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Ruthenium indenylidene complexes containing dichalcogenoimidodiphosphinate ligands

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ABSTRACT

Reactions of ruthenium indenylidene starting material $[Ru(PPh_3)_2(Ind)Cl_2]$ (Ind = 3-phenylinden-1-ylidene) with potassium dichalcogenoimidodiphosphinates $K[R_2P(E)NP(E')R_2]$ afforded a series of complexes $[Ru(PPh_3)(Ind)\{\kappa E,\kappa E'\text{-}R_2P(E)NP(E')R_2\}Cl]$ [R = Ph, E = E′ = S (**1a**); R = Ph, E = E′ = Se (**1b**); R = ^{i}Pr, E = E′ = S (**1c**); R = ^{i}Pr, E = E′ = Se (**1d**); R = Ph, E = S, E′ = Se (**1e**); R = ^{i}Pr, E = S, E′ = Se (**1f**)] which were characterized by microanalyses, IR and NMR spectroscopies. The molecular structure of **1a** has been confirmed by single-crystal X-ray diffraction. The catalytic reactivity of the ruthenium indenylidene complexes in the ring closing metathesis of diethyl 1,2-diallylmalonate has also been investigated.

1. Introduction

Olefin metathesis [1] is widely known as a powerful and versatile tool for the formation of C—C bond in organic synthesis [2] and polymer chemistry [3]. Ever since the first well-defined ruthenium-based catalyst discovered by Grubbs and coworkers in 1992 [4], considerable effort has been devoted to the catalyst modification in order to get enhanced performance for the transformation of functionalized olefins [5]. In recent years, ruthenium-indenylidene based catalysts have attracted great attention due to their convenient preparation and better stability under harsh conditions [6]. Ruthenium-indenylidene complexes containing *N*-heterocyclic carbenes (NHCs) are the typical examples for metathesis transformation [7]. Remarkable activity of two new ruthenium-indenylidene complexes with sterically demanding NHC ligand was observed in ring closing metathesis (RCM) of olefins at low catalyst loadings [5d].

Dichalcogenoimidodiphosphinates, $[N(R_2PE)_2]^-$ (R = aryl, alkyl; E = O, S, Se), having been recognized as chalcogenide analogues of acetylacetonate, can form stable complexes with a range of main group and transition metal ions [8–11]. These complexes have been widely used as molecular single-source precursors to thin films, nanoparticles, or quantum dots by chemical vapor deposition or solution methods [12,13]. Owing to their electron-donating ability and steric bulk, $[N(R_2PE)_2]^-$ can stabilize electron-rich 16e coordinatively unsaturated Ru(II) complexes $[Ru\{N(R_2PE)_2\}_2(PPh_3)]$ which are capable of activating H_2, SO_2 and hydrazine [14]. Herein we describe syntheses, characterization, and olefin metathesis reactivity of the ruthenium-indenylidene complexes bearing the dichalcogenoimidodiphosphinate ligands.

2. Results and discussion

Treatment of $[Ru(PPh_3)_2(Ind)Cl_2]$ with the anionic dichalcogenoimidodiphosphinate ligands in THF at room temperature afforded series of 16-electron ruthenium-indenylidene complexes $[Ru(PPh_3)(Ind)\{\kappa E,\kappa E'\text{-}R_2P(E)NP(E')R_2\}Cl]$ **1a**–**1f** in high yields, indicating the Ru—C(Ind) bond is stable enough towards the attack of 1 equiv. dichalcogenoimidodiphosphinate ligand (Scheme 1). Complexes **1a**–**1f** were isolated as air-stable dark red microcrystals and had good solubility in common organic solvents, such as THF, diethyl ether, and dichloromethane. However, they were air-sensitive in solution since colorless crystals of $Ph_3P{=}S$ and $Ph_3P{=}Se$, characterized by unit cell determination, were separated from the corresponding solution of **1a–1f** in air. The ^{1}H NMR spectra of **1a**–**1f** all showed the characteristic singlet for *H*-2 at = 5.78, 5.87, 6.05, 6.11, 5.89(5.80), and 6.11 ppm, respectively (*vide infra*). They all shifted upfield compared to $[Ru(PPh_3)_2(Ind)Cl_2]$ (6.42 ppm). The methyl protons of isopropyl group in complexes **1c** and **1d** split as dd peaks with coupling constant J_{HP} about 7.0 Hz and J_{HH} about 18.0 Hz, respectively. The ^{13}C NMR spectra of **1a**–**1f** presented signals around 290 ppm (J_{PC} = 15.0 Hz),

