**Reversible Photo-isomerization of *cis*-[Pd(L-κ*S,O*)2] (HL = *N N*-diethyl-*N’*-1-naphthoylthiourea) to *trans*-[Pd(L-κ*S,O*)2] and the Unprecedented Formation of *trans*-[Pd(L-κ*S,N*)2] in Solution.**

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**Abstract**

*Upon ex-situ UV-irradiation, complex cis-bis(N,N-diethyl-N’-naphthoylthioureato)-palladium(II), cis-[Pd(L-κS,O)2], undergoes isomerization in acetonitrile-d3 and chloroform-d to yield trans-[Pd(L-κS,O)2] which then rearranges thermally to novel trans-[Pd(L-κS,N)2] prior to returning to the cis isomer. The thermal isomerisation rate is highly solvent dependent and harnessed to enable each of these three geometric isomers to be isolated and characterized by 1H NMR spectroscopy, X-ray crystallography, melting point and thermal analysis. The formation of the trans-[Pd(L-κS,N)2] isomer as part of this isomerisation has only been observed with the sterically demanding cis-bis(N,N-diethyl-N’-(naphthoyl-thioureato)palladium(II) precursor based on our knowledge to date. In-situ irradiation with monochromatic laser light (=355 nm) coupled to 1H NMR spectroscopy of solutions of cis-[Pd(L-κS,O)2] in acetonitrile-d3 supports the ex-situ photo-induced isomerisation experiments.*

**Keywords:** Photo-induced *cis/trans* isomerization; palladium complexes; *cis*-[Pd(L-κ*S*,*O*)2]; *trans*-[Pd(L-κ*S*,*O*)2]; *trans*-[Pd(L-κ*S*,*N*)2]; *In-situ* laser photochemistry coupled to NMR

**Introduction**

The group of molecules generally known as the *N*,*N*-dialkyl-*N*’-acylthioureas (HL; R12NC(S)NHC(O)R2, R1 = alkyl, R2 = alkyl, aryl or aroyl groups) and their corresponding *N*-alkyl-*N’*-acylthiourea (H2L; R1HNC(S)NHC(O)R2) counterparts, have been known for almost a century.1 These ligands have a well-established coordination chemistry to many transition metal ions, which has been extensively reviewed.2-6 Metal complexes of these ligands show a diverse range of applications including as potential antitumor 7,8 and antibacterial agents.9 These complexes also displaycatalytic activity,10 havebeen used for solvent extraction of transition metal ions,11,12 and used in the quantitative chromatographic determination of precious metal complexes.13 More recently, applications include interesting supramolecular chemistry,14,15 and in materials chemistry.16

In general, these deceptively simple *N*,*N*-dialkyl-*N*’-acylthiourea molecules (HL) tend to overwhelmingly, although not exclusive, coordinate to divalent transition metal ions M2+ such as Cu(II),17 Ni(II),18, Pd(II),7,19,8 Pt(II),20-23 with loss of a proton in a stable monobasic bidentate κ-*S*,*O* mode of coordination, to give square-planar *cis*-[M(L-κ*S,O*)2] type complexes. In the case of trivalent transition metal ions such as Rh(III),13 Co(III)24,25 and Ru(III) 26 coordination of HL generally leads to mainly octahedral *fac*-[M(L-κ*S*,*O*)3].

As part of our interest, particularly in *cis*-[M(Ln-κ*S*,*O*)2] complexes of the noble metals M = Pt(II) & Pd(II) (‘n’ denoting variously substituted HL ligands) in the context of potential hydrometallurgical potential applications,3 we were intrigued by the rarity of the corresponding *trans*-[M(Ln-κ*S*,*O*)2] isomers obtained from *N*,*N*-dialkyl-*N*’-acylthioureas. In fact, the first example of a *trans*-*S*,*O* coordinated Pt(II) complex, *trans*-*bis*(*N*,*N*-(di-*n*)-butyl-*N*’-napthoylthioureo)platinum(II), was fortuitously isolated in low yields of *ca* 15% by Koch *et al,* more than 2 decades ago.27 Despite numerous attempts it was not possible, to reliably prepare *trans*-[Pt/Pd(L-κ*S*,*O*)2] complexes by conventional means with different ligands of this motif.5,6 Nevertheless, the synthesis of a few presumably thermodynamically less stable *trans*-[Cu(L-κ*S,O*)2] complexes has subsequently been achieved, as characterised by X-ray diffraction.28-31

Recently, Koch *et a*l demonstrated that the key to the formation of the geometrical *trans*-[Pt/Pd(Ln-κ*S*,*O*)2] isomers, is in fact a facile photo-induced isomerisation of the *cis*-[Pt/Pd(Ln-κ*S*,*O*)2] complexes in acetonitrile-*d3* if irradiated with intense polychromatic light of wavelength < 450 nm.32-35 Under such conditions *cis*-[Pt(Ln-κ*S*,*O*)2] and *cis*-[Pd(Ln-κ*S*,*O*)2] type complexes cleanly isomerize to the analogous *trans* isomersat room temperature.32,35 The extent of, and the relative rates of *cis* → *trans*, isomerization of these *cis* complexes were found to be dependent on the nature of the ligand, the polarity of the organic solvent, as well as the wavelength of the irradiating light. Moreover, the isomerisation is reversible in the absence of light, complete albeit slow *trans* → *cis* reversiontakes place at room temperature (Scheme1).32,33 Based on these observations, we developed a simple means of preparing and isolating several examples of pure *trans*-[Pt(Ln-κ*S*,*O*)2] and *trans*-[Pd(Ln-κ*S*,*O*)2] by photo-irradiation of their *cis* precursors in conjunction with simple vapour-diffusion crystallisation methodology.33,35



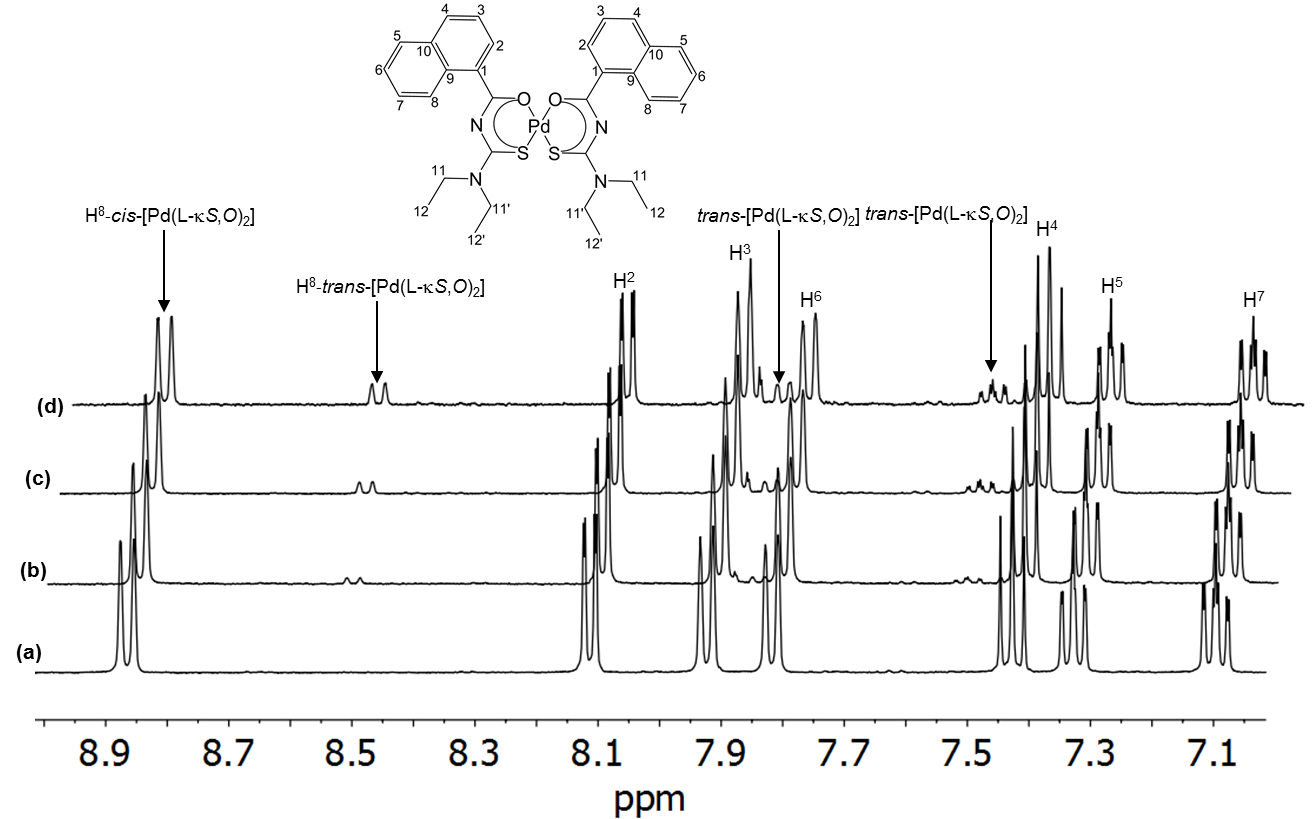
**Scheme1**

In this paper, we show that similar photo-induced isomerisation of *cis*-[Pd(L-κ*S*,*O*)2] in acetonitrile-*d3* leads not only to the expected *trans*-[Pd(L-κ*S*,*O*)2] isomer but also, and remarkably, to the unprecedented *trans*-[Pd(L-κ*S*,*N*)2] isomer, which could be isolated and characterised by exploiting their reactivity differences in chloroform or acetonitrile-*d3* solution, in the absence of light.

