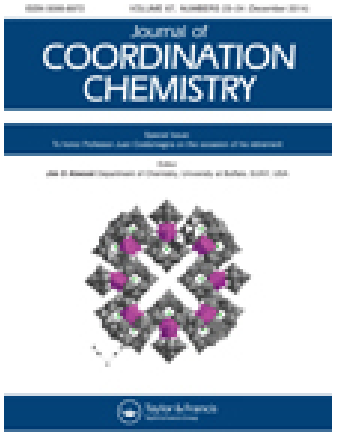

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Henry A. Nkabyo[a], D. Hannekom[a], Jean McKenzie[a] & Klaus R. Koch[a]

[a] Department of Chemistry and Polymer Science, University of Stellenbosch, Stellenbosch, South Africa

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Light-induced *cis/trans* isomerization of *cis*-[Pd(L-*S*,*O*)$_2$] and *cis*-[Pt(L-*S*,*O*)$_2$] complexes of chelating *N*,*N*-dialkyl-*N*′-acylthioureas: key to the formation and isolation of *trans* isomers

HENRY A. NKABYO, D. HANNEKOM, JEAN MCKENZIE and KLAUS R. KOCH*

Department of Chemistry and Polymer Science, University of Stellenbosch, Stellenbosch, South Africa

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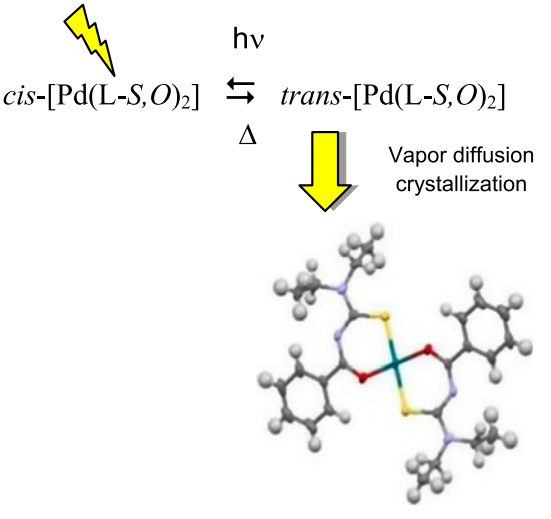


The dominantly formed *cis*-[M(L-*S*,*O*)$_2$] (M = Pt^{II} or Pd^{II}) complexes from *N*,*N*-dialkyl-*N*′-acyl-thioureas in solution undergo a facile *cis* → *trans* isomerization on irradiation with visible light at room temperature, allowing the predictable formation and isolation of the elusive *trans*-[Pd(L-*S*,*O*)$_2$] complexes.

Irradiation *cis*-[M(L^n-*S*,*O*)$_2$] complexes (M = Pt^{II}, Pd^{II}) derived from *N*,*N*-dialkyl-*N*′-benzoylthioureas (HL^n) with various sources of intense visible polychromatic or monochromatic light with $\lambda < 500$ nm leads to light-induced *cis* → *trans* isomerization in organic solvents. In all cases, white light derived from several sources or monochromatic blue-violet laser 405 nm light, efficiently results in substantial amounts of the *trans* isomer appearing in solution, as shown by ^{1}H NMR and/or reversed-phase HPLC separation in dilute solutions at room temperature. The extent and relative rates of *cis/trans* isomerization induced by *in situ* laser light (λ = 405 nm) of *cis*-[Pd(L^2-*S*,*O*)$_2$] was

*Corresponding author. Email: krk@sun.ac.za

directly monitored by ^{1}H NMR and ^{195}Pt NMR spectroscopy of selected *cis*-[Pt(L-*S,O*)$_2$] compounds in chloroform-*d*; both with and without light irradiation allows the $\delta(^{195}Pt)$ chemical shifts *cis*/*trans* isomer pairs to be recorded. The *cis/trans* isomers appear to be in a photo-thermal equilibrium between the thermodynamically favored *cis* isomer and its *trans* counterpart. In the dark, the *trans* isomer reverts back to the *cis* complex in what is probably a thermal process. The light-induced *cis/trans* process is the key to preparing and isolating the rare *trans* complexes which cannot be prepared by conventional synthesis as confirmed by the first example of *trans*-[Pd(L-*S,O*)$_2$] characterized by single-crystal X-ray diffraction, deliberately prepared after photo-induced isomerization in acetonitrile solution.

Keywords: Photo-induced *cis/trans* isomerization; *cis* → *trans* Isomerization; *N,N*-dialkyl-*N*′-benzoyl-thiourea complexes of Pt(II) and Pd(II); *In situ* laser ^{1}H NMR spectroscopy; ^{195}Pt NMR shifts of *cis/trans*-[Pt(L-*SO*)$_2$]; Separation with *rp*-HPLC; Molecular structure of *trans*-bis (*N,N*-diethyl-*N*′-benzoylthioureato)-palladium(II)

1. Introduction

Ligands of the general type *N,N*-dialkyl-*N*′-acyl(aroyl)thioureas (HL; $R^1{}_2NC(S)NHC(O)R^2$, R^1 = alkyl, R^2 = alkyl or aryl groups), first prepared more than 80 years ago [1], have long been known to readily form stable, uncharged coordination compounds with numerous transition metal ions as shown by the studies of Hoyer and Beyer more than three decades ago [2, 3], and later by *inter alia* Konig and Schuster [4–7]. We have been interested in fundamental aspects of the coordination chemistry of *N,N*-dialkyl-*N*′-acyl(aroyl)thioureas with some members of the platinum group metals (PGMs) in view of their potential application in solvent extraction, pre-concentration, separation, and even trace analytical determination of the PGMs [8]. A recent review for 2007–2013 on the coordination chemistry and the potential applications of this class of ligands attests to considerable growth in interest in these molecules worldwide [9].

Our focus on the coordination chemistry and use of this class of deceptively simple ligands arises in part from the relative ease of their synthesis, which together the favorable physiochemical properties of *N,N*-dialkyl-*N*′-acyl(aroyl)thioureas, allows for their selective *in situ* coordination of Pt^{II}, Pd^{II}, and Rh^{III} in acidic chloride-rich solutions, followed by easy quantification of the resultant complexes using reversed-phase high performance liquid chromatography (*rp*-HPLC) illustrates a practically useful application of such molecules [10]. Generally *N,N*-dialkyl-*N*′-acylthioureas show a marked tendency to coordinate to d^8 metal ions to give stable *cis*-[M(L-*S,O*)$_2$]-type complexes (M = Pt^{II}, Pd^{II}) upon loss of a proton; in the case of M^{III} transition metal ions, the corresponding *fac*-[M(L-*S,O*)$_3$] complexes are usually obtained, in which all sulfurs are coordinated *trans* to O donors [8, 10, 11]. The dominant tendency to form the *cis*-[M(L-*S,O*)$_2$] isomer of both Pt(II) and Pd (II) complexes may be exploited to design and prepare exclusively either the 2 : 2 *cis*-[Pt$_2$(L^m-*S,O*)$_2$] or the 3 : 3 *cis*-[Pt$_3$(L^p-*S,O*)$_3$] metallamacrocyclic Pt(II) complexes from bipodal ligands HL^m (3,3,3′,3′-tetraethyl-1,1-isophthaloylbis(thiourea) and HL^p (3,3,3′,3′-tetra(*n*-butyl)-1,1-terephthaloyl-bis(thiourea), essentially based on whether the two chelating *S,O* moieties are bound *meta* to each other in the bipodal ligand HL^m, or *para* in the HL^p ligand [11]. Moreover, the 2 : 2 *cis*-[Pt$_2$(L^m-*S,O*)$_2$] and 3 : 3 *cis*-[Pt$_3$(L^p-*S,O*)$_3$] readily react with halogens generated *in situ* electrochemically from halide ions to give the corresponding Pt(IV) analogs *cis*-[$Pt^{IV}{}_2$(L^m-*S,O*)$_2$Br$_4$], *cis*-[$Pt^{IV}{}_2$(L^m-*S,O*)$_2$Cl$_4$], and *cis*-[$Pt^{IV}{}_3$I$_6$(L^p-*S,O*)$_3$], not easily accessible by other means [12]. In this context, the

overwhelming tendency to form *cis* complexes of the numerous complexes of divalent transition metal ions with simple *N*,*N*-dialkyl-*N*′-acyl(aroyl)thioureas which have been structurally characterized is striking [9]. A search of the Cambridge Structural Database shows that of 40 single-crystal X-ray diffraction structures of Pt(II), Pd(II), Ni(II), and Cu(II) complexes from *N*,*N*-dialkyl-*N*′-acyl(aroyl)thiourea ligands which have been characterized in the solid state [13], at least 20 of them are d^8 Pt(II) and Pd(II) complexes. Remarkably out of all these, only one *trans*-bis(*N*,*N*-di(n-butyl)-*N*′-naphthoylthioureato)–platinum(II) complex, isolated serendipitously by us in ca. 15% yield two decades ago, has been characterized by single-crystal X-ray diffraction to date [14]. Only two other examples of *trans*-*S*,*O* chelated Cu(II) complexes have been unambiguously characterized to our knowledge [15, 16].

Despite considerable effort, we have not been able to predictably prepare substantial quantities of *trans*-[Pt(L-*S*,*O*)$_2$] or *trans*-[Pd(L-*S*,*O*)$_2$] complexes with *N*,*N*-dialkyl-*N*′-aroylthioureas by any conventional synthetic route. While intuitively it is not unreasonable to expect that the *cis*-[M(L-*S*,*O*)$_2$] (M = Pt^{II}, Pd^{II}) complexes are likely to be thermodynamically favored in view of the higher *trans* effect/influence of the *S* donor as compared to the *O* donor [17]. The corresponding *trans*-[M(L^n-*S,O*)$_2$] (M = Pt^{II}, Pd^{II}) isomers may be expected to be only of slightly higher energy overall. This is confirmed by the small energy difference of 10.1 kJ mol^{-1} for *cis*-[Pt(L-*S*,*O*)$_2$] and *trans*-[Pt(L-*S*,*O*)$_2$] with *N*,*N*-dimethyl-*N*′-methylacylthiourea in vacuum, based on DFT gas-phase calculations. Similar calculations using the conductor-like screening (COSMO) model for chloroform and acetonitrile show these energy differences range from 13.4 to 18.4 kJ mol^{-1}, respectively [18].

