

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

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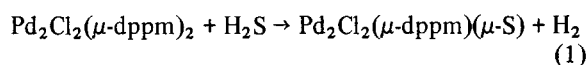
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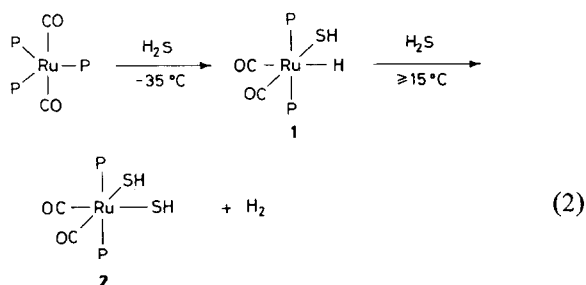
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Research into the reactions of transition metal complexes with H₂S has been intensifying, the systems being of interest both industrially and biologically [1, 2]. This, coupled with our recent report [3] describing quantitative conversion of H₂S to H₂ via a net oxidative addition process at a dimeric Pd₂^I centre (eqn. (1), dpmm = bis(diphenylphosphino)methane), encouraged us to test for reactivity at a Ru⁰ centre.

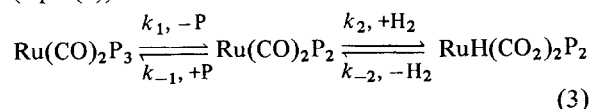


Treatment of the well-known ruthenium(0) complex Ru(CO)₂(PPh₃)₃ [4] with H₂S in THF for 2 h at -35 °C gives solely the oxidative addition product RuH(SH)(CO)₂(PPh₃)₂ (1), which is isolated in 95% yield by addition of hexane. At 65 °C, the H₂S reaction rapidly gives the single product Ru(SH)₂(CO)₂(PPh₃)₂ (2) again in 95% yield. At intermediate temperatures, mixtures of 1 and 2 are formed (monitored by NMR – see Table I), and under H₂S 1 is converted to 2 with the production of H₂. 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 = PPh₃). Formation of 1

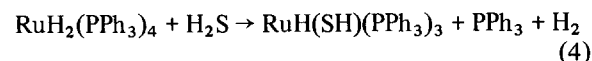


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almost certainly occurs via an intermediate 'Ru(CO)₂(PPh₃)₂' species generated by loss of phosphine from Ru(CO)₂(PPh₃)₃. Such a mechanism has been demonstrated for the formation of the dihydride RuH₂(CO)₂(PPh₃)₂ [4, 5] from Ru(CO)₂(PPh₃)₃ [4, 6] (eqn. (3)).



Reaction of H₂S with RuH₂(CO)₂(PPh₃)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 H₂ from this species which is governed by k₋₂ [6, 7], and thus the preferred mechanism invokes the acidic character of H₂S (⇌ H⁺ + SH⁻); protonation of a metal hydride would liberate H₂ 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)(PPh₃)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 H₂S yield dimers with bridging mercapto ligands [1, 8].



A range of thiols RSH (R = Et, Ph, CH₂Ph, and *o*-, *m*- and *p*-tolyl) readily oxidatively adds to Ru(CO)₂(PPh₃)₃ in THF solution at 20 °C, and the RuH(SR)(CO)₂(PPh₃)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(PPh₃)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 H₂S. Treatment of the dihydride 3 with RSH also gives only 4 (eqn. (5)). Chaudret and Poilblanc [10] have synthesized five-coordinate RuH(SR)(PPh₃)₃ complexes (R = Ph, CH₂Ph) but only from the hydrido precursors RuH₂(PPh₃)₄ and RuH₄(PPh₃)₃, presumably via the protonation/H₂ loss mechanism. We are unaware of reports on oxidative addition of thiols (or H₂S) to Ru⁰ species, although such chemistry for Ir^I and Rh^I is well documented [2, 11].

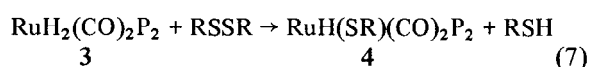
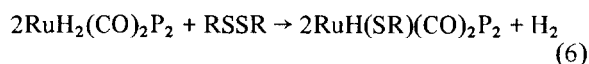


TABLE I. Spectroscopic Data for the Mercapto- and Thiolato-Ruthenium (II) Complexes

