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Unprecedented N,S,O co-ordination of the doubly deprotonated anion of *N*-benzoyl-*N*′-phenylthiourea (H_2L^2) bridging two rhodium(I) centres: crystal structure of the acetone solvate of [$(PPh_3)_2$(CO)Rh(μ-L^2-κ*N*′ : κ*O*,*S*)Rh(PPh_3)(CO)]

Gerdus Kemp,[a] **Andreas Roodt,***[†][a] **Walter Purcell**[a] **and Klaus R. Koch***[‡][b]

[a] *Department of Chemistry, University of the Free State, PO Box 339, Bloemfontein, 9300, Republic of South Africa*

[b] *Department of Chemistry, University of Cape Town, Private Bag, Rondebosch, 7700, Republic of South Africa*

Reaction of $[Rh(CO)_2Cl]_2$ with *N*-benzoyl-*N*′-phenylthiourea (H_2L^2) followed by PPh_3 resulted in an unprecedented tridentate (κ*N*′ : κ*O*,*S*) bonding mode of the doubly deprotonated anion of *N*-benzoyl-*N*′-phenylthiourea to yield a dinuclear rhodium(I) complex [$(PPh_3)_2$(CO)Rh(μ-L^2-κ*N*′ : κ*O*,*S*)Rh(PPh_3)(CO)]·$(CH_3)_2CO$, the structure of which was determined by X-ray crystallography.

The versatile ligands, *N*-benzoyl-*N*′-alkyl- (H_2L) and *N*-benzoyl-*N*′,*N*′-dialkylthiourea (HL), have recently attracted interest in view of their selective co-ordination of the platinum-group metals. This has led to some interesting practical applications of these ligands, ranging from liquid–liquid extraction,[1] pre-concentration and highly efficient chromatographic separation,[2] fluorimetric detection of the platinum-group metals,[3] to the selective on-line pre-concentration of ultra-traces of Pd, followed by its determination using graphite furnace atomic absorption spectrometry.[4]

There is nevertheless relatively little structural detail about the mode of co-ordination of these ligands in the literature. It has been shown previously that the co-ordination chemistry of *N*-benzoyl-*N*′-propylthiourea (H_2L^1) is dominated by an intramolecular H bond which locks the thiourea N′–H moiety and amidic O-donor atom into a six-membered ring, with the consequence that the ligand co-ordinates to the platinum(II) *via* the S atom only, yielding a mixture of *cis*- and *trans*-[Pt(H_2L^1-*S*)$_2$$Cl_2$] complexes; *cis*-[Pt($H_2L^1$-*S*)$_2$$Cl_2$] has been characterized by X-ray crystallography.[5] On the other hand, the *N*′,*N*′-dialkyl-substituted ligands tend to co-ordinate predominantly in a bidentate (κ*S*,*O*) fashion to the platinum-group metal ions, as has been illustrated by the crystal structures of their Pd^{II},[6] Pt^{II},[7] Rh^{III}[8] and Rh^{I} complexes.[9] The only notable exceptions to this mode of co-ordination of the *N*′,*N*′-dialkyl-substituted ligands can be seen in the complexes of Ag^{I},[10] Hg^{II}[11] and Au^{I},[12] in which the ligand binds to the metal ion through the S atom only.

We here show that *N*-benzoyl-*N*′-phenylthiourea (H_2L^2) displays yet another unprecedented, and indeed unexpected, mode of co-ordination to Rh^{I}. The doubly deprotonated anion of the ligand molecule forms a bridging ligand to two metal centres, the amidic nitrogen atom co-ordinating (κ*N*′) to one Rh^{I} atom, while the *N*-acylthiourea moiety binds to a second Rh^{I} atom in the more usual bidentate (κ*S*,*O*) fashion.

Treatment of $[RhCl(CO)_2]_2$ with *N*-benzoyl-*N*′-phenylthiourea (H_2L^2) followed by a slight excess of PPh_3 leads to the formation of [$(PPh_3)_2$(CO)Rh(μ-L^2-κ*N*′ : κ*O*,*S*)Rh(PPh_3)(CO)]·$(CH_3)_2CO$ **1**§ which has been characterized by X-ray diffraction (Fig. 1).¶

