Reduction–Oxidation Properties of Organotransition-metal Complexes. Part 6.[1] The Isomerization, and One-electron Oxidation, of *syn*- and *anti*-Di-μ-arylthio-bis[(η-cyclopentadienyl)rhodium]

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The reaction of $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ with R^1SSR^1 affords $[\{Rh(\mu\text{-}SR^1)(\eta\text{-}C_5H_5)\}_2]$ (R^1 = Ph or C_6H_4Me-*p*) as a mixture of *syn* and *anti* isomers. Each isomer is not fluxional but *syn–anti* isomerization, *via* a bridge-opening mechanism, occurs at room temperature. The isomerization process has been studied by ^1H n.m.r. spectroscopy and by cyclic voltammetry which also reveals that both isomers undergo irreversible one-electron oxidation at the platinum electrode in CH_2Cl_2. The complex *syn*-$[\{Rh(\mu\text{-}SC_6H_4Me\text{-}p)(\eta\text{-}C_5H_5)\}_2]$ reacts with di-*p*-tolyl disulphide, in the presence of $[NO][PF_6]$, to give $[Rh_2(\mu\text{-}SC_6H_4Me\text{-}p)_3(\eta\text{-}C_5H_5)_2][PF_6]$, and with $[N(C_6H_4Br\text{-}p)_3][SbCl_6]$ to give $[Rh_2(\mu\text{-}Cl)(\mu\text{-}SC_6H_4Me\text{-}p)_2(\eta\text{-}C_5H_5)_2][SbCl_6]$, *via* one-electron oxidation followed by insertion into the metal–metal bond of the radical cation $[\{Rh(\mu\text{-}SC_6H_4Me\text{-}p)(\eta\text{-}C_5H_5)\}_2]^+$.

IT has been reported previously that $[\{Co(\mu\text{-}SR)(\eta\text{-}C_5H_5)\}_2]$ (R = Me,[2,3] C_6H_4Me-*p*,[3] or C_6H_4Cl-*p* [3]) undergoes one-electron oxidation at a dropping mercury electrode [2] (in 1,2-dimethoxyethane) or at a platinum electrode [3] (in CH_2Cl_2). For R = Me or C_6H_4Cl-*p* the oxidation process was shown to be reversible, whereas that for R = C_6H_4Me-*p* was quasi-reversible. Although the monocation $[\{Co(\mu\text{-}SR)(\eta\text{-}C_5H_5)\}_2]^+$ has not been isolated, electrochemical oxidation of $[\{Co(\mu\text{-}SMe)(\eta\text{-}C_5H_5)\}_2]$ led to the observation of an e.s.r. spectrum attributable [2] to $[\{Co(\mu\text{-}SMe)(\eta\text{-}C_5H_5)\}_2]^+$. Frisch *et al.*[3] were, however, unable to detect such a spectrum on either chemical or electrochemical oxidation of $[\{Co(\mu\text{-}SR)(\eta\text{-}C_5H_5)\}_2]$ (R = Me, C_6H_4Me-*p*, or C_6H_4Cl-*p*).

The bonding in $[\{Fe(\mu\text{-}SR)(\eta\text{-}C_5H_5)(CO)\}_2]$, which contains no metal–metal bond, has been studied [4] by comparing the molecular structures of $[\{Fe(\mu\text{-}SPh)(\eta\text{-}C_5H_5)(CO)\}_2]$ [5] and $[\{Fe(\mu\text{-}SMe)(\eta\text{-}C_5H_5)(CO)\}_2][BF_4]$.[4] Oxidation is accompanied by a decrease in the metal–metal distance, implying removal of an electron from an orbital predominantly metal–metal antibonding in character. In order to investigate the effects of removing an electron from a molecule with a metal–metal bond, comparative structural studies on $[\{Co(\mu\text{-}SR)(\eta\text{-}C_5H_5)\}_2]^Z$ (Z = 0 or 1) seem worthwhile. Fruitless attempts [6] to synthesize the cobalt cation, however, have led us to prepare the analogous rhodium complexes and study their reduction-oxidation properties. Although we have found such species to undergo one-electron oxidation the process is irreversible implying that the isolation of, and therefore structural studies on, the monocation will be difficult, if not impossible. The isolation of isomers of $[\{Rh(\mu\text{-}SR^1)(\eta\text{-}C_5H_4R^2)\}_2]$ has, however, allowed us to make some comment on the bonding in such molecules, and also to investigate the isomerization of the *syn* to the *anti* form by cyclic-voltammetric and spectroscopic methods. In addition we have established that insertion into the metal–metal bond of $[\{Rh(\mu\text{-}SR^1)(\eta\text{-}C_5H_5)\}_2]$ may be effected *via* initial one-electron oxidation.