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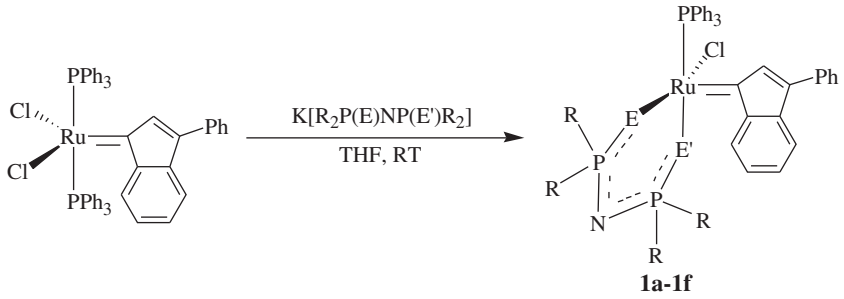


1a-1f

a, R = Ph, E = E' = S; b, R = Ph, E = E' = Se; c, R = ^{i}Pr, E = E' = S; d, R = ^{i}Pr, E = E' = Se; e(1), R = Ph, E = S, E' = Se; e(2), R = Ph, E = Se, E' = S; f, R = ^{i}Pr, E = S, E' = Se

Scheme 1. Synthesis of ruthenium indenylidene complexes **1a–1f**.

ascribed to Ru-*C*1(Ind). Resonances of both PPh_3 and dichalcogenoimidodiphosphinate ligands exhibited in the ^{31}P NMR spectra of **1a**–**1f**, for example, there were three ^{31}P signals, appearing at 38.8 (PPh_3), 36.0 [$P(S)Ph_2$], 35.2 [$P(S)Ph_2$] ppm in the ^{31}P NMR spectra of **1a**. The KBr IR spectra of **1a** and **1c** showed the ν(P═S) band at 703 and 699 cm^{-1}, respectively. The frequency of ν(P═Se) band in **1d** (528 cm^{-1}) increased compared to the $[N(^{i}Pr_2PSe)_2]^-$ (520 cm^{-1}) ligand (see Section 3).

It is worthy noting that complex **1e**, containing the mixed sulfur-selenium ligand, was found to be a mixture of two isomers **1e(1)** and **1e(2)**, as deduced from the NMR data. For example, there were two singlets of *H*-2, appeared at δ = 5.89 and 5.80 ppm in the ^{1}H NMR spectrum. Additionally, there were six ^{31}P signals in the ^{31}P NMR spectrum, exhibited at 39.2 (PPh_3), 38.2 (PPh_3), 35.9 ($P(S)Ph_2$), 35.2 ($P(S)Ph_2$), 24.6 ($P(Se)Ph_2$), 22.3 ($P(Se)Ph_2$), suggesting mixtures of compound **1e**. However, complex [Ru(PPh_3)(Ind){κ*S*,κ*Se*-$^{i}Pr_2P(S)NP(Se)^{i}Pr_2$}Cl] **1f** supported by bulky isopropyl substituted mixed donor ligand exists as one isomer only although we were unable to assign the exact geometry (*i.e. cis* or *trans*). For instance, there is one singlet signal around δ = 6.11 ppm in the ^{1}H NMR spectrum and three signals, showed at 36.2 (PPh_3), 51.4 (($P(Se)^{i}Pr_2$), 63.3 (($P(S)^{i}Pr_2$), in the ^{31}P NMR spectrum of **1f** (see Chart 1).

