A Dinuclear Palladium(I) Ethynyl Complex: Synthesis, Structure, and Dynamics

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The reaction of Pd(η^3-C_3H_5)$_2$ with P^{i}Pr$_3$ at −30 °C affords yellow crystals of the Pd^{II} complex (^{i}Pr$_3$P)Pd(η^3-C_3H_5)(η^1-C_3H_5) (**1**). At 20 °C **1** transforms into the dinuclear Pd^I complex {(^{i}Pr$_3$P)Pd}$_2$(μ-C_3H_5)$_2$ (**2**) due to oxidative C−C coupling of two allyl groups with elimination of 1,5-hexadiene. Heating **1** or **2** in 1,6-heptadiene to 80 °C produces the Pd^0 complex (^{i}Pr$_3$P)Pd(η^2,η^2-C_7H_{12}) (**3**). {(η^3-C_3H_5)PdCl}$_2$ reacts with ^{i}Pr$_3$P to give (^{i}Pr$_3$P)Pd(η^3-C_3H_5)Cl (**4b**), from which further derivatives (^{i}Pr$_3$P)Pd(η^3-C_3H_5)X (X = OSO_2CF_3 (**4a**), C≡CH (**5a**), CH_3 (**5b**)) are obtained by replacement reactions. The mononuclear Pd^{II}-acetylide **5a** and complex **3** combine to give the dinuclear Pd^I derivative {(^{i}Pr$_3$P)Pd}$_2$(μ-C_3H_5)(μ_2-η^2-C_2H) (**6**). The Pd−Pd bond in **6** is unsymmetrically bridged by a π-allyl and a σ−π-ethynyl group, as determined by X-ray structure analysis. The structures of **1**, **4a**,**b**, and **6** are dynamic in solution, with **1** undergoing an exchange of the binding modes of the π- and σ-coordinated allyl groups and **4a**,**b** displaying a π/σ-allyl group rearrangement, and in **6** the C≡CH substituent oscillates in its π-coordination from one Pd^I atom to the other.

Introduction

Some time ago we reported that the reaction of Pd(η^3-C_3H_5)$_2$ with bidentate phosphines $R_2PC_2H_4PR_2$ (R = ^{i}Pr, ^{t}Bu) and ethyne affords the mononuclear Pd^0-ethyne complexes ($R_2PC_2H_4PR_2$)Pd(HC≡CH) and the dinuclear derivatives {($R_2PC_2H_4PR_2$)Pd}$_2$(μ-HC≡CH).[1] In an attempt to prepare the analogous monodentate phosphine complexes[2] by a similar route, we have repeated the reaction using ^{i}Pr$_3$P as the phosphine. However, the in situ reaction of Pd(η^3-C_3H_5)$_2$, P^{i}Pr$_3$, and ethyne produces varying amounts of the novel dinuclear Pd^I-ethynyl complex {(^{i}Pr$_3$P)Pd}$_2$(μ-C_3H_5)(μ_2-η^2-C_2H) (**6**).

To throw some light on the mechanism of the formation of **6**, we have prepared, inter alia, the Pd^{II} compounds (^{i}Pr$_3$P)Pd(η^3-C_3H_5)(η^1-C_3H_5) (**1**), (^{i}Pr$_3$P)Pd(η^3-C_3H_5)Cl (**4b**), and (^{i}Pr$_3$P)Pd(η^3-C_3H_5)(C≡CH) (**5a**) and studied their chemical and physical properties. As a result, we have been able to develop a straightforward synthesis of **6**. Here we report the results of these investigations.[3]

Results and Discussion

Products from the Reaction of Pd(η^3-C_3H_5)$_2$ with P^{i}Pr$_3$: (^{i}Pr$_3$P)Pd(η^3-C_3H_5)(η^1-C_3H_5) (1), {(^{i}Pr$_3$P)Pd}$_2$(μ-C_3H_5)$_2$ (2), and (^{i}Pr$_3$P)Pd(η^2,η^2-C_7H_{12}) (3). The starting point for our study was the reaction of Pd(η^3-C_3H_5)$_2$ with P^{i}Pr$_3$ in the absence of ethyne. The reactions of Pd^{II}-allyl compounds with the monophosphines PMe_3, PPh_3, and PCy_3 have been intensively studied by Werner,[4] Jolly,[5] and co-workers. At low temperatures thermolabile square-planar 1:1 adducts (R_3P)Pd(η^3-C_3H_5)(η^1-C_3H_5) are formed, in which the allyl groups exhibit different bonding modes in the low-temperature conformation, as exemplified by the ^{1}H NMR data of (Me_3P)Pd(η^3-C_3H_5)(η^1-C_3H_5) at −110 °C.[5a,d] Above this temperature the complexes are fluxional due to an exchange of the bonding situations of the η^3- and the η^1-allyl groups. At 0 °C or above, two (R_3P)Pd(η^3-C_3H_5)(η^1-C_3H_5) molecules combine with elimination of 1,5-hexadiene to give dinuclear Pd^I complexes in which a central Pd^I−Pd^I moiety is sandwiched between two bridging allyl groups.[5b−d] For example, the reaction of Pd(η^3-C_3H_5)$_2$ with PPh_3 (1:1) in diethyl ether proceeds upon warming the mixture from −40 to 20 °C to yield the yellow solid {(Ph_3P)Pd}$_2$(μ-C_3H_5)$_2$.[5b]

When we react a light yellow diethyl ether solution of Pd(η^3-C_3H_5)$_2$ with P^{i}Pr$_3$ (1 equiv or excess) at −30 °C,[6] we observe that the color fades, and pale yellow cubes of the 1:1 adduct **1** crystallize out when the

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(2) The synthesis of the isolated complexes (R_3P)$_2$Pd(HC≡CH) and {(R_3P)$_2$Pd}$_2$(μ-HC≡CH) (e.g., R = Me, ^{i}Pr, OPh) will be described elsewhere. **3** reacts with ^{i}Pr$_3$P and ethyne to yield (^{i}Pr$_3$P)$_2$Pd(HC≡CH). For preliminary analytical data, see: Krause, J.; Pluta, C.; Pörschke, K.-R.; Goddard, R. *J. Chem. Soc., Chem. Commun.* **1993**, 1254. Krause, J.; Haack, K.-J.; Pörschke, K.-R.; Gabor, B.; Goddard, R.; Pluta, C.; Seevogel, K. *J. Am. Chem. Soc.* **1996**, *118*, 804.

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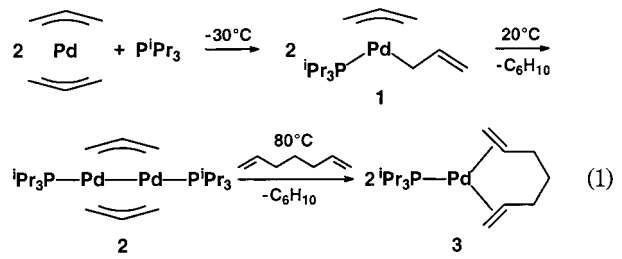
temperature is further reduced to −60 to −78 °C (eq 1). It is worth noting the absence of a bis(phosphine)



adduct $[(^iPr_3P)_2Pd(\eta^1\text{-}C_3H_5)_2]$ among the products, which is in contrast to the formation of $(^iPr_2PC_2H_4P^iPr_2)Pd(\eta^1\text{-}C_3H_5)_2$ we observed when using the chelating phosphine.[1] Solutions of **1** are only very briefly stable at ambient temperature. The IR spectrum exhibits a strong band at 1597 cm^{-1}, which can be assigned to the uncoordinated C=C bond.[7]

The low-temperature NMR spectra of **1** are consistent with those expected for $(^iPr_3P)Pd(\eta^3\text{-}C_3H_5)X$ complexes, including a chiral ground state structure, as described separately below in more detail. Thus, in the ^1H NMR spectrum at −80 °C all 10 allyl protons are inequivalent, and the corresponding ^{13}C NMR spectrum contains six somewhat broad signals for the two different types of allyl ligands. The signals at δ 118.5, 62.8, and 59.6 appear typical for a π-bonded allyl ligand (cf. Figure 2), and the signals at δ 149.5 (=CH−), 99.1 (=CH_2), and 18.3 ($PdCH_2$) can be attributed to a Pd^{II}-σ-allyl group. At 27 °C the allyl proton signals are coalesced to an AM_4 spin system (δ(H) 5.71 (quintet; meso), 3.11 (doublet; syn and anti)). At the same temperature the signals of the meso C atoms in the ^{13}C NMR spectrum are coalesced at δ 133.7 (calculated mean: 134.0), while the expected coalesced signal of the terminal allyl C atoms (predicted at δ 60.0) is still very broad and cannot be detected. The ambient temperature spectra are consistent with a dynamic structure which renders both allyl groups, and within these the various syn and anti protons, equivalent. Conversion between the various forms appears to occur slowly even at −80 °C, since it is clear that the limiting spectra have not been reached at this temperature.

