On the Reaction of $Ph_2PNHPPh_2$ with RNCS (R = Et, Ph, p-$NO_2C_6H_4$): Preparation of the Zwitterionic Ligand $EtNHC(S)Ph_2P{=}NPPh_2C(S)NEt$ (HSNS) and the Zwitterionic Metalate [(SNS)Rh(CO)]

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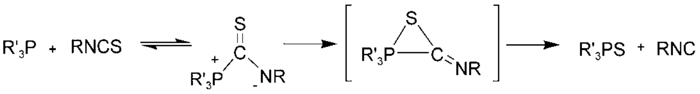
Abstract: The reaction of $Ph_2PNHPPh_2$ (PNP) with RNCS (Et, Ph, p-NO_2-(C_6H_4)) gives addition products resulting from the attack of the P atoms of PNP on the electrophilic carbon atom of the isothiocyanate. When PNP is reacted with EtNCS in a 1:2 molar ratio, the zwitterionic molecule $EtNHC(S)PPh_2{=}NP^+Ph_2C(S)N^-Et$ (HSNS) is obtained in high yield. HSNS can be protonated (H_2SNS^+) or deprotonated (SNS^-), behaving in the latter form as an *S,N,S*-donor pincer ligand. The reaction of HSNS with $[(acac)Rh(CO)_2]$ (acac = acetylacetonate) affords the zwitterionic metalate [(SNS)Rh(CO)]. Other products can be obtained depending on the R group, the PNP/RNCS ratio (1:1 or 1:2), and the reaction temperature. The proposed product of the primary attack of PNP on RNCS, $Ph_2PN{=}PPh_2C(S)NHR$ (**A**), cannot be isolated. Reaction of **A** with another RNCS molecule leads to 1:2 addition compounds of the general formula $RNHC(S)PPh_2{=}NP^+Ph_2C(S)N^-R$ (**1**), which can rearrange into the non-zwitterionic product $RNHC(S)PPh_2{=}NP(S)Ph_2$ (**2**) by eliminating a molecule of RNC. Two molecules of **A** can react together, yielding 1:1 PNP/RNCS zwitterionic products of the formula $RNHCH[PPh_2{=}NP(S)Ph_2]PPh_2{=}NP^+Ph_2C(S)N^-R$ (**3**). Compound **3** can then rearrange into $RNHCH[PPh_2{=}NP(S)Ph_2]_2$ (**4**) by losing a RNC molecule. When R = Et (**a**), compounds **1a**, **2a** (HSNS), and **4a** have been isolated and characterized. When R = Ph (**b**), compounds **2b** and **4b** can be prepared in high yield. When R = p-$NO_2C_6H_4$ (**c**), only compound **3c** is observed and isolated in high yield. The crystal structures of HSNS, [(SNS)Rh(CO)], and of the most representative products have been determined by X-ray diffraction methods.

Keywords: heterocycles • rhodium • synthetic methods • tridentate ligands • zwitterions

Introduction

The reaction of PEt_3 with EtNCS is known since the 1870s as a route to obtain ethyl isocyanide. In this reaction, the transfer of a sulfur atom from the NCS group to the phosphorus center is responsible for the formation of the corresponding phosphano-sulfide ($Et_3P{=}S$) and EtNC. In fact, in the reaction $PR'_3 + RNCS = R'_3PS + RNC$, a zwitterionic intermediate is formed, which is, in turn, dissociated in R'_3PS and RNC. This process is believed to proceed by the formation of a three-membered C-P-S non-zwitterionic ring (Scheme 1).[1]



Scheme 1. Addition reaction of alkylphosphanes to isothiocyanates and subsequent transformation in phosphano-sulfide and isocyanide.

Data reported in the literature indicates that only alkyl-substituted phosphanes, R_3P, or phosphanoamines, $(R'_2N)_xR''_{(3-x)}P$, which contain P–N bonds, can react with isothiocyanates. The zwitterion formation is an equilibrium depending on R, R′, and the solvent, and it is initiated by a nu-

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cleophilic attack of the phosphorus center on the carbon atom of the heterocumulene group.[2,3] The higher nucleophilic character of the P atom in phosphanoamines is due to the N lone pair delocalization, evidenced in Ph$_2$PNHPPh$_2$ (PNP) by the planarity of the P-NH-P system.[4]

Similar reactions of R$_3$P with CS$_2$ give zwitterionic adducts R$_3$PCS$_2$, whose ligating properties have been reviewed.[5] On the other hand, the coordination chemistry of phosphane- or phosphanoamine–isothiocyanate adducts has not been studied until now. As far as we know only one fully characterized complex containing a coordinated N$^-$C(S)P$^+$ zwitterionic group has been reported,[6] but is obtained by insertion of isothiocyanate in a preformed complex. In particular, the derivatives of PNP are potential multidentate ligands that can afford a new class of zwitterionic complexes.

Herein, we report the results of the reaction of PNP with some common isothiocyanates.

