Supplementary Material (ESI) for Chemical Communications

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Intra- and inter-molecular phosphoryl migration in phosphinothiazolines; precursors to polynuclear complexes and bimetallic coordination polymers.

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Experimental

1. General Considerations

All manipulations were carried out under inert dinitrogen atmosphere, using standard Schlenk-line conditions and dried and freshly distilled solvents. The ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded unless otherwise stated on a Bruker Avance 300 instrument at 300.13, 75.47 and 121.49 MHz, respectively, using TMS, or H_3PO_4 (85% in D_2O) as external standards with downfield shifts reported as positive. All NMR spectra were measured at 298 K, unless otherwise specified. The assignment of the signals was made by $^{1}H,^{1}H$-COSY and $^{1}H,^{13}C$-HMQC experiments. FT-IR spectra in the range of 4000-500 cm^{-1} were recorded on a Nicolet Nexus FT-IR spectrometer coupled with a continuum DRIFT microspectrometer, in diffuse reflectance mode. Elemental C, H, and N analyses were performed by the "Service de microanalyses", Université Louis Pasteur, Strasbourg.
The following compounds were prepared according to literature procedures: $[PtCl_2(NCPh)_2]$[S1] and [AuCl(THT)].[S2] PPh_2Cl was freshly distilled before use. Other chemicals were commercially available and used as received.

2. Synthesis

Preparation and Spectroscopic Data for 1.

Solid 2-amino-2-thiazoline (1.50 g, 14.7 mmol) was dissolved in 80 mL of THF and pure Et_3N (2.0 mL, 1.50 g, 14.8 mmol) was added. Pure PPh_2Cl (2.62 mL, 3.24 g, 14.7 mmol)

was added dropwise. The resulting solution was stirred under N_2 for 24 h. The volatiles were removed under vacuum and the resulting white solid was extracted with toluene (100 mL), the solution was filtered and the solvent removed under vacuum affording compound **1** as a colourless microcrystalline solid (3.84 g, yield 92%). If traces of the diphosphine ligand **2** (see below) are present, it can be converted to pure **1** by addition of an appropriate quantity of 2-amino-2-thiazoline to a THF solution of the crude product and stirring for 5 h. Single crystals of **1** suitable for X-ray analysis were obtained by layering a $CHCl_3$ solution with hexane or by evaporation of a $CHCl_3$ saturated solution of compound **1**. ^{1}H NMR ($CDCl_3$, 298 K) δ: 3.31 (t, 2H, ^3J(H,H) = 7.3 Hz, SCH_2), 3.67 (dt, 2H, ^3J(H,H) = 7.3 Hz, ^5J(P,H) = 2.2 Hz, NCH_2), 7.21-7.65 (m, 10H, aromatic); ^{1}H NMR ($CDCl_3$, 210 K) δ: 3.16 (t, br, 2H, ^3J(H,H) = 7.3 Hz, SCH_2), 3.08 (br, 2H, NCH_2), 7.21-7.65 (m, 10H, aromatic); ^{1}H NMR ($CDCl_3$, saturated solution, 298 K) δ: 3.12 (t, br, 2H, ^3J(H,H) = 6.9 Hz, SCH_2), 3.24 (dt, 2H, ^3J(H,H) = 6.9 Hz, ^5J(P,H) = 2.1 Hz, NCH_2), 7.21-7.58 (m, 10H, aromatic), 8.55 (br, 1H, NH). ^{1}H NMR (C_6D_6, 298 K) δ: 2.42 (t, 2H, ^3J(H,H) = 7.3 Hz, SCH_2), 2.80 (dt, 2H, ^3J(H,H) = 7.3 Hz, ^5J(P,H) = 2.2 Hz, NCH_2), 6.98-7.65 (m, 10H, aromatic), 8.61 (br, 1H, NH). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K) δ: 32.7 (d, ^4J(P,C) = 12 Hz, SCH_2), 51.7 (s, NCH_2), 128.0-140.7 (m, aromatic, PPh_2), 169.8 (d, ^2J(P,C) = 12 Hz, C=N). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K) δ: 47.9 (s); ^{31}P{^{1}H} NMR ($CDCl_3$, 210 K) δ: 51.9; ^{31}P{^{1}H} NMR (C_6D_6, 298 K) δ: 51.4. ^{31}P{^{1}H} NMR ($CDCl_3$, saturated solution, 298 K) δ: 50.7; (s). Anal. Calcd for $C_{15}H_{15}N_2PS$ (M = 286.33): C, 62.92; H, 5.28; N, 9.78. Found: C, 63.15; H, 5.26; N, 9.99.

The expected splitting of the ^{31}P signal at 210 K was not observed. However, the increased energy gap between the two tautomers in solution should be taken into account (see DFT section). The stabilization of isomer **1b** compared to **1a** is believed to increase the equilibrium constant value and therefore to preclude the observation of tautomer **1a** at low temperatures.

When a single crystal of **1a,b** was dissolved in $CDCl_3$, diphosphine **2** and **ATHZ** were detected by ^{1}H and ^{31}P NMR, both with a ca. 1:10 integration ratio with respect to **1a,b**. The ratio decreases to ca. 1:20 in d_6-toluene. Therefore, the reaction **2** + **ATHZ** → 2 **1** is an equilibrium, whose large K value seems to increase in non-polar solvents.

Preparation and Spectroscopic Data for 2.

Method A) A solution of *n*-BuLi in hexane (8.13 mL, 1.6 M, 13 mmol) was added dropwise via syringe to a THF solution (50 mL) of 2-amino-2-thiazoline (0.61 g, 6.0 mmol) at –78 °C. The cloudy solution was stirred for 30 min and degassed $SiClMe_3$ (1.42 g, 1.65 mL,

13 mol) was added. The clear solution was stirred for 30 min at –78 °C and then allowed to slowly warm to room temperature. After evaporation of the solvent under reduced pressure, the pale yellow residue was dissolved in diethyl ether (50 mL) and PPh_2Cl (2.65 g, 2.2 mL, 12 mmol) was added dropwise at –78 °C and stirring was maintained for 2 h. The solution was allowed to slowly reach room temperature and further stirred overnight. After evaporation of the solvent under reduced pressure, the yellow residue was triturated with hexane (20 mL) to eliminate residual THF and $SiClMe_3$. The pale yellow residue was then extracted with toluene (4 x 30 mL) and **2** was obtained as a white solid after evaporation of the toluene in vacuo (2.31 g, 4.90 mmol, 82%).

Method B) 2-amino-2-thiazoline (1.50 g, 14.7 mmol) was dissolved in 80 mL of toluene and PPh_2Cl (2.16 g, 1.81 mL, 9.8 mmol) was added dropwise at room temperature. The resulting solution was stirred under nitrogen for 2 h and then filtered. The solvent was removed under vacuum affording compound **2** as a colourless microcrystalline compound (2.17 g, 4.61 mmol, 94%). Suitable single crystals for X-ray analysis were obtained by slow cooling of a hot saturated toluene solution of **2**.

^{1}H NMR ($CDCl_3$) δ: 3.13 (t, 2H, ^3J(H,H) = 6.9 Hz, SCH_2), 3.41 (dt, 2H, ^3J(H,H) = 6.9 Hz, ^5J(P,H) = 2.1 Hz, NCH_2), 7.25-7.58 (m, 20H, aromatic). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 30.1 (d, ^4J(P,C) = 10.9 Hz, SCH_2), 49.7 (d, ^2J(P,C) = 6.1 Hz, NCH_2), 128.1-142.5 (m, aromatic, PPh_2), 168.7 (dd, ^2J(P,C) = 12.1 Hz, ^2J(P-C) = 36.6 Hz, CN). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 41.9 (s), 51.2 (s). Anal. Calcd for $C_{27}H_{24}N_2P_2S$ (M = 470.51): C, 68.92; H, 5.14; N, 5.95. Found: C, 68.07; H, 4.97; N, 5.84.

Preparation and Spectroscopic Data for 4.

Solid [AuCl(THT)] (0.103 g, 0.32 mmol) was added to a solution of **2** (0.075 g, 0.16 mmol) in CH_2Cl_2 (30 mL). The clear solution was stirred overnight and its volume reduced to 5 mL. Compound **4** was crystallized by slow diffusion of diethyl ether into the mother liquor (0.150 g, 0.147 mmol, 92%). The compound can be purified by crystallization at room temperature by slow diffusion of heptane into a solution in CH_2Cl_2. Suitable single crystals for X-ray analysis were obtained with the same technique using $CHCl_3$ instead of CH_2Cl_2.

^{1}H NMR ($CDCl_3$) δ: 3.37 (t, 2H, ^3J(H,H) = 6.6 Hz, SCH_2), 3.48 (dt, 2H, ^3J(H,H) = 6.6 Hz, ^5J(P,H) = 1.2 Hz, NCH_2), 7.27-7.75 (m, 20H, aromatic). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 31.7 (s, SCH_2), 51.3 (s, NCH_2), 127.9-133.3 (m, aromatic, PPh_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 65.3 (s), 68.6 (s). Anal. Calcd for $C_{27}H_{24}Au_2Cl_2N_2P_2S{\bullet}CH_2Cl_2$ (M = 1020.28): C, 32.96; H, 2.57; N, 2.75; Found: C, 33.40; H, 2.58; N, 2.62.

Preparation and Spectroscopic Data for 5.

A solution of *t*-BuLi (1.03 mL, 1.7 M, 1.75 mmol) was added to a solution of **1** (0.500 g, 1.75 mmol) in THF (50mL), at room temperature. The reaction mixture was stirred for 5 min. Solid $[PtCl_2(NCPh)_2]$ (0.412 g, 0.875 mmol) was added and the reaction mixture stirred for 30 min. The solvent was removed under vacuum and the residue redissolved in CH_2Cl_2 (30 mL). Filtration followed by evaporation of the volatiles afforded **5** as a white powder. This compound can be recrystallized from a 1:2:1 CH_2Cl_2, MeOH, MeCN solution (evaporation). Yield after recrystallization: 0.930 g, 0.60 mmol, 69%. ^{1}H NMR ($CDCl_3$) δ: 3.56 (t, 4H, ^3J(H,H) = 7.2 Hz, SCH_2), 4.33 (t, 4H, ^3J(H,H) = 7.2 Hz, NCH_2), 7.01-7.31 (m, 20H, aromatic). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 35.3 (s, SCH_2), 57.6 (s, NCH_2), 127.6-133.3 (m, aromatic, PPh_2), 188.2 (s, CN). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 65.17 (s, ^1J(P-Pt) = 3207 Hz). Anal. Calcd for $C_{30}H_{28}N_4P_2PtS_2$ (M = 765.73): C, 47.06; H, 3.69; N, 7.32. Found: C, 46.93; H, 3.83; N, 7.35.

Preparation and Spectroscopic Data for 6.

A solution of AgOTf (0.167 g, 0.65 mmol) in THF (10 mL) was added dropwise to a solution of compound **5** (0.500 g, 0.65 mmol) in CH_2Cl_2 (20 mL). A white microcrystalline solid precipitated instantaneously. The reaction mixture was stirred for 10 min. The solid was filtered and washed with amounts of CH_2Cl_2 (2x10 mL) and THF (2x10 mL). Evaporation of the solvents afforded **6** (0.590 g, 0.58 mmol, 90%) as a white powder. This compound can be crystallized by layering the two aforementioned starting solutions. The system was put in a dark place for two weeks. Crystals of **6** compound formed at the interface, were collected and dried under vacuum. Anal. Calcd for $C_{30}H_{28}N_4Ag_2P_2PtS_2{\cdot}CF_3O_3S$ (M = 1022.67): C, 36.41; H, 2.76; N, 5.48. Found: C, 36.82; H, 2.89; N, 5.27. The infrared spectrum is reported in figure S-1 and compared with that of compound **5.**

Reaction of 2 with 2-amino-2-thiazoline, conversion in 1.

