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Bent Nitrene Ligands Attached to Rhenium. Syntheses and Low-Temperature Structures of *trans*-$Re(OC_2H_5)(p\text{-}NC_6H_4CH_3)(S_2CN(CH_3)_2)_2$ and Related Compounds

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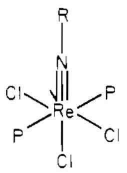
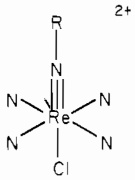
Received June 23, 1981

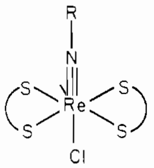
New rhenium nitrene complexes, $Re(NR)(S_2CNR'_2)_3$ and $Re(OR'')(NR)(S_2CNR'_2)_2$ (R = CH_3, C_6H_5, $p\text{-}CH_3C_6H_4$; R′ = CH_3, C_2H_5; R″ = CH_3, C_2H_5), have been prepared from $ReCl(NR)(S_2CNR'_2)_2$ by the action of $TlS_2CNR'_2$, $(CH_3)_3SiSC(S)NR'_2$, or NaOR″. Infrared and ^1H NMR spectroscopic data suggest that (1) the tris(dithiocarbamate) complexes possess cis, six-coordinate geometries with one monodentate dithiocarbamate group and that (2) *two* trans isomers of the alkoxy complexes are present in solution. Brown solvent-free crystals of $Re(OC_2H_5)(p\text{-}NC_6H_4CH_3)(S_2CN(CH_3)_2)_2$ were grown from methylene chloride–ethanol. The structure of the complex was determined at −175 °C with use of X-ray diffraction techniques. The complex is monomeric and six-coordinate and has a distorted, trans, octahedral geometry. The dithiocarbamate ligands have nearly identical structural parameters with S–Re–S bite angles of 71.97 (6) and 71.67 (6)°; the Re atom is 0.135 (3) Å out of the plane of the four sulfur atoms toward the nitrogen atom of the nitrene ligand. The nitrene ligand is significantly bent at the nitrogen atom (Re–N(3)–C(31) = 155.5 (5)°) with an abnormally long Re–N(3) distance of 1.745 (5) Å. The ethoxy ligand is also bent at the oxygen atom in the same plane as the nitrene with Re–O–C(41) = 131.7 (4)° and Re–O = 1.948 (4) Å. The title complex crystallizes in space group $P2_1/c$ with a = 9.190 (3) Å, b = 17.459 (4) Å, c = 14.082 (4) Å, β = 116.90 (2)°, and Z = 4. On the basis of 3315 unique reflections with $F_o^2 > 3\sigma(F_o^2)$, the structure was refined with use of full-matrix, least-squares methods to $R(F)$ = 0.035 and $R_w(F)$ = 0.043.

Introduction

Six-coordinate complexes of rhenium containing the linear Re≡N—R unit are well-known and have been extensively studied.[1] Complexes of this type, $ReCl_3(NR)(PPh_3)_2$, $ReCl(NR)(NH_2CH_3)_4^{2+}$, and $ReCl(NR)(S_2CNEt_2)_2$

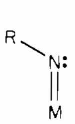






have been prepared from a variety of precursors and their structures are either known from X-ray diffraction studies or can be inferred with confidence from spectroscopic data.[2-4] These complexes seem to be quite stable and forcing conditions are usually required to produce reactions at the nitrogen atom of the tightly bound nitrene ligand.[5,17,29]

Oxo analogues of the above rhenium nitrene complexes are known ($ReOCl_3(PPh_3)_2$,[2] $ReOCl_3(NC_5H_5)_2$,[6] $ReOCl(S_2CNEt_2)_2$[4]) as well as their oxo–alkoxy analogues ($ReOCl_2(OEt)(PPh_3)_2$,[2] $ReO(OH)(NH_2CH_3)_4^{2+}$, $ReOCl_2(OH)(NC_5H_5)_2$,[7] $ReO(OMe)(S_2CNEt_2)_2$[8]). Trends in Re–O stretching frequencies suggest that the Re–O bond is weakened when an alkoxy group replaces a chloride ligand. Such weakening can be understood in terms of a competitive π donation of electrons from the oxo and alkoxy ligands. Our interest in these rhenium oxo and nitrene complexes stems from a desire to weaken and lengthen the short Re–NR bond in order to determine if enhanced reactivity would result. To this end, we have set out to prepare nitrene complexes of rhenium whose maximum electron counts (EAN rule) exceed 18 and whose ligand geometry would approach that shown in I with the −NR ligand acting as a two-electron-donor ligand instead of the more common circumstance in which the −NR ligand is linear and acts as a four-electron donor (II).



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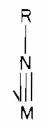

II

We now report the syntheses of new compounds of the types $Re(NR)(S_2CNR'_2)_3$ and $Re(OR'')(NR)(S_2CNR'_2)_2$ starting from $ReCl(NR)(S_2CNR'_2)_2$ (R = CH_3, C_6H_5, $p\text{-}CH_3C_6H_4$; R′ = CH_3, C_2H_5; R″ = CH_3, C_2H_5). The tris(dithiocarbamate) complexes each contain one monodentate dithiocarbamate ligand and probably nearly linear −NR ligands; however, the crystal structure of $Re(OEt)(NTo)(S_2CNMe_2)_2$ (To = *p*-tolyl) shows the presence of a bent nitrene ligand with an abnormally long Re–N distance. This is the second structurally characterized example of a bent nitrene ligand attached to Re.[9-11]

Experimental Section

Although most of the new Re complexes were not very air sensitive, all reactions were carried out under an inert (N_2) atmosphere with use of dry, freshly distilled solvents. Infrared spectra were measured in Fluorolube S-30 or Nujol mulls with a Perkin-Elmer 283 spectrometer and were calibrated with use of a polystyrene film. ^1H NMR spectra were measured in $CDCl_3$ or CD_2Cl_2 at the specified temperatures, with Varian Associates HR-220 and XL-100 spectrometers. Spectra were calibrated with use of internal tetramethylsilane. Elemental analyses were performed by Midwest Microlab, Ltd., Indianapolis, IN. X-ray data collection was carried out with use of a locally constructed diffractometer consisting of a Picker goniostat interfaced to a Texas Instruments TI980B computer; the attached low-temperature device has been described.[12] Rhenium metal and Re_2O_7 were obtained from Cleveland Refractory Metal Co., Solon (Cleveland), OH. Aniline-^{15}N (99% labeled) was purchased from Stohler Isotope Chemicals, Waltham, MA. Sodium dithiocarbamate salts were prepared from anhydrous secondary amines, CS_2, and NaOH in absolute ethanol and recrystallized from $EtOH–Et_2O$; the

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anhydrous forms of the sodium salts were obtained by heating them under vacuum (0.1 torr) at 80–100 °C for 1 week. Thallium dithiocarbamate salts were prepared from the sodium salts and $TlNO_3$ in water; the yellow Tl salts were dried and carefully recrystallized from hot benzene, toluene, or *p*-chlorotoluene. The moisture-sensitive trimethylsilyl dithiocarbamate compounds were prepared by the literature method[13] and vacuum distilled prior to use. Tetraarylphosphoranimines, $Ph_3P{=}NAr$, were conveniently prepared from triphenylphosphine and aromatic azides[14] (both ^{14}N and ^{15}N), which in turn were prepared from arenediazonium salts and NaN_3 in water. $ReCl_3(NAr)(PPh_3)_2$ was prepared by a modification of the literature method[15] with use of $ReOCl_3(PPh_3)_2$ and $Ph_3P{=}N(Ar)$; this method is superior to those that use ArNCO,[16] ArNSO,[5] and $ArNH_2$.[2] $ReCl_3(NCH_3)(PPh_3)_2$ was prepared with use of 1,2-dimethylhydrazine.[17] The $ReCl(NR)(S_2CNR'_2)_2$ complexes were prepared from $ReCl_3(NR)(PPh_3)_2$ and the respective thiuram disulfide.[4] $ReOCl_3(PPh_3)_2$ was prepared in acidic ethanol according to the literature method, starting with Re_2O_7 instead of $NaReO_4$.[2] Brown crystals of the title complex were grown by slow evaporation of a CH_2Cl_2–C_2H_5OH solution (dry solvents).

Trichloro(*p*-tolylnitrene)bis(triphenylphosphine)rhenium. A sample of $ReOCl_3(PPh_3)_2$ (10.00 g, 12.0 mmol) and p-$CH_3C_6H_4N{=}PPh_3$ (4.41 g, 12.0 mmol) was refluxed for 10 min in 200 mL of benzene. The cooled solution was reduced in volume to 30 mL, which caused the precipitation of the nicely crystalline, green product. The mixture was filtered, and the solid was washed with acetone and then dried under vacuum. Acetone (150 mL) was added to the filtrate to precipitate out a second crop of green crystals to bring the total yield to 9.81 g (88%) of the complex. The product could be conveniently recrystallized from CH_2Cl_2–EtOH.

Trichloro(phenylnitrene)bis(triphenylphosphine)rhenium was analogously prepared in 89% yield. This same complex was prepared on a $^1/_{20}$th scale with ^{15}N isotopic substituion (99%) on the nitrene ligand. The $^{31}P\{^1H\}$ NMR spectrum of $ReCl_3(^{15}NPh)(PPh_3)_2$ in CH_2Cl_2 at ambient temperature showed a doublet ($^2J_{PN}$ = 5 Hz) at δ −19.7 with respect to external 85% H_3PO_4; the spectrum of the unlabeled compound showed a singlet in the same position.

Chlorobis(dimethyldithiocarbamato)(*p*-tolylnitrene)rhenium. (a) Four grams of $ReCl_3(NTo)(PPh_3)_2$ (4.3 mmol) and tetramethylthiuram disulfide (2.6 g, 10.8 mmol) were added to 100 mL of dry acetone, and the mixture was refluxed for 1 h. The green solution was then reduced in volume to 25 mL and cooled to 10 °C in order to crystallize the green product. The mixture was filtered, and the product was washed with acetone and hexane to yield 2.05 g (83%) of the complex. **Chlorobis(dimethyldithiocarbamato)(phenylnitrene)rhenium** (84% yield), **chlorobis(diethyldithiocarbamato)(*p*-tolylnitrene)rhenium** (80% yield), and **chlorobis(dimethyldithiocarbamato)(methylnitrene)rhenium** (77% yield) were analogously prepared. $ReCl(^{15}NPh)(S_2CNMe_2)_2$ was also prepared on a $^1/_{10}$th scale.

(b) $Re(NTo)(S_2CNMe_2)_3$ (0.60 g, 0.92 mmol) was added to 50 mL of benzene, and the solution was heated to about 75 °C. Then anhydrous HCl gas was bubbled through the solution until there was a complete color change (2–5 min). The HCl addition was terminated, and the mixture was briefly refluxed (2–3 min). The volume of the cooled reaction mixture was reduced to about 20 mL, and it was filtered to give a green crystalline product, which was washed with hexane and dried to yield 0.48 g (92%) of the complex.

