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RESEARCH ARTICLE

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Synthesis of mononuclear and dinuclear palladium (II) complexes containing oxadithioether ligands and their catalytic activities in norbornene polymerization

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Abstract

The Pd (II) complexes *trans*-$[PdCl_2(\mu\text{-}L)]_2$ and $[Pd(acac)(L)][BF_4]$ (L = RS $(CH_2)_2O(CH_2)_2SR$, R = Me, Et, ^{n}Pr, ^{i}Pr, ^{n}Bu, ^{i}Bu, *n*-hexyl, benzyl) were obtained through the reaction of $Pd(cod)Cl_2$ or $[Pd(acac)(MeCN)_2][BF_4]$ with one equivalent of oxadithioether (L). The structural features of these complexes were analyzed by nuclear magnetic resonance (NMR) and Fourier-transform infrared spectroscopy (FTIR), as well as electrospray ionisation mass spectrometry and density functional theory calculations. The complexes di-μ-(2,10-dimethyl-6-oxa-3,9-dithiaundecane-κ^2S,S')-*bis*[*trans*-dichloropalladium (II)] and (acetylacetonate-κ^2O,O')(2,10-dimethyl-6-oxa-3,9-dithiaundecane-κ^2S,S')palladium (II) tetrafluoroborate were characterized by X-ray diffractometry. The X-ray structures of each complex indicate an axial M–O interaction formed by the endodentate conformation of the oxadithioether ligand. Palladium (II) dichloride complexes with oxadithioethers were demonstrated to have a 16-membered dinuclear structure with a *trans*-configured S_2PdCl_2 fragment. In the case of cationic palladium acetylacetonate complexes, only mononuclear complexes with a *cis* configuration of the oxadithioether fragment were observed. Variable temperature ^{1}H and ^{13}C NMR studies of the complexes demonstrate dynamic bonding of the oxadithioether ligands consistent with the presence of diastereoisomers that differ in the orientation of the S-R groups along with both endodentate and exodentate bonding modes in solution. FTIR studies of the complexes indicate the presence of isomers in the solid state. The palladium catalyst precursors *trans*-$[PdCl_2(\mu\text{-}L)]_2$ and $[Pd(acac)(L)][BF_4]$ were found to be active in the addition polymerization of norbornene. In the presence of cocatalysts, such as diisobutylaluminum chloride and boron trifluoride etherate, Pd (II) complexes exhibited activities in the range of 10^5 to 10^7 g of polymer (mol of Pd)$^{-1}$ h^{-1}. The catalyst systems

showed good thermostability with a high activity of 1.43×10^7 g of polymer (mol of Pd)$^{-1}$ h^{-1} at 75°C. These complexes are examples of Pd (II) complexes bearing thioether ligands, which are rarely observed in the field of olefin polymerization.

KEYWORDS

acetylacetonate, norbornene, palladium, polymerization, thioethers

1 | INTRODUCTION

Transition metal complexes with thioethers as ligands have been studied intensively for over five decades.[1–3] Among these complexes, particular attention has recently been given to palladium (II) complexes with sulfur-containing compounds, especially thiacrown ligands.[4–14] These compounds have interesting properties, including the stabilization of rare mononuclear trivalent oxidation states, C–H bond activation, anion recognition, photophysical properties, intermolecular π–π stacking motifs, and axial ligand–metal interactions in square planar complexes.[8,9,15–25] The last structural property for Pd (II) complexes are of theoretical interest, as these complexes may contain a weak bonding component and serve as important models in associative mechanisms for ligand substitution reactions in d^8 square planar complexes.[8,10]

Sulfur species are poisons for many catalytic processes; therefore, sulfur-containing compounds are not usually employed as ligands in transition metal-catalyzed reactions. In contrast to phosphorus, sulfur atoms in thioether ligands have only two substituents, which can create a less hindered environment.[3] Nevertheless, the application of palladium complexes with thioether ligands as precatalysts for allylic substitution, Suzuki–Miyaura coupling, and copolymerization of olefins with carbon monoxide has been reported.[3,13] Moreover, in recent years, various organic SNS-, SOS-, and SSS-type ligands have been shown to be useful in ethylene oligomerization catalyst systems based on chromium complexes.[26–30] In the past decades, palladium (II) catalysts for olefin (co)polymerization have attracted considerable attention in both the academic and industrial fields. This is mainly due to the great tolerance of palladium versus polar functional groups and their great reactivity toward polar comonomers.[31–35] However, Pd (II) complexes with bidentate oxadithioether ligands as catalysts for olefin polymerization have only rarely been applied. In previous research, our group reported the synthesis of various cationic acetylacetonate palladium complexes, as well their usage as efficient precursors for the polymerization of norbornene and its derivatives,[36–39] polymerization of phenylacetylene,[40] selective dimerization or hydroamination of vinylarenes,[39,41] and telomerization of butadiene with methanol.[42]

In this report, we describe the results of the synthesis of novel palladium complexes with SOS-type ligands *trans*-$[PdCl_2(\mu\text{-}L)]_2$ and $[Pd(acac)(L)][BF_4]$ (L = $RS(CH_2)_2O(CH_2)_2SR$, R = Me, Et, ^{n}Pr, ^{i}Pr, ^{n}Bu, ^{i}Bu, *n*-hexyl, benzyl). Sixteen new compounds were fully characterized, and crystal structures of [di-μ-(2,10-dimethyl-6-oxa-3,9-dithiaundecane-κ^2S,S')-bis [*trans*-dichloropalladium (II)] and (acetylacetonate-κ^2O,O')(2,10-dimethyl-6-oxa-3,9-dithiaundecane-κ^2S,S') palladium (II) tetrafluoroborate were determined by X-ray diffraction. Nuclear magnetic resonance (NMR) and infrared (IR) spectroscopic features of the prepared complexes are discussed. To examine the influence of the structural features of *trans*-$[PdCl_2(\mu\text{-}L)]_2$ and $[Pd(acac)(L)][BF_4]$ on their catalytic properties, the addition polymerization of norbornene with these complexes was also investigated in the presence of $BF_3{\cdot}OEt_2$ or Al^iBu_2Cl.

2 | EXPERIMENTAL SECTION

2.1 | General procedures and materials

All air- and/or moisture-sensitive compounds were manipulated by using standard high-vacuum line, Schlenk, or cannula techniques under an argon atmosphere. Argon (Arnika-Prom-Service) was purified before feeding to the reactor by passing through columns packed with oxygen scavenger and molecular sieve 4A (Aldrich). Diethyl ether, petroleum ether, and toluene (ZAO Vekton) were distilled from sodium−benzophenone. CH_2Cl_2 (ZAO Vekton), CH_3CN (ZAO Vekton), and methanol (ZAO Vekton) were distilled from CaH_2. Solvents were stored over molecular sieves. Other chemicals were obtained from Acros Organic, Sigma-Aldrich, or ABCR and employed without drying or any further purification. All glassware and steel reactors were dried for at least 3 h in a 150°C oven and cooled under an argon atmosphere.

$Pd(acac)_2$ was synthesized according to a published procedure[43] and recrystallized from acetone. The complexes $[Pd(acac)(MeCN)_2]BF_4$ and $Pd(cod)Cl_2$ were prepared according to published procedures.[39,40,44] 5-methoxycarbonylnorbornene was synthesized in stainless steel autoclave by the Diels–Alder reactions of dicyclopentadiene with methyl acrylate ($t = 180°C$, 6 h). The crude products were twice distilled over CaH_2 under argon. The mononomer *endo/exo*ratios were determined by GC. All other reagents were obtained commercially and used as received. All NMR spectra were recorded at room temperature on a Bruker DPX-400 spectrometer. IR spectra were recorded on a Simex Infralum FT 801 spectrometer. HPLC analyses were performed on a Thermo-Dionex HPLC system. GC-FID and GC–MS analyses were performed on Chromatec Crystall 5000.2 (SGE BPX-5 capillary column, benzene internal standard) and Shimadzu QP2010 Ultra (GSBP-5 MS capillary column), respectively. TGA/DSC measurements were performed with a Netzsch STA 449-F3 instrument with crucibles made of aluminum (sample masses were in the range of 3–4 mg) at a heating rate of 10 K/min in nitrogen atmosphere.

2.2 | Synthesis of ligands

Attention! These experimental methods for ligand synthesis carry the risk of producing mustard analogs. We have not studied the biological activity and toxicological properties of the substances. During the synthesis process and further use of these compounds, it is necessary to take appropriate precautions: use personal protective equipment for hands and respiratory organs, and all manipulations with these substances should be carried out in a fume hood. If these substances come in contact with exposed skin, rinse immediately with plenty of cold water and seek medical attention.

2.2.1 | General procedure for the synthesis of 5-oxa-2,8-dithianonane (**L1**) and 6-oxa-3,9-dithiaundecane (**L2**)[45]

KOH solution in hydrazine hydrate and R_2S_2 (molar ratio $KOH:R_2S_2 = 5:1$) was stirred for 4 h at 90°C. The reaction mixture was cooled to 25°C, and an equimolar amount of bis(2-chloroethyl) ether was added dropwise. The resulting mixture was stirred for 2 h at 90°C. The reaction product was extracted with diethyl ether (2 × 50 ml), and the extract was dried over $CaCl_2$. The solvent was removed under reduced pressure. The residue was distilled in a vacuum.

L1: Yield: 68%. $T_b = 90–92°C$ (2 mmHg). ^1H NMR (400 MHz, $CDCl_3$, 25°C): δ 3.65 (t, 4H), 2.68 (t, 4H), 2.14 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25°C): δ 70.35, 33.61, 16.12. IR (liquid film, KBr plates, cm^{-1}): 2956 ν_{as}(C–H from S-CH_3); 2916 ν_{as}(C–H from S-CH_2 and O-CH_2) and ν_s(C–H from S-CH_3); 2861 ν_s(C–H from S-CH_2 and O-CH_2); 1436 δ_{as}(C–H from S-CH_3); 1428 δ (HCH from O-CH_2, scissoring); 1406 δ (HCH from S-CH_2, scissoring); 1358 δ (CCH from O-*CH_2*-CH_2, wagging) with δ (HCH from S-CH_2, scissoring); 1321 δ_s(C–H from S-CH_3); 1288, 1233 δ (CCH from S-*CH_2*-CH_2, wagging) with δ (CCH from O-*CH_2*-CH_2, twisting); 1204, 1193 δ (CCH from S-*CH_2*-CH_2 and O-*CH_2*-CH_2, twisting); 1109 ν_{as}(C–O–C); 1042 ν(*C*–*C*–O); 959 ν_s(C–O–C) and δ(C–H from S–CH_3, rocking, not the main contribution); 857 δ(C–H from S–CH_3, rocking) and skeletal stretching vibrations; 815, 773, 724 δ(C–H from S-CH_2-CH_2-O, rocking); 700 ν_{as}(C–S–C); 660 ν_s(C–S–C).

L2: Yield: 72%. $T_b = 80–82°C$ (1 mmHg). ^1H NMR (400 MHz, $CDCl_3$, 25°C): δ 3.61 (t, 4H), 2.70 (t, 4H), 2,56 (m, 4H), 1.24 (t, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25°C): δ 70.54, 30.87, 26.26, 14.73. IR (liquid film, KBr plates, cm^{-1}): 2963 ν_{as}(C–H from CH_3); 2924 ν_{as}(C–H from S-CH_2 and O-CH_2); 2868 ν_s(C–H from CH_3) and ν_s(C–H from S-CH_2 and O-CH_2); 1453 δ_{as}(C–H from C-CH_3); 1426 δ (HCH from O-CH_2, scissoring); 1405 δ (HCH from S-CH_2, scissoring); 1374 δ_s(C–H from C-CH_3); 1357 δ (CCH from O-CH_2-C, wagging) with δ (HCH from S-CH_2, scissoring); 1294 δ (CCH from S-*CH_2*-CH_2, wagging) with δ (CCH from O-*CH_2*-CH_2, twisting); 1266 δ (CCH from S-*CH_2*-CH_3, wagging); 1235 δ (CCH from O-*CH_2*-CH_2, twisting) with δ (CCH from S-*CH_2*-CH_2, wagging); 1203, 1195 δ (CCH from S-*CH_2*-CH_2 and O-*CH_2*-CH_2, twisting); 1107 ν_{as}(C–O–C); 1063 ν(*C*–*C*–O); 1043, 1002 ν_s(C–O–C); 974 ν(*C*–*C*–S from S-CH_2-CH_3) and δ(C–H from CH_3, rocking); 783, 754 δ(C–H from S-CH_2-CH_2-O, rocking); 694 ν_{as}(C–S–C); 656 ν_s(C–S–C).

2.2.2 | General procedure for the synthesis of dithioether ligands **L3**–**L8**

To an ethanol (95%) solution of RSH and KOH (molar ratio 1:1), an equimolar amount of bis(2-chloroethyl) ether (10% solution in EtOH) was added dropwise for 30 min. The reaction mixture was stirred for 3 h at 80°C. The reaction mixture was cooled to 25°C and later neutralized using H_2SO_4. All volatiles were removed under reduced pressure. The product was extracted with diethyl ether (2 × 50 ml), and the extract was dried over $CaCl_2$. The solvent was removed, and the residue was distilled in a vacuum.

7-oxa-4,10-dithiatridecane (**L3**): Yield: 89%. T_b = 119–120°C (1.5 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 3.62 (t, 4H), 2.70 (t, 4H), 2.54 (m, 4H), 1.61 (m, 4H), 0.99 (t, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25°C): δ 70.81, 34.71, 31.50, 23.14, 13.48. IR (liquid film, KBr plates, cm^{-1}): 2960 ν_{as}(C–H from CH_3); 2927 ν_{as}(C–H from CH_2-groups); 2870 ν_s(C–H from CH_3) and ν_s(C–H from CH_2-groups); 1460 δ_{as}(C–H from C-CH_3) and δ (HCH from *CH_2*-CH_3, scissoring); 1424 δ (HCH from O-CH_2, scissoring); 1406 δ (HCH from S-CH_2, scissoring); 1376 δ_s(C–H from C-CH_3); 1357 δ (HCH from S-CH_2, scissoring) with δ (CCH from O-CH_2-C, wagging); 1289 δ (CCH from S-*CH_2*-CH_2, wagging) with δ (CCH from O-*CH_2*-CH_2, twisting) and δ (CCH from CH_2-*CH_2*-CH_3, wagging); 1235 δ (CCH from O-*CH_2*-CH_2, twisting) with δ (CCH from S-*CH_2*-CH_2, wagging); 1202, 1190 δ (CCH from S-*CH_2*-CH_2 and O-*CH_2*-CH_2, twisting) and δ (CCH from CH_2-*CH_2*-CH_3, twisting); 1109, 1100 (sh) ν_{as}(C–O–C); 1071 (sh), 1054 ν(*C–C*–O); 1035, 1009 ν_s(C–O–C); 969 (sh) ν(*C–C*–S from S-*CH_2*-*CH_2*-CH_3); 953 δ(C–H from CH_3, rocking); 896 ν(C–C from CH_2-CH_2-CH_3); 849 (sh), 835 skeletal stretching vibrations; 783, 740, 726 (sh) δ(C–H from CH_2-groups, rocking); 687 ν_{as}(C–S–C); 662, 649 ν_s(C–S–C).

2,10-dimethyl-6-oxa-3,9-dithiaundecane (**L4**): Yield: 92%. T_b = 117–119°C (2 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 3.62 (t, 4H), 2.73 (t, 4H), 2.97 (m, 2H), 1.27 (d, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25°C): δ 70.91, 35.26, 29.98, 23.52. IR (liquid film, KBr plates, cm^{-1}): 2959 ν_{as}(C–H from CH_3); 2924 ν_{as}(C–H from S-CH_2 and O-CH_2); 2896 (sh) ν(C–H from CH); 2866 ν_s(C–H from CH_3) and ν_s(C–H from S-CH_2 and O-CH_2); 1460, 1455(sh) δ_{as}(C–H from C-CH_3); 1427 δ (HCH from O-CH_2, scissoring); 1405 δ (HCH from S-CH_2, scissoring); 1382 and 1365 δ_s(C–H from C-CH_3, doublet); 1365 additional δ (HCH from S-CH_2, scissoring) with δ (CCH from O-CH_2-C, wagging); 1291 δ (CCH from S-*CH_2*-CH_2, wagging) with δ (CCH from O-*CH_2*-CH_2, twisting); 1244 δ (CCH from O-*CH_2*-CH_2, twisting) with δ (CCH from S-*CH_2*-CH_2, wagging); 1201, 1191 δ (CCH from S-*CH_2*-CH_2 and O-*CH_2*-CH_2, twisting); 1155 δ(C–H from CH_3, rocking); 1113 (sh), 1103 ν_{as}(C–O–C); 1055 ν(*C–C*–O); 1035, 1010 ν_s(C–O–C); 949 (sh) ν(*C–C*–S from S-*CH-(CH_3)$_2$*); 927 δ(C–H from CH_3, rocking); 882 ν(C–C–C from CH-(CH_3)$_2$); 768 δ(C–H from CH_2-groups, rocking); 698 (sh) and 683 ν_{as}(C–S–C); 645 (sh) and 635 ν_s(C–S–C).

8-oxa-5,11-dithiapentadecane (**L5**): Yield: 90%. T_b = 150–153°C (2 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 3.83 (t, 4H), 2.90 (t, 4H), 2.76 (t, 4H), 1.78 (m, 4H), 1.63 (m, 4H), 1.13 (t, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25°C): δ 71.21, 32.68, 32.30, 31.89, 22.37, 14.13. IR (liquid film, KBr plates, cm^{-1}): 2957 ν_{as}(C–H from CH_3); 2928 ν_{as}(C–H from CH_2-groups); 2870, 2862 (sh) ν_s(C–H from CH_3) and ν_s(C–H from CH_2-groups); 1463, 1440 (sh) δ_{as}(C–H from C-CH_3) and δ (HCH from *CH_2*-*CH_2*-CH_3, scissoring); 1424 δ (HCH from O-CH_2, scissoring); 1405 δ (HCH from S-CH_2, scissoring); 1378 δ_s(C–H from C-CH_3); 1357 δ (HCH from S-CH_2, scissoring) with δ (CCH from O-CH_2-C, wagging); 1290, 1275 δ (CCH from S-*CH_2*-CH_2, wagging) with δ (CCH from O-*CH_2*-CH_2, twisting) and δ (CCH from CH_2-*CH_2*-*CH_2*-CH_3, wagging); 1223 δ (CCH from CH_2-*CH_2*-*CH_2*-CH_3, twisting) and δ (CCH from O-*CH_2*-CH_2, twisting) with δ (CCH from S-*CH_2*-CH_2, wagging); 1203, 1192 (sh) δ (CCH from S-*CH_2*-CH_2 and O-*CH_2*-CH_2, twisting) and δ (CCH from CH_2-*CH_2*-*CH_2*-CH_3, twisting); 1110, 1100 (sh) ν_{as}(C–O–C); 1055 ν(*C–C*–O); 1036, 1014 ν_s(C–O–C); 968 ν(*C–C*–S from S-*CH_2*-*CH_2*-CH_2-CH_3); 950 (sh) δ(C–H from CH_3, rocking); 914, 877 ν(C–C–C from CH_2-CH_2-CH_2-CH_3); 785, 756, 745, 721 (sh) δ(C–H from CH_2-groups, rocking); 691 ν_{as}(C–S–C); 661 ν_s(C–S–C).

