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[9] Relevant analytical data for **6** and **7**. Compound **6**: yellow needles, m.p.: 139 °C; IR (KBr): $\tilde{\nu} = 2920$ (CH_2), 1630 cm^{-1} (C=C); UV (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 364 (2.35), 302 (3.24), 268 nm (4.31); ^1H NMR (500 MHz, C_6D_6): $\delta = 4.88$ (s, 5H; CH), 4.70 (s, 10H; CH), 2.17–1.75 (m, 48H; CH_2); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 82.9$ (C_{cbd}), 81.9 ($C_{\equiv}$), 80.2 (C_{Cp}), 79.8 (C_{cbd}), 79.5 (C_{Cp}), 79.0 (C_{cbd}), 32.0 (CH_2), 27.7 (CH_2), 25.5 (CH_2), 25.1 (CH_2), 24.1 (CH_2), 19.4 (CH_2); HRMS (FAB) calcd for $C_{55}H_{63}Co_3$: 900.2926, found: 900.2861; elemental analysis [%] calcd for $C_{55}H_{63}Co_3 \cdot 2\,CH_2Cl_2$: C 63.94, H 6.31, found: C 63.71, H 6.23; X-ray structure analysis of $C_{56}H_{65}Cl_2Co_3$: $M_r = 985.77$, $\mu = 1.184\ mm^{-1}$, $\rho_{calcd} = 1.378\ g\,cm^{-3}$, orthorhombic, space group *Pnma*, $Z = 4$, $a = 18.1815(3)$, $b = 30.8148(5)$, $c = 8.4824(1)$ Å, $V = 4752.34(12)$ Å^3, crystal dimensions $0.36 \times 0.30 \times 0.02\ mm^3$, $T = 200(2)$ K, $\lambda = 0.71073$ Å, Θ-range 2.24–27.48°, $-23 \leq h \leq 23$, $-40 \leq k \leq 39$, $-11 \leq l \leq 10$; 46290 reflections collected, 5531 unique reflections, 2889 observed reflections with $I > 2\sigma(I)$, transmission max/min 0.98/0.86, an empirical absorption correction was applied by using SADABS,[12] based on the Laue symmetry of the reciprocal space. The structure was refined against F^2 with a full-matrix least-squares algorithm, $R(F) = 0.054$, $\omega R_2(F^2) = 0.092$. Hydrogen atoms were included in calculated positions. Special position of the molecule on a crystallographic mirror plane, one equivalent of dichloromethane is cocrystallized. Compound **7**: orange crystals; m.p.: 144 °C; IR (KBr): $\tilde{\nu} = 2931$ (CH_2), 1699 cm^{-1} (C=O); UV (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 380 (2.75), 300 (2.20), 268 nm (4.42); ^1H NMR (300 MHz, C_6D_6): $\delta = 4.45$ (s, 5H; CH), 2.83–1.15 (m, 26H; CH_2); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 211.7$ (C=O), 82.8 (C_{cbd}), 82.3 (C_{cbd}), 81.5 (C_{Cp}), 80.9 (C_{cbd}), 79.0 ($C_{\equiv}$), 45.2 (CH_2), 36.2 (CH_2), 29.3 (CH_2), 27.6 (CH_2), 26.4 (CH_2), 24.4 (CH_2), 23.9 (CH_2), 22.9 (CH_2), 20.8 (CH_2), 20.2 (CH_2); HRMS (FAB) calcd for $C_{25}H_{31}CoO$: 406.1706, found: 406.1711; elemental analysis [%] calcd for $C_{25}H_{31}CoO$: C 73.87, H 7.69; found: C 73.76, H 7.66. X-ray structure analysis of $C_{25}H_{31}CoO$: $M_r = 406.43$, $\mu = 0.848\ mm^{-1}$, $\rho_{calcd} = 1.316\ g\,cm^{-3}$, orthorhombic, space group *Pbca*, $Z = 8$, $a = 14.4938(1)$, $b = 10.3639(1)$, $c = 27.4912(1)$ Å, $V = 4103.87(5)$ Å^3, crystal dimensions $0.26 \times 0.18 \times 0.06\ mm^3$, $T = 200(2)$ K, $\lambda = 0.71073$ Å, Θ-range 1.48–25.60°, $-17 \leq h \leq 17$, $-12 \leq k \leq 12$, $-32 \leq l \leq 32$; 28757 reflections collected, 3684 unique reflections, 2418 observed reflections with $I > 2\sigma(I)$, transmission max/min 0.95/0.80, an empirical absorption correction was applied by using SADABS,[12] based on the Laue symmetry of the reciprocal space. The structure was refined against F^2 with a full-matrix least-squares algorithm, $R(F) = 0.041$, $\omega R_2(F^2) = 0.094$. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were refined isotropically. CCDC-173922 (**7**) and CCDC-173921 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[11] Relevant analytical data of **4** and **5**. **4a**: HRMS (FAB) calcd for $C_{60}H_{68}Co_4$: 1024.2649; found: 1024.2693; ^1H NMR (500 MHz, C_6D_6): $\delta = 4.57$ (s, 20H; CH), 2.37 (m, 16H; CH_2), 2.04 (m, 32H; CH_2); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 84.0$ (C_{cbd}), 80.3 (C_{Cp}), 32.4 (CH_2), 28.3 (CH_2). **4b**: HRMS (FAB) calcd for $C_{62}H_{70}Co_4O_2$: 1082.2704, found: 1082.2699. **5a**: HRMS (FAB) calcd for $C_{120}H_{137}Co_8$: 2049.5376, found: 2049.5371. **5b**: HRMS (FAB) calcd for $C_{124}H_{140}Co_8O_4$: 2164.5408, found: 2164.5391.

