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Note

Cyclopentadienyl ruthenium alkynyldithiocarboxylate complexes

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Abstract

Treatment of the ruthenium chloride, $CpRu(PPh_3)_2Cl$, with the alkynyldithiocarboxylate anions, $RC{\equiv}CCS_2^-$, in refluxing THF affords the chelate complexes $CpRu(PPh_3)(\kappa^2S,S\text{-}S_2CC{\equiv}CR)$ (**1**) ($R = Bu^t$ (**a**), Bu^n (**b**), Ph (**c**), $SiMe_3$ (**d**)) in high yield. The room temperature reaction of the solvated species, $[CpRu(PPh_3)_2(NCPh)]^+$, with the alkynyldithiocarboxylate anions, $RC{\equiv}CCS_2^-$, produces the chelate complexes **1** and the mono-coordinated complexes $CpRu(PPh_3)_2(\kappa S\text{-}S_2CC{\equiv}CR)$ (**2**). Complexes **2** are converted to **1** in solution so that they were characterized spectroscopically.

Keywords: Ruthenium; Dithiocarboxylate; Alkynes; Structure; Chelates; Sulfur; Triphenylphosphine; Carbon disulfide; Complexes

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1. Introduction

Dithiocarboxylato complexes of the transition metals have been known for long time [1,2]. However, they have been much less investigated compared to complexes of other dithioacid ligands such as xanthates ($ROCS_2^-$), thioxanthate ($RSCS_2^-$) and dithiocarbamates ($R_2NCS_2^-$) [3–16]. The dithiocarboxylate ligands were usually prepared by the reaction of Grignard reagents or lithium aryls with CS_2 [1,2,17,18]. More recently, it was reported that the addition of the alkynyl anions, $RC{\equiv}C^-$ to CS_2 at low temperature is a convenient way to generate the alkynyldithiocarboxylate ligands [19,20]. These ligands were used in the preparation of several organic molecules such as dithioesters [21] and 1,2-dithiole-3-thiones [22]. In organometallic chemistry, these ligands were used in the preparation of the Ru-complexes $Ru(H)(CO)(PPh_3)_2(\kappa^2S,S\text{-}S_2CC{\equiv}CR)$ ($R = Bu^t, Ph, Mes$) by direct interaction of the ligands with $Ru(H)(Cl)(PPh_3)_3(CO)$ [23].

Several organotransition metal complexes of alkynyldithiocarboxylate ligands are reported in the literature. These include $Cp'Mo(CO)_2(\kappa^2S,S\text{-}S_2CC{\equiv}CR)$ ($Cp' = C_5H_5, C_5Me_5$) [24], $CpRu(PPh_3)(\kappa^2S,S\text{-}S_2CC{\equiv}CPh)$ [25] and $CpFe(L)(\kappa^2S,S\text{-}S_2CC{\equiv}CR)$ ($L = PPh_3$, dppe-P, dppm-P) [26]. All of these complexes have been made by CS_2 insertion into the metal–carbon bond of the corresponding alkynyl-complexes. The complex $Cp^*Ru(PPh_3)(\kappa^2S,S\text{-}S_2CC{\equiv}CBu^t)$ ($Cp* = C_5Me_5$) is prepared by the interaction of CS_2 with the carbene complex $Cp{*}Ru(PPh_3)Cl({=}C{=}CHBu^t)$ in the presence of a strong base [27].

The insertion of CS_2 into the Ru–C bond of $CpRu(PPh_3)_2C{\equiv}CPh$ is quite difficult. It took heating for four days in benzene for this insertion to give 56% yield of $CpRu(PPh_3)(\kappa^2S,S\text{-}S_2CC{\equiv}CPh)$. The complex $CpRu(PPh_3)_2Cl$ has a weak Ru–Cl bond, therefore, the Cl atom in this molecule is labile and easily substituted especially in polar solvents. Due to this fact, there should be an easier route to synthesize $CpRu(PPh_3)$-complexes containing dithiocarboxylato ligands by reaction of $CpRu(PPh_3)_2Cl$ with dithiocarboxylato ligands. Our interest in the reactions of $CpRu(PPh_3)_2Cl$ with sulfur containing ligands [28], and the availability of the anions, $RC{\equiv}CCS_2^-$, prompted us to carry a study of these anions with $CpRu(PPh_3)_2Cl$. In this report we describe the preparation

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and characterization of some alkynyldithiocarboxylate ruthenium complexes.

