Non-innocent Behaviour of Dithiocarboxylate Ligands Based on N-heterocyclic Carbenes

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While metal complexes of dithiocarbamate or xanthate ligands are well-known in the literature, only a few dithiocarboxylate compounds (LₙMS₂CR, where R is a carbon-based substituent) have been described to date.[1] This situation may be explained at least in part by the relative difficulty associated with the synthesis of dithiocarboxylate ligands compared to analogous dithiocarbamate or xanthate species. The lack of exploration in the field of dithiocarboxylate coordination chemistry may be contrasted with the explosion of interest in the use of N-heterocyclic carbenes (NHCs) as ligands over the past two decades.[2] Often seen as an excellent alternative to phosphines, these divalent carbon species have been embraced by those involved in catalysis.[3] Indeed, their tuneable, electron-rich nature, and steric bulk coupled with their lack of lability represent excellent attributes for the development of catalytic systems based on a wide range of transition metals, including ruthenium, palladium, gold and copper among many others.[4]

Although stable free carbenes were first isolated and characterized in the late 1980s,[5] the chemistry of their formal enetetramine dimers has been under investigation since the 1960s.[6] It was soon recognized that these electron-rich alkenes could be easily cleaved by various electrophiles to yield stable zwitterionic adducts.[7] This approach has been successfully extended to the reaction of free carbenes with CS₂ to afford the corresponding betaines in high yields and purities.[8] Despite this ease of preparation, the coordination chemistry of NHC•CS₂ adducts is still largely uncharted territory. Early exploratory work by Borer et al. showed that 1,3-dimethylimidazolium-2-dithiocarboxylate formed stable complexes with a number of transition metal halides or nitrates, although the intimate structure of these compounds remained elusive.[9] The organometallic chemistry of zwitterionic ligands derived from (benz)imidazolium salts such as the carbidicarbenes (or bent allenes) is also a rather unexploited field thus far.[10]

Our investigations of zwitterionic piperazine-based dithiocarbamates in the formation of multimetallic arrays[11] led to our interest in the very recent report of the compounds [RuCl(p-cymene)(NHC•CS₂)]PF₆ (p-cymene is 1-isopropyl-4-methylbenzene).[12a] This prompted us to further investigate the reaction of NHC•CS₂ betaines with transition metal complexes.[12b] An additional stimulus for this research is the low suitability of NHCs for high-valent metal centres.[12c] In contrast, NHC•CS₂ ligands would be able to combine a much greater stabilization of both high and low oxidation states, as seen for other 1,1'-dithio ligands, but with an adjustable steric profile. Here we report the synthesis and characterization of ruthenium-alkenyl complexes bearing NHC•CS₂ ligands and provide evidence of a remarkable rearrangement caused by their steric effect.

The most convenient triphenylphosphine-stabilized complexes to use as entry points for group 8 alkenyl chemistry are those of the form [Ru(CR¹=CHR²)Cl(CO)(PPh₃)₂][13] or [Ru(CR¹=CHR²)Cl(CO)(BTD)(PPh₃)₂][14] where BTD is the labile 2,1,3-benzothiadiazole ligand.
A bright red dichloromethane solution of [Ru(CH=CHC₆H₄Me-4)Cl(CO)(BTD)(PPh₃)₂] (1) was treated with a slight excess of 1,3-dicyclohexylimidazolium-2-dithiocarboxylate (ICy•CS₂) in the presence of NH₄PF₆ for an hour at room temperature (Scheme 1). The retention of the 4-tolylvinyl ligand in the product was indicated by the presence of typical features at 7.56 ppm (dt, Hα) and 5.67 ppm (dt, Hβ) in the ¹H NMR spectrum. These resonances displayed a mutual coupling of 16.8 Hz, while the former also showed coupling to the mutually trans phosphine ligands (J₃ Hp = 4.1 Hz), further confirmed by the singlet at 38.2 ppm in the ³¹P NMR spectrum. Multiplet resonances for the methylene cyclohexyl protons of the imidazolium-2-dithiocarboxylate ligand were observed between 0.85 and 1.87 ppm and a distinct, more deshielded resonance at 4.32 ppm for the methine protons adjacent to the nitrogen atoms. ¹³C NMR measurements showed characteristic features for the vinyl ligand and a triplet at 206.1 ppm (J₃ PC = 4.7 Hz) for the CS₂ moiety of the ICy•CS₂ ligand. The overall composition was confirmed by electrospray mass spectrometry (molecular ion at m/z 1079) and elemental analysis to be the expected complex [Ru(CH=CHC₆H₄Me-4)(κ²-S₂C•ICy)(CO)(PPh₃)₂]PF₆ (2). The formulation of this product was in accordance with the reaction of other dithio ligands, such as dithiocarbamates, xanthates and dithiophosphinates with vinyl precursors such as 1.