2,12-dimethyl-7-oxa-4,10-dithiatridecane (**L6**): Yield: 80%. T_b = 150–153°C (3.5 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 3.62 (t, 4H), 2.69 (t, 4H), 2.44 (d, 4H), 1.80 (m, 2H), 0.99 (d, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25°C): δ 70.80, 41.99, 32.15, 28.79, 22.03. IR (liquid film, KBr plates, cm^{-1}): 2956 ν_{as}(C–H from CH_3); 2926 ν_{as}(C–H from S-CH_2 and O-CH_2) and ν(C–H from CH); 2869 ν_s(C–H from CH_3) and ν_s(C–H from S-CH_2 and O-CH_2); 1464 δ_{as}(C–H from C-CH_3); 1428 δ (HCH from O-CH_2, scissoring); 1418 δ (HCH from S-CH_2 in *i*Bu, scissoring); 1405 (sh) δ (HCH from S-CH_2, scissoring); 1382 and 1365 δ_s(C–H from C-CH_3, doublet); 1365 additional δ (HCH from S-CH_2, scissoring) with δ (CCH from O-CH_2-C, wagging); 1334 δ(C–H from CH in *i*Bu); 1291 δ (CCH from S-*CH_2*-CH_2, wagging) with δ (CCH from O-*CH_2*-CH_2, twisting); 1247 δ (CCH from O-*CH_2*-CH_2, twisting) with δ (CCH from S-*CH_2*-CH_2, wagging); 1230 (sh) δ (CCH from S-*CH_2*-CH (CH_3)$_2$, twisting); 1204, 1191 δ (CCH from S-*CH_2*-CH_2 and O-*CH_2*-CH_2, twisting); 1168 δ(C–H from CH_3, rocking); 1108 ν_{as}(C–O–C); 1068 (sh) ν(*C–C*–O); 1037, 1015 ν_s(C–O–C); 945 ν(*C–C*–S from S-*CH_2*-*CH*-(CH_3)$_2$); 922 δ(C–H from CH_3, rocking); 859 ν(C–C–C from CH_2-CH-(CH_3)$_2$); 805,764, 735, 722 δ(C–H from CH_2-groups, rocking); 694 (sh) ν_{as}(C–S–C); 675 ν_s(C–S–C).

10-oxa-7,13-dithianonadecane (**L7**): Yield: 90%. T_b = 178–181°C (1 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 3.80 (t, 4H), 2.77 (t, 4H), 2.58 (t, 4H), 1.67 (m, 4H), 1.49 (m, 4H), 1.35 (m, 4H), 1.20 (m, 4H), 0.89 (t, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25°C): δ 71.52, 35.59, 34.22, 31.89, 28.31, 24.78, 22.35, 14.05. IR (liquid film, KBr plates, cm^{-1}): 2955 ν_{as}(C–H from CH_3); 2926 ν_{as}(C–H from CH_2-groups); 2870 (sh), 2856 ν_s(C–H from

CH_3) and ν_s(C–H from CH_2-groups); 1464, 1441 (sh) δ_{as}(C–H from C-CH_3) and δ (HCH from SCH_2-$(CH_2)_4$-CH_3, scissoring); 1424 δ (HCH from O-CH_2, scissoring); 1405 δ (HCH from S-CH_2, scissoring); 1377 δ_s(C–H from C-CH_3); 1356 δ (HCH from S-CH_2, scissoring) with δ (CCH from O-CH_2-C, wagging); 1287, 1260 δ (CCH from S-CH_2-CH_2, wagging) with δ (CCH from O-CH_2-CH_2, twisting) and δ (CCH from SCH_2-$(CH_2)_4$-CH_3, wagging); 1240 δ (CCH from SCH_2-$(CH_2)_4$-CH_3, twisting); 1206, 1190 (sh) δ (CCH from S-CH_2-CH_2 and O-CH_2-CH_2, twisting) and δ (CCH from SCH_2-$(CH_2)_4$-CH_3, twisting); 1109 ν_{as}(C–O–C); 1057 (sh) ν(C–C–O); 1037, 1007 (sh) ν_s(C–O–C); 962 (sh) ν(C–C–S from S-CH_2-CH_2-$(CH_2)_3$-CH_3) and δ(C–H from CH_3, rocking); 923, 890, 873, 857 ν(C–C–C from CH_2-$(CH_2)_4$-CH_3); 804 (sh), 760, 720 δ(C–H from CH_2-groups, rocking); 690 (sh) ν_{as}(C–S–C); 664 ν_s(C–S–C).

5-oxa-1,9-diphenyl-2,8-dithianonane (**L8**): Yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 7.30–7.22 (m, 10H), 3.73 (s, 4H), 3.51 (t, 4H), 2.57 (t, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25°C): δ 138.32, 128.88, 128.46, 127.00, 70.00, 36.61, 33.23. IR (liquid film, KBr plates, cm^{-1}): 3101 (sh), 3083, 3060, 3027, 3005 (sh) ν(C–H from Ph); 2950 ν_{as}(C–H from S-CH_2-Ph); 2916 ν_{as}(C–H from S-CH_2 and O-CH_2); 2858 ν_s(C–H from S-CH_2 and O-CH_2) and ν_s(C–H from S-CH_2-Ph); 1601, 1584 ν_{as}(C=C from Ph); 1493 ν_{as}(C=C from Ph) and δ (CCH from Ph); 1472 δ (HCH from S-CH_2-Ph, scissoring); 1453 δ (CCH from Ph) and ν_{as}(C=C from Ph); 1423 δ (HCH from O-CH_2, scissoring); 1404 δ (HCH from S-CH_2, scissoring); 1357 δ (HCH from S-CH_2, scissoring) with δ (CCH from O-CH_2-CH_2, wagging) and δ (CCH from S-CH_2-Ph, wagging); 1335 (weak), 1319 δ (CCH from Ph, plane); 1291 δ (CCH from S-CH_2-CH_2, wagging) with δ (CCH from O-CH_2-CH_2, twisting); 1239 δ (CCH from S-CH_2-Ph, twisting) and δ (CCH from S-CH_2-CH_2, twisting); 1200 δ (CCH from O-CH_2-CH_2 and S-CH_2-CH_2, twisting); 1185, 1154, 1146, 917 δ (CCH from Ph, plane); 1108 ν_{as}(C–O–C); 1073 ν(C–C–O) and δ (CCH from Ph, plane); 1028 ν_s(C–O–C) and δ (CCH from Ph, plane); 1040 (sh), 1018 (sh) ν_s(C–O–C); 1004 (sh) ν_s(C=C from Ph) with δ (CCH from Ph, plane) and ring deformations; 958 ν(C_{Ar}–C–S); 877 ν(C–C–S from S-CH_2-CH_2-O) and skeletal stretching vibrations; 845 δ (CCH from Ph, off-plane); 818, 804 skeletal stretching vibrations and δ(C–H from S-CH_2-CH_2-O, rocking); 767, 701 δ (CCH from Ph, off-plane) and δ(C–H from S-CH_2-CH_2-O, rocking); 676 (sh) ν_{as}(C–S–C); 655 (sh) ν_s(C–S–C); 620, 564 ring deformations (off-plane).

Further spectroscopic details are given in Figures S41–S50, S60–S67, and S107–S111 (see electronic supporting information file, SI).

2.3 | Synthesis of palladium complexes

The preparation of di-μ-(5-oxa-2,8-dithianonane-κ^2*S*,*S*′)-bis[*trans*-dichloropalladium (II)] (**1a**) was as follows. 5-Oxa-2,8-dithianonane (115 mg, 0.10 ml, 0.692 mmol) was dissolved in 10 ml of CH_2Cl_2, and $PdCl_2$(cod) (144 mg, 0.500 mmol) was added, forming an orange solution. The reaction mixture was stirred for 1.5 h at room temperature. The resulting yellow solution was concentrated to approximately 3 ml under vacuum. The addition of diethyl ether (10 ml) resulted in an orange oily precipitate, which was collected, washed with diethyl ether (2 × 10 ml), and dried (8 h) under vacuum to produce complex **1a** as a yellow powder (91 mg, 53%). Anal. Calcd for $C_6H_{14}Cl_2OPdS_2$: C, 20.97; H, 4.11; S, 18.66. Found: C, 20.24; H, 4.58; S, 17.66. Electrospray ionisation mass spectrometry (ESI-MS) (positive ion mode, MeCN): *m/z* 308.92 [$M^+ - Cl$]. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 4.15 (t, $J = 6.3$ Hz, 4H, CH_2O), 3.07 (t, $J = 6.3$ Hz, 4H, CH_2S), 2.39 (s, 6H, CH_3S). ^{1}H NMR (400 MHz, DMSO-d_6, 80°C): δ 3.82 (s, br, 4H, CH_2O), 2.94 (s, br, 4H, CH_2S), 2.29 (s, br, 6H, CH_3S). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 80°C): δ 67.87 (s, CH_2O), 35.54 (s, CH_2S), 17.50 (s, CH_3S). IR (KBr disk, cm^{-1}): 3009, 2986 ν_{as}(C–H from S-CH_3); 2919 ν_{as}(C–H from S-CH_2 and O-CH_2) and ν_s(C–H from S-CH_3); 2888 ν_s(C–H from S-CH_2); 2865 ν_s(C–Hfrom O-CH_2); 1478, 1464 δ_{as}(C–H from S-CH_3); 1423 δ (HCH from O-CH_2, scissoring); 1407 δ (HCH from S-CH_2, scissoring); 1357 δ (CCH from O-CH_2-CH_2, wagging) with δ (HCH from S-CH_2, scissoring); 1318 δ_s(C–H from S-CH_3); 1295, 1284 (sh), 1234 δ (CCH from S-CH_2-CH_2, wagging) with δ (CCH from O-CH_2-CH_2, twisting); 1202 (sh), 1189 δ (CCH from S-CH_2-CH_2 and O-CH_2-CH_2, twisting); 1125, 1107 (sh) ν_{as}(C–O–C); 1069, 1057, 1041ν(C–C–O); 964, 950 ν_s(C–O–C); 857 δ(C–H from S–CH_3, rocking) and skeletal stretching vibrations; 783, 734 δ(C–H from S-CH_2-CH_2-O, rocking); 655 ν_{as}(C–S–C); 640 ν_s(C–S–C).

The preparation of (acetylacetonate-κ^2*O*,*O*′)(5-oxa-2,8-dithianonane-κ^2*S*,*S*′)palladium (II) tetrafluoroborate (**1b**) was as follows. [Pd (acac)$(MeCN)_2$]BF_4 (185 mg, 0.495 mmol) was dissolved in 15 ml of CH_2Cl_2, and 5-oxa-2,8-dithianonane (1 ml of solution (0.495 M), 0.495 mmol) was added to this solution, forming an orange solution. The reaction mixture was stirred for 1.0 h at room temperature. The resulting orange solution was concentrated to approximately 3 ml under vacuum. The addition of diethyl ether (15 ml) resulted in an orange precipitate, which was collected, washed with diethyl ether (2 × 10 ml), and dried (8 h) under vacuum to produce complex **1b** as an orange powder (177 mg, 78%). The product contained traces (< 2%) of Et_2O by ^{1}H NMR analysis. Anal. Calcd for $C_{11}H_{21}BF_4O_3PdS_2$: C,

28.81; H, 4.62; S, 13.98. Found: C, 29.02; H, 4.65; S, 14.51. ESI-MS (positive ion mode, MeCN): *m/z* 370.99 [M^+]. ^{1}H NMR (400 MHz, CD_3CN, 25°C): δ 5.67 (s, 0.15H, CH_{acac}), 5.66 (s, 0.85H, CH_{acac}), 4.3–3.5 (m, 4H, CH_2O), 3.09 (t, br, $J \approx 12$ Hz, 2H, H^a, CH_2S), 2.84 (d, br, $J = 12.9$ Hz, 2H, H^a, CH_2S), 2.4–2.2 (m, 6H, CH_3S), 2.12 (s, 0.9H, C$H_{3,acac}$). 2.11 (s, 5.1H, C$H_{3,acac}$). ^{13}C{^{1}H} NMR (101 MHz, CD_3CN, 25°C): δ 187.24 (s, $C_{CO\text{-}acac}$), 187.21 (s, minor isomer signal, hereinafter referred to as "minor"), $C_{CO\text{-}acac}$), 100.96 (s, $C_{CH\text{-}acac}$), 100.83 (s, minor, $C_{CH\text{-}acac}$), 66.86 (s, minor, *C*H_2O), 66.46(s, *C*H_2O), 65.33 (s, minor, *C*H_2O), 39.61(s, *C*H_2S), 39.37 (s, minor, *C*H_2S), 25.70 (s, minor, $C_{Me\text{-}acac}$), 25.62 (s, $C_{Me\text{-}acac}$), 18.20 (s, minor, *C*H_3S), 16.69 (s, minor, *C*H_3S), 14.59 (s, *C*H_3S). IR (film, KBr plate, cm^{-1}): 3109 ν(C–H from CH in acac); 3015 ν_{as}(C–H from S-CH_3); 2931 ν_{as}(C–H from S-CH_2-CH_2-O), ν_s(C–H from S-CH_3) and ν_{as}(C–H from CH_3 in acac); 2872 ν_s(C–H from S-CH_2-CH_2-O); 1561 ν(C=O and C=C in acac); 1521 ν(C=C and C=O in acac); 1475 δ_{as}(C–H from S-CH_3 and C-CH_3 in acac); 1425 δ (HCH from S-*C*H_2-*C*H_2-O, scissoring) and δ(C–H from CH in acac, plane); 1369 δ_s(C–H from C-CH_3 in acac) and δ (CCH from O-*C*H_2-CH_2, wagging) with δ (HCH from S-CH_2, scissoring); 1322 δ_s(C–H from S-CH_3); 1277 δ (CCH from S-*C*H_2-CH_2, wagging) with δ (CCH from O-*C*H_2-CH_2, twisting); 1243 (sh) acac-chelate deformations; 1202 δ (CCH from S-*C*H_2-CH_2 and O-*C*H_2-CH_2, twisting); 1100 ν_{as}(B–F) and ν_{as}(C–O–C); 1056 ν_{as}(B–F) and ν(*C*–*C*–O); 1034 ν_{as}(B–F) and ν(*C*–*C*–O) and δ(C–H from CH_3 in acac, rocking) and acac-chelate deformations; 974 ν_s(C–O–C); 940 acac-chelate deformations and ν_{as}(C–CH_3 in acac); 866 δ(C–H from S–CH_3, rocking) and ν(*C*–*C*–S, from S-CH_2-CH_2-O) with skeletal stretching vibrations; 815 δ(C–H from CH in acac, off-plane) and δ(C–H from S-CH_2-CH_2-O, rocking); 790 ν_s(B–F) and δ(C–H from S-CH_2-CH_2-O, rocking); 766, 731 δ(C–H from S-CH_2-CH_2-O, rocking); 694 ν_{as}(C–S–C); 663 acac-chelate deformations and ν_s(C–CH_3 in acac); 636 ν_s(C–S–C).

The preparation of di-μ-(6-oxa-3,9-dithiaundecane-κ^2S,S')-bis[*trans*-dichloropalladium (II)] (**2a**) was as follows. 6-Oxa-3,9-dithiaundecane (100 mg, 0.10 ml, 0.515 mmol) was dissolved in 5 ml of CH_2Cl_2, and $PdCl_2$(cod) (143 mg, 0.502 mmol) was added, forming an orange solution. The reaction mixture was stirred for 3 h at room temperature. The resulting orange suspension was concentrated to approximately 3 ml under vacuum. The addition of diethyl ether (15 ml) resulted in a yellow precipitate, which was collected, washed with diethyl ether (2 × 10 ml), and dried (8 h) under vacuum to produce complex **2a** as a yellow powder (150 mg, 80%). Anal. Calcd for $C_8H_{18}Cl_2OPdS_2$: C, 25.85; H, 4.88; S, 17.25. Found: C, 25.87; H, 4.87; S, 16.82. ESI-MS (positive ion mode, MeCN): *m/z* 336.95 [$M^+ - Cl$]. ^{1}H NMR (400 MHz, DMSO-d_6, 90°C): δ 3.76 (s, br, 4H, CH_2O), 2.88 (s, br, 4H, CH_2S), 2.74 (q, br, $J = 7.4$ Hz, 4H, CH_2S) 1.30 (t, $J = 7.3$ Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 90°C): δ 69.25 (s, *C*H_2O), 34.48 (s, br, *C*H_2S), 29.33 (s, br, *C*H_2S), 14.18 (s, *C*H_3). IR (KBr disk, cm^{-1}): 2974, 2967 ν_{as}(C–H from CH_3); 2933 ν_{as}(C–H from S-CH_2); 2921 (sh) ν_{as}(C–H from O-CH_2); 2885 ν_s(C–H from CH_3); 2866 ν_s(C–H from S-CH_2); 2856 (sh) ν_s(C–H from O-CH_2); 1465 (sh), 1451 δ_{as}(C–H from C-CH_3); 1418 δ (HCH from O-CH_2, scissoring) and δ (HCH from S-CH_2, scissoring); 1377 δ_s(C–H from C-CH_3); 1359 δ (HCH from S-CH_2, scissoring) with δ (CCH from O-CH_2-C, wagging); 1291 δ (CCH from S-*C*H_2-CH_2, wagging) with δ (CCH from O-*C*H_2-CH_2, twisting); 1267 δ (CCH from S-*C*H_2-CH_3, wagging); 1235 δ (CCH from O-*C*H_2-CH_2, twisting) with δ (CCH from S-*C*H_2-CH_2, wagging); 1202, 1192 δ (CCH from S-*C*H_2-CH_2 and O-*C*H_2-CH_2, twisting); 1120 ν_{as}(C–O–C); 1073, 1053 ν(*C*–*C*–O); 1023, 1011 ν_s(C–O–C); 974, 963 ν(*C*–*C*–S from S-CH_2-CH_3) and δ(C–H from CH_3, rocking); 860 ν(*C*–*C*–S from S-*C*H_2-*C*H_2-O) and skeletal stretching vibrations; 779, 768, 757 δ(C–H from S-CH_2-CH_2-O, rocking); 686 ν_{as}(C–S–C); 627 ν_s(C–S–C).

