

Formation of the First Heterobimetallic Phosphido-bridged σ - π -Acetylide Complex $[(C_5H_5)_2Ti(\mu-\sigma, \eta^2-C\equiv CPh)(\mu-PPh_2)Ni(PPH_3)]$ by Cleavage of the Central C-C Single Bond in $PhC\equiv C-C\equiv CSiMe_3$ and of the P-C Bond in Ph_3P , and Coupling of the Fragments to $PhC\equiv CSiMe_3$

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An unexpected activation of the central C-C single bond of $PhC\equiv C-C\equiv CSiMe_3$ and of one P-C bond in Ph_3P and coupling of the fragments to $PhC\equiv CSiMe_3$ was observed in the reaction of $[Ni(PPH_3)_2(\eta^2-PhC\equiv C-C\equiv CSiMe_3)]$ with '(C₅H₅)₂Ti' providing, via the tweezer-like titanocene nickel(0) triphenylphosphine bisacetylide complex $[(C_5H_5)_2Ti(\mu-\sigma, \eta^2-C\equiv CSiMe_3)(C\equiv CPh)Ni(PPH_3)]$ **1**, the phosphido-bridged σ - π -acetylide complex $[(C_5H_5)_2Ti(\mu-\sigma, \eta^2-C\equiv CPh)(\mu-PPh_2)Ni(PPH_3)]$ **2**.

For some time we have been interested in the cleavage of the central C-C single bond of buta-1,4-diyne by titanocene and zirconocene,^{1,2} and we were able to show that $PhC\equiv C-C\equiv CSiMe_3$ is not cleaved by titanocene alone but heterobimetallic nickel(0)-titanium(II) systems work well giving a heterobimetallic tweezer-like bisacetylide complex (Scheme 1).³ In the reaction leading to complex **1** the phosphido-bridged titanium-nickel complex **2** (5–9% yield) and $PhC\equiv CSiMe_3$ were interesting by-products. Complex **2** was obtained in 30% yield by reaction of the tweezer complex **1** with triphenylphosphine in boiling dioxane (Scheme 2).[†]

One phenyl group of Ph_3P is coupled selectively with the trimethylsilylacetylide moiety of the starting tweezer complex **1** to give $PhC\equiv CSiMe_3$ which was detected by gas chromatography. Coordination of the remaining diphenylphosphido group leads to the first heterobimetallic phosphido-bridged σ - π -acetylide complex **2**. The existence of the phosphido group indicates that the phenyl group in $PhC\equiv CSiMe_3$ originates from the phosphine and not from butadiyne. The composition of complex **2** was verified as its thf adduct by elemental analysis, and IR and NMR spectra.[‡] Its ³¹P NMR spectrum shows an AX

spin system, one signal of which is found in the region expected for phosphines and the other shifted downfield at δ 188.6.

The X-ray crystal structure **2**§ (Fig. 1) exhibits a bent metallocene unit to which the atoms P(2) and C(1) are coordinated. The relatively long Ti-Ni distance of 2.834 Å cannot be considered as a bonding interaction between the metals. The short Ti-C(1) distance and the bonding geometry of the alkynyl group [C(1)-Ti 2.065(8) Å, Ti-C(1)-C(2) 163.2(6)°, C(1)-C(2)-C(3) 146.7(7)°] show the possibility of a π -interaction between titanium and the organic π -system along the σ -bond, e.g. Ti=C. The two Ni-P distances are different [Ni-P(1) 2.165(2), Ni-P(2) 2.181(2) Å]. Bond lengths and angles of **2** are similar to those in the phosphido-bridged homobimetallic σ - π -acetylide complexes $[Fe_2(CO)_5(C_2Ph)(PPh_2)(PPh_3)]$,⁴ $[Fe_2(CO)_6(C_2Ph)(PPh_2)]$,⁵ $[M_2(CO)_6\{\mu-\sigma, \eta^2(C\equiv CBut)\}(\mu-PPh_2)]$ (M = Fe, Ru, Os)⁶ prepared from phosphinoacetylenes $Ph_2PC\equiv CBut$ and metal carbonyls by cleavage of the P-C_{sp} bond. The preparation of **2** provides the first example of actually separating the two acetylide units of a butadiyne into two molecules. A possible mechanism for the reaction from **1** to **2** includes the transfer of one phenyl group (e.g. via *ortho*-metallation⁷) and the alkynyl group to the nickel