![Scheme 1. Synthesis of cationic 4-tolylvinyl complexes 2, 3 and 5. a) NHC•CS₂, NH₄PF₆, CH₂Cl₂, MeOH, RT, 1 h; b) ICy•CS₂, CH₂Cl₂, MeOH, RT, 1 h.](image)

In order to complete the characterization of 2, single crystals were grown by slow diffusion of ethanol into a dichloromethane solution of the complex, and a structural investigation undertaken by X-ray diffraction. The molecular structure depicted in Figure 1 reveals the expected
octahedral environment around the ruthenium centre with the ICy unit slightly twisted from the plane of the equatorial ligands. Structural data pertaining to the vinyl ligand are similar to those recorded previously for related thiocarbonyl–alkenyl complexes of ruthenium(II).[^19]

Figure 1. Molecular structure of complex 2 (thermal ellipsoids are shown at 50% probability). The hydrogen atoms and PF$_6^-$ counteranion are omitted for clarity.

The green cationic complex [Ru(CH=CHC$_6$H$_4$Me-4)(κ$_2$S$_2$C•IMes)(CO)(PPh$_3$)$_2$]PF$_6$ (3) was obtained in a similar fashion to 2 by treating [Ru(CH=CHC$_6$H$_4$Me-4)Cl(CO)(BTD)(PPh$_3$)$_2$] (1) with the mesityl-substituted IMes•CS$_2$ ligand[^8f] in the presence of NH$_4$PF$_6$ (Scheme 1). Spectroscopic data were largely similar to those recorded for 2 apart from the presence of resonances due to the methyl groups of the mesityl units at 1.53 (ortho) and 2.46 (para) ppm in the $^1$H NMR spectrum.

The coordinatively-unsaturated enynyl compound [Ru(C≡CPh)=CHPh)(CO)(PPh$_3$)$_2$] (4) underwent an analogous reaction with ICy•CS$_2$ to yield [Ru(C≡CPh)=CHPh)(κ$_2$-S$_2$C•ICy)(CO)(PPh$_3$)$_2$]PF$_6$ (5) in 61% yield (Scheme 1). Again, NMR data for this product were similar to those recorded for 2, other than the presence of a singlet for the HC=CH protons of the imidazole ring at 7.09 ppm, which was obscured by the other aromatic resonances in compounds 2 and 3.

