Synthesis, Solution Dynamics, and Crystal Structures of (2,2′:6′,2″-Terpyridine)(η^1- and η^3-allyl)palladium(II) Complexes

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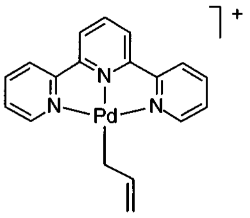
Received July 16, 1996⊗

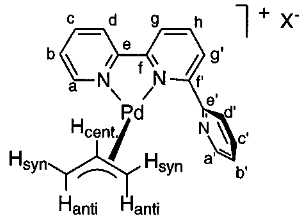
*Summary: The palladium allyl complexes [(2,2′:6′,2″-terpyridine)Pd(C_3H_5)]X (**1**, $X^- = BF_4^-$; **2**, $X^- = ClO_4^-$) were synthesized and characterized. The molecular structures of the η^3- and η^1-allyl isomeric forms of **2**, where the terpyridine ligand coordinates the palladium atom either in a bidentate or in a tridentate fashion, were determined by X-ray crystallography, whereas a variable-temperature ^1H NMR analysis of **1** shows that the complex is fluxional.*

Palladium allyl complexes have been heavily studied in the last 30 years and recently attracted much attention as a result of their importance as intermediates in palladium-catalyzed allylic substitution (*e.g.* alkylation) reactions. Attack of the nucleophile on a cationic palladium π-allyl complex is at present conventionally accepted as the crucial step in the catalytic cycle.[1] One major goal in alkylation catalysis is to gain regio-, stereo-, or enantioselectivity by modifying the nature of the ancillary ligand. To our knowledge, very few palladium complexes possessing a potentially tridentate ligand and an allyl moiety have been described so far.[2] We report herein the synthesis, characterization, and structural analysis of cationic allylpalladium(II) complexes with the tridentate ligand 2,2′:6′,2″-terpyridine (terpy).

Chart 1



1a : X = BF_4
2a : X = ClO_4



1b : X = BF_4
2b : X = ClO_4

Complex **1** is obtained in excellent yield by treatment of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with 2 equiv of silver tetrafluoroborate in CH_2Cl_2 at room temperature, followed by filtration of AgCl and addition of 2.1 equiv of terpy.[3] **1** is formulated as $[(terpy)Pd(C_3H_5)](BF_4)$ according to elemental analysis. In spite of the rigidity of the terpy ligand,[5] the ^1H NMR spectrum[6] of **1** at 188 K clearly indicates it adopts the configuration **1b** in solution (Chart 1), with the allyl ligand in a η^3 mode and the terpy binding nonsymmetrically. In the aromatic region 11 signals of terpyridine are displayed, which resemble very closely the spectra of bidentate metal terpy complexes previously reported in the literature.[7,8] The assignment was made on this basis and confirmed by decoupling experiments.[6] The five allylic signals are characteristic of a dissymmetrical π-allyl ligand (Figure 1). The two high-field resonances at 2.51 and 2.13 ppm can probably be assigned respectively to the H_{anti} and

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⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1996.

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(3) Experimental procedure for **1**: to a solution of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (50 mg, 0.137 mmol) prepared according to ref 4 in CH_2Cl_2 (5 mL) was added dropwise under nitrogen a solution of $AgBF_4$ (53.3 mg, 0.274 mmol) in CH_2Cl_2 (5 mL). The resulting suspension was stirred at room temperature for 4 h and then filtered on Celite, and a solution of terpy (67 mg, 0.287 mmol) in CH_2Cl_2 (5 mL) was added, after which the solution turned from yellow to orange. After it was stirred at room temperature for 30 min, the solution was evaporated to dryness and the resulting air-stable orange solid recrystallized from CH_2Cl_2/diethyl ether (yield 116 mg, 91%). Anal. Calcd for $C_{18}H_{16}N_3BF_4Pd$: C, 46.24; H, 3.45; N, 8.99. Found: C, 46.45; H, 3.23; N, 9.07. MS (FAB$^+$, NBA matrix): m/z 380.0 ($[M - BF_4]^+$, 100%), 339.0 ($[M - BF_4 - C_3H_5]^+$, 54%), 234.1 (terpy, $M + 1$, 61%). **2** was prepared by following an exactly similar procedure, replacing $AgBF_4$ by $AgClO_4$ (92% yield). Anal. Calcd for $C_{18}H_{16}N_3ClO_4Pd$: C, 45.02; H, 3.36; N, 8.75. Found: C, 44.18; H, 3.22; N, 8.24.