(c) Either 0.57 g of $[Re(NTo)(S_2CNMe_2)_2]_2O$ or 0.60 g of $Re(OEt)(NTo)(S_2CNMe_2)_2$ was dissolved in 60 mL of methylene chloride, and then 10 mL absolute ethanol was added. Anhydrous HCl gas was slowly bubbled through the stirring solution at room temperature for 5–10 min. The mixture was gently refluxed for 5 min, and the volume was reduced by half. Finally 40 mL of absolute ethanol was added to precipitate the product as green crystals. The mixture was filtered, and the product was washed with acetone and hexane and dried to yield about 0.5 g (80–86%) of the product, regardless of starting material.

***cis*-Tris(dimethyldithiocarbamato)(*p*-tolylnitrene)rhenium.** (a) To a solution of $ReCl_3(NTo)(PPh_3)_2$ (2.00 g, 2.17 mmol) in 50 mL of benzene was added trimethylsilyl dimethyldithiocarbamate (2.5 mL). The mixture was refluxed for 10 min, and the color turned deep brown. The solution was then reduced in volume to 5 mL, and then 15 mL of dry acetone was added to complete precipitation of the dark green product. This product was filtered off, washed with acetone and hexane, and dried to give 1.35 g (96%) of the complex. **Tris(dimethyldithiocarbamato)(phenylnitrene)rhenium** (91% yield), **tris(diethyldithiocarbamato)(*p*-tolylnitrene)rhenium** (79% yield), and **tris(diethyldithiocarbamato)(phenylnitrene)rhenium** (82% yield) were all analogously prepared in the stated yields.

(b) $ReCl_3(NTo)(PPh_3)_2$ (2.00 g, 2.17 mmol) and thallium dimethyldithiocarbamate (2.20 g, 6.79 mmol) were added to 100 mL of benzene, and the mixture was refluxed for 10 min; TlCl precipitated, and the solution was deep brown. The mixture was cooled and then filtered to remove TlCl. The brown solution was handled as in method a to yield 1.30 g (92%) of the compound. $Re(NTo)(S_2CNEt_2)_3$ was analogously prepared in 78% yield.

(c) To a refluxing solution of $ReCl(NTo)(S_2CNMe_2)_2$ (0.60 g, 1.1 mmol) in 30 mL of dry benzene was added trimethylsilyl dimethyldithiocarbamate (0.40 mL). The solution immediately turned dark brown and was refluxed for an additional 5 min. The cooled solution was reduced in volume to 5 mL, and dry acetone was added to precipitate dark green crystals of the complex. The mixture was filtered and the product washed with acetone and hexane to yield 0.57 g (83%) of the complex. $Re(NTo)(S_2CNEt_2)_3$ was analogously prepared in 80% yield.

(d) $Re(NTo)(OEt)(S_2CNMe_2)_2$ (0.40 g, 0.69 mmol) and trimethylsilyl dimethyldithiocarbamate (0.30 mL) were added to 25 mL of benzene, and the mixture was refluxed under nitrogen for 5 min. The volume of solution was then reduced to 5 mL, and dry acetone was added to complete precipitation of the product. The mixture was filtered, washed, and dried as before to yield 0.43 g (95%) of the complex.

(e) To a mixture of $[Re(NTo)(S_2CNMe_2)_2]_2O$ (0.50 g, 0.46 mmol) in 50 mL of dry methylene chloride was added trimethylsilyl dimethyldithiocarbamate (0.40 mL), and the mixture was stirred at room temperature under nitrogen for 10 min to produce a homogeneous brown solution. The volume of the solution was then reduced to 5 mL, and dry acetone was added to precipitate the green product. The mixture was filtered, and the product was washed with acetone and hexane to afford 0.56 g (93%) of the complex.

(f) To a mixture of $ReCl_3(NTo)(PPh_3)_2$ (1.00 g, 1.08 mmol) in dry acetone (100 mL) was added *anhydrous* NaS_2CNMe_2 (0.9 g, 6.3 mmol). The mixture was refluxed for 30 min, and the solution was then reduced in volume to 15 mL in order to precipitate the crude green product. The product was carefully recrystallized from dry CH_2Cl_2–Me_2CO to remove NaCl and traces of NaS_2CNMe_2 to afford 0.60 g (85%) of the pure complex.

***trans*-Ethoxybis(dimethyldithiocarbamato)(*p*-tolylnitrene)rhenium.** (a) To a suspension of $ReCl(NTo)(S_2CNMe_2)_2$ (0.50 g, 0.88 mmol) in 20 mL of absolute ethanol was added a sodium ethoxide solution (61 mg of freshly cut Na metal in 5 mL of absolute ethanol), and the mixture was refluxed for 2 min, causing the precipitation of a brown, microcrystalline product. The mixture was then filtered and the product washed with ethanol and hexane. The brown product was recrystallized from CH_2Cl_2–EtOH and dried to yield 0.38 g (75%) of brown crystals. **Ethoxybis(dimethyldithiocarbamato)(phenylnitrene)rhenium** (74% yield) and **ethoxybis(diethyldithiocarbamato)(*p*-tolylnitrene)rhenium** (65% yield) were analogously prepared. By extending refluxing time to 5 min and using absolute methanol instead of absolute ethanol, **methoxybis(dimethyldithiocarbamato)(*p*-tolylnitrene)rhenium** (93% yield) and **methoxybis(diethyldithiocarbamato)(*p*-tolylnitrene)rhenium** (89% yield) were similarly prepared.

(b) $Re(NTo)(S_2CNMe_2)_3$ (0.70 g, 1.08 mmol) was added to 40 mL of absolute ethanol, and to this mixture was added a sodium ethoxide solution (31 mg of freshly cut Na metal in 5 mL of absolute ethanol). The mixture was refluxed for 2 min, cooled, and filtered. The product was washed, dried, and recrystallized as before to yield 0.38 g (61%) of the complex. This reaction proceeded smoothly in the absence of added NaOEt but required 15 min of refluxing.

(c) $[Re(NTo)(S_2CNMe_2)_2]_2O$ (0.40 g, 0.37 mmol) was dissolved in 100 mL of methylene chloride, and then absolute ethanol (30 mL) was added. The brown solution was stirred for 1 h and then reduced

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in volume to 10 mL. Crystals of the brown complex precipitated from solution. The product was filtered off, washed with ethanol and hexane, and dried to give 0.37 g (87%) of the complex.

(μ-Oxo)bis[bis(dimethyldithiocarbamato)(*p*-tolylnitrene)rhenium]. (a) To a mixture of $ReCl(NTo)(S_2CNMe_2)_2$ (0.50 g, 0.87 mmol) in acetone (25 mL) was added an aqueous sodium hydroxide solution (41 mg of freshly cut Na metal in 1 mL of H_2O), and the mixture was refluxed for 10 min. The mixture was cooled and filtered. The product was washed with water (to remove NaCl), acetone, and hexane. The product was then recrystallized from CH_2Cl_2–Me_2CO and dried to afford 0.44 g (93%) of the complex. The compounds $[Re(NPh)(S_2CNMe_2)_2]_2O$ and $[Re(NTo)(S_2CNEt_2)_2]_2O$ were similarly prepared in 89% and 71% yields, respectively.

(b) $Re(NTo)(S_2CNMe_2)_3$ (0.50 g, 0.77 mmol) was dissolved in 50 mL of acetone that contained 1% H_2O by volume. The solution was refluxed for 8 h, during which time the brown product gradually precipitated out of solution. The mixture was cooled and filtered and the product washed with acetone and hexane to yield 0.31 g (75%) of the compound. $[Re(NTo)(S_2CNEt_2)_2]_2O$ was similarly prepared in 69% yield; on the basis of color change, this reaction went to completion in less than 1 h.

(c) $Re(NTo)(OEt)(S_2CNMe_2)_2$ (0.50 g, 0.87 mmol) was dissolved in 50 mL of CH_2Cl_2 to which several drops of water had been added. The brown solution was stirred for 1 h and then reduced in volume to 10 mL. Dry acetone (50 mL) was added to precipitate the brown product, which was separated from the solution by filtration and washed with hexane to yield 0.41 g (88%) of the complex.

(μ-Oxo)bis[bis(dimethyldithiocarbamato)(methylnitrene)rhenium]. To a mixture of $ReCl(NMe)(S_2CNMe_2)_2$ (0.25 g, 0.51 mmol) in acetone (15 mL) was added an aqueous sodium hydroxide solution (24 mg of freshly cut Na metal in 1 mL of H_2O), and the mixture was refluxed for 15 min. The mixture was cooled and filtered, and the product was washed with water (to remove NaCl), acetone, and hexane. The product was recrystallized from CH_2Cl_2–hexane and dried to afford 0.19 g (80%) of the orange complex.

***trans*-Methoxybis(dimethyldithiocarbamato)(methylnitrene)rhenium.** To a suspension of $ReCl(NMe)(S_2CNMe_2)_2$ (0.25 g, 0.51 mmol) in 10 mL of absolute methanol was added a sodium methoxide solution (35 mg of freshly cut Na metal in 5 mL of methanol), and the mixture was refluxed for 2 min, precipitating the orange product. The mixture was filtered, and the product was washed with methanol and hexane. The product was recrystallized from CH_2Cl_2–MeOH and dried to yield 0.22 g (88%) of the orange complex.

***cis*-Tris(dimethyldithiocarbamato)(methylnitrene)rhenium.** A mixture of $ReCl(NMe)(S_2CNMe_2)_2$ (0.25 g, 0.51 mmol) and thallium dimethyldithiocarbamate (0.17 g, 0.51 mmol) in benzene (20 mL) was refluxed for 15 min. The solution turned dark green, and TlCl precipitated out. The mixture was cooled and then filtered to remove TlCl. The filtrate was reduced in volume to 2 mL, and dry acetone was slowly added to precipitate the green product. The product was washed with acetone and hexane and dried to afford 0.24 g (82%) of the complex.

Crystallographic Data. A small regularly shaped prismatic crystal of the Re complex was mounted on the diffractometer, and monoclinic symmetry was identified. After data collection was under way, extinctions (*h0l*, *l* odd; *0k0*, *k* odd) characteristic of space group C^5_{2h}-$P2_1/c$ were evident. On the basis of a least-squares analysis of the angular positions of 12 strong, machine-centered reflections in diverse regions of reciprocal space (20° < 2θ < 31°), accurate unit cell dimensions were determined. See Table I for pertinent crystal information and details of data collection and processing. The mosaic character of the crystal was good; ω scans of strong, low-angle reflections using a normal source were 0.21° (fwhm) wide. Background counts were measured at both ends of the scan range with both crystal and counter stationary. The intensities of three standard reflections were measured frequently during the course of data collection; they were found to be constant within counting errors. The intensity data were corrected for background effects and for Lorentz polarization effects. A comparison of F_o and F_c in the final refined model showed no need for an extinction correction. Although some difficulty was encountered due to two poorly defined crystal faces, an adequate absorption correction was performed by using Gaussian integration.[18] Only reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in least-squares calculations. The values of $\sigma(F_o)$ were estimated in the usual way with use of a value of 0.05 for *p*.[9] A total of 4151 unique reflections was collected out to 52° in 2θ. Owing to highly unsymmetric backgrounds, six reflections were discarded.

