

Heterotrimetallic complexes of iron, ruthenium and palladium based on vinyliminium dithiocarboxylate ligands.

Lorenzo Mognon,[†] Samuel Richardson,[†] Gabriele Agonigi,[‡] Fabio Marchetti^{*‡} and James D. E. T. Wilton-Ely^{*†}

[†] *Department of Chemistry, Imperial College London, Molecular Sciences Research Hub, White City Campus, London W12 7SB, UK.*

[‡] *Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Moruzzi 13, 56124 Pisa, Italy.*

e-mail: fabio.marchetti1974@unipi.it
j.wilton-ely@imperial.ac.uk

Abstract

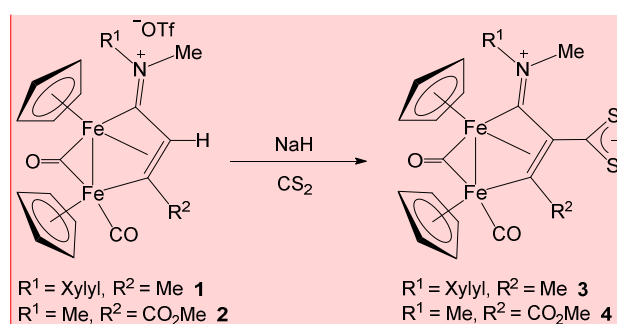
The diiron vinyliminium compounds $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(R}^2\text{)=C(H)C=N(Me)R}^1\}\{\mu\text{-CO}\}\{\text{CO}\}\{\text{Cp}\}_2]$ ($\text{R}^1 = \text{Xyl} = 2,6\text{-C}_6\text{H}_3\text{Me}_2$, $\text{R}^2 = \text{Me}$; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{CO}_2\text{Me}$) provide a versatile entry point for many subsequent transformations, such as their reaction with carbon disulfide to provide zwitterionic dithiocarboxylate products. These compounds react with the coordinatively-unsaturated ruthenium vinyl precursors $[\text{Ru}(\text{CH=CHR}^3)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ ($\text{R}^3 = \text{C}_6\text{H}_4\text{Me-4}$, 1-Pyrenyl) to yield heterotrimetallic Fe_2Ru compounds, exhibiting vinyl moieties at both iron and ruthenium centres.

Keywords: Ruthenium, diiron, dithiocarboxylate, multimetallics

Introduction

The ability to bring multiple metals together within the same molecular framework opens up the possibility of many fascinating interactions. These have been exploited in many areas, including catalysis,¹ sensing² and imaging.³ In particular, diiron assemblies are very well known and heavily investigated due to their important role in nature,⁴ such as hemerythrin, which reversibly binds dioxygen⁵ and [FeFe] hydrogenases.⁶ Many pioneering investigations have employed diiron units in the cleavage of challenging C-H and O-H bonds,⁷ oxidation of methane⁸ or form ammonia as a nitrogenase mimic.⁹ In many examples, the accessibility of different oxidation states is fundamental to the action of these diiron systems,¹⁰ which once again relies on the redox potential of the two iron centres in order to function. This has been used by Gibson and Long to modulate the lactide polymerisation behaviour of a ferrocenyl-derivatised salen-based ligand bonded to a titanium centre.¹¹ In oxidised form, the resulting positively charged complex is found to be a significantly less effective catalyst due to the electron withdrawing effect, allowing block copolymers to be prepared through sequential addition of monomers. This redox-switch catalysis is also explored in this contribution.

The potential for diiron units to be used themselves as ligands was indicated by the work of Busetto and Marchetti and coworkers, who prepared a series of vinyliminium diiron complexes (**1** and **2** in Scheme 1), which are susceptible to a variety of nucleophilic additions.¹²⁻¹³ Furthermore, ~~in contrast to the non-metallated conjugated iminium species,~~ these μ -vinyliminium ligands undergo deprotonation of the ~~the~~ α -C-H proton,¹⁴ which has been exploited to introduce a variety of substituents and functionalities into the diiron frame.¹⁵ In particular, the C-H activation in the presence of the heteroallene, CS₂, leads to the zwitterionic dithiocarboxylates shown in Scheme 1.¹⁶



Scheme 1. Preparation of diiron dithiocarboxylate betaine complexes **3** and **4**.

Commento [fabmar1]: once defined in the abstract, we may use "Xyl"

In recent years, our investigations have concentrated on the additional functionality afforded to metal complexes and gold nanoparticles by the addition of dithiocarbamate¹⁷ and xanthate¹⁸ ligands. In particular, their application in the formation of multimetallic assemblies is noteworthy.¹⁹ These studies on 1,1'-dithio ligands have been extended to ~~the investigation of dithiocarboxylate betaines based on N-heterocyclic carbenes (NHCs).~~²⁰

Commento [fabmar2]:

In this contribution, the dithiocarboxylate betaines shown in Scheme 1 are employed to form multimetallic compounds with other group 8 metals, forming heterotrinnuclear assemblies. In contrast to previous work, the availability of a 1,1'-dithio ligand with intimate connection to the diiron unit offers the possibility of influencing the behaviour of the metal centre to which the dithiocarboxylate is attached.

Results and Discussion

Ruthenium vinyl compounds of the form $[\text{Ru}(\text{CH}=\text{CHR})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ ²¹ and $[\text{Ru}(\text{CH}=\text{CHR})\text{Cl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$ (BTD = 2,1,3-benzothiadiazole)²² are readily accessible through hydorruthenation of alkynes by hydride precursors (R = alkyl or aryl substituents). These vinyl compounds have proved versatile precursors for many further transformations, including the addition of mono- and polydentate ligands.²³ The BTD compounds $[\text{Ru}(\text{CH}=\text{CHR})\text{Cl}(\text{CO})(\text{L})(\text{PPh}_3)_2]$ (L = BTD, thienyl-BTD) have recently been employed as highly selective and sensitive probes for carbon monoxide.²⁴

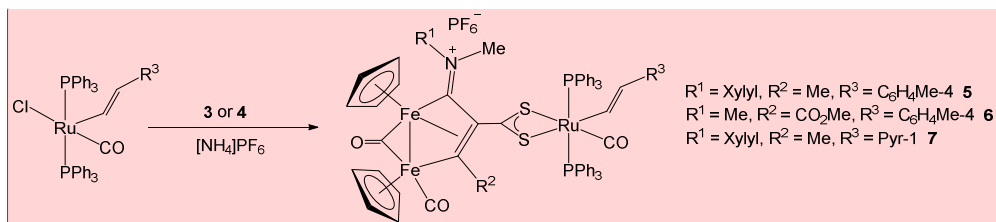
The two zwitterionic dithiocarboxylate complexes used in this study were chosen on the basis of their differing steric profiles. The diiron compound, $[\text{Fe}_2\{\mu-\eta^1:\eta^3\text{-C}(\text{Me})=\text{C}(\text{CS}_2)\text{C}=\text{N}(\text{Me})\text{Xyl}\}\{\mu\text{-CO}\}(\text{CO})(\text{Cp})_2]$ (**3**), has been reported previously,¹⁶ whereas the analogue, $[\text{Fe}_2\{\mu-\eta^1:\eta^3\text{-C}(\text{CO}_2\text{Me})=\text{C}(\text{CS}_2)\text{C}=\text{NMe}_2\}\{\mu\text{-CO}\}(\text{CO})(\text{Cp})_2]$ (**4**), was prepared for this study, in a moderate yield. Compound **4** has a less pronounced steric profile due to the less bulky NMe_2 and $\text{C}^{\delta-}$ -ester group. Due also to the presence of the CO_2Me ester group, **4** is less soluble in common organic solvents compared to **3**. The ¹H NMR spectrum of **4** displayed three methyl singlet resonances in the higher field region, at 3.28, 3.80 and 4.08 ppm. The former were attributed to the NMe_2 group and the latter to the CO_2Me ester unit. The spectrum was completed by two singlets at 5.12 and 5.25 ppm for the two cyclopentadienyl ligands.

