Journal of Organometallic Chemistry, 258 (1983) 73–79
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THIOCARBONYL COMPLEXES OF RUTHENIUM(II). SYNTHESIS OF $RuCl_2(CS)(H_2O)(PPh_3)_2$ AND $RuHCl(CS)(PPh_3)_3$

PENELOPE J. BROTHERS and WARREN R. ROPER*
Department of Chemistry, University of Auckland, Auckland (New Zealand)

(Received June 14th, 1983)

Summary

A high-yield synthesis of *trans*-$RuCl_2(CS)(H_2O)(PPh_3)_2$ from $RuCl_2(PPh_3)_3$ and CS_2 is described. The coordinated water molecule is labile, and introduction of CNR (R = *p*-tolyl or *p*-chlorophenyl) leads to yellow *trans*-$RuCl_2(CS)(CNR)(PPh_3)_2$, which isomerises thermally to colourless *cis*-$RuCl_2(CS)(CNR)(PPh_3)_2$. Reaction of $AgClO_4$ with *cis*-$RuCl_2(CS)(CNR)(PPh_3)_2$ gives $[RuCl(CS)(CNR)(H_2O)(PPh_3)_2]^+$, from which $[RuCl(CS)(CO)(CNR)(PPh_3)_2]^+$ and $[RuCl(CS)(CNR)_2(PPh_3)_2]^+$ are derived. Reaction of *trans*-$RuCl_2(CS)(H_2O)(PPh_3)_2$ with sodium formate gives $Ru(\eta^2\text{-}O_2CH)Cl(CS)(PPh_3)_2$, which undergoes decarboxylation in the presence of PPh_3 to give $RuHCl(CS)(PPh_3)_3$. $Ru(\eta^2\text{-}O_2CH)H(CS)(PPh_3)_2$ and $Ru(\eta^2\text{-}O_2CMe)H(CS)(PPh_3)_2$ are also described.

Introduction

The study of osmium thiocarbonyl chemistry was greatly facilitated by the discovery of $OsCl_2(CS)(PPh_3)_3$. This complex is prepared in high yield by the reaction of $OsCl_2(PPh_3)_3$ with CS_2 in the presence of excess PPh_3, and the lability of one phosphine ligand and one chloro ligand renders it an excellent substrate for further reaction [1]. In this paper we describe the incorporation of the thiocarbonyl ligand into the ruthenium coordination sphere in a one-step, high-yield synthesis of *trans*-$RuCl_2(CS)(H_2O)(PPh_3)_2$. This compound is easily converted into thiocarbonyl-containing cations suitable for the study of ligand reactions [2] and also into hydride thiocarbonyl complexes suitable for the investigation of migration reactions [1].

Results and discussion

Preparation of trans-$RuCl_2(CS)(H_2O)(PPh_3)_2$

The reaction of $RuCl_2(PPh_3)_3$ with CS_2 has been previously studied, but was found to be more complex than that of $OsCl_2(PPh_3)_3$ and CS_2 which leads cleanly

0022-328X/83/$03.00

to $OsCl_2(CS)(PPh_3)_3$ [1]. The ruthenium system was first investigated by Gilbert et al., and a species suggested to be $[RuCl_2(CS)(PPh_3)_2]_2$ was isolated [3]. Further work by Stephenson et al. gave the same complex in low yield, and additionally a triply-chloro-bridged dinuclear species $(PPh_3)_2ClRuCl_3Ru(PPh_3)_2(CS)$, which was fully characterised by X-ray crystal structure analysis [4,5]. In more recent studies further triply-chloro-bridged dinuclear species have been isolated and characterised [6]. We considered the dimer, $[RuCl_2(CS)(PPh_3)_2]_2$, to be a possible substrate for the study of ruthenium thiocarbonyl chemistry, and in an attempt to improve the low yield reported for this preparation the effects of solvent, reaction time, and addition of excess triphenylphosphine were examined.

On addition of $RuCl_2(PPh_3)_3$, CS_2 and excess PPh_3 to degassed toluene under nitrogen, a purple-red solution forms immediately. On heating this solution under reflux for a week the red colour disappears and the solution becomes light-brown in colour. Addition of hexane precipitates a yellowish product, in good yield, having the composition $RuCl_2(CS)(H_2O)(PPh_3)_2$. Use of xylene as solvent reduces the reaction time to 24 h, and addition of ethanol results in a more crystalline product of higher purity. Bands at 3541, 3488 and 1604 cm^{-1} in the IR spectrum indicate the presence of coordinated H_2O. The single band at 324 cm^{-1} indicates a *trans*-arrangement of the chloride ligands, and the reaction with CNR, described below, confirms this.