The preparation of (acetylacetonate-κ^2O,O')(6-oxa-3,9-dithiaundecane-κ^2S,S')palladium (II) tetrafluoroborate (**2b**) was as follows. [Pd (acac)$(MeCN)_2$]BF_4 (140 mg, 0.375 mmol) was dissolved in 19 ml of CH_2Cl_2, and 6-oxa-3,9-dithiaundecane (0.8 ml of solution (0.470 M), 0.375 mmol) was added, forming an orange solution. The reaction mixture was stirred for 3.0 h at room temperature. The resulting orange solution was concentrated to approximately 3 ml under vacuum. The addition of diethyl ether (15 ml) resulted in an orange oily precipitate, which was collected, washed with diethyl ether (2 × 10 ml), and dried (8 h) under vacuum to produce complex **2b** as an orange oil (162 mg, 89%). Anal. Calcd for $C_{13}H_{25}BF_4O_3PdS_2$: C, 32.08; H, 5.18; S, 13.18. Found: C, 31.96; H, 5.21; S, 13.22. ^{1}H NMR (400 MHz, CD_3CN, 25°C): δ 5.71 (s, 0.2H, CH_{acac}), 5.68 (s, 0.8H, CH_{acac}), 4.4–3.5 (m, 4H, CH_2O), 3.3–2.9 (m, 4H, CH_2S), 2.9–2.5 (m, 4H, CH_2S), 2.14 (s, 1.4H, C$H_{3,acac}$). 2.12 (s, 4.6H, C$H_{3,acac}$), 1.5–1.3 (m, 6H, CH_3). ^{13}C{^{1}H} NMR (101 MHz, CD_3CN, 25°C): δ 187.25 (s, $C_{CO\text{-}acac}$), 187.22 (s, minor, $C_{CO\text{-}acac}$), 100.78 (s, $C_{CH\text{-}acac}$), 67.15 (s, *C*H_2O), 66.65 (s, minor, *C*H_2O), 38.26 (s, br, *C*H_2S), 29.99(s, br, *C*H_2S), 25.72 (s, minor, $C_{Me\text{-}acac}$), 25.67 (s, $C_{Me\text{-}acac}$), 12.46 (s, *C*H_3), 11.86 (s, minor, *C*H_3). IR (film, KBr plate, cm^{-1}): 3108 ν(C–H from CH in acac); 2971 ν_{as}(C–H from CH_3); 2934 ν_{as}(C–H from S-CH_2-CH_2-O) and ν_{as}(C–H from CH_3 in acac); 2873 ν_s(C–H from S-CH_2-CH_2-O); 1560 ν(C=O and C=C in acac); 1521 ν(C=C and C=O in acac); 1473 (sh), 1453 δ_{as}(C–H from C-CH_3); 1428 δ (HCH from S-*C*H_2-*C*H_2-O, scissoring) and

δ(C–H from CH in acac, plane); 1367 δ_s(C–H from C-CH_3) and δ (CCH from O-CH_2-CH_2, wagging) with δ (HCH from S-CH_2, scissoring); 1294, 1276 δ (CCH from S-CH_2-CH_2, wagging) with δ (CCH from O-CH_2-CH_2, twisting); 1244 (sh) acac-chelate deformations; 1199, 1186 (sh) δ (CCH from S-CH_2-CH_2 and O-CH_2-CH_2, twisting); 1101 ν_{as}(B–F) and ν_{as}(C–O–C); 1057 ν_{as}(B–F) and ν(*C*–*C*–O); 1034 ν_{as}(B–F) and ν_s(C–O–C) and δ(C–H from CH_3 in acac, rocking) and acac-chelate deformations; 980 ν(*C*–*C*–S from S-CH_2-CH_3) and δ(C–H from CH_3, rocking); 940 acac-chelate deformations and ν_{as}(C–CH_3 in acac); 864 ν(*C*–*C*–S, from S-CH_2-CH_2-O) and skeletal stretching vibrations; 817 δ(C–H from CH in acac, off-plane) and δ(C–H from S-CH_2-CH_2-O, rocking); 782 ν_s(B–F) and δ(C–H from S-CH_2-CH_2-O, rocking); 733 δ(C–H from S-CH_2-CH_2-O, rocking); 693 ν_{as}(C–S–C); 680, 666 acac-chelate deformations and ν_s(C–CH_3 in acac); 636 ν_s(C–S–C).

The preparation of di-μ-(7-oxa-4,10-dithiatridecane-κ^2S,S')-bis[*trans*-dichloropalladium (II)] (**3a**) was as follows. 7-Oxa-4,10-dithiatridecane (88 mg, 0.394 mmol) was dissolved in 11 ml of CH_2Cl_2, and $PdCl_2$(cod) (112 mg, 0.392 mmol) was added, forming a yellow suspension. The reaction mixture was stirred for 3 h at room temperature. The resulting yellow solution was concentrated to approximately 2 ml under vacuum. The addition of diethyl ether (20 ml) resulted in a yellow precipitate, which was collected, washed with diethyl ether (2 × 10 ml), and dried (8 h) under vacuum to produce complex **3a** as a yellow powder (113 mg, 72%). Anal. Calcd for $C_{10}H_{22}Cl_2OPdS_2$: C, 30.05; H, 5.55; S, 16.04. Found: C, 30.86; H, 5.55; S, 15.78. ESI-MS (positive ion mode, MeCN): *m/z* 364.98 [M^+ − Cl]. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 4.20 (t, $J = 6.6$ Hz, 3.2H, CH_2O), 4.04 (t, $J = 6.1$ Hz, 0.8H, CH_2O), 3.05 (t, br, overlapping, $J \approx 6.0$ Hz, 0.9H, CH_2S), 2.99 (t, $J = 6.6$ Hz, 3.1H, CH_2S), 2.84 (m, br, 4H, CH_2S), 1.80 (h, $J = 7.4$ Hz, 4H, CH_2), 1.05 (t, $J = 7.4$ Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25°C): δ 69.80 (s, *C*H_2O), 69.22 (s, minor, *C*H_2O), 38.78 (s, minor, *C*H_2S), 38.16 (s, *C*H_2S), 35.96 (s, minor, *C*H_2S), 35.61 (s, minor, *C*H_2S), 21.85 (s, minor, *C*H_2), 21.51 (s, *C*H_2), 13.54 (s, minor, *C*H_3), 13.44 (s, *C*H_3). IR (KBr disk, cm^{-1}): 2964 ν_{as}(C–H from CH_3); 2929 ν_{as}(C–H from CH_2-groups); 2870 ν_s(C–H from CH_3) and ν_s(C–H from CH_2-groups); 1459 δ_{as}(C–H from C-CH_3) and δ (HCH from *C*H_2-CH_3, scissoring); 1415 δ (HCH from O-CH_2, scissoring); 1405 δ (HCH from S-CH_2, scissoring); 1380 δ_s(C–H from C-CH_3); 1360 δ (HCH from S-CH_2, scissoring) with δ (CCH from O-CH_2-C, wagging); 1340 δ (CCH from CH_2-*C*H_2-CH_3, wagging); 1293 δ (CCH from S-*C*H_2-CH_2, wagging) with δ (CCH from O-*C*H_2-CH_2, twisting) and δ (CCH from CH_2-*C*H_2-CH_3, wagging); 1240 δ (CCH from O-*C*H_2-CH_2, twisting) with δ (CCH from S-*C*H_2-CH_2, wagging) and δ (CCH from CH_2-*C*H_2-CH_3, twisting); 1202, 1184 δ (CCH from S-*C*H_2-CH_2 and O-*C*H_2-CH_2, twisting) and δ (CCH from CH_2-*C*H_2-CH_3, twisting); 1112, 1098 (sh) ν_{as}(C–O–C); 1078 (sh), 1061 ν(*C*–*C*–O); 1040, 1021 ν_s(C–O–C); 985 ν(*C*–*C*–S from S-*C*H_2-*C*H_2-CH_3); 964 δ(C–H from CH_3, rocking); 901 ν(C–C from CH_2-CH_2-CH_3); 859 ν(*C*–*C*–S from S-*C*H_2-*C*H_2-O) and skeletal stretching vibrations; 787, 739 δ(C–H from CH_2-groups, rocking); 672 (sh), 659 ν_{as}(C–S–C); 622 ν_s(C–S–C).

The preparation of (acetylacetonate-κ^2O,O')(7-oxa-4,10-dithiatridecane-κ^2S,S')palladium (II) tetrafluoroborate (**3b**) was as follows. [Pd (acac)$(MeCN)_2$]BF_4 (133 mg, 0.356 mmol) was dissolved in 16.5 ml of CH_2Cl_2, and 7-oxa-4,10-dithiatridecane (0.8 ml of solution (0.446 M), 0.356 mmol) was added, forming a yellow solution. The reaction mixture was stirred for 3.0 h at room temperature. The resulting yellow solution was concentrated to approximately 4 ml under vacuum. The addition of diethyl ether (25 ml) resulted in a yellow precipitate, which was collected, washed with diethyl ether (2 × 10 ml), and dried (8 h) under vacuum to produce complex **3b** as a yellow powder (121 mg, 66%). Anal. Calcd for $C_{15}H_{29}BF_4O_3PdS_2$: C, 35.00; H, 5.68; S, 12.46. Found: C, 34.61; H, 5.67; S, 11.87. ESI-MS (positive ion mode, MeCN): *m/z* 427.06 [M^+]. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 5.57 (s, 0.4H, CH_{acac}), 5.54 (s, 0.6H, CH_{acac}), 4.5–3.5 (m, 4H, CH_2O), 3.4–2.9 (m, 4H, CH_2S), 2.9–2.4 (m, 4H, CH_2S), 2.13 (s, 2.4H, C$H_{3,acac}$), 2.09 (s, 3.6H, C$H_{3,acac}$), 1.09 (dt, $J = 7.3$ Hz, 6H, *C*H_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25°C): δ 187.05 (s, minor, $C_{CO\text{-}acac}$), 186.68 (s, $C_{CO\text{-}acac}$), 101.39 (s, minor, $C_{CH\text{-}acac}$), 101.28 (s, $C_{CH\text{-}acac}$), 67.46 (s, br, *C*H_2O), 66.60 (s, minor, *C*H_2O), 37.08 (s, br, *C*H_2S), 36.85 (s, br, *C*H_2S), 36.20 (s, br, *C*H_2S), 33.98 (s, br, *C*H_2S), 26.71 (s, minor, $C_{Me\text{-}acac}$), 26.61 (s, $C_{Me\text{-}acac}$), 21.71 (br, *C*H_2), 21.20 (s, br, *C*H_2), 13.52 (s, minor, *C*H_3), 13.38 (s, *C*H_3). IR (film, KBr plate, cm^{-1}): 3106 ν(C–H from CH in acac); 2965 ν_{as}(C–H from CH_3); 2934 ν_{as}(C–H from CH_2-groups) and ν_{as}(C–H from CH_3 in acac); 2870 ν_s(C–H from CH_3) and ν_s(C–H from CH_2-groups); 1561 ν(C=O and C=C in acac); 1521 ν(C=C and C=O in acac); 1478 (sh), 1461 δ_{as}(C–H from C-CH_3) and δ (HCH from *C*H_2-CH_3, scissoring); 1426 δ (HCH from O-CH_2 and S-CH_2, scissoring) and δ(C–H from CH in acac, plane); 1368 δ_s(C–H from C-CH_3) and δ (CCH from O-*C*H_2-CH_2, wagging) with δ (HCH from S-CH_2, scissoring); 1294 (sh), 1276 δ (CCH from S-*C*H_2-CH_2, wagging) with δ (CCH from O-*C*H_2-CH_2, twisting) and δ (CCH from CH_2-*C*H_2-CH_3, wagging); 1247 (sh) acac-chelate deformations and δ (CCH from O-*C*H_2-CH_2, twisting) with δ (CCH from S-*C*H_2-CH_2, wagging) and δ (CCH from CH_2-*C*H_2-CH_3, twisting); 1200, 1186 δ (CCH from S-*C*H_2-CH_2 and O-*C*H_2-CH_2, twisting) and

δ (CCH from CH_2-CH_2-CH_3, twisting); 1102 ν_{as}(B–F) and ν_{as}(C–O–C); 1054 ν_{as}(B–F) and ν(*C*–*C*–O); 1034 ν_{as}(B–F) and ν_s(C–O–C) and δ(C–H from CH_3 in acac, rocking) and acac-chelate deformations; 963 ν(*C*–*C*–S from S-CH_2-CH_2-CH_3) and δ(C–H from CH_3, rocking); 940 acac-chelate deformations and ν_{as}(C–CH_3 in acac); 904 ν(C–C from CH_2-CH_2-CH_3); 869 (sh) ν(*C*–*C*–S from S-CH_2-CH_2-O) and skeletal stretching vibrations; 817 δ(C–H from CH in acac, off-plane) and δ(C–H from S-CH_2-CH_2-O, rocking); 789 ν_s(B–F) and δ(C–H from S-CH_2-CH_2-O, rocking); 765, 744 δ(C–H from CH_2-groups, rocking); 693 ν_{as}(C–S–C); 664 acac-chelate deformations and ν_s(C–CH_3 in acac); 636 ν_s(C–S–C).

The preparation of di-μ-(2,10-dimethyl-6-oxa-3,9-dithiaundecane-κ^2S,S')-bis[*trans*-dichloropalladium (II)] (**4a**) was as follows. 2,10-Dimethyl-6-oxa-3,9-dithiaundecane (97 mg, 0.436 mmol) was dissolved in 10 ml of CH_2Cl_2, and $PdCl_2$(cod) (124 mg, 0.434 mmol) was added, forming an orange solution. The reaction mixture was stirred for 2 h at room temperature. The resulting yellow solution was concentrated to approximately 3 ml under vacuum. The addition of diethyl ether (16 ml) resulted in a yellow precipitate, which was collected, washed with diethyl ether (2 × 10 ml), and dried (8 h) under vacuum to produce complex **4a** as a yellow powder (154 mg, 89%). Anal. Calcd for $C_{10}H_{22}Cl_2OPdS_2$: C, 30.05; H, 5.55; S, 16.04. Found: C, 30.88; 5.58, S, 15.79. T_m = 164°C. ESI-MS (positive ion mode, MeCN): *m/z* 364.98 [M^+ − Cl]. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 4.24 (t, *J* = 6.4 Hz, 3.2H, CH_2O), 4.11 (t, *J* = 6.1 Hz, 0.7H, CH_2O), 4.05 (br, 0.1H CH_2O), 3.56 (hept, *J* = 6.4 Hz, 2H, C*H*S), 2.99 (br, 4H, CH_2S), 1.50 (m, 12H, CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25°C): δ 69.67 (s, *C*H_2O), 68.96 (s, minor, *C*H_2O), 41.43 (s, minor, *C*H_2S), 40.94 (s, *C*H_2S), 34.34 (s, *C*HS), 34.03 (s, minor, *C*HS), 20.04 (br, *C*H_3). IR (KBr disk, cm^{-1}): 2975(sh), 2970 ν_{as}(C–H from CH_3); 2926 ν_{as}(C–H from S-CH_2 and O-CH_2); 2877 (sh) ν(C–H from CH); 2866 ν_s(C–H from CH_3) and ν_s(C–H from S-CH_2 and O-CH_2); 1465, 1447 δ_{as}(C–H from C-CH_3); 1402 δ (HCH from S-CH_2, scissoring) and δ (HCH from O-CH_2, scissoring); 1385 and 1368 δ_s(C–H from C-CH_3, doublet); 1368 additional δ (HCH from S-CH_2, scissoring) with δ (CCH from O-CH_2-C, wagging) and δ(C–H from CH); 1296 δ (CCH from S-*C*H_2-CH_2, wagging) with δ (CCH from O-*C*H_2-CH_2, twisting); 1252 δ (CCH from O-*C*H_2-CH_2, twisting) with δ (CCH from S-*C*H_2-CH_2, wagging); 1236 δ(C–H from CH_3, rocking); 1203, 1184 δ (CCH from S-*C*H_2-CH_2 and O-*C*H_2-CH_2, twisting); 1154 δ(C–H from CH_3, rocking); 1121, 1104 ν_{as}(C–O–C); 1059 ν(*C*–*C*–O); 1034, 1020 (sh) ν_s(C–O–C); 980 δ(C–H from CH_3, rocking); 976, 971 ν(*C*–*C*–S from S-*CH*-(CH_3)$_2$); 953 δ(C–H from CH_3, rocking), 931, 877 ν(C–C–C from CH-(CH_3)$_2$); 852 ν(*C*–*C*–S from S-*C*H_2-*C*H_2-O) and skeletal stretching vibrations; 803, 776 δ(C–H from CH_2-groups, rocking); 686 and 665 ν_{as}(C–S–C); 632 and 619 ν_s(C–S–C).

The preparation of (acetylacetonate-κ^2O,O')(2,10-dimethyl-6-oxa-3,9-dithiaundecane-κ^2S,S')palladium (II) tetrafluoroborate (**4b**) was as follows. [Pd(acac)(MeCN)$_2$]BF_4 (136 mg, 0.363 mmol) was dissolved in 16 ml of CH_2Cl_2, and 2,10-dimethyl-6-oxa-3,9-dithiaundecane (0.8 ml of solution [0.453 M], 0.363 mmol) was added, forming a yellow solution. The reaction mixture was stirred for 3 h at room temperature. The resulting yellow solution was concentrated to approximately 3 ml under vacuum. The addition of diethyl ether (25 ml) resulted in a yellow precipitate, which was collected, washed with diethyl ether (2 × 10 ml), and dried (8 h) under vacuum to produce complex **4b** as a yellow powder (147 mg, 77%). Anal. Calcd for $C_{15}H_{29}BF_4O_3PdS_2$: C, 35.00; H, 5.68; S, 12.46. Found: C, 35.45; H, 5.75; S, 12.14. T_m = 118°C (with decomposition). ESI-MS (positive ion mode, MeCN): *m/z* 427.06 [M^+]. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 5.52 (s, 1H, CH_{acac}), 4.65–3.55 (m, br, 4H, CH_2O), 3.55–3.30 (m, 2H, C*H*S), 3.30–2.65 (m, 4H, CH_2S), 2.08 (s, 6H, C$H_{3,acac}$), 1.60–1.40 (m, 12H, *C*H_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25°C): δ 186.64 (s, $C_{CO\text{-}acac}$), 101.63 (s, $C_{CH\text{-}acac}$), 67.08 (s, br, *C*H_2O), 39.29 (s, br, *C*H_2S), 35.90 (s, br, *C*HS), 26.63 (s, $C_{Me\text{-}acac}$), 23.22 (s, *C*H_3), 20.48 (s, *C*H_3). IR (film, KBr plate, cm^{-1}): 3114, 3066 ν(C–H from CH in acac); 2969 ν_{as}(C–H from CH_3); 2929 ν_{as}(C–H from S-CH_2-CH_2-O) and ν_{as}(C–H from CH_3 in acac); 2871 ν(C–H from CH) and ν_s(C–H from CH_3) and ν_s(C–H from S-CH_2 and O-CH_2); 1560 ν(C=O and C=C in acac); 1521 ν(C=C and C=O in acac); 1460 δ_{as}(C–H from C-CH_3); 1429 δ (HCH from O-CH_2, scissoring) with δ (HCH from S-CH_2, scissoring) and δ(C–H from CH in acac, plane); 1411 δ (HCH from S-CH_2, scissoring) and δ (HCH from O-CH_2, scissoring); 1387 (sh) and 1369 δ_s(C–H from C-CH_3 in i-Pr, doublet); 1367 additional δ_s(C–H from C-CH_3 in acac) and δ (CCH from O-*C*H_2-CH_2, wagging) with δ (HCH from S-CH_2, scissoring); 1293(sh) δ (CCH from S-*C*H_2-CH_2, wagging) with δ (CCH from O-*C*H_2-CH_2, twisting); 1276 δ (CCH from O-*C*H_2-CH_2, twisting) with δ (CCH from S-*C*H_2-CH_2, wagging); 1257 (sh) acac-chelate deformations and δ(C–H from CH_3, rocking); 1199, 1182 δ (CCH from S-*C*H_2-CH_2 and O-*C*H_2-CH_2, twisting); 1157 δ(C–H from CH_3, rocking); 1096 ν_{as}(B–F) and ν_{as}(C–O–C); 1055 ν_{as}(B–F) and ν(*C*–*C*–O); 1036 ν_{as}(B–F) and ν_s(C–O–C) and δ(C–H from CH_3 in acac, rocking) and acac-chelate deformations;962 δ(C–H from CH_3, rocking); 940 acac-chelate

deformations and ν_{as}(C–CH_3 in acac); 876, 866 ν(C–C–C from CH-$(CH_3)_2$); 855 ν(*C*–*C*–S from S-*CH_2*-*CH_2*-O) and skeletal stretching vibrations; 819 δ(C–H from CH in acac, off-plane) and δ(C–H from S-CH_2-CH_2-O, rocking); 789 ν_s(B–F) and δ(C–H from S-CH_2-CH_2-O, rocking); 765 (sh), 732 δ(C–H from CH_2-groups, rocking); 695 ν_{as}(C–S–C); 666 acac-chelate deformations and ν_s(C–CH_3 in acac); 636 ν_s(C–S–C).

