Mechanism of the Platinum-Promoted Conversion of $Cl_2C{=}PR$ to $R{-}C{\equiv}P$, Where R = 2,4,6-Tri-*tert*-butylphenyl

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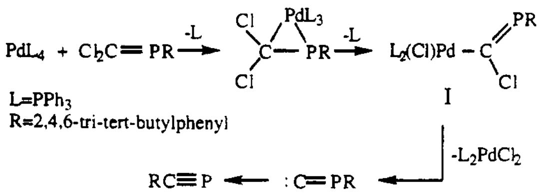
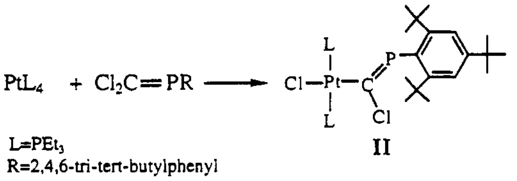
*Summary: The reaction of $Cl_2C{=}PR$ with $Pt(PEt_3)_4$ to give $R{-}C{\equiv}P$ and $Pt(PEt_3)_2Cl_2$ proceeds through intermediates **II** and **III**. An X-ray diffraction study shows that the 2,4,6-tri-tert-butylphenyl ring in **III** is no longer aromatic. However, the aromaticity is restored when migration of the R group from the P to C is completed in forming the $R{-}C{\equiv}P$ product.*

Recently, Romanenko and co-workers[1] reported that the reaction of $Pd(PPh_3)_4$ with $Cl_2C{=}PR$ gives the phosphaalkyne $R{-}C{\equiv}P$ and $Pd(PPh_3)_2Cl_2$ in greater than 85% yield (eq 1). This reaction involves the overall dechlorination of $Cl_2C{=}PR$ and the migration of the supermesityl (R) group from the phosphorus to the carbon. While no intermediates were detected, they proposed that the reaction proceeds by way of initial oxidative addition across a C–Cl bond to give an intermediate (I) which is analogous to **II**, a complex that we isolated previously[2] from the reaction of $Pt(PEt_3)_4$ with $Cl_2C{=}PR$ (eq 2). Their



(1)

mechanism (eq 1) involved elimination of L_2PdCl_2 from this intermediate to give the free aryl isocyaphide $:C{=}PR$, which rearranges to the well-known phosphaalkyne.[3] This latter rearrangement was based on the formation of $R{-}C{\equiv}P$ from the lithiated derivative (eq 3),[4] which was also proposed to occur through free $:C{=}PR$. In this paper, we describe the conversion of complex **II** to $R{-}C{\equiv}P$ and PtL_2Cl_2 (eq 4), as well as the isolation of intermediate **III**, which gives insight into the mechanism of formation of



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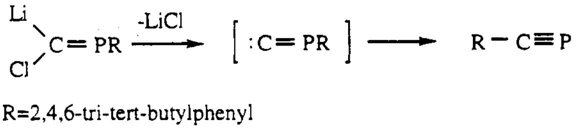
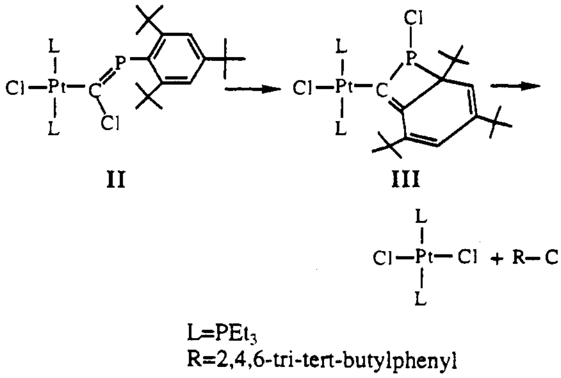


(3)

the phosphaalkyne $R{-}C{\equiv}P$ in this and presumably the similar palladium reaction (eq 1).



(4)

When a solution of complex **II**[2] (0.395 g, 0.500 mmol) in 10 mL of dry CH_2Cl_2 is stirred at room temperature under argon for 24 h, only **III**[5] is formed. It is isolated in 90% yield as air-stable colorless crystals by evaporating the reaction solution to dryness and recrystallizing the residue from hexanes at −30 °C. The structure of **III**, as established by a single-crystal X-ray diffraction study,[6] shows that it contains a remarkable phosphabicyclo ligand. The six-membered ring of this ligand is not aromatic but contains double bonds at C(4)–C(5) (1.348(7) Å) and C(6)–C(7) (1.339(8) Å) and single bonds at C(3)–C(4) (1.509(7) Å), C(2)–C(3) (1.533(6) Å), and C(2)–C(7) (1.490(8) Å), while the C(5)–C(6) distance (1.464(8) Å) is characteristic of the central C—C bond of a diene.[7] In the four-membered ring, C(2)–C(3) (1.533(6) Å) is a single bond, whereas C(1)–C(2) (1.389(8) Å) is a somewhat long double bond.[8] The P(3)–C(3) bond (1.911(6) Å) is also longer than a typical P–C single bond (1.85 Å),[7] but the P(3)–C(1) distance (1.802(5) Å) is close to that of a single bond.