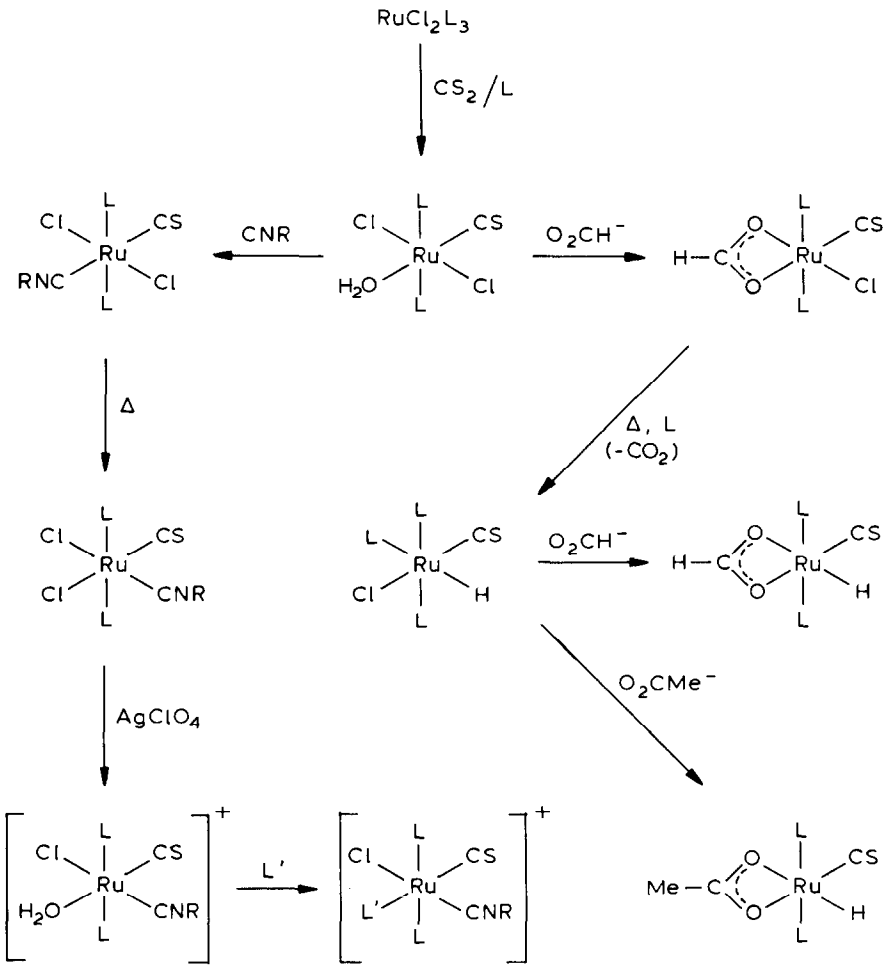
Preparation of ruthenium thiocarbonyl cations

In order to activate the thiocarbonyl ligand to nucleophilic attack, cationic complexes, preferably with other competing π-accepting ligands, are required [2]. *trans*-$RuCl_2(CS)(H_2O)(PPh_3)_2$ offers a simple route to such complexes (see Scheme 1). Treatment of *trans*-$RuCl_2(CS)(H_2O)(PPh_3)_2$ with one equivalent of CNR yields a bright yellow complex, *trans*-$RuCl_2(CS)(CNR)(PPh_3)_2$ (see Table 1 for IR and ^1H NMR data). This yellow complex readily isomerises to the thermodynamically stable product, the colourless *cis*-isomer, upon heating in toluene. On isomerisation, the value of ν(CS) decreases from 1295 to 1270 cm^{-1} for R = *p*-tolyl. In the *trans*-isomer both π-acceptor ligands are competing for the same metal *d*-electrons. In the *cis*-isomer this is not so and there is an increase in the amount of electron density available for back donation to the CS ligand, causing a decrease in ν(CS).

Reaction of *cis*-$RuCl_2(CS)(CNR)(PPh_3)_2$ with an equivalent of $AgClO_4$ abstracts a chloride ion from the complex, most likely from opposite the *trans*-labilising CS ligand, forming $[RuCl(CS)(H_2O)(CNR)(PPh_3)_2]ClO_4$. The coordinated H_2O molecule is readily displaced by CO or CNR leading to the cations $[RuCl(CS)(CO)(CNR)(PPh_3)_2]^+$ and $[RuCl(CS)(CNR)_2(PPh_3)_2]^+$ respectively.

