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Areneruthenium complexes with S_2CPR_3 and trichlorostannate

Bernardo Alvarez, Daniel Miguel, Julio A. Pérez-Martínez and Víctor Riera

Departamento de Química Organometálica, Universidad de Oviedo, E-33071 Oviedo (Spain)

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Abstract

Complexes $[\{(\eta^6\text{-arene})\,RuCl_2\}_2]$ (arene = benzene, *p*-cymene or hexamethylbenzene), react with trialkylphosphine-carbon disulfide adducts, S_2CPR_3 (R = cyclohexyl, Cy; or isopropyl, ^{i}Pr), in refluxing ethanol in the presence of KPF_6 to afford cationic complexes $[(\eta^6\text{-arene})Ru(S_2CPR_3)Cl]PF_6$, which have been characterized by analytical and spectroscopic methods. These complexes react with $SnCl_2$ in CH_2Cl_2/THF to afford trichlorostannato-derivatives $[(\eta^6\text{-arene})Ru(S_2CPR_3)(SnCl_3)]PF_6$ through insertion of $SnCl_2$ into the Ru–Cl bond.

Key words: Ruthenium; Tin; Arene

1. Introduction

In our studies of transition metal complexes with S_2CPR_3, we have found that mononuclear complexes of manganese that contain one halide ligand and one chelating adduct, S_2CPR_3, are convenient building blocks for the preparation of binuclear complexes [1,2]. This prompted us to undertake the preparation of similar complexes of other metals which could serve as starting materials for the synthesis of binuclear compounds.

We report here the preparation and characterization of a family of cationic complexes of ruthenium containing different arenes. η^6-arene complexes of Ru(II) have attracted considerable attention [3] and their chemistry has been recently reviewed [4]. However, there are few examples of this class of compound with *S*-donor [5–8]. Most reactions leading to heterobinuclear complexes containing "Ru(η^6-arene)" moieties take place with low yield. In contrast, we have reported [9] the preparation of $[Ru(\eta^6\text{-}C_6Me_6)(S_2CPCy_3)Cl]PF_6$ and of its use to prepare high yields of binuclear Ru–Mo and Ru–W complexes.

2. Results and discussion

The dimers $[\{(\eta^6\text{-arene})RuCl_2\}_2]$ (arene = benzene, **1a** [10]; *p*-cymene, $CH_3C_6H_4{}^iPr\text{-}4$, **1b** [11]; hexamethylbenzene, C_6Me_6, **1c** [11]), react with trialkylphosphine-carbon disulfide adducts, S_2CPR_3 (R = cyclohexyl, Cy; or isopropyl, ^{i}Pr), in a mixture of ethanol and CS_2 at reflux temperature in the presence of an excess of KPF_6, to afford red-brown solutions. After filtration to remove KCl and the excess of KPF_6, and evaporation of the solvents, mononuclear cationic complexes of formula $[(\eta^6\text{-arene})Ru(S_2CPR_3)Cl]PF_6$ (**2a**–**2f**, see Scheme 1) are obtained in good yield. Analytical (see Experimental details), and spectroscopic data fully support the structures proposed in Scheme 1. All show a singlet in their $^{31}P\{^1H\}$NMR spectra in a region characteristic of phosphorus of S_2CPR_3. As with other series of complexes, the resonances of those containing P^iPr_3 appear at higher frequencies than those of PCy_3.

Several octahedral mononuclear complexes of ruthenium with S_2CPR_3 have been reported previously [12–14]. In all of them, the S_2CPR_3 is proposed to be bidentate and chelate. However, no ^{13}C NMR data have been reported for these compounds. Since the discovery of the ability of S_2CPR_3 to act as $\eta^3(S,C,S')$ pseudo-allyl in mononuclear complexes [15–17], ^{13}C

Correspondence to: Dr. D. Miguel.

