Synthesis and structural characterisation of two η^1-bonded *N*-phenylthioformamidate complexes of rhodium

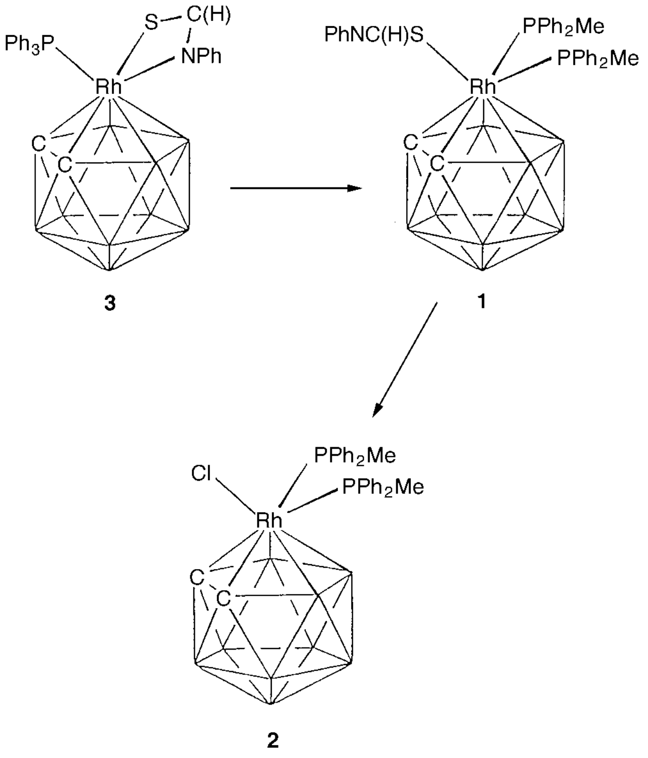
Patricia A. McEneaney,[a] **Trevor R. Spalding** *[,a] **and George Ferguson** *[,b]

[a] *Chemistry Department, University College, Cork, Ireland*
[b] *Chemistry Department, University of Guelph, Guelph, Ontario N1G 2W1, Canada*

The complexes [3-{η^1-SC(H)NPh}-3,3-$(PMe_2Ph)_2$-3,1,2-*closo*-$RhC_2B_9H_{11}$] and [2-{η^1-SC(H)NPh}-2,2-$(PMe_2Ph)_2$-2,1-*closo*-$RhTeB_{10}H_{10}$] have been structurally characterised using X-ray crystallography and are the first η^1-bonded thioformamidate complexes to be isolated.

Numerous metal complexes of ligands containing the S–C–N bond sequence have been characterised in the solid state. Reactions between isothiocyanates, RNCS, and metal hydrides usually lead to metal complexes with $[\eta^2\text{-SC(H)NR}]^-$ ligands which are bonded through both M–S and M–N bonds. A typical example is [ZrCl{η^2-SC(H)NPh}$(cp)_2$] (cp = η^5-C_5H_5).[1] Alternatively, more complex ligands derived from several SCNR molecules may be formed such as, $[\eta^2\text{-S}_2\text{C(H)NR}]^-$ in [2-{η^2-$S_2CN(H)Ph$}-2-(PPh_3)-2,1-*closo*-$RhTeB_{10}H_{10}$].[2] Although there have been several reports of complexes containing monodentate ligands derived from pyridine-2-thiol and related compounds (see ref. 3 for a recent review), there has been no report to our knowledge of the structural characterisation of any complex with an η^1-thioformamidato-to-metal functionality. Recently we proposed an $[\eta^1\text{-SC(H)NPh}]^-$ complex, [3-{η^1-SC(H)NPh}-3,3-$(PPh_2Me)_2$-3,1,2-*closo*-$RhC_2B_9H_{11}$] **1**, as an intermediate in the synthesis of the rhodacarborane [3,3-$(PPh_2Me)_2$-3-Cl-3,1,2-*closo*-$RhC_2B_9H_{11}$] **2**, from [3-{η^2-SC(H)-NPh}-3-(PPh_3)-3,1,2-*closo*-$RhC_2B_9H_{11}$] **3**, Scheme 1.[4] A study of the parallel reaction with PMe_2Ph as the phosphine has afforded [3-{η^1-SC(H)NPh}-3,3-$(PMe_2Ph)_2$-3,1,2-*closo*-$RhC_2B_9H_{11}$] **4**, Fig. 1. This compound was isolated from the reaction between a ten-fold excess of PMe_2Ph (0.109 g, 0.790 mmol) and a solution of **3** (0.050 g, 0.079 mmol) in CH_2Cl_2 (20 cm^3) at room temperature (r.t.) for 30 min. After evaporating the solvent under reduced pressure, the residue was washed with hexane (3 × 5 cm^3) to remove the excess phosphine. The single product was recrystallised from CH_2Cl_2–hexane solution affording orange crystals of [3-{η^1-SC(H)NPh}-3,3-$(PMe_2Ph)_2$-3,1,2-*closo*-$RhC_2B_9H_{11}$] **4**·$0.93CH_2Cl_2$, in 83% yield (0.047 g).† An analogous reaction (r.t., 15 min) with the rhodatelluraborane complex which is formally isoelectronic with **3**, *i.e.* [2-{η^2-SC(H)NPh}-2-(PPh_3)-*closo*-2,1-$RhTeB_{10}H_{10}$] **5**, produced [2-{η^1-SC(H)NPh}-2,2-$(PMe_2Ph)_2$-2,1-*closo*-$RhTeB_{10}H_{10}$] **6**, Fig. 2. The rhodatelluraborane **6** was recrystallised from a CH_2Cl_2–hexane solution in a yield of 86%.‡ Satisfactory microanalytic data (C, H, N) were obtained for both **4** and **6**.