RESULTS AND DISCUSSION

Disulphides, R^1SSR^1 (R^1 = Ph, C_6H_4Me-*p*, Me, Bu^t, or CH_2Ph) react with $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ in refluxing toluene or cyclohexane to give deep purple or brown-purple solutions containing mixtures of polynuclear products. Column chromatography on alumina allows removal of unchanged $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ and small quantities of $[Rh_3(\mu_3\text{-}CO)(\mu_3\text{-}S)(\eta\text{-}C_5H_5)_3]$ from mixtures of the *syn* and *anti* isomers of $[\{Rh(\mu\text{-}SR^1)(\eta\text{-}C_5H_5)\}_2]$. In most cases ($R^1$ = Me, Bu^t, or CH_2Ph) yields of the dimeric products are very low and full characterization has not been possible. In the context of the results described below it is interesting that if chromatography of the product of the reaction between $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ and MeSSMe is carried out in air the blue-purple band due to $[\{Rh(\mu\text{-}SMe)(\eta\text{-}C_5H_5)\}_2]$ rapidly becomes orange on the column. For the arenethiolato-complexes, and also for $[\{Rh(\mu\text{-}SR^1)(\eta\text{-}C_5H_4R^2)\}_2]$ (R^1 = Ph or C_6H_4Me-*p*; R^2 = Me) (prepared by treating $[\{Rh(\mu\text{-}SR^1)(CO)_2\}_2]$ with methylcyclopentadiene),[7] their dimeric nature is confirmed by mass spectrometry (Table 1). That the products are isomeric mixtures is shown by ^1H n.m.r. studies, and by cyclic-voltammetric measurements described below. In one case only (R^1 = C_6H_4Me-*p*, R^2 = H) have the isomers been separated. Washing

TABLE 1

Analytical data for $[\{Rh(\mu\text{-}SR^1)(\eta\text{-}C_5H_4R^2)\}_2]$ [a]

R^1	R^2	Yield (%)	*M* [b]	Analysis (%) [c] C	H
Ph	H	48	554	47.9 (47.7)	3.8 (3.6)
C_6H_4Me-*p*	H	56	582	49.1 (49.5)	4.2 (4.2)
Ph	Me	30 [d]	582	49.4 (49.5)	4.3 (4.2)
C_6H_4Me-*p*	Me	6 [d]	610	50.9 (51.2)	5.1 (4.6)
Bu^t	H	*e*	514	41.7 (42.0)	5.6 (5.5)
CH_2Ph	H	*e*	582	49.3 (49.5)	4.5 (4.2)

[a] Mixture of *syn* and *anti* isomers. [b] By mass spectrometry. [c] Calculated values are given in parentheses. [d] From $[\{Rh(\mu\text{-}SR^1)(CO)_2\}_2]$ and methylcyclopentadiene in refluxing toluene.[7] [e] Isolated only in quantities suitable for characterization by mass spectrometry and elemental analysis.

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[1] Part 5, N. G. Connelly and M. D. Kitchen, *J.C.S. Dalton*, 1977, 931.

[2] R. E. Dessy, R. Kornmann, C. Smith, and R. Haytor, *J. Amer. Chem. Soc.*, 1968, **90**, 2001.

[3] P. D. Frisch, M. K. Lloyd, J. A. McCleverty, and D. Seddon, *J.C.S. Dalton*, 1973, 2268.

[4] N. G. Connelly and L. F. Dahl, *J. Amer. Chem. Soc.*, 1970, **92**, 7472.

[5] G. Ferguson, C. Hannaway, and K. M. S. Islam, *Chem. Comm.*, 1968, 1165.

[6] L. F. Dahl, personal communication.

