Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Data

Rare, Hypodentate L-κ*S* Coordination Mode of *N,N*-dialkyl-*N'*-aroylthioureas leads to Unprecedented Mixed-ligand [Pt(phen)(L-κ*S*)$_2$] Complexes.

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Fig. S1. ^{1}H NMR spectra (a) of a sample of purified [Pt(phen)(L^1-κ*O,S*)]$^+$ as the chloride salt, in $CDCl_3$ and (b) the isolated crude reaction mixture obtained in the attempted synthesis of (a) containing a significant amount of the previously 'unknown' [Pt(phen)(L^1-κ*S*)$_2$]. Expansions are shown for both 'aromatic' and 'aliphatic' proton regions of the ^{1}H NMR spectrum for clarity, and to highlight the differences in the spectra of these complexes.

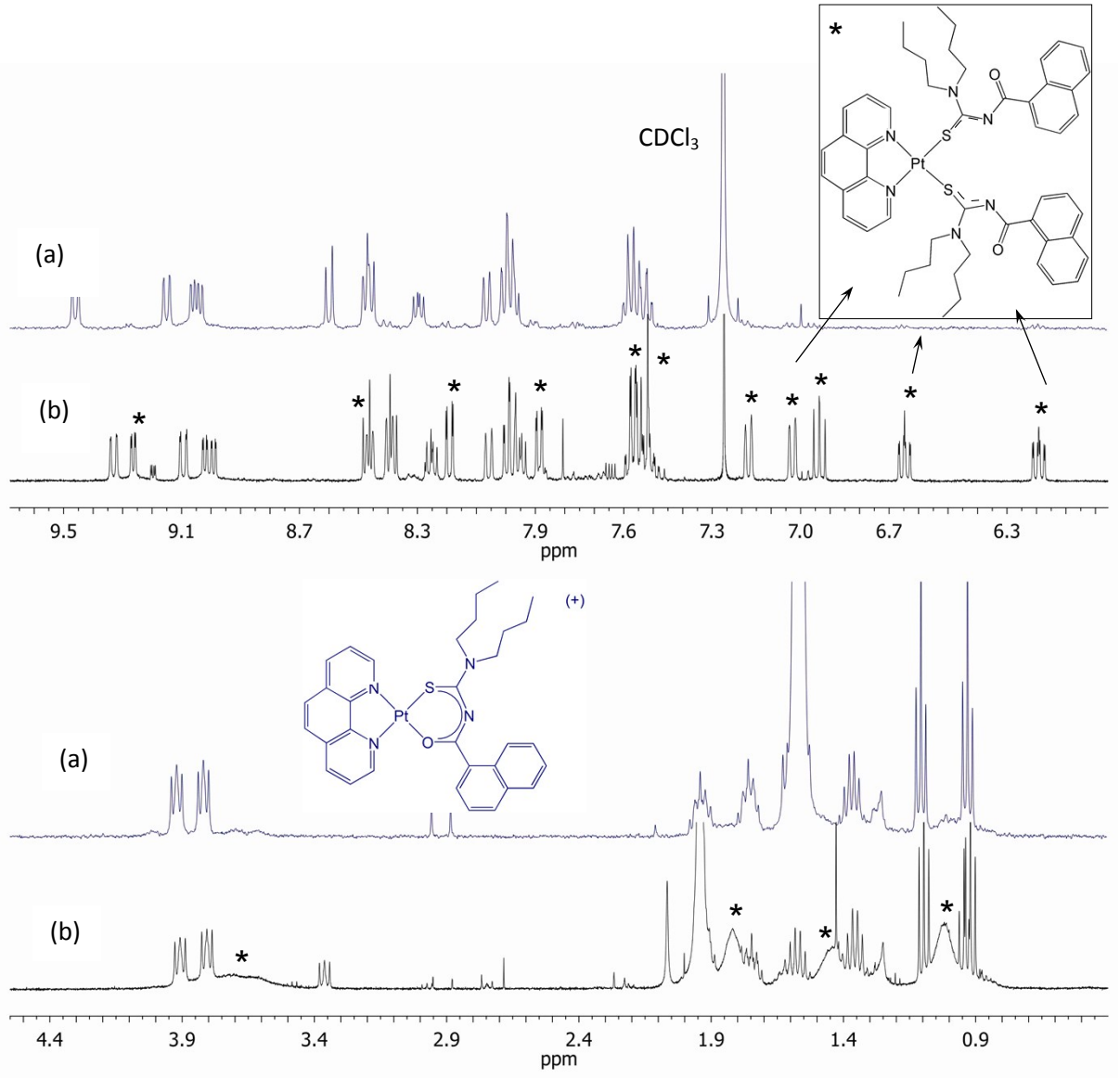

Fig. S2. A ^{1}H NMR spectrum of an isolated essentially 98% pure sample of [Pt(phen)(L^{1}-κ*S*)$_2$] in chloroform-d_1 with assignments (* traces of ethanol).

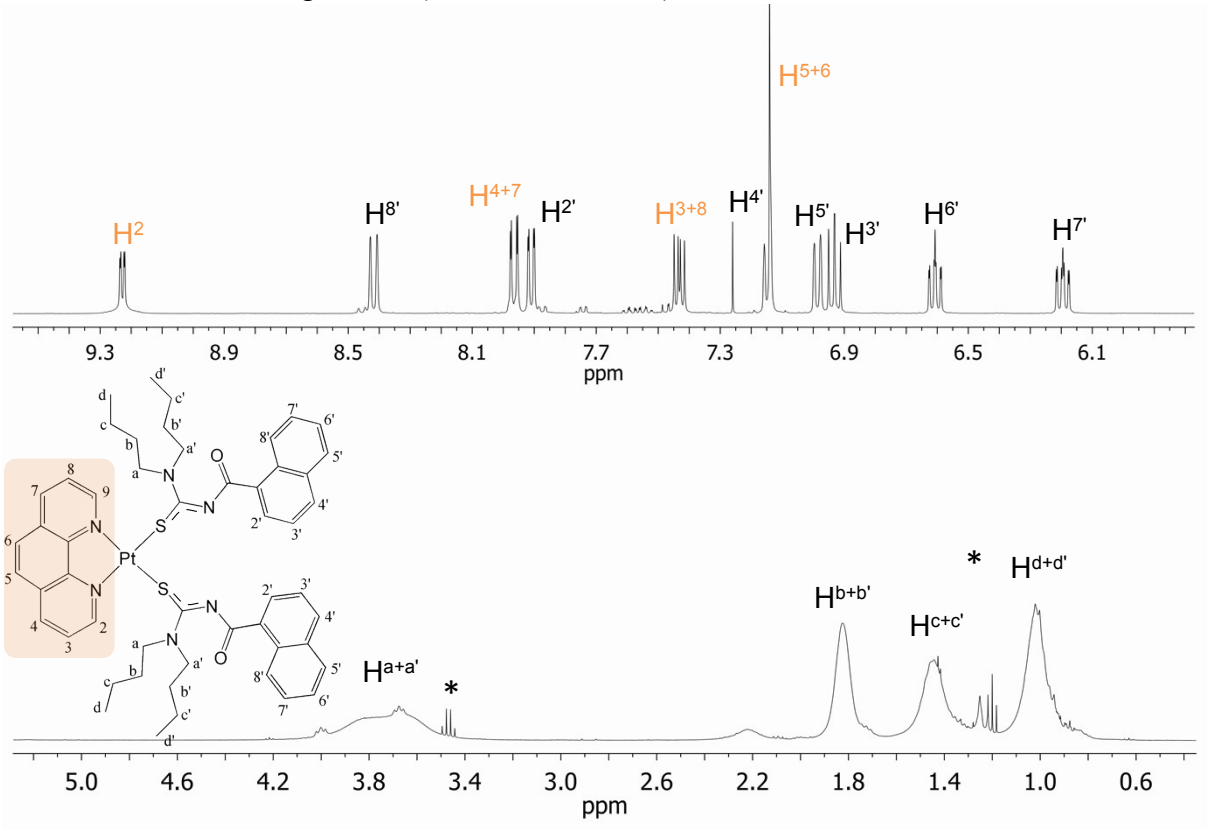

Fig. S3. The molecular structure and numbering of [Pt(phen)(L^{1}-κ*S*)$_2$], highlighting the striking offset *intra*-molecular stacking between the naphthoyl moieties and the Pt(phen)-moiety in this complex.

