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Preparation and characterization of rhenium (I) tricarbonyl dithiocarbamate compounds; $Re(CO)_3(S_2CNMe_2)(L)$

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ABSTRACT

The title compounds were prepared in good yield by treatment of $Re(CO)_5Cl$ or $[Re(CO)_3(H_2O)_3]Br$ with sodium dimethyldithiocarbamate hydrate ($NaS_2CNMe_2{\cdot}H_2O$) and a neutral ligand yielding eight $Re(CO)_3(S_2CNMe_2)(L)$ derivatives: L = NH_3 **1**, pyridine (py) **2**, imidazole (im) **3**, pyrazole (pz) **4**, triphenylphospine (PPh_3) **5**, 1,3,5-triaza-7-phosphaadamantane (PTA) **6**, *t*-butyl isocyanide (*t*-BuNC) **7**, and cyclohexyl isocyanide (CyNC) **8**. The resulting new complexes were characterized by ^1H and ^{13}C NMR and infrared spectroscopy. Each was also structurally elucidated by X-ray crystallography. General structural features in all eight compounds were similar. The orientation of the three single-faced ligands, py, im and pz, demonstrates an interaction with the filled π orbital of the dithiocarbamate. Compounds were tested for stability under conditions that mimic physiological conditions; **1**–**4** quickly decomposed, **7** and **8** decomposed over 24 h while **5** and **6** were stable.

1. Introduction

The dithiocarbamate anion is a versatile ligand in inorganic chemistry [1]. A monoanionic, four-electron donating ligand that is capable of either π-electron donation or withdrawal, dithiocarbamate has played a role in the study of a wide variety of compounds. It has been used in the synthesis of higher oxidation state transition metal compounds, including the modeling of molybdoenzymes [2,3], and in the creation of low oxidation state organometallic compounds [4,5]. The planar, delocalized π-system has also been useful in creating stable compounds that are electron-deficient or have unusual geometries. As one example, the trigonal prismatic geometry of the 16-electron compound, $Mo(CO)_2(S_2CN\text{-}i\text{-}Pr_2)_2$, is stabilized by concerted ligand π-donation to a single metal-based LUMO orbital [6].

The chemistry of the dithiocarbamate ligand has been investigated with rhenium; to date there are more than fifty structures of rhenium dithiocarbamates (dtc) in the CCDC database [7]. However, only six X-ray structures of rhenium carbonyl dithiocarbamates compounds have been reported, including $Re(CO)(S_2CNEt_2)_3$ [8], a manganese–rhenium heterobimetallic dimer with a bridging dithiocarbamate [9], and rhenium (I) dithiocarbamate compounds prepared by reactions of rhenium allyl or pseudo-allyl complexes with cumulenes or heterocumulenes [10,11]. Only two reported compounds are structurally analogous to the compounds in this report: a pair of rhenium (I) tricarbonyl dithiocarbamate compounds with derivatized phosphine ligands employed in an examination of the [2 + 1] strategy of preparing radiopharmaceuticals have been structurally characterized [12]. A similar study without crystallographically characterized compounds has been reported using derivatized dithiocarbamate ligands and isocyanide ligands [13]. There have been published studies of the synthesis and spectroscopic characterization of the fundamental members of the $Re(CO)_3(dtc)L$ series, however the compounds were prepared by multi-step reactions or by using thiuram disulfides or thallium salts [14–17].

Recently, we have been investigating the fundamental chemistry of the $Re(CO)_3^+$ fragment, largely driven by the use of this unit as a model for $^{99m}Tc(CO)_3^+$ based imaging agents as well as $^{186/188}Re$ radionuclide therapeutics [18–21]. One reason for this focus is that there remain common ligands that have not been extensively applied to the group 7 d^6 systems. We have presented reports on monodentate [22], bidentate [23,24], and tridentate [25,26] ligand systems over the past several years. In this paper we continue this series, looking at simple complexes of the dithiocarbamate ligand prepared in a straightforward manner.

