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Tricarbonylrhenium(I) Complexes with Thiosemicarbazone Derivatives of 2-Acetylpyridine and 2-Pyridine Formamide Showing Two Unusual Coordination Modes of Tridentate Thiosemicarbazone Ligands

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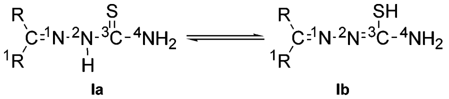
$[NEt_4]_2[Re(CO)_3Br_3]$ reacts with 2-acetylpyridine phenylthiosemicarbazone (HL^1) and 2-pyridine formamide thiosemicarbazone (HL^2) under formation of air-stable, neutral rhenium(I) complexes of the compositions $[Re(CO)_3(L^1\text{-}N,N,S)]$ and $[Re(CO)_3Br(HL^2\text{-}N,N)]$. Spectroscopic studies and X-ray crystallography show that the potentially tridentate thiosemicarbazones adopt unusual coordination modes. Whereas HL^1 deprotonates and binds to the metal in a nonplanar fashion, HL^2 acts as neutral N,N donor ligand. The bond lengths inside the chelate rings are almost uninfluenced by the overall bonding situation.

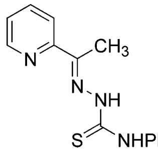
Thiosemicarbazones (tautomeric forms **Ia** and **Ib**) are versatile ligands which can coordinate as neutral ligands or in their deprotonated form. Numerous metal complexes have been studied chemically and by X-ray crystallography,[1] and some of them show interesting biological behavior.[2] Ligands with additional donor groups such as $-PR_2$, $-NH_2$, $-OH$, or $-SH$ at the substituent R^1 are of special interest since they can coordinate in a tridentate fashion which results in a significant increase of the stability of the complexes.



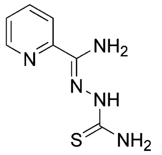
Ia **Ib**

Surprisingly, less is known about rhenium complexes with thiosemicarbazones. The first structural report on such compounds was published very recently dealing with cationic Re(III) compounds of the general composition $[Re(L^{1b})_2]^+$ where HL^{1b} represents a tridentate acetylpyridine thiosemicarbazonato ligand. They have been prepared by a reductive ligand exchange starting from $[ReOCl_3(PPh_3)_2]$ or $[ReO_4]^-$.[3] A series of tricarbonylrhenium(I) complexes have been prepared from $[Re(CO)_5Br]$ and ferrocenylcarbaldehyde thiosemicarbazones or methylacetoacetate thiosemicarbazones, and complexes of the composition $[Re(CO)_3Br(HL)]$ (**II**) and $[Re(CO)_3(L)]_2$ (**III**) have been isolated and structurally characterized.[4] The thiosemicarbazones act in both structure types as bidentate N,S donors. Deprotonation of the ligands and dimerization was achieved by the addition of sodium methoxide to complexes of type **II**.

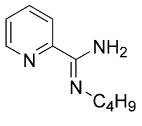
In the present Communication, we describe the products of the reactions of $[NEt_4]_2[Re(CO)_3Br_3]$, which has been shown to be an excellent starting material for the synthesis of tricarbonylrhenium(I) complexes,[5] with the potentially tridentate thiosemicarbazones derived from 2-acetylpyridine (HL^1) and 2-pyridineformamide (HL^2) and with a related Schiff base ligand (HL^3). The ligands have been prepared according to previously published procedures.[6]



HL^1



HL^2



HL^3

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(1) (a) Campbell, M. J. M. *Coord. Chem. Rev.* **1975**, *15*, 279. (b) West, D. X.; Padhye, S. B.; Sonawane, P. B. *Struct. Bonding (Berlin)* **1991**, *76*, 1. (c) Casas, J. S.; Garcia-Tasende, M. S.; Sordo, J. *Coord. Chem. Rev.* **2000**, *209*, 49.

(2) Klayman, D. L.; Scovill, J. P.; Bartosevich, J. F.; Bruce, J. *J. Med. Chem.* **1983**, *26*, 39.