Results and Discussion

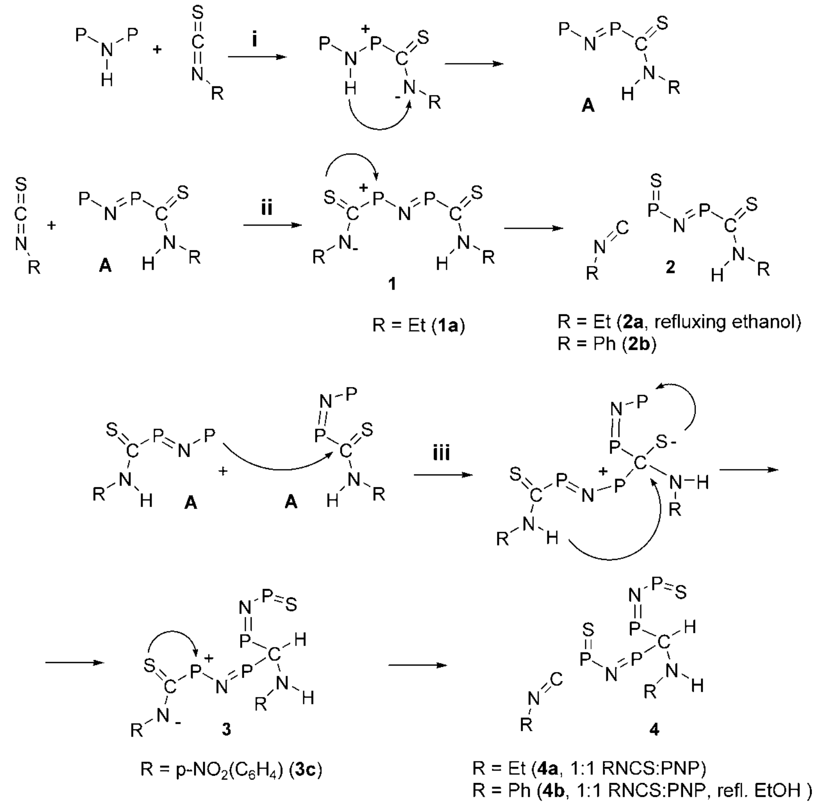
Four kinds of products (**1**–**4**) can be obtained in the reaction of PNP with RNCS, depending on R, the temperature, and the PNP/RNCS molar ratio (Scheme 2).

Reaction **i** represents the primary attack of PNP on RNCS giving the proposed intermediate **A**, via a proton migration. Intermediate **A** cannot be isolated because of the reactivity of its free P atom, which is able to react further with RNCS (pathway **ii**) or with another **A** molecule (pathway **iii**) on the electrophilic CS group.

Along pathway **ii**, the zwitterionic compound **1** is obtained, which, in turn, can rearrange to afford quantitatively compound **2** and an isocyanide molecule.

Along pathway **iii**, two molecules of **A** react with each other through the attack of the tertiary phosphorus of one molecule on the PC(S)N carbon atom of the second one. The resulting intermediate undergoes an S-atom transfer from the C–S group to the free P atom, probably through the formation of a *C,P,N,P,S* five-membered ring. After the S-atom transfer, the C atom is formally negative and can accept the thioamidic proton which migrates from N to C, leading to the formation of a zwitterionic N$^-$C(S)P$^+$ "arm" (compound **3**). An isocyanide molecule can be finally released by rearrangement of **3** into **4**, in the same way as the rearrangement of **1** to **2**.

These compounds can be purified by fractional crystallization, and identified in the crude reaction mixture by their ^{31}P NMR signals. In compound **2** the formation of the P=S group from the PC(S)N zwitterionic arm with the release of a RNC molecule depends on the temperature. When R = Et and the ratio of PNP/EtNCS is 1:2, compound **1a** (HSNS) is obtained in high yield (90 %, > 60 % after recrystallization) together with traces of **2a** and **4a**. Compound **2a** can be obtained almost quantitatively (50 % after recrystallization) by reacting PNP and EtNCS (1:2 ratio) in refluxing ethanol, or by refluxing an ethanol solution of compound **1a**. When R = Et and the ratio of PNP/EtNCS is 1:1, compound **4a** can be obtained (20–30 % yield, together with **1a**, **2a** and unreacted PNP), whereas formation of compound **3a** is not observed. When R = Ph and the PNP/PhNCS ratio is 1:2, the transformation of **1b** to **2b** occurs at lower temperatures, and only compound **2b** is obtained (Yield > 85 %). When the PNP/PhNCS ratio is 1:1, compounds **4b** is obtained (together with traces of a product that is probably **3b**, which can be detected in the reaction mixture by ^{31}P NMR spectroscopy). When



Scheme 2. Products and proposed intermediates of the 2:1 and 1:1 reactions of PNP with RNCS (Ph groups on P atoms are omitted. The isolated products are evidenced for every R group: **a** = Et, **b** = Ph, **c** = *p*-NO$_2$(C$_6$H$_4$). The zwitterionic Lewis structures have been drawn with the formal negative charge located on the nitrogen atom. Charge resonance on the sulfur atom has been omitted for clarity and will be omitted in all other schemes).

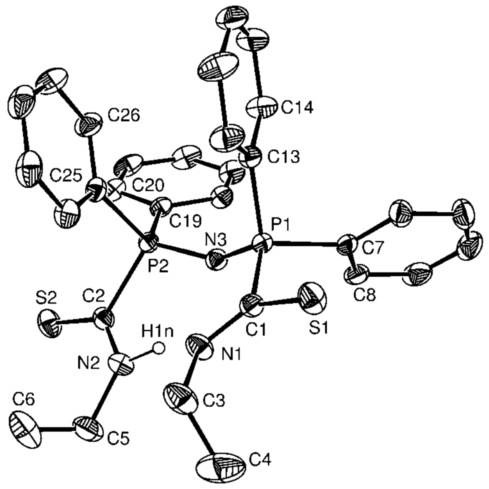


Figure 1. Molecular structure of **1a** (HSNS). Selected bond lengths [Å] and angles [°]: C1–N1 1.297(3), C1–S1 1.690(2), C2–N2 1.314(3), C2–S2 1.660(2), N3–P1 1.584(2), N3–P2 1.575(2); N1-C1-S1 132.1(2), N1-C1-P1 113.0(2), S1-C1-P1 115.0(1), N2-C2-S2 127.3(2), N2-C2-P2 112.2(2), S2-C2-P2 120.4(1), C1-N1-C3 116.4(2), C2-N2-C5 123.6(2), P1-N3-P2 140.3(1).

