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Rhenium Complexes with Triazine Derivatives Formed from Semicarbazones and Thiosemicarbazones

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Benzil bis(semicarbazone), H_2L^1, reacts with common rhenium(V) nitrido complexes such as $[ReNCl_2(PPh_3)_2]$ or $[ReNCl_2(PR_2Ph)_3]$ (R = Me, Et) under the release of one semicarbazone unit, cyclization, and formation of stable triazine-3-onato complexes of rhenium(V). The resulting 5,6-diphenyltriazine-3-one, HL^2, acts as monodentate or chelating, monoanionic ligand depending on the reaction conditions applied. Complexes of the compositions $[ReNCl(L^2\text{-}\kappa N^2,\kappa O)(PR_2Ph)_2]$ (R = Me, Et) or $[ReN(L^2\text{-}\kappa N^2,O)(L^2\text{-}\kappa N^2)(PPh_3)_2]$ were isolated. The N^2 nitrogen atom is the preferred binding site of the monodentate form of the ligand. This contrasts the behavior of the analogous thione HL^3, which preferably coordinates to nitridorhenium(V) centers via the sulfur atom. HL^3 is readily formed by the abstraction of methanol from 5-methoxy-5,6-diphenyl-4,5-dihydro-2H-[1,2,4]triazine-3-thione, $H_2L^3OCH_3$. In the presence of $[ReNCl_2(PPh_3)_2]$ or $[ReNCl_2(PR_2Ph)_3]$ complexes (R = Me, Et), this reaction yields stable complexes of the composition $[ReN(L^3\text{-}\kappa N^2,\kappa S)(L^3\text{-}\kappa S)(PR_2Ph)_2]$ (R = Me, Et, Ph) in good yields. Reduction of the metal atom and formation of the seven-coordinate $[Re(PPh_3)(L^3\text{-}\kappa N^2,\kappa S)_3]$ was observed during reactions of $H_2L^3OCH_3$ with $[ReOCl_3(PPh_3)_2]$ or $[ReO_2I(PPh_3)_2]$, while no rhenium complexes could be isolated during similar reactions with H_2L^1, although cyclization of the bis(semicarbazone) and the formation of H_2L^2OEt were observed.

Introduction

The increasing interest in the chemistry of thiosemicarbazones and their metal complexes is due to their interesting pharmacological properties, which have been found for some representatives.[1–3] The detected antibacterial, antiviral, and anticancer activity of the organic molecules is usually increased after complexation.[4] With respect to the large number of thiosemicarbazone complexes with many main group and transition metals,[5] the number of structurally characterized rhenium complexes with such ligands is small. The first structures of rhenium compounds with thiosemicarbazones, cationic $[Re^{III}(L)_2]^+$ complexes with HL = 2-acetylpyridinethiosemicarbazones, were published in 2003.[6] Only a few other examples involving oxorhenium(V) and tricarbonylrhenium(I) compounds have appeared since then.[7]

Relatively less attention has been devoted to the synthesis and biological properties of the structurally analogous semicarbazones and their metal complexes, despite the fact that, for some of these compounds, considerable anticonvulsant,[8] antimicrobial,[9] and antitumoral[10] activities have

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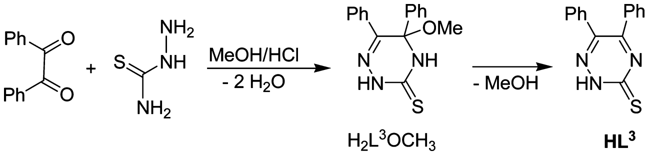
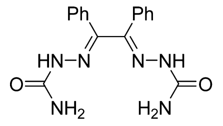
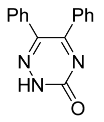
Chart 1. Formation of HL^3

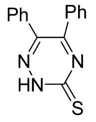


been found, and a great advantage of semicarbazone derivatives over their thiosemicarbazone analogues seems to be their lower toxicity. To the best of our knowledge, there exist only two reports about structurally fully characterized rhenium complexes with semicarbazones.[11] One reason for this might be the fact that they frequently undergo cyclization reactions, particularly in the presence of metal ions. This has also been observed for benzil semicarbazone (H_2L^1). It readily loses one of its hydrazinic units and forms a triazine-3-one (HL^2). Similar cyclization has been observed during the reaction of benzil with thiosemicarbazide in acidic methanol, and the heterocycle 5-methoxy-5,6-diphenyl-4,5-dihydro-2H-[1,2,4]triazine-3-thione, $H_2L^3OCH_3$, can be isolated from such reactions in good yields.[12] In the presence of metal ions, $H_2L^3OCH_3$ undergoes a further rearrangement and releases methanol under the formation of HL^3 (Chart 1).

Due to the possibility of electronic delocalization, which is enhanced upon deprotonation, these kinds of ligands are very versatile, and N,S chelate complexes of $(L^3)^-$ with metal ions such as Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Pb(II), and Sn(IV) have been isolated and structurally characterized. Monodentate coordination via the sulfur atom has been found in some Hg(II) complexes.[13] Much less is known about the coordination behavior of the heterocyclic ketone HL^2 and its open-chain precursor H_2L^1. A mixed monodentate, tetradentate coordination of the latter ligand is observed in the Pb(II) complex $[Pb(HL^1\text{-}\kappa N,\kappa N',\kappa O,\kappa O')(H_2L^1\text{-}\kappa O)(NO_3\text{-}\kappa O)]$.[14]


H_2L^1


HL^2


HL^3

In this paper, we report the synthesis of rhenium(III) and rhenium(V) complexes with triazine ligands derived from benzil semicarbazone and thiosemicarbazone. The rhenium(V) compounds are the first structurally characterized representatives of nitrido complexes with semicarbazone or thiosemicarbazone derivatives. The products were characterized by IR, mass spectrometry, ^1H and ^{31}P NMR, and X-ray diffraction.