Solid 2-amino-2-thiazoline (0.114 g, 1.064 mmol) was added to a solution of **2** (0.500 g, 1.064 mmol) in THF (50 mL). The reaction mixture was stirred for 16 h, the solvent removed under vacuum affording compound **1** quantitatively.

Formation and NMR spectroscopic identification of 3

A solution of *n*-BuLi (1.6 M, 3.09 mL, 4.95 mmol) was added dropwise at -78 °C to a solution of **ATHZ** (0.500 g, 4.95 mmol) in THF (30mL). Liquid Ph_2PCl (221 μL, 0.272 g, 1.24 mmol) was added dropwise over a period of 15 min at -78 °C. The reaction mixture was

allowed to warm to RT. *In situ* ^{31}P NMR revealed compound **3** as the only ^{31}P containing species present in solution. **3** was identified by comparison of its ^{31}P NMR chemical shift (singlet, δ 29 ppm) with those reported for secondary amino-diphenylphosphines.[S3] **3** was found to quantitatively isomerize in **1** over a period of 16 h.

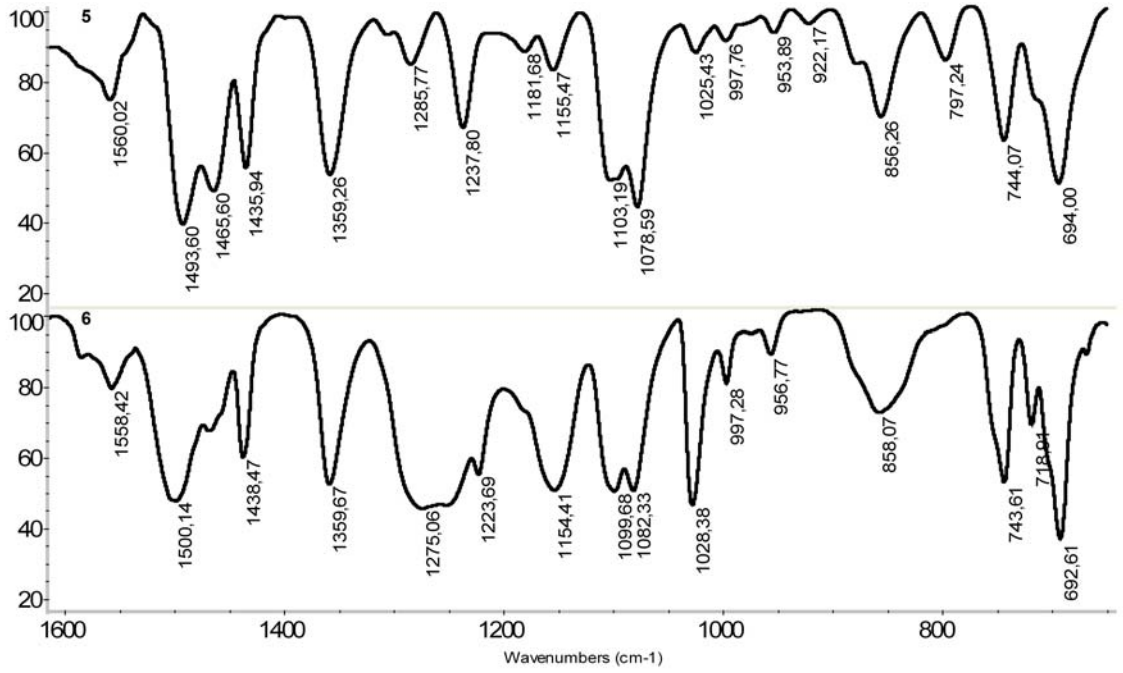


Figure S-1: comparison between the FTIR spectra of compounds **5** and **6**.

3. X-ray data collection, structure solution and refinement for compounds 1a,b, 2, 4·$CHCl_3$ and **6**·$3CH_2Cl_2$

Suitable crystals for the X-ray analysis of compounds **1a,b**, **2**, **4**·$CHCl_3$ and **6** ·$3CH_2Cl_2$ were obtained as described above. The intensity data was collected at 173(2) K on a Kappa CCD diffractometer[S4] (graphite monochromated MoK_α radiation, λ = 0.71073 Å). Crystallographic and experimental details for the structures are summarized in Table S-1. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97)[S5] with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined *riding* on the corresponding parent atoms. Tautomers **1a** and **1b** co-crystallized. In the asymmetric unit the N-H protons were found disordered in two positions, with occupancy factors ca. equal to 0.5. The C-N bond distances are in turn affected by this disorder, being inconsistent with the Lewis structure. For instance, the exo-cyclic distances C1-N1 and C16-N3 [1.321(2) and 1.314(2) Å, respectively]

are almost equal to the endo-cyclic C1-N2 and C16-N4 [1.313(2) and 1.320(2) Å, respectively]. Therefore, a detailed discussion on the structural parameters of compound **1** would be misleading. Attempts to resolve the disorder (i.e. decreasing the space group symmetry to P1 and P-1) were unsuccessful. The unit cell was measured at temperatures ranging from 293 to 173 K and varying the exposure time. CCDC-xxx (**1a,b**), xxx (**2**), xxx (**4**) and xxx (**6**) contain the supplementary crystallographic data for this paper that can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S-1: X-ray data collection and refinement parameters for compounds **1a,b**, **2, 4·$CHCl_3$** and **6** ·$3CH_2Cl_2$

Compound	**1a,b**	**2**	**4**·$CHCl_3$	**6**·$3CH_2Cl_2$
Formula	2 x $C_{15}H_{15}N_2S_1P_1$	$C_{27}H_{24}N_2S_1P_2$	$C_{27}H_{24}N_2S_1P_2Au_2Cl_2$ ·$CHCl_3$	$C_{30}H_{28}N_4S_2P_2$·CF_3SO_3· $3CH_2Cl_2$
FW	286.32	470.48	1054.68	1277.43
Crystal System	Monoclinic	Triclinic	Triclinic	Monoclinic
Space Group	*P21/c*	*P-1*	*P-1*	*P21/n*
***a*, Å**	15.5330(3)	9.1420(2)	9.6100(10)	9.185(3)
***b*, Å**	11.8340(2)	10.0760(2)	13.281(2)	19.488(6)
***c*, Å**	16.1740(3)	14.4330(4)	13.769(2)	25.892(9)
α, °	90	92.1400(9)	98.04(5)	92.1400(9)
β, °	105.3850(10)	100.10(3)	101.87(5)	90
γ,°	90	107.9900(12)	104.52(5)	99.74(2)
***V*, Å^3**	2866.52(9)	1205.47(5)	1630.5(4)	90
Z	8	2	2	4
D_{calcd}, g cm^{-3}	1.327	1.296	2.148	1.858
***F*(000)**	1200	492	992	2488
Crystal size (mm)	0.20 × 0.20 × 0.20	0.10 × 0.10 × 0.10	0.08 × 0.06 × 0.05	0.10 × 0.10 × 0.10
μ, cm^{-1}	3.25	2.85	95.82	40.97
Rflns. collected	15690	10874	9537	22964
Rflns. unique	5731	7015	9536	13265
Rflns. observed [$I > 2\sigma(I)$]	3562	4950	7031	10225
Parameters	359	289	361	514
***R* Indices [$I>2\sigma(I)$]**	*R1* = 0.0457, *wR2* = 0.1289	*R1* = 0.0480, *wR2* = 0.1229	*R1* = 0.0408 *wR2* = 0.1074	*R1* = 0.0503, *wR2* = 0.1198
***R* Indices (all data)**	*R2* = 0.0839, *wR2* = 0.1117	*R2* = 0.0792, *wR2* = 0.1401	*R2* = 0.0621, *wR2* = 0.1244	*R2* = 0.0720, *wR2* = 0.1295

4. Computational details

All calculations were done using the program system TURBOMOLE.[S6] If not mentioned explicitly otherwise, we used the DFT method with the Becke-Perdew functional (BP86).[S7] The Coulomb terms were treated by the RI-J approximation.[S8] For the structure optimizations we used SV(P) basis sets[S9] (single zeta for core orbitals, double zeta for the valence shells and one set of polarization functions for all centres except hydrogen). Single point energies were calculated with larger triple zeta valence plus polarization basis sets (TZVP).[S10] The total energies, computed with BP86/SV(P) and BP86/TZVP methods/bases are reported in Table S-2. For each compound, several conformers, whose computed structures are graphically reported below, were optimized. Single point calculation were carried out on **1a** and **1b** models in order to evaluate the influence of the solvent (COSMO method, $CHCl_3$).[S11] The absolute and relative energies listed in Tables S-2 to S-7 correspond to the most stable conformations.

Table S-2 Total energies (E_T, eV)

Species	**BP86/SV(P)**	**BP86/TZVP**
ATHZ/amino	-17017.5156510 eV	-17028.2102781 eV
ATHZ/imino	-17017.4190390 eV	-17028.0947530 eV
1a	-38886.4354574 eV	-38913.2069282 eV
1b	-38886.4613979 eV	-38913.2156757 eV
2	-60755.2460783 eV	-60798.1407216 eV
3	-38886.1947636 eV	-38913.0037599 eV
TS1	-38884.9040712 eV	-38911.6941540 eV
TS2a	-77771.1060425 eV	-77824.4708979 eV
TS2b	-94789.8206508 eV	-94853.6944888 eV
TS2	-77772.1858749 eV	-77825.4982314 eV
TS3	-77772.7504353 eV	-77825.9692023 eV

The unique imaginary frequencies of the transition states **TS1**, **TS2a, TS2b, TS2** and **TS3** are –86.35, –259.35, –197.03, –165.91 and –1667.74 cm^{-1}, respectively, and therefore these three transition states can be considered as real ones. According to the calculations of the BP86/SV(P) results, **TS1** connects **1a** with **3**, **TS2a** connects **2** and **ATHZ/amino** with **1a**, **TS2b** connects **2, ATHZ/imino** and **ATHZ/amino** with **1a, TS2** connects **2** and **ATHZ/imino** with **1a** and **TS3** connects **1a** with **1b**.

4.1 The 3 → 1a direct conversion and related proposed transition states

Although disfavored with respect to the indirect conversion *via* **2**, the **3** → **1a** direct conversion likely occurs via an intramolecular Ph_2P transfer from the endo- to the exo-nitrogen of **3**. Models a and b, idealized in Chart S-1**,** were used for the transition state search. Various geometries for both intra- (a) and inter-molecular (b) transfer were examined. Only the transition state model featuring an intramolecular transfer (b) showed an unique imaginary frequency. Moreover, when attempting to optimize model (c), with no geometrical constrains and the Ph_2P group equidistant from the two connected nitrogen atoms, it was found that the PPh_2 transfer did not occur (two separated molecules of **3** being preferred).

