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Phosphine-promoted ring-opening of benzisothiazolate ligands at a nickel(II) centre: A convenient synthesis of Ni(II)-thiolate complexes

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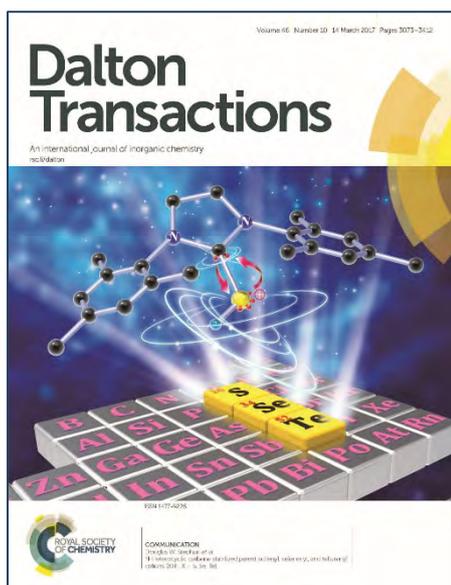
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Thank you very much for your assistance in evaluating this manuscript

Dr Andrew Shore (dalton@rsc.org)
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Editor, *Dalton Transactions*

Professor John Arnold
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4th March 2019

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Manuscript ID: DT-COM-12-2018-005027

Dear Helen,

I would be pleased if you would consider the revised version of the manuscript entitled "Phosphine-promoted ring-opening of benzisothiazolate ligands at a nickel(II) centre: A convenient synthesis of Ni(II)-thiolate complexes" by Subhi A. Al-Jibori, Samer Hussein Ali, Ahmed S. Al-Janabi, Christoph Wagner and Graeme Hogarth for publication as a *communication* in the issue of *Dalton Transactions* dedicated to Geoff Cloke FRS.

Following comments from four referees we have incorporated their suggested changes (in red) as listed below. Two of the four referees were favourable to publication, but the other two were less positive effectively saying that the work was in a preliminary stage and lacked mechanistic information. We do not disagree with this sentiment but believe that this is exactly why it warrants publication as a communication. We do not yet have "*sufficient information as to the pathways by which ring scission of the benzisothiazolate moiety takes place and why/how these are phosphine-dependent*" (Reviewer #2) and agree that "*it also lacks mechanistic insights of the unexpected S-N bond cleavage reaction*" (Reviewer #4). We also agree "*it is of interest to note that this observation is unprecedented*" (Reviewer #4) and believe that this *supports* our view that this work is very suitable for communication. There is much to do; arguably the work throws up more questions than answers and we are working actively towards a more detailed understanding, *but* the simple (in air and effectively one-step) reaction from commercially available starting materials to a range of new thiolate complexes, the synthesis of which are difficult to imagine by conventional methods, is we believe worthy of communication.

We had made this clear in our initial covering letter where we stated; "While the chemistry of the saccharinate ligand has been widely investigated, that of the related non-sulfur oxidised benzisothiazolate ligand remains virtually unexplored. We have recently published three articles concerning this chemistry and in all cases the benzisothiazolate ligand remains intact throughout. In this communication we report on reactions of a dimeric nickel-benzisothiazolate complex with some

phosphines and diphosphines. In all cases the chemistry is dominated by sulfur-nitrogen bond scission and this leads to a range of novel thiolate complexes which are otherwise inaccessible. We believe this novel transformation is worthy of communication and are currently trying to understand more about the mechanistic details ...". We still believe that this is the case and hope that the revised manuscript can be further considered for publication in the special issue dedicated to Geoff Cloke



Dr Graeme Hogarth

Referee: 1

There are 3 Structures in this paper. We examined this file: DT-COM-12-2018-005027

All three structures have been determined and reported in an exemplary fashion and I commend the authors on their excellent work. There is, however, a small problem with structure **i2t1674** -- there are three important CheckCif A alerts: H atoms are bumping into each other in the solvent water molecules. It is possible to sort this out, and I attach a file to show this. I am aware of the tentative nature of this assignment, but at least no direct H crashes are being reported.

Structure i2t1674 (CCDC 1884912): C34 H39 N Ni O5 P2 S These CheckCif A and B alerts are raised by this structure. This is for your information only - you may wish to address these issues before re-submitting your cif file to the CCDC.

417_ALERT_2_A Short Inter D-H..H-D H2B ..H5A .. 1.32 Ang.

417_ALERT_2_A Short Inter D-H..H-D H3B ..H4B .. 1.42 Ang.

417_ALERT_2_A Short Inter D-H..H-D H3B ..H5B .. 1.73 Ang.

417_ALERT_2_B Short Inter D-H..H-D H2A ..H3A .. 2.00 Ang.

The Ueq values of the following atoms are extremely large (Ueq = > 0.15). Either the occupancy is set too high for these atom, or you might need to explore the possibility that these atoms are involved in some form of disorder: O2 O4.

We thank the crystallographic referee for these comments and for help with removing the A alerts in the CheckCIF. We now submit new CIF and CHECKCIF and have acknowledged the referee's help.

"We thank the University of Tikrit and King's College London for partial support of this work and a referee for helpful suggestions regarding the structure refinement of the water molecules in **3b.4H₂O** (see ESI)".

Referee: 2

This manuscript describes the reaction of bimetallic nickel benzisothiazolate-bridge paddlewheel complexes with aryldiphosphines and PPh₃ and the characterisation of the resulting products. The various nickel complexes that arise form as a result of different types of ring scission of the benzisothiazolate motif.

Overall, this is not a particularly well-written paper, which, furthermore appears somewhat premature and lacks both a clear rationale for doing the work (see below) and also any mechanistic proposals. It is likely that a significantly improved manuscript would result from inclusion of additional material, in particular mechanistic studies probing the pathways for ring scission as a

function of phosphine/diphosphine. Indeed, the authors indicate that in this context a computational study is underway and the authors are strongly encouraged to consider waiting for these data and then re-submitting the manuscript to include them.

This is a communication. We report our preliminary findings. We believe that these warrant rapid publication but have not yet managed to elucidate the mechanism either experimentally or computationally. These studies are underway but are likely to take some time to complete. We would plan to produce a full paper at a later stage showing these aspects and also further developing the scope of these transformations.

In terms of the current submission, the abstract is rather vague and does not provide a stand-alone overview of the results described in the paper and should be re-written.

We disagree – but of course are constrained in length as it is a communication. If the editor will allow a more developed abstract then we can provide one but we feel that it highlights the key features of the work; access to novel nickel thiolate complexes via a one-pot reaction occurring through a novel N-S bond scission.

