Supplementary material

Volatile Pd-Pb and Cu-Pb heterometallic complexes: structure, properties and *trans*-to-*cis* isomerization under cocrystallization of Pd and Cu β -diketonates with Pb hexafluoroacetylacetonate

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S2 NMR Data

Fig. S2.1 ¹H NMR spectrum of PdL₂

Fig. S2.2 ¹³C NMR spectrum of PdL₂

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Fig. S3.1 Kinetic curves for ¹⁹F NMR signal corresponding to:

Table S3.1 Calculated constants for **2**

Fig. S3.2 Van 't Hoff plot for the estimation of enthalpy of the reaction (1).

Fig. S3.3 Arrhenius plot for the estimation of activation energy of the reaction (1).

S1 Structural data

Table 1. Crystallographic data and XRD experiment details.

	1 <i>trans</i> -PdL ₂	2 <i>cis</i> -PdL ₂ *Pb(hfa) ₂	3 <i>cis</i> -CuL ₂ *Pb(hfa) ₂
formula	C22H38O6Pd	C32H32F12O10PbPd	C32H40F12O10CuPb
fw	504.92	1118.17	1083.37
temp (K)	296	150	150
λ Mo K α (Å)	0.71073	0.71073	0.71073
Cryst syst	monoclinic	monoclinic	orthorhombic
space group	<i>P</i> 2 ₁ /c	<i>P</i> 2 ₁ /c	<i>P</i> 2 ₁ 2 ₁ 2 ₁
a (Å)	9.8399(3)	16.5709(8)	11.2895(7)
b (Å)	12.3641(4)	13.7306(6)	21.8043(11)
c (Å)	11.4366(3)	19.9942(9)	33.4418(18)
α (deg)	-	-	90
β (deg)	108.8160(10)	106.502(2)	90
γ (deg)	-	-	90
<i>V</i> (Å ³)	1317.04(7)	4361.9(3)	8232.0(8)
<i>Z</i>	2	4	8
<i>D</i> (calcd), g/cm ³	1.273	1.703	1.748
absorp coef	0.734 mm ⁻¹	4.364 mm ⁻¹	4.705 mm ⁻¹
F(000)	528	2160	4248
crystal size (mm)	0.20×0.10×0.06	0.25×0.20×0.05	0.50×0.50×0.50
θ record area (deg)	3.30 - 30.54	2.59 - 26.36	1.11 - 23.26
h, k, l range	-14≤h≤14, -15≤k≤17, -16≤l≤11	-20≤h≤20, -17≤k≤16, -24≤l≤24	-12≤h≤12, -17≤k≤24, -37≤l≤33
nbr. of measured /independent reflections	13764/4006 [R(int) = 0.0348]	48144/8885 [R(int) = 0.0607]	38705/11769 [R(int) = 0.0288]
completeness of data collection	on θ = 25.25° 99.5 %	on θ = 25.25° 99.9 %	on θ = 23.26° 99.8 %
max and min transmission	0.9573 and 0.8671	0.8113 and 0.4084	0.8779 and 0.8641
refinement method	Full-matrix	LSM against F ²	
nbr. of reflections /limits/parameters	4006 / 0 / 139	8885 / 0 / 568	11769 / 0 / 1033
S factor against F ²	1.015	0.986	1.060
R factor [I > 2 σ (I)]	R1 = 0.0432, wR2 = 0.1325	R1 = 0.0369, wR2 = 0.0772	R1 = 0.0276 wR2 = 0.0647
R factor (all data)	R1 = 0.0674, wR2 = 0.1465	R1 = 0.0789, wR2 = 0.0860	R1 = 0.0299, wR2 = 0.0655
max and min residual electron density	0.634 and -0.890 e/Å ³	0.910 and -0.570 e/Å ³	0.970 and -0.669 e/Å ³

