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Chelated Hydrazido(3–)rhenium(V) Complexes: On the Way to the Nitrido–M(V) Core (M = Tc, Re)

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Neutral and asymmetrical hydrazido(3–)rhenium(V) heterocomplexes of the type [Re(η^2-L^4)(L^n)(PPh$_3$)] (η^2-L^4 = NNC(SCH$_3$)S; H$_2$L^1 = *S*-methyl β-*N*-((2-hydroxyphenyl)ethylidene)dithiocarbazate, **1**, H$_2$L^2 = *S*-methyl β-*N*-((2-hydroxyphenyl)methylidene)dithiocarbazate, **2**) are prepared via ligand-exchange reactions in ethanolic solutions starting from [Re^V(O)Cl$_4$]$^-$ in the presence of PPh$_3$ or from [Re^V(O)Cl$_3$(PPh$_3$)$_2$]. The distorted octahedral coordination sphere of these compounds is saturated by a chelated hydrazido group, a facially ligated ONS Schiff base, and PPh$_3$. Reduction–substitution reactions starting from [NH$_4$][Re^{VII}O$_4$] in acidic ethanolic mixtures containing PPh$_3$ and H$_2$L^n (or its dithiocarbazic acid precursor H$_3$L^4) produce another example of chelated hydrazido(3–) rhenium(V) derivative, namely [Re(η^2-L^4)Cl$_2$(PPh$_3$)$_2$], **3**. On the contrary, the *N*-methyl-substituted dithiocarbazic acid H$_2$L^3 reacts with perrhenate to give the known nitrido complex [Re(N)Cl$_2$(PPh$_3$)$_2$]. Rhenium(V) complexes incorporating the robust η^2-hydrazido moiety represent key intermediates helpful for the comprehension of the reaction pathway which generates nitridorhenium(V) species starting from oxo precursors. An essential requirement for the stabilization of such chelated hydrazido–Re(V) units is the triple deprotonation at the hydrazine nitrogens, thereby providing efficient π-electron circulation in the resulting five-membered ring. The thermal stability of these units is affected by the nature of the anchoring donor, thione sulfur ensuring stronger chelation than nitrogen and oxygen. The η^2-hydrazido complexes are characterized by conventional physicochemical techniques, including the X-ray crystal structure determination of **1** and **3**.

Introduction

In the past two decades, the coordination chemistry of the group 7 metals technetium and rhenium has known a period of increasing investigation due to the widespread use of the metastable isomer ^{99m}Tc (pure γ-emitter with ideal physical properties for imaging: $t_{1/2}$ = 6 h, E_γ = 140 keV) in diagnostic nuclear medicine.[1] The recent advent of diphosphonate agents based on the β-emitters ^{186}Re ($t_{1/2}$ = 3.8 d, $E_{\beta\max}$ = 1.07 MeV) and ^{188}Re ($t_{1/2}$ = 0.7 d, $E_{\beta\max}$ = 2.11 MeV) as potential radiopharmaceuticals for the palliation of pain in patients with metastatic bone cancer[2] has made studies on these two elements even more attractive. The advantage of manipulating “cold” materials (the natural isotopic mixture of ^{185}Re and ^{187}Re) instead of using a radioactive nuclide (the soft β-emitter ^{99g}Tc; $t_{1/2}$ = 2.12 × 10^5 y, E_β = 292 keV) makes common inorganic chemistry studies on rhenium much easier to carry out. In fact, Re is often used as a technetium surrogate to study the macroscopic chemistry of potentially useful agents in nuclear medicine. However, while analogies such as synthetic and general chemistry seem to support this choice, a few important differences, lately disclosed, concerning the redox behavior and kinetics of substitution (rhenium species are more difficult to reduce to lower oxidation states and kinetically more inert toward substitution than technetium analogues),[3] suggest to use the chemical similarity of the two elements with some caution.

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The design of improved radiopharmaceuticals depends on the availability of both new ligand systems and new metal containing fragments. Studies concerning the $[M(O)]^{3+}$ core have played a prevalent role in the chemistry of Tc(V) and Re(V) since many of the radiopharmaceutical agents utilized for clinical purposes show a polydentate ligand coordinated to an oxo−metal core.[1a,4] Recent developments based on the incorporation of the nitrogen donor in the metal coordination sphere have led to the synthesis of complexes containing diazenido,[5] imido,[6] and nitrido[7] cores. Particular emphasis has been devoted to the latter $[Tc(N)]^{2+}$ moiety, for which a standard method of production at "noncarrier added" level (nca) has been proposed.[8] In this field, a new myocardial imaging agent $[^{99m}Tc(N)(NOEt)_2]$ (NOEt = *N*-ethyl-*N*-ethoxydithiocarbamate) has been prepared and is now under phase III clinical trials.[9] Various hydrazines and substituted hydrazines have been utilized as N^{3-} source in the preparation of the nitrido−^{99m}Tc core at nca level starting from the pertechnetate ion eluted from the commercially available ^{99}Mo/^{99m}Tc generator. Among substituted hydrazines, *S*-methyl *β*-*N*-((2-hydroxyphenyl)ethylidene)dithiocarbazate (H_2L^1) and *S*-methyl *β*-*N*-((2-hydroxyphenyl)methylidene)dithiocarbazate (H_2L^2) and the related dithiocarbazate precursors $H_2NN(CH_3)C(=S)SCH_3$ (H_2L^3) and $H_2NNHC(=S)SCH_3$ (H_3L^4) have been used as prototype ligands not only as potential source of nitrogen but also as suitable polydentate ligands able to stabilize the $[Tc(N)]^{2+}$ core both at macroscopic and nca levels.[10] Despite extensive effort aiming at the elucidation of the mechanism of formation of the nitrido group starting from (poly)oxo precursors, no exhaustive explanation has been produced so far. Some postulated intermediate species bearing alternatively the oxo or the nitrido group have been proposed in the case of technetium, i.e. the five-coordinate $[Tc^V(O)Cl(L^2)]$,[11] $[Tc^V(N)(L^2)(PPh_3)]$,[12] and $[Tc^V(N)(L^4)_2]$[12] complexes and the anomalous six-coordinate $[Tc^{III}Cl_2(HL^2)(PPh_3)_2]$[11] one. Additional investigation with the third row congener has produced similar five-coordinate $[Re^V(O)X(L^1)]$ (X = Cl or I)[13] and the six-coordinate phosphine-containing compounds $[Re^V(O)Cl(L^1)(PPh_3)]$ and $[Re^V(O)Cl(L^1)(OPPh_3)]$.[14]

