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Synthesis of *trans*-(σ -Allenyl)platinum(II) and -palladium(II) Compounds. X-ray Crystal Structure of *trans*-[PtBr{C(H)=C=CMe₂}(PPh₃)₂] and Highly Diastereoselective *trans*-*cis* Isomerization of (σ -Allenyl)palladium(II) Bromides

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The synthesis and characterization of new *trans*-bis(triphenylphosphine)(σ -allenyl)-platinum(II) and -palladium(II) halides, prepared by the oxidative-addition reaction of allenyl or propargyl halides with M(PPh₃)₄ (M = Pt, Pd), are described. Their molecular structure has been confirmed by an X-ray crystal structure determination of *trans*-[PtBr{CH=C=C(CH₃)₂}(PPh₃)₂]: space group C2/c, *a* = 11.498(3) Å, *b* = 15.511(3) Å, *c* = 19.570(6) Å, β = 90.06(3)°, *V* = 3490(2) Å³, *Z* = 4, *R* = 0.064, *R*_w = 0.123. Furthermore, a highly uncommon *trans* to *cis* isomerization was observed for *trans*-bis(triphenylphosphine)(σ -allenyl)palladium bromides which bear alkyl substituents at the γ -positions of the allenyl ligand, with formation of *cis*-(σ -allenyl)palladium bromides which exhibit double atropisomerism, *i.e.* around the allenic axis and around the Pd-C axis. The *trans* to *cis* isomerization proceeds diastereoselectively when the alkyl groups at the γ -position exhibit large steric differences; *i.e.*, for *cis*-[PdBr{CH=C=CMe(*t*-Bu)}(PPh₃)₂] only the *M,M/P,P* diastereoisomer was formed, whereas for *cis*-[PdBr{CH=C=CMe(Et)}(PPh₃)₂] equal amounts of the *M,M/P,P* and *M,P/P,M* diastereomers were observed.

Introduction

The chemistry of organometallic complexes containing one or more M-C σ - and/or π -bonds to 1,2-dienyl (allenyl) fragments continues to be a subject of interest, and they potentially possess a very rich chemistry.^{1,2} In the late 1960s σ -allenyl complexes were reported for Co,^{3,4} Fe,⁵ and Ir and Pt,⁴ which were all prepared by the oxidative-addition reaction of propargyl or allenyl halides with the appropriate metal nucleophile. Later, oxidative additions were also applied to the synthesis of (σ -allenyl)- and (σ -propynyl)Pd complexes,⁶ in order to substantiate the intermediacy of (σ -allenyl)palladium compounds in Pd-catalyzed cross-coupling reactions involving allenyl and propargyl compounds. Recently σ -allenyl complexes of Ru and W⁷ as well as novel transition-metal compounds containing the π -allenyl moiety have been reported.⁸

The mechanisms of the reactions of propargyl and allenyl halides with metal nucleophiles have not been proven rigorously, although it has been established by regio- and stereochemical studies on the organic starting materials and products that S_N2 and S_N2' processes are the principal ones.^{1,6,9} A few reports on palladium-catalyzed C-C coupling reactions of allenes with carbon monoxide,¹⁰ other allenes,¹¹ styrene,¹² and vinyl halides or triflates¹³ have appeared. For some of these reactions^{9,11} (σ -allenyl)palladium complexes were shown to be viable intermediates.⁶

One of the main objectives of our current work has been to study reactions of (σ -allenyl)palladium and -platinum complexes with isocyanides, carbon monoxide, and oxygen.¹⁴ Here we report on the synthesis and characterization of a series of novel (σ -allenyl)palladium

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(1) Jacobs, T. L. In *The Chemistry of The Allenes*; Landor, S. R., Ed.; Academic Press: London, 1982; Vol. 2, p 334.

(2) (a) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Chemistry*; Wiley-Interscience: New York, 1984. (b) Wojcicki, A.; Shuchart, C. E. *Coord. Chem. Rev.* **1990**, *105*, 35.

(3) Johnson, M. D.; Mayle, C. J. *Chem. Soc. D* **1969**, 192.

(4) Collman, J. P.; Cawse, J. N.; Kang, J. W. *Inorg. Chem.* **1969**, *8*, 2574. Mann, B. E.; Shaw, B. L.; Tucker, N. I. *J. Chem. Soc. A* **1971**, 2667.

(5) (a) Roustan, J.-L.; Cadot, P. C. R. *Seances Acad. Sci., Ser. C* **1969**, *268*, 734. (b) Jolly, P. W.; Pettit, R. *J. Organomet. Chem.* **1968**, *12*, 491. (c) Ariyaratne, J. K. P.; Green, M. L. H. *J. Organomet. Chem.* **1963-1964**, *1*, 90.

(6) (a) Elsevier, C. J.; Kleijn, H.; Ruitenberg, K.; Vermeer, P. *J. Chem. Soc., Chem. Commun.* **1983**, 1529. (b) Elsevier, C. J.; Kleijn, H.; Boersma, J.; Vermeer, P. *Organometallics* **1986**, *5*, 716.

(7) (a) Shuchart, C. E.; Willis, R. R.; Wojcicki, A. *J. Organomet. Chem.* **1992**, *424*, 185. (b) Keng, R.-S.; Lin, Y.-C. *Organometallics* **1990**, *9*, 289.

(8) (a) Gotzig, J.; Otto, H.; Werner, H. *J. Organomet. Chem.* **1985**, *287*, 247. (b) Bianchini, C.; Peruzzini, M.; Zanolini, F.; Frediani, P.; Albinati, A. *J. Am. Chem. Soc.* **1991**, *113*, 5453. (c) Casey, C. P. *Science* **1993**, *259*, 1552. (d) Blosser, P. W.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1993**, *12*, 1993. (e) Stang, P. J.; Crittall, C. M.; Arif, A. M. *Organometallics* **1993**, *12*, 4799. (f) Huang, T.-M.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *J. Am. Chem. Soc.* **1993**, *115*, 1170 and references cited herein.

(9) Elsevier, C. J.; Vermeer, P. *J. Org. Chem.* **1985**, *50*, 3042.

(10) (a) Nogi, T.; Tsuji, J. *Tetrahedron* **1969**, *25*, 4099. (b) Trieu, N. D.; Elsevier, C. J.; Vrieze, K. *J. Organomet. Chem.* **1987**, *325*, C23.

(11) Ruitenberg, K.; Kleijn, H.; Westmijze, H.; Meijer, J.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 405.

(12) Trost, B. M.; Kottirsch, G. *J. Am. Chem. Soc.* **1990**, *112*, 2816.

(13) Kopola, N.; Friess, B.; Cazes, B.; Gore, J. *Tetrahedron Lett.* **1989**, *30*, 3963.

and -platinum complexes, which were starting compounds for those studies, as well as the X-ray crystal structure determination of the (σ -allenyl)metal complex *trans*-[PtBr{CH=C=CMe₂}(PPh₃)₂].