Hydrido-thiocarbonyl ruthenium complexes

The stepwise reduction of the thiocarbonyl ligand, by successive hydride transfers, giving rise ultimately to the elimination of methylthiol, has been studied using the osmium complexes $OsH_2(CS)(PPh_3)_3$ and $OsHCl(CS)(PPh_3)_3$ [1]. The possibility of preparing analogous ruthenium complexes was examined using the formate ligand as a hydride-precursor [7]. The bright-yellow crystalline $Ru(\eta^2\text{-}O_2CH)Cl(CS)(PPh_3)_2$ is formed when $RuCl_2(CS)(H_2O)(PPh_3)_2$ in CH_2Cl_2/EtOH is treated with sodium formate in water. The characteristic stretching frequencies of the *dihapto*-formato ligand at 1547 and 1358 cm^{-1} are clearly identified in the IR



SCHEME 1. Synthesis of ruthenium thiocarbonyl complexes (L = PPh_3, R = *p*-tolyl or *p*-chlorophenyl, Me = methyl, L′ = CO or CNR).

spectrum. This complex readily decarboxylates on heating in methanol with excess PPh_3 to give, in high yield, fine cream crystals of $RuHCl(CS)(PPh_3)_3$. ν(Ru–H) and δ(Ru–H) occur at 2027 and 787 cm^{-1} respectively. The ^1H NMR spectrum exhibits a single high-field triplet (see Table 1 for details) implying that in solution one phosphine ligand is completely dissociated forming $RuHCl(CS)(PPh_3)_2$. The labile phosphine ligand in $RuHCl(CS)(PPh_3)_3$ facilitates the introduction of other ligands and this property is exploited in the syntheses of the *dihapto*-formato and -acetato complexes $Ru(\eta^2\text{-}O_2CH)H(CS)(PPh_3)_2$ and $Ru(\eta^2\text{-}O_2CMe)H(CS)(PPh_3)_2$ which form readily on treating $RuHCl(CS)(PPh_3)_3$ with sodium formate and sodium acetate respectively. $Ru(\eta^2\text{-}O_2CH)H(CS)(PPh_3)_2$ could not be successfully decarboxylated to $RuH_2(CS)(PPh_3)_3$. There are indications that these hydrido-thiocarbonyl derivatives readily rearrange to form complexes with thioformyl ligands but well-defined examples have not yet been isolated.

TABLE 1

IR DATA [a] (cm^{-1}) AND ^1H NMR DATA [b] FOR THIOCARBONYL RUTHENIUM COMPLEXES

Compound [c]	ν(CS)	ν(CN)	Other IR bands	Chemical shift (τ)
trans-$RuCl_2(H_2O)(CS)L_2$	1293		3488w,br ν(CH) 1604w δ(OH); 324m ν(RuCl)	
trans-$RuCl_2(CS)(CNR)L_2$	1270	2187	319m ν(RuCl)	7.64, s, 3H, CH_3
trans-$RuCl_2(CS)(CNR')L_2$	1273	2179	321m ν(RuCl)	
cis-$RuCl_2(CS)(CNR)L_2$	1295	2155		
cis-$RuCl_2(CS)(CNR')L_2$	1292	2150		
$[RuCl(CS)(H_2O)(CNR)L_2]ClO_4$	1305	2160	1090vs $\nu(ClO_4)$	
$[RuCl(CS)(H_2O)(CNR')L_2]ClO_4$	1309	2170	1092vs $\nu(ClO_4)$	
$[RuCl(CO)(CS)(CNR)L_2]ClO_4$	1335	2200 2160	2075vs ν(CO); 1090vs $\nu(ClO_4)$	
$[RuCl(CS)(CNR)_2L_2]ClO_4$	1310	2170	1088vs $\nu(ClO_4)$	7.68, s, 6H, CH_3
$[RuCl(CS)(CNR')_2L_2]ClO_4$	1309	2162br	1089vs $\nu(ClO_4)$	
$Ru(\eta^2\text{-}O_2CH)Cl(CS)L_2$	1290		1547s, 1358s ν(COO); 810s δ(CH)	3.27, m, 1H, CH
$RuHCl(CS)L_3$	1256		2031w ν(RuH); 787w δ(RuH)	16.65, t, Ru–H [d] ^2J(HP) 23 Hz
$Ru(\eta^2\text{-}O_2CH)H(CS)L_2$	1283		2030w ν(RuH); 1549s, 1366m ν(COO); 803m δ(RuH)	3.22, m, 1H, CH 23.29, t, 1H, Ru–H ^2J(HP) 21 Hz
$Ru(\eta^2\text{-}O_2CCH_3)H(CS)L_2$	1280		2004w ν(RuH); 1528, 1454 ν(COO) [e]	9.34, s, 3H, CH_3 23.18, t, 1H, Ru–H ^2J(HP) 21 Hz