The introduction to the manuscript is reasonable, but ends in a very speculative fashion (“...which may have interesting catalytic properties...”), which is not warranted and should be removed – unless the authors can include examples of where these systems have been used in catalysis.

This has now been removed. “Herein we communicate our preliminary results for nickel which, following subsequent rearrangements, lead to a range of mononuclear Ni(II) complexes containing otherwise inaccessible thiolate ligands.”

In general, the figures and schemes are acceptable, but it would be very useful to the reader if the authors included % conversions/ratios in the various synthetic schemes where multiple products are formed.

We don't feel that this is the focus of the communication and we don't see others doing this in Dalton Transactions.

Furthermore, although only a single synthetic methodology for each of the reactions is given in the body of the paper, the experimental section describes multiple methods for the preparation of 2a and 3.

We have provided as much experimental information as we currently have. We can remove some of this BUT prefer to keep it in the ESI to provide more information for readers. The key thing is that yields of **2** and **3** vary to some extent with the nature of the reaction solvent (dcm vs EtOH). We had initially said this in the paper. We have now edited to read “with a slight excess of the diphosphine for 4 h resulted in formation of two products; namely, maroon **2a-b** and orange **3a-b** (Scheme 1) the relative amounts of which vary as a function of both the diphosphine and the reaction solvent.

The work is appropriately referenced throughout.

In conclusion, this manuscript is not currently in a form where publication can be recommended in Dalton Trans. It comes across very much as being premature, in particular lacking sufficient information as to the pathways by which ring scission of the benzisothiazolinone moiety takes place and why/how these are phosphine-dependent.

We disagree with this comment and wonder if the referee realised that this was a communication and not a full paper. We agree that understanding the mechanism(s) is important but this will take much longer to address.

Additional Typos/Corrections:

Abstract bit must be defined **done**

p.1, line 9 “simple metal(II) salts” – vague what is meant by “simple”? Delete. **We mean commercially available halides (versus exotic M(II) salts that may be difficult to access) but have removed this comment in two places in the manuscript Removed “simple”**

- p.1, line 11 "centre" should be replaced by "core". We have used this term in many papers but change to "core" in line with referee's request
- p.2, line 7 "simple phosphines" – vague what is meant by "simple"? Delete/be specific. Again we mean cheap, commercially available phosphines, but have removed.
- p.2, lines 13-14 Not clear what is meant by "...and analytical-spectroscopic data"; re-word. I think this is straight-forward; spectroscopic summarise IR, NMR etc and analytical is elemental analysis. We have used this term many times to show that characterisation is not based only on the XRD structure. Hence we prefer to retain it here.
- P3, line 9 Replace "Both" by "All the complexes". We have done this
- p.4, lines 4-5 "...the structure of the isolated product 4...". We have changed this sentence to "With the latter the product 4 was confirmed by X-ray crystallography"
- p.4, line 8 Replace "phosphorus-imine" by "iminophosphorane" done
- p.4, line 9 "Reaction of 1 with...". Now reads "Reaction of 1 with PPh₃ another course"
- p.5, line 2 replace "stretch" by "band" done x 2
- p.5, line 4 "to an NH₂ group...". done
- P5, last sentence Very vague – not clear what the authors mean by this; revise. I think the referee is referring to the statement regarding related platinum and palladium chemistry. We wanted to acknowledge that M(II) thiolates were known for these heavier elements BUT that their chemistry differed from those described above for nickel – in that they readily lose one phosphine ligand. We think this is significant as it further justifies studying nickel(II) thiolate chemistry. We have edited the sentence slightly and hope that it is now clearer; "Analogous platinum and palladium complexes [M(k¹-PPh₃)₂(k¹-SPh)₂] have been reported [12-14] but this chemistry is complicated by facile loss of PPh₃ to afford dimeric complexes [M(k¹-PPh₃)(k¹-SPh)(m-SPh)]₂ [14]."
- p.5, line 12 This paragraph doesn't follow on from the previous paragraph. Re-word/re-write. We feel that it is adequate in its current form. It serves three purposes; (i) to very briefly summarise the findings reported, (ii) to suggest how these need to be further studied in order to fully understand them, (iii) suggest why how this can be exploited in future. We feel that as this is a communication this information will help others understand where we plan to take this chemistry.

GA Scheme This is very confused and misrepresents the actual chemistry described. This should be fully re-done.

We strongly disagree. It summarises the important transformations without complicating things by showing the different phosphines. We feel it is informative and easy to understand.

SI p.3, line 8 reference missing This has been removed as it is in the paper itself (reference 6 now published and updated in the manuscript)

Throughout "refluxed" should be replaced by "heated at reflux" done

SI p3, line 23 Not enough detail given to be able to be reproduced. The wording was poor and we have now clarified.

SI p3, line 27 Analytical data not in agreement – found/calculated. We believe data are fine. There was a typo in the data for 2a and the correct H found is 4.97 and not 5.97

Throughout the SI molar conductivity data cited, but not discussed. We routinely run this data but agree that it is of little use here (as all are neutral molecules) and hence we have removed it from the ESI

NMR data – where resonances are not singlets and have an established multiplicity, coupling constants should be given (additionally coupling data for ³¹P NMR spectra should be quoted to the nearest whole Hz). Coupling constants were given but we have now changed the format so that they appear alongside each of the chemical shift values

Replace "...suspension. This was filtered..." by "the suspension was isolated by filtration" done

dmso-d₆(subscript) not dmso-d₆(superscript) done

Where NMR resonances are reported as broad, they should ideally have a peak width at half-height cited and also should be recorded as a.bc – x.yz (...) we feel that this is unnecessary and is not commonly the case in Dalton

Referee: 3

In the manuscript, the authors report synthesis of novel Ni-complexes with complete characterization including comprehensive crystallographic data. The ring-opening reactions of the ligands involved are certainly providing new routes toward this category of metal complexes. Therefore it is recommended that the manuscript be considered for acceptance for publication.

We thank the referee for these positive comments.

Referee: 4

This manuscript describes a ring-opening reaction of benzoisothiazolate ligand that is bridged between two Ni(II) centers via a S-N bond cleavage upon reaction with phosphines resulting in a Ni(II) 2-cyanophenylthiolate complex. Some of these complexes have been structurally characterized. While it is of interest to note that this observation is unprecedented, this alone does not warrant its publication as a communication in a high quality journal like Dalton Trans. Additionally, the manuscript does not bring out any novel feature of the work, it also lacks mechanistic insights of the unexpected S-N bond cleavage reaction.