Commento [fabmar3]: I don't think the low yield is related to low solubility

Reaction of $[\text{Fe}_2\{\mu-\eta^1:\eta^3\text{-C}(\text{Me})=\text{C}(\text{CS}_2)\text{C}=\text{N}(\text{Me})(\text{Xyl})\}\{\mu\text{-CO}\}(\text{CO})(\text{Cp})_2]$ (**3**) with coordinatively-unsaturated $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{Me-4})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ and NH_4PF_6 in dichloromethane led to an immediate darkening of the solution. While anaerobic conditions were used as a precaution, the dark brown product isolated appeared to be indefinitely stable in air and light. The solid state infrared spectrum proved particularly diagnostic as the

absorptions for the terminal and bridging carbonyl ligands of the diiron unit were retained in the product at 1982 and 1820 cm^{-1} , respectively, alongside a new band at 1929 cm^{-1} , attributed to the Ru-CO ligand. In contrast to the singlet at 30.9 ppm observed for the precursor, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the product showed a pair of doublets at 37.2 and 39.6 ppm ($^2J_{\text{PP}} = 282$ Hz), showing substantial roofing effects. This indicated the inequivalence of the two phosphorus nuclei due to the orientation of the diiron unit. The ^1H NMR spectrum displayed the expected features for the diiron unit with resonances attributed to the Cp ligands at 4.58 and 5.23 ppm as well as the methyl groups of the vinyliminium and xylyl substituents between 1.80 and 3.36 ppm. It was not possible to unequivocally assign the methyl protons of the tolyl substituent, however, the presence of the ruthenium-bound vinyl ligand was confirmed by resonances for the H_β at 5.71 ppm ($^3J_{\text{HH}} = 16.0$ Hz). The resonance for the H_β proton was obscured by the aromatic protons of the triphenylphosphine ligands. A molecular ion at m/z 1330 in the electrospray mass spectrum (+ve mode) confirmed the overall composition for **5** as that shown in Scheme 2:

Commento [fabmar4]: there is a substantial decrease in the chemical shift for one Cp ligand. In principle, this might be due to electronic effect of the ruthenium complex, or to cis to trans rearrangement, anyway I believe that this latter is unlikely on considering steric factors. Probably the best choice is not to comment.



Scheme 2. Preparation of heterotrimetallic group 8 complexes **5 - 7**.

Commento [fabmar5]: "Xyl" instead of "xylyl"?

The analogous reaction of the new diiron compound, $[\text{Fe}_2\{\mu-\eta^1:\eta^3\text{-C}(\text{CO}_2\text{Me})=\text{C}(\text{CS}_2)\text{C}=\text{NMe}_2\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2]$ (**4**), with $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{Me-4})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ in the presence of NH_4PF_6 led to the formation of compound **6**. Similar features were observed as for **5** with the exception of a new feature at 1703 cm^{-1} in the solid state infrared spectrum for the C=O of the methyl ester group and additional resonances in the ^1H NMR spectrum corresponding to the CO_2Me and NMe_2 protons. The similarity in reactivity between **3** and **4**, despite their differing steric profiles, led to the more synthetically accessible **3** being used in the subsequent reactions.

The 1-pyrenyl vinyl complex, $[\text{Ru}(\text{CH}=\text{CHPyr-1})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$, was investigated partly due to the photophysical properties arising from the pyrenyl substituent. The closely-related precursor, $[\text{Ru}(\text{CH}=\text{CHPyr-1})\text{Cl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$, reacts with CO to afford the 36-times more fluorescent complex, $[\text{Ru}(\text{CH}=\text{CHPyr-1})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$, allowing CO to be detected in amounts as low as 1 ppb. This behaviour is partly attributed to the quenching

effect of the BTD ligand but the effect of the dithiocarboxylate ligand was unknown. Reaction of $[\text{Ru}(\text{CH}=\text{CHPyr-1})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ with **3** in the presence of ammonium hexafluorophosphate led to isolation of $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C}(\text{Me})=\text{C}(\text{CS}_2\{\text{Ru}(\text{CH}=\text{CHPyr-1})\text{Cl}(\text{CO})(\text{PPh}_3)_2\})\text{C}=\text{N}(\text{Me})\text{Xyl}\}\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2\}\text{PF}_6$ (**7**). Similar spectroscopic data were observed as for compound **5** apart from new features due to the pyrenyl unit (doublet at 6.86 ppm, $^3J_{\text{HH}} = 8.1$ Hz) in the ^1H NMR spectrum. The overall formulation was supported by the molecular ion at m/z 1440 in the electrospray mass spectrum (+ve mode). Effect of this on fluorescence?

Conclusions

This report illustrates how multimetallic compounds can be constructed in a controlled, stepwise manner by exploiting the reliable reactivity of 1,1'-dithio units. Heterotrimetallic Fe_2Ru compounds are formed from the reaction of zwitterionic diiron vinyliminium dithiocarboxylate units, $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C}(\text{R}^2)=\text{C}(\text{CS}_2)\text{C}=\text{N}(\text{Me})\text{R}^1\}\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2]$ ($\text{R}^1 = \text{Xyl}$, $\text{R}^2 = \text{Me}$; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{CO}_2\text{Me}$), acting as effective organometallic $k^2\text{S}$ -ligands, with the versatile five-coordinate ruthenium vinyl precursors $[\text{Ru}(\text{CH}=\text{CHR}^3)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ ($\text{R}^3 = \text{C}_6\text{H}_4\text{Me-4}$, 1-Pyrenyl). The novel products contain two group 8 metals with vinyl moieties at both iron and ruthenium centres.

Experimental

The compounds $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{Me-4})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$,²⁵ $[\text{Ru}(\text{CH}=\text{CHPyr-1})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ ²⁶ and $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C}(\text{R}^2)=\text{C}(\text{H})\text{C}=\text{N}(\text{Me})\text{R}^1\}\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2]\text{OTf}$ ($\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{CO}_2\text{Me}$ **1**; $\text{R}^1 = \text{Xyl}$, $\text{R}^2 = \text{Me}$ **2**) and **3**¹⁶ were prepared according to published procedures. All other chemicals and solvents were purchased from Alfa-Aesar, Sigma-Aldrich and VWR and were used without further purification, unless otherwise stated. Solvents used for UV-Vis measurements were thoroughly degassed with nitrogen before use. All experiments and manipulations of compounds were conducted under an inert atmosphere of nitrogen in dry solvents, unless otherwise specified. Schlenk line techniques were used as a precaution. Solvent mixtures are volume/volume mixtures. Solvents used in the reactions of oxygen and moisture sensitive compounds were dried and degassed according to standard techniques. Petroleum ether refers to the fraction boiling in the range 40-60 °C. A Waters LCT Premier ES-ToF (ESI) spectrometer were used for mass spectra. FTIR spectra were measured using

Commento [fabmar6]: correct reference:
V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, J. Organomet. Chem. 2004, 689, 528–538

Commento [fabmar7]: correct reference: V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, Organometallics 2003, 22, 1326 - 1331

a Perkin Elmer Spectrum GX spectrometer. NMR spectroscopy was performed at 25 °C using Bruker AV400 or AV500 spectrometers at room temperature in CD₂Cl₂ unless otherwise stated. ¹H NMR chemical shifts (δ) were referenced to the residual non-deuterated solvent signal. The deuterated solvents were all purchased from Sigma Aldrich. ³¹P{¹H} NMR chemical shifts were referenced externally to H₃PO₄ 85% in H₂O respectively and were all proton decoupled.