[7] R. Hill and S. A. R. Knox, personal communication.

the mixture of *syn*- and *anti*-[{Rh(μ-SC$_6$H$_4$Me-*p*)(η-C$_5$H$_5$)}$_2$], obtained by rapid column chromatography of the reaction products and evaporation to dryness, with a large volume of hexane gives a purple solution and a residue of near-black needles of the *syn* isomer; cooling the purple solution affords a precipitate which consists almost entirely of plate-like crystals of the *anti* isomer.

TABLE 2

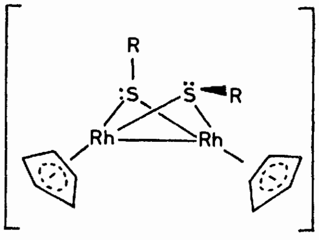
Hydrogen-1 n.m.r. and electrochemical data [a] for [{Rh(μ-SR^1)(η-C$_5$H$_4$R^2)}$_2$]

R^1	R^2	Isomer	$(E_p)_{ox}$ [b]/V	$(i_p)_{ox}$ [c]/μA	τ (in CDCl$_3$) [d]
Ph	H	*anti*	0.27	3.8	4.68 (5 H, s, C$_5$H$_5$), 2.68 (5 H, m, C$_6$H$_5$)
Ph	H	*syn*	0.11		4.85 (5 H, s, C$_5$H$_5$), 2.68 (5 H, m, C$_6$H$_5$)
C$_6$H$_4$Me-*p*	H	*anti*	0.24	3.7	7.75 (6 H, s, Me), 4.70 (10 H, s, C$_5$H$_5$), 3.14 (2 H, d, $\lvert J_o + J_p\rvert$ 8, *m*-C$_6$H$_4$), 3.12 (2 H, d, $\lvert J_o + J_p\rvert$ 8, *m*-C$_6$H$_4$), 2.69 (2 H, d, $\lvert J_o + J_p\rvert$ 8, *o*-C$_6$H$_4$), 2.66 (2 H, d, $\lvert J_o + J_p\rvert$ 8, *o*-C$_6$H$_4$),
C$_6$H$_4$Me-*p*	H	*syn*	0.11		7.70 (6 H, s, Me), 4.87 (10 H, s, C$_5$H$_5$), 3.05 (4 H, d, $\lvert J_o + J_p\rvert$ 8, *m*-C$_6$H$_4$), 2.48 (4 H, d, $\lvert J_o + J_p\rvert$ 8, *o*-C$_6$H$_4$)
Ph	Me	*anti*	0.18	3.1	8.08 (3 H, s, C$_5$H$_4$*Me*), 4.80 (4 H, m, C$_5$H$_4$*Me*), 2.60 (5 H, m, Ph)
Ph	Me	*syn*	0.05		8.49 (3 H, s, C$_5$H$_4$*Me*), 4.80 (4 H, m, C$_5$H$_4$*Me*), 2.60 (5 H, m, Ph)
C$_6$H$_4$Me-*p*	Me	*anti*	0.17	3.1	8.08 (3 H, s, C$_5$H$_4$*Me*), 7.76 (3 H, s, C$_6$H$_4$*Me*), 4.86 (4 H, m, C$_5$H$_4$*Me*), 2.88 (4 H, m, C$_6$H$_4$*Me*)
C$_6$H$_4$Me-*p*	Me	*syn*	0.05		8.46 (3 H, s, C$_5$H$_4$*Me*), 7.72 (3 H, s, C$_6$H$_4$*Me*), 4.86 (4 H, m, C$_5$H$_4$*Me*), 3.05 (2 H, d, $\lvert J_o + J_p\rvert$ 8, *m*-C$_6$H$_4$), 2.49 (2 H, d, $\lvert J_o + J_p\rvert$ 8, *o*-C$_6$H$_4$)

[a] In CH$_2$Cl$_2$. [b] *versus* a calomel electrode (1 mol dm^{-3} in LiCl), recorded at a scan rate of 100 mV s^{-1}. [c] Total peak current. For the reversible one-electron transfer process [Ni{S$_2$C$_2$(CN)$_2$}$_2$]$^{2-}$ $\rightleftharpoons$ [Ni{S$_2$C$_2$(CN)$_2$}$_2$]$^-$ + e, $(i_p)_{ox}$ = 3.6 μA. [d] *J* values in Hz.