Table I. Summary of Crystallographic Data

compd	$Re(OC_2H_5)(NC_6H_4CH_3)(S_2CN(CH_3)_2)_2$
formula	$C_{15}H_{24}N_3OReS_4$
fw	576.83
a, Å	9.190 (3)
b, Å	17.459 (4)
c, Å	14.082 (3)
β, deg	116.90 (1)
V, Å^3	2015
Z	4
space group	C^5_{2h}-$P2_1/c$
cryst size, mm	0.14 × 0.16 × 0.22
cryst vol, mm^3	7.2×10^{-3}
cryst shape	monoclinic prism with {011} and {$\bar{1}$01} faces
radiation	Mo Kα, λ = 0.710 69 Å, monochromatized with highly oriented graphite
density, g/cm^3	1.901 (calcd) 1.88 (2) (obsd at 25 °C)
μ, cm^{-1}	65.17
range of transmission factors	0.329–0.501
temp, °C	−175 (4)
scan speed, deg/min	3.0
bkgd counting, s	10
2θ limits, deg	4.0–52.0
aperture	2.5 mm wide by 3.5 mm high
takeoff angle, deg	2.0
scan range, deg	1.1 below Kα_1 to 1.0 above Kα_2
no. of variables	217
unique data with ($I_0 > 3\sigma(I_0)$)	3315
error in observn of unit wt, e	1.41
R(*F*)	0.035
$R_w(F)$	0.043

Structure Refinement. The structure was solved with use of a Patterson synthesis to locate Re and difference Fourier syntheses to locate the remaining non-hydrogen atoms. The structure was refined with use of full-matrix, least-squares techniques.[19] During the refinements, the quantity minimized was $Q = \sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factor amplitudes and where the weights, *w*, are taken as $4F_o^2/\sigma^2(F_o^2)$. Atomic scattering factors were taken from the usual sources,[20] and the anomalous dispersion terms for Re and S were included in F_c. *All* 24 hydrogen atoms were clearly located in a difference Fourier synthesis after the non-hydrogen atoms had refined to convergence. The positions of the H atoms were idealized (C–H = 0.95 Å) with isotropic thermal parameters 1.0 Å^2 larger than the isotropic equivalents of the respective carbon atoms to which each was attached.

The final structure model converged with 24 anisotropic non-hydrogen atoms and 24 fixed hydrogen atoms to $R(F) = \sum||F_o| - |F_c||/\sum|F_o| = 0.035$ and $R_w(F) = (Q/\sum wF_o^2)^{1/2} = 0.043$. A statistical analysis of the trends of *Q* as a function of observed structure amplitudes, diffractometer setting angles, and Miller indices showed nothing unusual and indicated that the weighting scheme was adequate. A final difference Fourier synthesis showed two residual peaks (1.8 e/Å^3, 1.3 e/Å^3) near Re; the remaining residual peaks were less than 0.8 e/Å^3 in size. Of the reflections with $3\sigma(F_o^2) > F_o^2$, only two had $|F_c^2 - F_o^2| > 4\sigma(F_o^2)$.

The final positional and thermal parameters of the atoms appear in Tables II and S-III, and the root-mean-square amplitudes of vi-

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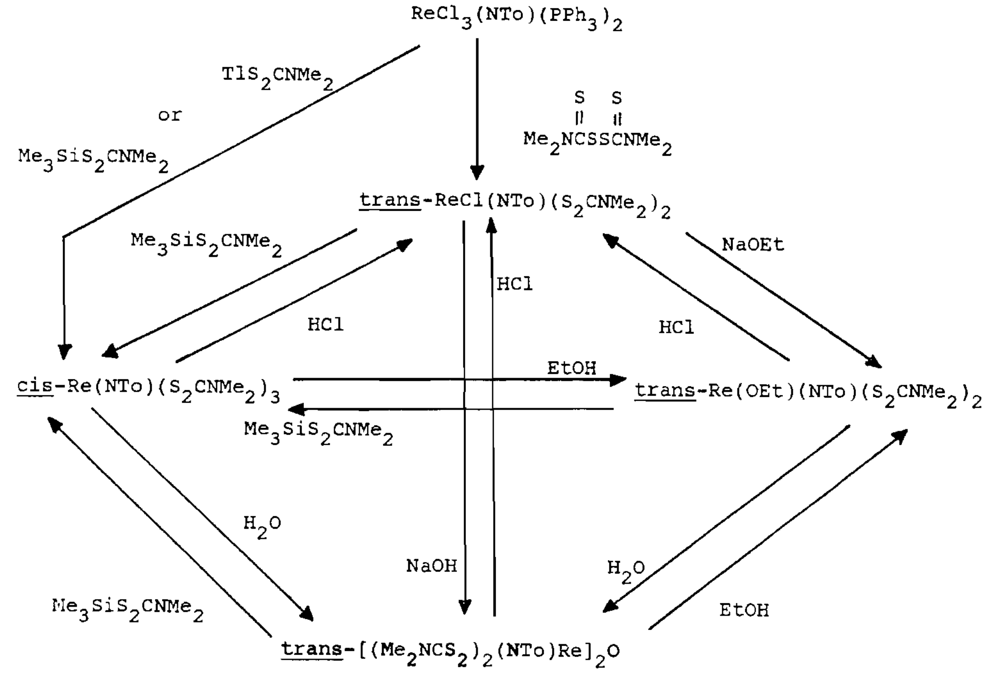
(18) Cahen, D.; Ibers, J. A. *J. Appl. Crystallogr.* **1972**, *5*, 298.

(19) In addition to various local programs for the CDC-6600 computer, modified versions of the following programs were employed: Zalkin's FORDAP Fourier summation program, Johnson's ORTEP thermal ellipsoid plotting program, Busing and Levy's ORFFE error function program, and the Northwestern full-matrix, least-squares program NUCLS, which, in its nongroup form, closely resembles the Busing and Levy ORFLS program.

(20) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Scheme I



bration are given in Table S-I.[21] Table S-II[21] contains the positional and thermal parameters for the hydrogen atoms. A listing of observed and calculated structure amplitudes for those data used in the refinements is available.[21]

Results and Discussion

Syntheses and Spectra. New nitrene complexes of rhenium have been prepared from the readily available starting material $ReCl_3(NTo)(PPh_3)_2$, which was prepared by the preferred method from $Ph_3P{=}NTo$ and $ReOCl_3(PPh_3)_2$ in refluxing benzene.[15] In turn, $ReCl(NTo)(S_2CNMe_2)_2$ was prepared by a modification of the published method[4] using tetramethylthiuram disulfide (2.5 equiv/Re) to displace two chloride and two phosphine ligands. The chloro ligand in $ReCl(NTo)(S_2CNMe_2)_2$ is readily displaced by a third dithiocarbamate in the presence of an anhydrous source of $S_2CNMe_2^-$. Although thiuram disulfides will not work, trimethylsilyl dithiocarbamates and thallous dithiocarbamates in benzene (80 °C) or methylene chloride (37 °C) give good yields of the brown-green $Re(NTo)(S_2CNMe_2)_3$. Indeed *anhydrous* sodium dithiocarbamate salts in dry acetone (56 °C) also produce the same products. The thallous dithiocarbamate is the preferred source of S_2CNMe_2 because truly anhydrous NaS_2CNMe_2 is difficult to obtain, and the preparation of $Me_3SiS_2CNMe_2$ requires several synthetic steps and vacuum distillations. One of the three dithiocarbamate ligands in $Re(NTo)(S_2CNMe_2)_3$ is readily susceptible to hydrolysis. Under mild conditions H_2O, EtOH, and HCl displace one dithiocarbamate group, forming $Re_2O(NTo)_2(S_2CNMe_2)_4$, $Re(OEt)(NTo)(S_2CNMe_2)_2$, and $ReCl(NTo)(S_2CNMe_2)_2$, respectively. The rapid hydrolysis of the tris(dithiocarbamate) complexes explains why Rowbottom and Wilkinson[4] never observed these complexes in their reactions. Commercially available NaS_2CNEt_2 has enough water in it to carry the reaction on to $Re_2O(NPh)_2(S_2CNEt_2)_4$. The analogous reaction with commercial NaS_2CNMe_2 produced small amounts of the less soluble $Re(NPh)(S_2CNMe_2)_3$, which subsequently hydrolyzed to the oxo-bridged dimer. If truly anhydrous sodium dithiocarbamate salts are employed in dry solvents, only the tris(dithiocarbamate) complexes are formed. In solution, $Re(NPh)(S_2CNMe_2)_3$ seemed to be somewhat less sensitive to hydrolysis than $Re(NPh)(S_2CNEt_2)_3$.

Table II. Positional Parameters for the Atoms of $Re(OC_2H_5)(p\text{-}NC_6H_4CH_3)(S_2CN(CH_3)_2)_2$

atom	x^a	y	z
Re	0.22146 (3)	0.170664 (13)	0.07043 (2)
S(11)	0.4665 (2)	0.24668 (9)	0.12140 (12)
S(12)	0.4554 (2)	0.08243 (9)	0.12031 (13)
S(21)	−0.0007 (2)	0.26203 (9)	0.00662 (13)
S(22)	−0.0380 (2)	0.09820 (9)	−0.00581 (13)
O	0.2022 (5)	0.1629 (2)	−0.0728 (3)
N(1)	−0.2601 (7)	0.1602 (3)	0.1948 (4)
N(2)	−0.2960 (7)	0.3057 (3)	0.4261 (4)
N(3)	0.2369 (6)	0.1552 (3)	0.1970 (4)
C(11)	−0.4216 (8)	0.1626 (3)	0.1515 (5)
C(12)	−0.1698 (8)	0.0882 (4)	0.2244 (6)
C(13)	−0.1606 (8)	0.2293 (4)	0.2131 (5)
C(21)	−0.1375 (8)	0.3142 (3)	0.4684 (5)
C(22)	−0.3728 (8)	0.2306 (4)	0.4075 (6)
C(23)	−0.4070 (9)	0.3716 (4)	0.3992 (6)
C(31)	0.2451 (7)	0.1112 (4)	0.2819 (5)
C(32)	0.2543 (8)	0.1468 (4)	0.3735 (5)
C(33)	0.2624 (8)	0.1010 (4)	0.4568 (5)
C(34)	0.2621 (9)	0.0214 (4)	0.4515 (5)
C(35)	0.2529 (9)	−0.0126 (4)	0.3586 (6)
C(36)	0.2436 (8)	0.0312 (4)	0.2747 (5)
C(37)	0.2748 (12)	−0.0264 (5)	0.5434 (7)
C(41)	0.1827 (8)	0.4007 (4)	0.3608 (5)
C(42)	0.1445 (9)	0.3743 (4)	0.2495 (6)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

In contrast to the case for $Re(NTo)(S_2CNMe_2)_3$, $ReCl(NTo)(S_2CNMe_2)_2$ is hydrolyzed only under more basic conditions. Whereas H_2O and EtOH do not affect the chloride ligand, NaOH and NaOEt displace NaCl and produce the oxo-bridged dimer and $Re(OEt)(NTo)(S_2CNMe_2)_2$, respectively. In turn, $Me_3SiS_2CNMe_2$, HCl, and H_2O react with $Re(OEt)(NTo)(S_2CNMe_2)_2$ to form $Re(NTo)(S_2CNMe_2)_3$, $ReCl(NTo)(S_2CNMe_2)_2$, and the oxo-bridged dimer. In fact, with HCl, NaOH (or H_2O), NaOEt (or EtOH), or $Me_3SiS_2CNMe_2$, the entire group of rhenium dithiocarbamate complexes can be interconverted as shown in Scheme I. The preferential attack of HCl at the OR ligand instead of the NR

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[21] See paragraph at the end of the paper regarding supplementary material.

