the Ph_2MeP and P-ol hydrogens may play an important role in stabilizing the precursor complex in order to account for the operation of an I_d mechanism. The idea of preassociation of the olefin moiety with the metal center in the precursor complex is also in agreement with the trend to more associative types of ligand substitution reactions for the larger W center as found for the displacement of solvent in $M(CO)_5S$ (Table V) and the displacement of CO during ring closure of $M(CO)_5(N\text{-}N)$, where N-N = 1,10-phenanthroline, 1,4-diisopropyl-1,4-diazabutadiene, and ethylenediamine.[17,18]

Conclusions. The results of this and earlier studies[1–3,8,9,15,17,18] have clearly demonstrated that there are quite a number of factors that can influence the intimate nature of ligand substitution reactions in general and solvent replacement reactions in particular. It is in the latter case, especially the size of the metal center, the nucleophilicity of the entering and departing ligands, the degree of bond formation and bond cleavage in the transition state, and the actual molecular packing around the metal center that will all contribute in determining the nature of the mechanism. This means that we are dealing with a very fine tuning effect between the the various contributions of the mentioned factors. The observed activation parameters, especially ΔV^{*}, will be a composite of the various contributions and only allow an overall mechanistic assignment. Larger metal centers tend to favor bond formation processes, stronger nucleophiles tend to exhibit more negative ΔV^{*} values during bond formation, and close-packed ring-opened species may facilitate interchange types of ring-closure reactions, as demonstrated by the results reported in this study. Some separation of the different contributions is possible when mixtures of solvents of different nucleophilicity are employed. We therefore conclude that combined pressure and solvent dependence studies as performed in this investigation can assist the elucidation of the intimate ligand substitution mechanism.

Acknowledgment. The support of this research by the National Science Foundation (Grant CHE-880127) and the Robert A. Welch Foundation (Grant B-0434) (G.R.D.) and the Deutsche Forschungsgemeinschaft and the Volkswagen-Stiftung (R.v.E.) is gratefully acknowledged. The high-pressure experiments were performed at the Center for Fast Kinetics Research (CFKR), University of Texas at Austin. The CFKR is supported jointly by the Biomedical Research Technology Program of the Division of Research Resources of the NIH (Grant RR 000886) and by the University of Texas at Austin. The advice and technical assistance of the staff at CFKR are much appreciated.

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$(R_2PC_2H_4PR_2)Pd^0$ Alkene and Ethyne Complexes

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The palladium η^3-allyl complex $Pd(\eta^3\text{-}C_3H_5)_2$ reacts with bidentate phosphanes $^{i}Pr_2PC_2H_4P^{i}Pr_2$ and $^{t}Bu_2PC_2H_4P^{t}Bu_2$ below −30 °C to yield the light yellow, microcrystalline palladium(II) η^1-allyl compounds $(R_2PC_2H_4PR_2)Pd(\eta^1\text{-}C_3H_5)_2$ (R = ^{i}Pr (**1**), ^{t}Bu (**2**)), which are stable to about −30 °C. Above −30 °C, the allyl substituents of **1** and **2** couple with reduction of palladium to form a mixture of $(R_2PC_2H_4PR_2)Pd^0$ 1,5-hexadiene complexes. When this reaction is carried out in 1,5-hexadiene, the complexes $(R_2PC_2H_4PR_2)Pd(\eta^2\text{-}C_6H_{10})$ (R = ^{i}Pr (**3**), ^{t}Bu (**4**)) are obtained in pure form. According to IR and NMR spectral data, the palladium atoms in **3** and **4** are coordinated at low temperature by the chelating diphosphane and (statically) by one of the two diene double bonds in a trigonal-planar geometry. At higher temperatures, a rapid exchange of the coordinated and uncoordinated double bonds occurs, passing through an intermediate with C_2 symmetry. When suspensions of **1** in pentane and **2** in THF are warmed to 20 °C, dinuclear diastereomers *rac-/meso-*$\{(R_2PC_2H_4PR_2)Pd\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_{10})$ (R = ^{i}Pr (**5a,b**), ^{t}Bu (**6a,b**)) are obtained, which upon treatment with 1,5-hexadiene furnish mononuclear derivatives **3** and **4**. Similarly, when **1** is reacted with 1,5-cyclooctadiene at 20 °C, the mono- and dinuclear interconvertible complexes $(^{i}Pr_2PC_2H_4P^{i}Pr_2)Pd(\eta^2\text{-}C_8H_{12})$ (**7**) and $\{(^{i}Pr_2PC_2H_4P^{i}Pr_2)Pd\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_8H_{12})$ (**8**) are produced. From the reaction of **1** and **2** with ethene, stable complexes $(R_2PC_2H_4PR_2)Pd(C_2H_4)$ (R = ^{i}Pr (**9**), colorless; R = ^{t}Bu (**10**), tan) result. The colorless mononuclear palladium(0) ethyne complexes $(R_2PC_2H_4PR_2)Pd(C_2H_2)$ (R = ^{i}Pr (**11**), ^{t}Bu (**12**)) may be prepared (a) by a displacement reaction of one of the isolated alkene complexes with ethyne, (b) by a reductive elimination and concomitant displacement reaction of the η^1-allyl complexes **1** and **2** with ethyne, or (c) in a one-pot synthesis from either $Pd(\eta^3\text{-}C_3H_5)_2$ or $Pd(\eta^3\text{-}2\text{-}MeC_3H_4)_2$ with $^{i}Pr_2PC_2H_4P^{i}Pr_2$ or $^{t}Bu_2PC_2H_4P^{t}Bu_2$, respectively, and ethyne in excess. When the mononuclear ethyne complexes **11** and **12** are combined with an equimolar amount of the corresponding η^1-allyl complex **1** or **2**, or the alkene complexes (especially the mononuclear 1,5-hexadiene (**3**, **4**) or ethene (**9**, **10**) derivatives), yellow dinuclear palladium(0) complexes $\{(R_2PC_2H_4PR_2)Pd\}_2(\mu\text{-}C_2H_2)$ (R = ^{i}Pr (**13**), ^{t}Bu (**14**)) are produced, in which the ethyne ligand bridges two palladium atoms. All the (diphosphane)palladium(0) alkene (**3**–**10**) and ethyne complexes (**11**–**14**) exhibit a trigonal-planar coordination geometry about the palladium atom. Most of the compounds have been isolated in high yield.

Introduction

In the context of our studies on the complexes of nickel(0) with ethyne, we have reported in detail the synthesis and characterization of monodentate ligand complexes, e.g. $(Ph_3P)_2Ni(C_2H_2)$,[1] as well as bidentate ligand complexes, e.g. $(^{i}Pr_2PC_2H_4P^{i}Pr_2)Ni(C_2H_2)$, $\{(^{i}Pr_2PC_2H_4P^{i}Pr_2)Ni\}_2(\mu\text{-}C_2H_2)$,[2] and $(^{t}Bu_2PC_2H_4P^{t}Bu_2)Ni(C_2H_2)$.[3] A similar

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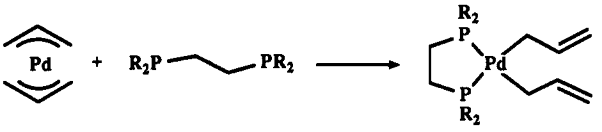
platinum(0) ethyne complex, namely $(Ph_3P)_2Pt(C_2H_2)$, has been known since 1957.[4] With our ongoing work in the field of transition-metal ethyne complexes, we became interested in preparing palladium(0) ethyne complexes to see what properties they would display, especially in comparison to the nickel(0) analogues. In general, π-complexes of palladium(0) are considered to be significantly less stable than those of nickel(0) and platinum(0) as a result of both weak σ- and π-bonding abilities of palladium(0).[5]

Previous reports on the reaction of palladium(0) complexes with terminal alkynes give the impression that the preferred reaction path is oxidative addition to yield alkynylhydridopalladium(II) complexes.[6] A major obstacle in the synthesis of palladium(0) alkyne complexes of terminal alkynes is the scarcity of appropriate starting complexes, e.g. palladium(0) alkene complexes,[7] in which the alkene ligand can readily be displaced by an alkyne, particularly ethyne.

We have developed general synthetic routes to palladium(0) ethyne complexes, $L_2Pd(C_2H_2)$ and $L_2Pd(\mu\text{-}C_2H_2)PdL_2$, with mono- and bidentate phosphane ligands. Suitable starting materials include the palladium(II) complexes $Pd(\eta^3\text{-}C_3H_5)_2$,[8,9] $Pd(\eta^3\text{-}2\text{-}MeC_3H_4)_2$,[8,9] $(\eta^5\text{-}C_5H_5)Pd(\eta^3\text{-}C_3H_5)$,[10] and $(tmeda)PdMe_2$,[11] together with the corresponding phosphanes and nonactivated alkenes. Herein we report in detail the reaction of $Pd(\eta^3\text{-}C_3H_5)_2$ with bidentate phosphanes ${}^iPr_2PC_2H_4P{}^iPr_2$ and ${}^tBu_2PC_2H_4P{}^tBu_2$ to form $(R_2PC_2H_4PR_2)Pd^0$ alkene complexes and their further conversion with ethyne to yield $(R_2PC_2H_4PR_2)Pd^0$ ethyne compounds. These results are taken in part from a Ph.D. thesis[12a] and a recent diploma thesis.[12b]

Results

$({}^iPr_2PC_2H_4P{}^iPr_2)Pd(\eta^1\text{-}C_3H_5)_2$ (1) and $({}^tBu_2PC_2H_4P{}^tBu_2)Pd(\eta^1\text{-}C_3H_5)_2$ (2). It has been shown by Jolly et al. that an ethereal suspension of $Pd(\eta^3\text{-}C_3H_5)_2$ reacts with chelating diphosphanes $R_2PC_2H_4PR_2$ (R = Me, Cyh) at −78 °C (for R = Me; rapidly) or −25 °C (for R = Cyh; slowly) to afford the corresponding $(R_2PC_2H_4PR_2)Pd(\eta^1\text{-}C_3H_5)_2$ adducts as off-white powders.[9] Similarly, when a mixture of $Pd(\eta^3\text{-}C_3H_5)_2$ and an equimolar amount of ${}^iPr_2PC_2H_4P{}^iPr_2$ or ${}^tBu_2PC_2H_4P{}^tBu_2$ is warmed from −78 to −40 °C with stirring, the starting complex dissolves and the light yellow, microcrystalline complexes **1** and **2** precipitate in 90% yield. It did not appear possible to grow larger crystals of **1** or **2**. The solids are stable up to about −30 °C (**1**) or −20 °C (**2**), temperatures at which they turn darker and become sticky.



