Electronic Supporting Information

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Palladium (II) complexes of tetradentate donor-acceptor Schiff base ligands: synthesis, spectral, structural, thermal and NLO properties

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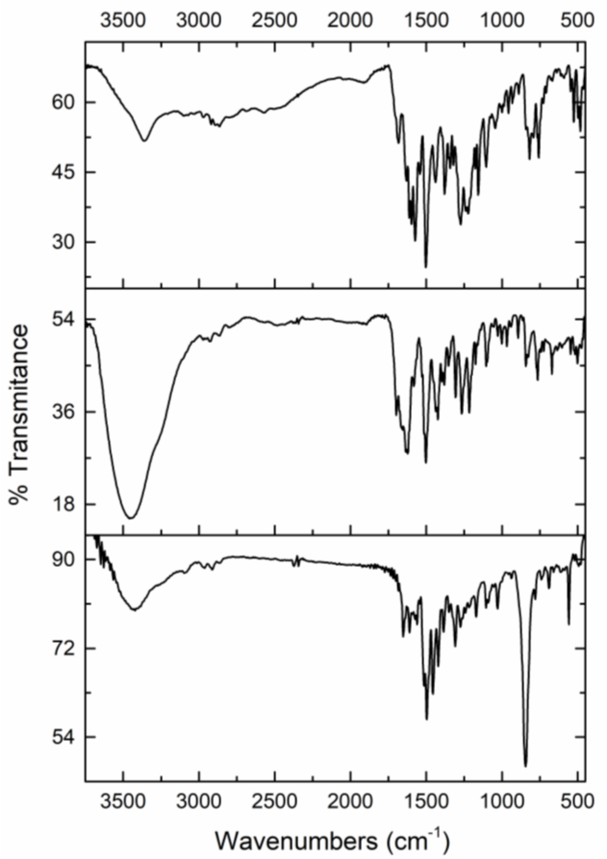

Fig. S1 Solid-state (KBr pellets) FT-IR spectra of proligand **2** (top), neutral bimetallic complex **3** (middle) and ionic trimetallic complex **4** (bottom).

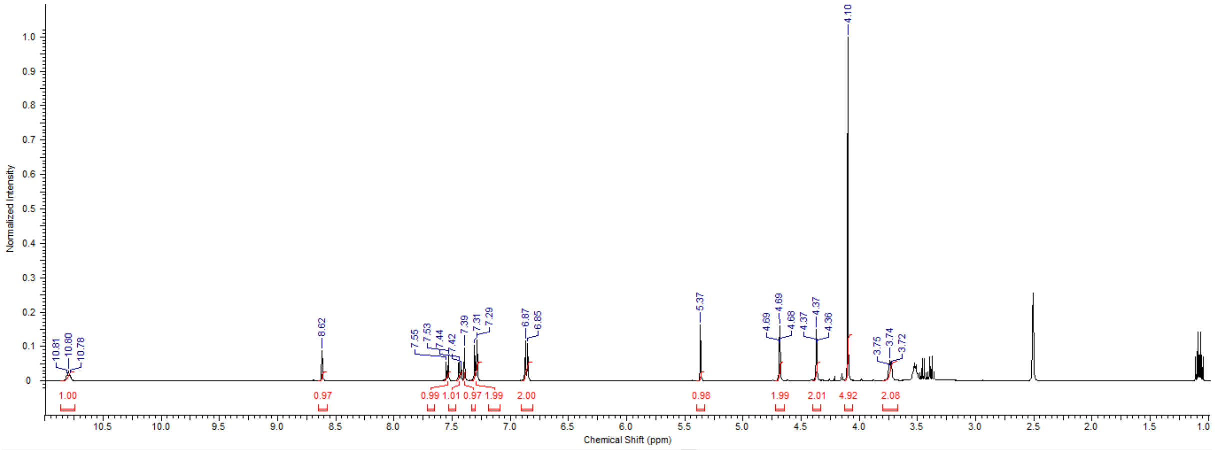

Fig. S2 ^{1}H NMR spectrum of **2** in $(CD_3)_2SO$ at 298 K.

