# Novel Air-Stable and Volatile Bis(pyridylalkenolato)palladium(II) and -platinum(II) Derivatives

Lisa Brückmann, Wieland Tyrra, Stefan Stucky, and Sanjay Mathur*

Chair, Inorganic and Materials Chemistry, Institute of Inorganic Chemistry, University of Cologne, Greinstrasse 6, 50939 Cologne, Germany

Ⓢ *Supporting Information*

ABSTRACT: Six novel homoleptic palladium(II) and platinum(II) complexes of donor-substituted alkenol ligands [PyCHC(R)OH; Py = pyridine, R = CH_3, CF_3, C_2F_5, C_3F_7] of the general formula $M[PyCHC(R)O]_2$ (M = Pd, Pt) were synthesized by reacting the deprotonated ligands with $PdCl_2$ and K_2PtCl_4, respectively. Molecular structures, revealed by single-crystal X-ray diffraction analyses, showed a square-planar arrangement of ligands around palladium and platinum centers, with the pyridine-ring nitrogen atoms situated in a mutually *trans* position. The monomeric nature of the compounds in the solution state was confirmed by multinuclear (^1H, ^{13}C, and ^{19}F) NMR spectroscopy. Thermal decomposition profiles recorded under a nitrogen atmosphere suggested their potential as volatile precursors to palladium and platinum materials. The volatility was increased upon elongation of the perfluoroalkyl chain, which suppressed the intermolecular interactions, as is evident in crystal packings. The volatility of these compounds was attributed to bidentate chelation of the alkenol units and cooperativity among the electron-back-donating nitrogen atom and interplay of electron-withdrawing C_xF_y groups, resulting in an effective steric shielding of the metal atoms.
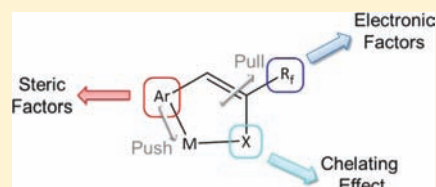
INTRODUCTION

Noble-metal coatings and clusters have found increasing applications in the recent past because of their useful optical and catalytic properties.[1,2] In particular, palladium and platinum nanostructures have generated a great deal of scientific and technological interest as electrodes in microelectronics,[3,4] as Ohmic and Schottky diode contacts in circuitry,[5,6] as solid-supported catalysts,[7,8] in the fabrication of hydrogen separation membranes,[9−11] and for enhanced gas sensing.[12,13]

The major limiting factor in the chemical synthesis of palladium and platinum material structures is the lack of adequate precursors that would produce high-purity materials under mild processing conditions. For gas-phase techniques such as chemical vapor deposition (CVD) and atomic layer deposition (ALD), suitable precursors are required to be volatile and thermally stable, to avoid premature decomposition, and should exhibit a clean ligand-stripping mechanism under deposition conditions. In addition, the precursors should be nontoxic, easy to prepare in high yields, and possess sufficiently long shelf-lives. The common class of CVD precursors to palladium and platinum include η^3-allyl,[7,14] η^1- or η^5-cyclopentadienyl,[15,16] and β-diketonato[17,18] derivatives. Among them, only a small number of compounds possess sufficient volatility to be used as valid metal organic CVD (MOCVD) sources, while others are air-sensitive. Therefore, the major thrust of this investigation was to design new palladium(II) and platinum(II) compounds with tunable physicochemical properties promising for CVD applications. For this purpose, substituted β-alkenols based on the cooperativity of electron-withdrawing perfluoroalkyl groups and electron-donating aromatic units in the ligand backbone

[PyCHC(R_f)OH; Py = pyridine, R_f = fluoroalkyl unit] were employed to obtain volatile palladium and platinum precursors. The ligand design enabled modulation of both steric and electronic elements to achieve an optimal coordinative saturation and stability of the metal centers.

RESULTS AND DISCUSSION

Synthesis of Palladium(II) and Platinum(II) Complexes (1−6). The precursor syntheses were performed using an alkenol (**A**) containing a pyridine substituent that exhibited chemical characteristics comparable to those found in β-diketones (**B**; Figure 1).
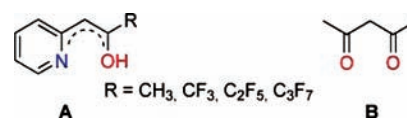
Figure 1. Schematic drawing of a donor alkenol **A** and a β-diketone **B**.

The chelating ability of the PyCHC(R_f)OH backbone and the stability of the resulting six-membered ring offer an interesting option to limit oligomerization of metal derivatives. The presence of an electron-withdrawing R_f group (R_f = CF_3, C_2F_5, C_3F_7) in **A** shifted the keto−enol equilibrium in favor of the enol tautomer. From this point of view, the presented ligand systems can be considered as hetero-aryl-substituted alkenols. The introduction of different alkyl groups with or

**Scheme 1. Syntheses of Complexes 1−3**

1; R_f = CF_3
2; R_f = C_2F_5
3; R_f = C_3F_7
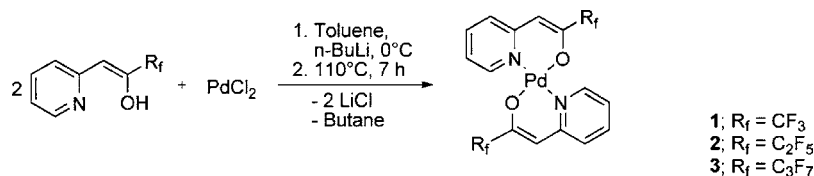
without fluorine revealed the influence of ligand periphery and associated electronic factors on the volatility of the complexes. The enhancement in the vapor pressure upon substitution of hydrogen with fluorine is well documented for metal β-diketonates and alkoxides.[19−21]

