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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 (L_nMS_2CR, in which 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 with 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 characterised in the late 1980s,[5] the chemistry of their formal enetetramine dimers has been under investigation since the 1960s.[6] It was soon recognised 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 CS_2 to afford the corresponding betaines in high yields and purities.[8] Despite this ease of preparation, the coordination chemistry of NHC·CS_2 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 carbodicarbenes (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·CS_2)][PF_6] (*p*-cymene = 1-isopropyl-4-methylbenzene).[12a] This prompted us to further investigate the reaction of NHC·CS_2 betaines with transition-metal complexes.[12b] An additional stimulus for this research is the low suitability of NHCs for high-valent metal centres.[2c] In contrast, NHC·CS_2 ligands would be able to combine a much greater stabilisation of both high and low oxidation states, as seen for other 1,1′-dithio ligands, but with an adjustable steric profile. Herein, we report the synthesis and characterisation of ruthenium–alkenyl complexes with NHC·CS_2 ligands and provide evidence of a remarkable rearrangement caused by their steric effect.

The most convenient triphenylphosphine-stabilised complexes to use as entry points for Group 8 alkenyl chemistry are those of the form [Ru(CR^1=CHR^2)Cl(CO)(PPh_3)$_2$][13] or [Ru(CR^1=CHR^2)Cl(CO)(btd)(PPh_3)$_2$],[14] in which BTD is the labile 2,1,3-benzothiadiazole ligand. A bright red solution of [Ru(CH=CHC_6H_4Me-4)Cl(CO)(btd)(PPh_3)$_2$] (**1**) in dichloromethane was treated with a slight excess of 1,3-dicyclohexylimidazolium-2-dithiocarboxylate (ICy·CS_2)[8f] in the presence of NH_4PF_6 for an hour at room temperature (Scheme 1). The retention of the 4-tolylvinyl ligand in the

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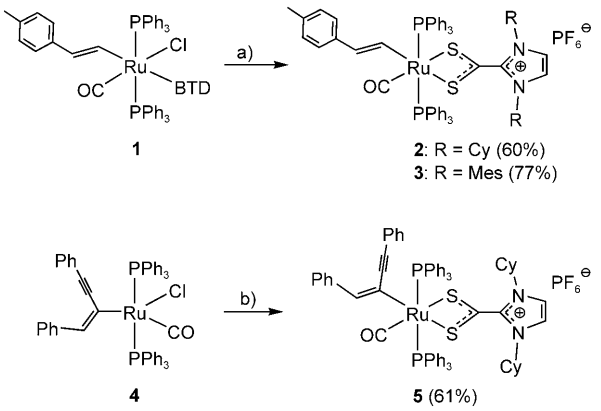
Supporting information (detailed experimental procedures for the synthesis of complexes **2**, **3**, **5** and **6**, and crystallographic data for the structures of **2** and **6**) for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201001235.



Scheme 1. Synthesis of cationic 4-tolylvinyl complexes **2**, **3** and **5**. a) NHC·CS_2, NH_4PF_6, CH_2Cl_2, MeOH, RT, 1 h; b) ICy·CS_2, CH_2Cl_2, MeOH, RT, 1 h.