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A *trans*-Platinum(II) Complex as a Single-Molecule Insulator**

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Heiko B. Weber,* Joachim Reichert, and
Detlef Beckmann

The use of single molecules as the ultimate tiny building blocks for electronic circuits would be an enormous step in terms of size reduction. This visionary concept in molecular electronics has its roots in theoretical studies of the 1970s.[1] A profound understanding of the correlation between the molecular structure and physical properties of single molecules is absolutely necessary for the design of such electronic circuits.[2] Numerous predictive correlation studies have been elaborated on the basis of electrochemical and/or spectroscopic investigations in solutions of different types of molecular wires[3] and monodisperse oligomers,[4] such as *trans*-platinum-linked oligo(tetraethenylethenes).[5]

Studies on electron transport through single-layer molecular films have been carried out between metallic electrodes.[6] Scanning tunneling microscopy has been used to investigate single or small numbers of molecules,[7] for example, in the switching behavior of molecular films supporting gold nanoclusters.[8] However, there are only a few studies on electron transport through single molecules which are covalently linked between two electrodes. Mechanically controlled break junctions have proven to be a very powerful tool for such investigations.[9] In previous work we studied the current through conjugated organic molecules[10] and generated

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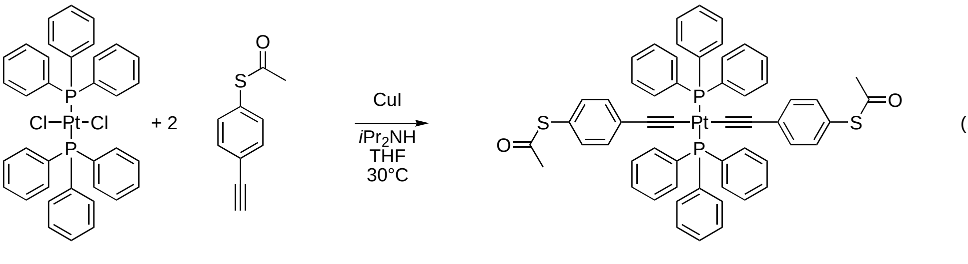
strong arguments that single molecules can indeed be studied in such a break junction. The enlargement of the "molecular toolbox" for the design of stiff, rodlike molecules with tailor-made conductivities has led us to consider *trans*-acetylene–platinum(II) complexes. The platinum–acetylene bond has hardly any π character and thus separates the molecular rod into two independent conjugated systems. This arrangement should therefore increase its resistance.[5]

