Notes

Monodentate Coordination of the Potentially Bidentate Ligand Methyl 2-(*N*-Ethylamino)-1-cyclopentenedithiocarboxylate to Rhenium(V) via a Neutral Thiocarbonyl Sulfur Atom

Giuliano Bandoli,† **Jan G. H. du Preez,**‡
Thomas I. A. Gerber,*,‡ **and Hannelie J. Kemp**‡

Department of Pharmaceutical Science, University of Padova,
Padova, Italy, and Department of Chemistry, University of
Port Elizabeth, 6000 Port Elizabeth, South Africa

Received February 4, 1993

As part of a program to develop the coordination chemistry of technetium and rhenium with the aim of synthesizing new complexes with possible nuclear medicinal application,[1] we are investigating the reactions of dithiocarboxylic acid derivatives with the above metals.

In this account we report on the unexpected results of the reaction of the ligand methyl 2-(*N*-ethylamino)-1-cyclopentenedithiocarboxylate[2] (HL′, Figure 1) with the rhenium(V) compound *trans*-$ReOCl_3(PPh_3)_2$. In principle, the ligand HL′ may exist in three tautomeric forms (Figure 1) in the free uncoordinated form, and it has the potential to coordinate in a bidentate manner (NS^-) to metal ions. The reactions of NS^- chelates with *trans*-$ReOCl_3(PPh_3)_2$ usually lead to six-coordinate products with the formulation $ReOCl_2(PPh_3)(NS)$.[3] However, in this account the unusual monodentate coordination of HL′ is illustrated by the X-ray molecular structure of the complex $ReOCl_3(PPh_3)(HL')$, in which coordination of HL′ occurs through the neutral thiocarbonyl sulfur atom only.

Synthesis

trans-$ReOCl_3(PPh_3)_2$ (100 mg, 120 μmol) was suspended in 5 cm³ of acetone. Methyl 2-(*N*-ethylamino)-1-cyclopentenedithiocarboxylate (48 mg, 240 μmol) was added to this solution, and the mixture was heated under reflux for 30 min. The initial pale green color turned dark red, and after cooling to room temperature, the solution was filtered and left to evaporate slowly overnight. Dark green crystals were obtained, and after filtration, they were washed with three 2-cm³ portions of ethanol and dried under vacuum (yield: 79% with respect to $ReOCl_3(PPh_3)_2$). Anal. Calcd for $C_{30}H_{30}Cl_3NO_2PReS_2$: C, 43.40; H, 4.37; N, 1.69; *Cl*, 12.81. Found: C, 43.70; H, 4.52; N, 1.48; *Cl*, 12.73. IR (KBr) (cm⁻¹): ν(Re═O) 974; ν($\overline{C---N}$) 1503; ν(N–H) 3161; ν(Re–Cl) 316, 289; ν(Re–P) 1090, 693. ¹H NMR [$(CD_3)_2SO$] (ppm): δ(N*H*) 12.18 (1H, s); δ$(CH_2)_{ring}$ 1.83 (2H, t), 2.71 (2H, t), 2.82 (2H, t); δ$(CH_3)_{acetone}$ 2.11 (6H, s); δ(SCH_3) 2.47 (3H, s); δ(CH_2CH_3) 1.22 (3H, t); δ(CH_2CH_3) 3.41 (2H, q); δ(PPh_3) 7.62 (15H, m).

Crystallography

A green-colored rectangular slab having approximate dimensions of 0.30 × 0.20 × 0.15 mm was mounted in a random orientation on a Siemens Nicolet R3m/V automatic diffractometer. The radiation used was Mo Kα, monochromatized by a highly ordered graphite crystal. Details of crystal data, measurement of intensities, and data processing are summarized in Table I. Intensities were measured using the ω–2θ technique, with the scan depending on the count obtained in rapid prescans of each reflections. Two standard reflections were monitored after every 150 data collected, and these showed no significant change during the course of the experiment. To the data, Lorentz and polarization corrections were applied as well as an empirical absorption correction based on ψ-scans of six reflections at χ *ca.* 90°. The structure was solved by standard heavy-atom methods and refined by least-squares methods. The hydrogen atoms were added in ideal calculated positions and constrained to riding motion, with a single variable isotropic temperature factor for all of them. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and the final difference density map showed a maximum peak of 1.1 e Å⁻³, located near Re. The molecular structure is shown in Figure 2, which also defines the atom-numbering scheme. The bond distances and angles are listed in Table II.