In this study we report on the synthesis and characterization of some hydrazido(3−) rhenium(V) species, namely $[Re(\eta^2-L^4)(L^1)(PPh_3)]$, **1**, $[Re(\eta^2-L^4)(L^2)(PPh_3)]$, **2**, and $[Re(\eta^2-L^4)Cl_2(PPh_3)_2]$, **3**, which are relevant for the comprehension of the mechanism of formation of the nitrido core starting from the high-valent perrhenate precursor. In this case we have utilized profitably the differences between the two elements. In particular, while the isolation of intermediate hydrazido−Tc species is extremely difficult because the kinetic of conversion of oxo−Tc into the corresponding nitrido−Tc compounds is very fast, the slower kinetic of substitution at the rhenium center, along with the careful choice of properly designed substituted hydrazines, has granted the isolation of stable intermediate (η^2-hydrazido)-rhenium species. Hence, a possible reaction pathway ongoing from perrhenate to nitrido−Re(V) through intermediate hydrazido−Re(V) derivatives is here proposed.

Experimental Section

Materials. Ethanol was distilled twice under dinitrogen over magnesium turnings. Dichloromethane and petroleum ether (30−60 °C) were distilled over calcium chloride. Perrhenate ammonium salt was purchased from STREM Chemicals (Newberyport). Carbon disulfide, hydrazine dihydrochloride, methyl iodide, triphenylphosphine, salicylaldehyde, and 2-hydroxyacetophenone are commercially available from Aldrich (Saint Quentin Fallavier, France). $[NBu_4][Re(O)Cl_4]$ and $[Re(O)Cl_3(PPh_3)_2]$ starting materials,[15] *S*-methyl *β*-*N*-((2-hydroxyphenyl)ethylidene)dithiocarbazate (H_2L^1) and *S*-methyl *β*-*N*-((2-hydroxyphenyl)methylidene)dithiocarbazate (H_2L^2) Schiff base ligands,[13] and the dithiocarbazic acid precursors $H_2NNHC(=S)SCH_3$ (H_3L^4) and $H_2NN(CH_3)C(=S)SCH_3$ (H_2L^3)[16] were prepared according to literature methods.

Instrumentation. Carbon, hydrogen, and sulfur analysis were performed by the ICSN (91198 Gif sur Yvette, France) on a model 1106 Carlo Erba elemental analyzer. IR spectra were obtained by a Nicolet 205 instrument in KBr pellets (4000−500 cm^{-1}). Mass spectrometry was carried out by the CRMPO (37500 Rennes, France) on a Zabspect TOF (Micromass) spectrometer (FAB+, NBA matrix). All prepared compounds were characterized by ^{1}H, ^{13}C, and ^{31}P NMR recorded with a Bruker ARX 400 at 400.13, 100.62, and 161.98 MHz, respectively. Chemical shift values are referred to residual $CHCl_3$ (7.26 ppm, ^{1}H NMR; 77.1 ppm, ^{13}C NMR).

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Syntheses of Complexes. [Re(η^2-L^4)(L^1)(PPh$_3$)], 1. Method A. To an ethanolic solution (20 mL) of [Re(O)Cl$_4$][NBu$_4$] (0.100 g, 0.17 mmol) were added dropwise H_2L^1 (0.082 g, 0.34 mmol) and triphenylphosphine (0.180 g, 0.68 mmol) in ethanol (10 mL), and the solution was stirred at room temperature for 7 days. The yellow brown precipitate was filtered out, washed several times with ethanol, and dried under reduced pressure. The resulting khaki powder was dissolved in a mixture of dichloromethane/petroleum ether (50/50; 10 mL). After 5 days at room temperature, dark crystals of **1** were collected, washed with petroleum ether, and dried under reduced pressure (0.064 g, yield = 47%). Anal. Calcd (found) for $C_{30}H_{29}N_4OPReS_4$: C, 44.71 (44.75); H, 3.50 (3.50); S, 15.91 (15.88). IR (KBr, cm^{-1}): 1596 (m, $\nu_{C=N}$), 1566 (m, $\nu_{N=N}$), 1527 (m, $\nu_{C=N}$), 1462 (m, ν_{PPh_3}), 1433 (s, ν_{PPh_3}), 1312 (m, ν_{C-O}), 1240 (m), 1191 (s), 1094 (m, ν_{PPh_3}), 1060 (m, ν_{C-S}), 992 (s, ν_{C-S}), 751 (m, ν_{PPh_3}), 692 (s, ν_{PPh_3}), 683 (m), 527 (s). FAB(+) (*m*/*z*): 807.0, [M + H]$^+$. ^{1}H NMR (CDCl$_3$, ppm): δ 2.36 (s, SC*H*$_3$, 3H), 2.69 (s, SC*H*$_3$, 3H), 2.99 (s, CC*H*$_3$, 3H), 6.46 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 6.94 (t, $^3J_{HH}$ = 8.1 Hz, 1H), 7.28 (t, $^3J_{HH}$ = 7.9 Hz, 1H), 7.40 (m, 9H), 7.55 (m, 6H); 7.59 (d, $^3J_{HH}$ = 8.1 Hz, 1H). ^{13}C NMR (CDCl$_3$, ppm): δ 18.1, 18.3, and 18.5 (*C*H$_3$), 119.1, 120.2, 126.0, and 133.7 (aromatic *C*), 128.2 (d, *J* = 10 Hz), 130.6 (d, *J* = 2 Hz), 132.7 (d, *J* = 41 Hz) and 134.5 (d, *J* = 10 Hz) (PPh$_3$−aromatic C), 164.1 (*C*−O), 166.5 (CH$_3$*C*═N), 191.5 and 192.2 (*C*S$_2$). ^{31}P NMR (CDCl$_3$, ppm): δ 13.8 (s, Re−*P*Ph$_3$).