[a] All spectra recorded in Nujol mulls. All ν(CS) absorptions are very strong; all ν(CN) vibrations are strong; other absorptions are denoted (vs), very strong; (s), strong; (m), medium; (w), weak; (br), broad. [b] All chemical shifts are quoted relative to the internal standard tetramethylsilane (τ, 10.0). $CDCl_3$ was used as the solvent for all spectra unless otherwise specified. [c] L = PPh_3, R = *p*-tolyl, R' = *p*-chlorophenyl. [d] CH_2Cl_2 used as solvent. [e] Spectrum recorded in "KEL-F" mull.

Experimental

General experimental conditions and instrumentation were as described previously [1].

$RuCl_2(CS)(H_2O)(PPh_3)_2$

$RuCl_2(PPh_3)_3$ [8] (4.0 g) and triphenylphosphine (2.0 g) were suspended in degassed xylene (60 ml). Carbon disulphide (1.0 ml) was added, and the resulting deep purple-red solution was heated under reflux until all traces of this red colour disappeared (24 h). On cooling the product began to crystallise from xylene solution. Ethanol (160 ml) was added and the suspension was stirred for 30 min to complete precipitation. The olive-green product was collected and washed with ethanol and hexane (2.46 g, 78%). Recrystallisation from dichloromethane/ethanol yielded chunky green-yellow crystals. M.p. 235–245°C. Anal. Found: C, 59.06; H, 4.72; P, 7.96. $C_{37}H_{32}Cl_2OP_2RuS$ calcd.: C, 58.58; H, 4.25; P, 8.17%.

trans-$RuCl_2(CS)(CNR)(PPh_3)_2$ (R = p-tolyl)

$RuCl_2(CS)(H_2O)(PPh_3)_2$ (0.50 g) was dissolved in dichloromethane (30 ml) and a solution of *p*-tolylisocyanide (0.085 g, 1.05 eq.) in ethanol was added. After stirring

for 5 min, further ethanol was added and the dichloromethane removed, giving a yellow crystalline solid. On filtration this was washed with ethanol and hexane (0.53 g, 94%). Recrystallisation from dichloromethane/ethanol yielded bright yellow crystals. M.p. 226–231°C. Anal. Found: C, 62.86; H, 4.45; N, 1.63; P, 7.23. $C_{45}H_{37}Cl_2NP_2RuS$ calcd.: C, 63.01; H, 4.35; N, 1.63; P, 7.22%.

trans-$RuCl_2(CNR)(CS)(PPh_3)_2$ (R = p-chlorophenyl)

$RuCl_2(CS)(H_2O)(PPh_3)_2$ (0.250 g) was treated with *p*-chlorophenylisocyanide (0.050 g) as above to yield yellow crystals of the title compound (0.290 g, 96%). Recrystallisation from dichloromethane/ethanol yielded bright yellow crystals. ^1H NMR ($CDCl_3$) showed that these crystals contain dichloromethane of solvation (τ 4.73 ppm) but the compound was too insoluble to obtain an accurate integral. Analysis indicated the presence of 0.5 mol dichloromethane. M.p. 268–273°C. Anal. Found: C, 58.26; H, 4.24; N, 1.45. $C_{44}H_{34}Cl_3NP_2RuS \cdot (CH_2Cl_2)_{0.5}$ calcd.: C, 58.06; H, 3.83; N, 1.52%.

cis-$RuCl_2(CS)(CNR)(PPh_3)_2$ (R = p-tolyl)

trans-$RuCl_2(CS)(CNR)(PPh_3)_2$ (0.54 g) was suspended in toluene (50 ml) and heated under reflux for 30 min. On cooling, white floccular crystals were formed which were collected and washed with ethanol and hexane (0.52 g, 97%). M.p. 222–227°C. Anal. Found: C, 63.14; H, 4.66; N, 1.67. $C_{45}H_{37}Cl_2NP_2RuS$ cald.: C, 63.01; H, 4.35; N, 1.63%.

cis-$RuCl_2(CNR)(CS)(PPh_3)_2$ (R = p-chlorophenyl)

trans-$RuCl_2(CNPhCl)(CS)(PPh_3)_2 \cdot (CH_2Cl_2)_{0.5}$ was treated as above to give white floccular crystals of the title compound (97%). Recrystallisation from dichloromethane/ethanol yielded white needles. M.p. 168–171°C. Anal. Found: C, 60.45; H, 4.51; N, 1.46. $C_{44}H_{34}Cl_3NP_2RuS$ calcd.: C, 60.18; H, 3.90; N, 1.59%.