This is a communication. We report our preliminary findings. We believe that these warrant rapid publication but have not yet managed to elucidate the mechanism either experimentally or computationally. These studies are underway but are likely to take some time to complete. We would plan to produce a full paper at a later stage showing these aspects and also further developing the scope of these transformations.

Further, the authors speculate that the thiolate complexes that result “may have interesting catalytic properties and be of biological relevance.” Such speculative statements have no place in Dalton Trans., they are not warranted unless supported by suitable studies.

This has now been removed. “Herein we communicate our preliminary results for nickel which, following subsequent rearrangements, lead to a range of mononuclear Ni(II) complexes containing otherwise inaccessible thiolate ligands.”

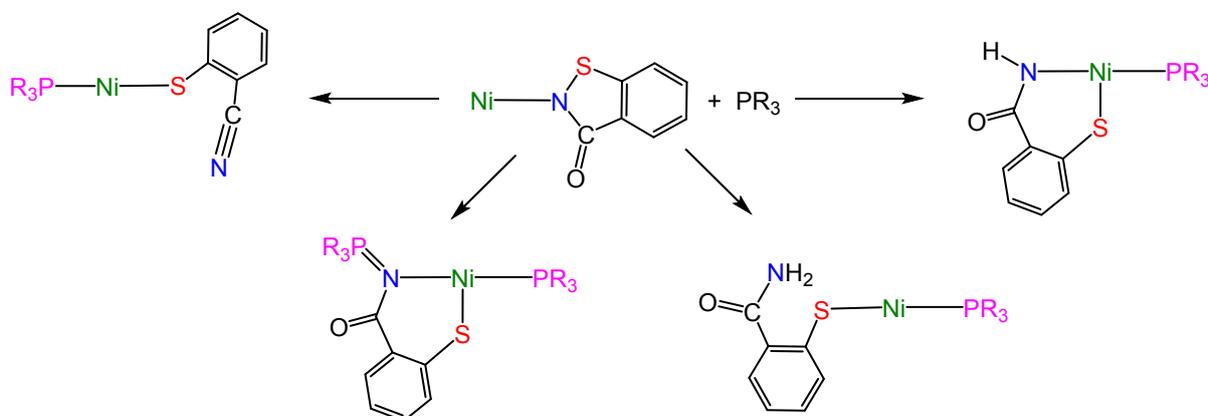
In summary, there is really no urgency for this work in its present form to be accepted for publication in Dalton Trans. When the authors have obtained more insights into the mechanism of the ring cleavage reaction and have substantiated their claims with experimental results about the catalytic potential and biological relevance of these complexes, they could submit a full paper for consideration.

We disagree. This is a simple route to otherwise inaccessible nickel-thiolate complexes. There is more work to be done but that is why we feel that a communication is warranted at this stage.

Phosphine-promoted ring-opening of benzisothiazolinate ligands at a nickel(II) centre: A convenient synthesis of Ni(II)-thiolate complexes

Subhi A. Al-Jibori^{a*}, Samer Hussein Ali^a, Ahmed S. Al-Janabi^b, Christoph Wagner^c and Graeme Hogarth^{d*}

Phosphines react with the benzisothiazolinate (bit) paddlewheel dimer, $[\text{Ni}_2(\mu\text{-bit})_4 \cdot 2\text{H}_2\text{O}]$, resulting in sulfur-nitrogen bond scission and a series unexpected transformations leading to novel Ni(II) complexes containing 2-cyanophenylthiolate and related thiolate ligands.



Phosphine-promoted ring-opening of benzisothiazolate ligands at a nickel(II) centre: A convenient synthesis of Ni(II)-thiolate complexes

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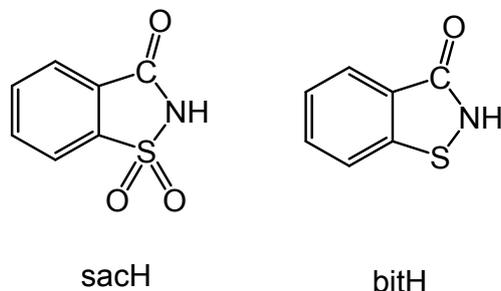
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Phosphines react with the benzisothiazolate (bit) paddlewheel dimer, [Ni₂(μ-bit)₄.2H₂O], resulting in sulfur-nitrogen bond scission and a series unexpected transformations leading to novel Ni(II) complexes containing 2-cyanophenylthiolate and related thiolate ligands.

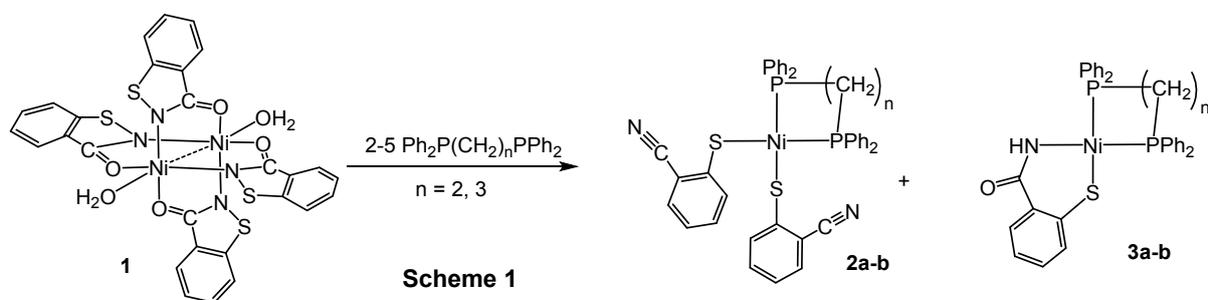
Saccharinate (sac) is a versatile poly-functional ligand with an extensive chemistry [1], while in contrast the coordination chemistry of the closely related, non-oxidised, benzisothiazolate (bit) ligand (Chart) remains virtually unexplored [2-6]. With this in mind we have initiated a systematic study of benzisothiazolate coordination chemistry [3,4] and recently showed that Na(bit) reacts cleanly with metal(II) salts to afford binuclear paddlewheel complexes, [M₂(μ-bit)₄(H₂O)₂] (M = Mn, Co, Ni, Cu, Pd), in which four benzisothiazolate ligands span the binuclear core, binding through both nitrogen and oxygen [6]. These dimers serve as synthons for development of benzisothiazolate chemistry, reactions with amines and diamines leading to metal-metal scission to afford a range of highly-colored paramagnetic mononuclear complexes in which the benzisothiazolate ligand coordinates in a monodentate fashion through nitrogen [6]. This chemistry is akin to that of saccharinate, and in all instances the ligand remains intact. In expanding the coordination chemistry of benzisothiazolate, we turned our attention to reactions of [M₂(μ-bit)₄(H₂O)₂] with phosphines, and find that the chemistry now differs

significantly from that of the saccharinate ligand, being dominated by facile sulfur-nitrogen bond scission. Herein we communicate our preliminary results for nickel which, following subsequent rearrangements, lead to a range of mononuclear Ni(II) complexes containing otherwise inaccessible thiolate ligands.