Both compounds **4** and **6** contain rhodium–sulfur bonded η^1-SC(H)NPh ligands. However, the orientation of these ligands with respect to the RhC_2B_3 or $RhTeB_4$ moieties in each of the compounds is clearly different. The phenylthioformamidate group in compound **4** interacts solely with the rhodium atom of the RhC_2B_9 cage, Fig. 1, whereas in compound **6** there is also a



Scheme 1

---

† Crystal data for **4**. $C_{25}H_{39}B_9NP_2RhS\cdot0.93CH_2Cl_2$, orange platelet, 0.39 × 0.26 × 0.12 mm, $M = 726.80$, monoclinic, $P2_1/c$, $a = 10.0955(12)$, $b = 21.897(2)$, $c = 15.960(2)$ Å, $\beta = 96.599(9)°$, $U = 3504.6(6)$ Å^3, $Z = 4$, $D_c = 1.39$ g cm^{-3}, λ(Mo-Kα) = 0.7107 Å, μ(Mo-Kα) = 0.81 mm^{-1}, $F(000) = 1484$, $T = 294$ K. Data for 8046 reflections were measured, of which 7625 reflections were unique ($R_{int} = 0.009$) and of these the 5575 with $I > 2\sigma(I)$ were labelled 'observed'. $R(F_o) = 0.0348$, $R'(F^2) = 0.0885$ for all measured data where $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R'(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(wF_o^2)\}^{\frac{1}{2}}$, and $w = 1/[\sigma^2(F_o^2)]$.

‡ Crystal data for **6**. $C_{23}H_{38}B_{10}NP_2RhSTe$, _ orange needle, 0.40 × 0.20 × 0.20 mm, $M = 761.15$, triclinic, $P\bar{1}$, $a = 9.7040(13)$, $b = 11.895(2)$, $c = 14.4469(15)$ Å, $\alpha = 76.211(11)$, $\beta = 80.557(11)$, $\gamma = 83.680(12)°$, $U = 1593.2(3)$ Å^3, $Z = 2$, $D_c = 1.587$ g cm^{-3}, λ(Mo-Kα) = 0.7107 Å, μ(Mo-Kα) = 1.616 mm^{-1}, $F(000) = 752$, $T = 294(1)$ K. Data for 5450 reflections were collected and of these the 4402 with $I > 2\sigma(I)$ were labelled 'observed'. $R(F_o) = 0.0292$, $R'(F^2) = 0.0800$ for all measured data, $R(F_o)$ and $R'(F^2)$ as for **4**.

