Formation of (σ-Alkenyl)- and (μ-Vinylidene)palladium and -platinum Complexes by Oxidative Addition of 4,4-Dichloro-1,1-diphenyl-2-azabuta-1,3-diene – The Molecular Structure of an Unusual Asymmetric (μ-Vinylidene)Pd–Pd Complex

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Keywords: Palladium / Vinylidene ligands / Platinum / Metal-metal interactions

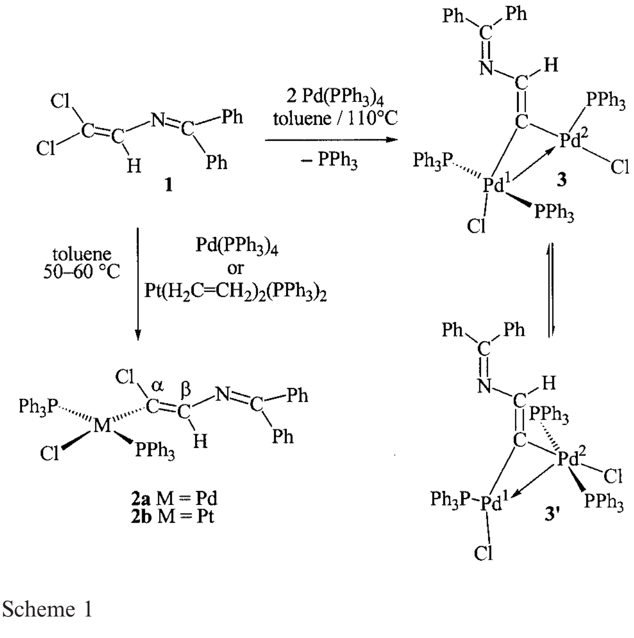
4,4-Dichloro-1,1-diphenyl-2-azabuta-1,3-diene (**1**) oxidatively adds to $[Pd(PPh_3)_4]$ and $[Pt(C_2H_4)(PPh_3)_2]$ giving rise to the σ-alkenyl complexes *trans*-$[MCl\{[C(Cl)=C(H)–N=CPh_2]\}(PPh_3)_2]$ (**2a**: M = Pd; **2b**: M = Pt). When **1** is treated with $[Pd(PPh_3)_4]$ in a 1:2 ratio in refluxing toluene, the dimetallic μ-vinylidene complex $[(PPh_3)ClPd\{\mu\text{-}[C=C(H)–N=CPh_2]\}PdCl(PPh_3)_2]$ (**3**) is formed. In this fluxional compound, a PPh_3 ligands migrates in a reversible manner between the two Pd centers. Substitution of the PPh_3 ligands of **3** by 2 equiv. of $Ph_2PCH_2PPh_2$ affords the A-frame complex $[ClPd(\mu\text{-}dppm)_2\{\mu\text{-}[C=C(H)–N=CPh_2]\}PdCl]$ (**4**).

Introduction

Due to the eminent role of palladium in organometallic synthesis and homogenous catalysis, several methods for the formation of palladium–carbon bonds have been developed.[1] Among them, the oxidative addition of alkyl and aryl halides to Pd^0 complexes is common. It has been shown that vinyl chlorides may also oxidatively add to $[Pd(PPh_3)_4]$ giving rise to σ-alkenyl complexes of the type *trans*-$[PdCl\{[C(R)=CR_2]\}(PPh_3)_2]$.[2] In the course of our earlier studies in the field of organic 1,3-dipolar cycloaddition reactions, we prepared the new dichloro vinyl-like compound 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene (**1**).[3,4] This compound exhibits some promising features for coordination to inorganic and/or organometallic units as it bears a conjugated π-system and a potentially reactive C=N double bond. Furthermore, the basic iminium nitrogen atom may act as a potential donor for coordination of further metal centres to assemble (hetero)dimetallic systems. The group-10 late transition metal (Pd, Pt) complexes seem to be particularly good candidates for activation and coordination of this compound. We present here the first application of **1** in the organometallic chemistry of palladium and platinum.