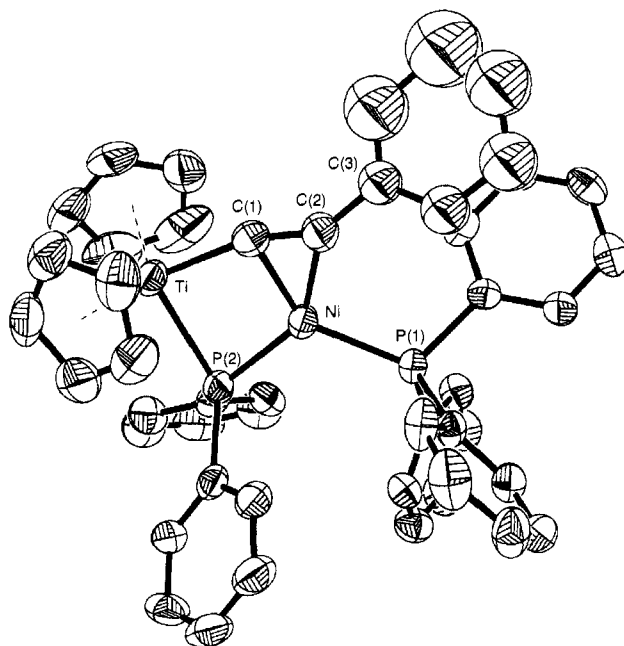
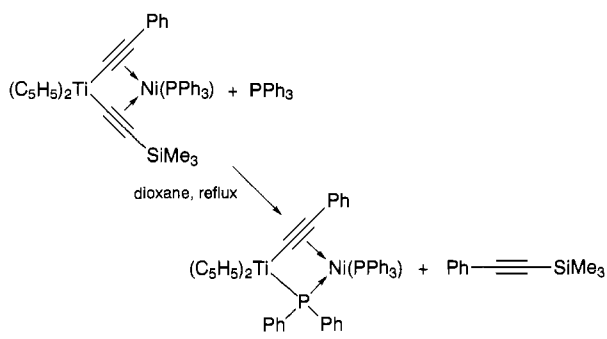
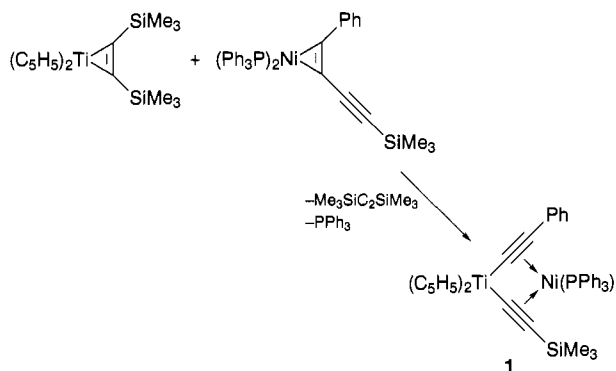


Fig. 1 Crystal structure of **2** at the 50% probability level for thermal ellipsoids. Solvent molecule is omitted. Selected bond lengths (Å) and angles (°): C(1)-C(2) 1.265(10), C(2)-C(3) 1.453(11), Ti-C(1) 2.065(8), Ti-Ni 2.834, Ti-P(2) 2.516(2), Ni-C(1) 1.943(6), Ni-C(2) 2.007(7), Ni-P(1) 2.165(2), Ni-P(2) 2.181(2), C(2)-C(1)-Ti 163.2(6), C(1)-C(2)-C(3) 146.7(7), Ni-P(2)-Ti 73.2(1), P(1)-Ni-Ti 172.8(1).

centre, formation of an unstable *cis*-phenyl-alkynyl nickel(II) complex and subsequent reductive elimination of $\text{PhC}\equiv\text{CSiMe}_3$.

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Footnotes

† *General procedure for preparation of 2*. A solution of **1** (90 mg, 0.129 mmol³) and PPh_3 (34 mg, 0.129 mmol) in dioxane (30 ml) was refluxed for 30 h. The crude product, obtained after evaporation of the volatile material, was analysed by ^1H NMR spectroscopy, which showed a 1 : 1 mixture of **1** and **2**. Recrystallization from thf-*n*-hexane gave 32 mg (0.038 mmol, 30% yield) of **2**: mp, 129 °C; *m/z*: 784 (M^+).

‡ *Spectral data for 2*: IR (Nujol): 1801 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$), elemental analysis for $\text{C}_{48}\text{H}_{40}\text{NiP}_2\text{Ti}\cdot 0.7\text{C}_4\text{H}_8\text{O}$ (M_r 835.32): calc.: C, 73.0; H, 5.5; found: C, 72.8; H, 5.6%; NMR ($\text{CD}_3\text{C}_6\text{D}_5$): ^1H : δ 5.07 (d, J 2 Hz, C_5H_5), 6.77–6.85 (m, *m*-*p*-Ph), 7.08 (m, *o*-C-Ph), 7.43 (m, *o*- PPh_3), 7.47 (m, *o*- PPh_2); ^{13}C { ^1H }: 101.5 (s, C_5H_5), 124.4 (s, *p*-C-Ph), 127.1 (d, J 1 Hz, *p*- PPh_2), 127.2 (d, J 9 Hz, *m*- PPh_2), 127.7 (s, *m*-C-Ph), 128.1 (d, J 9 Hz, *m*- PPh_3), 129.2 (d, J 1 Hz, *p*- PPh_3), 130.1 (s, *o*-C-Ph), 134.3 (d, J 9 Hz, *o*- PPh_2), 134.5 (d, J 13 Hz, *o*- PPh_3), 134.6 (d, J 5 Hz, *ipso*-C-Ph), 136.9 (dd, J 34, 2 Hz, *ipso*- PPh_3), 143.1 (d, J 17 Hz, β -C \equiv), 223.2 (d, J 10 Hz, α -C \equiv); the fifth quaternary C-atom could not be detected; ^{31}P NMR: δ 46.7 (d, J 22 Hz), 188.6 (d, J 22 Hz).

§ *X-Ray structure analysis of 2*: CAD4 diffractometer, graphite-monochromated Mo-K α radiation, solution of structures by direct methods (SHELXS 86);⁸ refinement with full-matrix least squares against F^2

(SHELXL 93).⁹ The red-brown crystals of **2** grew with 0.7 solvent molecule (thf) per formula unit; monoclinic, space group $P2_1/c$; $a = 16.446(1)$, $b = 13.371(1)$, $c = 20.272(1)$ Å, $\beta = 102.268(5)^\circ$; $V = 4356.0(5)$ Å³, $Z = 4$, $D_c = 1.274$ g cm^{-3} ; 7875 reflections measured, 4430 observed [$I > 2\sigma(I)$], $R = 0.0716$, $wR2 = 0.2060$ [$I > 2\sigma(I)$], 459 refined parameters; $2\theta_{\text{max}} = 49.92^\circ$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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