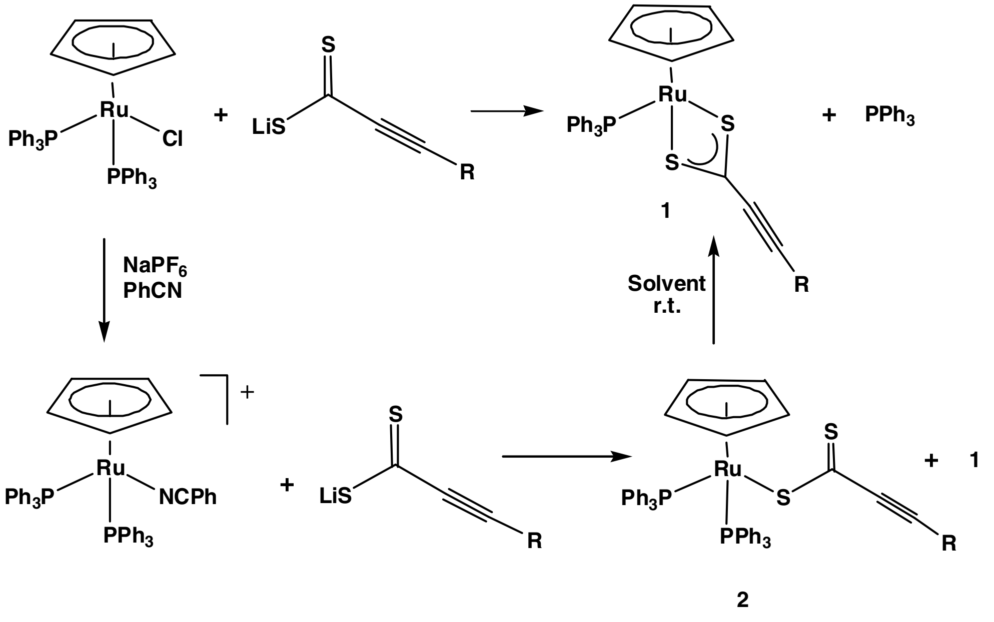
2. Results and discussion

The reaction of cyclopentadienylbis(triphenylphosphine)ruthenium chloride with various alkynyldithiocarboxylate anions in refluxing THF affords the complexes CpRu(PPh_3)($\kappa^2 S,S$-$S_2CC{\equiv}CR$) (**1**) (R = Bu^t (**a**), Bu^n (**b**), Ph (**c**), $SiMe_3$ (**d**)) in high yield (Scheme 1). The anionic ligands were prepared by the reaction of the alkynyl anions RC≡CLi with CS_2 at low temperature. Complexes **1** are new, but **1c** is known [25]. Complexes **1** are dark red solids, stable both as solids and in solutions. They are soluble in most common organic solvents and in some cases (**1c**, **1d**) are soluble in hydrocarbon solvents.

