Experimental

4-B(OH)$_2$C$_6$H$_4$C(Me)=NN(H)C(=S)NHMe (**a**). 4-Acetylphenylboronic acid (671 mg, 4.09 mmol) and hydrochloric acid (35%, 0.65 cm^3) were added to a suspension of 4−methyl−3−thiosemicarbazide (430 mg, 4.09 mmol) in water (40 cm^3) to give a clear solution, which was stirred at room temperature for 4 h. The white solid formed was filtered off, washed with cold water, and dried in *vacuo*. Yield: 924 mg, 90%. Anal. Found: C, 47.8; H, 5.6; N, 16.8; S, 12.7 %; $C_{10}H_{14}BN_3O_2S$ (251.11 g/mol) requires C, 47.8; H, 5.6; N, 16.7; S, 12.8 %. IR(cm^{-1}): υ(N−H) 3314, 3341; υ(C=N) 1570; υ(C=S) 831, υ(O−H) 3500; υ(B−O) 1363. ^{1}H NMR (DMSO): 2.29 (s, 3H, Me); 3.04 (d, 3H, NHC*H3*, ^3J(NHMe) = 4.2Hz); 7.80 (m, 2H, H3, H5, *N* = 8.3Hz); 7.90 (m, 2H, H2, H6, *N* = 8.3Hz); 8.12 (s, 2H, B(OH)$_2$); 8.47 (b, 1H, N*H*Me); 10.23 (bs, 1H, N*H*).

[Pd{4-B(OH)$_2$C$_6$H$_3$C(Me)=NN=C(S)NHMe}]$_4$ (**1**). To a stirred solution of potassium tetrachloropalladate (114 mg, 0.35 mmol) in water (6 cm^3) was added ethanol (40 cm^3). The resulting fine yellow suspension was treated with ligand **a** (88 mg, 0.35 mmol). The mixture was stirred for 24h at room temperature. The yellow precipitate was filtered off, washed with ethanol and dried. Yield: 105mg (89%). Anal. Found: C: 33.7; H: 3.3; N: 11.9; S: 8.9 %; $C_{40}H_{48}N_{12}B_4O_8S_4Pd_4$ (1422.08 g/mol) requires C: 33.8; H: 3.4; N: 11.8; S: 9.0 %. IR(cm^{-1}): υ(C=N) 1583; υ(N−H) 3256; υ(O−H) 3431; υ(B−O) 1382. ^{1}H NMR (DMSO): 2.28 (s, 12H, Me); 2.84 (d, 12H, NHC*H3*, ^3J(NHMe) = 4.6Hz); 6.50 (bs, 4H, N*H*Me); 6.68 (d, 4H, H3, ^3J(H3H2) = 7.6Hz); 7.33 (d, 4H, H2, ^3J(H2H6) = 7.6Hz); 7.61 (s, 8H, B(OH)$_2$); 7.79 (s, 4H, H5).

[Pd{4-B(OH)$_2$C$_6$H$_3$C(Me)=NN=C(S)NHMe}{PPh$_3$}] (**3**). The phosphine PPh$_3$ (42 mg, 1.2 mmol) was added to a suspension of complex **1** (57mg, 0.040 mmol) in acetone (20 cm^3). The mixture was stirred for 24h. The resulting yellow solid was filtered off and dried. Yield: 20 mg (80 %). Anal. Found: C, 54.2; H, 4.3; N, 6.6; S, 5.4 %, $C_{28}H_{27}N_3BO_2SPPd$ (617.18 g/mol) requires C, 54.4; H, 4.4; N, 6.8; S, 5.2 %. IR(cm^{-1}): υ(C=N) 1588; υ(N−H) 3284; υ(O−H) 3398; υ(B−O) 1371. ^{1}H NMR (CDCl$_3$): 2.25 (s, 3H, Me); 2.91 (d, 3H, NHC*H$_3$*, ^3J(NHMe) = 4.6Hz); 6.92 (bs, 1H, N*H*Me); 6.98 (d, 1H, H3, ^3J(H3H2) = 7.6Hz); 7.14 (s, 1H, H5); 7.25 (d, 1H, H2); 7.33-7.70 (m, 15H, P*Ph$_3$*); 7.93 (s, 2H, B(OH)$_2$). ^{31}P RMN (CDCl$_3$): 36.58 (s, *P*Ph$_3$).

