1 two iodine atoms (I(1) and I(3)) and one sulfur atom form the threefold coordination sphere, whereas for layer 2 copper is surrounded by two sulfur and only one iodine atom (I(4)). The central I(2) of layer 2 does not bond to three-coordinate copper. This fact and the well known flexibility of copper with respect to its trigonal or tetrahedral environment[20] can be regarded as the reason for the pronounced disorder of the copper atoms. Thus, several tetrahedral voids are partly occupied (Figure 3 right). The composition of these tetrahedra and their linkage is different for the two iodine layers. Around layer 1 they consist of one S, one I(1), and two I(3) atoms. These tetrahedra are linked through a common face to form trigonal bipyramids, in which copper partially occupies two positions. The bipyramids are linked through common corners. Around layer 2 the tetrahedral voids are built up by two S and two I atoms (I(2), I(4)). These tetrahedra share common edges (I(2), S(2)) and common corners. Temperature-dependent structure analyses and thermoanalytical investigations are in progress to check whether the disorder of copper in the title compound is dynamic in nature.

A fourfold, almost planar coordination by copper with distances $d(\mathrm{I(2)-Cu}) \approx 2.76$ Å is found for I(2). This results in channels in the crystal structure of $(CuI)_3Cu_2TeS_3$, in which one expects the lone pairs of the Te^{4+} ions to be situated (Figure 3 right).

Due to the strong two-dimensional character of $(CuI)_3Cu_2TeS_3$ this compound can be regarded as a composite material of the hitherto unknown Cu_2TeS_3 and CuI. Only one compound of similar composition, namely $Cu_{17.6}Te_8S_{26}$[21] $\approx 8 \times Cu_2TeS_3$, is known; however, it has a completely different structure that is closely related to that of the tetrahedrite type.[22]

We have some experimental evidence for the existence of similar compounds $(CuI)_nCu_mM^{(6-m)+}S_3$, with M for example As, Sb. Given that these colored materials also crystallize in acentric space groups interesting physical properties are to be expected.

Experimental Section

Pure $(CuI)_3Cu_2TeS_3$ was prepared by reaction of stoichiometric amounts of CuI, Cu, Te, and S (CuI:Cu:Te:S = 3:2:1:3) in evacuated quartz ampoules. After a period of 7 d at a temperature of 400 °C, black shiny hexagonal platelets with edges of up to 3 mm were obtained. The samples were characterized by powder X-ray diffraction and FT-IR spectroscopy. In addition to the characteristic vibrations of the $[TeS_3]^{2-}$ ion at 330 (s) and 374 (w) cm^{-1} a very broad band was observed around 125 cm^{-1}, which is probably to be assigned to Cu–I vibrations. From selected crystals the composition was determined by semiquantitative EDX analyses (EDX = energy dispersive X-ray analysis): Cu:I:Te:S = 0.40:0.23:0.09:0.28 (calc: 0.417:0.250:0.083:0.250).

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Intermediates in the Intermolecular, Asymmetric Heck Arylation of Dihydrofurans**

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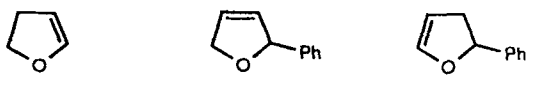
We recently reported the observation of a reactive alkylpalladium intermediate in the arylation of methyl acrylate with aryl triflates and its relationship to earlier and later species in the catalytic cycle.[1] This encouraged us to turn our attention to the intermolecular, asymmetric Heck reaction in the hope of gaining insight into the mechanism and origin of stereoselectivity.[2]

The most impressive examples in this class remain the arylation of dihydrofuran catalyzed by Pd–BINAP complexes discovered by Hayashi, Ozawa, and co-workers[3] and a series of closely related reactions. A consistent feature of this work, noted earlier by Larock et al.,[4] is the requirement for double-bond isomerization to release Pd and regenerate the catalyst. For phenylation of 2,3-dihydrofuran (**1**), this can lead to the 2,5-dihydrofuran **2** or to the doubly isomerized 2,3-dihydrofuran **3**. Characteristic of Hayashi's asymmetric synthesis is that the



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product ratio and *ee* values depend on a subtle interplay of catalyst precursor, solvent, and base, in which the predominant product **3** gains in enantiomeric enrichment at the expense of the singly isomerized product **2** as the yield of the latter increases.[5] With diphenylphosphinoaryloxazoline ligands,[6] high *ee* values are obtained but arylated 2,5-dihydrofuran is the predominant product.