At 20 °C the yellowish color of an ethereal solution of **1** slowly intensifies, and yellow needles of the dinuclear Pd^I complex **2** separate after several hours (84%). The mechanism of this reaction has been described previously.[8,9b] Accordingly, **1** partially thermolyzes with reductive elimination of 1,5-hexadiene to generate a $[(^iPr_3P)Pd^0]$ intermediate, which then nucleophilically attacks unreacted **1** to produce dinuclear **2**.[10] Complex **2** was first prepared by the reaction of $\{(^iPr_3P)Pd\}_2(\mu\text{-}C_5H_5)(\mu\text{-Br})$ with 2 equiv of C_3H_5MgCl.[11] The synthesis given in eq 1, however, provides a much easier route to **2**.[6]

The IR spectrum of **2** exhibits a C−H stretching band of the allyl groups at 3018 cm^{-1}, but the expected C=C stretching band (1580−1450 cm^{-1})[7] appears to be obscured by an intensive absorption band resulting from the phosphine ligand. Recording of the EI mass spectrum above 100 °C is accompanied by strong decomposition. In the ^1H and ^{13}C NMR spectra (27 °C) the allyl groups give rise to three proton signals (δ(H) 3.08 (2H, meso), 2.20 (4H, syn), 1.37 (4H, anti)) and two carbon resonances (δ(H) 83.1 (2C, CH), 30.1 (4C, CH_2)), all of which occur at considerably higher field than observed for Pd^{II}-π-allyl compounds (cf. **1** and Figure 2). Single ^1H and ^{13}C Me signals are observed for the $^iPr_3P$ ligands, and the ^{31}P NMR spectrum displays a singlet. The spectra indicate that both the allyl ligands and the $^iPr_3P$ ligands are equivalent and that the Me groups are enantiotopic, i.e., that at least one mirror plane is present that passes through the phosphine ligands. The spectra are consistent with a C_{2v} symmetric structure, in which a central Pd^I−Pd^I moiety, bearing a P^iPr_3 ligand at each Pd^I atom, is sandwiched between two equivalent and symmetrically coordinated allyl groups orientated cis to one other,[5e] as was found in an X-ray structure determination of the related $\{(Ph_3P)Pd\}_2(\mu\text{-}C_3H_5)_2$.[5b]

In contrast to the easy conversion of $(^iPr_3P)Ni(\eta^3\text{-}C_3H_5)_2$ into $(^iPr_3P)Ni(\eta^2,\eta^2\text{-}C_6H_{10})$ at −20 °C,[5a,12] **2** does not undergo further reductive elimination to yield the homologous Pd^0-1,5-hexadiene complex $(^iPr_3P)Pd(\eta^2,\eta^2\text{-}C_6H_{10})$. The analogous 1,6-heptadiene complex can, however, be prepared and is formed when a yellow solution of **1** or **2** in 1,6-heptadiene (bp 90 °C) is heated to 80 °C for 2 h. During this time the color fades completely, and after the evaporation of the excess of 1,6-heptadiene, colorless crystals of the Pd^0 complex **3** are obtained from pentane in 85% yield (eq 1).[9]

Reactivity of 1−3 toward Ethyne. Complex **2** does not react with ethyne at 20 °C, and **3** (in the absence of additional $^iPr_3P$)[2] initiates ethyne polymerization. When a solution of **1** saturated with ethyne (with or without additional P^iPr_3) is warmed from −78 to 20 °C and simultaneously monitored by ^{31}P NMR spectroscopy, signals of the Pd^{II}-ethynyl complex **5a** (δ(P) 57.3) (main component) and the Pd^I derivative **6** (δ(P) 52.2) are observed, in addition to signals of residual **1** (δ(P) 55.3) and a trace of **2** (δ(P) 47.4). The Pd^I complexes **2** and **6** appear to result from thermolysis reactions of **1** and **5a**. Thus, the major reaction of **1** with ethyne affords **5a**, and this reaction can be explained by a slow protolysis of the η^1-C_3H_5 substituent in **1** by the slightly acidic ethyne to give propene and the ethynyl substituent of **5a**.

Preparation of $(^iPr_3P)Pd(\eta^3\text{-}C_3H_5)X$ (X = OSO_2CF_3 (4a), Cl (4b), C≡CH (5a), CH_3 (5b)). We have subsequently developed an alternative synthesis of the $(^iPr_3P)Pd(\eta^3\text{-}C_3H_5)X$ complex **5a** (X = C≡CH) by starting from the derivative **4b** (X = Cl). Light yellow crystals of **4b** itself are obtained in 85% yield by addition of the

(6) No reaction occurs between $Pd(\eta^3\text{-}C_3H_5)_2$ and P^tBu_3 at −78 °C, while at 20 °C $Pd(P^tBu_3)_2$ is obtained. Therefore, $\{(^tBu_3P)Pd\}_2(\mu\text{-}C_3H_5)_2$ is not accessible by this route.

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(8) Yamamoto, T.; Akimoto, M.; Saito, O.; Yamamoto, A. *Organometallics* **1986**, *5*, 1559.

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(10) In fact, complex **1** reacts slowly with **3** at −30 °C to give **2**. Thus, already at this temperature **3** acts as a source[9] for the $[(^iPr_3P)Pd^0]$ unit, thereby avoiding the partial thermolysis (20 °C) of **1**.

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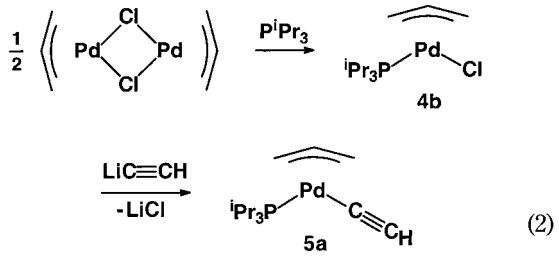
stoichiometric amount of $^{i}Pr_3P$ to the yellow suspension of $\{(\eta^3\text{-}C_3H_5)PdCl\}_2$[13] in THF (eq 2).



(2)

The light yellow THF solution of **4b** reacts with suspended $(H_2NC_2H_4NH_2)Li(C{\equiv}CH)$ at 20 °C with replacement of the chloride by an ethynyl substituent. After evaporation of the solvent the residue can be extracted with pentane to yield, upon cooling to −78 °C, pale yellow crystals of **5a** in up to 72% yield (eq 2).[14a] **5a** has a low melting point (ca. 20 °C) and is very soluble in pentane, where it slowly thermolyses. In the EI mass spectrum (20 °C) of **5a** the molecular ion *m/e* 332 (15%) is observed, which appears to readily eliminate propene to afford the base ion $[(^{i}Pr_3P)PdC_2]^+$. A further prominent ion is $[(^{i}Pr_3P)Pd]^+$ (28%). In the IR spectrum the ethynyl ligand shows ≡C−H and C≡C stretching vibration bands at 3280 and 1950 cm^{-1}, respectively. The latter absorption is similar to that of other Pd^{II}-ethynyl complexes with uncoordinated C≡C bonds (1970−1950 cm^{-1}).[15] An additional band at 1508 cm^{-1} is most likely due to an allylic C−C bond resonance. In the ambient temperature ^1H and ^{13}C NMR spectra of **5a** the ethynyl substituent gives rise to a proton doublet at δ(H) 1.95 with $^4J(PH) = 1.9$ Hz. The signal of the quaternary ethynyl carbon atom occurs at δ 101.9 and shows the couplings $^2J(PC)_{cis} = 25$ Hz and $^2J(CH) = 38$ Hz, while the terminal ethynyl carbon atom resonates at δ 98.2 with $^1J(CH) = 222$ Hz, similar to that found for other Pd-ethynyl complexes.[16]

Solution thermolysis (THF) of **5a** for several days at 20 °C affords the dinuclear Pd^{I} complex **6**. Similar to the (much faster) thermolysis of **1** to give **2**, the reaction can be explained by slow partial reductive elimination of pent-4-en-1-yne from **5a** to generate $[(^{i}Pr_3P)Pd^0]$, which is then trapped by the unreacted **5a** to give **6**.[17]

To gain a better understanding of the nature of the $(^{i}Pr_3P)Pd(\eta^3\text{-}C_3H_5)X$ complexes **4b** and **5a**, the derivatives **4a** ($X = OSO_2CF_3$) and **5b** ($X = CH_3$) have also been prepared. Thus, the reaction of **4b** with $AgOSO_2CF_3$ or protolysis of $(^{i}Pr_3P)Pd(\eta^2,\eta^2\text{-}C_6H_{10}O)$ with CF_3SO_3H affords pale yellow cuboids of **4a**. Common features of **4a**,**b**, with their inorganic substituents $X = OSO_2CF_3$ and Cl, are relatively high melting points (>100 °C), low solubility in pentane, and dynamic structures with respect to the allyl group coordination (see below). The reaction of **4b** with LiMe or, better, $(tmeda)MgMe_2$ affords colorless crystals of **5b**, which is analogous to the previously reported $(R_3P)Pd(allyl)Me$ complexes.[18] In the ^1H and ^{13}C NMR spectra of **5b** the $PdCH_3$ group is characterized by doublets at δ(H) 0.13 ($^3J(PH) = 4.9$ Hz) and δ(C) −17.6 ($^2J(PC)_{cis} = 14$ Hz). Both complexes **5a** and **5b**, with the organic substituents X = C≡CH and CH_3,[14b] display relatively low melting points (20−30 °C), good solubility in pentane, and a nonfluxional allyl group coordination.