[Fe₂{μ-η¹:η³-C(CO₂Me)=C(CS₂)C=NMe₂}(μ-CO)(CO)(Cp)₂] (4)

A solution of [Fe₂{μ-η¹:η³-C(CO₂Me)=CHC=NMe₂}(μ-CO)(CO)(Cp)₂]OTf (**2**, 260 mg, 0.44 mmol) in THF (10 mL) was treated first with CS₂ (1.0 mL, 16.60 mmol) and then NaH (45 mg, 1.13 mmol) in this order. After 30 minutes the mixture was filtered through an alumina pad and the solvent was removed. A solution of the green residue in CH₂Cl₂ was then transferred to an alumina column. Impurities were eliminated first with neat CH₂Cl₂, while the fraction containing the product was eluted with neat THF. Yield 76 mg, 32%. IR (CH₂Cl₂): ν (cm⁻¹) 1995 (CO), 1806 (μ-CO). ¹H NMR (CDCl₃): δ (ppm) 3.28, 3.79 (s x 2, 2 x 3H, NMe), 4.08 (s, 3H, CO₂Me), 5.12, 5.24 (s x 2, 2 x 5H, Cp). ¹³C{¹H} NMR (CDCl₃): δ (ppm) 257.8 (μ-CO), 244.6 (CS₂), 225.3 (C=N), 208.9 (CO), 177.2 (CO₂), 91.5 (C=C), 90.6, 90.3 (s x 2, Cp), 52.8 (OCH₃), 48.2, 45.1 (s x 2, NCH₃). MS (ES): *m/z* (abundance) 514 (100) [M]⁺. Elem. Anal. Calculated for C₂₀H₁₉Fe₂NO₄S₂ (M_w = 513.19): C 46.8, H 3.7, N 2.7; Found: C 47.1, H 3.8, N 3.0.

[Fe₂{μ-η¹:η³-C(Me)=C(CS₂{Ru(CH=CHC₆H₄Me-4)(CO)(PPh₃)₂})C=N(Me)(Xyl)}(μ-CO)(CO)(Cp)₂]PF₆ (5)

Compound **3** (18 mg, 0.0324 mmol) and [Ru(CH=CHC₆H₄Me-4)Cl(CO)(PPh₃)₂] (27 mg, 0.0334 mmol) were dissolved in 2 mL and 3 mL of dry DCM, respectively, before being combined and allowed to stir for 2 hrs. NH₄PF₆ (6 mg, 0.0368 mmol) was then dissolved in the minimum amount of MeOH, before being added to the reaction mixture and allowed to stir for 1 hr. All solvents were then removed, and the resulting solid was then redissolved in the minimum amount of DCM and filtered through celite, before being concentrated on a rotary evaporator, layered with diethyl ether, and left to precipitate overnight. The resulting dark brown precipitate was then filtered and washed with more diethyl ether to give the final product (Yield: 18 mg, 37%). Solubility in diethyl ether contributed to this low initial yield. A further crop of product could be obtained from the filtrate. IR: ν (cm⁻¹) 1982 (CO), 1929 (CO), 1820 (μ-CO), 1606 (CN). ¹H NMR (CD₂Cl₂): δ (ppm) 1.80 (s, 3H, Me^{xylyl}), 2.21 (s, 3H, Me^{tolylyl}), 2.25 (s, 3H, Me^{xylyl}), 2.66 (s, 3H, NMe), 3.36 (s, 3H, C³Me), 4.58, 5.23 (s x 2, 2 x 5H, Cp), 5.71 (d, 1 H, ³J_{HH} = 17.1 Hz, Hβ), 6.21, 6.85 (AB, 4H, ³J_{AB} = 7.9 Hz, C₆H₄), 7.38-7.59 (m, 30H

+ 2H + 1H + 1H, C₆H₅ + ^{3,5}H^{Xylyl} + ⁴H^{Xylyl} + H α). ³¹P{¹H} NMR (CD₂Cl₂): δ (ppm) 39.6 (d, ²J_{PP} = 282 Hz), 37.2 (d, ²J_{PP} = 282 Hz). MS (ES): *m/z* (abundance) 1330 (100) [M]⁺. Elem. Anal. Calculated for C₇₂H₆₄F₆Fe₂NO₃P₃RuS₂ (M_w = 1475.09): C 58.6, H 4.4, N 1.0; Found: C 59.0, H 4.4, N 0.9.

[Fe₂{ μ - η^1 : η^3 -C(CO₂Me)=C(CS₂{Ru(CH=CHC₆H₄Me-4)(CO)(PPh₃)₂)C=NMe₂}(μ -CO)(CO)(Cp)₂]PF₆ (6)

Complex **6** was prepared using the same procedure as described for **5**, by treating [Ru(CH=CHC₆H₄Me-4)Cl(CO)(PPh₃)₂] (38 mg, 0.0468 mmol) with **4** (24 mg, 0.0468 mmol) followed by NH₄PF₆ (8mg, 0.0468 mmol). The product was isolated by layering the reaction mixture with hexane. Yield: 30 mg, 44%. A further crop of product could be obtained from the filtrate. IR: ν (cm⁻¹) 3055 (sp²-CH), 2950 (sp³-CH), 1992 (CO), 1929 (CO), 1816 (μ -CO), 1704 (CO₂Me). ¹H NMR (CD₂Cl₂): δ (ppm) 2.26 (s, 3H, Me^{tolyl}), 2.48, 3.79 (s x 2, 2 x 3H, NMe), 3.90 (s, 3H, CO₂Me), 4.57, 5.14 (s x 2, 2 x 5H, Cp), 5.18 (d, 1 H, ³J_{HH} = 16.5 Hz, H β), 6.20, 6.86 (AB, 4H, ³J_{AB} = 7.9 Hz, C₆H₄), 7.35-7.53 (m, 30H, C₆H₅), 7.56 (m, 1H, H α). ³¹P{¹H} NMR (CD₂Cl₂): δ (ppm) 41.8 (d, ²J_{PP} = 276 Hz), 39.6 (d, ²J_{PP} = 276 Hz). MS (ES): *m/z* (abundance) 1284 (100) [M]⁺. Elem. Anal. Calculated for C₆₆H₅₈F₆Fe₂NO₅P₃RuS₂ (M_w = 1428.97): C 55.5, H 4.1, N 1.0; Found: C 55.3, H 3.9, N 1.1.