We have for some time been interested in the question of why *trans*-*S,O* chelated complexes are so rare compared with their *cis* analogs; of particular interest is the question how the *trans*-[M(L-*S*,*O*)$_2$] (M = Pt^{II}, Pd^{II}) complexes may reliably be prepared and isolated in reasonable yields. Recently, we discovered that the key to obtaining *trans*-[M(L-*S*,*O*)$_2$] (M = Pt^{II}, Pd^{II}) complexes in solution appears to be a facile photo-induced isomerization of the *cis*-[M(L^3-*S*,*O*)$_2$] complexes (HL^3 = *N*,*N*-diethyl-*N*′-3,4,5-trimethoxybenzoylthiourea) in acetonitrile solutions, as confirmed by RP-HPLC and ^{1}H NMR spectroscopy [19]. Irradiation of solutions of pure *cis*-[M(L^3-*S*,*O*)$_2$] in acetonitrile with intense white light results in substantial amounts of *trans*-[M(L^3-*S*,*O*)$_2$] appearing in solution at room temperature. The relative (conditional) rate of isomerization of the Pd(II) complexes was found to be significantly higher than that of the corresponding Pt(II) complexes (as might be expected). Interestingly, the *trans*-[Pd(L^3-*S*,*O*)$_2$] isomer formed by photo-induced isomerization was shown to readily revert back to the *cis* complex in the absence of light as schematically indicated below [19].

$$cis\text{-}[\mathrm{M}(\mathrm{L}^n\text{-}S,O)_2] \underset{\Delta}{\overset{h\nu}{\leftrightarrows}} trans\text{-}[\mathrm{M}(\mathrm{L}^n\text{-}S,O)_2]$$

This type of light-induced isomerization is reminiscent of the early work of Balzani *et al.* several decades ago, involving isomerization of a bis-chelated glycine complex of platinum (II), *cis*-[Pt(gly-*N*,*O*)$_2$], which readily undergoes *cis* → *trans* isomerization under the influence of light in dilute aqueous solutions [20, 21]. There are relatively few other systematic studies of photo-induced phenomena with Pt(II) and Pd(II) complexes in the literature.

In this paper, we report more detailed investigations of the facile photo-induced *cis*/*trans* isomerization of a series of *cis*-[M(L^n-*S*,*O*)$_2$] (M = Pd(II) and Pt(II)) complexes derived from several HL^n (*n* = 1–6) ligands shown in scheme 1 below, with the aim of understanding the

possible factors which may influence this reversible process in organic solvents. We examined the effect of differing light sources, as well as a preliminary assessment of the effects of ligand structure on the relative extent of *cis* → *trans* isomerization to steady state, using ^{1}H and ^{195}Pt NMR spectroscopy in relatively concentrated solutions of some *cis*-[M(L^n-*S*,*O*)$_2$] (M = Pd(II) and Pt(II)) complexes. Moreover, the photo-induced *cis*/*trans* isomerization of particularly *cis*-[Pd(L^n-*S*,*O*)$_2$] complexes in more dilute acetonitrile solutions can conveniently be monitored by *rp*-HPLC, leading to a semi-quantitative estimate of the extent of isomerization as indicated by a *trans : cis* ratio at steady state at room temperature.

We now demonstrate that *trans*-[Pd(L^n-*S,O*)$_2$] complexes can reliably be prepared and isolated from pure *cis*-[Pd(L^n-*S,O*)$_2$] in acetonitrile in the solid state under intense white light irradiation using a simple vapor diffusion crystallization technique. We believe this simple procedure to be more generally applicable, as illustrated by the first example of a *trans*-bis(*N,N*-diethyl-*N*′-benzoylthioureato)–palladium(II) complex characterized by single-crystal X-ray diffraction, deliberately prepared and isolated from its *cis* isomer, using a photo-induced isomerization process. Such a process was presumably responsible for the "accidental" isolation of a *trans*-bis(*N*,*N*-di(n-butyl)-*N*′-naphthoylthioureato)-platinum(II) complex by one of us, two decades ago [14].

2. Experimental setup

2.1. *Materials and general methods*

All chemicals used for the synthesis of ligands and complexes were commercially available from Sigma Aldrich SA and used without purification, while the platinum and palladium salts K_2PdCl_4 and K_2PtCl_4 of >99% purity were obtained from Johnson Matthey PLC. ^{1}H and ^{13}C NMR spectra of ligands and complexes were recorded at 25 °C in $CDCl_3$ solutions using various spectrometers, Varian VNMRS 300 MHz, or Varian UNITY INOVA 400 MHz or 600 MHz NMR spectrometers. All ^{195}Pt NMR spectra were recorded at 30 °C in the given solvents, usually $CDCl_3$ using a Varian INOVA 600 MHz spectrometer operating at 128 MHz. All ^{195}Pt chemical shifts are quoted for convenience relative to external H_2PtCl_6 (500 mg mL^{-1} in 30% v/v D_2O/1 M HCl) at $\delta(^{195}Pt) = 0$ ppm at 30 °C [or at ca + 4522 ppm relative to Ξ at 21.496 Hz], and are estimated to be accurate to ± 2 ppm.

Melting points were obtained using an Electrothermal IA 9000 series digital melting point apparatus. FT-IR analyses were performed on a Thermo Nicolet Avatar 330 Smart Performer ATR instrument using a ZnSe crystal. Thin layer chromatography (TLC) was carried out using silica plates (Merck) with dichloromethane/hexane mixtures of varying compositions as eluents, with visualization using either molecular iodine vapor or UV light.

2.2. *General procedure for synthesis of ligands and complexes*

2.2.1. Synthesis of ligands and complexes [M(L^n-S,O)$_2$] (M = Pt(II), Pd(II)). All ligands were prepared by the simple "one-pot" Douglass and Dains method [1] and characterized by standard procedures using melting points, elemental analyses, IR, ^{1}H, and ^{13}C

{^{1}H} NMR spectra in $CDCl_3$. The Pd(II) and Pt(II) complexes were prepared as previously described [10], from K_2PdCl_4 or K_2PtCl_4 as starting material.

A typical procedure for the Pd(II) complexes follows. Solutions containing 40 mg of K_2PdCl_4 (*ca* 0.12 mM Pd(II)) in 15 cm^3 water and 10 cm^3 acetonitrile were added dropwise to a stirred solution of 0.25 mM ligand HL^n in a mixture of 15 cm^3 acetonitrile and 10 cm^3 water containing ~0.25 mM of sodium acetate. The resulting mixture was stirred for 1 h at room temperature, during which a yellow precipitate was formed. Addition of *ca* 100 mL distilled water completed the precipitation, while dissolving excess soluble salts such as K/NaCl and sodium acetate. The precipitates were collected by centrifugation, rinsed with water, followed by drying at *ca* 60–70 °C in vacuum. Recrystallization of complexes from mixtures of chloroform and ethanol afforded yellow/orange crystals in good yields typically >80% of the expected, apart from mechanical losses.

2.2.1.1. *Ligand synthesis.* ***N,N*-diethyl-*N*′-benzoylthiourea (HL^1)**: Yield of 6.3 g (86.3%); m.p. 98–100 °C; (Found: C, 61.15; H, 6.93; N, 12.00; S, 13.61%; calculated for $C_{12}H_{16}N_2OS$: C, 60.98; H, 6.82; N, 11.85; S, 13.57%); IR (ATR, cm^{-1}): ν(N–H) 3258.84 cm^{-1} (br, sh), ν(C=O) 1649.35 cm^{-1} (vs); ^{1}H NMR (300 MHz, $CDCl_3$)/ppm δ 8.34 (singlet, 1H, N–H), 7.82 (doublet, 2H, Ar–H), 7.56 (triplet, 1H, Ar–H), 7.46 (triplet, 2H, Ar–H), 3.81 (doublet, 4H, N–CH_2), 1.32 (triplet, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$)/ppm δ 11.3, 13.1, 47.5, 50.6, 129.2, 131.7, 134.1, 137.9, 164.2, 180.0.

***N,N*-diethyl-*N*′-(4-methoxybenzoyl)thiourea (HL^2)**: Yield of 3.12 g (78%); m.p. 134–135 °C; (Found: C, 59.12; H, 7.45; N, 10.74; S, 11.74%; calculated for $C_{13}H_{18}N_2O_2S$: C, 56.73; H, 6.80%; ^{1}H NMR (300 MHz, $CDCl_3$)/ppm δ 1.27 (unresolved, 6H, CH_3), 3.57 (unresolved, 2H, CH_2), 3.84 (singlet, 3H, Ar–H), 6.93 (doublet, 2H, Ar–H), 8.21 (singlet, 1H, N–H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)/ppm δ 11.3, 12.9, 47.7, 51.4, 114.2, 125.0, 130.0, 163.6, 179.9.

***N,N*-diethyl-*N*′-(3,4,5-trimethoxybenzoy)thiourea (HL^3)**: Yield of 80%; m.p. 143–145 °C; (Found: C, 55.30; H, 7.16; N, 8.62; S, 9.37%; calculated for $C_{15}H_{22}N_2O_4S$: C, 55.19; H, 6.79; N, 8.58; S, 9.82%); ^{1}H NMR (300 MHz, $CDCl_3$)/ppm δ 1.31 (unresolved, 6H, CH_3), 3.55 (unresolved, 2H, CH_2), 3.85 (singlet, 3H, CH_3), 3.87 (singlet, 6H, CH_3), 7.05 (singlet, 2H, Ar-H), 8.82 (singlet, 1H, N–H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)/ppm δ 11.4, 13.3, 47.7, 56.4, 60.9, 105.2, 127.4, 142.1, 153.1, 163.3, 179.6.

***N,N*-diethyl-*N*′-(4-chlorobenzoyl)thiourea (HL^4)**: Yield of 83%; m.p. 163–165 °C; (Found: C, 48.00; H, 4.89; N, 9.42; S, 10.7%; calculated for $C_{12}H_{15}N_2OSCl$: C, 47.78; H, 48.68; N, 9.29; S, 10.63; Cl, 11.76%; ^{1}H NMR (600 MHz, $CDCl_3$)/ppm δ 1.33 (triplet, 6H, CH_3), 3.80 (quartet, 4H, CH_2), 7.44 (doublet, 2H, Ar–H), 7.77 (doublet, 2H, Ar–H), 8.35 (singlet, 1H, N-H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)/ppm δ 11.7, 13.5, 48.0, 48.3, 112.8, 129.3, 131.3, 139.6, 163.1, 179.3.

***N*-piperidyl-*N*′-benzoylthiourea (HL^5)**: Yield of 41.8%; m.p. 124–126 °C; (calculated for $C_{13}H_{16}N_2OS$: C, 62.86; H, 6.51; N, 11.28; S, 12.91%; Found: C, 62.86; H, 6.67; N, 11.39; S, 12.72%); ^{1}H NMR (600 MHz, $CDCl_3$)/ppm δ 1.71 (unresolved, 6H, CH_3), 3.87 (doublet, 4H, CH_2), 7.47 (triplet, 2H, Ar–H), 7.57 (unresolved, 1H, Ar–H), 7.83 (dd, 2H, Ar–H), 8.42 (singlet, 1H, N–H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)/ppm δ 23.9, 25.2, 52.8, 127.8, 128.9, 132.6, 132.9, 163.1, 178.2.

***N,N*-diethyl-*N*′-(3,5-dimethoxybenzoyl)thiourea (HL^6)**: Yield of 80%; m.p. 122–124 °C; (calculated for $C_{14}H_{20}N_2O_3S$: C, 56.73; H, 6.80; N, 9.45; S, 10.82%; Found: C, 57.06; H, 6.89; N, 9.51; S, 10.49%); ^{1}H NMR (300 MHz, $CDCl_3$)/ppm δ 1.27 (unresolved, 6H, 2 x CH_3), 3.55 and 4.00 (doublet, 4H, 2 × CH_2), 3.79 (singlet, 2 × OCH_3), 6.61 (1H,

triplet, H_4), 6.93 (2H, doublet, $H_{2/6}$), 8.38 (1H, singlet, N–H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)/ppm 11.2, 13.0, 47.5, 55.4, 105.3, 105.4, 134.8, 161.2, 163.8, 179.5.