[$RuCl(CS)(H_2O)(CNR)(PPh_3)_2$]$ClO_4$ (R = p-chlorophenyl)

cis-$RuCl_2(CNR)(CS)(PPh_3)_2$ (1.30 g) was dissolved in dichloromethane (110 ml) and a solution of silver perchlorate (0.370 g, 1.00 eq.) in ethanol (15 ml) was added. After stirring for 20 min the suspension was filtered through a celite pad to remove the precipitate of silver chloride. Removal of dichloromethane gave a cream coloured compound (1.32 g, 93%). Recrystallisation from dichloromethane/ethanol yielded cream crystals. ^1H NMR ($CDCl_3$) showed coordinated water (τ 8.48 ppm) but the compound was too insoluble to obtain an accurate integral. M.p. 188°C. Anal. Found: C, 54.55; H, 4.08; N, 1.44. $C_{44}H_{36}Cl_3NO_5P_2RuS$ calcd.: C, 55.04; H, 3.78; N, 1.46%.

[$RuCl(CS)(H_2O)(CNR)(PPh_3)_2$]$ClO_4$ (R = p-tolyl)

This was prepared exactly as described above for the R = *p*-chlorophenyl derivative, as a white solid. This was used without further characterisation for the preparation of the following two derivatives.

[$RuCl(CS)(CO)(CNR)(PPh_3)_2$]$ClO_4$ (R = p-tolyl)

[$RuCl(CS)(H_2O)(CNR)(PPh_3)_2$]$ClO_4$ (0.15 g) was dissolved in dichloromethane (30 ml) and ethanol (20 ml). The solution was placed in a Fischer-Porter bottle and

pressured with carbon monoxide (500 kPa) and heated to 100°C for 5 min. After cooling and reduction of the solvent volume under reduced pressure white crystals were deposited (0.15 g; 97.1%). M.p. 149–151°C. Anal. Found: C, 58.17; H, 4.22; N, 1.56. $C_{46}H_{37}Cl_2NO_5P_2RuS$ calcd.: C, 58.21; H, 3.93; N, 1.48%.

[RuCl(CS)(CNR)$_2$(PPh$_3$)$_2$]ClO$_4$ (R = p-tolyl)

[RuCl(CS)(H$_2$O)(CNR)(PPh$_3$)$_2$]ClO$_4$ (0.20 g) was dissolved in dichloromethane (30 ml), and a solution of *p*-tolylisocyanide (0.27 g) in ethanol (15 ml) was added. After stirring for 5 min further ethanol was added, and the dichloromethane was removed to give the white product, which was washed with ethanol and hexane (0.21 g, 93%). Recrystallisation from dichloromethane/ethanol/cyclohexane yielded fine white needles. M.p. 204°C. Anal. Found: C, 61.46; H, 4.46; N, 2.46%. $C_{45}H_{37}Cl_2N_2O_5P_2Ru$ calcd.: C, 61.27; H, 4.27; N, 2.70%.

[RuCl(CNR)$_2$(CS)(PPh$_3$)$_2$]ClO$_4$ (R = p-chlorophenyl)

[RuCl(CS)(H$_2$O)(CNR)(PPh$_3$)$_2$]ClO$_4$ (1.01 g) was treated with *p*-chlorophenylisocyanide (0.150 g) as above, to yield white crystals of the title compound (1.07 g, 94%). Recrystallisation from dichloromethane/ethanol yielded small white needles. M.p. 188°C. Anal. Found: C, 56.52; H, 3.59; N, 2.54%. $C_{51}H_{38}Cl_4N_2O_4P_2RuS$ calcd.: C, 56.73; H, 3.55; N, 2.59%.