Having investigated the reactivity of the vinyl complexes towards the ICy•CS$_2$ and IMes•CS$_2$ ligands, our attention turned to the more bulky derivative, 1,3-bis(2,6-
diisopropylphenyl)imidazolium-2-dithiocarboxylate (IDip•CS$_2$).\[8f\] Treatment of 4-tolylvinyl complex 1 with a slight excess of IDip•CS$_2$ in the presence of NH$_4$PF$_6$ using the same procedure that was applied to ICy•CS$_2$ and IMes•CS$_2$ afforded a pale brown solid in 62% isolated yield (Scheme 2). In this case, however, $^{31}$P NMR analysis immediately revealed that the reaction had taken a markedly different course, as a pair of doublets showing mutual coupling of 20.1 Hz were observed at 26.7 and 37.1 ppm. The inequivalence of two phosphorus nuclei suggested a mutually cis-arrangement. The retention of both the carbonyl and alkenyl ligands was confirmed by the IR spectroscopy (ν$_{CO}$ at 1962 cm$^{-1}$) and the $^1$H NMR spectrum, in which a doublet at δ 5.04 ppm ($^3$J$_{HH}$ = 15.8 Hz) was apparent for one of the alkenyl protons (the other being obscured by the aromatic resonances). The presence of the carbene moiety was evidenced by two septets at 2.35 and 2.46 ppm assigned to the isopropyl methine units of the diisopropylphenyl substituents and a singlet attributed to the central imidazole HC=CH backbone at 7.43 ppm. Additionally, a mysterious singlet was observed at 6.37 ppm, integrating to a single proton. The electrospray mass spectrum showed an abundant peak at m/z = 1271, apparently consistent with the formulation [Ru(CH=CHC$_6$H$_4$Me-4)(κ$^2$-S$_2$C•IDip)(CO)(PPh$_3$)$_2$]Cl, despite the expected elimination of NH$_4$Cl during the reaction. Elemental analysis, on the other hand, supported a structure with both a chloride and a hexafluorophosphate counteranion. To solve this contradiction, a single crystal was obtained with difficulty and a structural study undertaken.
Scheme 2. Possible mechanism for the synthesis of complex 6. a) IDip•CS\textsubscript{2}, NH\textsubscript{4}PF\textsubscript{6}, CH\textsubscript{2}Cl\textsubscript{2}, MeOH, RT, 1 h.

Although the crystals were twinned and some solvent loss occurred during data collection, the single crystal X-ray diffraction analysis showed that the phosphines were indeed mutually cis and that a chloride was present in the coordination sphere of the complex (Figure 2).\textsuperscript{18} Furthermore, migration of the alkenyl moiety onto the dithiocarboxylate ligand had apparently taken place. The crystals used for the structural determination were re-dissolved and gave identical NMR spectra to those obtained from the bulk sample. Two-dimensional NMR experiments (ROESY, COSY, HMBC, HMQC) confirmed the proton on the tetrahedral S\textsubscript{2}CHR unit to be responsible for the resonance at 6.37 ppm. In the \textsuperscript{13}C NMR spectrum, the resonance associated with the corresponding carbon had dramatically shifted upfield from 206.1 ppm in 2 to 59.5 ppm in compound 6. Mass spectrometry and elemental analysis data further supported the formulation as being [Ru{κ\textsuperscript{2}-SC(H)S(CH=CHC\textsubscript{6}H\textsubscript{4}Me-4)•IDip})Cl(CO)(PPh\textsubscript{3})\textsubscript{2}]PF\textsubscript{6} (6).

Figure 2. Structure of complex 6. For clarity, hydrogen atoms are omitted, phenyl substituents are drawn in outline, and only the heavy atoms are drawn as displacement ellipsoids (50% probability).
The rearrangement observed in product 6 is reminiscent of the phosphonium-2-dithiocarboxylate (A) / dithiomethylphosphonium (B) isomerism noted by Hector and Hill when investigating the reaction between [RuHCl(CO)(PPh3)3] and Cy3P•CS2 (Scheme 3a). It is likely that the greater steric bulk of the IDip•CS2 ligand, compared to its cyclohexyl or even mesityl-substituted analogues, forces adoption of a mutually cis arrangement of the two triphenylphosphines, therefore bringing the alkenyl and dithiocarboxylate ligands into close proximity. Nevertheless, the presence of an additional proton in complex 6 is perplexing. A possible explanation could lie with the initial formation of a carbene from the 4-tolylvinyl substituent through protonation by NH4+, followed by attack at the α-carbon by the neighbouring sulfur donor, and subsequent transfer of a proton onto the S2CR unit (Scheme 2) with addition of the still present chloride. The coupling of dithiocarbamates and carbene ligands has been observed previously (Scheme 3b) and lends some support to this aspect of the mechanism. Furthermore, performing the reaction with KPF6 instead of NH4PF6 does not lead to compound 6, but yields an intractable mixture of products instead, as does elimination of methanol (and hence dissolved NH4Cl) from the protocol.