(1)

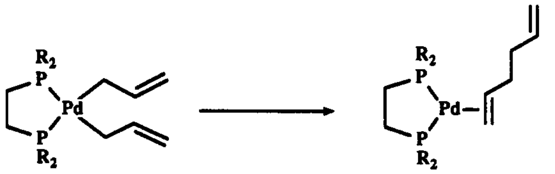
1 R = ${}^iPr$

2 R = ${}^tBu$

In the ^1H NMR spectra (THF-d_8) of **1** and **2** recorded at −30 °C, the expected four resonances of the two equivalent η^1-bonded 2-propenyl substituents are observed (e.g. for **1** δ(H) 6.18 (−CH=), 4.53 (=CHH_Z), 4.12 (=CH_EH), 2.15 ($PdCH_2$−); for **2** δ(H) 2.45 ($PdCH_2$−)). The low-temperature ^{31}P NMR spectra show singlets for **1** (δ(P) 66.8) and **2** (δ(P) 72.5). When the temperature is raised above −30 °C, these singlets disappear and new signals emerge, indicating a complete and rapid thermolysis of the starting compounds. The thermolysis products of **1** give rise to a singlet (δ(P) 60.1, main component) and two AB systems of equal intensity (δ(P) 61.1, 57.4 and 60.8, 57.3), which are similar to the resonances for the products from **2** (singlet at δ(P) 81.4 (main component); two AB systems at δ(P) 82.0, 79.6 and 81.9, 79.6).

By means of ^1H NMR spectroscopy the thermolysis products have been identified as mononuclear (**3**, **4**) and dinuclear (**5a**,**b**, **6a**,**b**) palladium(0) 1,5-hexadiene complexes, which could also be synthesized as described below. In addition, the ambient-temperature ^1H NMR spectra show the presence of uncoordinated 1,5-hexadiene in an amount equal to that of $\mu\text{-}\eta^2{:}\eta^2$-coordinated ligand present in the dinuclear complexes **5a**,**b** and **6a**,**b**.

$({}^iPr_2PC_2H_4P{}^iPr_2)Pd(\eta^2\text{-}C_6H_{10})$ (3) and $({}^tBu_2PC_2H_4P{}^tBu_2)Pd(\eta^2\text{-}C_6H_{10})$ (4). The preparation of pure **3** and **4** is possible, when suspensions of **1** and **2** *in small amounts of 1,5-hexadiene* are slowly warmed from −40 to 20 °C. **1** forms a colorless liquid from which, after cooling to −78 °C and the addition of pentane, colorless crystals of **3** are obtained. **2** reacts exothermically to generate a brown solution, which affords beige crystals of **4** after standing at −78 °C for a few days. Both **3** and **4** are isolated in 77% yields.



(2)

1 R = ${}^iPr$ **3** R = ${}^iPr$

2 R = ${}^tBu$ **4** R = ${}^tBu$

3 displays a melting point of about −5 °C, whereas **4** apparently decomposes, without a discernible melting point, above 220 °C (!) when quickly heated. The IR spectra (KBr, 20 °C) of the compounds show C—H alkene stretching bands of nearly equal intensity for uncoordinated and coordinated olefinic double bonds (ca. 3073 and 3025 cm^{-1}, respectively) as well as a C=C stretching band of an uncoordinated C=C bond (ca. 1640 cm^{-1}). No absorption bands, assignable to coordinated C=C bonds, appear at wavenumbers >1480 cm^{-1}, but two significant

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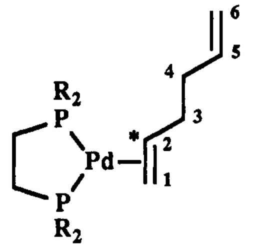

Figure 1. Chirality of L$_2$Pd(α-alkene) complexes, e.g. 3 and 4.

bands, attributable to coordinated vinylic groups, are found near 1200 cm^{-1}. From the IR and NMR data (discussed below) we conclude that 3 and 4 represent in their static low-temperature structures trigonal-planar palladium(0) complexes with a chelating diphosphane ligand and a diene ligand coordinated via *one* of the two double bonds.

^{1}H and ^{31}P NMR Spectra: Structure and Molecular Dynamics of 3 and 4. To clarify the bonding situation in 3 and 4, it is best to discuss at first the low-temperature ^{1}H and ^{31}P NMR spectra of 4. The ^{1}H NMR (400 MHz) spectrum of 4, recorded at −80 °C, shows 10 proton signals for the 1,5-hexadiene ligand. The three well-resolved resonances at δ(H) 5.85 (=C^{5}H–), 4.94 (=C^{6}H$_Z$H), and 4.85 (=C^{6}HH$_E$) correspond to an uncoordinated 1,5-hexadiene double bond. The three broadened signals at δ(H) 3.26 (=C^{2}H–), 2.40 (=C^{1}HH$_E$), and 2.36 (=C^{1}H$_Z$H) are attributed to a double bond coordinated to palladium. The 1,5-hexadiene methylene protons –C^{4}H$_a$H$_b$– and –C^{3}H$_a$H$_b$– give rise to four separate peaks (δ(H) 2.38, 2.17, 2.10, 1.47). In addition, two signals are obtained for the inequivalent PCH$_a$H$_b$ and P′CH$_a$H$_b$ groups (δ(H) 1.80, 1.70; CH$_a$H$_b$ unresolved), while the methyl signals of the four inequivalent *tert*-butyl groups are partially overlapping (δ(H) 1.2). In the ^{31}P NMR spectrum (81.0 MHz) of 4 (−80 °C), doublets of an AB system (δ(P) 82.0, 79.5; J(PP) = 70.4 Hz) are observed. The low-temperature NMR spectra of 4 are consistent with a trigonal-planar coordination of the palladium atom by the chelating diphosphane and one of the two 1,5-hexadiene double bonds. Because the β C atom becomes asymmetric upon coordination of the double bond to the metal atom,[13] the whole complex is chiral, thus causing all 1,5-hexadiene protons to be inequivalent (Figure 1). No rotation of the alkene double bond around the coordination axis to palladium(0) occurs.

For 3, all 1,5-hexadiene proton resonances are broad at −80 °C and can hardly be detected at −100 °C. Since 3 easily and reversibly liberates 1,5-hexadiene in solution (to afford the dinuclear derivatives **5a,b**), we recorded the ^{31}P NMR spectra of 3 in a solution of THF-d_8 containing excess 1,5-hexadiene. The ^{31}P NMR spectrum (81.0 MHz) so obtained at −100 °C shows only two signals (δ(P) 61.5, 58.9) of an unresolved AB spectrum, which coalesce at −80 °C to give a singlet at −30 °C (δ(P) 60.1). Without the addition of 1,5-hexadiene, essentially the same ^{31}P NMR spectra are observed for 3, but the signals of **5a,b** as minor components are also detected (see below). It is conceivable that 3 has a structure similar to that of 4 and that the low-temperature conformation has not yet been "frozen out" at −80 or −100 °C.

With rising temperatures, it becomes evident from the NMR spectra that both 3 and 4 exhibit dynamic solution structures. The ^{1}H NMR spectrum (200 MHz) of 3 recorded at −30 °C shows, for the 1,5-hexadiene ligand, three sharp olefinic resonances (δ(H) 4.63 (–C^{2,5}H=), 3.60 (=C^{1,6}HH$_Z$), 3.57 (=C^{1,6}H$_E$H)) and one sharp methylene resonances (δ(H) 2.02), compatible with equivalent "halves" of the ligand as a time average of different conformations. No significant change in the ^{1}H and ^{31}P NMR spectra of 3 is observed when the temperature is raised from −30 to +27 °C. In the case of 4, the coalesced 1,5-hexadiene signals are still broad at 27 °C (200 MHz, δ(H) 4.64 (=C^{2,5}H–), 3.70 (=C^{1,6}H$_E$H$_Z$), 2.09 (–C^{3,4}H$_2$–)), but the ^{31}P NMR spectrum shows a singlet (δ(P) 81.4). For 4 the proton chemical shifts observed for the 1,5-hexadiene ligand at 27 °C are the arithmetical mean of the corresponding proton shifts of the coordinated and uncoordinated double bonds at −80 °C. In addition, the proton chemical shifts observed for the 1,5-hexadiene ligand in 3 and 4 at 27 °C are the arithmetical mean of the corresponding proton shifts of uncoordinated 1,5-hexadiene and the 1,5-hexadiene ligand with both double bonds coordinated in **5a,b** or **6a,b**, respectively; e.g., δ(H) for =C^{2,5}H– in 3 is 4.63 and the mean of unbound 1,5-hexadiene (δ 5.81) and **5a,b** (δ 3.47) is δ 4.64.

Obviously, when the temperature is raised an exchange of the coordinated and uncoordinated 1,5-hexadiene double bonds takes place. This process occurs considerably faster for 3 (sterically less demanding phosphane) than for 4. Since the high-temperature ^{1}H NMR spectra of 3 and 4 also contain (due to partially formed **5a,b** and **6a,b**) sharp signals of uncoordinated 1,5-hexadiene, an exchange of 1,5-hexadiene ligands with the uncoordinated substrate is not observed on the NMR time scale. Therefore, we presume that the exchange of coordinated and uncoordinated double bonds in the complexes occurs intramolecularly.

When 3 is dissolved in THF-d_8, the formation of **5a,b** with liberation of 1,5-hexadiene cannot be totally avoided even at −78 °C without adding excess 1,5-hexadiene. In contrast, upon dissolution of 4 in THF-d_8 the ^{1}H and ^{31}P NMR resonances of the corresponding compounds **6a,b** together with those of 1,5-hexadiene are observed only at 27 °C. This transformation too can be suppressed by addition of excess 1,5-hexadiene. The ^{1}H and ^{31}P NMR spectra of 3 and 4 at 27 °C are, disregarding the different phosphane signals, quite similar in their general appearance.

Proposed Mechanism for the Molecular Dynamics of 3 and 4. It has been established by Jolly et al. that palladium(0) *butadiene* complexes (R$_2$PC$_2$H$_4$PR$_2$)Pd(η^2-C$_4$H$_6$) (R = Cyh, ^{i}Pr, ^{t}Bu)[14] exhibit a trigonal-planar geometry (η^2-bonded butadiene ligand). According to low-temperature ^{13}C NMR studies (75.5 MHz, −100 °C), the bonding of the butadiene ligand is static in the conformational ground state of these complexes (four broad signals). At higher temperatures (−10 to +20 °C) an exchange of the coordinated and uncoordinated butadiene double bonds is observed (two signals). In the ^{31}P NMR spectra the *AB systems are preserved* over the whole temperature range so that the butadiene ligand apparently exchanges coordinated and uncoordinated C=C bonds in its s-cis conformation via a transient species with *C$_s$ symmetry* (see eq 3). The same dynamics have been shown by ^{13}C CP/MAS NMR measurements to take place in the solid state.[15]

Similarly, a trigonal-planar coordination of the palladium atom by two phosphorus atoms and one 1,5-hexadiene double bond has been found in the conformational

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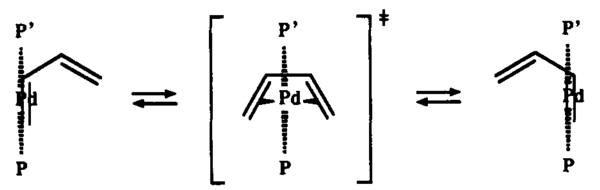
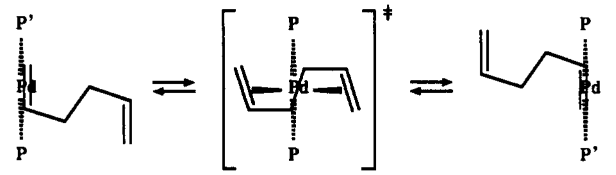


(3)

ground state for **3** and **4**. For the exchange process of the coordinated and uncoordinated *1,5-hexadiene* double bonds in **3** and **4**, as observed in the high-temperature NMR spectra, it is characteristic that both the corresponding 1,5-hexadiene protons and *the phosphorus atoms are equivalent*. It may be argued that the phosphorus atoms become equivalent by a simple rotation of the coordinated alkene around the bond axis to the palladium atom. However, such a rotation appears to be unlikely for **3** and **4**, since the derivatives **5a,b** and **6a,b**, which are structurally similar but with both double bonds coordinated to palladium atoms, exhibit an AB pattern in the ^{31}P spectra at all temperatures, thus excluding a rapid bond rotation.

