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Reactions of Dicarbonyltris(triphenylphosphine)ruthenium(0) and the Dicarbonyldihydridobis(triphenylphosphine)ruthenium(II) Derivative with Hydrogen Sulfide, Thiols, and Disulfides

CHUNG-LI LEE, JANET CHISHOLM, BRIAN R. JAMES*

Department of Chemistry, University of British Columbia, Vancouver, British Columbia V6T 1Y6, Canada

DAVID A. NELSON and MICHAEL A. LILGA

Pacific Northwest Laboratory, Richland, Wash. 99352, U.S.A.

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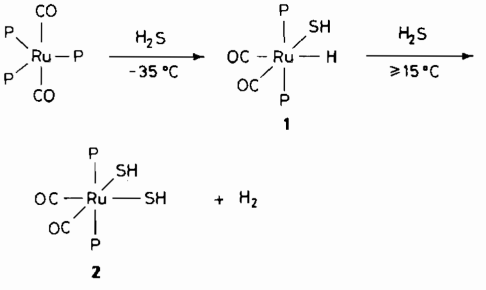
Research into the reactions of transition metal complexes with H_2S has been intensifying, the systems being of interest both industrially and biologically [1, 2]. This, coupled with our recent report [3] describing quantitative conversion of H_2S to H_2 via a net oxidative addition process at a dimeric Pd_2^I centre (eqn. (1), dppm = bis(diphenylphosphino)methane), encouraged us to test for reactivity at a Ru^0 centre.

$$Pd_2Cl_2(\mu\text{-dppm})_2 + H_2S \rightarrow Pd_2Cl_2(\mu\text{-dppm})(\mu\text{-S}) + H_2 \qquad (1)$$

Treatment of the well-known ruthenium(0) complex $Ru(CO)_2(PPh_3)_3$ [4] with H_2S in THF for 2 h at −35 °C gives solely the oxidative addition product $RuH(SH)(CO)_2(PPh_3)_2$ (**1**), which is isolated in 95% yield by addition of hexane. At 65 °C, the H_2S reaction rapidly gives the single product $Ru(SH)_2(CO)_2(PPh_3)_2$ (**2**) again in 95% yield. At intermediate temperatures, mixtures of **1** and **2** are formed (monitored by NMR – see Table I), and under H_2S **1** is converted to **2** with the production of H_2. Complexes **1** and **2** give the correct elemental analysis (C, H, and S) and are fully characterized by spectroscopy (Table I) with the geometries shown in eqn. (2) (here and elsewhere, $P = PPh_3$). Formation of **1** almost certainly occurs via an intermediate '$Ru(CO)_2(PPh_3)_2$' species generated by loss of phosphine from $Ru(CO)_2(PPh_3)_3$. Such a mechanism has been demonstrated for the formation of the dihydride $RuH_2(CO)_2(PPh_3)_2$ [4, 5] from $Ru(CO)_2(PPh_3)_3$ [4, 6] (eqn. (3)).



(2)

$$Ru(CO)_2P_3 \underset{k_{-1},\,+P}{\overset{k_1,\,-P}{\rightleftharpoons}} Ru(CO)_2P_2 \underset{k_{-2},\,-H_2}{\overset{k_2,\,+H_2}{\rightleftharpoons}} RuH(CO_2)_2P_2 \qquad (3)$$

Reaction of H_2S with $RuH_2(CO)_2(PPh_3)_2$ (**3**) (which has geometry analogous to that of **1** and **2** [4], see Table I) in THF at 20 °C shows clean formation of **1** over the first hour, with again subsequent complete conversion to **2**. The rate of formation of **1** from **3** is much faster than loss of H_2 from this species which is governed by k_{-2} [6, 7], and thus the preferred mechanism invokes the acidic character of H_2S ($\rightleftharpoons H^+ + SH^-$); protonation of a metal hydride would liberate H_2 and generate a vacant site for attack by SH^- [8]. A similar process presumably accounts for the formation of **2** from **1**. The previously reported formation of $RuH(SH)(PPh_3)_3$ from the stoichiometric reaction shown in eqn. (4) [9], could occur similarly. Mechanistic details will require more elaborate kinetic and deuterium labelling studies, work that is in progress. Other Ru^{II} hydrides reported to react with H_2S yield dimers with bridging mercapto ligands [1, 8].

$$RuH_2(PPh_3)_4 + H_2S \rightarrow RuH(SH)(PPh_3)_3 + PPh_3 + H_2 \qquad (4)$$

A range of thiols RSH (R = Et, Ph, CH_2Ph, and *o*-, *m*- and *p*-tolyl) readily oxidatively adds to $Ru(CO)_2(PPh_3)_3$ in THF solution at 20 °C, and the $RuH(SR)(CO)_2(PPh_3)_2$ adducts (**4**) are isolated in high yield by precipitation with hexane. The geometry of the hydrido(thiolato) species corresponds to that of **1** with *trans*-phosphines and *cis*-carbonyls; spectroscopic data for the ethanethiol and *p*-tolyl products $RuH(SR)(CO)_2(PPh_3)_2$, R = Et (**4a**), *p*-tolyl (**4b**), are given in Table I. There is no ready tendency to form the bis(thiolato) species (*cf.* **1** → **2**), presumably because of the weaker acidity of EtSH compared to that of H_2S. Treatment of the dihydride **3** with RSH also gives only **4** (eqn. (5)). Chaudret and Poilblanc [10] have synthesized five-coordinate $RuH(SR)(PPh_3)_3$ complexes (R = Ph, CH_2Ph) but only from the hydrido precursors $RuH_2(PPh_3)_4$ and $RuH_4(PPh_3)_3$, presumably via the protonation/H_2 loss mechanism. We are unaware of reports on oxidative addition of thiols (or H_2S) to Ru^0 species, although such chemistry for Ir^I and Rh^I is well documented [2, 11].