[Pd{4-(4-MeC(=O)C_6H_4)C_6H_3C(Me)=NN=C(S)NHMe}{PPh_3}] (**4**). Method **I**: To a stirred solution of compound **3** (39 mg, 0.06 mmol) in dry THF (10 cm^3) 4−bromoacetophenone (24 mg, 0.12 mmol), K_3PO_4 (51 mg, 0.24 mmol) and [Pd(PPh_3)$_4$] (58 mg, 0.005 mmol) were added and the mixture was refluxed for 24h. After cooling to room temperature water (10 cm^3) was added and the mixture was extracted with dichloromethane (2 x 20 cm^3). The combined extracts were dried over $MgSO_4$ and the solvent removed under vacuum. The residue was chromatographed on a column packed with silica gel. Elution with dichloromethane/methanol (2%) afforded the final product after concentration, as a yellow crystalline solid. The yellow precipitate was filtered off, washed with ethanol and dried. Yield: 15 mg, 36 %. Method **II**: An analogous procedure to that of method **I** was followed albeit without addition of [Pd(PPh_3)$_4$]. The resulting mixture was stirred for 15 min. at room temperature and refluxed for a further 30 minutes; the resulting crystals of **4** were separated by filtration. Anal. found: C, 62.7; H, 4.8; N, 6.0; S, 4.7 %, $C_{36}H_{32}N_3OSPPd$ (692.12 g/mol) requires C, 62.5; H, 4.7; N, 6.1; S, 4.6 %. IR(cm^{-1}): υC=N: 1593, υN-H: 3321, υO-H:3386, υ(B−O): 1353. ^{1}H NMR ($CDCl_3$): 2.43 (s, 3H, Me); 2.55 (s, 3H, COCH_3); 2.96 (d, 3H, NHCH_3, ^3J(NHMe) = 4.9Hz); 4.75 (b, 1H, N*H*Me); 6.60 (d, 1H, H3, ^3J(H3H2) = 7.6Hz); 6.82 (m, 2H, H12, H16, N = 8.3Hz); 7.14 (s, 1H, H5); 7.35-7.79 (m, 15H, PPh_3); 8.06 (m, 2H, H13, H15, N = 8.3Hz). ^{31}P−{^{1}H} RMN ($CDCl_3$): 37.89 (s, 1P, PPh_3).

X-ray Crystallographic Study: Three-dimensional, room temperature X-ray data were collected on a Siemens Smart CCD diffractometer by the w scan method using graphite-monochromated Mo-Kalpha radiation. All the measured reflections were corrected for Lorentz and polarisation effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined by full matrix least squares on *F2*. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final R = 0.0353 and wR_2 = 0.0721, with allowance for thermal anisotropy of all non-hydrogen atoms. A molecule of solvent was proven to be indeterminate as both THF and DCM where used in the preparation. Therefore PLATON Squeeze was used to create a solvent mask of 47e. this equates to approximately C2 H4 O1.

The structure solution and refinement were carried out using the program package SHELXS-97 and SHELXL-2013, respectively.

Crystallographic study:

Table 1. Crystal and structure refinement data for compound **4**.

Identification code	vi20la1n_sq_s	
Empirical formula	C38 H36 N3 O2 P Pd S	
Formula weight	736.13	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.7093(13) Å	α= 107.932(2)°.
	b = 11.0603(13) Å	β= 95.926(2)°.
	c = 15.9546(19) Å	γ = 104.175(2)°.
Volume	1710.2(4) Å^3	
Z	2	
Density (calculated)	1.429 Mg/m^3	
Absorption coefficient	0.688 mm^{-1}	
F(000)	756	
Crystal size	0.54 x 0.1 x 0.05 mm^3	
Theta range for data collection	1.999 to 26.021°.	
Index ranges	-13<=h<=13, -13<=k<=13, -19<=l<=19	
Reflections collected	6711	
Independent reflections	6711 [R(int) = 0.0402]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.91 and 0.65	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6711 / 0 / 392	
Goodness-of-fit on F^2	1.000	
Final R indices [I>2sigma(I)]	R1 = 0.0353, wR2 = 0.0721	
R indices (all data)	R1 = 0.0651, wR2 = 0.0817	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.372 and -0.517 e.Å^{-3}	

Table 2. Selected bond distances (Å) and angles (º) for compound **4**.