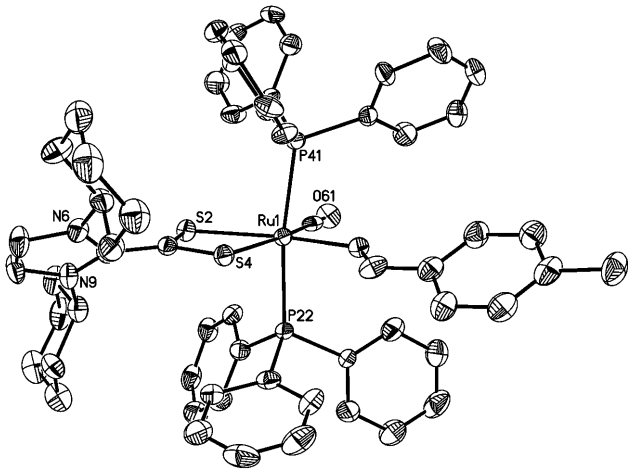


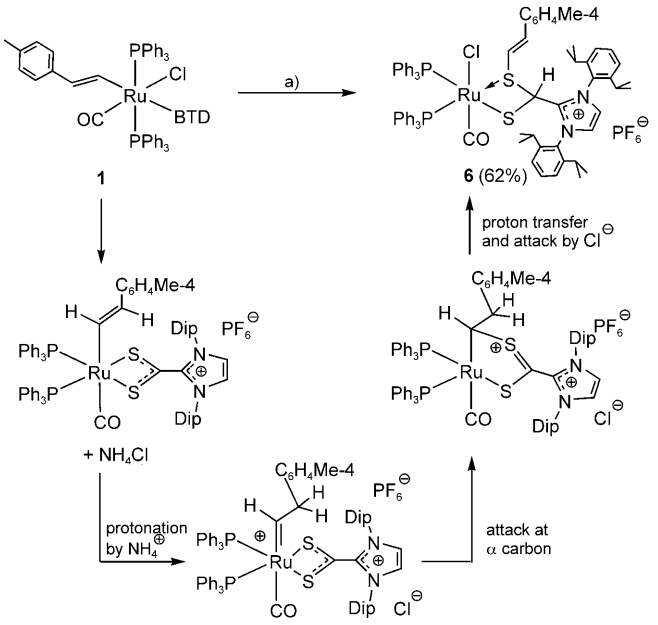
Figure 1. Molecular structure of complex **2** (thermal ellipsoids are shown at 50% probability). The hydrogen atoms and PF_6^- counteranion are omitted for clarity.

product was indicated by the presence of typical features at $\delta = 7.56$ (dt, Hα) and 5.67 ppm (dt, Hβ) in the ^{1}H NMR spectrum. These resonances displayed a mutual coupling of 16.8 Hz, while the former also showed coupling to the mutually *trans*-phosphine ligands (^3J(H,P) = 4.1 Hz), further confirmed by the singlet at $\delta = 38.2$ ppm in the ^{31}P NMR spectrum. Multiplet resonances for the methylene cyclohexyl protons of the imidazolium-2-dithiocarboxylate ligand were observed between $\delta = 0.85$ and 1.87 ppm and a distinct, more deshielded resonance at $\delta = 4.32$ ppm for the methine protons adjacent to the nitrogen atoms. ^{13}C NMR measurements showed characteristic features for the vinyl ligand and a triplet at $\delta = 206.1$ ppm (^3J(P,C) = 4.7 Hz) for the CS_2 moiety of the ICy·CS_2 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=CHC_6H_4Me-4)(κ^2-S_2C·ICy)(CO)(PPh_3)$_2$][PF_6] (**2**). The formulation of this product was in accordance with the reaction of other dithio ligands, such as dithiocarbamates,[11a,15] xanthates[16] and dithiophosphinates,[17] with vinyl precursors such as **1**.

To complete the characterisation of **2**, single crystals were grown by slow diffusion of ethanol into a solution of the complex in dichloromethane, and a structural investigation undertaken by X-ray diffraction.[18] 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]

The green cationic complex [Ru(CH=CHC_6H_4Me-4)(κ^2-S_2C·IMes)(CO)(PPh_3)$_2$][PF_6] (**3**) was obtained in a similar fashion to **2** by treating **1** with the mesityl-substituted IMes·CS_2 ligand[8f] in the presence of NH_4PF_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 $\delta = 1.53$ (*ortho*) and 2.46 ppm (*para*) in the ^{1}H NMR spectrum. The coordinatively unsaturated enynyl compound [Ru{C(C≡CPh)=CHPh}Cl(CO)(PPh_3)$_2$] (**4**) underwent an analogous reaction with ICy·CS_2 to yield [Ru{C(C≡CPh)=CHPh}(κ^2-S_2C·ICy)(CO)(PPh_3)$_2$][PF_6] (**5**) in 61% yield (Scheme 1). Again, NMR spectroscopy 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 $\delta = 7.09$ 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_4PF_6 by 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 spectroscopy analysis immediately revealed that the reaction had taken a markedly different course, since a pair of doublets showing mutual coupling of 20.1 Hz were observed at $\delta = 26.7$ 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 $\delta = 5.04$ ppm (^3J(H,H) = 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 $\delta = 2.35$ 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 $\delta = 7.43$ ppm. Additionally, a mysterious singlet was observed at $\delta = 6.37$ 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_6H_4Me-4)(κ^2-S_2C·IDip)(CO)(PPh_3)$_2$][Cl], despite the expected elimination of NH_4Cl



Scheme 2. Possible mechanism for the synthesis of complex **6**. a) IDip•CS_2, NH_4PF_6, CH_2Cl_2, MeOH, RT, 1 h.