Chart

The green paddlewheel dimer, $[\text{Ni}_2(\mu\text{-bit})_4(\text{H}_2\text{O})_2]$ (**1**), is easily prepared in high yields upon addition of Na(bit) to $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ [**6**], and readily reacts with a range of phosphines. With chelating diphosphines, $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 2$, dppe; $n = 3$, dppp), reactions of **1** with two equivalents of diphosphine for 4 h resulted in formation of two products; namely, maroon **2a-b** and orange **3a-b** (Scheme 1) the relative amounts of which vary as a function of both the diphosphine and the reaction solvent.



Characterisation of **2** as bis(2-cyanophenylthiolate) complexes, $[\text{Ni}\{\kappa^2\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}\{\kappa^1\text{-SC}_6\text{H}_4\text{-2CN}\}_2]$ (**2a-b**), was based on a preliminary X-ray crystal structure of **2a** (Fig. S1); which, while of poor quality, nevertheless firmly established the overall structure, and analytical-spectroscopic data are in full accord. While still retaining a ratio of nickel to sulfur-containing ligands of 1:2, the benzisothiazolinate ligands have undergone an unexpected rearrangement involving N-S bond scission and (presumably) dehydration, the amide being converted into a cyanide ligand. While a small number of derivatives of the type

$[\text{Ni}(\kappa^2\text{-diphosphine})(\kappa^1\text{-SAr})_2]$ and $[\text{Ni}(\kappa^2\text{-PR}_3)_2(\kappa^1\text{-SAr})_2]$ are known [7-11], as far as we are aware, the 2-cyanophenylthiolate is novel.

Complexes **3a-b** were characterised crystallographically (Fig. 1 and Fig. S2 respectively). Here there is a 1:1 ratio of Ni:S, one of the benzisothiazolate ligands having been lost, the fate of which is unknown. The remaining benzisothiazolate ligand has undergone N-S bond scission but now the carbonyl remains intact and the nitrogen remains bound to the nickel centre. Overall the generated ligand is best described as a thio-amide and carries a two-minus charge.

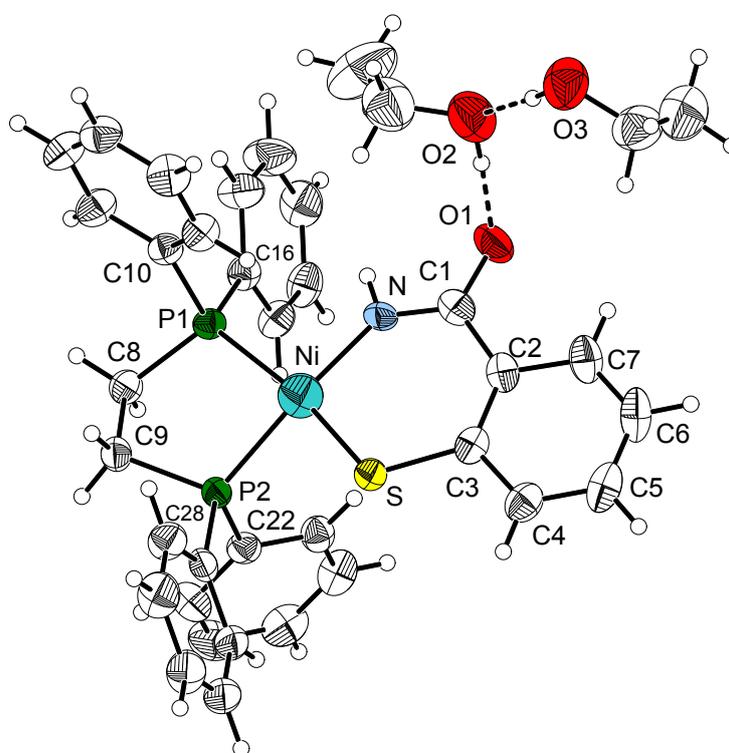
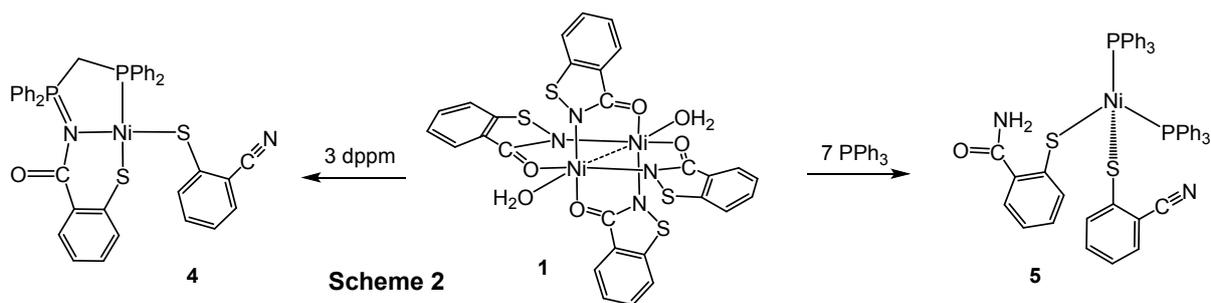


Fig. 1. Molecular structure of **3a**·(EtOH)₂ with thermal ellipsoids at the 50% level.

All the complexes **2** and **3** are square-planar and diamagnetic. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra reveal that these structures are maintained in solution, with **2** showing a singlet resonance due to the equivalence of the two ends of the diphosphine, while **3** shows two doublets associated with the unsymmetrical nature of the thio-amide ligand.



The unusual rearrangement of the nickel-bound benzisothiazolate ligand(s) is not restricted to these diphosphines but the precise nature of the isolated product(s) is phosphine-diphosphine dependent. Thus we have also investigated reactions of **1** with PPh_3 and the small bite-angle diphosphine, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm) (Scheme 2). With the latter the product **4** was confirmed by X-ray crystallography (Fig. 2). It contains a square-planar Ni(II) centre ligated by one 2-cyanophenylthiolate ligand, while the second benzisothiazolate has undergone an N-S scission but the product of this has been “trapped” by addition of one end of the diphosphine to form an iminophosphorane.