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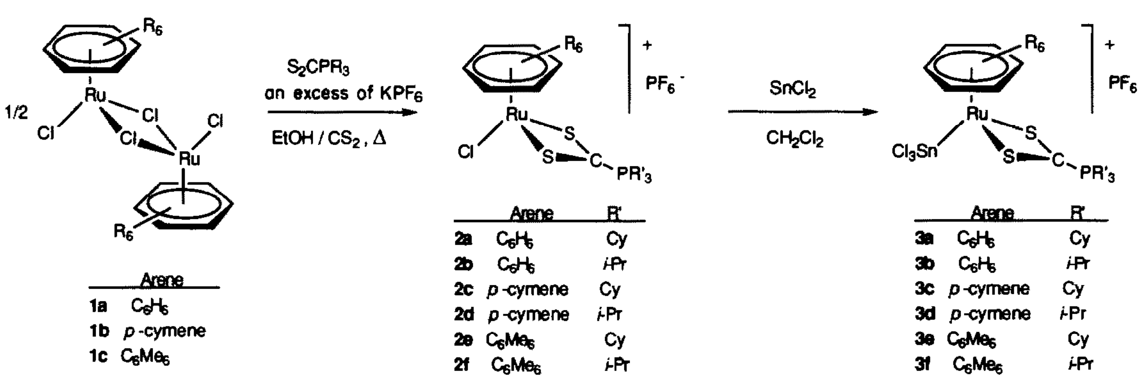

Scheme 1.

NMR spectroscopy has proved to be useful to distinguish between the two (chelate and pseudo-allyl) coordination modes. We have obtained ^{13}C NMR spectra for the complexes containing PCy_3 [**2a**, **2c** and **2e**], which are more soluble than their homologues with P^iPr_3. In the spectra, the signal attributable to the central carbon of the S_2CPCy_3 appears as a doublet in the range 215–225 ppm expected for chelating S_2CPR_3 with $J(PC)$ of *ca.* 35 Hz. These data are additional support for the structures proposed in Scheme 1.

Reaction of complexes **2a–2f** with an excess of tin(II) chloride in a mixture of CH_2Cl_2 and THF produces trichlorostannate derivatives through the insertion of $SnCl_2$ into the Ru–Cl bond. After appropriate workup (see Experimental details), these complexes can be isolated as hexafluorophosphate salts $[(\eta^6$-arene)