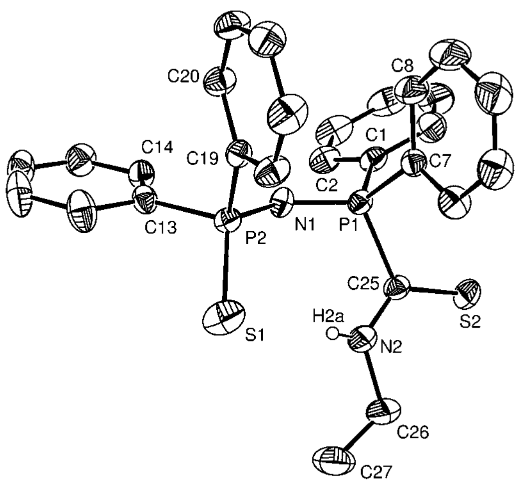


Figure 2. Molecular structure of **2a**. Selected bond lengths [Å] and angles [°]: C25–S2 1.657(4), C26–N2 1.470(5), C25–P1 1.844(4), C25–N2 1.313(5), P1–N1 1.566(3), P2–N1 1.613(3), P2–S1 1.942(2); C25-N2-C26 124.5(4), N2-C25-S2 125.5(3), N2-C25-P1 115.2(3), S2-C25-P1 119.3(2), P1-N1-P2 136.7(2), N1-P1-C25 113.8 (2), N1-P2-S1 119.6(1).

R = p-$NO_2(C_6H_4)$, only the formation of **3c** is observed regardless of the temperature or the PNP/PhNCS ratio.

At the moment the influence of the R group on the "choice" of the two reaction paths **ii** (yielding compound **1**) or **iii** (yielding compound **3**) and on the stability of the zwitterionic functional groups (transformations of **1** into **2**, and of **3** into **4**) is not rationalized. Only when R = p-$NO_2(C_6H_4)$ is the reaction driven towards the formation of a single zwitterionic product that is stable with respect to the subsequent P=S group and p-$NO_2(C_6H_4)NC$ formation. Apparently, the resonance effect of the p-$NO_2(C_6H_4)$ group stabilizes the negative charge on the N atom.

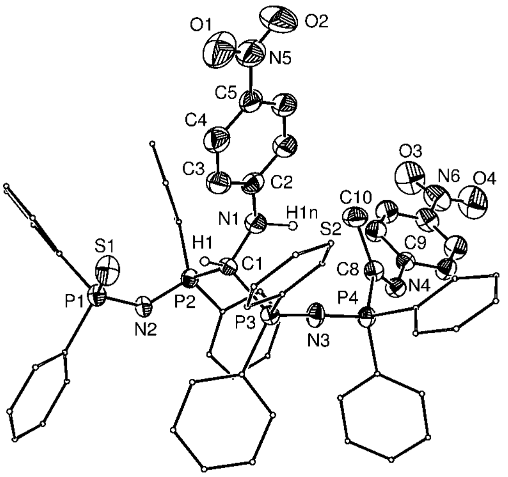


Figure 3. Molecular structure of **3c** (phenyl thermal ellipsoids omitted for clarity). Selected bond lengths [Å] and angles [°]: P1–S1 1.972(3), P4–C8 1.842(7), S2–C8 1.671(8), N1–C2 1.42(1), N1–C1 1.425(9), N4–C8 1.302(9), N2–P1 1.611(4), N2–P2 1.572(6), N3–P3 1.543(6), N3–P4 1.565(6); C2-N1-C1 125.3(7), P2-N2-P1 133.0(4), P3-N3-P4 166.0(4), C8-N4-C9 122.0(6), N4-C8-S2 134.4(6), N4-C8-P4 109.6(5), S2-C8-P4 115.9(4).

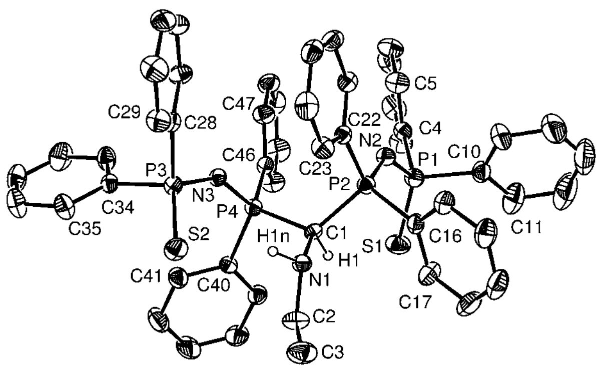


Figure 4. Molecular structure of **4a**. Selected bond lengths [Å] and angles [°]: P1–S1 1.967(2), P1–N2 1.616(2), P2–N2 1.572(2), P2–C1 1.844(3), N1–C1 1.459(3), P4–C1 1.852(3), P4–N3 1.571(2), P3–N3 1.602(2), P3–S2 1.954(2); N2-P1-S1 119.1(1), P2-N2-P1 130.9(2), N2-P2-C1 113.6(1), N1-C1-P4 111.0(2), P4-C1-P2 119.4(2), N3-P4-C1 111.0(1), P4-N3-P3 143.3(2), N3-P3-S2 119.5(1), N1-C1-P2 108.9(2).

As far as we know, **1a** (HSNS) and **3c** are the first compounds containing the new -N=P–C(S)NH- functional group, belonging to the isoelectronic series X=P–C(S)NH- (X = O, S, Se, NR).

Compounds **1a** (R = Et), **2a** (R = Et), **2b** (R = Ph), **3c** (R = p-$NO_2C_6H_4$), and **4a** (R = Et) were obtained as crystalline solids and their structures were determined by X-ray diffraction. Views of the structures of compounds **1a, 2a, 3c**, and **4a** are shown in Figure 1, Figure 2, Figure 3, and Figure 4, respectively, together with significant bond distances and angles. Structural data for **2b** has been deposited at the Cambridge Crystallographic Data Base.