^1H and ^{13}C NMR Spectra and Structural Dynamics of $(^{i}Pr_3P)Pd(\eta^3\text{-}C_3H_5)X$ (4a,b, 5a,b). The spectroscopic properties of complexes of the type $(R_3P)Pd(\pi\text{-allyl})X$ have been intensively studied, and several dynamic processes have been described. In particular, for the 2-methylallyl derivatives $(R_3P)Pd(\eta^3\text{-}C_3H_4Me)X$ partial or full equilibration of the allyl protons under various conditions has been reported.[19] Nevertheless, the complexes **4a**,**b** and **5a**,**b**, containing the parent allyl, show some NMR spectral and structural peculiarities, which are now described in more detail.

The ground state structures of all the complexes $(^{i}Pr_3P)Pd(\eta^3\text{-}C_3H_5)X$ (including **1**) are chiral. In the corresponding ^1H and ^{13}C NMR spectra for the $^{i}Pr_3P$ ligand, one PCH signal and two signals for the diastereotopic Me groups are observed, and the π-allyl group gives rise to five distinct proton multiplets and three carbon signals. With variation of $X = OSO_2CF_3$, Cl, C≡CH, and CH_3 marked changes in the chemical shifts of the π-allyl group resonances occur. Moreover, the spectra are partially dependent on both temperature (−80 to 20 °C) and solvent (THF-d_8, toluene-d_8, CD_2Cl_2).

Complex **4a** ($X = OSO_2CF_3$), which contains the least basic substituent of the series, as a solution in THF-d_8 serves here as a reference complex. In the −80 °C ^1H NMR spectrum H1 (H_{meso}) of the allyl ligand exhibits a 16-line multiplet at δ(H) 5.78, H2 (H_{syn} trans to P) a "triplet" at δ(H) 4.95, and H3 (H_{anti} trans to P) a double doublet at δ(H) 3.96, which thus occur at rather low field. The protons H4 (H_{syn} trans to SO_3CF_3) and H5 (H_{anti} trans to SO_3CF_3) give rise to two "doublets" at the substantially higher field of δ(H) 3.54 and 2.91, respectively (Figure 1). ^{31}P couplings are observed only for the protons trans to phosphorus. This assignment is in agreement with that reported previously.[20a] The ^{13}C NMR spectrum of **4a** displays a signal at δ(C) 119.3 with the small coupling $^2J(PC) = 3.2$ Hz for the central allyl C atom C2, a doublet at δ(C) 85.3 with the marked coupling $^2J(PC)_{trans} = 24.6$ Hz for the methylene allyl

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(14) (a) The yield and purity of the product seem to depend on the quality of $(H_2NC_2H_4NH_2)Li(C{\equiv}CH)$, which is about 90−95% pure.[14c] We realize that there is a dearth of well-defined transfer reagents for the C≡CH anion. (b) Complex **5b** does not react with ethyne at ambient temperature to give **5a** and methane. (c) Beumel, O. F., Jr.; Harris, R. F. *J. Org. Chem.* **1963**, *28*, 2775. Beumel, O. F., Jr.; Harris, R. F. *J. Org. Chem.* **1964**, *29*, 1872.

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(17) While the complexes $(^{i}Pr_3P)Pd(\eta^3\text{-}C_3H_5)X$ ($X = C_3H_5$ (**1**) and C≡CH (**5a**)) undergo reductive elimination reactions at ambient temperature, those with $X = SO_3CF_3$ (**4a**) and Cl (**4b**) fail to do so (for $X = CH_3$ (**5b**) the course of the thermolysis has not been clarified). Furthermore, no redox reaction occurs between **4a** or **5b** and **3** (as the source of $[(^{i}Pr_3P)Pd^0]$) to give the dinuclear PdI complexes $\{(^{i}Pr_3P)Pd\}_2(\mu\text{-}C_3H_5)(\mu\text{-}X)$ with $X = SO_3CF_3$ or CH_3. Apparently, such complexes are only stable for ligands X that can coordinate to both Pd^{I} centers by donation of (at least) four electrons.

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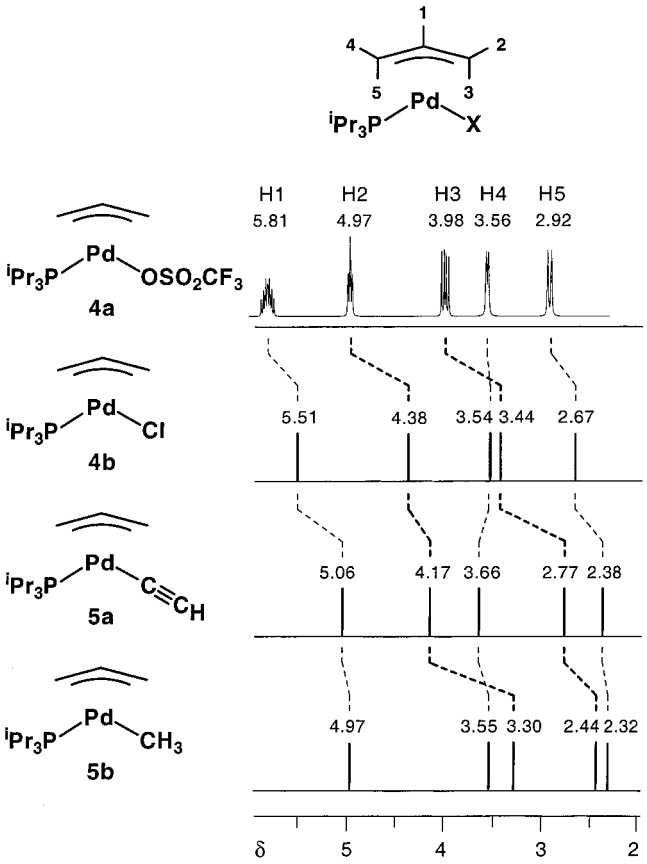


Figure 1. Schematic representation of the ^{1}H NMR π-allyl ligand resonances of the (η^3-C_3H_5)Pd(P^iPr_3)X complexes **4a**,**b** and **5a**,**b** (for **4a** the simulated spectrum is shown, while for **4b** and **5a**,**b** the changes in chemical shift are indicated). Chemical shifts refer to THF-d_8 as solvent.

C atom C3 (trans to P), and a signal at δ(C) 48.3 with a very small and unresolved coupling $^2J(PC)_{cis}$ for C1 (trans to SO_3CF_3) (Figure 2).

As X becomes more basic in the course **4a** → **4b** (Cl) → **5a** (C≡CH) → **5b** (CH_3), the signal of H1 gradually shifts to higher field, while the signals of the protons trans to X either remain at constant field (H4) or are moderately shifted to higher field (H5). At the same time, the signals of the allyl protons trans to P (H2, H3) shift so strongly to higher field that the sequence of the signals is changed (Figure 1). (The fundamental appearance of the individual signals remains, however, approximately the same.) In the ^{13}C NMR spectra the chemical shift of C2 is almost constant for all compounds in the series, whereas the signals of C3 and C1 move together, and the sequence of the signals is even reversed for **5b** (Figure 2). It is worth noting that although only X has been altered and the $^iPr_3P$ ligand remains constant, the chemical shift changes are much larger for the allyl methylene group at C3 *trans to P* (and thus *cis to X*) than for the C1 methylene *trans to X*. This "communicative effect" within the allyl group renders the methylene group at C3 a very sensitive probe for the trans influence[21] of X at C1.

When the temperature is raised to 27 °C, in the ^{1}H NMR spectra of a THF-d_8 solution of **4a**,**b** the doublets

(21) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemisty*, University Science Books: Mill Valley, CA, 1987; p 242.

