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Synthesis, spectral characterization, and X-ray crystal structure of Pd(II) complexes containing the orthometallated C,C-chelating ligand C₆H₄-PPh₂C(H)C(O)CH₂Cl

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Synthesis, spectral characterization, and X-ray crystal structure of Pd(II) complexes containing the orthometallated C,C-chelating ligand C₆H₄-PPh₂C(H)C(O)CH₂Cl

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The ylide-phosphonium salt [PPh₃CH₂C(O)CH₂Cl]⁺Cl⁻ (**1**) reacted with Pd(OAc)₂ to give the chloro-bridged dinuclear complex [Pd{C(H)PPh₃C(O)CH₂Cl}(μ-Cl)(OAc)]₂ (**2**), which underwent bridge cleavage reactions with a neutral bidentate N-donor to afford the cationic orthometallated complexes [Pd{(C,C)-C₆H₄PPh₂C(H)C(O)CH₂Cl}(N-N)]CF₃SO₃ [N=N=bipy (2,2'-bipyridine) (**3**), phen (1,10-phenanthroline) (**4**), 4-Me-phen (4-methyl-1,10-phenanthroline) (**5**), and 5-NO₂ phen (5-nitro-1,10-phenanthroline) (**6**)]. The complexes were identified and characterized by spectroscopic studies (IR and NMR). X-ray single-crystal analysis of **4** and **5** revealed the presence of an orthometallated C₆H₄-PPh₂ unit and a C-linked ylide Pd-C(H). Thermal behavior of **3–6** is investigated by thermogravimetry.

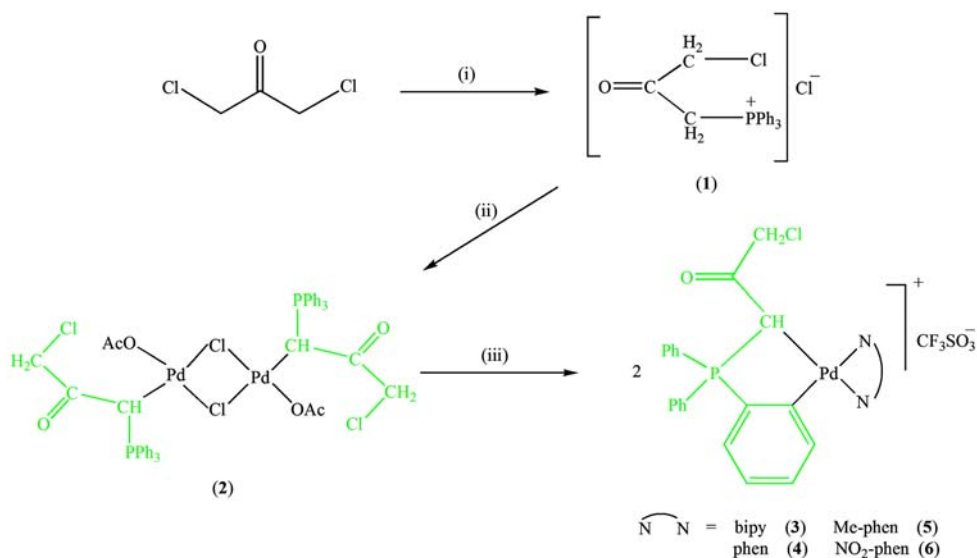
Keywords: CH-bond activation; Cyclopalladated complex; Phosphorus ylide; Crystal structure

1. Introduction

The reactivity and coordination chemistry of phosphorous ylides R₃P=C(R')(R'') (R=alkyl, aryl; R' and R''=H, alkyl, aryl, acyl, etc.) toward transition metals are important in organometallic chemistry [1–19]. They are versatile ligands due to their ambidentate character, in addition to their applicability in organic synthesis [20–22]. Carbonyl-stabilized phosphorus ylides are interesting ligands because they can behave as C or O donors owing to delocalization of the ylidic electron pair [23–29]. Orthometallation of phosphorous ylides [6–812, 1729–32] occurs in the vast majority of cases, regioselectively at Ph rings of the phosphine. Some recent contributions have shown that it is possible to obtain orthopalladated complexes derived from CH activation at Ph rings belonging to the R' or R'' substituents of the ylidic carbon and, more precisely, belonging to benzamide moieties [33].