Results and Discussion

Upon heating in toluene at 50 °C, complex **1** oxidatively adds to $[Pd(PPh_3)_4]$ to yield *trans*-$[PdCl\{[C(Cl)=C(H)–N=CPh_2]\}(PPh_3)_2]$ (**2a**) (Scheme 1). The expected



Scheme 1

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trans orientation of the two PPh_3 ligands follows from the $^{31}P\{^1H\}$ NMR spectrum, which displays a singlet at $\delta = 23.6$ ppm. In order to obtain an unambiguous assignment of the stereochemistry of **2a**, the Pt analogue *trans*-$[PtCl\{[C(Cl)=C(H)-N=CPh_2]\}(PPh_3)_2]$ (**2b**) was prepared by treating **1** in toluene with $[Pt(C_2H_4)(PPh_3)_2]$ at 60 °C. The ^1H NMR spectrum of **2b** indicates that the regioisomer with the hydrogen atom on C-β in the *cis* position relative to the platinum atom is formed exclusively.[5] Since the chemical shifts for the olefinic hydrogen atom of **2a** ($\delta = 6.21$ ppm) and **2b** [$\delta = 6.19$ ppm, $^3J_{cis}(Pt-H) = 27$ Hz] are quite close, we suggest a (*Z*) configuration for these complexes.

When **1** is treated with $[Pd(PPh_3)_4]$ in a 1:2 ratio in refluxing toluene, a two-centre, three-fragment oxidative addition of both vinylidene−chloride bonds across two Pd centers occurs affording the dimetallic μ-vinylidene complex $[(PPh_3)ClPd\{\mu\text{-}[C=C(H)-N=CPh_2]\}PdCl(PPh_3)_2]$ (**3**) in 49% yield {together with small amounts of **2a** and *trans*-$[PdCl_2(PPh_3)_2]$}. Suitable crystals of **3** for an X-ray diffraction study (Figure 1) were grown as red needles from a toluene/heptane solution. Surprisingly, this dimetallic complex possesses two different coordination spheres around each palladium atom; Pd(1) is ligated by P(1), P(2), and Cl(1), and the two Pd^{II} centers are bridged by C(1) in an slightly asymmetric manner [Pd(1)−C(1) 2.031(3), Pd(2)−C(1) 1.910(3) Å]. The close contact between Pd(1) and Pd(2) of 2.6785(3) Å is indicative of the existence of a metal−metal bond,[6,7] therefore Pd(1) may be described as five-coordinate. In contrast, Pd(2) is ligated with Cl(2) and only one phosphane ligand. To achieve the necessary 16-electron count, the metal−metal interaction is best described as a dative Pd1→Pd2 bond.

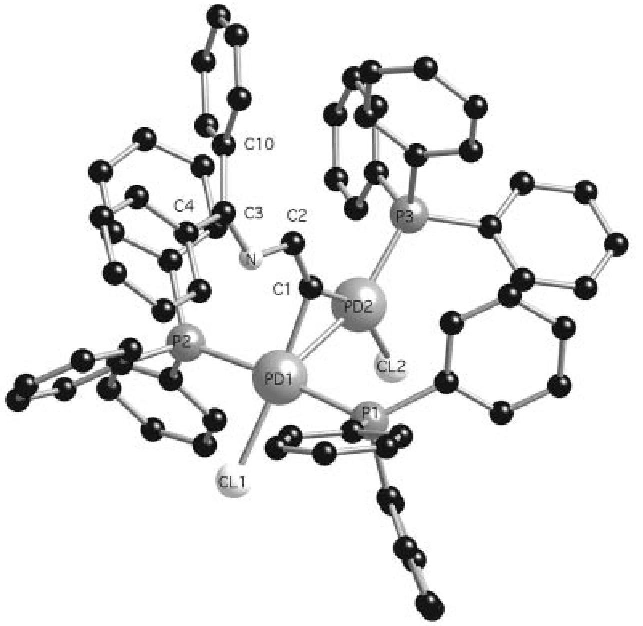


Figure 1. View of the crystal structure of **3**; selected bond lengths [Å] and angles [°]: Pd−Pd 2.6785(3), Pd(1)−P(1) 2.3375(9), Pd(1)−P(2) 2.3430(9), Pd(2)−P(3) 2.2399(9), Pd(1)−C(1) 2.031(3), Pd(2)−C(1) 1.910(3), Pd(1)−Cl(1) 2.3897(9), Pd(2)−Cl(2) 2.3887(9), C(1)−C(2) 1.339(4), N−C(2) 1.407(40), N−C(3) 1.302(4); Cl(1)−Pd(1)−C(1) 173.27(9), P(1)−Pd(1)−P(2) 174.82(3), P(1)−Pd(1)−C(1) 93.74(9), P(2)−Pd(1)−C(1) 91.28(9), P(3)−Pd(2)−C(1) 104.33(10), Pd(2)−C(1)−Pd(1) 85.58(13), C(1)−Pd(1)−Pd(2) 45.32(9), C(1)−Pd(2)−Pd(1) 49.10(10), C(1)−Pd(2)−Cl(2) 155.54(10), C(1)−C(2)−N 121.5(3)

