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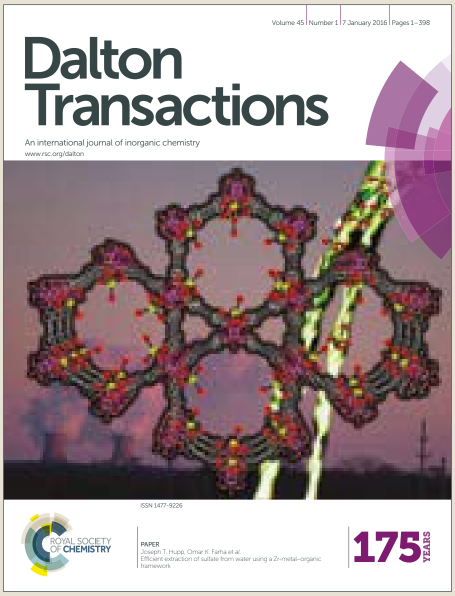
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COMMUNICATION

Homolytic cleavage of Lawesson's reagent: *N*-heterocyclic carbene complexes of ArPS$_2$ (Ar = 4-CH$_3$O-C$_6$H$_4$)

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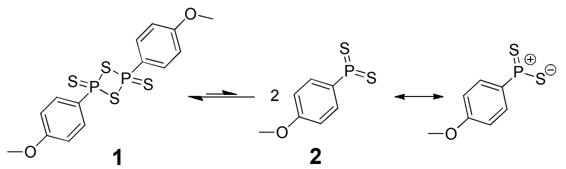
Ebrahim Soleimani,[a,b*] Katherine N. Robertson,[b] Cory C. Pye[b] and Jason A. C. Clyburne[b]*

Lawesson's reagent has been shown to react with the *N*-heterocyclic carbenes [1,3-*bis*(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) and 1,3-b*is*(2,6-diisopropylphenyl)imidazolidin-2-ylidene (SIPr)] to give adducts of the general form NHC•P(S)$_2$-C$_6$H$_4$OCH$_3$. Full characterizations, including X-ray crystal structures, are provided. The reaction of Woollin's reagent with IMes gave the known selanone, (IMes)Se.

Lawesson's reagent (LR) **1** is the compound of choice for the direct conversion of a wide array of carbonyl containing species into the corresponding thiocarbonyls.[1,2,3] It is commercially available, easy to handle, and usually gives the desired product in high yield. In spite of its versatility, reports regarding its actual mechanism(s) of reaction are few.[4,5] It is accepted that the initial step of the thionation reactions occur via cleavage of LR to give two equivalents of the neutral but reactive species **2**. LR and **2** exist in equilibrium in solution but with the equilibrium lying far in favour of LR remaining intact. Species **2** contains an unusual (and presumably highly reactive) pentavalent, tricoordinate phosphorus centre. It can be drawn in either neutral or zwitterionic form, the latter highlighting the Lewis acidic nature of the phosphorus centre. It is this Lewis acidity of phosphorus that facilitates the S/O exchange reactions of LR with organic carbonyl compounds.



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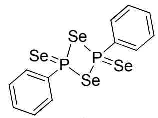

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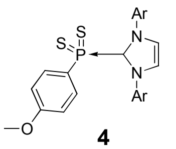
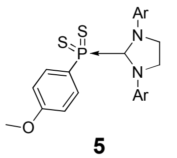
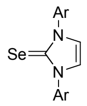


4
Ar = 2,4,6-trimethylphenyl



5
Ar = 2,6-diisopropylphenyl



6
Ar = 2,4,6-trimethylphenyl

The crystal structure of LR has been studied by both Kempe *et al.* (1992)[6] and Grossman *et al.* (1995),[7] the latter as a toluene solvate. However, the structure of the monomeric cleavage product **2** has never been reported. There are three structures similar to **2** that have been published but these all contain aromatic rings stabilized by very bulky and/or electron-withdrawing groups (2,6-CF$_3$[8]; 2,4,6-t-Bu[9]; 2,4-t-Bu and 6-Me[10]) which likely limits their reactivities. LR has also been reacted with many main group and transition metal complexes; see for examples the work of Carmalt *et al.*[11] and Weng *et al.*[12] Such reactions normally begin with cleavage of LR. The products formed most often feature interactions with the sulfur atoms of the monomer and less frequently involve interaction with the phosphorus centre. Very few simple adducts of **2** bonded through phosphorus have been crystallographically characterized and only one of these is an overall neutral molecule (the reaction of ethylenediamine with LR gives a zwitterionic product) rather than a salt.[13]