Following the protocols of earlier work[1] the aryl triflate **4a**, derived from (*S*)-BINAP ($\delta_P = 14.6$, 34.6; $J(P,P) = 35$ Hz; Scheme 1) was allowed to react with 2,3-dihydrofuran in THF at -70 to $-40\,^{\circ}C$. The reaction was followed by ^{31}P NMR spectroscopy (Figure 1). A single, new species **5a** was cleanly formed ($\delta_P = 22.5$, 37.0; $J(P,P) = 31$ Hz), which was stable in this temperature range but slowly decomposed at $-30\,^{\circ}C$ to form **6a** ($\delta_P = 22.4$, 38.7; $J(P,P) = 34$ Hz) and **6a'** ($\delta_P = 19.4$, 37.8; $J(P,P) = 27$ Hz), each associated with two low-field protons in the ^1H NMR spectrum, in comparable amounts with concomitant release of (*S*)-2-phenyl-2,3-dihydrofuran (**3**, 91 %*ee*). With the aid of electrospray mass spectrometry **5a** was identified as the formal product of Pd–Ph addition to the dihydrofuran (*m/z* 876), and **6a** and **6a'** as the products of addition of Pd–H to the dihydrofuran (*m/z* 800).

The structure of the first intermediate **5a** was determined by one- and two-dimensional NMR techniques and corroborated by a parallel reaction between **4a** and [2-D]**1**.[7] At $-35\,^{\circ}C$ the ^1H NMR displays six different, highly coupled, multiplet signals, each integrating for one proton. Connectivities between these protons and the carbon skeleton were established by TOCSY as well as phase-sensitive DQFCOSY and HMQC. Remarkably, the Pd atom has migrated from its original position at C3 by a double dyotropic shift, which must occur intramolecularly since there is no exchange with excess **1**. A complete assignment is as follows. Two low-field proton signals are observed. The ABX multiplet centered at $\delta = 5.5$ is assigned to H5 since it is absent in the sample generated from [2-D]**1**; the resonance at $\delta = 5.3$ is due to H2. The ^{13}C chemical shift of C2 is at very low field for a carbon atom that is σ-bonded to a metal center and implies significant oxonium ion character, as in **7**. The lack of large coupling of H2 to either proton on C3 is consistent with a φ-axial C–Pd bond, whereas H5 is clearly axial on the basis of the 12 Hz coupling to one H4 proton. Through-space interactions were studied with 1-D gradient ROESY (GROESY, which is effective since the gradients cleanly remove signals due to solvents and excess 2,3-dihydrofuran).[8] Given the ease with which complex **5a** is formed and the implications for the relative stability of the possible alkylpalladium species, there is a surprising paucity of crystallographic models for potentially anomeric C–M bonds in cyclic ethers.[9] However, in