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[5] **III**: ^1H NMR (C_6D_6) δ 6.11 (d, $^4J_{HH} = 1.46$ Hz, 1H, on C6), 6.04 (d, d, $^4J_{HH} = 1.46$ Hz, $^3J_{PH} = 18.80$ Hz, 1H, on C4), 2.14 (m, 6H, CH_2 of Et), 2.00 (m, 6H, CH_2 of Et), 1.54 (s, 9H, CH_3 of R), 1.10 (s, 9H, CH_3 of R), 1.08 (s, 9H, CH_3 of R), 1.18 (m, 9H, CH_3 of Et), 1.08 (m, 9H, CH_3 of Et); $^{31}P\{^1H\}$ NMR (C_6D_6, 85% H_3PO_4 external standard) δ 93.84 (s, $^2J_{PtP}$ = 387.66 Hz, P3), 12.86 (s, $^1J_{PtP}$ = 2737.06 Hz, PEt_3), 11.18 (s, $^1J_{PtP}$ = 2632.53 Hz, PEt_3). Anal. Calcd for $C_{31}H_{59}Cl_2P_3Pt$: C, 47.11; H, 7.46. Found: C, 47.46; H, 7.61.

[6] Crystallographic data for **III**: mol wt 790.7; space group $P\bar{1}$, a = 9.055(2) Å, b = 11.496(2) Å, c = 19.548(4) Å; V = 1825.3(6) Å^3, d_{calcd} = 1.439 g/cm^3 for $Z = 2$ at −80 ± 1 °C, μ = 4.141 mm^{-1} (Mo Kα). Diffraction data were collected at −80 ± 1 °C with an Enraf-Nonius CAD4 automated diffractometer. A total of 6846 reflections were collected. Of the 6404 unique data, 5608 were considered observed, having $F_o^1 > 6.0\sigma(F_o^1)$. R = 0.035 and R_w = 0.050. Details of data collection and refinement are given in the supplementary material.

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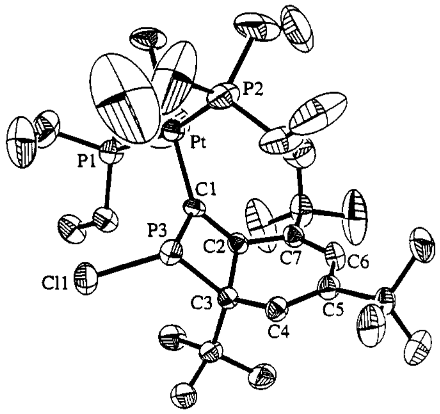
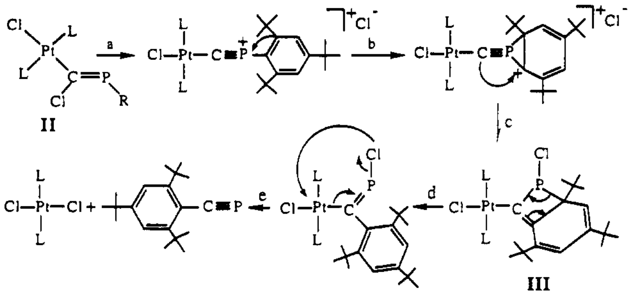


Figure 1. ORTEP Drawing of **III**. Selected bond distances (Å) and angles (deg) are Pt–C(1) = 1.982(4), C(1)–P(3) = 1.802(5), C(1)–C(2) = 1.389(8), C(3)–P(3) = 1.911(6), C(2)–C(3) = 1.533(6), C(4)–C(5) = 1.348(7), C(6)–C(7) = 1.339(8), C(5)–C(6) = 1.464(8), P(3)–Cl(1) = 2.118(2), Pt–C(1)–P(3) = 126.2(3), C(1)–C(2)–C(3) = 106.9(4), and C(2)–C(3)–P(3) = 82.3(3).

In CH_2Cl_2 at room temperature, **III** converts (eq 4) quantitatively within 72 h to R—C≡P and *trans*-Pt$(PEt_3)_2Cl_2$ without ^{31}P NMR evidence for intermediates. Under the same conditions, but in hexanes or benzene, the conversion is complete in less than 24 h.

On the basis of these reaction studies and the structure of **III**, we propose the mechanism in Scheme I for the reaction in eq 4. In step a, Cl^- dissociates to give a highly reactive aryl isocyaphide (C≡P—R) ligand whose positive phosphorus is attacked by an electron-rich carbon on the supermesityl to give a transient intermediate (step b). Addition of the isocyaphide carbon (step c) to the aryl ring carbon gives the characterized intermediate **III**. The formation of **III** clearly indicates that it is thermodynamically more stable than its isomer **II**. This is surprising, since the supermesityl group loses its aromaticity in this isomerization. The aromaticity is restored in the final steps (d and e), leading to *trans*-PtL_2Cl_2 and R—C≡P.

Scheme I



In summary, these studies provide details of the conversion of **II** to PtL_2Cl_2 and R—C≡P via the surprising non-aromatic intermediate **III**. It seems likely that the reaction (eq 1) of $Pd(PPh_3)_4$ with Cl_2C=PR to give analogous products proceeds by a similar mechanism. One might even speculate that the conversion (eq 3) of (Li)(Cl)C=PR to R—C≡P proceeds by the mechanism in Scheme I, where lithium plays the role of platinum.

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Supplementary Material Available: Text giving a description of the data collection and structure solution, a labeled drawing of **III**, and tables of crystal data, positional and thermal parameters, complete bond distances and angles, and least-squares planes (20 pages). Ordering information is given on any current masthead page.

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