Method B. To an ethanolic solution (20 mL) of [Re(O)Cl$_3$(PPh$_3$)$_2$] (1.0 g, 1.2 mmol) was added dropwise H_2L^1 (0.540 g, 2.4 mmol) in ethanol (10 mL), and the solution was stirred at room temperature for 7 days. The yellow brown precipitate was filtered out, washed several times with ethanol, and dried under reduced pressure. The resulting khaki powder was dissolved in a mixture of dichloromethane/petroleum ether (50/50; 10 mL) (0.490 g, yield = 51%). Spectroscopic data are as above.

[Re(η^2-L^4)(L^2)(PPh$_3$)], 2. Compound **2** was prepared using the same procedures above detailed for **1** (yield = 48%). Anal. Calcd (found) for $C_{29}H_{27}N_4OPReS_4$: C, 44.00 (43.85); H, 3.30 (3.60); S, 16.20 (16.36). IR (KBr, cm^{-1}): 1599 (m, $\nu_{C=N}$), 1579 (m, $\nu_{N=N}$), 1537 (m, $\nu_{C=N}$), 1479 (m, ν_{PPh_3}), 1432 (s, ν_{PPh_3}), 1309 (m, ν_{C-O}), 1274 (m), 1182 (s), 1100 (s, ν_{PPh_3}), 1065 (m, ν_{C-S}), 996 (m, ν_{C-S}), 750 (s, ν_{PPh_3}), 713 (s), 691 (s, ν_{PPh_3}), 637 (s), 612 (s). FAB(+) (*m*/*z*): 794, [M + H]$^+$. ^{1}H NMR (CDCl$_3$, ppm): δ 2.39 (s, SCH$_3$; 3H), 2.69 (s, SCH$_3$; 3H), 6.57 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 6.98 (t, $^3J_{HH}$ = 8.1 Hz, 1H), 7.04 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 7.40 (m, 9H), 7.56 (m, 6H); 7.99 (s, HC═N; 1H), 8.32 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (CDCl$_3$, ppm): δ 18.6 and 18.7 (S*C*H$_3$), 118.0, 119.6, 119.7, 121.3 and 121.8 (aromatic *C*), 128.6 (d, *J* = 10.1 Hz), 128.9 (d, *J* = 12.1 Hz), 134.8 (d, *J* = 10.1 Hz) and 136.4 (d, *J* = 38 Hz) (PPh$_3$−aromatic C), 160.4 (*C*−O), 161.4 (H*C*═N), 193.2 and 198.4 (*C*S$_2$). ^{31}P NMR (CDCl$_3$, ppm): δ 15.1 (s, Re−*P*Ph$_3$).

[Re(η^2-L^4)Cl$_2$(PPh$_3$)$_2$], 3. Method A. To an ethanolic solution (5 mL) of [NH$_4$][ReO$_4$] (0.100 g, 0.373 mmol) containing 1 mL of 12 M HCl were added dropwise H_2L^2 (0.169 g, 0.746 mmol) and triphenylphosphine (0.390 g, 1.491 mmol) in ethanol (30 mL), and the solution was kept at 60 °C for 3 h. The yellow green precipitate was filtered out, washed several times with hot ethanol, and dried under reduced pressure. The resulting olive-green powder was dissolved in a mixture of dichloromethane/petroleum ether (50/50; 10 mL). After standing at room temperature for few days, green crystals of **3** were collected, washed with petroleum ether, and dried under reduced pressure (0.195 g, yield = 76%). Anal. Calcd (found) for $C_{38}H_{33}Cl_2N_2P_2ReS_2$: C, 50.70 (50.62); H, 3.70 (3.72); S, 7.10 (7.14). IR (KBr, cm^{-1}): 1587 (w, $\nu_{C=N}$), 1571 (w, $\nu_{N=N}$), 1481 (s, ν_{PPh_3}), 1433 (s, ν_{PPh_3}), 1315 (m), 1286 (s), 1187 (m), 1157 (s), 1136 (m), 1093 (s, ν_{PPh_3}), 1070 (s, ν_{C-S}), 1028 (w), 997 (m, ν_{C-S}), 967 (m), 749 (s, ν_{PPh_3}); 693 (s, ν_{PPh_3}), 519 (s), 506 (s). FAB(+) (*m*/*z*): 900.0, [M + H]$^+$. ^{1}H NMR (CDCl$_3$, ppm): δ 2.25 (s, SC*H*$_3$, 3H), 7.30−7.60 (30 H; P*Ph*$_3$). ^{13}C NMR (CDCl$_3$, ppm): δ 17.3 (S*C*H$_3$), 128.0, 130.3, 131.5 and 134.6 (PPh$_3$−aromatic C), 207.2 (*C*S$_2$). ^{31}P NMR (CDCl$_3$, ppm): δ −6.2 (s, Re−*P*Ph$_3$).