We report a study of the fundamental series of eight compounds, $Re(CO)_3(dmtc)L$, dmtc = $S_2CNMe_2^-$, with varied neutral monodentate ligands: L = ammonia (NH_3) **1**, pyridine (py) **2**, imidazole (im) **3**, pyrazole (pz) **4**, triphenylphosphine (PPh_3) **5**, 1,3,5-triaza-7-phosphaadamantane (PTA) **6**, *t*-butyl isocyanide (*t*-BuNC) **7**, and cyclohexyl isocyanide (CyNC) **8**. Various ligand types, amines, N-heterocyclic amine, phosphines and isonitriles, were

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examined with the goal of seeing which type would give the compound most resistant to external nucleophiles. The compounds are readily prepared in methanol in good yield in a single step with simple reagents. Each compound was characterized spectroscopically and structurally elucidated by X-ray crystallography. The compounds were also exposed to conditions that mimic physiological conditions to test their ability to withstand decomposition following prolonged exposure to these conditions; **1–4** quickly decomposed, **5** and **6** decomposed over 24 h while **7** and **8** resisted decomposition over several days.

2. Results and discussion

2.1. Syntheses

The most efficient mode of synthesis of compounds **1–8** was found to be a one pot reaction in methanol. One equivalent each of the rhenium reagent and sodium dimethyldithiocarbamate hydrate and an excess of the neutral ligand were allowed to reflux in the solvent. It made no difference in outcome whether $Re(CO)_5Cl$ or $[Re(CO)_3(H_2O)_3]Br$ [27] (actually, $[Re(CO)_3(H_2O)_3]$ $Re_2(CO)_6(\mu_2\text{-}Br)_3]\cdot 6H_2O$ [28]) was used as the reagent. Previously, we found that $Re(CO)_3L_3^+$ (L = NH_3, tetrahydrothiophene, N-methylimidazole and pyridine) compounds could be readily prepared in water [22]. In this study, immediate precipitation, presumably of neutral $Re(CO)_3(dmtc)(H_2O)$, occurred when reactions were attempted in water; this compound was never isolated, and the use of water as a solvent was abandoned.

Pure compounds were obtained in good yield as colorless or pale yellow solids. Compounds were readily recrystallized by either vapor diffusion of a two solvent system, or by slow cooling of the reaction mixture, yielding pure crystals for spectroscopic and crystallographic analysis.

2.2. Molecular structures

Compounds **1–8** were characterized by single crystal X-ray crystallography. The molecular structures of **1–4** are shown in Fig. 1; the molecular structures of **5–8** are shown in Fig. 2. Crystal data and experimental details are listed in Table 1. The compounds share the same basic structural characteristics. Each $Re(CO)_3$ fragment has the carbon monoxide ligands in the expected *facial* arrangement, approximately 90° apart; each compound is pseudo-octahedral. The dithiocarbamate binds as a symmetric bidentate ligand. The ligand is essentially planar as a result of the π-electron delocalization through the sulfur, central carbon and nitrogen atoms. The placement of the rhenium atom with respect to the plane of the dithiocarbamate ligand varies in an apparently random fashion likely dictated by crystal packing. It lies as much as 8° below the plane (relative to ligand L) in **1** and 7° above the plane in **6**. The sixth ligand in each compound bends slightly toward the dithiocarbamate ligand with observed angles between 81 and 88°. The dithiocarbamate ligand has an average bite angle of 70.4(4)°, similar to the range of 69–71° measured for other rhenium (I) dithiocarbamates [10–12]. The Re–N distance of 2.228(5) Å measured for **1** is comparable to the average value of 2.23(1) Å recorded for $[Re(CO)_3(NH_3)_3]Br$ and $Re(CO)_3(NH_3)_2Br$ [22,29]. The average Re–N distance for **2** and **3** is 2.223(5) Å, comparable to the average value of 2.21(2) Å for the series of $[Re(CO)_3L_3][PF_6]$ and $Re(CO)_3L_2Br$ with N-heterocyclic base ligands [22]. The Re–N value of 2.173(10) Å measured for **4** is at the low end of the range of values, 2.17–2.20 Å, observed for comparable pyrazole complexes [30–34]. The Re–P distance for **5** is 2.470(3) Å [12]. The related compounds, $Re(CO)_3(dmtc)(PPh_2R)$ R = $CH_2CH_2CO_2Me$ and $CH_2CH_2CONHCH_2CH_2CO_2Me$, have Re–P distances of 2.495(2) and 2.492(2) Å, respectively, close to that observed in **5**. The Re–P distance in **6** is 2.437(4) Å, close to the average Re–P distance of 2.436(17) Å in the related neutral PTA complexes, $Re(CO)_3(PTA)_2(Br)$ and $[Re(CO)_3(PTA)_3][PF_6]$ [35]. The Re–C distances in **7** and **8** average 2.091(10) Å, similar to the range of values, 2.09–2.12 Å, measured in a series of mononuclear $Re(CO)_3$(CN-alkyl) compounds [36–40].