The palladium complexes **1−3** were prepared following a facile salt-elimination reaction between anhydrous $PdCl_2$ and *in situ* lithiated ligands (Scheme 1). $[Pd(PyCHC(CH_3)O)]_2$ (**4**) was based on the methyl derivative of the β-alkenolate unit and was synthesized following the procedure described by El-Dissouky et al.[22] $PdCl_2$ was added to an ethanolic solution of the ligand, and the resulting suspension was heated at reflux (5 h) until a white solid precipitated, which was identified by elemental analysis to be the complex $[PdL_2Cl_2]$. Treating a
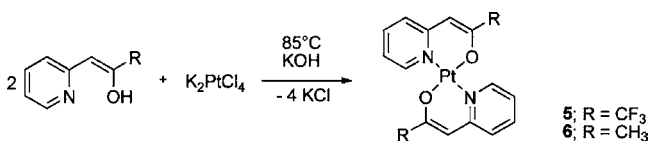
Scheme 2. Synthesis of Complex 4
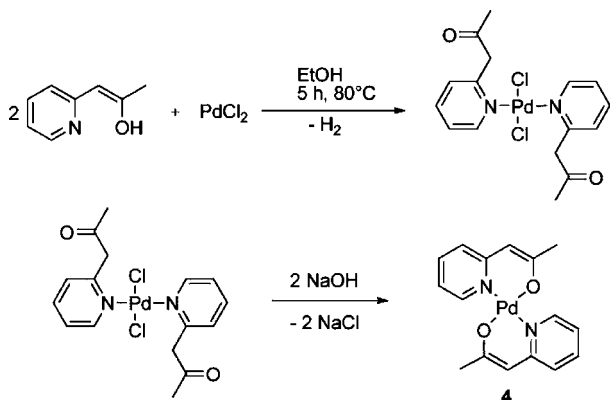
suspension of this complex in EtOH with NaOH (2 M) yielded the desired complex **4** (Scheme 2).

The platinum(II) complexes **5** and **6** were synthesized following a modified procedure reported by Behnke and Nakamoto.[23] They were obtained by a salt metathesis reaction

Scheme 3. Syntheses of Complexes 5 and 6

5; R = CF_3
6; R = CH_3

of K_2PtCl_4 and the ligand in an aqueous KOH solution (Scheme 3).

NMR Analysis. Multinuclear NMR data of **1−6** were recorded at room temperature in $CDCl_3$ solutions. The assignment of the NMR resonances (Scheme 4) was achieved by a combination of $^{13}C−^{19}F$, $^{13}C−^{1}H$, and $^{1}H−^{1}H$ correlation experiments.

The ^{1}H NMR spectra of compounds **1−6** showed the expected pattern of an ABCD spin system of the four

**Scheme 4. Molecular Structures and Arbitrary Atom Numbering for Complexes 3 and 5**
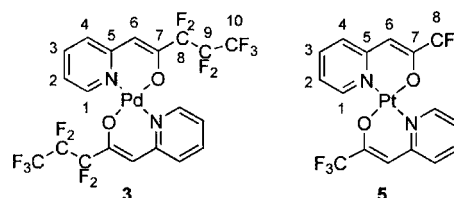
magnetically inequivalent protons for a pyridine ring and are in excellent agreement with the proposed molecular structures. For the sake of simplification, signals exhibiting doublets for H1 and H4 and triplets for H2 and H3 are considered first-order. The vinylic protons (H6) for complexes **1−3** and **5** are located around 5.85 ppm, while the resonances of H6 of **4** and **6** are significantly shifted to higher field (5.19 and 5.24 ppm, respectively). Although platinum satellites surrounding the H1 resonances were observed for both **5** and **6**, a ^{195}Pt NMR signal could only be detected for **5** at −1228 ppm. For **6**, a signal could not be detected, neither by direct methods (^{195}Pt) nor by inverse ($^{1}H−^{195}Pt$) HMBC experiments optimized for 35 Hz, in the range of +3000 to −6000 ppm, even after long acquisition times. The ^{19}F NMR signals for **1−3** and **5** were observed in the range expected for carboxylic moieties. In the ^{13}C NMR spectra, the chemical shifts of all six compounds showed similar patterns especially for the aromatic carbon atoms. The signals of C7 fall into the range of 152.6−154.1 ppm in complexes **1−3** and **5**, while in complexes **4** and **6**, they are detected significantly downfield at 169.2 and 168.1 ppm, respectively. This deshielding is attributed to the strong electron-withdrawing influence of the perfluoroalkyl groups.

In contrast to the investigation of Okeya et al.,[24] who found an equilibrium mixture of *cis* and *trans* isomers in solution for unsymmetrical square-planar $[M(\beta\text{-diketonates})_2]$ (M = Pd, Pt), only the *trans* isomer could be detected in complexes **1−6**. The geometrical arrangement could be proven unambiguously by $^{1}H−^{19}F$ HOESY NMR experiments.

X-ray Diffraction Analysis. Compounds **1** and **5** (Figures 2 and 6) crystallized in the triclinic space group $P\bar{1}$ (No. 2) with two independent molecules per unit cell. Because the values for bond lengths and angles in the two molecules are almost identical, only the molecules containing Pd1 and Pt1 are discussed. Compounds **2−4** (Figures 3−5) crystallized in the monoclinic space group $P2_1/c$ (No. 14). The central metal atoms in all five compounds display a square-planar arrangement of ligands with the nitrogen atoms of the pyridine ring situated mutually in the *trans* position.