To expand the scope of C,C-orthometallated complexes [29, 34–36], C–H bond activation processes induced on **2** by addition of bidentate N-donors under mild conditions

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Scheme 1. (i) PPh₃, dichloromethane, 60 °C; (ii) Pd(OAc)₂, dichloromethane, room temperature, 24 h; (iii) (Ag-CF₃SO₃), acetonitrile, bidentate ligand, room temperature.

have been investigated, resulting in synthesis of new mononuclear orthometallated **3–6** (scheme 1).

2. Experimental

2.1. General

Starting materials and solvents were purchased from Merck and used without purification. Infrared spectra were recorded on a FT-IR JASCO 680 spectrophotometer from 4000–400 cm⁻¹ using KBr pellets. NMR spectra were recorded in DMSO-d₆ at room temperature on a Bruker spectrometer at 400.13 MHz (¹H), 100.61 MHz (¹³C), and 161.97 MHz (³¹P). Chemical shifts (ppm) are reported according to internal TMS (¹H, ¹³C) and external 85% phosphoric acid (³¹P). Thermal analysis curves (TG) were obtained from a Labsys TG-DSC 1600 thermal analyzer in flowing air with a heating rate of 10 °C min⁻¹. Elemental analysis was performed on a Leco, CHNS-932 apparatus.

2.2. Synthesis of mono-phosphonium salt [PPh₃CH₂C(O)CH₂Cl]⁺Cl⁻ (1)

To a solution of 1,3-dichloro-2-propanone (0.504 g, 4 mM) in dichloromethane (15 mL) was added PPh₃ (1.048 g, 4 mM). The resulting solution was heated under reflux for 24 h and then filtered through a plug of MgSO₄. The filtrate was concentrated to ca. 2 mL, and n-hexane (15 mL) was added to precipitate **1** as a white solid, which was collected and air-dried. Yield 72%; IR (KBr, cm⁻¹): ν(CO)=1734. ¹H NMR (DMSO-d₆, ppm): δ=4.93 (s, 2H, CH₂Cl), 5.9 (d, 2H, CH₂P ²J_{PH}=12 Hz), 7.53–7.90 (m, 15H, PPh₃). ³¹P {¹H} NMR (DMSO-d₆, ppm): δ=19.84 (s, 1P, CH₂P).

2.3. Synthesis of $[Pd\{C(H)PPh_3C(O)CH_2Cl\}(\mu-Cl)(OAc)]_2$ (**2**)

Phosphonium salt (**1**) (0.116 g, 0.3 mM) was added to a dichloromethane (15 mL) solution of palladium(II) acetate (0.067 g, 0.3 mM) and the mixture was stirred for 24 h at room temperature. The resulting solution was concentrated to ca. 2 mL, and n-hexane (15 mL) was added to precipitate **2** as an orange solid, which was collected and air-dried. Yield: 76%. IR (KBr, cm^{-1}): $\nu(CO)=1671$; $\nu_{as}(COO)=1584$; $\nu_s(COO)=1334$; $\nu(Pd-OAc)=471$. Anal. calcd for $C_{46}H_{42}O_6P_2Cl_4Pd_2$: C, 49.89; H, 3.82. Found: C, 49.22; H, 3.67%.

2.4. Synthesis of $[Pd\{(C,C)-C_6H_4PPh_2C(H)C(O)CH_2Cl\}(bipy)]CF_3SO_3$ (**3**)

Silver triflate ($Ag-CF_3SO_3$) (0.03 g, 0.12 mM) was added to a solution of **2** (0.063 g, 0.06 mM) in acetonitrile (15 mL). The resulting mixture was stirred for 30 min in the absence of light and then filtered through a plug of $MgSO_4$ to remove $AgCl$. Bipyridine (0.018 g, 0.12 mM) was added to the filtrate, and the mixture was stirred for 2 h and then filtered again through $MgSO_4$. The solvent was removed to ca. 2 mL, and n-hexane (15 mL) was added to precipitate **3** as a light green solid, which was collected and air-dried. Yield: 84%. IR (KBr, cm^{-1}): $\nu(CO)=1677$. 1H NMR (DMSO- d_6 , ppm): $\delta=4.58$ (s, 2H, CH_2Cl), 5.04 (s, 1H, CHP) 7.49–7.84 (m, 14H, $(C_6H_4)PPh_2$), 7.95–8.74 (m, 8H, bipy). ^{31}P $\{^1H\}$ NMR (DMSO- d_6 , ppm): $\delta=19.65$ (s, 1P, CHP).

