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Preliminary Communication

Hydride-phosphoniodithiocarboxylate/ phosphonium-betaine isomerism in Cy_3PCS_2 complexes of ruthenium

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Abstract

Reaction of Cy_3PCS_2 (Cy = cyclohexyl) with the hydrido complexes $[RuClH(CA)(PPh_3)_3]$ (A = O, S), $[RuH(CO)(NCMe)_2(PPh_3)_2]^+$, and $[RuH(OClO_3)(CO)(CN^tBu)(PPh_3)_2]$ leads to the complex cations $[RuH(CA)(PPh_3)_2(\eta^2\text{-}S_2CPCy_3)]^+$, $[Ru(\eta^2\text{-}S_2CHPCy_3)(CO)(PPh_3)_2]^+$, $[RuH(\eta^1\text{-}S_2CPCy_3)(CO)(CN^tBu)(PPh_3)_2]^+$. The σ-vinyl complex $[Ru(CH{=}CHC_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]$ reacts with Cy_3PCS_2 to give the cationic complex $[Ru(CH{=}CHC_6H_4Me\text{-}4)(CO)(PPh_3)_2(\eta^2\text{-}S_2CPCy_3)]^+$, but this complex is not formed by hydroruthenation of $HC{\equiv}CC_6H_4Me\text{-}4$ by $[RuH(CO)(PPh_3)_2(\eta^2\text{-}S_2CPCy_3)]^+$. The inter-relationships between the above complexes are discussed.

The adducts formed between trialkylphosphines (PR_3) and carbon disulphide (S_2CPR_3) act as ligands to transition metals in a manner in some ways reminiscent of dialkyl dithiocarbamates, the predominant coordination mode being the formation of a MS_2C metallacycle (Scheme 1). The intriguing departure from this analogy comes from the possibility of P–C bond cleavage and/or the addition of nucleophiles to the carbon atom [1,2]. In particular the connection between dithioformate/phosphine (**A**, Scheme 1), phosphonium betaine [**B**, Scheme 1] and hydride/phosphoniodithiocarboxylate [**C**, Scheme 1] complexes raises the question of hydride and phosphine transfer to and from the metallacycle carbon. Singleton has shown that thermolysis of $[Ru(S_2CH)(PMe_2Ph)_4]^+$ leads to $[Ru(S_2CHPMe_2Ph)(PMe_2Ph)_3]^+$ and that replacement of the phosphine ligands by $P(OMe)_3$ induces the phosphine to return to the metal centre with formation of $[Ru(S_2CH)(PMe_2Ph)_2\{P(OMe)_3\}_2]^+$ [1], but there are no examples of cases in which the phosphonium betaine and phosphoniodithiocarboxylate isomers co-exist. We find that this situation arises in the reactions of C_3PCS_2 (Cy = cyclohexyl) with a variety of ruthenium hydride complexes featuring different electronic properties and coordinative saturation at the ruthenium centre.

The complex $[RuClH(CO)(PPh_3)_3]$ reacts with Cy_3PCS_2 to give a mixture of products. ^{31}P NMR and IR spectroscopy indicate that *ca.* 90% of the mixture consists of two compounds in a ratio of 1:3. A pure sample of these two complexes is obtained from the reaction of the salt $[RuH(CO)(NCMe)_2(PPh_3)_2]ClO_4$ [3] with S_2CPCy_3 ^1H, and ^{31}P NMR data (Table 1) indicate that two isomers are present, which we formulate as $[RuH(CO)(PPh_3)_2(S_2CPCy_3)]^+$ (minor) and $[Ru(S_2CHPCy_3)(CO)(PPh_3)_2]^+$ (major). The most informative spectroscopic data are associated with the proton which is either bound to ruthenium [δ −9.94 ppm, J(PH) 23.5, 5.3 Hz] or to the dithiocarboxylic carbon [δ 5.94 ppm, J(PH) not resolved at 400 MHz]. The formation of the minor hydrido isomer has precedent in the reaction of the 16-electron complex $[RuClH(CO)(PCy_3)_2]$ with Cy_3PCS_2 which provides $[RuH(CO)(PCy_3)_2(S_2CPCy_3)]^+$ [4]. It is not clear why replacement of PCy_3 by PPh_3 in the present case leads to a predominance of the betaine isomer. The implication that a less basic (or more π-acidic) phosphine disfavours the phosphoniodithiocarboxylate isomer is contradicted by the observation that Cy_3PCS_2 with $[RuClH(CS)(PPh_3)_3]$ leads exclusively to the complex $[RuH(CS)(PPh_3)_2(S_2CPCy_3)]^+$ [δ −7.76, $J(PH) = 23.5$, 5.5 Hz], given that carbon monosulphide is recognised to be a stronger π-acid than carbon monoxide. In the bis(tricyclohexylphosphine) complex it is possible that steric factors come into play, and indeed such an argument has been used by Singleton [1]. The results obtained with $[RuClH(CS)(PPh_3)_3]$ clearly indicate that both electronic and steric factors play a role in this isomerism.