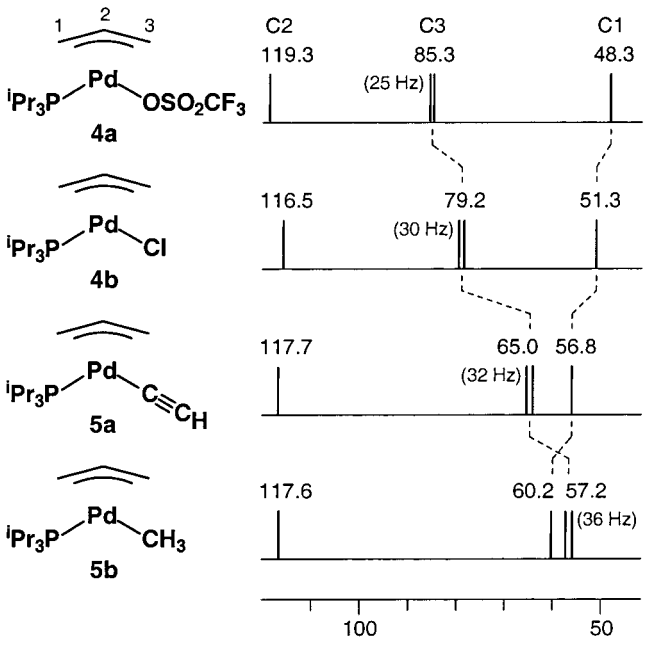
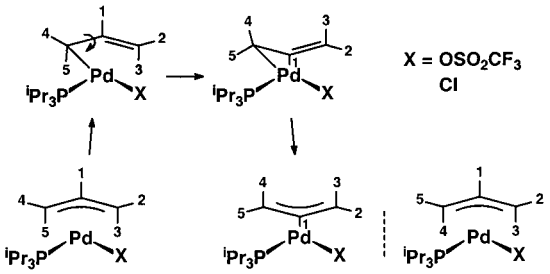


Figure 2. Schematic representation of the ^{13}C NMR resonances of the π-allyl ligands of the (η^3-C_3H_5)Pd(P^iPr_3)-X complexes **4a**,**b** and **5a**,**b.** Chemical shifts refer to THF-d_8 as solvent.

of H4 and H5 (trans to X) have either coalesced (**4a**) or become at least significantly broadened (**4b**), while the signals of H1−H3 are still very sharp. Simulation of the allyl part of the spectrum gave exchange rates for H4 and H5 of 280 s^{-1} (**4a**) and 45 s^{-1} (**4b**) at 27 °C. The ^{13}C NMR allyl group resonances are temperature independent, whereas for the $^iPr_3P$ ligand the Me groups are now enantiotopic and give rise to single ^{1}H and ^{13}C signals. The spectral changes for **4a**,**b** are indicative of the occurrence of a dynamic process, which can be explained by a 180° rotation of the vinyl moiety of the allyl group about the C−C bond to the methylene group trans to X, concomitant with a roughly 60° motion about the corresponding Pd−C bond. In the course of this rotation the complexes pass through a C_s symmetrical transition state structure, with the result that the enantiomers of each complex are interconverted (eq 3). It seems remarkable that this π−σ-allyl exchange



(3)

leads exclusively to the equilibration of H4 and H5, whereas the other allyl protons and the carbon atoms are unaffected. The dynamics appear to be essentially an intrinsic property of complexes with substituents X having a low basicity. They proceed both in THF-d_8 and, albeit somewhat slower, in noncoordinating solvents such as CD_2Cl_2[22] and toluene-d_8. For CD_2Cl_2 and toluene-d_8 as solvents the complexes pass through a formally 14e Pd^{II} intermediate,[23] whereas in THF-d_8 the

dynamics may be assisted by THF coordination,[24] thereby avoiding the 14e stage.

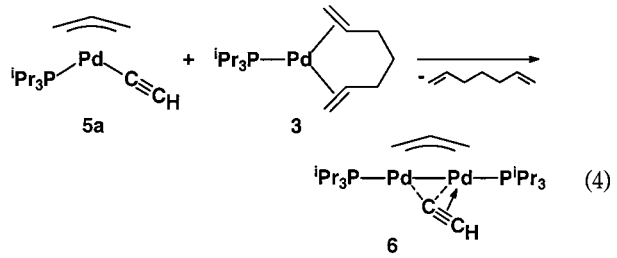
For **5a**,**b** with the rather basic substituents C≡CH and Me, the allyl group and phosphane ligand NMR resonances correspond to the chiral ground state structures in THF-d_8 and the other solvents at 27 °C, indicating that the structures of these complexes are static and not dynamic on the NMR time scale.

Why are **4a**,**b** fluxional whereas **5a**,**b** are not, and how do the allyl group NMR data correlate with this property? The relatively weak coordination of X = OSO_2CF_3 and Cl in **4a**,**b** presumably causes the π-allyl group to be polarized in the direction of a σ-allyl group, with the result that C1 (trans to X) is more strongly coordinated to Pd than C3 (trans to P), which consequently assumes partial olefinic character. This is reflected in the appearance of the signals of H4, H5, and C1 at relatively high field, those of H2, H3, and C3 at relatively low field, and the relatively small coupling $^2J(PC)_{trans}$ for C3 (≤30 Hz). The polarized allyl group readily undergoes reversible decoordination of the olefinic C=C bond, i.e., $\pi-\sigma$-allyl exchange.

In contrast, the substituents X = C≡CH and Me in **5a**,**b** are comparably or even more basic than the coligated P^iPr_3. This appears to initiate a weakening of the coordination of C1 in the trans position and a more balanced charge distribution within the allyl ligand results. While the chemical shifts of H4, H5, and C1 are only moderately affected by changing X, the signals of H2, H3, and C3 are shifted strongly to higher field, and for C3 the coupling $^2J(PC)_{trans}$ is markedly increased, indicative of a strengthening of the coordination of C3.

Preparation of {(^{i}Pr$_3$P)Pd}$_2$(μ-C$_3$H$_5$)(μ-η^1,η^2-C$_2$H) (6). We have seen that Pd(η^3-C_3H_5)$_2$ and P^iPr_3 form an adduct (^{i}Pr$_3$P)Pd(η^3-C_3H_5)(η^1-C_3H_5) (**1**). Moreover, **1** reacts slowly with ethyne to give **5a** as a further intermediate. Concomitant partial thermolysis of **1** and **5a** generates a [(^{i}Pr$_3$P)Pd^0] fragment, which is trapped by still unreacted **1** and **5a** to give the dinuclear **2** and **6** as products. On the basis of these considerations we felt that it should also be possible to obtain complex **6** from the reaction of **5a** with other sources of [(^{i}Pr$_3$P)-Pd^0], such as **3**.

Indeed, when a mixture of equimolar amounts of the Pd^{II} complex **5a** and the Pd^0 complex **3** dissolved in diethyl ether is warmed from −30 to 20 °C, yellow-greenish crystals of the dinuclear Pd^I complex **6** separate (eq 4). Recooling the mixture to −30 °C results in a final yield of 74%. The mechanism of the comproportionation reaction can be envisaged as involving nucleophilic attack of the [(R$_3$P)Pd^0] moiety at the Pd^{II} center.



(4)

Complex **6** is the first and also the parent representative of the {(R$_3$P)Pd^I}$_2$(μ-allyl)(μ-X) class of complexes for which X = alkynyl.

6 is stable at 20 °C and decomposes (when heated quickly) at 147 °C. In the EI mass spectrum (110 °C) the molecular ion *m*/*e* 598 (1.7%) is observed despite considerable decomposition. The compound is moderately soluble in diethyl ether, but dissolves well in THF. The IR spectrum (KBr) of **6** exhibits the characteristic C−H stretching bands of the ethynyl (3215 cm^{-1}) and the allyl ligands (3024 cm^{-1}). In addition, the C≡C stretching band of the ethynyl ligand is observed at 1796 cm^{-1}, which occurs at $\Delta\nu$ = 154 cm^{-1} lower wavenumbers than for the mononuclear Pd^{II}-ethynyl complex **5a**. The C≡C stretching band is indicative of an additional π-coordination of the triple bond and, hence, the presence of a $\sigma-\pi$-ethynyl ligand.[25a,b]

^{1}H, ^{13}C, and ^{31}P NMR Spectra of 6. The ^{1}H, ^{13}C, and ^{31}P NMR spectra of **6** are temperature dependent. In the −80 °C ^{31}P NMR spectrum the doublets of an AB system (δ(P) 58.3, 43.9; ^3J(PP) = 89 Hz) appear, which coalesce into a broad singlet at 27 °C (δ(P) 52.2).

The −80 °C ^{1}H and ^{13}C NMR spectra feature two PCH and four Me resonances (the latter are not resolved in the proton spectrum), which are attributable to two inequivalent ^{i}Pr$_3$P ligands with diastereotopic methyl groups. All protons (δ(H) 3.20 ($C_aH_{syn}H$), 3.06 ($C_bH_{syn}H$), 1.87 (CH_{meso}), 1.10 (C_aHH_{anti}), and 0.91 (C_bHH_{anti})) and carbon atoms (δ(C) 70.1 (C_{meso}), 35.6, and 29.3 (both $C_{terminal}$)) of the allyl group have different chemical shifts. The ethynyl proton gives rise to a double doublet at δ(H) 4.20 due to different couplings with the phosphorus atoms (^3J(PH) = 7.9 Hz, ^4J(P′H) = 1.1 Hz). Both the location of this signal at low field and the value of the coupling ^3J(PH) are in accordance with additional π-bonding of the ethynyl substituent (cf. **5a**). The quaternary C atom of the ethynyl ligand resonates at δ(C) 156.4, significantly downfield[26c] from the corresponding signal of **5a**, and displays different couplings to the two P atoms ($|^2J(PC)|$ = 23.8 Hz, $|^2J(P'C)|$ = 3.9 Hz (the couplings are of opposite sign)), whereas the signal of the terminal C atom at δ(C) 97.2 with ^1J(CH) = 219 Hz is almost unchanged as compared with that of **5a**.