Experimental Section

Materials. H_2L^1;[15] $H_2L^3OCH_3$;[12] and the rhenium precursors $[ReNCl_2(PPh_3)_2]$,[16] $[ReNCl_2(PEt_2Ph)_3]$,[16] $[ReNCl_2(PMe_2Ph)_3]$,[16] $[ReOCl_3(PPh_3)_2]$,[17] and $[ReO_2I(PPh_3)_2]$[18] were synthesized according to standard literature procedures. All reagents used in this study were reagent grade and were used without further purification.

Infrared spectra were measured as KBr pellets on a Shimadzu FTIR spectrometer between 400 and 4000 cm^{-1}. Fast atom bombardment (FAB^+) mass spectra were recorded with a TSQ (Finnigan) instrument using a nitrobenzyl alcohol matrix (results are given in the form *m/z*, assignment). Elemental analyses of carbon, hydrogen, nitrogen, and sulfur were determined using a Heraeus vario EL elemental analyzer. NMR spectra were taken in $CDCl_3$ at room temperature with a JEOL 400 MHz multinuclear spectrometer (chemical shifts relative to tetramethylsilane and H_3PO_4).

$[ReN(L^2\text{-}\kappa N^2,\kappa O)Cl(PEt_2Ph)_2]$ (1). H_2L^1 (32 mg, 0.1 mmol) was dissolved in 6 mL of ethanol, and two drops of NEt_3 were added. After the addition of solid $[ReNCl_2(PEt_2Ph)_3]$ (71 mg, 0.1 mmol), a red solution was immediately formed. The solution was stirred at room temperature for 4 h and kept overnight in the freezer. During this time, a colorless precipitate (consisting of semicarbazide hydrochloride and $NEt_3\cdot HCl$) appeared. This solid was filtered off, and the mother liquor was concentrated in vacuum to about 2 mL. Red crystals, which were suitable for X-ray diffraction, precipitated upon slow evaporation. Yield: 49 mg, 62%. ^1H NMR (δ (mult., int., assignment)): 7.76−6.96 (m, 20H, Ph), 3.10 (q, 8H, CH_2), 1.41 ppm (t, 12H, CH_3). ^{31}P NMR (δ): 12.66 ppm. FAB^+ MS: 817 $[M + H]^+$, 782 $[M - Cl]^+$, 650 $[M - PEt_2Ph]^+$, 568 $[M - L^2]^+$. IR (ν (int.)): 3055(m), 2932(m), 2872(w), 1689(m), 1674(m), 1643(m), 1543(s), 1481(m), 1434(m), 1350(m), 1149(m), 1076(s), 1041(s), 910(m), 763(m), 702(s), 609(w), 501(m), 452(w) cm^{-1}. Anal. calcd for $C_{35}H_{40}N_4OP_2ClRe$ (815.65): C, 51.49; H, 4.90; N, 6.86%. Found: C, 51.86; H, 4.97; N, 6.51%.

$[ReN(L^2\text{-}\kappa N^2,\kappa O)Cl(PMe_2Ph)_2]$ (2). The compound was prepared using the same procedure as described for **1** using H_2L^1 (32 mg, 0.1 mmol) and $[ReNCl_2(PMe_2Ph)_3]$ (68 mg, 0.1 mmol). Orange-

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Table 1. X-Ray Structure Data Collection and Refinement Parameters