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.

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).[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_2CHR unit to be responsible for the resonance at $\delta =$ 6.37 ppm. In the ^{13}C NMR spectrum, the resonance associated with the corresponding carbon had dramatically shifted upfield from $\delta = 206.1$ ppm in **2** to $\delta = 59.5$ ppm in compound **6**. Mass spectrometry and elemental analysis data further supported the formulation as being [Ru{κ^2-SC(H)S(CH=CHC_6H_4Me-4)•IDip)}Cl(CO)$(PPh_3)_2$][PF_6] (**6**).

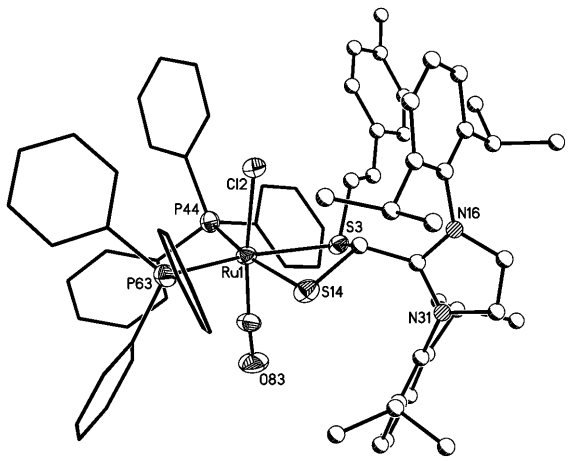
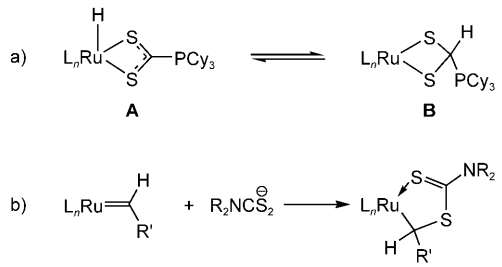


Figure 2. Structure of complex **6**. For clarity, hydrogen atoms are omitted, phenyl substituents are drawn in outline and only the heavy atoms are drawn as displacement ellipsoids (50% probability).

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)$(PPh_3)_3$] and Cy_3P•CS_2 (Scheme 3a).[17] It is likely that the greater steric bulk of the IDip•CS_2 ligand, compared with 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 NH_4^+, followed by attack at the α carbon by the neighbouring sulfur donor, and subsequent transfer of a proton onto the S_2CR unit (Scheme 2) with addition of the still present chloride. The coupling of dithiocarbamates and carbene ligands has been observed previously (Scheme 3b)[20] and lends some support to this aspect of the mechanism. Furthermore, performing the reaction with KPF_6 instead of NH_4PF_6 does not lead to compound **6**, but yields an intractable mixture of products instead, as does elimination of methanol (and hence dissolved NH_4Cl) 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 herein are some of the first known for the fascinating class of zwitterionic dithiocarboxylate ligands. The three NHC•CS_2 betaines under investigation have been shown to exhibit reliable reactivity as conventional dithio ligands,[21] 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 herein.

Keywords: alkene ligands · carbene ligands · dithiocarboxylates · ruthenium

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[18] Single crystal diffraction data were collected at low temperature[22] by using an Enraf–Nonius KCCD diffractometer.[23] The crystal structures of **2** and **6** were solved by using SIR92[24] and refined by using the CRYSTALS software suite,[25] as per the Supporting Information (CIF file). The data for **6** were shown to be twinned and were dealt with using ROTAX.[26] CCDC-767136 (**2**) and 767137 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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