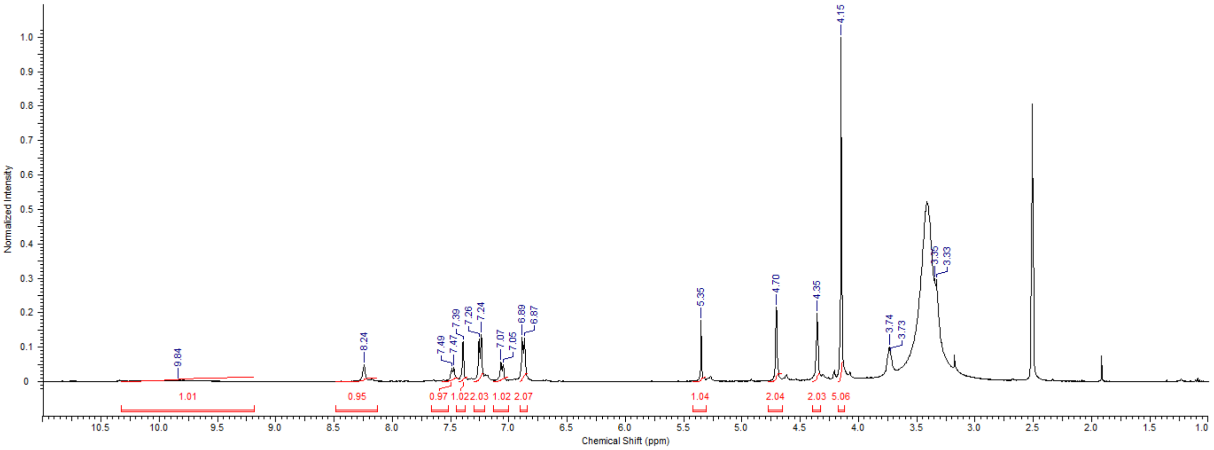

Fig. S3 ^{1}H NMR spectrum of **3** in $(CD_3)_2SO$ at 298 K.

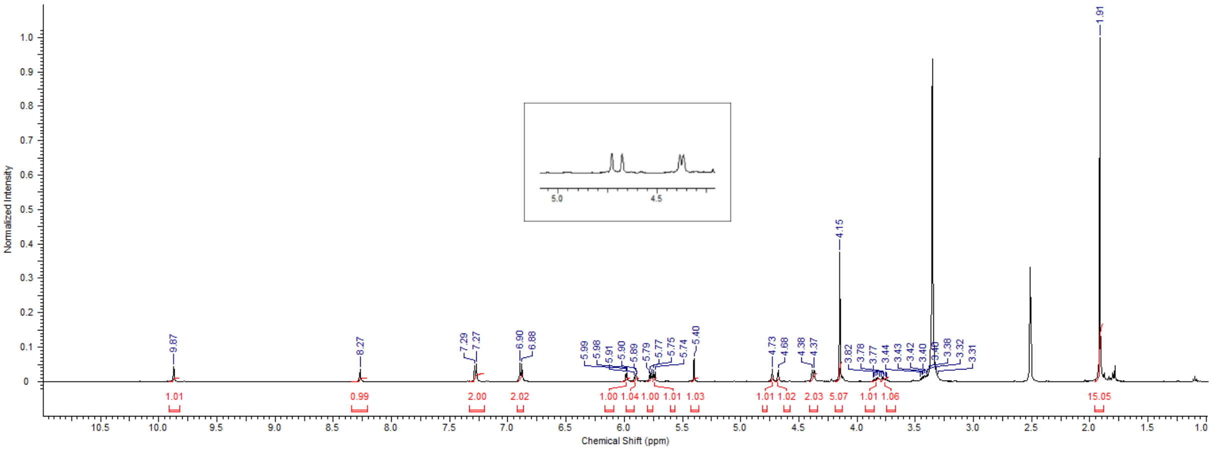

Fig. S4 ^{1}H NMR spectrum of **4** in $(CD_3)_2SO$ at 298 K. Inset: expansion of the chemical shift area of the substituted cyclopentadienyl proton.