(3) Cowley, A. R.; Dilworth, J. R.; Donnelly, P. S.; Woollard-Shore, J. *J. Chem. Soc., Dalton Trans.* **2003**, 748.

(4) (a) Carballo, R.; Casas, J. S.; Garcia-Martinez, E.; Pereiras-Gabian, G.; Sanchez, A.; Sordo, J.; Vazquez-Lopez, E. M.; Garcia-Monteagudo, J. L.; Abram, U. *J. Organomet. Chem.* **2002**, *656*, 1. (b) Carballo, R.; Casas, J. S.; Garcia-Martinez, E.; Pereiras-Gabian, G.; Sanchez, A.; Sordo, J.; Vazquez-Lopez, E. *Inorg. Chem.* **2003**, *42* 6395.

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The reaction of $[NEt_4]_2[Re(CO)_3Br_3]$ with HL^1 in methanol leads to a brown solution from which a stable, orange-brown crystalline solid can be isolated.[7] Addition of a few drops of triethylamine increases the rate of the reaction but is not mandatory to obtain the product. Strong bands at 2016, 1920, and 1898 cm^{-1} in the IR spectrum of the resulting complex clearly confirm the presence of three carbonyl ligands in a facial arrangement. The FAB^+ spectrum shows a peak at $m/z = 541$ which can be assigned to an ion of the composition $[Re(CO)_3(HL^1)]^+$. Fragmentation mainly occurs by the abstraction of carbonyl ligands ($m/z = 512$, 484, and 456) and sulfur ($m/z = 508$).

An X-ray structure determination on $[Re(CO)_3(L^1)]$[8] (Figure 1) confirms the spectroscopic results and shows the rhenium atom in a strongly distorted coordination environment. These distortion are caused by the restraints imposed by the skeleton of the thiosemicarbazonato ligand which contains a conjugated π-system. This is indicated by the bond length situation inside the chelate rings which are given in Table 1. The steric strain of the coordination sphere is also indicated by the long Re−S distance of 2.539(1) Å and the fact that this bond is obviously easily cleaved as is suggested by the preferred mass spectrometric abstraction of sulfur which has not been observed for uranium or gold complexes with the same type of ligands.[10,11]

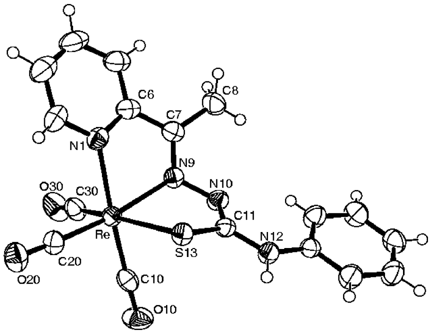

Figure 1. Molecular structure[9] of $[Re(CO)_3(L^1)]$.

Table 1. Selected Bond Lenghts (Å) and Angles (deg) in $[Re(CO)_3(L^1)]$, $[Re(CO)_3Br(HL^2)]$, and $[Re(CO)_3(HL^3)]$

	$[Re(CO)_3(L^1)]$	$[Re(CO)_3Br(HL^2)]$	$[Re(CO)_3Br(HL^3)]$
Re−N1	2.193(3)	2.174(8)	2.178(5)
Re−N9	2.131(3)	2.162(8)	2.174(5)
Re−S13/Br	2.539(1)	2.636(1)	2.610(2)
N1−C6	1.368(6)	1.37(1)	1.352(7)
C6−C7	1.466(6)	1.48(1)	1.452(8)
C7−N9	1.303(5)	1.32(1)	1.267(8)
N9−N10	1.403(5)	1.41(1)	
N10−C11	1.305(5)	1.33(1)	
C11−S13	1.776(4)	1.68(1)	
N1−Re−N9	72.3(1)	74.0(3)	74.3(2)
N1−Re−S13/Br	101.23(9)	81.3(2)	84.9(1)
N9−Re−S13/Br	71.00(9)	85.5(2)	85.7(2)

The facial coordination mode of 2-acetylpyridine thiosemicarbazones at a transition metal center is without precedent and underlines the coordination capacity of the tridentate ligand. There are spectroscopic indications that, in coordinating solvents such as acetonitrile, THF, or DMSO, the sulfur atom of the thiosemicarbazone is replaced by a molecule of the solvent, but we have not yet been able to isolate these species. All attempts to recrystallize the complex from these solvents resulted in the isolation of $[Re(CO)_3(L^1)]$.