Table 1. Crystallographic Data for **1** and **3**

	1	3
formula	$C_{30}H_{29}N_4OPS_4Re$	$C_{30}H_{29}N_4OPS_4Re$
fw	807.0	900.8
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	Cc
a, Å	20.916(3)	17.514(4)
b, Å	10.236(4)	10.639(2)
c, Å	29.463(7)	20.106(4)
β, deg	92.33(2)	102.29(3)
V, Å^3	6303(3)	3660(1)
Z; D_{calcd}, g cm^{-3}	8; 1.701	4; 1.635
μ(Mo Kα), cm^{-1}	4.20	3.70
T, °C	20	23
λ(Mo Kα), Å	0.710 69	0.710 73
θ_{max}, deg	27	27
obsd reflcns ($I > 2\sigma(I)$)	8713	3879
R1[a]	0.037	0.045
wR2[b]	0.072	0.114
GOF[c]	0.979	1.089

[a] $R1 = \Sigma(|F_o| \angle |F_c||)/\Sigma(|F_o|)$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o)^2]\}^{1/2}$. [c] $GOF = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ (n = reflections; p = parameters).

Method B. To an ethanolic solution (5 mL) of [NH$_4$][ReO$_4$] (0.100 g, 0.373 mmol) containing 1 mL of 12 M HCl were added dropwise H_3L^4 (0.091 g, 0.746 mmol) and triphenylphosphine (0.390 g, 1.491 mmol) in ethanol (30 mL), and the solution was kept at 60 °C for 3 h. The resulting yellow green precipitate was filtered off, washed several times with hot ethanol, and dried under vacuum. (0.285 g, yield = 85%). Spectroscopic data are as above.

[Re(N)Cl$_2$(PPh$_3$)$_2$], 4. To an ethanolic solution (5 mL) of [NH$_4$][ReO$_4$] (0.100 g, 0.373 mmol) containing 1 mL of 12 M HCl were added dropwise H_3L^3 (0.102 g, 0.746 mmol) and triphenylphosphine (0.390 g, 1.491 mmol) in ethanol (30 mL), and the solution was kept at 60 °C for 3 h. The resulting red-brick precipitate was collected by filtration, washed with ethanol, and dried under vacuum (0.202 g, yield = 68%). The spectroscopic data correspond to those reported in the literature for complex **4.**[17]

X-ray Crystallographic Study. Single crystals of complexes **1** and **3** were grown by slow evaporation of a petroleum ether/dichloromethane solutions. Pertinent crystallographic data and structure refinement for both compounds are summarized in Table 1, and the relevant bond lengths and angles in Table 2. The data sets of **1** and **3** were collected at room temperature on CAD4 Nonius and Philips PW 1100 automatic diffractometers, respectively, with graphite-monochromatized Mo Kα radiation. The cell parameters were obtained by fitting a set of 25 high-angle reflections. After Lorentz, polarization, and absorption corrections (ψ-scan method), the structures were solved using the SHELXS computer program[18] and refined with SHELXL-97[19] by the full-matrix least-squares techniques based on F^2. Atomic scattering factors were obtained from the *International Tables for X-ray Crystallography*, and the figures were performed with the ORTEP II program.[20]

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Table 2. Selected Bond Distances (Å) and Angles (deg) for **1** and **3**

	1	
	A	B
Re−S(1)	2.353(2)	2.348(2)
Re−S(3)	2.538(2)	2.541(2)
Re−N(1)	2.114(5)	2.103(5)
Re−N(3)	1.764(5)	1.769(5)
Re−P(1)	2.414(2)	2.426(2)
Re−O(1)	2.002(4)	1.995(4)
N(1)−N(2)	1.416(7)	1.426(6)
N(3)−N(4)	1.311(6)	1.312(6)
S(1)−Re−S(3)	168.6(1)	170.1(1)
S(1)−Re−N(1)	79.3(1)	79.3(1)
S(3)−Re−N(3)	72.9(2)	72.8(2)
N(1)−Re−P(1)	159.5(1)	166.1(1)
N(1)−Re−O(1)	80.6(2)	81.1(2)
N(3)−Re−O(1)	154.9(2)	155.7(2)
Re−S(1)−C(9)	95.3(2)	94.8(2)
Re−S(3)−C(11)	94.9(2)	94.8(2)
Re−N(1)−N(2)	116.9(4)	117.3(3)
Re−N(1)−C(7)	128.0(5)	128.3(4)
Re−N(3)−N(4)	143.3(4)	143.5(4)
Re−O(1)−C(1)	122.0(4)	123.2(4)

	3		
Re−P(1)	2.513(6)	Cl(1)−Re−Cl(2)	98.4(2)
Re−P(2)	2.451(6)	P(1)−Re−P(2)	170.5(1)
Re−Cl(1)	2.312(3)	P(2)−Re−Cl(1)	90.7(2)
Re−Cl(2)	2.422(3)	P(1)−Re−Cl(2)	88.2(2)

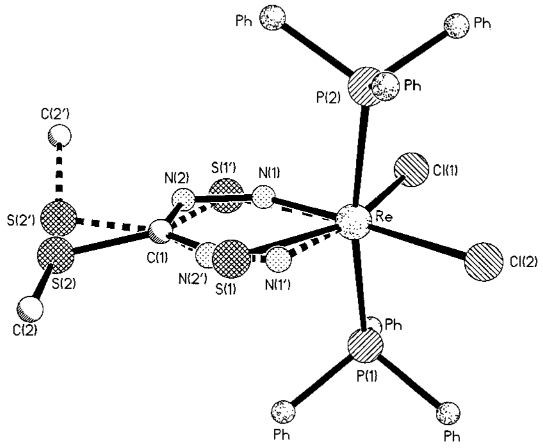


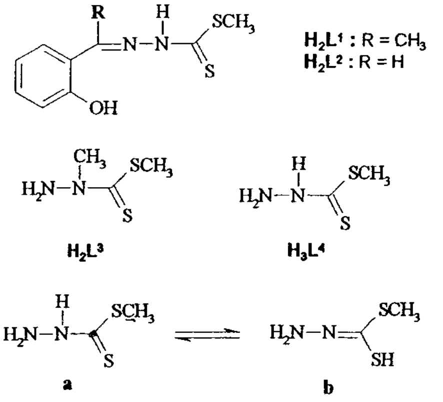
Figure 1. Two ligating modes of the η^2-hydrazido moiety in [Re(η^2-L^4)-Cl$_2$(PPh$_3$)$_2$], **3**.