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(6) ^1H NMR for **1** (300 MHz, CD_2Cl_2; δ (ppm)): $T = 298$ K, 8.81 (dt, 2H, $^3J_{HH} = 5.1$ Hz, $^4J_{HH} = {}^5J_{HH} = 1.3$ Hz, H_a), 8.35 (t, 1H, $^3J_{HH} = 7.9$ Hz, H_h), 8.24 (d, 2H, H_g), 8.13 (m, 4H, $H_c + H_d$), 7.63 (ddd, 2H, $^3J_{HH} = 5.1$ Hz, $^3J_{HH} = 7.1$ Hz, $^4J_{HH} = 2.0$ Hz, H_b), 5.55 (quintuplet, 1H, $^3J_{HH} = 9.8$ Hz, $H_{central}$), 3.14 (d, 4H, allylic CH_2); $T = 188$ K, 8.76 (d, 2H, $^3J_{HH} = 4.6$ Hz, $H_a + H_{a'}$), 8.40 (m, 2H, $H_d + H_g$), 8.32 (t, 1H, $^3J_{HH} = 7.9$ Hz, H_h), 8.22 (t, 1H, $^3J_{HH} = 7.6$ Hz, H_c), 7.96 (m, 2H, $H_{c'} + H_{g'}$), 7.81 (d, 1H, $^3J_{HH} = 6.3$ Hz, $H_{d'}$), 7.66 (t, 1H, $^3J_{HH} = 6.1$ Hz, H_b), 7.56 (t, 1H, $^3J_{HH} = 5.9$ Hz, $H_{b'}$), 5.47 (tt, 1H, $^3J_{HH} = 12.6$ Hz, $^3J_{HH} = 6.8$ Hz, $H_{central}$), 4.06 and 2.13 (2d, 2H, H_{syn}), 3.35 and 2.51 (2d, 2H, H_{anti}). The peak assignments were supported by irradiations. $^{13}C\{^1H\}$ NMR (50 MHz, CD_2Cl_2; δ (ppm)): 158.3, 157.2 ($C_e + C_f$), 152.1 (C_a), 141.8 (C_h), 139.4 (C_c), 126.7, 125.3, 124.6 ($C_b + C_d + C_g$), 118.4 (allylic CH), 63.7 (allylic CH_2).

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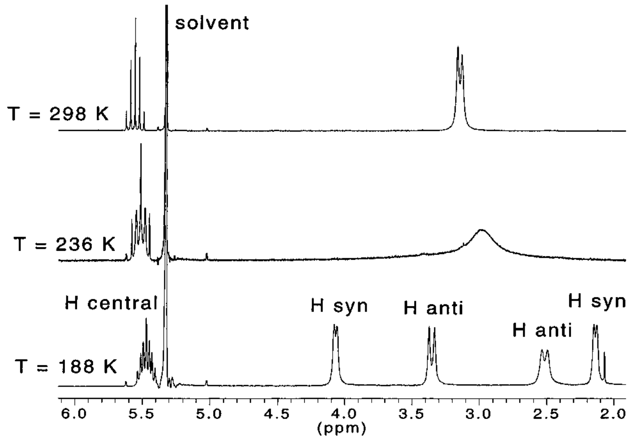

Figure 1. Variable-temperature ^{1}H NMR spectra of **1** in CD_2Cl_2.