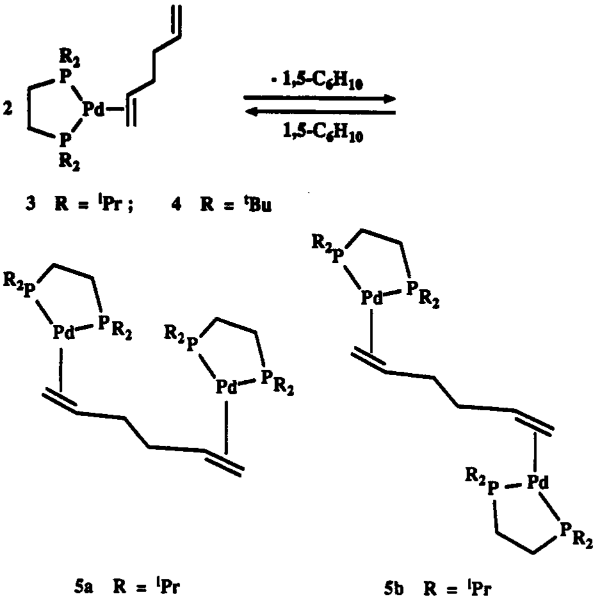
For the presumably intramolecular exchange process of the coordinated and uncoordinated 1,5-hexadiene double bonds in **3** and **4** we propose a "jump-over" of the double bonds of the 1,5-hexadiene ligand. The ligand is initially orientated in a "zigzag" conformation with one of the two double bonds coordinated to the metal center. During the exchange, the complex passes through a quasi-tetrahedral transition state with C_2 *symmetry* of the palladium(0) 1,5-hexadiene fragment. This molecular arrangement proposed for the *transition state* of the *(diphosphane)palladium(0) 1,5-hexadiene double-bond exchange process* has been ascertained for the complexes $(Et_3P)_2Ni(\eta^2{:}\eta^2\text{-}C_6H_{10})$ and $({}^iPr_2PC_2H_4P^iPr_2)Ni(\eta^2{:}\eta^2\text{-}C_6H_{10})$,[16] by X-ray single-crystal structural analyses, as the *low-energy conformation of (diphosphane)nickel(0) 1,5-hexadiene complexes*.



(4)

Coordination Geometry of (Diphosphane)palladium(0) Diene Complexes. From the results given above, it follows that both the (diphosphane)palladium(0) 1,3-butadiene and 1,5-hexadiene complexes are to be considered *trigonal-planar 16e complexes*, in which only one of the two diene double bonds is coordinated to palladium, although exchange of the double bonds occurs at elevated temperatures. It appears that in general there are *no 18e (diphosphane)palladium(0) diene complexes* in which both diene double bonds are bound to the palladium atom simultaneously in the ground state. This is indicated by the NMR spectra of the palladium(0) 1,3-butadiene[14] and 1,5-hexadiene complexes. It should be emphasized that both 1,3-butadiene and 1,5-hexadiene indeed form 18e (diphosphane)*nickel(0)* complexes in which the diene double bonds chelate the nickel atom (e.g. $(Cyh_2PC_2H_4PCyh_2)Ni(s\text{-}cis\text{-}\eta^4\text{-}C_4H_6)$[14,15] and the nickel(0) 1,5-hexadiene complexes cited above, of which $({}^iPr_2PC_2H_4P^iPr_2)Ni(\eta^2{:}\eta^2\text{-}C_6H_{10})$ is homologous to **3**). Examples of other dienes which tend to coordinate transition metals with both olefinic double bonds are 1,3-cyclohexadiene (1,3-C_6H_8), 1,3-cyclooctadiene (1,3-C_8H_{12}), fulvenes (e.g. $C_5Me_4{=}CH_2$), 1,5-cyclooctadiene (1,5-C_8H_{12}), and *p*-benzoquinone. It has been shown for $(Cyh_2PC_2H_4PCyh_2)Pd(1,3\text{-}C_6H_8)$ in solution,[14] and for $({}^tBu_2PC_2H_4P^tBu_2)Pd(1,3\text{-}C_8H_{12})$[15] and $(Me_3P)_2Pd(CH_2{=}C_5Me_4)$ (crystal structure)[17] in the solid state, that the diene ligands are η^2-bonded to palladium(0). In analogy to these results we found that also for 1,5-C_8H_{12} (cod) as the alkene ligand the palladium atom is trigonal-planar coordinated and the complexes $({}^iPr_2PC_2H_4P^iPr_2)Pd(\eta^2\text{-}1,5\text{-}C_8H_{12})$ (**7**) and $\{({}^iPr_2PC_2H_4P^iPr_2)Pd\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}1,5\text{-}C_8H_{12})$ (**8**) are formed (see below). In $(Ph_3P)_2Pd(p\text{-}C_6H_4O_2)$,[18] a bidentate binding mode of the *p*-benzoquinone ligand to palladium(0) has been reported. However, the ambient-temperature ^1H and ^{13}C NMR data[18] corresponding to the *p*-benzoquinone of this complex are best explained as the time average of the chemical shifts and coupling constants of $(Ph_3P)_2Pd(\eta^2\text{-}p\text{-}C_6H_4O_2)$, evidence for exchange of coordinated and uncoordinated olefinic double bonds.

***rac*-/*meso*-**$\mathbf{\{({}^iPr_2PC_2H_4P^iPr_2)Pd\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_{10})}$ **(5a,b) and *rac*-/*meso*-**$\mathbf{\{({}^tBu_2PC_2H_4P^tBu_2)Pd\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_{10})}$ **(6a,b).** When a −30 °C *pentane* suspension of **1** is warmed to 20 °C, the complex dissolves completely. After the volume of the solution is reduced (in the course of which some 1,5-hexadiene evaporates), a precipitate results that is collected by filtration and recrystallized from pentane at −30 °C to yield orange crystals of **5a,b** (60%), which turn beige when dried under vacuum. Solid **5a,b** is stable at room temperature but slowly decomposes at 20 °C in solution. The compound is sparingly soluble in diethyl ether or THF above −30 °C. The *tert*-butyl-substituted product is much easier to prepare: When the yellowish suspension of **2** in THF (−30 °C) is warmed to 20 °C, an orange-yellow solution is obtained (2 h) from which crystalline, beige **6a,b** separates (52%) on standing at 0 °C for 1 day. **6a,b** is sparingly soluble in THF and is almost completely insoluble in diethyl ether or pentane at 20 °C. The solid product is stable to at least 100 °C without melting.



3 R = ^{i}Pr ; 4 R = ^{t}Bu

(5)

5a R = ^{i}Pr
6a R = ^{t}Bu
5b R = ^{i}Pr
6b R = ^{t}Bu

The IR spectra (KBr) of **5a,b** and **6a,b** do not show absorption bands at wavenumbers near 1640, 990, and 910 cm^{-1}, attributable to an uncomplexed C=C bond. Al-

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[16] Mynott, R.; Pörschke, K. R.; Lutz, F.; Krüger, C. To be submitted for publication.

[17] Werner, H.; Crisp, G. T.; Jolly, P. W.; Kraus, H.-J.; Krüger, C. *Organometallics* **1983**, *2*, 1369.

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though there are no bands down to 1480 cm^{-1} as expected for complexed C=C bonds, the observed absorptions at 1205, 1188 cm^{-1} (**5a,b**) and 1238, 1217 cm^{-1} (**6a,b**) can be assigned to in-plane vibrations of vinylic C—H bonds of the coordinated alkene.

The ^{1}H NMR spectra of **5a,b** (200 MHz, -30 °C) and **6a,b** (400 MHz, 27 °C) confirm the compositions of the compounds but do not provide any structural evidence, due to partially unresolved resonances. Nevertheless, for **5a,b** resonances at δ(H) 3.47 (-CH=), 2.39 (=CH$_2$), and 2.0 (-CH$_2$-) can be assigned to symmetrically bonded 1,5-hexadiene.

The ^{31}P NMR spectrum at -30 °C of a freshly prepared solution of **5a,b** in THF-d_8 shows two AB systems (δ(P) 61.1, 57.4; δ(P) 60.8, 57.3; both J(PP) = 70.5 Hz). The AB spin systems show an initial intensity ratio of 8:1, but after several hours this ratio equalizes to 1:1. At 27 °C essentially the same spectrum is obtained for **5a,b** but slow decomposition is observed. Similarly the **6a,b** complexes (27 °C; stable) reveal two AB systems (δ(P) 82.0, 79.6; δ(P) 81.9, 79.6; both J(PP) = 81.0 Hz) with a 1:1 intensity ratio.

Obviously the substances **5a,b** and **6a,b** consist of two spectroscopically very similar components, which are at least partially interconvertible (**5a,b**). The ^{31}P NMR spectra are rationalized under the assumption that **5a,b** and **6a,b** represent mixtures of the racemic and meso forms of diastereomers of the dinuclear complexes. In these complexes the palladium atoms are trigonal-planar coordinated by a chelating diphosphane ligand and one olefinic double bond of a *bridging* 1,5-hexadiene molecule. The notations *rac* and *meso* refer to the relative configurations of the carbon atoms C^2,C^5 of the bridging 1,5-hexadiene ligand, which are asymmetric due to the coordination of the alkene to the metal center.[13] For each of the two *rac* diastereomers a conformation can be designated which shows a C_2 axis leading through the midpoint of the C^3–C^4 1,5-hexadiene bond, whereas the corresponding *meso* stereoisomer features a mirror plane. **5a,b** and **6a,b** therefore consist of a 25:25:50 mixture of *RR*,*SS* (racemic), and *RS*/*SR* (meso) diastereomers in slow equilibrium. Since the *RR*,*SS* enantiomers give rise to identical NMR signals, the number of NMR-detectable isomers in an achiral solvent is reduced to two.[19]

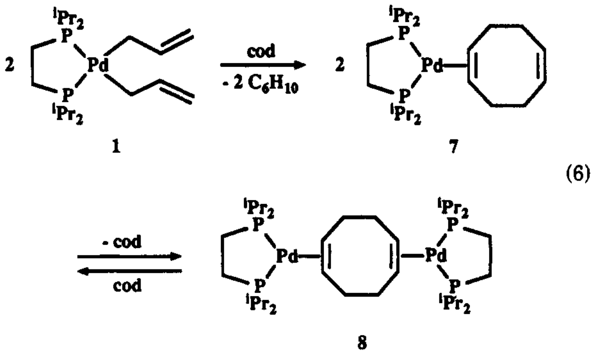
Dynamic Processes Concerning 5a,b and 6a,b. The changes observed in the ^{31}P NMR spectrum of **5a,b** at -30 °C fit well with a slow interchange of the diastereomers, requiring cleavage of the palladium(0)–alkene bond, turnover of the alkene double bond, and recomplexation of the other side of the double bond to palladium. A rapid (on the NMR time scale), reversible palladium(0)–alkene bond dissociation process can be excluded, since this would lead to an equilibration of the phosphorus atoms in the ^{31}P NMR spectra of **5a,b** and **6a,b** observed at 27 °C. It follows from the same argument that rapid rotation of the alkene double bonds around the bonding axis to palladium does not take place at 27 °C.