The ^{1}H n.m.r. spectra of *syn*- and *anti*-[{Rh(μ-SR^1)(η-C$_5$H$_4$R^2)}$_2$] (R^1 = C$_6$H$_4$Me-*p*, R^2 = H) are recorded in Table 2, together with data for other, unseparated, isomeric mixtures (R^1 = Ph, R^2 = H or Me; R^1 = C$_6$H$_4$Me-*p*, R^2 = Me). In each case, assignment of the spectrum of each isomer is possible due to the predominance of the *anti* form in the mixture. The ^{1}H n.m.r. spectrum, in C$_6$H$_5$Cl, of *anti*-[{Rh(μ-SC$_6$H$_4$Me-*p*)(η-C$_5$H$_5$)}$_2$], the solid-state structure of which has been determined,[8] shows the presence of two inequivalent *p*-phenylene groups (*i.e.* the *p*-tolyl groups are inequivalent) at all temperatures between —40 and 120 °C. (The resonances due to the inequivalent methyl groups are not resolved at 100 MHz.) The *anti* isomer (1) is therefore not fluxional in this temperature range. The ^{1}H n.m.r. spectrum of *syn*-[{Rh(μ-SC$_6$H$_4$Me-*p*)(η-C$_5$H$_5$)}$_2$] shows the presence of equivalent *p*-tolyl groups and is due to either one of the two symmetrical *syn* forms, (2) or (3), or to a rapidly equilibrating mixture of both. As the *anti* isomer is static it is unlikely that the *syn* isomer is otherwise and we assign its structure as (2). No examples of related dibridged bimetallic complexes are known with structure (3), presumably for steric reasons.

In solution, *syn*-[{Rh(μ-SR^1)(η-C$_5$H$_4$R^2)}$_2$] isomerizes to the *anti* form. While no detailed studies on the solvent dependence of the isomerization rate have been carried out, it is clear, qualitatively, that the isomerization process is far faster in CH$_2$Cl$_2$ than in less-polar solvents such as toluene or chlorobenzene. The mechanism of the *syn–anti* isomerization is of interest in connection with recent detailed studies of the fluxional properties of [{M(μ-X)(CO)$_3$}$_2$] (M = Fe, X = PMe$_2$, AsMePh, SMe, *etc.*; M = Co, X = GeMe$_2$ or SnMe$_2$)[9] and [{Rh(μ-SR)(diene)}$_2$] (R = alkyl or aryl, diene = cyclo-octatetraene or cyclo-octa-1,5-diene).[10] In the case of the cyclopentadienyl complexes described herein the *syn–anti* isomerization, which occurs at room temperature, is most likely to involve Rh–S bond cleavage, rotation about the resulting Rh–S terminal bond, and reformation of the Rh(μ-S)$_2$Rh ring. Since the terminal thiolato-sulphur atom has two lone pairs available for bonding, no inversion at sulphur is required during isomerization. For the μ-PMe$_2$ and μ-AsMePh complexes of iron *syn–anti* isomerization by a bridge-opening mechanism would require inversion at phosphorus (or arsenic) and therefore higher temperatures, as observed for [{Fe(μ-AsMePh)(CO)$_3$}$_2$].[9] The presence [8] of a metal–metal bond in [{Rh(μ-SR^1)(η-C$_5$H$_4$R^2)}$_2$] precludes inversion of the Rh(μ-S)$_2$Rh ring; such an inversion occurs for the fluxional molecules [{Rh(μ-SR)(diene)}$_2$] [10] which contain no Rh–Rh bond.