Bidentate coordination of a potentially tridentate thiosemicarbazone, however, is observed when $[NEt_4]_2[Re(CO)_3Br_3]$ reacts with HL^2.[12] 2-Pyridineformamide thiosemicarbazone does not deprotonate during this reaction and coordinates as a neutral bidentate ligand to give $[Re(CO)_3Br(HL^2)]$. The yellow solid which precipitates from the methanolic reaction mixture is only sparingly soluble in most common solvents and has been recrystallized from DMSO. The IR spectrum

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(5) Alberto, R.; Schibli, R.; Waibel, R.; Abram, U.; Schubiger, A. P. *Coord. Chem. Rev.* **1999**, *901*, 190.

(6) Synthesis of HL^1: Ortner, K.; Hilditch, L.; Yifan Zheng, Dilworth, J. R.; Abram, U. *Inorg. Chem.* **2000**, *39*, 2801. Synthesis of HL^2: West, D. X.; Swearingen, J. K.; Valdes-Martinez, J.; Hernandez-Ortega, S.; El-Sawaf, A. K.; van Meurs, F.; Castineiras, A.; Garcia Santos, I.; Bermejo, E. *Polyhedron* **1999**, *18*, 2919.

(7) Synthesis of $[Re(CO)_3(L^1)]$: $[NEt_4]_2[Re(CO)_3Br_3]$ (77 mg, 0.1 mmol) and HL^1 (30 mg, 1.2 mmol) were dissolved in 10 mL of MeOH and heated under reflux for 1 h. The color of the mixture changed to brown, and an orange-brown solid precipitated upon cooling. Recrystallization from a CH_2Cl_2/2-propanol mixture gave orange-brown crystals. Yield: 43 mg (80%). Anal. Calcd for $C_{17}H_{13}N_4O_3ReS$: C, 37.8; H, 2.4; N, 10.4; S, 5.9%. Found: C, 37.8; H, 2.6; N, 10.2; S, 5.7%. IR (ν, cm^{-1}): NH 3309, 3120, 3054; CO 2016, 1920, 1898; NHR + CN 1601, 1595, 1513; CS 824. FAB^+ MS (m/z (assignment, %B)): 541 ($[M + H]^+$, 25), 512 ($[M - CO]^+$, 55), 508 ($[M - S]^+$, 30), 484 ($[M - 2CO]^+$, 15), 456 ($[M - 3CO]^+$, 5).