The phosphonium betaine isomer is formally coordinatively unsaturated and accordingly it seemed plausible that the addition of small ligands L (L = CO, CN^tBu) would trap the betaine isomer as $[Ru(S_2CHPCy_3)(CO)(L)(PPh_3)_2]^+$. Treating the complex with either tert-butyl isonitrile or carbon monoxide did not lead to any reaction. An isomer of the desired complex was, however, formed by treatment of the σ-perchlo-

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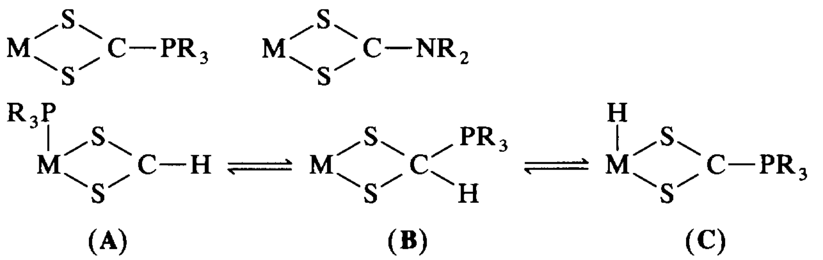
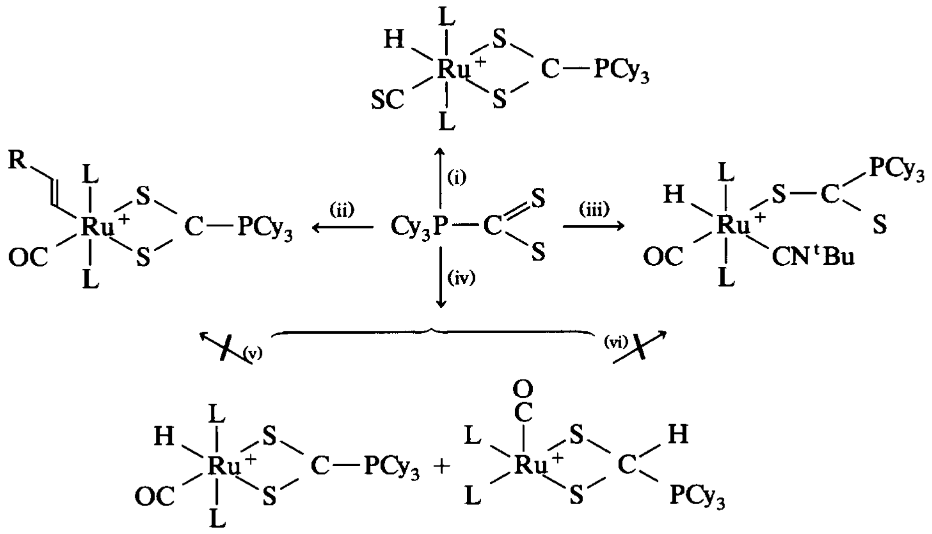


Scheme 1. Dialkyldithiocarbamate, phosphoniodithiocarboxylate, dithioformate and phosphonium betaine ligands.