There are a number of NHC-phosphorus compounds known, isolation of which began with the compounds described by Arduengo's group in 1997. All of the complexes then isolated feature the NHC IMes bonded to a phosphorus centre bearing electron withdrawing atoms or groups (PF$_4$Ph[14], P(BH$_3$)$_2$Ph[15], CF$_3$ and Ph[16]). Their incorporation of Lewis acidic phosphorus centres to form adducts with NHCs led to our conjecture that LR should also form neutral adducts with NHCs. A search of the literature revealed only one paper where the reactions of NHCs with LR or WR had been attempted.[17] Bockfeld *et al.* observed (^{1}H and ^{77}Se NMR) the

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Electronic Supplementary Information (ESI) available: Preparative details, spectroscopic and X-ray data, and computational results have been deposited. CCDC 1589387 (**4**) and 1589388 (**5**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

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formation of the diselenide (IMe)P(Se)$_2$Ph in ca. 25 % yield after addition of 1,3,4,5-tetramethylimidazolin-2-ylidene (IMe) to WR in [D$_8$]THF. However, the main product, which was formed in 75 % yield, was identified as the selenone, (IMe)Se.

Although largely unsuccessful in their attempts to react NHCs with LR or WR, Bockfeld *et al*. were successful in isolating compounds of the formula (IMe)P(E)$_2$Ph (E = S or Se) by an alternate route. (IMe)PPh was found to react readily with sulfur (S$_8$) and selenium (Se grey) in THF to afford the corresponding NHC-phosphinidene disulfide and diselenide as colourless solids. Reactions of more sterically demanding NHC-phosphinidenes (IMes and IPr) with elemental sulfur or selenium did not lead to the isolation of single products. Here we build on this previous work and report the successful preparation and isolation of crystalline complexes formed in the reaction of LR with the NHCs IMes and SIPr.

Solutions of LR in either THF or toluene solution exhibited a ^{31}P resonance for **1** at 15.9 ppm and did not show a resonance that could be attributed to **2**. This is not unexpected given the high Lewis acidity of the phosphorus site in **2** coupled with the strong phosphorus - sulphur bonds in **1**. Furthermore, **1** in pyridine-containing solutions did not exhibit any new ^{31}P NMR features suggesting that it does not form a stable complex with pyridine in solution. This is in contrast to both **2**, which might have been expected to be stabilized by pyridine based on the work of Meisel *et al*.,[18] and **3**, which has been shown to form pyridine stabilized PhPSe$_2$ in solution (Ascherl *et al.*[19]).

A stirred solution of LR in THF was treated with the NHC IMes in THF solution. The resulting solution was stirred for 30 minutes at room temperature under a nitrogen atmosphere. An aliquot of this solution exhibited a single phosphorus NMR resonance at 53 ppm. The solution was stirred overnight and the solvent was removed *in vacuo*. The residue was dissolved in CH$_2$Cl$_2$ and slow evaporation of the solvent resulted in the formation of crystalline material that was isolated in 91% yield.

Elemental analysis and HR-MS are consistent with the formation of compound **4**. The ^{31}P NMR spectrum of crystalline **4** dissolved in CD$_2$Cl$_2$ solution exhibits a single resonance at 52.6 ppm. The ^{1}H and ^{13}C NMR spectra suggest the formation of a species composed of the NHC moiety and a fragment derived from **2**. The equivalence of the Mes methyl groups is consistent with free rotation around a new dative C-P single bond. All of the NMR data is in agreement with that reported for (IMe)P(S)$_2$Ph by Bockfeld *et al*., particularly the ^{31}P resonance they observed at 52.9 ppm in CD$_2$Cl$_2$.[17]

Following a similar procedure, but using LR and SIPr, complex **5** was prepared and characterized, including an X-ray crystal structure. Lastly, and under similar conditions, reaction of IMes with **3** (Woollins' Reagent) resulted in the immediate formation of a purple solution and subsequent isolation of a crystalline solid. X-ray diffraction showed this compound to be the known selanone, **6**, by comparison of the experimental unit cell to that reported by Vummaleti *et al.*[20] Bockfeld *et al*. had observed similar reactivity in their investigation of IMe with WR, having isolated the related product (IMe)Se.[17]