	$[ReNCl(L^2\text{-}\kappa N^2,\text{-}\kappa O)(PEt_2Ph)_2]$ **1**	$[ReN(L^2\text{-}\kappa N^2,\text{-}\kappa O)(L^2\text{-}\kappa N^2)(PPh_3)_2]\cdot H_2O\cdot EtOH$ **3**$\cdot H_2O\cdot EtOH$	$[ReN(L^3\text{-}\kappa N^2,\text{-}\kappa S)(L^3\text{-}\kappa S)(PEt_2Ph)_2]$ **5**	$[ReN(L^3\text{-}\kappa N^2,\text{-}\kappa S)(L^3\text{-}\kappa S)(PMe_2Ph)_2]$ **4**	$[Re(L^3\text{-}\kappa N^2,\text{-}\kappa S)_3(PPh_3)]\cdot 0.5CH_3COCH_3$ **7**$\cdot 0.5CH_3COCH_3$
formula	$C_{35}H_{40}\,ClN_4OP_2Re$	$C_{68}H_{56}N_7O_4P_2Re$	$C_{50}H_{50}N_7P_2ReS_2$	$C_{46}H_{42}N_7P_2ReS_2$	$C_{64.50}H_{48}N_9O_{0.50}PReS_3$
M_w	816.30	1283.34	1061.23	1005,13	1270.4
cryst syst	monoclinic	orthorhombic	tetragonal	monoclinic	monoclinic
a/Å	11.981(2)	12.227(1)	12.387(2)	17.564(2)	9.564(1)
b/Å	24.215(2)	20.482(1)	12.387(2)	12.419(2)	22.511(1)
c/Å	13.531(1)	26.183(1)	30.963(2)	22.434(3)	13.818(1)
α/deg	90	90	90	90	90
β/deg	116.10(2)	90	90	106.81(2)	103.03(1)
γ/deg	90	90	90	90	90
V/ Å^3	3539.9(7)	6557.3(7)	4751(1)	4684(1)	2898.4(3)
space group	$P2_1/n$	$P2_12_12_1$	$P4_1$	$P2_1/n$	$P2_1$
Z	4	4	4	4	2
$D_{calcd.}$/g cm^{-3}	1.532	1.300	1.484	1.425	1.456
μ/mm^{-1}	3.631	1.952	2.755	2.790	2.282
no. of reflections	38137	54673	51670	28052	15844
no. of independent	9427	13926	12783	10163	10967
no. parameters	397	755	533	510	715
$R1/wR2$	0.0687/0.1289	0.0485/0.1168	0.0468/0.0782	0.0568/0.1165	0.0667/0.1372
GOF	0.865	0.905	0.885	0.772	0.986
Flack parameter		−0.002(8)	−0.018(7)		−0.001(11)

red solid, yield: 30 mg, 40%. ^{1}H NMR (δ (mult., int., assignment)): 7.79−6.98 (m, 20H, Ph), 1.79 ppm (d, 12H, CH_3). ^{31}P NMR (δ): –15.98 ppm. FAB$^+$ MS: 761 $[M + H]^+$, 726 $[M - Cl]^+$. IR (ν (int.)): 3055(w), 2977(w), 2916(w), 1697(s), 1681(s), 1558(m), 1436 (m), 1429(m), 1296(w), 1156(w), 1057(m), 910(s), 840(w), 748(s), 694(s), 601(w), 486(m), 417(m) cm^{-1}. Anal. calcd for $C_{31}H_{32}N_4OP_2ClRe$ (759.65): C, 48.97; H, 4.21; N, 7.37%. Found: C, 48.51; H, 4.06; N, 7.03%.

$[ReN(L^2\text{-}\kappa N^2,\kappa O)(L^2\text{-}\kappa N^2)(PPh_3)_2]$ (3). A suspension of $[ReNCl_2(PPh_3)_2]$ (80 mg, 0.1 mmol) in 10 mL of ethanol was added to a solution containing a mixture of H_2L^1 (66 mg, 0.2 mmol) and 2 drops of NEt_3 in 15 mL of ethanol. After 2 h of stirring at room temperature, the formed dark red solution was filtered in order to remove a small amount of unreacted $[ReNCl_2(PPh_3)_2]$. The resulting solution was concentrated by slow evaporation of the solvent, which resulted in the deposition of a red crystalline material. Single crystals for the X-ray diffraction were obtained from the mother liquor. Yield: 112 mg, 86%. ^{1}H NMR of the single crystals (δ (mult., int., assignment)): 7.64−7.03 (m, 50H, Ph), 3.13 (q, 3H, CH_2), 1.23 ppm (t, 4.5H, CH_3). ^{31}P NMR (δ): 24.96(s), 21.25 ppm(s). FAB$^+$ MS (m/z): 1222 $[M + H]^+$, 973 $[M - L^2]^+$, 959 $[M - (PPh_3)]^+$, 711 $[ReN(L^2)(PPh_3)]^+$. IR (ν (int.)): 3055(m), 1627(m), 1535(s), 1483(m), 1435(s), 1350(m), 1196(m), 1149(m), 1088(s), 1057(s), 926(w), 748(m), 694(s), 609(w), 517(s) cm^{-1}. Anal. calcd for $C_{68}H_{56}N_7O_4P_2Re$ (1283.34): C, 63.58; H, 4.36; N, 7.64%. Found: C, 63.87; H, 4.19; N, 7.44%.

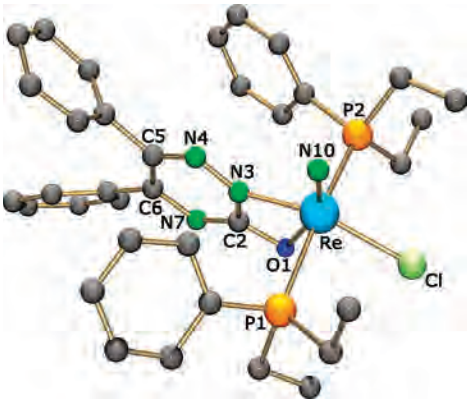

Figure 1. Molecular structure of $[ReNCl(L^2\text{-}\kappa N^2,\kappa O)(PEt_2Ph)_2]$ (**1**). H atoms have been omitted for clarity.