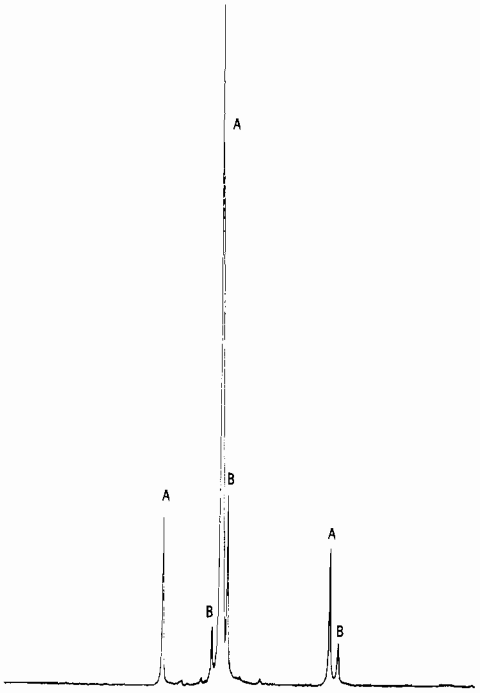
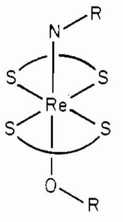


Figure 1. Proton NMR spectrum (220 MHz) of Re(OMe)(NMe)$(S_2CNMe_2)_2$ in CD_2Cl_2 at 20 °C. The two isomers are designated by A and B.

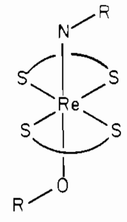
ligand has also been observed in Re(OH)$(NCH_3)(NH_2CH_3)_4^{2+}$.

The proton NMR spectra of the rhenium dithiocarbamate complexes are indicative of their respective coordination geometries (see Table III). At room temperature (30 °C), the dithiocarbamate methyl groups in Re(NTo)$(S_2CNMe_2)_3$ give rise to one broad singlet for all six groups, but at −65 °C, five sharp singlets are seen with one of them twice as intense as the other four. This resonance pattern is consistent with a cis, six-coordinate geometry with one unidentate dithiocarbamate ligand. Our attempts to produce a seven-coordinate, 20-electron complex with a bent NTo group apparently failed; instead, the nitrene probably remains linear and one of the six sulfur atoms is not coordinated to rhenium. The four dithiocarbamate methyl groups in ReCl(NTo)$(S_2CNMe_2)_2$ give rise to one sharp singlet, which does not change with temperature (+30 to −70 °C). At +30 °C, the four ethyl groups in ReCl(NTo)$(S_2CNEt_2)_2$ give rise to a single triplet for the CH_3 groups and a multiplet (ABX_3 pattern) for the CH_2 groups, indicating inequivalence of the methylene protons and slow rotation about the C–N multiple bond of the dithiocarbamate ligands. Because these six-coordinate dithiocarbamate complexes usually do not show fluxional behavior at low temperatures, we presume that ReCl(NTo)$(S_2CNR'_2)_2$ has a trans geometry, but a cis geometry with fluxional behavior in solution cannot be completely ruled out.

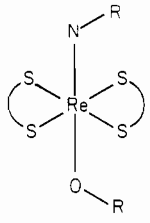
The trans geometry for Re(OEt)(NTo)$(S_2CNMe_2)_2$ is known (vide infra), and the same geometry is highly likely for $Re_2O(NTo)(S_2CNMe_2)_4$ by analogy to the known structure (trans geometry) of $Re_2O_3(S_2CNEt_2)_4$.[8,22] Furthermore, we have also determined the structure of $Re_2O(NPh)_2(S_2CNEt_2)_4$ and have found a trans geometry.[23] As expected for trans geometries, the NMR spectra of $Re_2O(NTo)_2(S_2CNMe_2)_4$ and Re(OEt)(NTo)$(S_2CNMe_2)_2$ show a single resonance (singlet) for the dithiocarbamate methyl groups in each compound. The NMR spectra of both compounds also show, however, extra resonances for all protons, indicating the presence of two isomers in solution with the same chemical constitution (see Figure 1). The relative intensities of these extra resonances indicate that the ratio of isomers ranges from 1:9 to 1:1 depending on the solvent, temperature, and organic groups attached to the –NR, –OR, and $-S_2CNR_2$ ligands; with S_2CNEt_2, both isomers are present in appreciable amounts, but with S_2CNMe_2, one isomer greatly predominates over the other. All reported compounds are pure, and the extra resonances are not caused by impurities. Although cis–trans isomerization about the metal or linear–bent isomerization at the nitrene ligand are two possibilities, we feel that isomerism (see III–V) about the Re–N and Re–O multiple bonds is a more likely explanation. Yet another type of isomerism could arise from the nonaxial disposition of the –OR and –NR ligands (see structure description), such as VI.



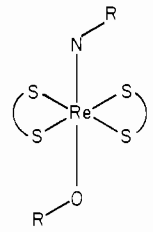
IIIa



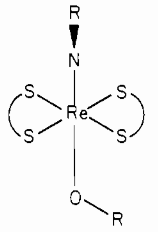
IIIb



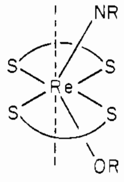
IVa



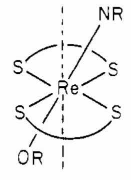
IVb



V



VIa



VIb

Chart I[a]

$Nb(NTo)(S_2CNEt_2)_3$	$Re(NTo)(S_2CNEt_2)_3$
1495, 1501	$\underline{1480}$, 1494, 1514
1325	$\underline{1414}$
1274	$\underline{1262}$, 1275
1145	$\underline{1131}$, 1151
1073	$\underline{1066}$, 1074

[a] All absorptions are in cm^{-1}.

For a confirmation of the presence of a unidentate dithiocarbamate ligand in the tris(dithiocarbamate) complexes, the infrared spectra of Nb(NTo)$(S_2CNEt_2)_3$[24] and Re(NTo)$(S_2CNEt_2)_3$ were carefully compared; the niobium structure is known to be seven-coordinate. This is similar to the comparison between Mo(NO)$(S_2CNEt_2)_3$[25] (seven-coordinate) and Ru(NO)$(S_2CNEt_2)_3$[26] (six-coordinate). In the

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(22) Fletcher, S. R.; Skapski, A. C. *J. Chem. Soc., Dalton Trans.* **1972**, 1073.

(23) Goeden, G. V.; Haymore, B. L., unpublished results. Owing to partial disorder, the quality of the structure is not good; however, the complex is clearly dimeric with two six-coordinate Re atoms and a nearly linear N–Re–O–Re–N arrangement of atoms.

(24) Tan, L. S.; Goeden, G. V.; Haymore, B. L. *Inorg. Chem.*, in press.

(25) Breenan, T. F.; Bernal, I. *Inorg. Chim. Acta* **1973**, *7*, 283. Johnson, B. F. G.; Al-Obaidi, K. H.; McCleverty, J. A. *J. Chem. Soc. A* **1969**, 1668.

(26) Domenicano, A.; Vaciago, A.; Zambonelli, L.; Loader, P. L.; Venanzi, L. M. *J. Chem. Soc., Chem. Commun.* **1966**, 476.

Table III. Physical, Spectroscopic, and Analytical Data for Rhenium Nitrene Complexes