[Fe₂{ μ - η^1 : η^3 -C(Me)=C(CS₂{Ru(CH=CHPyr-1)(CO)(PPh₃)₂)C=N(Me)Xylyl}(μ -CO)(CO)(Cp)₂]PF₆ (7)

Complex **7** was prepared by the same procedure as described for **5**, by treating [Ru(CH=CHPyr-1)Cl(CO)(PPh₃)₂] (38 mg, 0.0333 mol) with **3** (17 mg, 0.0295 mmol) followed by NH₄PF₆ (6 mg, 0.0295 mmol). Yield: 26 mg, 56%. IR: ν (cm⁻¹) 3055, (sp²-CH), 2973 (sp³-CH), 1982 (s, CO), 1930 (s, CO), 1821 (μ -CO), 1583 (CN). ¹H NMR (CD₂Cl₂): δ (ppm) 1.82, 2.27 (s x 2, 2 x 3H, Me^{xylyl}), 2.70 (s, 3H, NMe), 3.44 (s, 3H, C³Me), 4.61, 5.27 (s x 2, 2 x 5H, Cp), 7.10 (d, 1 H, ³J_{HH} = 16.5 Hz, H β), 6.86 (d, 1H, ³J_{HH} = 8.1 Hz, Pyr-1), 7.28-8.21 (m, 30H + 8H + 2H + 1H + 1H, C₆H₅ + 1-Pyr + ^{3,5}H^{Xylyl} + ⁴H^{Xylyl} + H α). ³¹P{¹H} NMR (CD₂Cl₂): δ (ppm) 38.7 (d, ²J_{PP} = 284 Hz), 36.4 (d, ²J_{PP} = 284 Hz). MS (ES): *m/z* (abundance) 1440 (100) [M]⁺. Elem. Anal. Calculated for C₈₁H₆₆F₆Fe₂NO₃P₃RuS₂·0.5CH₂Cl₂ (M_w = 1627.67 as solvate): C 60.1, H 4.2, N 0.9; Found: C 60.1, H 3.9, N 1.1.

Acknowledgements

L. M. thanks the Royal Society for a CNR-RS Fellowship.

References

1. a) M. Shibasaki, M. Kanai, S. Matsunaga and N. Kumagai, *Acc. Chem. Res.*, 2009, **42**, 1117-1127; b) M. Weber, J. E. M. N. Klein, B. Miehlich, W. Frey and R. Peters, *Organometallics*, 2013, **32**, 5810-5817; c) H. Sasai, T. Suzuki, S. Arai, T. Arai and M. Shibasaki, *J. Am. Chem. Soc.*, 1992, **114**, 4418-4420; d) J. H. H. Ho, J. Wagler, A. C. Willis and B. A. Messerle, *Dalton Trans.*, 2011, **40**, 11031-11042; e) W.-Z. Lee, T.-L. Wang, H.-C. Chang, Y.-T. Chen and T. S. Kuo, *Organometallics*, 2012, **31**, 4106-4109; f) Y. Yamaguchi, K. Yamanishi, M. Kondo and N. Tsukada, *Organometallics*, 2013, **32**, 4837-4842; g) B. Wu, J. C. Gallucci, J. R. Parquette and T. V. RajanBabu, *Chem. Sci.*, 2014, **5**, 1102-1117.
2. a) X. He, F. Herranz, E. C.-C. Cheng, R. Vilar and V. W.-W. Yam, *Chem. Eur. J.*, 2010, **16**, 9123-9131; b) J. S. Mendy, M. A. Saeed, F. R. Fronczek, D. R. Powell and Md. A. Hossain, *Inorg. Chem.*, 2010, **49**, 7223-7225; c) M. E. Moragues, J. Esteban, J. V. Ros-Lis, R. Martínez-Máñez, M.D. Marcos, M. Martínez, J. Soto and F. Sancenón, *J. Am. Chem. Soc.*, 2011, **133**, 15762-15772; d) J. Esteban, J. V. Ros-Lis, R. Martínez-Máñez, M. D. Marcos, M. Moragues, J. Soto and F. Sancenón, *Angew. Chem. Int. Ed.*, 2010, **49**, 4934-4937; *Angew. Chem.*, 2010, **122**, 5054-5057.
3. a) J. B. Livramento, E. Tóth, A. Sour, A. Borel, A. E. Merbach and R. Ruloff, *Angew. Chem. Int. Ed.*, 2005, **44**, 1480-1484; b) J. B. Livramento, A. Sour, A. Borel, A. E. Merbach and E. Tóth, *Chem. Eur. J.*, 2006, **12**, 989-1003; c) L. Moriggi, A. Aebischer, C. Cannizzo, A. Sour, A. Borel, J.-C. G. Bunzli and L. Helm, *Dalton Trans.*, 2009, 2088-2095; d) D. Kasala, T. S. Lin, C.-Y. Chen, G.-C. Liu, C.-L. Kao, T.-L. Cheng and Y.-M. Wang, *Dalton Trans.*, 2011, **40**, 5018-5025; e) P. Mieville, H. Jaccard, F. Reviriego, R. Tripier and L. Helm, *Dalton Trans.*, 2011, **40**, 4260-4267; f) G. Dehaen, P. Verwilst, S. V. Eliseeva, S. Laurent, L. Vander Elst, R. N. Muller, W. M. De Borggraeve, K. Binnemans and T. N. Parac-Vogt, *Inorg. Chem.*, 2011, **50**, 10005-10014; g) G. Dehaen, S. V. Eliseeva, K. Kimpe, S. Laurent, L. Vander Elst, R. N. Muller, W. Dehaen, K. Binnemans and T. N. Parac-Vogt, *Chem. Eur. J.*, 2012, **18**, 293-302; h) P. Verwilst, S. V. Eliseeva, L. Vander Elst, C. Burtea, S. Laurent, S. Petoud, R. N. Muller, T. N. Parac-Vogt and W. M. De Borggraeve, *Inorg. Chem.*, 2012, **51**, 6405-6411; i) G. Dehaen, S. V. Eliseeva, P. Verwilst, S. Laurent, L. Vander Elst, R. N. Muller, W. De Borggraeve, K. Binnemans and T. N. Parac-Vogt, *Inorg. Chem.*, 2012, **51**, 8775-8783.
4. S. Friedle, E. Reisner and S. J. Lippard, *Chem. Soc. Rev.*, 2010, **39**, 2768-2779.
5. R. Stenkamp, *Chem. Rev.*, 1994, **94**, 715-726