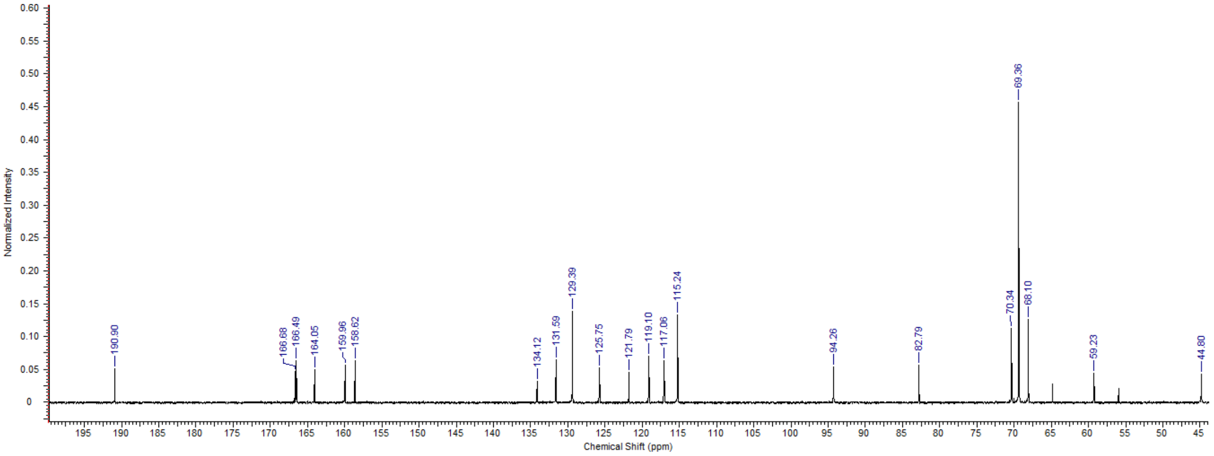

Fig. S5 ^{13}C{^{1}H} NMR spectrum of **2** in $(CD_3)_2SO$ at 298 K.

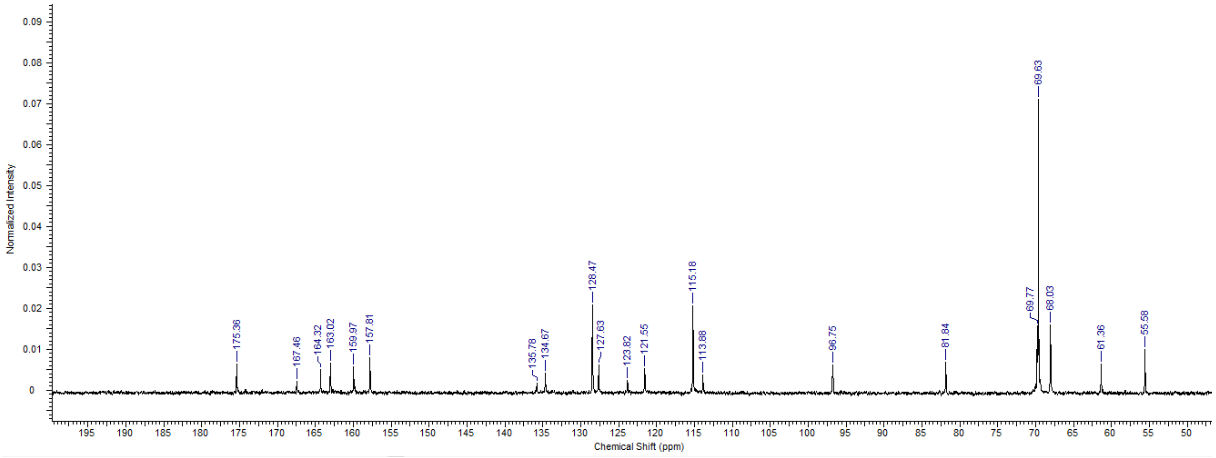

Fig. S6 $^{13}C\{^{1}H\}$ NMR spectrum of **3** in $(CD_3)_2SO$ at 298 K.