TABLE 1. $^{31}P\{^1H\}$ and ^1H NMR data [a] for the new complexes

Compound	$^{31}P\{^1H\}$ [b]	^1H [c]
2a $[(\eta^6\text{-}C_6H_6)Ru(S_2CPCy_3)Cl]PF_6$	33.2	5.95 [s, 6H, $C_6\mathit{H}_6$], 2.58 [m, 3H, $C^1\mathit{H}$ of Cy], 1.90–1.18 [m, 30H, $C\mathit{H}_2$ of Cy]
2b $[(\eta^6\text{-}C_6H_6)Ru(S_2CP^iPr_3)Cl]PF_6$ [d]	43.5	6.04 [s, 6H, $C_6\mathit{H}_6$], 2.99 [m, 3H, $C\mathit{H}$ of ^{i}Pr], 1.47 [dd, $J(PH) = 17$ Hz, $J(HH) = 7$ Hz, 18H, $C\mathit{H}_3$ of ^{i}Pr]
2c $[(\eta^6\text{-}p\text{-cymene})Ru(S_2CPCy_3)Cl]PF_6$	33.3	5.95, 5.71 [AB, $J = 6$ Hz, 4H, $C_6\mathit{H}_4$], 2.89 [m, 1H, $p\text{-}CH_3C_6H_4C\mathit{H}(CH_3)_2$], 2.67 [m, 3H, $C^1\mathit{H}$ of PCy_3], 2.36 [s, 3H, $C\mathit{H}_3\text{–}C_6H_4$], 1.95 to 1.33 [m, br, 30H, $C\mathit{H}_2$ of PCy_3], 1.32 [d, $J(HH) = 7$ Hz, 6H, $p\text{-}CH_3C_6H_4CH(C\mathit{H}_3)_2$]
2d $[(\eta^6\text{-}p\text{-cymene})Ru(S_2CP^iPr_3)Cl]PF_6$	42.5	5.94, 5.71 [AB, $J = 6$ Hz, 4H, $C_6\mathit{H}_4$], 3.01 [m, 3H, $C\mathit{H}$ of ^{i}Pr], 2.89 [m, 1H, $p\text{-}CH_3C_6H_4C\mathit{H}(CH_3)_2$], 2.37 [s, 3H, $p\text{-}C\mathit{H}_3C_6H_4CH(CH_3)_2$], 1.49 [dd, $J(PH) = 17$ Hz, $J(HH) = 7$ Hz, 18H, $C\mathit{H}_3$ of ^{i}Pr], 1.33 [d, $J(HH) = 7$ Hz, 6H, $p\text{-}CH_3C_6H_4CH(C\mathit{H}_3)_2$]
2e $[(\eta^6\text{-}C_6Me_6)Ru(S_2CPCy_3)Cl]PF_6$ [d]	33.9	2.96 [m, 3H, $C^1\mathit{H}$ of Cy], 2.27 [s, 18H, $C\mathit{H}_3$ of C_6Me_6], 1.97–1.30 [m, 30H, $C\mathit{H}_2$ of Cy]
2f $[(\eta^6\text{-}C_6Me_6)Ru(S_2CP^iPr_3)Cl]PF_6$	42.2	3.03 [m, 3H, $C\mathit{H}$ of ^{i}Pr] 2.25 [s, 18H, $C\mathit{H}_3$ of C_6Me_6], 1.49 [dd, $J(PH) = 17$ Hz, $J(HH) = 7$ Hz, 18H, $C\mathit{H}_3$ of ^{i}Pr]
3a $[(\eta^6\text{-}C_6H_6)Ru(S_2CPCy_3)(SnCl_3)]PF_6$	33.4 (123)	6.38 [s, 6H, $C_6\mathit{H}_6$], 2.73 [m, 3H, $C^1\mathit{H}$ of Cy], 2.12–1.14 [m, 30H, $C\mathit{H}_2$ of Cy]
3b $[(\eta^6\text{-}C_6H_6)Ru(S_2CP^iPr_3)(SnCl_3)]PF_6$ [d]	47.9 (128)	5.59 [s, 6H, $C_6\mathit{H}_6$], 3.33 [m, 3H, $C\mathit{H}$ of ^{i}Pr], 1.53 [dd, $J(PH) = 17$ Hz, $J(HH) = 7$ Hz, 18H, $C\mathit{H}_3$ of ^{i}Pr]
3c $[(\eta^6\text{-}p\text{-cymene})Ru(S_2CPCy_3)(SnCl_3)]PF_6$	32.6 (123)	6.59, 6.45 [AB, $J = 6$ Hz, 4H, $C_6\mathit{H}_4$], 2.89 [m, 1H, $p\text{-}CH_3C_6H_4C\mathit{H}(CH_3)_2$], 2.67 [m, 3H, $C^1\mathit{H}$ of PCy_3], 2.36 [s, 3H, $C\mathit{H}_3\text{–}C_6H_4$], 1.95 to 1.33 [m, br, 30H, $C\mathit{H}_2$ of PCy_3], 1.32 [d, $J(HH) = 7$ Hz, 6H, $p\text{-}CH_3C_6H_4CH(C\mathit{H}_3)_2$]
3d $[(\eta^6\text{-}p\text{-cymene})Ru(S_2CP^iPr_3)(SnCl_3)]PF_6$	42.1 (127)	6.33, 6.26 [AB, $J = 6$ Hz, 4H, $C_6\mathit{H}_4$], 3.05 [m, 3H, $C\mathit{H}$ of ^{i}Pr], 2.80 [m, 1H, $p\text{-}CH_3C_6H_4C\mathit{H}(CH_3)_2$], 2.33 [s, 3H, $p\text{-}C\mathit{H}_3C_6H_4CH(CH_3)_2$], 1.51 [dd, $J(PH) = 17$ Hz, $J(HH) = 7$ Hz, 18H, $C\mathit{H}_3$ of ^{i}Pr], 1.28 [d, $J(HH) = 7$ Hz, 6H, $p\text{-}CH_3C_6H_4CH(C\mathit{H}_3)_2$]
3e $[(\eta^6\text{-}C_6Me_6)Ru(S_2CPCy_3)(SnCl_3)]PF_6$ [d]	35.7 (125)	3.12 [m, 3H, $C^1\mathit{H}$ of Cy], 2.50 [s, 18H, $C\mathit{H}_3$ of C_6Me_6], 2.31–1.43 [m, 30H, $C\mathit{H}_2$ of Cy]
3f $[(\eta^6\text{-}C_6Me_6)Ru(S_2CP^iPr_3)(SnCl_3)]PF_6$	43.4 (125)	3.41 [m, 3H, $C\mathit{H}$ of ^{i}Pr], 2.47 [s, 18H, $C\mathit{H}_3$ of C_6Me_6], 1.56 [dd, $J(PH) = 17$ Hz, $J(HH) = 7$ Hz, 18H, $C\mathit{H}_3$ of ^{i}Pr]

[a] CD_2Cl_2 solutions unless otherwise stated. [b] Chemical shifts in δ (ppm) from external H_3PO_4. For complexes **3a–3f**, $J(Sn–P)$ is given in Hz, in parentheses. [c] Chemical shifts in δ (ppm) from internal $SiMe_4$. [d] In acetone-d_6.