H_{syn} protons which lie in the anisotropy cone of the noncoordinating pyridine.

When the temperature is raised to 298 K, a coalescence of certain of the aromatic signals takes place, indicative of the previouly reported fluxional process implicating the two lateral pyridine groups of the terpy ligand.[7,8] We also observe a coalescence of the four lateral allyl protons, the lower spectra shown in Figure 1 corresponding therefore to an AX_4 spin system. The activation barriers calculated from the pyridyl ring hydrogen exchange and the allyl hydrogen exchange are roughly the same ($\Delta G^{\ddagger} = ca.$ 44 kJ mol^{-1}), which infers that the fluxional processes are possibly concerted. The "tick-tock" twist mechanism proposed by Orrell *et al.* for similar "arm-off" intramolecular terpy exchanges is consistent with the observed exchange between the termini of the allyl ligand. However, such a mechanism does not explain the equilibration of the *syn* and *anti* allyl protons; this equilibration necessarily involves the intermediate **1a**. Besides, the ^{13}C NMR of **1** at room temperature is characteristic of an apparently symmetrical terpy ligand, like the ^{1}H NMR spectrum, and it exhibits a single signal for the two lateral allyl carbon atoms.

We prepared the analogous $[(terpy)Pd(C_3H_5)](ClO_4)$ (**2**) using $AgClO_4$ instead of $AgBF_4$, in order to get single crystals suitable for X-ray analysis.[3] Crystallization of **2** under a nitrogen atmosphere by slow diffusion of pentane into a solution of methylene chloride afforded a mixture of red (compound **2a**) and colorless (compound **2b**) crystals. Their molecular structures depicted in Figures 2 and 3 reveal two isomers.[9,11,12] **2a** and **2b** consist of discrete $[(terpy)Pd(C_3H_5)]^+$ cations and noncoordinating perchlorate anions.

In **2a** the terpyridine is acting as a tridentate ligand with the allyl ligand in a η^1 bonding mode (Chart 1). The coordination sphere exhibits a distorted-square-planar geometry, the distortion arising from the rigidity of the chelating terpyridine.[5,13] The Pd−N bond lengths (2.004−2.070 Å), Pd−C16 bond length (2.036(7) Å), N1−Pd−N2 bond angle (79.7(2)°), and N2−Pd−N3 bond

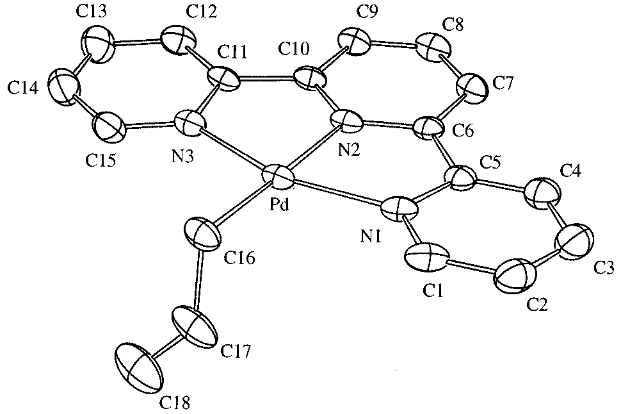

Figure 2. ORTEP drawing of **2a** showing 30% probability thermal ellipsoids and the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Pd−N1 = 2.070(6), Pd−N2 = 2.004(5), Pd−N3 = 2.067(6), Pd−Cl6 = 2.036(7), C16−C17 = 1.47(1), C17−C18 = 1.17(1); N1−Pd−N2 = 79.7(2), N1−Pd−N3 = 159.0(2), N1−Pd−C16 = 100.4(3), N2−Pd−N3 = 79.4(2), N2−Pd−C16 = 178.1(3), N3−Pd−C16 = 100.4(3), Pd−N1−C1 = 129.4(6), Pd−N1−C5 = 113.4(5), Pd−N2−C6 = 117.7(5), Pd−C16−C17 = 109.0(5), C16−C17−C18 = 134(1).