Experimental Section

General Considerations. Solvents were carefully dried and distilled prior to use. The reactions were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. The ¹H, ³¹P, and ¹³C NMR spectra were recorded on Bruker AC 100, WM 250, and AMX 300 spectrometers, and infrared spectra were measured on a Perkin-Elmer 283 spectrophotometer. Field desorption (FD) mass spectra were measured on a Varian MAT 711 double-focused mass spectrometer by the Institute for Mass Spectrometry of the University of Amsterdam. Elemental analyses were carried out at the Analytical Department of the Institute of Applied Chemistry, TNO, Zeist, The Netherlands.

The starting materials Pt(PPh₃)₄,¹⁵ Pd(PPh₃)₄,¹⁶ and allenyl and propargyl halides¹⁷ were synthesized by literature procedures.

Synthesis of (σ -allenyl)Pt^{II} and -Pd^{II} Compounds 1a–i and 2a–f. The synthesis of [PtBr{C(H)=C=CMe₂}(PPh₃)₂] (1a) from the reaction of Me₂C=C=C(H)Br and Pt(PPh₃)₄ is described in detail; the syntheses of 1b–i and 2a–f were carried out similarly. The only difference during the synthesis of the palladium complexes 2a–f was the observation that the reaction mixture remained yellow instead of changing from pale yellow to colorless as observed for the platinum compound.

***trans*-[PtBr{C(H)=C=CMe₂}(PPh₃)₂] (1a).** To a stirred solution of Pt(PPh₃)₄ (1.69 g, 1.35 mmol) in THF (200 mL) was added 1.5 equiv of Me₂C=C=C(H)Br (315 mg, 2.15 mmol) at ambient temperature. The yellow reaction solution rapidly turned colorless and was stirred for 1 h at 20 °C. The solvent was then evaporated *in vacuo* to 10% of its original volume, and pentane (100 mL) was added, which resulted in the precipitation of a white solid. The solid was filtered off, washed with diethyl ether (3 × 50 mL) and pentane (3 × 50 mL), and dried *in vacuo*, affording [PtBr{C(H)=C=CMe₂}(PPh₃)₂] (1.05 g, 89%) as a white powder. White crystals of 1a suitable for a single-crystal X-ray diffraction study were grown by slow diffusion of hexane into a THF solution of [PtBr{C(H)=C=CMe₂}(PPh₃)₂] at ambient temperature. Anal. Calcd for C₄₄H₄₃P₂BrPt: C, 56.82; H, 4.31; P, 7.15. Found: C, 56.79; H, 4.35; P, 7.21. FD-mass: found *m/z* 866; calcd M⁺ 866.7.

***trans*-[PtBr{C(H)=C=C(CH₂)₅}(PPh₃)₂] (1b).** The reaction of Pt(PPh₃)₄ (1.75 g, 1.41 mmol) in THF (200 mL) at ambient temperature with (CH₂)₅C=C=C(H)Br (415 mg, 2.22 mmol) yielded 1.23 g (96%) of 1b as a white powder. Anal. Calcd for C₄₄H₄₁P₂BrPt: C, 58.28; H, 4.56; P, 6.83. Found: C, 59.01; H, 4.81; P, 6.84. FD-mass: found *m/z* 907; calcd M⁺ 906.8.

***trans*-[PtBr{C(H)=C=CMe(Et)}(PPh₃)₂] (1c).** The reaction of Pt(PPh₃)₄ (1.00 g, 0.80 mmol) in THF (150 mL) at ambient temperature with Me(Et)C=C=C(H)Br (205 mg, 1.28 mmol) yielded 0.65 g (92%) of 1c as a white powder. Anal. Calcd for C₄₂H₃₉P₂BrPt: C, 57.28; H, 4.47; P, 7.03. Found: C, 56.82; H, 4.68; P, 6.93. FD-mass: found *m/z* 880; calcd M⁺ 880.

***trans*-[PtBr{C(H)=C=CH(*n*-C₅H₁₁)}(PPh₃)₂] (1d).** The reaction of Pt(PPh₃)₄ (1.95 g, 1.57 mmol) in THF (200 mL) at ambient temperature with *n*-C₅H₁₁–CH(Br)–C≡CH (468 mg, 2.48 mmol) yielded 1.18 g (83%) of 1d as a white powder. Anal. Calcd for C₄₄H₄₃P₂BrPt: C, 58.15; H, 4.77; P, 6.82. Found: C, 58.23; H, 5.16; P, 6.50. FD-mass: found *m/z* 909; calcd M⁺ 908.8.

***trans*-[PtBr{C(H)=C=CMe(*t*-Bu)}(PPh₃)₂] (1e).** The reaction of Pt(PPh₃)₄ (1.67 g, 1.34 mmol) in THF (200 mL) at ambient temperature with *t*-Bu(Me)C=C=C(H)Br (400 mg, 2.12 mmol) yielded 1.13 g (93%) of 1e as a white powder. Anal. Calcd for C₄₄H₄₃P₂BrPt: C, 58.15; H, 4.77; P, 6.82. Found: C, 58.05; H, 4.94; P, 6.77. FD-mass: found *m/z* 909; calcd M⁺ 908.8.

***trans*-[PtBr{C(H)=C=CH(Ph)}(PPh₃)₂] (1f).** The reaction of Pt(PPh₃)₄ (1.45 g, 1.17 mmol) in THF (200 mL) at ambient temperature with Ph(H)C=C=C(H)Br (360 mg, 1.85 mmol) yielded 0.97 g (90%) of 1f as a white powder. Anal. Calcd for C₄₅H₃₇P₂BrPt: C, 59.09; H, 4.08; P, 6.77. Found: C, 60.12; H, 4.31; P, 7.08. FD-mass: found *m/z* 915; calcd M⁺ 914.7.

***trans*-[PtCl{C(H)=C=CMe(*t*-Bu)}(PPh₃)₂] (1g).** The reaction of Pt(PPh₃)₄ (1.80 g, 1.45 mmol) in THF (200 mL) at ambient temperature with *t*-Bu(Me)C=C=C(H)Cl (315 mg, 2.18 mmol) yielded 1.00 g (80%) of 1g as a white powder. Anal. Calcd for C₄₄H₄₃P₂ClPt: C, 61.14; H, 5.02; P, 7.17. Found: C, 61.08; H, 4.99; P, 7.24. FD-mass: found *m/z* 864; calcd M⁺ 864.

***trans*-[PtI{C(H)=C=CMe(*t*-Bu)}(PPh₃)₂] (1h).** The reaction of Pt(PPh₃)₄ (1.48 g, 1.19 mmol) in THF (200 mL) at ambient temperature with *t*-Bu(Me)C=C=C(H)I (442 mg, 1.88 mmol) yielded 0.91 g (80%) of 1h as a white powder. Anal. Calcd for C₄₄H₄₃P₂IPt: C, 55.29; H, 4.53; P, 6.48. Found: C, 55.43; H, 4.60; P, 6.54. FD-mass: found *m/z* 956; calcd M⁺ 955.8.