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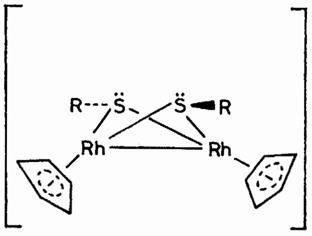

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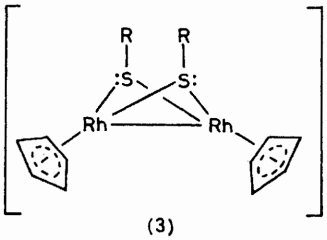

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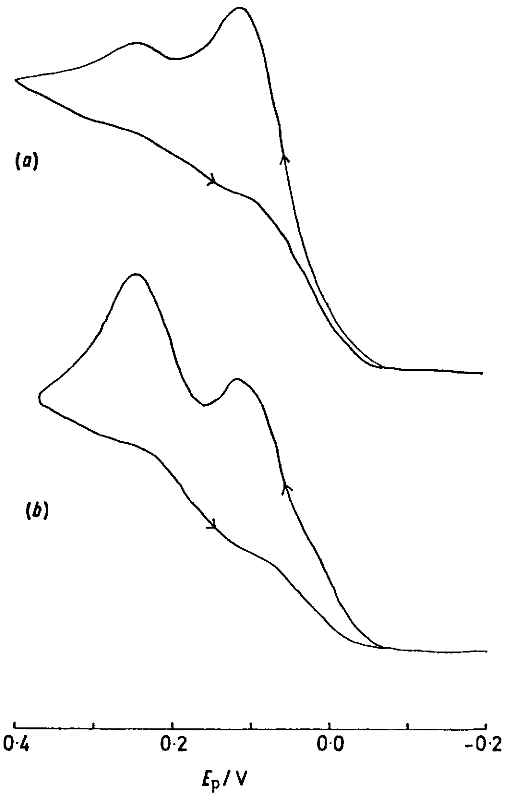
[8] N. G. Connelly, G. A. Johnson, B. A. Kelly, and P. Woodward, *J.C.S. Chem. Comm.*, 1977, 436.

[9] R. D. Adams, F. A. Cotton, W. R. Cullen, D. L. Hunter, and L. Mihichuk, *Inorg. Chem.*, 1975, **14**, 1395.

[10] R. Hill, B. A. Kelly, F. G. Kennedy, S. A. R. Knox, and P. Woodward, *J.C.S. Chem. Comm.*, 1977, 434.



Cyclic voltammograms of *syn*-$[\{Rh(\mu\text{-}SC_6H_4Me\text{-}p)(\eta\text{-}C_5H_5)\}_2]$ in CH_2Cl_2 after 1 (*a*) and 10 min (*b*) at 20 °C. The potential scale is *versus* a calomel electrode (1 mol dm^{-3} in LiCl) and the scan rate was 100 mV s^{-1}

The conversion of *syn*- into *anti*-$[\{Rh(\mu\text{-}SR^1)(\eta\text{-}C_5H_4R^2)\}_2]$ may be monitored by following changes in the ^1H n.m.r. or u.v.–visible spectrum. In the visible region *syn*-$[\{Rh(\mu\text{-}SC_6H_4Me\text{-}p)(\eta\text{-}C_5H_5)\}_2]$, for example, exhibits an intense absorption at $\lambda_{max.} = 563$ nm whereas the corresponding absorption for the *anti* isomer occurs at $\lambda_{max.} = 551$ nm. The isomerization process may also be followed by cyclic voltammetry. The Figure shows cyclic voltammograms taken (*a*) 1 min and (*b*) 10 min after dissolving pure *syn*-$[\{Rh(\mu\text{-}SC_6H_4Me\text{-}p)(\eta\text{-}C_5H_5)\}_2]$ in base electrolyte. It is clear that the peak at 0.11 V corresponds to oxidation of the *syn* isomer while that at 0.24 V, the peak current of which increases with time, corresponds to oxidation of the *anti* isomer; as the oxidation wave due to the *syn* isomer diminishes in height the deep blue colour of the solution becomes the deep purple of the *anti* isomer. That the oxidation processes each involve transfer of one-electron follows from the observation that the total peak current, at each scan, is that expected by comparison with the peak current measured for the oxidation of $[Ni\{S_2C_2(CN)_2\}_2]^{2-}$ to $[Ni\{S_2C_2(CN)_2\}_2]^{-}$, and from synthetic studies discussed below. It is also clear that the oxidation process is chemically irreversible and therefore that the isolation of $[\{Rh(\mu\text{-}SR^1)(\eta\text{-}C_5H_4R^2)\}_2]^+$ from CH_2Cl_2 will not be possible.*