Structure solution of **4** and **6**. Data were collected using an Enraf-Nonius CAD4 diffractometer to a maximum θ of 27° using graphite-monochromated Mo-Kα radiation. Data were corrected for Lorentz, polarisation and absorption effects (from ψ scans). The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations initially using the NRCVAX system of programs[5] and finally with SHELXL 93[6] using all F^2 data. The H atoms were allowed for as riding atoms using the appropriate AFIX commands in SHELX 93. Diagrams were prepared with the aid of ORTEP[7] and PLATON.[8] Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/334.

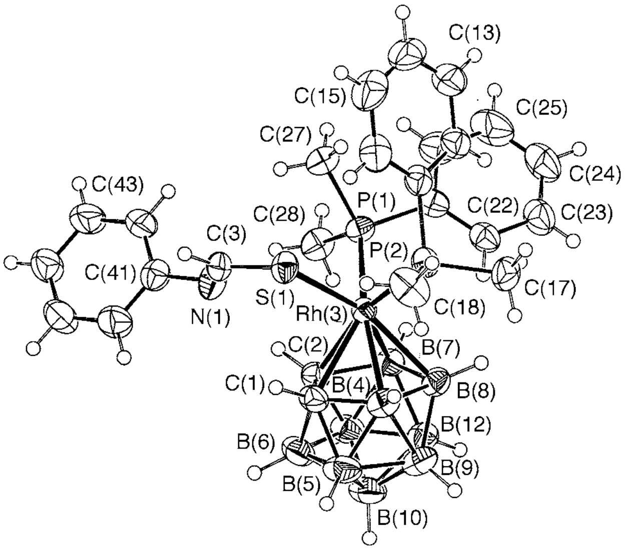


Fig. 1 An ORTEP view of compound **4** with the atom numbering scheme. Displacement ellipsoids are at the 50% level except for H atoms which are drawn as small spheres of an arbitrary size. Selected interatomic distances (Å) and angles (°): Rh(3)–S(1) 2.4010(8), Rh(3)–C(1) 2.246(3), Rh(3)–C(2) 2.212(3), Rh(3)–B(4) 2.280(4), Rh(3)–B(7) 2.216(3), Rh(3)–B(8) 2.274(3), Rh(3)–P(1) 2.3242(10), Rh(3)–P(2) 2.3346(8), C(1)–C(2) 1.613(4), S(1)–C(3) 1.724(3), C(3)–N(1) 1.254(4), N(1)–C(41) 1.424(4), C–B distances range from C(1)–B(6) 1.674(5) to C(2)–B(7) 1.753(4) and B–B distances from B(5)–B(6) 1.752(7) to B(4)–B(8) 1.818(5); C(3)–S(1)–Rh(3) 109.31(11), N(1)–C(3)–S(1) 126.7(2), C(41)–N(1)–C(3) 119.7(3), S(1)–Rh(3)–P(1) 82.11(3), S(1)–Rh(3)–P(2) 91.51(3), P(1)–Rh(3)–P(2) 95.83(3), S(1)–Rh(3)–C(1) 85.64(8), S(1)–Rh(3)–C(2) 103.55(8)