6. a) G. Berggren, A. Adamska, C. Lambertz, T. R. Simmons, J. Esselborn, M. Atta, S. Gambarelli, J. M. Mouesca, E. Reijerse, W. Lubitz, T. Happe, *Nature*, 2013, **499**, 66-69; b) C. Madden, M. D. Vaughn, I. Díez-Pérez, K. A. Brown, P. W. King, D. Gust, A. L. Moore and T. A. Moore, *J. Am. Chem. Soc.*, 2012, **134**, 1577-1582.
7. D. Wang, E. R. Farquhar, A. Stubna, E. Münck, L. Que, *Nature Chem.* 2009, **1**, 145-150.
8. E. V. Kudrik, P. Afanasiev, L. X. Alvarez, P. Dubourdeaux, M. Clémancey, J. M. Latour, G. Blondin, D. Bouchu, F. Albrieux, S. E. Nefedov, A. B. Sorokin, *Nature Chem.* 2012, **4**, 1024-1029.
9. Y. Li, Y. Li, B. Wang, Y. Luo, D. Yang, P. Tong, J. Zhao, L. Luo, Y. Zhou, S. Chen and F. Cheng, *Nature Chem.* 2013, **5**, 320-326.
10. Z. Cao and M. B. Hall, *J. Am. Chem. Soc.*, 2001, **123**, 3734-2742
11. C. K. A. Gregson, V. C. Gibson, N. J. Long, E. L. Marshall, P. J. Oxford, A. J. P. White, *J. Am. Chem. Soc.*, 2006, **128**, 7410-7411
12. F. Marchetti, *Eur. J. Inorg. Chem.* 2018, 3987-4003
13. a) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, *Organometallics*, 2004, **23**, 3348-3354; b) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, *J. Organomet. Chem.* 2006, **691**, 4234-4243; c) L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, *Eur. J. Inorg. Chem.* 2007, 1799-1807; d) F. Marchetti, S. Zacchini, V. Zanotti, *Organometallics* 2018, **37**, 107-115.
14. L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, *Organometallics* 2005, **24**, 2297-2306
15. a) L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, *Organometallics*, 2008, **27**, 5058-5066; b) L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, *Organometallics*, 2007, **26**, 3577-3584; c) L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, *Organometallics*, 2006, **25**, 4808-4816; d) L. Busetto, F. Marchetti, R. Mazzoni, M. Salmi, S. Zacchini, V. Zanotti, *J. Organomet. Chem.*, 2008, **693**, 3191-3196.
16. F. Marchetti, S. Zacchini, M. Salmi, L. Busetto, V. Zanotti, *Eur. J. Inorg. Chem.*, 2011, 1260-1268.
17. a) G. Hogarth, E.-J. C.-R. C. R. Rainford-Brent, S. E. Kabir, I. Richards, J. D. E. T. Wilton-Ely and Q. Zhang, *Inorg. Chim. Acta*, 2009, **362**, 2020-2026; b) S. Naeem, E. Ogilvie, A. J. P. White, G. Hogarth and J. D. E. T. Wilton-Ely, *Dalton Trans.*, 2010, **39**, 4080-4089; c) S. Naeem, A. J. P. White, G. Hogarth and J. D. E. T. Wilton-Ely, *Organometallics*, 2010, **29**, 2547-2556; d) S. Naeem, A. J. P. White, G. Hogarth and J. D. E. T. Wilton-Ely, *Organometallics*, 2011, **30**, 2068-2069; e) V. L. Hurtubise, J. M. McArdle, S. Naeem, A. Toscani, A. J. P. White, N. J. Long and J. D. E. T. Wilton-Ely, *Inorg. Chem.* 2014, **53**, 11740-11748; f) S. Naeem, S. A. Serapian, A. Toscani,

- A. J. P. White, G. Hogarth and J. D. E. T. Wilton-Ely, *Inorg. Chem.*, 2014, **53**, 2404-2416; g) R. Sherwood, F. González de Rivera, J. H. Wan, Q. Zhang, A. J. P. White, O. Rossell, G. Hogarth and J. D. E. T. Wilton-Ely, *Inorg. Chem.* 2015, **54**, 4222-4230; h) J. A. Robson, F. González de Rivera, K. Anuar Jantan, M. N. Wenzel, A. J. P. White, O. Rossell and J. D. E. T. Wilton-Ely, *Inorg. Chem.* 2016, **55**, 12982-12996.
18. Y. H. Lin, N. H. Leung, K. B. Holt, A. L. Thompson and J. D. E. T. Wilton-Ely, *Dalton Trans.*, 2009, 7891-7901.
19. a) J. D. E. T. Wilton-Ely, D. Solanki and G. Hogarth, *Eur. J. Inorg. Chem.*, 2005, 4027-4030; b) E. R. Knight, D. Solanki, G. Hogarth, K. B. Holt, A. L. Thompson and J. D. E. T. Wilton-Ely, *Inorg. Chem.*, 2008, **47**, 9642-9653; c) E. R. Knight, A. R. Cowley, G. Hogarth and J. D. E. T. Wilton-Ely, *Dalton Trans.*, 2009, 607-609; d) E. R. Knight, N. H. Leung, Y. H. Lin, A. R. Cowley, D. J. Watkin, A. L. Thompson, G. Hogarth and J. D. E. T. Wilton-Ely, *Dalton Trans.*, 2009, 3688-3697; e) E. R. Knight, N. H. Leung, A. L. Thompson, G. Hogarth and J. D. E. T. Wilton-Ely, *Inorg. Chem.*, 2009, **48**, 3866-3874; f) M. J. Macgregor, G. Hogarth, A. L. Thompson and J. D. E. T. Wilton-Ely, *Organometallics*, 2009, **28**, 197-208; g) K. Oliver, A. J. P. White, G. Hogarth and J. D. E. T. Wilton-Ely, *Dalton Trans.*, 2011, **40**, 5852-5864; h) S. Sung, H. Holmes, L. Wainwright, A. Toscani, G. J. Stasiuk, A. J. P. White, J. D. Bell and J. D. E. T. Wilton-Ely, *Inorg. Chem.*, *Inorg. Chem.* 2014, **53**, 1989-2005.
20. a) S. Naeem, A. L. Thompson, L. Delaude and J. D. E. T. Wilton-Ely, *Chem. Eur. J.*, 2010, **16**, 10971-10974; b) S. Naeem, A. L. Thompson, A. J. P. White, L. Delaude and J. D. E. T. Wilton-Ely, *Dalton Trans.*, 2011, **40**, 3737-3747; c) M. J. D. Champion, R. Solanki, L. Delaude, A. J. P. White and J. D. E. T. Wilton-Ely, *Dalton Trans.*, 2012, **41**, 12386-12394.
21. M. R. Torres, A. Vegas, A. Santos and J. Ros, *J. Organomet. Chem.*, 1986, **309**, 169-177.
22. M. C. J. Harris and A. F. Hill, *Organometallics*, 1991, **10**, 3903-3906
23. For an overview of vinyl chemistry of ruthenium(II), see: a) M. K. Whittlesey, in *Comprehensive Organometallic Chemistry III*; R. H. Crabtree, D. M. P. Mingos and M. I. Bruce, Eds.; Elsevier: Oxford, U.K., 2006; Vol. 6; b) A. F. Hill, in *Comprehensive Organometallic Chemistry II*; E. W. Abel, F. G. A. Stone and G. Wilkinson.; Eds.; Pergamon Press: Oxford, U.K., 1995, Vol. 7.
24. M. E. Moragues, A. Toscani, F. Sancenón, R. Martínez-Mañez, A. J. P. White and J. D. E. T. Wilton-Ely, *J. Am. Chem. Soc.*, 2014, **136**, 11930-11933; c) A. Toscani, C. Marín-Hernández, M. E. Moragues, F. Sancenón, P. Dingwall, N. J. Brown, R. Martínez-Mañez, A. J. P. White and J. D. E. T. Wilton-Ely, *Chem. Eur. J.*, 2015, **21**,

- 14529 – 14538; c) C. de la Torre, A. Toscani, C. Marín-Hernández, J. A. Robson, M. C. Terencio, A. J. P. White, M. J. Alcaraz, J. D. E. T. Wilton-Ely, R. Martínez-Máñez, F. Sancenón, *J. Am. Chem. Soc.*, 2017, **139**, 18484-18487.
25. J. D. Farmer, W. Y. Man, M. A. Fox, D. S. Yufit, J. A. K. Howard, A. F. Hill and P. J. Low, *J. Organomet. Chem.*, 2012, **721-722**, 173–185.
26. J. Maurer, M. Linseis, B. Sarkar, B. Schwederski, M. Niemayer, W. Kaim, S. Zálíš, C. Anson, M. Zabel, R. F. Winter, *J. Am. Chem. Soc.*, 2008, **130**, 259–268.

Supporting Information

Heterotrimetallic complexes of iron, ruthenium and palladium based on vinyliminium dithiocarboxylate ligands.