Compounds (**2–4**) each show an additional feature; the plane of the neutral sixth ligand is approximately perpendicular to the line that bisects the S–Re–S angle. The angle is 89(1)° for **2**, 79(1)° for **3**, and 74(1)° for **4**. This orientation is explained by orbital interactions. The neutral ligands are each single-faced π-acceptors ligands. One lobe of the π*-orbital points toward the center of one lobe of the dithiocarbamate π cloud (Fig. 3). The benefit gained by the interaction of the empty ligand π*-orbital with the filled, delocalized, dithiocarbamate π-orbital favors this orientation of the single-faced monodentate ligand. The skewing of the imidazole and pyrazole ligands by a few degrees away from this preferred geometry is most likely due to solid state packing effects. The pyrazole rings engage in π stacking in the extended solid state. In contrast, the imidazole ligand is twisted due to hydrogen bonding and smaller packing effects in the crystal.

2.3. Spectroscopic characterization

IR spectra of the new compounds displayed two metal carbonyl bands between about 2010 and 1840 cm^{-1}. This is consistent with a pseudo-C_{3v} symmetry for the compounds with an a_1 and an e band. Compound **6** shows splitting of the lower energy e band, the splitting is observed when the compound is dissolved in CH_2Cl_2 suggesting that this is a ligand-based effect. Compounds **7** and **8** each show a $\nu(C{\equiv}N)$ stretch around 2185 cm^{-1} comparable to where it is observed for related compounds [36]. ^1H and ^{13}C NMR spectra for all compounds were recorded and each showed the expected pattern for the dithiocarbamate ligand and for the sixth ligand.

2.4. Stability studies

An important characteristic of any compound or class of compounds that may be used *in vivo* is that it stands up to physiological conditions. In addition, diagnostic imaging agents administered by injection should clear the body in one day, thus drug candidates should not appreciably decompose during this period. The compounds reported here were all tested by setting up a $CDCl_3$ solution that was equimolar in the compound and in N-methylimidazole, a model for histidine. The solution was kept at 37 °C and monitored over time by ^1H NMR spectroscopy. Compounds **1–4** decomposed in less than 1 h under these conditions. Compounds **7** and **8** showed significant decomposition after 24 h. In contrast, **5** and **6** showed essentially no decomposition after one week under these conditions. Good σ donation and strong π back-donation for phosphines, characteristic of organometallic metal phosphine compounds [41], leads to inert M–L bonds that withstand the presence of strongly nucleophilic materials. Phosphines, both alkyl and aryl, would seem to be useful ligands to stabilize potential [2 + 1] candidates for radiopharmaceuticals. Isonitriles do not appear to be good candidates, while amines seem to impart little stability in the presence of nucleophiles.