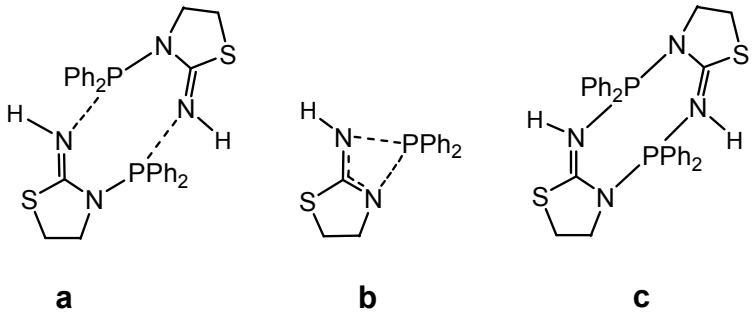


Chart S-1

Table S-3 Relative energies for the **3** → **1a** isomerization $E_R = E_T - [E(\mathbf{3})]$

Species	BP86/TZVP
	E_R, kJ mol^{-1}
3	0
TS1	+126.36
1a	-19.60

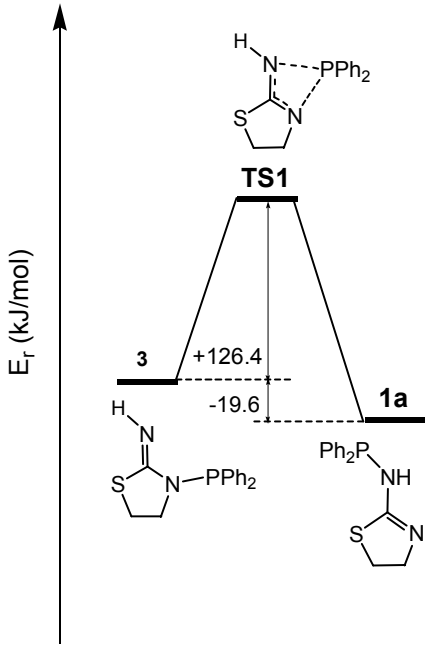


Figure S-2 Calculated potential energy E_R profiles for the direct **3** → **1a** conversion (BP86/TZVP)

4.2 The ATHZ + 2→ 2 1a reaction and related proposed transition states.

Three models for transition state **TS2** were examined in various geometries. The relative energy profiles and the structural diagrams of **TS2**, **TS2a** and **TS2b** are reported in Tables **S-4**, **S-5**, **S-6** and Figures **S-3**, **S-4**, **S-5**. **TS2a** was discarded because of its high energy, while **TS2b**, although energetically comparable to **TS2**, is expected to be entropically disfavored. Moreover, for **TS2b** the microreversibility principle would not be respected, because **pure 1a,b** is in equilibrium with **ATHZ** + **2** (see experimental section).

Table S-4 Relative energies for the **ATHZ/imino** + **2**→ 2 **1a** reaction (via the imino tautomer, E_R, kJ mol^{-1}), $E_R=E_T-[E(\textbf{ATHZ/imino} + \textbf{2})]$

Species	**BP86/TZVP**
	E_R, kJ mol^{-1}
[**ATHZ/imino** + **2**]	0
TS2	+71.13
2 × **1a**	-17.21
TS3	+25.69
2 × **1b**	-18.90

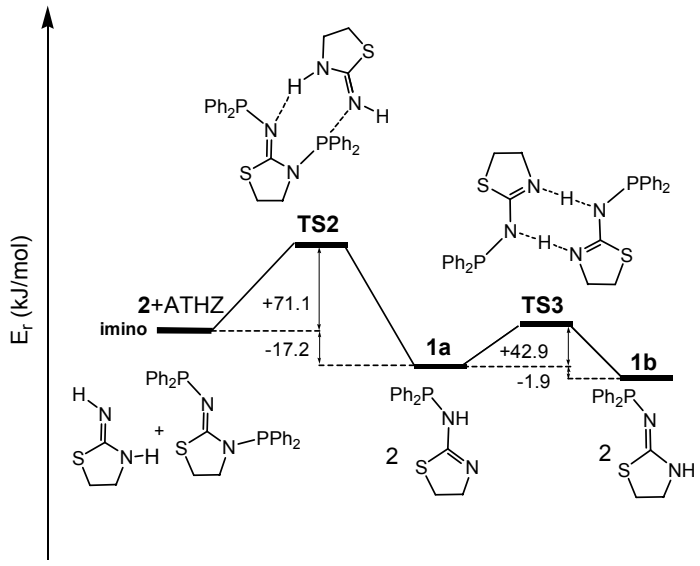


Figure S-3 Calculated potential energy E_R profiles (BP86/TZVP)

Table S-5 Relative energies for the **ATHZ/amino** + **2**→ 2 **1a** reaction (E_R, kJ mol^{-1}), $E_R=E_T-$ [E(**ATHZ/amino** + **2**)].

Species	**BP86/TZVP**
	E_R, kJ mol^{-1}
[**ATHZ** + **2**]	0
TS2a	+181.40
2 × **1a**	-6.06
TS3	+36.84
2 × **1b**	-7.75

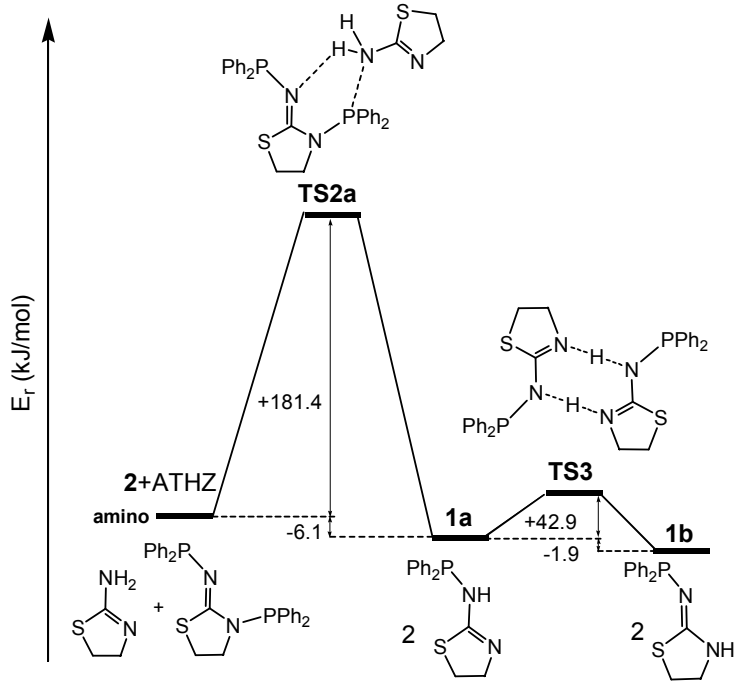


Figure S-4 Calculated potential energy E_R profiles (BP86/TZVP)

Table S-6 Relative energies for the **ATHZ/imino** + **2**→ 2 **1a** reaction (Via **TS2b**, E_R, kJ mol^{-1}), $E_R = E_T - [E(\textbf{ATHZ/amino} + \textbf{2})]$

Species	BP86/TZVP
	E_R, kJ mol^{-1}
[**ATHZ/amino** + **ATHZ/imino** + **2**]	0
TS2b	+72.53
2 × **1a** + **ATHZ/amino**	-17.21

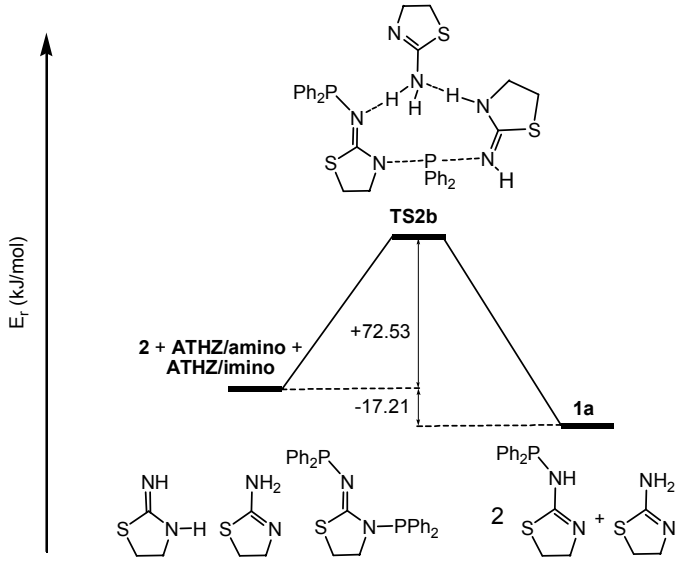


Figure S-5 Calculated potential energy E_R profiles (BP86/TZVP)

Table S-7. Relative energies for **1a** and **1b** after COSMO correction (E_R, kJ mol^{-1}), $E_R = E_T - [E(2 \times \textbf{1b}\ (CHCl_3)]$

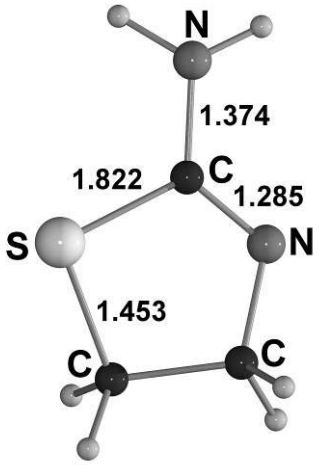
Species	BP86/TZVP/COSMO
2 × **1a** ($CHCl_3$)	0
2 × **1b** ($CHCl_3$)	-7.96

The geometrical parameters obtained from BP86/SV(P) for ATHZ (amino and imino tautomers), **1a**, **1b**, **2**, **3** and transition states **TS1**, **TS2**, **TS2a**, **TS2b** and **TS3** are given in Table S-8.

Table S-8: Comparison between selected computed bond distances [Å]

		d(C1-N1)	d(C1-N2)	d(N1-P2)	d(N2-P1)	d(C1-S1)
ATHZ/amino		1.374	1.285	-	-	1.822
ATHZ/imino		1.281	1.389	-	-	1.824
1a		1.382	1.284	1.748	-	1.816
1b		1.289	1.376	1.744	-	1.823
2		1.287	1.389	1.744	1.777	1.820
3		1.281	1.399	-	1.771	1.820
TS1		1.316	1.341	-	1.939	1.772
TS2a	**2**	1.313	1.367	1.751	1.840	1.800
	ATHZ/amino	1.430	1.282	1.890	-	1.808
TS2b	**2**	1.329	1.343	1.733	2.083	1.830
	ATHZ/amino	1.428	1.276	-	-	1.807
	ATHZ/imino	1.339	1.318	1.990	-	1.820
TS2	**2**	1.322	1.356	1.738	1.912	1.826
	ATHZ/imino	1.323	1.348	1.010	-	1.798
TS3	**1a**	1.335	1.324	1.737	-	1.815
	1a	1.334	1.324	1.739	-	1.812

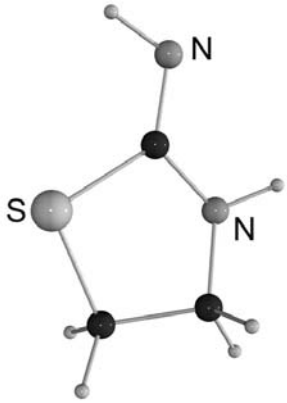
Table S-9: Total Energies and Cartesian Coordinates obtained from BP86/TZVP||BP86/SV(P) calculations.