Lorenzo Mognon, Samuel Richardson, Gabriele Agonigi, Fabio Marchetti* and James D. E. T. Wilton-Ely*

NMR and IR spectra

NMR and IR spectra for the new compounds prepared during this research are provided below:

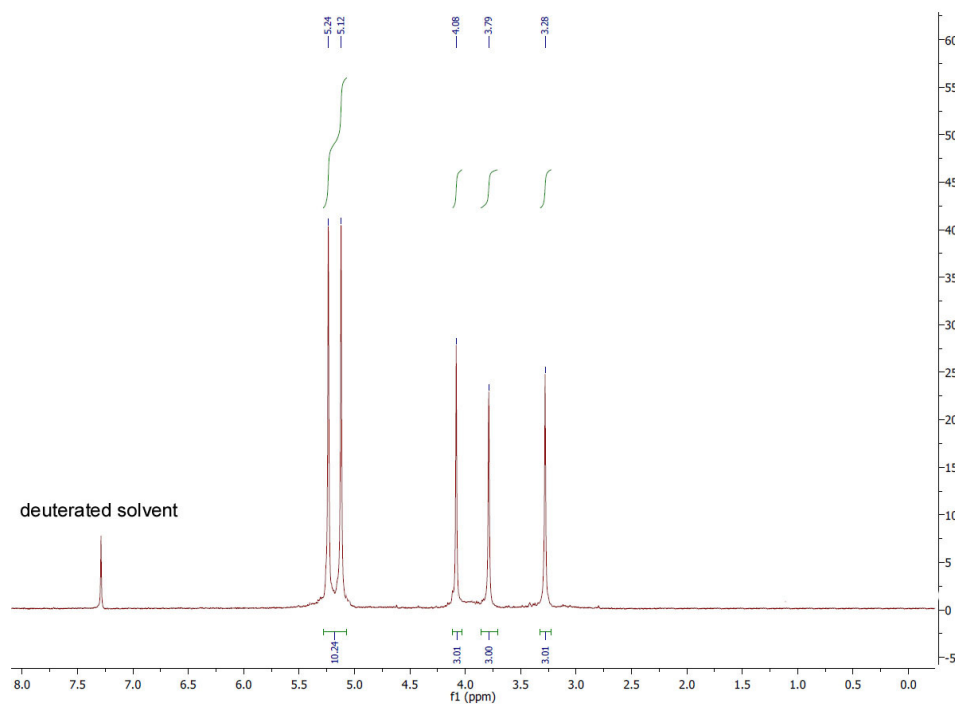


Figure S1. ¹H NMR spectrum of 4 in CDCl₃.

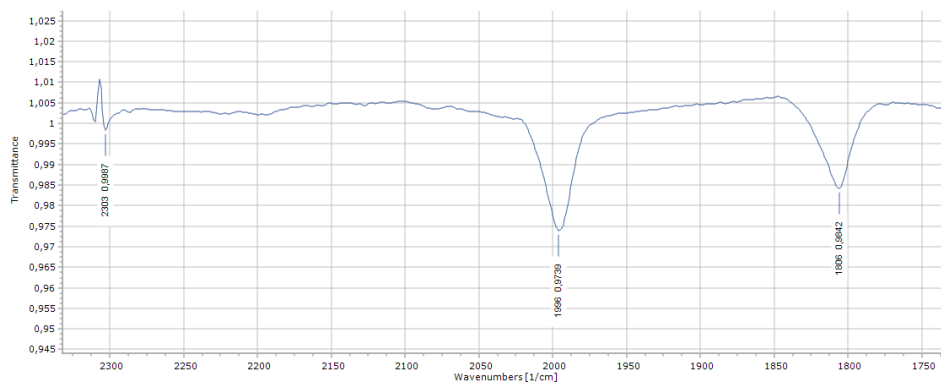


Figure S2. Solution IR spectrum of **4** in CH_2Cl_2 .

[Fe₂{μ-η¹:η³-C(Me)=C(CS₂{Ru(CH=CHC₆H₄Me-4)(CO)(PPh₃)₂}C=N(Me)Xylyl)](μ-CO)(CO)(Cp)₂PF₆ (5**)**

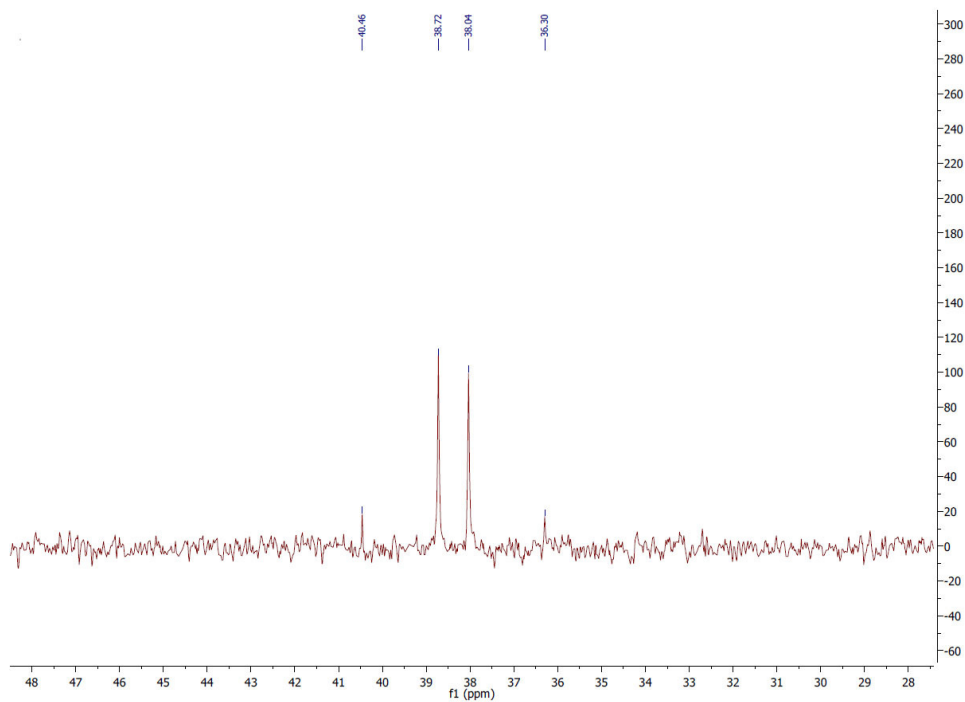


Figure S3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** in CD_2Cl_2 .