Scheme 3. a) Relationship between phosphonium-2-dithiocarboxylate (A) and dithiomethylphosphonium ligands (B); b) Addition of dithiocarbamates to ruthenium carbene compounds.

In summary, the compounds reported here are some of the first known for the fascinating class of zwitterionic dithiocarboxylate ligands. The three NHC•CS2 betaines under investigation have been shown to exhibit reliable reactivity as conventional dithio ligands, however the valuable steric tunability of the ligands can also cause them to display non-innocent behaviour. Both these aspects are demonstrated in their coordination chemistry with the ruthenium σ-vinyl complexes employed here.
Supporting Information Available:

Detailed experimental procedures for the synthesis of complexes 2, 3, 5 and 6, and crystallographic data for the structures of 2 and 6 are available in the Supporting Information.

References


Single crystal diffraction data were collected at low temperature\textsuperscript{[22]} using an Enraf-Nonius KCCD diffractometer.\textsuperscript{[23]} The crystal structures of 2 and 6 were solved using SIR92\textsuperscript{[24]} and refined using the CRYSTALS software suite,\textsuperscript{[25]} as per the supplementary information (CIF file). The data for 6 were shown to be twinned and were dealt with using ROTAX.\textsuperscript{[26]} Crystallographic data (excluding structure factors) for 2 and 6 have been deposited with the Cambridge Crystallographic Data Centre (CCDC 767136 and 767137) and copies of these data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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\bibitem{18} Single crystal diffraction data were collected at low temperature\textsuperscript{[22]} using an Enraf-Nonius KCCD diffractometer.\textsuperscript{[23]} The crystal structures of 2 and 6 were solved using SIR92\textsuperscript{[24]} and refined using the CRYSTALS software suite,\textsuperscript{[25]} as per the supplementary information (CIF file). The data for 6 were shown to be twinned and were dealt with using ROTAX.\textsuperscript{[26]} Crystallographic data (excluding structure factors) for 2 and 6 have been deposited with the Cambridge Crystallographic Data Centre (CCDC 767136 and 767137) and copies of these data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.
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Non-innocent Behaviour of Dithiocarboxylate Ligands Based on N-heterocyclic Carbenes

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Not so innocent: Sterically tuneable dithiocarboxylate ligands derived from N-heterocyclic carbenes act as excellent bidentate chelates for ruthenium(II) σ-alkenyl complexes. However, the most sterically demanding member of the ligand family causes a fascinating and unexpected rearrangement to occur.

Keywords: ruthenium, dithiocarboxylate, alkenyl, carbene ligands
Supporting information

'Non-innocent behaviour of dithiocarboxylate ligands based on N-heterocyclic carbenes'

Saira Naeem, Amber L. Thompson, Lionel Delaude, and James D. E. T. Wilton-Ely*

S1. Experimental

S2. X-ray Single Crystal Diffraction Studies

S3. References

S1. Experimental

General Comments

All experiments were carried out under aerobic conditions and the complexes appear indefinitely stable towards the atmosphere in solution or in the solid state. Solvents were used as received from commercial sources. The complex [Ru(CH=CHC₆H₄Me-4)Cl(CO)(BTD)(PPh₃)₂][Cl] was prepared by the literature procedure only using commercially available 2,1,3-benzothiadiazole (BTD) in place of 2,1,3-benzoselenadiazole (BSD). Syntheses of the following compounds have been described elsewhere: Ru(C(C≡CPh)=CHPh)Cl(CO)(PPh₃)₂, ICy•CS₂, IMes•CS₂, and IDip•CS₂. Electrospray mass spectra were obtained using a Micromass LCT Premier instrument. Infrared data were obtained using a Perkin Elmer Paragon 1000 FT-IR spectrometer, KBr plates were used for solid state IR spectroscopy, and characteristic phosphine-associated infrared data are not reported. NMR spectroscopy was performed at 25 °C using Varian Mercury 300 or 500 spectrometers in CDCl₃ unless otherwise indicated. All couplings are in Hertz. Elemental analysis data were obtained using the service provided by London Metropolitan University.