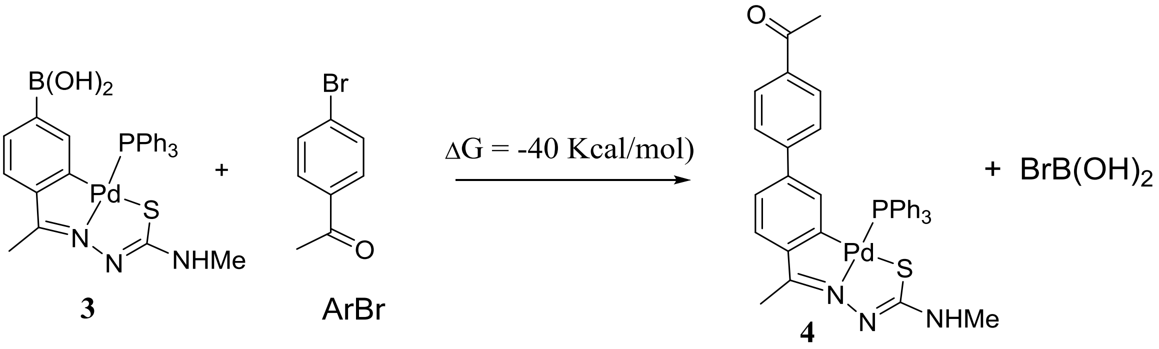
Pd(1)-C(1)	2.020(3)
Pd(1)-N(1)	2.028(2)
Pd(1)-P(1)	2.2520(9)
Pd(1)-S(1)	2.3484(9)
S(1)-C(5)	1.764(3)
N(1)-C(3)	1.295(4)
N(1)-N(2)	1.390(3)
N(2)-C(5)	1.303(4)
N(3)-C(5)	1.346(4)
N(3)-C(6)	1.447(4)
O(1)-C(10)	1.233(4)
C(1)-C(2)	1.414(4)
C(2)-C(3)	1.457(4)
C(3)-C(4)	1.496(4)
C(7)-C(8)	1.477(4)
C(9)-C(10)	1.464(5)
C(10)-C(11)	1.493(6)

C(1)-Pd(1)-N(1)	80.60(11)
C(1)-Pd(1)-P(1)	94.68(9)
N(1)-Pd(1)-S(1)	82.78(8)
P(1)-Pd(1)-S(1)	101.95(3)
C(5)-S(1)-Pd(1)	94.18(11)
C(3)-N(1)-N(2)	119.3(3)
C(3)-N(1)-Pd(1)	117.3(2)
N(2)-N(1)-Pd(1)	123.33(19)
C(5)-N(2)-N(1)	112.3(3)
N(1)-C(3)-C(2)	114.0(3)

N(1)-C(3)-C(4)	123.1(3)
C(2)-C(3)-C(4)	122.9(3)
C(5)-N(3)-C(6)	123.5(3)
C(1)-C(2)-C(3)	116.6(3)
N(2)-C(5)-N(3)	117.3(3)
N(2)-C(5)-S(1)	127.4(2)
N(3)-C(5)-S(1)	115.3(3)
O(1)-C(10)-C(11)	119.8(4)
C(9)-C(10)-C(11)	120.2(4)

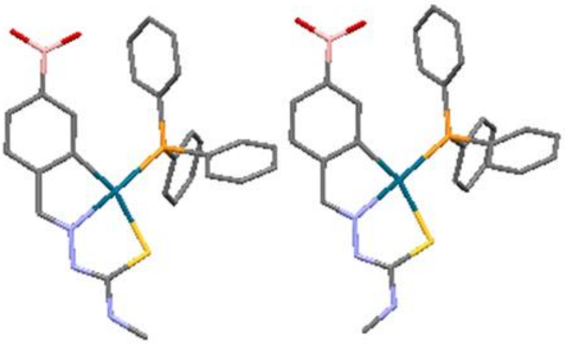
Computational details

The overall reaction studied was:



All the components which were optimized to ground state with the Gaussian g09[1] package of programs (M06/ ECP28MDF_GUESS[2]/6-31G(d)).

Structures obtained



3a **3b**

Figure 1.- 3b is slightly more stable than **3a** by 1.13 Kcal/mol.

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[1] M. J. Frisch *et al*. *Gaussian 09*, Revision D.01; Gaussian, Inc., Wallingford CT, **2013.**

[2] K. A. Peterson, D. Figgen, M. Dolg, H. Stoll, *J. Chem. Phys*. **2007** *126*, 124101.