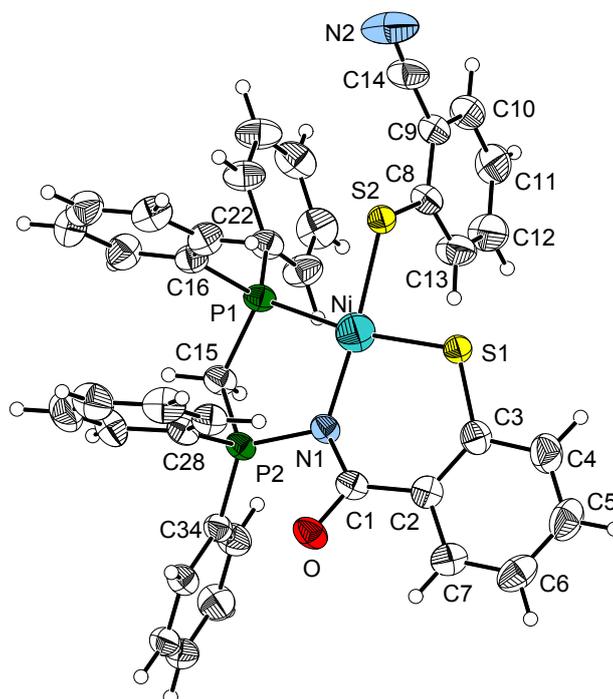


Fig. 2. Molecular structure of **4** with thermal ellipsoids at the 50% level.

Reaction of **1** with PPh_3 another course; the product is now paramagnetic being consistent with a tetrahedral Ni(II) centre and we tentatively assign this as $[\text{Ni}(\text{PPh}_3)_2(\kappa^1\text{-SC}_6\text{H}_4\text{-2-CN})(\kappa^1\text{-SC}_6\text{H}_4\text{-2-CONH}_2)]$ (**5**) (Scheme 2) on the basis of spectroscopic and analytical data.

The presence of a 2-cyanophenylthiolate ligand is shown by a $\text{C}\equiv\text{N}$ band at 2219 cm^{-1} in the IR spectrum. The latter also contains two weak bands at 3334 and 3147 cm^{-1} assigned to an NH_2 group and a medium intensity band at 1633 cm^{-1} assigned to a $\text{C}=\text{O}$ band. Thus we are confident that the two sulfur-containing ligands are inequivalent but await crystallographic confirmation that this is indeed the precise structure. Interestingly, while $[\text{Ni}(\kappa^2\text{-dppe})(\kappa^1\text{-SPh})_2]$ is known and has a square-planar geometry [11], the analogous PPh_3 derivative, $[\text{Ni}(\kappa^1\text{-PPh}_3)_2(\kappa^1\text{-SPh})_2]$ is unknown. Analogous platinum and palladium complexes $[\text{M}(\kappa^1\text{-PPh}_3)_2(\kappa^1\text{-SPh})_2]$ have been reported [12-14] but this chemistry is complicated by facile loss of PPh_3 to afford dimeric complexes $[\text{M}(\kappa^1\text{-PPh}_3)(\kappa^1\text{-SPh})(\mu\text{-SPh})_2]$ [14].

Thus ring-opening following N-S bond scission can be followed by dehydration to afford a 2-cyanophenylthiolate ligand (**2**, **4** and **5**), addition of a proton to give a chelating thio-amide ligand (**3**), addition of two protons to give a monodentate 2-amidophenylthiolate ligand (**5**) or trapped (by addition of a two-electron donor) as in **4**. All derive from a phosphine-induced N-S bond scission but how this occurs is currently unknown. We have previously shown that amines react with paddlewheel dimers to yield products containing the unit $[\text{M}(\text{amine})_2(\kappa^1\text{-bit})_2]$ in which the benzisothiazolate ligand binds in a monodentate fashion through nitrogen [6]. It may be that for similar complexes, $[\text{M}(\text{phosphine})_2(\kappa^1\text{-bit})_2]$, the softer nature of phosphorus favours S-bound coordination of the ligand and this in turn triggers N-S bond scission. Following this, the range of ligands generated appears to be a function of the ease of proton addition to nitrogen and dehydration. Synthetic and computational studies to fully elucidate the nature of these novel rearrangements are underway together with chemistry to exploit the fortuitous discovery of this one-pot, relatively high yielding, route to otherwise inaccessible Ni(II) thiolate complexes.

Acknowledgements

We thank the University of Tikrit and King's College London for partial support of this work and a referee for helpful suggestions regarding the structure refinement of the water molecules in **3b**.4H₂O (see ESI).

Conflicts of interest

There are no conflicts of interest.

Notes and references

- 1 E.J. Baran and V.T. Yilmaz, *Coord. Chem. Rev.*, 2006, **250**, 1980-1999.
- 2 D.M. Griffith, A. Haughey, S. Chahal, H. Muller-Bunz and C.J. Marmion, *Inorg. Chim. Acta*, 2010, **363**, 2333-2337.
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Appendix A Supplementary data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC 1884912-1884914. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.ac.uk](http://www.ccdc.ac.uk)).

Phosphine-promoted ring-opening of benzisothiazolate ligands at a nickel(II) centre: A convenient synthesis of Ni(II)-thiolate complexes

Electronic Supplementary Information

Fig. S1. Molecular structure of **2a**

Fig. S2. Molecular structure of **3b**.4H₂O

E1. General methods, reagents and instrumentation

E2. Synthesis of **2a** and **3a**

E3. Synthesis of **2b** and **3b**

E4. Synthesis of **4**

E5. Synthesis of **5**

E6. Crystal structure determinations

Table S1. Crystallographic data and structure refinement details

Table S2. Selected bond lengths (Å) and bond angles (°)