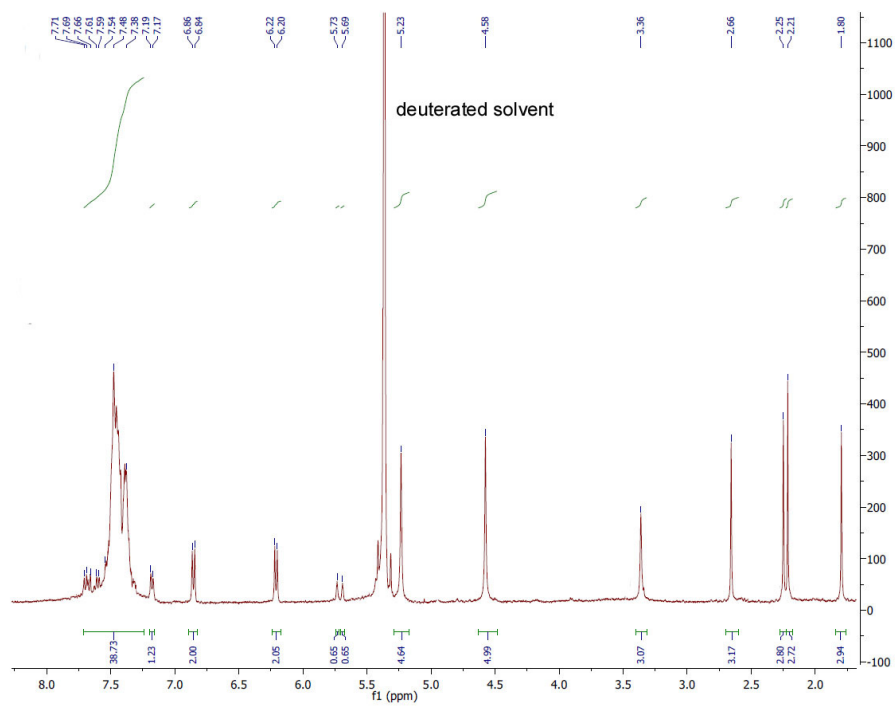


Figure S4. ^1H NMR spectrum of **5** in CD_2Cl_2 .

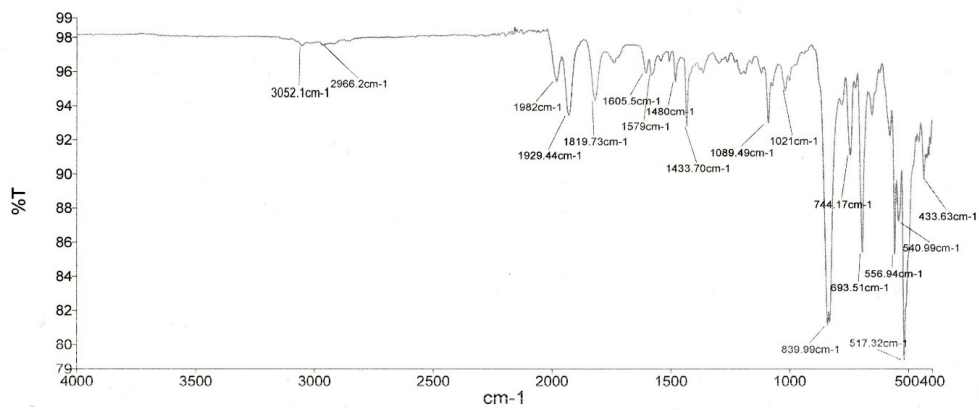


Figure S5. Solid-state IR spectrum of **5**.

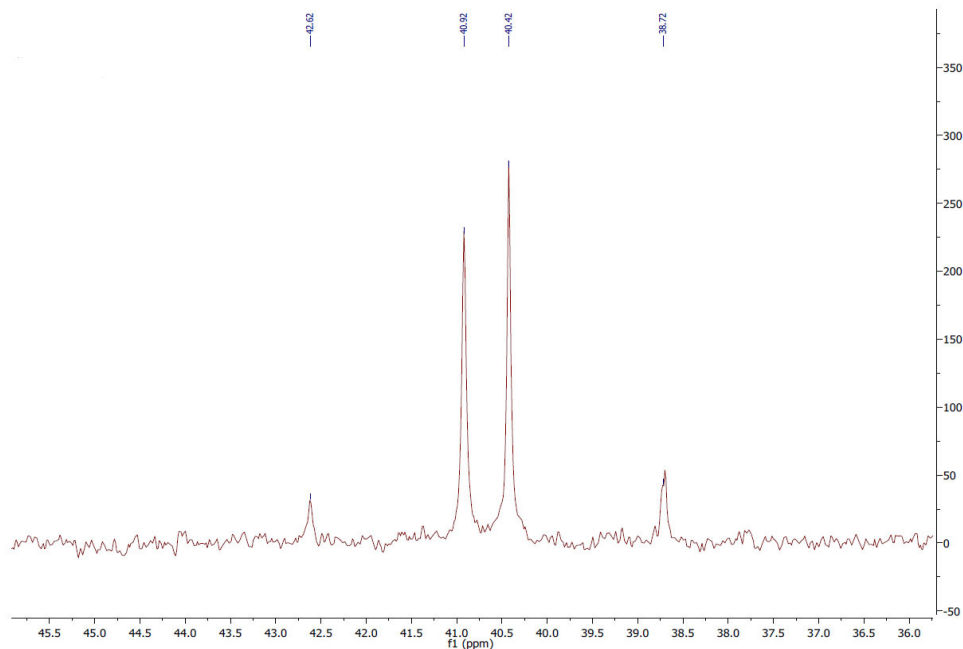
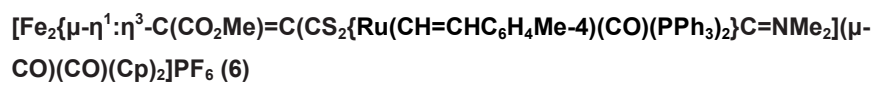


Figure S6. ³¹P{¹H} NMR spectrum of **6** in CD₂Cl₂.

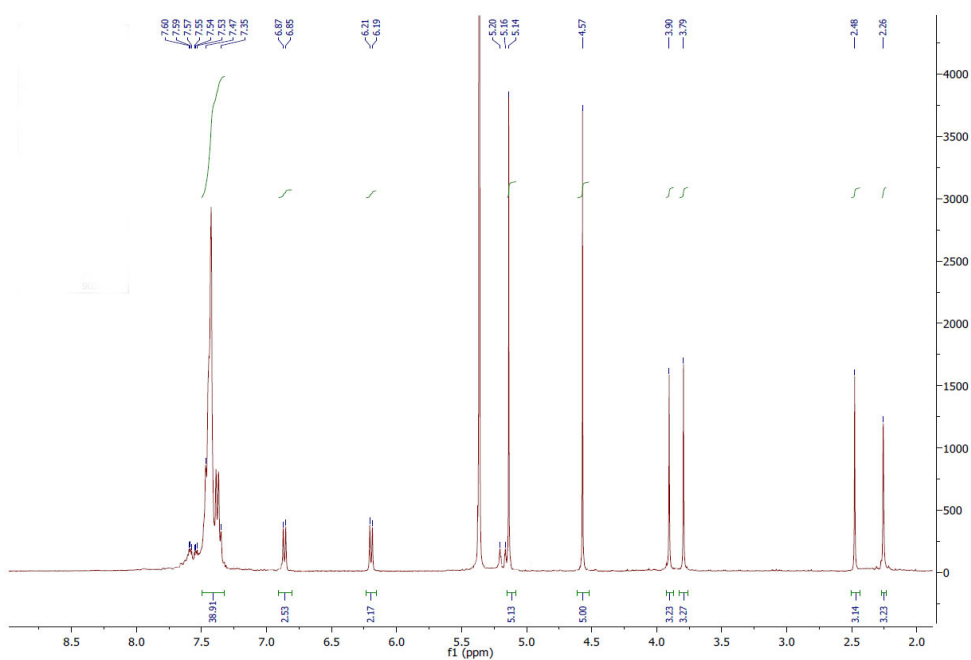


Figure S7. ¹H NMR spectrum of **6** in CD₂Cl₂.