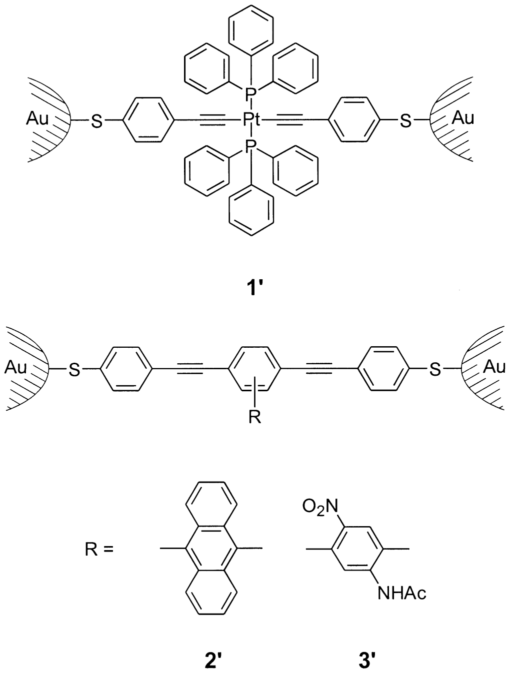
Here we present the synthesis and characterization of the platinum(II) complex **1** [Eq. (1)]. The complex has a molecular rod structure consisting of two conjugated π systems coordinated in a *trans* arrangement to a platinum(II) ion. Acetyl-protected sulfur functions at both ends of the rod allow for its immobilization between two gold electrodes. Deprotection of **1** in the presence of the gold surfaces of a mechanically controlled break junction gave **1′** anchored to the two gold electrodes through the two sulfur atoms (Figure 1).



1

(1)

Compound **1** was synthesized as shown in Equation 1 by a similar protocol as that described in ref. [5]; a solution of *trans*-bis(triphenylphosphane)platinum(II) chloride in THF, diisopropylamine (as base), and copper iodide (as catalyst) was treated with (4-ethynyl)phenyl thioacetate at 30 °C. The resulting ivory-colored solid was characterized by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) and ^1H, ^{13}C, and ^{31}P NMR spectroscopy as well as by X-ray analysis. Slow evaporation of a chloroform solution provided single crystals that were suitable for X-ray structure determination. The two triplets (C≡C-Pt$_\alpha$: $^2J_{P,C} = 6.2$ Hz, C≡C-Pt$_\beta$: $^3J_{P,C} = 5.4$ Hz) observed in the ^{13}C NMR spectrum of **1** suggested a *trans* conformation of the acetylene groups, which was confirmed by the crystal structure determination (Figure 2). Compound **1** crystallizes in the triclinic space group $P\bar{1}$, with one molecule in the unit cell.[11] The platinum ion is coordinated in a square-planar arrangement by two *trans*-PPh_3 groups and two *trans*-acetylene ligands. The intramolecular sulfur···sulfur distance determined from the crystal structure is 1.843(33) nm.



1′

2′ **3′**

Figure 1. Organic–inorganic hybrid structure of **1′** and organic compounds **2′** and **3′** immobilized between two gold electrodes.

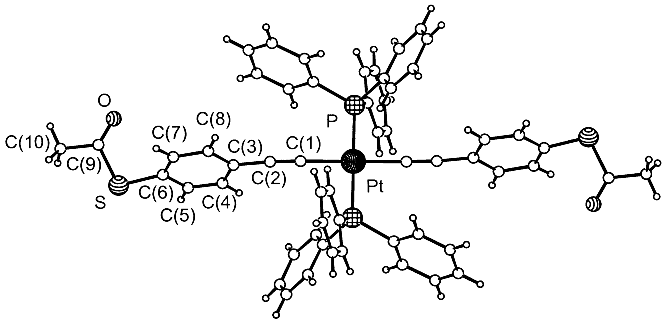


Figure 2. Molecular structure of **1** in the crystal. Selected bond lengths [pm] and bond angles [°]: Pt-P 231.77(15), Pt-C(1) 202.7(6), C(1)-C(2) 117.9(9), C(2)-C(3) 145.0(8), C(6)-S 177.8(6), S-C(9) 178.7(6), C(9)-O 118.1(9), C(9)-C(10) 149.6(10); P-Pt-C(1) 90.94(17), P′-Pt-C(1) 89.06(17), Pt-C1-C2 174.4(6), C1-C2-C3 173.7(8), C(6)-S-C(9) 103.0(3), S-C(9)-C(10) 111.0(6), S-C(9)-O 123.4(5), O-C(9)-C(10) 125.6(7).