Complexes **1** have been characterized by spectroscopic methods (^{1}H, ^{31}P NMR, IR), elemental analysis and X-ray diffraction for compound **1a**. The spectroscopic results are in agreement with the suggested structures. The presence of the alkynyldithiocarboxylate ligands is shown in the IR spectra of complexes **1** by the $\nu_{C\equiv C}$ bands between 2120 and 2197 cm^{-1}. This frequency is similar to those reported for analogous complexes, e.g., $Cp^*Ru(PPh_3)$-($\kappa^2 S,S$-$S_2CC{\equiv}CBu^t$) (2195 cm^{-1}) [27] and CpRu(PPh_3)-($\kappa^2 S,S$-$S_2CC{\equiv}CPh$) (2170 cm^{-1}) [25]. The ^{1}H NMR spectra of **1** exhibited Cp-protons in the range 4.50–4.56 ppm. The peaks for the R-groups and the PPh_3 ligand are also present in the spectra with the correct splitting and intensities. The ^{31}P NMR spectra of these complexes show a singlet in the range 56.77–57.14 ppm. These results suggested similar structures and negligible effects for the R-group at the end of the molecules.

The molecular structure of CpRu(PPh_3)($\kappa^2 S,S$-$S_2CC{\equiv}CBu^t$) (**1a**) was determined and is shown in Fig. 1. Selected bond distances and bond angles of **1a** are shown in Table 1. The structure definitively proves that both S-atoms are bonded to the Ru-center with Ru–S distances of 2.3627(5) and 2.3667(5) Å. These distances are similar to those of CpRu(PPh_3)($\kappa^2 S,S$-$S_2CC{\equiv}CPh$) (2.336(3), 2.353(4) Å) [25] and also similar to those found for $Cp^*Ru(PPh_3)$($\kappa^2 S,S$-$S_2CC{\equiv}CBu^t$) (2.37(1), 2.350(9) Å) [27]. The Cp-ligand is bonded to the Ru atom in η^5-fashion with Ru–C bond distances ranging from 2.197(2) to 2.210(2) Å. The Ru–P bond distance of 2.3004(5) Å is similar to those of complexes containing the CpRu(PPh_3) moiety [10–13,29,30].

Complexes **1** are believed to be obtained from the corresponding bis(triphenylphosphine) complexes, **2** by loss of PPh_3 ligand (Scheme 1). In order to prove this suggestion, the complexes CpRu$(PPh_3)_2$(κS-$S_2CC{\equiv}CR$) (**2**) were prepared from the reaction of $[CpRu(PPh_3)_2(NCPh)]^+$ with $RC{\equiv}CCS_2^-$. However, this reaction always gives a mixture of **1** and **2**. Our attempts to isolate pure samples of **2** failed, they spontaneously converted to **1** in solution. This is not a surprising result on the basis that some complexes containing the CpRu$(PPh_3)_2$-moiety have a high tendency to loss PPh_3 ligand in solution [31]. Also, the ability of the dithiocarboxylate ligand to act as a chelate ligand is high, even it is higher than that of the bis(phosphine) ligands [26]. Complexes **2** have been characterized by ^{1}H and ^{31}P NMR spectroscopy. However, their spectra always display signals for



R= Bu^t (**a**), Bu^n (**b**), Ph (**c**), $SiMe_3$ (**d**)

Scheme 1.