***trans*-[PtCl{C(H)=C=CMe₂}(PPh₃)₂] (1i).**⁴ The reaction of Pt(PPh₃)₄ (1.00 g, 0.80 mmol) in THF (150 mL) at ambient temperature with Me₂C=C=C(H)Cl (130 mg, 1.27 mmol) yielded 0.63 g (96%) of 1i as a white powder. Anal. Calcd for C₄₁H₃₇P₂ClPt: C, 59.89; H, 4.54; P, 7.53. Found: C, 59.99; H, 4.61; P, 6.42. FD-mass: found *m/z* 822; calcd M⁺ 822.3.

***trans*-[PdBr{C(H)=C=CMe₂}(PPh₃)₂] (2a).** The reaction of Pd(PPh₃)₄ (1.00 g, 0.87 mmol) in THF (100 mL) at ambient temperature with Me₂C=C=C(H)Br (192 mg, 1.30 mmol) yielded 0.63 g (90%) of 2a as a yellow powder. Anal. Calcd for C₄₁H₃₇P₂BrPd: C, 63.30; H, 4.80; P, 7.96. Found: C, 63.36; H, 4.89; P, 7.89.

***trans*-[PdBr{C(H)=C=C(CH₂)₅}(PPh₃)₂] (2b).** The reaction of Pd(PPh₃)₄ (2.42 g, 2.10 mmol) in THF (200 mL) at ambient temperature with (CH₂)₅C=C=C(H)Br (589 mg, 3.15 mmol) yielded 1.63 g (95%) of 2b as a yellow powder. Anal. Calcd for C₄₄H₄₁P₂BrPd: C, 64.60; H, 5.06; P, 7.57. Found: C, 64.67; H, 5.24; P, 7.74.

***trans*-[PdBr{C(H)=C=CMe(Et)}(PPh₃)₂] (2c).** The reaction of Pd(PPh₃)₄ (1.99 g, 1.72 mmol) in THF (150 mL) at ambient temperature with Me(Et)C=C=C(H)Br (415 mg, 2.58 mmol) yielded 1.10 g (81%) of 2c as a yellow powder. Anal. Calcd for C₄₂H₃₉P₂BrPd: C, 63.69; H, 4.97; P, 7.82. Found: C, 63.79; H, 5.10; P, 7.74.

***trans*-[PdBr{C(H)=C=CH(*n*-C₅H₁₁)}(PPh₃)₂] (2d).** The reaction of Pd(PPh₃)₄ (1.50 g, 1.30 mmol) in THF (200 mL) at ambient temperature with *n*-C₅H₁₁–CH(Br)–C≡CH (368 mg, 1.95 mmol) yielded 0.83 g (78%) of 2d as a yellow powder. Anal. Calcd for C₄₄H₄₃P₂BrPd: C, 64.44; H, 5.29; P, 7.55. Found: C, 64.58; H, 5.36; P, 7.36.

***trans*-[PdBr{C(H)=C=CMe(*t*-Bu)}(PPh₃)₂] (2e).** The reaction of Pd(PPh₃)₄ (2.04 g, 1.77 mmol) in THF (200 mL) at ambient temperature with *t*-Bu(Me)C=C=C(H)Br (502 mg, 2.66 mmol) yielded 1.25 g (86%) of 2e as a yellow powder. Anal. Calcd for C₄₄H₄₃P₂BrPd: C, 64.44; H, 5.29; P, 7.55. Found: C, 64.61; H, 5.34; P, 7.41.

(14) (a) Wouters, J. M. A.; Avis, M. W.; Elsevier, C. J.; Kyriakidis, C. E.; Stam, C. H. *Organometallics* **1990**, *9*, 2203. (b) Wouters, J. M. A.; Klein, R. A.; Elsevier, C. J.; Vrieze, K.; Zoutberg, M. C.; Stam, C. H. *Organometallics* **1993**, *12*, 3864. (c) Wouters, J. M. A.; Elsevier, C. J.; Vrieze, K.; Zoutberg, M. C.; Goubitz, K. *Organometallics* **1994**, *13*, 1510.

(15) Ugo, R.; Cariati, F.; LaMonica, G. *Inorg. Synth.* **1968**, *11*, 105.

(16) Titus, D.; Orto, A. A.; Gray, H. B. *Inorg. Synth.* **1972**, *13*, 117.

(17) Brandsma, L.; Verkrujse, H. D. *Syntheses of Acetylenes, Allenes and Cumulenes*; Elsevier: Amsterdam, 1981.

Table 1. Crystal Data and Details of the Structure Determination of *trans*-[PtBr{C(H)=C=CMe₂}(PPh₃)₂] (1a)

A. Crystal Data	
formula	C ₄₁ H ₃₇ BrP ₂ Pt
mol wt	866.68
cryst syst	monoclinic
space group	C2/c
<i>a</i> , Å	11.498(3)
<i>b</i> , Å	15.511(3)
<i>c</i> , Å	19.570(6)
β, deg	90.06(3)
<i>V</i> , Å ³	3490(2)
<i>Z</i>	4
<i>D</i> _{calc} , g cm ⁻³	1.65
<i>F</i> ₀₀₀ , e	1704
μ(Mo Kα), cm ⁻¹	5.31
abs cor max	1.145
abs cor min	0.997
approx cryst size, mm ³	0.23 × 0.30 × 0.38
B. Data Collection	
radiation	Mo Kα (λ = 0.710 69 Å)
temp, K	293
θ _{max} , deg	25
data set	1
ω/2θ	θ/2θ
horiz and vert aperture, mm	3.5, 4
max time/rfln, s	40
ref rflns	200 and 111
no. of rflns	6538
no. of unique (rflns)	6436
no. of obs rflns (<i>I</i> > 2.5σ(<i>I</i>))	2444
exposure time, h	82
C. Refinement	
no. of params	596
weighting scheme	(6.5 + <i>F</i> _o + 0.034 <i>F</i> _o ²) ⁻¹
final <i>R</i> _F , <i>R</i> _w	0.064, 0.123
max shift/error	0.11
residual density max, e Å ⁻³	2.0
residual density min, e Å ⁻³	-2.1

***trans*-[PdBr{C(H)=C=CH(Ph)}(PPh₃)₂] (2f).** The reaction of Pd(PPh₃)₄ (2.29 g, 1.98 mmol) in THF (200 mL) at ambient temperature with Ph(H)C=C=C(H)Br (579 mg, 2.97 mmol) yielded 1.44 g (88%) of **2f** as a yellow powder. Anal. Calcd for C₄₅H₃₇P₂BrPd: C, 65.43; H, 4.52; P, 7.50. Found: C, 65.49; H, 4.57; P, 7.48.