Complex **1** crystallises as a dinuclear moiety with the acetone solvate molecule showing only weak intermolecular interactions >3.2 Å with the phenyl hydrogen atoms. The two rhodium(I) metal centres are linked *via* the amidic nitrogen atom [N(1)] of the *N*-benzoyl-*N*′-phenylthiourea ligand to yield the dinuclear complex with the Rh^{I} atoms in different environments. The Rh(1) centre can be thought of as forming a Rh^{I} 'Vaska'-type analogue, of the general type *trans*-[Rh$(PPh_3)_2$(CO)(R)], where R = Cl^- in the typical Ir^{I} complex,[14] in which for **1**, the 'Vaska' core is slightly modified, with R = amidic nitrogen [N(1)] of the fuctionalised thiourea ligand. Interestingly, there is a weak but significant S(1)–Rh(1) interaction, rendering the Rh(1) atom pseudo-five-co-ordinate (see below). The second four-co-ordinate rhodium centre, Rh(2), exhibits the expected κ*S*,*O* co-ordination by the *N*-acylthiourea ligand, as has been observed previously for related complexes.[9]

The infrared data for complex **1** in the solid state shows only one strong ν(CO) vibration, suggesting very similar metal–ligand interactions of the two CO ligands at the different Rh(1) and Rh(2) centres. This is not necessarily unexpected since the ν(CO) vibrations in the solid state for the closely related

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† E-Mail: roodta@cem.nw.uovs.ac.za

‡ E-Mail: kkoch@psipsy.uct.ac.za

§ The compounds $[RhCl(CO)_2]_2$ (20 mg, 5.1×10^{-5} mol) and *N*-benzoyl-*N*′-phenylthiourea (27 mg, 1.02×10^{-5} mol) were dissolved separately in a minimum of dimethylformamide (*ca.* 2 cm^3 each) and the two solutions were then slowly mixed at room temperature. Ice (*ca.* 0.5 g) was added to the mixture and the resulting yellow-brown precipitate was collected by centrifugation (40 mg, yield >60%); ν(CO)/cm^{-1} (KBr) 2004s, 2082s. The product was dissolved in cold acetone (≈0 °C, 3 cm^3), followed by the addition of a slight excess of PPh_3 (≈20 mg; 8×10^{-5} mol) which resulted in the liberation of CO gas. Orange blocks of **1** were obtained from this solution after about 6 h on ice (50 mg, yield 45%); ν(CO)/cm^{-1} (KBr) 1968s, 1714w; (C_6H_6) 2004s, 1984s; ^{31}P-{^{1}H} NMR (400 MHz Varian Unity operating at 161.943 MHz, $CDCl_3$, relative to external 85% H_3PO_4 in D_2O): δ 36.02 [d, P(3), $^{1}J(^{103}Rh–^{31}P) = 147.9$], 33.44 [d, P(1) + P(2), $^{1}J(^{103}Rh–^{31}P) = 137.3$ Hz].

¶ Crystal data for complex **1**. $C_{73}H_{61}N_2O_4P_3Rh_2S$, *M* = 1361.03, space group $P2_1/c$, $a = 12.282(3)$, $b = 26.539(5)$, $c = 20.079(4)$ Å, $\beta = 100.20(2)°$, $V = 6441(2)$ Å^3, $Z = 4$, $D_m = 1.392$ g cm^{-3}, $T = 293(2)$ K, $\mu = 0.670$ mm^{-1}. Of 4145 reflections collected, 3868 were unique, with $R_{int} = 0.0522$. No absorption corrections were applied. Data reduction and structure solution/refinement[13] (SHELXS 86 and SHELXL 93); full-matrix least-squares on F_o^2; to $R = 0.0456$ and $R' = 0.998$, $w = [\sigma^2(F_o^2) + (0.022P)^2 + 33P]^{-1}$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. Hydrogen positions were calculated as riding on the adjacent carbon atom. The acetone solvent molecule showed indications of multiple disorder, but refinement of this moiety with restrained (FLAT[13]) movement perpendicular to the plane (defined by the four solvent atoms) resulted in a reasonable model with acceptable bond distances within experimental error, although the anisotropic thermal parameters were quite large. CCDC reference number 186/765.