$Ru(S_2CPR_3)(SnCl_3)]PF_6$ (**3a**–**3f**, see Scheme 1). The structures depicted in the Scheme are fully supported by analytical and spectroscopic data. The presence of the tin-containing ligand is unambiguously demonstrated by a set of satellites with ^4J(P–Sn) = 125 ± 3 Hz in the ^{31}P NMR spectra of all the complexes of the series.

We have recently reported several examples of transition metal–tin complexes containing S_2CPR_3 [18,19]. In one case, the S_2CPR_3 bridges between the two metal atoms, displaying $\eta^3(S,C,S')$; $\eta^2(S,S')$ coordination [18]; in the other, there is no interaction between the chelating S_2CPR_3 and the tin atom [19]. In the present case, the ^{13}C NMR spectra of complexes containing $SnCl_3$ (**3a**, **3c** and **3e**) show the doublet (with J(PC) = 31 ± 2 Hz), in the range expected for chelating S_2CPR_3. This allows us to rule out the involvement of the central carbon of the S_2CPR_3 in the bond with the metals, and supports the structures proposed for **3a**–**3f** in Scheme 1 with chelate S_2CPR_3.

Insertion of $SnCl_2$ into Ru–Cl bonds has been used to prepare octahedral carbonyl complexes of ruthenium [20]. However, as far as we know, there is only one example of such an insertion in η^6-arene complexes of ruthenium [21*].

3. Experimental details

All reactions were carried out in dry solvents under dinitrogen. Literature procedures for the preparation of starting materials are quoted in each case. Reagents were purchased and used without purification unless otherwise stated. ^1H, ^{31}P, and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer. Elemental analyses were carried out on a Perkin-Elmer 240B analyzer.

3.1. *[Ru(η^6-C_6H_6)(S_2CPCy_3)Cl]PF_6, (**2a**)*

A mixture of $[\{Ru(\eta^6\text{-}C_6H_6)Cl_2\}_2]$ [10] (0.13 g, 0.25 mmol), S_2CPCy_3 (0.18 g, 0.5 mmol), KPF_6 (0.5 g, an excess), and CS_2 (1 cm^3, an excess) was heated under reflux in ethanol (20 cm^3) for 4 h, and then the solvents were evaporated to dryness *in vacuo*. The residue was extracted with CH_2Cl_2 (3 × 10 cm^3) and the extracts were filtered. Slow evaporation *in vacuo* gave brown microcrystals of **2a**, which were washed with Et_2O (3 × 15 cm^3). Yield 0.34 g, 94%. (Anal. Found: C, 42.02; H, 5.40. $C_{25}H_{38}ClF_6P_2RuS_2$ calc.: C, 41.00; H, 5.36%.

3.2. *[Ru(η^6-C_6H_6)($S_2CP^iPr_3$)Cl]PF_6, (**2b**)*

Compound **2b** was prepared as described for **2a** from $[\{Ru(\eta^6\text{-}C_6H_6)Cl_2\}_2]$ [10] (0.13 g, 0.25 mmol), P^iPr_3 (80 μl, 0.5 mmol), KPF_6 (0.5 g, an excess), and CS_2 (1 cm^3, an excess); in ethanol (20 cm^3). Yield 0.26 g, 88%. (Anal. Found: C, 32.20; H, 4.35. $C_{16}H_{26}ClF_6P_2RuS_2$ calc.: C, 32.30; H, 4.41%).

3.3. *[Ru(η^6-p-cymene)(S_2CPCy_3)Cl]PF_6, (**2c**)*

Compound **2c** was prepared as described for **2a** from $[\{Ru(\eta^6\text{-}p\text{-cymene})Cl_2\}_2]$ [11], (0.15 g, 0.25 mmol), S_2CPCy_3 (0.18 g, 0.5 mmol), KPF_6 (0.5 g, an excess), and CS_2 (1 cm^3, an excess); in ethanol (20 cm^3). Yield 0.36 g, 92%. (Anal. Found: C, 45.22; H, 6.10. $C_{29}H_{47}ClF_6P_2RuS_2$ calc.: C, 45.10; H, 6.13%).