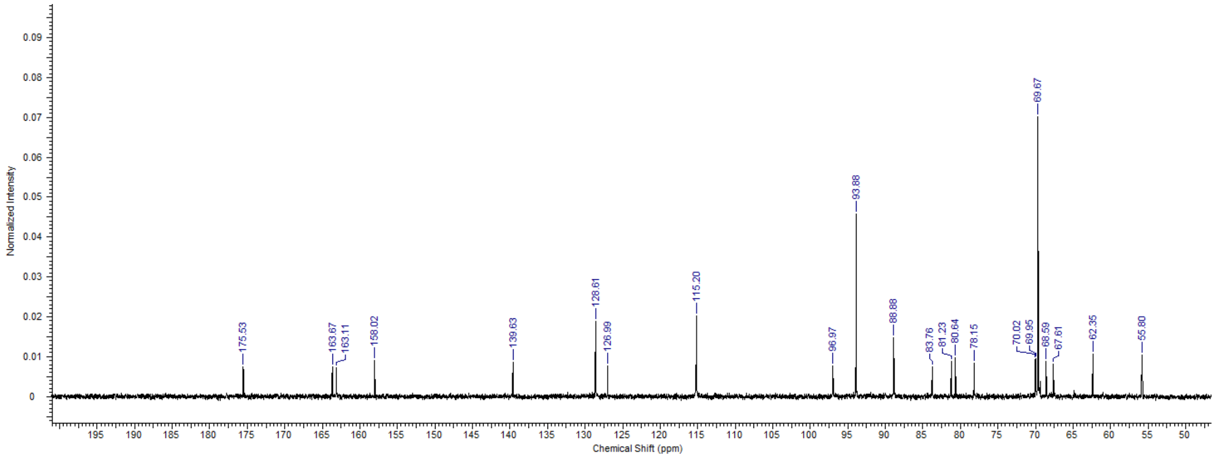

Fig. S7 $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $(CD_3)_2SO$ at 298 K. Inset: expansion of the chemical shift area of substituted cyclopentadienyl carbons.

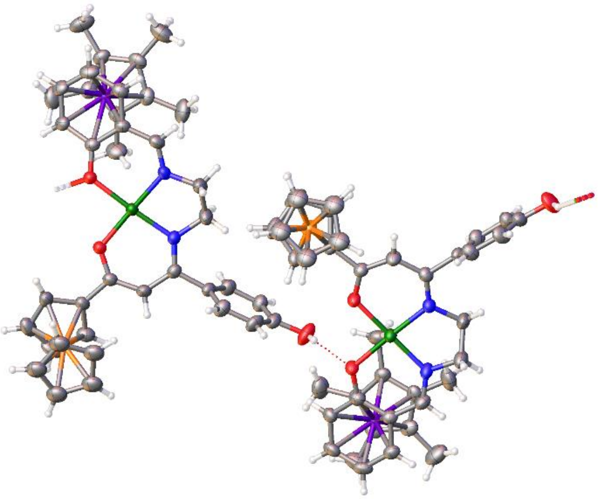

Fig. S8 Packing diagram of the bimetallic complex **4** showing the molecular arrangement within the crystal lattice through intermolecular hydrogen bonds.