**Results and Discussion**

**Preparation and Isolation of *trans*-[Pd(L-κ*S*,*O*)2] and *trans*-[Pd(L-*S*,*N*)2] by photo-induced isomerisation of *cis*-[Pd(L-κ*S*,*O*)2].**

The aromatic region of the 1H NMR spectrum of *cis*-[Pd(L-κ*S*,*O*)2] in acetonitrile-*d3* containing *N*,*N*-diethyl-*N*’-naphthoylthiourea that resulted from a literature procedure is shown Figure 1(a).13,14 Photo-irradiation of this solution in an NMR tube with polychromatic light from a 5 Watt LED lamp leads to a slow photo-induced isomerization resulting in the formation of *trans*-[Pd(L-κ*S*,*O*)2] at 298 K. Figure 1(b-c) shows how this 1H NMR spectrum changes over time. The new resonances are readily assignedto *trans*-[Pd(L-κ*S*,*O*)2] as they are comparable to those of *trans*-*bis*(*N*,*N*-(di-*n*)-butyl-*N*’-1-napthoylthioureo)platinum(II).27



**Figure 1.** 1H NMR spectra of an acetonitrile-*d*3 solution *cis*-[Pd(L-κ*S*,*O*)2] (a) fresh solution *ex-situ* irradiation with polychromatic light of a 5 Watt LED lamp for (b) 3 min, (c) 10 min, (d) 15 min at 25 °C, showing the emergence of the *trans*-[Pd(L-κ*S*,*O*)2].

Good crops of crystals of *trans*-[Pd(L-κ*S*,*O*)2] could reproducibly be isolated from acetonitrile solutions of the *cis*-[Pd(L-κ*S*,*O*)2] complex, following irradiation by a procedure we recently reported33,35 involving continuous irradiation with polychromatic light and *in-situ* crystallisation by vapour diffusion using diethylether at room temperature.

In the case of complexes derived from *N*,*N*-diethyl-*N*’-1-naphthoylthiourea however, mixtures of *cis*-[Pd(L-κ*S*,*O*)2] and *trans*-[Pd(L-κ*S*,*O*)2] are obtained depending on the irradiation time. The unprecedented *trans*-[Pd(L-*S*,*N*)2] isomer is also seen in these solutions. Prolonged continuous irradiation of a more concentrated in acetonitrile for *ca* 4 days, and subsequent crystallization, results in the isolation of a second crop of yellow crystals due to *trans*-[Pd(L-κ*S*,*N*)2]. The isolated crystals of the *cis*-[Pd(L-κ*S*,*O*)2], *trans*-[Pd(L-κ*S*,*O*)2] and *trans*-[Pd(L-κ*S*,*N*)2] isomers are not easily distinguishable visually, all being yellowish and rod-shaped (see insert in Figure 2). After careful physical separation though they could be distinguished by their melting points. The pure *cis*-[Pd(L-κ*S*,*O*)2] isomer exhibits a low melting point of between 157 and 159 °C when compared to both of the other forms; *trans*-[Pd(L-κ*S*,*O*)2] (174 - 176 °C) and *trans*-[Pd(L-κ*S*,*N*)2] (187-189 °C). The relatively higher melting point of the *trans* isomer is consistent with the situation reported in the literature for related complexes.33,35

Differential scanning calorimetry (DSC) confirms the differing melting points of the three geometric isomers over the temperature range 25 – 220 °C under a heating rate of 10 °C min-1 and a dinitrogen atmosphere (Figure 2). The red DSC curve, obtained from a sample of pure *cis*-[Pd(L-κ*S*,*O*)2], shows a single sharp endothermic event at 153.8 oC, corresponding to the melting of this complex. The blue curve reflects a mixture of the *trans*-[Pd(L-κ*S*,*O*)2] and *trans*-[Pd(L-κ*S*,*N*)2] that was obtained after evaporation of a previously irradiated solution of the *cis*-[Pd(L-κ*S*,*O*)2] complex. Now two endothermic events are seen, in the range 160 - 200 °C, which confirms both isomers are present. The additional 154 °C event, suggests the occurrence of thermal *trans* → *cis* isomerization during this observation. These endothermic events are consistent with the conventionally measured melting points of the isolated *trans*-[Pd(L-*S*,*O*)2] (174 – 176 °C) and *trans*-[Pd(L-κ*S*,*N*)2] (187 -189 °C). The broad endothermic peak (blue line) at *ca* 183 °C is ascribed to the thermal interconversion process that leads to the more stable *cis*-[Pd(L-κ*S*,*O*)2] form.

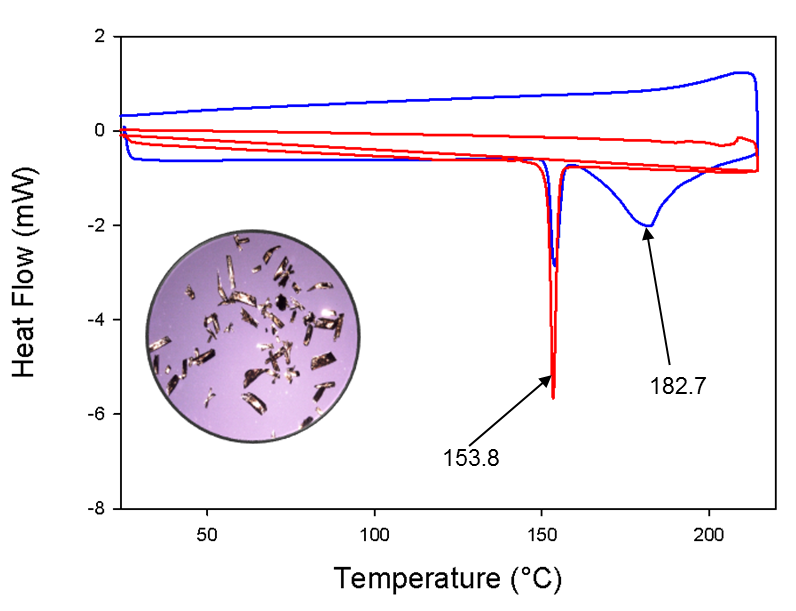
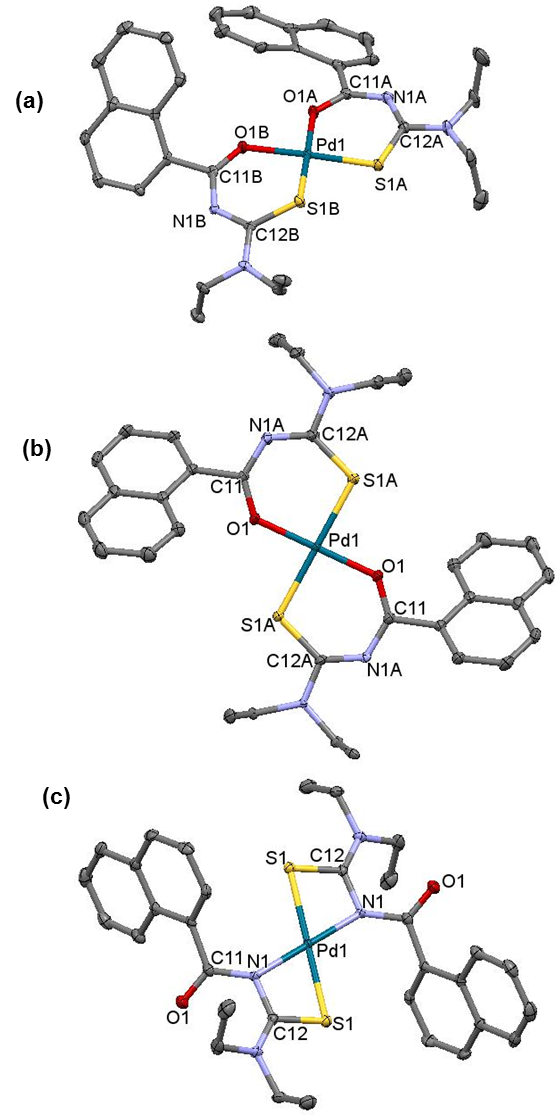


Figure 2. Differential Scanning Calorimetry curves of pure *cis*-[Pd(L-κ*S*,*O*)2] (red line); A sample of a mixture *trans*-[Pd(L-κ*S*,*O*)2] and *trans*-[Pd(L-κ*S*,*N*)2] complexes at a heating rate of 10 °C min-1  (blue line). Note the physical similarity of the crystals on the mixture of the *trans*-[Pd(L-κ*S*,*O*)2] and *trans*-[Pd(L-κ*S*,*N*)2] complexes in the inset with optical microscopy.