The preparation of di-μ-(8-oxa-5,-11-dithiapentadecane-κ^2*S*,*S*′)-bis[*trans*-dichloropalladium (II)] (**5a**) was as follows. 8-Oxa-5,11-dithiapentadecane (94 mg, 0.373 mmol) was dissolved in 10 ml of CH_2Cl_2, and $PdCl_2$(cod) (106 mg, 0.372 mmol) was added, forming a yellow solution. The reaction mixture was stirred for 6 h at room temperature. The resulting yellow solution was concentrated to approximately 4 ml under vacuum. The addition of diethyl ether (20 ml) resulted in a yellow precipitate, which was collected, washed with diethyl ether (2 × 10 ml), and dried (8 h) under vacuum to produce complex **5a** as a yellow powder (121 mg, 76%). Anal. Calcd for $C_{12}H_{26}Cl_2OPdS_2$: C, 33.69; H, 6.13; S, 14.99. Found: C, 33.61; H, 6.11; S, 14.55. ESI-MS (positive ion mode, MeCN): *m/z* 393.01 [M^+ − Cl]. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 4.19 (t, *J* = 6.6 Hz, 2.5H, C*H*$_2$O), 4.06 (m (t, overlapping, *J* = 6.6 Hz), 1.5H, C*H*$_2$O), 3.30–3.00 (m, br, overlapping, 1.5H, C*H*$_2$S), 2.99 (t, br, overlapping, *J* = 6.4 Hz, 2.5H, C*H*$_2$S), 1.80–1.69 (m (p, overlapping, *J* = 7.4 Hz), 4H, C*H*$_2$), 1.46 (m (h, overlapping, *J* = 7.3 Hz), 4H, C*H*$_2$), 0.92 (m (t, overlapping, *J* = 7.3 Hz, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25°C): δ 69.79 (s, *C*H$_2$O), 69.21 (s, minor, *C*H$_2$O), 36.69 (s, minor, *C*H$_2$S), 36.06 (s, *C*H$_2$S), 36.01 (sh, minor, *C*H$_2$S), 35.68 (s, *C*H$_2$S), 30.35 (s, minor, *C*H$_2$), 30.01 (s, *C*H$_2$), 22.09 (s, minor, *C*H$_2$), 22.02 (s, *C*H$_2$), 13.73 (s, minor, *C*H$_3$), 13.68 (s, *C*H$_3$). IR (KBr disk, cm^{-1}): 2958 ν_{as}(C–H from CH_3); 2929 ν_{as}(C–H from CH_2-groups); 2870 ν_s(C–H from CH_3) and ν_s(C–H from CH_2-groups); 1462 δ_{as}(C–H from C-CH_3) and δ (HCH from *CH_2*-*CH_2*-CH_3, scissoring); 1416 δ (HCH from O-CH_2, scissoring); 1402 δ (HCH from S-CH_2, scissoring); 1380 δ_s(C–H from C-CH_3); 1360 δ (HCH from S-CH_2, scissoring) with δ (CCH from O-CH_2-C, wagging); 1314 (sh), 1290, 1275, 1242 (sh) δ (CCH from S-*CH_2*-CH_2, wagging) with δ (CCH from O-*CH_2*-CH_2, twisting) and δ (CCH from CH_2-*CH_2*-*CH_2*-CH_3, wagging); 1226 δ (CCH from CH_2-*CH_2*-*CH_2*-CH_3, twisting) and δ (CCH from O-*CH_2*-CH_2, twisting) with δ (CCH from S-*CH_2*-CH_2, wagging); 1203, 1192 (sh) δ (CCH from S-*CH_2*-CH_2 and O-*CH_2*-CH_2, twisting) and δ (CCH from CH_2-*CH_2*-*CH_2*-CH_3, twisting); 1111 (sh), 1100 ν_{as}(C–O–C); 1077, 1057 ν(*C*–*C*–O); 1042, 1023 ν_s(C–O–C); 986, 968 ν(*C*–*C*–S from S-*CH_2*-*CH_2*-CH_2-CH_3); 953 δ(C–H from CH_3, rocking); 942, 915, 877 ν(*C*–*C*–C from CH_2-CH_2-CH_2-CH_3); 849 ν(*C*–*C*–S from S-*CH_2*-*CH_2*-O) and skeletal stretching vibrations, 802, 780, 747, 729 δ(C–H from CH_2-groups, rocking); 667 ν_{as}(C–S–C); 638, 614 (very weak) ν_s(C–S–C).

The preparation of (acetylacetonate-κ^2*O*,*O*′)(8-oxa-5,11-dithiapentadecane-κ^2*S*,*S*′)palladium (II) tetrafluoroborate (**5b**) was as follows. [Pd (acac)$(MeCN)_2$]BF_4 (117 mg, 0.314 mmol) was dissolved in 16 ml of CH_2Cl_2, and 8-oxa-5,11-dithiapentadecane (0.8 ml of solution (0.492 M), 0.314 mmol) was added, forming a yellow solution. The reaction mixture was stirred for 3.0 h at room temperature. The resulting yellow solution was concentrated to approximately 3 ml under vacuum. The addition of diethyl ether (25 ml) resulted in a yellow precipitate, which was collected, washed with diethyl ether (2 × 10 ml), and dried (8 h) under vacuum to produce complex **5b** as a yellow powder (115 mg, 68%). Anal. Calcd for $C_{17}H_{33}BF_4O_3PdS_2$: C, 37.62; H, 6.13; S, 11.81. Found: C, 37.26; H, 6.10; S, 11.35. ESI-MS (positive ion mode, MeCN): *m/z* 455.09 [M^+]. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 5.59 (s, 0.2H, C*H*$_{acac}$), 5.57 (s, 0.4H, C*H*$_{acac}$), 5.54 (s, 0.4H, C*H*$_{acac}$), 4.5–3.6 (m, 4H, C*H*$_2$O), 3.4–3.0 (m, 4H, C*H*$_2$S), 3.0–2.4 (m, 4H, C*H*$_2$S), 2.13 (s, 3.6H, C*H*$_{3,acac}$), 2.09 (s, 2.4H, C*H*$_{3,acac}$), 1.9–1.6 (m, 4H, C*H*$_2$), 1.6–1.4 (m, 4H, C*H*$_2$), 0.95 (t, *J* = 7.4 Hz, 6H, *C*H$_3$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25°C): δ 187.07 (s, minor, $C_{CO\text{-}acac}$), 186.68 (s, $C_{CO\text{-}acac}$), 101.42 (s, minor, $C_{CH\text{-}acac}$), 101.31 (s, $C_{CH\text{-}acac}$), 67.57 (s, br, *C*H$_2$O), 66.62 (s, minor, *C*H$_2$O), 39.11 (s, br, *C*H$_2$S), 37.04 (s, minor, *C*H$_2$S), 34.96 (s, *C*H$_2$S), 30.25 (s, minor, *C*H$_2$), 29.73 (s, br, *C*H$_2$), 26.74 (s, minor, $C_{Me\text{-}acac}$), 26.63 (s, $C_{Me\text{-}acac}$), 22.19 (s, minor, *C*H$_2$), 22.02 (s, *C*H$_2$), 13.62 (s, minor, *C*H$_3$), 13.58 (s, *C*H$_3$). IR (film, KBr plate, cm^{-1}): 3107 ν(C–H from CH in acac); 2958 ν_{as}(C–H from CH_3); 2932 ν_{as}(C–H from S-CH_2-CH_2-O) and ν_{as}(C–H from CH_3 in acac); 2873 ν_s(C–H from CH_3) and ν_s(C–H from CH_2-groups); 1560 ν(C=O and C=C in acac); 1521 ν(C=C and C=O in acac); 1465 δ_{as}(C–H from C-CH_3) and δ (HCH from *CH_2*-*CH_2*-CH_3, scissoring); 1425 δ (HCH from S-*CH_2*-*CH_2*-O, scissoring) and δ(C–H from CH in acac, plane); 1369 δ_s(C–H from C-CH_3) and δ (CCH from O-*CH_2*-CH_2, wagging) with δ (HCH from S-CH_2, scissoring); 1294 (sh), 1277 δ (CCH from S-*CH_2*-CH_2, wagging) with δ (CCH from O-*CH_2*-CH_2, twisting) and δ (CCH from CH_2-*CH_2*-*CH_2*-CH_3, wagging); 1257 (sh) acac-chelate deformations; 1232 δ (CCH from CH_2-*CH_2*-*CH_2*-CH_3, twisting) and δ (CCH from O-*CH_2*-CH_2, twisting) with δ (CCH from S-*CH_2*-CH_2, wagging); 1198, 1186 (sh) δ (CCH from S-*CH_2*-CH_2 and O-*CH_2*-CH_2, twisting) and δ (CCH from CH_2-*CH_2*-*CH_2*-CH_3, twisting); 1099 ν_{as}(B–F) and ν_{as}(C–O–C); 1056 ν_{as}(B–F) and ν(*C*–*C*–O); 1036 ν_{as}(B–F) and ν_s(C–O–C) and δ(C–H from CH_3 in acac, rocking) and acac-chelate deformations;

992 (sh) ν(*C*–*C*–S from S-*CH*$_2$-*CH*$_2$-CH$_2$-CH$_3$); 940 acac-chelate deformations and ν_{as}(C–CH$_3$ in acac); 923, 872 ν(*C*–*C*–C from CH$_2$-CH$_2$-CH$_2$-CH$_3$); 858 (sh) ν(*C*–*C*–S from S-*CH*$_2$-*CH*$_2$-O) and skeletal stretching vibrations; 823 δ(C–H from CH in acac, off-plane) and δ(C–H from S-CH$_2$-CH$_2$-O, rocking); 787 ν_s(B–F) and δ(C–H from S-CH$_2$-CH$_2$-O, rocking); 763, 744, 739 (sh) δ(C–H from CH$_2$-groups, rocking); 693 ν_{as}(C–S–C); 665 acac-chelate deformations and ν_s(C–CH$_3$ in acac), 636 ν_s(C–S–C).

The preparation of di-μ-(2,12-dimethyl-7-oxa-4,10-dithiatridecane-κ^2*S*,*S*′)-bis[*trans*-dichloropalladium (II)] (**6a**) was as follows. 2,12-Dimethyl-7-oxa-4,10-dithiatridecane (100 mg, 0.398 mmol) was dissolved in 5 ml of CH_2Cl_2, and $PdCl_2$(cod) (113 mg, 0.397 mmol) was added, forming a yellow solution. The reaction mixture was stirred for 3 h at room temperature. The resulting yellow solution was concentrated to approximately 2 ml under vacuum. The addition of diethyl ether (20 ml) resulted in a yellow precipitate, which was collected, washed with diethyl ether (2 × 10 ml), and dried (8 h) under vacuum to produce complex **6a** as a yellow powder (134 mg, 79%). Anal. Calcd for $C_{12}H_{26}Cl_2OPdS_2$: C, 33.69; H, 6.13; S, 14.99. Found: C, 33.63; H, 6.11; S, 14.70 ESI-MS (positive ion mode, MeCN): *m/z* 393.01 [M^+ − Cl]. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 4.22 (t, *J* = 6.7 Hz, 3.2H, C*H*$_2$O), 4.09 (t, *J* = 6.7 Hz), 0.8H, C*H*$_2$O), 3.03 (s, br, 0.8H, C*H*$_2$S), 2.97 (t, *J* = 6.7 Hz, 3.2H, C*H*$_2$S), 2.74 (s, br, 4H, C*H*$_2$S), 2.08 (hept, *J* = 6.8 Hz, 1.6H, C*H*), 1.93 (s, br, 0.4H, C*H*), 1.06 (two overlapping doublets, *J* = 6.7 Hz), 12H, C*H*$_3$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25°C): δ 69.99 (s, *C*H$_2$O), 69.35 (s, minor, *C*H$_2$O), 45.45 (s, minor, *C*H$_2$S), 44.91 (s, *C*H$_2$S), 36.99 (s, minor, *C*H$_2$S), 36.93 (s, *C*H$_2$S), 27.57 (s, *C*H), 22.18 (s, minor, *C*H$_3$), 22.12 (s, *C*H$_3$). IR (KBr disk, cm^{-1}): 2958 ν_{as}(C–H from CH$_3$); 2929 ν_{as}(C–H from S-CH$_2$ and O-CH$_2$); 2897 ν(C–H from CH); 2870 ν_s(C–H from CH$_3$) and ν_s(C–H from S-CH$_2$ and O-CH$_2$); 1464 δ_{as}(C–H from C-CH$_3$); 1412 δ (HCH from S-CH$_2$ in *i*Bu, scissoring) and δ (HCH from O-CH$_2$, scissoring); 1403 δ (HCH from S-CH$_2$, scissoring); 1386 and 1366 δ_s(C–H from C-CH$_3$, doublet); 1366 additional δ (HCH from S-CH$_2$, scissoring) with δ (CCH from O-CH$_2$-C, wagging); 1338 δ(C–H from CH in *i*Bu); 1323 δ (CCH from S-*CH*$_2$-CH$_2$ in *i*Bu, wagging); 1291 δ (CCH from S-*CH*$_2$-CH$_2$, wagging) with δ (CCH from O-*CH*$_2$-CH$_2$, twisting); 1261 δ (CCH from O-*CH*$_2$-CH$_2$, twisting) with δ (CCH from S-*CH*$_2$-CH$_2$, wagging) and δ (CCH from S-*CH*$_2$-CH (CH$_3$)$_2$, twisting); 1222, 1202 δ (CCH from S-*CH*$_2$-CH$_2$ and O-*CH*$_2$-CH$_2$, twisting); 1172 δ(C–H from CH$_3$, rocking); 1114 (sh), 1101 ν_{as}(C–O–C); 1082, 1058 ν(*C*–*C*–O); 1042, 1021 ν_s(C–O–C); 984 δ(C–H from CH$_3$, rocking); 968 ν(*C*–*C*–S from S-*CH*$_2$-*CH*-(CH$_3$)$_2$); 954, 928, 863 ν(C–C–C from CH$_2$-CH-(CH$_3$)$_2$); 815, 783, 736 (sh), 729 δ(C–H from CH$_2$-groups, rocking); 664 ν_{as}(C–S–C); 638 (sh), 619 ν_s(C–S–C).

The preparation of (acetylacetonate-κ^2*O*,*O*′)(2,12-dimethyl-7-oxa-4,10-dithiatridecane-κ^2*S*,*S*′)palladium (II) tetrafluoroborate (**6b**) was as follows. [Pd (acac)(MeCN)$_2$]BF_4 (118 mg, 0.316 mmol) was dissolved in 15 ml of CH_2Cl_2, and 2,12-dimethyl-7-oxa-4,10-dithiatridecane (0.8 ml of solution [0.395 M], 0.316 mmol) was added, forming a yellow solution. The reaction mixture was stirred for 3 h at room temperature. The resulting yellow solution was concentrated to approximately 3 ml under vacuum. The addition of diethyl ether (25 ml) resulted in a yellow precipitate, which was collected, washed with diethyl ether (2 × 10 ml), and dried (8 h) under vacuum to produce complex **6b** as a yellow powder (107 mg, 62%). Anal. Calcd for $C_{17}H_{33}BF_4O_3PdS_2$: C, 37.62; H, 6.13; S, 11.81. Found: C, 37.31; H, 6.13; S, 11.63. ESI-MS (positive ion mode, MeCN): *m/z* 455.09 [M^+]. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 5.57 (s, 0.6H, C*H*$_{acac}$), 5.54 (s, 0.4H, C*H*$_{acac}$), 4.6–3.6 (m, br, 4H, C*H*$_2$O), 3.50–3.05 (m, 4H, C*H*$_2$S), 3.05–2.50 (m, 4H, C*H*$_2$S), 2.20–2.00 (m, 8H, C*H*$_{3,acac}$+C*H*), 1.09 (d, *J* = 7.2 Hz, 12H, *C*H$_3$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25°C): δ 187.10 (s, $C_{CO\text{-}acac}$), 186.67 (s, minor, $C_{CO\text{-}acac}$), 101.44 (s, $C_{CH\text{-}acac}$), 101.29 (s, minor, $C_{CH\text{-}acac}$), 66.59 (s, br, *C*H$_2$O), 43.58 (s, *C*H$_2$S), 37.64 (s, *C*H$_2$S), 28.16 (s, *C*H), 26.75 (s, minor, $C_{Me\text{-}acac}$), 26.60 (s, $C_{Me\text{-}acac}$), 23.00–21.00 (m, br, *C*H$_3$). IR (film, KBr plate, cm^{-1}): 3115 ν(C–H from CH in acac); 2960 ν_{as}(C–H from CH$_3$); 2933 ν_{as}(C–H from S-CH$_2$-CH$_2$-O) and ν_{as}(C–H from CH$_3$ in acac); 2874 ν(C–H from CH) and ν_s(C–H from CH$_3$) and ν_s(C–H from S-CH$_2$ and O-CH$_2$); 1560 ν(C=O and C=C in acac); 1521 ν(C=C and C=O in acac); 1466 δ_{as}(C–H from C-CH$_3$); 1422 δ (HCH from S-*CH*$_2$-*CH*$_2$-O, scissoring) and δ(C–H from CH in acac, plane); 1385 (sh) and 1368 δ_s(C–H from C-CH$_3$, doublet); 1368 additional δ_s(C–H from C-CH$_3$) and δ (CCH from O-*CH*$_2$-CH$_2$, wagging) with δ (HCH from S-CH$_2$, scissoring); 1324 δ (CCH from S-*CH*$_2$-CH$_2$ in *i*Bu, wagging); 1293 (sh) δ (CCH from S-*CH*$_2$-CH$_2$, wagging) with δ (CCH from O-*CH*$_2$-CH$_2$, twisting); 1277 δ (CCH from O-*CH*$_2$-CH$_2$, twisting) with δ (CCH from S-*CH*$_2$-CH$_2$, wagging) and δ (CCH from S-*CH*$_2$-CH (CH$_3$)$_2$, twisting); 1262 (sh) acac-chelate deformations δ (CCH from S-*CH*$_2$-CH$_2$ and O-*CH*$_2$-CH$_2$, twisting); 1200, 1181 δ (CCH from S-*CH*$_2$-CH$_2$ and O-*CH*$_2$-CH$_2$, twisting); 1170 δ(C–H from CH$_3$, rocking); 1103 ν_{as}(B–F) and ν_{as}(C–O–C); 1057 ν_{as}(B–F) and ν(*C*–*C*–O); 1036 ν_{as}(B–F) and ν_s(C–O–C) and δ(C–H from CH$_3$ in acac, rocking) and acac-chelate deformations; 991(sh) δ(C–H from CH$_3$, rocking); 965 (sh) ν(*C*–*C*–S from S-*CH*$_2$-*CH*-(CH$_3$)$_2$); 940 acac-chelate deformations and ν_{as}(C–CH$_3$ in acac); 895 ν(C–C–C from CH$_2$-CH-(CH$_3$)$_2$); 814 δ(C–H from CH

in acac, off-plane) and δ(C–H from CH_2-groups, rocking); 788 ν_s(B–F) and δ(C–H from CH_2-groups, rocking); 764, 729 δ(C–H from CH_2-groups, rocking); 693 ν_{as}(C–S–C); 665 acac-chelate deformations and ν_s(C–CH_3 in acac); 636 ν_s(C–S–C).