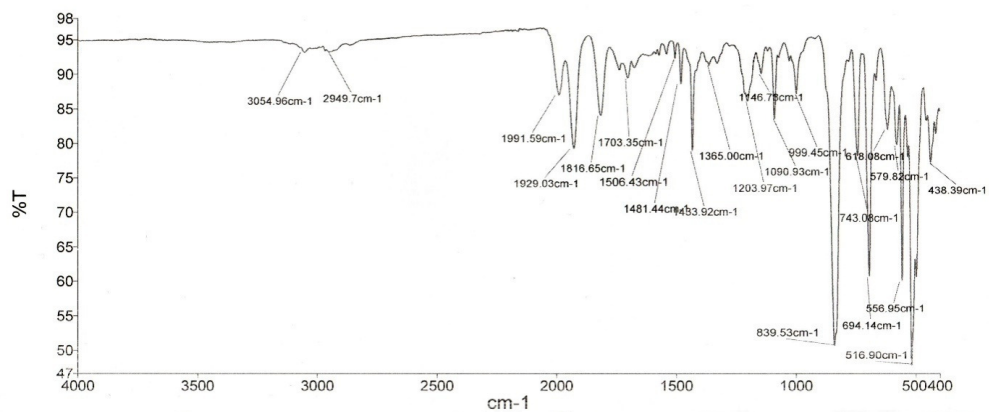


Figure S8. Solid-state IR spectrum of **6**.

[Fe₂{μ-η¹:η³-C(Me)=C(CS₂{Ru(CH=CHPyr-1)(CO)(PPh₃)₂)}C=N(Me)Xylyl}]{μ-CO)(CO)(Cp)₂PF₆ (7**)**

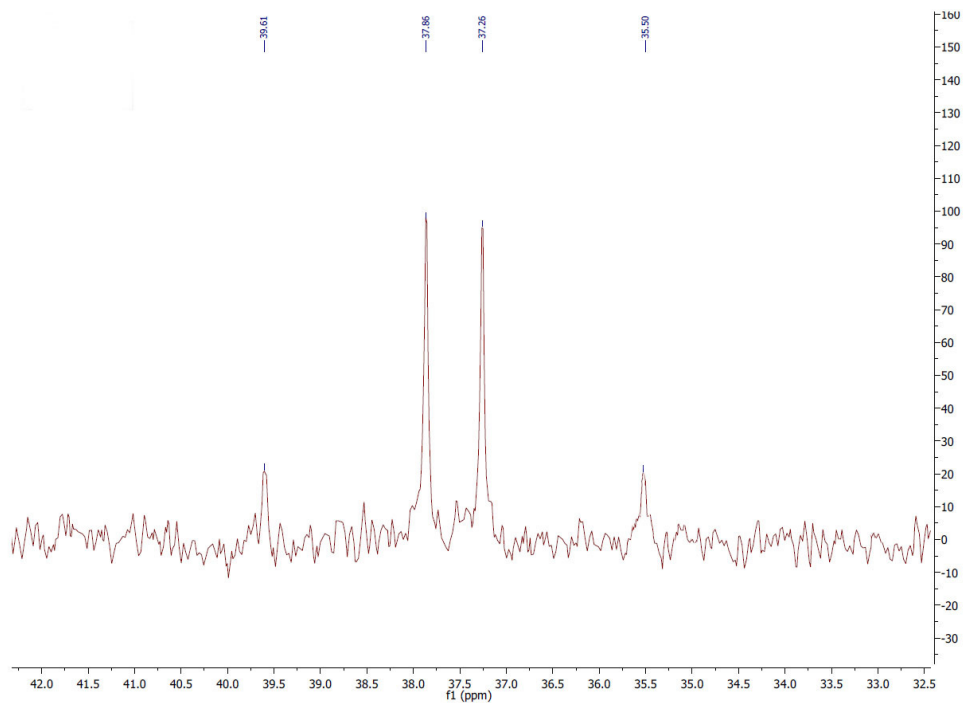


Figure S9. ³¹P{¹H} NMR spectrum of **7** in CD₂Cl₂.

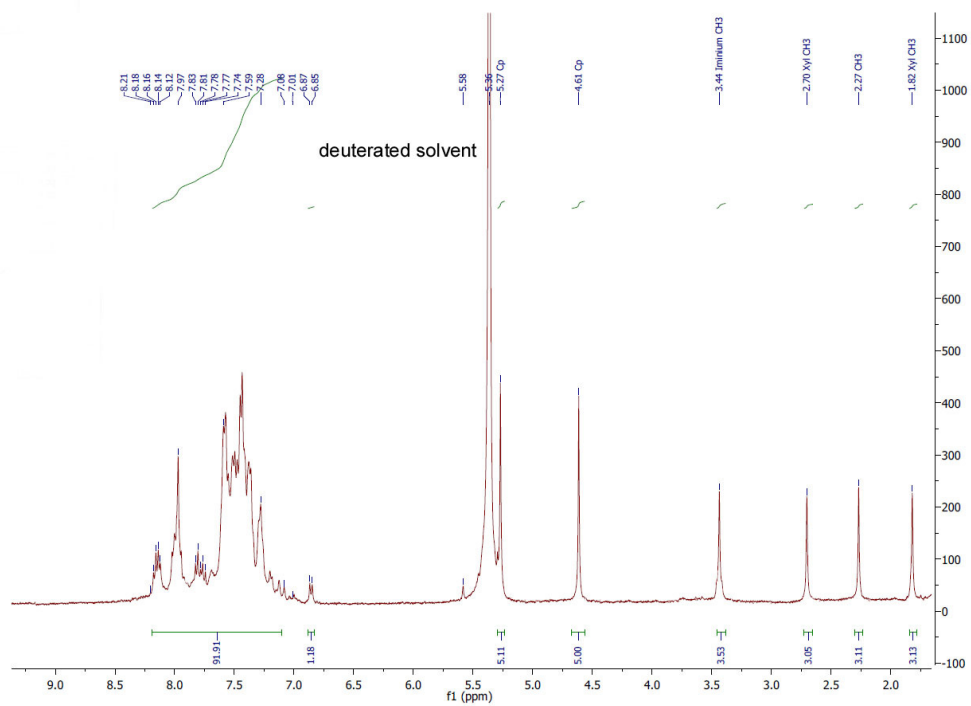


Figure S10. ^1H NMR spectrum of **7** in CD_2Cl_2 .

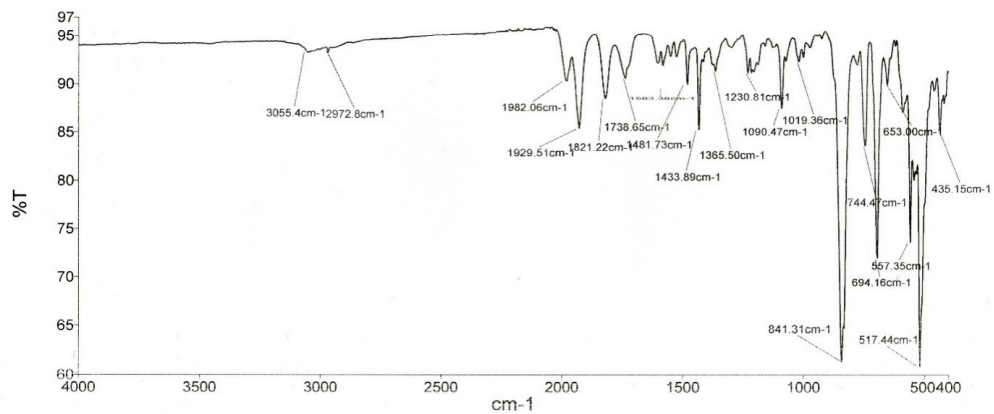


Figure S11. Solid-state IR spectrum of **7**.