The single crystal X-ray diffraction structures of all three *cis*-[Pd(L-κ*S*,*O*)2], *trans*-[Pd(L-κ*S*,*O*)2] and *trans*-[Pd(L-κ*S*,*N*)2] complexes are shown in Figure 3. Their refinement data is given in Table 1. The *cis*-[Pd(L-κ*S*,*O*)2] complex (Figure 3(a)) crystallizes in the orthorhombic space group P*bcn*, with the palladium atom coordinating to the sulfur and oxygen atoms in a *cis-*κ*S,O* manner. There are no significant differences in the average Pd-S (2.234(1) Å) and Pd-O (2.023(2) Å) bond lengths, in this isomer as compared to those of the corresponding *cis*-*bis*(*N*,*N*-dialkyl-*N*’-benzoylthioureato)palladium(II) complex,33-35 suggesting that the presence of the napthoyl-moiety does not significantly affect distribution of delocalized electrons density in the six-membered chelate ring of the *cis*-[Pd(L-κ*S*,*O*)2] isomer. Closer inspection of the latter crystal structure shows a detectable deviation from square planarity of the six-membered chelate ring, resulting in the S(1A)-Pd1-O(1B) and S(1B)-Pd1-O(1A) bond angles being 177.99 (7)° in *cis*-[Pd(L-κ*S*,*O*)2] compared to that of *cis*-*bis*(*N*,*N*-dialkyl-*N*’-benzoylthioureato)palladium(II) of 179.09 (8)° respectively.33 In *cis*-[Pd(L-κ*S*,*O*)2], the two naphthoyl groups are not coplanar with the six-membered chelate rings reflected by differences in the torsion angles C(12B)-N(1B)-C(11B)-C(1B) -172.5(2)° compared to C(12A)-N(1A)-C(11A)-C(1A) -167.3 (3)°, presumably due to the bulky nature of the napthoyl-moiety. The crystal packing of *cis*-[Pd(L-κ*S*,*O*)2] shows intermolecular π-π interactions of the naphthoyl rings (Figure S1(a)) with weak intermolecular C-H interactions between the naphthoyl moieties and the methyl hydrogen atoms of the thioamidic group (Fig S1).



**Figure 3.** Molecular structure from single-crystal X-ray diffraction of (a) *cis*-[Pd(L-κ*S*,*O*)2] isolated from acetonitrile by slow evaporation in the dark, (b) *trans*-[Pd(L-κ*S*,*O*)2] and (c) *trans*-[Pd(L-κ*S*,*N*)2] isolated after irradiation with a 5 Watt LED lamp at 25 °C by vapour diffusion crystallization with diethylether. All hydrogen atoms are omitted for clarity. The displacement ellipsoids are drawn at 50 % probability level. Selected bond lengths (Å) and angles (°); *cis*-[Pd(L-κ*S*,*O*)2]: Pd-S 2.224, 2.2458, Pd-O 2.032, 2.015, S-Pd-O 177.19, S-Pd-S 86.93; *trans*-[Pd(L-κ*S*,*O*)2]: Pd-S 2.29, Pd-O 1.978, S-Pd-S/O-Pd-O 180.00; *trans*-[Pd(L-κ*S*,*N*)2]: Pd-S 2.3252, Pd-N 2.050, S-Pd-S/N-Pd-N 180.00

The molecular structure of the *trans*-[Pd(L-κ*S*,*O*)2] complex (Figure 3(b)) shows bidentate *trans*-κ*S*,*O* coordination of the ligand to Pd(II) in the six-membered Pd1-S1-C12-N1-C11-O1 chelate ring. The *trans*-[Pd(L-κ*S*,*O*)2] complex crystallizes in a monoclinic space group, P21/c. This structure is complicated by crystallographic disorder at two positions corresponding to one of the ethyl moieties linked to section C12-N1B of the chelate ring. The average Pd-S [2.281(12) Å] bond length in the *trans*-[Pd(L-κ*S*,*O*)2] isomer is slightly longerthan that of the *cis*-[Pd(L-κ*S*,*O*)2] [Pd-S = 2.234(1) Å] complex, while the corresponding and Pd-O [1.9789(13) Å] bonds are shorter [ Pd-O = 2.023(2) Å], respectively. This may be ascribed to the higher *trans*-influence of the sulfur donor atom,36 leading to the expected longer Pd-S and shorter Pd-O bond distances, in the *trans*-[Pd(L-κ*S*,*O*)2] isomer. The *trans*-[Pd(L-κ*S*,*O*)2] structure assumes an almost perfectly square planar configuration, represented by S1-Pd1-S1 and O1-Pd1-O1 bond angles of 180°. The two napthoyl-moieties are not coplanar with the six-membered chelate system as evident by the torsion angles C12A-N1A-C11-C1=171.19°, C12B-C-11B-C11-C1=-175.00°.

The novel *trans*-[Pd(L-κ*S*,*N*)2] complex crystallizes in a monoclinic space group P21/n shown in Figure 3(c). The structure illustrates a rare four-membered *trans*-*S*,*N* chelate ring, which is almost perfectly square-planar as indicated by the S1-Pd1-S(1\_a) bond angles of 180°. The napthoyl-moieties are not coplanar with the four-membered chelate, with torsion angles of S1-C12-N2-C11= 138.93°. The Pd-S bonds are significantly longer (2.325(3) Å) compared to both the *trans*-[Pd(L-κ*S*,*O*)2] (2.281(12) Å) and *cis*-[Pd(L-κ*S*,*O*)2] (2.234(1) Å) isomers. The longer Pd-S bonds are ascribed to a higher *trans* influence of the sulfur donor atom relative to either oxygen or nitrogenwhich consequently weakens the Pd-S bonds, as well as the effect of the four membered chelate ring imposes. A shortening of the uncoordinated C=O bond distance (1.225(4) Å) in the *trans*-[Pd(L-*S*,*N*)2] complex is also observed compared to the average bond distances of the coordinated C-O bond in either *cis*-[Pd(L-κ*S*,*O*)2] (1.272(4) Å) or *trans*-[Pd(L-κ*S*,*O*)2] [1.282(2) Å]. This is probably due to extensive delocalization of the oxygen donor electrons into the six-membered chelate rings in both *cis*-[Pd(L-κ*S*,*O*)2] and *trans*-[Pd(L-κ*S*,*O*)2], a situation that is absent in the *trans*-[Pd(L-κ*S*,*N*)2] complex, resulting in the double bond character in the uncoordinated C=O bond being similar to that in the free ligand.

**Table 1.** Crystallographic refinement data for *cis*-[Pd(L-κ*S*,*O*)2], *trans*-[Pd(L-κ*S*,*O*)2] and *trans*-[Pd(L-κ*S*,*N*)2].

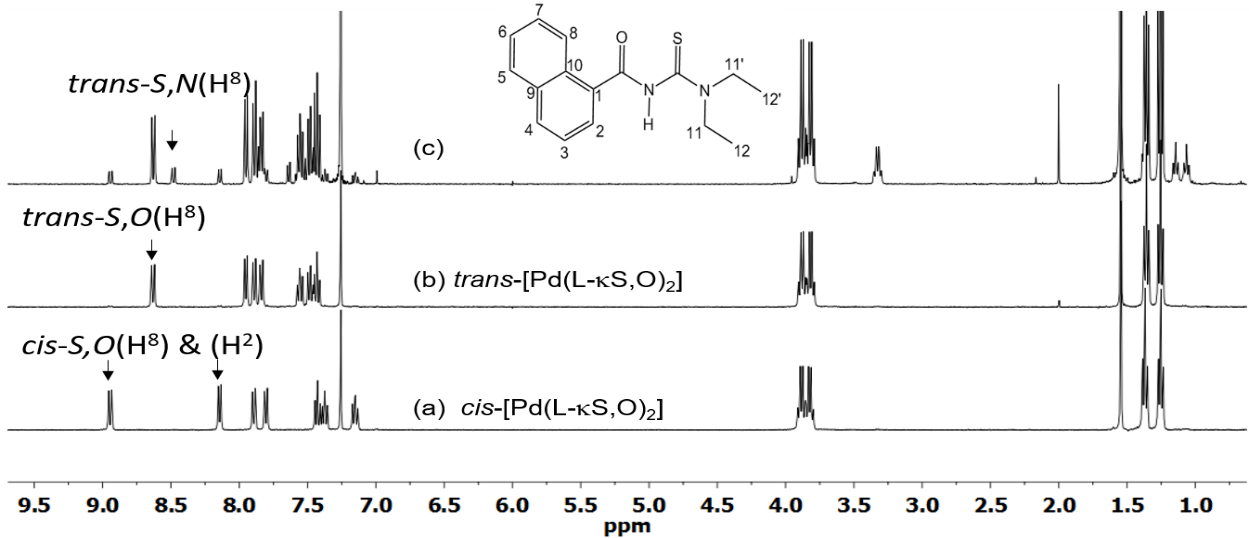
|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Compound | *cis*-[Pd(L-κ*S*,*O*)2] | | *trans*-[Pd(L-κ*S*,*O*)2] | | *trans*-[Pd(L-κ*S*,*N*)2] | |
| Empirical formula | C32H34N4O2PdS2 | | C32H34N4O2PdS2 | | C32H34N4O2PdS2 | |
| Formula weight | 677.11 | | 677.11 | | 677.11 | |
| Crystal system | orthorhombic | | monoclinic | | monoclinic | |
| Space group | P*cbn* | | *P*21/*c* | | *P*21/*n* | |
| a (Å) | 43.068(8) | | 11.640(15) | | 12.471(3) | |
| b (Å) | 9.323(18 ) | 8.444(11) | | 7.397(2) | |
| c (Å) | 15.204(3) | 14.795(19) | | 15.924(5) | |
| α/° | 90.000 | 90.000 | | 90.000 | |
| β/° | 110.198 | 96.132(2) | | 92.975(4) | |
| γ/° | 90.000 | 90.000 | | 90.000 | |
| Z | 8 | 2 | | 2 | |
| T/K | 100 | 100 | | 100 | |
| μ/mm-1 | 0.781 | 0.824 | | 0.812 | |
| Independent reflections | 7077 | 3344 | | 3387 | |
| Rint | 0.080 | 0.017 | | 0.045 | |
| Final R1, wR2[I > 2σ(I)] | 0.0490, 0.1043, 1.04 | 0.0245, 0.0668, 1.07 | | 0.0245, 0.0668, 1.07 | |