ATHZ/amino

E = -625.7748692870 H; E = -17028.2102781 eV (TZVP)

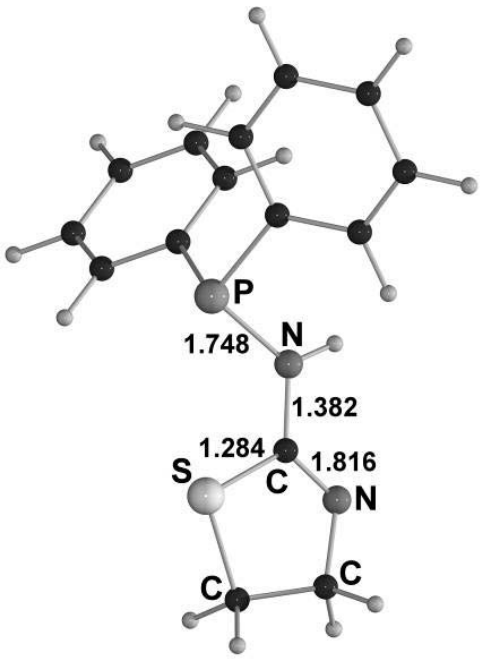
```
H -0.5600443  2.5353360 -0.3048169
S -1.2410447  0.1981220 -0.0927389
H -0.7452146 -2.5572415  0.4625106
H  1.4001899  1.4566652 -1.2576978
C -0.1818078  1.6599344  0.2623424
N  0.0992381 -2.1820575  0.0228546
C  0.2671349 -0.8182224  0.0245491
C  1.2422699  1.2188899 -0.1760080
N  1.3992312 -0.2101963  0.0353511
H -0.2306704  1.8864678  1.3502435
H  2.0128325  1.7846077  0.3945639
H  0.9585878 -2.7200503  0.1751325
```



ATHZ/imino

E = -625.7706238210 H; E = -17028.0947530 eV (TZVP)

```
N  0.0064404 -0.1816727  2.2233845
S -0.0688491  1.2466018 -0.1916778
C  0.0331654 -0.1778129  0.9422899
N  0.1458436 -1.3315407  0.1774776
H -0.3216286  0.5603424 -2.5291283
C  0.2378425  0.1701348 -1.6548882
H -1.3602299 -1.2955785 -1.3539984
C -0.2512188 -1.2181773 -1.2156665
H  1.3249682  0.1659803 -1.8846811
H  0.2286155 -2.0181527 -1.8220931
H -0.0240896 -2.2038939  0.6877149
H -0.0094544  0.7713591  2.6148376
```



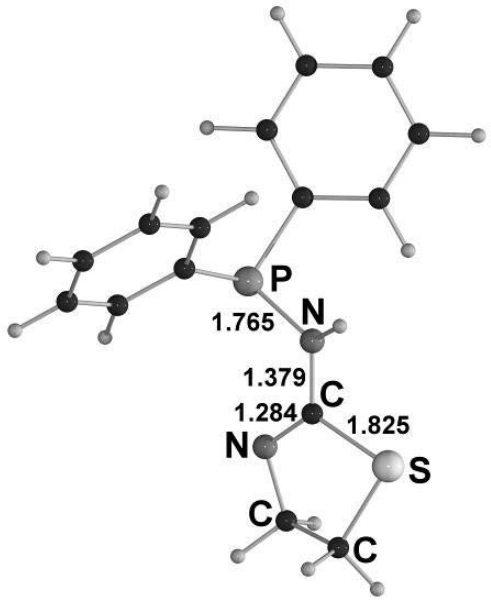
1a

E = -1430.0332554800 H; E = -38913.2069282 eV (TZVP)

```
H -1.7731649 -1.3993733 -4.3361191
H -4.0283774 -0.2960266 -4.2206957
C -2.0333434 -0.7593592 -3.4763895
C -3.2942357 -0.1434263 -3.4123427
H -0.1039251 -1.0435159 -2.5093182
C -1.0945274 -0.5641169 -2.4477138
C -3.6124193  0.6742705 -2.3126014
H -4.5987324  1.1644182 -2.2542143
H  5.4258254  0.9102477 -0.7763304
C -1.4083570  0.2463233 -1.3356748
C -2.6765114  0.8719965 -1.2853616
S  3.0251690  1.1489438 -0.3801934
H  0.6640156 -1.6446331 -0.1317926
H  4.8389652 -1.3227895 -1.4666970
C  4.6946359  0.4115251 -0.1072687
N  0.9666879 -0.6651458 -0.2241637
C  2.3414561 -0.5291881 -0.2547032
H -2.9404939  1.5180671 -0.4301371
C  4.5338725 -1.1071195 -0.4129895
N  3.1555399 -1.5216686 -0.2222887
H  0.1059906  1.6441806  2.6538667
H  4.9948262  0.5962309  0.9470674
P -0.1540309  0.6630560 -0.0395117
H  5.2094813 -1.7037637  0.2407305
C -0.6594635  0.8505662  2.7043325
C -1.0452067  0.1814647  1.5209466
H -0.9298401  1.0422731  4.8547115
C -1.2394148  0.5119692  3.9386698
C -2.0327215 -0.8266322  1.5950120
H -2.3570736 -1.3484717  0.6789472
C -2.2168154 -0.4958474  4.0024142
C -2.6125498 -1.1635004  2.8291917
H -2.6755687 -0.7608871  4.9696109
H -3.3814978 -1.9529387  2.8758205
```

$1a^{II}$

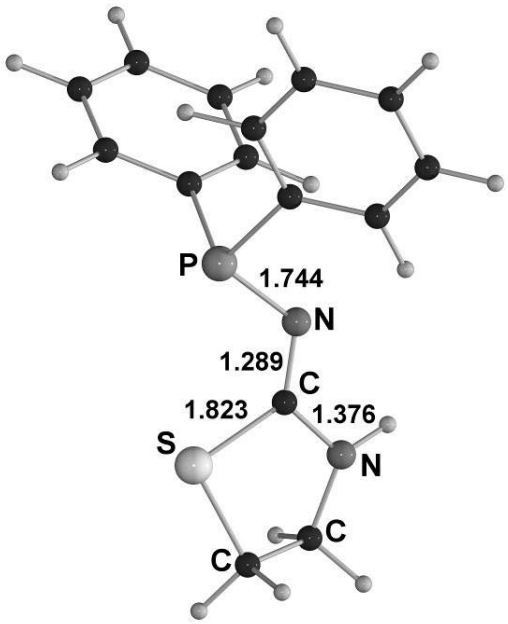
E = -1430.0312573720 H; E = -38913.1525569 eV (TZVP)




```
H -0.9959236 -2.3689259 -4.2415795
H -0.4307968 -4.7244387 -3.5692527
C -0.5210654 -2.5680748 -3.2660462
C -0.2047941 -3.8843159 -2.8917817
H -0.4692993 -0.4651713 -2.7158977
C -0.2322835 -1.4955718 -2.4039340
C  0.4078148 -4.1221848 -1.6479952
H  0.6644584 -5.1513003 -1.3454030
H -0.2676759  5.6370402 -1.1448478
C  0.3692653 -1.7241276 -1.1461243
C  0.6959648 -3.0534438 -0.7852840
S -1.1626740  3.3665722 -1.2769187
H -1.2214231  0.6420872 -0.6797581
H  1.8121009  4.3745131 -1.1363615
C -0.2553078  4.7522448 -0.4757775
N -0.2279561  0.8888520 -0.5883291
C  0.0486318  2.2372843 -0.5094562
H  1.1778858 -3.2578996  0.1863589
C  1.1728574  4.1881912 -0.2379639
N  1.0980711  2.7594229  0.0136236
H -1.4804594 -2.0051461  0.8798213
H -0.7635865  5.0128467  0.4785723
P  0.9322095 -0.3320674 -0.0604262
H  1.6563555  4.7095766  0.6181801
C -0.9535752 -1.5998317  1.7604968
C  0.2156396 -0.8245623  1.5891433
H -2.3603010 -2.4754457  3.1687335
C -1.4472352 -1.8684523  3.0475610
C  0.8803759 -0.3284158  2.7328783
H  1.7921653  0.2802783  2.6069716
C -0.7794827 -1.3665938  4.1797184
C  0.3841609 -0.5952593  4.0207714
H -1.1677448 -1.5805317  5.1895604
H  0.9126579 -0.2016241  4.9051760
```

1b

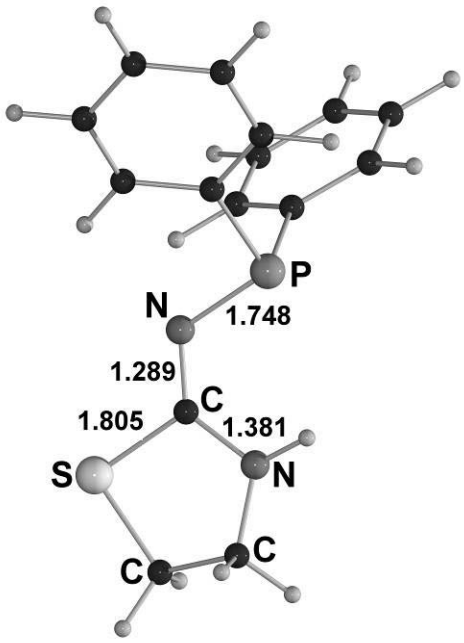
E = -1430.0335769440 H; E = -38913.2156757 eV (TZVP)




```
H -1.3074395  2.2740598 -4.5802528
H  0.4340004  4.0477995 -4.1983371
C -0.7322932  2.2916474 -3.6390678
C  0.2431753  3.2833183 -3.4266094
H -1.7553235  0.5571874 -2.8274450
C -0.9809367  1.3247941 -2.6522604
C  0.9703387  3.2944970 -2.2243164
H  1.7380027  4.0680474 -2.0511883
C -0.2469132  1.3247191 -1.4450315
C  0.7292123  2.3208117 -1.2385289
H -2.1724728 -2.0443093 -1.4581837
H -1.5138141 -4.1624818 -2.6233545
C -1.1065974 -2.3238580 -1.5308416
C -0.7380836 -3.5170707 -2.1777046
P -0.6849641  0.0851856 -0.1302015
H  1.3048052  2.3148587 -0.2989455
C -0.1250363 -1.4845487 -0.9628086
C  0.6143773 -3.8917985 -2.2418882
H  0.9051188 -4.8319384 -2.7400980
C  1.2312004 -1.8708959 -1.0247214
C  1.5964864 -3.0689728 -1.6588063
N  0.6305673  0.3584449  0.9811870
H  1.9957925 -1.2235396 -0.5647963
H  2.6588392 -3.3641160 -1.7037625
S -1.2387118  0.0720177  3.0451687
C  0.3821338  0.3046926  2.2445715
N  1.3515793  0.4260281  3.2140587
H -1.0997768  0.4191125  5.4675431
C -0.4330818 -0.0333118  4.7060669
H  0.7275287  1.8246916  4.7089774
C  0.8909408  0.7275016  4.5620497
H -0.2638940 -1.1027450  4.9560928
H  1.6384325  0.3850885  5.3111019
H  2.2718745  0.7398929  2.8918235
```