The mechanically controlled break-junction technique enabled the two gold electrodes to be adjusted with sub-angstrom resolution.[9b, 12] At the beginning of the experiment the electrodes were fixed at a distance of 10 nm and exposed to a 5×10^{-4} M solution of **1** in THF for 30 s. The thioacetyl protecting group is readily hydrolyzed on the gold surface and a covalent sulfur–gold bond is formed.[10, 13] The gold surface of the electrodes is now partially covered by molecules which are covalently linked to the surface on one side, while the second sulfur atom is still protected by an acetyl group. The acetyl protecting group also prevents oxidative disulfide formation, and is only cleaved by contact with the second gold electrode.[13] After a short exposure of the break junction to the solution of **1** it was extensively rinsed with THF and subsequently transferred to a vacuum (5×10^{-7} mbar). The two gold electrodes were then slowly moved toward each other while the current was monitored at a bias voltage of 4 V. A sudden "lock-in" behavior with an immediate increase of the current to a plateau of about 0.2 nA was indicative of the first bridging contact of a molecule between the two electrodes. This observed current plateau is insensitive to small variations in the distance between the electrodes. However, an increase in the current was observed on further pushing the two electrodes together. This phenomenon can be explained by additional contributions of further molecules that bridge the electrodes at smaller distances. In some cases a doubling of the current was observed, which is the expected behavior for the bridging of a second molecule, followed by a further drastic increase in the current as the electrodes further approach one another. However, currents smaller than 0.2 nA (the first plateau) were never observed.

The configuration is stable at room temperature and reproducible I/V curves could be recorded. Experiments have shown that such a stable, reproducible behavior could not be obtained without molecules between the electrodes; gold-vacuum-gold setups were unstable, presumably because of the high mobility of gold atoms at the surface. The overall behavior of our experiment resembles the observations already made for the organic systems **2′** and **3′**. A comparison of the I/V curves with the spatial symmetry of the molecules (together with further considerations) in these systems showed that single molecules could indeed be observed.[10] Therefore, we are convinced that in our described experiment we observe electron transport through a single molecule covalently linked on both sides to gold electrodes.

The I/V curves recorded on **1′** immobilized in the gold break junction are shown in Figure 3. The curves are symmetric with respect to voltage inversion, as expected for the symmetric structure of **1′**. An exponential increase in the current with applied voltage is observed, which corresponds to the behavior of a classical insulator. The resistance of the organic–inorganic hybrid structure **1′** between the two gold electrodes at 5 V is in the range of 5–50 GΩ, which is about three orders of magnitude larger than that observed for the organic compounds **2′** and **3′**. The current/voltage relationship can best be described by the model for a rectangular tunnel barrier,[14] with a tunnel barrier height of 2.5 eV giving the best fit to our data (circles in Figure 3). The origin of the insulating behavior of **1′** can be explained by the pure σ character of the Pt–C(sp) bonds between the Pt^{II} ion and the acetylene ligands.[15] However, both the stability of the setup and the stability of the insulating behavior up to such a high bias voltage of 5 V are remarkable.