2.5. Summary

This study was undertaken with the goal of developing simple syntheses of $Re(CO)_3(dmtc)L$ compounds, to characterize the new compounds and examine their stability. Eight new compounds were prepared and characterized by spectroscopy and elemental

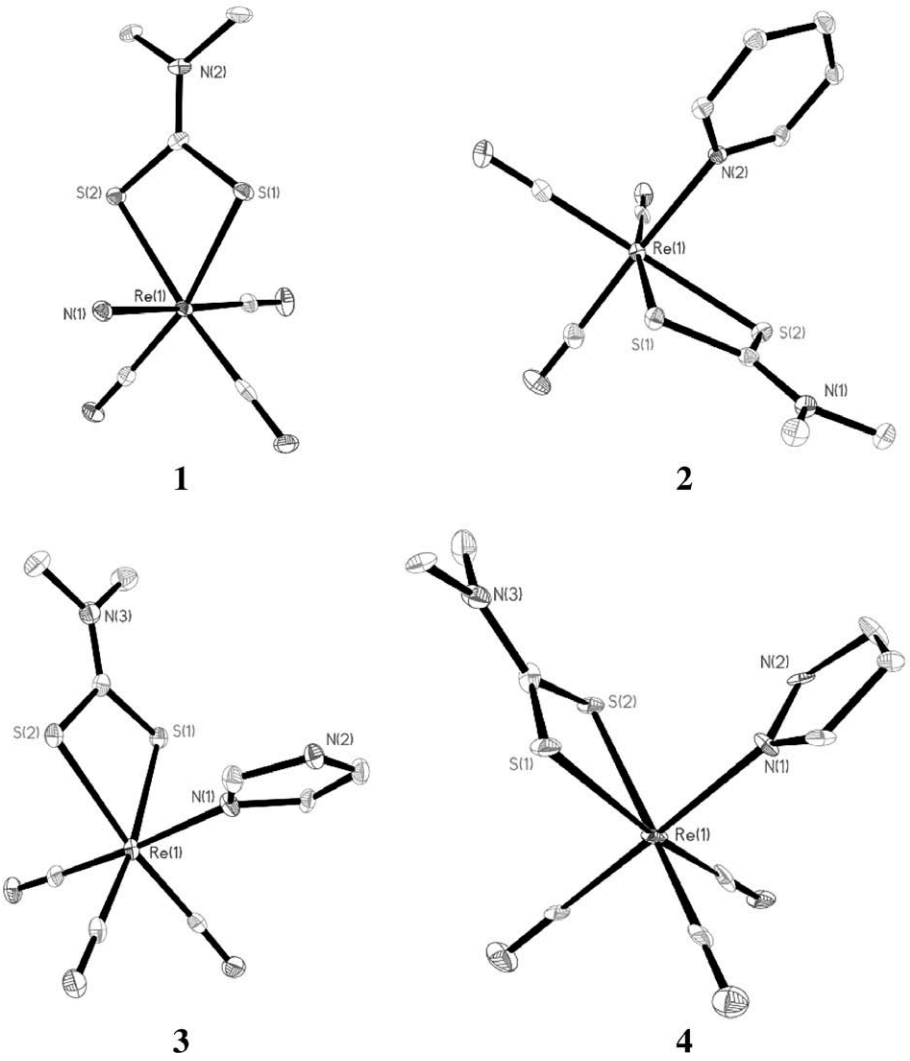

Fig. 1. Structures of **1–4** with 35% ellipsoids. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) for **1**: Re(1)–S(1) 2.5065(2), Re(1)–S(2) 2.497(2), Re(1)–N(1) 2.228(5), S(2)–Re(1)–S(1) 70.64(5), N(1)–Re(1)–S(1) 83.60(12), N(1)–Re(1)–S(2) 85.89(14); for **2**: Re(1)–S(1) 2.498(2), Re(1)–S(2) 2.5051(15), Re(1)–N(2) 2.219(4), S(1)–Re(1)–S(2) 70.83(4), N(2)–Re(1)–S(1) 85.1(1), N(2)–Re(1)–S(2) 83.39(1); for **3**: Re(1)–S(1) 2.517(2), Re(1)–S(2) 2.501(2), Re(1)–N(1) 2.189(6), S(2)–Re(1)–S(1) 70.83(6), N(1)–Re(1)–S(1) 83.5(2), N(1)–Re(1)–S(2) 85.6(2); for **4**: Re(1)–S(1) 2.489(4), Re(1)–S(2) 2.501(4), Re(1)–N(1) 2.17(1), S(1)–Re(1)–S(2), 70.2(1), N(1)–Re(1)–S(1) 85.9(3), N(1)–Re(1)–S(2) 87.1(3).