When the PNP group bears a positive charge as in the zwitterionic compounds **1a** (HSNS) and **3c**, the two P–N bond lengths are comparable, being 1.575(2) and 1.584(2) Å in **1a**, 1.543(6) and 1.565(6) Å in **3c**, indicating that the positive charge is delocalized on the two P atoms. The P-N-P angles are 140.3(1) and 166.0(4)°, respectively. When the PNP group is not charged, as in **2a**, **4a** and for the P1-N2-P2 group in **3c**, the P–N bond lengths differ more, (minimum difference for the P4-N3-P3 group in **4a**: P4–N3 1.571(2) Å and P3–N3 1.602(2) Å) suggesting a less delocalized character of the double bond. The P-N-P angles are narrower (in the range 130.9(2)–143.3(2)°). In **1a** an intramolecular hydrogen bond is present between the N atoms of the two EtNC(S)P phosphothioamidic moieties (N1···N2 = 2.885(4) Å, N1–H···N2 = 162(7)°). It is noteworthy that in all molecules of **3c** the chiral C1 atom adopts an *R* configuration, indicating spontaneous enantiomeric resolution during crystallization. When a P=S group is present, intramolecular NH···S=P interactions are observable (H···S distances 2.475(6) and 2.556(8) Å for **2a** and **4a**, respectively), having hydrogen-bonding character in **3c** (N1···S2, H1n···S2 distances 3.295(9) and 2.043(5) Å, respectively, N1···H1n···S2 angle 163.9(7)°). In **3c**, this hydrogen bond creates a second chiral center on the aminic N atom.

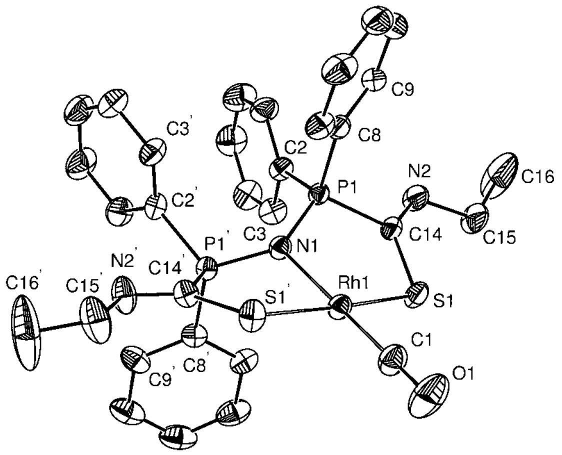
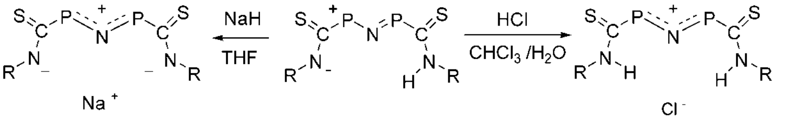


Figure 5. Molecular structure of **5**. Selected bond lengths [Å] and angles [°]: Rh1–C1 1.815(8), Rh1–N1 2.158(5), Rh1–S1 2.367(2), S1–C14 1.764(5), P1–N1 1.643(2), P1–C14 1.851(5), N2–C14 1.288(7); C1-Rh1-N1 180.0(0), C1-Rh1-S1 91.92(3), N1-Rh1-S1 88.08(3), S1'-Rh1-S1 176.15(7), C14-S1-Rh1 102.5(2), N1-P1-C14 106.2(2), P1-N1-P1' 134.3(3), P1-N1-Rh1 112.8(2), N2-C14-S1 131.8(4), N2-C14-P1 111.5(4), S1-C14-P1 116.7(3). (symmetry transformation used to generate equivalent atoms: ′ = $-x+1, y, -z+1/2$)

HSNS is easily and quantitatively protonated to give the H_2SNS^+ ion (Scheme 3). By shaking a chloroform solution of HSNS with concentrated hydrochloric acid, $[H_2SNS]Cl$ was prepared and its crystal structure was determined (structural data for this salt have been deposited at the Cambridge Crystallographic Data Base). By reacting HSNS with NaH in THF, the anion SNS^- can be prepared as a sodium salt, (Scheme 3) but it has not been isolated and characterized because of its instability (this anion may also be referred to as a cation–dianion or a zwitterion–anion).



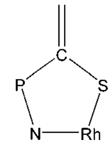
Scheme 3. Protonation and deprotonation of HSNS (Ph groups are omitted for clarity).

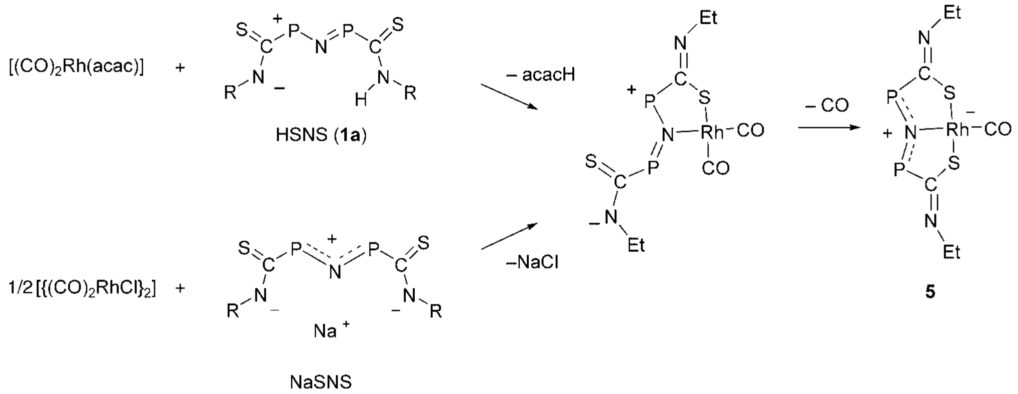
HSNS reacts with $[(acac)Rh(CO)_2]$ (FTIR, CH_2Cl_2 solution: $\nu(CO) = 2023$, 2011 cm^{-1}) through loss of the thioamidic proton and formation of acetylacetone. The anion SNS^- is then coordinated by the $\{Rh(CO)_2\}^+$ moiety, affording a biscarbonyl labile intermediate ($\nu(CO) = 2066$, 2003 cm^{-1} after some minutes), which quickly loses CO, to form [(SNS)Rh(CO)] (**5**) ($\nu(CO) = 1967$ cm^{-1}) in a quantitative yield. Compound **5** can be also obtained by reaction of $[\{(CO)_2RhCl\}_2]$ with NaSNS. The molecular structure of **5** is shown in Figure 5.