$[ReN(L^3\text{-}\kappa N^2,\kappa S)(L^3\text{-}\kappa S)(PMe_2Ph)_2]$ (4). A solution of $[ReNCl_2(PMe_2Ph)_3]$ (68 mg, 0.1 mmol) in ethanol was added to a mixture of $H_2L^3OCH_3$ (53 mg, 0.2 mmol) and three drops NEt_3 in 20 mL of ethanol. The mixture was refluxed for 30 min. The resulting red solution was allowed to evaporate slowly, and red crystals suitable for X-ray measurement were formed. Yield: 60 mg, 60%. ^{1}H NMR (δ (mult., int., assignment)): 7.38−6.97 (m, 30H, Ph), 2.15 ppm (s, 12H, CH_3). ^{31}P NMR (δ): –13.57 ppm. FAB$^+$ MS: 1006 $[M + H]^+$, 867 $[M - (PMe_2Ph)]^+$, 741 $[M - L^3]^+$, 726 $[M - 2(PMe_2Ph)]^+$, 603 $[ReN(L^3)(PMe_2Ph)]^+$. IR (ν (int.)): 3055(w), 2908(w), 1650(w), 1627(w), 1481(m), 1434(m), 1335(s), 1283(w), 1173(s), 1103(s), 1049(s), 949(m), 910(s), 872(w), 830(w), 764(m), 748(m), 694(s), 586(m), 532(m), 486(m) cm^{-1}. Anal. calcd for $C_{46}H_{42}N_7S_2P_2Re$ (1005.20): C, 54.97; H, 5.68; N, 9.76; S, 9.56%. Found: C, 54.59; H, 5.77; N, 9.51; S, 9.41%.

$[ReN(L^3\text{-}\kappa N^2,\kappa S)(L^3\text{-}\kappa S)(PEt_2Ph)_2]$ (5). The compound was prepared from $H_2L^3OCH_3$ (53 mg, 0.2 mmol) and $[ReNCl_2(PMe_2Ph)_3]$ (71 mg, 0.1 mmol) as described for **4**. Purple crystals, which were suitable for X-ray diffraction, were deposited upon evaporation of the solvent. Yield: 76 mg, 72%. ^{1}H NMR (δ (mult., int., assignment)): 7.51−6.98 (m, 30H, Ph), 2.16 (q, 8H, CH_2), 1.59 ppm (t, 12H, CH_3). ^{31}P NMR (δ): 3.70 ppm. FAB$^+$ MS: 1062.4 $[M + H]^+$, 895 $[M - (PEt_2Ph)]^+$, 797 $[M - L^3]^+$, 729 $[M - 2(PEt_2Ph)]^+$. IR (ν (int.)): 3047(w), 2962(w), 2932(w), 2878(w), 1643(w), 1625(w), 1481(m), 1435(m), 1327(s), 1246(w), 1209(w), 1172(s), 1103(s), 1049(s), 864(w), 764(m), 733(w), 694(s), 640(w), 586(w), 493(m), 455(w) cm^{-1}. Anal. calcd for $C_{50}H_{50}N_7S_2P_2Re$ (1062.20): C, 56.59; H, 5.66; N, 9.24; S, 9.05%. Found: C, 56.50; H, 5.38; N, 9.16; S, 9.08%.

$[ReN(L^3\text{-}\kappa N^2,\kappa S)(L^3\text{-}\kappa S)(PPh_3)_2]$ (6). Solid $[ReNCl_2(PPh_3)_2]$ (80 mg, 0.1 mmol) was added to a mixture of $H_2L^3OCH_3$ (53 mg, 0.2 mmol) and three drops of NEt_3 in 10 mL of ethanol. The resulting suspension was heated under reflux for 30 min and stirred for an additional 3 h at room temperature. During this time, the sparingly soluble rhenium precursor dissolved completely, and a red solution was obtained. The resulting mixture was concentrated until a dark red solid appeared, which was filtered off, washed with cold ethanol and diethyl ether, and dried in a vacuum. Yield: 106 mg, 85%. ^{1}H NMR (δ (mult., int., assignment)): 7.60−7.39 ppm (m, Ph). ^{31}P NMR (δ): 29.64 ppm. FAB$^+$ MS: 989 $[M - L^3]^+$, 730 $[M - 2(PPh_3)+H]^+$. IR (ν (int.)): 3055(m), 1648(w), 1628(w), 1484(m), 1434(s), 1342(w), 1188(w), 1095(s), 1025(w), 995(w),

Table 2. Selected Bond Lengths (Å) and Angles (deg) in $[ReNCl(L^2\text{-}\kappa N^2,\kappa O)(PEt_2Ph)_2]$ (**1**) and $[ReN(L^2\text{-}\kappa N^2,\kappa O)(L^2\text{-}\kappa N^2)(PPh_3)_2]$ (**3**)

	1	**3**		**1**	**3**
Re−N10	1.59(1)	1.631(6)	Re−P1	2.479(4)	2.477(2)
Re−P2	2.465(4)	2.451(2)	Re−N3	2.05(1)	2.127(6)
Re−O1	2.42(1)	2.355(5)	Re−Cl	2.402(4)	
O1−C2	1.30(1)	1.259(9)	Re−N13		2.127(6)
O11−C12		1.22(1)			
N10−Re−O1	155.3(5)	159.1(2)	N10−Re−P1	96.6(5)	98.4(3)
N10−Re−P2	95.5(5)	93.8(3)	N10−Re−N3	97.7(5)	101.2(3)
N10−Re−Cl	109.7(5)		N10−Re−N13		107.0(3)

847(w), 748(m), 694(s), 586(w), 517(s), 447(w) cm^{-1}. Anal. calcd for $C_{66}H_{50}N_7S_2P_2Re$ (1252.20): C, 63.25; H, 4.79; N, 7.83; S, 7.67%. Found: C, 62.98; H, 4.56; N, 7.28; S, 7.35%.