The preparation of di-μ-(10-oxa-7,-13-dithianonadecane-κ^2S,S')-bis[*trans*-dichloropalladium (II)] (**7a**) was as follows. 10-oxa-7,13-dithianonadecane (94 mg, 0.307 mmol) was dissolved in 10 ml of CH_2Cl_2, and $PdCl_2$(cod) (87 mg, 0.305 mmol) was added, forming a yellow solution. The reaction mixture was stirred for 3 h at room temperature. The resulting yellow solution was concentrated to approximately 2 ml under vacuum. The addition of diethyl ether (20 ml) resulted in a yellow precipitate, which was collected, washed with diethyl ether (2 × 10 ml), and dried (8 h) under vacuum to produce red brick powder. The residue was recrystallized from CH_2Cl_2-diethyl ether mixture to give **7a** (73 mg, 50%). Anal. Calcd for $C_{16}H_{34}Cl_2OPdS_2$: C, 39.71; H, 7.08; S, 13.25. Found: C, 39.65; H, 7.12; S, 12.94. ESI-MS (positive ion mode, MeCN): *m/z* 449.08 [$M^+ - Cl$]. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 4.18 (t, $J = 6.6$ Hz, 2.5H, CH_2O), 4.10–3.70 (m (t, overlapping, $J = 6.1$ Hz), 1.5H, CH_2O), 3.25–3.00 (m, br, overlapping, 1.5H, CH_2S), 2.98 (t, br, overlapping, $J = 6.6$ Hz, 2.5H, CH_2S), 2.90–2.65 (m, br, 4H, CH_2S), 1.97–1.68 (m (p, overlapping, $J = 7.8$ Hz), 4H, CH_2), 1.50–1.36 (m, br, 4H, CH_2), 1.34–1.19 (m, br, 8H, CH_2), 0.92 (m, br, 6H, CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25°C): δ 69.79 (s, *C*H_2O), 69.72 (s, minor, *C*H_2O), 36.97 (s, minor, *C*H_2S), 36.35 (s, *C*H_2S), 36.02 (minor, *C*H_2S), 35.66 (s, *C*H_2S), 31.38 (s, minor, *C*H_2), 31.33 (s, *C*H_2), 28.58 (s, minor, *C*H_2), 28.44 (s, *C*H_2), 28.31 (s, minor, *C*H_2), 27.96 (s, *C*H_2), 22.53 (s, minor, *C*H_2), 22.50 (s, *C*H_2), 14.04 (m, br, *C*H_3). IR (KBr disk, cm^{-1}): 2957 ν_{as}(C–H from CH_3); 2926 ν_{as}(C–H from CH_2-groups); 2870 (sh), 2858 ν_s(C–H from CH_3) and ν_s(C–H from CH_2-groups); 1461 (sh), 1456 (sh) δ_{as}(C–H from C-CH_3) and δ (HCH from SCH_2-(*CH_2*)$_4$-CH_3, scissoring); 1416 δ (HCH from O-CH_2, scissoring); 1403 δ (HCH from S-CH_2, scissoring); 1377 δ_s(C–H from C-CH_3); 1371 δ (HCH from S-CH_2, scissoring) with δ (CCH from O-CH_2-C, wagging); 1362 δ (CCH from SCH_2-(*CH_2*)$_4$-CH_3, wagging); 1344 δ (CCH from O-CH_2-C, wagging) with δ (HCH from S-CH_2, scissoring); 1292, 1263 δ (CCH from S-*CH_2*-CH_2, wagging) with δ (CCH from O-*CH_2*-CH_2, twisting) and δ (CCH from SCH_2-(*CH_2*)$_4$-CH_3, twisting); 1215, 1205, 1174 δ (CCH, twisting, from O-*CH_2*-CH_2, SCH_2-(*CH_2*)$_4$-CH_3 and S-*CH_2*-CH_2, respectively); 1122 (sh), 1103 ν_{as}(C–O–C); 1077, 1052 (sh) ν(*C*–*C*–O); 1045, 1034, 1018 ν_s(C–O–C); 984, 967 (sh) ν(*C*–*C*–S from S-*CH_2*-*CH_2*-$(CH_2)_3$-CH_3); 952 δ(C–H from CH_3, rocking); 917, 888 (sh), 874 (sh), ν(*C*–*C*–C from CH_2-$(CH_2)_4$-CH_3); 863 ν(*C*–*C*–S from S-*CH_2*-*CH_2*-O) and skeletal stretching vibrations; 813, 789, 760, 725 δ(C–H from CH_2-groups, rocking); 674 (sh), 666 ν_{as}(C–S–C); 644 (sh), 624 (very weak) ν_s(C–S–C).

The preparation of (acetylacetonate-κ^2O,O')(10-oxa-7,13-dithianonadecane-κ^2S,S')palladium (II) tetrafluoroborate (**7b**) was as follows. [Pd (acac)$(MeCN)_2]BF_4$ (83 mg, 0.222 mmol) was dissolved in 16 ml of CH_2Cl_2, and 10-oxa-7,13-dithianonadecane (0.8 ml of solution (0.279 M) in CH_2Cl_2, 0.223 mmol) was added, forming a yellow solution. The reaction mixture was stirred for 3.0 h at room temperature. The resulting yellow solution was concentrated to approximately 2 ml under vacuum. The addition of *n*-pentane (12 ml) resulted in a yellow precipitate, which was collected, washed with *n*-pentane (2 × 10 ml), and dried (8 h) under vacuum to produce complex **7b** as a yellow oily powder (81 mg, 60%). Anal. Calcd for $C_{21}H_{41}BF_4O_3PdS_2$: C, 42.11; H, 6.90; S, 10.71. Found: C, 42.17; H, 6.88; S, 10.15. ESI-MS (positive ion mode, MeCN): *m/z* 511.15 [M^+]. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 5.60 (s, 0.8H, CH_{acac}), 5.56 (s, 0.2H, CH_{acac}), 4.5–3.5 (m, 4H, CH_2O), 3.4–3.1 (m, 4H, CH_2S), 3.1–2.4 (m, 4H, CH_2S), 2.15 (s, 4.9H, C$H_{3,acac}$), 2.11 (s, 1.1H, C$H_{3,acac}$), 1.81 (s, br, 4H, CH_2), 1.48 (s, br, 4H, CH_2), 1.32 (s, br, 8H, CH_2), 0.90 (s, br, 6H, CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25°C): δ 187.07 (s, minor, $C_{CO\text{-}acac}$), 186.68 (s, $C_{CO\text{-}acac}$), 101.32 (s, $C_{CH\text{-}acac}$), 100.51 (s, minor, $C_{CH\text{-}acac}$), 67.58 (s, br, *C*H_2O), 67.13 (s, br, minor, *C*H_2O), 39.17 (s, br, *C*H_2S), 38.10 (s, br, minor, *C*H_2S), 35.22 (s, br, minor, *C*H_2S), 34.42 (s, br, *C*H_2S), 32.17 (s, br, *C*H_2), 31.24 (s, br, minor, *C*H_2), 28.48 (s, br, *C*H_2), 28.35–27.25 (m, br, *C*H_2), 26.73 (s, minor, $C_{Me\text{-}acac}$), 26.63 (s, $C_{Me\text{-}acac}$), 22.44 (s, br, *C*H_2), 13.98 (s, br, *C*H_3). IR (film, KBr plate, cm^{-1}): 3113 ν(C–H from CH in acac); 2955 ν_{as}(C–H from CH_3); 2929 ν_{as}(C–H from CH_2-groups) and ν_{as}(C–H from CH_3 in acac); 2869, 2859 ν_s(C–H from CH_3) and ν_s(C–H from CH_2-groups); 1560 ν(C=O and C=C in acac); 1521 ν(C=C and C=O in acac); 1465, 1459 (sh) δ_{as}(C–H from C-CH_3) and δ (HCH from SCH_2-(*CH_2*)$_4$-CH_3, scissoring); 1425 δ (HCH from S-*CH_2*-*CH_2*-O, scissoring); 1401 δ(C–H from CH in acac, plane); 1369 δ_s(C–H from C-CH_3) and δ (CCH from O-*CH_2*-CH_2, wagging) with δ (HCH from S-CH_2, scissoring); 1294 (sh), 1279 δ (CCH from S-*CH_2*-CH_2, wagging) with δ (CCH from O-*CH_2*-CH_2, twisting) and δ (CCH from SCH_2-(*CH_2*)$_4$-CH_3, twisting); 1245 (sh) acac-chelate deformations; 1201, 1186 δ (CCH, twisting, from O-*CH_2*-CH_2, SCH_2-(*CH_2*)$_4$-CH_3 and S-*CH_2*-CH_2, respectively); 1098 ν_{as}(B–F) and ν_{as}(C–O–C); 1057 ν_{as}(B–F) and ν(*C*–*C*–O); 1036 ν_{as}(B–F) and ν_s(C–O–C) and δ(C–H from CH_3 in acac, rocking) and acac-chelate deformations; 984 (sh) ν(*C*–*C*–S from S-*CH_2*-*CH_2*-$(CH_2)_3$-CH_3);

940 acac-chelate deformations and ν_{as}(C–CH_3 in acac); 865 ν(*C*–*C*–S from S-*CH_2*-*CH_2*-O) and skeletal stretching vibrations; 816 δ(C–H from CH in acac, off-plane) and δ(C–H from S-CH_2-CH_2-O, rocking); 788 ν_s(B–F) and δ(C–H from S-CH_2-CH_2-O, rocking); 763, 728 δ(C–H from CH_2-groups, rocking); 693 ν_{as}(C–S–C); 666 acac-chelate deformations and ν_s(C–CH_3 in acac); 635 ν_s(C–S–C).

The preparation of di-μ-(5-oxa-1,9-diphenyl-2,8-dithianonane-κ^2S,S')-bis[*trans*-dichloropalladium (II)] (**8a**) was as follows. 5-Oxa-1,9-diphenyl-2,8-dithianonane (112 mg, 0.10 ml, 0.350 mmol) was dissolved in 10 ml of CH_2Cl_2, and $PdCl_2$(cod) (100 mg, 0.350 mmol) was added, forming an orange solution. The reaction mixture was stirred for 7 h at room temperature. The resulting orange solution was concentrated to approximately 3 ml under vacuum. The addition of diethyl ether (15 ml) resulted in an orange precipitate, which was collected, washed with diethyl ether (2 × 10 ml), and dried (8 h) under vacuum to produce complex **8a** as an orange powder (134 mg, 69%). Anal. Calcd for $C_{18}H_{22}Cl_2OPdS_2$ C, 43.60; H, 4.47; S, 12.93. Found: 43.98; H, 4.42; S, 13.49. ESI-MS (positive ion mode, MeCN): *m/z* 460.98 [M^+ – Cl]. ^{1}H NMR (400 MHz, DMSO-d_6, 70°C): δ 7.60–7.20 (m, br, 10H, Ph), 3.97 (s, br, 4H, C*H_2*O), 3.68 (s, br, 4H, C*H_2*S), 2.79 (s, br, 4H, C*H_2*S). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 70°C): δ 129.78 (s, Ph), 128.99 (s, Ph), 127.88 (s, Ph), 69.40 (s, br, *C*H_2O). IR (KBr disk, cm^{-1}): 3105 (sh), 3085, 3061, 3029, 3002 (sh) ν(C–H from Ph); 2975 ν_{as}(C–H from S-*CH_2*-Ph); 2925 ν_{as}(C–H from S-CH_2 and O-CH_2); 2880 ν_s(C–H from S-*CH_2*-Ph); 2860 ν_s(C–H from S-CH_2 and O-CH_2); 1602, 1584 ν_{as}(C=C from Ph); 1494 ν_{as}(C=C from Ph) and δ (CCH from Ph); 1473 δ (HCH from S-*CH_2*-Ph, scissoring); 1454 δ (CCH from Ph) and ν_{as}(C=C from Ph); 1418 δ (HCH from S-CH_2, scissoring) and δ (HCH from O-CH_2, scissoring); 1365 δ (CCH from S-*CH_2*-Ph, wagging) and δ (CCH from O-*CH_2*-CH_2, wagging) with δ (HCH from S-CH_2, scissoring); 1359 δ (HCH from S-CH_2, scissoring) with δ (CCH from O-*CH_2*-CH_2, wagging) and δ (CCH from S-*CH_2*-Ph, wagging); 1342 (sh), 1323 (sh) δ (CCH from Ph, plane); 1296 δ (CCH from S-*CH_2*-CH_2, wagging) with δ (CCH from O-*CH_2*-CH_2, twisting); 1246 δ (CCH from S-*CH_2*-Ph, twisting) and δ (CCH from S-*CH_2*-CH_2, twisting); 1202 δ (CCH from O-*CH_2*-CH_2 and S-*CH_2*-CH_2, twisting); 1185, 1155 (sh), 1143 δ (CCH from Ph, plane); 1110 ν_{as}(C–O–C); 1072 ν(*C*–*C*–O) and δ (CCH from Ph, plane); 1045 (sh), 1018 (sh) ν_s(C–O–C); 1027 ν_s(C–O–C) and δ (CCH from Ph, plane); 1004 (sh) ν_s(C=C from Ph) with δ (CCH from Ph, plane) and ring deformations; 958 ν (*C_{Ar}*–*C*–S); 917 δ (CCH from Ph, plane); 877 ν(*C*–*C*–S from S-*CH_2*-*CH_2*-O) and skeletal stretching vibrations; 845 δ (CCH from Ph, off-plane); 818, 804 skeletal stretching vibrations and δ(C–H from S-CH_2-CH_2-O, rocking); 769, 698 δ (CCH from Ph, off-plane) and δ(C–H from S-CH_2-CH_2-O, rocking); 668 (sh) ν_{as}(C–S–C); 642 (sh) ν_s(C–S–C); 619, 591, 564 ring deformations (off-plane).

The preparation of (acetylacetonate-κ^2O,O')(5-oxa-1,9-diphenyl-2,8-dithianonane-κ^2S,S')palladium (II) tetrafluoroborate (**8b**) was as follows. [Pd (acac)(MeCN)$_2$]BF_4 (103 mg, 0.275 mmol) was dissolved in 15 ml of CH_2Cl_2, and 5-oxa-2,8-dithianonane (0.8 ml of solution (0.345 M), 0.276 mmol) was added, forming a yellow solution. The reaction mixture was stirred for 1.0 h at room temperature. The resulting orange solution was concentrated to approximately 3 ml under vacuum. The addition of diethyl ether (25 ml) resulted in a yellow precipitate, which was collected, washed with diethyl ether (2 × 10 ml), and dried (8 h) under vacuum to produce complex **8b** as a yellow powder (143 mg, 85.0%). The product contained races (<2%) of Et_2O by ^{1}H NMR analysis. Anal. Calcd for $C_{23}H_{29}BF_4O_3PdS_2$: C, 45.22; H, 4.79; S, 10.50. Found: C, 45.50; H, 4.85; S, 10.16. ESI-MS (positive ion mode, MeCN): *m/z* 523.06 [M^+]. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 7.1–7.6 (m, 10H, Ph), 5.58 (s, 0.6H, C*H_{acac}*), 5.54 (s, 0.4H, C*H_{acac}*), 4.4–2.6 (m, br, 12H, C*H_2*O), 2.15 (s, 3.6H, overlapping, C*$H_{3,acac}$*). 2.11 (s, 2.4H, overlapping, C*$H_{3,acac}$*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25°C): δ 187.04 (s, $C_{CO\text{-}acac}$), 130.12 (s, Ph), 129.97(s, Ph), 129.32 (s, Ph), 129.01 (s, Ph), 128.93 (s, Ph), 101.37 (s, $C_{CH\text{-}acac}$), 68.52 (s, br, *C*H_2O), 26.80 (s, $C_{Me\text{-}acac}$). IR (film, KBr plate, cm^{-1}): 3106 ν(C–H from CH in acac) and ν(C–H from Ph); 3087, 3062, 3030, 3003 (sh) ν(C–H from Ph); 2994 ν_{as}(C–H from S-*CH_2*-Ph); 2931 ν_{as}(C–H from S-CH_2-CH_2-O) and ν_{as}(C–H from CH_3 in acac); 2871 ν_s(C–H from S-*CH_2*-Ph)and ν_s(C–H from S-CH_2 and O-CH_2) and ν_s(C–H from CH_3 in acac); 1599 (sh) ν_{as}(C=C from Ph); 1558 ν(C=O and C=C in acac); 1520 ν(C=C and C=O in acac); 1496 ν_{as}(C=C from Ph) and δ (CCH from Ph); 1474 δ (HCH from S-*CH_2*-Ph, scissoring) and δ_{as}(C–H from C-CH_3); 1455 δ (CCH from Ph) and ν_{as}(C=C from Ph); 1425 δ (HCH from S-*CH_2*-*CH_2*-O, scissoring) and δ(C–H from CH in acac, plane); 1367 δ_s(C–H from C-CH_3) and δ (CCH from S-*CH_2*-Ph, wagging) and δ (CCH from O-*CH_2*-CH_2, wagging) with δ (HCH from S-CH_2, scissoring); 1294 (sh), 1277 δ (CCH from S-*CH_2*-CH_2, wagging) with δ (CCH from O-*CH_2*-CH_2, twisting) and δ (CCH from S-*CH_2*-Ph, twisting); 1247 (sh) acac-chelate deformations; 1199 δ (CCH from O-*CH_2*-CH_2 and S-*CH_2*-CH_2, twisting); 1184, 1159 (sh) δ (CCH from Ph, plane); 1098 ν_{as}(B–F) and ν_{as}(C–O–C); 1056 ν_{as}(B–F) and ν(*C*–*C*–O); 1036 ν_{as}(B–F) and ν_s(C–O–C) and δ(C–H from CH_3 in acac, rocking) and acac-chelate deformations; 1002 (sh) ν_s(C=C from Ph); 940 acac-chelate deformations and ν_{as}(C–CH_3 in

acac) and ν (C_{Ar}–C–S); 925 (sh) δ (CCH from Ph, plane); 880 ν(C–C–S from S-CH_2-CH_2-O) and skeletal stretching vibrations; 851 δ (CCH from Ph, off-plane); 820 (sh) δ(C–H from CH in acac, off-plane) and δ(C–H from S-CH_2-CH_2-O, rocking); 820 (sh) skeletal stretching vibrations and δ(C–H from S-CH_2-CH_2-O, rocking); 804 ν_s(B–F) and δ(C–H from S-CH_2-CH_2-O, rocking); 771, 704 δ (CCH from Ph, off-plane); 731 δ(C–H from S-CH_2-CH_2-O, rocking); 669 (sh) ν_{as}(C–S–C); 663 (sh) acac-chelate deformations and ν_s(C–CH_3 in acac); 637 (sh) ν_s(C–S–C); 619, 568 ring deformations (off-plane).

Further spectroscopic details are given in Figures S6–S40, S68–S83, and S97−S106 (see SI).

2.4 | Polymerization experiments

Polymerizations were performed in a 10-ml glass reactor equipped with a magnetic stirrer under purified argon. The reactor was filled with norbornene as a solution in CH_2Cl_2; the solution was kept at the desired temperature for 15 min before the palladium complex was added. Polymerizations were initiated by the injection of boron or aluminum compound. After stirring, the polymers formed were precipitated in ethanol. The precipitated polymers were washed three times with ethanol and dried in vacuum at 80°C for 6 h.

2.5 | Calculations

All density functional theory calculations were performed with the ORCA program.[46] All geometry optimizations were run with tight convergence criteria using the BP86 functional,[47,48] using the resolution of the identity technique.[49] The applicability of gradient-corrected functionals such as BP86 for the structural prediction of transition metal compounds and reliable determination of the kinetic balance are well documented.[50–55] The Weigend−Ahlrichs basis sets were used.[56,57] Triple ξ-quality basis sets with one set of polarization functions (def2-TZVP) were used for palladium, chlorine, and sulfur in connection with effective core potentials for Pd. The remaining atoms were described by slightly smaller def2-SVP basis sets.

2.6 | X-ray crystallographic studies

Data were collected on a BRUKER D8 VENTURE PHOTON 100 CMOS diffractometer with MoK_α radiation (λ = 0.71073 Å) using the φ and ω scans technique. The structures were solved by direct methods using the SHELX program.[58] Data were corrected for absorption effects using the multiscan method (SADABS).[59] All nonhydrogen atoms were refined anisotropically using SHELX.[58] The coordinates of the hydrogen atoms were refined using a riding model. The resulting structure was refined by the least squares method using SHELXL. Note for Alert Level B in checkCIF/PLATON report for **4b**. The *R*-factor for compound **4b** is high, and this is due to the data quality, which is a consequence of the characteristics of the crystal. There have been repeated attempts at recrystallization, but they did not give the best results. Due to the poor quality of the data, geometric restraints were not investigated, and disorder was not considered. The crystal data and experimental details are given in Table S1 (SI). The selective bond lengths, bond angles, and torsion angles are given in Tables S2 and S3 (SI). Table S1 (SI) contains the CCDC reference number of the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (http://www.ccdc.cam.ac.uk).