TABLE 2. $^{13}C\{^1H\}$ NMR Data for the complexes with S_2CPCy_3 [a]

Compound	S_2C–P [b]	Arene	Cyclohexyl
2a	224.2 [d (31)]	88.4 [s, C_6H_6]	30.6 [d, (36), C^1], 27.0 [s, C^2 and C^6] 26.6 [d, (13), C^3 and C^5], 25.3 [s, C^4]
2c	222.3 [d (31)]	108.6 and 104.9 [s, C^1 and C^4 of *p*-cymene] 87.0 and 85.9 [s, C^2 and C^6, C^3 and C^5 of *p*-cymene], 32.3 [s, $C(CH_3)_2$], 22.9 [s, $C(CH_3)_2$], 19.5 [s, C_6H_4–CH_3].	30.6 [d (36), C^1], 26.7 [d (12), C^3 and C^5] 26.3 [s, C^2 and C^6], 25.2 [s, C^4]
2e	217.6 [d (31)]	97.7 [s, $C_6(CH_3)_6$], 16.7 [s, $C_6(CH_3)_6$]	30.5 [d (37), C^1], 26.8 [d (12), C^3 and C^5] 26.4 [d (3), C^2 and C^6], 25.4 [s, C^4]
3a	218.4 [d (33)]	90.8 [s, C_6H_6]	31.7 [d (36), C^1], 27.0 [s, C^2 and C^6] 26.9 [d (13), C^3 and C^5], 25.5 [s, C^4]
3c	213.8 [d (33)]	114.2 and 105.9 [s, C^1 and C^4 of *p*-cymene] 89.7 and 89.6 [s, C^2 and C^6, C^3 and C^5 of *p*-cymene], 32.3 [s, $CH(CH_3)_2$], 23.3 [s, $CH(CH_3)_2$], 19.9 [s, C_6H_4–CH_3].	30.6 [d (36), C^1], 26.7 [d (12), C^3 and C^5] 26.3 [s, C^2 and C^6], 25.2 [s, C^4]
3e [c]	217.2 [d (30)]	101.7 [s, $C_6(CH_3)_6$], 16.8 [s, $C_6(CH_3)_6$]	30.7 [d (36), C^1], 26.0 [s, C^2 and C^6] 25.9 [d (13), C^3 and C^5], 24.8 [s, C^4]

[a] CD_2Cl_2 solutions unless otherwise stated. Chemical shifts in δ (ppm) from internal $SiMe_4$. [b] J(PC) in Hz in parentheses. [c] In acetone-d_6.

3.4. [Ru(η⁶-p-cymene)(S₂CPⁱPr₃)Cl]PF₆, (2d)

Compound **2d** was prepared as described for **2a** from [{Ru(η^6-*p*-cymene)Cl_2}$_2$] [11], (0.15 g, 0.25 mmol), P^iPr_3 (80 μl, 0.5 mmol), KPF_6 (0.5 g, an excess), and CS_2 (1 cm^3, an excess); in ethanol (20 cm^3). Yield 0.28 g, 86%. (Anal. Found: C, 36.78; H, 5.36. $C_{20}H_{35}ClF_6P_2RuS_2$ calc.: C, 36.84; H, 5.41%).

3.5. [Ru(η⁶-C₆Me₆)(S₂CPCy₃)Cl]PF₆,(2e)

Compound **2e** was prepared as described for **2a** from [{Ru(η^6-C_6Me_6)Cl_2}$_2$] [11] (0.17 g, 0.25 mmol), S_2CPCy_3 (0.18 g, 0.5 mmol), KPF_6 (0.5 g, an excess), and CS_2 (1 cm^3, an excess); in ethanol (20 cm^3). Yield 0.38 g, 95%. (Anal. Found: C, 46.35; H, 6.26. $C_{31}H_{51}ClF_6P_2RuS_2$ calc.: C, 46.52; H, 6.42%).