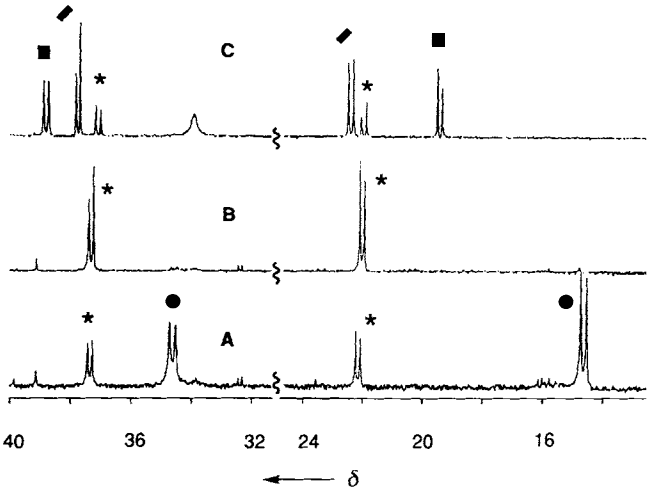
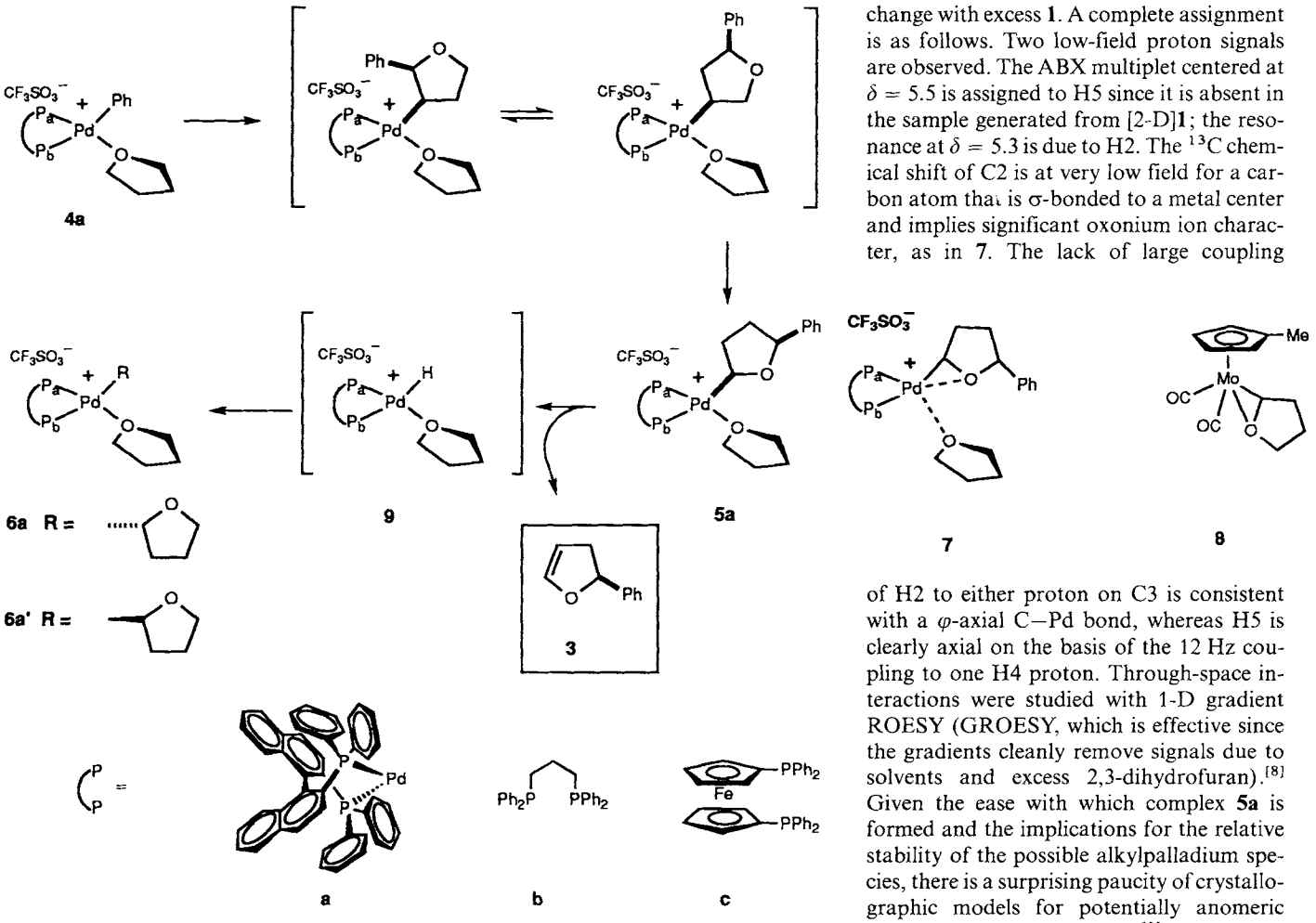


Figure 1. ^{31}P NMR spectra of the reaction sequence between **4a** and **1**; complex **4a** ●, complex **5a** *, complex **6a** ■, complex **6a'** ◢. A) Partial conversion of **4a** to **5a** at $-50\,^{\circ}C$; B) after complete formation of **5a** at $-40\,^{\circ}C$; C) nearly complete decomposition of **5a** at $-30\,^{\circ}C$ to form **6a** and **6a'**; a peak due to an impurity is at about $\delta = 34$. The downfield phosphorus atom is P_a.



Scheme 1. Sequence of intermediates for the (*S*)-BINAP complex **4a** (similar for **b** and **c**).