This complex, having a crystallographically imposed C_2 symmetry, is a zwitterionic metalate.[7] The anion SNS^- coordinates as an *S,N,S* pincer ligand to the Rh atom, which is found in a square-planar environment. It is noteworthy that the two fused pentaatomic chelating rings contain five different atoms (Rh, S, C, P, N), and therefore can be considered as "true heterocycles".[8] The two P–N bond lengths, 1.643(2) Å, are longer than in **1a** and **3c**, with a P-N-P′ bond angle of 134.3(3)°. The PNP coordinated group, can be associated to the well-known $(Ph_3P)_2N^+$ (PPN^+) cation. As far as we know this is the first example of such a cation coordinated by a metal atom.

To gain insight on the electronic charge distribution in complex **5**, density functional theory (DFT) calculations were performed. The relevant electronic properties of chelation rings, Mulliken atomic charges, and the total electric dipole moment, as obtained by the DFT calculations are reported in Table 1. The electronic structure is characterized by a high charge separation between the phosphorus atoms and the neighboring nitrogen and carbon atoms. In the Lewis structure of [(SNS)Rh(CO)], the negative charge would be located on the Rh atom, as shown in Scheme 4 (for this reason these complexes are called "metalates"), instead it is mainly found on the coordinated N atom. The

Table 1. Mulliken atomic net charges and calculated molecular dipole moment in gas phase and in cyclohexane and THF solutions.

	N	P	C	S	Rh	μ/D	
gas	–0.439	0.205	–0.280	0.017	–0.150	12.870	
C_6H_{12}	–0.442	0.207	–0.270	–0.010	–0.157	14.923	
THF	–0.447	0.210	–0.268	–0.044	–0.177	17.664	



Scheme 4. Reaction of Rh^I precursors, $[(CO)_2Rh(acac)]$ and $[\{(CO)_2RhCl\}_2]$, with HSNS and its deprotonated form SNS^- (Ph groups are omitted for clarity).

charge separation also determines the high value of the total electric dipole moment (12.9 D in the gas phase), which is the sum of the local dipoles on the two chelation rings. Its direction is the same as the twofold axis found in the solid-state structure. The PNP system is the location of the charge separation, with a total positive charge of +0.41 found on the two P atoms and a negative charge of −0.439 on the N atom.

The value of the dipole moment was calculated in nonpolar (cyclohexane) and polar (THF) solvents. Its value is higher than in the gas phase, showing that the molecule is highly polarizable.

In the solid state, molecules all oriented in the same direction are disposed in layers in a head-to-tail fashion (see Figure 6a). Adjacent layers contain molecules with opposite orientations. A perpendicular view with respect to the layers shows that the molecules form "columns" defined by alternated opposite orientations (Figure 6b). The shortest intermolecular Rh···Rh separation, between two molecules with different orientations in two adjacent layers in the same column, is 9.0 Å. The shortest Rh···Rh separation between two equally oriented molecules in the same layer is 10.3 Å.

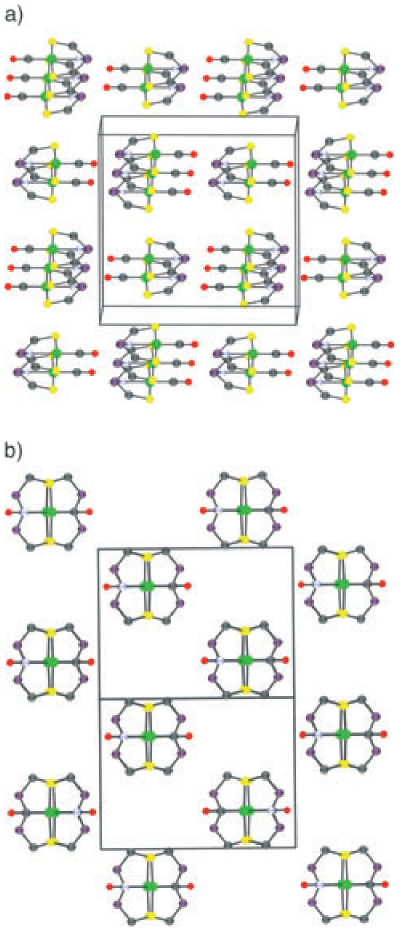


Figure 6. Two views of the [(SNS)Rh(CO)] crystal packing. The unit cell axes are highlighted.

Conclusion

The reaction of PNP with isothiocyanates, RNCS, yields four kinds of structurally characterized products that depend mainly on the R group of RNCS. Among these new products there are zwitterionic molecules that are able or potentially able to coordinate to metal species. In particular, we have found that the ligand HSNS behaves, in its deprotonated form, as an efficient *S,N,S*-donor pincer ligand. The complex [(SNS)Rh(CO)] is the first member of a series (e.g., Pd^{II}, Pt^{II}, Cu^{I}, Co^{III}, Hg^{II} etc) that will be studied to produce a new class of zwitterionic complexes whose properties should be promising in catalysis and in nonlinear optics.

Experimental Section

General remarks: The starting reagents Ph_2PCl, EtNCS, $Me_3SiNHSiMe_3$, p-$NO_2(C_6H_4)NCS$, PhNCS, $[(acac)Rh(CO)_2]$, $[\{(CO)_2RhCl\}_2]$, and NaH were pure commercial products (Aldrich and Fluka) and were used as received. $Ph_2PNHPPh_2$ (PNP) was prepared by reacting Ph_2PCl and Me_3-

$SiNHSiMe_3$ in 2:1 ratio in refluxing diethyl ether and purified by recrystallization. The solvents (C. Erba, Fluka) were dried and distilled by standard techniques before use. Purity was checked by elemental analysis and/or by ^1H and ^{31}P NMR spectroscopy. Elemental (C, H, N, S) analyses were performed with a Carlo Erba EA 1108 automated analyzer. IR spectra (KBr discs or CH_2Cl_2 solutions) were recorded on a Nicolet Nexus FT spectrometer. ^1H (300 MHz, $CDCl_3$), NMR spectra were recorded on Bruker instruments, AC 300, Avance 300 (^1H). ^{31}P (162.0 MHz, 85% H_3PO_4 as external reference, $CDCl_3/CHCl_3$) NMR spectra were recorded on a Bruker AMX400. Multiplicity and coupling constants for ^1H NMR spectra of **2a**, **4a**, and $(H_2SNS)Cl$ compounds were simulated, in very good accordance with those observed experimentally, by using MestRe-C program.[9] Mass spectra were recorded on a Fennigan MAT SSQ710.