The metal−ligand interactions and stereochemical features of **1−5** are comparable with other reported palladium and platinum complexes with chelating N,O ligands.[25−27] The Pd−N bond lengths of 2.03−2.06 Å as well as the Pd−O bond lengths of 1.97−1.98 Å are similar to the interatomic distances observed in comparable complexes. Likewise, the bite angles
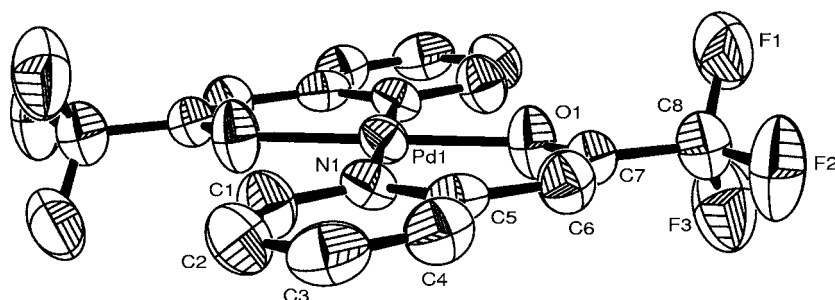
Figure 2. Molecular structure of **1** with an atomic labeling scheme (hydrogen atoms are omitted for clarity). Thermal ellipsoids are shown at 50% probability level. Selected bond lengths (Å) and angles and torsion angles (deg): Pd1−O1 1.974(3), Pd1−N1 2.060(4), O1−C7 1.286(6), C7−C6 1.330(7); O1−Pd1−N1' 87.54(15), O1−Pd1−N1 92.46(15); O1−Pd1−N1'−C1 4.88(36), N1−Pd1−O1−C7 5.86(49).
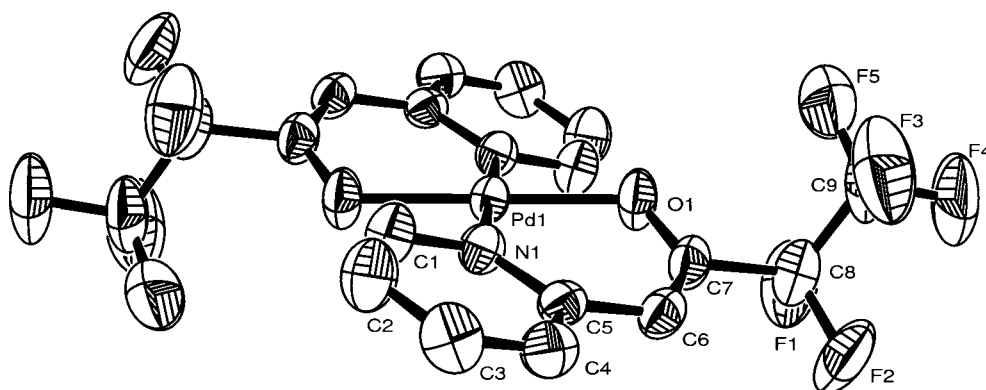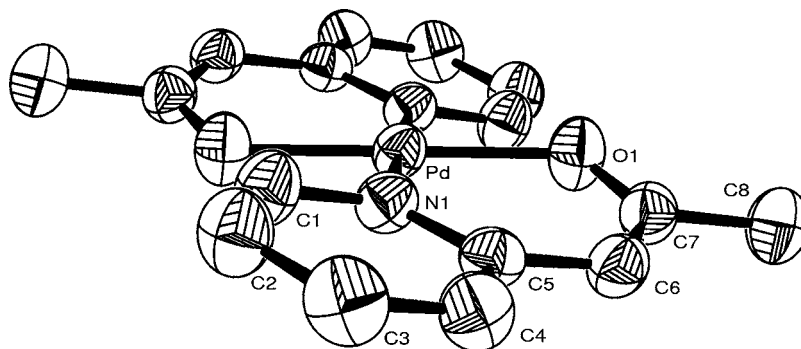

Figure 3. Molecular structure of **2** with an atomic labeling scheme (hydrogen atoms are omitted for clarity). Thermal ellipsoids are shown at 50% probability level. Selected bond lengths (Å) and angles and torsion angles (deg): Pd1−O1 1.985(2), Pd1−N1 2.042(3), O1−C7 1.301(4), C7−C6 1.338(5); O1−Pd1−N1' 88.53(10), O1−Pd1−N1 91.48(9); O1−Pd1−N1'−C1 19.53(25), N1−Pd1−O1−C7 29.38(24).
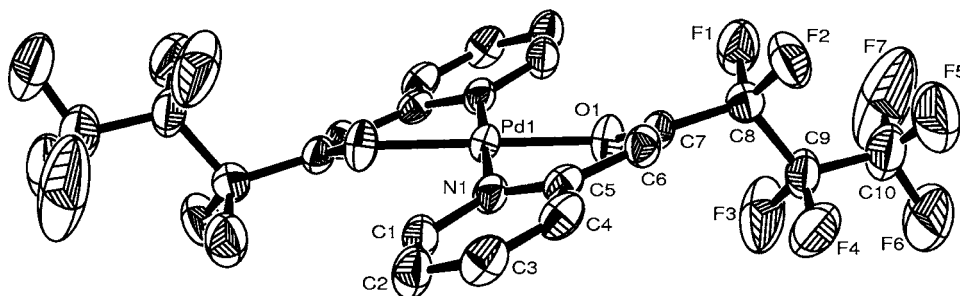
Figure 4. Molecular structure of **3** with an atomic labeling scheme (hydrogen atoms are omitted for clarity). Thermal ellipsoids are shown at 50% probability level. Selected bond lengths (Å) and angles and torsion angles (deg): Pd1−O1 1.981(4), Pd1−N1 2.027(6), O1−C7 1.298(8), C7−C6 1.339(8); O1−Pd1−N1' 88.21(19), O1−Pd1−N1 91.79(19); O1−Pd1−N1'−C1 20.98(53), N1−Pd1−O1−C7 29.55(49).
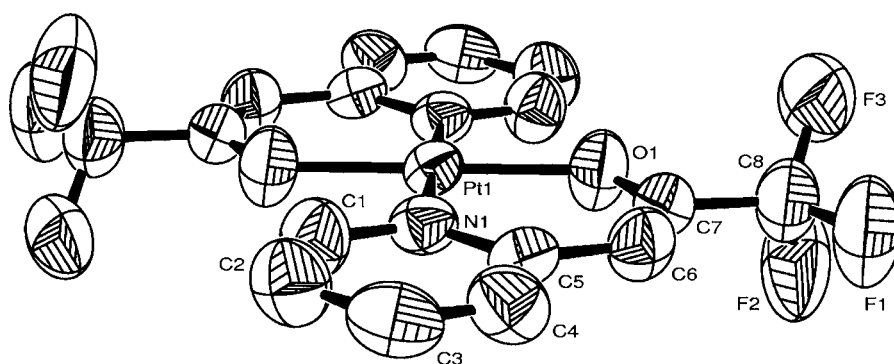