Single crystals of **1a** were obtained by slow diffusion of *n*-hexane to a concentrate solution of the complex in dichloromethane. The ORTEP diagram for the structure with selected bond lengths and angles is shown in Fig. 1. The X-ray crystal structure determination clearly shows coordination of the Ru center to the indenylidene moiety. The coordination geometry around the ruthenium center is distorted square pyramidal, with the strongest ligand (indenylidene) assuming the unique apical site. The square base is defined by one chloride, the donor atom of the phosphine and the dithioimidodiphosphinate ligand with the ruthenium center lying above this plane, the phosphine and chloride being in mutually *cis* positions. The six-membered ring RuS_2P_2N adopts chair-like conformation. The bond distance of Ru—C of 1.860(5) Å in **1a** is

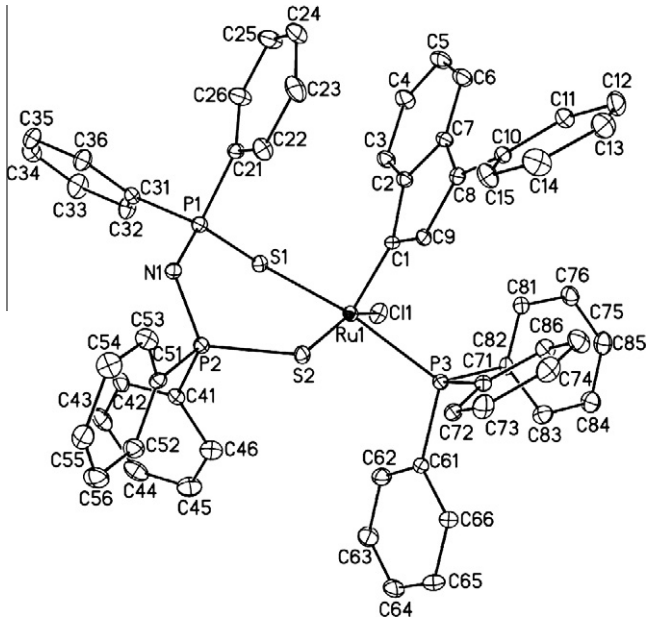
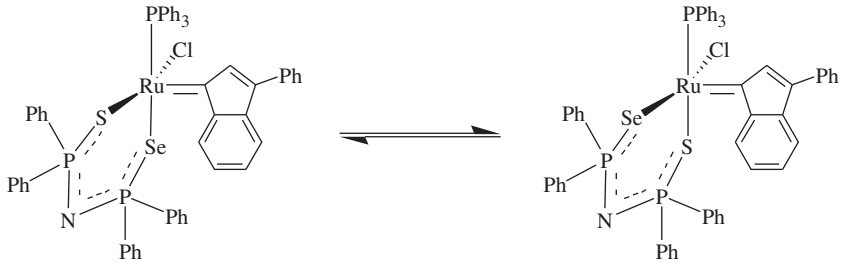


Fig. 1. ORTEP drawing of the molecular structure of [Ru(PPh_3)(Ind)(κ^2*S*,*S*-N($Ph_2PS)_2$)Cl] (**1a**). The hydrogen atoms are omitted for clarity. Selected bonds (Å) and angles (°): Ru(1)—C(1) 1.860(5), Ru(1)—S(1) 2.406(1), Ru(1)—S(2) 2.384(2), Ru(1)—Cl(1) 2.363(2), Ru(1)—P(3) 2.359(1), P(3)—Ru(1)—Cl(1) 87.84(5), S(1)—Ru(1)—S(2) 99.31(5), C(1)—Ru(1)—S(1) 101.03(2), C(1)—Ru(1)—P(3) 91.75(15), C(1)—Ru(1)—Cl(1) 107.02(16), P(3)—Ru(1)—S(1) 164.48(5), P(3)—Ru(1)—S(2) 88.26(5), Cl(1)—Ru(1)—S(1) 80.05(5), Cl(1)—Ru(1)—S(2) 157.97(5).