Although comparative structural studies of $[\{Rh(\mu\text{-}SR^1)(\eta\text{-}C_5H_4R^2)\}_2]^Z$ ($Z = 0$ and 1) have not been carried out the relative potentials at which the *syn* and *anti* isomers are oxidized allow some comment to be made on the bonding in $[\{Rh(\mu\text{-}SR^1)(\eta\text{-}C_5H_4R^2)\}_2]$. The electrochemical data in Table 2 show that for each R^1 and R^2 the thermodynamically less-stable *syn* isomer is more readily oxidized than the *anti* isomer. Current bonding theories, reinforced by e.s.r. studies on the cation $[\{Co(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)\}_2]^+$, suggest [11] that the highest-occupied molecular orbital (h.o.m.o.) of bridged bimetallic species such as $[\{Rh(\mu\text{-}SR^1)(\eta\text{-}C_5H_4R^2)\}_2]$ will have considerable metal–metal bonding character. That the *anti* isomer is the more difficult to oxidize suggests a lower-energy h.o.m.o. than for the *syn* isomer and therefore a stronger metal–metal interaction. Formation of a stronger Rh–Rh bond may therefore contribute to the driving force for the *syn*–*anti* isomerization.

Although the electrochemical studies reported suggest that $[\{Rh(\mu\text{-}SR^1)(\eta\text{-}C_5H_4R^2)\}_2]^+$ is unlikely to exist as a stable salt, the values of $(E_p)_{ox}$ show that the oxidation of the neutral precursor is likely to be extremely easy Assuming that generation of the radical cation is followed by a rapid chemical reaction, we have treated *anti*-$[\{Rh(\mu\text{-}SC_6H_4Me\text{-}p)(\eta\text{-}C_5H_5)\}_2]$ with oxidizing agents in the presence of a source of radicals. Thus, addition of $[NO][PF_6]$, as a one-electron oxidant, to a mixture of the rhodium complex and di-*p*-tolyl disulphide in CH_2Cl_2 at 20 °C causes rapid formation of an orange solution from which $[Rh_2(\mu\text{-}SC_6H_4Me\text{-}p)_3(\eta\text{-}C_5H_5)_2][PF_6]$ may be isolated. Hydrogen-1 n.m.r. spectroscopy (Table 3) reveals the equivalence of the three bridging thiolato-ligands and thus that the cation has structure (4). The reaction between *anti*-$[\{Rh(\mu\text{-}SC_6H_4Me\text{-}p)(\eta\text{-}C_5H_5)\}_2]$ and $[N(C_6H_4Br\text{-}p)_3][SbCl_6]$ in CH_2Cl_2 similarly affords orange $[Rh_2(\mu\text{-}Cl)(\mu\text{-}SC_6H_4Me\text{-}p)_2(\eta\text{-}C_5H_5)_2][SbCl_6]$. In this case

TABLE 3

Analytical and ^1H n.m.r. data for $[Rh_2(\mu\text{-}X)(\mu\text{-}SC_6H_4Me\text{-}p)_2(\eta\text{-}C_5H_5)_2][Y]$

		Analysis [a] (%)		τ [in $(CD_3)_2CO$] [b]
X	Y	C	H	
SC_6H_4Me-*p*	PF_6	43.5 (43.8)	3.9 (3.7)	7.65 (9 H, s, Me), 4.29 (10 H, s, C_5H_5), 2.80 (6 H, d, $\lvert J_o + J_p\rvert$ 8, *m*-C_6H_4), 2.23 (6 H, d, $\lvert J_o + J_p\rvert$ 8, *o*-C_6H_4)
Cl	$SbCl_6$	29.4 (30.3)	2.5 (2.5) [c]	7.64 (3 H, s, Me), 7.62 (3 H, s, Me), 4.17 (10 H, s, C_5H_5), 2.78 (4 H, d, $\lvert J_o + J_p\rvert$ 8, *m*-C_6H_4), 2.33 (2 H, d, $\lvert J_o + J_p\rvert$ 8, *o*-C_6H_4), 2.03 (2 H, d, $\lvert J_o + J_p\rvert$ 8, *o*-C_6H_4)

[a] Calculated values are given in parentheses. [b] *J* values in Hz. [c] Cl, 26.1 (26.1%).