8 the oxygen atom occupies a vacant coordination site to give a metallaoxacyclopropane structure. This cannot be ruled out in the present case, and the 8 Hz five-bond coupling between P_a and H2 strengthens the case for σ contact between the palladium and oxygen centers. Taking the evidence in sum provides a unique structure and conformation (Figure 2). An O1–C2 half-chair conformation for the five-membered ring is supported by the three contiguous ax–ax ^3J(H,H) couplings and the observed NOE between H3 (ax) and H5.

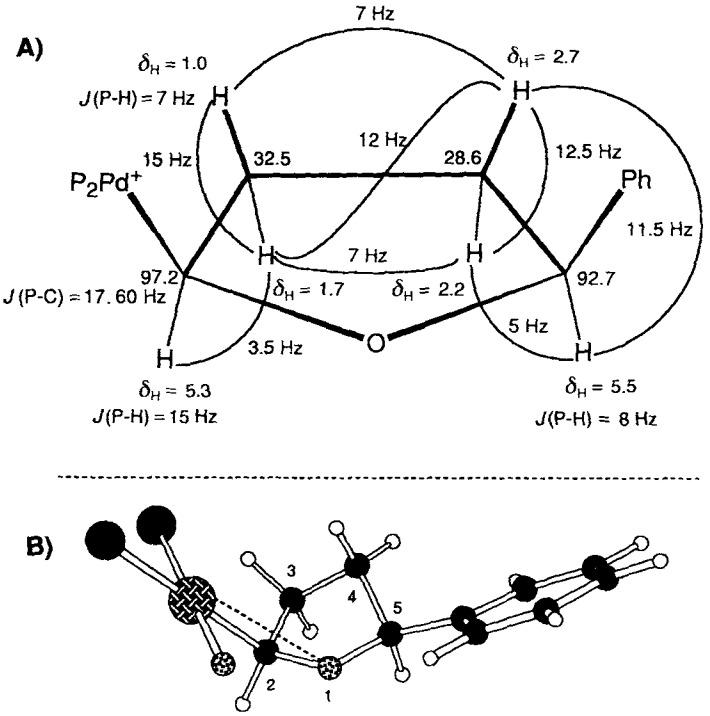


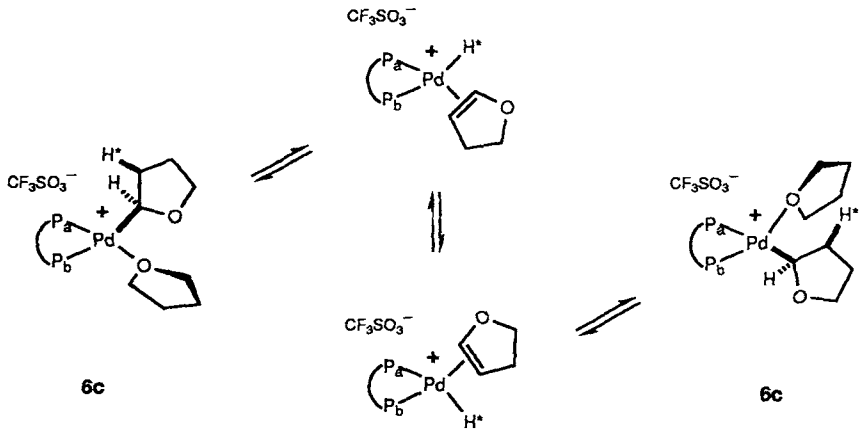
Figure 2. A) ^{13}C and ^1H NMR chemical shifts as well as J(H,H), J(H,P), and J(C,P) for **5a** in [D_8]THF at −40 °C. The experimental spectrum was matched against δ and J values simulated with gNMR [11]. B) Chem-3D model in a minimized conformation based on the NMR data.

The formation of two isomers of **6a** in comparable amounts concurrent with the disappearance of **5a** indicates decomposition to **3** and the Pd–H complex **9**. Further addition of **1** (Scheme 1) occurs with regiochemistry opposite to that of Pd–Ph addition of the first step. As before, it was possible to assign some of the NMR signals of the two diastereomers,[10] thereby demonstrating the structural similarity between **5** and **6**. When [2-D]**1** is employed, the H2 signal is absent in both **6a** and **6a′**, which demonstrates that the Pd–H addition is not stereospecific, and migration of palladium between C2 and C5 does not occur.