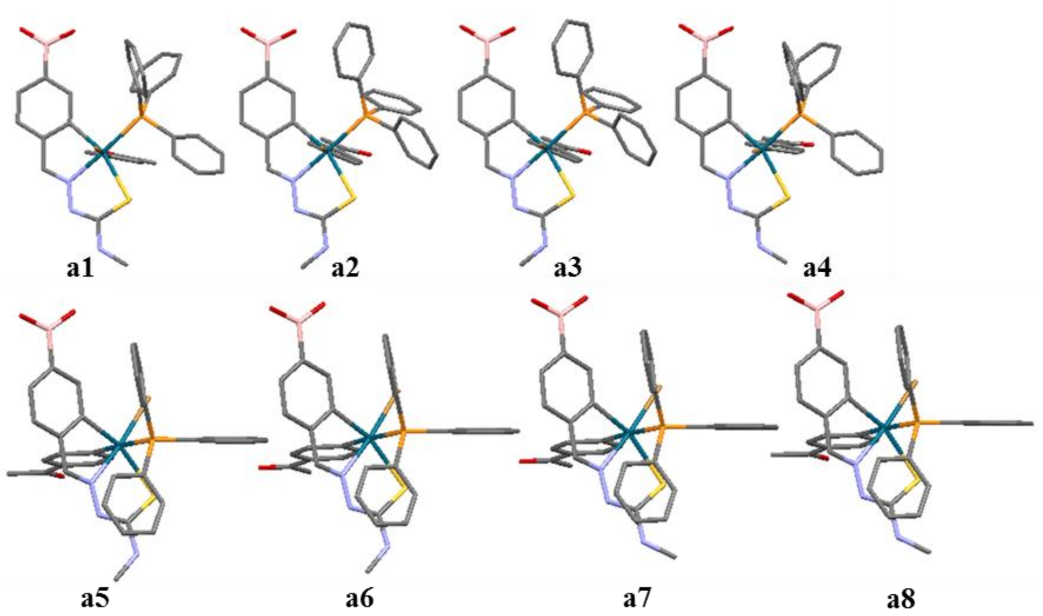
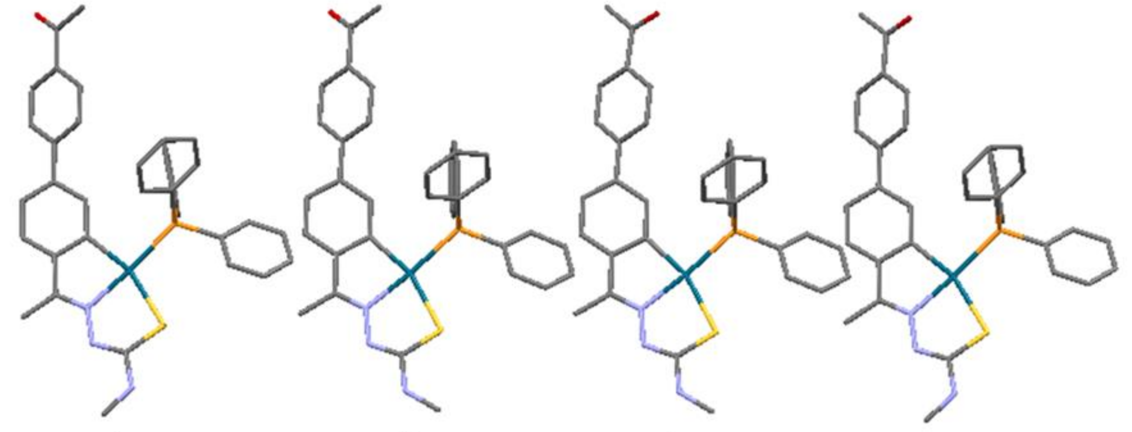


Figure 2.- The eight conformers derived from **a**. The most stable one is **a6**, as shown in Table 3.

Table 3.- Related energies to the most stable conformer (**a6**)

Compound	Energy/(Kcal/mol)
a6	0
a5	0,29806725
a7	1,10755515
a8	1,47841356
a2	9,64796625
a3	10,04831763
a4	10,05082767
a1	10,6583201

The results show that the energy difference between the species with the same conformation (*cis*- or *trans*-) is *ca.* 1 Kcal/mol, thus being nearly isoenergetic. The difference of 10 Kcal/mol between the *cis*- and the *trans*- conformers corroborates our assumption of a *cis*-fashion addition.



4a 4b 4c 4d

Figure 3.- The four conformers derived from **4**. The most stable one is **4d**, as shown in Table 4.

Table 4.- Related energies to the most stable conformer (**4d**)

Compound	Energy/(Kcal/mol)
4d	0
4a	0,298067
4c	0,968875
4b	1,146461

Crystallographic data comparison

In the case of compound **4**, suitable crystals for X-ray diffraction were obtained. In order to compare the crystal structure with the conformers studied, the results showed that the structure matches conformer **4d**; this is in accordance with the experimental data, and shows the wellness of the model.

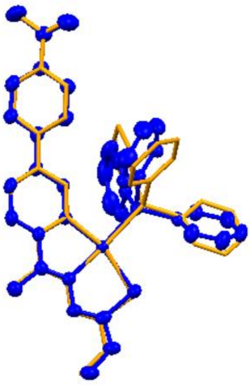


Figure 4.- Comparison of the DFT optimized conformer **4d** (orange) and the crystal structure (blue) for **4**.