Figure 5. Molecular structure of **4** with an atomic labeling scheme (hydrogen atoms are omitted for clarity). Thermal ellipsoids are shown at 50% probability level. Selected bond lengths (Å) and angles and torsion angles (deg): Pd−O1 1.985(13), Pd−N1 2.055(18), O1−C7 1.296(2), C7−C6 1.360(4); O1−Pd−N1' 87.65(6), O1−Pd−N1 92.35(6); O1−Pd−N1'−C1 14.62(15), N1−Pd−O1−C7 20.80(16).
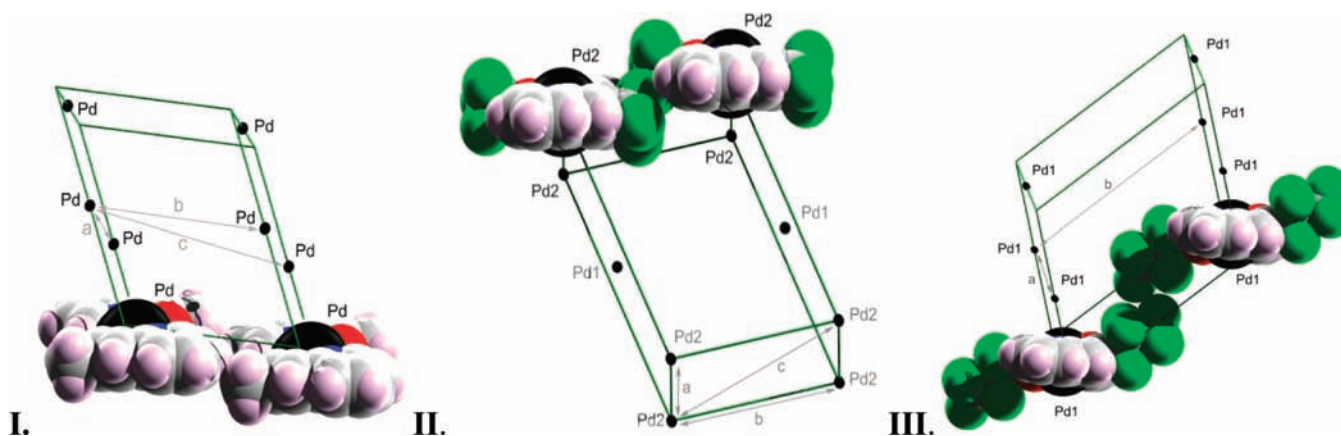
Figure 6. Molecular structure of **5** with an atomic labeling scheme (hydrogen atoms are omitted for clarity). Thermal ellipsoids are shown at 50% probability level. Selected bond lengths (Å) and angles and torsion angles (deg): Pt1−O1 2.006(6), Pt1−N1 2.088(7), O1−C7 1.317(11), C7−C6 1.310(14); O1−Pt1−N1′ 87.90(3), O1−Pt1−N1 92.10(3); O1−Pt1−N1′−C1 1.11(69), N1−Pt1−O1−C7 3.26(73).

Figure 7. Systematic views of intermolecular packing in **4** (I), **1** (II), and **3** (III).

Table 1. Selected Crystallographic Data and Collection Parameters for Compounds 1−5

	1	2	3	4	5
formula	$C_{16}H_{10}F_6N_2O_2Pd$	$C_{18}H_{10}F_{10}N_2O_2Pd$	$C_{20}H_{10}F_{14}N_2O_2Pd$	$C_{16}H_{16}N_2O_2Pd$	$C_{16}H_{10}F_6N_2O_2Pd$
fw	482.66	582.68	682.70	374.71	571.35
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a, Å	5.0335(7)	11.411(5)	14.295(3)	10.1229(19)	4.9630(10)
b, Å	9.8636(14)	5.940(5)	5.7769(6)	5.8527(6)	9.939(2)
c, Å	16.915(3)	14.471(5)	14.940(3)	12.7090(24)	17.939(4)
α, deg	100.258(18)	90.000	90.00	90.000	100.436(17)
β, deg	92.229(19)	96.453(5)	116.47(2)	106.872(14)	92.178(17)
γ, deg	94.336(17)	90.000	90.00	90.000	94.890(17)
V, Å^3	822.8(2)	974.6(10)	1104.4(3)	720.6(2)	865.7(3)
Z	2	2	2	2	2
D_{calcd}, g cm^{-3}	1.948	1.985	2.053	1.727	2.192
total reflns	9723	8789	10 141	9244	9120
unique reflns	3613	2165	2504	1988	3566
R1, wR2 [$I_0 > 2\sigma(I)$]	0.0383, 0.0798	0.0330, 0.0641	0.0472, 0.1010	0.0272, 0.0779	0.0362, 0.0838
R1, wR2 [all data]	0.0820, 0.0904	0.0592, 0.0686	0.1250, 0.1203	0.0321, 0.0810	0.0715, 0.0938
GOF	0.973	0.892	0.814	1.009	0.984

(O−Pd−N) of 91.5−92.5° and the angles O−Pd−N′ of 87.5−88.5° are in the range typically found in related palladium derivatives.[25,27,28] The bonding parameters in platinum derivative **5** [Pt−N, 2.006(6) Å; Pt−O, 2.088(7) Å] are in good agreement with those reported for other platinum complexes with chelating N,O ligands.[26,29]

The deviations of the ligands out of the MN_2O_2 planes (M = Pd, Pt) can be measured by the torsion angles O−M−N′−C1 and N−M−O−C7. According to these values, **1** and **5** exhibit nearly planar structures, whereas **2**−**4** show a higher distortion. The spatial distance between two adjacent molecules is best expressed in a simplified manner by the distance between two metal centers (abbreviated as the M−M distance). The higher

distortion of **2**−**4** causes longer M−M distances *a* in the intermolecular stacking arrangements for **2** (5.94 Å), **3** (5.78 Å), and **4** (5.85 Å) compared to **1** (5.03 Å) and **5** (4.96 Å). Upon elongation of the perfluoroalkyl chain in the ligand backbone, the M−M distance *b* increases because of steric crowding [9.86 Å (**1**), 9.94 Å (**5**), 11.41 Å (**2**), and 14.29 Å (**3**)]. The crystal packing of compound **4**, which does not contain any fluorine atoms, differs from the others because the neighboring molecules showed head-to-head packing instead of a staggered configuration, as found in **1**−**3** and **5** (Figure 7). The perfluoroalkenolates favor staggered packing because of fluorophilic interactions (refs 30 and 31 and references cited therein), which also explains the longer intermolecular M−M distance *b* of 10.12 Å in **3** in comparison to 9.86 Å in **1** and 9.94 Å in **5**. In compounds **1** and **5**, head-to-head packing of the molecules can also be found, but as expected, the M−M distances *c* were longer [10.72 Å (**5**) and 11.41 Å (**1**)] than those in **4** because of the more space-demanding CF_3 group. These trends in the relative M−M distances indicate decreasing intermolecular interactions with increasing amounts of fluorine in the molecules, which is reflected in the improved volatility of these derivatives (see later). The decreasing intermolecular interactions are partially caused by higher steric demands in crystal packing as well as fluorophilic interactions that influence the packing arrangement.