(22) In the ^{13}C NMR spectrum of a solution of **4a** in CD_2Cl_2 at 27 °C the signals of the terminal allyl C atoms (C1 and C3) are broadened, indicating the occurrence of an additional dynamic process in this solvent.

(23) Van Leeuwen and Praat considered whether acetate in (R$_3$P)-Pd(allyl)(acetate) complexes can act as a bidentate ligand during the course of the $\pi-\sigma$-allyl exchange process, but they concluded that it does not.[23a] However, other authors have found favor with this idea.[8,20b] Since (R$_3$P)Pd(allyl)(acetate) complexes appear to exhibit the same dynamic behavior as **4a** and it is accepted that trifluormethanesulfonate acts purely as a monodentate ligand, there is no need to postulate that acetate functions as a bidentate ligand. (a) Van Leeuwen, V. N. M.; Praat, A. P. *J. Organomet. Chem.* **1970**, *21*, 501.

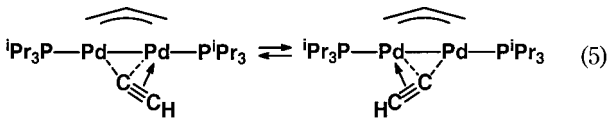
(24) For **4b** the exchange rate was not visibly affected by addition of either (η^3-C_3H_5)$_2$$Pd_2Cl_2$ (in order to abstract P^iPr_3 or Cl from **4b**) or uncoordinated P^iPr_3, but addition of LiCl and pyridine enhanced the exchange.

(25) (a) For another dinuclear complex with a $\sigma-\pi$-C≡CH ligand, see: Franzreb, K. H.; Kreiter, C. G. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1984**, *39*, 81. (b) A binding mode similar to a dinuclear Pd^I complex has been recently found for the ionic [{(Ph$_3$P)Pd}$_2$(μ-C_4H_6)-(μ-C≡CPh)][PF_6]. Murahashi, T.; Otani, T.; Okuno, T.; Kurosawa, H. *Angew. Chem.* **2000**, *112*, 547; *Angew. Chem., Int. Ed.* **2000**, *39*, 537.

(26) (a) Patel, H. A.; Fischer, R. G.; Carty, A. J.; Naik, D. V.; Palenik, G. J. *J. Organomet. Chem.* **1973**, *60*, C49. (b) Smith, W. F.; Yule, J.; Taylor, N. J.; Paik, H. N.; Carty, A. J. *Inorg. Chem.* **1977**, *16*, 1593. (c) Carty, A. J.; Cherkas, A. A.; Randall, L. H. *Polyhedron* **1988**, *7*, 1045. (d) Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113. (e) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203.

At 27 °C (^{1}H NMR) and 38 °C (^{13}C NMR) the ^{i}Pr$_3$P ligands are equivalent (a single PCH resonance), but the Me groups are still diastereotopic (two resonances). According to the spectra the allyl group is symmetrically bound at this temperature and gives rise to three proton resonances (δ(H) 3.23 (CH_{syn}H), 1.92 (CH$_{meso}$), 1.04 (CHH_{anti})) and two carbon resonances for the meso (δ-(C) 70.5) and terminal (δ(C) 32.3) allyl C atoms. A triplet (δ(H) 4.00; $^{3/4}J$(PH) = 4.5 Hz) is observed for the ethynyl proton. The ethynyl ligand carbon resonances are unshifted, but show simplified spin−spin coupling patterns due to the equivalence of the P nuclei; for the quaternary C atom, the sum of the couplings is $|^2J(PC) + {}^2J(P'C)| = 20$ Hz.

These results are consistent with the view that in **6** the ethynyl ligand coordinates to both Pd^I atoms by the carbanionic α-C atom, and in addition, the C≡C group is π-bonded to *one* of the Pd^I atoms. In the ground state structure the complex is chiral with inequivalent (R$_3$P)-Pd^I moieties and an asymmetric allyl group, as evidenced by the low-temperature NMR spectra. At ambient temperature the structure of **6** is dynamic, with the result that both (R$_3$P)Pd^I moieties and the terminal parts of the allyl group are equivalent as the time average of different conformations (apparent C_s symmetry). The fluxionality of the structure of **6** can be explained in such a way that the C≡C group of the ethynyl ligand oscillates in its π-coordination from one Pd^I atom to the other (eq 5). The alignment of the allyl



(5)

group along the Pd−Pd axis (as opposed to a transverse bridging orientation) precludes a plane of symmetry passing through the Pd−P bonds and invokes the diastereotopy of the methyl groups of the P^{i}Pr$_3$ ligand. Since the diastereotopy of the methyl groups is maintained as the temperature is raised from −80 to 27 °C, it follows that there is no rotation of the allyl ligand about the normal to the Pd−Pd bond at ambient temperature.

Molecular Structure of 6. The results of an X-ray crystal structure determination of **6** are summarized in Figure 3, which shows a view perpendicular to a mean plane through the two metal atoms, the bridging ethynyl ligand, and the two P atoms. The atoms of this moiety are approximately coplanar (rms deviation 0.045 Å) and define a local mirror plane, which is broken only by the isopropyl groups and the bridging allyl group. Unfortunately, the latter is disordered (50:50), but the two components could be resolved, and they are related to one another by the same approximate mirror plane. The Pd1−Pd2 bond distance is 2.6597(4) Å and lies within the expected range of bond distances observed for two Pd^I atoms (2.53−2.70 Å)[27] and close to that found in complexes containing the related structural element Pd$^I_2$(μ-allyl)(μ-X) (X = I,[28] C$_5$H$_5$,[4a,b] C$_3$H$_5$,[5b] Cl,[18] SPh;[29]

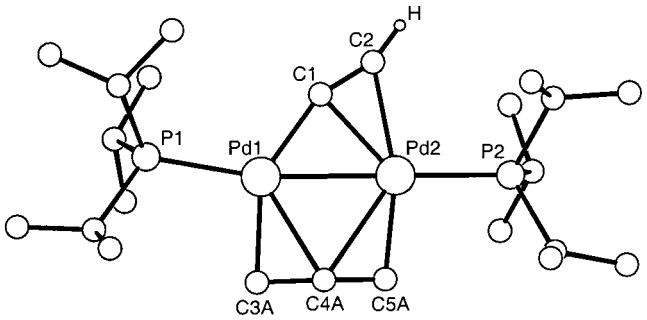


Figure 3. Structure of **6** in the crystal. The μ_2-η^2,η^2-allyl group is disordered over two positions (50:50), only one of which is shown for clarity (C3A−C5A). Selected distances (Å) and angles (deg): Pd1−Pd2 = 2.6597(4), Pd1−P1 = 2.294(1), Pd2−P2 = 2.295(1), Pd1−C1 = 2.004(3), Pd2−C1 = 2.188(3), Pd2−C2 = 2.284(3), C1−C2 = 1.219(4), C2−H = 0.90(4), Pd1−C3A = 2.106(6), Pd1−C4A = 2.426-(6), Pd2−C4A = 2.579(6), Pd2−C5A = 2.104(6), C3A−C4A = 1.455(8), C4A−C5A = 1.434(8); Pd2−Pd1−C1 = 53.8-(1), Pd1−C1−C2 = 157.2(3), C1−C2−H = 158(2), P1−Pd1−Pd2 = 168.89(2), Pd1−Pd2−P2 = 177.98(2), Pd1−C1−Pd2 = 78.6(1), C2−C1−Pd2 = 78.6(2), C1−C2−Pd2 = 69.9(2).

2.61−2.72 Å). Each of the Pd atoms carries a single phosphine ligand, and the Pd−P bond distances are normal (2.30 Å).