Crystal Structure Determination of *trans*-[PtBr{C(H)=C=CMe₂}(PPh₃)₂] (1a). Crystals of **1a** are monoclinic, space group C2/c, with *Z* = 4, *a* = 11.498(3) Å, *b* = 15.511(3) Å, *c* = 19.570(6) Å, β = 90.06(3)°, *V* = 3490(2) Å³, μ(Mo Kα) = 5.31 cm⁻¹, *d*_{calc} = 1.65 g cm⁻³, and crystal dimensions 0.23 × 0.30 × 0.38 mm. A total of 6436 intensities were measured on a Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα (λ = 0.710 69 Å) radiation (1.1 ≤ θ ≤ 25°; -23 ≤ *h* ≤ 23, 0 ≤ *k* ≤ 13, 0 ≤ *l* ≤ 18). Of these, 2444 were above the 2.5σ(*I*) level and were treated as observed. The asymmetric unit contains half of a molecule. As the molecule is not centrosymmetric in itself, the only way to describe it satisfactorily was to introduce disorder by placing half of a Br atom and half of an allenyl moiety at either position on the Pt atom. Trying to describe the structure in a noncentrosymmetric space group (*Cc*), thus avoiding the disorder, led to a refinement result in which all C atoms could only be refined isotropically. Although the final *R* factor in *Cc* was somewhat better (0.054) than in the case of C2/c, anisotropic refinement was possible in C2/c for all but the allenyl C atoms. The Pt and Br positions were determined using the Patterson method, and the remainder of the non-hydrogen atoms were found in a Δ*F* synthesis. The positions of the hydrogen atoms were calculated. Full-matrix least-squares refinement on *F*, anisotropic for all non-hydrogen atoms except those of the allenyl moiety, which were kept isotropic while the hydrogen atoms were kept fixed at their calculated positions with a temperature factor of *U* = 0.038 Å², converged to *R* = 0.064 (*R*_w = 0.123). The atoms of the allenyl moiety were restrained in

such a way as to ensure that the distances within this group stayed at acceptable values. A weighting scheme was applied with *w* = 1/(6.5 + *F*_o + 0.034*F*_o²), and the anomalous dispersion of Pt and Br was taken into account. The programs used were from XRAY76^{19a} and XTAL3.2;^{19b} the scattering factors²⁰ and the dispersion corrections²¹ were taken from the literature.

Results and Discussion

The (σ-allenyl)metal halides [MX{C(H)=C=CRR'}-(PPh₃)₂] (**1a–i**, M = Pt; **2a–f**, M = Pd) have been prepared by the reaction of tetrakis(triphenylphosphine)palladium(0) and -platinum(0) with several appropriately substituted allenyl halides or propargyl halides in THF (eq 1).

- a:** R = R' = Me, X = Br
b: R–R' = -(CH₂)₅-, X = Br
c: R = Me, R' = Et, X = Br
d: R = *n*-C₅H₁₁, R' = H, X = Br
e: R = *t*-Bu, R' = Me, X = Br
f: R = Ph, R' = H, X = Br
g: R = *t*-Bu, R' = Me, X = Cl
h: R = *t*-Bu, R' = Me, X = I
i: R = R' = Me, X = Cl

The (σ-allenyl)platinum compounds **1a–i** are white solids which are soluble in dichloromethane, THF, and toluene but insoluble in apolar solvents such as pentane and hexane. They can be stored without decomposition for several months if kept at -20 °C under an inert atmosphere in the dark. They have been characterized by ¹H, ³¹P, and ¹³C NMR, IR, FD mass spectrometry, and elemental analysis and by a single-crystal X-ray structure determination of **1a**.

The (σ-allenyl)palladium compounds **2a–f** are yellow solids which are soluble in toluene, benzene, and THF but insoluble in pentane and other apolar solvents. In the solid state **2a–f** can be stored for approximately 1 month if kept at -20 °C under an inert atmosphere. The compounds have been characterized by ¹H and ³¹P NMR, IR, and elemental analysis and by ¹³C NMR for **2f**.

In contrast to the analogous chloride complexes,⁶ the *trans*-bis(triphenylphosphine)(σ-allenyl)palladium(II) bromides **2a–e** are not configurationally stable in chlorinated solvents. After approximately 10 min in a CH₂Cl₂ or CHCl₃ solution at room temperature, isomerization

(18) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

(19) (a) Stewart, J. M. *The XRAY 76 system*; Technical Report TR 446; Computer Science Center, University of Maryland: College Park, MD, 1976. (b) Hall, S. R.; Flack, H. D.; Stewart, J. M., Eds. *XTAL3.2 Reference Manual*; Universities of Western Australia, Geneva, and Maryland, 1992.

(20) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *24*, 321.

(21) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

Figure 1. ORTEP drawing of $\text{trans-[PtBr}\{\text{C(H)=C=Me}_2\}(\text{PPh}_3)_2]$.

of **2a-e** started and formation of the new compounds **3a-e** occurred, which was completed in ca. 10 h, during

which period the initially yellow color of the solution gradually changed to orange. Attempts to isolate **3a-e** were unsuccessful. For instance, attempts to crystallize **3a** yielded crystals of $\text{Pd}(\text{PPh}_3)_4$ (according to elemental analysis), palladium metal, and unidentified organic material. ^1H and ^{31}P NMR spectroscopy of the solutions of **3a-e** revealed that these products are actually the *cis* isomers of **2a-e** (see below). When the solid (σ -allenyl)palladium compounds **2a-e** were stored for prolonged periods, i.e. several months at -20°C or several days at room temperature, the originally yellow color turned orange also in the solid state. NMR of a solution of this orange species revealed that the same compounds **3a-e** had been formed.

Solid-State Structure of $\text{trans-[PtBr}\{\text{C(H)=C=Me}_2\}(\text{PPh}_3)_2]$ (1a). The molecular geometry of $\text{trans-[PtBr}\{\text{C(H)=C=Me}_2\}(\text{PPh}_3)_2$ (**1a**) and its atomic numbering scheme is shown in Figure 1, and bond distances and angles are listed in Table 2. The crystal structure is one of the very few known for mononuclear

Table 2. Relevant Bond Lengths ($\text{\AA}$) and Bond Angles (deg) for **1a**

Around Pt			
Pt-Br	2.443(4)	Br-Pt-P	92.9(1)
Pt-P	2.301(4)	Br-Pt-C(40)	178(3)
Pt-C(40)	2.10(3)	P-Pt-C(40)	88(1)
Within Ligand			
C(40)-C(41)	1.30(5)	Pt-C(40)-C(41)	131(4)
C(41)-C(42)	1.30(4)	C(40)-C(41)-C(42)	173(5)
C(42)-C(43)	1.50(6)	C(41)-C(42)-C(43)	124(3)
C(42)-C(44)	1.50(5)	C(41)-C(42)-C(44)	123(3)
		C(43)-C(42)-C(44)	112(3)

metal σ -1,2-dienyl compounds, i.e. where the allenyl-metal bond is not supported by additional $\pi\text{-C}=\text{C}$ bonding to another (or the same) metal atom. Apart from an early report by Struchkov, only two recent examples are known.²²

The platinum-phosphorus bond distances in **1a** of 2.301(4) $\text{\AA}$ are similar to those for other $\text{trans-[PtBr(R)(PR}_3)_2]$ complexes^{14,23} (see Table 3). The Pt-Br distance of 2.443(4) $\text{\AA}$ is the shortest, while the Pt-C(40) bond distance of 2.10(3) $\text{\AA}$ is one of the longest Pt-C(allenyl) distances in Table 3 and is longer than a normal Pt-C(sp^2) bond of 1.98 $\text{\AA}$.²⁴ The dihedral angle between the allenyl-Pt moiety and the coordination plane amounts to $85(2)^\circ$.