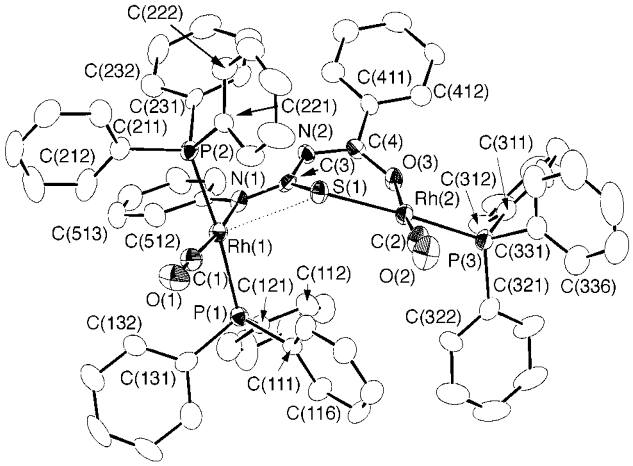

Fig. 1 Perspective view of complex **1** with 30% probability ellipsoids shown [parentheses have been omitted for simplification; the third numbering digit of the phenyl carbon atom always refers to the number (1–6) of the atom in the ring]. The most important bond lengths (Å) and angles (°): Rh(1)–C(1) 1.744(13), Rh(1)–P(1) 2.328(3), Rh(1)–P(2) 2.330(3), Rh(1)–N(1) 2.122(8), Rh(1)–S(1) 2.815(3), Rh(2)–P(3) 2.275(3), Rh(2)–S(1) 2.353(3), Rh(2)–C(2) 1.773(13), Rh(2)–O(3) 2.037(7), S(1)–C(3) 1.747(11), N(2)–C(3) 1.349(12), C(3)–N(1) 1.333(12), N(2)–C(4) 1.319(12), C(4)–O(3) 1.302(12); C(1)–Rh(1)–N(1) 171.9(5), C(1)–Rh(1)–P(1) 88.6(4), N(1)–Rh(1)–P(1) 91.9(2), C(1)–Rh(1)–P(2) 88.5(4), N(1)–Rh(1)–P(2) 90.4(2), P(1)–Rh(1)–P(2) 174.78(11), C(1)–Rh(1)–S(1) 127.7(4), N(1)–Rh(1)–S(1) 60.3(3), P(1)–Rh(1)–S(1) 95.06(10), P(2)–Rh(1)–S(1) 90.15(10), C(2)–Rh(2)–O(3) 174.3(5), C(2)–Rh(2)–P(3) 89.7(4), O(3)–Rh(2)–P(3) 88.9(2), C(2)–Rh(2)–S(1) 90.6(4), O(3)–Rh(2)–S(1) 91.1(2), P(3)–Rh(2)–S(1) 176.76(12), C(3)–S(1)–Rh(2) 103.1(4), C(3)–S(1)–Rh(1) 75.4(4), Rh(2)–S(1)–Rh(1) 143.57(13), C(4)–O(3)–Rh(2) 127.5(7), C(3)–N(1)–C(511) 123.7(9), C(3)–N(1)–Rh(1) 113.0(7), C(511)–N(1)–Rh(1) 123.3(7), C(4)–N(2)–C(3) 125.0(9), O(1)–C(1)–Rh(1) 178.8(11), O(2)–C(2)–Rh(2) 174.8(13), N(1)–C(3)–N(2) 124.3(10), N(1)–C(3)–S(1) 111.2(8), N(2)–C(3)–S(1) 123.7(9), O(3)–C(4)–N(2) 127.1(10)

monomeric complexes, [Rh(PPh$_3$)$_2$(CO)Cl][14] and [Rh(DBBTU-*S*,*O*)(CO)(PPh$_3$)][9] (DBBTU = *N*-benzoyl-*N′N′*-dibenzylthiourea), are identical (1983 cm^{-1}); moreover the ν(CO) vibration of [Rh(PPh$_3$)$_2$(CO)Cl] in the solid state has been shown to be dependent on the mode of packing of the complex,[14] with ν(CO) being lowered to 1965 cm^{-1} by variations in the mode of packing. On the other hand, in a solution of **1** in benzene, two characteristic peaks at 1984 and 2004 cm^{-1} assigned to the ν(CO)$_{Rh(2)}$ and ν(CO)$_{Rh(1)}$ respectively, are observed. The presence of an acetone solvent molecule is also confirmed by a weak ν(CO) vibration at 1714 cm^{-1}.

