Inorganic Chemistry
Article

Inorg. Chem. **2009**, *48*, 11945–11953 **11945**
DOI: 10.1021/ic9018458

Efficient Transfer of Either One or Two Dithiolene Ligands from Nickel to Ruthenium: Synthesis and Crystal Structures of [Ru(SCR=CPhS)$_2$(PPh$_3$)] and [RuCl$_2$(SCR=CPhS)(PPh$_3$)$_2$] (R = Ph, H)

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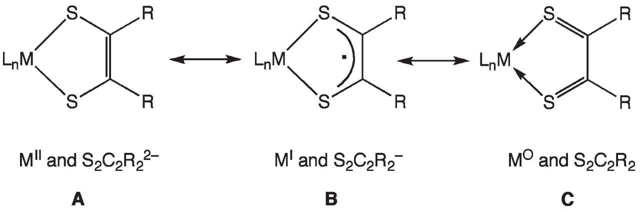
Received September 18, 2009

High yields of two different types of ruthenium dithiolene complex have been obtained by reactions that involve transfer of the dithiolene ligands from the nickel complexes [Ni(SCR=CPhS)$_2$] (R = Ph, H) to [RuCl$_2$(PPh$_3$)$_3$]. At room temperature one dithiolene is rapidly transferred to yield [RuCl$_2$(SCR=CPhS)(PPh$_3$)$_2$], whereas under thermal conditions (refluxing toluene) two dithiolene ligands are incorporated to give [Ru(SCR=CPhS)$_2$(PPh$_3$)]. The crystal structures of the ruthenium bis(dithiolene) complexes indicate that the dithiolene ligands are bonded in the monoanionic form, whereas in the monodithiolene complexes the dithioketone canonical form of the dithiolene ligand is more in evidence, as shown by the average C—S and C=C bond distances in the ligands. This is consistent with both complexes containing Ru(II) centers. The synthesis of the mixed-ligand bis(dithiolene) complex [Ru(SCH=CPhS)(S$_2$C$_2$Ph$_2$)(PPh$_3$)] has been achieved and it is shown that the bis(dithiolene) complexes undergo relatively slow scrambling of the dithiolene ligands in solution. The complex [Ru(SCH=CFcS)$_2$(PPh$_3$)], containing two ferrocenyl-substituted dithiolene ligands, was also prepared, but attempts to establish the degree of electrochemical communication between them were hampered by instability and the irreversible nature of the redox processes.

Introduction

Complexes of dithiolene (1,2-enedithiolate) ligands often display unusual properties such as multiple redox states, for example in [Ni(S$_2$C$_2$R$_2$)$_2$]$^{n-}$ ($n = 0-2$), or unusual coordination geometries, for example, trigonal prismatic [M(S$_2$C$_2$R$_2$)$_3$] (M = Mo, W).[1] The existence of the three canonical forms depicted in Chart 1 (dianionic dithiolate **A**, radical monoanion **B**, and neutral dithioketone **C**) which are interconvertible by one-electron redox processes can be considered responsible for the unique electronic properties of the ligand. Potential applications in near-IR dyes,[2] gas purification,[3] conducting and superconducting solids, and molecular magnets,[4] as well as their role in the bioinorganic chemistry of molybdenum and tungsten,[5] have ensured that the study of dithiolene complexes has remained an active and fertile area of research.

Chart 1. Canonical Forms of the Dithiolene Ligand: **A**, Dianionic Dithiolate; **B**, Radical Monoanion; and **C**, Neutral Dithioketone



Iron dithiolene complexes of the type [Fe(S$_2$C$_2$R$_2$)$_2$]$_2$, which exist as dimeric structures through coordination of one dithiolene sulfur atom to a second iron center, were first synthesized in the 1960′s by reaction of iron(II) sulfate with Na$_2$S$_2$C$_2$H$_2$ (for R = H) or with the solution obtained by refluxing benzoin with P$_2$S$_5$ in xylene (for R = Ph).[6] It was rapidly established that cleaving the dimeric unit with ligands

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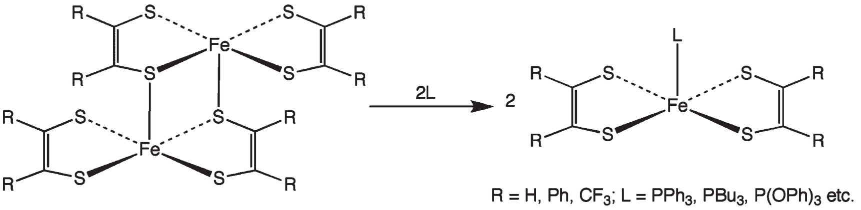
Scheme 1. Cleavage Reactions of the Dimeric Iron Dithiolene Complexes $[Fe(S_2C_2R_2)_2]_2$



such as phosphines or NO produced square pyramidal species of the formula $[Fe(S_2C_2R_2)_2(L)]$ (Scheme 1),[7,8] which have been receiving renewed research interest of late: in a series of papers Wieghardt and co-workers have examined the electronic structures of such species by a variety of techniques including X-ray crystallography, Mossbauer spectroscopy, electron paramagnetic resonance (EPR), spectroelectrochemistry, and density-functional theory (DFT) calculations.[9−12] More recently, the irreversible electrochemical reduction undergone by $[Fe(S_2C_2R_2)_2(PR_3)]$ has been linked to the dissociation of the phosphine ligand.[13,14]

In contrast the chemistry of the analogous ruthenium complexes is virtually unexplored. Early work mentions the preparation of ill-defined dithiolene complexes from $RuCl_3$ and the benzoin-P_2S_5 reagent, but this does not appear have been followed up.[15] A further paper reported that $[Ru_3(CO)_{12}]$ reacted with bis(perfluoromethyl)dithiete to give either an orange compound thought to be $[Ru(CO)_3\{S_2C_2(CF_3)_2\}]$ or at higher temperatures a carbonyl-free green material which reacted with EPh_3 (E = P, As, Sb) to give $[Ru\{S_2C_2(CF_3)_2\}_2(EPh_3)]$;[16] the structures of two isomeric forms of $[Ru(CO)(PPh_3)_2\{S_2C_2(CF_3)_2\}]$ were subsequently determined.[17] Cyclopentadienyl species such as anionic $[CpRu(PPh_3)(mnt)]^-$ (made by treatment of $[CpRu(PPh_3)_2Cl]$ with Na_2mnt) and neutral [Cp*Ru(NO)(dithiolene)] were reported by Prasad[18] and by Bott and Richmond, respectively,[19] but apart from some additional complexes with polypyridine ligands,[20] most new ruthenium dithiolene complexes prepared since then have been polynuclear species.[21] More recently, however, mononuclear complexes of the type $[(\eta^6\text{-arene})Ru\{S_2C_2(CO_2Me)_2\}]$ have been prepared and studied electrochemically, though these also undergo association into dimers.[22]

We have recently examined reactions in which dithiolene ligands are transferred from the readily available square planar nickel complex $[Ni(S_2C_2Ph_2)_2]$ to molybdenum centers, which provide useful routes to new and otherwise inaccessible Mo and W dithiolene species.[23] We therefore sought to extend these studies to other metals, and here we report the high yield preparation of two new mononuclear ruthenium dithiolene complexes in which the redox state of the dithiolene ligands is clearly indicated by their structural parameters.