$[Re(L^3\text{-}\kappa N^2,\kappa S)_3(PPh_3)]$ (7). Solid $[ReOCl_3(PPh_3)_2]$ (84 mg, 0.1 mmol) was added to a mixture of $H_2L^3OCH_3$ (89 mg, 0.3 mmol) and 3 drops of NEt_3 in 6 mL of ethanol. The suspension was heated under reflux for 3 h, after which a green solution and a dark blue precipitate were formed. The solid was filtered off, washed with diethyl ether, and dried in a vacuum. Yield: 118 mg, 95%.

The same complex was obtained by the reaction between $[ReO_2I(PPh_3)_2]$ (0.087 g, 0.1 mmol) and $H_2L^3OCH_3$, applying the same conditions. Yield: 110 mg, 90%.

Single crystals were grown by slow evaporation of a solution of the complex in acetone. ^{1}H NMR (δ (mult., int., assignment)): 7.38−7.08 ppm (m, Ph). ^{31}P NMR (δ): 30.21 ppm. FAB$^+$ MS (*m*/*z*): 1242.4 $[M + H]^+$, 979.3 $[M - L^3]^+$, 978.3 $[M - (PPh_3){+}H]^+$. IR (ν (int.)): 3055(w), 1651(w), 1628(w), 1473(m), 1435(m), 1361(m), 1334(s), 1226(w), 1173(m), 1119(s), 1057(s), 918(w), 879(w), 849(w), 764(m), 694(s), 586(w), 525(m), 432(w) cm^{-1}. Anal. calcd for $C_{63}H_{45}N_9S_3PRe$ (1242.20): C, 60.96; H, 3.63; N, 10.16; S, 7.74%. Found: C, 60.31; H, 3.32; N, 9.87; S, 7.84%.

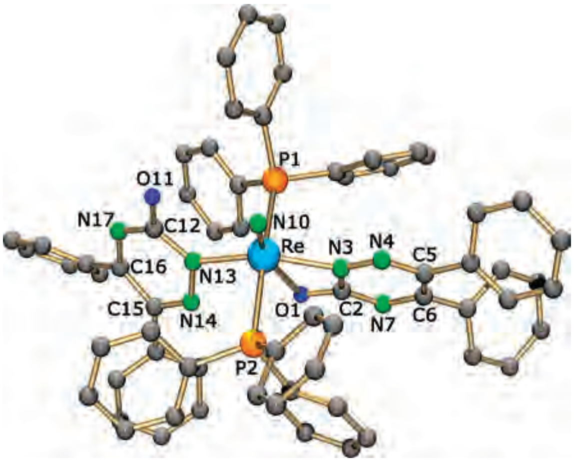

Figure 2. Molecular structure of $[ReN(L^2\text{-}\kappa N^2,\kappa O)(L^2\text{-}\kappa N^2)(PPh_3)_2]$ (**3**). H atoms have been omitted for clarity.

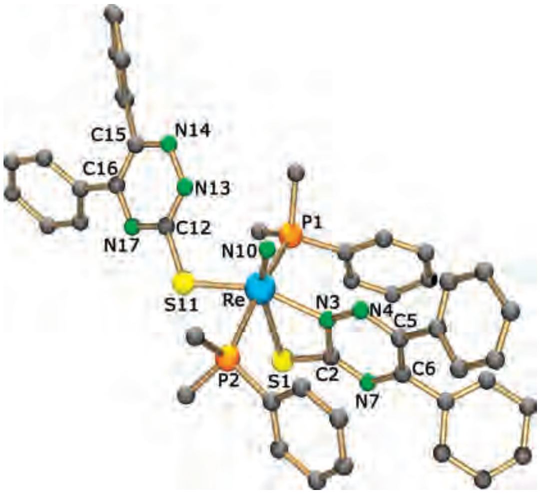

Figure 3. Molecular structure of $[ReN(L^3\text{-}\kappa N^2,\kappa S)(L^3\text{-}\kappa S)(PMe_2Ph)_2]$ (**4**). H atoms have been omitted for clarity.

X-Ray Crystallography. The intensities for the X-ray structure determinations were collected on a STOE IPDS 2T instrument with Mo Kα radiation (λ = 0.710 73 Å). Standard procedures were applied for data reduction and absorption correction. Structure solution and refinement were performed with SHELXS97 and SHELXL97.[16] Hydrogen atom positions were calculated for idealized positions. More details on data collections and structure calculations are contained in Table 1.

Additional information on the structure determinations have been deposited with the Cambridge Crystallographic Data Centre. Crystallographic data is also available in the Supporting Information.