**Monitoring photo-induced *cis*/*trans* isomerisation of the *cis*-[Pd(L-κ*S*,*O*)2] by 1H NMR spectroscopy.**

The 1H NMR spectra of samples of pure *cis*-[Pd(L-κ*S*,*O*)2] and *trans*-[Pd(L-κ*S*,*O*)2] isomers in CDCl3 differ significantly as shown in Figure 4 (a) and (b) respectively. These are very similar to the respective *cis-* and *trans-*isomers in CD3CN, after short periods of *ex-situ* irradiation with polychromatic light (Figure 1). The 1H NMR spectrum of a freshly prepared solution of pure *trans*-[Pd(L-κ*S*,*O*)2] in CDCl3 shows that the H8 and H2 resonances of the *trans*-[Pd(L-κ*S*,*O*)2] isomer are more shielded by *ca* 0.32 ppm and 0.19 ppm, compared to their counterparts in the *cis*-[Pd(L-κ*S*,*O*)2] isomer. The H7 multiplets in this *trans*-[Pd(L-κ*S*,*O*)2] complex are significantly de-shielded by *ca* 0.40 ppm compared to its *cis* isomer. This makes 1H NMR a good tool for monitoring the *cis/trans* isomerisation processes in organic solvents of these complexes as previously shown for similar complexes. 32,33,34 For all known *cis → trans* isomerisation of related *cis*-[M(L-*S*,*O*)2] (M=Pt(II), Pd(II)) to date, it was found that after photo-irradiation by polychromatic light, onlythe *trans*-[M(L-*S*,*O*)2] isomer is formed, which reverts back to the corresponding *cis*-[M(L-*S*,*O*)2] complex in the absence of light.32,33,34

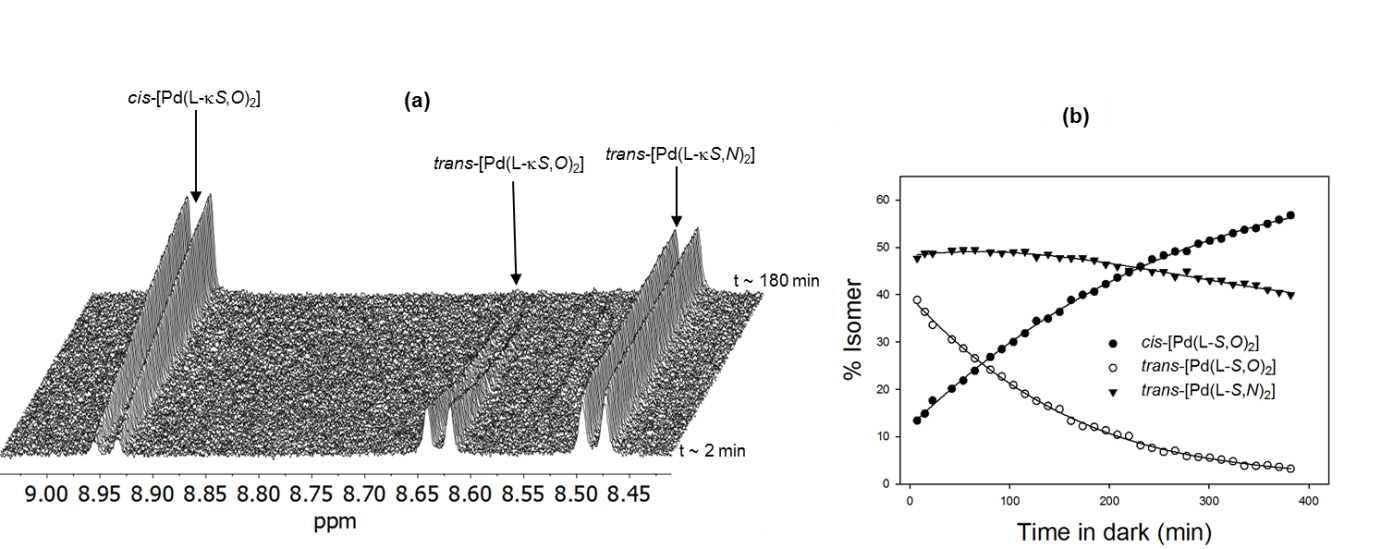
Figure 4 shows a series of 1H NMR spectra of *cis*-[Pd(L-κ*S,O*)2] and *trans*-[Pd(L-κ*S,O*)2] in CDCl3 solution. As described above, these two complexes are readily distinguished by inspection of the aromatic region of the spectrum in CDCl3. The corresponding chemical shifts are almost identical in CD3CN.Upon short periods of *ex-situ* irradiation of a solution of *cis*-[Pd(L-κ*S,O*)2] the signals for *trans*-[Pd(L-κ*S,O*)2] become readily visible.

Interestingly, if a solution of pure *trans*-[Pd(L-κ*S,O*)2] (Fig. 4(c)) is left in the dark for more than 25 min at 298 K, peaks due to the *cis*-[Pd(L-κ*S,O*)2] emerge in addition to several new peaks, most clearly indicated by the doublet at *δ* 8.48 ppm. This doublet is shielded relative to H8 of *trans*-[Pd(L-κ*S,O*)2] and accompanied by other new resonances in the aliphatic region at *δ* 3.45 and *δ* 1.05 ppm. These are due to -N(CH2) and -CH3 protons of an -N(ethyl)2 moiety and have similar appearance to those of *cis*- and *trans*-[Pd(L-κ*S,O*)2], respectively. These new peaks are assigned to novel *trans*-[Pd(L-κ*S,N*)2]. This isomer forms slowly from *trans*-[Pd(L-κ*S,O*)2] in the absence of light and eventually reverts to *cis*-[Pd(L-κ*S,O*)2]. This behaviour has not previously been observed for any of the related Pt(II) and Pd(II) complexes with a variety of *N,N*-dialkyl-*N’*-benzoylthiourea ligands.32-35



**Figure 4.** 1H NMR spectra of (a) pure *cis*-[P(L-κ*S*,*O*)2]; (b) isolated pure *trans*-[Pd(L-κ*S*,*O*)2] and (c) the solution (b) of *trans*-[Pd(L-κ*S*,*O*)2] after allowing it to stand for 25 min in dark in chloroform-*d* at 25 °C, showing clearly the slow emergence of the *trans*-[Pd(L-κ*S*,*N*)2] complex.

To investigate further the evolution of the intermediate *trans*-[Pd(L-κ*S,N*)2] we recorded a series of time-arrayed 1H NMR spectra on a sample prepared from an isolated *mixture* of *trans*-[Pd(L-κ*S*,*O*)2] and *trans*-[Pd(L-κ*S*,*N*)2] containing a trace of residual *cis*-[Pd(L-κ*S*,*O*)2]. The resulting 1H NMR spectra in chloroform-*d* in Figure 5, indicate that *cis*-[Pd(L-κ*S,O*)2]reforms essentially over 370 minutes in the dark *via* presumably the conversion of *trans*-[Pd(L-κ*S,*O)2] into the intermediate *trans*-[Pd(L-κ*S,N*)2] as in Scheme 2. It is important to note that the reaction *trans*-[Pd(L-κ*S,N*)2] → *cis*-[Pd(L-κ*S,O*)2]takes ca 84 h to completion, suggestive of an associative reaction pathway, as shown in the NMR spectra in Figure S2.



**Figure 5**. Time-dependent 1H NMR changes in peak intensities in the dark, of the H8 protons for a mixture of *trans*-[Pd(L-κ*S*,*O*)2] and *trans*-[Pd(L-κ*S*,*N*)2] freshly dissolved in chloroform-*d* at 298 K. The first 1H NMR spectrum recorded 2 min after dissolution shows *cis*-[Pd(L-κ*S*,*O*)2] present. Clearly the rates of reversion of *trans*-[Pd(L-κ*S*,*O*)2] → *cis*-[Pd(L-κ*S*,*O*)2] at 298 K in the dark differ significantly from the *trans*-[Pd(L-κ*S*,*N*)2] → *cis*-[Pd(L-κ*S*,*O*)2].