Results and Discussion

Bis(dithiolene) Complexes. Treatment of $[RuCl_2(PPh_3)_3]$ **1** with 2 equiv of $[Ni(S_2C_2Ph_2)_2]$ **2a** in refluxing toluene afforded the new complex $[Ru(S_2C_2Ph_2)_2(PPh_3)]$ **3a** as an air-stable blue-green crystalline solid in quantitative yield after purification by column chromatography (Scheme 2). The ^1H NMR spectrum consisted only of phenyl resonances, but the ^{13}C NMR spectrum also showed the presence of dithiolene carbon atoms at δ 179.5. The observation of a singlet at δ 52.4 in the ^{31}P NMR spectrum indicated that at least one PPh_3 ligand was still coordinated. The mass spectrum displayed a highest mass envelope at m/z 847, corresponding to the molecular ion. Unlike in our recent synthesis of $[CpMo(S_2C_2Ph_2)_2]$,[23] no evidence was found for the formation of any heterometallic complexes in this reaction.

The structure of **3a** as its ethyl acetate solvate is shown in Figure 1, with selected bond lengths and angles collected in Table 1. The molecule adopts a square-based pyramidal structure with the PPh_3 ligand at the apex. Interestingly the phosphine ligand is somewhat tilted away from the normal to the S_4 plane; as a result the P(1)−Ru(1)−S angles can be divided into two groups, two smaller [S(2) 92.42(5) and S(3) 94.32(5)°] and two larger [S(1) 100.38 (5) and S(4) 108.96(5)°]. The angles S(1)−Ru(1)−S(2) and S(3)−Ru(1)−S(4), that is, the bite

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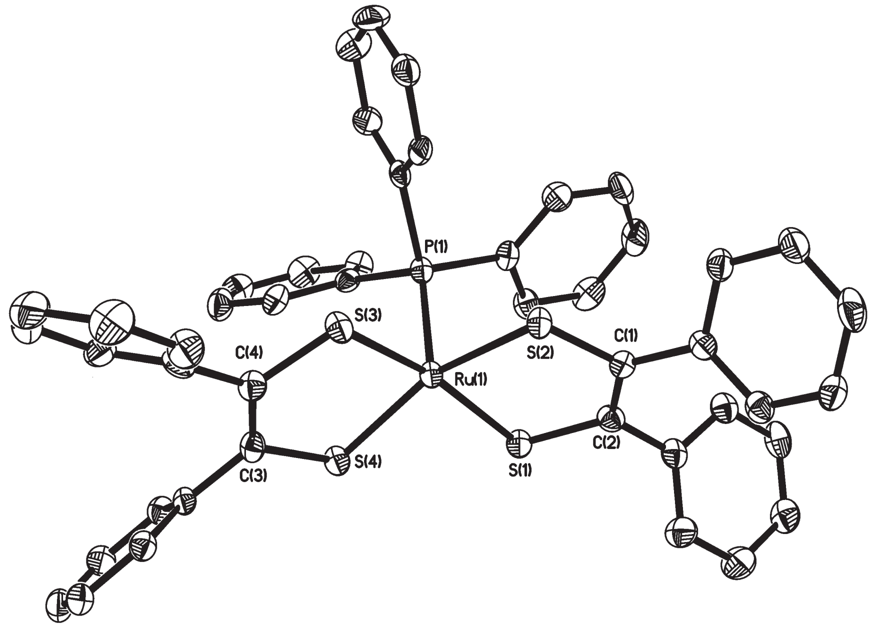

Figure 1. Molecular structure of $[Ru(S_2C_2Ph_2)_2(PPh_3)]\cdot EtOAc$ (**3a**·EtOAc) in the crystal (ORTEP plot, 50% probability ellipsoids). Hydrogen atoms and the ethyl acetate of crystallization have been omitted for clarity.

Scheme 2. Synthesis of the New Ruthenium Complexes **3** and **4**

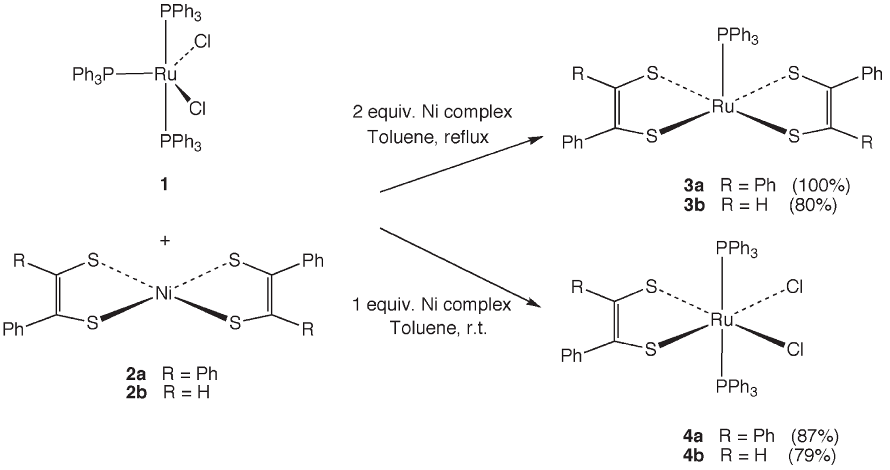

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex **3a**·EtOAc

Ru(1)−S(2)	2.2526(14)	Ru(1)−P(1)	2.2616(15)
Ru(1)−S(4)	2.2638(14)	Ru(1)−S(1)	2.2686(14)
Ru(1)−S(3)	2.2696(14)	S(1)−C(2)	1.710(6)
S(2)−C(1)	1.707(5)	S(3)−C(4)	1.708(6)
S(4)−C(3)	1.729(5)	C(1)−C(2)	1.398(7)
C(3)−C(4)	1.390(8)		
S(2)−Ru(1)−P(1)	92.42(5)	S(2)−Ru(1)−S(4)	158.61(6)
P(1)−Ru(1)−S(4)	108.96(5)	S(2)−Ru(1)−S(1)	85.28(5)
P(1)−Ru(1)−S(1)	100.38(5)	S(4)−Ru(1)−S(1)	90.19(5)
S(2)−Ru(1)−S(3)	93.49(5)	P(1)−Ru(1)−S(3)	94.32(5)
S(4)−Ru(1)−S(3)	85.62(5)	S(1)−Ru(1)−S(3)	165.29(6)

angles of the two dithiolene ligands, are 85.28(5) and 85.62(5)°, respectively. The Ru−S distances (av. 2.264 Å) are comparable to those in other Ru dithiolene complexes, such as $[(\eta\text{-}C_6Me_6)Ru\{S_2C_2(CO_2Me)_2\}]$,[22] even though the oxidation state of the ruthenium is formally higher. The C(1)−C(2) and C(3)−C(4) bond lengths of 1.398(7) and 1.390(8) Å are toward the longer end of the range usually found for dithiolene ligands, and the C−S bonds are relatively short (av. 1.7135 Å), which indicates a considerable contribution of the monoanionic form of the dithiolene ligands. Hence, although the replacement of two PPh_3 ligands and two chlorides by two dithiolene ligands during the reaction *formally* means that the oxidation state of the metal atom has increased to Ru(IV), it seems that a more accurate description would involve Ru(II).