2.5. Synthesis of $[Pd\{(C,C)-C_6H_4PPh_2C(H)C(O)CH_2Cl\}(phen)]CF_3SO_3$ (**4**)

Silver triflate ($Ag-CF_3SO_3$) (0.025 g, 0.1 mM) was added to a solution of **2** (0.05 g, 0.005 mM) in acetonitrile (15 mL). The resulting mixture was stirred for 30 min in the absence of light and then filtered through a plug of $MgSO_4$ to remove $AgCl$. 1,10-phenanthroline (0.018 g, 0.1 mM) was added to the filtrate, and the mixture was stirred for 2 h and then filtered again through $MgSO_4$. The solvent was removed to ca. 2 mL, and n-hexane (15 mL) was added to precipitate **4** as a cream solid, which was collected and air-dried. Yield: 64%. IR (KBr, cm^{-1}): $\nu(CO)=1678$. 1H NMR (DMSO- d_6 , ppm): $\delta=4.73$ (s, 2H, CH_2Cl), 5.24 (s, 1H, CHP) 7.45–7.96 (m, 14H, $(C_6H_4)PPh_2$), 8.32–9.73 (m, 7H, phen), 9.74 (br s, H_a , phen). ^{13}C $\{^1H\}$ NMR (DMSO- d_6 , ppm): $\delta=37.1$ (d, $^1J_{Pc}=56$ Hz), 49.34 ($C_{aliphatic}$), 119.05, 122.26, 123.44, 124.42, 125.07, 125.54, 126.05, 126.64, 127.32, 128.43, 129.34, 129.56, 129.71, 129.83, 131.37, 131.50, 132.07, 132.12, 133.29, 133.35, 135.44, 135.68, 135.82, 137.10, 138.38, 138.90, 142.72, 148.60, 150.61, 152.32 ($C_{aromatic}$), 195.08 (s, CO), ^{31}P $\{^1H\}$ NMR (DMSO- d_6 , ppm): $\delta=19.82$ (s, 1P, CHP).

2.6. Synthesis of $[Pd\{(C,C)-C_6H_4PPh_2C(H)C(O)CH_2Cl\}(4-Me-phen)]CF_3SO_3$ (**5**)

Silver triflate ($Ag-CF_3SO_3$) (0.025 g, 0.1 mM) was added to a solution of **2** (0.05 g, 0.005 mM) in acetonitrile (15 mL). The resulting mixture was stirred for 30 min in the dark and then filtered through a plug of $MgSO_4$ to remove $AgCl$. 4-Me-Phenanthroline (0.019 g, 0.1 mM) was added to the filtrate, and the mixture was stirred for 2 h and then filtered again through $MgSO_4$. The solvent was removed to ca. 2 mL, and n-hexane (15 mL) was added to precipitate **5** as a light purple solid, which was collected and air-dried. Yield: 72%. IR (KBr, cm^{-1}): $\nu(CO)=1677$. 1H NMR (DMSO- d_6 , ppm): $\delta=2.88$

(m, 3H, CH₃), 4.71 (s, 2H, CH₂Cl), 5.23 (s, 1H, CHP) 7.44–8.03 (m, 14H, (C₆H₄)PPh₂), 8.15–9.56 (m, 6H, phen), 9.70 (br s, H_a, phen). ¹³C{¹H} NMR (DMSO-d₆, ppm): δ = 18.76, 36.5 (d, ¹J_{pc} = 57 Hz), 49.28 (C_{aliphatic}), 119.06, 122.26, 123.44, 124.40, 124.78, 125.05, 125.59, 126.08, 126.22, 126.72, 127.15, 128.24, 129.42, 129.51, 129.70, 129.80, 131.34, 131.50, 132.01, 133.27, 133.37, 135.64, 135.85, 136.97, 138.33, 138.77, 141.75, 149.90, 150.59, 151.23 (C_{aromatic}), 194.91 (s, CO), ³¹P {¹H} NMR (DMSO-d₆, ppm): δ = 19.68 (s, 1P, CHP).