compd[a] (color, NMR solvent)	elemental anal. found (calcd)	ν(CN)[b] (ν(ReO))	^{1}H NMR resonances (δ)[c]			isomer ratio (A/B)
			NR	S_2CNR_2	OR	
$\mathrm{ReCl(NTo)(S_2CNMe_2)_2}$ (green, CD_2Cl_2)	C, 27.81 (27.53) H, 3.49 (3.38) N, 7.31 (7.41)	1546	2.27 (s) CH_3 7.30 (qt) C_6H_4	3.44 (s) 4 CH_3		
$\mathrm{ReCl(NTo)(S_2CNEt_2)_2}$ (green, CD_2Cl_2)	C, 32.88 (32.76) H, 4.28 (4.37) N, 6.68 (6.74)	1512	2.19 (s) CH_3 7.17 (qt) C_6H_4	1.33 (t) 4 CH_3 3.72 (ab) 4 CH_2		
$\mathrm{ReCl(NPh)(S_2CNMe_2)_2}$ (green, CD_2Cl_2)	C, 25.89 (26.05) H, 3.19 (3.10) N, 7.48 (7.60)	1543	7.43 (m) C_6H_5	3.42 (s) 4 CH_3		
$\mathrm{ReCl(NMe)(S_2CNMe_2)_2}$ (pink, $CDCl_3$)	C, 17.44 (17.12) H, 3.37 (3.08) N, 8.84 (8.56)	1542	2.21 (s) CH_3	3.40 (s) 4 CH_3		
$\mathrm{Re(NTo)(S_2CNMe_2)_3}$ (olive green, CD_2Cl_2)	C, 29.82 (29.47) H, 3.99 (3.87) N, 8.66 (8.59)	1545 (sh), 1533, 1499 (sh)	2.20 (s) CH_3 7.29 (qt) C_6H_4 2.21 (s) CH_3[h] 7.32 (qt) C_6H_4[h]	3.47 (s, br) 6 CH_3 3.21 (s) CH_3[h] 3.44 (s) CH_3[h] 3.41 (s) CH_3[h] 3.48 (s) CH_3[h] 3.69 (s) 2 CH_3[h]		
$\mathrm{Re(NTo)(S_2CNEt_2)_3}$ (green-brown, CD_2Cl_2)	C, 35.99 (35.90) H, 5.07 (5.07) N, 7.92 (7.61)	1514, 1494, 1480	2.18 (s) CH_3 7.27 (qt) C_6H_4	1.30 (t, br) 6 CH_3 3.88 (qt, br) 6 CH_2		
$\mathrm{Re(NPh)(S_2CNMe_2)_3}$ (olive green, $CDCl_3$)	C, 28.39 (28.34) H, 3.75 (3.63) N, 8.61 (8.78)	1544 (sh), 1531, 1498 (sh)	7.20 (t) 2 CH(meta) 7.47 (t) CH(para) 7.69 (d) 2 CH(ortho)	3.48 (s, br) 6 CH_3		
$\mathrm{Re(NPh)(S_2CNEt_2)_3}$ (green-brown, $CDCl_3$)	C, 35.19 (34.93) H, 4.98 (4.89) N, 7.72 (7.79)	1514, 1495, 1475	7.18 (t) 2 CH(meta) 7.43 (t) CH(para) 7.67 (d) 2 CH(ortho)	1.32 (t, br) 6 CH_3 3.92 (q, br) 6 CH_2		
$\mathrm{Re(NMe)(S_2CNMe_2)_3}$ (green, $CDCl_3$)	C, 20.95 (20.86) H, 3.88 (3.68) N, 9.94 (9.73)	1545, 1520, 1495	2.20 (s) CH_3	3.50 (s, br) 6 CH_3		
$\mathrm{Re(OEt)(NTo)(S_2CNMe_2)_2}$ (brown, CD_2Cl_2)	C, 31.29 (31.23) H, 4.26 (4.19) N, 7.19 (7.28)	1535	2.25 (s) CH_3, B 2.22 (s) CH_3, A 7.10 (qt) C_6H_4, A (C_6H_4, B)[f]	3.36 (s) 4 CH_3, B 3.33 (s) 4 CH_3, A	(CH_3, B)[f] 1.15 (t) CH_3, A (CH_2, B)[f] 3.46 (q) CH_2, A	6/1
$\mathrm{Re(OEt)(NPh)(S_2CNMe_2)_2\cdot CH_2Cl_2}$ (brown, CD_2Cl_2)	C, 28.15 (27.86) H, 3.97 (3.74) N, 6.67 (6.50)	1532	7.4 (m) C_6H_5[d]	3.38 (s) 4 CH_3[d]	1.02 (t) CH_3[d] 4.22 (q) CH_2[d]	*d*
$\mathrm{Re(OEt)(NTo)(S_2CNEt_2)_2}$ (brown, CD_2Cl_2)	C, 36.45 (36.06) H, 5.29 (5.10) N, 6.33 (6.64)	1503	2.18 (s) CH_3, B 2.12 (s) CH_3, A 7.07 (qt) C_6H_4, B 6.97 (qt) C_6H_4, A	1.31 (t) 4 CH_3, A 3.7 (m) 4 CH_2, A + B[e] 1.33 (t) 4 CH_3, B	0.93 (t) CH_3, B 1.14 (t) CH_3, A (CH_2, B)[g] 4.04 (q) CH_2, B	2/1
$\mathrm{Re(OMe)(NTo)(S_2CNMe_2)_2}$ (brown, CD_2Cl_2)	C, 29.68 (29.88) H, 3.99 (3.94) N, 7.26 (7.47)	1537	2.23 (s) CH_3, B 2.19 (s) CH_3, A 7.16 (qt) C_6H_4, B 7.06 (qt) C_6H_4, A	3.35 (s) 4 CH_3, B 3.30 (s) 4 CH_3, A	4.01 (s) CH_3, B 3.46 (s) CH_3, A	1/3
$\mathrm{Re(OMe)(NTo)(S_2CNEt_2)_2}$ (brown, CD_2Cl_2)	C, 34.78 (34.93) H, 4.81 (4.89) N, 6.57 (6.79)	1500	2.18 (s) CH_3, B 2.13 (s) CH_3, A 7.08 (qt) C_6H_4, B 6.97 (qt) C_6H_4, A	1.30 (t) 4 CH_3, A + B[e] 3.7 (m) 4 CH_2, A + B[e]	3.83 (s) CH_3, B 3.35 (s) CH_3, A	1.2/1
$\mathrm{Re(OMe)(NMe)(S_2CNMe_2)_2}$ (orange, CD_2Cl_2)	C, 19.76 (19.74) H, 3.83 (3.73) N, 8.52 (8.63)	1523	2.33 (s) CH_3, B 2.40 (s) CH_3, A	3.24 (s) 4 CH_3, B 3.31 (s) 4 CH_3, A	3.36 (s) CH_3, B 3.76 (s) CH_3, A	4/1
$\mathrm{Re_2O(NTo)_2(S_2CNMe_2)_4}$ (brown, $CDCl_3$)	C, 38.82 (28.93) H, 3.59 (3.55) N, 7.50 (7.78)	1525 (730)	2.22 (s) 2 CH_3, A 2.26 (s) 2 CH_3, B 7.10 (qt) 2 C_6H_4, A 7.25 (qt) 2 C_6H_4, B	3.32 (s) 8 CH_3, A 3.38 (s) 8 CH_3, B		1/6
$\mathrm{Re_2O(NPh)_2(S_2CNMe_2)_4}$ (brown, $CDCl_3$)	C, 27.09 (27.41) H, 3.29 (3.26) N, 7.58 (7.99)	1526 (718)	7.3 (m) 2 C_6H_5, A + B[e]	3.34 (s) 8 CH_3, A 3.38 (s) 8 CH_3, B		1/1.5
$\mathrm{Re_2O(NTo)_2(S_2CNEt_2)_4}$ (brown, $CDCl_3$)	C, 34.04 (34.26) H, 4.71 (4.57) N, 7.26 (7.05)	1492 (719)	2.14 (s) 2 CH_3, A 2.22 (s) 2 CH_3, B 7.05 (qt) 2 C_6H_4, A 7.21 (qt) 2 C_6H_4, B	1.32 (t) 8 CH_3, A 1.34 (t) 8 CH_3, B 3.7 (m) 8 CH_2, A + B[e]		2/1
$\mathrm{Re_2O(NMe)_2(S_2CNMe_2)_4}$ (orange, $CDCl_3$)	C, 18.36 (18.13) H, 3.45 (3.26) N, 9.00 (9.06)	1524 (729)	2.44 (s) 2 CH_3, A 2.38 (s) 2 CH_3, B	3.27 (s) 8 CH_3, A 3.34 (s) 8 CH_3, B		1/5

[a] Abbreviations: Me = CH_3, Et = C_2H_5, Ph = C_6H_5, To = p-$C_6H_4CH_3$. [b] Infrared spectra measured in both Nujol and Fluorolube mulls; ν(CN) is for dithiocarbamate; ν(ReO) is for the antisymmetric Re–O–Re stretching vibration sh = shoulder. [c] Measured at ambient temperature in indicated solvent with tetramethylsilane as internal standard: ab = AB part of ABX_3, s = singlet, t = triplet ($^3J_{HH} \simeq 7$ Hz), q = quartet ($^3J_{HH} \simeq 7$ Hz), m = multiplet, qt = AA'BB' quartet ($^3J_{HH} \simeq 8$ Hz, $^5J_{HH}$ small), br = broad. [d] Low solubility prevents detection of minor isomer. [e] Overlapping resonances for the two isomers. [f] Resonances too weak to be observed. [g] Resonance obscured by dithiocarbamate methylene group. [h] Measured at −65 °C.

region 800–2000 cm^{-1}, five infrared bands appear in the spectrum of the Re complex that do not appear in the Nb complex (Chart I). These bands (underlined in Chart I) are probably associated with the monodentate diethyldithiocarbamate ligand. All but the band at 1131 cm^{-1} compare favorably with the corresponding infrared bands in Ru(NO)(S_2CNEt_2)$_3$, which has one monodentate dithiocarbamate group. On the basis of the observations of others,[26,27] we expected to see some additional changes in the ν(CS) region near 1000 cm^{-1} (970–1030 cm^{-1}); however, only minor changes in the spectrum of Re(NTo)(S_2CNEt_2)$_3$ are seen in this region. In Nb(NTo)(S_2CNEt_2)$_3$, a band at 1325 cm^{-1} is seen, which is absent in the Re complex, and a band at 1414 cm^{-1} is present in Re(NTo)(S_2CNEt_2)$_3$ but not in the Nb complex. These data indicate that the presence of the monodentate dithiocarbamate ligand in Re(NTo)(S_2CNEt_2)$_3$ gives the appearance of splitting some of the bands due to the dithiocarbamate groups. The infrared and ^{1}H NMR spectra of the rhenium tris(dithiocarbamate) complexes taken together indicate that the Re(NTo)(S_2CNR_2)$_3$ complexes are six-coordinate with the –NTo and monodentate –SC(S)NR_2 ligands cis to each other.

Efforts to identify ν(ReN) in the infrared spectra of the phenylnitrene complexes were not entirely successful. The only band in $ReCl_3$(NPh)(PPh_3)$_2$ that was observed to shift upon ^{15}N substitution was one at 1347 cm^{-1}, which moved to 1317 cm^{-1} with ^{15}N. In ReCl(NPh)(S_2CNMe_2)$_2$ four bands shifted upon isotopic substitution; bands at 1353, 1025, 1009, and 991 cm^{-1} moved to 1328, 1019, 1004, and 986 cm^{-1}. In both compounds, the band that was observed to shift the most was one near 1350 cm^{-1}. This band is in the region of ν(CN) bands for aromatic amines; thus, it is possible that the band is primarily a C–N stretch rather than an N–Re stretch. Furthermore, it is generally felt that Re–N stretching bands in nitrene complexes occur at lower energy (1000–1300 cm^{-1}), although few thorough vibrational analyses supported by isotopic labeling have been carried out. On the other hand, 25–30-cm^{-1} shifts with ^{15}N labeling seem to be large for simple C–N stretches. Until we obtain more information, we cannot definitely conclude whether the 1350-cm^{-1} bands belong to ν(CN), ν(ReN), or a combination of both vibrations.

Alternate synthetic routes to Re(NTo)(S_2CNR_2)$_3$ were attempted, but the desired products were not obtained. Re(CO)(S_2CNEt_2)$_3$[28] and Re(S_2CNEt_2)$_3$[28] were allowed to react with ToN_3 or PhN_3 under varying conditions. In all cases, only starting materials were recovered. It is noteworthy that the formal replacement of a two-electron donor (CO) in Re(CO)(S_2CNR_2)$_3$ by a two/four electron donor (NTo) in Re(NTo)(S_2CNR_2)$_3$ caused one of the three chelating dithiocarbamate ligands in the carbonyl complex to become monodentate in the nitrene complex.

The syntheses of the methylnitrene (–NCH_3) complexes were very similar to those for the arylnitrene analogues. The same types of products in reasonable yields were obtained. Although $ReCl_3$(NCH_3)(PPh_3)$_2$ is known to deprotonate in the presence of base and excess ligand (L) to form $ReCl_2$(NCH_2)L(PPh_3)$_2$, the dithiocarbamate derivatives, ReCl(NCH_3)(S_2CNMe_2)$_2$, do not deprotonate even under highly basic conditions. Efforts to convert ReCl(NCH_3)(S_2CNMe_2)$_2$, Re(OMe)(NMe)(S_2CNMe_2)$_2$, or $ReCl_3$(NCH_3)(PPh_3)$_2$ into Re(NCH_2)(L)(S_2CNMe_2)$_2$ (L = PPh_3, C_5H_5N) failed. Reducing the electron density on the metal by replacing phosphine and chloride ligands with dithiocarbamate ligands significantly inhibits this unusual deprotonation reaction probably because –NCH_2 is stabilized by metal-to-ligand π donation. Although both $ReCl_2$(NCH_2)(PR_3)$_3$[29] and $ReCl_2$(NO)(PR_3)$_3$[30] are known, we have not been able to prepare the –NCH_2 analogue of the known Re(NO)(PPh_3)(S_2CNMe_2)$_2$.[31]

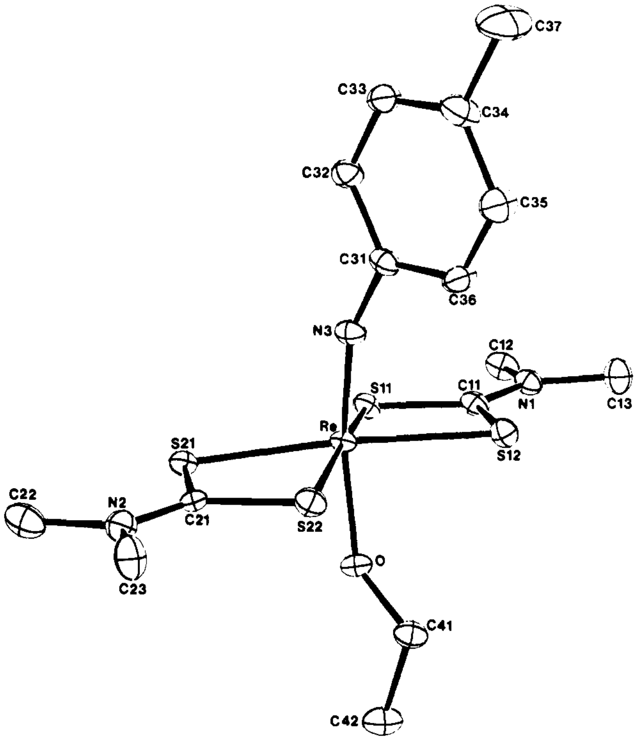

Figure 2. Drawing of a molecule of Re(OEt)(p-$NC_6H_4CH_3$)(S_2CNMe_2)$_2$. The hydrogen atoms have been omitted. Vibrational ellipsoids are drawn at the 50% probability level.