Results and Discussion

Reactions of benzil bis(semicarbazone), H_2L^1, with common nitridorhenium(V) complexes such as $[ReNCl_2(PR_2Ph)_3]$ (R = Et, Me) or $[ReNCl_2(PPh_3)_2]$ result in the loss of one of the semicarbazone units and cyclization. The resulting 5,6-diphenyl-1,2,4-triazine-3-one, HL^2, deprotonates and substitutes chloro and/or phosphine ligands of the rhenium precursors. Depending on the reaction conditions and the rhenium starting materials, one or two of the heterocyclic ligands are coordinated in the products. Complexes with each $(L^2)^-$ ligand are formed with the six-coordinate precursors $[ReNCl_2(PR_2Ph)_3]$ (R = Me, Et) by replacement of a chloro and a phosphine ligand. The resulting $[ReNCl(L^2\text{-}\kappa N^2,\kappa O)(PR_2Ph)_2]$ complexes (**1** and **2**) contain the triazine ketonate in a chelate-bonded mode. We were not able to isolate products with more than one $(L^2)^-$ ligand during such reactions. Even the use of an excess of H_2L^1 resulted in the formation of the monosubstituted products.

A complex with two $(L^2)^-$ ligands was isolated with the five-coordinate precursor $[ReNCl_2(PPh_3)_2]$. Similar differences in the ligand exchange behavior of the related phosphine complexes of nitridorhenium(V) were observed previously during reactions with bidentate ligands such as dialkyldithiocarbamates or N,N-dialkylthiocarbamoylbenzamidines.[20] The differences in the reactivity in the referred examples are readily explained by the different basicity of the used phosphines. In the present case, however, both phosphine ligands remain coordinated. The reason for the formation of different ligand exchange products is most

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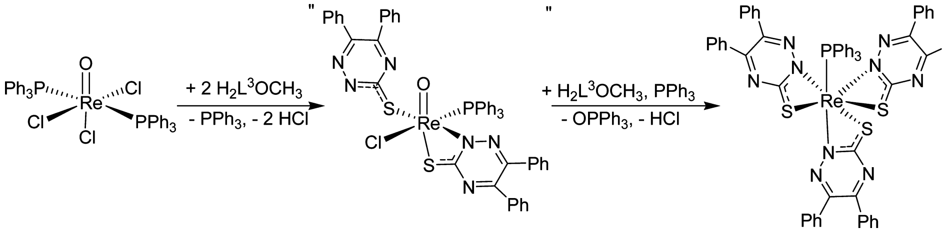
(20) (a) Abram, U.; Ritter, S. *Inorg. Chim. Acta* **1993**, *210*, 99. (b) Ritter, S.; Abram, U. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1443.



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probably a kinetic one, since the low solubility of [ReNCl$_2$(PPh$_3$)$_2$] in ethanol (even in the presence of NEt$_3$) provides a high local excess of HL^2 in the reaction mixture, which finally leads to the formation of a bis triazine-3-ketonato complex.

The products are air-stable, crystalline solids which are soluble in polar organic solvents such as THF or chloroform. FAB$^+$ mass spectra confirm the composition of the products by the detection of the molecular ions. The loss of Cl$^-$ ligands dominates the mass spectra of **1** and **2**, while ions at m/z = 973 and 959 can be assigned to the release of PPh$_3$ and (L^2)$^-$, respectively, in the spectrum of **3**. Strong infrared bands at 1076, 1057, and 1057 cm^{-1} can be attributed to the rhenium−nitrogen triple bonds. The NMR spectra of the complexes provide additional evidence for the proposed composition and molecular structures of the complexes. Each one ^{31}P signal is detected in the spectra of **1** and **2**, while two singlets are observed in **3**. This can be understood by the coordination of the second (L^2)$^-$ ligand via its nitrogen atom (*vide infra*), which results in a hindered rotation around the rhenium−imido bond and the formation of two diastereoisomers.

Figure 1 shows the molecular structure of **1**. Selected bond lengths and angles are summarized in Table 2. The rhenium atom has a strongly distorted octahedral coordination environment with the two phosphine ligands in trans positions to each other. The monoanionic triazine ketonate (L^2)$^-$ binds bidentate via its oxygen atom and N3, with O1 trans to the nitrido ligand. This bonding mode is also the main reason for the distortions from an ideal octahedron. The restricting bite angle of the four-membered chelate ring causes a N10−Re−O1 angle of 155.3(5)°, which is far from the ideal value of 180°. The N10−Re distance of 1.59(1) Å can clearly be assigned to a metal−nitrogen triple bond, and as a consequence of the high electron density in this axial bond, the angles between N10, Re, and the equatorial ligands are significantly larger than 90°. A remarkable feature of the structure of **1** is the long Re−O1 bond of 2.42(1) Å, which can also be addressed to the influence of the "N^{3-}" ligand. Nitrido ligands belong to the most powerful σ donors and exert a strong structural trans influence, which drastically weakens the bonds to the trans ligands and leads in many examples to the formation of five-coordinate rhenium nitrido complexes.[21] A survey of the hitherto crystallographically studied rhenium complexes with terminal nitrido ligands shows that almost 50% of the compounds are five-coordinate,[22] and there exists experimental proof that the coordination number of the metal atom is increased when the trans influence of the "N^{3-}" is reduced (e.g., by reaction with a Lewis acid).[23] The bonding situation inside the planar heterocyclic ligand shows an extensive delocalization of electron density. A value of 1.30(1) Å is observed for the O1−C2 bond, which reflects a high degree of double-bond character for the ketone fuctionality in the complex.