$\mathbf{1b^{II}}$

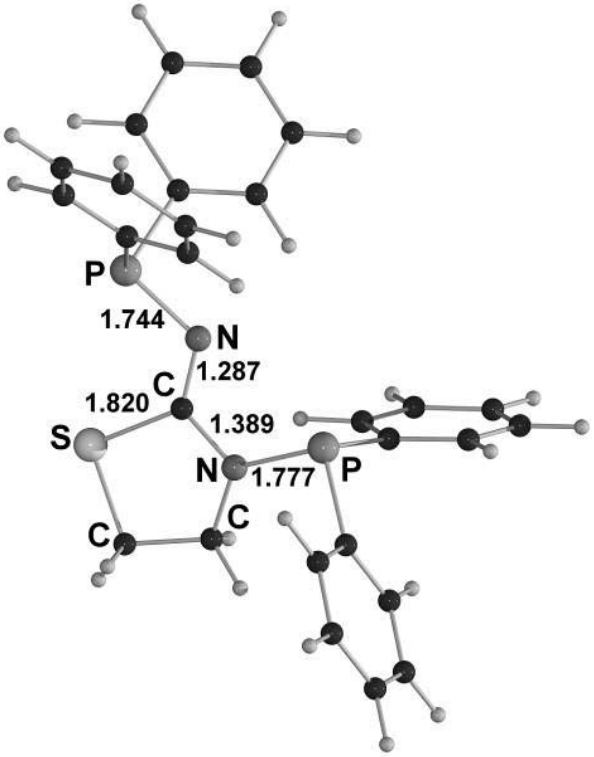
E = -1430.311450560 H; E = -38913.1495006 eV (TZVP)



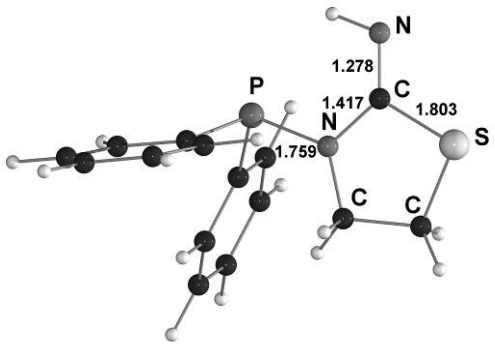
N	-0.3033513	-0.3287450	1.0043905
S	-0.6127903	-1.1512578	3.5575854
C	-0.2263905	0.0227851	2.2421157
N	0.1320692	1.2330589	2.8033693
H	-0.6494777	-0.0852267	5.7620412
C	-0.0358083	0.0332669	4.8467378
H	-1.2536879	1.7841269	4.3378514
C	-0.2039194	1.4201795	4.2072659
H	1.0277371	-0.1804704	5.0878208
H	0.4808689	2.1614188	4.6750415
H	0.1562692	2.0343585	2.1581197
P	-0.0646452	0.8689089	-0.2466410
C	1.4913412	0.2143777	-1.0398697
C	2.0154077	-1.0600893	-0.7389799
C	3.2030496	-1.4979786	-1.3488014
C	3.8763453	-0.6727247	-2.2671367
C	3.3611033	0.6002133	-2.5679703
C	2.1802643	1.0450550	-1.9494430
H	1.4816639	-1.7021171	-0.0192491
H	3.6050629	-2.4966702	-1.1070614
H	4.8077490	-1.0201394	-2.7449258
H	3.8878082	1.2562898	-3.2814925
H	1.7934474	2.0550467	-2.1734665
C	-1.3346570	0.2910005	-1.4768614
C	-1.6160415	1.1199655	-2.5841652
C	-2.5694114	0.7327047	-3.5406370
C	-3.2661129	-0.4791741	-3.3882610
C	-3.0035599	-1.2991608	-2.2762232
C	-2.0430892	-0.9185219	-1.3235227
H	-1.0858802	2.0821171	-2.6991087
H	-2.7763726	1.3865770	-4.4044943
H	-4.0205896	-0.7808861	-4.1340416
H	-3.5527168	-2.2478426	-2.1501213
H	-1.8311199	-1.5517798	-0.4467171

2

E = -2234.2893317370 H; E = -60798.1407216 eV (TZVP)

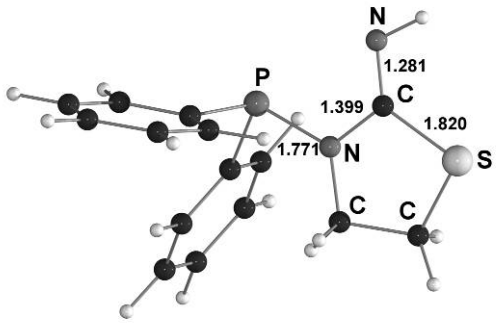


H	0.5177985	0.2126474	-6.8615054
H	2.9463896	0.8514836	-6.8346230
C	1.0194629	0.4369418	-5.9051279
C	2.3798171	0.7923312	-5.8904188
H	-5.5834656	0.6830032	-2.9409820
H	-0.7707818	0.0774613	-4.7254041
C	0.2940851	0.3612064	-4.7033899
H	-4.0876265	2.5248643	-3.7750112
C	-4.4985949	0.6462104	-2.7477577
H	-4.5938076	-1.2297286	-1.6447785
C	-3.6615001	1.6757854	-3.2146137
C	3.0132227	1.0798284	-4.6682460
C	-3.9445666	-0.4234294	-2.0250373
H	4.0775475	1.3676474	-4.6495992
C	-2.2809116	1.6321268	-2.9632315
C	0.9196256	0.6481074	-3.4691163
H	-1.6395707	2.4548760	-3.3251668
C	-2.5611331	-0.4723160	-1.7780821
C	2.2850066	1.0185700	-3.4687147
C	-1.7101873	0.5472605	-2.2561228
H	-2.1427596	-1.3095661	-1.1961247
H	2.7799297	1.2664862	-2.5133826
P	0.0872234	0.6266358	-1.8037360
H	-4.0327359	1.3779112	2.6255329
H	-0.4446860	-2.6894601	-2.3781060
H	0.9382845	-1.8949919	-3.2152110
C	0.5535472	-2.2136205	-2.2245309
C	-3.2843342	0.8255775	3.2191713
H	-1.8964223	0.6120635	1.5460484
N	0.4413945	-1.0507505	-1.3349297
H	-4.4617956	0.8908676	5.0527580
C	-2.0914615	0.3997063	2.6096323
C	-3.5249207	0.5547274	4.5774687
H	1.2611292	1.7083597	1.4266730
H	2.8689139	3.4770260	2.2023793
H	1.3482339	-4.2388521	-1.8608799
C	1.5146607	-3.1906954	-1.5389404
C	0.5294194	-1.3445346	0.0200349
N	0.1925970	-0.5112925	0.9414941
H	2.5771034	-2.9180230	-1.7180538
C	1.8211937	1.5795236	2.3674558
C	2.7236353	2.5637556	2.8042926
C	-1.1260748	-0.3067826	3.3560169
C	-2.5681722	-0.1541308	5.3256435
S	1.1481075	-3.0394601	0.2615804
H	-2.7522910	-0.3779380	6.3900719
P	0.4549598	-0.9466330	2.6100354
C	-1.3810659	-0.5908983	4.7154426
C	1.6260894	0.4079920	3.1297085
H	4.1433642	3.1677430	4.3450443
C	3.4367766	2.3921119	4.0047971
H	-0.6441400	-1.1643282	5.3055463
C	2.3588576	0.2322715	4.3230572
C	3.2521415	1.2238923	4.7643730
H	2.2359856	-0.6943488	4.9110199
H	3.8163582	1.0776286	5.7009092



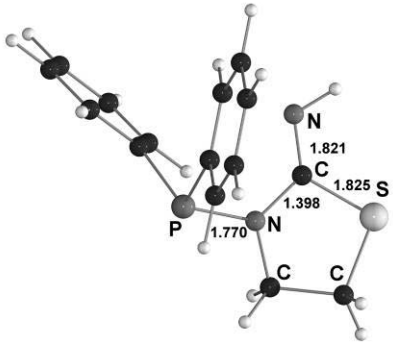
E = -1430.0243635260 H; E = -38912.9649657 eV (TZVP)

H	3.0690442	-2.0815322	-2.7269042
H	5.1275982	-0.8403017	-2.0022417
C	2.9796815	-1.1969438	-2.0740946
C	4.1326701	-0.5037631	-1.6663019
H	-4.2026260	-0.7798692	-3.7190850
H	0.8125589	-1.3191158	-1.9813029
C	1.7091785	-0.7684193	-1.6518175
H	-2.0923995	0.2232873	-4.6476610
C	-3.3900297	-0.4721005	-3.0404393
H	-4.4552839	-1.0601305	-1.2331332
C	-2.2103927	0.0902295	-3.5591293
C	4.0124910	0.6252975	-0.8372239
C	-3.5304496	-0.6285669	-1.6509743
H	4.9121570	1.1785222	-0.5200521
C	-1.1755867	0.4860800	-2.6957890
C	1.5762845	0.3654568	-0.8186689
H	-0.2606304	0.9339464	-3.1201100
C	-2.4959861	-0.2344093	-0.7851775
C	2.7429997	1.0606028	-0.4235562
C	-1.2993102	0.3157102	-1.2968783
H	-2.6253299	-0.3473602	0.3042324
H	2.6514115	1.9553540	0.2163349
P	-0.0256914	1.0345600	-0.1605361
H	-0.9952408	-1.9058918	1.1499962
H	0.7386800	-1.7177161	0.6965470
C	-0.0462964	-1.3765873	1.4052800
N	-0.2126434	0.0791087	1.2999711
H	0.0847973	-2.6977492	3.1666024
C	0.3570159	-1.6684832	2.8565191
C	-0.6127172	0.7276996	2.4950915
N	-0.9637418	1.9387516	2.7031708
H	1.4457543	-1.5147273	3.0196055
S	-0.5930627	-0.4548059	3.8556396
H	-0.9725853	2.4818722	1.8190451



E = -1430.0257891870 H; E = -38913.0037599 eV (TZVP)

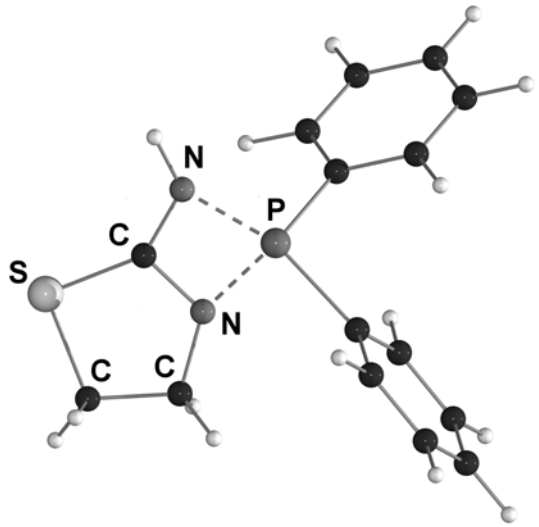
H	2.5531822	-1.9536330	-3.3235970
H	4.7355266	-0.8061169	-2.8436014
C	2.5910681	-1.1148329	-2.6081925
C	3.8131704	-0.4745798	-2.3380339
H	-4.6452342	-0.9710155	-2.9811472
H	0.4609950	-1.2046127	-2.1838011
C	1.4131568	-0.6932518	-1.9667506
H	-2.9073380	0.3937390	-4.1818027
C	-3.7527725	-0.6117888	-2.4422477
H	-4.3481362	-1.4898173	-0.5399742
C	-2.7795386	0.1502620	-3.1135373
C	3.8529987	0.5957815	-1.4269347
C	-3.5848363	-0.9029952	-1.0782327
H	4.8062201	1.1090141	-1.2163979
C	-1.6457144	0.6115929	-2.4260409
C	1.4398256	0.3817627	-1.0503601
H	-0.8980656	1.2201639	-2.9642907
C	-2.4472929	-0.4462387	-0.3899705
C	2.6735513	1.0261985	-0.7973950
C	-1.4557322	0.3036595	-1.0581245
H	-2.3359881	-0.6648832	0.6845328
H	2.7048223	1.8825079	-0.1010697
P	-0.0346940	1.0795559	-0.1499380
H	-0.3411998	-1.9936077	1.2996954
H	1.2765237	-1.4972159	0.6824948
C	0.5050110	-1.2799551	1.4500835
N	0.0551607	0.1084538	1.3287412
H	1.0626815	-2.4788634	3.2199319
C	1.0780248	-1.4274625	2.8667063
C	-0.4662220	0.6597508	2.5044072
N	-1.1523814	1.7412599	2.5209114
H	2.1141479	-1.0313381	2.9372691
S	-0.0396501	-0.4101505	3.9131492
H	-1.3767019	2.0507552	3.4779776