$$RuH_2(CO)_2P_2 + RSH \rightarrow RuH(SR)(CO)_2P_2 + H_2 \qquad (5)$$

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*Author to whom correspondence should be addressed.

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TABLE I. Spectroscopic Data for the Mercapto- and Thiolato-Ruthenium (II) Complexes

Compound[a]	^{1}H NMR[b]	^{31}P NMR[c]	ν(Ru–H)[d]	ν(CO)[d]
RuH(SH), **1**	−3.59 (SH, dt, *J*(HH) 2.9, *J*(PH) 5.04) −5.29 (RuH, dt, *J*(HH) 2.9, *J*(PH) 19.9)	42.1	1901	2029 1984
Ru(SH)$_2$, **2**	−2.62 (SH, t, *J*(PH) 6.7)	21.6	–	2046 1981
RuH$_2$, **3**	−6.30 (RuH$_2$, t, *J*(PH) 23.1)[e]	56.1	1880[e] 1825	2012[e] 1975
RuH(SEt), **4a**	0.77 (CH$_2$, q, *J*(HH) 7.2)[f] 0.36 (CH$_3$, t, *J*(HH) 7.2)[f] −5.16 (RuH, t, *J*(PH) 20.1)	38.7	1925	2025 1964
RuH(*p*-SC$_6$H$_4$Me), **4b**	2.0 (CH$_3$, s)[f] −4.35 (RuH, t, *J*(PH) 20.2)	38.6	1900	2021 1987

[a] Ru implies Ru(CO)$_2$(PPh$_3$)$_2$. [b] At 25 °C, in CD$_2$Cl$_2$ except for **4b** (in C$_6$D$_6$); δ in ppm w.r.t. TMS; *J* values in Hz; s = singlet, dt = doublet of triplets, t = triplet, q = quartet. [c] In CD$_2$Cl$_2$ at 25 °C; all singlets downfield w.r.t. external 85% H$_3$PO$_4$. [d] IR (cm^{-1}) measured in Nujol. [e] The data agree well with those in the literature [5]. [f] ^{13}C{^{1}H}NMR, δ (25 °C, CD$_2$Cl$_2$ for **4a**, C$_6$D$_6$ for **4b**, w.r.t. TMS): singlets at 28.0(CH$_2$) and 19.9(CH$_3$) for **4a**, and 20.9(CH$_3$) for **4b**.

The dihydride reacts with disulfides at ambient conditions in THF, again to give **4**; preliminary data suggest the stoichiometry shown in eqn. (6), although small amounts of free RSH are also seen. The reaction could well proceed via reaction (7), followed by the more rapid reaction shown in eqn. (5). Cleavage of the disulfide is faster with R = *p*-tolyl ($t_{1/2} \sim 1$ h) than with R = CH$_2$Ph, Et, or Me ($t_{1/2}$ = several hours).

$$2\mathrm{RuH_2(CO)_2P_2} + \mathrm{RSSR} \rightarrow 2\mathrm{RuH(SR)(CO)_2P_2} + \mathrm{H_2} \qquad (6)$$

$$\underset{\mathbf{3}}{\mathrm{RuH_2(CO)_2P_2}} + \mathrm{RSSR} \rightarrow \underset{\mathbf{4}}{\mathrm{RuH(SR)(CO)_2P_2}} + \mathrm{RSH} \qquad (7)$$

We have no data on the mechanism of reaction (6) which appears a useful model for catalytic hydrogenolysis of disulfides, a process of industrial importance [12, 13.] A plausible mechanism for reaction (7) involves initial H atom abstraction from **3** by the disulfide; hydrogen atom transfer from transition metal hydrido complexes (especially hydridocarbonyls) is becoming increasingly well-documented [14] but has not been demonstrated for Ru systems. Reaction of RuH$_2$(PPh$_3$)$_4$ with MeSSMe has been reported to give similarly RuH(SMe)(PPh$_3$)$_3$ [10]. Non-hydridic Ru complexes such as [Ru(CO)$_2$(η-C$_5$H$_5$)]$_2$ react with disulfides to give thiolate-containing products but only under UV irradiation [15]. Of note, we find that the complex Ru(CO)$_2$(PPh$_3$)$_3$ is unreactive toward the disulfides; for example, the species formed from a room temperature reaction with the *p*-tolyl disulfide appears to be the oxidative addition product Ru(SR)$_2$(CO)$_2$(PPh$_3$)$_2$, R = *p*-tolyl, of geometry analogous to that of **1**, as judged by NMR data: a singlet in both the ^{1}H spectrum (δ 2.02 ppm, 6H, CH$_3$) and ^{31}P spectrum (δ 11.2 ppm), cf. Table I.

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