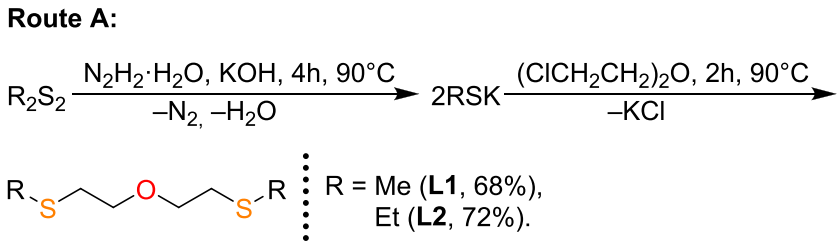
3 | RESULTS AND DISCUSSION

3.1 | Synthesis of oxadithioether ligands

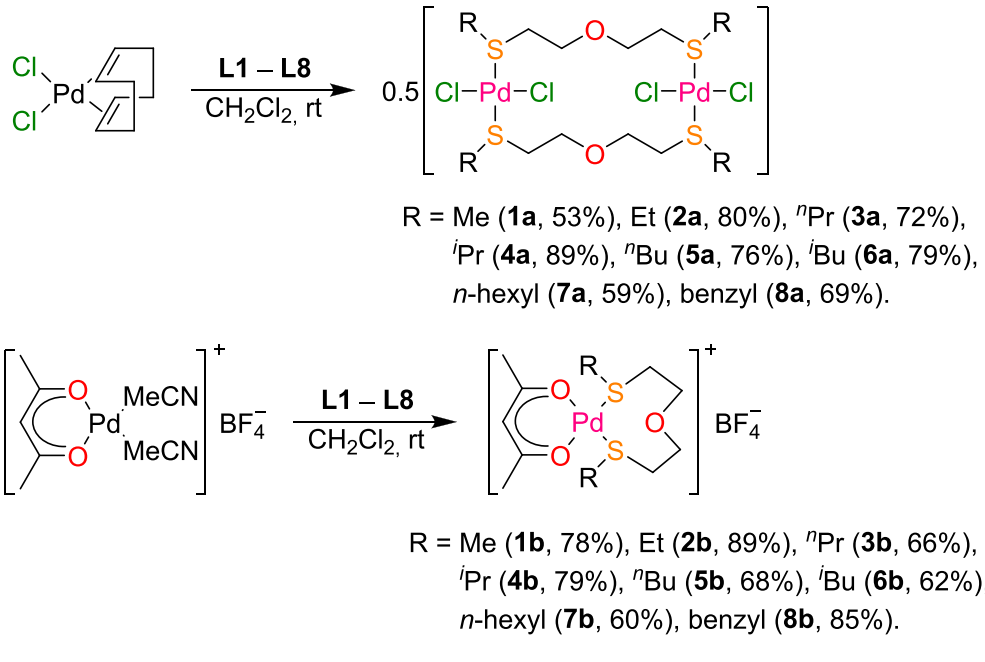
The synthetic strategies for the oxadithioether ligands **L1**–**L8** are shown in Scheme 1. Two well-known methods of synthesis were employed based on bis(2-chloroethyl) ether, thiols, or diorganyldisulfides in the presence of KOH or hydrazine hydrate/base.[60–63] Methyl- and ethyl-substituted oxadithioethers (**L1**, **L2**) were synthesized by the reaction of potassium alkyl sulfides prepared by the reaction of R_2S_2 (R = Me, Et) and hydrazine hydrate/KOH with chlorex (Scheme 1). The reaction of bis(2-chloroethyl) ether with RSH/KOH produced other oxadithioethers **L3–L8**. The oxadithioethers **L3**, **L4**, and **L6** are new compounds, whereas **L1**, **L2**, **L5**, **L7**, and **L8** are known.[45,60–62,64–68] The compounds were fully characterized by NMR and Fourier-transform infrared spectroscopy (FTIR). Purity of the obtained ligands was confirmed by GC.

3.2 | Synthesis of palladium (II) dichloride complexes

The synthesis of complexes **1a**–**8a** was achieved by reacting (1,5-cyclooctadiene)palladium (II) dichloride with one equivalent of **L1**–**L8** in dichloromethane, which led to the formation of *trans*-[$PdCl_2$(μ-**L**)]$_2$ (**1a**–**8a**, **L** – oxadithioether ligands), as depicted in Scheme 2. Two



SCHEME 1 Routes for oxadithioether ligand synthesis (**L1**–**L8**). Percentages in parentheses represent yields



SCHEME 2 Synthesis of palladium chlorido (**1a**–**8a**) and cationic acetylacetonato complexes (**1b**–**8b**) with oxadithioether ligands. Percentages in parentheses represent yields

sulfur atoms coordinate to palladium (II), replacing the labile cod ligand. The new complexes were fully characterized by NMR and FTIR spectroscopy, ESI-MS, and elemental analysis.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **1a–8a** in $CDCl_3$ or DMSO-d_6 are generally consistent with the structure presented in Scheme 2. For **1a** and **2a**, DMSO-d_6 was the most suitable solvent, as these complexes were poorly soluble in other solvents. The formation of 16-membered dinuclear complexes is supported by an X-ray study of **4a** (vide infra). In the ^{1}H NMR spectra, the resonances in the range of 3.6–4.3 ppm are attributable to the four hydrogens of the -CH_2OCH_2- group and are at a lower field than the corresponding resonances of the free ligands. Signals from eight hydrogens in the -SCH_2- units appear in the 2.8–3.6 ppm range. Notably, for a solution of **2a** in dimethyl sulfoxide, raising the temperature from 25°C to 90°C causes the broad multiple -CH_2O-signals to coalesce to a single narrower band, and peaks in the -SC$H_2$$CH_3$ and -SC$H_2$$CH_2$O- regions have two narrower resonances (Figure S51, SI). These observations are indicative of dynamic behavior in solution. The signals due to the methylene protons from the -CH_2O moiety obtained in $CDCl_3$ at room temperature are more informative. For example, for **4a**, three signals of different intensities are observed between 4.05 and 4.24 ppm with $J_{H\text{-}H}$ couplings of 6.1–6.4 Hz (Figure 1). This observation demonstrates the presence of at least three isomers in solution in a 3.2/0.8/0.1 ratio. Two major signals can be attributed to the known pyramidal inversion of sulfur atoms occurring

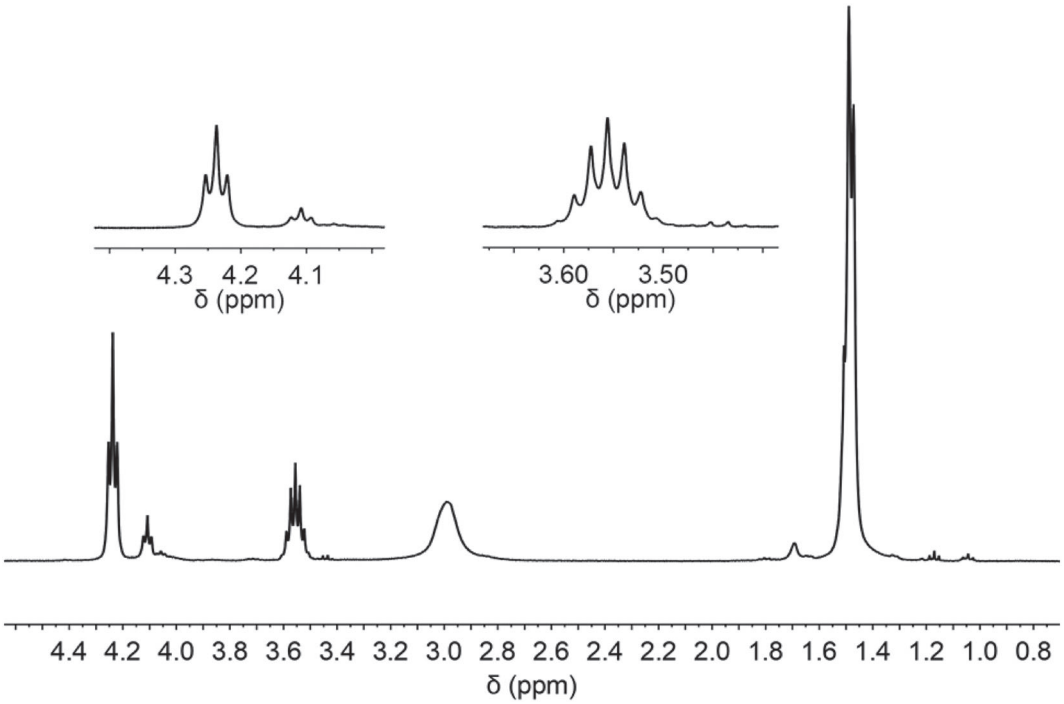
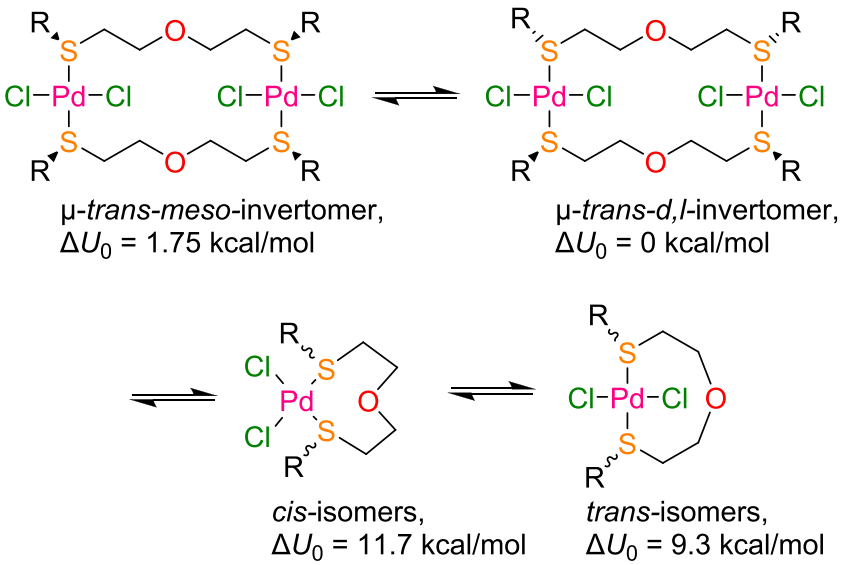


FIGURE 1 ^{1}H NMR of **4a** in $CDCl_3$ at room temperature

FIGURE 2 Plausible invertomers and isomers of **1a–8a** (ΔU_0 – zero point energy from DFT calculation for **1a**)



in palladium oxadithioether complexes.[69,70] As shown in Figure 2, two diastereoisomers (invertomers) can exist in solution, which differ in the orientation of the S-R groups. The S-R groups are *cis*-arranged in the *meso*-invertomer, whereas they are *trans*-arranged in the *d*,*l*-invertomer. The presence of an additional isomer may be associated with the formation of a mononuclear Pd (II) complex chelated by an eight-membered ring (Figure 2). Similar mononuclear complexes (*cis*-$[PdCl_2$(1-oxa-4,7-dithiacyclononane)] and *cis*-$[PdCl_2\{(PhSCH_2SiMe_2)_2O\}]$) are known in the literature and have been evidenced by X-ray studies.[63,70] ESI-MS analysis (positive mode, MeCN) of **1a–8a** demonstrated the molecular peaks of complex cations, which can be attributed to mono- ($[Pd(\mathbf{L})Cl]^+$) or dicationic ($[Pd_2(\mathbf{L})_2Cl_2]^{2+}$) species, for example, **4a** $m/z = 364.98$ Da. For complexes **5a** and **7a**, ESI-MS analysis also showed minor peaks of dimers with one chorine dissociated ($[Pd_2(\mathbf{L})_2Cl_3]^+$) and coordination oligomers $[Pd_3(\mathbf{L})_2Cl_5]^+$. Thus, the formation of di- or mononuclear complexes in solution was not clear from ESI-MS experiments.

Therefore, we performed density functional theory (DFT) calculations on the BP86/def2-TZVP$_{Pd,S,Cl}$/def2-SVP$_{C,H,O}$ level regarding the most plausible isomers (*meso*-, *d*,*l*-invertomers) for mononuclear species related to **1a** and two conformational isomers of dinuclear **1a**. The energy gap between dinuclear **1a** and its mononuclear version is greater than that between the *meso*- and *d*,*l*-isomers (see Table S4, SI). The energy difference between di- and mononuclear complexes calculated with the DFT method is approximately 7 kcal/mol (Figure 2). The energetic ($\Delta_r U_0$) gap between the two optimized isomers of **1a** accounts for ≈1.7 kcal/mol. These calculations confirm the coexistence of the two dinuclear isomers in solution as a consequence of interconversion equilibrium. The formation of monomeric *cis*-chelated palladium complexes is energetically less favored, and such species probably exist in negligible amounts in solution.

For oxadithioether ligands **L1**–**L8** and complexes **1a**–**8a**, IR spectroscopy enables the confirmation of successful complex formation, as well as helping to elucidate their structural and spectroscopic features. In the range of 2850–2960 cm^{-1}, stretching vibrations of C−H bonds from CH_3, CH_2, and CH groups were observed; for **L1**–**L8**, there are no deviations from the generally accepted frequency values. However, upon coordination to palladium, the bands of the stretching vibrations of C−H bonds in groups at S are shifted toward higher frequencies. Moreover, this effect weakens with an increase in the length of the substituent chain and is practically not observed for the groups located in the γ-position relative to the sulfur atom. For example, the band at ≈2960 cm^{-1} is caused by antisymmetric stretching vibrations of C−H bonds in the methyl group in most organic compounds. However, in complex **1a**, this band splits into two bands and shifts by 40 cm^{-1} (average value, 3009 and 2986 cm^{-1}). In complexes **2a** and **4a**, where the methyl group is in the β-position, the band increases to ≈2970 cm^{-1} on average. A similar trend for the vibrations of methylene groups was observed for complex **8a**. In **L8**, the antisymmetric C−H stretching vibrations of the CH_2 groups of the benzyl moiety appear as a band at 2950 cm^{-1} and do not overlap with bands from the S-*CH$_2$*-CH$_2$-O-fragment. In the IR spectrum of **8a**, the frequency of this band increases to 2975 cm^{-1}. For **L1**, characteristic bands at 1436 and 1320 cm^{-1} should be noted, corresponding to bending antisymmetric and symmetric vibrations in S-CH_3, respectively.[71] Upon coordination to Pd, the δ_{as}(C-H from S-CH_3) band is shifted up to ≈1470 cm^{-1} and splits, while δ_s does not change its position in the spectrum. In the IR spectra of **L1**–**L8**, the bands of scissoring vibrations in the OCH_2 groups (≈1427 cm^{-1}) and SCH_2 groups (≈1405 cm^{-1}) are also observable. In the spectra of complexes **1a**–**8a**, the vibration band in the OCH_2 groups decreases by 5–10 cm^{-1} and appears as a shoulder on the vibration band from the SCH_2 groups, increasing 2–3 times in intensity compared to free ligand. For example, upon coordination to palladium, the intensity ratio $I(\delta_{HCH,\ scissoring})/I(\nu_{as\ C-O-C})$ increases 1.8, 2.5, 2.3, 2.7, and 3.5 times in **L1**, **L2**, **L3**, **L5**, and **L7**, respectively. Bands of mixed wagging and twisting vibrations of methylene groups at various substituents are observed in the spectra at 1100–1400 cm^{-1}. In this case, the bands, which are primarily attributable to the vibrations of the SCH_2 groups, increase in intensity upon coordination to Pd. For example, for **L1**, the 1190 cm^{-1} band appears in the spectrum as a shoulder at 1200 cm^{-1}, but an increase in its intensity is observed in the spectrum of complex **1a**. Thus, twisting vibrations in SCH_2 groups make a greater contribution to the 1190 cm^{-1} band.

The IR spectrum of **L1** contains an intense band of antisymmetric stretching vibrations of C−O−C bonds at 1110 cm^{-1}, with a full width at half maximum (FWHM) of 123 cm^{-1}. The large width of this line is due to the presence of a significant number of conformational isomers in equilibrium in **L1**. Upon coordination to palladium, the geometric structure of **L1** is stabilized, and as a result, this band is narrowed by a factor of 2.5. Notably, the FWHM of the 1110 cm^{-1} bands in the other ligands is considerably narrower and decreases from 58 cm^{-1} for **L2** to 48 cm^{-1} for **L8**. In complexes **1a**, **3a**–**8a**, the FWHM of the corresponding band decreases insignificantly (Δ (FWHM) = 2–12 cm^{-1}). An exception is **2a**, for which the narrowest ν_{as}(C−O−C) band with an FWHM of 33 cm^{-1} was observed. This result may indicate the stabilization of a small number of conformers. For complex **4a**, this band is split into two bands (the FWHM is 43 cm^{-1}), which indicates the formation of two types of isomers (in the solid). In addition, splitting of the ν_s(C−O−C) band was observed in the IR spectra of complexes **1a**–**8a**. It should be noted that the peak of ν_{as}(C−O−C) in complexes **1a**, **2a**, **3a**, **5a**, and **7a** shifts as the substituent lengthens from 1125 cm^{-1} (for **1a**) to 1003 cm^{-1} (for **7a**). Weak bands from antisymmetric and symmetric stretching vibrations of C−S−C bonds were observed in the IR spectra of **L1**–**L8** at 600–700 cm^{-1}. Moreover, the heavier the substituents on sulfur were, the weaker the intensity of these bands was. The shift of these bands to lower frequencies in the IR spectra of complexes **1a**–**8a** by 10–50 cm^{-1} confirms the coordination of ligands to palladium through sulfur atoms. This shift was most clearly recorded for **L1** (ν_{as}(C−S−C) = 700 cm^{-1} and ν_s(C−S−C) = 660 cm^{-1}) and **1a** (655 and 640, respectively). Notably, for complex **4a**, splitting of the ν_{as}(C−S−C) and ν_s(C − S − C) bands in the IR spectrum was observed (ν_{as} = 686, 665 cm^{-1} and

ν_s = 632, 619 cm^{-1}), which indicates the formation of at least two types of isomers.

3.3 | X-ray crystal structure of 4a

Single crystals of **4a** suitable for X-ray crystallography were obtained by slow vapor diffusion of diethyl ether into 1,2-dichloroethane solutions of the complex. Complex **4a** contains two four-coordinate palladium (II) centers.

The solid-state molecular structure of **4a** is depicted in Figure 3 with selected interatomic distances and angles listed in the figure caption. The Pd–S bond lengths of 2.331 and 2.325 Å are similar to those reported for *trans*-[Pd_2Cl_4{μ-^{t}BuS $(CH_2)_5S^tBu$}$_2$] ($d_{Pd\text{-}S,\ av.}$ = 2.33 Å) but longer than *cis*-[$PdCl_2$(1-oxa-4,7-dithiacyclononane)], *cis*-[$PdCl_2${$(PhSCH_2SiMe_2)_2O$}], and *cis*-[$PdCl_2$([9]aneS_3)], with Pd–S bond lengths of 2.26–2.31 Å.[63,70,72] The average Pd–Cl bond length (2.301 Å) lies in the usual range found for four-coordinate Pd (II) complexes.[1]

The two trans-arranged Cl atoms form a Cl1-Pd1-Cl2 angle of 179.347(19), and the angle between the sulfur atoms of S1-Pd1-S2 of 173.760(16) indicates slight deformation of the square planar geometry for palladium. The 16-member ring has a "parallelogram shape" when viewed along the Cl–Pd bond with sides formed by the extended S-$(CH_2)_2O(CH_2)_2$-S chains and the *trans* S-Pd-S linkages. From an overhead point of view, the 16-membered ring adopts a chair-like conformation. Surprisingly, the ligand 1,5-bis(*tert*-butylthio)pentane, which is comparable to ligand **L4**, adopted an elongated boat-like conformation when coordinated to palladium.[73] Most likely, a chair-like conformation is preferred due to a weak dative Pd1···O1 bond in **4a**. In the crystal structure of **4a**, the oxygen atom of **L4** is oriented toward palladium and lies inside the coordination macrocycle at a Pd1···O1 distance of 3.011 Å. The sum of the van der Waals radii of the atoms in question is 3.10 Å.