Crystallographic data of the X-ray diffraction analysis of compounds **1**−**5** are summarized in Table 1.

Electron Impact Mass Spectrometry (EI-MS). EI-MS spectra of **1**−**6** demonstrated their considerable thermal stability with parent molecular ions [*m/z* 482 (**1**), 582 (**2**), 682 (**3**), 374 (**4**), 571 (**5**), 463 (**6**)] observable with the highest intensity for each complex. The fragmentation pattern of the fluorinated complexes showed the loss of fluoroalkyl groups and $[OCCF_3]$, $[OCC_2F_5]$, and $[OCC_3F_7]$ fragments. Evidently, the bonds of the ligand moiety appear to cleave more preferentially than the metal−ligand bonds. In contrast, the metal−ligand bonds in **4** and **6**, which contained no fluorinated groups, were found to be less stable under EI-MS conditions, which suggested the enhanced volatility of metal derivatives due to the stability of the metal−ligand framework based on fluorinated ligands.
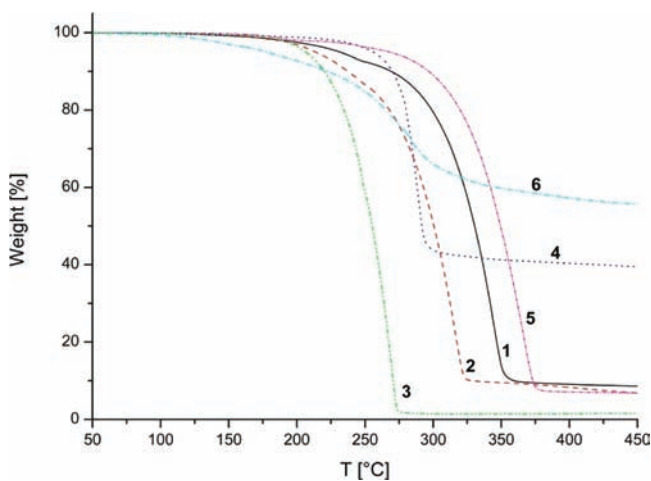
Figure 8. TGA profiles of compounds **1**−**6** under a nitrogen atmosphere with a heating rate of 10 °C min^{-1}.

Thermogravimetric Analysis/Differential Thermal Analysis (TG/DTA). TGA of complexes **1**−**6** showed just one major decomposition step (Figure 8) indicating a quantitative vaporization for **1**−**3** and **5** at 280−370 °C (**1**), 260−325 °C (**2**), 200−275 °C (**3**), and 280−370 °C (**5**) with minimal residue (<5 wt %) left at 800 °C, whereas **4** and **6** decomposed at 275−300 °C (**4**) and 200−400 °C (**6**) with ca. 35 and 50 wt % residues left at 800 °C. The minimal decomposition of complexes **1**−**3** and **5** suggested their high thermal stability. These observations demonstrate the expected increase of the volatility by introducing fluorine atoms to the complexes, as is already known for *β*-diketonates[19] as well as palladium(II) *β*-iminoketonates.[32] In this study, the most volatile derivatives are those with the highest fluorine content (**3** and **5**), which is explained by the decreasing intermolecular interactions exhibited in the different M−M distances in the solid-state structures (Figure 7).

■ CONCLUSION

New palladium(II) and platinum(II) complexes were synthesized using donor-substituted *β*-alkenols as chelating anions. The presence of fluorine atoms in the ligand periphery, effective steric shielding, and bidentate chelating behavior toward the metal centers imparted these compounds a remarkable stability against air and moisture. Further, the higher the number of fluorine atoms, the more the intermolecular stacking arrangement was found to be influenced, partly caused by steric demands in the crystal packing as well as fluorophilic interactions. For instance, the metal−metal distance among neighboring molecules was found to increase with increasing length of the perfluoralkyl chain, which enhanced the volatility of the compounds compared to the crystal packing found in alkyl derivatives. In addition to the straightforward accessibility of the herein presented complexes **1**−**6** (Table 2), the high solubility in organic solvents as well as the good vapor pressure makes them promising and scalable precursors for the synthesis of platinum- and palladium-based phases by gas-phase techniques.

■ EXPERIMENTAL SECTION

Reagents and General Procedures. All manipulations of air- and moisture-sensitive materials were carried out under nitrogen using Stock-type all-glass assemblies. The organic ligands 2-PyCH-COHCF$_3$[33] and 2-PyCH$_2$COCH$_3$[34] were prepared according to procedures previously described; 2-PyCHCOHC$_3$F$_7$ was prepared following procedures described for 2-PyCHCOHCF$_3$ but using heptafluorobutyric anhydride instead of trifluoroacetic anhydride. K$_2$PtCl$_4$ (Acros Organics), *n*-butyllithium (Acros Organics, 1.6 M solution in hexane), and PdCl$_2$ (Merck) were used without further purification. Solvents were dried by standard methods with the appropriate desiccating reagents and distilled prior to their use. Elemental analyses were performed on a HEKAtech CHNS Euro EA 3000. MS spectra were obtained on a Finnigan MAT 95 (20 eV) in *m/z* (relative percent). NMR spectra were recorded on a Bruker Avance II 300 spectrometer; chemical shifts are quoted in parts per million relative to tetramethylsilane (^{1}H, 300.1 MHz; ^{13}C, 75.7 MHz) and CCl$_3$F (^{19}F, 282.4 MHz). DTA measurements were performed on a TGA/DSC1 (Mettler-Toledo GmbH, Giessen, Germany) apparatus. Data collection for X-ray structure elucidation was performed on a STOE IPDS I/II diffractometer using graphite-monochromated Mo Kα radiation (0.710 73 Å). The programs used in this work are STOE's *X-Area*[35] and the *WINGX* suite of programs,[36] including *SIR-92*[37] and *SHELXL-97*[38] for structure solution and refinement.