2.3.1.2. *Pd(II) and Pt(II) complex synthesis.* ***cis*-bis(*N,N*-diethyl-*N′*-(benzoylthioureato) palladium(II), *cis*-[Pd(L^1-*S,O*)$_2$]**: Yield of 0.106 g (88.3%); m.p. 159–163 °C; IR (ATR, cm^{-1}): ν(C=O) 1583.74 cm^{-1} (w); ^1H NMR (400 MHz, $CDCl_3$)/ppm δ 8.26 (doublet, 2H, Ar–H), 7.50 (unresolved, 1H, Ar–H), 7.44 (unresolved, 2H, Ar–H), 3.85 (quartet, 4H, N–CH_2), 3.50 (quartet, 4H, CH_2), 1.33 (unresolved, 4H, CH_2), 1.23 (triplet, 6H, CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)/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.

***cis*-bis(*N,N*-diethyl-*N*-(4-methoxybenzoylthioureato)palladium(II), *cis*-[Pd(L^2-*S,O*)$_2$]**: Yield of 0.069 g (86.5%); m.p. 138–140 °C; IR (ATR, cm^{-1}): ν(C=O) 1579.25 cm^{-1} (w); ^1H NMR (600 MHz, $CDCl_3$)/ppm δ 1.33 (dt, 6H, CH_3), 3.84 (unresolved, 4H, CH_2), 3.87 (singlet, 3H, O–CH_3), 7.29 (unresolved, 2H, Ar–H), 7.03 (unresolved, 2H, Ar–H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)/ppm δ 12.6, 13.1, 46.1, 47.2, 55.2, 114.3, 117.8, 122.1, 128.8, 138.6.

***cis*-bis(*N,N*-diethyl-*N′*-(3,4,5-trimethoxybenzoylthioureato)palladium(II), *cis*-[Pd(L^3-*S,O*)$_2$]**: Yield of 0.081 g (85.3%); m.p. 198–202 °C; IR (ATR, cm^{-1}): ν(C=O) 1589.40 cm^{-1} (w); ^1H NMR (300 MHz, $CDCl_3$)/ppm, δ 1.28 (triplet, 6H, CH_3), 1.32 (triplet, 6H, CH_3), 3.82 (quartet, 4H, CH_2), 3.83 (singlet, 12H, CH_3), 6.85 (triplet, 2H, Ar–H), 7.44 (doublet, 4H, Ar–H); $^{13}C\{^1H\}$ NMR (300 MHz, $CDCl_3$)/ppm δ 12.3, 13.1, 46.2, 47.23, 55.3, 103.9, 107.4, 139.2, 160.2, 170.0, 171.2.

***cis*-bis(*N,N*-diethyl-*N′*-(4-chlorobenzoylthioureato)palladium(II), *cis*-[Pd(L^4-*S,O*)$_2$]**: Yield of 0.072 g (88.9%); m.p. 179–181 °C; IR (ATR, cm^{-1}): ν(C=O) 1577.73 cm^{-1} (w); ^1H NMR (600 MHz, $CDCl_3$)/ppm δ 1.30 (dt, 6H, CH_3), 3.83 (quarter, 4H, CH_2), 7.38 (unresolved, 2H, Ar–H), 8.14 (unresolved, 2H, Ar–H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)/ppm δ 12.6, 13.1, 46.1, 47.3, 128.2, 131.0, 135.6, 137.7, 169.6, 171.2.

***cis*-bis(*N*-piperidyl-*N′*-(benzoylthioureato)palladium(II), *cis*-[Pd(L^5-*S,O*)$_2$]**: Yield of 0.062 g (82.7%); m.p. 130–134 °C; IR (ATR, cm^{-1}): ν(C=O) 1583.89 cm^{-1} (w); ^1H NMR (600 MHz, $CDCl_3$)/ppm δ 1.72 (unresolved, 6H, CH_2), 4.11 (unresolved, 4H, CH_2), 7.41 (triplet, 2H, Ar–H), 7.48 (triplet, 1H, Ar–H), 8.23 (unresolved, 2H, Ar–H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)/ppm δ 24.5, 26.1, 48.6, 51.1, 127.9, 129.7, 131.5, 131.1, 171.1, 171.4.

***cis*-bis(*N,N*-diethyl-*N′*-(benzoylthioureato)platinum(II), *cis*-[Pt(L^1-*S,O*)$_2$]**: Yield of 0.1025 g (63%); m.p. 152–156 °C; (Found: C, 43.57; H, 4.48; N, 8.91; S, 9.32%; calculated for $C_{28}H_{30}N_4O_2PtS_2$: C, 43.30; H, 4.54; N, 8.42; S, 9.63%); ^1H NMR (600 MHz, $CDCl_3$)/ppm δ 1.28 (6H, triplet, CH_3), 1.34 (6H, triplet, CH_3), 3.77 (4H, quartet, CH_2), 3.83 (4H, quartet, CH_2), 7.42 (4H, triplet, Ar–H), 7.51 (2H, triplet, Ar–H), 8.26 (4H, doublet, Ar–H); $^{13}C\{^1H\}$ (400 MHz, $CDCl_3$)/ppm δ 12.3, 13.1, 46.0, 128.1, 129.3, 131.3, 137.6, 167.0, 168.4. $\delta(^{195}Pt$, 128 MHz, $CDCl_3$)/ppm, −2720.1 (*cis*), −1980.8 (*trans*, post irradiation; white Quartz Halogen light).

***cis*-bis(*N,N*-diethyl-*N′*-(4-methoxybenzoylthioureato)platinum(II), *cis*-[Pt(L^2-*S,O*)$_2$]**: Yield of 0.1444 g (82%); m.p. 198–200 °C; (Found: C, 43.57; H, 4.58; N, 8.91; S, 7.82%; calculated for $C_{28}H_{34}N_4O_4PtS_2$: C, 42.79; H, 5.25; N, 7.68; S, 8.79%); ^1H NMR (600 MHz, $CDCl_3$)/ppm δ 1.27 (6H, triplet, CH_3), 1.33 (6H, triplet, CH_3), 3.77 (4H, quartet, NCH_2), 3.81 (4H, quartet, NCH_2), 3.87 (6H, singlet, O–CH_3), 6.92 (4H, doublet, Ar–H), 8.22 (4H, doublet, Ar–H). $\delta(^{195}Pt$ 128 MHz, $CDCl_3$)/ppm, −2733.8 (*cis*), −1991.0 (*trans*, post irradiation; white Quartz Halogen light).

***cis*-bis(*N,N*-diethyl-*N′*-(3,4,5-trimethoxybenzoylthioureato)platinum(II), *cis*-[Pt(L^3-*S,O*)$_2$]**: Yield of 0.1617 g (79%); m.p. 218–221 °C (decomposition); (Found: C, 42.43; H, 4.88; N, 6.55; S, 7.00; calculated for $C_{30}H_{46}N_4O_8PtS_2$: C, 42.39; H, 5.46; N, 6.59; S, 7.55); ^{1}H NMR (600 MHz, $CDCl_3$)/ppm δ 1.29 (6H, triplet, CH_3), 1.32 (6H, triplet, CH_3), 3.75 (4H, quartet, NCH_2), 3.80 (4H, quartet, NCH_2), 3.87 (12H, singlet, O-CH_3), 3.88 (6H, singlet, CH_3), 7.55 (4H, singlet Ar–H); ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$)/ppm δ 12.4, 13.1, 30.8, 47.1, 107.4, 132.9, 141.6, 152.6, 166.9, 167.9. δ(^{195}Pt 128 MHz, $CDCl_3$)/ppm, −2723.5 (*cis*), −1982.5 (*trans*, post irradiation; white Quartz Halogen light).

***cis*-bis(*N,N*-diethyl-*N′*-3,5-dimethoxybenzoylthioureato)platinum(II), *cis*-[Pt(L^6-*S,O*)$_2$]**: Yield of 0.1758 g (88%); m.p. 211–212 °C; (Found: C, 42.96; H, 4.47; N, 7.06; S, 7.82; calculated for $C_{28}H_{42}N_4O_6PtS_2$: C, 42.58; H, 5.36; N, 7.09; S, 8.17); ^{1}H NMR (600 MHz, $CDCl_3$)ppm: 1.29 (6H, triplet, CH_3), 1.33 (6H, triplet, CH_3), 3.75 (4H, quartet, NCH_2), 3.81 (4H, quartet, NCH_2), 3.84 (12H, singlet, H_1), 6.61 (2H, singlet, H_2), 7.47 (4H, singlet, H_3) ^{13}C{^{1}H} (75 MHz, $CDCl_3$)ppm: 12.4, 13.1, 46.1, 47.1, 55.4, 103.7, 107.2, 139.7, 160.4, 167.0, 167.7. δ(^{195}Pt 128 MHz, $CDCl_3$)/ppm −2706.7 (*cis*), −1974.5 (*trans*, post irradiation; white Quartz Halogen light).

2.3. *Photo-induced isomerization experiments and rp-HPLC separation of Pt and Pd complexes*

Photo-induced isomerization experiments were performed with several light sources, including an intense white light quartz-halogen lamp (150 Watt), a low-heat (5 Watt OSRAM superstar) white light-emitting diode (LED) lamp, as well as a hand-held blue–violet laser diode (100 mW, λ = 405 nm). Irradiation of complexes prior to *rp*-HPLC was achieved with a homemade pre-column "photo-reactor", constructed using a commercially available Hg UV/visible (PHILIPS TL 4 W/05 4 Watt, 112 × 15 mm) cylindrical lamp as shown schematically in figure S1 (see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.974584) of the electronic supplementary data. This device allows for direct on-line pre-column irradiation of an injected sample aliquot of [M(L^n-*S,O*)$_2$] (M = Pt(II), Pd(II)) complexes, passing through a Teflon tube (61.6 cm, 3 μm ID) coiled around the air-cooled Hg UV/visible lamp *ca* 110 cm long, which is transparent to a large portion of the spectrum of Hg-vapor generated UV/visible light. In this way, a sample aliquot may be exposed to light irradiation prior to entering the analytical *rp*-HPLC column, at a constant flow rate. The relative time of light exposure may be controlled as a function of the effective coil length at a given flow rate. Typical Teflon coil lengths used ranged from 9.4 to 61.6 cm, the longest of which resulted in sufficient exposure time to allow for steady state to be reached (*vide infra*). A disadvantage of this simple but effective device is that the actual spectrum of light that the sample is exposed to is not well known, since it is difficult to estimate the effective photon flux to which a sample is subjected to. Nevertheless, the pre-column photochemical reactor allows for a semi-quantitative estimation of the distribution of *cis/trans* isomers of [M(L^n-*S,O*)$_2$] (M = Pt(II), Pd(II)) generated at steady state, from their subsequent separation and quantification by means of *rp*-HPLC. However, we find that presumably the high energy UV component of Hg-vapor light spectrum results in evidence of some photochemical decomposition after longer exposure times, particularly for the *cis*-[Pt(L^n-*S,O*)$_2$] complexes, although this is not evident for the corresponding palladium complexes, under similar conditions (figure S2, electronic supplementary data).