To the best of our knowledge, no related Pd−Pd compound has been structurally characterized to date. However, the overall core structure in **3** is quite similar to that found in a platinum derivative $[(PEt_3)BrPt\{\mu\text{-}[C=C(H)-Ph]\}PtBr(PEt_3)_2]$.[8] Compound **3** is fluxional in solution, since a very broad singlet resonance at $\delta = 27.4$ ppm is observed in the $^{31}P\{^1H\}$ NMR spectrum at 293 K, which sharpens upon heating to 323 K. At low temperature (223 K), the spectrum consists of distinct triplet and doublet resonances in a 1:2 ratio at $\delta = 34.0$ and 24.8 ppm (see Figure 2). Addition of 2 equiv. of PPh_3 (at 293 K) to a sample of **3** has no influence on the chemical shift or shape of the resonance.

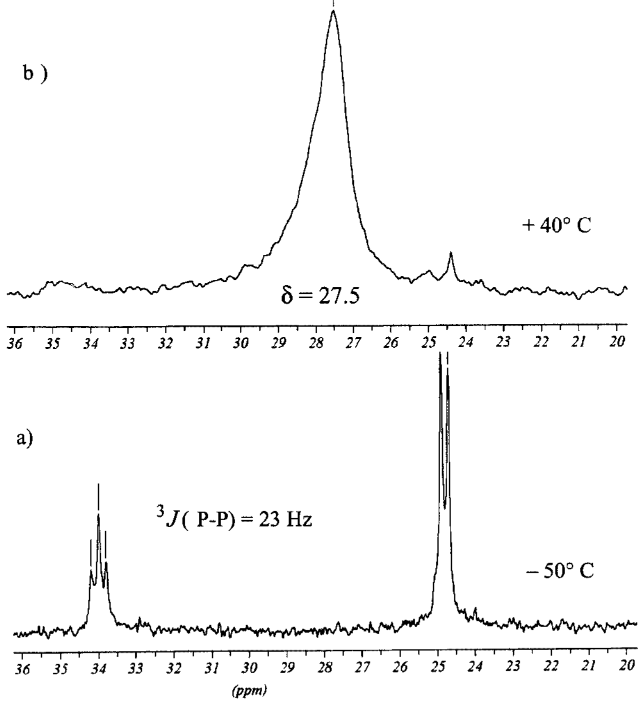
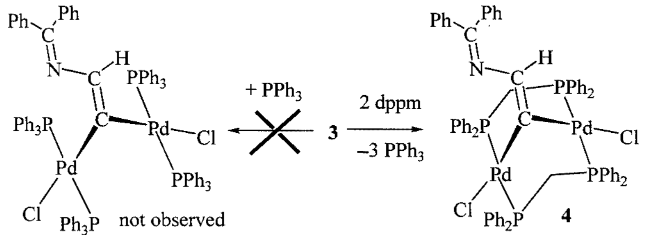


Figure 2. $^{31}P\{^1H\}$ NMR spectrum of **3** recorded in $CDCl_3$ at 223 K (a) and 313 K (b)

This fluxionality may be explained by a nondissociative intramolecular flipping[9a] of one PPh_3 ligand between Pd(1) and Pd(2) with concomitant switching of the vector of the dative bond, resulting in an averaged $\mathbf{3} \rightleftarrows \mathbf{3'}$ equilibrium on the NMR time scale. Note that this hypothesis involving the intermediacy of a μ-PPh_3 ligand is supported by the structural characterization of a stable $Rh(\mu\text{-}PMe_3)_2Rh$ complex.[9b,9c] Furthermore, a related reversible and nondissociative migration of a PR_3 ligand has been studied in detail very recently for the dimetallic system $[\{(\eta^5\text{-}C_5Me_5)Ru\}_2(PR_3)(\mu\text{-}H)_2]$.[9d] The ligation of Pd(2) by *just one* PPh_3 ligand is probably due to steric reasons. To avoid steric overcrowding by four bulky PPh_3 ligands in a mutual *trans* arrangement on each Pd center, steric repulsion is minimized by dissociation of one of the four PPh_3 ligands, followed by an electronic *quasi* saturation of Pd(2) (up to 16 e^-) by formation of a dative Pd→Pd bond during formation of **3**. This hypothesis is corroborated by the observation that after addition of 2 equiv. of dppm, the three PPh_3 ligands are instantaneously replaced by two diphosphane ligands giving complex **4** quantitatively ($^{31}P\{^1H\}$ NMR monitoring, Scheme 2). As expected for an unsymmetrical dipalladium A-frame complex,[10−12] **4** displays an AA′BB′ pattern in the $^{31}P\{^1H\}$ NMR spectrum centered at δ = 16.3 ppm. This asymmetry may be explained by the coplanar orientation of the μ-azabutadiene unit with the $Cl-Pd-C_\mu-Pd-Cl$ array, thus rendering the two Pd environments nonequivalent.