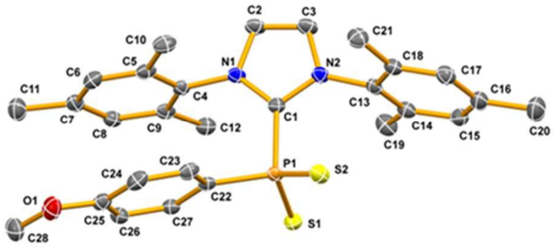

Figure 1. Solid state structure of **4.** Hydrogen atoms and co-crystallized solvent (CH$_2$Cl$_2$) have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

The X-ray crystal structures of both **4** (as a dichloromethane solvate) and **5** (as a toluene hemi-solvate) have been determined and the final results are shown in Figures 1 and 2, respectively. In addition, Table 1 summarizes selected metrical parameters and there are further diagrams and tables of crystallographic data in the Supplementary Information. Our results can be compared to the reported crystal structures for Lawesson's reagent.[6,7] In addition to the Arduengo structures previously mentioned,[14–16] and the IMePS$_2$Ph structure of Bockfeld *et al.*,[17] a search of the Cambridge Structural Database (Version 5.38, November 2017) revealed only one other structure, IMes=P-Mes, suitable for comparison to **4**.[21] There are even fewer structures with which to compare **5**; all of the relevant SIPr-P containing species have additional P-P rather than P-C bonds.[22]

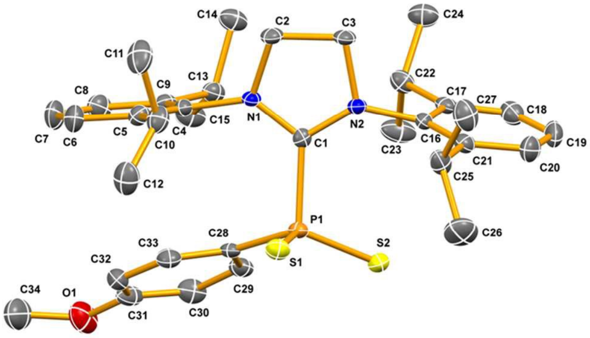

Figure 2. Solid state structure of **5.** Hydrogen atoms and co-crystallized solvent (C$_6$H$_5$CH$_3$) have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

The carbene rings in **4** and **5** are planar, although the nitrogen atoms lie slightly further out of the defined plane in **5** (0.0500 Å) than in **4** (0.0005 Å). The average C1-N bond lengths are slightly longer in **4** (1.357(2) Å) than they are in **5** (1.338(3) Å). The N-C1-N angle in **5** is considerably larger than those in either **4** or IMeP(S)$_2$Ph. The angle in **4** is typical of that in similar IMes carbene phosphorus complexes.[14,15] The angle in **5** is larger than other such angles reported for SIPr-P complexes in the literature (~107°)[22] but this is perhaps unsurprising as the structures are not that similar.

Table 1. Selected bond lengths [Å] and angles [°] for compounds **4** and **5** and IMeP(S)$_2$Ph.[17]

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	4	**5**	**IMeP(S)$_2$Ph**
S(1)-P(1)	1.9741(5)	1.9674(10)	1.9780(4)
S(2)-P(1)	1.9620(5)	1.9577(10)	1.9688(4)
P(1)-C(NHC)	1.8822(14)	1.905(2)	1.8659(12)
P(1)-C(Ph)	1.8139(15)	1.817(3)	1.8164(12)
S(1)-P(1)-S(2)	119.79(3)	120.70(5)	120.01(2)
C(NHC)-P(1)-C(Ph)	103.71(6)	106.98(11)	103.41(5)
N(1)-C(NHC)-N(2)	105.27(12)	110.3(2)	106.62(10)