We find that the photo-induced *cis/trans* isomerization of the [M(L^n-*S,O*)$_2$] complexes can also conveniently be achieved using a simple hand-held AC-powered blue–violet laser

diode (100 mW, 405 nm). This allows the use of monochromatic light to be investigated, immediately prior to manual sample injection onto the analytical *rp*-HPLC column. Interestingly, the laser light generally results in clean and efficient *cis/trans*-isomerization (*vide infra*) of complexes. Since we could not estimate accurately the photon flux which the sample aliquot is exposed to using a hand-held laser, no absolute rates of isomerization can be inferred although semi-quantitative estimates of the conditional steady-state *trans : cis* ratio (K_e = [*trans*-(M(L^n-*S,O*)$_2$)]/[*cis*-(M(L^n-*S,O*)$_2$)] for a given injected [M(L^n-*S,O*)$_2$] complex is possible. Surprisingly, reproducible steady-state *trans : cis* ratios were obtained with the monochromatic laser light irradiation using a hand-held blue–violet laser diode (100 mW, 405 nm) at room temperature. Finally, some *in situ* irradiation experiments using an optical fiber to direct blue–violet laser light directly into an NMR tube containing samples of selected [M(L^n-*S,O*)$_2$] (M = Pt(II), Pd(II)) in several solvents were also carried out, allowing for simultaneous recording the ^{1}H NMR spectra of such samples as a function of irradiation time. Moreover for the more soluble *cis*-[Pt(L^n-*S,O*)$_2$] complexes in $CDCl_3$, we also obtained the 128 MHz ^{195}Pt{^{1}H} NMR spectra, resulting in the chemical shifts $\delta(^{195}\text{Pt})$ of several *cis*-[Pt(L^n-*S,O*)$_2$] and those of their *trans* isomers for the first time.

Reversed-phase HPLC was performed using an Agilent system with Quaternary pump equipped with automatic sample injector; typically, 20 µL aliquots consisting of [M(L^n-*S,O*)$_2$] (M = Pt(II), Pd(II)) solutions in acetonitrile at typical concentrations of 100–200 mg L^{-1} gave good separations. A GEMINI 150 × 4.6 mm column packed with "end-capped" 5 µm C_{18}-ODS particles was used throughout together with photometric detection using a UV150 Photo-diode array (PDA) detector; generally maximum sensitivity is obtained by monitoring peaks at 262 nm. A mobile phase of variable composition from 85 : 15 to 90 : 10 (v/v%) acetonitrile:0.1 M acetate buffer (pH 6) using isocratic elution gave optimum separations at room temperature for most complexes. Only de-ionized water and HPLC grade acetonitrile filtered through a 0.45 µm was used to make up the mobile phase. Off-line UV–vis absorption spectra of *cis*-[M(L^n-*S,O*)$_2$] (M = Pt(II), Pd(II)) solutions in acetonitrile were recorded using a Varian Cary 50 Bio single-beam spectrophotometer (figure S3, supplementary material).

2.4. *Single-crystal X-ray diffraction*

Crystals suitable for single-crystal X-ray diffraction of *cis*-[Pd(L^2-*S,O*)$_2$] and *cis*-[Pd(L^3-*S,O*)$_2$] were grown from a solvent mixture of a ~80 : 20 (v/v%) acetonitrile–chloroform in a glass vial sealed with a perforated wax-film under slow evaporation of the solvent at room temperature without protection from ambient light.

Crystals of *trans*-[Pd(L^1-*S,O*)$_2$] were prepared from authentic *cis*-bis(*N,N*-diethyl-*N*′-(benzoylthioureato)palladium(II) dissolved in acetonitrile, subjected to intense polychromatic LED white light irradiation in a specially designed two-chamber closed glass vessel interconnected by means of a Teflon tap, to allow for slow vapor diffusion of diethyl ether from one chamber into the chamber containing the solution of *cis*-[Pd(L^1-*S,O*)$_2$] at room temperature. Over a period of several hours at room temperature, pale yellow needle-shaped crystals of *trans*-[Pd(L^1-*S,O*)$_2$] suitable for X-ray diffraction analysis were formed. Significantly, the melting point of *trans*-[Pd(L^1-*S,O*)$_2$] is at 194–196 °C, significantly higher than that of the starting *cis*-[Pd(L^1-*S,O*)$_2$] compound.

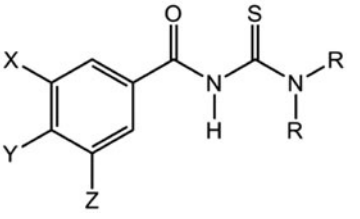
X-ray diffraction intensity data were collected on a Bruker SMART APEX single-crystal X-ray diffractometer equipped with a Mo fine-focus sealed tube, Monocap collimator, and

an APEXII detector with Incoatec IμS molybdenum and copper micro-focus X-ray sources and an APEXII detector. The temperature in both systems was regulated using an Oxford Cryosystem. Data were reduced using SAINT [22] and empirical corrections were performed where necessary using multi-scan SADABS [23]. The crystal structures were solved and refined using the SHELX-97 [24] suite of programs and mainly from direct methods. X-seed software [25] was used as a graphic interface for SHELX. All non hydrogen atoms were refined anisotropically by means of full-matrix least-squares calculations for F^2 using SHELXL-97, which is incorporated into the X-seed software package. Hydrogens were placed using a 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 X-seed.

3. Results and discussion

3.1. *Preparation and configuration of cis-[M(L^n-S,O)$_2$] (M = Pt^{II}, Pd^{II}), HL^n (n = 1–6)*

The preparation of pure *cis*-[M(L^n-*S*,*O*)$_2$] (M = Pt^{II}, Pd^{II}) complexes derived from the series of HL^n (R$^1{}_2$NC(S)NHC(O)R^2, R^1 = alkyl or aryl groups, n = 1–6) ligands as shown in scheme 1 was carried out as described previously based on literature methods [8, 10]. All ligands and complexes were fully characterized by conventional means, including melting points, elemental analysis, IR and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy as indicated in the experimental section. The purity and particularly the isomeric homogeneity of the recrystallized [M(L^n-*S*,*O*)$_2$] (M = Pt^{II}, Pd^{II}) complexes from chloroform/ethanol/methanol under ambient light conditions is confirmed by the narrow melting point range found for these [M(L^n-*S*,*O*)$_2$] (M = Pt^{II}, Pd^{II}) complexes, as well as their chromatographic homogeneity on TLC plates, showing only a single spot on elution (Merck silica-gel) with chloroform as the eluent.



Scheme 1.

HL^1: R = ethyl; X, Y, Z = H; **HL^2:** R = ethyl; X, Z = H, Y = MeO; **HL^3**: R = ethyl; X, Y, Z = MeO; **HL^4**: R = ethyl; X, Z = H, Y = Cl; **HL^5**: R = piperidyl; X, Y, Z = H; **HL^6**: R = ethyl; X, Z = MeO; Y = H.

^{1}H and ^{13}C{^{1}H} NMR spectra of all recrystallized [M(L^n-*S*,*O*)$_2$] (M = Pt(II), Pd(II)) complexes (under low light conditions) recorded in $CDCl_3$ or acetonitrile-d_6 where solubility permits, confirm that these complexes where exclusively the *cis* isomers. These spectra did not contain any trace of peaks ascribable to the *trans* isomers. In the case of soluble Pt(II) complexes in $CDCl_3$, the ^{195}Pt{^{1}H} NMR spectra recorded from freshly prepared solutions under subdued light, showed only a single ^{195}Pt NMR resonance in the ^{195}Pt chemical shift range −2700 ± 100 ppm, characteristic of *cis*-[Pt(L^n-*S*,*O*)$_2$] complexes in $CDCl_3$ (relative to external H_2PtCl_6 (500 mg mL^{-1} in 30% v/v D_2O/1 M HCl) at $\delta(^{195}Pt) = 0$ ppm) [8].

For completeness, particularly for Pd(II) complexes, the single-crystal structure of two representative examples of *cis*-[Pd(L^2-*S*,*O*)$_2$] (figure 1) and *cis*-[Pd(L^3-*S*,*O*)$_2$] (figure S4 in supplementary electronic data) complexes derived from the *N*,*N*-diethyl-*N*′-(4-methoxy-benzoyl)thiourea (HL^2) and *N*,*N*-diethyl-*N*′-(3,4,5-trimethoxybenzoy)thiourea (HL^3), respectively, were determined. The *cis*-[Pd(L^2-*S*,*O*)$_2$] complex crystallizes in a monoclinic space group $P2_1/c$, while *cis*-[Pd(L^3-*S*,*O*)$_2$] crystallizes in the $P2_1/n$ space group, with relevant crystal data given in table S1. The structure of *cis*-[Pd(L^3-*S*,*O*)$_2$] unfortunately displays some slight crystallographic disorder in one of the ethyl moieties over two positions in this complex, although this does not compromise the isomeric veracity of the structure. As anticipated in both cases, the Pd(II) coordinates to two deprotonated *N*,*N*-diethyl-*N*′-benzoylthioureato anions with the *S*- and *O*-donors mutually *cis* to each other forming a square planar complex. The *cis*-[Pd(L^2-*S*,*O*)$_2$] and *cis*-[Pd(L^3-*S*,*O*)$_2$] structures are essentially isostructural with numerous other examples of similar Pt(II), and relatively fewer Pd(II) complexes with related ligands in the Cambridge crystallographic database (CCD) [13], including those described in the recent review [9].

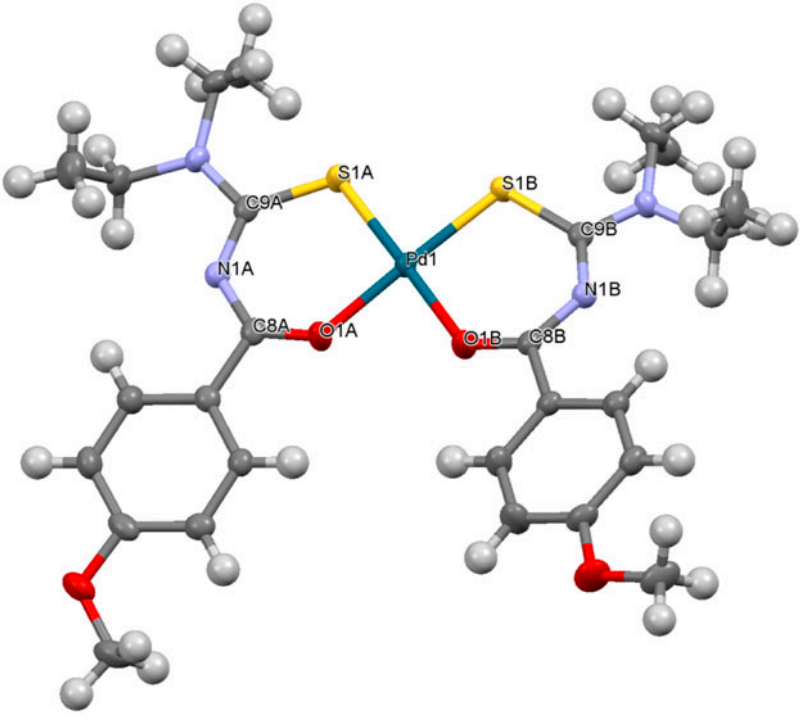


Figure 1. Molecular structure of *cis*-bis(*N*,*N*-diethyl-*N*′-4-methoxy-benzoylthioureato)-palladium(II), *cis*-[Pd(L^2-*S*,*O*)$_2$] with selected bond lengths (Å) and angles (°): Pd(1)–S(1A) 2.2364(4), Pd(1)–O(1A) 2.0085(11), Pd(1)–S(1B) 2.2351(4), Pd(1)–O(1B) 2.0147(12), S(1A)–C(9A) 1.7441(16), O(1A)–C(8A) 1.2636(18), N(1A)–C(8A) 1.3371 (19), N(1A)–C(9A) 1.3354(19); S(1A)–Pd(1)–S(1B) 86.62(1), S(1A)–Pd(1)–O(1A) 94.16(3), S(1A)–Pd(1)–O(1B) 178.94(3), S(1B)–Pd(1)–O(1A) 177.52(3), S(1B)–Pd(1)–O(1B) 94.44(3), O(1A)–Pd(1)–O(1B) 84.78(5), Pd1–S (1A)–C(9A) 107.92(5), Pd(1)–S(1B)–C(9B) 107.53(3), Pd(1)–O(1A)–C(8A) 131.28(10), Pd(1)–O(1B)–C(8B) 129.69(10).