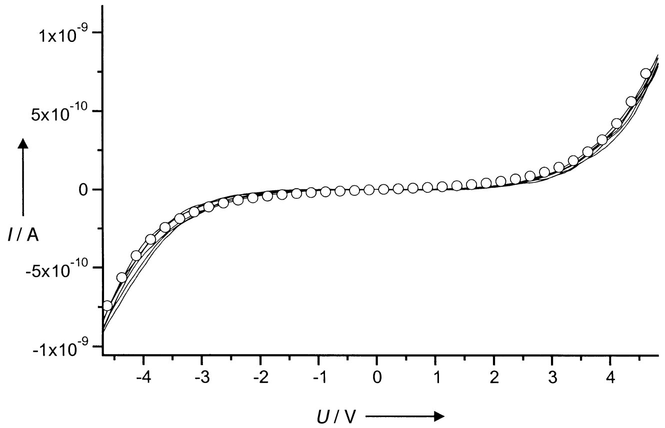


Figure 3. I/V curves for a gold-**1′**-gold setup. Consecutively recorded I/V curves (solid lines) and simulated current with a barrier height of 2.5 eV (circles) are shown.

The results indicate the potential of platinum(II) complexes as single-molecule electronic junctions. Measurement of the current transport through single molecules provide important insight for controlling and tuning electron transport through molecular structures, a crucial requirement for the design of electronic circuits based on single to small numbers of molecules.

Experimental Section

(4-ethynyl)phenyl thioacetate (30.5 mg, 173 mmol) was dissolved in N_2-saturated THF (10 mL). *trans*-Bis(triphenylphosphane)platinum(II) chloride (60.7 mg, 76.8 mmol) and copper iodide (3.6 mg, 18.9 mmol) were added, followed by diisopropylamine (1 mL). The reaction mixture was stirred at 30 °C under a N_2 atmosphere for 1 h. Filtration through silica with THF and subsequent column chromatography (silica gel, CH_2Cl_2/toluene 1/1–3/1) yielded **1** (12.6 mg, 11.8 mmol, 15 %) as an ivory solid. M.p. 205 °C (decomp); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.72-7.85$ (m, 12H), 7.31–7.42 (m, 18H), 6.94 (d, $J = 8$ Hz, 4H), 6.27 (d, $J = 8$ Hz, 4H), 2.33 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 194.75$, 135.03 (t, C≡C-Pt_{α}, $^2J_{P,C} = 6.2$ Hz), 133.18, 131.56, 131.20, 130.81, 130.32, 129.05, 128.24, 127.91 (t, C≡C-Pt_{β}, $^3J_{P,C} = 5.4$ Hz), 123.22, 30.04; $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 20.02$ (s, $J_{Pt,P} = 2630$ Hz); MALDI-TOF-MS: 1071.55 [M^++H], 894.46 [M^+ – C≡CPhSAc], 719.38 [M^+ – 2C≡CPhSAc].

Nanostructured mechanically controlled break junctions were fabricated as described in ref. [12]. This setup allows the distance of the gap to be adjusted with sub-angstrom resolution. A 5×10^{-4} M solution of **1** in THF was applied for 30 s, and the junction was subsequently rinsed with THF under a N_2 atmosphere. The controlled approach of the two electrodes and transport measurements were investigated in a metallic ultrahigh-vacuum box at 5×10^{-7} mbar with a Keithley 6430 subfemtoamp remote source meter.

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[11] **1**: $a = 964.8(2)$, $b = 1079.9(2)$, $c = 1271.7(3)$ pm, $\alpha = 76.69(3)$, $\beta = 75.67(3)$, $\gamma = 64.67(3)^\circ$, $V = 1148.6(4) \times 10^6$ pm^3; triclinic, space group $P\bar{1}$, $Z = 1$, $\rho_{\text{calcd}} = 1.547$ g cm^{-1}, $\mu = 3.258$ mm^{-1}, STOE IPDS2, Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 200$ K, $2\theta_{\max} = 52^\circ$; 5297 reflections measured, 3692 independent reflections ($R_{\text{int}} = 0.0312$), 3690 independent reflections with $F_o > 4\sigma(F_o)$. The structure was solved by direct methods and refined by full-matrix least-square techniques against F^2, 286 parameters (Pt, P, S, O, C refined anisotropically, H atoms were calculated at ideal positions); $R1 = 0.0401$; $wR2 = 0.1058$ (all data); GOF = 1.058; max. residual electron density 1.032 e Å^{-3}. CCDC 169386 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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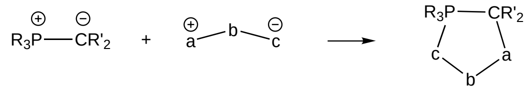
Intramolecular [3+2] Cycloaddition of a Nitrilium Phosphane Ylide Complex to the *P*-Phenyl Group of a Wittig Ylide[**]