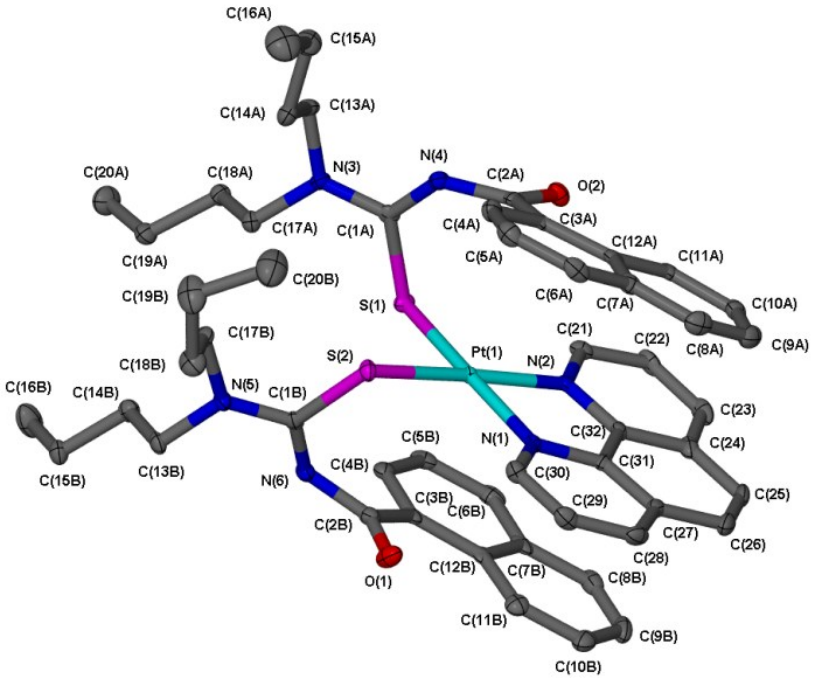

Fig. S4. Packing diagram of the crystal structure of [Pt(phen)(L^1-κ*S*)$_2$] viewed along the *b* axis.

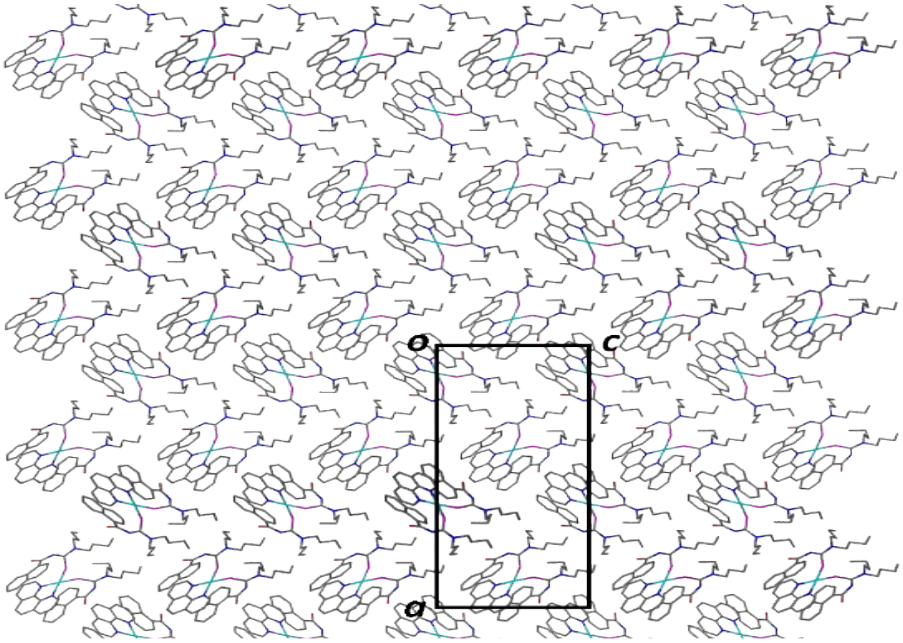

Table S1. Selected bond lengths for [Pt(phen)(L^1-κ*S*)$_2$].