3.2. *Photo-induced cis → trans isomerization of [M(L^n-S,O)$_2$] (M = Pt(II), Pd(II)): ^{1}H and ^{195}Pt NMR studies*

Given the limited scope of our previous communication on the photo-induced *cis*/*trans* isomerism of *cis*-[Pd(L-*S,O*)$_2$] complexes in solution [19], we specifically examined the photo-induced *cis* → *trans* phenomenon to include several *cis*-[Pd(L^n-*S,O*)$_2$] and *cis*-[Pt(L^n-*S,O*)$_2$] complexes from a selection of *N,N*-dialkyl-*N′*-aroylthiourea ligands HL^n (n = 1–6) by means of NMR spectroscopy in more detail. As a precaution, solutions of all complexes examined by means of ^{1}H NMR (and *rp*-HPLC see below) were freshly prepared under subdued light, and solutions were always stored in the dark. Irradiation of solutions of *cis*-[Pd(L^n-*S,O*)$_2$] complexes in organic solvents such as chloroform or acetonitrile in normal glass vessels with one of several sources of visible light, including intense white light quartz-halogen (150 Watt lamp) light, a low-heat 5 Watt LED source, a Hg UV/visible lamp (4 Watt), and a 100 mW blue–violet laser (λ = 405 nm) *all* result in some degree of *cis* → *trans* isomerization, as conveniently monitored by ^{1}H NMR spectroscopy in reasonably concentrated solutions. This can be illustrated by the partial ^{1}H NMR spectrum of the representative *cis*-[Pd(L^1-*S,O*)$_2$] complex of *N,N*-diethyl-*N′*-benzolythiourea of *ca* 10 mg mL^{-1} in acetonitrile-d$_6$ shown in figure 2(a), confirming that only a single compound is present in solution not subjected to intense light. On irradiation with intense white LED light of a solution of *cis*-[Pd(L^1-*S,O*)$_2$] directly in an NMR tube for 20 and 30 min, followed by the rapid acquisition of a ^{1}H NMR spectrum shows clear evidence of *cis* → *trans* photo-induced isomerization of this complex by the appearance of additional peaks ascribed to the *trans* isomer [figure 2(b) and (c)]. Similar results are obtained for all other soluble palladium(II) complexes. Moreover, on allowing the sample to stand in the dark for sufficiently long, these additional peaks vanish from the ^{1}H NMR spectrum on reacquisition of the ^{1}H NMR spectrum.

The reversion of the *trans* isomer back to the *cis* isomer in the dark takes place for all Pd as well as Pt(II) complexes in either chloroform or acetonitrile solution (see below).

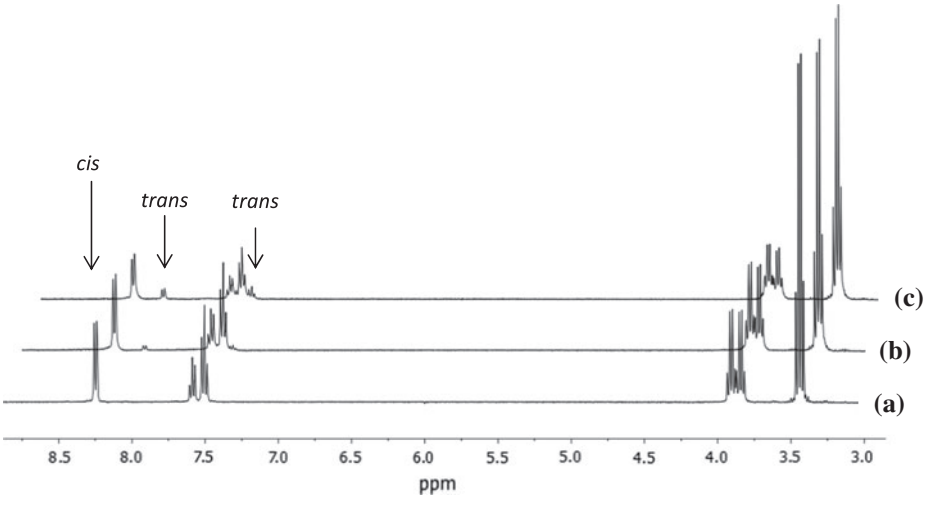


Figure 2. ^{1}H NMR spectra of aromatic region of *cis*-[Pd(L^1-*S,O*)$_2$] in acetonitrile-d$_6$ (400 MHz, 298 K): (a) (in dark); (b) (after irradiation with white light for 20 min); (c) (after irradiation with white light for 30 min).

The extent of conversion to the *trans* isomer as measured by the *trans:cis* ratio (K_e = [*trans*-(Pd(L^n-*S,O*)$_2$)]/[*cis*-(Pd(L^n-*S,O*)$_2$)] at steady state varies significantly for these complexes, depending on the structure of HL^n examined, as well as the solvent acetonitrile-d_6 or $CDCl_3$ used (*vide infra*). For *cis*-[Pd(L^n-*S,O*)$_2$] complexes in acetonitrile-d_6, the relative rate of isomerization takes place on a timescale suitable to be readily measurable by means of ^{1}H NMR. In the case of the corresponding *cis*-[Pt(L^n-*S,O*)$_2$] complexes, however, the relative rates of photo-induced *cis* → *trans* isomerization are generally very much lower (including the reverse reaction in the dark). Moreover, for the generally less soluble *cis*-[Pt(L^n-*S,O*)$_2$] complexes in acetonitrile, prolonged irradiation by polychromatic light sources used in this work (particularly with a strong UV component) indicates some photochemical decomposition in solution after irradiation.

Nevertheless for the most soluble *cis*-[Pt(L^n-*S,O*)$_2$] (*n* = 1–3,6) complexes in $CDCl_3$ at concentrations of ~50 mg mL^{-1}, we recorded the 128.8 MHz ^{195}Pt{^{1}H} NMR spectra both with and without prior irradiation with intense white light directly in the NMR tube. In the absence of light irradiation, clean single resonance ^{195}Pt{^{1}H} NMR spectra are obtained with δ(^{195}Pt) in the characteristic range of the *cis*-[Pt(L^n-*S,O*)$_2$] complexes typically at −2700 (±30) ppm, depending on the structure of coordinated ligand (table 1). Irradiation of these Pt(II) complexes with intense white light for approximately 30–40 min (but avoiding sample heating), followed by rapid ^{195}Pt{^{1}H} NMR spectral acquisition (ca 15–20 min) results in one additional ^{195}Pt{^{1}H} peak of lower intensity appearing in each spectrum; the major peak corresponds to the *cis*-[Pt(L^n-*S,O*)$_2$] isomer as obtained before, while the minor peak at δ(^{195}Pt) at *ca* −1980 (±15 ppm) is assigned to the *trans*-[Pt(L^n-*S,O*)$_2$] isomer. This is illustrated for *cis*-[Pt(L^3-*S,O*)$_2$] in $CDCl_3$ in figure 3. The ^{195}Pt{^{1}H} chemical shift data similarly recorded for the most soluble *cis/trans*-[Pt(L^n-*S,O*)$_2$] (*n* = 1–3,6) complexes is listed in table 1. To our knowledge, this is the first ^{195}Pt NMR shielding data corresponding to *trans*-[Pt(L^n-*S,O*)$_2$] (*n* = 1–3,6) complexes available.

Interestingly, the ^{195}Pt{^{1}H} NMR chemical shifts of *trans*-[Pt(L^n-*S,O*)$_2$] (*n* = 1–3,6) are significantly less shielded than the corresponding *cis*-[Pt(L^n-*S,O*)$_2$] complexes by an average of some 748 ± 5 ppm (table 1). This difference in shielding between *cis* and *trans* isomers of [Pt(L^n-*S,O*)$_2$] complexes is substantially larger than for similar differences observed in other four-coordinate square planar Pt(II) complexes, based on available data in the literature [26–27]. In the case of *cis* and *trans* PtX_2Cl_2 complexes with X being monodentate ligands with relatively "harder" donors (e.g. N or O) [17] compared with "softer" donor ligands such as phosphines or arsines, similar shielding differences between the *cis* and

Table 1. ^{195}Pt NMR chemical shifts relative to external reference of selected *cis*- and *trans*-[Pt(L^n-*S,O*)$_2$] complexes in $CDCl_3$ at 303 K after irradiation of samples with intense white light, not at steady state.

	δ(^{195}Pt)/ppm in $CDCl_3$[b]	
Complex[a]	*cis* isomer	*trans* isomer
[Pt(L^1-*S,O*)$_2$]	−2720	−1981
[Pt(L^2-*S,O*)$_2$]	−2733	−1991
[Pt(L^3-*S,O*)$_2$]	−2721	−1978
[Pt(L^6-*S,O*)$_2$]	−2707	−1975

[a]Concentration ~50 mg mL^{-1}.
[b]δ(^{195}Pt) ±2 ppm relative to external reference of $[PtCl_6]^{2-}$ at δ^{195}Pt = 0 ppm (+4522 ppm relative to Ξ at 21.496 Hz]).