analysis. The structure of each compound was also elucidated by X-ray crystallography. The general structure of each was as expected. The three compounds with planar heterocyclic amines as the sixth ligand showed a preferential geometric orientation of this planar ligand with respect to the dithiocarbamate ligand, indicating that there is an orbital interaction between the filled dithiocarbamate π-orbital and the ligand π^*-orbital. The ability of each compound to withstand the presence of strong nucleophiles was tested. Compounds **1–4** showed little stability under these conditions. Compounds **7** and **8** were marginally stable as they showed significant decomposition in 24 h. Compounds **5** and **6** are promising. Each withstood these conditions for seven days with essentially no decomposition. Further studies are in progress.

3. Experimental

3.1. Materials and methods

All reagents were purchased from Strem, Acros Organics or Sigma–Aldrich and used as received. Solution NMR spectroscopy was performed on Varian VXR 300 MHz and Varian 400MH NMR instruments. IR spectra were recorded on a Nicolet NEXUS 870 FT-IR Esp and Perkin Elmer Spectrum One FT-IR spectrometers. Elemental analyses were carried out at the School of Chemical Sciences Microanalytical Laboratory at the University of Illinois at Urbana-Champaign or Atlantic Microlab of Norcross, GA 30091. The synthesis of $[Re(CO)_3(H_2O)_3]Br$ was carried out as previously described [27].

3.2. Synthesis of *1*

$[Re(CO)_3(H_2O)_3]Br$ (0.100 g, 0.247 mmol), Sodium dimethyldithiocarbamate monohydrate (0.0354 g, 0.247 mmol) and 30% ammonium hydroxide (0.0150 g, 0.247 mmol) were added to 10 mL of methanol. The reaction was refluxed for 4 h producing a clear homogeneous solution. The round bottom was slowly cooled to room temperature generating small, white crystals. The crystalline solid was filtered and dried under air and collected. Yield 69%. IR: 2008(s), 1865(vs) cm^{-1}. Anal. Calc. for $C_6H_{11}N_2O_4S_2Re$: C, 16.94; H, 2.61; N, 6.58. Found: C, 16.58; H, 2.04; N, 6.23%. M.p. = 175.8° ^1H NMR ($CDCl_3$): δ 3.24 (m, 6H, CH_3), 2.55 (s, 3H, NH_3). ^{13}C NMR ($CDCl_3$): δ 212.2, 195.2, 194.9, 34.95.