When **5a,b** and **6a,b** are dissolved in a 1:1 mixture of THF-d_8 and 1,5-hexadiene, the ^{31}P NMR spectra do not show the 2-fold AB pattern of **5a,b** and **6a,b** but rather reveal the coalesced resonances of the corresponding mononuclear complexes **3** and **4** (27 °C). Obviously, the dinuclear complexes are easily cleaved by 1,5-hexadiene in excess to yield the mononuclear derivatives, which in turn can liberate 1,5-hexadiene and form the dinuclear compounds **5a,b** and **6a,b**. Therefore, the reactions of eq 5 represent an equilibrium, and the dinuclear and mononuclear complexes are interconvertible by addition or depletion of 1,5-hexadiene.

The solution behavior of **3**, **4**, **5a,b**, and **6a,b** described above provides a qualitative picture of the degree of the palladium(0)–alkene bond stability in (diphosphane)palladium(0) alkene complexes.

(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Pd(η^2-1,5-C$_8$H$_{12}$) (7) and {(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Pd}$_2$(μ-η^2:η^2-1,5-C$_8$H$_{12}$) (8). When a mixture of **1** and a small amount of 1,5-C$_8$H$_{12}$ is warmed from -30 °C to room temperature, the complex dissolves and a light yellow solution is obtained. Addition of pentane does not cause the precipitation of a solid (-78 °C). It is assumed that the mononuclear **7** with a trigonal-planar coordination geometry about the palladium(0) and a η^2-bonded 1,5-C$_8$H$_{12}$ ligand is present at this stage. When the volatile components are removed under reduced pressure at 20 °C, colorless crystals of the dinuclear complex **8** can be isolated (93%). In **8**, the two palladium atoms are trigonal-planar coordinated by the chelating diphosphane and one double bond of the 1,5-C$_8$H$_{12}$ ligand, which bridges the palladium atoms. The bridging 1,5-C$_8$H$_{12}$ ligand is characterized in the IR spectrum by a C=C stretching vibration at 1548 cm^{-1} and in the ^{1}H NMR spectrum (-30 °C) by one signal for the vinylic protons (-CH=CH-, δ(H) 3.70) and two signals for the diastereotopic methylene protons (-CH$_a$H$_b$-, δ(H) 2.58, 1.9). In the ^{31}P NMR spectrum (-30 °C) of **8** a singlet appears at δ(P) 57.9, so that apparently only one stereoisomer is formed. Some samples also gave a minor signal at δ(P) 57.4 due to **7** (see below).

Solid **8** is stable at 20 °C. It is scarcely soluble in pentane and only moderately soluble in diethyl ether or THF, in which it slowly decomposes at 20 °C. However, **8** dissolves readily in 1,5-C$_8$H$_{12}$ at 20 °C and such a solution does not decompose up to 90 °C, nor does a precipitate form when pentane is added. In the ^{31}P NMR spectrum of a solution of **8** in THF-d_8/1,5-C$_8$H$_{12}$ (1:1) only the signal at δ(P) 57.4 is observed. The greater solubility of **8** in solvents containing 1,5-C$_8$H$_{12}$ and the increased thermal stability of these solutions can be explained by the formation of the mononuclear **7**, which is stabilized by the excess 1,5-C$_8$H$_{12}$, and for which a ^{31}P chemical shift similar to that for **8** would be conceivable. Assuming the existence of **7**, the complexes **7** and **8** are obviously easily interconvertible by depletion or addition of 1,5-C$_8$H$_{12}$.



(6)

Unlike the palladium(0) complexes **7** and **8**, *nickel*(0) forms the mononuclear homologue (^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Ni(η^2:η^2-C$_8$H$_{12}$),[12a] in which both the phosphane and 1,5-C$_8$H$_{12}$ ligands are chelating the nickel atom, yielding a *tetrahedral* coordination geometry.

(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Pd(C$_2$H$_4$) (9) and (^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Pd(C$_2$H$_4$) (10). When a light green-

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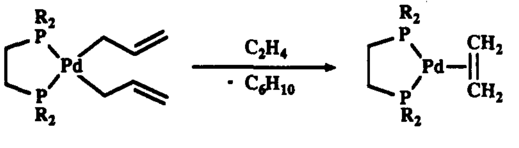
[19] Similar bonding situations have recently been described for both nickel(0)[19a] and platinum(0):[19b] (a) Proft, B. Diplomarbeit, Universität Düsseldorf, 1990. Proft, B.; Pörschke, K. R.; Lutz, F.; Krüger, C. *Chem. Ber.* **1991**, *124*, 2667. (b) Hitchcock, P. B.; Lappert, M. F.; Warhurst, N. J. W. *Angew. Chem.* **1991**, *103*, 440; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 438.

yellow solution of **1** in diethyl ether is saturated with ethene at −30 °C and warmed to 0 °C, the color disappears almost completely. At −78 °C, colorless crystals of the palladium(0) ethene complex **9** precipitate after 1 or 2 days (62%). **9** dissolves very well in ether and THF even at low temperatures, and the solutions are stable at room temperature for at least several days. Similarly, when an ethene-saturated ether suspension of **2** is warmed from −30 °C to room temperature, a brownish yellow reaction solution is obtained from which large, tan needles of **10** separate (−30 °C, 84%). **10** is stable as a solid and in solution at room temperature but is less soluble than **9**.



(7)

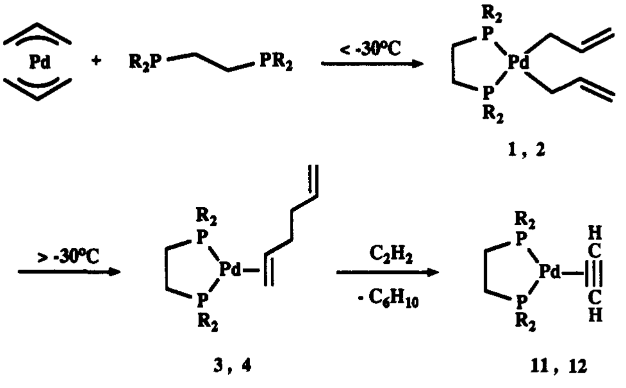
1 R = ^{i}Pr **9** R = ^{i}Pr

2 R = ^{t}Bu **10** R = ^{t}Bu

In the IR spectra of **9** and **10** the ethene ligands are characterized by C—H stretching bands at 3045 and 3035 cm^{-1}, respectively. Signals assignable to C═C stretching and symmetric CH$_2$ deformation modes which are strongly coupled are found at 1572 and 1179 cm^{-1} for **9** and 1572 and 1175 cm^{-1} for **10**.[20] Both **9** (δ(P) 62.7) and **10** (δ(P) 84.8) show singlets in the ^{31}P NMR spectra (27 °C). ^{1}H NMR analysis (27 °C) of **9** and **10** revealed that the ethene protons give rise to doublets at δ(H) 2.30 and 2.41, respectively, with small couplings (1–2 Hz) to the "trans"-located phosphorus atoms.

In contrast to the multitude of ethene complexes known for nickel(0) and platinum(0), only a few palladium(0) ethene complexes have been described so far. Compounds Pd(C_2H_4)$_3$,[21] (R_3P)$_2$Pd(C_2H_4) (R = Cyh, Ph, O-2-tolyl),[22] and (diop)Pd(C_2H_4) (X-ray structure)[23] have been isolated, and complexes (n-Bu$_3$P)$_2$Pd(C_2H_4) and ($Ph_2PC_2H_4PPh_2$)Pd(C_2H_4)[24] were spectroscopically identified in solution, all of which are apparently stable in solution only in the presence of additional ethene. In the ^{1}H NMR spectra of these solutions, broadened signals of coordinated and uncoordinated ethene are observed due to ligand exchange. In contrast, **9** and **10** give rise to sharp ^{1}H NMR signals for the ethene protons and do not require excess ethene as a stabilizing factor. Thus, **9** and **10** can be considered the first palladium(0) ethene complexes that are stable in solution without additional ethene.

(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Pd(C$_2$H$_2$) (11) and (^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Pd(C$_2$H$_2$) (12). When an ethereal suspension of **3** (likewise a suspension or solution of **5a,b** and **7–9**) is treated with excess ethyne at 0 °C, the alkene ligand is displaced, and at −78 °C colorless crystals of the palladium(0) ethyne complex **11** are obtained (87%). Similarly, ligand displacement on **4** (or **6a,b** and **10**) by ethyne affords, when the temperature is lowered below −30 °C, colorless crystals of **12** (90%). **11** and **12** may also be prepared from the Pd(II) η^1-allyl complexes **1** and **2**, respectively, through reductive elimination followed by alkene displacement. A one-pot synthesis of **11** and **12** is realized by starting from η^3-allyl complexes Pd(η^3-C_3H_5)$_2$ or Pd(η^3-2-MeC$_3$H$_4$)$_2$, ethyne, and ^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$ or ^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$, respectively (eq 8). Exploratory studies have shown that (η^5-C_5H_5)Pd(η^3-C_3H_5) can also be used as a starting complex for the synthesis of **11** and **12** via a one-pot reaction. In all cases ethyne should be present in slight excess, since some of the ethyne may be consumed by polymerization.



1, 2

3, 4 **11, 12**

1, 3, 11 R = ^{i}Pr; **2, 4, 12** R = ^{t}Bu

(8)

Compounds **11** and **12** are the first reported Pd(0) complexes in which the palladium atom is trigonal-planar coordinated by a chelating diphosphane and an ethyne ligand. Solid **12** is stable at room temperature, while **11** is only briefly stable. In solution they decompose slowly to yield, with partial liberation of ethyne, dinuclear complexes **13** and **14** (discussed below). Spectroscopically, **11** and **12** were characterized by IR (KBr) and ^{1}H, ^{13}C, and ^{31}P NMR (−30 °C) data. In the IR spectra for the η^2-bonded ethyne ligands, ≡C—H (**11**, 3125, 3085 cm^{-1}; **12**, 3125 cm^{-1}) and C≡C (**11**, 1619 cm^{-1}; **12**, 1626 cm^{-1}) stretching vibrations are observed ((^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Pd(C_2D_2) (**12a**), ≡C—D 2418 cm^{-1}, C≡C 1531 cm^{-1}). The C≡C stretching vibrations for the (diphosphane)palladium(0) complexes are lower than those of gaseous ethyne (ν(≡C—H) 3373 (sym), 3282 (asym) cm^{-1}; ν(C≡C) 1974 cm^{-1}), but the magnitude of the shift ($\Delta\nu \approx 350$ cm^{-1}) is somewhat less than observed for the corresponding nickel(0) complexes (cf. (^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Ni(C_2H_2), 1598 cm^{-1}, $\Delta\nu \approx 375$ cm^{-1}).[2]

In the ^{1}H NMR spectra the η^2-ethyne protons show the AA′ portion of an AA′XX′ pattern (**11**, δ(H) 6.91; **12**, δ(H) 6.78) due to inequivalent couplings with both phosphorus atoms. The ^{13}C NMR spectrum of **12** reveals for the η^2-ethyne carbon atoms a multiplet at δ(C) 105.1 with ^1J(CH) = 211 Hz (cf. (^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Ni(C_2H_2), δ(H) 7.29, δ(C) 123.8, ^1J(CH) = 202 Hz).[2] For both complexes the phosphorus atoms (**11**, δ(P) 69.5; **12**, δ(P) 91.3) are markedly *de*shielded as compared to those of ethene complexes **9** and **10**.