A very similar bonding situation is observed in compound **3**, in which PEt$_2$Ph is replaced by PPh$_3$ and the chloro ligand of **1** is formally replaced by a second (L^2)$^-$ ligand. Figure 2 depicts the molecular structure of this complex, and selected bond lengths are compared with the values of **1** in Table 2. The second triazine ketonato ligand does not form a chelate but is coordinated solely via the N13 atom. The ketone oxygen atom O11 is directed toward the molecular hemisphere of the nitrido nitrogen atom, and the resulting O11···N10 distance is only 3.156 Å. The C12−O11 distance of 1.26 Å is slightly shorter than that in the chelate-bonded ligand.

The cyclization of H$_2$L^1 and the formation of the heterocyclic ligand HL^2 during reactions with metal ions are hitherto without precedent, and the complexes reported above are the first representatives of such metal complexes. However, benzil and thiosemicarbazide under acidic conditions readily undergo cyclization (Chart 1), which can be utilized for the direct synthesis of 5-methoxy-5,6-diphenyl-4,5-dihydro-2H-[1,2,4]triazine-3-thione, H$_2$L^{3}OCH$_3$, in a methanol/HCl mixture.[12]

H$_2$L^{3}OCH$_3$ reacts in a one-pot protocol with [ReNCl$_2$(PPh$_3$)$_2$] or [ReNCl$_2$(PR$_2$Ph)$_3$] (R = Me, Et) complexes under abstraction of methanol and the formation of 1:2 ligand exchange products. Complexes of the general formula [ReN(L^3-κN^2,κS)(L^3-κS)(phosphine)$_2$] are formed as air-stable, orange-red solids. No evidence was found for the formation of reasonable amounts of products with only one triazine thionato ligand, as was the case for the corresponding ketonates (L^2)$^-$ (compounds **1** and **2** *vide supra*). The products are readily soluble in polar solvents such as THF, CHCl$_3$, or CH$_2$Cl$_2$. Their FAB$^+$ mass spectra show the molecular ions only with low intensity. Intense peaks, however, are due to ions which are formed by the abstraction of complete ligands. ^{31}P NMR spectra display each one resonance, which suggests a magnetic equivalence of the phosphine ligands. This is unlike the situation in compound **3**, where the coordination of a second (L^2)$^-$ ligand (in comparison to **1** and **2**) made the phosphines inequivalent. The spectrum of **3** can be understood with regard to the monodentate N-coordination of the second triazine ketonate

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(21) Abram, U.; Schmidt-Brücken, B.; Hagenbach, A.; Hecht, M.; Kirmse, R.; Voigt, A. *Z. Anorg. Allg. Chem.* **2003**, *629*, 838.

(22) *Cambridge Crystallographic Database*, Release 5.28, May 2007; Cambridge Crystallographic Data Centre: Cambridge, U.K.

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Table 3. Selected Bond Lengths (Å) and Angles (deg) in $[ReN(L^3\text{-}\kappa N^2,\kappa S)(L^3\text{-}\kappa S)(PMe_2Ph)_2]$ (**4**) and $[ReN(L^3\text{-}\kappa N^2,\kappa S)(L^3\text{-}\kappa S)(PEt_2Ph)]$ (**5**)

	4	5		4	5
Re−N10	1.704(9)	1.639(7)	Re−P1	2.452(3)	2.445(2)
Re−P2	2.444(3)	2.478(2)	Re−N3	2.13(1)	2.136(5)
Re−S1	2.739(1)	2.769(2)	Re−S11	2.409(3)	2.386(1)
S1−C2	1.74(1)	1.720(7)	S11−C12	1.74(1)	1.747
C2−N3	1.36(1)	1.360(8)	C2-N7	1.31(1)	1.336(8)
C12−N13	1.31(2)	1.342	C12−N17	1.32(2)	1.334
N10−Re−S1	156.1(4)	156.1(2)	N10−Re−P1	98.1(3)	91.5(2)
N10−Re−P2	95.3(3)	97.6(2)	N10−Re−N3	94.3(4)	95.0(2)
N10−Re−S11	110.0(4)	107.3	Re−N3−C2	110.2(9)	109.3(4)
Re−S1−C2	77.1(4)	76.0(2)	Re−S11−C12	116.4(5)	116.1
S1−C2−N7	124(1)	125.2(5)	S1−C2−N3	111(1)	112.8(7)
S11−C12−N17	114.9(9)	115.5	S11−C12−N13	120(1)	119.5

(Figure 2) and suggests a different coordination mode in the compounds **4**–**6**, with less restriction for the monodentate heterocyclic ligand. This can in principle be achieved by its coordination via the sulfur atom and is confirmed by the solid-state structures of compounds **4** and **5**, which have been determined by X-ray diffraction.

Figure 3 depicts the molecular structure of complex **4**. The coordination sphere of the rhenium atom is a distorted octahedron, and the compound contains, similarly to complex **3**, one chelate-bonded and one monodentate heterocyclic ligand. In contrast to its nitrogen-bonded oxygen analogue, the monodentate $(L^3)^-$ ligand prefers the sulfur atom for coordination. The chelate-bonded ligand directs its sulfur atom to the position trans to the nitrido nitrogen. This results in a similar bonding mode to that observed in **3** and in an exceptionally long Re−S1 bond of 2.739(3) Å.

