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SUBSTITUTED CYCLOPENTADIENYLRUTHENIUM COMPLEXES CONTAINING (S,S) DONOR LIGANDS

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Summary

The complexes $Ru(\eta\text{-}RC_5H_4)Cl(PPh_3)_2$ (R = H, CH_3, CH_3CO) have been shown to react with the anionic S–S donor ligands M^IS_2CX, (M^I = Na, K, NH_4^+; X = OR′, NR''_2, CN) to give cyclopentadienyl dithiolate complexes of ruthenium(II). Analogous compounds have been obtained from thallium cyclopentadienide and $Ru(S_2CX)_2(PPh_3)_2$. $Ru(\eta\text{-}CH_3COC_5H_4)Cl(PPh_3)_2$ (III) has been made by reaction between acetylcyclopentadiene, $RuCl_3$(aq.), and PPh_3 in absolute ethanol. Complexes of formula $Ru(\eta\text{-}RC_5H_4)(S_2CX)(PPh_3)_2$, with the dithiolate ligand monodentate, are obtained when R = H, X = OC_6H_{11}; R = CH_3, X = OCH_3; R = H, CH_3, X = CN. In the other cases studied the isolated complexes contain a bidentate S–S ligand. Steric effects as well as the electronic properties of dithiolate ligands, seem to influence the choice between the two coordination modes. Reaction of III with NaS_2CNEt_2 affords $Ru(S_2CNEt_2)_2(PPh_3)_2$ as the sole product. Carbonylation of complex VI, $Ru(\eta\text{-}C_5H_5)(S_2COC_6H_{11})(PPh_3)_2$ takes place in solution, but the carbonyl complex could not be isolated.

Introduction

The reactions of $Ru(\eta\text{-}C_5H_5)Cl(PPh_3)_2$ provide an interesting area of the chemistry of the organoruthenium compounds [1]. Its behaviour is characterised by the ready displacement of one or both triphenylphosphine ligands; many substitution complexes have been obtained, but reactions with dithiolate anionic ligands are scarce [2,3].

We have prepared $Ru(\eta\text{-}CH_3COC_5H_4)Cl(PPh_3)_2$ (III) from acetylcyclopentadiene. In contrast to the much studied rhodium complexes, [4,5], only a few functionally monosubstituted cyclopentadienyls of ruthenium have been reported [6]. We now describe the reactions of the complexes $Ru(\eta\text{-}RC_5H_4)Cl(PPh_3)_2$ (I, R = H; II, R = CH_3; III, R = CH_3CO) with the anionic dithiolate ligands ^-S_2CX, showing a range of electronic and steric properties, viz. those with X = OCH_3 (the ligand, S_2COMe then being denoted by Mexant), OC_2H_5 (Etxant), OC_6H_{11} (Cyxant), $N(C_2H_5)_2$ (Et_2dtc), $N(CH_2)_4$ (pyrrdtc), and CN (cyanodithioformate).

The results reported for the reactions with xanthates reveal their ability to take part in monodentate or bidentate coordination to ruthenium. On the other hand, the dithiocarbamates give only bidentate complexes.

Results and discussion

Synthesis of $Ru(\eta\text{-}RC_5H_4)Cl(PPh_3)_2$ (II, $R = CH_3$; III, $R = CH_3CO$)

The complexes II and III were obtained by a method similar to that described by Bruce [7] for complex I. Complex II was isolated in a higher yield than that achieved by a different procedure by Haines and Du Preez [6]. The low yield for the synthesis of III ($RuCl_2(PPh_3)_3$ was the main product) reflects the lower reactivity of cyclopentadiene bearing an acetyl substituent.

The IR and ^1H NMR spectra of II and III are consistent with a coordination similar that in complex I. Substitution in the cyclopentadienyl ring produces a splitting in its NMR signal, and in line with previous studies on substituted metallocenes [8,9] we have assigned the signal at higher field to protons 3 and 4, and that at lower field to protons 2 and 5. The diamagnetic anisotropic effect of the electron-withdrawing acetyl substituent is expected to effect mainly the 2- and 5-positions, whereas an electron-donating alkyl substituent is thought to shield the 3- and 4-protons.