E = -1430.0245834280 H; E = -38912.9709495 eV (TZVP)

H	4.7758768	2.8707376	-0.7202580
H	-1.2471413	0.7244078	-2.6890002
H	2.5178560	3.9746475	-0.6705536
C	3.8890220	2.3050589	-0.3894455
C	2.6262187	2.9220969	-0.3587750
H	4.9980420	0.4669937	-0.0143173
C	4.0123981	0.9618453	0.0046229
N	-0.7819850	0.6358392	-1.7733851
C	1.4947786	2.2026532	0.0573972
H	0.5091316	2.6955956	0.0688644
S	-3.3006406	1.4830588	-0.9397193
C	-1.5809652	0.8878020	-0.8040484
C	2.8819340	0.2408945	0.4244010
C	1.6068326	0.8506769	0.4465159
H	2.9975425	-0.8122786	0.7332816
N	-1.2421110	0.7506897	0.5449517
H	-4.3288095	1.9159588	1.2351528
C	-3.5970451	1.1782259	0.8473304
H	-1.9948706	2.4327477	1.6309715
P	0.1873222	-0.0562427	1.2062666
C	-2.2096881	1.3472179	1.4763466
H	-0.6221089	-2.6142397	2.1619743
H	-3.9980751	0.1508759	0.9880032
H	-2.1382736	0.8401304	2.4615683
C	-0.2620142	-2.7943828	1.1336909
C	0.2177404	-1.7086824	0.3650060
H	-0.6523358	-4.9343091	1.2186675
C	-0.2743592	-4.0974395	0.6078123
C	0.7060406	-1.9539034	-0.9388966
H	1.0691734	-1.1114091	-1.5456676
C	0.2095280	-4.3302081	-0.6904103
C	0.7015335	-3.2586731	-1.4581193
H	0.2088155	-5.3522170	-1.1054823
H	1.0807703	-3.4412849	-2.4777778

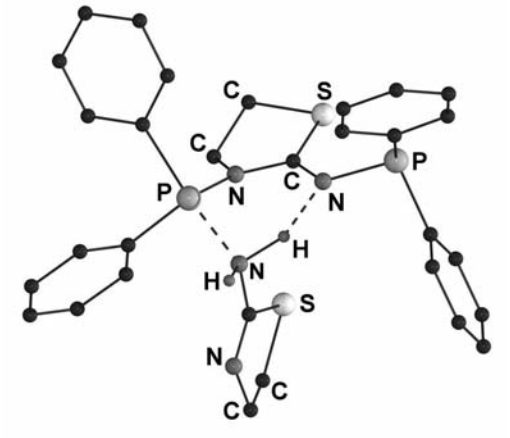
TS1 (Imaginary frequency -86.35 cm^{-1})



E = -1429.9776620830 H; E = -38911.6941540 eV (TZVP)

H	-3.7016482	-0.9567684	-4.1101090
H	-4.1059751	-1.6608137	-1.7304092
C	-3.0331821	-0.6068819	-3.3057865
C	-3.2587909	-0.9980702	-1.9762986
H	-1.7566408	0.5483554	-4.6438202
C	-1.9435078	0.2320343	-3.6038055
N	-1.6163501	1.0347657	1.3657152
C	-2.4132458	-0.5424766	-0.9474240
H	-2.6156239	-0.8421872	0.0934621
S	-0.9549172	-0.1582158	3.9212829
C	-0.9232088	0.3027674	2.2110338
C	-1.0877817	0.6679681	-2.5810825
C	-1.3129639	0.2949844	-1.2336514
H	-0.2274117	1.3116027	-2.8327772
N	0.1705995	-0.1095701	1.5548076
H	1.0049335	-1.5575578	4.4182634
C	0.8359773	-0.6710427	3.7736940
H	0.9155567	-2.0384207	2.0340621
P	-0.1666900	1.0415608	0.0317977
C	1.0943333	-0.9616842	2.2694926
H	0.7270475	-1.6499991	-1.3980051
H	1.4562171	0.1735864	4.1412875
H	2.1456911	-0.7261919	1.9985643
C	1.5922398	-0.9642346	-1.3611007
C	1.4410174	0.3240978	-0.8000096
H	2.9240850	-2.3978785	-2.3188360
C	2.8264153	-1.3877089	-1.8844393
C	2.5653611	1.1770202	-0.7871479
H	2.4649082	2.1911114	-0.3571134
C	3.9374326	-0.5234841	-1.8613772
C	3.8050014	0.7629623	-1.3124961
H	4.9050661	-0.8528605	-2.2766716
H	4.6694437	1.4492028	-1.2978066
H	-2.3724041	1.6616818	1.6630515

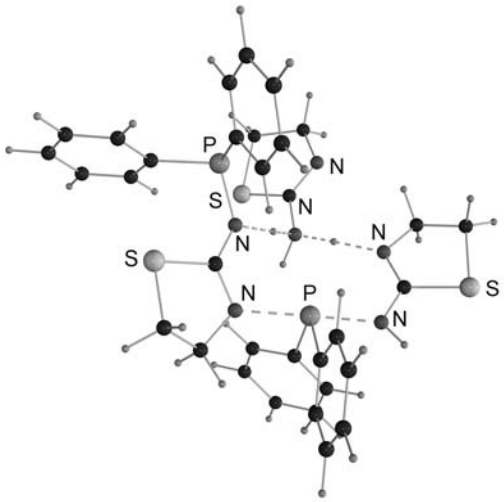
TS2a (Imaginary frequency -259.53 cm^{-1})



E = -2859.9951085890 H; E = -77824.4708979 eV (TZVP)

N	0.4888884	-1.0346262	-1.0354625
S	0.2407490	-2.8738743	1.0504258
C	0.5141838	-2.4183985	-0.6775121
N	0.7337291	-3.3526734	-1.5267859
H	1.8634044	-4.6886992	0.9444100
C	0.8057265	-4.5757998	0.6217978
H	1.4403013	-5.3373148	-1.3492144
C	0.6557124	-4.6735372	-0.9227730
H	0.1853629	-5.3159437	1.1670842
H	-0.3302569	-5.1238399	-1.1928129
H	-5.0190941	-2.4871001	-2.4102979
H	-5.3735465	-4.2513414	-0.6596360
C	-4.7071658	-2.3018158	-1.3685048
C	-4.9036640	-3.2910565	-0.3884237
H	-3.9697133	-0.3009588	-1.7980244
C	-4.1152267	-1.0743229	-1.0258711
C	-4.5063745	-3.0495035	0.9381488
H	-4.6633008	-3.8190362	1.7126022
C	-3.7112293	-0.8230562	0.3035810
C	-3.9180157	-1.8210804	1.2820197
H	-5.4349781	2.0579375	0.2673679
H	-6.1592504	3.7225747	-1.4445787
C	-4.7113040	2.4146891	-0.4870049
C	-5.1200063	3.3530095	-1.4474393
H	6.3747383	-2.7085490	-1.7513083
P	-2.9046701	0.7546426	0.8733020
H	-3.6153234	-1.6294393	2.3261651

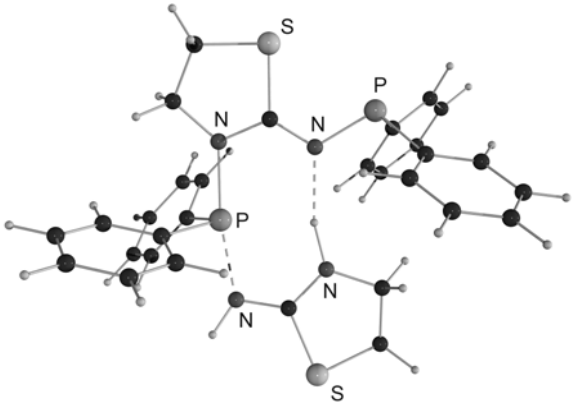
TS2b (Imaginary frequency -197.03 cm^{-1})



E = -3485.8072164170 H; E = -94853.6944888 eV

C	0.7909338	3.6410859	-1.6674157
C	-0.3733371	2.7200702	-2.0571625
S	2.1378652	2.4793337	-1.2101563
C	0.8888359	1.2138522	-0.7768995
N	1.1927190	0.0723416	-0.1671139
N	-0.3484789	1.5591187	-1.1691591
H	0.5425314	4.2796836	-0.7917515
H	1.1300350	4.2850872	-2.5049685
H	-0.2628510	2.3930368	-3.1213741
H	-1.3458838	3.2471031	-1.9684950
P	2.6733324	-0.4276739	0.5813866
P	-1.9484831	0.6191161	-0.2219325
C	-3.5689599	-3.0865960	3.2486726
C	-2.6757835	-3.4182084	2.0366715
S	-4.6811210	-1.7611675	2.6253308
C	-3.3976608	-1.2975825	1.4205141
N	-3.5027081	-0.1330315	0.7673890
N	-2.4394006	-2.1918062	1.2849511
H	-2.9798253	-2.6919962	4.1053536
H	-4.1751412	-3.9511662	3.5891105
H	-3.1882451	-4.1762151	1.3903030
H	-1.7041052	-3.8544931	2.3552783
H	-4.2417163	0.4857617	1.1208818
H	-0.7272505	-2.0938005	-1.2735924
N	-0.3396893	-2.1380514	-0.3118475
H	-1.2503829	-2.1319128	0.4226578
H	0.2400273	-1.1752789	-0.1939629

TS2 (Imaginary frequency -165.91 cm^{-1})