The chemical shifts (^{1}H NMR) of the protons in –NCH_3 ligands vary widely depending on the nature of the metal–nitrogen interaction. In $ReCl_3$(NCH_3)(PPh_3)$_2$ the resonance is shifted to high field at δ 0.36 ($CDCl_3$, triplet, $^4J_{PH}$ = 4 Hz) whereas the resonances in Re(NCH_3)(S_2CNMe_2)$_3$ and ReCl(NCH_3)(S_2CNMe_2)$_2$ occur near δ 2.2 and those in Re(OCH_3)(NCH_3)(S_2CNMe_2)$_2$ and Re_2O(NCH_3)$_2$(S_2CNMe_2)$_4$ occur near δ 2.4; the methyl proton chemical shift of free $(CH_3)_2NH$ is δ 2.38 in $CDCl_3$. In contrast, the –NCH_3 protons in Nb(NCH_3)(S_2CNEt_2)$_3$ (δ 3.6) and WF_4(NCH_3)($NCCH_3$) (δ 5.5) are shifted further downfield. It seems that metals with lower formal oxidation states, with larger numbers of valence electrons in d orbitals, and with more basic electron-donating coligands induce higher field chemical shifts in attached methylnitrene ligands.

Description of the Structure. The structure of Re(OEt)(NTo)(S_2CNMe_2)$_2$ consists of well-separated monomeric molecules. Careful examination of electron density maps showed the absence of any molecules of solvent (CH_2Cl_2/C_2H_5OH) in the lattice. There are no short or unusual intermolecular, nonbonded contacts less than 2.5 Å except H(2)C(37)–H(3)C(22) and H(3)C(23)–H(1)C(41) at 2.3 Å. Figure 2 contains a drawing and labeling scheme for the entire molecule, which has a distorted, trans, octahedral geometry. The major distortions from octahedral geometry are caused by the small bite angles (71.67 (6) and 71.97 (6)°) of the dithiocarbamate chelates and by the bending of the –OEt (4.2 (3)°) and –NTo (8.7 (3)°) ligands off the true axial sites as defined by the normals to the plane of the four sulfur atoms; the largest deviation from this plane is S(11), which is dis-

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(27) O'Connor, C.; Gilbert, J. D.; Wilkinson, G. *J. Chem. Soc. A* **1969**, 84.

(28) Rowbottom, J. F.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1974**, 684.

(29) Chatt, J.; Dosser, R. J.; King, F.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2435.

(30) Adams, R. W.; Chatt, J.; Hooper, N. E.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1974**, 1075.

(31) Haymore, B. L., unpublished results.

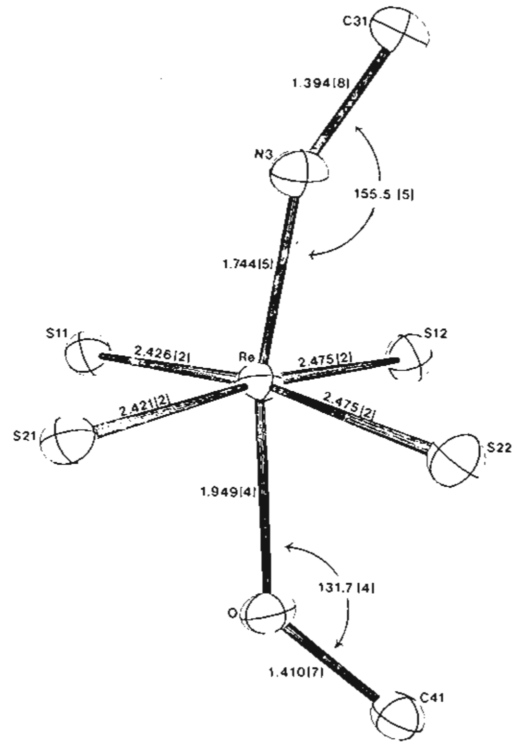

Figure 3. Coordination sphere of Re(OEt)(*p*-$NC_6H_4CH_3$)$(S_2CNMe_2)_2$. The tolyl group (except C(31)), atom C(42), all hydrogen atoms, and all but the sulfur atoms of the dithiocarbamate ligands have been omitted for clarity. Vibrational ellipsoids are drawn at the 50% probability level.

placed by 0.017 (2) Å. The –OEt and –NTo ligands are bent toward each other about Re in a pseudo mirror plane that relates one dithiocarbamate ligand to the other; the resulting O–Re–N(3) angle is 167.1 (2)°. Indeed, the title complex has very nearly C_s symmetry in the solid state. The torsion angles about O–C(41) and N(3)–C(31) are such that even the ethyl and *p*-tolyl groups lie quite close to this pseudo mirror plane. A clear view of the coordination sphere about Re can be seen in Figure 3. The complex is sterically unencumbered due to the presence of the small dithiocarbamate ligands. There are no unusual intramolecular contacts; the shortest contact is H(1)C(42)–O at 2.55 Å (calculated by using C–H = 1.08 Å).

The dithiocarbamate ligands adopt the usual geometry seen for these groups. The ligands are very nearly planar; the dihedral angles about N(1)–C(11) and N(2)–C(21) are 4.0 (5) and 1.5 (5)°, respectively. The average length of the N(1)–C(11) and N(2)–C(21) bonds at 1.32 Å is considerably shorter than the average of the four other C–N single bonds at 1.46 Å but somewhat longer than the expected C–N double-bond length of 1.27 Å. The coordination geometries at C(11), C(21), N(1), and N(2) are planar within experimental error. The two planar dithiocarbamate ligands are nearly coplanar; the angle between the S(11)–C(11)–S(12) and S(21)–C(21)–S(22) planes is 1.6 (3)°. The average N(3)–Re–S angle is 93.3° with the sulfur chelates bent away from N(3), which forms a significantly shorter bond to Re than does O. In other words, the Re atom is displaced 0.135 (3) Å out of the plane of the four sulfur atoms toward N(3). This distance compares favorably with 0.14-Å displacement of Re toward the terminal oxo ligands in $ORe(S_2CNEt_2)_2$–O–$(S_2CNEt_2)_2ReO$,[22] which has a trans geometry about Re, but these distances are much smaller than the 0.73-Å displacement in the square-pyramidal $ReN(S_2CNEt_2)_2$,[32] which has the vacant coordination site trans to N. The average Re–S distance in $Re(OEt)(NTo)(S_2CNMe_2)_2$ is 2.45 Å, which is nearly the same as that in $Re_2O_3(S_2CNEt_2)_4$[22] (2.44 Å). The average Re–S distance in $ReN(S_2CNEt_2)_2$,[32] however, is shorter (2.39 Å), but this shortening is not unexpected considering the lower coordination number about Re. Tables IV and V contain additional bond distances and angles for $Re(OEt)(NTo)(S_2CNMe_2)_2$.

Table IV. Selected Bond Distances (Å) in Re(OEt)(*p*-$NC_6H_4CH_3$)$(S_2CNMe_2)_2$

atoms	dist	av	atoms	dist	av
Re–S(11)	2.425 (2)	2.449	N(1)–C(2)	1.458 (8)	1.462
Re–S(12)	2.475 (2)		N(1)–C(13)	1.464 (8)	
Re–S(21)	2.421 (2)		N(2)–C(22)	1.457 (9)	
Re–S(22)	2.475 (2)		N(2)–C(23)	1.469 (9)	
Re–N(3)	1.745 (5)		O–C(41)	1.410 (7)	
Re–O	1.948 (4)		C(41)–C(42)	1.515 (9)	
S(11)–C(11)	1.732 (6)	1.733	N(3)–C(31)	1.394 (8)	
S(12)–C(11)	1.726 (6)		C(31)–C(32)	1.400 (9)	1.394
S(21)–C(21)	1.741 (6)		C(32)–C(33)	1.394 (9)	
S(22)–C(22)	1.734 (6)		C(33)–C(34)	1.391 (9)	
C(11)–N(1)	1.325 (8)	1.317	C(34)–C(35)	1.402 (9)	
C(21)–N(2)	1.309 (8)		C(35)–C(36)	1.379 (9)	
			C(36)–C(31)	1.400 (9)	
			C(34)–C(37)	1.499 (10)	

Table V. Selected Bond Angles (deg) in Re(OEt)(*p*-$NC_6H_4CH_3$)$(S_2CNMe_2)_2$

atoms	angle	av
Re–N(3)–C(31)	155.5 (5)	
O–Re–N(3)	167.1 (2)	
S(11)–Re–S(22)	172.50 (5)	
S(12)–Re–S(21)	173.82 (5)	
S(11)–Re–S(12)	71.67 (6)	
S(21)–Re–S(22)	71.97 (6)	
S(11)–Re–S(21)	105.27 (6)	
S(12)–Re–S(22)	110.36 (6)	
N(3)–Re–S(11)	98.5 (2)	
N(3)–Re–S(21)	98.4 (2)	
N(3)–Re–S(12)	87.4 (2)	
N(3)–Re–S(22)	88.9 (2)	
O–Re–S(11)	88.9 (1)	
O–Re–S(21)	89.7 (1)	
O–Re–S(12)	84.9 (1)	
O–Re–S(22)	84.1 (1)	
Re–O–C(41)	131.7 (4)	
O–C(41)–C(42)	110.3 (5)	
S(11)–C(11)–S(12)	112.1 (4)	
S(21)–C(21)–S(22)	111.8 (4)	
Re–S(11)–C(11)	88.7 (2)	88.0
Re–S(12)–C(11)	87.3 (2)	
Re–S(21)–C(21)	88.9 (2)	
Re–S(22)–C(21)	87.3 (2)	
S(11)–C(11)–N(1)	123.8 (5)	124.0
S(12)–C(11)–N(1)	124.0 (5)	
S(21)–C(21)–N(2)	123.6 (5)	
S(22)–C(21)–N(2)	124.6 (5)	
C(11)–N(1)–C(12)	122.2 (5)	122.2
C(11)–N(1)–C(13)	122.3 (5)	
C(21)–N(2)–C(22)	122.2 (6)	
C(21)–N(2)–C(23)	121.9 (6)	
C(12)–N(1)–C(13)	115.5 (5)	
C(22)–N(2)–C(23)	115.8 (6)	
N(3)–C(31)–C(32)	120.2 (6)	
N(3)–C(31)–C(36)	119.5 (6)	
C(37)–C(34)–C(33)	120.8 (7)	
C(37)–C(34)–C(35)	121.2 (6)	
C(36)–C(31)–C(32)	120.3 (6)	120.0
C(31)–C(32)–C(33)	118.6 (6)	
C(32)–C(33)–C(34)	122.0 (6)	
C(33)–C(34)–C(35)	118.0 (6)	
C(34)–C(35)–C(36)	121.3 (6)	
C(35)–C(36)–C(31)	119.8 (6)	

The Tolylnitrene Ligand. The most noticeable feature of the structure of $Re(OEt)(NTo)(S_2CNMe_2)_2$ is the presence

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[32] Fletcher, S. R.; Skapski, A. C. *J. Chem. Soc., Dalton Trans.* **1972**, 1079.

