A New and Versatile Chelating Dithio Ligand: *X*-Ray Crystal Structure of $[Ru(CO)(SC_6H_3Me\text{-}o\text{-}SC_6H_4Me)(\eta\text{-}C_5H_5)]$

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Summary Under u.v. radiation diaryl disulphides $(C_6H_4\text{-}p\text{-}R)_2S_2$ (R = H or Me) yield $(C_6H_3R\text{-}o\text{-}SC_6H_4R)_2S_2$, which reacts with a variety of transition metal complexes to provide metallacycles $\overline{MSC_6H_3R\text{-}o\text{-}S}C_6H_4R$; one of these $[Ru(CO)(SC_6H_3Me\text{-}o\text{-}SC_6H_4Me)(\eta\text{-}C_5H_5)]$, has been structurally identified by *X*-ray diffraction.

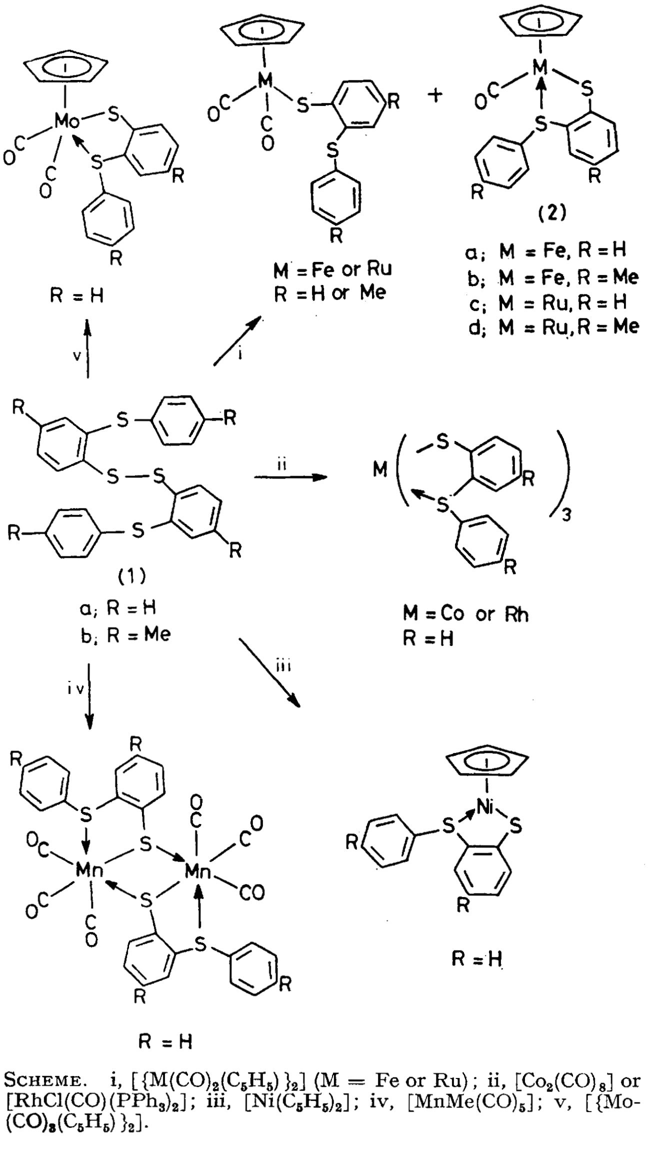
THE rearrangements of hydrazobenzene and its derivatives have received much attention.[1] In the presence of acid the classic 'benzidine rearrangement' predominates but under thermal or photochemical inducement semidines are produced. We now report that diaryl disulphides undergo a related rearrangement upon u.v. irradiation to yield *ortho*-*S*-aryl-substituted diaryl disulphides which are highly reactive and an excellent source of a new chelating dithio ligand. Previously, photolysis of diaryldisulphides has been reported to afford only the corresponding thiols.[2]

U.v. irradiation (250 W mercury vapour lamp) of a toluene solution of diphenyl- or di-*p*-tolyl-disulphide contained in a silica glass flask produces the colourless crystalline *ortho*-substituted disulphides (**1a**; m.p. 121 °C) and (**1b**; m.p. 111 °C), respectively.† Optimum yields (**1a**, 20%; **1b**, 6%) are achieved after 4—7 days; prolonged irradiation reduces the yield in favour of oily intractable products. The ^{1}H and ^{13}C n.m.r. spectra of (**1b**) show the expected presence of two types of methyl group [^{1}H: τ 7·84 (6H) and 7·89 (6H); ^{13}C: δ 21·1 and 20·8 p.p.m. (downfield of Me_4Si)], while the mass spectrum of each disulphide has a prominent molecular ion M^+ and also $(M/2)^+$. Experiments bearing on the mechanism of formation of (**1**) are in hand.