One of the indicators of the degree of aromaticity in a metal dithiolene complex can be the chemical shift of protons attached to the dithiolene ligand. To explore this aspect, we also prepared the analogous unsymmetrical dithiolene complex $[Ru(SCH{=}CPhS)_2(PPh_3)]$ **3b** from the nickel complex $[Ni(SCH{=}CPhS)_2]$ **2b**. This reaction occurred under the same conditions as those leading to **3a**, and in similarly good yield, demonstrating the generality of this synthetic method.

In the nickel complex $[Ni(SCH{=}CPhS)_2]$ the dithiolene proton appears at δ 9.85 in the ^1H NMR spectrum, and this signal splits into two peaks at low temperature

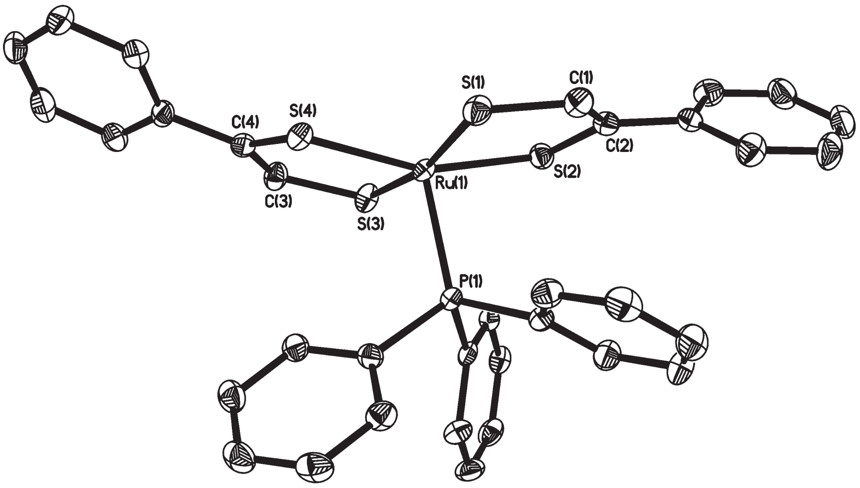

Figure 2. Molecular structure of $[Ru(SCH{=}CPhS)_2(PPh_3)]$ **3b** in the crystal (ORTEP plot, 50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

(193 K). This indicates that both possible isomers (*cis* and *trans*) are present and interconvert on the NMR time scale at room temperature.[24] The ^{1}H NMR spectrum of **3b** displays a singlet at δ 9.79 which remains invariant at low temperature (190 K) and in the ^{13}C NMR spectrum, the two dithiolene carbons resonate at δ 183.3 (CPh) and 165.9 (CH). There is no evidence for the presence of more than one isomer in either spectrum, and in the solid state structure of **3b** (Figure 2, Table 2) only the *trans* isomer was observed. The C−S bonds in the dithiolene ligands are again relatively short, with those involving the CH carbons [1.697(3) and 1.692(3) Å] being shorter than those for the CPh carbons [1.716(3) and 1.717(3) Å], whereas the C(1)−C(2) and C(3)−C(4) distances are relatively long, 1.368(4) and 1.373(4) Å, though shorter than those in **3a**. The tilting of the phosphine ligand toward two of the sulfur atoms is more pronounced in this compound than in **3a**, with the smaller P(1)−Ru(1)−S angles being 89.10(3) and 91.25(3)° for S(2) and S(3), respectively, and the larger ones being 101.44(3) and 111.64(3)° for S(1) and S(4), respectively.

The structures of **3a** and **3b** are the first of this type of complex for ruthenium. However, four structures of analogous iron complexes have been reported previously: $[Fe\{S_2C_2(CF_3)_2\}_2(AsPh_3)]$,[8] $[Fe(S_2C_2Ph_2)_2\{P(OMe)_3\}]$,[25] $[Fe(S_2C_2Ph_2)_2\{P(OPh)_3\}]$,[9] and most recently $[Fe(S_2C_2R_2)_2(PPh_3)]$ where R = *p*-anisyl.[13] The average C−S distances in these four complexes were 1.702 Å, 1.717 Å, 1.705 Å, and 1.710 Å, respectively, and the average C═C distances in the dithiolene ligands were 1.372 Å, 1.397 Å, 1.395 Å, and 1.383 Å, respectively. In their recent publication in which they examine the electronic structure of such compounds by a variety of spectroscopic techniques as well as X-ray crystallography, Wieghardt and co-workers conclude that these are typical parameters for dithiolene ligands which are bound in the radical anion state, that is, canonical form **B** in Chart 1.[9]

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex **3b**

Ru(1)−S(1)	2.2671(8)	Ru(1)−P(1)	2.2700(7)
Ru(1)−S(2)	2.2716(7)	Ru(1)−S(3)	2.2731(8)
Ru(1)−S(4)	2.2871(7)	S(1)−C(1)	1.697(3)
S(2)−C(2)	1.716(3)	S(3)−C(3)	1.692(3)
S(4)−C(4)	1.717(3)	C(1)−C(2)	1.368(4)
C(3)−C(4)	1.373(4)		
S(1)−Ru(1)−P(1)	101.44(3)	S(1)−Ru(1)−S(2)	86.08(3)
P(1)−Ru(1)−S(2)	89.10(3)	S(1)−Ru(1)−S(3)	167.25(3)
P(1)−Ru(1)−S(3)	91.25(3)	S(2)−Ru(1)−S(3)	95.48(3)
S(1)−Ru(1)−S(4)	88.65(3)	P(1)−Ru(1)−S(4)	111.64(3)
S(2)−Ru(1)−S(4)	159.24(3)	S(3)−Ru(1)−S(4)	85.45(3)

The similarity of these values to those found in complexes **3a** and **3b** leads us to assert that these too contain monoanionic dithiolene ligands.

Further confirmation of this is obtained from the UV−visible spectra of **3a** and **3b**, which contain strong absorptions at 682 nm (ε = 21307 M^{-1} cm^{-1}) and 821 nm (ε = 6570 M^{-1} cm^{-1}), respectively. In the spectrum of $[Fe(S_2C_2Ph_2)_2\{P(OPh)_3\}]$, which shows a feature-by-feature correspondence with the spectra of **3**, Wieghardt observed a band at 687 nm and assigned it as a ligand to ligand charge transfer band between the two monoanionic dithiolenes.