(22) (a) Andrianov, B. G.; Zlotina, I. B.; Chomutov, M. A.; Kolobova, N. E.; Struchkov, Yu. T.; *Koord. Khim.* **1978**, *4*, 298. (b) Wojcicki, A. *New J. Chem.* **1994**, *18*, 61. (c) Huang, T.-M.; Hsu, R.-H.; Yang, C.-S.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *Organometallics* **1994**, *13*, 3657.

(23) (a) Huffman, J. C.; Laurent, M. P.; Kochi, J. K. *Inorg. Chem.* **1977**, *16*, 2639. (b) Rajaram, J.; Pearson, R. G.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 2103. (c) Gassman, P. G.; Gennick Cesa, I. *Organometallics* **1984**, *3*, 119. (d) Cardin, C. J.; Cardin, D. J.; Parge, H. E.; Sullivan, A. C. *J. Chem. Soc., Dalton Trans.* **1986**, 2315.

(24) 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; p 532.

(25) (a) Leiserowitz, L.; Nader, F. *Angew. Chem.* **1973**, *85*, 150. (b) Groth, P. *Acta Chem. Scand.* **1973**, *27*, 3302. (c) Irngartinger, H.; Jäger, H.-U. *Acta Crystallogr., Sect. B* **1978**, *34*, 2943. (d) Karle, I. L. *J. Am. Chem. Soc.* **1973**, *95*, 4036. (e) Luche, J. L.; Damiano, J. C.; Crabbé, P.; Cohen-Addad, C.; Lajzerowicz, J. *Tetrahedron* **1977**, *33*, 961.

Table 3. Bond Distances and Δ Values^a for *trans*-[PtBr(R)(PR'₃)₂] Complexes

R	R'	ref	Pt-P (Å)	Pt-Br (Å)	Pt-C (Å)	Δ
CH=C=CH ₂	Ph	22c	2.313(2), 2.307(2)	2.4914(8)	2.040(5)	
η^1 -C ₃ H ₅	Et	23a	2.301(2), 2.294(2)	2.543(1)	2.086(7)	0.93
(<i>E</i>)-CH=CHC ₆ H ₅	Ph	23b	2.310(2), 2.304(2)	2.5021(12)	2.022(8)	0.96
3-bromobicyclo[2.2.1]hept-2-en-2-yl	Ph	23c	2.32(1), 2.31(1)	2.52(5)	1.90(3)	0.93
C(C ₁₀ H ₁₅)=CH ₂	Et	23d	2.301(5), 2.310(5)	2.549(2)	2.14(2)	0.89
C(C ₁₀ H ₇)=CMe ₂	Et	23d	2.297(5), 2.320(5)	2.537(2)	2.086(16)	0.93
C(H)=C=CMe ₂	Ph	this work	2.301(4)	2.443(4)	2.10(3)	0.92
C=C(C ₃ H ₅)-CH ₂ -C(=O)-O	Ph	14a	2.321(4), 2.325(4)	2.504(2)	2.00(1)	0.93
C(CMe ₂)(CH=C=N- <i>t</i> -Bu)	Ph	14b	2.324(2), 2.312(2)	2.5464(9)	2.050(6)	0.93
C=CCMe ₂ OOH	Ph	14c	2.317(2), 2.310(2)	2.479(1)	1.979(7)	0.95

^a $\Delta = [\sum_{i=1}^6 \delta_i - 657.0]/63$, in which δ_i values are the dihedral angles formed by the normals to adjacent faces. For a perfect tetrahedron $\Delta = 0$, and for a perfect square-planar geometry $\Delta = 1$ (De Ridder, D. J. A., University of Amsterdam, to be submitted for publication).

Table 4. ¹H and ³¹P NMR and IR Data for *trans*-[MX{C(H)=C=CRR'}(PPh₃)₂] (1a-i, 2a-f)^a

compd	$\delta(R)$	$\delta(R')$	$\delta(H)$	$\delta(P)^b$	$\nu(C=C=C)^c$
PtBr{C(H)=C=CMe ₂ }(PPh ₃) ₂ (1a)	0.89 (d, 2.8, ^d 26 ^e)		4.91 (m, 104 ^e)	22.38 (3079)	1928
PtBr{C(H)=C=C(CH ₂) ₅ }(PPh ₃) ₂ (1b)	1.20 (m)		5.02 (m, 102 ^e)	22.53 (3109)	1910
PtBr{C(H)=C=CMe(Et)}(PPh ₃) ₂ (1c)	0.72 (d, 2.6, ^d 25 ^e)	0.56 (t, 7.0 ^d), 1.23 (m)	5.05 (m, 107 ^e)	22.99 (3077)	1905
PtBr{C(H)=C=CH(<i>n</i> -C ₅ H ₁₁)}(PPh ₃) ₂ (1d)	0.85 (t, 7.1 ^d), 0.99 (m), 1.18 (m), 1.28 (m)	3.13 (m, 51 ^e)	4.96 (m, 109 ^e)	23.12 (3028)	1909
PtBr{C(H)=C=CMe(<i>t</i> -Bu)}(PPh ₃) ₂ (1e)	0.61 (s)	0.53 (d, 2.9, ^d 18 ^e)	5.17 (m, 72 ^e)	23.13 (3090)	1895
Pt{C(H)=C=CH(Ph)}(PPh ₃) ₂ Br (1f)	6.51 (m), 6.92 (m)	4.10 (m, 57 ^e)	5.57 (m, 135 ^e)	22.77 (2968)	1911
PtCl{C(H)=C=CMe(<i>t</i> -Bu)}(PPh ₃) ₂ (1g)	0.56 (s)	0.40 (br)	5.15 (m, 91 ^e)	23.85 (3112)	1905
PtI{C(H)=C=CMe(<i>t</i> -Bu)}(PPh ₃) ₂ (1h)	0.65 (s)	0.54 (d, 2.8 ^d)	5.16 (m, 60 ^e)	20.96 (3062)	1906
PtCl{C(H)=C=CMe ₂ }(PPh ₃) ₂ (1i)	0.84 (d, 3.1, ^d 25.8 ^e)		4.80 (m, 117 ^e)	23.45 (3094)	1920
PdBr{C(H)=C=CMe ₂ }(PPh ₃) ₂ (2a)	0.77 (d, 2.3 ^d)		4.65 (m)	22.92	1930
PdBr{C(H)=C=C(CH ₂) ₅ }(PPh ₃) ₂ (2b)	1.20 (m, br)		4.72 (t, 8.5 ^f)	22.62	1910
PdBr{C(H)=C=CMe(Et)}(PPh ₃) ₂ (2c)	0.68 (d, 2.0 ^d)	0.59 (t, 7.4 ^d), 1.17 (m)	4.74 (m)	23.04	1907
PdBr{C(H)=C=CH(<i>n</i> -C ₅ H ₁₁)}(PPh ₃) ₂ (2d)	0.86 (t, 7.1 ^d), 1.00 (m), 1.17 (m), 1.27 (m)	3.63 (m)	4.68 (m)	23.75	1908
PdBr{C(CH ₃)=C=CMe(<i>t</i> -Bu)}(PPh ₃) ₂ (2e)	0.63 (s)	0.52 (d, 2.6 ^d)	4.83 (dt)	22.89	1900
Pd{C(H)=C=CH(Ph)}(PPh ₃) ₂ Br (2f)	6.48 (m), 6.91 (m)	4.45 (t, 6.1 ^f)	5.31 (dt)	24.12	1910