Bonds:	Å
Pt1-S2	2.2838(8)
Pt1-N1	2.056(2)
Pt1-N2	2.056(2)
S1-C1A	1.784(3)
S2-C1B	1.779(3)
O1-C2B	1.225(4)
O2-C2A	1.238(3)
N1-C30	1.328(3)
N1-C31	1.373(4)
N2-C21	1.327(4)
N2-C32	1.368(5)
N3-C1A	1.361(4)
N3-C13A	1.459(4)
N3-C17A	1.469(4)
N4-C1A	1.295(4)
N4-C2A	1.362(4)
N5-C1B	1.353(4)
N5-C13B	1.468(4)
N5-C17B	1.471(4)
N6-C1B	1.304(4)
N6-C2B	1.375(5)

Fig. S5. A representative portion of an ^{1}H NMR spectrum of the isolated product of a reaction of 2.02 eq. HL^3 with 1 eq. of $[Pt(phen)Cl_2]$ in methanol; Note that the major product is $[Pt(phen)(L^3\text{-}\kappa S,O)]^+Cl^-$, while the minor product $[Pt(phen)(L^3\text{-}\kappa S)_2]$ is only formed in a *ca* 9 % overall yield (highlighted ^{1}H NMR peaks). Repetition of such synthesis with higher ratios of HL^3 : $[Pt(phen)Cl_2]$ of up to 4:1, did not result in significantly larger amounts of $[Pt(phen)(L^3\text{-}\kappa S)_2]$ being found upon work up of this relatively unstable product.

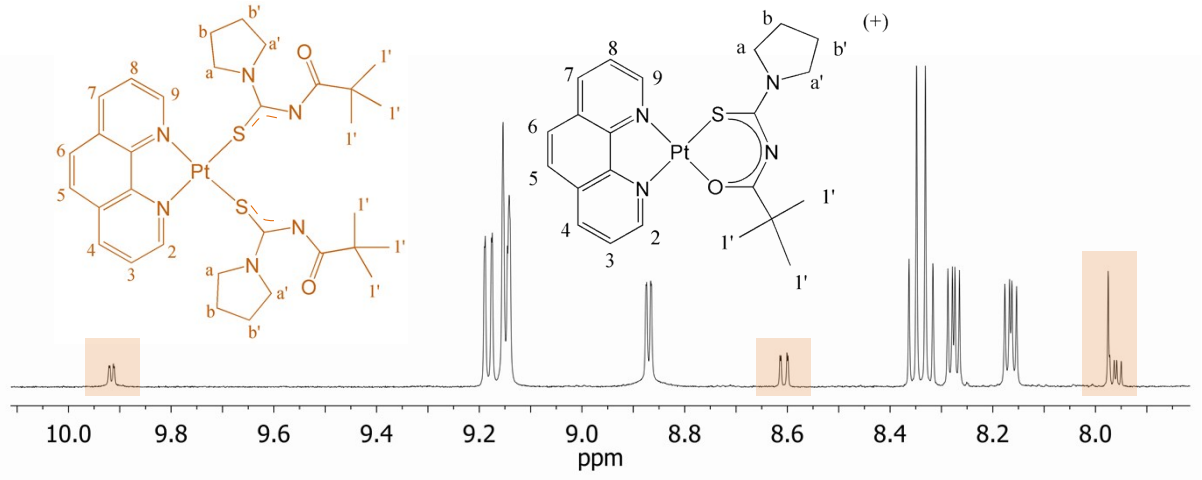

Fig. S6. Numbering scheme of selected atoms and groups of the molecular structure of $[Pt(phen)(L^2\text{-}\kappa S)_2]$. Hydrogen atoms omitted for clarity, with the exception of a water molecule, H-bonded to the pendant C(O) group of the phenyl amide moiety of this complex.