{(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Pd}$_2$(μ-C$_2$H$_2$) (13) and {(^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Pd}$_2$(μ-C$_2$H$_2$) (14). A light yellow solution of mononuclear ethyne complex **11**, after standing at room temperature for 2 days, slowly turns yellow-brown and some polyacetylene deposits. At −78 °C brownish crystals of the dinuclear ethyne complex **13** can be isolated in about 50% yield. Pure yellow crystals of **13** are almost quantitatively accessible by a 1:1 reaction of **11** with either the Pd(II) η^1-allyl complex **1** or an appropriate Pd(0) alkene complex (**3**, **5a,b**, **7–9**) at 0 °C. Similarly, from a 1:1 mixture of mononuclear ^{t}Bu derivative **12** with Pd(0) ethene complex **10** in diethyl ether, the light yellow, dinuclear ethyne complex **14** precipitates as fine needles. **14**

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[21] Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 271.

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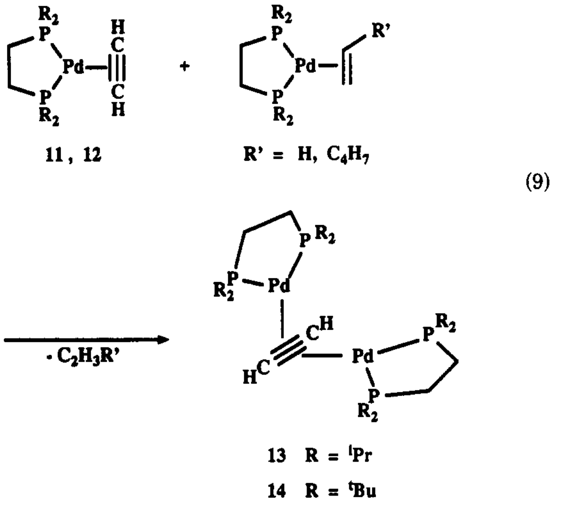
[23] Hodgson, M.; Parker, D.; Taylor, R. J.; Ferguson, G. *J. Chem. Soc., Chem. Commun.* **1987**, 1309.

[24] Paonessa, R. S.; Prignano, A. L.; Trogler, W. C. *Organometallics* **1985**, *4*, 647.

may also be obtained from the reaction of **12** with either **2** or **4**, but a side reaction leads to **6a,b**, which is only slowly converted to **14**. Whereas **13** slowly decomposes at 20 °C, **14** is stable. The latter dissolves poorly in diethyl ether and only slightly in THF.



11, 12   R' = H, C_4H_7 (9)

13 R = ^iPr

14 R = ^tBu

In both **13** and **14**, two (diphosphane)palladium(0) moieties are bound to a bridging ethyne ligand. Both palladium atoms exhibit a trigonal-planar coordination geometry with the coordination planes perpendicular to each other because of the orthogonal ethyne π-orbitals. **13** is analogous to the nickel(0) complex $\{(^iPr_2PC_2H_4P^iPr_2)Ni\}_2(\mu\text{-}C_2H_2)$, whose molecular structure is known.[2] In contrast, **14** was obtained even though its nickel(0) analogue cannot be made.[3] Thus, the binding of the two $(R_2PC_2H_4PR_2)M^0$ moieties to a common ethyne ligand can be accommodated by the large palladium atoms even for the bulky ^{t}Bu substituents, whereas for the smaller nickel atoms steric hindrance prevents this.

The proposed constitution of **13** and **14** is evident from the IR and ^1H, ^{13}C, and ^{31}P NMR spectra. In the IR and Raman spectra of **14**, bands due to C—H and C≡C stretching vibrations of the coordinated ethyne are observed at 3065, 3024, and 1370 cm^{-1}. These assignments were established unequivocally by use of deuterium-labeled $\{(^tBu_2PC_2H_4P^tBu_2)Pd\}_2(\mu\text{-}C_2D_2)$ (**14a**), which shows two C—D stretching modes at 2325 and 2255 cm^{-1} and one C≡C stretching mode at 1320 cm^{-1}. Thus, in the dinuclear ethyne complex **14**, the C—H and C≡C stretching frequencies are markedly lower in comparison to those of mononuclear derivatives **11** and **12**. In the NMR spectra, the μ-ethyne protons of **13** (δ(H) 5.75) and **14** (δ(H) 5.66) give rise to the AA′ portion of an $AA'X_2X'_2$ pattern due to coupling to the phosphorus atoms. Similarly, the ethyne carbon atoms of **13** show a multiplet at δ(C) 67.7 with ^1J(CH) = 200 Hz (cf. $\{(^iPr_2PC_2H_4P^iPr_2)Ni\}_2(\mu\text{-}C_2H_2)$, δ(H) 5.52, δ(C) 86.3, ^1J(CH) = 188 Hz).[2] Both ^1H and ^{13}C resonances of the μ-ethyne ligands are shifted to high field as compared to those of η^2-ethyne derivatives **11** and **12**. For the chelating diphosphanes, the four PCH_2 positions are equivalent but the bent structure of the complexes causes the "inner" and "outer" substituents R at phosphorus to be different. In addition, the methyl groups of the ^{i}Pr substituents in **13** are diastereotopic, so that four methyl resonances result. In the ^{31}P NMR spectra the phosphorus resonances of the dinuclear palladium(0) ethyne compounds **13** (δ(P) 60.2) and **14** (δ(P) 80.0) appear about 10 ppm to high field from the resonances of the mononuclear derivatives **11** and **12** and therefore at an even higher field than those of the ethene complexes **9** and **10**.

Discussion

The purpose of this study was to synthesize palladium(0) ethyne complexes from suitable starting compounds. The only previously reported palladium(0) alkyne complexes contain disubstituted alkynes.[9,24,25]

Synthesis. It has been shown that the palladium(II) η^3-allyl complexes $Pd(\eta^3\text{-}C_3H_5)_2$, $Pd(\eta^3\text{-}2\text{-}MeC_3H_4)_2$, and also $(\eta^5\text{-}C_5H_5)Pd(\eta^3\text{-}C_3H_5)$ may be converted with the bidentate phosphanes $^iPr_2PC_2H_4P^iPr_2$ and $^tBu_2PC_2H_4P^tBu_2$ and ethyne in a "one-pot" reaction to palladium(0) ethyne complexes of type $(R_2PC_2H_4PR_2)Pd(C_2H_2)$ (**11**, **12**; eq 8). $Pd(\eta^3\text{-}2\text{-}MeC_3H_4)_2$ and $(\eta^5\text{-}C_5H_5)Pd(\eta^3\text{-}C_3H_5)$ may be preferred for the "one-pot" synthesis of **11** and **12** because of their easy handling, whereas $Pd(\eta^3\text{-}C_3H_5)_2$ is best suited for mechanistic studies.

A plausible scheme for the synthesis of the ethyne complexes, starting from $Pd(\eta^3\text{-}C_3H_5)_2$ as the source of palladium, proceeds through several intermediates, all of which have been isolated and characterized. At rather low temperatures (<−40 °C), palladium η^1-allyl complexes $(R_2PC_2H_4PR_2)Pd(\eta^1\text{-}C_3H_5)_2$ (**1**, **2**) are initially formed; i.e., at these temperatures $Pd(\eta^3\text{-}C_3H_5)_2$ coordinates the phosphanes but does not yet react with ethyne. At −30 °C or above, these complexes undergo a reductive coupling reaction of the η^1-allyl groups to yield 1,5-hexadiene complexes of palladium(0), in which the palladium atoms are trigonal-planar coordinated by a chelating diphosphane ligand and one alkene double bond. Due to the difunctional character of the diene, these complexes are either mononuclear with one uncoordinated double bond (**3**, **4**) or dinuclear with both double bonds of the bridging diene ligand complexed to different palladium atoms (**5a,b**, **6a,b**). The mono- and dinuclear complexes are easily interconverted by depletion or addition of 1,5-hexadiene. Moreover, the 1,5-hexadiene double bonds coordinated to the $(R_2PC_2H_4PR_2)Pd^0$ fragments are readily exchanged by other olefinic double bonds, such as (a) the uncomplexed double bond of the η^2-coordinated 1,5-hexadiene ligand in **3** and **4** through an intramolecular exchange process, (b) $1,5\text{-}C_8H_{12}$ to yield the corresponding mononuclear (**7**) and dinuclear (**8**) derivatives, or (c) ethene to yield the parent complexes **9** and **10**. Any one of the isolated Pd(II) η^1-allyl (**1**, **2**) or Pd(0) alkene (**3**–**10**) complexes reacts with ethyne to yield the ethyne derivatives **11** and **12**.

The reaction of the Pd(0) alkene complexes with ethyne is a simple displacement of the alkene ligand by an ethyne molecule, while the Pd(II) η^1-allyl complexes first undergo an η^1-allyl coupling reaction with reduction of the palladium to form an intermediate Pd(0) 1,5-hexadiene complex. This reductive-elimination reaction is rate determining and is independent of the presence of ethyne; hence, it is not "ethyne induced". It could be shown by NMR spectroscopy that $(^iPr_2PC_2H_4P^iPr_2)Pd(\eta^1\text{-}C_3H_5)_2$ (**1**) reacts above −30 °C (at −10 °C 50% reaction after 50 min) to form Pd(0) hexadiene complexes **3** and **5a,b**. In the presence of ethyne the disappearance of **1** occurs at the same rate and the ethyne complex **11** and free hexadiene are obtained. Complexes **3** and **5a,b** are not observed, since they react with ethyne instantaneously even at −80 °C, as has been shown separately. Therefore, the formation of the ethyne complexes proceeds formally in a subsequent reaction step, where the intermediately formed Pd(0)

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[25] (a) Greaves, E. O.; Maitlis, P. M. *J. Organomet. Chem.* **1966**, *6*, 104. Greaves, E. O.; Lock, C. J. L.; Maitlis, P. M. *Can. J. Chem.* **1968**, *46*, 3879. Moseley, K.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1974**, 169. (b) Krause, H.-J. *Z. Anorg. Allg. Chem.* **1982**, *490*, 141. (c) Urata, H.; Suzuki, H.; Moro-oka, Y.; Ikawa, T. *J. Organomet. Chem.* **1989**, *364*, 235.