The P-C bond between the carbene and the phosphorus centre is slightly longer in **5** than in **4**. This again is reflective of the unsaturation of the carbene ring in **4** and substantiated by the similarity to the length of the same bond in IMeP(S)$_2$Ph. All three bond lengths are indicative of predominantly single bond character and are similar to other P-C carbene single bond lengths reported in the literature.[14,15] In addition to the carbene P-C bond, each complex also forms a second P-C bond to a carbon atom of an aromatic ligand. These bonds are more invariant in the three compounds, being almost equal in each. The bond to the $C_6H_4OCH_3$ group is shorter than that to the carbene in **4** and **5**, but the distances are still indicative of single bonds. These P-C bonds are, however, slightly longer than those reported in LR itself.[6,7] The remainder of the bonds and angles in the $C_6H_4OCH_3$ groups are unsurprisingly very similar in **4**, **5** and both LR structures.

In each compound the phosphorus centre forms two P-S bonds in addition to the two P-C bonds. The two bond lengths are roughly equal and they are similar between the two compounds. The bonds are intermediate in length between those reported in LR,[6,7] where the P-S$_{\text{terminal}}$ bonds are shorter and the P-S$_{\text{bridge}}$ bonds are longer than all of the P-S$_{\text{terminal}}$ bonds in **4** and **5**. They are very similar to the bond lengths reported for IMeP(S)$_2$Ph by Bockfeld *et al*. and are longer than P=S double bonds.[17]

Each phosphorus centre forms a total of four bonds (2 P-C and 2 P-S) with most of the angles at phosphorus falling in the range of 103-111°. The range of angles is in agreement with that reported for the tetrahedral phosphorus centre in the IMeP(S)$_2$Ph complex.[17] There are notable outliers from ideal tetrahedral angles in the two structures. Both **4** and **5** have S(1)-P(1)-S(2) angles that lie well outside the expected tetrahedral values and in **5** the C(1)-P(1)-S(1) angle (99.13(8)°) is also smaller than expected. Thus they should be described as having distorted tetrahedral geometries at phosphorus. The S-P-S angles in **4** and **5** are larger than those found in LR, which is not surprising given that the latter are geometrically constrained. The observed S-P-S angles are again best compared to that in IMeP(S)$_2$Ph. Overall, they bracket the angle reported by Bockfeld *et al*. and all are notably similar.[17]

The unexpectedly small C(1)-P(1)-S(1) angle in **5**, relative to **4**, highlights their major structural differences. These are also visibly evident if Figures 1 and 2 are contrasted and is further substantiated by examining the interplanar angles in the two compounds. In **4**, the aryl rings of both IMes groups are planar, including the methyl carbon atoms, and lie almost perpendicular to the carbene ring plane (88.90(5) and 87.38(5)°, respectively). The aryl ring of the $C_6H_4OCH_3$ ligand is also planar (including the methoxy oxygen and carbon atoms) and almost perpendicular to the carbene ring (83.73(5)°). It lies directly below one of the IMes groups in the solid state, and is oriented almost parallel to it. There is no steric interference and the two rings can approach each other quite closely. This results in **4** having an interplanar angle of only 12.29(8)° and a distance of only 3.5072(9) Å between the ring centroids. Close intramolecular interactions thus form between the two rings.

This is in contrast to the geometry adopted in **5**, where steric effects result in a more distorted structure. The isopropyl groups of the di-isopropylphenyl (dipp) ligands do not lie in the plane of the aryl rings, but protrude above and below them. This would bring one of them into close contact with the $C_6H_4OCH_3$ group below it, if the geometry of **5** did not adapt. In **5**, the NHC aryl ring planes lie at angles of 76.3(1) and 88.7(1)° relative to the carbene ring plane. The dipp group lying above the $C_6H_4OCH_3$ ligand is the one that has closed up as the two rings (dipp and $C_6H_4OCH_3$) rotate away from each other. This results in an angle of 22.8(1)° between the rings and an increased distance (relative to **4**) of 3.889(2) Å between the ring centroids. The plane of the $C_6H_4OCH_3$ ligand is also no longer perpendicular to the carbene ring plane, this angle having decreased to 55.3(1)°.