Bis[3,3,3-trifluoro-1-(pyridin-2-yl)propen-2-olato]palladium(II) (1). 2-PyCHCOHCF$_3$ (0.38 g, 2 mmol) was dissolved in 25 mL of

Table 2. Physicochemical Properties of 1−6

compound	MW [g mol^{-1}]	MP [°C]	$T_{1/2}$ [°C]^a	space group	M−M distances [Å] head-to-head	staggered
1	482.7	250	330	P$\bar{1}$	11.41 (c)	9.86 (b)
2	582.7	240	301	P2$_1$/c		11.41 (b)
3	682.7	208	259	P2$_1$/c		14.29 (b)
4	374.6	192	291	P2$_1$/c	10.12 (b)	11.63 (c)
5	571.3	250	350	P$\bar{1}$	10.72 (c)	9.94 (b)
6	463.4	dec 185−195	b	c		

^{a}Temperature at which 50 wt % of the sample has been lost during TGA (heating rate = 10 °C min^{-1}). ^{b}The complex decomposes with 53 wt % residue at 800 °C. ^{c}No crystallographic data were collected.

anhydrous toluene under an inert atmosphere. The solution was cooled to 0 °C, and n-butyllithium (2 mmol) was added. The reaction mixture was allowed to warm to ambient temperature, and then PdCl$_2$ (0.18 g, 1 mmol) was added and the suspension heated at reflux for 7 h. The product was separated by filtration, and excess solvent was removed under reduced pressure. Excess 2-PyCHCOHCF$_3$ was sublimed at 55 °C/10^{-3} mbar from the orange product. Yield: 92% (0.44 g). ^{1}H NMR (CDCl$_3$): δ 8.76 (d, J = 7.2 Hz, H1), 7.65 (t, J = 7.6 Hz, H3), 7.12 (d, J = 8.5 Hz, H4), 7.07 (t, J = 6.7 Hz, H2), 5.82 (s, H6). ^{13}C NMR (CDCl$_3$): δ 153.7 (C7), 151.2 (C5), 147.1 (C1), 138.2 (C3), 123.5 (C4), 119.5 (C2), 118.3 (C8), 97.5 (C6). ^{19}F NMR (CDCl$_3$): δ −72.4 (^{1}J$_{C,F}$ = 280 Hz, ^{2}J$_{C,F}$ = 32 Hz). EI-MS: 482 (100, M$^+$), 413 (6, M$^+$ − CF$_3$), 385 (6, M$^+$ − OCCF$_3$), 294 (8, M$^+$ − 2-PyCHCOCF$_3$). Elem anal. Calcd for C$_{16}$H$_{10}$F$_6$N$_2$O$_2$Pd: C, 39.81; H, 2.09; N, 5.80. Found: C, 40.89; H, 2.46; N, 5.88. Sublimation temperature: 110 °C/10^{-3} mbar.

Bis[3,3,4,4,4-pentafluoro-1-(pyridin-2-yl)buten-2-olato]-palladium(II) (2). The synthetic procedure was similar to that described for **1**, with 2-PyCHCOHC$_2$F$_5$ (0.36 g, 1.5 mmol), n-butyllithium (1.5 mmol), and PdCl$_2$ (0.13 g, 0.75 mmol). Yield: 95% (0.42 g) of orange solid. ^{1}H NMR (CDCl$_3$): δ 8.75 (d, J = 6.2 Hz, H1), 7.68 (t, J = 8.1 Hz, H3), 7.14 (d, J = 7.9 Hz, H4), 7.05 (t, J = 7.2 Hz, H2), 5.86 (s, H6). ^{13}C NMR (CDCl$_3$): δ 154.1 (C7), 151.1 (C5), 146.9 (C1), 137.9 (C3), 123.3 (C4), 119.0 (C2), 118.9 (C9), 108.2 (C8), 98.5 (C6). ^{19}F NMR (CDCl$_3$): δ −119.4 (F8, ^{1}J$_{C,F}$ = 278 Hz), −82.5 (F9, ^{1}J$_{C,F}$ = 287 Hz). EI-MS: 582 (100, M$^+$), 463 (6, M$^+$ − C$_2$F$_5$), 435 (8, M$^+$ − OCC$_2$F$_5$), 344 (6, M$^+$ − 2 C$_2$F$_5$), 287 (4, M$^+$ − 2 OCC$_2$F$_5$). Elem anal. Calcd for C$_{18}$H$_{10}$F$_{10}$N$_2$O$_2$Pd: C, 37.10; H, 1.73; N, 4.81. Found: C, 36.81; H, 1.85; N, 4.17. Sublimation temperature: 100 °C/10^{-3} mbar.