1,5-hexadiene complexes undergo a displacement reaction.

As long as the ethyne concentration is low, it is likely that the formation of the $(R_2PC_2H_4PR_2)Pd(C_2H_2)$ complexes from the Pd(0) alkene precursors involves dinuclear $(R_2PC_2H_4PR_2)Pd^0$ intermediate complexes with a bridging ethyne ligand. Such complexes of type $\{(R_2PC_2H_4PR_2)Pd\}_2(\mu\text{-}C_2H_2)$ (**13**, **14**) are obtainable in a pure state by the stoichiometric interaction of $(R_2PC_2H_4PR_2)Pd$ alkene complexes (or the η^1-allyl analogues) with mononuclear $(R_2PC_2H_4PR_2)Pd(C_2H_2)$ (eq 9).

Spectroscopic Properties. The isolated trigonal-planar $(R_2PC_2H_4PR_2)Pd^0$ alkene complexes exhibit, in their ^1H NMR spectra for the coordinated alkene double bonds, proton signals in the approximate range δ(H) 3.5–2.0, which are at higher field than those of the uncoordinated alkene (cf. ethene, δ(H) 5.40; $(^iPr_2PC_2H_4P^iPr_2)Pd(C_2H_4)$ (**9**), δ(H) 2.30) but at lower field than those of the corresponding nickel(0) complexes ($(^iPr_2PC_2H_4P^iPr_2)Ni(C_2H_4)$, δ(H) 1.74).[2] Comparison of the IR data reveals that the C—H and C=C stretching vibrations of the alkene ligands (**9**, ν(C—H) 3045 cm^{-1}, ν(C=C) 1572 cm^{-1}) are not as strongly shifted to higher wavelengths as in the nickel(0) compounds ($(^iPr_2PC_2H_4P^iPr_2)Ni(C_2H_4)$, ν(C—H) 3020 cm^{-1}, ν(C=C) 1530 cm^{-1}).[2] These observations are in accord with the anticipated lower back-bonding ability of palladium(0), as compared to that of nickel(0), into acceptor orbitals of π-bonded ligands.

For the mononuclear $(R_2PC_2H_4PR_2)Pd^0$ ethyne complexes, the ethyne protons give rise to a signal at about δ(H) 6.9, which is between that observed for unbound ethyne (δ(H) 2.40) and the corresponding $(R_2PC_2H_4PR_2)Ni^0$ complexes (δ(H) 7.3). The deshielding of the ethyne ligand protons reflects the lower bond order of the original triple bond when coordinated to palladium(0) or nickel(0) and can be explained by a vinylic proton character (cf. cyclopropene, δ(H) 7.01). In contrast, coordination of an additional palladium or nickel atom to a palladium(0) or nickel(0) ethyne complex causes a high-field shift, an effect which is slightly smaller for palladium(0) (**13**, δ(H) 5.75) than for nickel(0) ($\{(^iPr_2PC_2H_4P^iPr_2)Ni\}_2(\mu\text{-}C_2H_2)$, δ(H) 5.52),[2] resulting in similar δ values for $\{(R_2PC_2H_4PR_2)M\}_2(\mu\text{-}C_2H_2)$ complexes (M = Ni, Pd). Similarly, the ethyne carbon atoms (unbound ethyne, δ(C) 71.9, $^1J(CH)$ = 259 Hz) are deshielded in the mononuclear palladium(0) complexes (**12**, δ(C) 105.1, $^1J(CH)$ = 211 Hz), but to a lesser extent than in the nickel(0) analogues ($(^iPr_2PC_2H_4P^iPr_2)Ni(C_2H_2)$, δ(C) 123.8, $^1J(CH)$ = 202 Hz). In contrast, for the dinuclear complexes of both palladium(0) (**13**, δ(C) 67.7, $^1J(CH)$ = 200 Hz) and nickel(0) ($\{(^iPr_2PC_2H_4P^iPr_2)Ni\}_2(\mu\text{-}C_2H_2)$, δ(C) 86.3, $^1J(CH)$ = 188 Hz), the μ-C_2H_2 resonances are shifted equally (37 ppm) to high field. This shift observed for the μ-C_2H_2 protons and carbon atoms is explained by a further reduction of the bond order, now formally from double- to single-bond character, so that the signals are shifted in the direction typical for coordinated alkenes and for alkanes. The reduction of the bond order is, moreover, reflected by a steady decrease in the C,H coupling constant, although this reduction is less pronounced for palladium than for nickel, and is accompanied by a steady decrease in the C≡C stretching frequencies (**11**, ν(C≡C) 1619 cm^{-1}; **14**, ν(μ-C≡C) 1370 cm^{-1}; $(^iPr_2PC_2H_4P^iPr_2)Ni(C_2H_2)$, ν(C≡C) 1598 cm^{-1}; $\{(^iPr_2PC_2H_4P^iPr_2)Ni\}_2(\mu\text{-}C_2H_2)$, ν(μ-C≡C) 1315 cm^{-1}).[2]

Essentially the same trends are reflected in the ^{31}P NMR spectra. The $(R_2PC_2H_4PR_2)Pd^0$ alkene complexes show phosphorus resonances of about δ(P) 60 (R = ^iPr) or 83 (R = ^tBu). For the ethyne derivatives these resonances are shifted downfield (**11**, δ(P) 69.5; **12**, δ(P) 91.3), consistent with a diminution of charge at the phosphorus atoms due to a stronger back-bonding from palladium to the ethyne than to an alkene ligand. Coordination of a second $(R_2PC_2H_4PR_2)Pd^0$ fragment to ethyne causes an opposite shift (**13**, δ(P) 59.9; **14**, δ(P) 80.0) to a value below those typical for the palladium(0) alkene complexes. This behavior parallels that of the corresponding nickel complexes ($(^iPr_2PC_2H_4P^iPr_2)Ni(C_2H_4)$, δ(P) 73.4; $(^iPr_2PC_2H_4P^iPr_2)Ni(C_2H_2)$, δ(P) 82.3; $\{(^iPr_2PC_2H_4P^iPr_2)Ni\}_2(\mu\text{-}C_2H_2)$, δ(P) 69.2),[2] for which the differences are greater.

Chemical Properties. Even though $^iPr_2PC_2H_4P^iPr_2$ and $^tBu_2PC_2H_4P^tBu_2$ exhibit largely different ligand properties with respect to nickel(0),[2,3] the properties these ligands induce to palladium(0,II) complexes are less distinguishing. In this study, essentially the same types of palladium(0,II) complexes could be realized for both phosphanes. Nevertheless, each ligand turned out to show its own character. In the case of ^iPr derivatives generally excellent solubility is found, which is advantageous for NMR studies, especially at low temperature. On the other hand, the lower solubility of the ^tBu derivative complexes simplifies isolation. The ^tBu derivative complexes are thermally more stable than the ^iPr analogues.

Owing to the larger bulk of the ^tBu phosphane ligand, (a) the double-bond exchange process of the $(R_2PC_2H_4PR_2)Pd(\eta^2\text{-}C_6H_{10})$ complexes (**3**, **4**) is slower for the ^tBu derivative **4**, for which it has been possible to "freeze out" the ground-state conformation by low-temperature NMR spectroscopy and (b) the conversion of the ethyne complexes $(R_2PC_2H_4PR_2)Pd(C_2H_2)$ (**11**, **12**) into the dinuclear compounds $\{(R_2PC_2H_4PR_2)Pd\}_2(\mu\text{-}C_2H_2)$ (**13**, **14**) proceeds significantly slower (20 °C) for the ^tBu derivative **12** than for the ^iPr derivative **11**.

Experimental Section

To exclude oxygen and moisture, all operations were conducted under an atmosphere of argon by means of the Mülheim open-bench technique with Schlenk-type glassware. $\{(\eta^3\text{-}C_3H_5)PdCl\}_2$,[10b] $^iPr_2PC_2H_4P^iPr_2$,[26] and $^tBu_2PC_2H_4P^tBu_2$[3] were prepared by published procedures. Microanalyses were performed by the Mikroanalytisches Labor Dornis und Kolbe, Mülheim a.d. Ruhr, Germany. ^1H NMR spectra were measured at 200 and 400 MHz on Bruker AM-200 and WH 400 instruments (relative to internal TMS), ^{13}C NMR spectra at 75.5 MHz on a Bruker WM-300 instrument (relative to internal TMS), and ^{31}P NMR spectra at 81.0 MHz on a Bruker AM-200 instrument (relative to external 85% aqueous H_3PO_4). For all NMR spectra solutions of the compounds in THF-d_8 were used.

$\{(\eta^3\text{-}2\text{-}MeC_3H_4)PdCl\}_2$[27] is prepared in analogy to $\{(\eta^3\text{-}C_3H_5)PdCl\}_2$ from Na_2PdCl_4 (29.5 g, 0.1 mol), 2-methallyl chloride (36 g, 0.4 mol), and CO in methanol/water: yellow crystals; yield 18.3 g (93%).

$Pd(\eta^3\text{-}C_3H_5)_2$ (According to Ref 9). A solution of $(C_3H_5)MgCl$ (110 mmol) in diethyl ether (270 mL) is slowly added to a magnetically stirred suspension of $\{(\eta^3\text{-}C_3H_5)PdCl\}_2$ (18.3 g, 50 mmol) in diethyl ether (70 mL) below −50 °C. The reaction mixture is stirred for 12 h at −78 °C and the solvent removed at −50 °C under reduced pressure to give a brownish solid. $Pd(\eta^3\text{-}C_3H_5)_2$ is isolated by high-vacuum sublimation at 0 °C as a light-yellow crystalline solid, yield 14.0 g (74%).

$Pd(\eta^3\text{-}2\text{-}MeC_3H_4)_2$ (According to Ref 9). The methallyl complex was prepared analogously to $Pd(\eta^3\text{-}C_3H_5)_2$ from $\{(\eta^3\text{-}2\text{-}MeC_3H_4)PdCl\}_2$ (19.7 g, 50 mmol) and $(2\text{-}MeC_3H_4)MgCl$ (110

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mmol) in a total volume of 400 mL of diethyl ether. The product sublimes from a cream-colored residue: yellow crystals; yield 17.3 g (80%).

$({}^iPr_2PC_2H_4P{}^iPr_2)Pd(\eta^1\text{-}C_3H_5)_2$ (1) (in Analogy to Ref 9). A solution of $^iPr_2PC_2H_4P^iPr_2$ (2.62 g, 10.0 mmol) in ether (10 mL) is added to a light yellow suspension of $Pd(\eta^3\text{-}C_3H_5)_2$ (1.89 g, 10.0 mmol) in ether (20 mL) at -78 °C. The reaction mixture is allowed to reach -50 to -40 °C and is stirred for 30 min at this temperature. During the course of the reaction the product precipitates from an intermediately homogeneous bright yellow reaction mixture as a cream-colored solid. The fine crystalline product is filtered off at -78 °C, washed twice with cold ether, and dried below -40 °C under high vacuum for several hours; yield 4.06 g (90%). Anal. Calcd for $C_{20}H_{42}P_2Pd$ (450.9): C, 53.28; H, 9.39; P, 13.74; Pd, 23.60. Found: C, 53.18; H, 9.45; P, 13.68; Pd, 23.64. ^{1}H NMR (200 MHz, -30 °C): δ 6.18 (m, 2 H, $=$CH–), 4.53 (m, 2 H, $=CH_ZH$), 4.12 (m, 2 H, $=CHH_E$), 2.15 (m, 4 H, $PdCH_2$–; allyl); δ 2.32 (m, 4 H, PCH), 1.71 (m, 4 H, PCH_2), 1.14, 1.10 (each m, 12 H, CH_3; phosphane). ^{31}P NMR (-30 °C): δ 66.8.