^a δ (ppm) measured at 100.13 or 300.13 MHz, solvent CD₂Cl₂ or CDCl₃, at 293 K. Abbreviations: s = singlet, d = doublet, t = triplet, dt = doublet of triplets, m = multiplet. Compounds **1a-i** and **2a-f** all show multiplets at 7.4 and 7.7 ppm due to $\text{Ph}_{m,p}$ and Ph_o , respectively. ^b Chemical shift in ppm relative to external 85% H₃PO₄; ¹J(Pt,P) in Hz in parentheses. ^c KBr pellets; ν in cm⁻¹. ^d J(H,H) in Hz. ^e J(Pt,H) in Hz. ^f J(P,H) in Hz.

The P and C(40) atoms lie above and the Pt and Br atoms below the least-squares plane defined by these five atoms. Accordingly, the coordination geometry can be described as a square plane with a distortion toward a tetrahedron. A measure for such distortions is the parameter Δ (see footnote a in Table 3). The Δ value calculated for **1a** is 0.92, which is similar to those calculated for known comparable *trans*-Pt(PPh₃)₂(R)Br complexes ($\Delta = 0.89$ – 0.96),^{14,23} which indicates that the square-planar coordination mode is only slightly distorted.

Characterization of the *trans*-(σ -Allenyl)metal Compounds 1a-i and 2a-f. The ¹H and ³¹P NMR data of *trans*-[MX{C(H)=C=CRR'}(PPh₃)₂] (**1a-i** and **2a-f**) have been collected in Table 4. In the ³¹P NMR spectra the (σ -allenyl)palladium compounds all show a singlet for the ³¹P nuclei, whereas the (σ -allenyl)-platinum compounds likewise show a singlet with satellites due to ¹J(Pt,P) coupling of ca. 3100 Hz. These observations indicate that the two phosphines in these complexes are situated in mutually *trans* positions.²⁶

Whereas the different R and R' groups of **1c-h** and **2c-f** are observed as separate signals in the ¹H NMR spectra, the σ -allenyl complexes **1a,b,i** and **2a,b**, which have C_s symmetry, show one signal for the equivalent R groups: a doublet for the methyl groups of **1a,i** and **2a** and a multiplet for the CH₂ groups of the cyclohexyl moiety of **1b** and **2b**. Furthermore, a multiplet (1H) originating from the proton bonded at C_α is observed

at approximately 5 ppm for each compound, which is a characteristic value for metalated allenes.⁴⁻⁹

Homonuclear decoupling experiments on R and R' converted these multiplets at approximately 5 ppm into triplets (³J(P,H) $\approx$ 7.0–9.0 Hz), which are due to a ³J(P,H) coupling of the two equivalent phosphorus nuclei to the proton bonded at C_α. In case of complexes **1a-i**, platinum satellites due to a ²J(Pt,H) coupling of approximately 110 Hz are observed on these multiplets, which are normal values for such complexes.²⁷ In the case of **2b**, a triplet is observed at 4.72 ppm for the proton bonded at C_α, due to ³J(P,H) coupling of 8.5 Hz, while no J(H,H) is observed.

The ¹³C{¹H} NMR data for compounds **1a-f** and **2f** have been collected in Table 5 and are in agreement with the proposed structures. The signal at high frequency (ca. 194–200 ppm) points to the presence of a =C= unit (C_β), which is important evidence for the σ -allenic structure in solution. The presence of the allenic moiety has been corroborated by IR spectroscopy, where the typical absorption band due to the asymmetric stretching mode of the allene ligand was observed around 1915 cm⁻¹. The absorption is situated at a ca. 40 cm⁻¹ lower value compared to noncoordinated allenes,²⁸ but in the region where $\nu(C=C=C)$ for (σ -allenyl)palladium chlorides has been found.⁶ The spec-

(27) ³¹P and ¹³C NMR of Transition Metal Phosphine Complexes; Pregosin, P. S.; Kunz, R. W., Springer-Verlag: Berlin, 1979.

(28) (a) Munson, J. W. In *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; Wiley: Chichester, U. K., 1980; p 172. (b) Irngartinger, H.; Jäger, H.-U. *Tetrahedron Lett.* **1976**, 3595.

Table 5. ^{13}C NMR^a Data for *trans*-[MBr{C(H)=C=CRR'}](PPh₃)₂ (1a–f, 2f)

	1a	1b	1c	1d	1e	1f	2f
C _i	131.5 (28.0, ^b 30.0 ^c)	131.0 (28.0, ^b 30.0 ^c)	131.1 (26.7, ^b 26.9 ^c)	130.9, (27.9, ^b 27.9 ^c)	131.1 (27.8, ^b 29.8 ^c)	130.6 (27.8, ^b 28.3 ^c)	131.4 (37.0 ^b)
C _o	135.5 (6.1 ^b)	135.1 (6.0 ^b)	135.2 (6.4 ^b)	135.2 (5.7 ^b)	135.2 (5.8 ^b)	135.0 (5.6 ^b)	135.0 (10.3 ^b)
C _m	128.2 (5.0 ^b)	127.7 (5.2 ^b)	127.8 (4.8 ^b)	127.8 (5.0 ^b)	127.8 (5.0 ^b)	127.8 (5.2 ^b)	128.0 (7.9 ^b)
C _p	130.6	129.8	130.1	130.1	130.1	130.2	130.1
M–C=	75.1 (8.7 ^b)	75.0 (8.5 ^b)	74.9 (8.5 ^b)	84.4 (8.4 ^b)	75.4 (8.1 ^b)	79.9 (8.3 ^b)	88.8
=C=	197.8 (4.2 ^b)	194.1 (3.5 ^b)	197.2 (6.0 ^b)	200.3 (3.3 ^b)	196.0 (3.5 ^b)	200.2 (3.6 ^b)	194.4 (4.3 ^b)
=CRR'	89.6	96.7	95.0	110.0	103.0	88.1	91.1
R/R'	19.2	29.9, 27.2, 26.2	16.2, 26.7, 12.7	28.0, 30.0, 31.6, 22.6, 14.2	13.0, 32.7, 29.1	129.7 (i), 137.0 (o), 124.5 (m), 125.9 (p)	130.3 (i), 137.5 (o), 124.8 (m), 126.1 (p)