2.7. Synthesis of [Pd{(C,C)-C₆H₄PPh₂C(H)C(O)CH₂Cl}(5-NO₂-phen)]CF₃SO₃ (**6**)

Silver triflate (Ag-CF₃SO₃) (0.038 g, 0.12 mM) was added to a solution of **2** (0.068 g, 0.06 mM) in acetonitrile (15 mL). The resulting mixture was stirred for 30 min in the dark and then filtered through a plug of MgSO₄ to remove AgCl. 5-Nitro-phenanthroline (0.023 g, 0.12 mM) was added to the filtrate, and the mixture was stirred for 2 h and then filtered again through MgSO₄. The solvent was removed to ca. 2 mL, and n-hexane (15 mL) was added to precipitate **6** as a yellow solid, which was collected and air-dried. Yield: 63%. IR (KBr, cm⁻¹): ν(CO) = 1679. ¹H NMR (DMSO-d₆, ppm): δ = 4.71 (s, 2H, CH₂Cl), 5.26 (s, 1H, CHP) 7.48–7.79 (m, 14H, (C₆H₄)PPh₂), 9.01–9.35 (m, 6H, phen), 9.86 (br s, H_a, phen). ¹³C{¹H} NMR (DMSO-d₆, ppm): δ = 37.5 (d, ¹J_{pc} = 57 Hz), 49.43 (C_{aliphatic}), 119.05, 121.13, 122.40, 124.22, 125.94, 126.07, 126.27, 126.35, 126.92, 127.25, 129.33, 129.45, 129.75, 129.87, 132.05, 132.15, 133.17, 133.29, 133.40, 133.65, 134.46, 135.59, 135.84, 136.31, 140.61, 141.89, 143.89, 144.08, 152.21, 154.28 (C_{aromatic}), 195.6 (s, CO), ³¹P {¹H} NMR (DMSO-d₆, ppm): δ = 20.32 (s, 1P, CHP).

2.8. X-ray structure determinations

X-ray diffraction data for **4** and **5** were collected at 295 K using a Bruker APEX-II CCD diffractometer and corrected for absorption using SADABS [37]. The structures were solved by direct methods using SIR97 [38] and refined with SHELXL97 [39]. Hydrogens were positioned geometrically and refined using a riding model approximation, with C–H = 0.93–0.98 Å and with U_{iso}(H) = 1.2 U_{eq}(C) or 1.5 U_{eq}(C) for methyl H. In **4**, chloride is disordered over two orientations with refined site occupancies of 0.824(2) and 0.176(2) for the major and minor components, respectively.

3. Results and discussion

3.1. Spectral characterization

The IR spectrum of **1** shows a strong absorption at 1734 cm⁻¹, due to the C=O stretch. The simultaneous presence of an ylide and a phosphonium is clearly inferred from the NMR spectra of **1**. The ¹H NMR spectrum of **1** shows, in addition to the aromatic resonances, two signals centered at 4.93 (s) and 5.9 (d, ²J_{PH} = 12 Hz) attributed, respectively, to the CH₂Cl and CH₂–P⁺ protons. The ³¹P {¹H} NMR spectrum of **1** shows one broad resonance, centered at 19.84 ppm, and attributed to PCH₂.

The treatment of Pd(OAc)₂ with **1** (1 : 1 M ratio) gives an insoluble solid, whose stoichiometry corresponds to the chloro-bridged dinuclear complex [Pd{C(H)PPh₃C(O)CH₂Cl}]

(μ -Cl)(OAc)₂ (**2**) (scheme 1). The C-bonding of the ylide-phosphonium salt can be inferred from the IR spectrum, since a decrease in the C=O stretch is observed [40, 41]. The IR spectrum also showed strong bands at 1584 and 1334 cm⁻¹ due to asymmetric and symmetric ν (COO) stretching bands, respectively, which were consistent with monodentate [42] acetate. The band at 471 cm⁻¹ was assigned to ν (Pd-OAc) [42]. The high insolubility of **2** in the usual organic solvents prevented a more detailed spectroscopic characterization of **2**. Reactivity of the dimeric complex **2** was studied toward bipy, phen, 4-methyl-1,10-phenanthroline (4-Me-phen), and 5-nitro-1,10-phenanthroline (5-NO₂ phen). The reaction of **2** with 2 equiv of bidentate N-donor results in formation of the cationic orthometalated derivatives [Pd{(C,C)-C₆H₄PPh₂C(H)C(O)CH₂Cl}(N-N)]CF₃SO₃ (**3–6**) (N–N=bidentate N-donor) in good yields. The spectroscopic data of **3–6** are in keeping with the proposed structure in scheme 1.