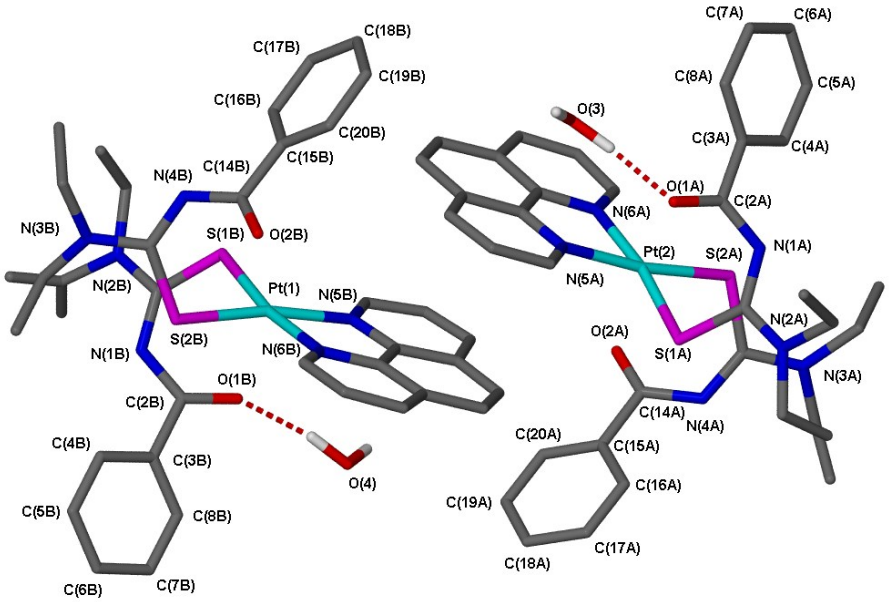

Table S2. Selected bond lengths for [Pt(phen)(L^2-κ*S*)$_2$].

Bonds:	Å
Pt1-S1B	2.280(2)
Pt1-S2B	2.280(2)
Pt1-N5B	2.060(6)
Pt1-N6B	2.050(6)
Pt2-S1A	2.279(2)
Pt2-S2A	2.284(2)
Pt2-N5A	2.057(6)
Pt2-N6A	2.063(6)
S1B-C1B	1.746(7)
S2B-C13B	1.751(8)
S1A-C1A	1.741(7)
S2A-C13A	1.748(7)
O1B-C2B	1.242(9)
O2B-C14B	1.233(10)
O2A-C14A	1.238(9)
O1A-C2A	1.242(9)
N1B-C2B	1.359(9)
N1B-C1B	1.320(9)
N2B-C11B	1.474(9)
N2B-C1B	1.349(9)
N2B-C9B	1.480(9)
N3B-C13B	1.343(10)
N3B-C17	1.511(12)
N3B-C14	1.472(12)
N4B-C13B	1.310(10)
N4B-C14B	1.349(11)
N5B-C32B	1.365(9)
N5B-C21B	1.327(10)
N6B-C31B	1.369(9)
N6B-C30B	1.317(10)
N1A-C1A	1.320(9)
N1A-C2A	1.333(9)
N2A-C1A	1.352(9)
N2A-C9A	1.480(9)
N2A-C11A	1.439(9)

Table S2. Selected bond lengths for [Pt(phen)(L^2-κ*S*)$_2$].

Bonds:	Å
N3A-C13A	1.356(9)
N3A-C21A	1.516(11)
N3A-C23A	1.493(9)
N4A-C14A	1.353(9)
N4A-C13A	1.318(9)
N5A-C25A	1.340(10)
N5A-C36A	1.348(9)
N6A-C34A	1.324(10)
N6A-C35A	1.381(9)

Table S3. Selected hydrogen bond distanced in [Pt(phen)(L^2-κ*S*)$_2$]

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H-Bond		D…A (Å)	D…A (º)	Symm. Op
O4—HB... O1B	1.88(6)	2.877(8)	170(5)	-x,-y,-z
O4—HA... O2A	1.87(3)	2.837(7)	163(7)	1-x,-y,-z
O3-- H3A... O2B	1.93(5)	2.914(8)	167(6)	1-x,-y,-z
O3-- H3B... O1A	1.83(7)	2.812(8)	168(6)	1-x,1-y,-z