Like complex I, complexes II and III are appreciable ionized in methanol, according to the equilibrium:

$$Ru(\eta\text{-}RC_5H_4)Cl(PPh_3)_2 + MeOH \rightarrow [Ru(\eta\text{-}RC_5H_4)(PPh_3)_2(MeOH)]^+ + Cl^-$$

In keeping with this observation, addition of a methanolic solution of $M^I(S_2CX)$ readily brings about substitution. Similar reactions can be carried out in chloroform, but complexes I–III are not ionized in this solvent and the yield is lower.

Sythesis of complexes IV–XX

Addition of a methanolic solution of M^IS_2CX to a suspension of I–III in methanol gave complexes IV–XX. The isolated complexes are stable to air and water, and can be precipitated from the methanolic solutions by addition of water. Table 1 lists the analytical data and yields for these compounds; when a complex was synthesized by more than one method, the yield in each case is indicated.

The reaction of $Ru(S_2CX)_2(PPh_3)_2$ ($X = OC_2H_5$, $N(CH_2)_4$) with thallium cyclopentadienide gave cyclopentadienyl complexes (V and VIII, respectively, which were shown to be identical with those obtained from complex I by halide substitution.

The most characteristic stretching frequencies in the IR spectra are listed in Table 2. The ν(C–X) bands at about 1200–1250 cm^{-1} for xanthates and at 1470–1500 cm^{-1} for dithiocarbamates correspond to a bidentate coordination of the S–S ligand; for complexes VI and XI the spectral data reveal monodentate coordination of the dithiolate ligand.

Wilczewski et al. [2] previously synthesised complexes IV, V, VIII and IX, and reported the preparation of the monodentate dithiolate complex $Ru(\eta\text{-}C_5H_5)$(Mexant)$(PPh_3)_2$, but in our hands their procedure always gave complex IV.

TABLE 1

YIELDS AND ANALYTICAL DATA FOR THE COMPLEXES

Complex		Colour	Method used and yield (%) [a]	Analyses (Found (calcd.) (%))		
				C	H	N
I	$Ru(\eta\text{-}C_5H_5)Cl(PPh_3)_2$	orange	85	67.35	4.71	
				(67.80)	(4.87)	
II	$Ru(\eta\text{-}CH_3C_5H_4)Cl(PPh_3)_2$	orange	90	68.24	5.00	
				(68.14)	(5.05)	
III	$Ru(\eta\text{-}CH_3COC_5H_4)Cl(PPh_3)_2$	red	30	66.87	4.79	
				(67.22)	(4.86)	
IV	$Ru(\eta\text{-}C_5H_5)(Mexant)(PPh_3)$	orange	A-63	56.24	4.74	
				(56.05)	(4.34)	
V	$Ru(\eta\text{-}C_5H_5)(Etxant)(PPh_3)$	yellow-orange	A-80 C-36	57.10	4.43	
				(56.81)	(4.59)	
VI	$Ru(\eta\text{-}C_5H_5)(Cyxant)(PPh_3)_2$	orange	A-34	64.98	5.12	
				(66.56)	(5.36)	
VII	$Ru(\eta\text{-}C_5H_5)(Cyxant)(PPh_3)$	orange	A-53	59.41	5.05	
				(59.67)	(5.19)	
VIII	$Ru(\eta\text{-}C_5H_5)(pyrrdtc)(PPh_3)$	orange	A-88 C-39	58.13	5.59	2.81
				(58.51)	(4.92)	(2.44)
IX	$Ru(\eta\text{-}C_5H_5)(Et_2dtc)(PPh_3)$	orange	A-85 B-18	58.23	5.20	2.70
				(58.37)	(5.25)	(2.48)
X	$Ru(\eta\text{-}C_5H_5)(S_2CCN)(PPh_3)_2$	purple	A-93 B-32	62.98	4.57	1.51
				(65.13)	(4.46)	(1.77)
XI	$Ru(\eta\text{-}CH_3C_5H_4)(Mexant)(PPh_3)_2$	yellow-orange	A-48	63.75	4.77	
				(65.08)	(4.98)	
XII	$Ru(\eta\text{-}CH_3C_5H_4)(Mexant)(PPh_3)$	yellow-orange	A-41	57.03	4.60	
				(56.81)	(4.59)	
XIII	$Ru(\eta\text{-}CH_3C_5H_4)(Etxant)(PPh_3)$	yelow	A-85 B-38	58.10	4.93	
				(57.52)	(4.84)	
XIV	$Ru(\eta\text{-}CH_3C_5H_4)(Cyxant)(PPh_3)$	yellow	A-64	60.70	5.51	
				(60.26)	(5.39)	
XV	$Ru(\eta\text{-}CH_3C_5H_4)(pyrrdtc)(PPh_3)$	orange	A-81 B-24	59.44	5.14	2.57
				(59.16)	(5.15)	(2.38)
XVI	$Ru(\eta\text{-}CH_3C_5H_4)(Et_2dtc)(PPh_3)$	orange	A-72	58.81	5.33	2.44
				(58.95)	(5.47)	(2.37)
XVII	$Ru(\eta\text{-}CH_3C_5H_4)(S_2CCN)(PPh_3)_2$	purple	A-95	66.10	4.49	2.10
				(65.49)	(4.63)	(1.73)
XVIII	$Ru(\eta\text{-}CH_3COC_5H_4)(Mexant)(PPh_3)$	orange	A-82	55.98	4.29	
				(56.13)	(4.37)	
XIX	$Ru(\eta\text{-}CH_3COC_5H_4)(Etxant)(PPh_3)$	orange	A-79 B-33	55.94	4.26	
				(56.83)	(4.61)	
XX	$Ru(\eta\text{-}CH_3COC_5H_4)(pyrrdtc)(PPh_3)$	orange	A-62	58.83	5.05	2.60
				(58.42)	(4.91)	(2.27)
XXI	III + $NaEt_2dtc$ [b]	green		59.31	5.49	3.71
				(59.90)	(5.47)	(3.04)