The IR spectra show ν (CO) as a strong band at 1671–1679 cm⁻¹, lower than the parent phosphonium salt **1**. This lowering is well-established in complexes containing other carbonyl-stabilized phosphorus ylides [40, 41] and shows that the ligand coordinates through the carbon and not through oxygen; this has been confirmed for **4** and **5** by X-ray diffraction. The ν (P–C), which is also sensitive to coordination, occurs at 871 cm⁻¹ in the phosphonium salt **1** and shifts to lower frequencies for the complexes, suggesting removal of electron density of the P–C bands [29, 43]. The IR spectra of **3–6** also show significant absorptions at 1029–1057 cm⁻¹ according to the presence of uncoordinated CF₃SO₃⁻.

The ¹H NMR spectra of **3–6** show broad signals for the PC(H) at 5.04–5.26 ppm, shifted upfield in comparison with the parent phosphonium salt. Similar behavior has already been observed for other C-coordinated phosphonium ylide complexes [41].

In ³¹P {¹H} NMR spectra of **3–6**, signals due to PC(H) groups are 19.58–19.68 ppm. ¹³C {¹H} NMR spectra of **4–6** show signals due to the ylidic carbon at 37.1 (¹J_{pc} = 56 Hz), 36.5 (¹J_{pc} = 57 Hz), and 37.5 ppm (¹J_{pc} = 57 Hz), respectively, with characteristic coupling constants for a C-bonded ylide [32, 35, 41].

There are two factors that promote ortho-metallation: (i) the presence of the acetate in **2** which helps the C–H bond breaking by acting as an intramolecular base for deprotonation [44] and (ii) coordination of chelating (N–N) ligands to **2** which leaves the phenyl groups of the phosphine in close proximity to the ylidic fragments C(H)PPh₃ and promotes ortho-metallation to minimize steric repulsions [41].

3.2. Crystal structures

Single crystals suitable for structure determinations were obtained by slow diffusion of diethyl ether into chloroform solutions of **4** and **5**, respectively. Crystallographic data and parameters concerning data collection and structure solution and refinement are summarized in table 1. Selected bond lengths (Å) and angles (°) are listed in table 2. An ORTEP view of the cation of **4** and **5** is shown in figures 1 and 2, respectively. The geometric parameters describing the coordination environment of the metal and the conformation of the five-membered metallacycles in the cations of **4** and **5** are very similar. The square planar coordination geometry of Pd is slightly tetrahedrally distorted, with palladium protruding from the plane of the N₂C₂ core by 0.01073(15) and 0.0239(3) Å in **4** and **5**, respectively. Distortion from the regular square planar geometry is indicated by bond angles subtended at the Pd centers (table 2). The Pd–C_{aryl} bond distances (1.994(2) and 1.993(4) Å for **4** and **5**, respectively) are within the range usually reported for C,C-ortho-palladated complexes [29, 35]. The Pd–N₂ distances (2.1388(17) and 2.135(3) Å) are

Table 1. X-ray crystallographic data for **4** and **5**.