comparable to those in other limited reported ruthenium indenylidene complexes (1.850–1.908 Å) [15]. The average Ru—S bond length in **1a** (2.395(2) Å) lies well in other reported ruthenium complexes with dithioimidodiphosphinate ligands, such as [Ru{$N(Ph_2PS)_2$}$_2$(PPh_3)] (2.400(2) Å) and [Ru{$N(^{i}Pr_2PS)_2$}$_2$(PPh_3)]

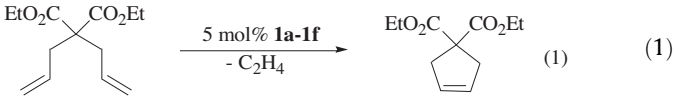


1e(1) **1e(2)**

Chart 1. Transformation of complex **1e(1)** and **1e(2)**.

(2.404(2) Å) [14b]. The Ru—P bond length in **1a** (2.359(1) Å) is slightly longer than that in [Ru{N(Ph_2PS)$_2$}$_2$(PPh_3)] (2.218(2) Å). The Ru—Cl bond length in **1a** (2.363(2) Å) is slightly shorter than those in [Ru(Ind)(PhobCy)$_2$$Cl_2$] (Phob = phosphabicyclononane) (av. 2.393(2) Å) [15a] and [Ru(Ind)(SIMes)(Py)Cl_2] (SIMes = 1,3-bis(1,3,5-trimethylphenyl)-4,5-dihydroimidazolin-2-ylidene) (av. 2.384(2) Å) [15b]. The bond angle of S(1)—Ru(1)—S(2) of 99.31(5)° in **1a** is more obtuse than that in [Ru{N(Ph_2PS)$_2$}$_2$(PPh_3)] 94.34(4)° [14b].

The catalytic activity of complexes **1a**–**1f** in ring closing metathesis (RCM) of dienes has been briefly investigated for comparison. The catalytic reactions are depicted in Eq. (1).



(1)

Complex **1a** showed no activity in the RCM at room temperature or at reflux condition for 6 h in dichloromethane. When the reaction with **1a** was tried in toluene at 80 °C for 2 h, a conversion of 38% by NMR analysis was found. Other ruthenium indenylidene complexes **1b**–**1f** were tested under the same conditions. Generally, the activities of ^{i}Pr substituted complexes **1c** and **1d** (65%, 57%) are more active catalysts than those of the corresponding phenyl complexes **1a** and **1b** (48%, 39%), possibly reflecting better electron donating abilities of ^{i}Pr towards the ruthenium center. The activity of ruthenium sulfide complexes **1a** (48%) and **1c** (65%) is slightly higher than those of their selenium analogous **1b** (39%) and **1d** (57%). Complexes **1e** (45%) and **1f** (53%) containing mixed donor ligand also exhibited moderate catalytic behavior. Previously, Buchmeiser has shown that the replacement of tricyclohexylphosphine to triphenylphosphine has a tremendous effect on the stability/reactivity of Grubbs' complexes [16]. When PCy_3 was introduced into the ruthenium-indenylidene complex [RuCl(PPh_3)(Ind)(κ^2*S*,*S*-N(^{i}$Pr_2$$PS)_2$)] (**1c**) *in situ* to replace PPh_3, the RCM catalytic activity was improved to ca. 86%. Overall, compared to other ruthenium based catalysts [17], the catalytic activity of complexes **1a-f** for ring closing metathesis is a little disappointing for the tested system.

In summary, a series of ruthenium indenylidene complexes containing dichalcogenoimidodi-phosphinate ligands [R_2P(E)NHP(E′)R_2] (R = Ph or ^{i}Pr; E/E′ = S or Se) were synthesized and well characterized. Complex **1e** with the mixed S/Se donor ligand [Ph_2P(S)NP(Se)Ph_2]$^-$ was isolated as a mixture of two isomers, while a single isomer was found for complex **1f** with [^{i}Pr_2P(S)N^iPr_2P(Se)]$^-$ probably due to steric effect of the bulky isopropyl group. The Ru—C bond length of 1.860(6) Å in **1a** is normal for the ruthenium-carbene complexes. These complexes exhibited moderate catalytic activity for the RCM reaction of diethyl diallylmalonate.