Preparation of [Ru(CH=CHC₆H₄Me-4)(κ²-S₂C•ICy)(CO)(PPh₃)₂]PF₆ (2)

A dichloromethane solution (10 mL) of [Ru(CH=CHC₆H₄Me-4)Cl(CO)(BTD)(PPh₃)₂] (I) (100 mg, 0.106 mmol) was treated with a solution of ICy•CS₂ (36 mg, 0.117 mmol) in dichloromethane (5 mL). On addition of NH₄PF₆ (65 mg, 0.211 mmol) in methanol (5 mL), a green colouration appeared. The reaction mixture was stirred for 1 h and then all solvent removed. The residue was dissolved in dichloromethane (10 mL) and filtered through celite to remove NH₄Cl and excess NH₄PF₆. Ethanol (20 mL) was added and the solvent volume reduced to precipitate a pale green
solid. This crude product was filtered, washed with ethanol (10 mL) and hexane (10 mL), and dried. Yield: 78 mg (60%). IR (nujol/KBr): 1933 ν(CO), 1710, 1571, 1506, 1308, 1277, 1251, 1191, 1048, 941, 841 ν(PF) cm⁻¹. ¹H NMR: 0.85–1.01, 1.45–1.64, 1.74–1.87 (m × 3, Cy, 6H + 6H + 8H), 2.23 (s, CH₃, 3H), 4.32 (m, NCH², 2H), 5.67 (dt, JHβ, 1H, JHH = 16.7 Hz, JHP = 2.4 Hz), 6.30, 6.86 (AB, C₆H₄, 4H, JAB = 7.9 Hz), 7.35–7.52 (m, C₆H₅ + HC=CH, 30H + 2H), 7.56 (dt, JHα, 1H, JHH = 16.8 Hz, JHP = 4.1 Hz) ppm. ¹³C NMR: 206.1 (t, CS, JPC = 4.7 Hz), 205.2 (t, CO, JPC = 15.2 Hz), 145.4 (t, Cα, JPC = 15.3 Hz), 141.6 (t, CN₂, JPC = 2.5 Hz), 138.5 (t, Cβ, JPC = 5.3 Hz), 138.2 (t, tolyl-С₁, JPC = 5.3 Hz), 134.7 (s, CMe), 134.3 (virtual t, o/m-C₆H₅, JPC = 5.3 Hz), 133.4 (virtual t, ipso-C₆H₅, JPC = 22.4 Hz), 130.7 (s, p-C₆H₅), 128.9 (s, tolyl-C₂β), 128.7 (virtual t, o/m-C₆H₅, JPC = 5.3 Hz), 125.0 (s, tolyl-C₃β), 120.0 (s, NС₂H₂N), 59.3 (s, Cy-C₁), 34.1 (s, Cy-C₂β), 25.5 (s, Cy-C₃β), 24.5 (s, Cy-C₄), 21.1 (s, CH₃) ppm. ³¹P NMR: 38.2 ppm (s, PPh₃). MS (ES +ve) m/z (abundance): 1079 (100) [M]+. Calcd. for C₆₂H₆₃F₆N₂OP₃RuS₂: C 60.8, H 5.2, N 2.3%. Found: C 60.9, H 5.3, N 2.3%.