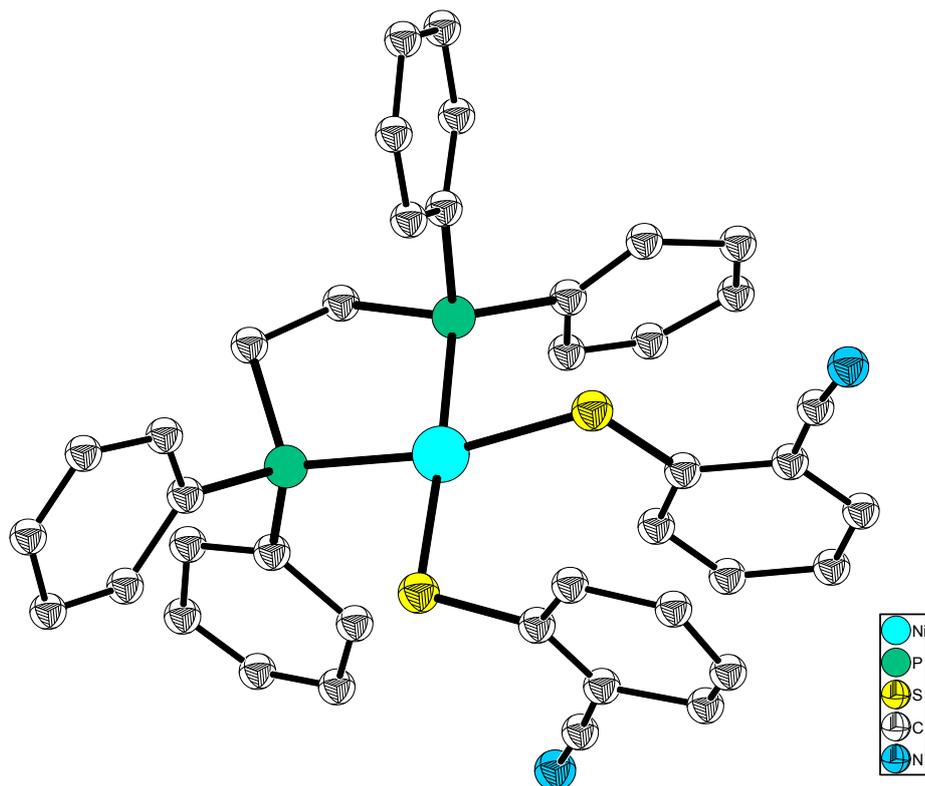


Fig. S1. Molecular structure of **2a**

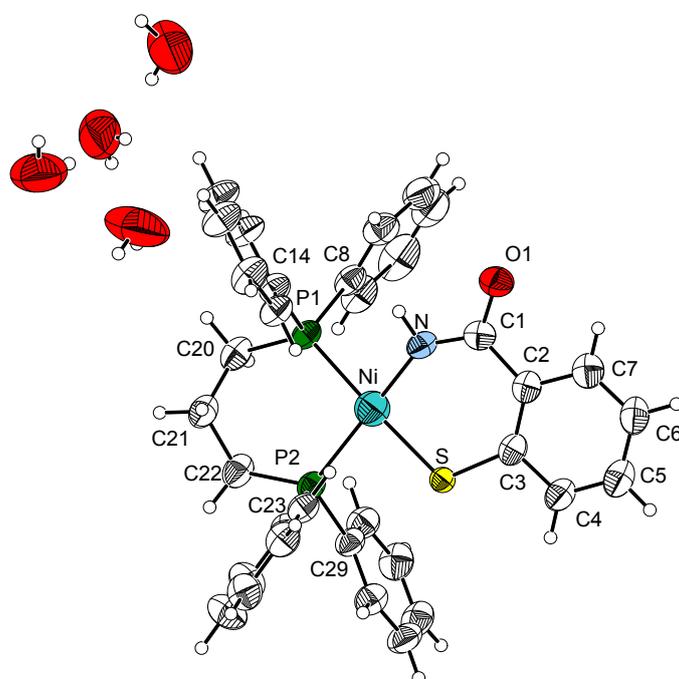


Fig. S2. Molecular structure of **3b.4H₂O**.

General methods, reagents and instrumentation - ^1H NMR spectra were recorded on a Varian Unity spectrometer using $\text{d}^6\text{-DMSO}$ as solvent. IR spectra were recorded on Shimadzu FT-IR 8400 spectrophotometer in the $400\text{-}4000\text{ cm}^{-1}$ range as KBr discs and in the $200\text{-}600\text{ cm}^{-1}$ as CsI discs Elemental analyses were carried out at Al Al-Bayt University, Jordan using a Euro vector EURO EA300 elemental analyzer. Melting points measured on a Gallenkamp melting point apparatus and are uncorrected. Conductivity measurements were carried out on 10^{-3} molar solutions using a digital conductivity meter. $[\text{Ni}_2(\mu\text{-bit})_4(\text{H}_2\text{O})_2](1)\cdot 3\text{H}_2\text{O}$ was prepared by the literature method.

Synthesis of 2a and 3a - Three slightly different procedures have been employed. **(a)** EtOH (20 cm^3) and CH_2Cl_2 (5 cm^3) were added to a mixture of dppe (0.30 g, 0.74 mmol) and **1** (0.30 g, 0.37 mmol). The mixture was stirred for 30 mins then heated at reflux for 4 h. Filtration gave an orange solid which was dried under vacuum and recrystallized from $\text{CH}_2\text{Cl}_2/\text{EtOH}$ to afford orange needles crystals of **3a** (0.30 g, 58%). The maroon mother liquor was left to evaporate at room temperature to give a maroon solid, which was recrystallized from $\text{CH}_2\text{Cl}_2/\text{EtOH}$ to afford maroon plate-like crystals of **2a** (0.10 g, 18%). **(b)** CH_2Cl_2 (20 cm^3) was added to a mixture of dppe (0.58 g 1.46 mmol) and **1** (0.30 g, 0.37 mmol). The mixture was stirred at room temperature for 30 mins to afford a maroon solution. The solution was heated at reflux for 4 h, filtered and the filtrate was set aside to evaporate at room temperature. The resulting maroon solid was recrystallized from $\text{CH}_2\text{Cl}_2/\text{EtOH}$ to give a mixture of orange needles of **3a** (5%) and maroon plates of **2a** (95%). Combined yield 0.30 g, 80%. **(c)** EtOH (20 cm^3) was added to a mixture of dppe (0.30 g, 0.74 mmol and **1** (0.30 g, 0.37 mmol). The mixture was stirred for 4h at room temperature to afford an orange precipitate which was collected and dried under vacuum. Recrystallisation from $\text{CH}_2\text{Cl}_2/\text{EtOH}$ afforded orange needle crystals of **3a**. Yield 0.10 g, 76%. Characterising data for **2a**: Dark maroon plates. *Anal.* Calc. for $\text{C}_{40}\text{H}_{32}\text{N}_2\text{NiP}_2\text{S}_2$: C 66.22, H 4.45, N 3.86, S 8.84. Found: C 66.55, H 4.97, N 3.80, S 8.59. IR: 3053w, 2921w, 2858w, 2214m, 1579m, 1483w, 1429s, 1101m, 876w, 810w, 748s, 700s, 528s, 478m cm^{-1} . UV-Vis (λ_{max} nm): 540, 376, 310. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): 55.6 (s) ppm. ^1H NMR (dmsO-d_6): δ 8.01 (d, J 7.6 Hz, 1H, Ph), 7.91-7.45 (m, 20H, Ph), 7.36 (d, J 7.6 Hz, 1H, Ph), 7.25 (d, J 7.6, 1H, Ph), 7.17 (d, J 7.6 Hz, 1H, Ph), 7.02 (d, J 7.6 Hz, 1H, Ph), 6.94 (t, J 4.0 Hz, 1H, Ph), 6.86 (t, J 4.0 Hz, 1H, Ph), 6.80 (t, J 4.0 Hz, 1H, Ph), 2.50 (s, 4H, 2CH_2). Mp: 244 °C. Characterising data for **3a**: Orange needles. *Anal.* Calc. for $\text{C}_{33}\text{H}_{29}\text{NNiOP}_2\text{S}$: C 65.16, H 4.81, N 2.30, S 5.52. Found: C 65.55, H 4.84, N