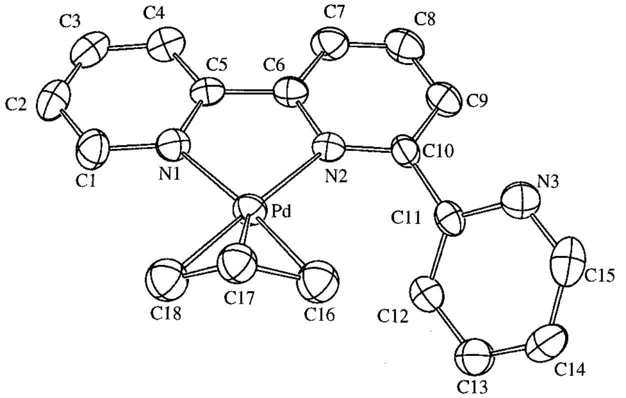

Figure 3. ORTEP drawing of **2b** showing 30% probability thermal ellipsoids and the atom-numbering scheme. Hydrogen atoms and C17′ are omitted for clarity. Selected bond distances (Å) and angles (deg): Pd−N1 = 2.089(6), Pd−N2 = 2.141(6), Pd−C16 = 2.118(9), Pd−C17 = 2.13(1), Pd−C18 = 2.12(1); C16−C17 = 1.41(2), C17−C18 = 1.36(2), N1−Pd−N2 = 78.8(2), N1−Pd−C18 = 102.4(3), N2−Pd−C16 = 110.0(3), C16−Pd−C18 = 68.8(4), Pd−N1−C1 = 125.8(5), Pd−N1−C5 = 115.2(5), Pd−N2−C6 = 111.6(5), Pd−N2−C10 = 129.7(5), C16−C17−C18 = 120(1).

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[9] Crystal data were obtained at 20 °C using an Enraf-Nonius CAD4-F diffractometer with Mo Kα graphite-monochromated radiation ($\lambda = 0.7107$ Å). The scan width (deg) in the $\theta/2\theta$ mode was $\Delta\theta = 0.96 + 0.34 \tan\theta$ (**2a**) or $1.23 + 0.34 \tan\theta$ (**2b**). A total of 4452 $+h+k+l$ (**2a**) or 4460 $+h+k+l$ (**2b**) reflections were recorded within $2° < \theta < 26°$, and 2095 (**2a**) or 2070 (**2b**) relections having $I > 3\sigma(I)$ were used for determining and refining the structure. Absorption corrections derived from the ψ scans of four reflections were applied. The structures were solved using the heavy-atom method and refined using full-matrix least squares to $R(F) = 0.043$ (**2a**) or 0.047 (**2b**) and $R_w(F) = 0.063$ (**2a**) or 0.066 (**2b**). The C16, C17, C17′, and C18 atoms of **2b** have been refined isotropically. The Nonius OpenMolen/Alpha[10] package was used for all calculations.

[10] Fair, C. K. In *MolEN*: *An Interactive Intelligent System for Crystal Structure Analysis*; Nonius: Delft, The Netherlands, 1990.

angle (79.4(2)°) are closely similar to the values found by Vrieze *et al*. for the similar complex [(terpy)Pd(CH_3)]-Cl.[5] As in other tridentate terpyridine complexes,[7a] the Pd−N2 distance is significantly shorter (−0.07 Å) than the Pd−N1 and Pd−N3 distances. The palladium atom lies approximately in the plane defined by N1, N2, N3, and C16, with a deviation of 0.0253(5) Å. The C−C bonds and angles of the allyl fragment are unexceptional when compared with other examples of transition-metal η^1-allyl complexes described in the literature.[14]