The tilting of the axial phosphine ligand observed in **3a** and **3b** is also present in the four iron structures referred to above. This suggests that it is a consistent feature of bonding in these molecules rather than simply the consequence of crystal packing forces. Calculations by Donahue on the neutral iron complex $[Fe(S_2C_2R_2)_2]$ where R = *p*-anisyl indicate that the lowest unoccupied molecular orbital (LUMO) is the d_{z^2} orbital, as expected for a square pyramidal d^6 system, and the phosphine ligand interacts with this.[13] We suggest the tilting may be a manifestation of an interaction between filled d orbitals and the π-acceptor orbitals of the phosphine (either an empty d-orbital or the P−C σ^* orbitals). Tilting of the axial ligand has been noted in Fe(II) porphyrin complexes with an axial nitrosyl group, and ascribed to a similar interaction.[26]

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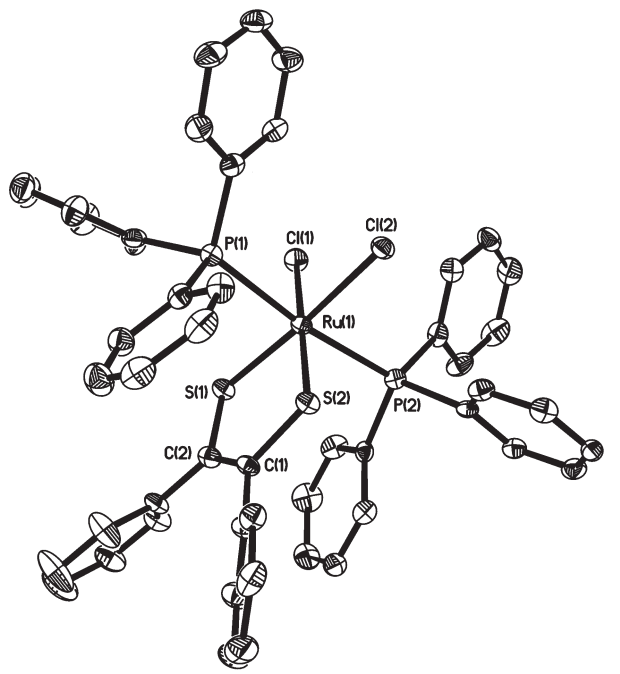


Figure 3. Molecular structure of $[\mathrm{RuCl_2(S_2C_2Ph_2)(PPh_3)_2}]\cdot 2\mathrm{CHCl_3}$ **4a** in the crystal (ORTEP plot, 50% probability ellipsoids). Hydrogen atoms and the chloroform molecules of crystallization have been omitted for clarity.

Monodithiolene Complexes. During the preparation of **3a**, we noticed that while the solution was heating to reflux, it initially adopted a purple coloration. We therefore explored the reaction of **1** with $[\mathrm{Ni(S_2C_2Ph_2)_2}]$ at room temperature, and discovered that with a 1:1 ratio of the two reagents, the new purple monodithiolene complex $[\mathrm{RuCl_2(S_2C_2Ph_2)(PPh_3)_2}]$ **4a** could be isolated by crystallization in yields of around 70% (Scheme 2). The ^{31}P NMR spectrum of this species consists of a singlet at 12.9 ppm, and in the ^{13}C NMR spectrum the dithiolene carbons are shifted to lower field (δ 209.7, as compared to 179.5 for **3a**). The mass spectrum in this case displays a highest mass ion envelope corresponding to $[\mathrm{M}-\mathrm{Cl}]^+$, though the retention of both chloride ligands was indicated by the elemental analysis.

Again an analogous reaction of **1** with $[\mathrm{Ni(SCH{=}CPhS)_2}]$ afforded the corresponding complex $[\mathrm{RuCl_2(SCH{=}CPhS)(PPh_3)_2}]$ **4b** as a purple solid which displays a singlet in its ^{1}H NMR spectrum at δ 10.18 due to the dithiolene proton, and peaks at δ 210.4 and 196.1 in the ^{13}C NMR spectrum which are assigned to the CPh and CH carbons, respectively. The low field shifts of these signals indicate an increased contribution of the dithioketone form of the dithiolene ligand in **4a** and **4b** compared to **3a** and **3b**.

The structural type represented by **4a** and **4b** is unprecedented in iron chemistry. The solid state structure of $[\mathrm{RuCl_2(S_2C_2Ph_2)(PPh_3)_2}]\cdot 2\mathrm{CHCl_3}$ **4a** is depicted in Figure 3, and that of **4b** in Figure 4. Selected bond lengths and angles are collected in Tables 3 and 4, respectively. In each complex the two phosphine ligands adopt *trans* positions in the octahedral structure. The most interesting feature is the bonding of the dithiolene ligands: in **4a** the C(1)−C(2) bond length of 1.412(5) appears to be slightly longer than in **3a** and the C−S bond lengths of 1.690(4) and 1.695(4) Å are possibly slightly shorter, although the differences are not significant given the esd values. In the structure of **4b**, however, the situation is more clear-cut. The C(1)−C(2) bond length is 1.408(7) Å, which is now significantly longer than the corresponding distances of 1.368(4) and 1.373(4) Å in **3b**, and moreover the C−S distances of 1.662(5) and 1.675(5) Å for the CH and CPh carbons, respectively, are significantly shorter than the corresponding ones in **3b**. Such changes are expected as the contribution of the dithioketone canonical form **C** increases.

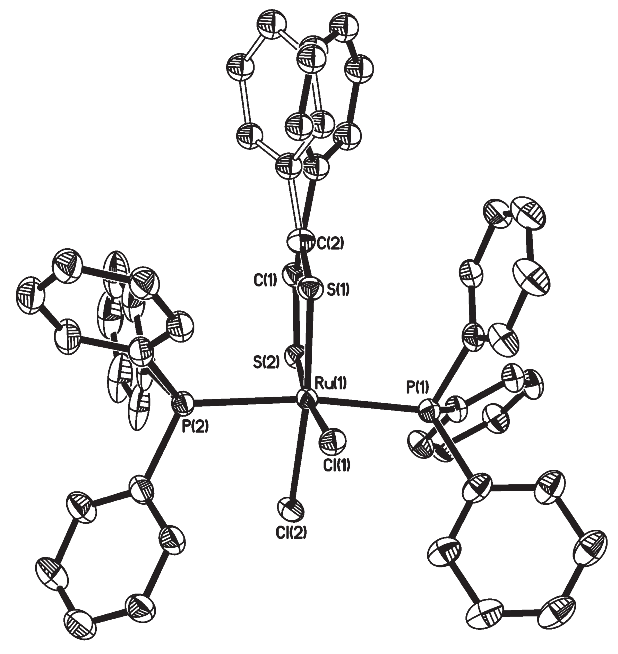


Figure 4. Molecular structure of $[\mathrm{RuCl_2(SCH{=}CPhS)(PPh_3)_2}]$ **4b** in the crystal (ORTEP plot, 50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex **4a**·2CHCl$_3$