A relevant anomaly was encountered in the refinement of **3**. Refinement of the non-hydrogen atoms converged with $R = 0.073$, and a Fourier-difference map at this stage revealed maxima in the vicinity of the hydrazido ligand, indicating a second complete image of the ligand. The orientation, position, and relative occupancy for it were refined, along with the parameters of the other atoms. The two alternative ligating modes (*i* and *ii*) (Figure 1) refined satisfactorily with occupancies of ca. 0.5; no significant matrix correlation was observed, and refinement converged at $R = 0.045$. Anisotropy was applied only to Re, Cl, and P atoms, and the phenyl rings were treated as rigid idealized hexagons. The maximum residual peak in the final difference map corresponded to 1.12 e Å^{-3}, 1.14 Å from rhenium.

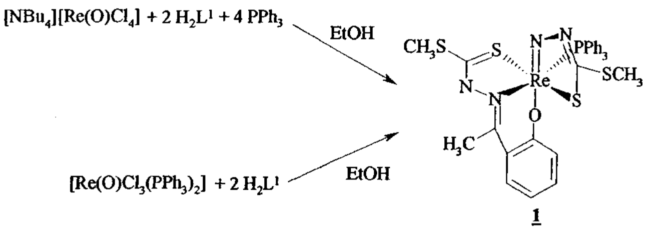
Results

Synthesis of Chelated Hydrazido−Re(V) Complexes. The Schiff base ligands H$_2$L^1 and H$_2$L^2 have been prepared from condensation of 2-hydroxyacetophenone or salicylaldehyde with dithiocarbazic acid methyl ester (H$_3$L^4). These potentially tridentate chelates as well as the related dithiocarbazic acid precursors undergo a tautomeric equilibrium in solution as shown in Scheme 1. Equimolar amounts of H$_2$L^n react with [Re(O)Cl$_4$]$^-$ giving the five-coordinate [Re(O)Cl(L^n)] complexes,[13] whereas the presence of triphenylphosphine in the coordination sphere of the [Re(O)Cl$_3$(PPh$_3$)$_2$] starting material induces the formation of the six-coordinate mixed-ligand [Re(O)Cl(L^n)(PPh$_3$)] complexes.[14] On the contrary, excess of H$_2$L^n react with monooxorhenium precursors in the presence of triphenylphosphine to afford the novel mixed hydrazido−Re(V) heterocomplexes [Re(η^2-L^4)(L^n)(PPh$_3$)], **1** and **2** (Scheme 2), in which the original oxo group has been abstracted and replaced by a multiple metal−nitrogen hydrazido bond.

Scheme 1



Scheme 2



Reaction of perrhenate with excess of H$_2$L^n and triphenylphosphine in acidic ethanolic solutions affords another chelated hydrazido species, the six-coordinate green complex [Re(η^2-L^4)Cl$_2$(PPh$_3$)$_2$], **3**. The same compound is obtained by adopting similar reaction conditions but replacing the Schiff base with the dithiocarbazic acid precursor H$_3$L.^{4} It is worth noting that the use of the *N*-methyl-substituted hydrazine H$_2$L^3 instead of H$_3$L^4 does not give hydrazido−Re(V) species under the conditions utilized above, the red-brick nitrido complex [Re(N)Cl$_2$(PPh$_3$)$_2$] being recovered as the resulting product.

Characterization of Chelated Hydrazido−Re(V) Complexes. Elemental analyses of complexes **1**−**4**, as given in the Experimental Section, are in good agreement with the proposed formulations. Compounds **1**−**3** show the [MH]$^+$ molecular ion peaks when subjected to FAB mass spectroscopy in the positive mode, with no significant fragmentation in the three cases. The IR spectra of all of the complexes do not show bands characteristic of the [Re≡O] stretching vibration, while peaks attributable to coordinated triphen-

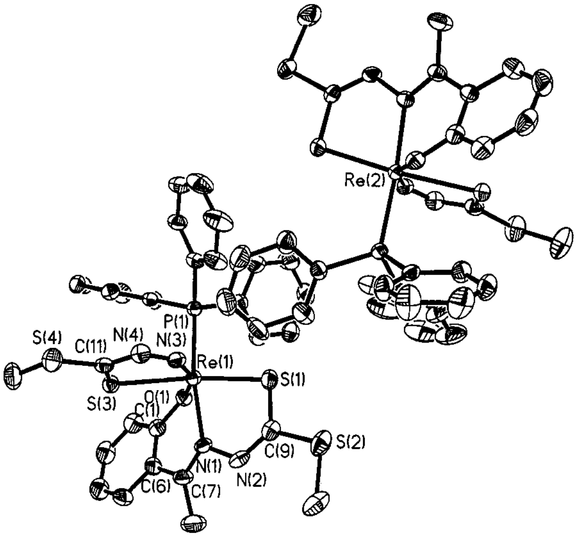


Figure 2. ORTEP view of molecules A and B of [Re(η^2-L^4)(L^1)(PPh$_3$)$_2$], **1**. Ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity, and the atom numbering scheme only for A is reported.

ylphosphine appear around 1100 and 700 cm^{-1}. Moreover, the absence of significant bands over 3000 cm^{-1} in complexes **1** and **2** indicates coordination of the Schiff base in the classical tridentate fashion as dianionic SNO chelate,[11,13] via charged phenolate oxygen, neutral imine nitrogen, and charged thiolate sulfur.

Quite narrow profiles, characteristic of diamagnetic species, are shown in ^{1}H, ^{13}C, and ^{31}P spectra of complexes **1**−**3**. Upon coordination the ^{31}P phosphine signal moves downfield from −5.0 ppm in the free ligand to 13.8 and 15.1 ppm in complexes **1** and **2**, respectively. A singlet at −6.2 ppm is observed in complex **3** as well, indicating magnetic equivalence of the two phosphine phosphorus. Proton and carbon spectra of complexes **1** and **2** show peaks characteristic of coordinated Schiff bases and triphenylphosphine.[14] However, an extra proton signal attributable to a methyl group and two dithiocarbazate carbon signals appear in the spectra. These features are consistent with the coordination of an additional ligand, which may be generated in situ by the cleavage of the Schiff base carboimine function.