The bridging ethynyl ligand assumes the familiar planar unsymmetrical trans-bent μ_2-η^2 or σ−π-C≡CR coordination.[26b−e] The σ-bond distance of the α-C atom (C1) to Pd1 (2.004(3) Å) corresponds to that of complexes with Pd^{II}−C(sp) bonds (1.95−2.04 Å)[30] (there appear to be no comparative values for Pd^I−C(sp) bonds). The distance of C1 to Pd2 (2.188(3) Å) is significantly longer, as is also the distance of C2 to Pd2 (2.284(3) Å). The ethynyl ligand is tilted toward Pd2 in order that both C1 and C2 can coordinate to Pd2, and as a result the Pd1−C1−C2 angle deviates considerably from linearity (157.2(3)°). The Pd2−C1 and Pd2−C2 distances of **6** are longer than the Pd^0−C π-bonds in Pd^0-alkyne complexes such as (^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Pd(HC≡CH) (2.04 Å) or {(^{i}Pr$_2$-PC$_2$H$_4$P^{i}Pr$_2$)Pd}$_2$(μ-HC≡CH) (mean 2.09 Å),[31] but it can be anticipated that Pd^I−C (and Pd^{II}−C) π-bonds will generally be longer than Pd^0−C π-bonds, due to the weaker back-bonding ability of palladium[32] in its higher oxidation states. In accord with this, the C1−C2 bond of the ethynyl ligand (1.219(4) Å) is barely lengthened in comparison with the C≡C bond of uncoordinated ethyne (1.18 Å).[33] The ethynyl H atom could be located and refined (U_H = 0.07(1) Å^2, C−H 0.90(4) Å), and it is found to be slightly tilted away from Pd2 (C1−C2−H 158(2)°), as expected. Although the disorder in the allyl group precludes a detailed discussion of its geometry, the meso C atom (C4, and its disordered adjunct) is significantly closer to Pd1 (mean, 2.41(3) Å) than Pd2 (mean, 2.57(1) Å), indicating increased π-character in

(27) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. *Palladium(I) and Cluster Complexes*. In *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, U.K., 1982; Vol. 6, p 265.
(28) Kobayashi, Y.; Iitaka, Y.; Yamazaki, H. *Acta Crystallogr. B* **1972**, *28*, 899.
(29) Osakada, K.; Ozawa, Y.; Yamamoto, A. *J. Organomet. Chem.* **1990**, *399*, 341.
(30) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. Compounds with Palladium−Carbon σ-Bonds. In *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, U.K., 1982; Vol. 6, p 279.
(31) Krause, J.; Goddard, R.; Pörschke, K.-R. Unpublished results.
(32) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. Monoolefin and Acetylene Complexes of Palladium. In *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, U.K., 1982; Vol. 6, p 351.
(33) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

the C3−C4···Pd1 bond. As a result of the binding modes of the two bridging ligands, the P1−Pd1−Pd2−P2 moiety deviates from linearity at the Pd1 end (P1−Pd1−Pd2 = 168.9(1)°; Pd1−Pd2−P2 = 178.0(1)°).

Examples of structurally characterized dinuclear complexes with substituted $\sigma-\pi$-C≡CR ligands include $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}C_2Ph)$,[26a,b] $Fe_2(CO)_5(PPh_3)(\mu\text{-}PPh_2)(\mu\text{-}C_2Ph)$,[26b] $(Ch_3P)_2Pt_2(C_2Ph)(\mu\text{-}SiMe_2)(\mu\text{-}C_2Ph)$,[34a] $[Cp_2W_2(CO)_4(PhC_2H)(\mu\text{-}C_2Ph)][BF_4]$,[34b] and $(C_5Me_5)(PhMe_2P)ReWCp(\mu\text{-}CO)(\mu\text{-}C_2Ph)$,[34c] but **6** is the first example with R = H.

Conclusions

We have shown that the in situ reaction of $Pd(\eta^3\text{-}C_3H_5)_2$, P^iPr_3, and ethyne to afford variable amounts of the dinuclear Pd^I-ethynyl complex **6** proceeds in a stepwise fashion. Initially, $Pd(\eta^3\text{-}C_3H_5)_2$ and P^iPr_3 form the adduct **1**, containing both σ- and π-bonded allyl groups. **1** can then follow two reaction paths. In one it partly gives the dinuclear Pd^I byproduct **2** due to rapid thermolysis, but mainly it undergoes a protolysis reaction with ethyne to afford the mononuclear Pd^{II}-ethynyl complex **5a**. The latter undergoes slow solution thermolysis to yield **6**.

A clean synthesis of **6** has been achieved by a modular synthesis route, combining **5a** (which was obtained by a standard method) with **3** as a source of the $[(^iPr_3P)Pd^0]$ building unit. The synthesis of **6** by this method demonstrates once more the utility of L-Pd(1,6-diene) complexes as an effective source for $[L\text{-}Pd^0]$ building blocks in palladium chemistry.[9]

Complexes of the type $\{(R_3P)Pd^I\}_2(\mu\text{-allyl})(\mu\text{-X})$ are apparently confined to those ligands X which provide (at least) four electrons for the bridge bond. Such ligands include halogenide, sulfide, carboxylate, allyl anion, and cyclopentadienide, but exclude, for example, the methyl group, which bridges metal centers by electron-deficient binding. The function of the ethynyl ligand in **6** is similar to that of an allyl anion or cyclopentadienide in related complexes in that donation of π-electrons—in addition to the formal σ-donation of a carbanion—stabilizes the bridge bond. The prerequisite for four electrons explains the unsymmetrical ground state structure of **6**, in contrast to a C_s symmetrical structure (with no or significantly reduced π-bonding) which is suggested for the transition state of the dynamic process.

Finally, variable-temperature NMR studies indicate that the $\pi-\sigma$-allyl exchange dynamics of $(^iPr_3P)Pd(\eta^3\text{-}C_3H_5)X$ complexes is an intrinsic property of complexes with substituents X having a low basicity.

Experimental Section

All manipulations were carried out under argon with Schlenk-type glassware. Solvents were dried prior to use by distillation from $NaAlEt_4$. $\{(\eta^3\text{-}C_3H_5)PdCl\}_2$,[13] $(^iPr_3P)Pd(\eta^2,\eta^2\text{-}C_7H_{12})$ (**3**), and $(^iPr_3P)Pd(\eta^2,\eta^2\text{-}C_6H_{10}O)$[9] were prepared as published. P^iPr_3 (Alfa), 1,6-heptadiene (Aldrich), and $(H_2NC_2H_4NH_2)LiC{\equiv}CH$ (Fluka; 95% pure) were commercially available. Microanalyses were performed by the local Mikroanalytisches Labor Kolbe. Mass spectra were recorded at 70 eV and refer to ^{106}Pd and ^{35}Cl. ^1H NMR spectra were measured at 300 MHz, ^{13}C NMR spectra at 75.5 MHz (both relative to TMS), and ^{31}P NMR spectra at 121.5 MHz (relative to external 85% aqueous H_3PO_4) on Bruker AMX-300 and DPX-300 instruments. The given NMR data refer to solutions of the compounds in THF-d_8.

$(^iPr_3P)Pd(\eta^3\text{-}C_3H_5)(\eta^1\text{-}C_3H_5)$ (1). To the yellow solution of $Pd(\eta^3\text{-}C_3H_5)_2$ (367 mg, 2.00 mmol) in diethyl ether (5 mL) was added an ethereal solution (1 mL) of P^iPr_3 (320 mg, 2.00 mmol) at −30 °C. Immediately the color faded almost completely, and at −78 °C pale yellow crystals separated. These were freed from the mother liquor by means of a capillary, washed with a small volume of cold pentane, and dried under high vacuum at −78 °C: yield 420 mg (60%). IR (KBr): 3064 (=CH_2), 1597 (C=C), 1506, 1014 cm^{-1} (π-C_3H_5). ^1H NMR (−80 °C): δ 6.34 (CH), 5.13 (CH), 4.38, 3.99, 3.44, 3.44, 2.50, 2.37, 2.25, 2.21 (each broad, 1H, CH_2), π/σ-allyl; 2.37 (m, 3H, PCH), 1.24, 1.21 (each 9H, diastereotopic Me), $^iPr_3P$; (27 °C): δ 5.71 (quintet, 2H, CH), 3.11 (d, 8H, CH_2); 2.35 (m, 3H, PCH), 1.24 (dd, 18H, Me). ^{13}C NMR (−80 °C): δ 149.5 (=CH−), 99.1 (=CH_2), 18.3 ($PdCH_2$), σ-allyl; 118.5 (C2), 62.8 (d, $^2J(PC)$ = 28 Hz, C3), 59.6 (C1), π-allyl; 25.9 (d, 3C, PCH), 20.1 (d, 6C, unresolved diastereotopic Me), $^iPr_3P$; (27 °C): δ 133.7 (2C, CH), CH_2 is not detected; 26.2 (d, 3C, PCH), 20.3 (d, 6C, Me). ^{31}P NMR (−80 °C): δ 52.8. (27 °C): δ 55.3. Anal. Calcd for $C_{15}H_{31}PPd$ (348.8): C, 51.65; H, 8.96; P, 8.88; Pd, 30.51. Found: C, 51.88; H, 8.86; P, 8.93; Pd 30.42. **1** melts at 20 °C to give **2**.