3.4 | Synthesis of cationic palladium (II) Acetylacetonate complexes

The synthesis of complexes **1b–8b** was achieved by reacting bis(acetonitrile)(acetylacetonate)palladium (II) tetrafluoroborate with one equivalent of **L1–L8** in dichloromethane, which led to the formation of [Pd(acac)(**L**)][BF_4] (**1b–8b**), as depicted in Scheme 2. The new complexes were fully characterized by NMR and FTIR spectroscopy, ESI-MS and elemental analysis.

In contrast to **1a–8a**, these complexes are most likely mononuclear. In our opinion, this is due to destabilization of the dinuclear 16-member ring structure forced by the acac ligand *cis*-structure. DFT calculations regarding the most plausible conformational isomers for the cation of **1b** (**1b**+) and dinuclear dication of **1b** showed an energy gap of ≈15 kcal/mol (Figure 4). Notably, the geometrical conformers of [Pd(acac)(**L**)]BF_4 can exist in two *exo*- or *endo*-type conformations (Figure 4). In the

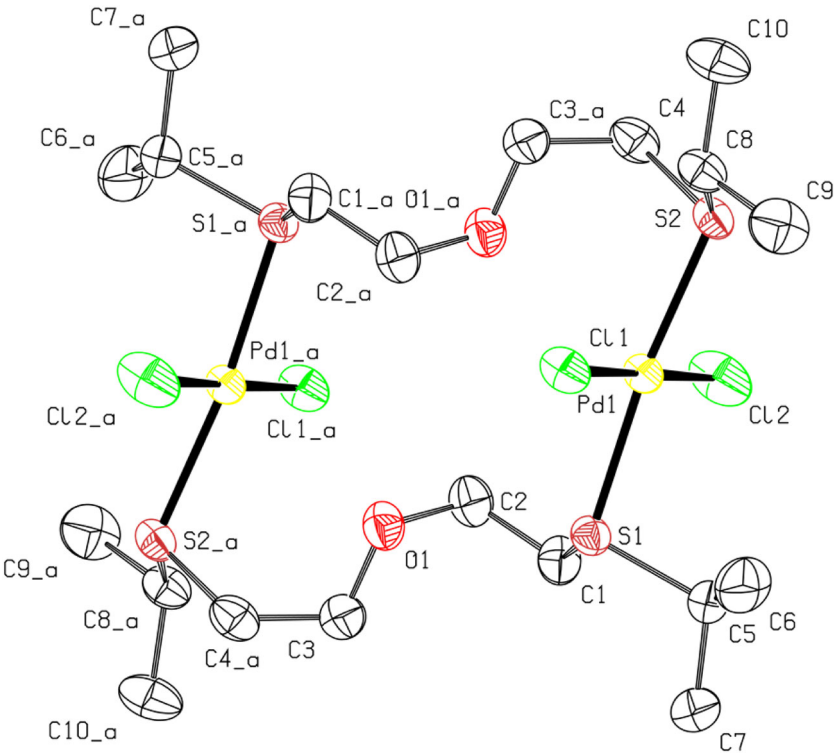


FIGURE 3 An ORTEP drawing of **4a** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Details of the structure refinement are given in Table S1, SI. Selected bond distances (Å) and angles (°): Pd1—S1 = 2.3253(4), Pd1—S2 = 2.3311(5), Pd1—Cl1 = 2.3005(4), Pd1—Cl2 = 2.3011(5); ∠Cl1—Pd1—S1 = 86.286(16), ∠Cl2—Pd1—S2 = 84.683(18), ∠S1—Pd1—S2 = 173.760(16), ∠Cl1—Pd1—Cl2 = 179.347(19)

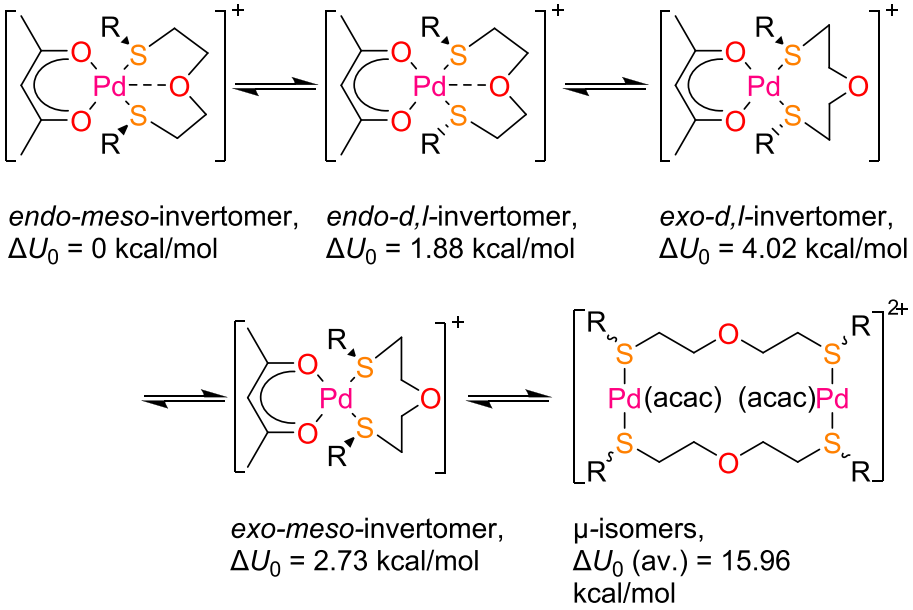


FIGURE 4 Plausible invertomers and isomers for cations of **1b–8b** in solution (ΔU_0 – zero point energy from DFT calculation for cations of **1b**)

endocomplexes, an oxygen atom on the ligand is directed toward the inner side of the central metal. The oxygen atom of the endocomplex plays the role of a weak electron donor group to the central Pd (II) metal.[74] As a result, the DFT-calculated structures for **1b**+ show that the more stable conformers are *endo*-ones. The oxygen atom in *endo*-**1b**+ lies above the coordination plane with a (Pd···O) distance of 2.991–3.101 Å. The average zero point energy difference between *endo*- and *exo*-**1a** + - (Figure 4) calculated with the DFT-BP86 method is approximately 2.5 kcal/mol (see Table S4, SI). The formation of mononuclear complexes was also evident from HPLC analysis of the complex solutions (MeCN). The retention times (R_t) for **1b–8b** were 1.70–1.95 min; for dinuclear complexes **1a–8a**, R_t = 2.20–2.65 min.

Since the small energy changes in solvent incorporation (especially coordinating forces) or crystal packing forces may switch the endodentate and exodentate coordinations of the Pd (II) metal cation with the ligands,[74] four isomeric complexes can be formed from **1b–8b** in solution. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **1b–8b** in $CDCl_3$ or CD_3CN are consistent with the presence of isomers (Figure 4) in a solution. The spectra of all complexes ligated with the **L1–L8** ligands show the presence of two or more structures. In particular, resonances from the Me-S fragment in the ^{1}H NMR spectrum of **1b** appear as four broad signals (2.37 (12%), 2.31 (19%), 2.24 (48%), 2.18 (21%) ppm). In the NMR spectra of **1b–8b**, two or three signals can be easily distinguished from the CH- and CH_3-protons of acetylacetonate ligands.

It was concluded from ^{1}H and ^{13}C{^{1}H} NMR spectroscopy that the length and structure of the alkyl group at the sulfur atom of the ligand influence the isomer distribution. For example, when the ligand with the Me-S group is used, the ratio of the integrals from C*H*-acac protons in the ^{1}H NMR spectrum ($CDCl_3$, 5.56 and 5.53 ppm) was 0.5; for **7b** (*n*-hexyl-S group), the integral ratio of the corresponding signals (5.60 and 5.56 ppm) was 4.0. In general, the signals in the ^{1}H NMR spectra (at 25°C) are relatively broad, which is indicative of a dynamic exchange process. The ^{1}H,^{1}H NOESY spectra of **1b** and **5b** exhibit an exchange of cross-peaks arising from the dynamic exchange between the -CH_2O- and -CH_2S- groups of the chelated oxadithioether ligands (Figure S52, SI). This result clearly indicates the presence and interconversion of isomers in solution, which differ in the orientation of the S–R groups, as well as in structures involving a weak apical Pd···O contact.

To further investigate the dynamic behavior of the oxadithioether ligands, we performed variable temperature ^{1}H NMR experiments with cationic complex **2b**. Figure 5a presents the region of the ^{1}H NMR spectra in CD_3CN or $CDCl_3$ from −50°C to 70°C. In CD_3CN, the fast exchange limit is almost reached at 70°C. All signals in the spectrum decoalesce into two or more signals at lower temperatures. The same trend was observed in the ^{13}C NMR spectra of **2b** (Figure 5b). Two signals from -CH_2O-, -CH_2S-, and acac groups are apparent in the ^{13}C NMR spectrum of **2b** at 25°C, with coalescence occurring at ≈70°C in CD_3CN. The free energy of activation estimated according to the equation $\Delta G^{\#} = RT_c[22.96 + \ln(T_c/\delta_\nu)]$[10,75] for the dynamic fluxional behavior of **2b** from NMR at coalescence temperatures suggests a barrier of approximately 16 kcal/mol. An activation energy $\Delta G^{\#}$ of 16.9 kcal/mol was determined for the process of pyramidal inversion of sulfur atoms occurring at the chelate

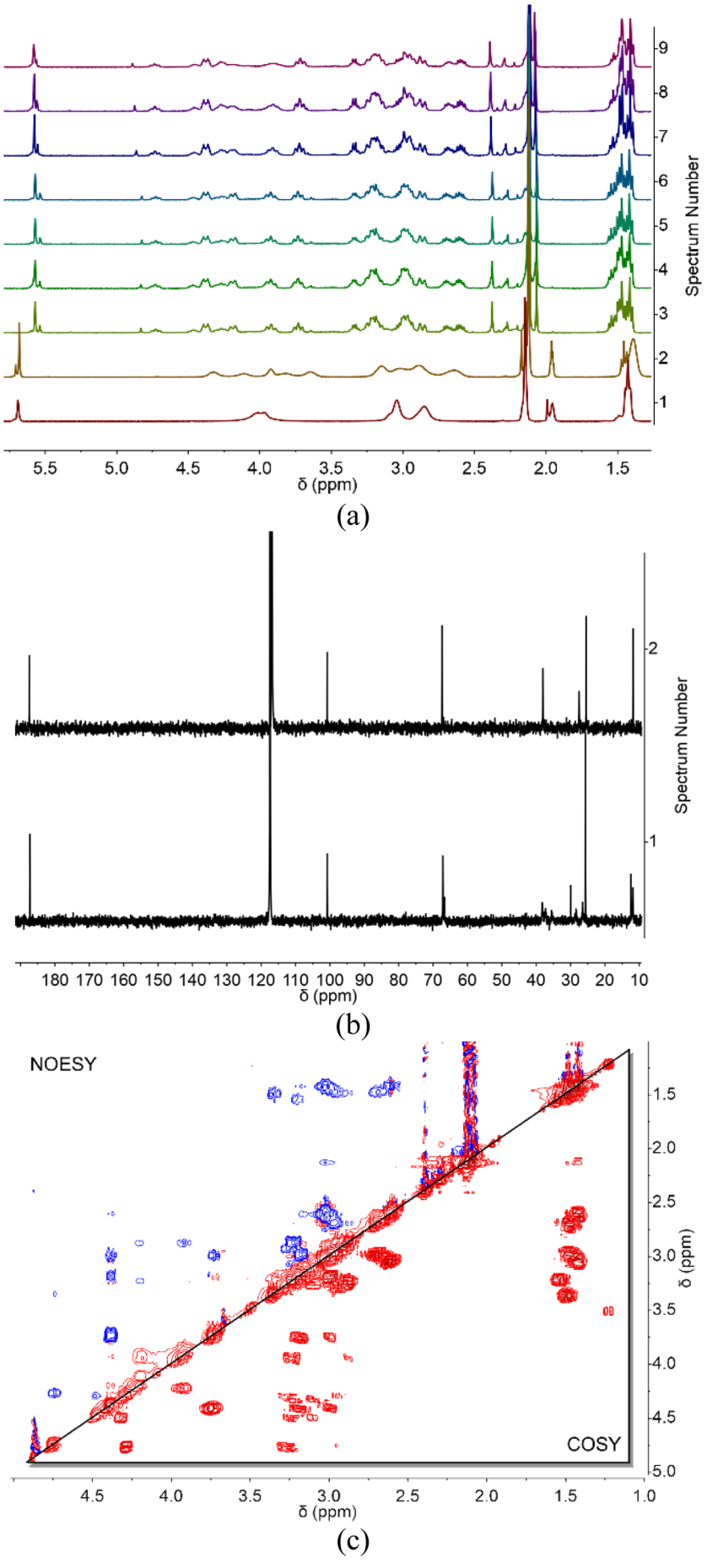


FIGURE 5 NMR spectra of **2b** at various temperatures: ^{1}H [CD_3CN: 1–343 K, 2–298 K; $CDCl_3$: 3–293 K, 4–283 K, 5–263 K, 6–253 K, 7–243 K, 8–233 K, 9–223 K] (a);$^{13}C\{^{1}H\}$ [CD_3CN: 1–298 K, 2–343 K] (b); and $^{1}H,^{1}H$ NOESY and COSY [$CDCl_3$, 263 K] (c)

complex *cis*-[$PdCl_2$(MeSCH$_2$CH$_2$SMe)].[69] The ^{1}H NMR spectra of **2b** recorded in $CDCl_3$ were notably complicated (Figure 5). To elucidate the structural features of the complex, correlation spectroscopy (COSY), nuclear Overhauser effect spectroscopy (NOESY), and heteronuclear single-quantum correlation spectroscopy (HSQC) 2D procedures were used in addition to analysis of the one-dimensional ^{1}H and ^{13}C NMR spectra.

Analysis of the ^{1}H NMR spectrum of **2b** showed the presence of four isomeric complexes. For example, resonances from the Me fragment appear as four triplets (1.54 (11%), 1.50 (19%), 1.47 (34%), and 1.41 (36%) ppm). The complication of the spectral pattern in the aliphatic region is also related to the restriction of the mobility of oxadithioether units in the rigid spatial structure of **2b**. A similar phenomenon was reported[7] for palladium (II) complexes with benzothiacrown ethers as ligands. Restriction of the ligand mobility in **2b** results in splitting of the proton signals of the oxadithioether methylene groups. Chemical shifts for the axial and equatorial protons in the spectrum of **2b** were interpreted using quantum-chemical calculation of the nitrobenzodithiacrown ether palladium (II) complexes with similar structural SOS patterns.[7] Figure 5 shows fragments of the NOESY and COSY spectra of **2b**, where the cross-peaks correspond to coupling of the methylene-group geminal and methylene-methyl-group protons from four different isomers. In contrast to the results obtained for **1b** and **5b** in CD_3CN, in the ^{1}H,^{1}H NOESY spectra of **2b** (−10°C, $CDCl_3$), there are no exchange cross-peaks arising from the dynamic exchange between -CH_2O- and -CH_2S- groups. This result suggests that interconversions of the isomers, which differ in the orientation of the weak apical Pd···O contact, are slow on the NMR timescale in $CDCl_3$ at −10°C. An interpretation of the major isomer peaks in the aliphatic region suggests that these represent invertomers of an endodentate conformation of the coordinated 6-oxa-3,9-dithiaundecane. The resonances at 4.38 (m), 4.10 (dt) and 3.92 (t), 3.73 (dt) ppm are assigned as the two axial and two equatorial hydrogens of the -CH_2O-group from two invertomers of the *endo*-SOS-chelate and are shifted downfield compared with the peak of the free ligand (3.61 ppm). The resonances from 4.0 to 4.9 ppm are assigned as invertomers of an exodentate conformation of **L2**. Notably, the signals observed in the ^{1}H NMR spectra of **2b** from one of the major isomers (see resonances at 4.19, 3.92, and 2.69 ppm, Figure 5) broaden when the temperature drops below 263 K. The resonances at 2.69 (dq) and 2.61 (dq) ppm are assigned as the two equatorial hydrogens of the -S*C*H_2CH$_3$-group from two major invertomers. As several peaks of the -CH_2S*C*H_2-group attributed to *endo*-, *exo*-, *meso*- and *d*,*l*- forms overlap, further analysis of the peaks is precluded.

Complexes **1b**–**8b** were characterized by IR spectroscopy (see Section 2). The spectra contain all the vibration bands of the fragments of the **L1**–**L8** ligands (vide supra), as well as intense bands of stretching vibrations of C=O and C=C bonds of the acetylacetonate chelate at 1560 and 1520 cm^{-1}. In addition, the spectra show two bands at 693 and 636 cm^{-1} from antisymmetric and symmetric stretching vibrations of C−S−C bonds, respectively. Moreover, the position of these bands is unchanged in all complexes. This evidences the formation of identical structures in complexes **1b**–**8b**. The 1150–1000 cm^{-1} region is uninformative, since it is almost completely overlapped by intense bands of antisymmetric stretching vibrations of the $[BF_4]^-$ anion. Therefore, further analysis to determine populations of the two forms or more isomeric forms is precluded in the solid phase. Notably, in all spectra of the complexes at 780–790 cm^{-1}, there is a band of symmetric stretching vibrations of the $[BF_4]^-$ anion, which is forbidden in the IR spectrum of an ideal tetrahedron. This result indicates a distortion of the ideal tetrahedral geometry of the anion molecule caused by the interaction of the latter with the fragments of the cation.

3.5 | X-ray crystal structure of 4b

Single crystals of **4b** suitable for X-ray crystallography were obtained by slow vapor diffusion of diethyl ether into 1,2-dichloroethane solutions of the complex. Figure 6 shows the structure of **4b**. Selected bond lengths and angles are given in the figure captions. Ligand **L4** assumes a facial coordination mode in **4b**. Complex **4b** has a distorted square planar geometry for palladium, shown by the ∠O3—Pd1—O2 and ∠S1—Pd1—S2 bond angles of 93.2(6)° and 91.23(18)°, respectively. The average Pd–S bond distance of 2.275 Å is comparable with those found in other Pd (II) complexes of macrocyclic thioethers.[1,63,70] As in the case of **4a** in the crystal structure of **4b**, the oxygen atom of **L4** is oriented toward palladium at a Pd···O distance of 2.893 Å, indicating weak dative Pd···O bond formation. In addition, short contacts between the fluorine atoms of $[BF_4]^-$ and the hydrogens of the methylene groups (F···H-C, 2.449–2.661 Å) are observed in the crystallographic packing of **4b**, presumably forming minor C–H···F hydrogen bonds. Consequently, distortion of the idealized tetrahedral geometry of the anion $[BF_4]^-$ (e.g., ∠F4—B1—F3 = 106(3)°) leads to the appearance of symmetric stretching vibration at 789 cm^{-1} in the IR

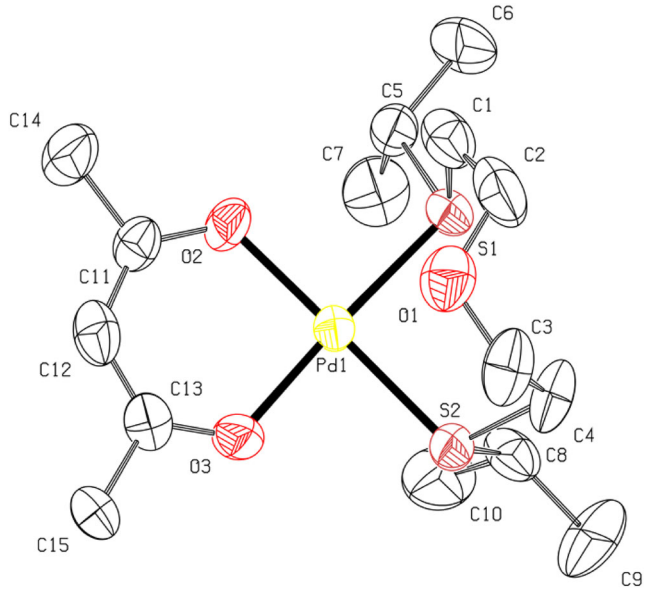
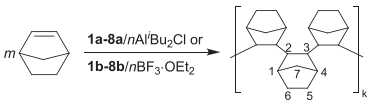


FIGURE 6 An ORTEP drawing of **4b** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and BF_4 counterion are omitted for clarity. Details of the structure refinement are given in Table S1, SI. Selected bond distances (Å) and angles (°): Pd1—O3 = 2.018(13), Pd1—O2 = 2.018(13), Pd1—S1 = 2.278(5), Pd1—S2 = 2.273(5); ∠O2—Pd1—O3 = 93.2(6), ∠S1—Pd1—S2 = 91.23(18), ∠O2—Pd1—S2 = 178.0(5), ∠O3—Pd1—S1 = 176.6(4)

spectrum of **4b**, which is forbidden in the infrared absorption spectrum.