	4	5
Empirical formula	C ₃₄ H ₂₅ ClN ₂ OPPd·CF ₃ O ₃ S	C ₃₅ H ₂₇ ClN ₂ OPPd·CF ₃ O ₃ S
Formula weight	787.44	801.47
<i>T</i> /K	295(2)	295(2)
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	10.3399(5)	10.822(2)
<i>b</i> /Å	10.7947(5)	10.854(2)
<i>c</i> /Å	15.0333(7)	14.801(3)
<i>α</i> /°	82.6359(7)	84.721(3)
<i>β</i> /°	82.5068(7)	76.596(3)
<i>γ</i> /°	77.8977(7)	83.400(4)
<i>V</i> /Å ³	1617.83(13)	1676.1(6)
<i>Z</i>	2	2
<i>μ</i> (mm ⁻¹)	0.83	0.80
<i>D</i> _{cal} /Mg m ⁻³	1.616	1.588
<i>F</i> (000)	792	808
<i>θ</i> Range/°	1.4–30.0	1.4–25.3
Independent reflections	9399	6066
Data/restraints/parameters	9399/0/434	6066/0/434
Goodness-of-fit on <i>F</i> ²	1.037	1.046
Final <i>R</i> indices	<i>R</i> ₁ = 0.0323, <i>wR</i> ₂ = 0.0854	<i>R</i> ₁ = 0.0448, <i>wR</i> ₂ = 0.1114
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0383, <i>wR</i> ₂ = 0.0900	<i>R</i> ₁ = 0.0514, <i>wR</i> ₂ = 0.1161
Largest diff. peak and hole (e Å ⁻³)	0.75, -0.68	1.86, -0.87

Table 2. Selected bond lengths (Å) and angles (°) for **4** and **5**.

	4	5
<i>Bond lengths</i> (Å)		
Pd1–C5	1.994(2)	1.993(4)
Pd1–C1	2.0894(18)	2.097(4)
Pd1–N1	2.1074(17)	2.109(3)
Pd1–N2	2.1388(17)	2.135(3)
P1–C1	1.7857(18)	1.789(4)
P1–C10	1.805(2)	1.802(4)
P1–C4	1.777(2)	1.778(4)
P1–C16	1.809(2)	1.809(4)
<i>Bond angles</i> (°)		
C5–Pd1–C1	85.13(7)	84.94(16)
C5–Pd1–N1	98.18(8)	98.93(16)
C1–Pd1–N1	175.93(7)	173.46(14)
C5–Pd1–N2	176.86(7)	175.95(15)
C1–Pd1–N2	97.73(7)	97.84(14)
N1–Pd1–N2	79.03(7)	78.57(14)

longer than the Pd–N1 distances (2.1074(17) and 2.109(3) Å) for **4** and **5**, respectively, due to the greater *trans* influence of the aryl carbon with respect to the ylidic carbon.

The stabilized resonance structure for the parent ylide-phosphonium is destroyed due to complexation, thus the C1–C2 bond lengths (1.480(3) and 1.478(5) Å) in **4** and **5**, respectively, are significantly longer than the corresponding distances found in similar uncomplexed phosphoranes (1.407(8) Å [45]), meaning that this bond has been relaxed,

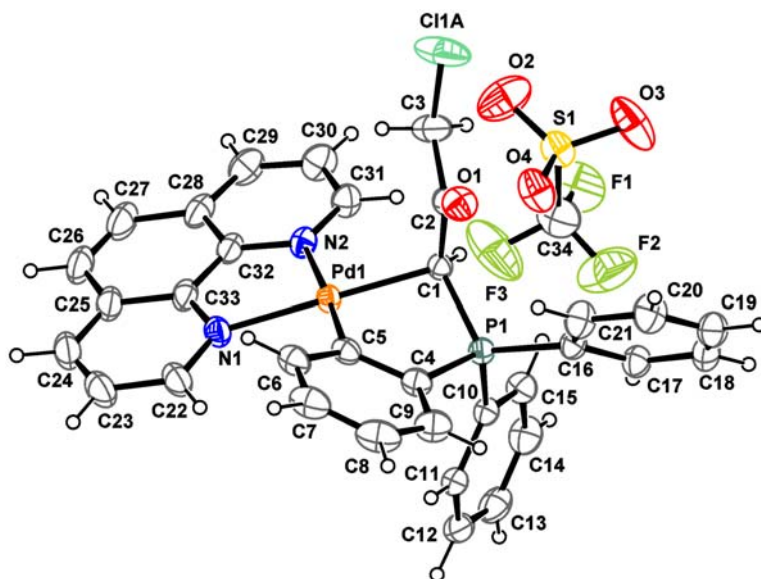


Figure 1. ORTEP plot of **4** with displacement ellipsoids drawn at the 30% probability level. Only the major component of the disordered chloride is shown.

