benzyl protection efficiently provided the needed stereochemistry in diol **6**. Activation of the diol as the dimesylate and displacement with diphenylphosphide as above afforded the enantiomerically pure diphosphine **2**.

The formation of (π-allyl)palladium complexes containing the new diphosphine ligands **1** and **2** was accomplished by transallylation following the procedure used above for the palladium complex containing the chairphos

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(8) The crystal structures of related unsymmetrical (η^3-allyl)palladium complexes have been determined.[6a]

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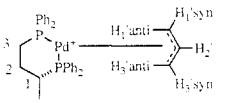
(10) The formation of the allyl complexes was also successful with use of tetrafluoroborate, but characterization was best accomplished when the perchlorate salt (*Caution!*) was employed. All new compounds have been purified and characterized spectroscopically. For example, the parent η^3-allyl complex of **3**-Pd$^+$ was isolated as a 50:50 mixture of isomers; mp 253–254 °C dec. The ^{1}H NMR assignments were made with the aid of a COSY spectrum:



^{1}H NMR ($CDCl_3$, 400 MHz, δ): major isomer, 7.52–7.20 (m, 10 H, C_6H_5), 5.65 (m, 1 H, $H_{2'}$), 3.97 (m, 1 H, $H_{1'syn}$ or $H_{3'syn}$), 3.85 (m, 1 H, $H_{1'syn}$ or $H_{3'syn}$), 3.16 (m, 3 H, $H_{1'anti}$, $H_{3'anti}$, H_1), 2.67 (m, 2 H, H_3), 2.01 (m, 1 H, H_{2_a}), 1.92 (m, 1 H, H_{2_b}), 1.06 (dd, J = 14.1, 7.1 Hz, 3 H, CH_3); minor isomer, 7.52–7.20 (m, 10 H, C_6H_5), 5.65 (m, 1 H, $H_{2'}$), 3.97 (m, 2 H, $H_{1'syn}$ and $H_{3'syn}$), 3.39 (m, 1 H, $H_{1'anti}$ or $H_{3'anti}$), 3.24 (m, 1 H, $H_{1'anti}$ or $H_{3'anti}$), 2.85 (m, 1 H, H_1), 2.67 (m, 1 H, H_3), 2.53 (m, 1 H, H_3), 2.01 (m, 2 H, H_{2_a}, H_{2_b}), 1.18 (dd, J = 14.7, 7.1 Hz, 3 H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 135–128 (complex), 123.5 (br t), 122.9 (br t), 75.5 (29), 75.0 (26), 73.4 (24), 73.0 (27), 28.9 (24), 28.4 (24), 26.9, 23.9 (26), 22.9 (27), 16.6, 16.1. ^{31}P NMR (160 MHz, $CDCl_3$, 85% H_3PO_4 at 0 ppm, δ): 17.86 (62), 17.62 (62), 9.33 (62), 8.43 (62). IR ($CHCl_3$): 3060, 1640, 1440, 1050 cm^{-1}.

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ligand.[10] The ratios achieved with use of diphosphine ligand 1 were 57:43, 83:17, and 88:12 and with the myrtenol-derived diphosphine 2 were 64:36, 64:36, and 88:12 for the complexes with allyl, 1,3-diphenylallyl, and cyclohexenyl, respectively.[14] In both cases the stereoselectivity for the formation of the cyclohexenyl complexes is better than that for the diphenylallyl compounds. This would be expected since the staggered form of the diphenylallyl complex has the allyl substituents gauche to both phenyl groups on each phosphine, whereas the staggered cyclohexenyl complex has its substituents gauche to only one phenyl group, resulting in a smaller energy difference in the two diphenylallyl isomers.

Having established the ability to coordinate at least one class of C_s-symmetrical π-allyls selectively to C_s-symmetric (diphosphine)palladium complexes containing diphenylphosphines, we are now pursuing the preparation of related diphosphines in which the two phosphines are electronically different, which we anticipate will function as efficient asymmetric ligands.

Acknowledgment. We thank the Graduate Research School of Boston University for financial support of this work.

Supplementary Material Available: A table listing ^1H, ^{13}C, and ^{31}P NMR data for the diastereomeric mixtures of the nine (η^3-allyl)(diphosphine)palladium complexes (2 pages). Ordering information is given on any current masthead page.