(8) X-ray crystal structure calculations. $[Re(CO)_3(L^1)]$: CAD4 (Enraf Nonius), Cu Kα radiation ($\lambda = 1.54184$ Å), $C_{17}H_{13}N_4O_3ReS$, orange-red plates, monoclinic, space group $P2_1/c$, $a = 11.705(1)$ Å, $b = 13.552(1)$ Å, $c = 11.389(1)$ Å, $\beta = 90.31(1)°$, $V = 1806(3)$ Å^3, $Z = 4$. $D_{calcd} = 1.984$ g/cm^3, $\theta = 5.07-64.92°$, 3878 reflections collected, 3063 independent, $\mu = 14.461$ mm^{-1} (absorption correction Psi Scans, $T_{min} = 0.3842$, $T_{max} = 0.6229$), solved by Patterson methods, and refined by full-matrix least-squares procedures using SHELXS and SHELXL (G. M. Sheldrick, University of Göttingen, Germany), 287 parameters, $R = 0.029$, wR2 = 0.056. $[Re(CO)_3Br(HL^2)]$·4DMSO: CAD4 (Enraf Nonius), Mo Kα radiation ($\lambda = 0.71073$ Å), $C_{18}H_{33}N_5O_7ReS_5Br$, yellow needles, monoclinic, space group $P2_1/n$, $a = 18.067(2)$ Å, $b = 9.479(1)$ Å, $c = 20.290(2)$ Å, $\beta = 111.00(1)°$, $V = 3243(3)$ Å^3, $Z = 4$. $D_{calcd} = 1.757$ g/cm^3, $\theta = 3.01-26.98°$, 7709 reflections collected, 7034 independent, $\mu = 5.341$ mm^{-1} (absorption correction DELABS, $T_{min} = 0.540$, $T_{max} = 0.857$), solved by Patterson methods and refined by full-matrix least-squares procedures using SHELXS and SHELXL (G. M. Sheldrick, University of Göttingen, Germany), 330 parameters, $R = 0.059$, wR2 = 0.115. $[Re(CO)_3Br(L^3)]$: CAD4 (Enraf Nonius), Mo Kα radiation ($\lambda = 0.71073$ Å), $C_{13}H_{14}N_2O_3ReBr$, orange-red needles, triclinic, space group $P\bar{1}$, $a = 7.088(6)$ Å, $b = 8.088(6)$ Å, $c = 13.936(9)$ Å, $\alpha = 77.57(5)°$, $\beta = 77.81(5)°$, $\gamma = 82.06(5)°$, $V = 772.9(9)$ Å^3, $Z = 2$. $D_{calcd} = 2.202$ g/cm^3, $\theta = 3.01-27.01°$, 4190 reflections collected, 3377 independent, $\mu = 10.453$ mm^{-1} (absorption correction Psi Scans, $T_{min} = 0.733$, $T_{max} = 0.942$), solved by Patterson methods and refined by full-matrix least-squares procedures using SHELXS and SHELXL (G. M. Sheldrick, University of Göttingen, Germany), 181 parameters, $R = 0.030$, wR2 = 0.078.

(9) Farrugia, L. J. *J. Appl. Chem.* **1997**, *30*, 565.

(10) Abram, U.; Schulz Lang, E.; Bonfada, E. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1873.

(11) Ortner, K.; Abram, U. *Inorg. Chem. Commun.* **1998**, *1*, 251. (b) Abram, U.; Ortner, K.; Gust, R.; Sommer, K. *J. Chem. Soc., Dalton Trans.* **2000**, 735.

(12) Synthesis of $[Re(CO)_3Br(HL^2)]$: $[NEt_4]_2[Re(CO)_3Br_3]$ (77 mg, 0.1 mmol) and HL^1 (20 mg, 0.1 mmol) were dissolved in 20 mL of MeOH and heated under reflux for 2 h. The solvent was removed in a vacuum, the residue was dissolved in acetone, and the volume was slowly reduced at room temperature. A crystalline precipitate was formed which was recrystallized from DMSO. Yield: 20 mg (23%). Anal. Calcd for $C_{18}H_{33}N_5O_7ReS_5Br$ (tetra(dimethyl sulfoxide) solvate): C, 25.2; H, 3.9; N, 8.2; S, 18.7%. Found: C, 25.4; H, 4.0; N, 8.1; S, 17.1%. IR (ν, cm^{-1}): NH 3319, 3084; CO 2019, 1915, 1881; NHR + CN 1666−1485; CS 837. FAB^+ MS (m/z (assignment, %B)): 466 ($[M - Br]^+$, 10), 438 ($[M - Br - CO]^+$, 15), 410 ($[M - Br - 2CO]^+$, 5), 382 ($[M - Br - 3CO]^+$, 5).

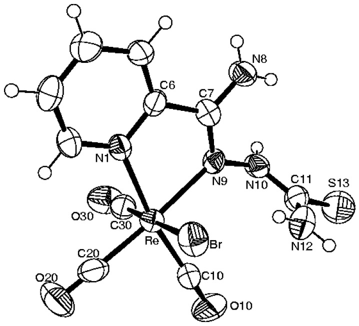

Figure 2. Molecular structure[9] of [Re(CO)$_3$Br(HL^2)].