[a] For methods see Experimental. [b] Analyses calculated for $Ru(Et_2dtc)_2(PPh_3)_2$.

The complexes $Ru(\eta\text{-}RC_5H_4)(S_2COR')(PPh_3)_2$ (IV, $R = H$, $R' = C_6H_{11}$ and XI, ($R = CH_3$, $R' = CH_3$) were made in refluxing methanol, and immediately separated out. After filtration the solutions yielded, complexes VII and XII. We assume that in all cases reaction involves chlorine displacement and formation of the dithiolate

TABLE 2

INFRARED SPECTRAL DATA

Complex		Cp def [a]	ν(CS)	ν(CX)	Others
I	$Ru(\eta\text{-}C_5H_5)Cl(PPh_3)_2$	810m 840m			280w ν(RuCl)
II	$Ru(\eta\text{-}CH_3C_5H_4)Cl(PPh_3)_2$	810m 840m			285w ν(RuCl)
III	$Ru(\eta\text{-}CH_3COC_5H_4)Cl(PPh_3)_2$	805m 855m			280w ν(RuCl) 1680s ν(C=O)
IV	$Ru(\eta\text{-}C_5H_5)$(Mexant)(PPh_3)	810m 840m 860w	1045m	1240s	
V	$Ru(\eta\text{-}C_5H_5)$(Etxant)(PPh_3)	805m 830w 855w	1040s	1230s	
VI	$Ru(\eta\text{-}C_5H_5)$(Cyxant)$(PPh_3)_2$	810m 830w 840w	1040s	1150s 1180s	
VII	$Ru(\eta\text{-}C_5H_5)$(Cyxant)(PPh_3)	810w 835w 860w	1035m	1235s	
VIII	$Ru(\eta\text{-}C_5H_5)$(pyrrdtc)(PPh_3)	790m 830m 840m	1005m	1450s 1470s	
IX	$Ru(\eta\text{-}C_5H_5)(Et_2dtc)(PPh_3)$	800w 835w 860w	1010w	1490s	
X	$Ru(\eta\text{-}C_5H_5)(S_2CCN)(PPh_3)_2$	815m 840m	1005s	1055s ν(C=S)	2200m ν(CN)
XI	$Ru(\eta\text{-}CH_3C_5H_4)$(Mexant)$(PPh_3)_2$	825m 840m	1050s	1140s 1200s	
XII	$Ru(\eta\text{-}CH_3C_5H_4)$(Mexant)$(PPh_3)$	800m 840m	1055m	1250s	
XIII	$Ru(\eta\text{-}CH_3C_5H_4)$(Etxant)$(PPh_3)$	810m 835m	1025s	1220s	
XIV	$Ru(\eta\text{-}CH_3C_5H_4)$(Cyxant)$(PPh_3)$	840m	1035m	1225s	
XV	$Ru(\eta\text{-}CH_3C_5H_4)$(pyrrdtc)$(PPh_3)$	805m 840m	1030m	1440s 1470s	
XVI	$Ru(\eta\text{-}CH_3C_5H_4)(Et_2dtc)(PPh_3)$	810w 830w 860w	1010m	1490s	
XVII	$Ru(\eta\text{-}CH_3C_5H_4)(S_2CCN)(PPh_3)_2$	820m 845m	1005m	1060s ν(C=S)	2210m ν(CN)
XVIII	$Ru(\eta\text{-}CH_3COC_5H_4)$(Mexant)$(PPh_3)$	800w 840w 850w	1045m	1245s	1670s ν(C=O)
XIX	$Ru(\eta\text{-}CH_3COC_5H_4)$(Etxant)$(PPh_3)$	810w 835w	1030m	1240s	1660s ν(C=O)
XX	$Ru(\eta\text{-}CH_3COC_5H_4)$(pyrrdtc)$(PPh_3)$	840m	1005m	1455s 1470s	1665m ν(C=O)

[a] Deformation ring modes attributable to π(CH) and Cp tilt.

monodentate complex. Subsequent loss of a bulky triphenylphosphine ligand then gives the bidentate complex. The reaction can be represented as follows:

$$\begin{tikzcd} Ru(\eta\text{-}RC_5H_4)Cl(PPh_3)_2 \arrow[r, "MS_2CX"] & Ru(\eta\text{-}RC_5H_4)(S_2CX)(PPh_3)_2 \arrow[d, "-PPh_3"] \\ & Ru(\eta\text{-}RC_5H_4)(S_2CX)(PPh_3) \end{tikzcd}$$

It was possible to isolate compounds VI and XI because their insolubility prevents occurrence of the second step. In supporting of our proposed route we note that the product of reaction of III with NaS_2COCH_3 (aimed at complex XVIII) sometimes had an IR spectrum indicating it to be a mixture, with a strong band at 1135 cm^{-1} attributable to the ν(C–O) for the monodentate methylxanthate complex along with a band at 1245 cm^{-1} due to the ν(C–O) of a bidentate xanthate. The ^{1}H NMR spectrum does not show separate signals for the cyclopentadienyl protons of the monodentate and bidentate complexes, but integration of the resonances is consistent with the presence of a mixture.

We failed to obtain $Ru(\eta\text{-}RC_5H_4)$(Cyxant)$(PPh_3)_2$ by refluxing a mixture of $Ru(\eta\text{-}RC_5H_4)$(Cyxant)(PPh_3) and PPh_3 in toluene.

No reaction was detected when carbon monoxide was bubbled through a solution of $Ru(\eta\text{-}CH_3C_5H_4)$(Etxant)$(PPh_3)$ (XIII) in methanol or chloroform, with the objective of obtaining the related carbonyl complex containing monodentate xanthate.

Bubbling carbon monoxide through a solution of $Ru(\eta\text{-}C_5H_5)$(Cyxant)$(PPh_3)_2$ (VI) in chloroform gave rise to a strong band at 2020 cm^{-1} (ν(C≡O)), along with bands attributable to monodentate xanthate at 1145 and 1180 cm^{-1}. These bands may correspond to a monocarbonyltriphenylphosphine complex. We assume that the following equillibrium is present in solution:

$$\mathrm{Ru}(\eta\text{-}C_5H_5)(\mathrm{Cyxant})(\mathrm{PPh}_3)_2 + \mathrm{CO} \rightleftharpoons \mathrm{Ru}(\eta\text{-}C_5H_5)(\mathrm{Cyxant})(\mathrm{CO})(\mathrm{PPh}_3) + \mathrm{PPh}_3$$

The greater ease of carbonylation of the xanthate complex than of the chloro complex, which is carbonylated only under forcing conditions [10], as well as a marked lability of one PPh_3 ligand due to steric effects, allow carbonylation to proceed. However, attempts to isolate the formed complex result in displacement of the equilibrium to the left, and recovery of the starting complex.