***In-situ* laser irradiation of *cis*-[Pd(L-κ*S*,*O*)2] in acetonitrile monitored by 1H NMR spectroscopy.**

The photo-induced isomerism of an optically dilute solution of *cis*-[Pd(L-κ*S,O*)2] in acetonitrile-*d3* was studied by 1H NMR spectroscopy with *in-situ* monochromatic laser irradiation (λ = 355 nm) where the complex shows an absorption. These experiments were carried out to assess the role of the solvent and possible wavelength dependence on the photo-isomerisation of *cis*-[Pd(L-κ*S,O*)2]in the product distribution. Figure 6(a) shows the effect of irradiation time on the growth of the H8 NMR signal of *trans*-[Pd(L-κS,O)2], with the concomitant decrease in the peak of the same proton for *cis*-[Pd(L-κ*S,O*)2] precursor. After 16 min of irradiation, a photo-stationary state is achieved with ca 64% *cis*-[Pd(L-κ*S,O*)2] and 36% *trans*-[Pd(L-κ*S,O*)2] in solution. This ratio is approximately consistent with similar *ex-situ* irradiation with polychromatic light experiments in chloroform-*d*, shown in Figure 1. A nominal *k*obs of 1.2 ± 0.2 x 102 s-1 for the growth of the 1H NMR peak intensity of the *trans*-[Pd(L-κ*S,O*)2] complex was obtained (Figure 6b); a similar pseudo-first order rate constant (1.3 ± 0.2 x102 s-1 Figure 6b) is obtained for the decrease in the concentration of the *cis*-[Pd(L-κ*S,O*)2] species, confirming that the photo-isomerization proceeds cleanly from the photo-excited *cis*-[Pd(L-κ*S,O*)2] to form the *trans*-[Pd(L-κ*S,O*)2] species. Evidently, the *cis*-[Pd(L-κ*S,O*)2] → *trans*-[Pd(L-κ*S,O*)2] isomerisation achieves a photo-stationary state fairly rapidly during the first 400 seconds, which persists to at least ~ 900 sec. During this time-interval there is no evidence for the formation of *trans*-[Pd(L-κ*S,N*)2] by *in-situ* irradiation with the monochromatic laser light. After switching the laser irradiation off at 900 sec, continued monitoring of the 1H NMR spectrum in the dark shows that this system thermally relaxes by slow reversion of the *trans*-[Pd(L-κ*S,O*)2] species *via* the formation of the *trans*-[Pd(L-κ*S,N*)2] complex, to regenerate the precursor *cis*-[Pd(L-κ*S,O*)2] species (Figure 6(c)). The growth of a signal for *trans*-[Pd(L-κ*S,N*)2] is consistent with the disappearance of the *trans*-[Pd(L-κ*S,O*)2] peaks which commences after the laser is switched off at 900 seconds, as seen by the first spectrum in the array of spectra in Figure 6(c). From this time onwards, the signals of *trans*-[Pd(L-κ*S,N*)2] species grow much more slowly in intensity only to eventually decline again to give rise to the *cis*-[Pd(L-κ*S,O*)2] complex.

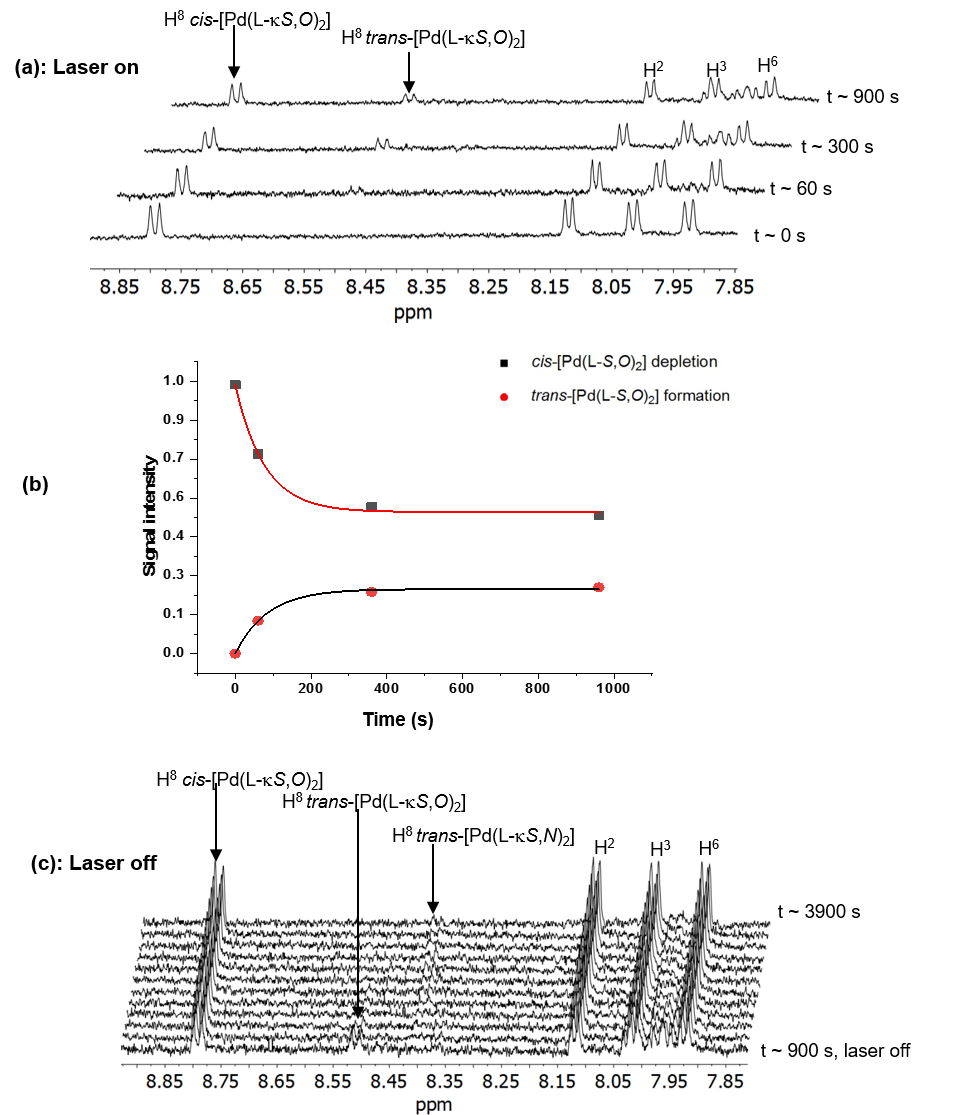
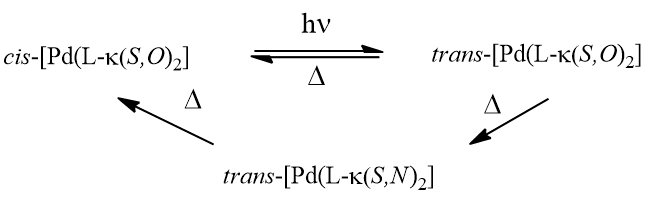


Figure 6. (a) 1H NMR spectra of a fresh acetonitrile-*d3* solution (~ 0.1 mgml-1) of *cis*-[Pd(L-κ*S,O*)2] before (t = 0 s) and after *in-situ* irradiation with λ = 355 nm laser for t = 60 s, 300 s, 900 s at 25 °C; (b) plot of the signal intensity *vs* photolysis time for both the *cis* and *trans* isomers in acetonitrile-*d3*; The squares/circles are the experimental points while the lines show the fit according to an exponential decay function (c) After t = 900 s, the laser was switched off with continued 1H NMR monitoring of the thermal *trans* → *cis* reversion reaction in the dark; the slow emergence of the intermediate *trans*-[Pd(L-κ*S,N*)2] isomer is observed in these spectra (see text).

Collectively, these data indicate that the *cis*-[Pd(L-κ*S*,*O*)2] converts photo-chemically into *trans*-[Pd(L-κ*S*,*O*)2] to reach a photo-stationary state in acetonitrile-*d3*, during continuous*in-situ* laser irradiation proposed in Scheme 2. After switching off the laser, a thermal rearrangement of the *trans*-[Pd(L-κ*S,O*)2] to the *trans*-[Pd(L-κ*S,N*)2] species takes place, which in turn reverts slowly and cleanly, back to the thermodynamically more stable *cis*-[Pd(L-κ*S*,*O*)2] complex.



**Scheme 2**

Unfortunately, due to the need of using optically dilute solutions for *in-situ* laser irradiation, as well as due to the low overall solubility of the *cis*-[Pd(L-κ*S*,*N*)2] complex in acetonitrile-*d3* (typically at best ~ 0.1 mg ml-1) the S/N ratio of these time arrayed 1H NMR spectra precluded a more quantitative analysis of the rate of formation of the *trans*-[Pd(L-κ*S*,*N*)2] complex by such NMR experiments. Nevertheless, the reversion of the *trans* → *cis* isomerization *via* the *trans*-[Pd(L-κ*S*,*N*)2] species in the dark, monitored by 1H NMR in a more concentrated solution of aphysical mixture of *trans*-[Pd(L-κ*S*,*O*)2], *trans*-[Pd(L-κ*S*,*N*)2] in the presence of a small quantity of *cis*-[Pd(L-κ*S*,*O*)2] in chloroform-*d* (Figure 5)*,* qualitatively correspond to the trends in observed in Figure 6 in acetonitrile-*d3*. The relative rates of the *trans* → *cis* reactions in the dark in chloroform-*d* are several orders of magnitude lower compared to the corresponding processes in acetonitrile-*d3;* this also nicely illustrates the role of the solvent in these isomerization reactions. In chloroform-*d* the *trans*-[Pd(L-κ*S*,*N*)2] complex persists in solution for more than *ca* 400 min, by which time the *trans*-[Pd(L-κ*S*,*O*)2] has completely disappeared from solution (Figure 5 and S2).