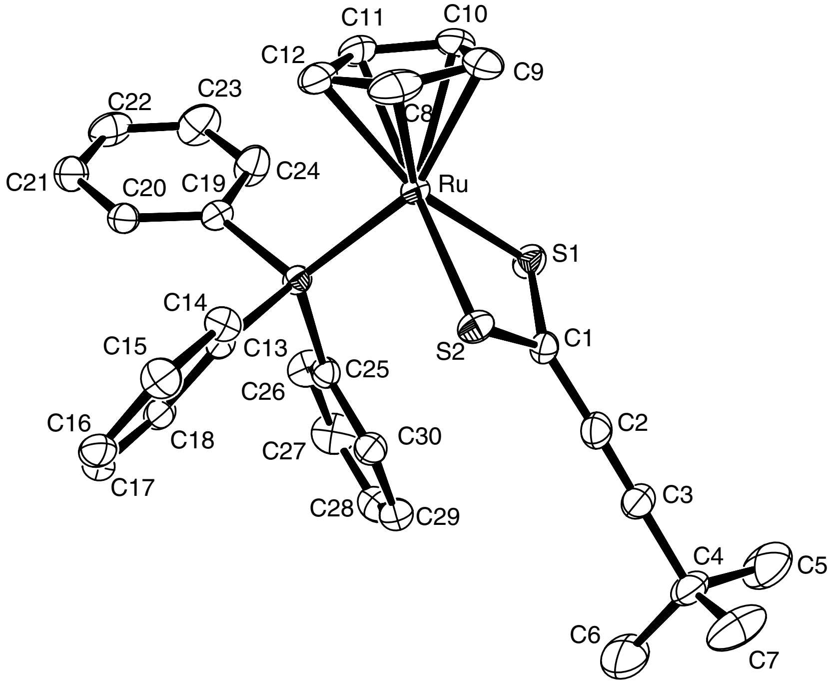


Fig. 1. ORTEP drawing of CpRu(PPh$_3$)(κ^2*S*,*S*-S$_2$CC≡CBu^t), **1a**.

Table 1
Selected bond length (Å) and angles (°) of CpRu(PPh$_3$)(κ^2*S*,*S*-S$_2$CC≡CBu^t) (**1a**)

Ru–S1	2.3627(5)	P1–Ru–S1	94.726(19)
Ru–S2	2.3667(5)	P1–Ru–S2	89.930(18)
Ru–C8	2.197(2)	S1–Ru–S2	71.520(19)
Ru–C9	2.203(2)	S1–C1–C2	109.62(11)
Ru–C10	2.202(2)	C1–S1–Ru	89.43(7)
Ru–C11	2.210(2)	C1–S2–Ru	89.28(7)
Ru–P1	2.3005(5)	C1–C2–C3	178.4(2)
S1–C1	1.691(2)	C2–C3–C4	178.4(2)
S2–C1	1.691(2)		
C1–C2	1.418(3)		
C2–C3	1.200(3)		
C3–C4	1.478(3)		

1 in some percent depending on how long they stayed in solution. Their spectra show the signals for the Cp-ligands in the range 4.40–4.50 ppm and the corresponding ^{31}P NMR spectra show singlets for the phosphine ligand in the range of 47.10–47.14 ppm.

3. Experimental

All manipulations were performed under an inert atmosphere of argon, using standard Schlenk line techniques. Tetrahydrofuran (THF) and hexane were dried and freshly distilled over sodium/benzophenone under argon prior to use. The reagents: CpRu(PPh$_3$)$_2$Cl [32], [CpRu(PPh$_3$)$_2$(NCPh)]PF$_6$ [33] and alkynyldithiocarboxylate anions [21] were prepared as previously reported. Infrared spectra were recorded on a Perkin–Elmer AC 2000 FT-IR spectrometer in KBr. ^{1}H and ^{31}P NMR spectra were recorded using a Varian Avance 200 or 400 MHz spectrometer. Chemical shifts are quoted in ppm downfield of TMS and referenced using the chemical shifts of residual solvent resonances. Elemental analyses were performed by the Institute of Organic and Macromolecular Chemistry, FSU-Jena. Melting points were recorded on a polarization-microscope (Axiolab) connected to a heating unit (THMS-600) using the software Linkam LNP and CI 93.

3.1. General procedure for the preparation of CpRu(PPh$_3$)(κ^2S,S-S$_2$CCCR) (*1*)

A 100-mL two-neck flask fitted with a reflux condenser was charged with CpRu(PPh$_3$)$_2$Cl (0.50 g, 0.68 mmol) and 50.0 mL of THF. A 10.0 mL THF solution of the alkynyldithiocarboxylate anion (0.55 mmol) was added in one portion. The resulting orange solution was refluxed for 2 h at which the color becomes dark red. The solvent was removed under vacuum and the resulting red solid was redissolved in a minimum amount of THF and was introduced to a silica gel column made up in hexane. Elution with THF:hexane (1:1 v:v ratio) gave a red band which was collected, dried and was recrystallized from THF/hexane.