Dithiocarbamates gave only the bidentate complexes, whereas complexes X and XVII contain a monodentate cyanodithioformate ligand, as indicated by the bands at 1060 (ν(C=S)) and 1005 cm^{-1} (ν(C–S)).

The behaviour of the dithiolate ligands can be explained in terms of electronic and steric effects. The donor ability of ^-S_2CX ligands shows some correlation with the lowering of the frequency of the ν(C–S) absortion on going to the complex and also the higher shielding of the cyclopentadienyl protons. Examination of the spectral data (Tables 2 and 3) suggests that the donor ability towards the cyclopentadienylruthenium moiety falls in the sequence $^-S_2CNR''_2 > {}^-S_2COR' > {}^-S_2CCN$, in keeping with the ease of displacement of the phosphine ligand. The smaller size and thus lower steric hindrance of the ligand cyanodithioformate, along

TABLE 3

PROTON NMR DATA[a]

Complex		Ph	Cp		R-Cp	S–S ligand
			H(2,5)	H(3,4)		
I	Ru(η-C_5H_5)Cl(PPh_3)$_2$	7.16m	4.01s			
II	Ru(η-$CH_3C_5H_4$)Cl(PPh_3)$_2$	7.20m	4.0s	3.30s	1.93s	
III	Ru(η-$CH_3COC_5H_4$)Cl(PPh_3)$_2$	7.30m	5.1s	3.6s	2.20s	
IV	Ru(η-C_5H_5)(Mexant)(PPh_3)	7.37m	4.40s			3.6s OCH_3
V	Ru(η-C_5H_5)(Etxant)(PPh_3)	7.45m	4.37s			4.0q OCH_2; 1.07t CH_3
VI	Ru(η-C_5H_5)(Cyxant)(PPh_3)$_2$	7.27m	4.41s			3.48m OCH; 1.54m CH_2
VII	Ru(η-C_5H_5)(Cyxant)(PPh_3)	7.30m	4.42s			3.45m OCH; 1.71m CH_2; 1.32m CH_2; 0.92 m CH_2
VIII	Ru(η-C_5H_5)(pyrrdtc)(PPh_3)	7.23m	4.10s			3.05m NCH_2; 1.70m CH_2
IX	Ru(η-C_5H_5)(Et_2dtc)(PPh_3)	7.40m	4.25s			3.37q NCH_2; 0.83t CH_3
X	Ru(η-C_5H_5)(S_2CCN)(PPh_3)$_2$	7.20m	4.84s			
XI	Ru(η-$CH_3C_5H_4$)(Mexant)(PPh_3)$_2$	7.23m	4.4s	3.83s	1.97s	3.72s OCH_3
XII	Ru(η-$CH_3C_5H_4$)(Mexant)(PPh_3)	7.40m	4.13s		1.9s	3.60s OCH_3
XIII	Ru(η-$CH_3C_5H_4$)(Etxant)(PPh_3)	7.35m	4.77m	3.60m	1.9s	4.06q OCH_2; 1.23t CH_3
XIV	Ru(η-$CH_3C_5H_4$)(Cyxant)(PPh_3)	7.30m	4.13s		1.90s	3.43m OCH; 1.50m CH_2; 1.27m CH_2; 0.75 CH_2
XV	Ru(η-$CH_3C_5H_4$)(pyrrdtc)(PPh_3)	7.50m	4.03s		1.87s	3.00m NCH_2; 1.73m CH_2
XVI	Ru(η-$CH_3C_5H_4$)(Et_2dtc)(PPh_3)	7.53m	4.0s		1.9s	3.37q NCH_2; 0.97t CH_3
XVII	Ru(η-$CH_3C_5H_4$)(S_2CCN)(PPh_3)$_2$	7.23m	5.03s	3.87s	1.9s	
XVIII	Ru(η-$CH_3COC_5H_4$)(Mexant)(PPh_3)	7.23m	5.35m	4.05m	2.20s	3.63 OCH_3
XIX	Ru(η-$CH_3COC_5H_4$)(Etxant)(PPh_3)	7.33m	5.4m	3.97m	2.20s	4.06q OCH_2; 1.23t CH_3
XX	Ru(η-$CH_3COC_5H_4$)(pyrrdtc)(PPh_3)	7.29m	5.3m	3.90m	2.20s	3.0m NCH_2; 1.73m CH_2