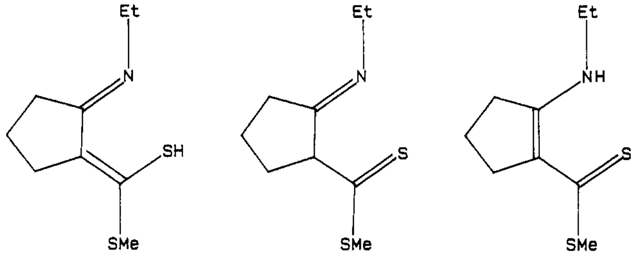

Figure 1. Tautomeric forms of ligand HL′.

Table I. Crystallographic Data for $ReOCl_3(PPh_3)(HL')\cdot Me_2CO$

chem formula $C_{30}H_{30}Cl_3NO_2PReS_2$
fw 824.2
$a = 9.333(2)$ Å
$b = 13.297(4)$ Å
$c = 14.496(4)$ Å
$\alpha = 97.91(2)°$
$\beta = 105.66(2)°$
$\gamma = 99.91(2)°$
$V = 1673.9(8)$ Å³
$Z = 2$

space group $P\bar{1}$ (No. 2)
$T = 21$ °C
$\lambda = 0.710\,73$ Å
$\rho_{obsd}{}^{a} = 1.64$ g cm⁻³
$\rho_{calcd} = 1.633$ g cm⁻³
$\mu = 40.7$ cm⁻¹
transm coeff = 0.73–0.90
$R(F_o^2)^b = 0.0314$
$R_w(F_o^2)^b = 0.0445$

[a] By neutral buoyancy in bromoform–carbon tetrachloride. [b] $R = \omega\Delta F/\omega|F_o|$. $R_w = \omega w\Delta F/\omega w|F_o|$.

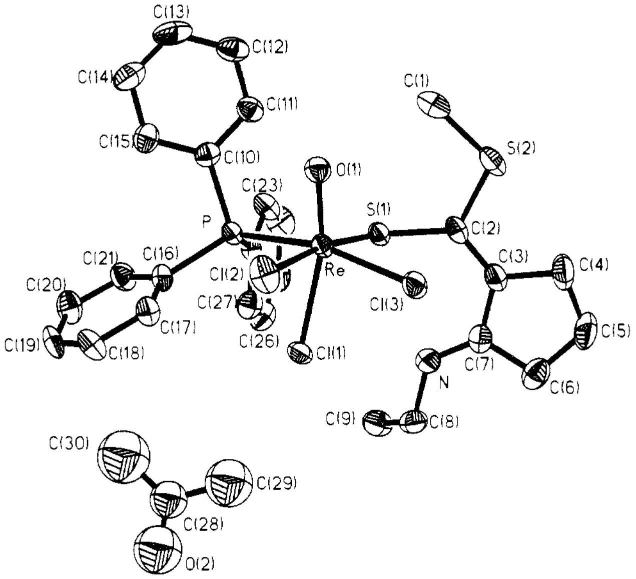

Figure 2. View of the $[ReOCl_3(PPh_3)(HL')]\cdot Me_2CO$ complex, with atom-numbering scheme and thermal ellipsoids at the 40% probability level.

Results and Discussion

The compound $ReOCl_3(PPh_3)(HL')\cdot Me_2CO$ (Figure 2) is built up by the juxtaposition at van der Waals distances of well-

---

† University of Padova.

‡ University of Port Elizabeth.

(1) *Technetium and Rhenium in Chemistry and Nuclear Medicine 3*; Nicolini, M, Bandoli, G., Mazzi, U., Eds.; Cortina International: Verona, Italy, 1990.

(2) Bordás, B.; Sohár, P.; Matolocsy, G.; Berencsi, P. *J. Org. Chem.* **1972,** *37,* 1727.

(3) Du Preez, J. G. H.; Gerber, T. I. A.; Kemp, H. J.; Van Brecht, B. J. A. M. *J. Coord. Chem.* **1991,** *24,* 159.