^a δ (ppm) measured at 75.54 MHz, solvent CDCl₃, at 293 K. ^b Virtual triplet due to $J(\text{P},\text{C})$ in Hz. ^c $J(\text{Pt},\text{C})$ in Hz.

Table 6. ^1H ^a and ^{31}P ^b NMR Data for *cis*-[PdBr{C(H)=C=CRR'}](PPh₃)₂ (3a–e)

compd	$\delta(\text{R})$	$\delta(\text{R}')$	$\delta(\text{H})$	$\delta(\text{P})$	$\delta(\text{P}')$
PdBr{C(H)=C=CMe ₂ }(PPh ₃) ₂ (3a)	1.53 (dd, 1.3, ^c 4.0 ^d)	0.85 (dd, 2.0, ^c 5.2 ^d)	3.31 (m)	14.14 (d, 5.9 ^e)	34.28 d (5.9 ^e)
PdBr{C(H)=C=C(CH ₂) ₅ }(PPh ₃) ₂ (3b)		1.26 (m br)	3.31 (dd, 6.6, ^c 13.1 ^d)	14.39 (d, 6.0 ^e)	34.63 (d, 6.0 ^e)
PdBr{C(H)=C=CMe(Et)}(PPh ₃) ₂ (3c)	0.60 (t, 7.3 ^d), 1.49 (dd, 1.6, ^c 4.1 ^d), 1.77 (m)	0.06 (t, 7.3 ^d), 0.83 (dd, 2.0, ^c 5.2 ^d), 1.24 (m)	3.35 (m)	14.06 (d, 7.2 ^e), 14.45 (d, 3.6 ^e)	34.33 (d, 7.2 ^e), 35.25 (d, 3.6 ^e)
PdBr{C(H)=C=CH(<i>n</i> -C ₅ H ₁₁)}(PPh ₃) ₂ (3d)	6.13 (m)	0.75 (t, 7.2 ^d), 0.80 (m), 1.26 (m), 1.01 (m)	3.01 (m)	14.50 (d, 6.9 ^e), 14.85 (d)	29.80 d (6.9 ^e), 29.12 (d)
PdBr{C(H)=C=CMe(<i>t</i> -Bu)}(PPh ₃) ₂ (3e)	1.66 (dd, 2.6, ^c 7.0 ^d)	0.81 (s)	3.41 (m)	14.76 (br)	34.88 (br)

^a δ (ppm) measured at 300.13 MHz, solvent CDCl₃, at 293 K. All complexes reveal a multiplet from 7.1 to 7.9 ppm due to the phenyl protons of the PPh₃ groups. ^b Measured at 40.5 MHz, δ (ppm) relative to external 85% H₃PO₄. ^c $J(\text{P}_{\text{trans}},\text{H})$ in Hz. ^d $J(\text{H},\text{H})$ in Hz. ^e $J(\text{P},\text{P})$ in Hz.

tropic data for the platinum compound 1a compare very well with those of the known compound 1i.⁴

trans-cis Isomerization of 2a–e into 3a–e. The conversion of 2a–e into 3a–e could be monitored conveniently by ^1H and ^{31}P NMR. After approximately 15 min, the ^{31}P NMR spectrum in CD₂Cl₂ revealed the appearance and increase of an AX pattern centered at ca. 14 and 34 ppm, with concomitant decrease of the singlet of the starting compounds 2a–e at ca. 22 ppm. Similarly, in the ^1H NMR spectra the signals of the starting compounds 2a–e slowly decreased, while new signals belonging to 3a–e increased. After 10 h the conversion was complete, whereafter 3a–e started to decompose, as evidenced by the appearance of a palladium mirror on the NMR tube. Due to the relatively instability of 3a–e and the fact that diagnostic allenyl carbon nuclei in these compounds have a very long T_1 , it was not possible to obtain adequate ^{13}C NMR data.

Conductivity measurements of (mixtures of) 2a and 3a revealed that bromine is covalently bonded to the metal. The rate of the isomerization reaction of 2a into 3a appeared to be independent of the concentration of 2a, which points to an intramolecular isomerization.

The ^1H and ^{31}P NMR data for the new compounds 3a–e are listed in Table 6. The structure of the new compounds 3a–e, on the basis of these data, may be considered as approximately square planar, with two mutually *cis* triphenylphosphine groups, a σ -bonded allenyl ligand, and a bromide in the fourth coordination position. Compound 3a showed in the ^{31}P NMR spectra two doublets at 14.1 and 34.3 ppm, with a $^2J(\text{P},\text{P})$ value of 5.9 Hz. This AX pattern indicates that the two triphenylphosphine groups are situated in mutually *cis* positions, and the chemical shifts point to dissimilar groups (such as C and Br) in *trans* positions relative to the phosphorus nuclei. The ^1H NMR is in full agreement with the proposed structure of 3a–e (see below for discussion of the stereochemical intricacies). The relatively low frequency of the Pd–CH= proton in 3a–e as compared to that for 2a–e must be ascribed to anisotropic shielding by the aryl groups of the phosphine

Figure 2. Atropisomeric enantiomers (*M,M/P,P*)-3 ($R > R'$).

moiety in *cis* positions, which is another, albeit indirect, support of the structure proposed for 3a–e.