2.02, S 5.59. IR: 3299w, 3051w, 2908w, 1589s, 1573s, 1535m, 1483w, 1434s, 1375m, 1101s, 746s, 692m, 532vs, 484m cm^{-1} . UV-Vis (λ_{max} nm): 530, 380, 305. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): 59.3 (d, J 51 Hz), 56.1 (d, J 51) ppm. ^1H NMR (CDCl_3): δ 7.91-7.78 (m, 6H, Ph), 7.57-7.38 (m, 14H, Ph), 7.32 (d, 8.0 Hz, 1H, Ph), 6.94 (dd, J 8.0, 4.0 Hz, 1H, Ph), 6.77 (td, J 4.0, 8.0 Hz, 1H, Ph), 6.69 (td, J 4.0, 8.0 Hz, 1H, Ph), 2.35 (d, J 4.0 Hz, 4H, 2 CH_2). Mp: 173 °C decomposes.

Synthesis of 2b and 3b - EtOH (25 cm^3) and CH_2Cl_2 (5 cm^3) was added to dppp (0.37 g 0.89 mmol) and **1** (0.30 g, 0.37 mmol). The resulting mixture was stirred for 30 mins then heated at reflux for 4 h to give a maroon suspension. This was filtered to give a light maroon solid which was dried under vacuum and recrystallized from $\text{CH}_2\text{Cl}_2/\text{EtOH}$ to afford light maroon crystals of **2b** (Yield 0.25 g, 40%). The filtrate was left to evaporate at room temperature to give a dark maroon solid which was recrystallized from $\text{CH}_2\text{Cl}_2/\text{EtOH}$ to afford dark maroon crystals **3b** (Yield 0.17 g, 26%). Characterising data for **2b**: Light maroon. *Anal.* Calc. for $\text{C}_{41}\text{H}_{34}\text{N}_2\text{NiP}_2\text{S}_2$: C 65.01, H 4.97, N 3.70, S 8.46. Found: C 65.00, H 4.77, N 3.66, S 8.40. IR: 3062w, 2925m, 2856w, 2221m, 1674w, 1581s, 1494s, 1429m, 1166w, 1060w, 894w, 750s, 570w, 499w cm^{-1} . UV-Vis (λ_{max} nm): 510, 380, 305. $^{31}\text{P}\{^1\text{H}\}$ NMR (dmsO-d_6) 29.9 ppm. ^1H NMR (dmsO-d_6): δ 8.0-7.15 (m, 26H, Ph), 6.95 (bs, 2H, Ph), 6.74 (bs, 2H, Ph), 2.50 (s, 4H, 2 CH_2), 1.61 (bs, 2H, CH_2) Mp: 184 °C decomposed. Characterising data for **3b**: Dark maroon. *Anal.* Calc. for $\text{C}_{34}\text{H}_{31}\text{NNiOP}_2\text{S}_2$: C 65.62, H 5.02, N 2.25, S 5.15. Found: C 65.67, H 5.10, N 2.22, S 5.10. IR: 3049w, 2920w, 2852w, 1575vs, 1521m, 1483w, 1434s, 1305m, 1097m, 981w, 844w, 748s, 698s, 513m cm^{-1} . UV-Vis (λ_{max} nm): 538, 351, 322. $^{31}\text{P}\{^1\text{H}\}$ NMR (dmsO-d_6): 13.8 (d, J 90 Hz), 11.42(d, J 90 Hz). ^1H NMR (dmsO-d_6): δ 7.85 (d, 1H, Ph), 7.82-7.73 (m, 8H, Ph), 7.60-7.35 (m, 12H, Ph), 7.02 (d, J 8.0 Hz, 1H, Ph), 6.92 (d, J 8.0 Hz, 2H, Ph), 2.60 (d, J 8.0 Hz, 4H, 2 CH_2), 1.75 (s, 2H, CH_2). Mp: 246 °C.

Synthesis of 4 - A solution of dppm (0.25 g, 0.65 mmol) in CH_2Cl_2 (3 cm^3) was added to **1** (0.20 g, 0.25 mmol) suspended in EtOH (15 cm^3). The mixture was heated under reflux for 3 h to afford a maroon suspension. The suspension was filtered and the solid dried under vacuum. It was then extracted into CHCl_3 (ca. 10 cm^3) and EtOH (10 cm^3) was added. The mixture was left to evaporate at room temperature to afford a mixture of maroon needles and plate-like crystals. Yield 0.28 g, 80%. Characterising data for **4**: *Anal.* Calc. for $\text{C}_{39}\text{H}_{30}\text{N}_2\text{NiO}_2\text{P}_2\text{S}_2$: C 64.39, H 4.16, N 3.85, S 8.85. Found: C 64.35, H 4.12, N 3.84, S 8.81. IR: 3049w, 2910, 2212, 1583m, 1556s, 1527m, 1425s, 1321m, 1101m, 1062w, 773m, 738s,

686s, 509w, 478w cm^{-1} . UV-Vis (λ_{max} nm): 530, 365, 300. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): 45.3 (d, J 57 Hz), 15.5 (d, J 57 Hz) ppm. ^1H NMR (CDCl_3): δ 7.8-7.11 (m, 24H, Ph), 7.02 (t, J 7.8 Hz, 1H, Ph), 6.95 (d, J 7.8 Hz, 1H, Ph), 6.84 (t, J 4.0 Hz, 1H, Ph), 6.76 (t, J 4.0 Hz, 1H, Ph), 2.99 (dd, J 7.6, 1.8 Hz 2H, CH_2). Mp: 237-238°C.