(14) The ratios of all compounds were determined by examination of the crude ^1H NMR spectra. Characterization was done on purified materials. The ratios reflect kinetically formed products (reaction time 30 min). Both diastereomers of 3-Pd$^+$(η^3-1,3-diphenylallyl) were isolated by crystallization, and both isomers were observed to equilibrate slowly in solution, reaching the same 55:45 ratio in 48 h, where the major isomer corresponds to the original minor isomer.

(t-Bu)$_2$GaAs(t-Bu)$_2$: A Volatile Monomeric Arsinogallane

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Summary: The 1:1 reaction of t-Bu$_2$GaCl and t-Bu$_2$AsLi in benzene affords the volatile monomeric compound (t-Bu)$_2$GaAs(t-Bu)$_2$ as a yellow solid. The single-crystal X-ray structure, ^1H and ^{13}C NMR, IR, and mass spectroscopy, elemental analysis, and isopiestic molecular weight determination are reported.

Although arsinogallanes have been known for over 25 years,[1] monomeric arsinogallanes are rare. Arsinogallanes are usually found as dimers, trimers, or adducts due to the proclivity of Ga(III) toward tetracoordination.[2-5] Monomeric arsinogallanes are expected to exhibit a pπ-pπ interaction between the unoccupied p orbital on gallium and the filled p orbital on arsenic. Multiple bonding between main-group elements[6-8] has been well documented, but not for third-row or higher group III-V compounds. Attempts to prepare monomeric arsinogallanes have focused on the use of the bulky substituents. The first monomeric arsinogallane, [(mesityl)$_2$As]$_3$Ga, was reported by Wells et al.[9] in 1986, and subsequently, the *tert*-butyl derivative was reported by Cowley[10] and co-workers. Only recently, Theopold[11] and co-workers reported the first mono(arsino)gallane monomer, (C$_5$Me$_5$)$_2$GaAs(SiMe$_3$)$_2$, and its conversion to amorphous GaAs powder via reaction with alcohol.

Here we report the synthesis and crystal structure of (t-Bu)$_2$GaAs(t-Bu)$_2$ (1), the first volatile monomeric mono(arsino)gallane, and its conversion to polycrystalline GaAs by pyrolysis at 400-450 °C. Benzene (20 mL) was added to t-Bu$_2$GaCl[12] (0.66 g, 3.0 mmol) and t-Bu$_2$AsLi[13]

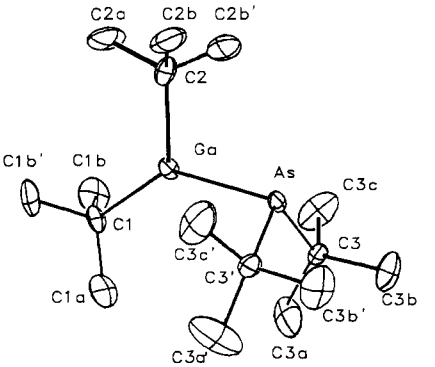

Figure 1. Structure of (t-Bu)$_2$GaAs(t-Bu)$_2$ (1). Hydrogen atoms are omitted for clarity.

Table I. Selected Bond Lengths (Å) and Bond Angles (deg) for (t-Bu)$_2$GaAs(t-Bu)$_2$

Ga-As	2.466 (3)	C(2)-C(2b)	1.510 (16)
Ga-C(1)	2.016 (13)	C(2)-C(2b')	1.510 (16)
Ga-C(2)	1.961 (17)	C(3)-C(3a)	1.490 (18)
As-C(3)	1.982 (10)	C(3)-C(3b)	1.504 (14)
As-C(3')	1.982 (10)	C(3)-C(3c)	1.505 (17)
C(1)-C(1a)	1.483 (24)	C(3')-C(3a')	1.490 (18)
C(1)-C(1b)	1.536 (14)	C(3')-C(3b')	1.504 (14)
C(1)-C(1b')	1.536 (14)	C(3')-C(3c')	1.505 (17)
C(2)-C(2a)	1.541 (22)		
As-Ga-C(1)	132.7 (4)	Ga-C(1)-C(1b)	106.6 (8)
As-Ga-C(2)	106.8 (4)	Ga-C(2)-C(2a)	118.3 (11)
C(1)-Ga-C(2)	120.5 (6)	Ga-C(2)-C(2b)	108.9 (8)
Ga-As-C(3)	103.4 (3)	As-C(3)-C(3a)	110.2 (6)
Ga-As-C(3')	103.4 (3)	As-C(3)-C(3b)	110.0 (7)
C(3)-As-C(3')	110.2 (6)	As-C(3)-C(3c)	107.3 (7)
Ga-C(1)-C(1a)	116.3 (9)		

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