3. Experimental section

3.1. General

All the operations were carried out under pure nitrogen atmosphere using standard Schlenk techniques, solvents were distilled prior to use. Compounds K[R_2P(E)NR_2P(E′)}] (R = Ph/^{i}Pr; E, E′ = S/Se) [18] and [Ru(Ind)(PPh_3)$_2$$Cl_2$] [19] were prepared according to modified literature methods. NMR spectra were recorded on a BrukerALX400 spectrometer operating at 400, 100, and 162 MHz for ^{1}H, ^{13}C and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^{1}H), the residual solvent peak (^{13}C) and H_3PO_4 (^{31}P). Infrared spectra (KBr) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer with the use of pressed KBr pellets, and elemental analyses for C and H were carried out on an Elementar III Vario EI analyzer (see Fig. 2).

3.2. Syntheses of complexes [RuCl(PPh_3)(Ind){κE,κE′-R_2P(E)NR_2P(E′)}] [R = Ph, E = E′ = S (**1a**); R = Ph, E = E′ = Se (**1b**); R = ^{i}Pr, E = E′ = S (**1c**); R = ^{i}Pr, E = E′ = Se (**1d**); R = Ph, E = S, E′ = Se (**1e**); R = ^{i}Pr, E = S, E′ = Se (**1f**)]

To a stirred solution of [$RuCl_2$(PPh_3)$_2$(Ind)] (44.3 mg, 0.05 mmol) in 10 mL of THF was added K[R_2P(E)NR_2P(E′)}] (0.05 mmol) at room temperature. The mixture was stirred for 12 h and the solvent was removed in vacuum, the residue was extracted with dichloromethane and filtered, the filtrate was removed in vacuum and the residue was washed with *n*-hexane for three times, affording complexes **1a**–**1f** in quantitive yields.

For **1a**, IR (KBr): *ν* 3054, 1478, 1437, 1151, 1105, 1088, 744, 702, 574, 524 cm^{-1}. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 38.8 (s, PPh_3), 36.0 (s, P(S)Ph_2), 35.2 (s, P(S)Ph_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.37–8.35 (m, 1H, Ar—H), 8.02–7.97 (m, 2H, Ar—H), 7.71–7.60 (m, 5H, Ar—H), 7.46–7.01 (m, 34H, Ar—H), 6.88–6.83 (m, 2H, Ar—H), 5.78 (s, 1H, H-2); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 294.9 (d, J_{PC} = 14.9 Hz, C-1), 145.6 (s), 140.8 (s), 139.2–127.5 (m), 127.1 (s), 117.7 (s). Anal. Calc. for $C_{57}H_{45}ClNP_3S_2Ru$: C 65.98%; H 4.37%; N 1.35%; Found: C, 65.95%; H, 3.39%; N, 1.34%.

For **1b**, IR (KBr): *ν* 3050, 1611, 1487, 1437, 1192, 1097, 744, 690, 524 cm^{-1}. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.1 (s, PPh_3), 24.7 (s, P(Se)Ph_2), 22.3 (s, P(Se)Ph_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.33–8.32 (m, 1H, Ar—H), 7.98–7.93 (m, 2H, Ar—H), 7.80–7.75 (m, 2H, Ar—H), 7.73–7.05 (m, 37H, Ar—H), 6.90–6.84 (m, 2H, Ar—H), 5.87 (s, 1H, H-2); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 292.6 (d, J_{PC} = 15.1 Hz, C-1), 145.2 (s), 140.5 (s), 137.9–127.6 (m), 127.0 (s), 117.8 (s). Anal. Calc. for $C_{57}H_{45}ClNP_3Se_2Ru$: C 60.37%; H 4.00%; N 1.24%; Found: C, 60.34%; H, 4.01%; N, 1.22%.