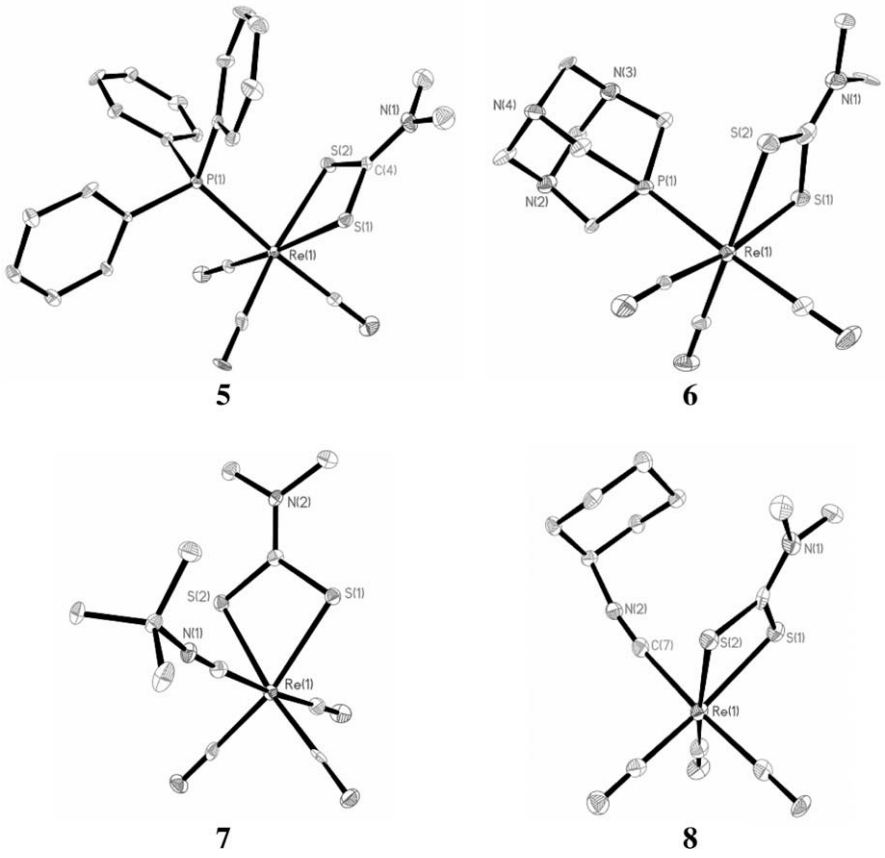

Fig. 2. Structures of **5–8** with 35% ellipsoids. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) for **5**: Re(1)–S(1) 2.495(3), Re(1)–S(2) 2.513(3), Re(1)–P(1) 2.470(3), S(1)–Re(1)–S(2) 69.95(9), P(1)–Re(1)–S(1) 90.74(8), P(1)–Re(1)–S(2) 85.94(9); for **6**: Re(1)–S(1) 2.527(5), Re(1)–S(2) 2.529(5), Re(1)–P(1) 2.437(4), S(1)–Re(1)–S(2) 69.90(14), P(1)–Re(1)–S(1) 86.68(15), P(1)–Re(1)–S(2) 84.69(15); for **7**: Re(1)–S(1) 2.521(2), Re(1)–S(2) 2.512(2), Re(1)–C(4) 2.101(8), S(2)–Re(1)–S(1) 70.22(7), C(4)–Re(1)–S(1) 84.2(2), C(4)–Re(1)–S(2) 85.1(2); for **8**: Re(1)–S(1) 2.502(2), Re(1)–S(2) 2.513(2), Re(1)–C(7) 2.081(10), S(1)–Re(1)–S(2) 69.91(8), C(7)–Re(1)–S(1) 83.8(3), C(7)–Re(1)–S(2) 85.2(3).

3.3. Synthesis of ***2–8***

Compounds **2–7** were prepared by similar methods. In a typical reaction, 0.150 g of $Re(CO)_5Cl$ or $[Re(CO)_3(H_2O)_3]Br$, along with one equivalent of sodium dimethyldithiocarbamate hydrate and the monodentate ligand were added to a round bottom flask. The reaction was refluxed for 4 h in methanol producing a clear, homogeneous solution. The round bottom was slowly cooled to room temperature affording colorless or pale yellow crystals. The crystals were filtered, washed with ether and dried. In some cases crystals

Table 1
Crystal Data and Structure Refinement for **1–8**.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Formula	$C_6H_9N_2O_3ReS_2$	$C_{11}H_{11}N_2O_3ReS_2$	$C_{12}H_{16}N_3O_4ReS_2$	$C_9H_{10}N_3O_3ReS_2$	$C_{24}H_{21}NO_3PReS_2$	$C_{15}H_{21}NO_3PReS_2$	$C_{11}H_{15}N_2O_3ReS_2$	$C_{13}H_{17}N_2O_3ReS_2$
FW	407.47	469.54	516.6	458.52	652.74	544.62	473.57	623.72
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*c*	$P\bar{1}$	*P*2(1)/*c*	*C*2/*c*	*P*2(1)/*n*	*P*2(1)2(1)2(1)	*P*2(1)/*n*
a (Å)	10.656(5)	13.236(5)	8.273(6)	9.303(4)	55.78(3)	8.032(3)	5.837(4)	6.5075(17)
b (Å)	10.354(5)	7.993(3) Å	8.335(6)	6.306(2)	8.795(5)	23.326(9)	15.104(9)	18.724(5)
c (Å)	10.656(5)	14.782(6)	13.255(9)	22.046(9)	19.782(11)	9.168(4)	17.514(10)	13.387(3)
α (Å)	90	90	76.355(11)	90	90	90	90	90
β (Å)	113.15	112.507(6)	74.601(11)	96.918(7)	102.446(13)	90.278(6)	90	94.431(4)
γ (Å)	90	90	83.047(11)	90	90	90	90	90
V (Å^3)	1080.9(9)	1444.7(10)	854.6(10)	1283.9(8)	9476(9)	1717.7(12)	1544.1(16)	1626.2(7)
Z	4	4	2	4	16	4	4	4
ρ_{calc} (mg/m^3)	2.504	2.1593	2.007	2.372	1.830	2.106	2.037	2.548
Absorption coefficient (mm^{-1})	11.611	8.703	7.372	9.792	5.400	7.423	8.144	11.454
$2\theta_{max}$ (°)	54.00	56.62	53.98	54.96	54	53.98	54.48	56.46
R indices[a]	0.0300	0.0314	0.0390	0.0669	0.0598	0.0808	0.0329	0.0557
$wR_2 = [I > 2\sigma(I)]$	0.0711	0.0679	0.0890	0.1522	0.1053	0.1884	0.0641	0.1131
Data/parameters	2344/130	3408/174	3660/203	2880/165	10 349/581	3729/210	3442/178	3804/190