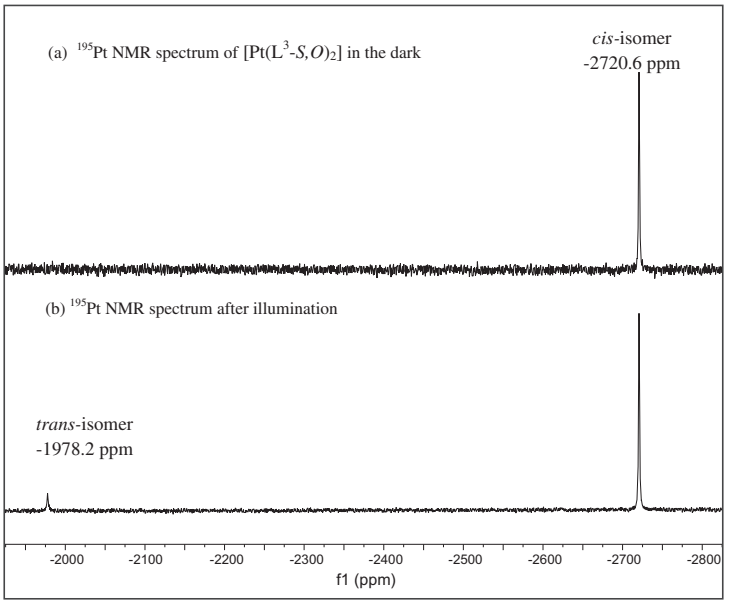


Figure 3. (a) ^{195}Pt{^{1}H} NMR spectrum of *cis*-[Pt(L^3-*S,O*)$_2$] in $CDCl_3$ in dark; (b) after irradiation with intense white light for 30 min show both the *cis* and *trans*-isomers in solution at 298 K.

trans geometric isomers ranging from ~250 to ~500 ppm, respectively, have been reported [26, 27]. Given the lack of reliable ^{195}Pt shielding trends particularly for [PtS_2O_2]-type complexes similar to the *cis/trans*-[Pt(L^n-*S,O*)$_2$] (n = 1–3,6) complexes studied here, any generalizations on the origin of the observed ^{195}Pt NMR shielding trends of these compounds must remain speculative until insights from more detailed computational studies currently in progress are available.

In view of the relatively long spectral acquisition times for ^{195}Pt{^{1}H} NMR spectra (*ca* 15–20 min) using typical complex concentrations of *ca* 50 mg mL^{-1} in $CDCl_3$, it is not sensible to estimate a *trans : cis* ratio from relative ^{195}Pt NMR peak intensities, since during acquisition, the intensities of the ^{195}Pt{^{1}H} peaks may change as a result of slow reversion of the *trans* → *cis* complexes (in the dark). While the above ^{1}H and ^{195}Pt{^{1}H} NMR results are useful in elucidating the nature of the light-induced *cis* → *trans* isomerization of the Pt complexes, the disadvantage of using ^{195}Pt NMR for these studies is the requirement for fairly concentrated solutions. This limitation, together with the potential photochemical decomposition of *cis*-[Pt(L^n-*S,O*)$_2$] alluded to above on prolonged irradiation with light, complicated further study of these complexes using NMR spectroscopy. For this reason we will focus only on the *cis*-[Pd(L^n-*S,O*)$_2$] complexes for the remainder of this study.

Preliminary experiments show that the *cis*-[Pd(L^n-*S,O*)$_2$] complexes are more kinetically labile requiring shorter light irradiation times as well as being more soluble in solvents other than chloroform, such as acetonitrile. In order to probe the relative rates of isomerization in differing solvents, we carried out a preliminary *in situ* laser-induced isomerization of *cis*-[Pd(L^2-*S,O*)$_2$] in $CDCl_3$ using a blue–violet laser (λ = 405 nm) guided directly into an NMR tube using an optical fiber, while monitoring the ^{1}H NMR signals as a function of

irradiation time (figure 4). This experiment clearly confirms a facile photo-isomerization of *cis*-[Pd(L^2-*S,O*)$_2$] → *trans*-[Pd(L^2-*S,O*)$_2$] induced by monochromatic 405 nm laser light; when the laser is switched off a slow reversion of the *trans*-[Pd(L^2-*S,O*)$_2$] complex back to its *cis* isomer commences as illustrated in figure 4(a). The relatively rapid *cis* → *trans* isomerism in the fairly concentrated 20–25 mg mL^{-1} solutions of *cis*-[Pd(L^2-*S,O*)$_2$] in $CDCl_3$ which reach steady state in approximately 20 min, with low power (~100 mW) laser light is noteworthy, in contrast to the very slow reversion of the *trans*-[Pd(L^2-*S,O*)$_2$] complex to the *cis* commencing with the laser "off" in figure 4(a). By contrast in acdetonitrile-d_6 (not shown), the overall relative rate of *cis*-[Pd(L^2-*S,O*)$_2$] → *trans*-[Pd(L^2-*S,O*)$_2$] is significantly more rapid.

To illustrate the importance of the solvent for the *cis* ⇆ *trans* isomerization of *cis*-[Pd(L^2-*S,O*)$_2$], we estimated qualitatively the relative rates of the reversion *trans* → *cis* reaction in the absence of light at 298 K by ^{1}H NMR, immediately after a laser light-induced steady-state *trans : cis* ratio had been reached in chloroform-d, benzene-d_6, and acetonitrile-d_6 [figure 4(b)]. It is clear that in both $CDCl_3$ and C_6D_6, the "dark" *trans* → *cis* (presumably

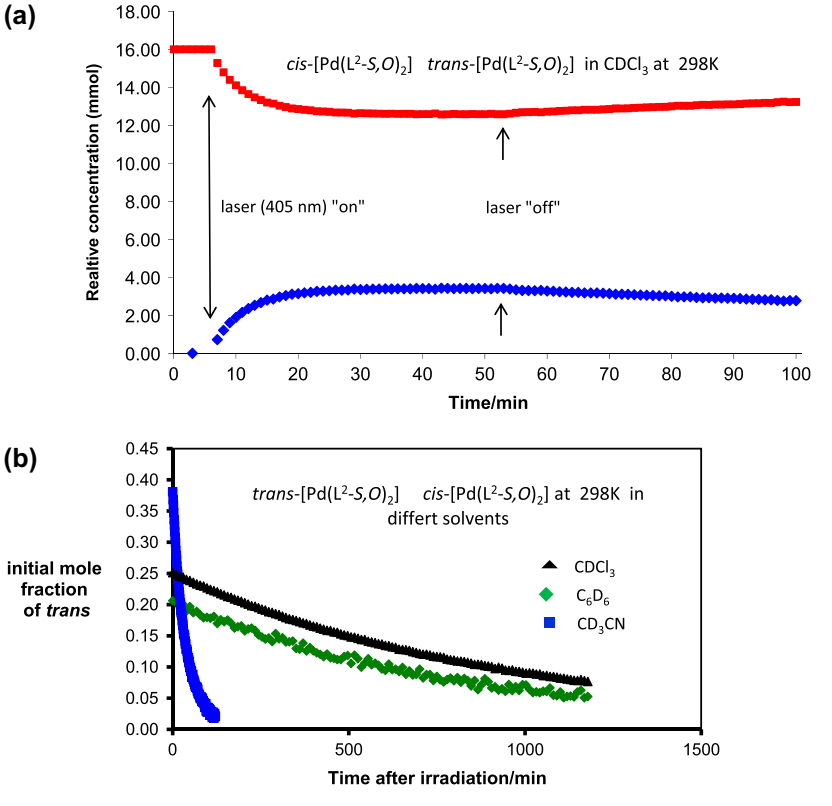


Figure 4. (a) *In situ* laser irradiation with ^{1}H NMR monitoring of the isomerism *cis*-[Pd(L^2-*S,O*)$_2$] → *trans* in $CDCl_3$ at 298 K as a function of time: (■) indicates the relative intensity of the $\delta(^1H)$ ~7.29 ppm doublet corresponding to the $H^{3/5}$ of *cis*-[Pd(L^2-*S,O*)$_2$], while (♦) represents the growth of the corresponding resonance at $\delta(^1H)$ ~7.13 ppm of the *trans* complex. The *trans* complex only disappears entirely from the spectrum after *ca* 17 h in the dark. (b) Reversion of the *trans*-[Pd(L^2-*S,O*)$_2$] → *cis* in the dark as in $CDCl_3$. C_6D_6 and CD_3CN at 298 K, after reaching steady state on laser irradiation.

thermal) reaction is extremely slow; it takes more than 1000 min (*ca* 17 h) for the *trans* to completely disappear from solution, with concomitant growth of ^{1}H NMR peaks of the *cis* compound back to their original intensity. The thermal nature of the reverse reaction is supported by higher rates of disappearance of the *trans* complex in chloroform at 323 K (50 °C) in the dark; the last trace of *trans* isomer vanishes from the ^{1}H NMR spectrum in *ca* 500 min. By contrast, in acetonitrile-d_6, the relative rate of disappearance of ^{1}H NMR peaks of the *trans*-[Pd(L^2-*S,O*)$_2$] complex is much higher than in chloroform or benzene, with all traces of the *trans* isomer vanishing from the ^{1}H NMR spectrum after *ca* 180 min. These experiments indicate that the solvent plays a significant role at least for the *trans* → *cis* process in the absence of light. This may be the result of differences in the relative solvent polarity and/or differences in solvent donor properties. The trends in figure 4(b) also indirectly confirm that the extent of *cis* → *trans* isomerization under the influence of light similarly depends on the nature of the solvent, as indicated by the initial mole fraction of the *trans* isomer in acetonitrile being almost double that in chloroform/benzene after laser irradiation for *ca* 30 min to steady state, at the start of the ^{1}H NMR monitoring of the reversion reaction at 298 K. The role of acetonitrile is reasonable in the light of studies by Kukushkin *et al.* who have shown that nitriles, such as CH_3CN used as solvent in this work, are well known to coordinate with Pt(II) complexes resulting in stable, isolable *cis/trans*-[MX_2(R-CN)$_2$] (M = Pt(II) and X = Cl^-) complexes [28]. Thus in the case of photo-induced isomerization in question here, it is likely that CH_3CN is in not an innocent solvent involved in the overall photo-induced *cis* → *trans* isomerization, as well as in the reverse *trans* → *cis* "dark" reaction of [M(L^n-*S,O*)$_2$]. Such postulated effects are supported by a preliminary theoretical DFT study of the possible mechanism of the interesting *cis* ⇆ *trans* process, suggesting that on irradiation, the S,O-chelate undergoes ring opening, which would certainly be stabilized in the presence of coordinating acetonitrile [18]. It should, nevertheless, be emphasized that any conclusions concerning relative rates of *cis/trans* isomerization should only be viewed as qualitative at this stage, since it has not been possible to estimate the laser light intensity accurately nor has any reliable measurement of the quantum yields of this interesting photo-induced isomerization process been possible to date.

3.3. *Monitoring of the light-induced isomerization of cis-[Pd(L^n-S,O)$_2$] complexes by rp-HPLC*

To circumvent the limitations of ^{1}H NMR spectroscopy for the study of the photo-induced isomerization, we used *rp*-HPLC to examine the isomerization of several of the *cis*-[Pd(L^n-*S,O*)$_2$] complexes in much more dilute acetonitrile solutions, since this separation methodology has been shown to be useful for easy separation of uncharged *cis*-[Pt/Pd(L^n-*S,O*)$_2$] complexes [10, 19]. However, the very much lower rates of isomerization of the corresponding platinum complexes found by means of ^{1}H NMR above necessitating prolonged irradiation times, which result in apparent photo-decompostion products as indicated above, is also evident for the *cis*-[Pt(L^3-*S,O*)$_2$] complexes by *rp*-HPLC (figure S2b), so that only palladium compounds will be discussed further.