For **1c**, IR (KBr): *ν* 3058, 2963, 2872, 1623, 1482, 1433, 1188, 1092, 752, 699, 524 cm^{-1}. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 37.6 (s, PPh_3), 59.3 (s, P(S)^iPr_2), 60.4 (s, P(S)^iPr_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.58–8.55 (m, 1H, Ar—H), 7.78–7.24 (m, 23H, Ar—H), 6.05 (s, 1H, H-2), 2.12–1.99 (m, 2H, CH), 1.85–1.78 (m, 1H, CH), 1.62–1.58 (m, 1H, CH), 1.32–0.88 (m, 18H, CH_3), 0.78 (dd, J_{HH} = 17.4 Hz, J_{HP} = 6.8 Hz, 3H, CH_3), 0.56 (dd, J_{HH} = 17.8 Hz, J_{HP} = 6.8 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 291.8 (d, J_{PC} = 15.0 Hz, C-1), 145.1 (s), 141.3 (s), 139.8 (d, J_{PC} = 15.6 Hz), 138.3 (s), 136.7 (s), 135.4 (d, J_{PC} = 15.2 Hz), 132.6–128.1 (m), 126.9 (s), 117.6 (s), 34.3–31.5 (m, *C*H(CH_3)$_2$), 18.2–16.4 (m, CH(*C*H_3)$_2$). Anal. Calc. for $C_{45}H_{53}ClNP_3S_2Ru$: C 59.92%; H 5.93%; N 1.55%; Found: C, 59.95%; H, 5.96%; N, 1.54%.

For **1d**, IR (KBr): *ν* 3058, 2959, 2868, 1611, 1482, 1441, 1151, 1093, 1026, 752, 699, 528, 412 cm^{-1}. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 38.2 (s, PPh_3), 51.5 (s, P(Se)^iPr_2), 50.1 (s, P(Se)^iPr_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.52–8.50 (m, 1H, Ar—H), 7.57–7.19 (m, 23H, Ar—H), 6.11 (s, 1H, H-2), 2.27–2.24 (m, 1H, CH), 2.10–2.04 (m, 1H, CH), 1.86–1.84 (m, 1H, CH), 1.80–1.72 (m, 1H, CH), 1.31–0.88 (m, 18H, CH_3), 0.79 (dd, J_{HH} = 18.0 Hz, J_{HP} = 7.2 Hz, 3H, CH_3), 0.57 (dd, J_{HH} = 18.4 Hz, J_{HP} = 7.2 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 290.3 (d, J_{PC} = 15.1 Hz, C-1), 145.0 (s), 140.9–128.1

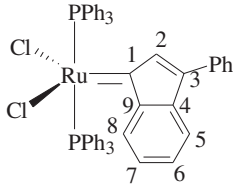


Fig. 2. Numbering of ruthenium indenylidene complex [Ru(Ind)(PPh_3)$_2$$Cl_2$].

(m), 126.8 (s), 117.6 (s), 34.5–31.1 (m, $CH(CH_3)_2$), 18.4–16.6 (m, $CH(CH_3)_2$). Anal. Calc. for $C_{45}H_{53}ClNP_3Se_2Ru$: C 54.31%; H 5.37%; N 1.41%; Found: C, 54.27%; H, 5.39%; N, 1.44%.

For **1e(1)** and **1e(2)**, IR (KBr): ν 3046, 1482, 1171, 1101, 757, 694, 670, 537, 429 cm^{-1}. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 39.2 (s, PPh_3), 38.2 (s, PPh_3), 35.9 (s, $P(S)Ph_2$), 35.2 (s, $P(S)Ph_2$), 24.6 (s, $P(Se)Ph_2$), 22.3 (s, $P(Se)Ph_2$); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.37–8.33 (m, 2H, Ar—H), 8.07–6.78 (m, 86H, Ar—H), 5.89 (s, 1H, H-2), 5.80 (s, 1H, H-2); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 292.2 (d, J_{PC} = 15.0 Hz, C-1), 145.4 (s), 145.3, 140.9–127.0 (m), 117.7 (s), 117.6 (s). Anal. Calc. for $C_{57}H_{45}ClNP_3SSeRu$: C 63.13%; H 4.18%; N 1.29%; Found: C, 63.10%; H, 4.20%; N, 1.31%.