Preparation of 1a (HSNS): A solution of $HN(PPh_2)_2$ (3.86 mmol, 1.387 g) in CH_2Cl_2 (15 mL) was added to a stirred solution of EtNCS (7.72 mmol, 0.697 mL, 97%) in CH_2Cl_2 (10 mL) and left at room temperature for 3 h. The resulting yellow solution was concentrated under reduced pressure. Hexane (10 mL) was added to give, after two days at 4°C, a yellow crystalline product. Yield: 67%; ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta = 13.0$ (s, br, 1H; NH), 7.7–7.3 (m, 20H; Ph), 3.7 (qd, $^3J(H,H) = 7.2$, $^4J(H,P) = 2.0$ Hz, 4H; CH_2), 1.2 ppm (t, $^3J(H,H) = 7.2$ Hz, 6H; CH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25°C): $\delta = 8.4$ ppm (s); MS (CI): *m/z* (%): 473 (15), 417 (100), 384(40), 308 (10), 262 (15); elemental analysis calcd (%) for $C_{30}H_{31}N_3P_2S_2$: N 7.51, C 64.38, H 5.58, S 11.46; found: N 7.24, C 64.03, H 5.49, S 11.25.

Preparation of 2a: A solution of $HN(PPh_2)_2$ (2.6 mmol, 1 g) in EtOH (20 mL) was added to a solution of EtNCS (5.2 mmol, 0.469 mL, 97%) in refluxing EtOH (30 mL). After 3 h, the heating was stopped and at room temperature a yellow crystalline product was obtained. The product was washed with hexane. Yield: 48%; ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta = 11.4$ (s, br, 1H; N-H), 7.7–7.2 (m, 20H; Ph), 3.8 (obsd multiplicity: m, simulated: qdd, $^3J(H,H) = 7.4$, $^4J(H,P) = 5.6$, $^6J(H,P) = 1.8$ Hz, 2H; CH_2), 1.4 ppm (t, $^3J(H,H) = 7.4$ Hz, 3H; CH_3), $^{31}P\{^1H\}$ NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 44.4$ (s, P=S), 11.4 ppm (s, P-C(S)NEt); MS (CI): *m/z* (%): 504 ($[M]^+$, 60), 417 (100), 385 (20), 308 (20); elemental analysis calcd (%) for $C_{27}H_{26}N_2P_2S_2$: N 5.55, C 64.27, H 5.19, S 12.71; found: N 5.61, C 64.46, H 5.08, S 12.84.

Preparation of 2b: A solution of $HN(PPh_2)_2$ (2.7 mmol, 1.04 g) in CH_2Cl_2 (20 mL) was added to a stirred solution of PhNCS (5.4 mmol, 0.659 mL, 98%) in CH_2Cl_2 (20 mL) at room temperature over 3 h. The resulting yellow solution was concentrated under reduced pressure. Hexane (10 mL) was added to give, after two days at 4°C, a yellow crystalline product. Yield: 85%; ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta = 12.4$ (s, br, 1H; N-H), 8.1–6.8 ppm (m, 25H; Ph); $^{31}P\{^1H\}$ NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 44.5$ (s, P=S), 12.1 ppm (s, P-C(S)NPh); MS (CI): *m/z* (%): 550 ($[M]^+$, 20), 522 (70), 446 (56), 418 (100), 385 (30); elemental analysis calcd (%) for $C_{31}H_{26}N_2P_2S_2$: N 5.07, C 67.37, H 4.74, S 11.60; found: N 5.12, C 67.52, H 4.64, S 11.46.

Preparation of 3c: A solution of $HN(PPh_2)_2$ (1.2 mmol, 0.462 g) in CH_2Cl_2 (20 mL) was added under stirring to a solution of *p*-NO_2-$(C_6H_4)NCS$ (1.2 mmol, 0.220 g, 98%) in CH_2Cl_2 (10 mL) at room temperature over 3 h. The resulting orange solution was concentrated under reduced pressure. Hexane (10 mL) was added to give, after 3–4 days at 4°C, an orange product. Yield: 91%; ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta = 8.7$ (br, 1H; NH), 8.3–6.9 (m, br, 48H; Ph, $C_6H_4NO_2$), 6.75 ppm (t, br, $^2J(H,P) = 8.0$ Hz, 1H; CHP_2); ^{31}P NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 44.6$ (s; P=S), 20.3 (dd, $^2J(P,P) = 12$, $^2J(P,P) = 27$ Hz; S=CPN*P*), 17.4 (d, $^2J(P,P) = 12$ Hz; S=PN*P*), 8.0 ppm (d, $^2J(P,P) = 12$ Hz; PC=S); MS (70 CI): *m/z* (%): 566 (18), 446 (18), 417 (100), 401 (34), 384 (30), 340 (24), 308 (30), 262 (58), 217 (20), 181 (34), 139 (28). elemental analysis calcd (%) for $C_{62}H_{50}N_6P_4O_4S_2$: N 7.43, C 65.83, H 4.45, S 5.67; found: N 7.36, C 65.69, H 4.44, S 5.71.