A representative mixture of *cis*-[Pd(L^1-*S,O*)$_2$], *cis*-[Pd(L^3-*S,O*)$_2$], *cis*-[Pd(L^4-*S,O*)$_2$], and *cis*-[Pd(L^5-*S,O*)$_2$] complexes freshly dissolved in acetonitrile in typical concentrations between 100 and 200 μg mL^{-1} show these compounds to be readily separable by *rp*-HPLC using isocratic elution with a buffered aqueous acetonitrile mobile phase (typically 85 : 15

v/v% acetonitrile:0.1 M acetate buffer pH 6) at room temperature, illustrated in figure 5(a). The influence of ligand structure on the retention behavior of these complexes is also clearly apparent, with retention times differing significantly for various ligand structures in these complexes. Although this retention behavior is not the focus of this study, it is noteworthy that the retention time of *cis*-[Pd(L^1-*S*,*O*)$_2$] from the unsubstituted *N*,*N*-diethyl-*N*′-benzoylthiourea is much shorter (t_R = 23.2 min) than, for example, the corresponding 4-chlorobenzoylthiourea *cis*-[Pd(L^4-*S*,*O*)$_2$] complex (*ca* t_R = 62.2 min), while being similar

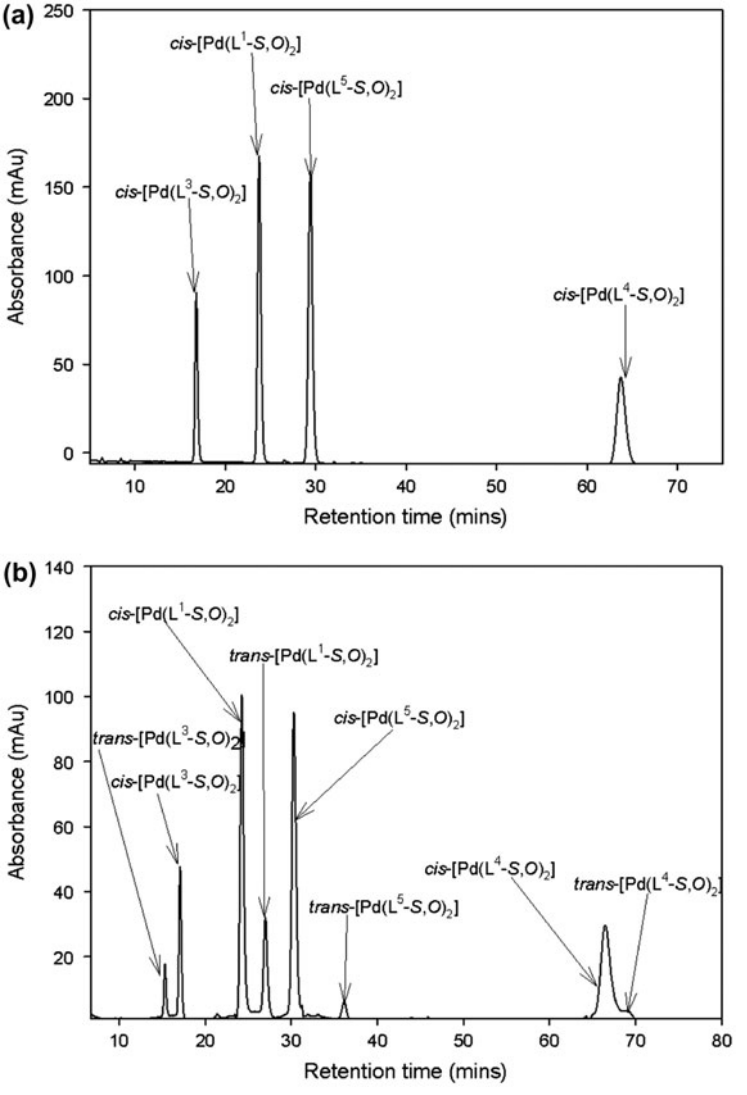


Figure 5. (a) Chromatogram representing the RP-HPLC separation of acetonitrile solution of a mixture of *cis*-[Pd(L^1-*S*,*O*)$_2$], *cis*-[Pd(L^3-*S*,*O*)$_2$], *cis*-[Pd(L^4-*S*,*O*)$_2$], and *cis*-[Pd(L^5-*S*,*O*)$_2$] in the dark; (b) Chromatogram of *cis* and *trans* isomers of [Pd(L^1-*S*,*O*)$_2$], [Pd(L^3-*S*,*O*)$_2$], [Pd(L^4-*S*,*O*)$_2$], and [Pd(L^5-*S*,*O*)$_2$] in acetonitrile, after irradiation with Hg UV light; conditions: GEMINI C_{18} 5 μm, 150 × 4.6 mm column, mobile phase 85 : 15 (% v/v) acetonitrile:0.1 M acetate buffer (pH 6) flow rate 1 mL min^{-1}, injection volume 20 μL, 262 nm detection.

to that of the 4-methoxybenzolyl complex *cis*-[Pd(L^2-*S*,*O*)$_2$] (ca t_R = 25.5 min), but longer than the 3,4,5-trimethoxybenzoylthiourea complex *cis*-[Pd(L^3-*S*,*O*)$_2$] (16.3 min). Under similar conditions, the corresponding *N*-piperidylbenzoylthiourea complex *cis*-[Pd(L^5-*S*,*O*)$_2$] shows a longer retention time (28.5 min) than its *N,N*-diethyl-*N′*-benzoylthiourea analog, *cis*-[Pd(L^1-*S*,*O*)$_2$]. These trends suggest that the *rp*-HPLC retention times of the series of complexes are sensitive indicators of the relative polarity of the individual compounds, and consequently their degree of partition between the less polar stationary phase and the more polar mobile phase. Such arguments qualitatively account for the long retention time of the more hydrophobic 4-chlorobenzoylthiourea *cis*-[Pd(L^4-*S*,*O*)$_2$] complex compared with the presumably more hydrophillic 3,4,5-trimethoxybenzoylthiourea *cis*-[Pd(L^3-*S*,*O*)$_2$] complex. Evindently, the use of *rp*-HPLC not only confirms the isomeric purity of the above (*cis*) complexes in dilute solutions not previously exposed to light, but confirms this to be an excellent separation technique for the study of photo-induced isomerization of *cis*-[Pd(L^n-*S*,*O*)$_2$] complexes, at two orders of magnitude lower complex concentrations.

The *rp*-HPLC chromatogram obtained after injection of a 20 μL aliquot of a mixture of *cis*-[Pd(L^1-*S*,*O*)$_2$], *cis*-[Pd(L^3-*S*,*O*)$_2$], *cis*-[Pd(L^4-S,O)$_2$], and *cis*-[Pd(L^5-*S*,*O*)$_2$] in acetonitrile irradiated using the pre-column Hg UV lamp photo-reactor (figure S1) clearly shows that good separation between the *cis* and photo-induced *trans* isomers is achieved in most cases. With the exception of the *cis*-[Pd(L^3-*S*,*O*)$_2$] complex, the *trans* isomer of the other three complexes tend to have longer retention times compared with their *cis* analogs under identical conditions, consistent with the expected low relative dipole moment of the symmetrical *trans* isomers. The above chromatographic assignments were confirmed by comparison of retention times obtained from single-component sample aliquots containing only one of the *cis*-[Pd(L^n-*S*,*O*)$_2$] (n = 1–5) complexes with and without sample irradiation. The retention times of individual *cis/trans* pairs so generated gave consistent retention times, and from the relative chromatographic peak areas, the *trans : cis* ratios could readily be measured at 262 nm photometrically for each individual complex. The validity of using chromatographic peak areas as a measure of the *trans : cis* ratios of the separated *cis/trans* isomer pairs was confirmed by the UV/visible light absorption profiles determined for all individual *cis/trans* complexes recorded by means of diode-array detector. Virtually identical absorption profiles and molar absorptivities at 262 nm are obtained for all *cis/trans* complex pairs, which allow for the photometric determination of the chromatographic area ratio directly proportional to the *trans : cis* ratio within minimal experimental error, without a need to perform any calibration (see figure S2). In this way, steady-state *trans : cis* ratios (K_e) for each of the *cis*-[Pd(L^n-*S*,*O*)$_2$] (n = 1–5) complexes can be estimated by variation of the effective flow rate and the Teflon coil length in the photo-reactor as described in the experimental section; thus, the length of time for which each particular complex is exposed to the Hg UV lamp irradiation can be varied until ultimately a steady-state *trans : cis* ratio K_e may be determined. While this methodology gives reproducible K_e values, unfortunately several disadvantages using the Hg UV lamp pre-column photo-reactor are apparent. One is the degree of photochemical decomposition of complexes which occurs under prolonged UV light irradiation times using the Hg lamp, particularly at relatively low flow-rates necessary for the optimum analytical *rp*-HPLC separation of products. Moreover at the low flow rates necessary for optimum analytical separations, a previously irradiated sample spends a substantial time in the "dark", while being transported to the analyitcal column. This could result in the *trans/cis* ratio measured in this way and may not be an accurate reflection of a "true" steady-state *trans/cis* ratio, since the reversion *trans* → *cis* commences immediately in the dark, while being transported to the analytical column.

For this reason, we explored an alternative "off-line" photo-induced isomerization methodology using a manual irradiation of samples to steady state with 100 mW blue–violet laser light (405 nm), followed by immediate injection of a laser light-irradiated aliquot into the analytical *rp*-HPLC column. This procedure gave good, reproducible results, showing also that treatment with 405 nm laser light apparently results in more rapid *cis* → *trans* conversion for these [Pd(L^n-*S*,*O*)$_2$] (n = 1–5) complexes in acetonitrile, and generally results in much "cleaner" chromatograms free from potential photochemical decomposition. In this way, steady-state K_e values could be measured in an overall shorter time. The conditional experimental K_e values obtained using blue–violet laser light at room temperature are listed in table 2 for selected *cis*-[Pd(L^n-*S*,*O*)$_2$] (n = 1–5) complexes.

The data are interesting, showing differences in the relative K_e values measured from chromatographic peak areas for the selected [Pd(L^n-*S*,*O*)$_2$] complexes in acetonitrile after irradiation by blue–violet laser light. Comparison of K_e values of these *cis/trans* pairs of [Pd(L^n-*S*,*O*)$_2$] complexes indicates some influence of ligand structure on the apparent steady-state K_e values as obtained by this methodology. Thus, the *cis*-[Pd(L^1-*S*,*O*)$_2$] and *cis*-[Pd(L^2-*S*,*O*)$_2$] derived from the unsubstituted benzoyl and 4-methoxy-benzoyl ligands, respectively, show virtually identical relative K_e values at ~1.5, indicating that the *para* methoxy-substituent in *cis*-[Pd(L^2-*S*,*O*)$_2$] has little effect on the effective steady-state *trans/cis* ratio under these conditions. By contrast, significantly lower K_e values of ~0.33 and ~0.13 for the *cis*-[Pd(L^3-*S*,*O*)$_2$] and *cis*-[Pd(L^5-*S*,*O*)$_2$], are obtained under identical conditions respectively. These K_e values should not be seen as "absolute" thermodynamic or equilibrium values since they are conditional on the experimental methodology used, given the lack of estimates of the quantum yield for the photo-induced process at 405 nm which may differ for different complexes. The monochromatic laser light at 405 nm appears to efficiently and rapidly induce isomerization to steady state as is apparent from the data in table 2, showing fairly short times of between 3 and 4 min to attain the steady-state K_e value in dilute acetonitrile solutions at room temperature. While the polychromatic UV/visible spectrum from a Hg lamp as well as those from conventional tungsten or LED white light sources also result in such isomerism, this appears to take place at differing relative rates and to differing extents, requiring generally longer exposure times. Since it is known that the reverse *trans* → *cis* reaction takes place in the absence of light at differing rates for the *cis*-[Pd(L^3-*S*,*O*)$_2$] complex as shown from *in situ* ^{1}H NMR data in significantly more concentrated solutions [figure 4(b)], quantitative comparisons of K_e cannot reasonably be made from the current data. The K_e values presumably reflect equal relative rates of the forward photo-induced *cis* → *trans* process relative to the thermal reverse *trans* → *cis* reversion rate under particular conditions. The apparent steady state probably depends also on

Table 2. Approximate relative times to steady state and the K_e value for *cis* → *trans* photo-induced isomerization of [Pd(L^1-*S*,*O*)$_2$], [Pd(L^2-*S*,*O*)$_2$], [Pd(L^3-*S*,*O*)$_2$], [Pd(L^5-*S*,*O*)$_2$], and [Pt(L^3-*S*,*O*)$_2$] in acetonitrile as monitored by PR-HPLC after irradiation of injected aliquots with a blue–violet laser (100 mW, 450 nm) at room temperature. (chromatographic conditions in figure 5).