[a] All structures collected at 100(2) K.

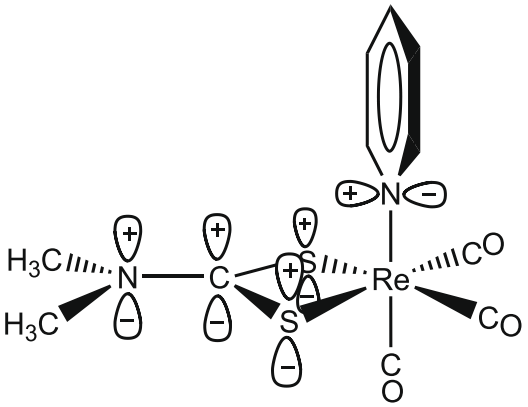

Fig. 3. Interaction between filled, delocalized dithiocarbamate ligand orbital and empty π^* N-heterocyclic orbital.

suitable for X-ray diffraction were grown by vapor diffusion. The crystalline solid was filtered and dried under air and collected.

Compound **2**: 63% yield. IR: 2005(s), 1863(vs) cm^{-1}. Anal. Calc. for $C_{11}H_{11}N_2O_3S_2Re$; C, 28.14; H, 2.36; N, 5.97%. Found: C, 28.08; H, 2.30; N, 5.88%. M.p.= 184.3 °C (d). ^1H NMR ($CDCl_3$): δ 8.96 (m, 2H, *H* on py), 7.83 (m, 1H, *H* on py), 7.35 (m, 2H, *H* on py), 3.16 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 215.6, 155.5, 137.7, 125.2, 39.6. Crystals suitable for X-ray diffraction were grown by vapor diffusion of CH_2Cl_2 into a methanol solution of the complex.

Compound **3**: 56% yield. IR: 2004(s), 1838(vs) cm^{-1}. Anal. Calc. for $C_6H_{10}N_3O_3S_2Re$; C, 23.57; H, 2.20; N, 9.16%. Found: C, 23.77; H, 2.17; N, 8.79%. M.p.= 178.6 °C (d). ^1H NMR ($CDCl_3$): δ 8.31 (s, 1H, *H* on imidazole), 7.40(s, 1H, *H* on imidazole), 7.28 (s, 1H, *H* on imidazole), 3.20 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 214.8, 139.9, 131.4, 117.4, 38.7. Crystals suitable for X-ray diffraction were grown by vapor diffusion of heptane into an acetone solution of the complex.

Compound **4**: 93% yield. IR: 2001(s), 1856(vs) cm^{-1}. Anal. Calc. for $C_6H_{10}N_3O_3S_2Re$: C, 23.57; H, 2.20; N, 9.16. Found: C, 23.49; H, 2.21; N, 8.95%. M.p. = 147.5 °C (d). ^1H NMR ($CDCl_3$): δ 7.95 (s, 1H, *H* on pz), 7.63 (s, 1H, *H* on pz), 6.44 (s, 1H, *H* on pz) 3.26 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 215.0, 144.7, 129.8, 107.62, 39.8. Crystals suitable for X-ray diffraction were grown by vapor diffusion of methanol into a CH_2Cl_2 solution of the compound.