Preparation of 4a: A solution of EtNCS (2.6 mmol, 0,235 mL, 97%) in CH_2Cl_2 (20 mL) was added dropwise to a stirred solution of $HN(PPh_2)_2$ (2.6 mmol, 1 g) in CH_2Cl_2 (10 mL) at 0°C. After 4 h, the solution was concentrated under reduced pressure and hexane was added to obtain, after two days, a yellow powder. The solution was filtered and after two days a crystalline white product was obtained. Yield: 37%. ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta = 8.0$–6.9 (m, 40H; Ph), 6.48 (td, $^2J(H,P) = 15.9$, $^3J(H,H) = 9$ Hz, 1H; CHP_2), 3.40 (ttd, $^3J(H,H) = 6.7$, $^3J(H,H) = 9$ Hz, $^3J(H,P) =$ sim. 7.8 Hz, 1H; NH), 2.49 (qd, $^3J(H,H) = 6.7$, $^3J(H,H) = 6.7$ Hz, 2H; CH_2), 0.58 ppm (t, $^3J(H,H) = 6.7$ Hz, 3H; CH_3); $^{31}P\{^1H\}$ NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 44.0$ (s, P=S), 18.4 ppm (s, CH-P); MS (CI): *m/z* (%): 472 (15), 417 (100), 384 (20), 308 (10); elemental analysis calcd (%) for $C_{51}H_{47}N_3P_4S_2$: N 4.72, C 68.83, H 5.32, S 7.21; found: N 4.79, C 68.49, H 5.32, S 7.15;

Preparation of 4b: A solution of PhNCS (2.6 mmol, 0.317 mL, 98%) in CH_2Cl_2 (20 mL) was added to a stirred solution of $HN(PPh_2)_2$ (2.6 mmol, 1 g) in refluxing EtOH (10 mL). After 45 min, the solution was concentrated under reduced pressure. After two days at 4°C a white solid was filtered. Yield: 60%. ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta = 7.9$–6.65 (m, 45H; Ph), 6.55 (t, $^2J(H,P) = 7$ Hz, 1H; CHP_2), 3.75 ppm (s, br, 1H; NH); $^{31}P\{^1H\}$ NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 44.7$ (s, P=S), 17.9 ppm (s, CH-P); elemental analysis calcd (%) for $C_{55}H_{47}N_3P_4S_2$: N 4.48, C 70.42, H 5.05, S 6.83; found: N 4.52, C 70.81, H 4.99, S 6.81.

Preparation of [(SNS)Rh(CO)] (5): Method a): A solution of HSNS (**1a**) (0.65 mmol, 0.364 g) in THF (5 mL) was added to a stirred solution of $[(acac)Rh(CO)_2]$ (0.65 mmol, 0.168 g) in THF (5 mL) at room temperature over 3 h. Hexane (5 mL) was added to the orange resulting solution to give, after 2–3 days, a crystalline orange-red solid [Rh(SNS)CO] (**5**) (yield 82%).

Method b): NaSNS in THF (15 mL) was prepared by adding a suspension of NaH (0.2 mmol, 5 mg in THF (15 mL)) to a HSNS solution (0.2 mmol, 112 mg in THF (30 mL). The color turned from yellow to white in few seconds. A solution of $[\{(CO)_2RhCl\}_2]$ (0.1 mmol, 40 mg) in THF (15 mL) was then added at room temperature under stirring. After 3 h, the solvent was evaporated under reduced pressure, and CH_2Cl_2 (10 mL) was added to the orange resulting powder. After the color of the solution turned to orange, the NaCl precipitated was filtered off. The solvent was then evaporated to give an orange-red powder (**5**), which was recrystallized from CH_2Cl_2/hexane. Yield: 80%; ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta = 7.48$ (m, 12H; Ph), 7.26 (m, 8H; Ph), 3.75 (qd, $^3J(H,H) = 7.2$, $^4J(H,P) = 3.9$ Hz, 4H; -CH_2-), 1.19 ppm (t, $^3J(H,H) = 7.2$ Hz, 6H; -CH_3); ^{31}P NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 16.6$ ppm (s); FTIR (CH_2Cl_2): $\tilde{\nu} = 1967$ cm^{-1} (CO); elemental analysis calcd (%) for $RhC_{31}H_{30}N_3OP_2S_2$: N 6.09, C 53.99, H 4.38, S 9.30; found: N 6.12, C 54.25, H 4.46, S 9.18.

Preparation of $(H_2SNS)Cl$: HSNS (0.13 mmol, 73 mg) was dissolved in CH_2Cl_2 (20 mL) to give a yellow solution; HCl (1 mL, 37%) was added and the reaction mixture was vigorously shaken. The upper aqueous phase was eliminated and the resulting organic phase was dried on anhydrous Na_2SO_4 and evaporated under reduced pressure to obtain a yellow powder. Yield: 98%; ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta = 12.8$ (s, 2H; NH), 8.0–7 (m, 40H; Ph), 4.05 (obsd. multiplicity: q, $J = 6.7$ Hz, simulated qd, $^3J(H,H) = 7.2$, $^4J(H,P) = 7$ Hz, 4H; CH_2), 1.41 ppm (t, $^3J(H,H) = 7.2$ Hz, 6H; CH_3); ^{31}P NMR ($CDCl_3$, 25°C): $\delta = 12.8$ ppm (s); elemental analysis calcd (%) for $C_{30}H_{32}N_3P_2S_2Cl$: N 7.05, C 60.44, H 5.41, S 10.76; found: N 7.00, C 60.18, H 5.24, S 10.88.

X-ray data collection, structure solution and refinement for complexes 1a, 2a, 3c, 4a, and 5: Crystals suitable for X-ray analysis of **1a, 2a, 3c, 4a,** and **5** were obtained by layering hexane on a dichlorometane solution. The intensity data were collected at room temperature on a Philips PW 1100 (**1a, 4a**), on a Bruker area detector AXS Smart 1000 (**2a, 5**), and on a Enraf-Nonius CAD4 diffractometers (**3c**) (the first two using graphite-monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, while the latter using $Cu_{K\alpha}$ radiation, $\lambda = 1.54183$ Å). Crystallographic and experimental details of the structures are summarized in Table 2. An empirical correction for absorption was made for **1a, 3c, 4a** (maximum and minimum value for the transmission coefficient: 1.000 and 0.473 (**1**), 1.000 and 0.7227 (**3**), 1.000 and 0.623 (**4**)).[10a,b] For complex **2a** and **5** (maximum and minimum effective transmission value 1.000 and 0.827, 1.000 and 0.591, respectively) the raw frame data were processed by using SAINT and SADABS to yield the reflection data file and the Bruker software was used for the absorption correction.[10c–e] The structures were solved by Patterson and Fourier methods and refined by full-matrix least-

Table 2. Crystal data and structure refinement for compounds **1a**, **2a**, **3c**, **4a**, and **5**.