Bis[3,3,4,4,5,5,5-heptafluoro-1-(pyridin-2-yl)penten-2-olato]-palladium(II) (3). The synthetic procedure was similar to that described for **1**, with 2-PyCHCOHC$_3$F$_7$ (0.29 g, 1 mmol), n-butyllithium (1 mmol), and PdCl$_2$ (0.09 g, 0.5 mmol). Yield: 91% (0.31 g) of orange solid. ^{1}H NMR (CDCl$_3$): δ 8.75 (d, J = 6.8 Hz, H1), 7.68 (t, J = 8.4 Hz, H3), 7.15 (d, J = 8.3 Hz, H4), 7.05 (t, J = 6.7 Hz, H2), 5.84 (s, H6). ^{13}C NMR (CDCl$_3$): δ 153.8 (C7), 150.9 (C5), 147.1 (C1), 138.1 (C3), 123.4 (C4), 119.1 (C2), 117.8 (C10), 109.7 (C8), 109.0 (C9), 99.0 (C6). ^{19}F NMR (CDCl$_3$): δ −126.2 (s, ^{1}J$_{C,F}$ = 268 Hz, ^{2}J$_{C,F}$ = 42 Hz, F9), −117.1 (q, F8, J$_{F,F}$ = 9.1 Hz), −80.7 (t, F10, J$_{F,F}$ = 9.0 Hz). EI-MS: 682 (100, M$^+$), 632 (12, M$^+$ − CF$_2$), 513 (8, M$^+$ − C$_3$F$_7$), 485 (8, M$^+$ − OCC$_3$F$_7$), 394 (4, M$^+$ − 2-PyCHCOHC$_3$F$_7$). Elem anal. Calcd for C$_{20}$H$_{10}$F$_{14}$N$_2$O$_2$Pd: C, 35.19; H, 1.48; N, 4.10. Found: C, 35.05; H, 1.46; N, 4.31. Sublimation temperature: 90 °C/10^{-3} mbar.

Bis[1-(pyridin-2-yl)propen-2-olato]palladium(II) (4). **4** was synthesized following a procedure described by El-Dissouky et al.[22] PdCl$_2$ (0.09 g, 0.5 mmol) was added to a solution of 2-PyCH$_2$COCH$_3$ (0.16 g, 1.1 mmol) in EtOH (20 mL). The suspension was heated at reflux for 5 h, and a microcrystalline solid precipitated upon cooling. The formed suspension was treated with 2 N aqueous NaOH until the reaction mixture became clear. Upon standing, the product was obtained as a red-orange solid. Yield: 80% (0.15 g). ^{1}H NMR (CDCl$_3$): δ 8.69 (d, J = 6.2 Hz, H1), 7.39 (t, J = 8.0 Hz, H3), 6.82 (d, J = 8.1 Hz, H4), 6.71 (t, J = 6.7 Hz, H2), 5.19 (s, H6), 2.04 (s, H8).

^{13}C NMR (CDCl$_3$): δ 169.2 (C7), 153.4 (C5), 145.5 (C1), 136.4 (C3), 121.2 (C4), 115.2 (C2), 96.7 (C6), 24.4 (C8). EI-MS: 374 (100, M$^+$), 359 (4, M$^+$ − CH$_3$), 331 (6, M$^+$ − OCCH$_3$), 287 (4, M$^+$ − 2 OCCH$_3$), 240 (16, M$^+$ − 2-PyCH$_2$COCH$_3$), 211 (6, M$^+$ − 2-PyCH$_2$COCH$_3$, − CH$_3$, − CO). Elem anal. Calcd for C$_{16}$H$_{16}$N$_2$O$_2$Pd: C, 51.28; H, 4.30; N, 7.48. Found: C, 51.67; H, 4.47; N, 7.73. Sublimation temperature: 140 °C/10^{-3} mbar.

Bis[3,3,3-trifluoro-1-(pyridin-2-yl)propen-2-olato]platinum(II) (5). The method described by Behnke and Nakamoto[23] was modified to synthesize the platinum complex. K$_2$PtCl$_4$ (0.21 g, 0.5 mmol) was dissolved in 2 mL of boiling water. While the temperature was maintained at 65 °C, 2-PyCHCOHCF$_3$ (0.76 g, 4 mmol) dissolved in 1 mL of acetone and 1 mL of 7.8 M KOH were added. The solution was rapidly stirred for 10 min. Then 2 mL of additional KOH was added followed by extraction with ethyl acetate. After the solvent was removed under reduced pressure, the product was obtained as a yellow solid. Yield: 39% (0.11 g). ^{1}H NMR (CDCl$_3$): δ 9.03 (d, J = 6.4 Hz, H1), 7.71 (t, J = 8.4 Hz, H3), 7.10 (d, J = 7.9 Hz, H4), 7.06 (t, J = 6.9 Hz, H2), 5.83 (s, H6). ^{13}C NMR (CDCl$_3$): δ 152.6 (C7), 150.6 (C5), 145.7 (C1), 137.1 (C3), 123.8 (C4), 119.4 (C2), 117.6 (C8), 97.9 (C6). ^{19}F NMR (CDCl$_3$): δ −72.6 (^{1}J$_{C,F}$ = 279 Hz, ^{2}J$_{C,F}$ = 33 Hz). ^{195}Pt NMR (CDCl$_3$): δ −1228. EI-MS: 571 (100, M$^+$), 474 (32, M$^+$ − OCCF$_3$), 377 (4, M$^+$ − 2 OCCF$_3$). Elem anal. Calcd for C$_{16}$H$_{10}$F$_6$N$_2$O$_2$Pt: C, 33.82; H, 1.76; N, 4.90. Found: C, 33.82; H, 2.12; N, 5.55. Sublimation temperature: 135 °C/10^{-3} mbar.

Bis[1-(pyridin-2-yl)propen-2-olato]platinum(II) (6). The synthetic procedure was similar to that described for **5**, from 2-PyCH$_2$COCH$_3$ (0.54 g, 4 mmol) and K$_2$PtCl$_4$ (0.21 g, 0.5 mmol). Yield: 34% (0.08 g). ^{1}H NMR (CDCl$_3$): δ 9.00 (d, J = 6.4 Hz, H1), 7.4 (t, J = 8.2 Hz, H3), 6.82 (d, J = 8.7 Hz, H4), 6.73 (t, J = 6.7 Hz, H2), 5.24 (s, H6), 2.040 (s, H8). ^{13}C NMR (CDCl$_3$): δ 168.1 (C7), 152.1 (C5), 144.2 (C1), 135.5 (C3), 121.8 (C4), 115.4 (C2), 97.8 (C6), 24.40 (C8). EI-MS: 463 (100, M$^+$), 448 (16, M$^+$ − CH$_3$), 420 (20, M$^+$ − OCCH$_3$), 377 (16, M$^+$ − 2 OCCH$_3$), 314 (4, M$^+$ − 2-PyCH$_2$COCH$_3$), 299 (6, M$^+$ − 2-PyCH$_2$COCH$_3$, − CH$_3$), 93 (18, 2-PyCH$_2$COCH$_3$$^+$ − OCCH$_3$), 43 (4, OCCH$_3$$^+$). Sublimation temperature: 170 °C/10^{-3} mbar.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR and MS spectra, TGA/DTA data, and X-ray crystallographic data files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sanjay.mathur@uni-koeln.de.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Fender, J. H. *Nanoparticles and Nanostructured Films: Preparation, Characterization and Application*; Wiley-VCH Verlag GmbH: Weinheim, Germany, 1998.