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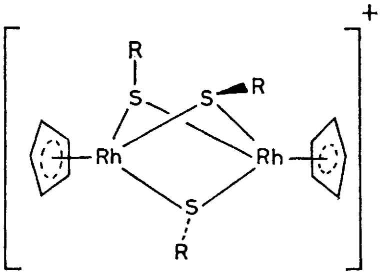
* Brief electrochemical studies have shown that the oxidation process is also chemically irreversible in MeCN.

[11] B. K. Teo, M. B. Hall, R. F. Fenske, and L. F. Dahl, *Inorg. Chem.*, 1975, **14**, 3103.

the ^{1}H n.m.r. spectrum (Table 3) reveals inequivalent bridging thiolato-groups and thus structure (5) for the cation. Similar reactions between *anti*-$[\{Rh(\mu\text{-}SC_6H_4Me\text{-}p)(\eta\text{-}C_5H_5)\}_2]$ and oxidizing agents such as halogens, arenediazonium salts, and tetracyanoethylene (tcne) also afford orange to orange-brown solids. Unfortunately, full characterization of the products was not possible even though, in the last case, a product analyzing (C, H, and N) for $[\{Rh(\mu\text{-}SC_6H_4Me\text{-}p)(\eta\text{-}C_5H_5)\}_2]\cdot$tcne was obtained.

It is clear that $[\{Rh(\mu\text{-}SR^1)(\eta\text{-}C_5H_4R^2)\}_2]$ (R^1 = alkyl) will have values of $(E_p)_{ox}$ lower than those measured for the arenethiolato-complexes described. It is probable, therefore, that the decomposition of $[\{Rh(\mu\text{-}SMe)(\eta\text{-}C_5H_5)\}_2]$ to an orange species on chromatography in air involves formation of a tribridged complex of the type described.

The combined chemical and electrochemical studies reported demonstrate that the metal–metal bond in $[\{Rh(\mu\text{-}SR^1)(\eta\text{-}C_5H_4R^2)\}_2]$ is activated towards insertion by initial one-electron oxidation. A similar mechanism was proposed by Jones and McCleverty [12] to account for the formation of $[Fe_2(\mu\text{-}SR)_3(CO)_6]^+$ in the reaction of $[\{Fe(\mu\text{-}SR)(CO)_3\}_2]$ with oxidizing agents such as $S_2C_2(CF_3)_2$ or $[NO]^+$, and it is clear that the formation of $[Fe_2(\mu\text{-}I)(\mu\text{-}SR)_2(CO)L]^+$ (L = phosphine) and related products [13] in the reaction of derivatives of $[\{Fe(\mu\text{-}SR)(CO)_3\}_2]$ with iodine occurs by a similar path.



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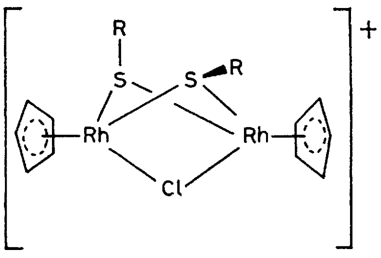

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EXPERIMENTAL

The preparation, purification, and reactions of the complexes described were carried out under atmospheres of dry nitrogen. The compounds $Tl(C_5H_5)$,[14] $[\{RhCl(CO)_2\}_2]$,[15] $[\{Rh(\mu\text{-}SR)(CO)_2\}_2]$,[16] and $[N(C_6H_4Br\text{-}p)_3][SbCl_6]$ [17] were prepared by published methods. Nitrosyl hexafluorophosphate and silver(I) salts were purchased from Ozark Mahoning Co., Tulsa, Oklahoma.

Hydrogen-1 n.m.r. spectra were recorded on a Varian Associates HA 100 instrument and mass spectra on an A.E.I. MS9 spectrometer. Electrochemical studies were carried out at 20 °C on 10^{-3} mol dm^{-3} solutions of the complex in purified CH_2Cl_2 with $[NEt_4][ClO_4]$ (0.05 mol dm^{-3}) as base electrolyte. Cyclic voltammograms were recorded on a Beckmann Electroscan 30 instrument using platinum-wire working and auxiliary electrodes and a calomel electrode (1 mol dm^{-3} in LiCl) as reference. Microanalyses were carried out by the staff of the Microanalytical Laboratory of the School of Chemistry, University of Bristol.