The disulphides (**1**) are very reactive towards a variety of transition metal complexes under both thermal and photochemical conditions (Scheme), a reactivity we attribute to the relief of steric crowding within (**1**) brought about by S–S bond fission. This reactivity is exemplified by the reactions of (**1a**) with $[\{M(CO)_2(C_5H_5)\}_2]$ (M = Fe or Ru), $[\{Mo(CO)_3(C_5H_5)\}_2]$, and $[RhCl(CO)(PPh_3)_2]$, each of which reaches completion within 10 min, accompanied by visible CO evolution, and yields the products quantitatively. The versatility of the new chelating dithio ligand derived from (**1**) is evident in the Scheme. The nature of the chelate and, by implication, of (**1**) were established by an *X*-ray diffraction study of $[Ru(CO)(SC_6H_3Me\text{-}o\text{-}SC_6H_4Me)(\eta\text{-}C_5H_5)]$ (**2d**) [orange crystals, m.p. 150—151 °C; ν(CO) 1967 cm^{-1} (cyclohexane)].

Crystal data: $C_{20}H_{18}ORuS_2$, *M* 439·6, monoclinic, space group $P2_1/c$, $a = 6{\cdot}5858(17)$, $b = 15{\cdot}568(8)$, $c = 18{\cdot}322(8)$ Å, $\beta = 92{\cdot}43(3)°$, $U = 1876{\cdot}8(14)$ Å^3, $Z = 4$, $D_c = 1{\cdot}555$, $\mu(\text{Mo-}K_\alpha) = 10{\cdot}3$ cm^{-1}.

The structure was solved by Patterson and Fourier techniques and refined by least-squares to *R* 0·063 for 1945 independent reflections to $\theta = 25°$ (Mo-K_α radiation, Syntex $P2_1$ diffractometer).‡ The molecular geometry is shown in the Figure. Bond lengths Ru–C(cyclopentadienyl)



SCHEME. i, $[\{M(CO)_2(C_5H_5)\}_2]$ (M = Fe or Ru); ii, $[Co_2(CO)_8]$ or $[RhCl(CO)(PPh_3)_2]$; iii, $[Ni(C_5H_5)_2]$; iv, $[MnMe(CO)_5]$; v, $[\{Mo(CO)_3(C_5H_5)\}_2]$.

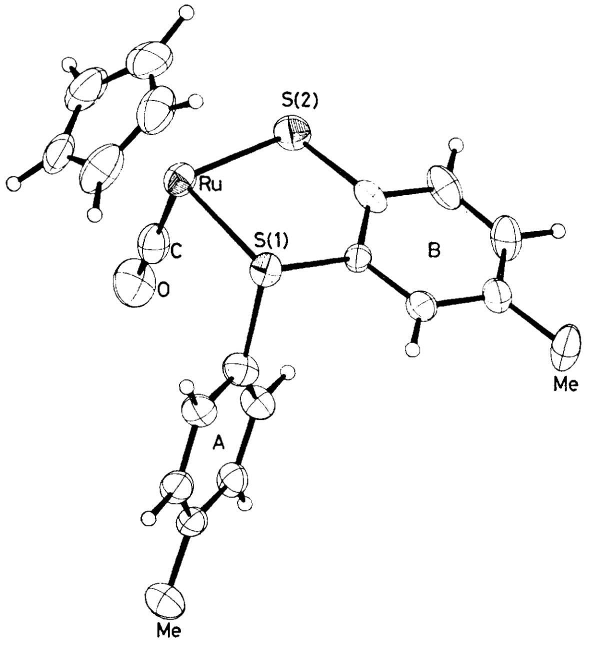


FIGURE. Molecular structure of $[Ru(CO)(SC_6H_3Me\text{-}o\text{-}SC_6H_4Me)(\eta\text{-}C_5H_5)]$ (**2d**).

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† Satisfactory analytical data were obtained for all new compounds.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

range from 2·20(3) to 2·29(3) Å and Ru–C(O) is 1·84(2) Å. The metal atom lies in the plane of S(1)S(2) and the ring B, bonding unevenly to the dithioaryl fragment with Ru–S(1) 2·323(4) and Ru–S(2) 2·379(4) Å.

For the complexes (**2**) two orientations of the phenyl ring A with respect to the metal are possible, that observed in crystalline (**2d**) being the one which minimises steric interaction with the cyclopentadienyl ligand. N.m.r. spectra reveal, however, that for each complex (**2**) the alternative orientation is accessible in solution and that there is a rapid interconversion of the two forms.

Thus, for example, (**2a**) shows at −60 °C ($CDCl_3$ solution) a limiting low temperature ^1H n.m.r. spectrum with two η-C_5H_5 signals (τ 5·24 and 5·64) in the intensity ratio 7·5 : 1, which coalesce on warming to *ca.* −5 °C and at +25 °C appear as a sharp singlet (τ 5·38). The changes are reversed on cooling. We attribute this temperature dependent behaviour to an inversion at S(1). Somewhat surprisingly, the free energies of activation of the inversion are insensitive to the nature of M or R within the complexes (**2**), falling in the narrow range $56·5 \pm 1·0$ kJ mol^{-1}.

It has been reported[3] recently that the reaction of $[\{Fe(CO)_2(C_5H_5)\}_2]$ with Ph_2S_2 in benzene under u.v. irradiation gives a complex identified tentatively as a third isomer ('C') of $[\{Fe(CO)(\mu_2\text{-}SPh)(C_5H_5)\}_2]$. The physical and spectroscopic properties of this complex are identical to those of (**2a**), which might be expected to be formed under these conditions.

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[2] W. E. Lyons, *Nature*, 1948, **162**, 1004.
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