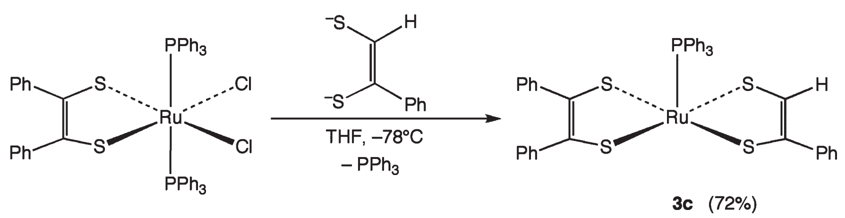
Ru(1)−S(1)	2.2127(17)	Ru(1)−S(2)	2.2207(14)
Ru(1)−P(2)	2.4225(15)	Ru(1)−P(1)	2.4332(16)
Ru(1)−Cl(2)	2.4387(18)	Ru(1)−Cl(1)	2.4610(15)
S(1)−C(2)	1.690(4)	S(2)−C(1)	1.695(4)
C(1)−C(2)	1.412(5)		
S(1)−Ru(1)−S(2)	85.29(4)	P(2)−Ru(1)−P(1)	172.91(4)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex **4b**

Ru(1)−S(2)	2.2214(13)	Ru(1)−S(1)	2.2288(13)
Ru(1)−P(1)	2.4129(12)	Ru(1)−Cl(2)	2.4170(12)
Ru(1)−P(2)	2.4174(12)	Ru(1)−Cl(1)	2.4567(12)
S(1)−C(2)	1.675(5)	S(2)−C(1)	1.662(5)
C(1)−C(2)	1.408(7)		
S(2)−Ru(1)−S(1)	86.37(5)	P(1)−Ru(1)−P(2)	171.80(4)

If we compare the average bond lengths in **4b** and **3b**, the C−S bonds are shorter [Δ(C−S) = 0.0365 Å] and the C−C bonds are longer [Δ(C−C) = 0.037 Å respectively]. Wieghardt and co-workers point out that the change from a dianionic dithiolene ligand to a monoanionic one is accompanied by bond length changes which are typically 0.05 Å for Δ(C−S) and 0.04 Å for Δ(C−C).[9] If a similar figure holds true for the change from monoanionic dithiolene to the neutral dithioketone form (which

Scheme 3. Synthesis of the Mixed-Ligand Complex [Ru(SCH=CPhS)($S_2C_2Ph_2$)(PPh_3)] **3c**



seems a reasonable assumption since the usual bond length ranges in dithiolene ligands are relatively narrow, specifically 1.642−1.777 Å for C−S and 1.284−1.520 Å for C−C in bis(dithiolene) complexes),[27] then the changes observed in **4b** particularly signify a definite shift toward canonical form **C** in Chart 1. In the synthesis of this complex the dithiolene has replaced only a PPh_3 ligand, accompanied by a *formal* increase in metal oxidation state from Ru(II) to Ru(IV). However, if the dithiolene was acting as a neutral ligand, the Ru could again retain an oxidation state of II.

Perhaps the closest structural comparison in this case is provided by [$RuCl_2(PPh_3)([9]aneS_3)$] ($[9]aneS_3$ = 1,4,7-trithiacyclononane), which indisputably contains Ru(II).[28] In this complex the Ru−Cl distances *trans* to S are 2.456(2) and 2.449(2) Å, whereas in **4a** the corresponding distances are 2.4387(18) and 2.4610(15) Å. The Ru−S distances are, however, somewhat shorter in **4a** [2.2127(17) and 2.2207(14) Å] compared to 2.270(2) and 2.269(2) in the thioether complex.

Synthesis of a Mixed Bis(thiolene) Complex. The dithiolene transfer reaction from nickel to ruthenium is the most efficient route to the bis(dithiolene) complexes **3a** and **3b**. To demonstrate this we also carried out the synthesis of **3b** by treatment of **1** with the dianion derived by base deprotection of 4-phenyl-1,3-dithiol-2-one. Although this reaction was successful, the yield was only 45% compared to the virtually quantitative one obtained by dithiolene transfer from the nickel complex.

However, the transfer reaction is evidently not as straightforward as it first appears. Despite the fact that the purple complex **4a** was observed transiently during the synthesis of **3a**, implying that it is an intermediate, we were surprised to discover that isolated **4a** did not react rapidly with further [$Ni(S_2C_2Ph_2)_2$] to give **3a**. In fact this reaction required 60 h to reach completion as opposed to the 4 h used for the one-pot reaction. One possible interpretation of this result is that in the original reaction, **4a** does not react with further [$Ni(S_2C_2Ph_2)_2$] itself, but with a compound formed from it by the transfer of the first dithiolene ligand. The obvious candidate is the oligomeric species $[Ni(S_2C_2Ph_2)]_n$ (where *n* is probably equal to 6), which is known to be produced in many dithiolene transfer reactions of this type;[29] however, **4a** appeared to undergo no detectable reaction at all with $[Ni(S_2C_2Ph_2)]_n$ in refluxing toluene.

Further investigation showed that there was also complete scrambling of dithiolene ligands during the reaction, as heating isolated **4a** with [$Ni(SCH{=}CPhS)_2$] in an attempt to produce the mixed-ligand complex [Ru(SCH=CPhS)($S_2C_2Ph_2$)(PPh_3)] **3c** gave instead, according to the ^1H NMR and mass spectra of the product, a statistical 1:2:1 mixture of **3a**:**3c**:**3b**. However a more successful strategy proved to be the reaction of **4a** with the dianion derived by deprotection of 4-phenyl-1,3-dithiol-2-one; when carried out at −78 °C with immediate purification by chromatography, this gave **3c** in good yield (72%) but still contaminated with approximately 5% of **3b** (Scheme 3).

Attempts to obtain crystals of **3c** for structural analysis were frustrated by the fact that a slow exchange of dithiolene ligands evidently occurs in solution even at room temperature and below, which meant that the crystals isolated turned out to be of **3a**. Investigation of an equimolar mixture of **3a** and **3b** in $CDCl_3$ in an NMR tube showed no evidence for the formation of **3c** after 20 min, but after 9 days at room temperature (even in the dark) the ^1H NMR spectrum showed the presence of both **3b** and **3c** in a 1:5 ratio estimated by integration of the peaks at δ 9.79 for **3b** and δ 9.93 for **3c**; the amount of **3a**, which has no dithiolene-bound proton, present is assumed to be similar to that of **3b**. A similar experiment was conducted with a sample of **3c**; after 9 days the same equilibrium position was attained. An equilibrium constant of K = 25 can thus be calculated for the conproportionation reaction of **3a** and **3b** to give **3c** (eq 1).

$$\mathbf{3a} + \mathbf{3b} \rightleftharpoons 2\ \mathbf{3c} \qquad K = 25 \qquad (1)$$

Ferrocenyl-Substituted Dithiolene Complex [Ru(SCH=CFcS)$_2$(PPh$_3$)] 3d. We have recently been investigating the incorporation of redox-active substituents into bis(dithiolene) complexes in an attempt to discover whether some degree of electronic communication is possible through the highly delocalized ligand system. The ferrocenyl group is an ideal candidate for study as it is relatively easily introduced, and displays a reversible oxidation at an accessible potential. The ferrocenyl-substituted nickel complex [$Ni(SCH{=}CFcS)_2$] has been previously prepared by Underhill and Mueller-Westerhoff; a difference of 187 mV was observed between the ferrocene oxidations.[30,31] The fully ferrocenyl-substituted [$Ni(S_2C_2Fc_2)_2$] was also made, and in the presence of noncoordinating anions such as $[B(C_6F_5)_4]^-$ in the supporting electrolyte, four separate oxidations for the ferrocene

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[27] Beswick, C. L.; Schulman, J. M.; Stiefel, E. I. *Prog. Inorg. Chem.* **2004**, *52*, 55.