To confirm this hypothesis we have grown crystals of complex **1** to perform the X-ray diffraction analysis. The unique portion of the unit cell comprises two molecules (A and B), and as illustrated in Figure 2, each neutral [Re(η^2-L^4)(L^1)(PPh$_3$)] molecule displays a distorted octahedral environment around the rhenium atom. Since A and B are practically superimposable (rms of 0.08 Å when the fitting is performed on the 13 atoms nearest to Re) in the discussion the mean values for bond lengths and angles are reported. An intact Schiff base ligand acts as classical tridentate donor in a facial manner having the triphenylphosphine phosphorus trans to its central imine nitrogen. The coordination is completed by a chelated hydrazido-*N,S* fragment placing the N(3) atom trans to the phenolate oxygen and the S(2) atom trans to the thiolate sulfur. Major distortions from the ideal octahedron arise from the chemical unequivalence of the three chelate rings and from significant steric interactions with the bulky triphenylphosphine molecule. Hence, the O(1)−Re═N(3) and S(1)−Re−S(3) angles deviate significantly from linearity (155.3(2) and 169.3(1)°, respectively), and the η^2-hydrazido N(3)−Re−S(3) bite angle is constrained at 72.9(2)°. The Re atom is displaced by 0.11 Å from the mean plane defined by N(1), S(1), S(3), and P(1), pointing toward the imine N(3) atom. According to the different coordination mode (facial vs meridional) and the increased coordination number (6 vs 5), the metal−donor distances of the tridentate Schiff base are slightly lengthened (by 0.05−0.10 Å) in complex **1** compared to those exhibited by less crowded [Re(O)I(L^1)].[14] The Re−N(1) distance of 2.109(5) Å attests a single bond in contrast with the Re−N(3) bond distance of 1.766(5) Å, which indicates strong multiple bond character (vide infra). The five-membered chelate ring of the η^2-hydrazido moiety is essentially planar (perfectly planar in A, deviation within 0.03 Å in B). Despite the scattered bond angles (between 72.8 and 143.5°) the ring reaches the planarity and the sum of the internal angles approaches 540°. The hydrazido ring is perpendicular to the mean plane of the other five-membered ring Re(1)N(1)N(2)C(9)S(1) and to the six-membered one Re(1)N(1)C(7)C(6)C(1)O(1), dihedral angles being 90.8 and 95.5°, respectively.

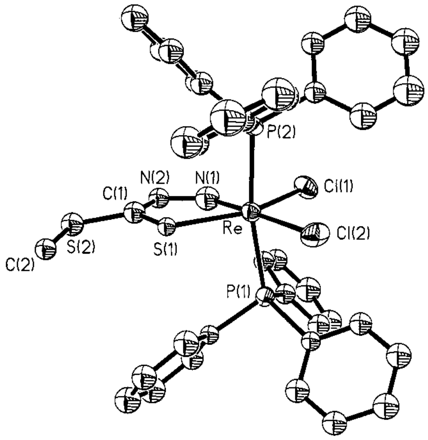


Figure 3. ORTEP representation of [Re(η^2-L^4)Cl$_2$(PPh$_3$)$_2$], **3**. Ellipsoids are drawn at the 40% probability level, and for clarity, only one liganting mode is shown.

For **3**, the solution of the structure was relatively difficult due to the two ligating modes of the hydrazido ligand (see Experimental Section and Figure 1) and, consequently, only the metrical data for the remaining portion of the complex are quoted in Table 2. In any case, in both the orientations *i* and *ii*, the five-membered ring is substantially planar with the N−Re−S bite angle of 73(1)°. As outlined in Figure 3, the coordination octahedron is somewhat distorted, as evidenced by the dihedral angle between the triangular faces Cl(1)P(1)N(1) and S(1)P(2)Cl(2) (16.3 and 18.0° in *i* and *ii*, respectively).

Discussion

The determination of the metal oxidation state in hydrazido-type technetium and rhenium compounds is not always straightforward,[21] formal oxidation states from 1+

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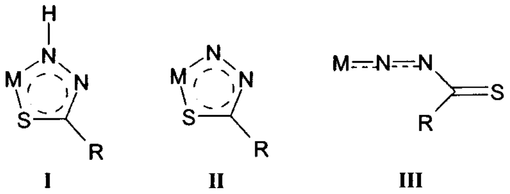
[21] Nicholson, T.; Davison, A.; Jones, A. *Inorg. Chim. Acta* **1990**, *168*, 227.

Chart 1



to 5+ being reported.[4b,c] This uncertainty is mainly related with the degree of protonation at the α and/or β nitrogens, which, in turn, determines various M−NN− arrangements and, eventually, the rich geometrical versatility of these ligands. For example, as shown in Chart 1, (thiobenzoyl)-hydrazine-type ligands may adopt the η^2-diazene I, the η^2-hydrazido II, and the η^1-diazenido coordination mode III,[22] with the pertinent metal−nitrogen distances moving from 1.76 Å (form II) to 2.16 Å (form I).