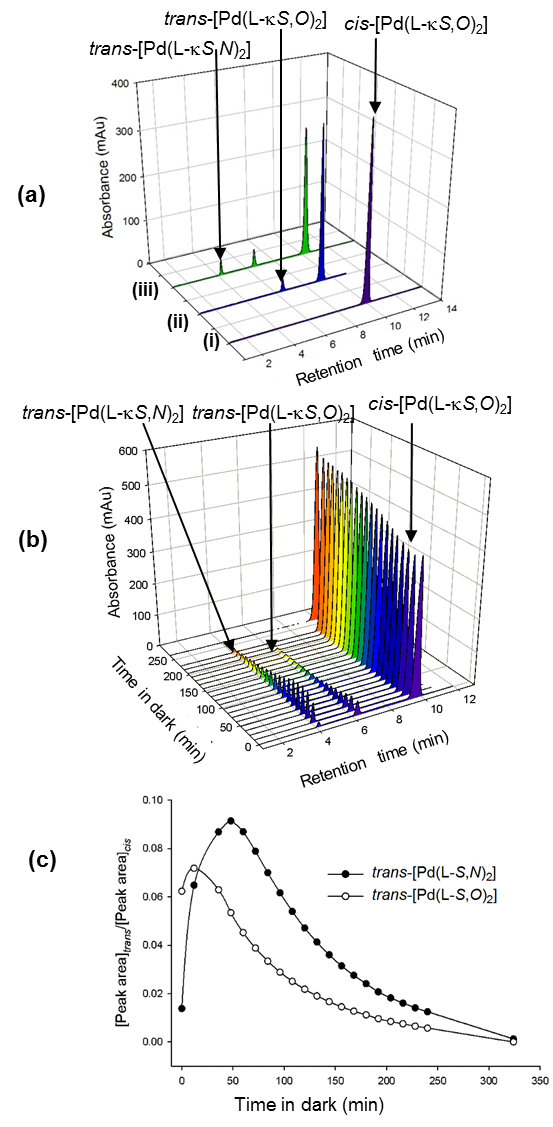
It is worth emphasising that this mechanism has so far only been observed for the *cis*-*bis*(*N*,*N*-dialkyl-*N*’-naphthoylthioureato)palladium(II) complex but not for the analogous *cis*-*bis*(*N*,*N*-diethyl-*N*’-benzoylthioureato)palladium(II) complexes.33-35

**Photo-isomerization of *cis*-[Pd(L-κ*S*,*O*)2] → *trans*-[Pd(L-κ*S*,*O*)2] and its reversion via the *trans*-[Pd(L-κ*S*,*N*)2] in the dark, monitored by *Reversed Phase*-HPLC**

The low solubility of *cis*-[Pd(L-κ*S,O*)2] in acetonitrile suggests that the use of *RP*-HPLC with photodiode array UV/vis detection could be used to examine the photo-induced *cis*-*trans* isomerism of *cis*-[Pd(L-κ*S*,*O*)2] together with the formation of the *trans*-[Pd(L-κ*S*,*N*)2]. This assumption is confirmed by Figure 7 which shows a series of overlaid *RP*-HPLC chromatograms of *cis*-[Pd(L-κ*S*,*O*)2] before and after *ex-situ* irradiation with polychromatic light. Prior to irradiation, only a single chromatographic peak is observed, with retention time ~ 10.1 min, for *cis*-[Pd(L-κ*S*,*O*)2] (Figure 7 (a)i). After exposure of a freshly prepared solution of the *cis* isomer to intense daylight (sunshine) for *ca.* 2 min, followed by injection into the *RP*-HPLC, a second peak appears which corresponds to *trans*-[Pd(L-κ*S*,*O*)2] at ~ 6.4 min (Figure 7 (a)ii). Irradiation of the freshly prepared solution of the *cis* complex for *ca.* 5 min with intense polychromatic light results in a small additional peak at retention time ~ 4.2 min (Figure 7 (a)iii). The latter peak is assigned to the *trans*-[Pd(L-*S*,*N*)2] isomer. This peak presumably forms in the dark during the time in which the irradiated sample is injected into the *RP*-HPLC. The *RP*-HPLC data confirms that *trans*-[Pd(L-κ*S,O*)2] reverts into *cis*-[Pd(L-κ*S,O*)2] *via* the much longer lived *trans*-[Pd(L-κ*S,N*)2] species.

Figure 7(b) shows a series of chromatograms obtained after repeated injections of 20 L aliquots of a solution of the precursor *cis*-[Pd(L-κ*S*,*O*)2] in acetonitrile which has undergone 30 min of *ex-situ* irradiation with polychromatic light. Injection was now achieved by means of an auto-sampler at 13 minute intervals and the sample was stored at room temperature in the dark. The resulting *RP*-HPLC trends as a function of time show that at the first time point, three species already exist in solution; *cis*-[Pd(L-κ*S*,*O*)2] dominates with small amounts of the photo-induced *trans*-[Pd(L-κ*S*,*O*)2] and a trace of the *trans*-[Pd(L-κ*S*,*N*)2] being detected. Repeated injections of this solution show chromatograms in which the peak areas of both *trans*-[Pd(L-κ*S*,*O*)2] and *trans*-[Pd(L-κ*S*,*N*)2] initially increase slightly over the first 26 mins. This is followed by a gradual decrease in the peak area for *trans*-[Pd(L-κ*S*,*O*)2] with concomitant increase in the peak due to *trans*-[Pd(L-κ*S*,*N*)2], reaching a zenith at *ca* 60 min after which it too falls off reaching zero at about 325 min. The concomitant growth of the *cis*-[Pd(L-κ*S*,*O*)2] peak tracks these changes, until after *ca* 6 hr full reversal is indicated.

These peak intensities were monitored at = 262 nm where the absorbance of the three species is very similar, although not identical (Figure S3). In this way qualitative relative rates of reversion of the *trans*-[Pd(L-κ*S*,*O*)2] and *trans*-[Pd(L-κ*S*,*N*)2] → *cis*-[Pd(L-κ*S*,*O*)2] isomer in the dark can extracted by taking the peak area ratios of *trans*-[Pd(L-κ*S*,*O*)2]/*cis*-[Pd(L-κ*S*,*O*)2] and *trans*-[Pd(L-κ*S*,*N*)2]/*cis*-[Pd(L-κ*S*,*O*)2] as a function of time (Figure 7 (c)). It is clear that these data match the trends observed in the NMR studies of Figs. 1, 6 and S2.



**Figure 7.** Overlaid *RP*-HPLC chromatograms of **(a)** (i) 20 µL of an acetonitrile solution of *cis*-[Pd(L-κ*S*,*O*)2] in the dark, (ii) 20 µL acetonitrile solution of *cis*-[Pd(L-κ*S,O*)2] exposed to intense daylight for 2 min, (iii) acetonitrile solution of *cis*-[Pd(L-κ*S,O*)2] after irradiation with polychromatic light from a 5 Watt LED lamp for 5 min; **(b)** *trans* → *cis* isomerism in the dark from a photo-irradiated solution of *cis*-[Pd(L-κ*S*,*O*)2] injected successively into the HPLC at 13 min time intervals; **(c)** Plot of the time-dependent changes in relative peak areas of *trans*-[Pd(L-κ*S*,*O*)2] and *trans*-[Pd(L-κ*S*,*N*)2] in acetonitrile; (Chromatographic conditions: mobile phase acetonitrile/water (97:3 %v/v); GEMINI C18, 5 µm, 250 x 4.6 mm column; 20 µL injection volume; flow rate 1 ml min-1; detection at 262 nm.

The unambiguous molecular compostion of the three isomers (and their relative retention times) was confirmed by *RP*-HPLC coupled to an ESI-TOF-mass-spectrometer (Figure S5). This gives three total-ion chromatographic peaks at 1.4 min, 1.8 min, and 2.8 min, all of which have identical low resolution *m/z* values of 677.12. Figure S6(b-d) shows the high resolution ESI mass spectra of the three isomeric species. The most intense set of peaks observed are in the *m/z* range 673.123-683.125 which corresponds exactly to the parent molecular ion [C32H34N4O2PdS2 + H]+,taking isotopic elemental distribution into account. Similarly, high resolution mass spectra of the *trans*-[Pd(L-κ*S*,*O*)2] (Fig S6(c)) and *trans*-[Pd(L-κ*S*,*N*)2] isomers (Fig. S6(d)) have essentially identical isotopic distibution peak patterns.

In summary the photo-induced isomerisation of pure *cis*-[Pd(L-κ*S*,*O*)2] in either acetonitrile or chloroform solution results in the fairly rapid formation of a *trans*-[Pd(L-κ*S*,*O*)2] complex, and much slower formation of the unprecedented *trans*-[Pd(L-κ*S*,*N*)2] species. This enables the isolation of both the *trans*-[Pd(L-κ*S*,*O*)2] and the *trans*-[Pd(L-κ*S*,*N*)2] complex in pure form, by careful timing of their crystalisation. The relative rate of the *in-situ* laser photo-induced *cis*-[Pd(L-κ*S*,*O*)2] → *trans*-[Pd(L-κ*S*,*O*)2] isomerism is significantly higher than the formation of the *trans*-[Pd(L-κ*S*,*N*)2] complex (Fig. 6(a-c)). The formation of the unusual *trans*-[Pd(L-κ*S*,*N*)2] complex not easily prepared by convetional means, appears to result from a thermal *trans*-[Pd(L-κ*S*,*O*)2] → *trans*-[Pd(L-κ*S*,*N*)2] isomerisation. Qualitatively, the rate of thermal *trans*-[Pd(L-κ*S*,*N*)2] → *cis*-[Pd(L-κ*S*,*O*)2] occurs at a much lower rate at room temperature. Nevertheless both *trans-*isomers are isolable and stable in the solid state; in organic solvents they slowly and cleanly revert back to the thermodynamically more stable *cis* precursor in solution in the absence of light.

All available evidence to date indicates that *only* the *cis*-bis(*N,N*-diethyl-*N’*-(naphthoylthioureato)palladium(II) compound undergoes photo-induced isomerization to give both the *trans*-[Pd(L-κ*S*,*O*)2] and *trans*-[Pd(L-κ*S*,*N*)2] complexes, and that the reversion reaction in the absence of light proceeds by a more complicated pathway shown in Scheme 2, in contrast to the simpler bimolecular process known for all the related *cis*-[M(Ln-κ*S*,*O*)2] complexes of the noble metals M = Pt(II) & Pd(II), derived from *N*,*N*-dialkyl-*N*’- benzoylthiourea ligands.32-35 to date (Scheme 1).