**Preparation of [Ru(CH=CHC₆H₄Me-4)(κ²-S₂C•IMes)(CO)(PPh₃)₂]PF₆ (3)**

A dichloromethane solution (10 mL) of [Ru(CH=CHC₆H₄Me-4)Cl(CO)(BTD)(PPh₃)₂] (1) (100 mg, 0.106 mmol) was treated with a solution of IMes•CS₂ (44 mg, 0.116 mmol) in dichloromethane (5 mL). On addition of NH₄PF₆ (81 mg, 0.213 mmol) in methanol (5 mL), a green colouration appeared. The reaction mixture was stirred for 1 h and then all solvent removed. The residue was dissolved in dichloromethane (10 mL) and filtered through celite to remove NH₄Cl and excess NH₄PF₆. Ethanol (20 mL) was added and the solvent volume reduced to precipitate a pale green solid. This crude product was filtered, washed with ethanol (10 mL) and hexane (10 mL), and dried. A second crop could be obtained from evaporation solvent from the filtrate and triturating in diethyl ether. Yield: 106 mg (77%). IR (nujol/KBr): 1934 ν(CO), 1606, 1552, 1310, 1230, 1185, 840 ν(PF) cm⁻¹. ¹H NMR: 1.53 (s, o-CH₃, 12H), 2.29 (s, tolyl-CH₃, 3H), 2.46 (s, p-CH₃, 6H), 5.05 (dt, JHβ, 1H, JHH = 17.0 Hz, JHP = 2.0 Hz), 5.84, 6.66 (AB, C₆H₄, 4H, JAB = 7.7 Hz), 6.94 (s, m-CH, 4H), 6.91–7.36 (m, C₆H₅ + HC=CH + Hα, 15H + 2H + 1H) ppm. ³¹P NMR: 40.1 ppm (s, PPh₃). MS (ES +ve) m/z (abundance): 1151 (100) [M]+. Calcd. for C₆₈H₆₃F₆N₂OP₃RuS₂: C 63.0, H 4.9, N 2.2%. Found: C 63.1, H 4.9, N 2.3%.

**Preparation of [Ru(C(C≡CPh)=CHPh)(κ²-S₂C•ICy)(CO)(PPh₃)₂]PF₆ (5)**

A dichloromethane solution (10 mL) of [Ru(C(C≡CPh)=CHPh)Cl(CO)(PPh₃)₂] (4) (100 mg, 0.112 mmol) was treated with a solution of ICy•CS₂ (38 mg, 0.123 mmol) in dichloromethane (5 mL). On addition of NH₄PF₆ (37 mg, 0.227 mmol) in methanol (5 mL), a green colouration appeared. The
reaction mixture was stirred for 1 h and then all solvent removed. The residue was dissolved in dichloromethane (10 mL) and filtered through celite to remove NH₄Cl and excess NH₄PF₆. Ethanol (20 mL) was added and the solvent volume reduced to precipitate a pale green solid. This crude product was filtered, washed with ethanol (10 mL) and hexane (10 mL), and dried. A second crop could be obtained from evaporation solvent from the filtrate and triturating in diethyl ether. Yield: 89 mg (61%). IR (nujol/KBr): 2143 v(C=O), 1941 v(CO), 1593, 1562, 1307, 1250, 1189, 1049, 940, 915, 839 v(PF) cm⁻¹. ¹H NMR: 0.77–0.90, 1.49–1.65, 1.70–1.80 (m × 3, Cy, 20H), 4.32 (m, NCH₁⁻, 2H), 6.03 (t, Hβ, 1H, J_HH = 2.1 Hz), 7.09 (s, HC=CH, 2H), 7.19–7.55 (m, C₆H₅, 40H) ppm. ₃¹P NMR: 36.2 ppm (s, PPh₃). MS (ES +ve) m/z (abundance): 1165 (100) [M]+. Calcd. for C₆₀H₆₅F₆N₂OP₃RuS₂: C 63.2, H 5.0, N 2.1%. Found: C 63.3, H 5.1, N 2.2%.