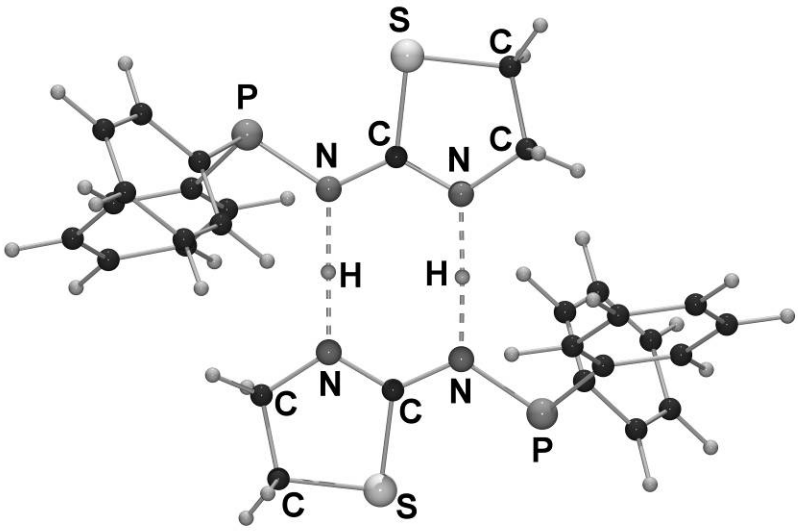


E = -2860.0328623820 H; E = -77825.4982314 eV

N	1.5095395	1.5102954	1.8696924
S	2.9712333	3.3053494	0.3803225
C	1.8451497	1.9323451	0.6617483
N	1.3852501	1.4164302	-0.4958390
H	3.1041333	3.8618928	-1.9964408
C	3.0100463	2.9172892	-1.4244824
H	0.8647844	2.9219147	-1.9060352
C	1.6820202	2.1922739	-1.6941136
H	3.8902033	2.2710737	-1.6286525
H	1.7667158	1.5178766	-2.5725719
H	3.8908057	-3.9242415	3.3754909
H	0.4424215	0.6281144	-0.4455140
H	2.3360768	-4.3087005	1.4341273
C	3.1465632	-3.1589051	3.0990251
C	2.2750101	-3.3744149	2.0171136
H	3.7364065	-1.7753150	4.6759613
C	3.0602625	-1.9580316	3.8235926
N	-0.9137867	-0.5848759	-0.8770848
C	1.3235975	-2.4012730	1.6674361
H	0.6558870	-2.5844052	0.8103089
S	-2.9971742	-2.3214972	-0.2970448
C	-1.5999083	-1.2040934	0.0688154
C	2.1112963	-0.9835828	3.4682258
C	1.2217719	-1.1881784	2.3875452
H	2.0586818	-0.0514617	4.0542025
N	-1.3496535	-1.1124309	1.3983146
H	-3.7647648	-3.4300611	1.7395153
C	-3.4049220	-2.4094890	1.4966349

H 5.0062661 -3.2505053 0.2844581	C -2.6235684 0.0468037 -1.8892657	H -1.4860464 -2.9767149 2.4069994
C -3.3842632 1.9261891 -0.4779221	C -3.9985622 -0.2138542 -2.1007694	P 0.0442758 0.1366542 1.7908869
C 5.4661008 -2.1269224 -1.5227312	C -4.4615759 -0.7690257 -3.3062222	C -2.0979112 -2.0585350 2.2256558
C -4.2033834 3.8294399 -2.4031120	C -3.5598506 -1.1046736 -4.3298010	H -0.3928886 -0.9225856 4.6452388
H -4.5222075 4.5719380 -3.1536091	C -2.1886238 -0.8684322 -4.1348021	H -4.2122637 -1.6788601 1.7197490
C 4.6995295 -2.4300382 -0.3865245	C -1.7302165 -0.2918762 -2.9370089	H -2.3167943 -1.6014357 3.2143329
C -2.4698210 2.4116653 -1.4362745	H -4.7187931 0.0033000 -1.2981958	C -0.8274927 0.0873381 4.5658637
H 5.6593908 -0.8267050 -3.2615227	H -5.5418538 -0.9495019 -3.4399095	C -0.7196555 0.8046316 3.3540653
C -2.8799122 3.3582725 -2.3926338	H -3.9221950 -1.5498579 -5.2713479	H -1.5393421 0.0783004 6.6222406
C 5.0661713 -1.0741721 -2.3650595	H -1.4636221 -1.1254254 -4.9256959	C -1.4663293 0.6548485 5.6845849
N -1.2431084 0.4099498 0.4396629	H -0.6538961 -0.0877437 -2.8170187	C -1.2650279 2.1078793 3.2939840
H -1.4303666 2.0424066 -1.4297967	C -2.7138909 2.3005913 0.0771939	H -1.1906423 2.6818847 2.3547007
H -2.1548761 3.7292184 -3.1364999	C -2.3939542 2.9288070 1.3018360	C -2.0017655 1.9510514 5.6102583
C 3.5371114 -1.6921187 -0.0943347	C -2.9433354 4.1777177 1.6365714	C -1.8975321 2.6780385 4.4104421
H 2.9417843 -1.9592722 0.7937253	C -3.8229691 4.8227501 0.7486637	H -2.4987031 2.3981809 6.4874780
S -0.5486187 0.9854925 3.0552512	C -4.1493952 4.2082416 -0.4715027	H -2.3149433 3.6969654 4.3442395
C -0.2877737 0.5388796 1.3307078	C -3.6001037 2.9555190 -0.8044895	H 2.0076320 1.9900014 2.6344988
C 3.9123573 -0.3320466 -2.0683237	H -1.7094101 2.4252217 2.0065024	P -1.4205729 -0.8230522 -2.5220082
C 3.1264651 -0.6317602 -0.9303868	H -2.6837164 4.6493451 2.5993955	C -1.4122269 0.9355569 -3.1326585
H 3.6183918 0.5018578 -2.7291672	H -4.2556997 5.8025793 1.0109470	C -1.0453606 1.2803720 -4.4530193
N 1.0299710 0.3246592 1.0389900	H -4.8400829 4.7056320 -1.1734415	C -1.1798976 2.6012010 -4.9138430
H 1.5446221 0.8841176 4.3134937	H -3.8709071 2.4822747 -1.7631760	C -1.6886434 3.6011064 -4.0660992
C 1.2736399 1.1855730 3.2815225	C 2.8401038 0.6408266 2.0894158	C -2.0553275 3.2688066 -2.7495827
H 1.9406353 -0.7798840 2.5973632	C 1.8450266 1.5582552 2.4879523	C -1.9221635 1.9484490 -2.2876696
P 1.6231101 0.4393174 -0.6991224	C 1.9608469 2.2560250 3.7029792	H -0.6378420 0.5116135 -5.1311403
C 1.8964329 0.2704179 2.2242595	C 3.0700029 2.0469214 4.5403368	H -0.8798020 2.8510379 -5.9457391
H 4.7107323 1.1833467 0.1626754	C 4.0590759 1.1207594 4.1622145	H -1.8041777 4.6351366 -4.4316655
H 1.5398151 2.2518651 3.1221755	C 3.9379144 0.4149913 2.9542108	H -2.4502427 4.0456661 -2.0729658
H 2.9184796 0.6034876 1.9542123	H 0.9664605 1.7182004 1.8430502	H -2.2060155 1.6976145 -1.2517076
C 4.0948908 2.0994934 0.1501603	H 1.1754800 2.9728187 3.9971232	C 0.1102208 -1.5074872 -3.3252657
C 2.7138336 2.0183692 -0.1414242	H 3.1583321 2.5957531 5.4927328	C -0.0249846 -2.0925188 -4.6047599
H 5.7978827 3.3679862 0.6442012	H 4.9271268 0.9392650 4.8182734	C 1.0846024 -2.6583911 -5.2564354
C 4.7169029 3.3349451 0.4215166	H 4.7096282 -0.3255268 2.6794129	C 2.3401650 -2.6710827 -4.6249559
C 1.9828315 3.2294306 -0.1575739	C 4.0611727 0.1642339 -0.5226140	C 2.4770003 -2.1202897 -3.3381062
H 0.9051847 3.2014361 -0.4104017	C 4.1781131 -0.4917728 -1.7714015	C 1.3712554 -1.5417495 -2.6915470
C 3.9659312 4.5222794 0.4109938	C 5.2316509 -0.1879512 -2.6474547	H -1.0164649 -2.1211884 -5.0904600
C 2.5896618 4.4660170 0.1210022	C 6.2040342 0.7594980 -2.2791655	H 0.9625658 -3.1091432 -6.2557946
H 4.4517399 5.4906992 0.6192990	C 6.1079572 1.4039941 -1.0338183	H 3.2107098 -3.1219703 -5.1300378
H 1.9905977 5.3930704 0.1012534	C 5.0429812 1.1135920 -0.1638159	H 3.4552984 -2.1456553 -2.8284043
H -0.5129726 -0.5217908 -0.6195541	H 3.4301680 -1.2533477 -2.0551343	H 1.4802792 -1.1204059 -1.6789071
H 0.4271273 -1.0223738 -2.0702705	H 5.2994593 -0.7018519 -3.6212505	
	H 7.0379543 0.9919413 -2.9624808	
	H 6.8643750 2.1512203 -0.7391972	
	H 4.9673881 1.6456688 0.7983194	
	C 0.5078349 -3.2758581 -0.1461324	
	N 0.6083136 -3.9091947 0.9575734	
	S 1.5023086 -3.8214102 -1.5522690	
	C 1.5386189 -5.0250089 0.8628022	
	C 2.4671556 -4.8563778 -0.3727466	
	H 0.9426793 -5.9666892 0.7899793	
	H 2.1419106 -5.0946383 1.7943408	
	H 3.3965256 -4.3034830 -0.1185616	
	H 2.7333724 -5.8203366 -0.8522427	

TS3 (Imaginary frequency -1667.74 cm^{-1})

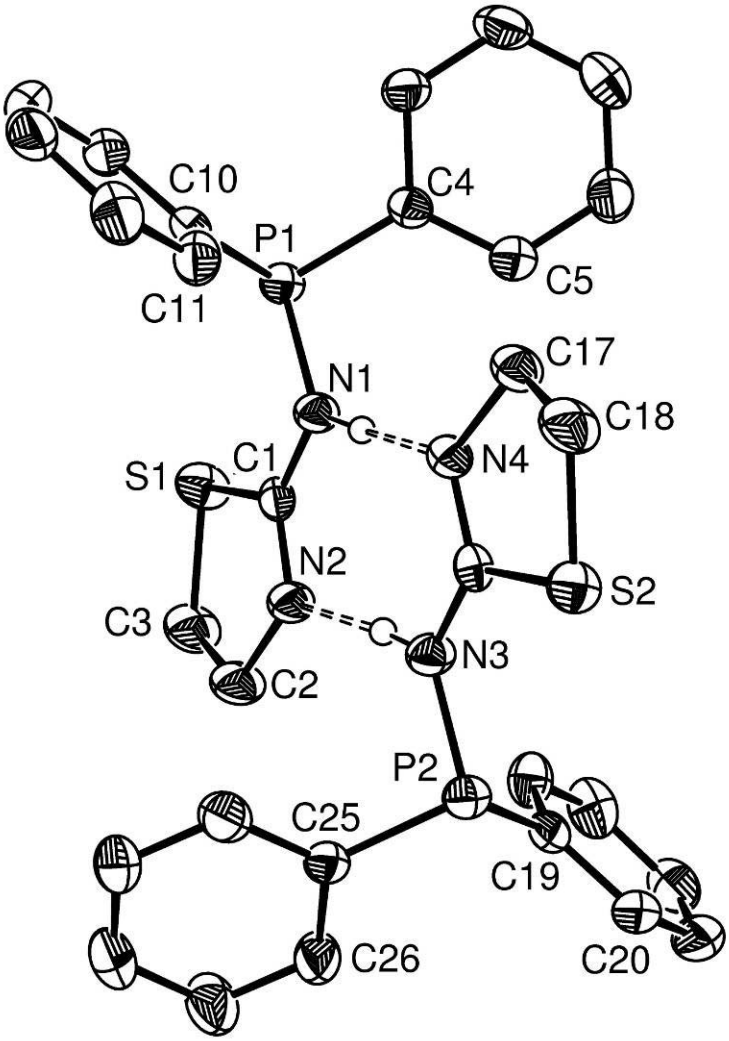


E = -2860.0501702340 H; E = -77825.9692023 eV (TZVP)