3.1.1. CpRu(PPh$_3$)(κ^2S,S-S$_2$CC≡CBu^t) (*1a*)

Dark red crystals (90%). m.p.: 222–223 °C. IR (KBr, cm^{-1}): $\nu_{C\equiv C}$ 2194 (s). ^{1}H NMR (CDCl$_3$): δ 1.16 (s, 9H, CMe$_3$); 4.50 (s, 5H, C$_5$H$_5$); 7.30 (m, 9H, PPh$_3$); 7.41 (m, 6H, PPh$_3$). ^{31}P NMR (CDCl$_3$): δ 57.07. Anal. Calc. for C$_{30}$H$_{29}$PRuS$_2$: C, 61.52; H, 4.99; S, 10.95. Found: C, 61.31; H, 4.90; S, 10.96%.

3.1.2. *CpRu(PPh$_3$)(κ^{2}S,S-S$_2$CC≡CBu^n) (**1b**)*

Dark red crystals (87%). m.p.: 107–108 °C. IR (KBr, cm^{-1}): $\nu_{C\equiv C}$ 2197 (s). ^{1}H NMR (CDCl$_3$): δ 0.86 (t, 3H, CH$_3$); 1.25 (m, 2H, CH$_2$); 1.53 (m, 2H, CH$_2$); 3.45 (t, 2H, CH$_2$); 4.51 (s, 5H, C$_5$H$_5$); 7.32 (m, 9H, PPh$_3$); 7.44 (m, 6H, PPh$_3$). ^{31}P NMR (CDCl$_3$): δ 57.10. Anal. Calc. for C$_{30}$H$_{29}$PRuS$_2$: C, 61.52; H, 4.99; S, 10.95. Found: C, 59.02; H, 5.05; S, 14.33%.

3.1.3. *CpRu(PPh$_3$)(κ^{2}S,S-S$_2$CC≡CPh) (**1c**)*

Dark red crystals (85%). m.p.: 118–120 °C. IR (KBr, cm^{-1}): $\nu_{C\equiv C}$ 2174 (s). ^{1}H NMR (CDCl$_3$): δ 4.56 (s, 5H, C$_5$H$_5$); 7.30 (m, 9H, PPh$_3$); 7.40 (m, 6H, PPh$_3$); 7.70 (m, 5H, Ph). ^{31}P NMR (CDCl$_3$): δ 57.14. Anal. Calc. for C$_{33}$H$_{25}$PRuS$_2$: C, 63.45; H, 4.16; S, 10.59. Found: C, 62.98; H, 4.37; S, 10.78%.

3.1.4. *CpRu(PPh$_3$)(κ^{2}S,S-S$_2$CC≡CSiMe$_3$) (**1d**)*

Dark red crystals (82%). m.p.: 130–131 °C. IR (KBr, cm^{-1}): $\nu_{C\equiv C}$ 2120 (s). ^{1}H NMR (CDCl$_3$): δ 0.12 (s, 9H, SiMe$_3$); 4.53 (s, 5H, C$_5$H$_5$); 7.31 (m, 9H, PPh$_3$); 7.40 (m, 6H, PPh$_3$). ^{31}P NMR (CDCl$_3$): δ 56.77. Anal. Calc. for C$_{29}$H$_{29}$PRuS$_2$Si: C, 57.88; H, 4.68; S, 10.66. Found: C, 57.98; H, 5.10; S, 10.66%.