[28] Alcock, N. W.; Cannadine, J. C.; Clark, G. R.; Hill, A. F. *J. Chem. Soc., Dalton Trans.* **1993**, 1131.

[29] Schrauzer, G. N.; Mayweg, V. P.; Heinrich, W. *J. Am. Chem. Soc.* **1966**, *88*, 5174. See also: Beswick, C. L.; Terroba, R.; Greaney, M. A.; Stiefel, E. I. *J. Am. Chem. Soc.* **2002**, *124*, 9664 for the structure of a Pd analogue.

[30] (a) Wilkes, S. B.; Butler, I. R.; Underhill, A. E.; Kobayashi, A.; Kobayashi, H. *J. Chem. Soc., Chem. Commun.* **1994**, 53. (b) Underhill, A. E.; Charlton, A.; Wiles, S. B.; Butler, I. R.; Kobayashi, A.; Kobayashi, H. *Synth. Met.* **1995**, *70*, 1101.

[31] Mueller-Westerhoff, U. T.; Sanders, R. W. *Organometallics* **2003**, *22*, 4778.

units could be distinguished.[32] We have observed a similar peak separation in dinuclear complexes such as [Mo_2(μ-SCH=CFcS)$_2$$Cp_2$].[33]

The reaction of [$RuCl_2(PPh_3)_3$] with [Ni(SCH=CFcS)$_2$] duly afforded [Ru(SCH=CFcS)$_2$(PPh_3)], though the yield of 21% was much lower because of decomposition of the product during purification. The ^{1}H NMR spectrum contained a peak at δ 9.72 due to the dithiolene protons; as in the case of **3b** only one isomer was detected, presumably the *trans* isomer.

Electrochemistry. The electrochemistry of the iron bis(dithiolene) phosphine adducts has been investigated first by McCleverty[7a] and more recently by Wieghardt[9] and Donahue.[13] For example [Fe($S_2C_2Ph_2$)$_2${P(OPh)$_3$}] and [Fe($S_2C_2R_2$)$_2${P(OMe)$_3$}] (R = p-$C_6H_4{}^tBu$) were shown to undergo one reversible oxidation and one essentially irreversible reduction, which was accompanied by the dissociation of the axial phosphine ligand.[9] The same conclusion was reached with regard to [Fe($S_2C_2R_2$)$_2$(PPh_3)] (R = p-anisyl).[13]

The cyclic voltammograms of ruthenium complexes **3a**, **3b**, and **3c** were recorded in dichloromethane. All undergo an irreversible oxidation between + 0.85 and 0.91 V versus Ag/AgCl and a reduction in the range −0.56 to −0.65 V; in the case of **3b** this reduction is reversible, and presumably represents the formation of a monoanion. A second irreversible reduction was observed in the range −1.40 to −1.48 V. The cyclic voltammograms of the monodithiolene species **4a** and **4b** displayed only one irreversible oxidation at about +1.20 V and an irreversible reduction at about −0.40 V.

The cyclic voltammogram of the ferrocenyl-substituted complex **3d** revealed a reversible reduction at −0.67 V and a further irreversible one at −1.55 V. Two oxidations were observed, at +0.53 V and +0.68 V; however, both of these were irreversible and thus it is not possible to determine with any certainty whether the two ferrocene units are in electrochemical communication. However, it should be noted that both oxidations appear to be one-electron processes, which could indicate an interaction between the iron centers.

Conclusions

This work has provided further examples of the use of dithiolene ligand transfer reactions as a high yield route to new dithiolene complexes. The use of three different nickel dithiolene complexes (one symmetrical, and the other two unsymmetrical) suggests that the reactions are general ones. Moreover, by adjusting the reaction conditions, it is possible to access the new monodithiolene species **4** of an unprecedented structural type, as well as the bis(dithiolene) complexes **3** which are analogues of previously known iron compounds. The electronic state of the dithiolene ligands in these complexes is clearly indicated not only by the crystallographically determined bond lengths but also by the chemical shifts of the dithiolene carbons in the ^{13}C NMR spectrum. According to these criteria the dithiolene ligands in **3** are, as expected, bonded in the monoanionic form, whereas in **4** the neutral dithioketone canonical form is much more in evidence.

Although the introduction of the dithiolene ligands is not a simple stepwise process, we have also shown that it is possible to synthesize in **3c** a rare example of a bis(dithiolene) complex which contains two different dithiolene ligands. Attempts to characterize this structurally were, however, hindered by a slow redistribution of the dithiolene ligands in solution.

Further examples of the use of nickel bis(dithiolene) complexes as dithiolene transfer agents, particularly those facilitated by the presence of labile ligands on the receiving metal center, will be reported in due course.

Experimental Section

Materials. General experimental techniques were as described in recent work from this laboratory.[23] All reactions were routinely carried out under an argon or nitrogen atmosphere, though separation procedures were carried out without any special precautions since the products described are all relatively air-stable. Solvents were purified with a Grubbs-type purification system manufactured by Innovative Technology, Newburyport, MA. The complexes [Ni($S_2C_2Ph_2$)$_2$], [Ni(SCH=CPhS)$_2$], and [$RuCl_2(PPh_3)_3$] were prepared by the literature procedures.[34,24,35] The radical method of Gareau and Beauchemin was used to prepare 4-phenyl-1,3-dithiole-2-one.[36] All other chemicals were obtained from commercial sources and used as supplied. Light petroleum refers to the fraction with a boiling range of 60−80 °C.

Physical Measurements. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained in $CDCl_3$ solution on a Bruker AC250 Fourier transform machine with automated sample-changer or on Bruker AMX400 or DRX-500 spectrometers. Chemical shifts are given on the δ scale relative to $SiMe_4$ = 0.0 ppm for ^{1}H and ^{13}C, and relative to 85% H_3PO_4 for ^{31}P. The ^{13}C{^{1}H} NMR spectra were routinely recorded using an attached proton test technique (JMOD pulse sequence). Mass spectra were recorded on a Fisons/BG Prospec 3000 instrument operating in fast atom bombardment mode with m-nitrobenzyl alcohol as matrix; the figures reported are the highest intensity peak of each isotope envelope. UV−visible absorption spectra were recorded in dichloromethane solution on a Varian Cary 50 instrument in the range 200−800 nm with a path length of 1 cm. Elemental analyses were carried out by the Microanalytical Service of the Department of Chemistry with a Perkin-Elmer 2400 analyzer. Cyclic voltammetry was carried out using an EG&G 273A potentiostat. Measurements were carried out under dinitrogen in dry freshly distilled dichloromethane solutions of approximate concentration 1 mM, containing 0.1 M Bu_4NBF_4 as supporting electrolyte. Potentials were measured relative to a Ag/AgCl electrode; under these conditions the ferrocene/ferrocenium redox couple was observed at 0.50 V. Processes are described as reversible if ΔE < 100 mV and $|I_pa/I_pc|$ = 1.