$({}^tBu_2PC_2H_4P{}^tBu_2)Pd(\eta^1\text{-}C_3H_5)_2$ (2) (in Analogy to Ref 9). A suspension of $Pd(\eta^3\text{-}C_3H_5)_2$ (1.89 g, 10.0 mmol) in diethyl ether (40 mL) is combined with an ethereal solution (30 mL) of $^tBu_2PC_2H_4P^tBu_2$ (3.18 g, 10.0 mmol) at -60 °C. When the mixture is stirred, a light yellow solution results, from which the microcrystalline product precipitates. After the mixture is stirred at -50 °C for 30 min to complete the reaction, the product is filtered off at -78 °C, washed twice with cold ether, and dried under high vacuum at -40 °C; yield 4.66 g (92%). Anal. Calcd for $C_{24}H_{50}P_2Pd$ (507.0): C, 56.86; H, 9.94; P, 12.22; Pd, 20.99. Found: C, 56.70; H, 10.24; P, 12.09; Pd, 20.91. ^{1}H NMR (200 MHz, -30 °C): δ 6.24 (m, 2 H, $=$CH–), 4.67 (m, 2 H, $=CH_ZH$), 4.25 (m, 2 H, $=CHH_E$), 2.45 (m, 4 H, $PdCH_2$–; allyl); δ 1.84 ("q", 4 H, PCH_2), 1.31 (d, 36 H, CH_3; phosphane). ^{31}P NMR (-30 °C): δ 72.5.

$({}^iPr_2PC_2H_4P{}^iPr_2)Pd(\eta^2\text{-}C_6H_{10})$ (3). A suspension of 1 (902 mg, 2.00 mmol) in cold 1,5-hexadiene (2 mL) is warmed from -30 to +20 °C, whereupon 1 dissolves completely. After 1 h the pale greenish yellow solution is cooled to -78 °C and pentane (2 mL) is added. At -78 °C colorless crystals slowly (2 days) separate, from which the mother liquor is siphoned off by means of a capillary. The product is washed with cold pentane and dried under high vacuum at -78 °C; yield 695 mg (77%). Anal. Calcd for $C_{20}H_{42}P_2Pd$ (450.9): C, 53.28; H, 9.39; P, 13.74; Pd, 23.60. Found: C, 53.36; H, 9.48; P, 13.71; Pd, 23.49. IR (KBr, -60 °C): 3074, 1639, 994, 904 cm^{-1} (uncomplexed); 3025, ~1200 cm^{-1} (complexed vinylic group). ^{1}H NMR (200 MHz, -30 °C): δ 4.63 (m, 2 H, $=$CH–), 3.60 (d, 2 H, $=CH_ZH$), 3.57 (d, 2 H, $=CHH_E$), 2.02 (m, 4 H, –CH_2–; alkene); δ 2.00 (m, 4 H, PCH), 1.62 (m, 4 H, PCH_2), 1.07, 0.99 (each m, 12 H, CH_3; phosphane). The ^{1}H NMR signals (200 and 400 MHz) are broad at lower temperatures (down to -100 °C). ^{31}P NMR: δ 60.1 (-30 °C); δ 61.5, 58.9 (unresolved AB spectrum) (-110 °C).

$({}^tBu_2PC_2H_4P{}^tBu_2)Pd(\eta^2\text{-}C_6H_{10})$ (4). The yellowish suspension of 2 (1.014 g, 2.00 mmol) in 1,5-hexadiene (2 mL) is warmed slowly from -30 to +20 °C. The complex dissolves exothermally to afford a red-brown solution, from which beige crystals separate at -78 °C. The crystals are freed from the mother liquor by means of a capillary, washed twice with cold pentane, and dried under high vacuum at -40 °C: yield 780 mg (77%); dec pt >220 °C. Anal. Calcd for $C_{24}H_{50}P_2Pd$ (507.0): C, 56.86; H, 9.94; P, 12.22; Pd, 20.99. Found: C, 56.92; H, 10.27; P, 12.03; Pd, 20.84. IR (KBr): 3072, 1641, 994, 902 cm^{-1} (uncomplexed); 3026, 1234, 1210 cm^{-1} (complexed vinylic group). MS (70 eV, 45 °C): *m/e* 506 (M^+, 0.06), 424 ($[M - C_6H_{10}]^+$, 1.6 relative intensity). ^{1}H NMR (400 MHz, -80 °C): δ 5.85 (m, 1 H, $=$CH– unbound), 4.94 (d, 1 H, $=CH_ZH$ unbound), 4.85 (d, 1 H, $=CHH_E$ unbound), 3.26 (broad, 1 H, $=$CH– bound), 2.40 (broad, 1 H, $=CHH_E$ bound), 2.36 (broad, 1 H, $=CH_ZH$ bound), 2.38, 2.17, 2.10, 1.47 (each 1 H, –CH_aH_b–, –$C'H_aH_b$–; alkene); δ 1.80, 1.70 (each m, 2 H, PCH_aH_b and $P'C'H_aH_b$), 1.2 (four unresolved signals, 36 H, $C(CH_3)_3$; phosphane). ^{1}H NMR (200 MHz, 27 °C): δ 4.64 (broad, 2 H, $=$CH–), 3.70 (broad, 4 H, $=CH_2$), 2.09 (broad, 4 H, –CH_2–; alkene); δ 1.76 (m, 4 H, PCH_2), 1.20 (m, 36 H, $C(CH_3)_3$; phosphane). ^{31}P NMR: δ 82.0 (d), 79.5 (d), J(PP) = 70.4 Hz (AB) (-80 °C); δ 81.4 (27 °C).

***rac*-/*meso*-$\{({}^iPr_2PC_2H_4P{}^iPr_2)Pd\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_{10})$ (5a,b).** 1 (902 mg, 2.00 mmol) suspended in pentane (20 mL, -30 °C) affords a yellow-green solution at -20 °C and a yellow-orange reaction solution at 20 °C. When part of the solvent is evaporated, a precipitate is formed, which is isolated by filtration and recrystallized from pentane to yield orange crystals, which after drying in vacuo turn beige; yield 492 mg (60%). Anal. Calcd for $C_{34}H_{74}P_4Pd_2$ (819.7): C, 49.82; H, 9.10; P, 15.12; Pd, 25.96. Found: C, 48.68; H, 8.83; P, 14.85; Pd, 25.46. IR (KBr): 3026, 1205, 1188 cm^{-1} (complexed vinylic group). ^{1}H NMR (200 MHz, -30 °C): δ 3.47 (2 H, $=$CH–), 2.39 (4 H, $=CH_ZH_E$), 2.0 (4 H, –CH_2–; alkene); δ 2.0 (8 H, PCH), 1.6 (8 H, PCH_2), 1.0 (48 H, CH_3; phosphane); signals not resolved due to a mixture of stereoisomers. ^{31}P NMR (-30 °C; two AB systems of isomeric compounds): δ 61.1, 57.4, J(PP) = 70.5 Hz; δ 60.8, 57.3, J(PP) = 70.5 Hz.

***rac*-/*meso*-$\{({}^tBu_2PC_2H_4P{}^tBu_2)Pd\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_{10})$ (6a,b).** A yellowish suspension of 2 (1.014 g, 2.00 mmol) in THF (7 mL, -30 °C) is warmed to 20 °C to afford an orange-yellow solution, which is kept at this temperature for 2 h. At 0 °C within 24 h beige crystals precipitate, which are freed from the mother liquor by means of a capillary, washed twice with cold pentane, and dried under vacuum; yield 485 mg (52%). Anal. Calcd for $C_{42}H_{90}P_4Pd_2$ (931.9): C, 54.13; H, 9.73; P, 13.30; Pd, 22.84. Found: C, 53.94; H, 9.94; P, 13.20; Pd, 22.86. IR (KBr): 1238, 1217 cm^{-1} (complexed vinylic group). ^{1}H NMR (400 MHz, 27 °C): δ 3.50 (2 H, $=$CH–), 2.50 (4 H, $=CH_ZH_E$), ca. 1.75 (4 H, –CH_2–; alkene); δ ca. 1.75 (8 H, PCH_2), 1.18 (72 H, CH_3; phosphane); signals not resolved due to a mixture of stereoisomers. ^{31}P NMR (27 °C; two AB systems of isomeric compounds): δ 82.0, 79.6, J(PP) = 81.0 Hz; δ 81.9, 79.6, J(PP) = 81.0 Hz.

$({}^iPr_2PC_2H_4P{}^iPr_2)Pd(\eta^2\text{-}C_8H_{12})$ (7). 1,5-C_8H_{12} (2 mL) is added to 1 (902 mg, 2.0 mmol) at -30 °C, and the reaction mixture is warmed to 20 °C to yield a yellow solution of the complex, which has not been isolated. ^{31}P NMR (27 °C): δ 57.4.

$\{({}^iPr_2PC_2H_4P{}^iPr_2)Pd\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_8H_{12})$ (8). From the 1,5-C_8H_{12} solution of 7, the volatile components are evaporated under vacuum at 20 °C, and the resulting solid is treated with pentane, isolated by filtration, and dried under vacuum at 20 °C; yield 790 mg (93%). Anal. Calcd for $C_{36}H_{76}P_4Pd_2$ (845.7): C, 51.13; H, 9.06; P, 14.65; Pd, 25.16. Found: C, 51.45; H, 9.21; P, 14.06; Pd, 23.86. IR (KBr): 1548, 1436, ca. 780 (overlapped) cm^{-1} (complexed 1,5-C_8H_{12}). ^{1}H NMR (200 MHz, -30 °C): δ 3.70 (m, 4 H, $=$CH–), 2.58 (m, 4 H, –CH_aH–), 1.9 (m, 4 H, –CHH_b–; alkene); δ 1.9 (m, 8 H, PCH and PCH′), 1.57 (m, 8 H, PCH_2), 1.0 (m, 48 H, CH_3 and CH_3'; phosphane). ^{31}P NMR (-30 °C): δ 57.9.