[a] In $CDCl_3$ with TMS as internal standard.

with its lower donor ability, leads to formation of the monodentate complex as the only isolated product.

The ^{1}H NMR spectra (Table 3) of the substituted cyclopentadienyl complexes XI–XX show a sharp singlet at 1.9–2.2 ppm arising from the methyl protons of the substituent. Complexes XI, XIII, XVII, XVIII, XIX and XX exhibit two signals in the δ 5.4–3.6 ppm range, which are assigned to the 2,5 and 3,4 protons of the substituted cyclopentadienyl rings. These two resonances are shifted to lower field with respect to those of the chloro-complexes II and III. Methylcyclopentadienyl complexes XII, XIV, XV and XVI show only one resonance for cyclopentadienyl protons, we expect that the effect of the dithiolate ligand on the 3 and 4 protons results in the undetectable separation of the two signals expected for an AA′BB′ pattern of a monosubstituted cyclopentadienyl ring. We have previously observed such behaviour for methylcyclopentadienylnickel complexes [11].

Reaction of III with sodium diethyldithiocarbamate gives only $Ru(Et_2dtc)_2(PPh_3)_2$ with loss of both chloride and cyclopentadiene ligands; this may be attributed to the high donor ability of the dithiocarbamate ligand and low donor ability of the acetylcyclopentadiene ligand.

Experimental

All reactions were carried out under oxygen-free nitrogen. $Ru(\eta\text{-}C_5H_5)Cl(PPh_3)_2$ [7], $RuCl_2(PPh_3)_3$ [12], sodium acetylcyclopentadienide [13] and sodium cyanodithioformate [14] were prepared by published methods. Analyses were by Elemental Microanalyses Ltd. (Devon). IR spectra were recorded on a Perkin–Elmer 1300 spectrophotometer with KBr pellets. ^{1}H NMR spectra were recorded on a Varian EM-390 spectrometer at room temperature. Melting points were measured in open capillaries and are uncorrected.

Preparation of $Ru(\eta\text{-}CH_3C_5H_4)Cl(PPh_3)_2$ (II)

A solution $RuCl_3$aq. (0.3 g, 1.4 mmol) in 20 ml of 96% ethanol was added to a boiling solution of 1.2 g (4.6 mmol) of PPh_3 in 50 ml of 96% ethanol, followed immediately by addition of 1.5 ml of a solution of freshly distilled methylcyclopentadiene in 5 ml of 96% ethanol. The solution was refluxed for 1 h then cooled, to give orange crystals, which were recrystallized from dichloromethane/n-hexane. M.p. 138°C.

Preparation of $Ru(\eta\text{-}CH_3COC_5H_4)Cl(PPh_3)_2$ (III)

A solution of 1.2 g of sodium acetylcyclopentadienide in diluted HCl was stirred for 15 min. The acetylcyclopentadiene was extracted with diethyl ether, and the ethereal solution was concentrated, dried over $MgSO_4$, and added to a boiling solution of 0.48 g (1.83 mmol) of PPh_3 and 0.12 g (0.6 mmol) of $RuCl_3$ aq. in 20 ml of absolute ethanol. The mixture was refluxed for 2 h then filtered, and the filtrate was cooled. The brown precipitate of $RuCl_2(PPh_3)_3$ was filtered off and the filtrate was then kept cold concentrated overnight, to give red crystals of III. The product can be recrystallized from chloroform/n-hexane. M.p. 110–112°C.