The ^{31}P NMR spectrum of **1** is well defined, showing two definite P-environments [at δ(^{31}P-{^{1}H}) = 33.44 and 36.02 in the expected 2 : 1 ratio] with the ^1J(^{103}Rh–^{31}P) coupling constants§ correlating well with the bond distances, as has been shown for related complexes elsewhere.[15] The Rh(1)–P(1) and Rh(1)–P(2) bond distances of 2.328(3) and 2.330(3) Å respectively are relatively long, but normal for a *trans* P–Rh–P moiety.[15,16]

The Rh(2)–P(3) bond distance of 2.275(3) Å in **1** is somewhat shorter than the corresponding distance of 2.282(1) Å found in [Rh(DBBTU-*S,O*)(CO)(PPh$_3$)],[9] which is reflected by the simultaneous lengthening of the *trans* Rh(2)–S(1) bond at 2.353(3) Å compared to 2.289(1) and 2.307(1) Å in [Rh(DBBTU-*S,O*)(CO)(PPh$_3$)] and [Rh(DBBTU-*S,O*)(CO)(AsPh$_3$)],[9] respectively. This effect can be attributed to the weak interaction between the S-donor atom of the *N*-acylthiourea and Rh(1) [interaction distance 2.815(3) Å], which is likely to result in the removal of some electron density from S(1), so decreasing its bonding abiliy to Rh(2), resulting in a stronger *trans* Rh(2)–P(3) bond.

The weak Rh(1)–S(1) interaction results in the distortion from ideal square planar geometry of the Rh(1) co-ordination centre to what may be considered a five-co-ordinate polyhedron. The geometry of this polyhedron may be described either as a square-based pyramid [defined by the plane P(1)–C(1)–N(1)–P(2), with the Rh(1) atom displaced by a significant 0.114(4) Å from this plane], or as an extensively distorted trigonal bipyramid (*TBPY*) [trigonal plane defined by C(1)–Rh(1)–N(1)–C(3)–S(1)] with the maximum deviation from planarity by any individual atom of only 0.050(4) Å. The extent of the distortion from ideal *TBPY* geometry is illustrated by the bond angles C(1)–Rh(1)–N(1) 171.9(5), C(1)–Rh(1)–S(1) 127.7(4) and S(1)–Rh(1)–N(1) 60.3(3)°, respectively, while the angle between the trigonal plane described above and that defined by P(1)–C(1)–N(1)–P(2) is 87.7(2)°.

Of further interest is the substantial rearrangement of sp^2 delocalised electron density in the S,O backbone of the co-ordinated *N*-acylthiourea ligand. Although extensive sp^2 delocalization is maintained in the S(1)–C(3)–N(2)–C(4)–O(3) moiety of these ligands in their κ*S* and κ*S*,*O* modes of co-ordination,[6–9] such sp^2 delocalization is significantly altered in **1**, *i.e.*, C(4) and C(3) lie 0.356(13) and 0.487(13) Å respectively above and below the S(1)–N(2)–O(3) plane. This 'loss' in sp^2 delocalization from bonds N(2)–C(3) and S(1)–C(3) is illustrated by the observed angles between the two different planes associated with the S,O backbone. There is for example a significant 36.0(4)° deviation from co-planarity between the C(2)–S(1)–O(3)–P(3) and N(2)–C(4)–C(411)–O(3) planes [where maximum deviation of individual atoms from the two planes are only 0.010(3) and 0.010(9) Å respectively], and a similar deviation of 39.3(2)° between the S(1)–C(3)–N(2)–C(4)–O(3) and the C(1)–Rh(1)–N(1)–C(3)–S(1) planes. Moreover, the trends observed in the bond distances in the S,O backbone are also consistent with a decrease in sp^2 delocalization, in the N(2)–C(3), and especially the S(1)–C(3) bonds of **1**, which are significantly weakened (lengthened) compared to the κ*S,O* co-ordination of the ligand in the [Rh(DBBTU-*O,S*)(CO)(PPh$_3$)] and [Rh(DBBTU-*S*,*O*)(CO)(AsPh$_3$)] complexes[9] {*e.g.* S(1)–C(3) at 1.747(11) and N(2)–C(3) at 1.349(12) Å in **1** compared to 1.715(5) and 1.337(6) Å in [Rh(DBBTU-*S*,*O*)(CO)(PPh$_3$)] respectively}. The comparatively short C(3)–N(1) bond [1.333(12) Å] suggests an increased imine character, consistent with the increased sp^2 delocalization of the electron density, as compared to the N(2)–C(3) bond.

In conclusion the versatility and interesting behaviour of *N*-acylthiourea ligands has again been demonstrated by an unusual κ*N′* : κ*S*,*O* bonding of the doubly deprotonated anion of H$_2$L^2 to two Rh$^{\text{I}}$ atoms. Complex **1** as well as mononuclear [Rh(*N*-benzoyl-*N*,*N′*-dialkylthiourea-*S*,*O*)X(Y)] moieties are currently being investigated further in terms of kinetic behaviour towards oxidative addition and a range of other reactions.

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