	1a	**2a**	**3c**	**4a**	**5**
formula	$C_{30}H_{31}N_3P_2S_2$	$C_{27}H_{26}N_2P_2S_2$	$C_{62}H_{50}N_6P_4O_4S_2$	$C_{51}H_{47}N_3P_4S_2$	$RhC_{31}H_{30}N_3OP_2S_2$
FW	559.64	504.56	1131.08	889.92	689.55
crystal system	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic
space group	$P2_1/n$	$C2/c$	$P2_12_12_1$	$P\ -1$	$C2/c$
a [Å]	14.718(4)	17.506(5)	21.820(5)	16.778(5)	13.810(5)
b [Å]	11.178(3)	14.626(5)	20.636(5)	12.958(4)	15.389(5)
c [Å]	18.263(5)	20.601(5)	12.492(5)	12.765(4)	16.236(5)
α [°]	90	90	90	64.94(5)	90
β [°]	102.41(5)	97.404(5)	90	70.51(5)	106.88(5)
γ [°]	90	90	90	71.99(5)	90
V [Å^3]	2934(2)	5231(3)	5625(3)	2323.7(1)	3302(2)
Z	4	8	4	2	4
ρ_{calcd} [g cm^{-3}]	1.267	1.281	1.336	1.272	1.387
$F(000)$	1176	2112	1162	932	1408
crystal size [cm]	0.14×0.21×0.15	0.17×0.21×0.15	0.24×0.18×0.14	0.22×0.11×0.20	0.12×0.20×0.25
μ [cm^{-1}]	3.14	3.44	23.70	2.91	7.68
rflns collected	5710	10240	4637	6866	7474
rflns unique	5710	3204	4637	6866	2300
rflns observed [$I>2\sigma(I)$]	3641	2262	3581	3559	1879
parameters	338	309	443	556	187
R indices $R1$[a]	0.0511	0.0484	0.0388	0.0499	0.0389
[$I>2\sigma(I)$] $wR2$[b]	0.1468	0.1357	0.0604	0.1264	0.0750
R indices	$R1$ 0.0797	0.0746	0.0662	0.1049	0.0637
(all data) $wR2$	0.1572	0.1357	0.0711	0.1349	0.0834

[a] $R1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR2=[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

squares procedures (based on F_o^2) (SHELX-97),[11] first with isotropic thermal parameters and then with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms or except those bound to nitrogen atoms and H1 in compound **3a**, which were found and refined isotropically.

CCDC-246734 (**1a**), CCDC-246735 (**2a**), CCDC-246737 (**3c**), CCDC-246738 (**4a**), and CCDC-246740 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Calculations: DFT calculations were performed by using the B3LYP[12a–c] exchange-correlation functional with LanL2DZP effective core potential basis function,[13] augmented by a supplemented set of d valence orbitals on the phosphorus atoms to properly describe the low-lying empty d orbitals. All calculations were performed with the Gaussian 03 program.[14] The equilibrium geometry of the molecular systems was obtained by applying a standard criterion of convergence of the molecular forces. The computed geometry is in reasonable agreement with the structure obtained by single-crystal X-ray analysis.

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[1] a) A. W. Hofmann, *Ber. Dtsch. Chem. Ges.* **1870**, *3*, 761; b) A. Hantzsch, H. Hibbert, *Chem. Ber.* **1907**, *40*, 1511.

[2] L. Engel, O. Dahl, *Acta Chem. Scand. B* **1974**, *9*, 28.

[3] K. Akiba, T. Yoneyama, H. Hamada, N. Inamoto, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1970.

[4] N. Noth, E. Fluck, *Z. Naturforsch. B* **1984**, *39*, 744.

[5] A. Galindo, D. Miguel, J. Perez, *Coord. Chem. Rev.* **1999**, *193*, 643.

[6] R. Chauvin, *Eur. J. Inorg. Chem.* **2000**, 577.

[7] V. Cadierno; Maria. Zablocka, B. I. Donnadieu, J.-P. Alain; Majoral, *Organometallics* **1999**, *18*, 1882.

[8] P. Cheshire, A. M. Z. Slawin, J. D. Woollins, *Inorg. Chem. Commun.* **2002**, *5*, 803.

[9] MestRe-C: J. Carlos Cobas Gomez, F. Javier Sardina Lòpez, Mestrelab Research, Acoruña, Spain, **2004**.

[10] a) S. Parkin, B. Moezzi, H. Hope, *J. Appl. Crystallogr.* **1995**, *28*, 53; b) F. Ugozzoli, *Comput. Chem.* **1987**, *11*, 109; c) *SMART Software Users Guide, Version 5.0*; Bruker Analytical X-ray Systems, Madison, WI, **1999**; d) *SAINT Software Users Guide*; Bruker Analytical X-ray Systems: Madison, WI, **1999**; e) G. M. Sheldrick, SADABS, Bruker Analytical X-ray Systems, Madison, WI, **1999**.

[11] a) G. M. Sheldrick, SHELXL-93, a program for crystal structure determination, University of Göttingen, Germany, **1993**; b) G. M. Sheldrick, SHELXL-97, Program for crystal structure refinement, University of Göttingen, Germany, **1997**.

[12] T. H. Dunning, Jr., P. J. Hay in *Modern Theoretical Chemistry, vol. 3* (Ed.: H. F.Schaefer, III), Plenum, New York, **1976**, p. 1.

[13] a) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270; b) W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284; c) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**. *82*, 299.

[14] Gaussian 03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **2003**.

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