Nils Hoffmann, Peter G. Jones, and Rainer Streubel[*]

Dedicated to Professor Masaaki Yoshifuji
on the occasion of his 60th birthday

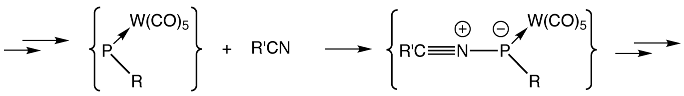
Wittig ylides[1, 2] of the general type $R_3PCR'_2$ **I** are some of the most widely used and thus most extensively investigated phosphorus compounds in organic synthesis; cycloaddition reactions such as those of **I** with 1,3-dipoles **II** belong to the classical repertoire of heterocyclic chemistry. Such reactions, which exploit the P,C-ylide function, generally proceed smoothly and lead to the five-membered phosphorus(V) heterocycles **III** (Scheme 1).[1] Until now, cycloadditions to a *P*-bonded phenyl group of Wittig ylides, involving the former as a 2π-cycloaddition component, were unknown (as indeed were similar reactions involving any other benzene derivatives[3]). Cyclometalations of *P*-phenyl Wittig ylide derivatives are known, but are rare; they have been observed, for example, in reactions with zirconium[4] and platinum[5] complexes.



I **II** **III**

Scheme 1. Cycloaddition of Wittig ylides with 1,3-dipoles (R, R′ = arbitrary organic substituents; a, b, c denote organoelement fragments).

Nitrilium phosphane ylide complexes **VI**, whose existence as intermediates we were able to demonstrate by trapping reactions,[6] now represent a new and well-established 1,3-dipole system in heterocyclic chemistry.[7–9] We recently discovered the 1,1-addition of electrophilic terminal phosphanediyl complexes **IV** to nitriles **V**, providing an independent access to **VI** (Scheme 2), so that the synthetic potential of **VI** could be extended further by the use of 7-phosphanorbornadiene complexes.[10, 11]



IV **V** **VI**

Scheme 2. Formation of nitrilium phosphane ylide complexes by 1,1-addition of electrophilic terminal phosphanediyl complexes with nitriles (R, R′ = arbitrary organic substituents).

For some time we have been investigating the possibility of obtaining kinetically stabilized nitrilium phosphane ylide complexes, in order to study their properties. Promising candidates in this respect are, for example, Wittig ylide derivatives that contain a nitrile function at the ylide carbon atom. Because of their variable stereoelectronic properties, these are potential reaction partners for 1,1-additions to **IV**. Surprisingly, however, heating the 2*H*-azaphosphirene complex **1**[12] in toluene in the presence of the Wittig ylide derivative **2**[13] led diastereoselectively to the new tricycle **5**, whose formation we explain by a [3+2] cycloaddition of the intermediate 1,3-dipole **4** to a phenyl group of **2** (Scheme 3). Monitoring the reaction by ^{31}P NMR spectroscopy indeed revealed the appearance and disappearance of a further product ($\delta = 22.3$ (d, $J(\text{P,P}) = 10.8$, $^1J(\text{W,P}) = 243.9$ Hz) and -0.7 (d)), which however could not be more precisely characterized because it was a minor component of the product mixture. A previous study using other, sterically more demanding, ylide-*C*-substituted triorganosilyl derivatives of **2** provided support for our interpretation via 1,1-addition as a primary step, in that here also the same tricyclic ring systems were formed as in **5**.[14] The results presented here are also interesting in view of recently reported first examples of reactions of other benzene derivatives with μ^1- and μ^2-phosphanediyl complexes. In the first case a [5]metacyclophane[15] reacted as a 4π-cycloaddition component,[16] whereas the second example involved the phenyl group of benzonitrile

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