Similar observations were made when the triflates **4b** and **4c**, derived from 1,3-bis(diphenylphosphino)propane (dppp) and 1,1′-bis(diphenylphosphino)ferrocene (dppf), respectively, were employed, but without the potential complexity of diastereoisomerism in the alkyl intermediates. The palladium complex **5b** was found to be less thermally stable. At −60 °C β-H elimination occurred at a rate comparable to that of alkyl formation to give the turnover products **3** and **6b**. The dppf complex **5c** is stable up to −40 °C and was characterized by NMR spectroscopy. Its ^1H NMR spectrum is similar to that of the BINAP analogue **5a**, but the corresponding complex **6c** exhibits interesting dynamic NMR behavior. Unlike all related complexes, the two ^{31}P nuclei exchanged above −50 °C, and the signal for H2 broadened from the A component of an AMX system at the low-temperature limit towards the A component of an AMX_2 system; the AX coupling was halved. This is most simply explained by the process shown in Scheme 2 ($k_1 \approx 40\ s^{-1}$ at −40 °C),[11] since it formally requires that the alkyl group exchanges intramolecularly between adjacent sites on the square plane. There is evidence for stereochemical lability in square-planar hydrides of d^8 metals.[12]

What is the relationship of these intermediates to the catalytic asymmetric Heck reaction? The observed regiochemistry in catalysis depends on the base employed; the maximum *ee* and, concomitantly, the lowest ratio of **3** to **2** is associated with 1,8-bis-(dimethylamino)naphthalene.[5] When the NMR experiment was repeated in the presence of a twentyfold excess of this base, formation of **5** proceeded as before, but **6a** and **6a′** were not observed. Therefore, the base competes successfully for Pd–H under these conditions. A catalytic reaction (5 mol% Pd, $Me_2NC_{10}H_6NMe_2$, THF, 40 °C, 140 h) with **4a**, prepared in situ led only to doubly isomerized **3** in 78% *ee*, but using $Pd(OAc)_2$ and (*S*)-BINAP under otherwise identical conditions gave (*S*)-**3** (86% *ee*) as well as (*R*)-**2** (55% *ee*).[13] Careful examination of the initial ^1H NMR spectrum of **5a** indicates that trace amounts (<5%) of other transient species are observed below −40 °C concurrent with or immediately subsequent to formation of **5a**. We speculate that they arise from the less favored (*S,R*)-diastereomer of the initial Pd–Ph addition product. The observed *ee* of **3** (91%) under stoichiometric conditions at −40 °C reflects the enantioselectivity of the alkene addition step and correlates reasonably with the value (78%) obtained with **4a** as catalyst.

The strong driving force towards an α-oxoalkyl palladium intermediate points to the possibility of a second route for catalysis under Hayashi–Ozawa conditions, which favors the opposite enantiomer and is less disposed to double isomerization.[14] We note the precedent for two competing catalytic pathways with opposite enantioselectivity in earlier asymmetric Heck chemistry[15] and consider that a parallel study of the singly isomerizing P–N palladium catalysts[6, 16] will be enlightening.



Scheme 2. A pathway for the interconversion leading to dynamic NMR spectra for **6c** with reversible transfer of hydrogen H* to Pd.

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Experimental Section

Enantiomeric excesses were determined by gas chromatography, with a 25 m, CHIRAL-DEX-bonded silica column. Electrospray MS was performed by Dr. H. E. K. Matimba and Dr. R. T. Aplin. All NMR spectra were recorded on a Bruker AMX 500 spectrometer (^{1}H: 500 MHz) with an inverse gradient probe at low temperatures; the heteronuclear experiments (^{31}P: 202 MHz, ^{13}C: 125 MHz) were carried out with a broad-band probe. TOCSY was performed with the MLEV-17 spin lock (8.3 kHz) with a mixing time of 70 ms (bracketed by 2.5 ms "trim pulses"). Signals for a modified 1-D gradient ROESY (GROESY) were selected by 25 ms Gaussian 180° pulses with application of a continuous-wave spin lock (2.6 kHz), a relaxation delay, and mixing times of 4 s and 300 ms. The gradients used were 14: −6: −20% of the maximum gradient strength (about 45 G cm^{-1}).