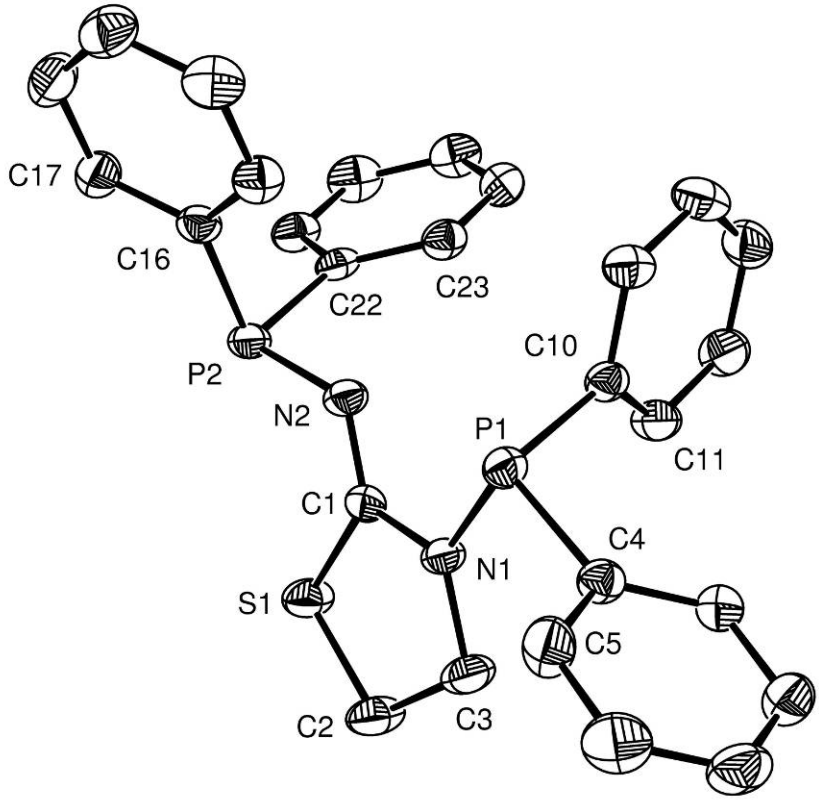
H	-1.0961590	-4.7013114	-5.0129561	P	-1.2481387	-3.3152279	0.6104310
H	-2.1592358	-2.5559921	-4.2406075	N	-0.8271818	-1.6319927	0.5342698
H	-3.5955278	5.5360247	-2.9647330	H	-0.1217788	1.1171563	0.4561685
H	-1.4028112	6.7538316	-3.1264158	H	0.0427251	5.7421961	0.7103991
C	-1.0961210	-4.4355246	-3.9426536	H	-3.9782689	0.8341845	2.1127240
C	-1.6906202	-3.2366439	-3.5098806	C	-1.4436295	-0.7356728	1.3063970
C	-2.6875332	5.1045010	-2.5112578	N	-1.1984397	0.5653294	1.2950212
C	-1.4622595	5.7866266	-2.5997129	H	-2.0717153	2.3537930	2.0129818
H	-3.7074068	3.3198452	-1.7900415	H	1.6250269	-2.4135273	1.0710571
H	-0.0299071	-6.2334859	-3.3290352	S	-2.7164634	-1.2174548	2.5075460
C	-2.7492341	3.8629689	-1.8527334	C	1.1245806	3.8879642	1.1131389
C	-0.5031074	-5.2929049	-2.9999290	C	0.5445812	5.1244544	1.4737380
H	3.4197636	-0.8188484	-3.7067552	C	-1.8359623	1.3241196	2.3596790
C	-1.6943113	-2.9002819	-2.1462718	C	-3.1157817	0.5690558	2.7622405
H	-2.1621343	-1.9572800	-1.8177680	C	0.2754794	-4.1066547	1.3214211
C	-0.3040925	5.2258118	-2.0333812	C	1.5173295	-3.4465507	1.4404227
H	0.6627137	5.7499508	-2.1338207	H	-0.8270524	-5.9343712	1.7764027
H	1.2178578	-1.5530205	-2.9942294	C	0.1491052	-5.4200808	1.8267776
C	-1.5958548	3.3087378	-1.2727395	H	-3.3965398	0.7340454	3.8223434
C	3.1730066	-0.6087400	-2.6462415	H	-1.1453807	1.4191211	3.2332728
C	-0.3618785	3.9907362	-1.3501528	H	0.1254369	6.5384829	3.0696900
C	-0.5001617	-4.9550653	-1.6353794	H	2.2159048	2.1491230	1.8500157
C	-1.0915225	-3.7516510	-1.1912605	C	0.5889232	5.5730958	2.8049012
C	1.9369429	-1.3835340	-2.1564730	C	1.7564026	3.1159586	2.1150140
H	-1.6527101	2.3337932	-0.7615735	C	2.6127715	-4.0954873	2.0348050
S	2.7229122	1.1756798	-2.4682050	H	3.5770070	-3.5670701	2.1255533
H	4.0677841	-0.8101124	-2.0183068	C	1.2495612	-6.0738166	2.4076290
H	-0.0190432	-5.6329973	-0.9109261	C	2.4844142	-5.4114037	2.5141418
H	2.2222511	-2.3827139	-1.7614766	H	1.1365707	-7.1006782	2.7941114
N	1.3103899	-0.5874194	-1.1108936	C	1.2118093	4.7952139	3.7961037
C	1.5150221	0.7182762	-1.1978196	C	1.7934268	3.5637680	3.4459452
H	0.2501562	-1.1045028	-0.3203707	H	3.3454636	-5.9173028	2.9820183
P	1.2307034	3.3296813	-0.6556437	H	1.2441419	5.1475323	4.8405062
N	0.9042208	1.6349891	-0.4442608	H	2.2852192	2.9450394	4.2155317

Figure S-6: ORTEP plots of the molecular structures of compound **1, 2, 4** and **6** (solvent molecules omitted for clarity, only tautomer **1a** is depicted for **1**). Thermal ellipsoids include 50% of the electron density

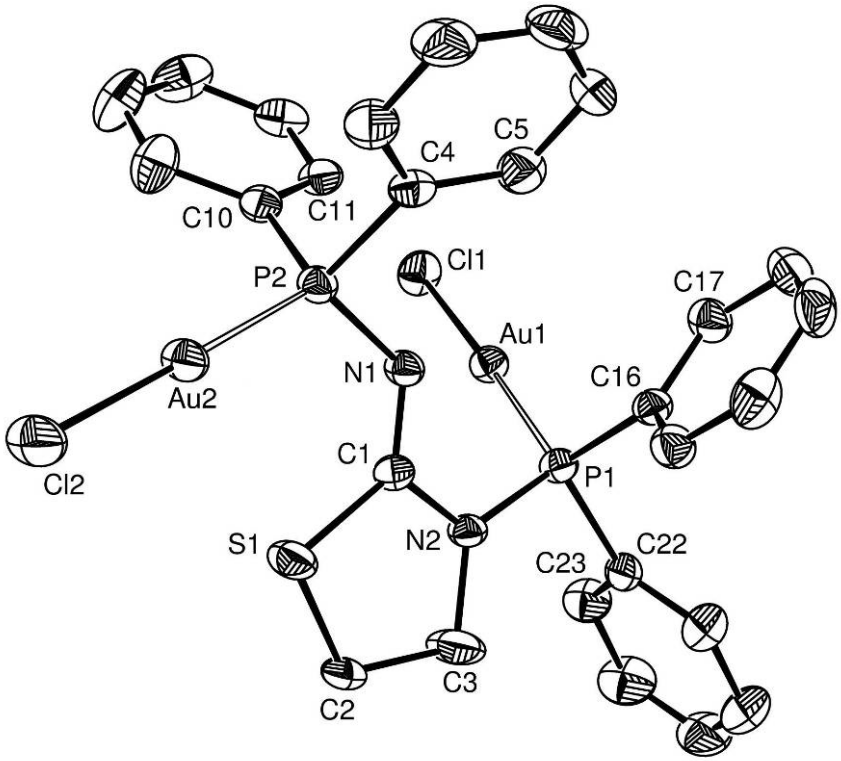
Compound 1a,b



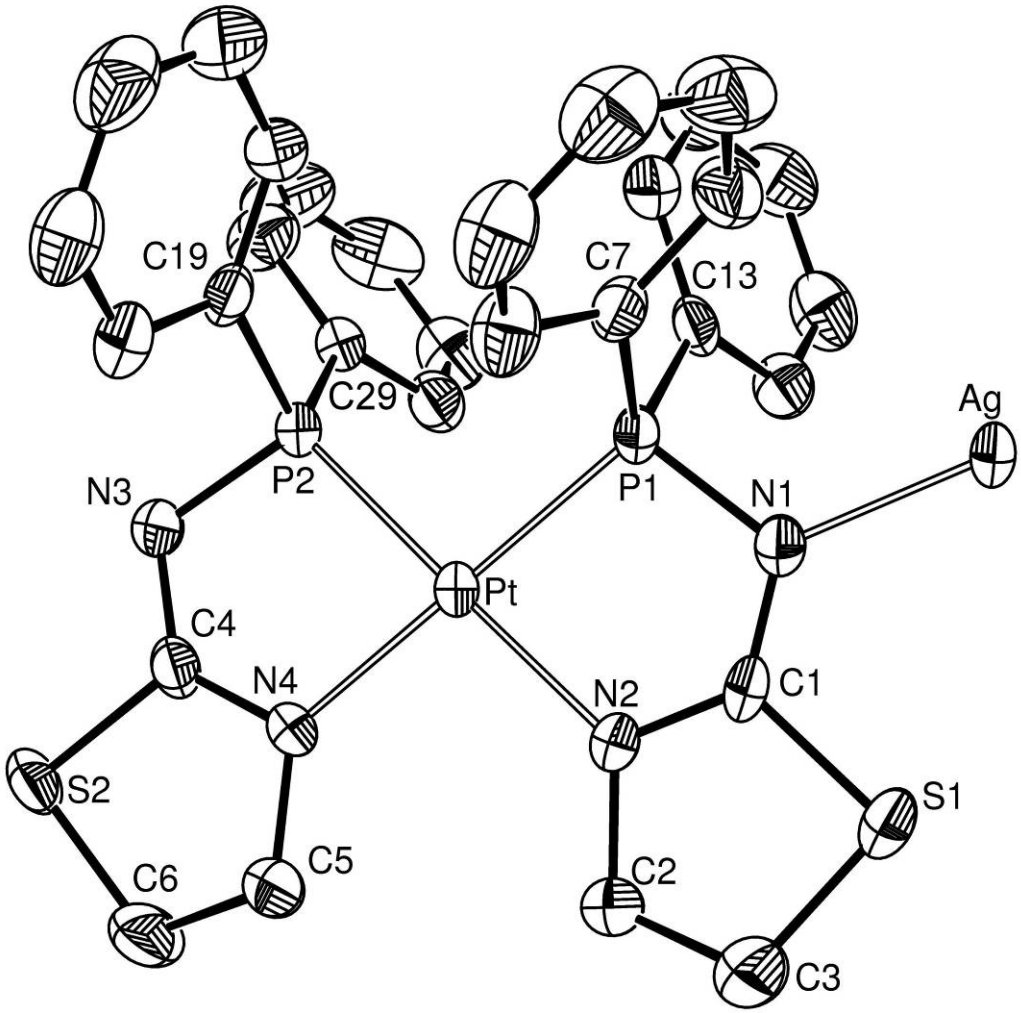
Compound 2



Compound 4



Compound 6



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