3.2. *General procedure for the preparation of CpRu(PPh$_3$)$_2$(κ^{1}S-S$_2$CCCR) (2)*

A 100-mL two-neck flask was charged with [CpRu(PPh$_3$)$_2$(NCPh)]PF$_6$ (0.50 g, 0.53 mmol) and 50.0 mL of THF. A 10.0 mL THF solution of the alkynyldithiocarboxylate anion (0.55 mmol) was added in one portion. The resulting yellow solution was stirred overnight. TLC (THF/hexane 1:1 v:v ratio) showed two products are formed. The solvent was removed under vacuum and the resulting red solid was redissolved in a minimum amount of THF and was introduced to a silica gel column made up in hexane. Elution with THF:hexane (1:1 v:v) ratio gave a red band which was collected and identified as **1** followed by another red band which was also collected and dried and was identified as CpRu(PPh$_3$)$_2$(κ^1*S*-S$_2$CC≡CR).

3.2.1. *CpRu(PPh$_3$)$_2$(κ^{1}S-S$_2$CC≡CBu^t) (**2a**)*

^{1}H NMR (CDCl$_3$): δ 4.49 (s, 5H, C$_5$H$_5$). ^{31}P NMR (CDCl$_3$): δ 47.14.

3.2.2. *CpRu(PPh$_3$)$_2$(κ^{1}S-S$_2$CC≡CBu^n) (**2b**)*

^{1}H NMR (CDCl$_3$): δ 4.40 (s, 5H, C$_5$H$_5$). ^{31}P NMR (CDCl$_3$): δ 47.10.

3.2.3. *CpRu(PPh$_3$)$_2$(κ^{1}S-S$_2$CC≡CPh) (**2c**)*

^{1}H NMR (CDCl$_3$): 4.41 (s, 5H, C$_5$H$_5$). ^{31}P NMR (CDCl$_3$): δ 47.11.

3.2.4. *CpRu(PPh$_3$)$_2$(κ^{1}S-S$_2$CC≡CSiMe$_3$) (**2d**)*

^{1}H NMR (CDCl$_3$): 4.40 (s, 5H, C$_5$H$_5$). ^{31}P NMR (CDCl$_3$): δ 47.10.

Table 2
Selected crystal data and refinement parameters for CpRu(PPh$_3$)(κ^2*S*,*S*-S$_2$CC≡CBu^t) (**1a**)

Empirical formula	C$_{30}$H$_{29}$PRuS$_2$
Crystal size (mm)	0.10 × 0.10 × 0.08
Crystal system	Triclinic
Space group	$P\bar{1}$
Volume (Å^3)	1329.15(7)
Z	2
Unit cell dimensions	
a (Å)	11.2606(3)
b (Å)	11.2890(4)
c (Å)	11.7437(3)
α (°)	63.936(2)
β (°)	84.948(2)
γ (°)	82.641(2)
Index range	$-14 \leqslant h \leqslant 14$, $-12 \leqslant k \leqslant 14$, $-14 \leqslant l \leqslant 15$
Formula weight	585.69
Radiation type	Mo Kα
Density (Mg/m^3)	1.463
μ (mm^{-1})	0.824
λ (Å)	0.71069
θ (°)	1.93–27.43
$R[F^2 > 2\sigma(F^2)]$	0.0278
$\omega R(F^2)$[a]	0.0684

[a] $\omega = 1/[\sigma^2(F_o^2) + (0.0598P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

3.3. *Crystallographic analysis of CpRu(PPh$_3$)(κ^{2}S,S-S$_2$CCCBu^t) (**1a**)*

Single crystals suitable for the X-ray study were obtained by recrystallization of **1a** from THF/hexane mixture. A crystal of size 0.10 × 0.10 × 0.08 mm was used for data collection. The crystallographic data are shown in Table 2. The geometric and intensity data were collected at 173(2) K on a KappaCCD diffractometer. There was 8948 total reflections with 5889 independent reflections (R_{int} = 0.017). The structures were solved by direct methods using SHELXS [34] and refined by full-matrix least-squares on F_o^2 using SHELX-97 [35]. All non-hydrogen atoms were refined anisotropically. The crystal data and structure refinement details are shown in Table 2.

4. Supplementary materials

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, (deposition No. CCDC No. 289730) for compound **1a**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1233 336 033, e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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