Selected bond lengths and angles are summarized in Table 3. They clearly show that the double-bond character of the carbon−sulfur bond in $H_2L^3OCH_3$ (1.628 Å)[15] is reduced upon complex formation and the C−S bond lengths in the complex come closer to the expected values of a single bond. It is interesting to note that this holds true for the chelate-bonded as well as for the monodentate ligands. The triazine rings of both ligands are essentially planar, reflecting an extended π system.

All structural features which have been discussed for **4** are also true for complex **5**. The corresponding bond lengths and angles are contained in Table 3. Since the molecular structure of this complex is virtually the same as that of compound **4** and the same molecular labeling scheme has been applied, we have refrained from depicting another structural plot in this communication.

Table 4. Selected Bond Lengths (Å) and Angles (deg) in $[Re(L^3\text{-}\kappa N^2,\kappa S)_3(PPh_3)]$ (**7**)

Re−P	2.405(3)	Re−S1	2.494(3)
Re−S11	2.490(3)	Re−S21	2.491(3)
Re−N3	2.055(9)	Re−N13	2.082(9)
Re−N23	2.061(8)	S1−C2	1.71(1)
C2−N3	1.36(2)	C2−N7	1.31(2)
C12−N13	1.40(1)	C12−N17	1.32(1)
C22−N23	1.38(2)	C22−N27	1.34(2)
P−Re−S1	84.2(1)	P−Re−N3	103.1(3)
P−Re−S11	101.9(1)	P−Re−N13	83.7(3)
P−Re−S21	103.4(1)	P−Re−N23	168.7(3)
N3−Re−S11	133.1(3)	N3−Re−N13	78.9(4)
N3−Re−S21	132.7(3)	N3−Re−N23	81.9(6)
S11−Re−N13	65.2(3)	S11−Re−S21	77.4(1)
S11−Re−N23	81.2(4)	N13−Re−S21	142.5(3)
N13−Re−N23	107.4(4)	S21−Re−N23	66.4(5)
S1−Re−N3	64.6(3)	S1−Re−S11	157.3(1)
S1−Re−N13	137.5(3)	S1−Re−S21	80.0(1)
S1−Re−N23	88.9(3)		

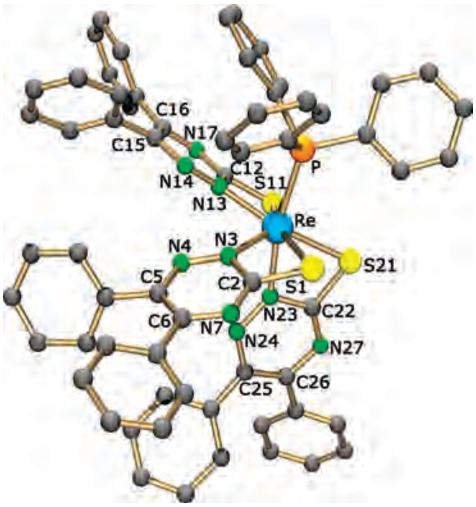

Figure 4. Molecular structure of $[Re(L^3\text{-}\kappa N^2,\kappa S)_3(PPh_3)]$ (**7**). H atoms have been omitted for clarity.

Despite the fact that ligands HL^2 and HL^3 perfectly stabilize the oxidation state at "5+" in the nitrido complexes described above, a completely different reaction pattern is observed for reactions of HL^3 with the oxorhenium(V) precursors $[ReOCl_3(PPh_3)_2]$ and $[ReO_2I(PPh_3)_2]$. Here, we found reduction of the metal and the formation of a rhenium(III) complex, as is shown in the above reaction with $[ReOCl_3(PPh_3)_2]$. The intermediate formation of the first ligand exchange product "$[ReOCl(L^3\text{-}\kappa N^2,\kappa S)(L^3\text{-}\kappa S)(PPh_3)]$" and the subsequent reduction of the metal by the released PPh_3 is strongly suggested and confirmed by the detection of $OPPh_3$.

Similar reactions have been described previously during ligand exchange reactions starting from $[ReOCl_3(PPh_3)_2]$.[24] The seven-coordinate product $[Re(L^3\text{-}\kappa N^2,\kappa S)_3(PPh_3)]$ (**7**) is diamagnetic and shows a ^{31}P NMR resonance at 30.2 ppm. A structural determination of **7** shows a strongly distorted pentagonal-bipyramidal environment of rhenium with PPh_3 and a nitrogen atom in the axial positions. The molecular structure is shown in Figure 4.

Table 4contains selected bond lengths and angles. Main distortions from an ideal pentagonal bipyramid are found in the pentagonal plane with a maximum deviation from a mean least-squares plane of 0.500 Å for N3, while the axial P−Re−N23 angle is 168.7(3)°. This can be understood in regard to the bite angles of chelate ligands and the steric demands of the phenyl rings in the peripheries of $(L^3)^-$. The bonding situation in **7** well resembles those in a number of other seven-coordinate mixed-ligand Re(III) complexes with a monodentate phosphine and three bidentate ligands.[25]

In conclusion, it can be stated that benzil bis(semicarbazone) undergoes cyclization and loses one of the semicarbazone side arms during reactions with rhenium nitrido complexes. The resulting triazine ketone can act as a bidentate or monodentate ligand. In the latter case, the N^2 nitrogen atom of the triazine is coordinated. A different coordination pattern is observed for the analogous triazine thione, which coordinates via the thione sulfur atom, when it acts as a monodentate ligand.

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

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