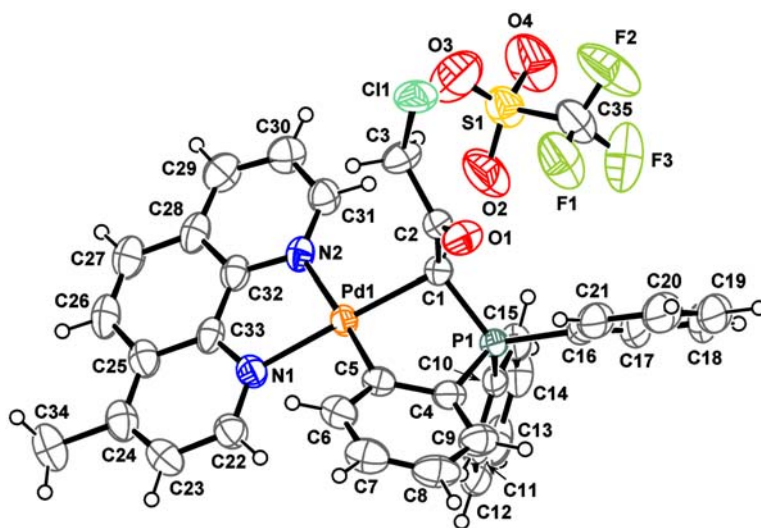


Figure 2. ORTEP plot of **5** with displacement ellipsoids drawn at the 40% probability level.

while the C2–O1 bond lengths (1.204(3) and 1.202(5) Å in **4** and **5**, respectively) are shorter than observed in similar ligand (1.256(2) Å) [45], which indicates that the C-bonding of the ligand fixes the charge density at C and breaks the conjugation. In the crystal structures of **4** and **5**, the complexes are stabilized by intramolecular C–H...O hydrogen bonds (figures 3 and 4, respectively).

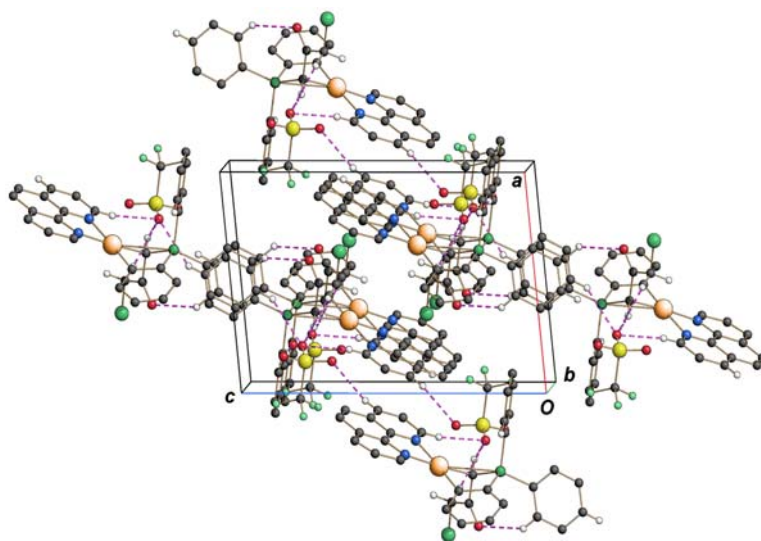


Figure 3. Packing diagram of **4**. Dashed lines represent the hydrogen bonding interactions. Hydrogens not involved in hydrogen bonding are omitted for clarity.

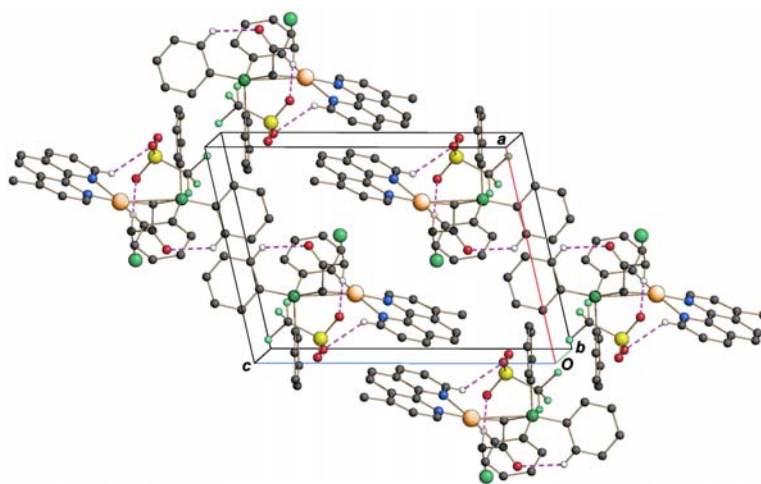


Figure 4. Packing diagram of **5**. Dashed lines represent the hydrogen bonding interaction. Hydrogens not involved in hydrogen bonding are omitted for clarity. Only the major component of the disordered chloride is shown.