**Conclusions**

The irradiation of pure *cis*-[Pd(L-κ*S*,*O*)2] in acetonitrile or in chloroform solution with polychromatic light or *in-situ* irradiation with  = 355 nm laser light in acetonitrile leads to the formation of the *trans*-[Pd(L-κ*S*,*O*)2] species and the unprecedented detection of *trans*-[Pd(L-κ*S*,*N*)2] isomer. The previously unknown *trans*-[Pd(L-κ*S*,*N*)2] isomer has been successfully detected only with *cis*-bis(*N,N*-diethyl-*N’*-(naphthoylthioureato)palladium(II) complex, and not from any of the other *cis*-bis(*N,N*-diethyl-*N’*-(benzoylthioureato)palladium(II) analogues that are known. *This appears to be a consequence of the nature of the N,N-diethyl-N’-naphthoylthiourea ligand which is sterically more demanding than the benzoyl analogue*. The *cis*-[Pd(L-κ*S*,*O*)2], *trans*-[Pd(L-κ*S*,*O*)2] and the *trans*-[Pd(L-κ*S*,*N*)2] have been characterised by means of single crystals X-ray diffraction structure determination thereby illustrating a series of three interconverting geometric isomers, which show significantly different melting points as confirmed by DSC analysis. Both 1H NMR spectroscopy and reversed phase-HPLC allow for the estimation of the relative rates of the photo-induced *cis*→*trans* process, as well as its thermal reversion in the dark. The relative rate of *trans*-[Pd(L-κ*S*,*O*)2]→ *cis*-[Pd(L-κ*S*,*O*)2] and *trans*-[Pd(L-κ*S*,*N*)2]→ *cis*-[Pd(L-κ*S*,*O*)2] complexes differ substantially in the solvents chloroform and acetonitrile. It appears that for these complexes, the reversion of the *trans*-[Pd(L-κ*S*,*O*)2] proceeds very slowly in chloroform, most probably *via* the intermediate formation of the *trans*-[Pd(L-κ*S*,*N*)2] species *en route* to the *cis*-[Pd(L-κ*S*,*O*)2] complex. In acetonitrile the corresponding thermal isomerisation occurs more rapidly at room temperature thereby implicating possible solvent coordination and a role for the *trans* effect. Significantly in the absence of light, given enough time both *trans*-isomers cleanly revert back to the *cis*-[Pd(Lκ-*S*,*O*)2] precursor.

**Experimental**

**Materials and general methods**

All reagents and solvents used for synthesis were commercially available, and were all used without purification, except for acetone which was distilled before use during ligand synthesis, meanwhile palladium salt K2PdCl4 of > 99% purity was obtained from Johnson Matthey PLC.

**NMR spectroscopy**

1H and 13C NMR spectra of ligands and complexes were recorded at 25°C in CDCl3 solutions using Varian UNITY INOVA 600 MHz NMR spectrometer. Photochemical NMR experiments were recorded as a function of time using standard time-arrayed experiments after *ex-situ* sample irradiation of solutions directly in a NMR tube at 298 K. The time delay to staring the recording after irradiation was typically 2 min, with total acquisition times for each spectrum in the array was typically 3-4 min. Long time arrayed experiments were typically recorded over night or weekends. *Ex-situ* light irradiation was performed using a low-heat polychromatic light-emitting diode (LED) lamp (5 Watt OSRAM, Germany), or in some cases by a modified constant voltage hand held blue-violet diode laser (100 mW,  = 405 nm)

***In-situ* laser coupled 1H NMR photochemistry**

All laser-coupled NMR experiments were recorded with a Bruker Avance II 600 MHz spectrometer with a widebore magnet fitted with a 5 mm BBO probe. *In-situ* laser photolyis was carried out with a pulsed Nd:Yag (Continuum Surelite II) fitter with a frequency tripling crystal (output 355 nm). Operating conditions were typically: a 10 Hz repetition rate flash lamp voltage 1.49 kV, and Q-switch delay increased to 320 ms, yielding a laser power of 75 mW in internal mode. The energy of a single laser energy meter calibrated for 355 nm to ca 29.8 mJ at our operating conditions (external triggering Q-switch delay set to 150 s). The unfocussed laser beam is directed to the base of the spectrometer, and focused into the NMR probe as previously reported.40

***Reversed Phase-*HPLC**

*RP*-HPLC-UV-vis experiments were performed using an Agilent 1260 Infinity system fitted with a Photodiode Array (PDA) detector and an Autosampler (Agilent Technologies, Waldronn, Germany) meanwhile separation was achieved at room temperature on a GEMINI C18 Column (4.6 x 150 mm) of particle size 5 μm and with a flow rate of 1 ml min-1. A mobile phase composition of 95:5 (% v/v) acetonitrile:water was used under isocratic elution and detection of chromatographic traces was carried out at 262 nm, with 20 μL sample injection volume. In all cases, the mobile phase was composed only of de-ionized water filtered through a 0.45 μm filter and HPLC grade acetonitrile.

All LC-MS experiments were performed using a Waters Synapt G2 mass spectrometer equipped with an ESI source (Waters, Milford, MA, USA). All UHPLC-ESI-MS experiments were carried out in the positive mode using a Waters BEH C18 (2.1 X 100 mm) column with the mobile phase composed of acetonitrile and 0.1 % formic acid under isocratic conditions.

**Thermal analysis**

Differential Scanning Calorimetry (DSC) was performed using a TA Instrument Q20 with Refrigerated Cooling System (RCS90). Typically a sample of 1.3 mg was heated from ambient temperature to 230 °C in a standard TA Instruments aluminium pan at a ramp rate of 10 °C min-1. Samples were analysed under constant purge of dry nitrogen gas at a flow rate of 50 ml min-1. Additional figures were generated using SigmaPlot 11.0.

**X-ray crystallography**

Crystals suitable for single-crystal X-ray diffraction for the *cis*-[Pd(L-κ*S*,*O*)2] complex were grown from acetonitrile solutions in a glass vial sealed with a perforated wax-film under slow evaporation of the solvent at room temperature and in the dark. Crystals of the *trans*-[Pd(L-κ*S*,*O*)2] and *trans*-[Pd(L-κ*S*,*N*)2] complexes suitable for X-ray diffraction were obtained either by slow evaporation or vapour diffusion of diethyl ether into acetonitrile solutions of the *cis*-[Pd(L1-κ*S*,*O*)2] complex irradiated with a 5 Watt LED lamp. X-ray diffraction intensity data was collected on a Bruker SMART APEX single-crystal X-ray diffractometer equipped with a molybdenum fine-focus sealed tube, monocap collimator and an APEXII detector with Incoatec IμS molybdenum and copper micro-focus X-ray sources. The temperature of the crystals was regulated to 100 K using an Oxford Cryostream Cooler. The crystal structures were all solved and refined using the SHELXS-97.37 X-seed software38 was used as a graphic interface for SHELX. All non-hydrogen atoms were refined anisotropically by means of full-matrix least-squares calculations for F2 using SHELXL-97. Hydrogen atoms were placed using riding model and isotropic thermal parameters were assigned values of 1.2 – 1.5 times the *U*eq of their parent atoms. Molecular graphics were generated using POV-Ray.39

**Ligand and complex synthesis**

The HL ligand, ***cis*-[Pd(L-κ*S*,*O*)2] and *trans*-[Pd(L-κ*S*,*O*)2] complexes** were prepared as described in the literature.13,34,35

***N,N-diethyl-N’-naphthoylthiourea (HL).*** Yield of 84.7%; m.p. 138-140°C; (Found: C, 66.21; H, 6.45; N, 9.78; S, 10.80%; calculated for C16H18N2OS: C, 67.13; H, 6.29; N, 9.79; S, 11.20%); 1H NMR (400 MHz, CDCl3)/ppm δ 8.44 (d, 1H, Ar-H8), 8.34 (s, 1H, N-H), 7.98 (d, 1H, Ar-H2), 7.88 (m, 1H, Ar-H4), 7.76 (m, 1H, Ar-H5), 7.58 (m, 1H, Ar-H3), 7.53 (m, 1H, Ar-H6), 7.47 (m, 1H, Ar-H7), 3.86 (d, 4H, N-CH2), 1.37 (t, 6H, CH3); 13C NMR (100 MHz, CDCl3)/ppm δ 178.9, 165.4, 133.8, 132.4, 131.5, 130.3, 128.5, 127.8, 126.7, 126.5, 125.2, 124.5, 47.9, 13.4, 11.6.

***cis-bis(N,N-diethyl-N’-(naphthoylthioureato)-palladium(II), cis-[Pd(L-κS,O)2]:*** Yield of 86.6%; m.p. 159-163 °C (*cis*-*S*,*O*); (Found: C, 56.08; H, 5.11; N, 7.67; S, 9.15%; calculated for C32H34N4O2S2Pd: C, 56.77; H, 5.03; N, 8.28; S, 9.46%); 1H NMR (400 MHz, CDCl3)/ppm δ 8.94 (d, 1H, Ar-H8), 8.14 (d, 1H, Ar-H2), 7.89 (d, 1H, Ar-H4), 7.80 (d, 1H, Ar-H5), 7.43 (t, 1H, Ar-H3), 7.37 (m, 1H, Ar-H6), 7.15 (m, 1H, Ar-H7), 3.88 (q, 4H, N-CH2), 3.82 (q, 4H, N-CH2) 1.37 (t, 3H, CH3), 1.25 (t, 3H, CH3); 13C{1H} NMR (100 MHz, CDCl3)/ppm δ 12.6, 13.1, 15.3, 46.1, 47.2, 65.9, 127.9, 129.7, 131.4, 137.1, 170.6, 171.1.