This has consequences in the packing and intermolecular interactions of **4** and **5**. In **4**, the alignment of the planar Mes and $C_6H_4OCH_3$ groups leaves the sulfur atoms relatively unshielded. There is also a solvent molecule with potential hydrogen bonding acceptors (Cl atoms) and donors (C-H). Compound **4** forms 14 contacts that are less than the sum of the van der Waals radii, 9 of which go to the best acceptors available (Cl or S), and 7 of which are intermolecular in nature. These are all listed in Table S2 (and Table S3 for **5**) of the Supplementary Information. Of note are the contacts made by the protons on the back side of the central carbene ring and the contacts from the solvent to the sulfur atoms, which bind everything together in an extended network. There are very few short C-H…C or C-H…H-C contacts in **4**. The sulfur atoms accept both inter- and intra-molecular contacts, the latter particularly with protons on the IMes methyl groups and with aryl protons of the $C_6H_4OCH_3$ ligand.

Compound **5** forms many more short contacts than **4**, but almost all of them are intramolecular in nature. The bulky dipp groups shield the sulfur atoms, so sulfur accepts only 3 contacts and all of these are intramolecular. Compound **5** forms many more (usually weaker) C-H…C and C-H…H-C type contacts than **4**, and almost all of these are also intramolecular in nature. The dipp groups themselves, and the change in geometry relative to **4** to accommodate steric interactions, result in **5** being less available to neighbouring molecules to form intermolecular type interactions, and thus, intra-type contacts are favoured.

At the MP2/6-31G* level of theory,[23] the calculated standard gas-phase dissociation enthalpy (free energy) of **1** to produce **2** is calculated to be 108 (46) kJ/mol. For the simpler model systems, RPS$_2$ (R = H, Me, Ph), the corresponding numbers are 74 (21), 114 (43), and 110 (51) kJ/mol, respectively. The electronic-only dimerization energies at the

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MP2/6-311+G* level are higher than those at MP2/6-31G* by 20-30 kJ/mol. The frontier MOs of **2** reveal that the compound has the potential to be amphoteric, with Lewis acidity at phosphorus and Lewis basicity at sulphur. The electrostatic potential plot for **2** is shown (Figure 3 left) and from this one can see the probability of **2** engaging bases at the phosphorus site. In the case of the formation of analogues of **4**, combination of the model systems RPS_2 (above) with the simplified carbene 1,3-dimethylimidazol-2-ylidene is predicted to be exothermic (exergonic) by 179 (130), 172 (108), and 185 (127) kJ/mol, respectively. The overall process from dimer to two adduct molecules is therefore favourable. Combination of the model systems with pyridine, is predicted to be much less exothermic (exergonic) by 73 (26), 79 (21), and 78 (29) kJ/mol, and the overall reaction is nearly thermoneutral. Lastly, the electrostatic potential plot for the complex **4** is also shown (Figure 3 right), highlighting the changes induced by coordination of the carbene to **2**. Consonant with the electrostatic potential plot, **4** possesses a large dipole moment, 10.5 D, when calculated at the B3LYP/6-31G* level.

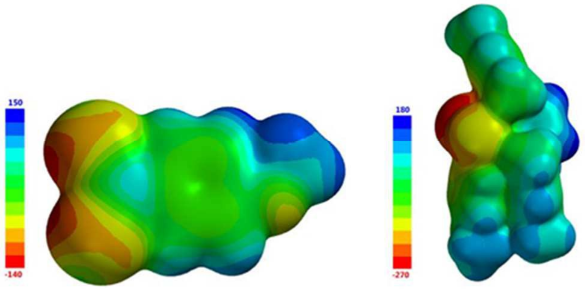

Figure 3. Electrostatic potentials [atomic units (au)] super-imposed on the total electron density isosurface ($3x10^{-3}$ au) of (left) **2** and (right) **4** calculated using DFT [B3LYP/6-31G*].[24]

Compounds **4** and **5** are examples of a rare type of complex in which an NHC is bonded to a low coordinate and high oxidation state phosphorus centre. They represent the ultimate products formed in the stepwise oxidation of the arylphosphinidene complexes, NHC•PAr, species that can be considered to be formed between a neutral carbene and a phosphinidene. A full discussion is beyond the scope of this report, but we note that during the preparation of this manuscript the first phosphinidene structure, the intermediate oxidation product ArP(S)•NHC, was published.[25] In summary, the first adducts between NHCs and the cleavage product of LR have been prepared. These have been fully characterized, with X-ray crystal structures and *ab initio* calculations included.

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Conflicts of interest

The authors have no conflicts to declare.

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