The disorder at the hydrazido moiety of complex **3** (vide supra) does not allow one to use the structural parameters for a comparison with those exhibited by similar compounds of formula [M(η^2-hydrazido)$Cl_2(PPh_3)_2$] (M = Tc, Re),[23−25] cumulated in Table 3. However, the related complex **1** contains an identical not disordered η^2-hydrazido group, whose parameters can in turn be utilized for a detailed correlation. Its multiple Re−N bond distance of 1.763(5) Å falls in the narrow range exhibited by isosterical η^2-hydrazido(3−) compounds (Table 3). Although their chelated moieties hold different anchoring donors (S or N or O), the bite angles are homogeneous in the restricted 70−75° region as well. In these compounds extended delocalization of the electronic density is warranted by the planar five-membered ring through the π-network system. Also η^1-hydrazido(3−) groups, frequently referred to as metal−diazenido units, show multiple Tc−N bond distances in the identical 1.76−1.78 Å narrow range[26−29] (Table 3). The strict analogy in the M−N bond distances along with the diamagnetism shown in solution for both linear and chelated hydrazido(3−) complexes are in agreement with the metal exhibiting a low-spin d^2 configuration typical of Tc(V) and Re(V) species.[4]

As previously mentioned, the chelated hydrazido(3−) moiety in [M(η^2-hydrazido)$Cl_2(PPh_3)_2$] complexes can hold different anchoring donors. The stability of the complexes depends on the chelate donor set according to the series *N*,*S* ≫ *N*,*N* ≅ *N*,*O*. In fact, attempts to open and/or cleave the N−N group of the η^2-*S*,*N*-hydrazido(3−) moiety of the rhenium complex **3** always failed, even under drastic conditions. In fact, after prolonged reflux in ethanol at pH = 1 complex **3** was recovered intact (see route B of Scheme 3). Analogously, reaction with diethyldithiocarbamate sodium salt (Na(dedc)), under the conditions utilized to convert the chelated hydrazido complex [Re(η^2-*N*,*O*-hydrazido)$Cl_2(PPh_3)_2$] into the linear hydrazido [Re(η^1-*N*-hydrazido)$(dedc)_2(PPh_3)$] species,[28] gives complex **3** unmodified. It has to be noted that chelated hydrazido [Re(η^2-*N*,*O*-hydrazido)$Cl_2(PPh_3)_2$]-type complexes represent ideal starting materials to produce linear diazenido derivatives,[30] confirming the hemilability of *N*,*O*-chelated moieties. Similar hemilability, followed by rapid N−N cleavage to yield the terminal $[Tc(N)]^{2+}$ group under relatively mild conditions (refluxing dichloromethane), was observed in the related [Tc(η^2-*N*,*N*-hydralazino)$Cl_2(PPh_3)_2$] complex.[23]

The substitution inert complex **3** crumbles only by removing the π-electron delocalization at the η^2-*S*,*N*-hydrazido(3−) moiety, i.e by insertion of a methyl group at the β-hydrazine nitrogen, as in H_2L^3. As depicted in route A of Scheme 3, the chelated hydrazido adduct [Re(η^2-hyd-L^3)$Cl_2(PPh_3)_2]^+$ may form, but it is rapidly converted through N−N cleavage into [Re(N)$Cl_2(PPh_3)_2$]. A similar behavior was previously reported in related [Re(η^2-*N*,*S*-thiosemicarbazido)$Cl_2(PPh_3)_2$] compounds,[31] in which a flipping proton delocalized over the hydrazido ring partially removes π-electron circulation, thereby promoting cleavage of the N−N bond to give eventually the [Re(N)$Cl_2(PPh_3)_2$] species.

On the basis of the above arguments, we can say that perrhenate can be converted into nitrido−Re(V) species through intermediate η^2-hydrazido(3−) rhenium(V) derivatives, according to the simplified reaction pathway depicted in Scheme 4. Since the reduction of perrhenate operated by tertiary phosphines in acid media is a consolidated route of synthesis of monooxo−Re(V) compounds[32] and these species can be also converted into η^2-hydrazido(3−)−Re(V) ones by oxo abstraction operated by PPh_3 or by condensation-type reactions in absence of PPh_3,[33] monooxo−Re(V) derivatives may also represent other intermediate species in the process.

The mechanism underlying the conversion of hydrazido-(3−) into nitridorhenium and technetium compounds has been proposed by other authors.[31,33] Imido−technetium adducts have been postulated,[33] and imido−hydrazido(1−)−rhenium derivatives have been isolated[31] as intermediates in the process. Thus, it is reasonable to apply the same reaction pathway of Scheme 4 to the second-row congener technetium. However, the faster kinetic of substitution at the technetium center[3] does not allow easy isolation of η^2-hydrazido(3−)−Tc(V) intermediate species, which quickly rearrange to the more stable nitrido species. This drawback at macroscopic level becomes an advantage at the nca level,

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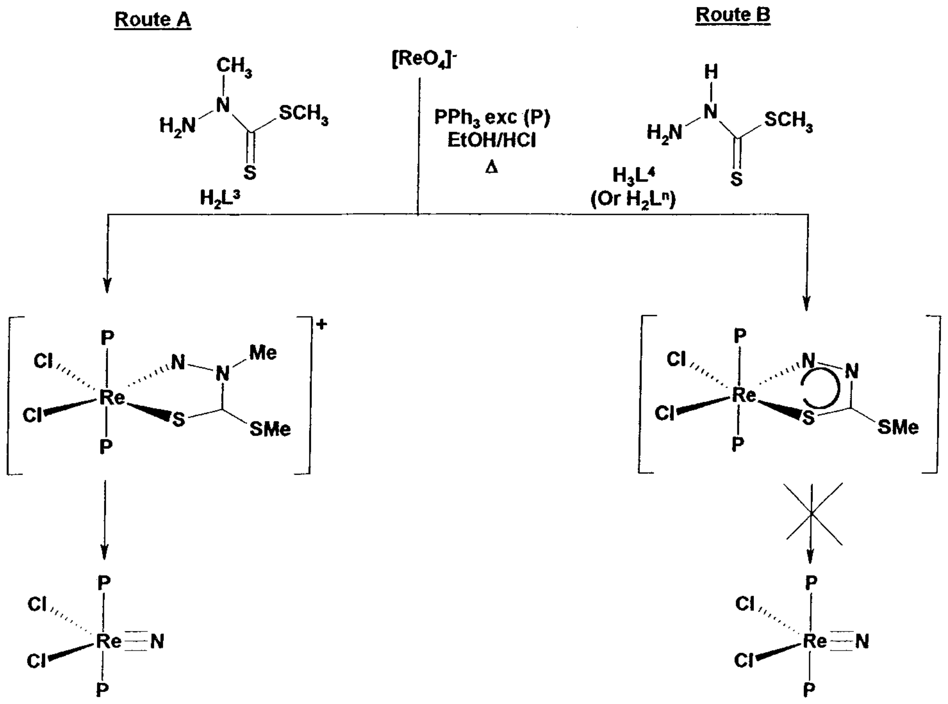
Table 3. Relevant Structural Parameters for Selected η^2-Hydrazido(3−)- and η^1-Hydrazido(3−)-Containing Technetium and Rhenium Complexes