3.6 | Catalytic studies

Bicyclo[2,2,1]hept-2-ene (norbornene, **NB**) can be polymerized in three different ways: ring opening metathesis polymerization, cationic or radical polymerization, and vinyl/addition polymerization. Addition polynorbornene (**PNB**) has received considerable attention due to its dielectric and mechanical properties for technical application as an interlevel dielectric in microelectronics applications.[76–79] Catalyst systems based on palladium and nickel complexes in different oxidation states exhibit high activity (usually in the range of 10^5–10^7 g_{NB} mol^{-1} cat h^{-1}) in the addition polymerization of NB.[76–79] A variety of palladium complexes have been reported to be active for the polymerization of norbornene,[76,79] but the application of oxadithioether-chelated palladium complexes in this reaction is not known to date. We studied the polymerization of norbornene (Scheme 3) with chlorido palladium complexes (**1a–8a**) in the presence of typical Ziegler–Natta alkylating cocatalyst (Al^iBu_2Cl). Cationic acetylacetonate complexes (**1b–8b**) were activated with $BF_3{\cdot}OEt_2$. It is known that aluminum alkyl-



SCHEME 3

free cationic Pd-catalyzed systems with O^O-chelating ligands (O^O = β-diketonates or carboxylates) activated with Lewis acid such as $BF_3{\cdot}OEt_2$ have shown promising results for polymerization of norbornene and its derivates.[36,38,39,80,81] The main results are listed in Tables 1 and 2. All **1a–8a** complexes produce polynorbornene, showing moderate to high activities on the order of $1.5{\cdot}10^5$–$1.4{\cdot}10^7$ g_{PNB} mol_{Pd}^{-1} h^{-1}. Table 1 shows that for oxadithioether-ligated complexes, the catalytic productivity under the same conditions decreased in the following order: **6a**, **5a**, **3a** > **4a** > **1a**, **8a** > **2a**, **7a**. This can be attributed to the influence of electronic or steric properties of oxadithioether ligands and to differences in the reactivity of these ligands with Al^iBu_2Cl if they dissociate. Upon activation, oxadithioether ligands can be lost to give a "naked" Pd as the active species. Hence, more weakly bound ligands that can be removed faster will lead to the more active palladium "naked" species more quickly.[82,83] In blank experiments, no activity was observed with any of the complexes in the absence of the cocatalyst or with Al^iBu_2Cl alone. The use of $BF_3{\cdot}OEt_2$ as a cocatalyst to activate **1a–8a** led to low catalytic activity.

In contrast to the results for **1a–8a**, catalyst systems (**1b–8b**)/$BF_3{\cdot}OEt_2$ generally showed moderate polymerization activities (Table 2) of $1.2{\cdot}10^5$–$8.0{\cdot}10^5$ g_{PNB} (mol Pd)$^{-1}$ h^{-1}. The yield, as well as the catalyst activity, also depends significantly on the reaction parameters applied, such as the cocatalyst/catalyst ratio, monomer/catalyst ratio, and reaction temperature (Table S5 and Figures S1 and S2, SI). Table 2 shows that the catalytic productivity for *n*-alkyl-oxadithioether-ligated *cis*-complexes under the same conditions decreased in the following order: **5b**, **7b** > **3b** > **1b** ≫ **2b**. The most active complex **5b** was chosen as the precatalyst for the study of the polymerization in detail. A linear relation between activity and the initial molar ratio of norbornene to **5b** of up to $[NB]_0/[Pd]_0$ of 5000 was found (Figure S2, SI). A further increase of $[NB]_0/[Pd]_0$ lowered the activity. Such concentration effect of palladium precatalyst was reported for norbornene polymerization by C. Janiak et al[84] and may be explained by impurities which are contained in the monomer and eventually decrease the number of active centers. Variation of the ratio of $BF_3{\cdot}OEt_2$ to **5b** showed considerable effect on the catalytic activities (Table 2, Entries 9–12). When the [B]/[Pd] ratio was increased, the catalytic ability of **5b** first increased rapidly

TABLE 1 Polymerization of norbornene by (**1a**–**8a**)/nAl^{i}Bu$_2$Cl

Entry[a]	Complex (R)	$[NB]_0$: $[Pd]_0$	$[Cocat.]_0$: $[Pd]_0$	Y/%[b]	TON[c]	A[d]
1	**1a** (Me)	5000	75	27	1400	260
2	**2a** (Et)	5000	75	16	800	150
3	**3a** (^{n}Pr)	5000	75	62	3100	580
4	**4a** (^{i}Pr)	5000	75	48	2400	450
5	**5a** (^{n}Bu)	5000	75	62	3100	590
6	**6a** (^{i}Bu)	5000	75	73	3700	690
7[e]	**6a** (^{i}Bu)	50,000	250	22	11,200	2110
8[f]	**6a** (^{i}Bu)	500,000	2500	5	26,800	5060
9[g]	**6a** (^{i}Bu)	500,000	2500	15	75,900	14,290
10	**7a** (*n*-hexyl)	5000	75	17	800	160
11	**8a** (benzyl)	5000	75	20	1000	190
12[h]	**4a** (^{i}Pr)	5000	50	<0.1	2	0.4
13[h]	**6a** (^{i}Bu)	5000	50	2	90	20

[a]Reaction conditions: $t = 25$°C, 0.02 mol.% Pd, $n_{Pd} = 4.9$ μmol, dichloromethane, $V_0 = 9$ ml, reaction time—0.5 h.
[b]Yield of PNB.
[c]*TON* in (mol NB) (mol Pd)$^{-1}$.
[d]Average activity of the catalyst in (kg NB) (mol Pd h)$^{-1}$.
[e]0.002 mol.% Pd, $n_{Pd} = 0.49$ μmol.
[f]2 ppm (mol.) Pd, $n_{Pd} = 0.05$ μmol.
[g]2 ppm (mol.) Pd, $n_{Pd} = 0.05$ μmol, $t = 75$°C.
[h]Cocatalyst—$BF_3{\cdot}OEt_2$.

and then increases smoothly (also see Figure S1 (SI) for the same trend with **1b** as precatalyst). It was found that the activity of **5b** increased with increasing temperature from 25°C to 100°C (Table 2, Entries 14, 18–20). The highest activity was found at 100°C, indicating that the active species is stable at high temperature. Along with an increase of $[NB]_0/[Pd]_0$ ratio and reaction time at 100°C resulted in high *TON* of 44,000 with the activity up to $2.7{\cdot}10^6$ g_{PNB} (mol Pd)$^{-1}$ h^{-1}. Solvent dependence of the polymer yields was found for catalyst system **5b**/$n$$BF_3{\cdot}OEt_2$. No activity was observed in polar coordinating solvents such as acetonitrile and *N*,*N*-dimethylformamide (Table 2, Entries 15 and 16), while in weakly coordinating solvents (Table 2, Entries 14 and 17) the catalyst activity was practically the same. The high-temperature stability of the catalyst system **5b**/$n$$BF_3{\cdot}OEt_2$ prompted us to investigate whether it also had high activities toward polymerization of polar NB derivative (5-methoxycarbonylnorbornene), but almost no polymer of NB-$COOCH_3$ was obtained. This is common for ester-functionalized norbornene derivatives,[77] for which the carbonyl oxygen atom competes with the vinyl double bond for the coordination. Thus, in contrast to the known steric hindered phosphine-ligated palladium catalysts,[36,77,85] nonbulky *n*-alkyl-oxadithioether-ligated palladium complexes cannot inhibit this chelation.

Notably, complexes **2b** and **4b** activated with boron trifluoride etherate showed low activity in the polymerization of NB. Proposed mechanism of the formation of the active species is shown in Figure 7. Beginning with the BF_3 adduct, the first step of the catalytic reaction involves the transformation of κ^2-O,O-acetylacetonate to a π-complex with a γ-bonded acetylacetonate ligand.[39,86–88] In the next step, insertion of the coordinated NB into the Pd–C bond occurs (Figure 7). The reaction of **1b**–**7b** with $BF_3{\cdot}OEt_2$ in the presence of hex-1-ene as a model substrate was monitored by FTIR (see Figures S84–S91, SI). The IR spectrum of the reaction mixture **6b**/20(hex-1-ene)/3$BF_3{\cdot}OEt_2$ exhibits a decrease in the intensity of the absorbance band at 1520 cm^{-1} with the reaction time (Figure S91, SI). The band at 1520 cm^{-1} is due to stretching vibrations of the C=O and C=C bonds in the chelate-bonded acac group.[89] Upon the addition of $BF_3{\cdot}OEt_2$ to a solution of **6b** and hex-1-ene, new bands appear at 1555 and 580 cm^{-1}. The band at 1555 cm^{-1} characterizes acac ligated with boron trifluoride (C=O·BF_3).[90] The band at 580 cm^{-1} can be assigned to the stretching vibrations of the Pd–C bond.[91] When the reaction was performed using **4b**/20(hex-1-ene)/3$BF_3{\cdot}OEt_2$, similar results were obtained but with substantially slower acac-group transformation from the O^O-bonded to C-bonded form (Figure S87, SI). For

TABLE 2 Polymerization of norbornene by (**1b**–**8b**)/$n$$BF_3$·$OEt_2$

Entry[a]	Complex (R)	$[NB]_0$: $[Pd]_0$	$[Cocat.]_0$: $[Pd]_0$	t/ °C	τ[b]/h	Solvent	Y/%[c]	TON[d]	A[e]
1	**1b** (Me)	2000	30	25	0.5	CH_2Cl_2	63	1260	240
2	**2b** (Et)	2000	30	25	0.5	CH_2Cl_2	5	100	20
3	**3b** (^{n}Pr)	2000	30	25	0.5	CH_2Cl_2	73	1460	280
4	**4b** (^{i}Pr)	2000	30	25	0.5	CH_2Cl_2	2	40	10
5	**5b** (^{n}Bu)	2000	30	25	0.5	CH_2Cl_2	89	1780	340
6	**6b** (^{i}Bu)	2000	30	25	0.5	CH_2Cl_2	80	1600	300
7	**7b** (*n*-hexyl)	2000	30	25	0.5	CH_2Cl_2	79	1560	290
8	**8b** (benzyl)	2000	30	25	0.5	CH_2Cl_2	41	820	150
9	**5b** (^{n}Bu)	5000	10	25	0.5	CH_2Cl_2	24	1200	225
10	**5b** (^{n}Bu)	5000	30	25	0.5	CH_2Cl_2	57	2850	540
11	**5b** (^{n}Bu)	5000	70	25	0.5	CH_2Cl_2	93	4650	880
12	**5b** (^{n}Bu)	5000	100	25	0.5	CH_2Cl_2	96	4810	910
13	**5b** (^{n}Bu)	15,000	70	25	0.5	CH_2Cl_2	7	1100	210
14	**5b** (^{n}Bu)	15,000	70	75	0.5	DCE[f]	21	3150	600
15	**5b** (^{n}Bu)	15,000	70	75	0.5	MeCN[g]	0	–	–
16	**5b** (^{n}Bu)	15,000	70	75	0.5	DMF[g]	0	–	–
17	**5b** (^{n}Bu)	15,000	70	75	0.5	CH_3NO_2[g]	15	2250	430
18	**5b** (^{n}Bu)	15,000	70	75	1.0	DCE[f]	47	7050	670
19	**5b** (^{n}Bu)	15,000	70	75	1.5	DCE[f]	70	10,500	660
20	**5b** (^{n}Bu)	15,000	70	100	0.5	DCE[f]	91	13,650	2580
21	**5b** (^{n}Bu)	30,000	70	100	0.5	DCE[f]	42	12,500	2370
22	**5b** (^{n}Bu)	50,000	70	100	0.5	DCE[f]	29	14,400	2730
23	**5b** (^{n}Bu)	50,000	70	100	1.5	DCE[f]	88	44,000	2760
24[h]	**5b** (^{n}Bu)	500	70	100	5.0	DCE[f]	0	–	–
25[i]	**4b** (^{i}Pr)	5000	50	25	0.5	CH_2Cl_2	20	1000	200
26[i]	**6b** (^{i}Bu)	5000	50	25	0.5	CH_2Cl_2	19	930	180

[a]Reaction conditions: $n_{NB} = 24.6$ mmol, $V_0 = 9$ ml.
[b]Reaction time.
[c]Yield of PNB.
[d]*TON* in (mol NB) (mol Pd)$^{-1}$.
[e]Average activity of the catalyst in (kg NB) (mol Pd h)$^{-1}$.
[f]Solvent—1,2-dichloroethane.
[g]80/20 v/v mixture of the solvent/1,2-dichloroethane was used.
[h]5-methoxycarbonylnorbornene was used as monomer (*exo*/*endo* = 53/47).
[i]Cocatalyst—Al^iBu_2Cl.

example, after 3 min, only 14% of the initial amount of **4b** transformed, whereas more than 44% of the O^O-bonded acac groups are transformed for **6b**. For **1b**, **2b**, **3b**, **5b**, and **7b**, the same trends in the FTIR monitoring results were observed (Figures S84–S91, SI). We presume that these observations indicate that the nature of the oxadithioether ligand influences the acac-group activation step. Additional details of the activation hypothesis were obtained from NMR (^{1}H and ^{19}F) investigations (see for spectroscopic details Figures S54–S59 and Tables S6–S7, SI). The reaction of **4b** and **6b** with BF_3·OEt_2 (5 equiv) in $CDCl_3$ in an NMR tube at room temperature led to the transformation of κ^2-O,O-acetylacetonate ligand within 6 min (the conversion was 39% for **4b** and 68% for **6b** based on ^{1}H NMR data for C*H*-acac at 5.0–5.7 ppm) and appearance of a new signal at 6.0 ppm attributed to BF_2(acac). New signals from BF_4 anion coordination were also detected by ^{19}F NMR (−150.83, −149.57 ppm), BF_2(acac) (−138.71 ppm), and an unidentified signal that was observed at −153.87 ppm. No Pd-black was observed. The NMR data were assigned to "$L_nPd(F{\cdot}BF_3)$" species and BF_2(acac) by comparison with values in the

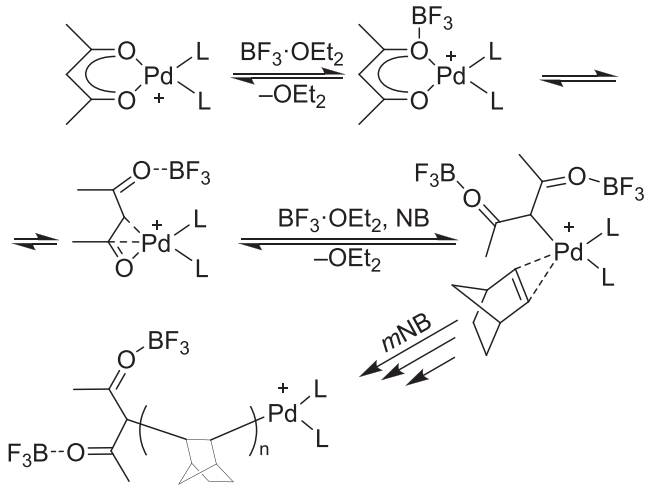


FIGURE 7 Proposed mechanism of the formation of the active species using (**1b–8b**)/$n$$BF_3$·$OEt_2$. The anion is omitted for clarity

literature.[92–95] Observation of the signals from BF_2(acac) suggests the formation of dicationic palladium species (see Figure S53, SI) and, in our opinion, presents a catalyst deactivation pathway that occurs in the catalyst systems under study. It should be noted that the significant decrease in activity of the monuclear complexes compared with the dinuclear complexes (e.g., **4a**, **6a** vs **4b**, and **6b**) can also be explained by metal–metal cooperativity effect, which was reported by C. Chen et al[96–98] in ethylene polymerization by dinuclear α-diimine Ni (II) and Pd (II) complexes.

The resulting polynorbornenes were insoluble in common solvents, such as benzene, chloroform, methylene chloride, THF, toluene, and 1,2,4-trichlorobenzene. Therefore, we cannot measure the molecular weights of the polymers by GPC. Insolubility of addition PNBs is frequently observed and considered indicative of high stereoregularity or the existence of a cross-linking structure by the C7-linkage, since intramolecular σ-bond metathesis leads to a rigid helical structure of the PNB, which strongly affects its solubility.[83,99,100] IR (KBr disk) analysis of polynorbornene (Figure S3, SI) showed no absorbance in the 1600–1670 cm^{-1} range, indicating that polymerization occurred via a vinyl addition pathway.[101] Notably, the IR spectrum of PNB obtained using **4b** showed the presence of weak bands at 1732 and 1717 cm^{-1}, indicative of C=O from the acac end group in the polymer (Figure S3, SI). Thermogravimetric analyses (Figures S4 and S5, SI) of the polymers also yielded typical high decomposition temperatures between 400°C and 420°C for the vinyl addition PNB.

4 | CONCLUSIONS

Palladium complexes *trans*-[$PdCl_2$(μ-L)]$_2$ and [Pd(acac)(L)][BF_4] (L = RS $(CH_2)_2O(CH_2)_2SR$, R = Me, Et, ^{n}Pr, ^{i}Pr, ^{n}Bu, ^{i}Bu, *n*-hexyl, benzyl) were synthesized and characterized by multinuclear NMR spectroscopy, FTIR spectroscopy, and mass spectrometry. Two palladium (II) complexes were characterized by X-ray crystallography. Variable temperature NMR spectroscopic studies and DFT calculations confirmed dynamic bonding of the oxadithioether ligands, which was consistent with the presence of diastereoisomers that differ in the orientation of the S-R groups along with both endodentate and exodentate bonding modes in solution. The flexibility of oxadithioether ligands expressed as different conformations in different complexes parallels the experience with the ligand series described in this report. The catalytic potential of *trans*-[$PdCl_2$(μ-L)]$_2$ and [Pd(acac)(L)][BF_4] was demonstrated in the polymerization of norbornene.

ELECTRONIC SUPPLEMENTARY INFORMATION AVAILABLE

XRD, NMR, FTIR, ESI-MS, EI-MS spectral data, DFT calculations and NB polymerization results.

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AUTHOR CONTRIBUTIONS

Dmitry Suslov: Conceptualization; investigation; supervision. **Zorikto Abramov:** Investigation. **Ilya Babenko:** Investigation. **Viktor Bezborodov:** Investigation. **Tatyana Borodina:** Investigation. **Mikhail Bykov:** Investigation. **Marina Pakhomova:** Investigation. **Vladimir Smirnov:** Investigation. **Anastasia Suchkova:** Investigation. **Gennadii Ratovskii:** Investigation. **Igor Ushakov:** Investigation. **Alexey Vilms:** Investigation.

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DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article

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