0020-1669/93/1332-3964$04.00/0

Table II. Relevant Bond Lengths (Å) and Angles (deg) with Esd's in Parentheses

Re–Cl(1)	2.481(2)	Re–Cl(2)	2.441(2)	Re–Cl(3)	2.364(1)
Re–S(1)	2.369(2)	Re–P	2.490(2)	Re–O(1)	1.671(4)
S(1)–C(2)	1.772(6)	S(2)–C(1)	1.803(7)	S(2)–C(2)	1.738(7)
P–C(10)	1.833(6)	P–C(16)	1.840(7)	P–C(22)	1.845(7)
N–C(7)	1.281(9)	N–C(8)	1.477(9)		

Cl(1)–Re–Cl(2)	84.7(1)	Cl(1)–Re–Cl(3)	87.6(1)
Cl(2)–Re–Cl(3)	84.5(1)	Cl(1)–Re–S(1)	89.2(1)
Cl(2)–Re–S(1)	172.1(1)	Cl(3)–Re–S(1)	90.1(1)
Cl(1)–Re–P	77.9(1)	Cl(2)–Re–P	97.8(1)
Cl(3)–Re–P	165.0(1)	S(1)–Re–P	85.9(1)
Cl(1)–Re–O(1)	165.0(1)	Cl(2)–Re–O(1)	88.9(2)
Cl(3)–Re–O(1)	105.3(1)	S(1)–Re–O(1)	98.2(2)
P–Re–O(1)	89.5(1)	Re–S(1)–C(2)	110.6(2)
Re–P–C(10)	109.2(2)	Re–P–C(16)	121.2(2)
Re–P–C(22)	113.2(2)		

separated units of complex and solvent, and there were no unusual nonbonded interactions. The rhenium atom resides in a distorted octahedral coordination environment; as a common feature, it lies out of the mean equatorial PC*l*(2)C*l*(3)S(1) plane by 0.22 Å toward the apical oxo ligand and the C*l*(1)–Re–O_{oxo} angle, departing from linearity by 15°, represents, along with the C*l*(3)–Re–P angle (165.0°), the maximum angular deviation from ideal octahedral values. Since the rhenium(V) complex is neutral, the HL′ ligand acts as unidentate, *via* the uncharged thiocarbonyl sulfur atom. The Re–S(1) distance (2.369(2) Å) lies in the wide range (from 2.31 to 2.54 Å)[4–7] of Re–S lengths found in other six-coordinate rhenium complexes, and the Re–Cl(3) distance of 2.364(1) Å, *trans* to the PPh_3 ligand, parallels the value (2.360 Å) found in *trans*-[$ReOCl_2(PPh_3)L$] (L = 4,6-dimethylpyrimidine-2-thiolato).[6] The five-membered carbon ring, in envelope (C_s) arrangement, is virtually normal (93.2°) to the mean equatorial plane, and the C(2)–C(3) (1.386(8) Å) and C(7)–N (1.281(9) Å) distances reflect, along with the angular values around the C(2), C(3), C(7), and N atoms and the pertinent torsion angles, double-bond character. There is nothing remarkable about the other bond lengths and angles.

Monodentate coordination of potentially bidentate NS donor ligands, and of neutral sulfur donor atoms, to rhenium(V) has not been observed previously. Another surprising feature of the structure is that the coordination of HL′ occurs *cis* to the PPh_3 molecule, which contrasts with the *trans* geometry found in the starting complex *trans*-$ReOCl_3(PPh_3)_2$.

Acknowledgment. J.G.H.d.P. and T.I.A.G. gratefully acknowledge financial support by the Medical Research Council of South Africa and the Foundation for Research Development.

Supplementary Material Available: A summary of the structure determination (Table A), full listings of bond lengths (Table B) and angles (Table C), anisotropic displacement coefficients (Table D), and H-atom coordinates (Table E), and a listing of atomic coordinates and equivalent isotropic displacement coefficients (Table F) (5 pages). Ordering information is given on any current masthead page.

---

(4) Blower, P. J.; Dilworth, J. R.; Hutchinson, J. P.; Zubieta, J. *Transition Met. Chem.* **1982**, *7*, 353.

(5) Rossi, R.; Marchi, A.; Duatti, A.; Magon, L.; Casellato, U.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1988**, 899.

(6) Baltistuzzi, R.; Manfredini, T.; Bataglia, L. P.; Corradi, A. B.; Marzotto, A. *J. Crystallogr. Spectrosc. Res.* **1989**, *19*, 513.

(7) Cockerton, B.; Deeming, A. J.; Karim, A.; Hardcastle, K. I. *J. Chem. Soc., Dalton Trans.* **1991**, 431.