3.3. Thermogravimetric analysis

Thermogravimetric analyses [46] of **3–6** were carried out to define the influence of N-donor on the initial decomposition temperature and on the thermal decomposition mechanism. The steps, initial and final temperatures ($^{\circ}\text{C}$), partial mass losses (%) for the thermal decompositions of four complexes, are given in table 3. The thermal decomposition of **3** occurs in two consecutive steps. The first mass loss occurs between $350\text{--}450\text{ }^{\circ}\text{C}$

Table 3. Thermal analysis data for **3–6**.

Complex	Step	$\Delta T/^\circ\text{C}$	Δm (%)		Assignment
			Found	Calcd	
3	1	350–450	38.16	39.89	bipy, CF_3SO_3
	2	450–560	45.23	46.07	$-\text{C}_6\text{H}_4\text{-PPh}_2\text{C(H)C(O)CH}_2\text{Cl}$
4	1	360–450	30.82	30.41	$-\text{C(H)C(O)CH}_2\text{Cl}$, CF_3SO_3
	2	450–550	56.45	56.06	phen, $-\text{C}_6\text{H}_4\text{PPh}_2$
5	1	360–455	29.94	29.88	$-\text{C(H)C(O)CH}_2\text{Cl}$, CF_3SO_3
	2	455–560	57.12	56.83	4-Me-phen, $-\text{C}_6\text{H}_4\text{PPh}_2$
6	1	355–500	28.79	28.77	$-\text{C(H)C(O)CH}_2\text{Cl}$, CF_3SO_3
	2	500–620	58.61	58.44	5- NO_2 -phen, $-\text{C}_6\text{H}_4\text{PPh}_2$

corresponding to, by mass calculation, loss of CF_3SO_3 and bipy and the uptake of O_2 . The second mass loss takes place between 450–560 °C and corresponds to elimination of $-\text{C}_6\text{H}_4\text{-PPh}_2\text{C(H)C(O)CH}_2\text{Cl}$. Complexes **4–6** present similar decomposition patterns. The first step of decomposition corresponds to release of CF_3SO_3 and $-\text{C(H)C(O)CH}_2\text{Cl}$ from 355–500 °C and uptake of O_2 . From 450–620 °C, a mass loss occurs which was attributed to elimination of the bidentate N-donor and $-\text{C}_6\text{H}_4\text{-PPh}_2$ group. All complexes also exhibited a mass gain from 550–850 °C, attributed to PdO formation (ASTM card file 6-0515). This behavior was already observed for other palladium complexes [46, 47]. By taking into account the initial temperature of the decomposition process, **3–6** show similar thermal stabilities, indicating that the presence of different N-donor ligands has a minor influence on the thermal behavior.

4. Conclusion

A new dinuclear complex has been obtained through reaction of the ylide-phosphonium salt $[\text{PPh}_3\text{CH}_2\text{C(O)CH}_2\text{Cl}]^+\text{Cl}^-$ (**1**) with Pd(OAc)_2 giving $[\text{Pd}\{\text{C(H)PPh}_3\text{C(O)CH}_2\text{Cl}\}(\mu\text{-Cl})(\text{OAc})_2]$ (**2**). Orthometallation can be promoted under mild conditions by reacting **2** with bidentate N-donor chelating ligands resulting in synthesis of mononuclear orthometalated complexes (**3–6**), in which a five-membered metallacycle is formed. The crystal structures of **4** and **5** allowed complete characterization of the cyclometallated ligand. The thermoanalytical data of **3–6** show that the thermal degradation consists of elimination of the ligands and oxidation of the remaining Pd to PdO.

Supplementary data

CCDC 913735 and 913734 contain the supplementary crystallographic data for **4** and **5**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/contents/retrieving.html>, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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