$({}^iPr_2PC_2H_4P{}^iPr_2)Pd(C_2H_4)$ (9). A suspension of 1 (451 mg, 1.00 mmol) in diethyl ether (10 mL) is saturated with ethene at -60 °C, and the mixture slowly warmed. At -30 °C a clear greenish yellow solution is obtained, which becomes almost colorless at 20 °C. When the mixture is cooled to -78 °C, colorless crystals slowly separate, and the reaction mixture is further concentrated under vacuum. The crystals are isolated by means of a capillary, washed with cold ether, and dried under high vacuum at -78 °C; yield 246 mg (62%). Anal. Calcd for $C_{16}H_{36}P_2Pd$ (396.8): C, 48.43; H, 9.14; P, 15.61; Pd, 26.81. Found: C, 48.58; H, 9.23; P, 15.48; Pd, 26.59. IR (KBr): 3045 cm^{-1} (ν(=C—H)); 1572, 1179 cm^{-1} (ν(C=C), $\delta(CH_2)$). ^{1}H NMR (200 MHz, 27 °C): δ 2.30 (d, 4 H, J(PH) = 1.8 Hz; C_2H_4); δ 2.00 (m, 4 H, PCH), 1.67 (m, 4 H, PCH_2), 1.08, 1.00 (each m, 12 H, CH_3; phosphane). ^{31}P NMR (27 °C): δ 62.7.

$({}^tBu_2PC_2H_4P{}^tBu_2)Pd(C_2H_4)$ (10). A yellowish suspension of 2 (1.014 g, 2.00 mmol) in diethyl ether (20 mL) is saturated with ethene at -30 °C. When the mixture is warmed to 20 °C, a yellow-brown solution is obtained, from which large tan needles separate at -30 °C. After the mother liquor is siphoned off, the crystals are washed with cold ether and dried under high vacuum at -30 °C; yield 760 mg (84%). Anal. Calcd for $C_{20}H_{44}P_2Pd$ (452.9): C, 53.04; H, 9.79; P, 13.68; Pd, 23.49. Found: C, 52.80; H, 9.75; P, 13.70; Pd, 23.71. IR (KBr): 3035 cm^{-1} (ν(=C—H)), 1572, 1175 cm^{-1} (ν(C=C), $\delta(CH_2)$). ^{1}H NMR (200 MHz, 27 °C): δ 2.41 (d, 4 H, C_2H_4); δ 1.81 (m, 4 H, PCH_2), 1.20 (m, 36 H, CH_3; phosphane). ^{31}P NMR (27 °C): δ 84.8.

$({}^iPr_2PC_2H_4P{}^iPr_2)Pd(C_2H_2)$ (11). To a suspension of 1 (902 mg, 2.00 mmol) in diethyl ether (10 mL) is added ethyne gas (100 mL) in excess at -78 °C and the reaction mixture slowly warmed to 0 °C. A greenish yellow solution then forms, which fades to almost colorless when kept at 0 °C for 30 min. At -78 °C colorless crystals separate (1 day), from which the supernatant liquid is removed by capillary. The product is washed with two portions of cold diethyl ether and dried under vacuum at −30 °C: yield 690 mg (87%). Anal. Calcd for $C_{16}H_{34}P_2Pd$ (394.8): C, 48.68; H, 8.68; P, 15.69; Pd, 26.95. Found: C, 48.38; H, 8.70; P, 15.61; Pd, 27.18. IR (KBr, −30 °C): 3125, 3085 cm^{-1} (≡C—H bound), 1619 cm^{-1} (C≡C bound). ^{1}H NMR (200 MHz, −30 °C): δ 6.91 (m, 2 H, C_2H_2); δ 2.02 ("octet", 4 H, PCH), 1.67 (m, 4 H, PCH_2), 1.11, 1.01 (each m, 12 H, CH_3; phosphane). ^{31}P NMR (−30 °C): δ 69.5.

$(^iPr_2PC_2H_4P^iPr_2)Pd(C_2D_2)$ (11a): synthesis as for 11 but with C_2D_2.

$(^tBu_2PC_2H_4P^tBu_2)Pd(C_2H_2)$ (12). When a suspension of 4 (1.014 g, 2.00 mmol) in diethyl ether (20 mL), containing dissolved ethyne (100 mL) in excess, is warmed from −30 to 0 °C, cooled to −30 °C, and cooled further to −78 °C, colorless crystals form. After the supernatant liquid is removed through a capillary, the crystals are washed with cold ether and dried under vacuum at −30 °C; yield 810 mg (90%). Anal. Calcd for $C_{20}H_{42}P_2Pd$ (450.9): C, 53.28; H, 9.39; P, 13.74; Pd, 23.60. Found: C, 52.88; H, 9.67; P, 13.61; Pd, 23.78. IR (KBr): 3125 cm^{-1} (≡C—H bound), 1626 cm^{-1} (C≡C bound). ^{1}H NMR (400 MHz, 27 °C): δ 6.78 (m, 2 H, C_2H_2); δ 1.80 (m, 4 H, PCH_2), 1.23 (m, 36 H, CH_3; phosphane). ^{13}C NMR (75.5 MHz, −30 °C): δ 105.1 (m, 2 C, ^1J(CH) = 211 Hz, C_2H_2); δ 34.3 ("t", 4 C, $PCMe_3$), 30.6 (m, 12 C, CH_3), 24.5 (m, 2 C, PCH_2; phosphane). ^{31}P NMR (27 °C): δ 91.3.

$(^tBu_2PC_2H_4P^tBu_2)Pd(C_2D_2)$ (12a): synthesis as for **12** but with C_2D_2. IR (KBr): 2418 cm^{-1} (≡C—D bound), 1531 cm^{-1} (C≡C bound).

$\{(^iPr_2PC_2H_4P^iPr_2)Pd\}_2(\mu\text{-}C_2H_2)$ (13). A solution of the ethyne complex **11** (790 mg, 2.00 mmol) in diethyl ether (20 mL) is added at −50 °C to solid 1 (902 mg, 2.00 mmol). The suspension is warmed to 20 °C, whereupon an intensely yellow reaction solution slowly develops (2 h). At −78 °C, yellow crystals deposit. The supernatant liquid is removed by capillary and the product washed with cold diethyl ether and dried under vacuum at −30 °C; yield 1.51 g (99%). Anal. Calcd for $C_{30}H_{66}P_4Pd_2$ (763.6): C, 47.19; H, 8.71; P, 16.23; Pd, 27.87. Found: C, 47.21; H, 8.83; P, 16.18; Pd, 27.74. Raman: 1370 cm^{-1} (μ-C≡C, bound). ^{1}H NMR (400 MHz, 27 °C): δ 5.75 (m, 2 H, μ-C_2H_2); δ 1.89, 1.93 (each 4 H, PCH and PCH′), 1.49 (8 H, PCH_aH_b), 1.18, 1.08, 1.03, 0.99 (each 12 H, CH_3; phosphane). ^{13}C NMR (75.5 MHz, −30 °C): δ 67.7 (m, 2 C, ^1J(CH) = 200 Hz, μ-C_2H_2); δ 26.1, 25.9 (each m, 4 C, PCH and PC′H), 21.1, 20.2, 19.4, 18.7 (each m, 4 C, CH_3), 22.7 (m, 4 C, PCH_2; phosphane). ^{31}P NMR (−30 °C): δ 59.9.

$\{(^iPr_2PC_2H_4P^iPr_2)Pd\}_2(\mu\text{-}C_2D_2)$ (13a): synthesis as for **13** but with **11a**. IR (KBr): 1316 cm^{-1} (μ-C≡C, bound).

$\{(^tBu_2PC_2H_4P^tBu_2)Pd\}_2(\mu\text{-}C_2H_2)$ (14). Solutions of the ethyne complex **12** (451 mg, 1.00 mmol) and the ethene complex **10** (453 mg, 1.00 mmol) in diethyl ether (each 15 mL) are combined at 20 °C. Within 2 days light yellow needles crystallize. The supernatant liquid is removed by capillary and the product washed with diethyl ether and dried under vacuum; yield 725 mg (80%). Anal. Calcd for $C_{38}H_{82}P_4Pd_2$ (875.8): C, 52.12; H, 9.44; P, 14.15; Pd, 24.30. Found: C, 52.08; H, 9.54; P, 14.11; Pd, 24.21. IR (KBr) and Raman: 3065, 3024 cm^{-1} (≡C—H, bound), 1370 cm^{-1} (C≡C bound). ^{1}H NMR (400 MHz, 27 °C): δ 5.66 (m, 2 H, μ-C_2H_2); δ 1.67 (8 H, PCH_aH_b), 1.26, 1.21 (each 36 H, $C(CH_3)_3$ and $C'(CH_3)_3$; phosphane). ^{31}P NMR (27 °C): δ 80.0.

$\{(^tBu_2PC_2H_4P^tBu_2)Pd\}_2(\mu\text{-}C_2D_2)$ (14a): synthesis as for **14** but with **12a**. IR (KBr) and Raman: 2325, 2255 cm^{-1} (≡C—D, μ-bound), 1320 cm^{-1} (C≡C, μ-bound).

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η^2-(C,O) Ketene Coordination at Nickel(0). Synthesis, Bonding, and Molecular Structure of (dtbpm)Ni[η^2-(*C*,*O*)-Ph_2C_2O][†]

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Qualitative electronic structure considerations and MO model calculations are presented, which predict η^2-(C,O) coordination to be preferred over η^2-(C,C) coordination for ketene complexes of P_2Ni^0 and P_2Pt^0 (d^{10}) bis(phosphane) metal fragments. The relative energetic preference for an η^2-(C,O)-bonding mode of ketenes is shown to increase with a decreasing P–M–P angle. Bis(di-*tert*-butylphosphino)methane ($^tBu_2PCH_2P^tBu_2$, dtbpm) is a tailor-made chelating bis(phosphane) ligand, which allows one to realize P–Ni–P angles below 80° within four-membered NiPCP chelate rings. Starting from the stilbene complex (dtbpm)Ni(η^2-*trans*-PhCH═CHPh) (**25**), the 14-electron intermediate [(dtbpm)Ni^0] could be generated and trapped by diphenylketene to yield the η^2-(C,O)-coordinated diphenylketene complex (dtbpm)Ni-[η^2-(*C*,*O*)-Ph_2C_2O] (**30**), which has been characterized spectroscopically and by X-ray diffraction. Crystals of compound **30**·C_6D_6 ($C_{31}H_{48}OP_2Ni\cdot C_6D_6$) are monoclinic, space group $P2_1/n$, with a = 11.957 (2) Å, b = 14.911 (2) Å, c = 20.111 (2) Å, β = 99.73 (1)°, V = 3534.0 Å^3, and Z = 4. The molecular structure of **30** provides the first example of a nickel triad ketene complex, for which ketene to metal bonding has been established unequivocally. Its η^2-(C,O) geometry is in accord with EH model calculations for Ni and Pt, but it contrasts ab initio results for analogous platinum systems reported in the literature and may have interesting consequences for understanding reactivity patterns of d^{10}-ML_2 ketene complexes (M = Ni(0), Pd(0), Pt(0)).

Introduction

Transition-metal complexes with ketene ligands have found much attention in recent years, and their chemistry has been extensively reviewed by Geoffroy and Bassner.[1] To a large part the impetus to synthesize and to study transition-metal ketene complexes comes from the assumption that they might play an important role as model compounds for homogenous or heterogeneous Fischer–

[†] Dedicated to Prof. Wolfgang Beck on the occasion of his 60th birthday.

(1) Geoffroy, G. L.; Bassner, S. L. *Adv. Organomet. Chem.* **1988**, *28*, 1.

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