The molecular structure of **2b** shows that the allyl moiety is η^3-bonded, with the terpyridine behaving as a bidentate ligand. The coordination sphere presents roughly the same structural features as the related (bipyridine)allylpalladium complex.[15] The distances for Pd−N (2.089−2.141 Å) and Pd−C (2.09−2.13 Å), as well as the angles for N1−Pd−N2 (78.8(2) Å), C16−Pd−C18 (68.8(4) Å), and the angle made by the allyl plane with the N1−Pd−N2 plane (112.9(8)°) are all within the expected range. The two coordinating pyridine rings are nearly coplanar, with a N1−C5−C6−N2 torsion angle of only 1.5(9)°, which is small compared to other known bidentate terpy metal complexes.[7,16] This fact can be related to the absence of an axial ligand in these square-planar complexes and the relatively small size of the allyl ligand. The dihedral angle N2−C10−C11−N3 is 135.4(7)°; such a twist of the noncoordinating pyridine is common in bidentate metal terpy complexes.[7,16] The Pd−N2 bond is *ca*. 0.05 Å longer than the Pd−N1 bond, the Pd−N1−C5 angle is *ca* 4° larger than the Pd−N2−C6 angle, and the N1−Pd−N2 plane is tilted by 11.2(9)° with regard to the least-squares plane defined by N1, C5, C6, and N2; these observations indicate that the palladium atom is repelled by the noncoordinating pyridine. The central allyl carbon atom occupies two sites, one (C17, 70% occupancy) above the plane defined by Pd, N1, and N2 (Figure 3) and the other (C17′, 30% occupancy) below. The allyl ligand is doubly tilted, along the *z* axis (a N1−Pd−C18 angle of 102.4(3)° is observed, while the N2−Pd−C16 angle reaches 110.0(3)°), and along an equatorial axis (C16 is 0.141(9) Å above the N1−Pd−N2 plane, whereas C18 lies 0.043(9) Å below). It is again probable that this tilt arises from a steric interaction between the pendant pyridine and the palladium allyl fragment.

This combined analysis of the (terpy)Pd(allyl) cationic complex in solution and in the solid state establishes that the η^3-allyl and the η^1-allyl forms are both present in solution in a dynamic equilibrium, which is very strongly displaced toward the η^3-allyl form in a CD_2Cl_2 solution at low temperature. A similar example of intramolecular η^3-/η^1-allyl interconversion where both forms are present has been described by Werner *et al*.,[17] but to our knowledge, the results presented here are the first example of an equilibrium between the bidentate (arm-off) and tridentate bonding modes of terpy. Work is in progress in our laboratory to extend this study to other allyl complexes containing tridentate ligands.

Acknowledgment. We thank Gary S. Hanan, Jack W. Faller, and Marie-Thérèse Youinou for helpful discussions, Nathalie Kyritsakas for X-ray analysis, and the Centre National de la Recherche Scientifique for supporting this work. S.R. is indebted to the Ministère de l'Education et de la Recherche Scientifique for a grant.

Supporting Information Available: Tables of positional and thermal parameters, bond distances and angles, and least-squares planes for **2a** and **2b** (20 pages). Ordering information is given on any current masthead page.

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(11) Crystal data for **2a**: $C_{18}H_{16}N_3PdClO_4$, red crystals, $M_r = 480.2$, orthorhombic, space group *Pccn*, $a = 7.223(2)$ Å, $b = 19.446(5)$ Å, $c = 25.595(7)$ Å, $V = 3595.0$ Å^3, $Z = 8$, $D_{calc} = 1.774$ g cm^{-3}, $\mu = 11.969$ cm^{-1}.

(12) Crystal data for **2b**: $C_{18}H_{16}N_3PdClO_4$, colorless crystals, $M_r = 480.2$, orthorhombic, space group *Pbca*, $a = 9.683(2)$ Å, $b = 18.644(5)$ Å, $c = 20.226(6)$ Å, $V = 3651.3$ Å^3, $Z = 8$, $D_{calc} = 1.747$ g cm^{-3}, $\mu = 11.784$ cm^{-1}.

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