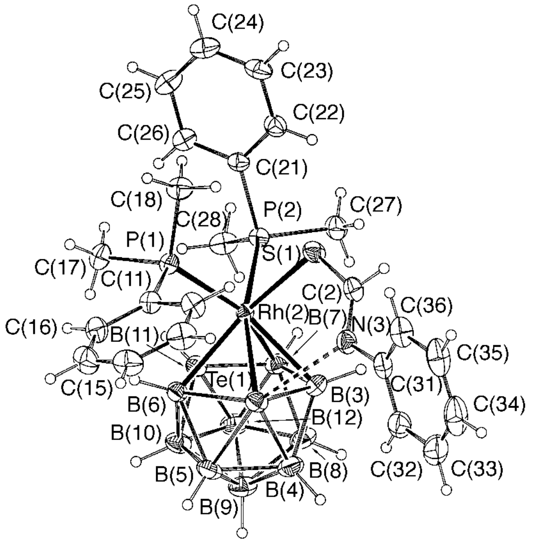


Fig. 2 An ORTEP view of compound **6** with the atom numbering scheme. Displacement ellipsoids are at the 30% level except for H atoms which are drawn as small spheres of an arbitrary size. Selected interatomic distances (Å) and angles (°): Rh(2)–S(1) 2.4147(10), Rh(2)–Te(1) 2.5788(4), Rh(2)–B(3) 2.336(4), Rh(2)–B(6) 2.362(4), Rh(2)–B(7) 2.241(4), Rh(2)–B(11) 2.253(4), Rh(2)–P(1) 2.3732(10), Rh(2)–P(2) 2.3601(10), S(1)–C(2) 1.712(4), C(2)–N(3) 1.256(5), N(3)–C(31) 1.423(5), Te(1)···N(3) 2.737(3), Te–B distances range from Te(1)–B(4) 2.288(5) to Te(1)–B(3) 2.390(5) and B–B distances from B(10)–B(12) 1.745(7) to B(5)–B(6) 1.896(6); C(2)–S(1)–Rh(2) 114.83(14), N(3)–C(2)–S(1) 127.7(3), C(31)–N(3)–C(2) 120.1(3), S(1)–Rh(2)–P(1) 87.41(4), S(1)–Rh(2)–P(2) 81.74(4), P(1)–Rh(2)–P(2) 96.58(3), S(1)–Rh(2)–Te(1) 93.27(3)

weak but significant intramolecular Te···N contact, Fig. 2. The S(1)–C(3)–N(1)–C(41) plane in **4** is at an angle of 37.5(3)° to the best-fit plane containing the C_2B_3 face, while the S(1)–C(2)–N(1)–C(31) plane in **6** is at an angle of 60.8(3)° to the TeB_4 face. The SC(H)NPh ligand in **6** is clearly positioned to facilitate the Te···N interaction.

Within each SC(H)NPh ligand, the bond lengths and most of the bond angles are essentially the same. In both cases the S–C–N–C atoms are virtually coplanar with torsion angles of 177.5(3)° in compound **4** and 178.3(3)° in **6**. The S(1)–C(3)–N(1) and C(3)–N(1)–C(41) angles in **4** are 126.7(2) and 119.7(3)°, while the corresponding angles in **6** are 127.7(3) and 120.1(3)°. The S–C distances of 1.724(3) and 1.712(4) Å respectively in **4** and **6** are typical of delocalised sp^2 hybridised carbon–sulfur bonds (1.720 Å), *i.e.* longer than the typical $S{=}C_{sp^2}$ distance of 1.681 Å in thioureas and shorter than the typical $S{-}C_{sp^3}$ distance of 1.808 Å in thiols.[5] The phenyl carbon-to-nitrogen and the methine carbon-to-nitrogen distances are respectively 1.424(4) and 1.254(4) Å in **4** and 1.423(5) and 1.256(5) Å in **6**, and are essentially identical. These bond lengths are respectively longer than typical $N{-}C_{ar}$ bonds and shorter than typical $N{=}C_{sp^2}$ bonds.[9]

The Te···N interaction in compound **6** has implications for cluster electron counting. Although the Te···N distance in **6** is long, 2.737(3) Å compared with a typical Te–N distance (in covalent bonds 2.15 Å), it is considerably shorter than the sum of the van der Waals' radii of Te and N, 3.61 Å. Similar Te···N distances of 2.702 and 2.752 Å respectively have previously been reported in the compounds bis[2-(4′-methoxyphenyl)iminomethinylphenyl]telluride[10] and 1,6-bis[(2-butyltelluro)phenyl]-2,5-diazahexa-1,5-diene.[11] If the donation of electron density from the nitrogen lone pair to the tellurium in the $RhTeB_{10}$ cage was strong it would imply an electronic character for **6** which is *nido*-type, but because the Te···N interaction is weak, a *nido* structure for **6** is not observed and the *closo* structure of the system is maintained. It is noteworthy, however, that the Rh–S bond length in **6**, 2.4147(10) Å, is significantly longer than that in **4**, 2.4010(8) Å. In overall electron density terms, the relative weakening of the Rh–S bond in **6** may be considered to balance the Te···N interaction. The rhodium–tellurium distance in **6**, 2.5788(4) Å, is well within the known range of 2.529(4)[12] to 2.6172(4) Å[13] for rhodatelluraboranes and is close to the distance found in [2-{η^2-S_2CN-(H)Ph}-2-(PPh_3)-*closo*-2,1-$RhTeB_{10}H_{10}$] [2.5812(3) Å].[2] The dimensions of the $RhC_2B_9H_{11}$ and $RhTeB_{10}H_{10}$ cages, Figs. 1 and 2 respectively, are typical of such structures and require no further comment.[14]