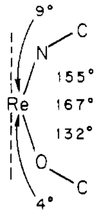
Table VI. Structural Data for Terminal Nitrene Complexes of Rhenium

complex[a]	R	Re–N, Å	Re–N–C, deg	ref
$[\mathrm{ReCl(NR)(NH_2Me)_4}][\mathrm{ClO_4}]_2$[b]	CH_3	1.694 (11)	180 (2)	*c*
$\mathrm{ReCl_3(NR)(PPhEt_2)_2}$	p-$\mathrm{CH_3C(O)C_6H_4}$	1.690 (5)	171.9 (2)	*d*
$\mathrm{ReCl_3(NR)(PPhEt_2)_2}$[b]	p-$\mathrm{CH_3OC_6H_4}$	1.709 (4)	175.8 (1)	*d*
$\mathrm{ReCl_3(NR)(PPh_2Et)_2}$	CH_3	1.685 (11)	173.4 (10)	*e*
$\mathrm{Re(OEt)(NR)(S_2CNMe_2)_2}$	p-$\mathrm{CH_3C_6H_4}$	1.745 (5)	155.5 (5)	this work
$\mathrm{Re_3(NR)_4O_5(OSiMe_3)_3}$	CMe_3	1.70 (1)	166 (1)	*f*
	CMe_3	1.72 (1)	153 (1)	
	CMe_3	1.70 (1)	168 (1)	
	CMe_3	1.69 (1)	155 (1)	

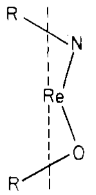
[a] Abbreviations: Me = CH_3, Et = C_2H_5, Ph = C_6H_5. [b] Partial disorder present. [c] Shandles, R. S.; Murmann, R. K.; Schlemper, E. O. *Inorg. Chem.* 1974, *13*, 1373. [d] Bright, D.; Ibers, J. A. *Ibid.* 1968, *7*, 1099. [e] Bright, D.; Ibers, J. A. *Ibid.* 1969, *8*, 703. [f] Reference 11.

of a bent nitrene ligand with Re–N(3)–C(31) equal to 155.5 (5)°; this bending is associated with an unusually long Re–N(3) distance of 1.745 (5) Å. This value can be compared with Re–N distances of 1.69 Å and linear Re–N–C angles (172–180°) in 18-electron rhenium nitrene complexes (see Table VI). The C(31) carbon atom of the nitrene is bent in the pseudo mirror plane noted earlier; the angles between the vectors, S(12)–S(22) and S(11)–S(21), and the normal to the bending plane, Re–N(3)–C(31), are 2.2 (9) and 1.2 (9)°, respectively. Furthermore, the entire planar aromatic ring very nearly lies on the pseudo mirror plane; the angle between the Re–N(3)–C(31) plane and the C_6 plane is only 2.1 (9)°.

The ethoxy ligand adopts a geometry that is not uncommon for these groups. The Re–O distance is 1.948 (4) Å and the Re–O–C(41) angle is 131.7 (4)°. The ethoxy ligand is bent in the same plane as the nitrene; the angle between Re–N(3)–C(31) and Re–O–C(41) is 3.1 (11)°. Furthermore, the dihedral angle about O–C(41) is only 9.9 (4)°, causing the terminal carbon atom of the ethyl group to lie very near the pseudo mirror plane as well (see VII). Thus, we find a remarkable situation in which there is bending about N(3), Re, and O all in the same plane in such a way as to bring the atoms of the axial ligands closer to each other. It is noteworthy that there are no short intra- or intermolecular nonbonded contacts that can account for the direction or magnitude of bending in this pseudo mirror plane. However the Re–O–C(41) angle may be opened up somewhat due to intramolecular contacts; the H(2)C(41)–S(22) (2.71 Å) and H(1)C(41)–S(12) (2.81 Å) distances are somewhat shorter than the sum of the hydrogen and sulfur van der Waals radii[33] (3.0 Å). These distances are not too unusual, however, because two intermolecular contacts are about the same; H(1)C(13)–S(21) = 2.82 Å and H(1)C(33)–S(11) = 2.83 Å.

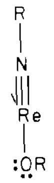


VII

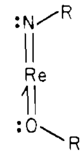


VIII

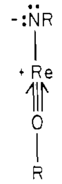
Simple electron counting using the EAN rule shows that $\mathrm{Re(OEt)(NTo)(S_2CNMe_2)_2}$ can exceed the usual number of 18 electrons. Alkoxy ligands are good π-donor ligands, and structural data suggest that they are quite capable of forming double bonds, Re=ÖR, and acting as three-electron-donor ligands. In principle, alkoxy ligands could also act as five-electron-donor ligands by forming triple bonds, Re≡OR, and donating both pair of electrons of the metal. In fact, the electronegative oxygen is reluctant to do this and five-electron-donor alkoxy ligands are infrequently found, yet nonbridging three-electron-donor alkoxy ligands are often observed. Thus, we consider $\mathrm{Re(OEt)(NTo)(S_2CNMe_2)_2}$ to have a maximum electron count of 20 electrons, and several valence bond forms (IX–XI) of the complex can be envisioned.



IX



X



XI

Formalism XI is unlikely to contribute to the ground state of the molecule for reasons noted earlier. In the chloro complex $\mathrm{ReCl(NTo)(S_2CNMe_2)_2}$, only formalism IX (OR replaced by Cl) would appreciably contribute to the ground state of this compound because Cl is a poor π donor in comparison to OR. However, in $\mathrm{Re(OEt)(NTo)(S_2CNMe_2)_2}$ both the IX and X formalisms can contribute to the ground state of the complex.

Careful consideration of metrical parameters in $\mathrm{Re(OEt)(NTo)(S_2CNMe_2)_2}$ and comparisons with other structures suggest the formalisms IX and X contribute nearly equally to the ground state and that the observed angles and distances in the Re complex can be rationalized in terms of a 50:50 mixture of the two formalisms. The first example of a complex containing a bent nitrene ligand was $\mathrm{Mo(NPh)_2(S_2CNEt_2)_2}$,[9] which was shown to have an average Mo–N bond order of 2.5 with Mo–N = 1.77 Å (average) and Mo–N–C = 154° (average). In the present Re complex, Re–N = 1.75 Å and Re–N–C = 155°. With correction for the smaller size (0.01–0.02 Å) of Re,[34] the agreement is remarkable, and we estimate that the Re–N bond order is near 2.5. Using the structure of $\mathrm{(HB(Pz)_3)MoCl(NO)(OCHMe_2)}$[35] (Mo–O = 1.86 Å) to estimate the Re=ÖR double-bond distance as 1.85 Å in alkoxy complexes with minimal steric hindrance, we estimate that a bond order of 1.5 for Re–OR should be 1.95 Å,[36] which is close to the observed value in $\mathrm{Re(OEt)(NTo)(S_2CNMe_2)_2}$. The Re–O–C(41) angle of 131.7 (4)° is about 15° too large based on simple formalisms such as IX and X. However, steric interactions frequently prevent M–O–C angles from decreasing less than 130° in alkoxy complexes. The foregoing bond-distance, bond-order correlations are supported by other structural data. We have noted that M≡N and M≡O distances are nearly equal (±0.02 Å) if the metal, coordination number, and electron count (EAN rule) are the same. Furthermore, comparable M≡NR distances are about 0.06 Å longer than M≡O distances.[1,9] With use of a Re=O double-bond length in oxo complexes of 1.78

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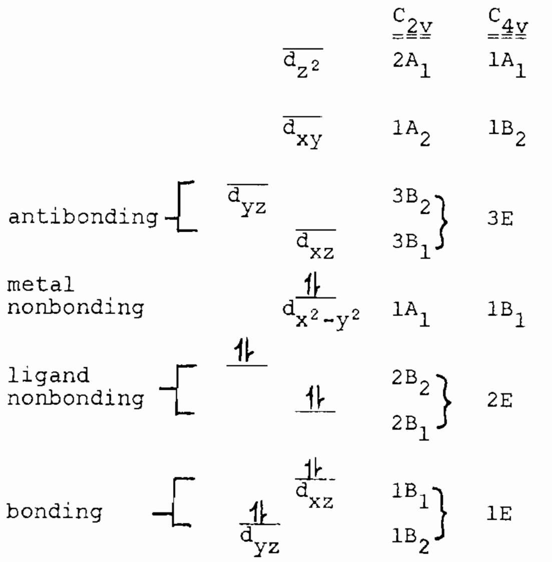
(33) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(34) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 256.

(35) McCleverty, J. A.; Seddon, D.; Bailey, N. A.; Walker, N. W. *J. Chem. Soc., Dalton Trans.* **1976**, 898.

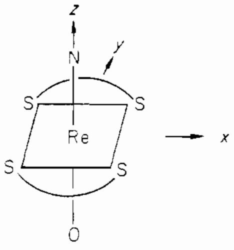
(36) Reference 34, p 239.

Chart II



Å[37] and a Re≡O triple-bond length of 1.63 Å,[38] a Re–O bond order of 2.5 should have a length of 1.70 Å, and a Re–NR bond order of 2.5 should be about 1.76 Å in length, which also compares favorably with the Re–N(3) distance in the present structure.

It is instructive to redescribe the foregoing valence bond description in molecular orbital terms. As with *cis*-$Mo(NR)_2(S_2CNEt_2)_2$,[9] only the interactions of the metal d orbitals with the π orbitals on –OR and –NR are considered, and nine molecular orbitals are formed (see XII). At first C_{4v} symmetry is considered (Chart II), and then the symmetry restrictions are relaxed to account for the sulfur chelates (C_{2v} symmetry) and then bending of the –NR and –OR ligands (C_s symmetry). The degeneracy in the E orbitals (C_{4v}) is broken by the dithiocarbamate chelates, whose π system causes the d_{yz} orbital to be lower in energy than the d_{xz} orbital. Owing to strong σ interactions, d_{xy} and d_{z^2} are high in energy. The $d_{x^2-y^2}$ orbital is essentially nonbonding with repsect to the π and σ ligand systems. The three B_2 orbitals and three B_1 orbitals form pairs of bonding ($1B_1$, $1B_2$), antibonding ($3B_1$, $3B_2$) and ligand-centered nonbonding ($2B_1$, $2B_2$) orbitals. As in $Mo(NMe_2)_4$,[39] it is assumed that the O/N p orbitals are lower in energy than the metal d orbitals; hence, $2B_1$ and $2B_2$ orbitals are probably lower in energy than the $d_{x^2-y^2}$ orbital (nonbonding $1A_1$). Since there are 10 π electrons, the two bonding and three nonbonding π orbitals are filled. The highest occupied orbitals ($1A_1$, $2B_1$, $2B_2$) have no significant σ components in the plane of the sulfur atoms, and the Re–S σ bonding is not strongly affected. It might be expected that these filled nonbonding ligand orbitals would have stereochemical consequences and would cause bending of the π-bonded ligands in the plane with the weakest π-bonding component, the *xz* plane. This MO description correlates nicely with the delocalized model (analogous to X) for the hypothetical compounds $Re(NR)_2(S_2CNR'_2)_2^-$ or $Os(NR)_2(S_2CNR'_2)_2$: two equal metal–nitrogen bonds on bond order 2.0 with equal bending of the nitrene ligands. If one nitrene is allowed to bend more than the other, the $2B_1$ and $2B_2$ orbitals will be localized on the more bent nitrene, and its metal–nitrogen distance will increase due to reduced overlap in the bonding $1B_1$ orbital. In turn π-bonding orbitals will be more localized on the other nitrene, which would respond in an opposite manner with a shorter metal–nitrogen bond and less bending at nitrogen. In the extreme case, the complex would adopt the fully localized geometry (analogous to IX) with the four electrons in the two nonbonding ligand orbitals being represented as lone pairs of electrons on the bent ligand. Although it is conceivable that the hypothetical $Os(NR)_2(S_2CNR'_2)_2$ could adopt the delocalized geometry, it is unlikely that $Re(OR'')(NR)(S_2CNR'_2)_2$ would do the same owing to the electronegativity differences between the oxygen and nitrogen ligands. Indeed, the Re complex seems to adopt a geometry intermediate between IX and X with bond orders of 2.5 (Re–N) and 1.5 (Re–O), which roughly corresponds to equal participation of the –NR and –OR ligands in dative π donation to the metal.