**Preparation of [Ru(κ²-SC(H)S(=CHC₆H₄Me-4)-IDip)]Cl(CO)(PPh₃)₂PF₆** (6)
A dichloromethane solution (10 mL) of [Ru(CH=CHC₆H₄Me-4)Cl(CO)(BTD)(PPh₃)₂] ([1] (50 mg, 0.053 mmol) was treated with a solution of IDip•CS₂ (25 mg, 0.054 mmol) in dichloromethane (5 mL). After addition of NH₄PF₆ (17 mg, 0.104 mmol) in methanol (5 mL) the reaction mixture was stirred for 2 h and then all solvent removed. The residue was dissolved in dichloromethane (10 mL) and filtered through celite to remove NH₄Cl and excess NH₄PF₆. Ethanol (20 mL) was added and the solvent volume reduced to precipitate a pale brown solid. This crude product was filtered, washed with ethanol (10 mL) and hexane (10 mL), and dried. Yield: 45 mg (62%). IR (nujol/KBr): 1962 v(CO), 1556, 1511, 1388, 1367, 1326, 1274, 1183, 835 v(PF) cm⁻¹. ¹H NMR (500 MHz, CD₂Cl₂): 1.05 (d, aryl-CH₃, 6H, J_HH = 6.7 Hz), 1.07 (d, aryl-CH₃, 6H, J_HH = 7.0 Hz), 1.13 (d, aryl-CH₃, 6H, J_HH = 7.0 Hz), 1.33 (d, aryl-CH₃, 6H, J_HH = 6.7 Hz), 2.34 (s, tolyl-CH₃, 3H), 2.35, 2.46 (sept. × 2, CHMe₂, 2 × 2H, J_HH = 6.7 Hz), 5.04 (d, Hβ, 1H, J_HH = 15.8 Hz), 6.37 (s, 1H, CHS), 6.89 (d, C₆H₄, 2H, J_HH = 8.1 Hz), 6.99–7.06, 7.10–7.15, 7.24–7.29, 7.34–7.36 (m × 4, C₆H₅ + m-C₆H₃ + C₆H₄ + Hα, 30H + 2H + 2H + 1H), 7.43 (s, HC=CH, 2H), 7.52 (dd, m-C₆H₃, 2H, J_HH = 7.9 Hz, 1.2 Hz), 7.72 (t, p-C₆H₃, 2H, J_HH = 7.9 Hz) ppm. ¹³C NMR (500 MHz, CD₂Cl₂): 198.1 (t, CO, J_PC = 12.9 Hz), 147.6 (t, NCN, J_PC = 2.9 Hz), 146.0, 145.9 (s × 2, o-C₆H₃), 140.8 (tolyl-C₄), 138.9 (s, SC=C), 134.7 (d, o-PC₆H₅, J_PC = 10.5 Hz), 134.6 (d, o-PC₆H₅, J_PC = 9.5 Hz), 133.5 (d, ipso-PC₆H₅, J_PC = 47.7 Hz), 132.9 (s, p-C₆H₃), 132.4 (d, ipso-PC₆H₅, J_PC = 40.1 Hz), 131.8 (s, ipso-C₆H₄), 130.6 (d, p-PC₆H₅, J_PC = 2.8 Hz), 130.5 (d, p-PC₆H₅, J_PC = 1.9 Hz), 130.0, 130.6 (s, ipso-C₆H₄), 129.8 (s, m-C₆H₄), 128.7 (d, m-PC₆H₅, J_PC = 9.5 Hz), 128.1 (d, m-PC₆H₅, J_PC = 10.5 Hz), 127.8 (s, o-C₆H₄), 125.9 (s, HC=CH), 125.4, 125.0 (s × 2, m-C₆H₃), 113.7 (SC=C), 59.5 (S₂CH), 30.4, 30.1 (s × 2, CHMe₂), 26.3, 26.2, 23.2, 22.3 (s × 4, Prᵢ-CH₃), 21.6 (s, tolyl-CH₃) ppm. ₃¹P NMR (500 MHz, CD₂Cl₂): 26.7, 37.1 ppm (d × 2, PPh₃, J_pp = 20.1 Hz). MS (ES +ve) m/z
(abundance): 1271 (100) [M]+, 1236 (68) [M−Cl]+. Calcd. for C74H76ClF6N2OP3Ru2: C 62.7, H 5.4, N 2.0%. Found: C 62.4, H 5.2, N 1.9%.