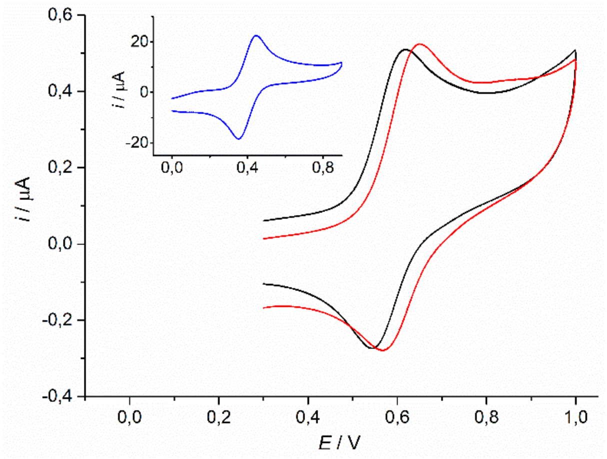

Fig. S9 Cyclic voltammograms of complexes **3** (black curve) and **4** (red curve) recorded in DMF containing 0.1 M n-Bu$_4$N$^+$PF$_6^-$ at T = 298 K with a sweep rate v = 0.1 V s^{-1}, reference electrode Ag/AgCl; external reference: ferrocene/ferrocenium couple (blue curve).

Table S1 Selected bond distances (Å) and angles (°) of the Schiff base ligand in compounds **3**·H_2O and **4**.

	3·H_2O	**4**
Bond distances		
O(1)-C(11)	1.300(4)	1.296(8)
O(2)-C(28)	1.321(4)	1.298(7)
O(3)-C(17)	1.371(4)	1.366(9)
N(1)-C(13)	1.321(4)	1.309(8)
N(1)-C(20)	1.468(4)	1.484(9)
N(2)-C(21)	1.473(4)	1.484(9)
N(2)-C(22)	1.297(4)	1.273(8)
C(10)-C(11)	1.484(4)	1.476(9)
C(11)-C(12)	1.387(4)	1.388(9)
C(12)-C(13)	1.409(4)	1.408(9)
C(13)-C(14)	1.491(4)	1.502(9)
C(20)-C(21)	1.521(5)	1.475(11)
C(22)-C(23)	1.435(5)	1.460(9)
C(23)-C(28)	1.438(5)	1.436(9)
C(29)-O(4)	1.240(4)	-
C(29)-O(5)	1.298(5)	-
Angles		
Pd(1)-O(1)-C(11)	122.1(2)	122.4(4)
Pd(1)-O(2)-C(28)	125.4(2)	123.3(4)
Pd(1)-N(1)-C(13)	124.6(2)	124.9(5)
Pd(1)-N(1)-C(20)	112.4(2)	111.7(4)
Pd(1)-N(2)-C(21)	113.4(2)	113.0(4)
Pd(1)-N(2)-C(22)	126.3(2)	127.1(5)
O(1)-C(11)-C(12)	126.5(3)	125.7(6)
N(1)-C(13)-C(12)	123.5(3)	123.1(6)
O(2)-C(28)-C(23)	124.3(3)	126.2(6)
N(2)-C(22)-C(23)	125.9(3)	125.0(6)
C(11)-C(12)-C(13)	127.6(3)	128.4(6)
C(22)-C(23)-C(28)	124.7(3)	124.0(6)
O(4)-C(29)-O(5)	122.9(3)	-

Table S2 Metrical parameters of the ferrocenyl units in compounds **3**·H_2O and **4**.

Compd	Fe-Cp_{CNT} (Å)	Fe-Cp'_{CNT} (Å)	Cp_{CNT}-Fe-Cp'_{CNT}(°)	Cp/Cp' (°)
3·H_2O	1.651	1.647	176.3	2.4
4	1.654	1.650	178.1	1.9

Abbreviations: Cp = C_5H_5, Cp' = C_5H_4, CNT = centroid.

Table S3 Hydrogen bond interactions in **3**·H2O and **4**.

Compd.	D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A (°)
3·H2O	O3-H3…Ow1$^{\#1}$	0.80(4)	1.91(4)	2.713(4)	178(5)
	O5-H5O…O4$^{\#2}$	0.81(5)	1.79(5)	2.594(2)	172(5)
	Ow1-Hw1…O2	0.87(2)	1.81(2)	2.669(3)	170(4)
4	O3-H3…O2$^{\#3}$	0.82	2.02	2.801(6)	146.6

Symmetry transformations used to generate equivalent atoms: #1 x, y, z; #2 -x, -y, -z; #3 x-1/2, -y-1/2, z-1/2