$\{(^iPr_3P)Pd\}_2(\mu\text{-}C_3H_5)_2$ (2). To a yellow suspension of $Pd(\eta^3\text{-}C_3H_5)_2$ (943 mg, 5.00 mmol) in diethyl ether (10 mL) was added an ethereal solution (5 mL) of P^iPr_3 (802 mg, 5.00 mmol) at −30 °C. The resulting light-yellow solution of **1** was warmed to 20 °C, and in the course of several hours yellow needles crystallized. After 2 days the mixture was slowly cooled to −30 °C to complete the crystallization, and the product was isolated as for **1**, albeit dried under vacuum at 20 °C: yield 1.29 g (84%); >100 °C dec. IR (KBr): 3018 cm^{-1} (C−H, μ-allyl). ^1H NMR (27 °C): δ 3.08 (m, 2H, CH_{meso}), 2.20 ("quintet", 4H, $^3J(HH)_{cis}$ = 7.7 Hz, CH_{syn}), 1.37 ("d", 4H, $^3J(HH)_{trans}$ = 12.1 Hz, CH_{anti}), μ-allyl; 2.44 (m, 6H, PCH), 1.18 ("q", 36H, Me), P^iPr_3. ^{13}C NMR (27 °C): δ 83.1 (2C, CH), 30.1 (4C, CH_2), μ-allyl; 26.3 (6C, PCH), 20.4 (12C, Me), P^iPr_3. ^{31}P NMR (27 °C): δ 47.4. Anal. Calcd for $C_{24}H_{52}P_2Pd_2$ (615.4): C, 46.84; H, 8.52; P, 10.07; Pd, 34.58. Found: C, 46.96; H, 8.78; P, 10.06; Pd, 34.28.

$(^iPr_3P)Pd(\eta^3\text{-}C_3H_5)(OSO_2CF_3)$ (4a). (a) From $(^iPr_3P)Pd(\eta^3\text{-}C_3H_5)Cl$ (4b). A solution of **4b** (343 mg, 1.00 mmol) and $AgOSO_2CF_3$ (257 mg, 1.00 mmol) in 10 mL of diethyl ether was stirred at 20 °C for 1 h. The resulting suspension was filtered to remove the precipitated AgCl. At −30 °C pale yellow cuboids formed, which were freed from the mother liquor, washed with cold pentane, and dried under vacuum at −30 °C: yield 330 mg (72%).

(b) From $(^iPr_3P)Pd(\eta^2,\eta^2\text{-}C_6H_{10}O)$. A solution of $(^iPr_3P)Pd(\eta^2,\eta^2\text{-}C_6H_{10}O)$[9] (365 mg, 1.00 mmol) in 5 mL of diethyl ether was treated with a solution of CF_3SO_3H (150 mg, 1.00 mmol) in 1 mL of ether at −78 °C. Immediately a colorless precipitate formed, which was dissolved at ambient temperature. Cooling the solution to −30 and −78 °C gave crystals which were isolated as described: yield 356 mg (78%); mp 109 °C dec. IR (KBr): 3086, 3068, 3037 (C−H), 1522 cm^{-1} (C=C), π-allyl. EI-MS (80 °C): The complex decomposed. ^1H NMR (−80 °C): δ 5.81 (m, H1), 4.97 ("t", ^3J(H1H2) = 7.6 Hz, ^4J(H2H4) = 1.6 Hz, ^3J(PH) = 6.1 Hz, H2), 3.98 (dd, ^3J(H1H3) = 14.1 Hz, ^3J(PH) = 7.2 Hz, H3), 3.56 (d, ^3J(H1H4) = 6.8 Hz, ^4J(H2H4) = 1.6 Hz, H4), 2.92 (d, ^3J(H1H5) = 11.6 Hz, H5), π-allyl; 2.40 (m, 3H, PCH), 1.31, 1.26 (each dd, 9H, diastereotopic Me), $^iPr_3P$; (27 °C): δ 5.69 (m, H1), 5.09 ("t", H2), 4.01 (dd, H3), ≈3.5 (br, H4), ≈2.85 (br, H5), π-allyl; 2.38 (m, 3H, PCH), 1.31 (dd, 18H, Me), $^iPr_3P$. ^{13}C NMR (−80 °C): δ 120.9 (q), SO_3CF_3;

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119.3 (d, ^2J(PC) = 3.2 Hz, C2), 85.3 (d, ^2J(PC) = 24.6 Hz, C3), 48.3 (s, C1), π-allyl; 24.8 (d, 3C, PCH), 19.8, 19.6 (each 3C, diastereotopic Me), ^{i}Pr$_3$P; (27 °C): δ 121.1 (q), SO_3CF_3; 118.3 (d, ^2J(PC) = 4.4 Hz, C2), 86.6 (d, ^2J(PC) = 24.4 Hz, C3), 47.0 (s, C1), π-allyl; 25.1 (d, 3C, PCH), 19.9 (6C, Me), ^{i}Pr$_3$P. ^{31}P NMR (−80 °C): δ 52.5. (27 °C): δ 54.4. Anal. Calcd for $C_{13}H_{26}F_3O_3PPdS$ (456.8): C, 34.18; H, 5.74; F, 12.48; O, 10.51; P, 6.78; Pd, 23.30; S, 7.02. Found: C, 34.18; H, 5.62; P, 6.89.

(^{i}Pr$_3$P)Pd(η^3-C$_3$H$_5$)Cl (4b). To a yellow suspension of $\{(C_3H_5)PdCl\}_2$ (1.83 g, 5.00 mmol) in THF (15 mL) was added P^{i}Pr$_3$ (1.60 g, 10.0 mmol). Upon stirring the solid dissolved and the color faded. From the resulting solution light yellow crystals were obtained at −30 to −78 °C. After the supernatant liquid was removed through a capillary, the crystals were washed with pentane and dried under vacuum (20 °C): yield 2.92 g (85%); mp 107 °C. IR (KBr): 3071 (=C−H), 1508, 1008 cm^{-1} (C=C), π-allyl. EI-MS (90 °C): *m*/*e* (%) 342 (M$^+$, 1), 306 ([M − HCl]$^+$, 1). ^{1}H NMR (−80 °C): δ 5.51 (m, H1), 4.38 ("t", ^3J(H1H2) = 7.5 Hz, ^4J(H2H4) = 1.8 Hz, ^3J(PH) = 7.0 Hz, H2), 3.54 (d, ^3J(H1H4) = 6.7 Hz, ^4J(H2H4) = 1.8 Hz, H4), 3.44 (dd, ^3J(H1H3) = 13.7 Hz, ^3J(PH) = 9.2 Hz, H3), 2.67 (d, ^3J(H1H5) = 12.0 Hz, H5), π-allyl; 2.52 (m, 3H, PCH), 1.27, 1.26 (each dd, 9H, diastereotopic Me), P^{i}Pr$_3$. At 27 °C the signals of H4 and H5 are broad and the Me signals have coalesced. ^{13}C NMR (27 °C): δ 116.5 (d, ^2J(PC) = 5 Hz, C2), 79.2 (d, ^2J(PC) = 30 Hz, C3), 51.3 (d, ^2J(PC) = 2 Hz, C1), π-allyl; 25.4 (d, 3C, ^1J(PC) = 19 Hz, PCH), 20.2 (d, 6C, ^2J(PC) = 2 Hz, Me), ^{i}Pr$_3$P. ^{31}P NMR (27 °C): δ 53.8. Anal. Calcd for $C_{12}H_{26}ClPPd$ (343.2): C, 42.00; H, 7.64; Cl, 10.33; P, 9.03; Pd, 31.01. Found: C, 42.12; H, 7.55; P, 9.11.