Scheme 2

The potential of **1** and its derivatives as pincer ligands for cyclometallation and carbon−carbon coupling reactions as well for synthesis of other (hetero)dimetallic compounds is currently under investigation.[13]

Experimental Section

General: All reactions were performed in Schlenk-tube flasks under purified nitrogen. Solvents were dried and distilled under nitrogen before use: toluene and heptane from sodium, dichloromethane from P_4O_{10}. The ^1H, $^{31}P\{^1H\}$ NMR, and $^{195}Pt\{^1H\}$ NMR spectra were recorded with a Bruker Avance 300 MHz spectrometer (300.13, 121.49 MHz, and 64.52 MHz for ^1H, ^{31}P, and ^{195}Pt, respectively). Phosphorus chemical shifts are referenced to 85% H_3PO_4 in H_2O with downfield shifts reported as positive. ^{195}Pt chemical shifts are referenced to external K_2PtCl_4 in water with downfield chemical shifts reported as positive. All NMR spectra were recorded in $CDCl_3$.

Preparation of *trans*-[PdCl{[C(Cl)=C(H)−N=CPh$_2$]}(PPh$_3$)$_2$] (2a): Complex **1** (122 mg, 0.44 mmol) was added to a suspension of $[Pd(PPh_3)_4]$ (462 mg, 0.4 mmol) in toluene (15 mL) and the mixture warmed to 50 °C for 5 h. The resulting clear, orange solution was then concentrated to 8 mL, and layered with heptane. After keeping overnight in a refrigerator, **2a** crystallized. The yellow microcrystalline compound was rinsed with hexane (4 mL) and dried in vacuo. Yield: 66% (241 mg). ^1H NMR: δ = 6.21 (s, 1 H, C=CH), 6.49−7.86 (m, 40 H, phenyl) ppm. $^{31}P\{^1H\}$ NMR: δ = 23.6 (s) ppm. $C_{51}H_{41}Cl_2NP_2Pd$ (907.15): calcd. C 67.53, H 4.56, N 1.54; found C 67.98, H 4.56, N 1.90.

Preparation of *trans*-[PtCl{[C(Cl)=C(H)−N=CPh$_2$]}(PPh$_3$)$_2$] (2b): A mixture of $[Pt(C_2H_4)(PPh_3)_2]$ (750 mg, 1 mmol) and **1** (304 mg, 1.1 mmol) in toluene (20 mL) was heated to 60 °C for 14 h. The resulting clear yellowish solution was concentrated to ca. 10 mL and layered with heptane. After keeping at −25 °C, **2b** precipitated as an off-white, air-stable, microcrystalline solid, which was dried in vacuo. Yield: 79% (778 mg). ^1H NMR: δ = 6.19 [s, 1 H, C=CH, $^3J_{cis}$(Pt-H) = 27 Hz], 6.94−7.92 (m, 23 H, phenyl) ppm. $^{31}P\{^1H\}$ NMR: δ = 24.8 (s, $^1J_{Pt,P}$ = 3015 Hz). $^{195}Pt\{^1H\}$ NMR: δ = −2641 (t, $^1J_{Pt,P}$ = 3015 Hz) ppm. $C_{51}H_{41}Cl_2NP_2Pt$ (995.85.): calcd. C 61.51, H 4.15, N 1.41; found C 61.89, H 4.02, N 1.21.