(2) Chow, G.-M.; Ovid'ko, I. A.; Tsakalakos, T. *Nanostructured Films and Coatings*; Kluwer Academic: Amsterdam, The Netherlands, 2000.

(3) Lee, J. M.; Kang, S. Y.; Shin, J. C.; Kim, W. J.; Hwang, C. S.; Kim, H. J. *Appl. Phys. Lett.* **1999**, *74*, 3489−3491.

(4) Aaltonen, T.; Ritala, M.; Sajavaara, T.; Keinonen, J.; Leskelä, M. *Chem. Mater.* **2003**, *15*, 1924−1928.

(5) Erhardt, M. K.; Nuzzo, R. G. *Langmuir* **1999**, *15*, 2188−2193.

(6) Lim, H.; Song, H. J.; Lee, Y.; Shin, H.-J.; Choi, H. C. *Langmuir* **2010**, *26*, 1464−1467.

(7) Hierso, J.-C.; Feurer, R.; Kalck, P. *Chem. Mater.* **2000**, *12*, 390−399.

(8) Dossi, C.; Pozzi, A.; Recchia, S.; Fusi, A.; Psaro, R.; Dal Santo, V. *J. Mol. Catal. A: Chem.* **2003**, *204−205*, 465−472.

(9) Itoh, N.; Akiha, T.; Sato, T. *Catal. Today* **2005**, *104*, 231−237.

(10) Yan, S.; Maeda, H.; Kusakabe, K.; Morooka, S. *Ind. Eng. Chem. Res.* **1994**, *33*, 616−622.

(11) Jun, C.-S.; Lee, K.-H. *J. Membr. Sci.* **2000**, *176*, 121−130.

(12) Briand, D.; Labeau, M.; Currie, J. F.; Delabouglise, G. *Sens. Actuators, B* **1998**, *48*, 395−402.

(13) Majoo, S.; Gland, J. L.; Wise, K. D.; Schwank, J. W. *Sens. Actuators, B* **1996**, *36*, 312−319.

(14) Henc, B.; Jolly, P. W.; Salz, R.; Wilke, G.; Benn, R.; Hoffmann, E. G.; Mynott, R.; Schroth, G.; Seevogel, K.; Sekutowski, J. C.; Krüger, C. *J. Organomet. Chem.* **1980**, *191*, 425−448.

(15) Gozum, J. E.; Pollina, D. M.; Jensen, J. A.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 2688−2689.

(16) Kwon, J.-H.; Yoon, S.-G. *Thin Solid Films* **1997**, *303*, 136−142.

(17) Hierso, J.-C.; Feurer, R.; Kalck, P. *Coord. Chem. Rev.* **1998**, *178−180*, 1811−1834.

(18) Thurier, C.; Doppelt, P. *Coord. Chem. Rev.* **2008**, *252*, 155−169.

(19) Sievers, R. E.; Sadlowski, J. E. *Science* **1978**, *201*, 217−223.

(20) Herrmann, W. A.; Huber, N. W.; Runte, O. *Angew. Chem., Int. Ed.* **1995**, *34*, 2187−2206.

(21) Ozawa, T. *Thermochim. Acta* **1991**, *174*, 185−199.

(22) El-Dissouky, A.; Mohamed, G. B.; Refaat, L. S. *Transition Met. Chem.* **1984**, *9*, 23−28.

(23) Behnke, G. T.; Nakamoto, K. *Inorg. Chem.* **1967**, *6*, 433−440.

(24) Okeya, S.; Ooi, S.; Matsumoto, K.; Nakamura, Y.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1085−1095.

(25) Lobmaier, G. M.; Frey, G. D.; Dewhurst, R. D.; Herdtweck, E.; Herrmann, W. A. *Organometallics* **2007**, *26*, 6290−6299.

(26) Chang, S.-Y.; Cheng, Y.-M.; Chi, Y.; Lin, Y.-C.; Jiang, C.-M.; Lee, G.-H.; Chou, P.-T. *Dalton Trans.* **2008**, 6901−6911.

(27) Liu, Y.-H.; Cheng, Y.-C.; Tung, Y.-L.; Chi, Y.; Chen, Y.-L.; Liu, C.-S.; Peng, S.-M.; Lee, G.-H. *J. Mater. Chem.* **2003**, *13*, 135−142.

(28) Prout, C. K.; Wheeler, A. G. *J. Chem. Soc. A* **1966**, 1286−1290.

(29) Hubel, R.; Polborn, K.; Knizek, J.; Nöth, H.; Beck, W. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1701−1708.

(30) Ramasubbu, N.; Parthasarathy, R.; Murray-Rust, P. *J. Am. Chem. Soc.* **1986**, *108*, 4308−4314.

(31) Castillo, N.; Matta, C. F.; Boyd, R. J. *Chem. Phys. Lett.* **2005**, *409*, 265−269.

(32) Zharkova, G. I.; Sysoev, S. V.; Stabnikov, P. A.; Logvinenko, V. A.; Igumenov, I. K. *J. Therm. Anal. Calorim.* **2011**, *103*, 381−385.

(33) Giebelhaus, I.; Müller, R.; Tyrra, W.; Pantenburg, I.; Fischer, T.; Mathur, S. *Inorg. Chim. Acta* **2011**, *372*, 340−346.

(34) Wang, D.; Ding, K. *Chem. Commun.* **2009**, 1891−1893.

(35) *X-Area 1.16*; Stoe & Cie GmbH: Darmstadt, Germany, 2003.

(36) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838.

(37) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343−350.

(38) Sheldrick, G. M. *SHELXL-97, Programs for Crystal Structure Analysis*; University of Göttingen: Göttingen, Germany, 1997.