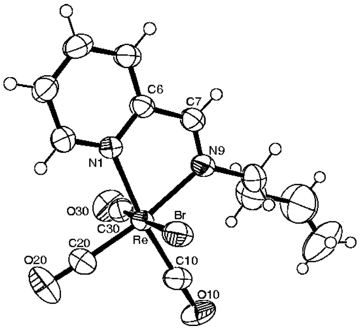

Figure 3. Molecular structure[8] of [Re(CO)$_3$Br(HL^3)].

shows the typical facial tricarbonyl pattern with intense bands at 1998, 1867, and 1855 cm^{-1}. FAB mass spectrometry gives evidence for a potential molecular ion at $m/z = 466$ which corresponds to a tentative composition of "[Re(CO)$_3$(L^2)]". Main fragmentation products are due to the subsequent abstraction of CO ligands. The intensities of the mass spectral peaks of [Re(CO)$_3$Br(HL^2)] are generally lower than those of [Re(CO)$_3$(L^1)] which is most probably caused by the lower solubility of the bromo derivative in the FAB matrix nitrobenzyl alcohol.

X-ray crystallography[8] confirms the composition of [Re(CO)$_3$Br(HL^2)] as containing a nondeprotonated thiosemicarbazone in the very unusual N,N coordination mode together with a bromo ligand. Figure 2 shows the molecular structure of the complex, and Table 1 contains selected bond lengths and angles. The short C11−S13 bond of 1.687(10) Å clearly shows the domination of the tautomeric form **Ia**, but some delocalization of electron density is indicated for the C−N bonds inside the chelate ring. The sulfur atom is bent away from the rhenium atom and does not contribute to the coordination of the metal. This results in a bonding situation which has been found in the related Schiff base complex [Re(CO)$_3$Br(HL^3)] which can readily be prepared be the reaction of [NEt$_4$][Re(CO)$_3$Br$_3$] with HL^3 in ethanol following the protocol given for the thiosemicarbazone derivatives. Selected bond lengths and angles of [Re(CO)$_3$Br(HL^3)] are given in Table 1 to allow comparison with the thiosemicarbazone complexes. The molecular structure of the Schiff base complex together with the atomic labeling scheme is given in Figure 3.

All isolated complexes are stable, and no oxidation has been observed at ambient conditions. The coordination of a potentially tridentate thiosemicarbazone in [Re(CO)$_3$Br(HL^2)] without the use of its sulfur donor site is without precedent. A similar coordination mode, however, has been reported for a nickel(II) complex with a related, potentially pentadentate diacetylpyridine bis(thisosemicarbazonato) ligand.[13] In this case, only four of the five donor functions of the ligand are used to form the square-planar coordination sphere around the nickel atom. In the present rhenium complex, however, a clear preference for the pyridine donor site over the sulfur atom of the thiosemicarbazone must be stated. This behavior seems to be typical for rhenium(I) and technetium(I) tricarbonyl centers and can be applied for the design of new radiopharmaceuticals as has been demonstrated recently with the preferred coordination of the [^{99m}Tc(CO)$_3$]$^+$ core to the imidazole donor sites of histidine-tagged recombinant proteins.[14]

The identification of two novel coordination modes of potentially tridentate thiosemicarbazones just on rhenium centers is remarkable in light of the fact that the first structural reports on a rhenium thiosemicarbazone complex dates from 2003.[3,4] This underlines the versatility of this ligand class. The formation of an N,N-chelate with ligands of the type HL^2 may contribute to understand the cleavage of the N−N bonds in some thiosemicarbazones during reactions with rhenium complexes, which lead to the isolation of methyl(2-pyridyl)methyleneimine and amino(2-pyridyl)methyleneimine complexes of Re(III) and Re(V).[3,15] Further studies on the reactivity of the new compounds and their potential use in the design of new metal-based pharmaceuticals are in progress in our laboratories.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Kasuga, N. C.; Sekino, K.; Koumo, C.; Shimada, N.; Ishikawa, M.; Nomiya, K. *J. Inorg. Biochem*. **2001**, *84*, 55.

(14) Waibel, R.; Alberto, R.; Willuda, J.; Finnern, R.; Schibli, R.; Stichelberger, A.; Egli, A.; Abram, U.; Mach, J.-P.; Plückthun, A.; Schubiger, P. A. *Nat. Biotechnol.* **1999**, *17*, 897.

(15) Garcia, I.; Abram, U. Unpublished.