Finally, with respect to the previous suggestion that [3-{η^1-SC(H)NPh}-3,3-(PPh_2Me)$_2$-3,1,2-*closo*-$RhC_2B_9H_{11}$] **1** is an intermediate in the formation of [3,3-(PPh_2Me)$_2$-3-Cl-3,1,2-*closo*-$RhC_2B_9H_{11}$] **2** from [3-{η^2-SC(H)NPh}-3-(PPh_3)-3,1,2-*closo*-$RhC_2B_9H_{11}$] **3**,[4] Scheme 1, we wish to report that the rhodacarborane **1** has now been isolated from this reaction in 70% yield and characterised spectroscopically. The formation of the rhodium–chloride containing compounds [3-Cl-3,3-(PPh_2Me)$_2$-3,1,2-*closo*-$RhC_2B_9H_{11}$] **2** (quantitative yield) or [3-Cl-3,3-(PMe_2Ph)$_2$-3,1,2-*closo*-$RhC_2B_9H_{11}$] **7** (16% yield) is observed when the complexes **1** and **4** respectively are refluxed in CH_2Cl_2 solution for 48 h.

Acknowledgements

The generous loan of Rh salts by Johnson Matthey plc is gratefully acknowledged (T. R. S.). G. F. thanks the Natural Sciences and Engineering Research Council (Canada) for Grants in Aid of Research, P. McE. thanks Forbairt, Ireland for support. Thanks are due to Dr. B. Štíbr and his colleagues in the Czech Republic for discussions. We wish to thank a referee for drawing our attention to ref. 3.

References

1 W. Mei, L. Shiwei, B. Meizhi and G. Hefu, *J. Organomet. Chem.*, 1993, **447**, 227.
2 G. Ferguson, D. O'Connell and T. R. Spalding, *Acta Crystallogr., Sect. C*, 1994, **50**, 1432.

3 E. S. Raper, *Coord. Chem. Rev.*, 1996, **153**, 199.

4 G. Ferguson, J. Pollock, P. A. McEneaney, D. P. O'Connell, T. R. Spalding, J. F. Gallagher, R. Maciás and J. D. Kennedy, *Chem. Commun.*, 1996, 679.

5 E. J. Gabe, Y. LePage, J. P. Charland, F. J. Lee and P. S. White, *J. Appl. Crystallogr.*, 1989, **22**, 384.

6 G. M. Sheldrick, SHELXL 93, A program for the refinement of crystal structures, University of Göttingen, 1993.

7 C. K. Johnson, ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

8 A. L. Spek, Molecular Graphics Program, University of Utrecht, 1994.

9 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, in *Structure Correlation*, eds. H.-B. Burgi and J. D. Dunitz, VCH, Weinheim, 1994, vol. 2, Appendix.

10 V. I. Minkin, I. D. Sadekov, A. A. Maksimenko, O. E. Kompan and Yu. T. Struchkov, *J. Organomet. Chem.*, 1991, **402**, 331.

11 N. Al-Salim, T. A. Hamor and W. R. McWhinnie, *J. Chem. Soc., Chem. Commun.*, 1986, 453.

12 Faridoon, M. McGrath, T. R. Spalding, X. L. R. Fontaine, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1990, 1819.

13 Faridoon, O. Ni Dhubhghaill, T. R. Spalding, G. Ferguson, B. Kaitner, X. L. R. Fontaine, J. D. Kennedy and D. Reed, *J. Chem. Soc., Dalton Trans.*, 1988, 2739.

14 See, for example, M. F. Hawthorne, *J. Organomet. Chem.*, 1975, **100**, 97 and refs. therein; R. N. Grimes, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982 and refs. therein.

Received 11*th September* 1996; *Communication* 6/06276H