	Retention time (min)			
Complex	*cis*	*trans*	Time to steady state (min)	K_e ~[*trans*]/[*cis*]
[Pd(L^1-*S*,*O*)$_2$]	21.03	23.15	4	1.46
[Pd(L^2-*S*,*O*)$_2$]	25.97	24.73	3	1.52
[Pd(L^3-*S*,*O*)$_2$]	15.58	14.26	3	0.33
[Pd(L^5-*S*,*O*)$_2$]	25.93	30.51	3	0.13

the nature of the palladium complex and the experimental conditions after irradiation by whatever means from a particular light source at room temperature. Preliminary results show that after laser light irradiation of dilute solutions of the *cis*-[Pd(L^3-*S*,*O*)$_2$] complex in acetonitrile, the *trans* isomer rapidly reverts completely back to the *cis* after only *ca* 3 min in the absence of light, while the corresponding *trans*-[Pd(L^1-*S*,*O*)$_2$] and *trans*-[Pd(L^2-*S*,*O*)$_2$] complexes persist in solution for approximately 420 min in solution, before the last traces of *trans* isomer vanishes from solution after irradiation is discontinued (figure S5). Therefore, in view of the potential complexity of this interesting photochemical/thermal *cis* ⇆ *trans* isomerism, a more detailed mechanistic and thermodynamic interpretation based on current data is beyond the scope of this paper.

In summary, all the experimental findings described point to the interesting photo-induced *cis* → *trans* isomerization in *cis*-[M(L^n-*S*,*O*)$_2$] (M = Pd(II) and Pt(II)) complexes of *N*,*N*-dialkyl-*N*′-aroylthioureas. This process is the key factor in the formation of the *trans*-[M(L^n-*S*,*O*)$_2$] complexes, at least of complexes with the d^8 Pt(II) and Pd(II) metal ions, which to our knowledge have not been obtainable by any conventional synthetic means.

Finally, to confirm the above conclusions in particular with the practical objective of reliably preparing and isolating *trans*-[Pd(L^n-*S*,*O*)$_2$] in the solid state, we devised a simple procedure with which it is possible to reliably isolate *trans* complexes of palladium(II) under conditions of photo-isomerization. Thus, the *trans*-[Pd(L^1-*S*,*O*)$_2$] complexes could readily be isolated by means of a vapor diffusion-induced crystallization from solutions of authentic *cis*-[Pd(L^1-*S*,*O*)$_2$] complexes in acetonitrile under continuous irradiation with a low-heat LED white light source at room temperature. Irradiation of an acetonitrile solution of *cis*-bis(*N*,*N*-diethyl-*N*′-benzoylthioureato)-palladium(II) at room temperature between 30 and 60 min with simultaneous slow vapor diffusion of diethylether in a closed specifically designed glass apparatus results in the crystallization of a good crop of pure yellow needles of the sparingly soluble *trans*-bis(*N*,*N*-diethyl-*N*′-benzoylthioureato)palladium(II). The crystal and molecular structure of which were established by single-crystal X-ray diffraction shown in figure 6. To the best of our knowledge, this is a first example of a *trans*-[Pd(L^1-*S*,*O*)$_2$] complex prepared by *deliberate experimental* design involving irradiation. It is of interest to note that the crystals of *trans*-[Pd(L^1-*S*,*O*)$_2$] have a significantly higher melting point (194–196 °C) compared with the *cis* isomer (159–163 °C). The molecular structure of the corresponding *cis*-bis(*N*,*N*-diethyl-*N*′-benzoylthioureato)palladium(II) previously prepared by conventional means has been characterized by X-ray diffraction [29, 30] and is as expected, isostructural with the analogous *cis*-bis(*N*,*N*-diethyl-*N*′-benzoylthioureato) platinum(II) [31].

The square planar *trans*-[Pd(L^1-*S*,*O*)$_2$] complex crystallizes in a monoclinic $P2_1/n$ space group, with relevant crystallographic details given in table S3 in supplementary data. Inspection of the molecular structure of *trans*-[Pd(L^1-*S*,*O*)$_2$] shows that in the six-membered Pd1–S1–C8–N1–C7–O1 chelate ring, the Pd–S (2.2830 Å) and the Pd–O (1.9920 Å) bond lengths are significantly longer and shorter than in the previously *cis*-[Pd(L-*S*,*O*)$_2$] complex at 2.2310 and 2.0170 Å, respectively. This is consistent with the higher *trans* influence expected for the *S*-donor resulting in somewhat longer Pd–S and concomitant shorter bond Pd–O distances in the *trans* isomer. Moreover, the *trans* structure shows virtually ideal square planar coordination to Pd as indicated by the S(1)–Pd(1)–S(1a) and O(1)–Pd(1)–O(1a) bond angles of 180°, whereas the bite angle S(1)–Pd(1)–O(2) of 178.34(4)° in the *cis* isomers deviates somewhat from the ideal linearity, as has been noted in some of the many analogous *cis*-[M(L^n-*S*,*O*)$_2$] (M = Pt and Pd) complexes [8–10, 14, 31] in the literature.

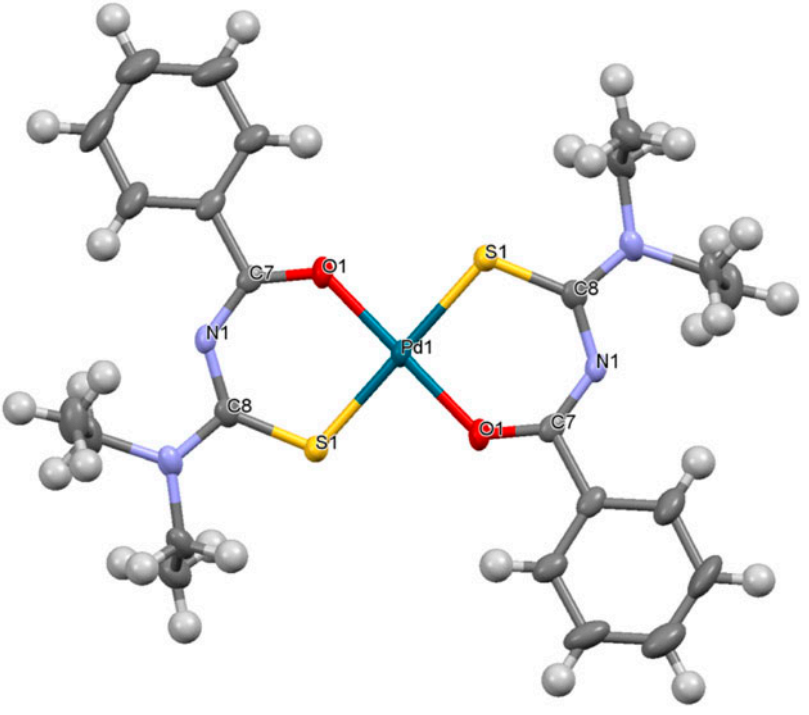


Figure 6. Molecular structure of the first example of a *trans*-bis(*N,N*-diethyl-*N*′-(benzoyl-thioureato)palladium(II), *trans*-[Pd(L^1-*S,O*)$_2$] isolated by irradiation of *cis*-[Pd(L^1-*S,O*)$_2$] in acetonitrile with while light and vapor diffusion crystallization; selected bond lengths (Å) and angles (°):Pd(1)–S(1) 2.2830(11), Pd(1)–O(1) 1.992(2), Pd(1)–S(1_a) 2.2830(11), Pd(1)–O(1_a) 1.992(2), S(1)–C(8) 1.713(4), O(1)–C(7) 1.286(5), N(1)–C(7) 1.321(5), N(1)–C(8) 1.344 (5); S(1)–Pd(1)–O(1) 94.23(7), S(1)–Pd(1)–(S1_a) 180.00, S(1)–Pd(1)–O(1_a) 85.77(7), S(1_a)–Pd(1)–O(1) 85.77 (7), O(1)–Pd(1)–O(1_a) 180.00, S(1_a)–Pd(1)–O(1_a) 94.23(14), Pd(1)–S(1)–C(8) 107.20(2), Pd(1)–O(1)–C(7) 128.8(2), C(7)–N(1)–C(8) 126.9(3).

4. Conclusion

The uncharged *cis*-[M(L-*S,O*)$_2$] complexes prepared by conventional synthetic means from *N,N*-dialkyl-*N*′-benzoylthiourea (LH) and the d^8 metals Pt(II) and Pd(II), which are usually the sole reaction product, undergo a facile light-induced *cis* → *trans* isomerization in organic solvents such as chloroform and particularly acetonitrile. This deceptively simple photo-induced *cis* → *trans* isomerization of the series of *cis*-[M(L-*S,O*)$_2$] (M = Pt^{II}, Pd^{II}) complexes results in significant quantities of the corresponding *trans* isomer appearing in solution at room temperature on irradiation with various sources of intense polychromatic or monochromatic light with $\lambda < 500$ nm. The rate and extent of the *cis* → *trans* conversion appears to depend on several factors, such as the ligand structure, the solvent the *cis* isomer is dissolved in, the d^8 metal ion (Pt or Pd), the temperature, and the light source. A simple 100 mW blue–violet laser emitting at 405 nm, efficiently results in substantial amounts of the *trans* isomer appearing in solutions. These geometrical isomers are apparently in a photo-thermal equilibrium between the thermodynamically favored *cis* isomer and its light-induced *trans* counterpart. In the absence of light, the *trans* isomer reverts back to the *cis* complex in a thermal process. This *cis* → *trans* process is the key to preparing and

isolating examples of the rare *trans* complexes. This is confirmed by the first deliberately prepared example of *trans*-[Pd(L^1-*S*,*O*)$_2$] characterized by single-crystal X-ray diffraction, after photo-induced isomerization from its corresponding *cis* complex.in acetonitrile solution and crystallization by vapor diffusion.

Supplementary material

Crystallographic data for *cis*-[Pd(L^2-*S*,*O*)$_2$], *cis*-[Pd(L^3-*S*,*O*)$_2$] and *trans*-[Pd(L^1-*S*,*O*)$_2$] have been deposited with the Cambridge Crystallographic Data Center, CCDC Numbers 1022563, 1005249 and 1022562, 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 or http://www.ccdc.cam.ac.uk).

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