For **1f**, IR (KBr): ν 3058, 2963, 2930, 2868, 1930, 1478, 1441, 1196, 1093, 1030, 752, 703, 549, 528, 512 cm^{-1}. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 36.2 (s, PPh_3), 51.4 (s, $P(Se)^iPr_2$), 63.3 (s, $P(S)^iPr_2$); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.53–8.47 (m, 1H, Ar—H), 7.70–7.21 (m, 23H, Ar—H), 6.11 (s, 1H, H-2), 2.27–2.20 (m, 1H, CH), 2.10–1.62 (m, 3H, CH), 1.31–0.54 (m, 24H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 292.2 (d, J_{PC} = 15.1 Hz, C-1), 144.8 (s), 141.3–128.2 (m), 126.8 (d, J_{PC} = 2.2 Hz), 117.6 (s), 34.5–31.0 (m, $CH(CH_3)_2$), 18.3–16.4 (m, $CH(CH_3)_2$). Anal. Calc. for $C_{45}H_{53}ClNP_3SSeRu$: C 56.99%; H 5.63%; N 1.48%; Found: C, 56.93%; H, 5.69%; N, 1.49%.

3.3. X-ray diffraction measurements

Intensity data were collected on a Bruker SMART APEX 2000 CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The collected frames were processed with the software SAINT [20]. The data were corrected for absorption using the program SADABS [21]. Structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [22]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C_{sp3}—H = 0.96 and C_{sp2}—H = 0.93), assigned isotropic thermal parameters, and allowed to ride on their respective parent carbon or oxygen atoms before the final cycle of least-squares refinement. The solvent molecules hexane in **1a** was isotropically refined without hydrogen atoms due to disorder. Crystallographic data and experimental details for [Ru(PPh_3)(Ind)(κ^2*S*,*S*-N(Ph_2PS)$_2$)Cl] (**1a**·hexane) is given in Table 1.

Table 1
Crystallographic data and experimental details for [Ru(PPh_3)(Ind)(κ^2*S*,*S*-N(Ph_2PS)$_2$)Cl] (**1a**·hexane).

Complex	**1a**·Hexane
Empirical formula	$C_{66}H_{58}NClP_3S_2Ru$
Formula weight	1158.68
Crystal system	Triclinic
a (Å)	12.7779(19)
b (Å)	13.7203(19)
c (Å)	17.624(3)
α (°)	75.478(2)
β (°)	88.514(2)
γ (°)	64.692(2)
V (Å^3)	2692.3(7)
Space group	$P-1$
Z	2
D_{calc} (g cm^{-3})	1.429
Temperature (K)	296(2)
$F(000)$	1340
μ(Mo Kα) (mm^{-1})	0.552
Total refln	16,737
Independent refln	11,855
R_{int}	0.0582
$R1$[a], $wR2$[b] ($I > 2\sigma(I)$)	0.0593, 0.0969
$R1$, $wR2$ (all data)	0.0806, 0.1257
Parameter	676
GoF[c]	0.829

[a] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[b] $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.
[c] GoF = $[\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{param})]^{1/2}$.

3.4. General procedure for ring closing metathesis reactions

Under nitrogen, a Schlenk flask was charged with the substrate diethyl diallylmalonate (0.5 mmol) and dry dichloromethane or toluene (5 mL, C = 0.1 M), then pre-catalyst (5×10^{-6} mol) was added. The reaction mixture was magnetically stirred at room temperature or at 80 °C for 2 h. The volatiles were removed under vacuum and the crude residue was analyzed by ^1H NMR. Product formation and diene disappearance were monitored by integrating the allylic methylene peaks. Product formation was confirmed by comparison with literature NMR data [23].

Supplementary data

CCDC 831918 contain the supplementary crystallographic data for complex **1a** can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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