Preparation of dithiolate complexes (IV–XX)

Method A: To a suspension of complexes I, II or III (0.1 g, 0.13 mmol) in 20 ml methanol was added an excess (0.2 mmol) of the alkali metal or ammonium salt of the dithiolate ligand in 10 ml of methanol. The mixture was refluxed for about 15 minutes, then concentrated in vacuum and cooled, to give orange microcrystals of the product. (In some cases water was added to the methanolic solution to precipitate the complex.) All the products were recrystallized from chloroform/n-hexane. Compounds VI and XI separated form the refluxing mixture and were filtered off; the filtrate then gave products VII and XII, respectively.

Method B: Refuxing in chloroform of a mixture of complexes I, II or III and the S–S ligand for 3 h, following by fitration and addition of n-hexane gave the product in 20–40% yield.

Method C: A solution of 0.05 g (ca. 0.06 mmol) of $Ru(S_2CX)_2(PPh_3)_2$ (prepared from $RuCl_2(PPh_3)_3$ and KEtxant or NH_4pyrrdtc in refluxing acetone [15]) was mixed with a suspension of 0.02 g (0.07 mmol) of thallium cyclopentadienide in 30 ml of benzene, and the mixture was refluxed for 2 h, then evaporated to dryness. The residue was extracted with chloroform, and concentration of the extract followed by addition of n-hexane gave the orange solid in 30–40% yield.

Reaction of VI with carbon monoxide

Carbon monoxide was bubbled for 15 min at room temperature, through a solution of 0.03 g (0.035 mmol) of $Ru(\eta\text{-}C_5H_5)$(Cyxant)$(PPh_3)_2$ in 15 ml of chloroform. The solution shows a strong band at 2020 cm^{-1}. Concentration and addition of light petroleum gives a yellow orange solid whose IR and ^1H NMR spectra are identical to the starting product.

Reaction of III with $NaEt_2dtc \cdot 3H_2O$

When a solution of 0.03 g (0.04 mmol) of III and 0.014 g (0.06 mmol) of $NaEt_2dtc \cdot 3H_2O$ in 20 ml of methanol was refluxed, the colour changed from red-orange to green. Concentration of the solution and cooling gave a green solid, which analysed for $Ru(Et_2dtc)_2(PPh_3)_2$, in 60% yield.

References

1 M.A. Bennett, M.I. Bruce and T.W. Matteson in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 4, p. 783, Pergamon Press, Oxford, 1982.
2 T. Wilczewski, M. Bochenska and J.F. Biernat, J. Organomet. Chem., 215 (1981) 87.
3 T. Wilczewski, J. Organomet. Chem., 244 (1982) Cl.
4 M. Arthurs, S.M. Nelson and M.G.B. Drew, J. Chem. Soc. Dalton Trans., (1977) 779.
5 M.-D. Rausch, W.P. Hart, J.L. Atwood and M.J. Zaworotko, J. Organomet. Chem., 197 (1980) 225.
6 R.J. Haines and A.L. Du Preez, J. Organomet. Chem., 84 (1975) 357.
7 M.I. Bruce and N.J. Windsor, Aust. J. Chem., 30 (1977) 1601.
8 D.W. Slocum, and C.R. Ernast, Organometallic Chem. Rev. A, 6 (1970) 346.
9 D.W. Slocum, C.R. Ernst and W.E. Jones, J. Org. Chem., 37 (1972) 4278.
10 T. Blackmore, M.I. Bruce and F.G.A. Stone, J. Chem. Soc. A, (1971) 2376.
11 L.R. Byers and L.F. Dahl, Inorg. Chem., 19 (1980) 680.
12 P.S. Hallman, T.A. Stephenson and G. Wilkinson, Inorg. Synth., 12 (1970) 237.
13 W.P. Hart, D.W. Macomber and M.D. Rausch, J. Am. Chem. Soc., 102 (1980) 1196.
14 G. Bähr and G. Scheitzer, Chem. Ber., 88 (1955) 1771.
15 C. O'Connor, J.D. Gilbert and G. Wilkinson, J. Chem. Soc. A, (1969) 84.