(^{i}Pr$_3$P)Pd(η^3-C$_3$H$_5$)(C≡CH) (5a). A solution of **4b** (686 mg, 2.00 mmol) in THF (15 mL) was added to a suspension of $(H_2NC_2H_4NH_2)Li(C{\equiv}CH)$ (300 mg, in excess) in THF (15 mL) at −30 °C. The reaction mixture was stirred at 20 °C for 1 h. After removing the solvent under vacuum the remaining solid was partially dissolved in a small portion of pentane (5 mL). LiCl and the excess of lithium acetylide were separated by filtration. When the resulting solution was cooled to −30 and −78 °C, pale yellow crystals were obtained. These were freed from the mother liquor by means of a capillary, washed with cold pentane, and dried under vacuum (−30 °C): yield 480 mg (72%); mp ∼20 °C.[14a] Because of its low melting point and possible thermolysis, the complex must be stored in the cold. IR (KBr): 3280 (≡C−H), 1950 (C≡C), 1508 cm^{-1} (C=C, π-allyl). EI-MS (20 °C): *m*/*e* (%) 332 (M$^+$, 15), 290 ([(^{i}Pr$_3$P)-PdC$_2$]$^+$, 100), 266 ([(^{i}Pr$_3$P)Pd]$^+$, 28). ^{1}H NMR (27 °C): δ 5.06 (m, H1), 4.17 ("t", H2), 3.66 (dd, ^3J(H1H2) = 7.3 Hz, ^4J(H2H4) = 2.3 Hz, H4), 2.77 (dd, ^3J(H1H3) = 13.6 Hz, ^3J(PH) = 9.3 Hz, H3), 2.38 (d, ^3J(H1H5) = 13.1 Hz, H5), π-allyl; 1.95 (d, ^4J(PH) = 1.9 Hz, ≡CH); 2.49 (m, 3H, PCH), 1.31, 1.26 (each dd, 9H, diastereotopic Me), ^{i}Pr$_3$P. ^{13}C NMR (27 °C): δ 117.7 (d, ^2J(PC) = 5 Hz, C2), 65.0 (d, ^2J(PC) = 32 Hz, C3), 56.8 (d, ^2J(PdC) = 2 Hz, C1), π-allyl; 101.9 (d, ^2J(CH) = 38 Hz, ^2J(PC) = 25 Hz, PdC≡), 98.2 (d, ^1J(CH) = 222 Hz, ^3J(PC) = 3 Hz, ≡CH), C$_2$H; 26.4 (d, 3C, ^1J(PC) = 19.5 Hz, PCH), 20.5, 20.4 (each d, 3C, ^2J(PC) = 2 Hz, diastereotopic Me), ^{i}Pr$_3$P. The signal of quaternary PdC≡ is broad at 27 °C and has been taken from a −80 °C spectrum. Due to the thermal instability of the complex the proton gated-decoupled spectrum has been recorded also at −80 °C. ^{31}P NMR (27 °C): δ 57.3. Anal. Calcd for $C_{14}H_{27}PPd$ (332.8): C, 50.53; H, 8.18; P, 9.31; Pd, 31.98. Found: C, 49.79; H, 8.22; P, 9.31; Pd, 32.42.

(^{i}Pr$_3$P)Pd(η^3-C$_3$H$_5$)(CH$_3$) (5b). Complex **4b** (686 mg, 2.00 mmol) was stirred with (tmeda)MgMe$_2$ (200 mg, 1.2 mmol) in diethyl ether (15 mL) at −10 to 0 °C for 1 h. The solvent was removed in a vacuum, and the residue was extracted with 10 mL of pentane (0 °C). After filtration the solution was cooled to −78 °C to give colorless crystals, which were washed with pentane and dried under vacuum (−30 °C): yield 305 mg (47%); mp ∼30 °C. The complex sublimes under high vacuum above 30 °C with partial decomposition. IR (KBr): 3062 (=CH−), 1506, 996 (C=C) cm^{-1}. EI-MS (15 °C): *m*/*e* (%) 322 (M$^+$, 4), 307 ([M − Me]$^+$, 42), 181 ([(H$_3$P)Pd(C$_3$H$_5$)]$^+$, 26), 175 ([^{i}Pr$_3$-PMe]$^+$, 100). ^{1}H NMR (27 °C): δ 4.97 (m, H1), 3.55 (dd, ^3J(H1H4) = 7.6 Hz, ^4J(H2H4) = 2.5 Hz, H4), 3.30 ("t", H2), 2.44 (dd, ^3J(H1H3) = 12.9 Hz, ^3J(PH) = 8.7 Hz, H3), 2.32 (strongly overlapped d, ^3J(H1H5) ≈ 13 Hz, H5), π-allyl; 2.32 (m, 3H, PCH), 1.25, 1.21 (each dd, 9H, diastereotopic Me), ^{i}Pr$_3$P; 0.13 (d, ^3J(PH) = 4.9 Hz, PdCH$_3$). ^{13}C NMR (27 °C): δ 117.6 (d, ^2J(PC) = 4 Hz, C2), 60.2 (^2J(PdC) = 1.5 Hz, C1), 57.2 (d, ^2J(PC) = 36 Hz, C3), π-allyl; 25.8 (d, 3C, ^1J(PC) = 17 Hz, PCH), 20.4, 20.3 (each d, 3C, ^2J(PC) = 3 Hz, diastereotopic Me), ^{i}Pr$_3$P; −17.6 (d, $^2J(PC)_{cis}$ = 14 Hz, PdCH$_3$). ^{31}P NMR (27 °C): δ 56.5. Anal. Calcd for $C_{13}H_{29}PPd$ (322.8): C, 48.38; H, 9.06; P, 9.60; Pd, 32.97. Found: C, 48.45; H, 8.85; P, 9.60; Pd, 33.04.

{(^{i}Pr$_3$P)Pd}$_2$(μ-C$_3$H$_5$)(μ-η^1,η^2-C$_2$H) (6). A solution of **5a** (333 mg, 1.00 mmol) in diethyl ether (15 mL) was combined with a solution of **3** (363 mg, 1.00 mmol) in diethyl ether (10 mL) at −30 °C. When the reaction mixture was warmed to 20 °C, some greenish-yellow crystals separated. For complete crystallization the mixture was left overnight at −30 °C. The mother liquor was siphoned off by means of a capillary, and the crystals were washed with cold pentane (−78 °C) and dried under vacuum (20 °C): yield 445 mg (74%). IR (KBr): 3223 (≡C−H), 3028 (=C−H), 1796 cm^{-1} (C≡C). ^{1}H NMR (−80 °C): δ 4.20 (dd, ≡CH), 3.20 (m, C$_a$*H*$_{syn}$H), 3.06 (m, C$_b$*H*$_{syn}$H), 1.87 (m, CH$_{meso}$), 1.10 (d, C$_a$H*H*$_{anti}$), 0.91 (d, C$_b$H*H*$_{anti}$), μ-allyl; 2.49, 2.29 (each m, 3H, PCH and P′CH), 1.35−1.20 (36H, unresolved Me), ^{i}Pr$_3$P; (27 °C): δ 4.00 (t, ≡CH), 3.23 (q, 2H, C$_{a,b}$*H*$_{syn}$H), 1.92 (m, CH$_{meso}$), 1.04 (d, 2H, C$_{a,b}$H*H*$_{anti}$), μ-allyl; 2.35 (m, 6H, PCH), 1.27 ("dd", 36H, unresolved diastereotopic Me), ^{i}Pr$_3$P. ^{13}C NMR (−80 °C): δ 156.4 (m, ^2J(PC = 23.8 Hz, ^2J(P′C) = 3.9 Hz, PdC≡), 97.2 (m, ^1J(CH) = 219 Hz, ≡CH), C≡CH; 70.1 (m, =CH−), 35.6, 29.3 (each m, 1C, CH$_2$), μ-allyl; 25.7, 25.5 (each m, 3C, PCH), 21.1, 20.6, 20.0, 20.0 (each m, 3C, Me), ^{i}Pr$_3$P; (38 °C): δ 156.1 (m, 1C, PdC≡), 96.3 (m, 1C, ≡CH), C≡CH; 70.5 (m, 1C, =CH−), 32.3 (m, 2C, CH$_2$), μ-allyl; 26.1 (m, 6C, PCH), 20.7, 20.6 (each m, 6C, diastereotopic Me), ^{i}Pr$_3$P. ^{31}P NMR (−80 °C): δ 58.3 (d), 43.9 (d, ^3J(PP) = 89 Hz); (27 °C): δ 52.2. Anal. Calcd for $C_{23}H_{48}P_2Pd_2$ (599.4): C, 46.09; H, 8.07; P, 10.33; Pd, 35.50. Found: C, 46.01; H, 7.96; P, 10.28; Pd, 35.58.

X-ray Crystal Structure Analysis of 6. $C_{23}H_{48}P_2Pd_2$: M_r = 599.4, yellow prism, crystal size 0.28 × 0.35 × 0.42 mm, a = 11.667(1) Å, b = 15.686(1) Å, c = 15.0290(1) Å, β = 100.400-(6)°, U = 2705.3(4) Å^3, T = 293 K, monoclinic, $P2_1/c$ [No. 14], Z = 4, d_{calcd} = 1.47 g cm^{-3}, λ = 0.710 69 Å, μ(Mo Kα) = 1.454 mm^{-1}, Enraf-Nonius CAD-4 diffractometer, 1.77° < θ < 29.96°, 8251 measured, 7854 independent reflections, 6304 with $I > 2\sigma(I)$. The structure was solved by the heavy atom method and refined by least-squares using Chebyshev weights on F_o^2 to R_1 = 0.035 [$I > 2\sigma(I)$], wR_2 = 0.088, 245 parameters, μ_2−η^2,η^2-allyl group C3−C5 is disordered over two positions (50:50); H atoms riding, except for ethynyl H atom, which was refined isotropically [U_H = 0.07(1) Å^2], S = 1.022, residual electron density +0.479/−1.069 e Å^{-3}.

Supporting Information Available: Tables of X-ray data collection information, atom coordinates and thermal parameters, and bond lengths and angles, together with CIF data, for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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