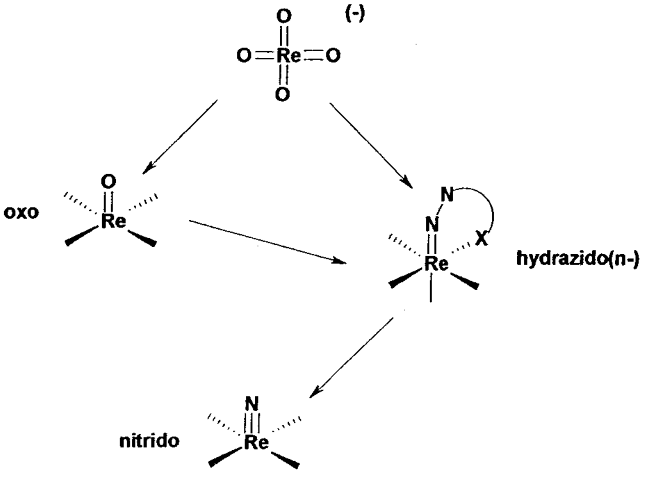
compd	M∠η^2−N−N--, Å	M∠η^2−X−C−, Å (X, anchor donor)	M∠η^1-*N*,*N*-R, Å	X−M−N, deg	ref
$[Tc(\eta^2\text{-}N^\frown N)Cl_2(PPh_3)_2]^a$	1.77(1)	2.15(1) (N)		69.8(4)	23
$[Re(\eta^2\text{-}N^\frown O)Cl_2(PPh_3)_2]^b$	1.77(1)	2.12(1) (O)		71.0(5)	24
$[Re(\eta^2\text{-}N^\frown S)(L^1)(PPh_3)]$, **1**[c]	1.763(5)	2.538(2) (S)		72.9(2)	this work
$[Re(\eta^2\text{-}N^\frown P)Cl_2(\eta^2\text{-}P^\frown NH)]^d$	1.780(7)	2.492(2) (P)		75.2(2)	25
$[Re(\eta^2\text{-}N^\frown S)Cl_2(PPh_3)_2]$, **3**[c]				73(1)	this work
$[Tc(\eta^2\text{-}HN^\frown N)(\eta^1\text{-}NNR)(S^\frown N)(SR)]^e$	1.985(9)	2.150(7) (N)	1.767(9)	74.5(4)	26
$[Re(\eta^2\text{-}HN^\frown N)(\eta^1\text{-}NNR)(S^\frown N)(SR)]^e$	1.956(6)	2.127(5) (N)	1.766(6)	73.3(3)	26
$[Tc(\eta^1\text{-}NNPh\text{-}Cl)(salen)(PPh3)]^f$			1.764(8)		27
$[Tc(\eta^1\text{-}NNPh\text{-}Cl)(dmdc)_2(PPh_3)]^g$			1.763(3)		28
$[Tc(\eta^1\text{-}NNPh)Br_2(PMe_2Ph)_3]^h$			1.77(1)		29

[a] $(\eta^2\text{-}N^\frown N)$ = η^2-hydralazine ($C_8H_5N_4$). [b] $(\eta^2\text{-}N^\frown O)$ = η^2-acetylhydrazide. [c] $(\eta^2\text{-}N^\frown S)$ = L^4. [d] $(\eta^2\text{-}N^\frown P)$ = η^2-(2-diphenylphosphino)benzeneamide. [e] $(\eta^2\text{-}HN^\frown N)$ = η^2-hydrazinonicotinamide; $(\eta^1$-NNR) = η^1-hydrazinonicotinamide; $(S^\frown N)$ = η^2-pyridine-2-thiolate; (SR) = η^1-pyridine-2-thiolate. [f] $(\eta^1$-NNPh-Cl) = η^1-*p*-Cl-phenyldiazenido; salen = *N*,*N*′-ethylenebis(salicylideneimine). [g] dmdc = dimethyldithiocarbamate. [h] $(\eta^1$-NNPh) = η^1-phenyldiazenido.

Scheme 3



Scheme 4



promoting the clean formation of the [^{99m}Tc(N)] group. In this connection, the substitution of the *N*,*S*-dithiocarbazic acid (utilized in early preparations as the nitrogen source for the formation of the [^{99m}Tc(N)] core at nca level) with the bis-(*N*,*O*-hydrazine) succinic acid in the kit formulation, initially justified by experimental evidence only, has now a chemical explanation. This study demonstrates that the use of *N*,*S*-dithiocarbazic ligands favors the obtainment of substitution-inert intermediates such as chelated hydrazido−Re(V) species. In the case of technetium, similar adducts likely make more difficult the clean formation of the [^{99m}Tc(N)] group. On the contrary, the hemilability of the *N*,*O*-succinic chelate, followed by rapid N−N cleavage, appears to be the key factor for the easy formation of the [^{99m}Tc(N)] moiety starting from pertechnetate.

Supporting Information Available: X-ray cystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. Supplementary data for complexes **1** and **3** have been deposited at the Cambridge Crystallographic Data Centre. Copies of this information are available free of charge on request from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk), quoting the deposition numbers CCDC 140023 and 172547 for complex **1** and **3**, respectively.

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