*Di-μ-*p*-tolylthio-bis[(η-cyclopentadienyl)rhodium]*, $[\{Rh(\mu\text{-}SC_6H_4Me\text{-}p)(\eta\text{-}C_5H_5)\}_2]$.—To a solution of $[Rh(\eta\text{-}C_5H_5)(CO)_2]$, prepared from $Tl(C_5H_5)$ (1.08 g, 4.01 mmol) and $[\{RhCl(CO)_2\}_2]$ (0.76 g, 1.94 mmol), in toluene (100 cm^3) was added di-*p*-tolyl disulphide (0.50 g, 2.02 mmol). After heating the mixture under reflux for 4 h the resulting deep purple solution was evaporated to dryness and the residue chromatographed rapidly on an alumina column. Elution with hexane afforded unchanged $[Rh(\eta\text{-}C_5H_5)(CO)_2]$, and with 40% CH_2Cl_2 (in hexane) gave a blue-purple band. Evaporation of the purple eluate gave a near-black crystalline product which was washed with a large volume of hexane (*ca.* 500 cm^3) to give a purple solution and a residue of black needles shown to be *syn*-$[\{Rh(\mu\text{-}SC_6H_4Me\text{-}p)(\eta\text{-}C_5H_5)\}_2]$ (yield 0.20 g, 18%). On cooling the purple solution to 0 °C dark plates of *anti*-$[\{Rh(\mu\text{-}SC_6H_4Me\text{-}p)(\eta\text{-}C_5H_5)\}_2]$ (contaminated with small amounts of the *syn* isomer) were isolated (yield 0.30 g, 27%). The *syn* isomer is only sparingly soluble in hexane but is soluble in all other common organic solvents to give deep blue solutions which become purple on standing. The *anti* isomer is soluble in all common organic solvents to give deep purple, air-stable, solutions.

The *complex* $[\{Rh(\mu\text{-}SPh)(\eta\text{-}C_5H_5)\}_2]$ was prepared by the same method but the *syn* and *anti* isomers were not separated.

*Tri-μ-*p*-tolylthio-bis[(η-cyclopentadienyl)rhodium] Hexafluorophosphate*, $[Rh_2(\mu\text{-}SC_6H_4Me\text{-}p)_3(\eta\text{-}C_5H_5)_2][PF_6]$.—To a vigorously stirred solution of *anti*-$[\{Rh(\mu\text{-}SC_6H_4Me\text{-}p)(\eta\text{-}C_5H_5)\}_2]$ (0.10 g, 0.17 mmol) and di-*p*-tolyl disulphide (0.21 g, 0.85 mmol) in CH_2Cl_2 (15 cm^3) was added solid $[NO][PF_6]$ (0.03 g, 0.17 mmol). After 5 min the initial intense purple solution had become orange. On filtration, addition of hexane, and recrystallization of the precipitate twice from CH_2Cl_2–hexane the *complex* was isolated as an orange solid (yield 0.10 g, 68%). It is soluble in polar solvents such as acetone and CH_2Cl_2 to give moderately air-stable orange solutions.

*μ-Chloro-di-μ-*p*-tolylthio-bis[(η-cyclopentadienyl)rhodium] Hexachloroantimonate*(V), $[Rh_2(\mu\text{-}Cl)(\mu\text{-}SC_6H_4Me\text{-}p)_2(\eta\text{-}C_5H_5)_2][SbCl_6]$.—To a stirred solution of *anti*-$[\{Rh(\mu\text{-}SC_6H_4Me\text{-}p)(\eta\text{-}C_5H_5)\}_2]$ (0.20 g, 0.34 mmol) in CH_2Cl_2 (30 cm^3) was added $[N(C_6H_4Br\text{-}p)_3][SbCl_6]$ (0.28 g, 0.34 mmol). After 5 min the orange solution was filtered and hexane added. Recrystallization of the precipitate three

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times from CH_2Cl_2–hexane gave the *complex* as an orange solid (yield 0.10 g, 20%). It is soluble in polar solvents such as acetone and CH_2Cl_2 to give moderately air-stable orange solutions.

G. A. J. thanks the S.R.C. for the award of a postgraduate studentship.

[7/1664 *Received, 20th September,* 1977]