XII

The above molecular orbital description gives some insight into the stereochemistry of the title complex. The trans geometry with the linear π system seems to be preferred over the cis geometry for $Re(OR)(NR)L_4^{2+}$ and $Os(NR)_2L_4^{2+}$ (L = neutral ligand) owing to the favorable bonding overlap in the $1B_1$ and $1B_2$ orbitals. Let us consider the removal of the two electrons from the $1A_1$ ($d_{x^2-y^2}$) orbital; this would lead to a less favorable situation in which there would be little overlap between the empty $1A_1$ and the filled $2B_1$ or $2B_2$ orbitals. However, a cis geometry would result in appreciable overlap and a third important π-bonding interaction would result; thus $Re(OR)(NR)L_4^{4+}$ and $Mo(NR)_2L_4^{2+}$ would be expected to have cis geometries. Similar arguments can be used to rationalize the cis geometry in d^0 dioxo complexes (e.g., $WO_2Cl_2L_2$) and the trans geometry in d^2 dioxo complexes (e.g., $OsO_2Cl_2L_2$).[40]

The displacement of the axial ligands off the ideal axial sites was noted above. This effect is quite obvious and is *not* a result of intramolecular steric effects. The absence of any unusual intermolecular contacts also precludes crystal packing forces as being the determining causes. Careful scrutiny of the structures of $Re_2O_3(S_2CNEt_2)_4$[22] and $ReOCl_2(OEt)(C_5H_5N)_2$[41] shows that the *same distortions* also occur in these compounds despite the different ligands and different solid-state packing! In $Re_2O_3(S_2CNEt_2)_4$, the terminal oxo ligands are bent off the axial sites between the respective pair of dithiocarbamate ligands. The sulfur chelates respond by

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(37) Re–O = 1.781 (3) Å; see: Murmann, R. K.; Schlemper, E. O. *Inorg. Chem.* **1971**, *10*, 2352.

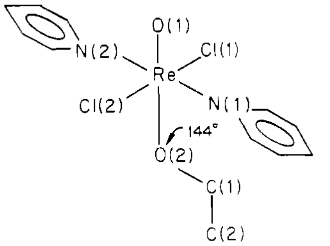
(38) Unlike the Mo≡O distance, which is reasonably well-known to be 1.66 ± 0.01 Å, Re≡O is much less well documented. We chose 1.63 Å to be a lower estimate of the Re–O distance on the basis of available (mediocre to poor quality) structural data: $ReOCl_4(OH_2)$ [1.63 (2) Å], $ReOCl_4(OH_2)^-$ [1.660 (9) Å], $ReOCl_5^{2-}$ [1.65 (2) Å], $ReOCl_2(OH_2)(thiourea)_2^+$ [1.65 (1) Å]. See: Lis, T. *Acta Crystallogr., Sect. B* **1979**, *B35*, 3041. The Re–O distance in *trans*-$ReOCl_3(PPhEt_2)_2$ is 1.60 Å, but the structural precision is too poor to be reliable. One might argue that 1.64 or 1.65 Å may be a better estimate for Re≡O than 1.63 Å, but the difference is not great and the semiquantitative discussions about bond lengths are not substantially changed. In the choice of reference complexes (above), those containing bulkier groups (Br^-) or π-donating groups (OR′) as auxiliary ligands must be excluded from consideration. By choosing Re≡O to be 1.63 Å and Re═O to be 1.78 Å, we calculate the Re–O distance to be 2.036 Å. Obtaining similar results to ours, Lock and Turner (*Acta Crystallogr., Sect. B* **1978**, *B34*, 923) chose Re═O to be 1.765 Å and fixed Re–O to be 2.04 Å; from this, Re≡O is calculated to be 1.604 Å.

(39) Chisholm, M. H.; Cotton, F. A.; Extine, M. W. *Inorg. Chem.* **1978**, *17*, 1329.

(40) Griffith, W. P. *Coord. Chem. Rev.* **1970**, *5*, 459.

(41) Lock, C. J. L.; Turner, G. *Can. J. Chem.* **1977**, *55*, 333.

folding back from the direction of the bending (109.2° − 106.5° = 2.7° on Re_1; 110.0° − 105.4° = 4.7° on Re_2) and by increasing the Re–S distances associated with the largest interchelate angle (Re–S(12), Re–S(21) > Re–S(11), Re–S(22) by 0.024 Å (average); Re–S(32), Re–S(41) > Re–S(31), Re–S(42) by 0.042 Å (average)). In $ReOCl_2(OEt)(C_5H_5N)_2$ (see XIII), both O(1) and O(2) are bent away from N(2) and Cl(2) toward Cl(1) and N(1); C(1) is bent in a plane that contains Re and O(2) and nearly bisects the Cl(1)–N(1) vector. Furthermore, Re–Cl(1) > Re–Cl(2) (by 0.075 Å), Re–N(1) > Re–N(2) (by 0.012 Å), and Cl(1)–Re–N(1) > Cl(2)–Re–N(2) (by 0.8°). If steric effects played a dominant role in determining the geometry of $Re(OEt)(NTo)(S_2CNMe_2)_2$ and $ReOCl_2(OEt)(C_5H_5N)_2$, then a geometry similar to VIII rather than the observed geometry VII would be expected. In the title complex, the bending of the –NR and –OR ligands at N or O in the *xz* plane reduces the bonding overlap in the bonding $1B_1$ orbital and increases the interaction (absent when –OR and –NR are linear) between the metal $d_{x^2-y^2}$ orbital ($1A_1$) and the nonbonding combination of O/N p_x orbitals ($2B_1$). Moving the –NR and –OR ligands off the axial sites *in the direction of the bending* of the two nonlinear, axial ligands reduces the decrease in bonding overlap in the $1B_1$ orbital and increases the bonding interaction between the $1A_1$ and $2B_1$ orbitals. Thus, the movement of the –NR and –OR ligands off the ideal axial sites minimizes the decrease in π bonding caused by the bending of the axial ligands. We find that these simple molecular orbital considerations seem to rationalize the unusual distortions seen in the geometry of $Re(OEt)(NTo)(S_2CNMe_2)_2$ and related complexes.



XIII

This study illustrates that the EAN rule is useful in predicting when a bent nitrene will be found in a particular complex provided that something is known about the coordination modes of ambidentate ligands such as dithiocarbamates. When the electron count exceeds the usual 18 electrons, the amphoteric nitrene ligand can bend with a concomitant increase in the metal–nitrogen bonding distance.[42] It would be interesting to know if the lengthening of the metal–nitrogen distances in bent nitrenes appreciably weakens the metal–nitrogen bonds to the extent that the nitrenes are rendered more susceptible toward external chemical attack at nitrogen. Experiments to determine the chemical reactivity of some of these bent nitrene ligands are in progress.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also acknowledge the Marshall H. Wrubel Computing Center for the use of computing facilities.

Registry No. $ReCl_3(NTo)(PPh_3)_2$, 83461-46-5; $ReCl_3(NPh)(PPh_3)_2$, 83461-47-6; $ReCl(NTo)(S_2CNMe_2)_2$, 83399-38-6; $ReCl(NPh)(S_2CNMe_2)_2$, 83399-39-7; $ReCl(NTo)(S_2CNEt_2)_2$, 83399-40-0; $ReCl(NMe)(S_2CNMe_2)_2$, 83399-41-1; *cis*-$Re(NTo)(S_2CNMe_2)_3$, 83399-42-2; *cis*-$Re(NPh)(S_2CNMe_2)_3$, 83399-43-3; *cis*-$Re(NTo)(S_2CNEt_2)_3$, 83399-44-4; *cis*-$Re(NPh)(S_2CNEt_2)_3$, 83399-45-5; *trans*-$Re(NTo)(OEt)(S_2CNMe_2)_2$, 83399-46-6; *trans*-$Re(NPh)(OEt)(S_2CNMe_2)_2$, 83399-47-7; *trans*-$Re(NTo)(OEt)(S_2CNEt_2)_2$, 83399-48-8; *trans*-$Re(NTo)(OMe)(S_2CNMe_2)_2$, 83399-49-9; *trans*-$Re(NTo)(OMe)(S_2CNEt_2)_2$, 83399-50-2; $[Re(NTo)(S_2CNMe_2)_2]_2O$, 83399-51-3; $[Re(NMe)(S_2CNMe_2)_2]_2O$, 83399-52-4; *trans*-$Re(NMe)(OMe)(S_2CNMe_2)_2$, 83399-53-5; *cis*-$Re(NMe)(S_2CNMe_2)_3$, 83399-54-6; *p*-$CH_3C_6H_4N{=}PPh_3$, 2327-67-5; $PhN{=}PPh_3$, 2325-27-1; $ReOCl_3(PPh_3)_2$, 34248-12-9; tetramethylthiouram disulfide, 137-26-8; trimethylsilyl dimethyldithiocarbamate, 18140-13-1; thallium dimethyldithiocarbamate, 83399-37-5.

Supplementary Material Available: Listings of root-mean-square amplitudes of vibration, positional parameters of hydrogen atoms, thermal parameters, and observed and calculated structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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(42) The EAN rule yields useful results when applied to a wide variety of mono- and bis(nitrene) complexes. Notable exceptions are the bis(aminonitrene) (1,1-diazene, hydrazido(2−)) complexes of the type $Mo(NNR_2)_2(S_2CNR'_2)_2$. Both $Mo(N_2Ph_2)_2(S_2CNMe_2)_2$ and $Mo(N_2MePh)_2(S_2CNMe_2)_2$ have similar structural parameters: N–N = 1.30 Å, Mo–N = 1.79 Å, Mo–N–N = 171°. The absence of significant bending at the Mo–NN angle makes these compounds unique and points to their unusual electronic characteristics. See ref 1 and: Chatt, J.; Crichton, B. A. L.; Dilworth, J. R.; Dahlstrom, P.; Gutkoska, R.; Zubieta, J. A. *Transition Met. Chem.* (*Weinheim, Ger.*) **1979**, *4*, 271.