Synthesis of [Ru($S_2C_2Ph_2$)$_2$(PPh_3)] 3a. A solution of [$RuCl_2(PPh_3)_3$] (149.4 mg, 0.156 mmol) and [Ni($S_2C_2Ph_2$)$_2$] (164.9 mg, 0.303 mmol) in toluene (125 cm^3) was heated to reflux for 4 h. After cooling and addition of a small amount of silica, the solvent was removed in vacuo. The resulting powder was loaded onto a silica chromatography column. Elution with dichloromethane/light petroleum (1:4) afforded a green band

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[34] (a) Schrauzer, G. N.; Mayweg, V. P.; Heinrich, W. *Inorg. Chem.* **1965**, *4*, 1615. (b) Schrauzer, G. N.; Mayweg, V. P. *J. Am. Chem. Soc.* **1965**, *87*, 1483.

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Table 5. Summary of Crystallographic Data for Complexes **3a**·EtOAc, **3b**, **4a**·2CHCl$_3$, and **4b**

	3a·EtOAc	**3b**	**4a**·2CHCl$_3$	**4b**
empirical formula	$C_{50}H_{43}O_2PRuS_4$	$C_{34}H_{27}PRuS_4$	$C_{52}H_{42}Cl_8P_2RuS_2$	$C_{44}H_{36}Cl_2P_2RuS_2$
formula weight	936.12	695.84	1177.59	862.76
T/K	150(2)	150(2)	150(2)	150(2)
$\lambda(Mo-K_\alpha)$/Å	0.71073	0.71073	0.71073	0.71073
crystal system	orthorhombic	triclinic	triclinic	monoclinic
space group	*Pbca*	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a/Å	15.556(2)	10.7650(6)	11.684(7)	10.1008(4)
b/Å	20.523(3)	10.8154(7)	15.101(9)	36.5535(16)
c/Å	27.394(3)	13.4584(8)	16.227(10)	12.2298(5)
α/deg	90	100.495(2)	70.154(10)	90
β/deg	90	91.637(2)	69.881(10)	107.620(2)
γ/deg	90	105.421(2)	82.166(11)	90
V/Å^3	8745.6(19)	1480.34(15)	2528(3)	4303.6(3)
Z	8	2	2	4
density (calcd)/Mg m^{-3}	1.422	1.561	1.547	1.332
final R1, wR2 [$I > 2\sigma(I)$]	0.0592, 0.1281	0.0344, 0.0829	0.0506, 0.1078	0.0530, 0.1240
(all data)	0.1411, 0.1742	0.0407, 0.0865	0.0948, 0.1230	0.0750, 0.1325

containing a small amount of the starting nickel complex. Further elution with a 3:7 mixture of the same solvents produced an intense blue-green zone which yielded [Ru($S_2C_2Ph_2$)$_2$(PPh$_3$)] (131.4 mg, 0.155 mmol, 100%). Recrystallization from ethyl acetate and hydrocarbons (pentane, hexane, heptane) gave crystals of the ethyl acetate monosolvate suitable for X-ray analysis; all other recrystallizing solvents failed to produce crystals.

Data for **3a**: mp 235−237 °C. ^{1}H NMR δ 7.33−7.05 (m, Ph). ^{13}C NMR δ 179.5 (CPh), 143.3 (C$_{ipso}$ of dithiolene), 135.9 (d, J = 56.7 Hz, C$_{ipso}$ of PPh$_3$), 133.1−127.4 (m, Ph). ^{31}P NMR: δ 52.4. Found: C, 64.15; H, 4.47; S, 13.69. Calcd for $C_{46}H_{35}PRuS_4$·EtOAc: C, 64.17; H, 4.60; S, 15.02%. Mass spectrum: *m/z* 848 (M$^+$), 605 (M − $S_2C_2Ph_2$)$^+$, 583 (M − PPh$_3$)$^+$. UV−vis spectrum λ_{max} = 680 nm (ε = 21307 M^{-1} cm^{-1}), 552 nm (ε = 2623 M^{-1} cm^{-1}), 460 nm (ε = 5429 M^{-1} cm^{-1}).

Synthesis of [Ru(SCH=CPhS)$_2$(PPh$_3$)] 3b. (i). By Dithiolene Transfer. To a solution of [Ni(SCH=CPhS)$_2$] (58.0 mg, 0.15 mmol) in toluene, [RuCl$_2$(PPh$_3$)$_3$] (71.0 mg, 0.07 mmol) was added and the mixture was heated to reflux for 4 h. The solvent was removed in vacuo, and the solid residue was redissolved in dichloromethane and adsorbed onto silica, which was loaded onto a silica column prepared in light petroleum or hexanes. Elution of the column with hexane-dichloromethane (5:1) produced a dark green band of unreacted [Ni(SCH=CPhS)$_2$]. A 3:1 mixture of the same solvents was then used to elute a turquoise band of [Ru(SCH=CPhS)$_2$(PPh$_3$)] (41.7 mg, 80%).

Data for **3b**: ^{1}H NMR δ 9.79 (s, 2 H, H of dithiolene), 7.72−6.82 (m, 25 H, Ph). ^{13}C NMR δ 183.3 (CPh), 165.9 (CH), 140.9 (C$_{ipso}$ of dithiolene), 135.5 (s, C$_{ipso}$ of PPh$_3$), 133.6−125.6 (m, Ph). ^{31}P NMR δ 52.5. Found: C, 58.78; H, 3.97; S, 18.28. Calcd for $C_{34}H_{27}PRuS_4$: C, 58.68; H, 3.91; S, 18.43%. Mass spectrum: *m/z* 696 (M$^+$), 561 (M − SCH=CPhS)$^+$, 434 (M − PPh$_3$)$^+$. UV−vis spectrum: λ_{max} = 821 nm (ε = 6570 M^{-1} cm^{-1}), 580 nm (ε = 394 M^{-1} cm^{-1}).

(ii). From 4-Phenyl-1,3-dithiol-2-one. Hexane-washed sodium (0.0240 g, 1.03 mmol) was dissolved in methanol (2.25 mL), and this solution was added to a slurry of 4-phenyl-1,3-dithiol-2-one (0.1003 g, 0.52 mmol) in methanol. After the mixture was stirred at room temperature for 1 h, the resulting dithiolene dianion solution was cooled to −78 °C. Over a period of 25 min, [RuCl$_2$(PPh$_3$)$_3$] (0.2502 g, 0.26 mmol) dissolved in THF was added dropwise with stirring. The solvent was removed, and the solid residue was redissolved in dichloromethane and adsorbed onto silica, which was loaded onto a silica column prepared in hexanes. Elution of the column with hexane-dichloromethane (3:1) produced a turquoise band of **3b** (0.0814 g, 45%).