Typical procedure for preparing samples for in situ NMR experiments: Silver triflate (0.006 g, 0.02 mmol) was added to a vigorously stirred solution of [(*S*)-(BINAP)Pd(Ph)(I)] [17] (0.020 g, 0.02 mmol) in [D$_8$]THF (0.5 mL) at −78 °C. Stirring was continued for 10 min, during which time a white precipitate formed. The suspension was centrifuged cold, and the pale colored liquid rapidly decanted over a cannula into a 5 mm NMR tube containing 2,3-dihydrofuran (10 μL, 0.13 mmol, excess) at −78 °C. The tube was transferred to the pre-cooled probe, and spectra measured as described.

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[13] With the use of **4a** as catalyst with proton sponge, turnover was slower than for the Pd(dba)$_2$/BINAP (dba = dibenzylideneacetone, 1,5-diphenylpenta-1,4-diene-3-one)or Pd(OAc)$_2$/BINAP protocols. However, using 5 mol% **4a** with NEt$_3$ in THF gave complete reaction in 21 h (100% **3**, 75% *ee*).

[14] The effect of deliberate addition of OAc$^-$ has been explored. In the absence of any other additives **4b** catalyzed arylation in the presence of NEt$_3$ or proton sponge to give **3** as the sole product. The ratio of **3** to **2** decreased with increasing amounts of tetra-*n*-butylammonium acetate. The reverse result was achieved (97% **2**) when acetate was added as the base in stoichiometric amount.

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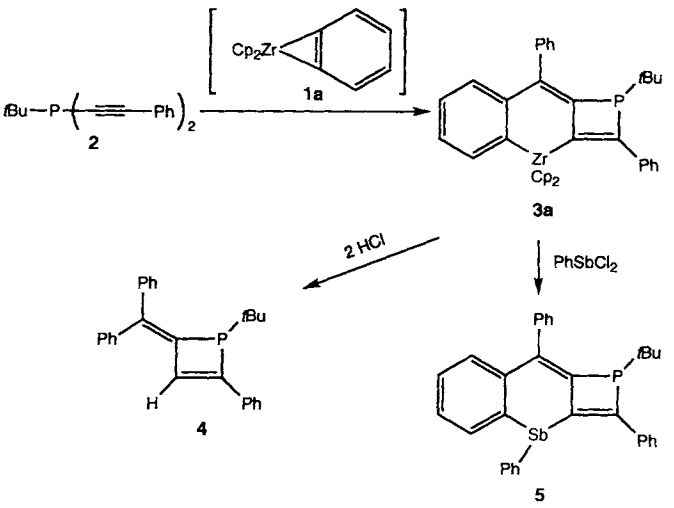
Zirconocene–Benzyne-Mediated Intramolecular Coupling of Bis(alkynyl)phosphane: A Way to Mono- and Tricyclic 1,2-Dihydrophosphetes**

Laurence Dupuis, Nadine Pirio, Philippe Meunier,* Alain Igau, Bruno Donnadieu, and Jean-Pierre Majoral*

In recent years, much attention has been paid to the chemistry of zirconocene complexes,[1] which show versatile behavior in a number of coupling and insertion reactions. The zirconocene synthon [Cp$_2$Zr] has, for example, promoted intramolecular coupling of alkynyl groups with formation of cyclic derivatives,[2] coupling of diynes with generation of zirconacyclic cumulenes,[3] and cleavage of the central C–C single bond of butadiynes.[3, 4] Insertion of acetylenic systems into zirconocene–benzyne has also been described,[5] but to our knowledge, there is no example of a reaction of dialkynes with zirconocene–aryne complexes.

Here we report a novel, intramolecular coupling reaction of a dialkynylphosphane (tBuP(C≡C–Ph)$_2$) and zirconocene–benzyne, which provides unusual 1,2-dihydrophosphete–zirconium complexes. One of these complexes is a useful reagent for the synthesis of a stilbene tricyclic system and a 1,2-dihydrophosphete bearing an exocyclic carbon–carbon double bond.

Addition of bis(alkynyl)phosphane **2** to one equivalent of the transient benzyne complex [Cp$_2$Zr(η^2-C$_6$H$_4$)] (**1a**), generated in situ by thermolysis of a solution of [Cp$_2$ZrPh$_2$] in toluene at 80 °C over 24 h, resulted in the unexpected zirconacycle **3a** in 65% yield ($\delta(^{31}P) = 59.9$, Scheme 1). Complex **3a** was fully characterized by usual methods, but identification based only on spectroscopic data was uncertain (Table 1). The molecular



Scheme 1. Synthesis and reactivity of **3a**.

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