Table S1.2 Main interatomic distances (Å) and angles (°) for **1**

Pd(1)-O(1)	1.9738(17)
Pd(1)-O(2)	1.9774(18)
O(1)-C(1)	1.273(3)
O(2)-C(3)	1.261(4)
C(1)-C(4)	1.526(4)
C(2)-C(1)#1	1.373(4)
C(2)-C(3)	1.406(5)
C(3)-C(5)	1.531(5)
C(4)-C(42)	1.474(5)
C(4)-C(43)	1.475(7)
C(4)-C(41)	1.571(7)
C(5)-O(3)	1.381(6)
C(5)-C(51)	1.491(6)
C(5)-C(52)	1.593(10)
O(3)-C(53)	1.618(13)

O(1)-Pd(1)-O(2)	86.00(7)
C(1)-O(1)-Pd(1)	124.11(17)
C(3)-O(2)-Pd(1)	123.2(2)
O(1)-C(1)-C(2)#1	125.8(3)
O(1)-C(1)-C(4)	112.4(3)
C(2)#1-C(1)-C(4)	121.8(3)
C(1)#1-C(2)-C(3)	126.3(3)
O(2)-C(3)-C(2)	126.6(3)
O(2)-C(3)-C(5)	114.1(3)
C(2)-C(3)-C(5)	119.3(3)
C(42)-C(4)-C(43)	112.9(5)
C(42)-C(4)-C(1)	111.7(3)
C(43)-C(4)-C(1)	109.1(3)
C(42)-C(4)-C(41)	108.1(4)
C(43)-C(4)-C(41)	107.6(4)
C(1)-C(4)-C(41)	107.2(3)
O(3)-C(5)-C(51)	122.9(5)
O(3)-C(5)-C(3)	112.7(4)
C(51)-C(5)-C(3)	112.0(3)
O(3)-C(5)-C(52)	90.0(8)
C(51)-C(5)-C(52)	109.8(5)
C(3)-C(5)-C(52)	105.8(5)
C(5)-O(3)-C(53)	95.3(7)

#1 -x+1,-y,-z+1

Fig. S1.1 Unit cell and packing of molecules in *trans*-PdL₂.

Fig. S1.2 View of the unit cell along the Y axis for **2**.

Fig. S1.3 View of the unit cell for **3**.

Fig. S1.4 Coordination in **3** with Pb...Cu = 3,44 Å.

Fig. S1.5. X-ray diffraction pattern of sublimed compound powder (upper curve) and monocrystal of **3** (lower curve). The difference between experimental and theoretical curves is explained by the different temperature of powder (298K) and single crystal (150K) X-ray diffraction experiments. Rough Rietveld refinement was carried out to proof that sublimed compound is single phase. The diffraction pattern of the compound was completely indexed by the results of the single crystal study. No extra lines were found, which indicates that the product is a single phase. Refined cell parameters are: $a = 16.375(3)$, $b = 13.194(3)$, $c = 19.992(3)$ Å, $\beta = 101.83(2)^\circ$. R-values are: $R_p = 7.77$, $R_{wp} = 10.20$.

S2 NMR Data

Fig. S2.1 ¹H NMR spectrum of PdL₂

Fig. S2.2 ¹³C NMR spectrum of PdL₂

Fig. S2.3 ^1H NMR spectrum of *cis*-PdL₂*Pb(hfa)₂

Fig. S2.4 ^{19}F NMR spectrum of *cis*-PdL₂*Pb(hfa)₂

S3 Kinetics study for 2.

Fig. S3.1 Kinetic curves for F19 NMR signal corresponding to: ● – free $\text{Pb}(\text{hfa})_2$ and ■ - $\text{Pb}(\text{hfa})_2$ in **2**.

Table S3.1 Calculated constants for **2**.

T, K	K	Ln(K)	k_{obs}	Ln(k_{obs})
298	23.93755	3.17545	5.19E-5	-9.86619
308	176.70006	5.17445	1.8E-4	-8.62255
318	328.13919	5.79301	8E-4	-7.1309
328	569.70102	6.34511	0.00141	-6.56417

Fig. S3.2 Van 't Hoff plot for the estimation of enthalpy of the reaction (1).

Fig. S3.3 Arrhenius plot for the estimation of activation energy of the reaction (1).

Rough Rietveld refinement results.