***trans-bis(N,N-diethyl-N’-(1-naphthoyl)thioureato-κ2S,O)palladium(II) trans-[Pd(L-κS,O)2].*** Yield of 62 %; m.p. 174-176 °C (*trans*-*S*,*O*); 1H NMR (400 MHz, CDCl3)/ppm δ 8.63 (d, 1H, Ar-H8((*trans*-*S*,*O*)), 8.48 (d, 1H, Ar-H8((*trans*-*S*,*N*)), 7.96 (d, 1H, Ar-H2), 7.89 (d, 1H, Ar-H4), 7.84 (d, 1H, Ar-H5), 7.56 (m, 1H, Ar-H3), 7.48 (m, 1H, Ar-H6), 7.43 (m, 1H, Ar-H7), 3.88 (q, 4H, N-CH2), 3.82 (q, 4H, N-CH2), 1.36 (t, 3H, CH3), 1.26 (t, 3H, CH3).

**Electronic Supplementary material**

Crystallographic data for *cis*-[Pd(L-κ*S*,*O*)2], *trans*-[Pd(L-κ*S*,*O*)2] and *trans*-[Pd(L-*S*,*N*)2] have been deposited with the Cambridge Crystallographic Data Centre, CCDC Numbers 1403030, 1403032 and 1403031 respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (E-mail: [deposit@ccdc.cam.ca.uk](mailto:deposit@ccdc.cam.ca.uk) or <http://www.ccdc.cam.ac.uk>).

**Conflict of interest**

There are no conflicts of interest to declare.

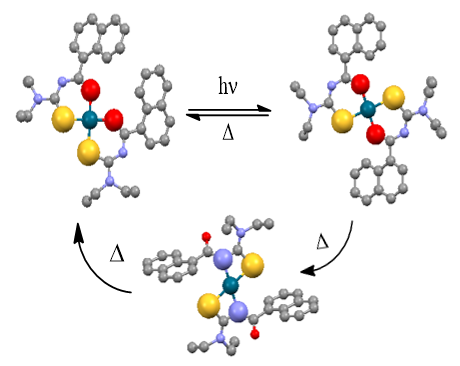
**Acknowledgements**

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**References.**

1. K. Neucki, *Ber. Dtsch. Chem. Ges*., 1873, **6**, 598.
2. A. N. Westra, S. A. Bourne, C. Esterhuysen, and K. R. Koch, *Dalton Trans*., 2005, 2162-2172.
3. K. R. Koch, *Coord. Chem. Rev*., 2001, **216-217**, 473-488.
4. K. R. Koch, C. Sacht, T. Grimmbacher, S. Bourne*, S. Afr. J. Chem*., 1995, **48**, 71-77.
5. K. R. Koch, C. Sacht, S. Bourne, *Inorg. Chim. Acta,* 1995*,* **232**, 109-115.
6. A.Saeed, U Flӧrke, F Erben, *J. Sulfur Chem*., 2014, **35**, 318-355.
7. N. Selvakumaran, S. W. Ng, E. R. T. Tiekink, R. Karvembu, *Inorg. Chim. Acta*., 2011, **376**, 278-284.
8. A. M. Plutin, R. Mocelo, A. Alvarez, R. Ramos, E. E. Castellano, M. R. Cominetti, A. E. Graminha, A. G. Ferreira, A. A. Batista; *J. Inorg. Biochem.,* 2014, **134**, 76-82.
9. W. Yang, L. Huanhuan, L. Mengying, F. Wang, Z. Weiqun, F. Jianfen, *J. Inorg. Biochem*., 2012, **116**, 97-105.
10. N. Gunasekaran, P. Jerome, S. N. Weng, E. R. T. Tiekink, R. Karvembu, *J. Mol. Catal. A: Chem*., 2012, **353-354**, 156-162.
11. M. Dominguez, E. Antico, L. Beyer, A. Aguirre, S. Garcia-Granda, V. S. Alvado, *Polyhedron*, 2002, **21**, 1429-1437.
12. P. Vest, M. Schuster, K.-H. König, *Fresenius Z. Anal. Chem*., 1989, **335**, 759-763.
13. A. N. Mautjana, J. D. Miller, A. Gie, S. A. Bourne and K. R. Koch, *J. Chem. Soc. Dalton Trans.*, 2003, 1952-1960.
14. K. R. Koch, S. A. Bourne, A. Coetzee, J. Miller, *J. Chem. Soc., Dalton Trans*., 1999, 3157-3161.
15. A. N. Westra, S. A. Bourne, K. R. Koch, *Dalton Trans*., 2005, 2916-2924.
16. C. Viorel, I. Mihaela, I. Monica, D. Florea, N. Ionela, P. Simona, *Polyhedron*, 2009, **28**, 3739-3746.
17. F. Z. El Aamrani, A. Kumar, J. L. Cortina, A. M. Sastre, *Anal. Chim. Acta*., 1999, **382**, 205-213.
18. R. A. Bailey, K. L. Rothaupt, R. K. Kulling, *Inorg. Chim. Acta*, 1988, **147**, 233-236.
19. A. M. Plutin, R. Mocelo, A. Alvarez, R. Ramos, E. E. Castellano, M. R. Cominetti, A. E. Graminha, A. G. Ferreira, A. A. Batista, *J. Inorg. Biochem*., 2014, **134**, 76-82.
20. K. R. Koch, C. Sacht, S. Bourne, *Inorg. Chim. Acta*, 1995, **232**, 109-115.
21. K. R. Koch, Y. Wang, A. Coetzee, *J. Chem. Soc., Dalton Trans.*,1999, 1013-1016.
22. K. R. Koch, T. Grimmbacher, C. Sacht, *Polyhedron*, 1998, **17**, 267-274.
23. K. R. Koch. S. Bourne, *J. Mol. Struct*., 1998, **441**, 11-16.
24. S. Yaseen, M. K. Rauf, S. Zaib, A. Badshah, M. N. Tahir, M. I. Ali, I. Ud-Din, M. Sahid, J. Iqbal, *Inorg. Chim. Acta*, 2016, **443**, 69-77.
25. Z. Weiqun, Y. Wen, X. Liqun, C. Xian, *J. Inorg. Biochem.*, 2005, **99**, 1314-1319.
26. N. Gunasekaran, R. Karvembu, *Inorg. Chem. Commun*., 2010, **13**, 952-955.
27. K. R. Koch, J. Du Toit, M. R. Caira and C. Sacht, *J. Chem. Soc. Dalton Trans*., 1994, 785-786.
28. Arslan A., Florke U., Kulcu N., Emen M. F., *J. Coord. Chem*., 2006, **59**, 223.
29. Hernandez W., Spodine E., Vega A., Richter R., Griebel J., Kirmse R., Schroder U., Beyer L., *Z. Anorg. Allg. Chem*., 2004, **630**, 1381.
30. Ramasamy K., Malik M. A., O’Brien P., Raftery J., *Dalton Trans.*, 2010, **39**, 1460-1463.
31. Su-Yun W., Xiao-Ya Z., Hai-Pu L., Ying Y., Roesky H. W., *Z. Anorg. Allg. Chem*., 2015, **641**, 883-889.
32. D. Hanekom, J. M. McKenzie, N. M. Derix and K. R. Koch, *Chem. Commun.*, 2005, 767-769.
33. H. A. Nkabyo, D. Hannekom, J. McKenzie, K. R. Koch, *J. Coord. Chem.*, 2014, **76**, 4039-4060.
34. H. A. Nkabyo, K. R. Koch, *Inorg. Chim. Acta*., 2018, **483**, 440-447.
35. H. A. Nkabyo, K. R. Koch, *J. Mol. Struct*., 2019, **1190**, 47-53.
36. J. A. Lewis, D. T. Puerta, S. M. Cohen, *Inorg. Chem*., 2003, **42**, 7455-7459.
37. G. M. Sheldrick, *Acta Crystallogr., Sect. A.: Found. Crystallogr.*, 2008, **64**, 112.
38. L. J. Barbour, *J. Supramol. Chem*., 2003, **1**, 189.
39. POV-RayTM for windows, Persistence of vision Raytracer Pty. Ltd., Williamstown, Australia, 2004.
40. B. Procacci, P. M. Aguiar, M. E. Halse, R. N. Perutz and S B. Duckett, *Chem. Sci*., 2016, 7, 7087 -7093

**Table of Content**



**Reversible Photo-isomerization of *cis*-[Pd(L-κ*S,O*)2] (HL = *N N*-diethyl-*N’*-1-naphthoylthiourea) to *trans*-[Pd(L-κ*S,O*)2] and the Unprecedented Formation of *trans*-[Pd(L-κ*S,N*)2] in Solution**

*Ex-situ* with broadband polychromatic or *in-situ* laser light irradiation of solutions of pure *cis*-[Pd(L-κ*S*,*O*)2] in acetonitrile or chloroform, lead to the formation of *trans*-[Pd(L-κ*S*,*O*)2] species, which reverts cleanly, *via* an unprecedented *trans*-[Pd(L-κ*S*,*N*)2] species, to the *cis*-[Pd(L-κ*S*,*O*)2] in the dark.

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