Compound **5**: 68.8% yield. IR: 2005(s), 1863(vs) cm^{-1}. Anal. Calc. for $C_{24}H_{21}NPO_3S_2Re$: C, 44.18; H, 3.24; N, 2.15. Found: C, 44.52; H, 3.28; N, 2.25%. M.p. = 196.0 °C (d). ^1H NMR ($CDCl_3$): δ 7.55 (m, 6H, *H* on PPh_3), 7.40 (m, 9H, *H* on PPh_3), 2.71 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 211.6, 134.9, 131.4, 130.2, 127.8, 38.4. Crystals suitable for X-ray diffraction and characterization purposes were formed by vapor diffusion of diethyl either into a CH_2Cl_2.

Compound **6**: 99% yield IR: 2010(vs), 1927(s), 1878(vs) cm^{-1}. Anal. Calc. for $C_{12}H_{18}N_4O_3RePS_2$: C, 26.32; H, 3.31; N, 10.23. Found: C, 26.44; H, 3.30; N, 9.89%. M.P. = 210.0 °C. ^1H NMR ($CDCl_3$): δ 4.63 (d, 3H, $NCH_{ax}N$, J_{HH} = 13.2 Hz), 4.50 (d, 3H, $NCH_{eq}N$, J_{HH} = 13.2 Hz), 4.22 (s, 6H, PCH_2N), 3.22 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ213.4, 73.5, 50.7 (d, PCH_2N, J_{PC} = 16.1 Hz), 39.2. Crystals suitable for X-ray diffraction and characterization purposes were obtained by single solvent crystallization from a $CHCl_3$ solution.

Compound **7**: 72% yield. IR: 2185(m), 2011(s), 1886(vs) cm^{-1}. Anal. Calc. for $C_{11}H_{15}N_2O_3S_2Re$: C, 27.90; H, 3.19; N, 5.92. Found: C, 27.60; H, 3.13; N, 5.62%. M.P. = 158.0 °C. ^1H NMR ($CDCl_3$): δ3.21 (s, 6H, NCH_3), 1.53 (s, 9H, *H*, CCH_3). ^{13}C NMR ($CDCl_3$): δ 214.8, 191.0, 190.8, 39.0, 30.8. Slow evaporation of the methanol reaction solution produced crystals suitable for X-ray diffraction.

Compound **8**: 59.2% yield. IR: 2186(m), 2010(s), 1879(vs) cm^{-1}. Anal. Calc. for $C_{13}H_{17}N_2O_3S_2Re$: C, 31.31; H, 3.23; N, 5.62. Found: C, 31.06; H, 3.39; N, 5.43%. M.P. = 110.4 °C (d). ^1H NMR (d_6-DMSO): δ 3.99 (s, H, *CH*), 3.21 (s, 6H, CH_3), 1.84 (m, 6H, CH_2), 1.48 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ 206.6, 197.5, 54.1, 39.2, 32.5, 25.2, 22.0. Crystals suitable for X-ray diffraction were grown by vapor diffusion of hexane into an acetone solution of the compound.

3.4. X-ray data collection and structure determination

X-ray intensity data were measured at 100 K (Bruker KYROFLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (λ = 0.71073 Å) operated at 2000 W power. The crystals were mounted on a cryoloop using Paratone N-Exxon oil and placed under a stream of nitrogen at 100 K. The detector was placed at a distance of 5.009 cm from the crystals. The data was corrected for absorption with the SADABS program. The structures were refined using the Bruker SHELXTL Software Package (Version 6.1), and were solved using direct methods until the final anisotropic full-matrix, least squares refinement of F^2 converged [42]. Additional experimental details are provided in Table 1.

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Appendix A. Supplementary material

CCDC 731465 through 731472 contain the supplementary crystallographic data for **1** through **8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.08.008.

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