TABLE 1. Spectroscopic data for the complexes ($L = S_2CPCy_3$; $L'' = PPh_3$; $R = C_6H_4Me$-4)

Compound	IR [a] $\nu(CO)/\nu(CS)$	NMR [b] ^{31}P (δ) [$J(PP)$] (Hz)	^1H (δ)
$[RuH(CO)(\eta^2\text{-}L)L''_2]^+$	1935	50.1 (d)	-9.94 [dt, 0.24H, $J(PH)$ 23.5 (RuP), 5.3 Hz (S_2CP)]
(colour unknown)	(1930)	29.9 (t), [5.0]	
$[Ru(CO)(\eta^2\text{-}HL)L''_2]^+$	1951	50.3 (s)	5.94 [dt [c], 0.76H, RuS_2CH PCy_3]
(red)	(1961)	27.9 (s)	
$[RuH(\eta^1\text{-}L)(CN^tBu)(CO)L''_2]^+$	1976	45.4 (s)	-10.66 [dt, 1H, $J(PH)$ 17.8 (RuP), 8.1 Hz (S_2CP)]
(yellow)	(1992)	30.2 (s)	
$[RuH(\eta^2\text{-}L)(CS)L''_2]^+$	1267	48.9 (d)	-7.76 [dt, 1H, $J(PH)$ 23.5 (RuP), 5.5 (S_2CP)]
(orange)	–	30.9 (t), [6.8]	
$[Ru(CH_\alpha{=}CH_\beta R)(CO)(\eta^2\text{-}L)L''_2]^+$	1940	39.3 (d)	2.25 [s, 3H, $C_6H_4CH_3$], 5.42 [dt [c], 1H, $J(H_\alpha H_\beta)$ 16.8 Hz,
(solid: purple; CH_2Cl_2 soln.: green)	(1947)	31.2 (t), [4.9]	$RuCH{=}CH_\beta$], 6.26, 6.87 [$(AB)_2$, 4H, $J(AB) = 8.0$ Hz, $C_6H_4CH_3$], 7.66 [m [b], 1H, $RuCH_\alpha{=}CH_\beta$].

[a] Nujol mulls, values in parentheses for CH_2Cl_2 solution. [b] From saturated solutions of the complex in $CDCl_3$ at ambient temperature. Chemical shifts are given relative to internal Me_4Si (0.00 ppm). ^1H Resonances due to PPh_3 and PCy_3 omitted. [c] $J(PH)$ Not resolved at 400 MHz. [d] $\nu(CN) = 2156$ (2144) cm^{-1}.



Scheme 2. Synthesis of phosphoniodithiocarboxylate complexes ($L = PPh_3$; $R = C_6H_4Me$-4) (i) $[RuClH(CS)L_3]$; (ii) $[Ru(CH{=}CHR)(CO)(NCMe)_2L_2]^+$ or $[RuCl(CH{=}CHR)(CO)L_2]$; (iii) $[RuH(OClO_3)(CO)(CN^tBu)L_2]$; (iv) $[RuClH(CO)L_3]$ or $[RuH(CO)(NCMe)_2L_2]^+$; (v) $HC{\equiv}CR$; (vi) CN^tBu.

rato complex $[RuH(OClO_3)(CO)(CN^tBu)(PPh_3)_2]$ [5*] with Cy_3PCS_2. Spectroscopic data (Table 1) indicate that it is in fact a monodentate adduct of S_2CPCy_3, viz. $[RuH(CO)(CN^tBu)(PPh_3)_2(S_2CPCy_3)]^+$ [J(PH) 8.0, 16.7 Hz], and not $[Ru(S_2CHPCy_3)(CO)(CN^tBu)(PPh_3)_2]^+$ or the alternative iminoformyl isomer $[Ru(CH{=}N^tBu)(CO)(PPh_3)_2(S_2CPCy_3)]^+$ [6*].

The possible application of $[RuH(CO)(PPh_3)_2(S_2CPCy_3)]^+/[Ru(S_2CHPCy_3)(CO)(PPh_3)_2]^+$ to the hydroruthenation of alkynes was next investigated, and for conditions under which the complexes were stable there was no evidence for the hydroruthenation of 4-ethynyltoluene to give $[Ru(CH{=}CHC_6H_4Me\text{-}4)(S_2CPCy_3)(CO)(PPh_3)_2]^+$. This complex (and a range of analogues) were, however, prepared by addition of S_2CPCy_3 to the preformed σ-vinyl complex $[Ru(CH{=}CHC_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]$ [7*] (Scheme 2).

Note added in proof: Since the submission of this manuscript, we have obtained $[Ru(S_2CHPCy_3)(CO)(PPh_3)_2]BF_4$ by fractional crystallisation and crystallographically verified the formulation [8].

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* Reference number with asterisk indicates a note in the list of references.

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References and notes

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