S2. X-ray Single Crystal Diffraction Studies

Crystals of 2 and 6 were grown by slow diffusion of ethanol into a dichloromethane solution of the complexes. Single crystal X-ray diffraction data were collected using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) on an Enraf-Nonius KappaCCD diffractometer. The diffractometer was equipped with a Cryostream N₂ open-flow cooling device, and the data were collected at 150(2) K. Series of ω-scans were performed in such a way as to cover a sphere of data to a maximum resolution between 0.70 and 0.77 Å. Cell parameters and intensity data for 2 and 6 were processed using the DENZO-SMN package. Intensities were corrected for absorption effects by the multi-scan method based on multiple scans of identical and Laue equivalent reflections (using the SCALEPACK). The structures were both solved by direct methods using SIR92 and refined by full-matrix least-squares on F² using the CRYSTALS software suite.

All non-hydrogen atoms were refined with anisotropic displacement parameters and in general, the hydrogen atoms were visible in the difference map, refined with soft restraints to give the starting positions for a riding model. In the case of complex 6, structure refinement was complicated by the presence of twinning, so ROTAX was used within CRYSTALS to determine a twin law (rotation of 180° around the [1 0 0] direct lattice direction, twin scale factor 0.402(2)). Data quality was further reduced by damage to the crystal thought to be caused by solvent loss. The combined effect of this and the twinning caused data processing difficulties exacerbated by the slight weakness of the data. Although, inclusion of restraints improved the refinement convergence leading to reduce the R-indices, the results are less than optimal. However, the connectivity seems in little doubt, especially when taken together with the other analytical data, and the structure is included given the insight it gave to the structure of the dithioimidazolium betaine. See the CIF for further details.

Crystal data and structure refinement parameters are included in Table 1. Crystallographic data (excluding structure factors) for the structures of 2 and 6 will be deposited with the Cambridge Crystallographic Data Centre (CCDC 767136 and 767137). Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Table 1. Crystallographic Data for Complexes 2 and 6.

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<thead>
<tr>
<th>Complex</th>
<th>2</th>
<th>6</th>
</tr>
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<tbody>
<tr>
<td>Chemical Formula</td>
<td>C_{62}H_{63}F_{6}N_{2}OP_{3}Ru_{2}</td>
<td>C_{74.50}H_{77}Cl_{2}F_{6}N_{2}O_{1}P_{3}RuS_{2}</td>
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<tr>
<td>Fw</td>
<td>1224.31</td>
<td>1459.46</td>
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<td>Crystal system</td>
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<td>monoclinic</td>
</tr>
<tr>
<td>Crystal color</td>
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<td>yellow block</td>
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<td>Crystal size (mm)</td>
<td>0.22 x 0.16 x 0.06</td>
<td>0.09 x 0.21 x 0.40</td>
</tr>
<tr>
<td>Space group</td>
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<td>P 21/n</td>
</tr>
<tr>
<td>a (Å)</td>
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<td>13.4320(2)</td>
</tr>
<tr>
<td>b (Å)</td>
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<td>14.4151(2)</td>
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<tr>
<td>c (Å)</td>
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<td>37.1742(4)</td>
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<tr>
<td>β (°)</td>
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<td>93.1758(5)</td>
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<tr>
<td>V (Å³)</td>
<td>5539.19(9)</td>
<td>7186.75(16)</td>
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<tr>
<td>Z</td>
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<td>4</td>
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<tr>
<td>D_{calc} (g/cm³)</td>
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<td>1.349</td>
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<td>T (K)</td>
<td>150(2)</td>
<td>150(2)</td>
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<tr>
<td>μ(Mo Kα) (mm⁻¹)</td>
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<td>0.477</td>
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<td>F(000)</td>
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<td>3020</td>
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<td>Reflections collected</td>
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<td>22441</td>
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<td>Unique reflections (R_{int})</td>
<td>12640 (0.087)</td>
<td>14461(0.053)</td>
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<tr>
<td>R₁ (I&gt;2σ(I))</td>
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<td>0.1074</td>
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<tr>
<td>wR₂ (all data)</td>
<td>0.1281</td>
<td>0.2542</td>
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</tbody>
</table>

S3. References