Preparation of [(PPh$_3$)ClPd{μ-[C=C(H)−N=CPh$_2$]}PdCl(PPh$_3$)$_2$] (3): Complex **1** (55 mg, 0.2 mmol) was added to a suspension of $[Pd(PPh_3)_4]$ (462 mg, 0.4 mmol) in toluene (10 mL) and the mixture heated under reflux for 5 h. The solvent was then evaporated and the residue was washed with Et_2O (5 mL). The remaining solid was redissolved in warm toluene and layered with heptane. A mixture of red, air-stable, needle-shaped crystals of **3** and yellow crystals of **2a** and of *trans*-$[PdCl_2(PPh_3)_2]$ co-crystallized; they were separated manually. Yield: 49% (134 mg). ^1H NMR: δ = 6.30 (s, 1 H, C=CH), 6.32−7.98 (m, 55 H, phenyl) ppm. $^{31}P\{^1H\}$ NMR (223 K): δ = 24.8 (d, 2 P, $^3J_{P,P}$ = 23 Hz), 34.0 (t, 1 P, $^3J_{P,P}$ = 23 Hz) ppm. $C_{69}H_{56}Cl_2NP_3Pd_2 \cdot C_7H_8$ (1367.99): calcd. C 66.73, H 4.72, N 1.02; found C 66.98, H 4.54, N 0.97.

Preparation of [ClPd(μ-dppm)$_2${μ-[C=C(H)−N=CPh$_2$]}PdCl] (4): To a solution of **3** (14 mg, 0.01 mmol) in CH_2Cl_2 (2 mL) was added dppm (8 mg, 0.021 mmol). The resulting orange solution was stirred for a further 10 min, and then the solvent was removed under reduced pressure. The residue was rinsed with Et_2O (2 mL) and than dried to afford orange, air-stable **4** in almost quantitative yield (12 mg). ^1H NMR: δ = 2.55 (m, 2 H, PCH_AP), 3.02 (m, 2 H, PCH_BP), 6.53 (m, 1 H, C=CH), 6.70−7.94 (m, 50 H, phenyl) ppm. $^1H\{^{31}P\}$ NMR: δ = 2.55 (d, 2 H, PCH_AP), 3.02 [d, 2 H, PCH_BP, $J(H_A\text{-}H_B)$ = 12.9 Hz], 6.53 (s, 1 H, C=CH), 6.70−7.94 (m, 50 H, phenyl) ppm. $^{31}P\{^1H\}$ NMR: δ = 16.3 (m, AA′BB′ pattern) ppm. $C_{65}H_{55}Cl_2NP_4Pd_2$ (1257.78): calcd. C 62.07, H 4.41, N 1.12; found C 61.68, H 4.24, N 0.96.

X-ray Crystal Structure Determination of 3·Toluene: A small (0.10 × 0.08 × 0.05 mm) irregularly shaped solvated (toluene) single crystal of **3** was mounted on a Nonius Kappa CCD diffractometer. The unit cell determination and intensity data collection were carried out with Mo-K_α radiation (λ = 0.71073 Å) at 120 K. The measured intensities were reduced with the DENZO program.[14] The structure was solved by both Patterson and direct methods using the routines incorporated in SHELXS-97.[15] The asymmetric unit contains one dinuclear complex and one toluene molecule. The model was further refined with SHELXL-97.[15]

Crystallographic Data: $C_{76}H_{64}Cl_2NP_3Pd_2$ (M = 1367.89): monoclinic, space group $P2_1/n$; a = 16.2461(2), b = 25.3368(3), c = 16.7569(2) Å, β = 108.934(1)°, V = 6524.34(14) Å^3, Z = 4, $\rho_{calcd.}$ = 1.393 g·cm^{-3}, $F(000)$ = 2792; 35364 measured reflections in the scan range 5.4° < 2θ < 61.0°, of which 18823 independent and 9156 observed with $I > 2\sigma(I)$ were used in the structure solution and refinement for 757 parameters; $R1 = \Sigma|F_o - F_c|/\Sigma|F_o| = 0.049$ [$I > 2\sigma(I)$], $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2} = 0.101$ (all data), S(GoF) = 0.929; anisotropic refinement for non-hydrogen atoms; hydrogen atoms in idealized (riding model) geometries. The highest residual electron-density peak in the differential Fourier map of 0.98 e·Å^{-3} is quasi-symmetrically located between the heavy palladium atoms (1.38 Å from Pd1 and 1.40 Å from Pd2). CCDC-185833 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. An ORTEP Plot of compound **3** (at the 50% probability level) and the SFC Eurochem 2002 abstract P2-41[13b] are available as Supporting Information.

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