The presence of a η^3 -allenyl moiety in 3a–e was borne out because of their behavior as nonelectrolytes and, furthermore, because of the rather large difference in ^{31}P chemical shifts of the two phosphorus sites (as would be expected for two very distinct ^{31}P nuclei as in 3a–e), which in the case of η^3 -allenyl bis(phosphine) complexes tend to be more similar.⁸

Stereochemistry of 3a–e. Due to restricted rotation around the Pd–Ca axis (see Figure 2), the *cis* compounds 3a,b exist as two atropisomers; hence, the diastereotopicity of the Me groups in 3a can be determined by the appearance of two double doublets in the ^1H NMR spectra at 0.85 and 1.53 ppm with coupling constants of 2.0 and 5.2 Hz and 1.3 and 4.0 Hz, respectively, due to $^5J(\text{H},\text{H})$ coupling and $^6J(\text{P}_{\text{trans}},\text{H})$ coupling. Furthermore, at 3.31 ppm a multiplet (1H) has been observed for the Pd–CH=proton. In the ^1H NMR of 3b one multiplet has been observed for the protons of the cyclohexenyl ring, whereas a double doublet (1H) at 3.31 ppm has been observed for the Pd–CH= proton, due to a $^3J(\text{P}_{\text{trans}},\text{H})$ coupling of 13.1 Hz and a $^3J(\text{P}_{\text{cis}},\text{H})$ coupling of 6.6 Hz.

The fact that complexes 3a,b are chiral has been confirmed by the NMR data for 3c, in which, unlike 3a,b, the allenyl moiety is also chiral. In this and similar cases two sources of atropisomerism can be discerned, *i.e.* restricted rotation around the axis of the

Scheme 1. Viable Mechanisms of Isomerization of 2a-e into 3a-e

A:

B:

allenyl moiety and, furthermore, around the C_α -Pd axis (see Figure 2).

Indeed, the ^{31}P NMR spectrum of **3c** showed two sets of AX patterns in the same region as observed for **1a**, indicating that two diastereomeric *cis* products have been formed. The ^1H NMR spectrum of **3c** showed double signals for each R group: two triplets at respectively 0.06 and 0.60 ppm, each with a $J(\text{H},\text{H})$ coupling of 7.3 Hz, and two multiplets at 1.24 and 1.77 ppm for the ethyl group. Furthermore, two double doublets, at 0.83 and 1.49 ppm, were observed for the methyl group. As one goes from **3c** to **3d** to **3e**, the diastereoisomeric ratio increases from approximately 1:1 for **3c** to 9:1 for **3d** and >99:1 for **3e**. Consistently the ^1H NMR data for **3e** show a singlet at 0.81 ppm for the *tert*-butyl protons and a double doublet at 1.66 ppm for the methyl group, with coupling constants of 2.6 Hz due to $^5J(\text{H},\text{H})$ and 7.0 Hz due to $^6J(\text{P}_{\text{trans}},\text{H})$.

cis-trans isomerizations are common processes in organometallic Pt(II) and Pd(II) square-planar complexes; however, the reverse process has been scarcely documented.²⁹ A few examples are the *trans-cis* isomerizations of $[\text{PtCl}_2\{\text{C}(\text{NPhCH}_2)_2\}]$,³⁰ $[\text{PtCl}_2(\text{CO})\text{L}]$,³¹ and $[\text{PdMe}_2\text{L}_2]$ ³² in solution. The mechanisms proposed for both *trans-cis* and *cis-trans* isomerizations are (i) rearrangements catalyzed by the solvent or a ligand, via a five-coordinate intermediate, (ii) reactions involving ligand loss and rearrangement of a three-coordinate intermediate, and (iii) reactions involving a straightforward change of geometry by a concerted mechanism, via a tetrahedral intermediate.

When the behavior of the known *trans*-bis(triphenylphosphine)palladium chlorides⁶ is compared with that of the new palladium bromides **2a-e**, the striking difference is that the latter show a *trans-cis* rearrangement in chlorinated solvents and in the solid state, whereas the other complexes do not. Although this is

at present not well understood, the presence of bromide instead of chloride seems to be crucial to the *trans-cis* rearrangement. The formation of the *cis* Pd complexes is favored in polar chlorinated solvents, which could be explained by an increase of the molecular dipole upon isomerization of **2** into **3**, which will result in a better solvation of the molecule in such a solvent.²⁹ Possibly, the size and increased polarizability of bromide as compared to chloride plays a crucial role in the initiation of the *trans-cis* isomerization process.

The *trans* influence exerted by the allenyl moiety destabilizes the metal-bromide bond, and the square-planar coordination mode may become distorted toward a tetrahedron (route A, Scheme 1) by elongation of the Pd-Br bond. Subsequently, rearrangement to a *cis* geometry takes place. Alternatively, the Pd-Br bond may break (route B, scheme 1), followed by isomerization through e.g. π -allenyl type intermediates.⁸ However, the latter option seems less likely in view of the absence of conductivity and that fact that added bromide did not affect the rate of isomerization. Therefore, our interpretation of the isomerization of **2** into **3** as a geometrical change via the intermediacy of a distorted-tetrahedral structure (route A) is in line with the fact that the isomerization is an intramolecular process, which also takes place in the solid state.

In the case of the asymmetric *cis* complexes **3a-e** hindered rotation about the Pd-C bond is present, which cannot be observed in the *trans* complexes **2a,b** of C_s symmetry. The atropisomerism becomes apparent by introduction of a prochiral element such as the 3-methylbuta-1,2-dienyl group as in **3a** or the helical chirality of appropriately substituted allenyl moieties such as in **3c-e**. The combined sources of helical chirality in the latter cases give rise to the formation of diastereoisomers. As is seen from the results for **3d,e**, the *trans-cis* isomerization takes place diastereoselectively when the relative steric demands of the groups R and R' on the allenic terminal C atom are sufficiently different. In the case of **3e** (R = Me, R' = *t*-Bu), the induced diastereoselectivity amounts to (close to) 100%. The observation that the diastereoselectivity during the

(29) Anderson, G. K.; Cross, R. J. *Chem. Soc. Rev.* **1980**, 9, 185.

(30) Cardin, D. J.; Cetinkaya, B.; Cetinkaya, E.; Lappert, M. F.; Manojlovic-Muir, L.; Muir, K. W. *J. Organomet. Chem.* **1972**, 44, C59.

(31) Anderson, G. K.; Cross, R. J. *Inorg. Chim. Acta* **1979**, 38, L21.

(32) Ozawa, F.; Kurihara, K.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1985**, 297, 233.

trans–*cis* isomerization increases in the order **3c**, **3d**, **3e** is consistent with the increasing steric demand of one of the groups R (or R') at the terminal allenic sp² carbon atom. When steric arguments are taken into account, the relative configuration of the two stereogenic axes will be as shown in Figure 2 (if both priority order and steric bulk for R > R'); *i.e.*, the abundant diastereomer is (*M,M/P,P*)-**3**. Clearly, in the series of chiral *trans*-bis(triphenylphosphine)(σ -allenyl)palladium(II) bromides **2c**–**e**, the *trans*–*cis* isomerization proceeds with increasing diastereoselectivity, the conversion of **2e** into **3e** being completely diastereoselective. As far as we

know, this reaction represents the first example of a *trans*–*cis* isomerization of a metal complex resulting in complete regio- and diastereocontrol.

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Supplementary Material Available: Tables of positional coordinates, anisotropic thermal parameters, and bond distances and angles for **1a** (7 pages). Ordering information is given on any current masthead page.

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