3.6. [Ru(η⁶-C₆Me₆)(S₂CPⁱPr₃)Cl]PF₆, (2f)

Compound **2f** was prepared as described for **2a** from [{Ru(η^6-C_6Me_6)Cl_2}$_2$] [11] (0.17 g, 0.25 mmol), P^iPr_3 (80 μl, 0.5 mmol), KPF_6 (0.5 g, an excess), and CS_2 (1 cm^3, an excess); in ethanol (20 cm^3). Yield 0.31 g, 92%. (Anal. Found: C, 38.96; H, 5.70. $C_{22}H_{39}ClF_6P_2RuS_2$ calc.: C, 38.85; H, 5.78%).

3.7. [Ru(η⁶-C₆H₆)(S₂CPCy₃)(SnCl₃)]PF₆,(3a)

Compound [Ru(η^6-C_6H_6)(S_2CPCy_3)Cl]PF_6 (**2a**) (0.14 g, 0.20 mmol) and $SnCl_2$ (0.05 g, 0.25 mmol) were stirred in a mixture of CH_2Cl_2 (10 cm^3) and THF (10 cm^3) for 1 h, and the resulting solution was filtered. Slow evaporation *in vacuo* gave red-brown microcrystals of **3a**, which were washed with Et_2O (2 × 20 cm^3). Yield 0.17 g, 92%. (Anal. Found: C, 32.96; H, 4.30. $C_{25}H_{38}Cl_3F_6P_2RuS_2Sn$ calc.: C, 33.19; H, 4.23%).

3.8. [Ru(η⁶-C₆H₆)(S₂CPⁱPr₃)(SnCl₃)]PF₆, (3b)

Compound **3b** was prepared as described for **3a** from [Ru(η^6-C_6H_6)($S_2CP^iPr_3$)Cl]PF_6, (**2b**) (0.12 g, 0.20 mmol), and $SnCl_2$ (0.05 g, 0.25 mmol). Yield 0.14 g, 87%. (Anal. Found: C, 24.66; H, 3.24. $C_{16}H_{26}Cl_3F_6P_2RuS_2Sn$ calc.: C, 24.50; H, 3.34%).

3.9. [Ru(η⁶-p-cymene)(S₂CPCy₃)(SnCl₃)]PF₆, (3c)

Compound **3c** was prepared as described for **3a** from [Ru(η^6-*p*-cymene)(S_2CPCy_3)Cl]PF_6 (**2c**) (0.15 g, 0.20 mmol), and $SnCl_2$ (0.05 g, 0.25 mmol). Yield 0.17 g, 90%. (Anal. Found: C, 36.45; H, 4.86. $C_{29}H_{47}Cl_3F_6P_2RuS_2Sn$ calc.: C, 36.21; H, 4.93%).

3.10. [Ru(η⁶-p-cymene)(S₂CPⁱPr₃)(SnCl₃)]PF₆, (3d)

Compound **3d** was prepared as described for **3a** from [Ru(η^6-*p*-cymene)($S_2CP^iPr_3$)Cl]PF_6 (**2d**) (0.13 g, 0.20 mmol), and $SnCl_2$ (0.05 g, 0.25 mmol). Yield 0.15 g, 88%. (Anal. Found: C, 28.58; H, 4.26. $C_{20}H_{35}Cl_3F_6P_2RuS_2Sn$ calc.: C, 28.51; H, 4.31%).

3.11. [Ru(η⁶-C₆Me₆)(S₂CPCy₃)(SnCl₃)]PF₆, (3e)

Compound **3e** was prepared as described for **3a** from [Ru(η^6-C_6Me_6)(S_2CPCy_3)Cl]PF_6 (**2e**)(0.16 g, 0.20 mmol), and $SnCl_2$ (0.05 g, 0.25 mmol). Yield 0.19 g, 94%. (Anal. Found: C, 38.02; H, 5.03. $C_{31}H_{51}Cl_3F_6P_2RuS_2Sn$ calc.: C, 37.61; H, 5.19%).

3.12. [Ru(η⁶-C₆Me₆)(S₂CPⁱPr₃)(SnCl₃)]PF₆, (3f)

Compound **3f** was prepared as described for **3a** from [Ru(η^6-C_6Me_6)($S_2CP^iPr_3$)Cl]PF_6 (**2f**) (0.14 g, 0.20 mmol), and $SnCl_2$ (0.05 g, 0.25 mmol). Yield 0.16 g, 90%. (Anal. Found: C, 30.52; H, 4.63. $C_{22}H_{39}Cl_3F_6P_2RuS_2Sn$ calc.: C, 30.38; H, 4.52%).

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