Compound ^a	¹ H NMR ^b	³¹ P NMR ^c	$\nu(\text{Ru-H})^d$	$\nu(\text{CO})^d$
RuH(SH), 1	−3.59 (SH, dt, $J(\text{HH})$ 2.9, $J(\text{PH})$ 5.04) −5.29 (RuH, dt, $J(\text{HH})$ 2.9, $J(\text{PH})$ 19.9)	42.1	1901	2029 1984
Ru(SH) ₂ , 2	−2.62 (SH, t, $J(\text{PH})$ 6.7)	21.6	—	2046 1981
RuH ₂ , 3	−6.30 (RuH ₂ , t, $J(\text{PH})$ 23.1) ^e	56.1	1880 ^e 1825	2012 ^e 1975
RuH(SET), 4a	0.77 (CH ₂ , q, $J(\text{HH})$ 7.2) ^f 0.36 (CH ₃ , t, $J(\text{HH})$ 7.2) ^f −5.16 (RuH, t, $J(\text{PH})$ 20.1)	38.7	1925	2025 1964
RuH(<i>p</i> -SC ₆ H ₄ Me), 4b	2.0 (CH ₃ , s) ^f −4.35 (RuH, t, $J(\text{PH})$ 20.2)	38.6	1900	2021 1987

^aRu implies Ru(CO)₂(PPh₃)₂. ^bAt 25 °C, in CD₂Cl₂ except for 4b (in C₆D₆); δ in ppm w.r.t. TMS; J values in Hz; s = singlet, dt = doublet of triplets, t = triplet, q = quartet. ^cIn CD₂Cl₂ at 25 °C; all singlets downfield w.r.t. external 85% H₃PO₄. ^dIR (cm^{−1}) measured in Nujol. ^eThe data agree well with those in the literature [5]. ^f¹³C{¹H}NMR, δ (25 °C, CD₂Cl₂ for 4a, C₆D₆ for 4b, w.r.t. TMS): singlets at 28.0(CH₂) and 19.9(CH₃) for 4a, and 20.9(CH₃) 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 ($t_{1/2}$ ~ 1 h) than with R = CH₂Ph, Et, or Me ($t_{1/2}$ = several hours).



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 RuH₂(PPh₃)₄ with MeSSMe has been reported to give similarly RuH(SMe)(PPh₃)₃ [10]. Non-hydridic Ru complexes such as [Ru(CO)₂(η -C₅H₅)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(PPh₃)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(PPh₃)₂, R = *p*-tolyl, of geometry analogous to that of 1, as judged by NMR data: a singlet in both the ¹H spec-

trum (δ 2.02 ppm, 6H, CH₃) and ³¹P spectrum (δ 11.2 ppm), cf. Table I.

Acknowledgements

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References

- 1 K. Osakada, T. Yamamoto, A. Yamamoto, A. Takenaka and Y. Sasada, *Inorg. Chim. Acta*, **105**, L9 (1985) and refs. therein.
- 2 A. M. Muetting, P. Boyle and L. H. Pignolet, *Inorg. Chem.*, **23**, 44 (1984).
- 3 C-L. Lee, G. Besenyey, B. R. James, D. A. Nelson and M. A. Lilga, *J. Chem. Soc., Chem. Commun.*, 1175 (1985).
- 4 B. E. Cavit, K. R. Grundy and W. R. Roper, *J. Chem. Soc., Chem. Commun.*, 60 (1972).
- 5 S. Cenini, F. Porta and M. Pizzotti, *Inorg. Chim. Acta*, **20**, 119 (1976).
- 6 D. A. Nelson, R. T. Hallen, C-L. Lee and B. R. James, in N. N. Li and J. M. Calo (eds.), 'Recent Developments in Separation Science', Vol. IX, CRC Press, Boca Raton, 1986, p. 1.
- 7 C-L. Lee, B. R. James, D. A. Nelson and M. A. Lilga, to be published.
- 8 T. V. Ashworth, M. J. Nolte and E. Singleton, *J. Chem. Soc., Chem. Commun.*, 936 (1977).
- 9 K. Osakada, T. Yamamoto and A. Yamamoto, *Inorg. Chim. Acta*, **90**, L5 (1984).

- 10 B. Chaudret and R. Poilblanc, *Inorg. Chim. Acta*, **34**, L209 (1979).
- 11 J. L. Herdé and C. V. Senoff, *Can. J. Chem.*, **51**, 1016 (1973).
- 12 B. C. Gates, J. R. Katzer and G. C. A. Schuit, 'Chemistry of Catalytic Processes', McGraw-Hill, New York, 1979, Chap. 5.
- 13 R. Bader, H. U. Blaser and H. Thies, *Eur. Pat. Appl. EP 134 200*, Ciba-Geigy A.-G.; *Chem. Abst.*, **102**, 220429 (1985).
- 14 T. M. Bockman, J. F. Garst, R. B. King, L. Marko and F. Ungvary, *J. Organomet. Chem.*, **279**, 165 (1985) and refs. therein.
- 15 S. D. Killops and S. A. R. Knox, *J. Chem. Soc., Dalton Trans.*, 1260 (1978).