Ru(η^2-O$_2$CH)Cl(CS)(PPh$_3$)$_2$

RuCl$_2$(CS)(H$_2$O)(PPh$_3$)$_2$ (0.5 g) was dissolved in dichloromethane (100 ml), and a solution of sodium formate (0.14 g) in water (4.5 ml) was added. A homogeneous solution was effected by the addition of ethanol (60 ml). The solution was stirred for 1 h, after which time crystallisation had begun. The dichloromethane was removed, and the yellow crystals washed with water and ethanol (0.48 g, 95%). Recrystallisation from dichloromethane/ethanol yielded chunky yellow crystals containing 0.17 mol dichloromethane of solvation. ^{1}H NMR ($CDCl_3$) shows τ 4.73 ppm [s, 0.33 H, CH_2Cl_2]. M.p. 145°C. Anal. Found: C, 59.77; H, 4.75; P, 8.25%. $C_{38}H_{31}ClO_2P_2RuS \cdot (CH_2Cl_2)_{0.17}$ calcd.: C, 59.98; H, 4.13; P, 8.11%.

RuHCl(CS)(PPh$_3$)$_3$

Ru(η^2-O$_2$CH)Cl(CS)(PPh$_3$)$_2$ · (CH$_2$Cl$_2$)$_{0.17}$ (0.73 g) and triphenylphosphine (0.75 g) were heated under reflux in degassed methanol (200 ml) for 1 h. The resulting suspension was cooled and the fine cream crystals collected. These were washed with methanol, dried, then washed with hot hexane (100 ml) to remove traces of excess triphenylphosphine (0.78 g, 83%). M.p. 164–169°C. Anal. Found: C, 67.99; H, 4.80. $C_{55}H_{46}ClP_2RuS$ calcd.: C, 68.21; H, 4.79%.

Ru(η^2-O$_2$CH)H(CS)(PPh$_3$)$_2$

RuHCl(CS)(PPh$_3$)$_3$ (0.20 g) was dissolved in dichloromethane (40 ml) and mixed with a solution of sodium formate (0.20 g) in water (3 ml). Ethanol (30 ml) was added in order to achieve a homogeneous solution which was stirred under nitrogen for 4.5 h. During this time a fine cream solid crystallised from the solution. This was collected after removal of the dichloromethane, and washed with water, ethanol and hexane (0.14 g, 89%). Recrystallisation from dichloromethane/ethanol yielded chunky pale yellow crystals, containing 0.25 mol dichloromethane of solvation. ^{1}H

NMR ($CDCl_3$) shows τ 4.73 ppm [s, 0.5H, CH_2Cl_2]. M.p. 174–184°C. Anal. Found: C, 62.75; H, 4.65. $C_{38}H_{32}O_2P_2RuS \cdot (CH_2Cl_2)_{0.25}$ calcd.: C, 62.34; H, 4.45%.

$Ru(\eta^2\text{-}O_2CCH_3)H(CS)(PPh_3)_2$

$RuHCl(CS)(PPh_3)_3$ (0.20 g) was dissolved in dichloromethane (40 ml), and a solution of sodium acetate (0.40 g) dissolved in water (4.0 ml), and ethanol (35 ml) were added. The homogeneous solution was stirred under nitrogen for 1.5 h, during which time the crystallisation of a fine white product began. This was collected by filtration and washed with ethanol, water, ethanol, and hexane (0.14 g, 92%). Recrystallisation of an analytical sample from dichloromethane/ethanol gave fine cream crystals. M.p. 196°C. Anal. Found: C, 63.87; H, 4.74. $C_{39}H_{34}O_2P_2RuS$ calcd.: C, 64.19; H, 4.70%.

Acknowledgements

We thank the New Zealand Universities Grants Committee for grants towards instrumental facilities and Johnson Matthey Ltd for a generous loan of $RuCl_3$.

References

1 T.J. Collins and W.R. Roper, J. Organomet. Chem., 159 (1978) 73.
2 P.J. Brothers, C.E.L. Headford and W.R. Roper, J. Organomet. Chem., 195 (1980) C29.
3 J.D. Gilbert, M.C. Baird and G. Wilkinson, J. Chem. Soc. (A), (1968) 2198.
4 T.A. Stephenson, E.S. Switkes and P.W. Armit, J. Chem. Soc., Dalton Trans., (1974) 1134.
5 A.J.F. Fraser and R.O. Gould, J. Chem. Soc., Dalton Trans., (1974) 1139.
6 P.W. Armit, W.J. Sime and T.A. Stephenson, J. Chem. Soc., Dalton Trans., (1976) 2121.
7 W.R. Roper and L.J. Wright, J. Organomet. Chem., 234 (1982) C5.
8 T.A. Stephenson and G. Wilkinson, J. Inorg. Nuclear Chem., 28 (1968) 945.