Synthesis of [RuCl$_2$($S_2C_2Ph_2$)(PPh$_3$)$_2$] 4a. A solution of [Ni($S_2C_2Ph_2$)$_2$] (158.4 mg, 0.29 mmol) and [RuCl$_2$(PPh$_3$)$_3$] (280.1 mg, 0.29 mmol) in toluene was stirred at room temperature for 10 min, causing a color change from green to purple. The solvent was removed in vacuo, and the solid residue washed with diethyl ether. Recrystallization from dichloromethane-hexane afforded the pure product (234.4 mg, 87%).

Data for **4a**: ^{1}H NMR: δ 7.66−7.10 (m, Ph). ^{13}C NMR: δ 209.7 (CPh), 141.0 (C$_{ipso}$ of dithiolene), 134.2 (s, C$_{ipso}$ of PPh$_3$), 134.1−127.5 (m, Ph). ^{31}P NMR: δ 12.9. Found: C, 63.86; H, 4.09; Cl, 7.45; S, 5.01. Calcd for $C_{50}H_{40}Cl_2P_2RuS_2$: C, 63.96; H, 4.29; Cl, 7.55; S, 6.83%. Mass spectrum *m/z* 903 (M − Cl)$^+$, 641 (M − PPh$_3$)$^+$. UV−vis spectrum: λ_{max} = 665 nm (ε = 2729 M^{-1} cm^{-1}), 551 nm (ε = 4802 M^{-1} cm^{-1}).

Synthesis of [RuCl$_2$(SCH=CPhS)(PPh$_3$)$_2$] 4b. Solid [RuCl$_2$(PPh$_3$)$_3$] (200.7 mg, 0.21 mmol) was added to a solution of [Ni(SCH=CPhS)$_2$] (82.0 mg, 0.21 mmol) in toluene which was then stirred at room temperature for 10 min. The solvent was removed in vacuo, and the solid residue triturated with diethyl ether. Recrystallization from dichloromethane-hexane afforded the pure purple product (141.5 mg, 79%).

Data for **4b**: ^{1}H NMR: δ 10.18 (s, 1 H, H of dithiolene), 7.88−6.85 (m, 20 H, Ph). ^{13}C NMR: δ 210.4 (CPh), 196.1 (CH), 138.5−125.8 (m, Ph). ^{31}P NMR: δ 10.7. Found: C, 61.16; H, 4.20; Cl, 8.20; S, 6.41. Calcd for $C_{44}H_{36}Cl_2P_2RuS_2$: C, 61.25; H, 4.21; Cl, 8.22; S, 7.43%. Mass spectrum: *m/z* 827 (M − Cl)$^+$. UV−vis spectrum: 642 nm (ε = 1010 M^{-1} cm^{-1}), 528 nm (ε = 3029 M^{-1} cm^{-1}).

Synthesis of [Ru(SCH=CPhS)($S_2C_2Ph_2$)(PPh$_3$)] 3c. To a slurry of 4-phenyl-1,3-dithiol-2-one (0.0713 g, 0.367 mmol) in methanol was added a solution of NaOMe, freshly prepared by dissolving sodium (0.0264 g, 1.148 mmol) in dry methanol (2.84 mL). After stirring the mixture at room temperature for 1 h, it was cooled to −78 °C, and a solution of [RuCl$_2$($S_2C_2Ph_2$)(PPh$_3$)$_2$] (0.3365 g, 0.358 mmol) in THF was added dropwise. The solvent was removed in vacuo, and the solid residue redissolved in dichloromethane, adsorbed onto silica, and loaded onto a silica column. Elution of the column with hexane-dichloromethane (3:1) produced a turquoise band of **3c** (0.2002 g, 72%).

Data for **3c**: ^{1}H NMR δ 9.93 (s, 1 H, CH), 7.80−6.95 (m, 30 H, Ph). ^{13}C NMR δ 183.0 (CPh), 179.5 (CPh), 165.7 (CH), 143.2−127.2 (Ph). ^{31}P NMR δ 52.2. Found: C, 62.54; H, 4.29; S, 16.96. Calcd for $C_{40}H_{31}PRuS_4$: C, 62.23; H, 4.05; S, 16.61%. Mass spectrum *m/z* 772 (M$^+$). UV−vis spectrum: λ_{max} = 669 nm (ε = 16814 M^{-1} cm^{-1}), 547 nm (ε = 2419 M^{-1} cm^{-1}), 458 nm (ε = 3603 M^{-1} cm^{-1}).

Synthesis of [Ru(SCH=CFcS)$_2$(PPh$_3$)] 3d. A solution of [RuCl$_2$(PPh$_3$)$_3$] (0.2774 g, 0.289 mmol) and [Ni(SCH=CFcS)$_2$][31]

(0.3518 g, 0.580 mmol) in toluene (150 mL) was heated to reflux for 4 h. After the solvent was removed, the residue was dissolved in dichloromethane and loaded on silica preparative TLC plates, which were then run with hexane-dichloromethane (7:3). The turquoise band was quickly removed and extracted to give **3d** (55.6 mg, 21%). The complex decomposes as it travels up the plate, leaving a black streak.

Data for **3d**: ^{1}H NMR δ 9.72 (s, 2 H, CH); 7.80−6.94 (m, 15 H, Ph), 4.89 (s, 4 H, CH of Fc), 4.31 (s, 4 H, CH of Fc), 4.00 (s, 10 H, Cp). ^{13}C NMR: δ 133.1−127.3 (m, Ph), 86.8 (C_{ipso} of Fc), 70.2, 69.9 (C_5H_4), 69.6 (Cp); the dithiolene carbons were not observed. ^{31}P NMR: δ 53.4. Found: C, 55.93; H, 3.97; S, 14.77. Calcd for $C_{42}H_{35}Fe_2PRuS_4$: C, 55.33; H, 3.87; S, 14.07%. Mass spectrum m/z 912 (M^+).

Crystal Structure Determinations. The crystal data for the four structures are collected in Table 5. General procedures were as described in previous publications.[23] A Bruker Smart CCD area detector with Oxford Cryosystems low temperature system was used for data collection at 150(2) K. Complex scattering factors were taken from the program package SHELXTL as implemented on a Viglen Pentium computer.[37] Hydrogen atoms were placed geometrically and refined in riding mode (including torsional freedom for methyl groups) with U_{iso} constrained to be 1.2 times U_{eq} of the carrier atom (1.5 for methyl groups). In the structure of **4b**, the phenyl ring of the dithiolene ligand is disordered over two positions, each refined at 50% occupancy.

Acknowledgment. This work was supported by the EPSRC through a studentship awarded to A.M.C., and also by the University of Sheffield. We also thank Johnson Matthey for a generous loan of ruthenium trichloride, and the ACS Division of Inorganic Chemistry for the award of a travel grant to A.M.C. to present this work at the 236th ACS National Meeting in Philadelphia in August 2008.

Supporting Information Available: Fully labeled thermal ellipsoid plots and crystallographic information files for the four structure determinations, with NMR spectra illustrating the dithiolene ligand exchange reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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(37) Sheldrick, G. M. *SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data* (*Revision 5.1*); Bruker AXS Ltd.: Madison, WI, 1997.