Synthesis of 5 - PPh_3 (1.02 g, 3.90 mmol) and **1** (0.45 g, 0.56 mmol) were dissolved in a mixed of EtOH (7 cm^3), isopropanol (3 cm^3) and CHCl_3 (3 cm^3). The mixture was stirred for 30 min then heated at reflux for 6 h to give a maroon solid. This was filtered off and dried under vacuum. Yield 0.60 g, 60%. Characterising data for **5**: Maroon solid *Anal.* Calc. for $\text{C}_{50}\text{H}_{40}\text{N}_2\text{NiOP}_2\text{S}_2$: C 69.06, H 4.64, N 3.22, S 7.37. Found: C 69.10, H 4.59, N 3.20, S 7.30. μ_{eff} : 3.95 BM. IR: 3334w, 3269m, 3056w, 2220m, 1633m, 1577s, 1490s, 1429s, 1062w, 891w, 750s, 484m cm^{-1} . UV-Vis (λ_{max} nm): 700, 510, 318, 280. Mp: 320 °C decomposes.

Crystal structure determinations - Crystals of suitable for X-ray crystallography were mounted on a glass fiber and all geometric and intensity data were taken from this sample using a STOE-IPDS diffractometer. Absorption corrections were made using the IPDS software package. All structures were solved by direct methods and refined using full-matrix least-square routines against F^2 with SHELXL-97. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the models by calculating the positions (riding model) and refined with calculated isotropic displacement parameters. Illustrations were generated using DIAMOND 3.0. Crystallographic data is summarised in Table 1.

Table S1. Crystallographic data and structure refinement details

Compound	3a.(2EtOH)	3b.(4H₂O)	4
Empirical formula	C ₃₇ H ₄₁ NNiO ₃ P ₂ S	C ₃₄ H ₃₈ NNiO ₅ P ₂ S	C ₃₉ H ₃₀ N ₂ NiOP ₂ S ₂
Formula weight	700.42	694.37	727.42
Temperature (K)	213(2)	200(2)	213(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system,	Monoclinic	Monoclinic	Monoclinic
space group	P2 ₁ /n	P2 ₁ /n	P2 ₁ /c
Unit cell dimensions			
a (Å)	15.7991(6)	15.5162(7)	10.9912(4)
b (Å)	14.1552(5)	13.4129(6)	27.0617(12)
c (Å)	16.1484(6)	16.3229(6)	11.4178(4)
α (°)	90	90	90
β (°)	106.07(8)	104.39(2)	98.521(3)
γ (°)	90	90	90
Volume (Å ³)	3470.3(2)	3290.5(2)	3358.6(2)
Z	4	4	4
Density (calc.) (g/cm ³)	1.341	1.400	1.439
Absorption coefficient (mm ⁻¹)	0.748	0.793	0.833
F(000)	1472	1456	1504
Crystal size (mm)	0.21 x 0.09 x 0.06	0.46 x 0.45 x 0.37	0.33 x 0.28 x 0.05
Theta range for data collection (°)	1.596 to 25.000°.	1.991 to 26.857°.	1.505 to 24.999
Limiting indices	-17<=h<=18, -16<=k<=16, -19<=l<=19	-17<=h<=19, -16<=k<=16, -20<=l<=20	-13<=h<=12, -30<=k<=32, -13<=l<=13
Refln collected/ Indep.refln	31463/6114	19782/6939	17246/5910
R _{int}	0.0570	0.1023	0.0301
Completeness to θ	100.0 %	99.7 %	100.0 %
Data / restraints / parameters	6114 / 1 / 420	6939 / 4 / 409	5910 / 0 / 424
Goodness-of-fit on F ²	1.012	0.956	1.015
Final R indices [I>2σ(I)]	R1 = 0.0329, wR2 = 0.06995	R1 = 0.0549, wR2 = 0.1482	R1 = 0.0292, wR2 = 0.0677
R indices (all data)	R1 = 0.0520, wR2 = 0.0759	R1 = 0.0719, wR2 = 0.1561	R1 = 0.0416, wR2 = 0.0724
Largest diff. peak/hole (e ⁻ Å ⁻³)	0.350 and -0.250	1.075 and -0.674	0.379 /-0.185

Table S2. Selected bond lengths (Å) and bond angles (°)

4				3a			
Bond lengths		Bond angles		Bond lengths		Bond angles	
Ni-S(1)	215.17(6)	N(1)-Ni-S(1)	96.63(5)	Ni-N	189.60(19)	N-Ni-S	95.31(6)
Ni-S(2)	222.18(5)	N(1)-Ni-P(1)	92.97(5)	Ni-S	213.78(6)	N-Ni-P(2)	169.35(7)
Ni-P(1)	215.99(6)	S(1)-Ni-P(1)	170.16(2)	Ni-P(1)	219.10(6)	S-Ni-P(2)	86.53(2)
Ni-N(1)	193.27(15)	N(1)-Ni-S(2)	174.22(5)	Ni-P(2)	215.66(6)	N-Ni-P(1)	93.85(6)
N(1)-P(2)	167.98(8)	S(1)-Ni-S(2)	85.75(2)			S-Ni-P(1)	169.13(3)
		P(1)-Ni-S(2)	84.88(2)			P(2)-Ni-P(1)	85.54(2)
		C(1)-N(1)-Ni	130.30(13)			C(28)-P(2)-Ni	121.12(8)
		P(2)-N(1)-Ni	117.82(9)			C(22)-P(2)-Ni	107.48(8)
		C(3)-S(1)-Ni	112.66(8)			C(9)-P(2)-Ni	110.20(8)
		C(8)-S(2)-Ni	106.60(7)				
		C(22)-P(1)-Ni	118.24(7)				
		C(16)-P(1)-Ni	118.43(7)				
		C(15)-P(1)-Ni	102.90(7)				
3b							
Bond lengths		Bond angles					
Ni-S	215.98(8)	N-Ni-S	93.40(8)				
Ni-P(1)	220.56(8)	N-Ni-P(2)	171.68(8)				
Ni-P(2)	218.14(9)	S-Ni-P(2)	85.26(3)				
Ni-N	188.5(3)	N-Ni-P(1)	87.58(8)				
		S-Ni-P(1)	171.70(3)				
		P(2)-Ni-P(1)	94.92(3)				
		C(22)-P(2)-Ni	120.67(12)				
		C(23)-P(2)-Ni	109.74(11)				
		C(29)-P(2)-Ni	113.23(11)				
		C(1)-N-Ni	139.6(2)				