



## Experimental and theoretical studies of new rhenium carbonyls containing 4,5-bis(chalcogenodiphenylphosphinoyl)-1,2,3-triazolates



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### ABSTRACT

The novel binuclear complexes  $[\text{Re}(\text{CO})_3-\mu\{-\kappa^3\text{-N,N',E-L}^{\text{T-E2}}\}_2 \text{E} = \text{S and Se}]$  were prepared upon reaction of the corresponding potassium bis(chalcogenodiphenylphosphinoyl)triazolate,  $\text{K}[\text{L}^{\text{T-E2}}]$ , and  $[\text{ReBr}(\text{CO})_5]$ .  $^{31}\text{P}\{^1\text{H}\}$ -NMR monitoring studies showed that formation of the binuclear complexes was preceded by the corresponding mononuclear complex  $[\text{Re}(\text{CO})_4\{\kappa^2\text{-N,E-L}^{\text{T-E2}}\}]$  ( $\text{E} = \text{S, Se}$ ). Theoretical calculations indicated that a faster reaction time for the formation of the sulfur binuclear complex in comparison with its selenium analog stems from thermodynamic considerations. The new complexes herein reported were characterized by standard spectroscopic techniques and single crystal X-ray analysis.

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### 1. Introduction

Rhenium carbonyl species have attracted widespread attention due to their numerous applications in bioorganometallic chemistry as luminophores in fluorescence cell imaging [1,2], as catalysts for the isomerization of propargylic alcohols [3], as electrocatalysts for  $\text{CO}_2$  reduction [4], and CO-releasing molecules (CORMs) [5], to mention but a few. In all the areas where rhenium carbonyl cores play a part, the ligands to which they are bound are determinant for their specific application. Thus, coordination studies of unexplored ligands pose a challenge and a necessity for suitable complex formation.

The 4,5-bis(chalcogenodiphenylphosphinoyl)-1,2,3-triazoles,  $[\text{L}^{\text{T-E2}}]\text{H}$ ,  $\text{E} = \text{O, S, and Se}$ , comprise a set of compounds that has attracted great attention since they are thermally, oxidatively, and hydrolytically stable. The first congener of the series, the 4,5-bis(diphenylphosphinoyl)-1,2,3-triazole, was reported several years ago by Trofimenko et al. [6] and its molecular structure is shown in Chart 1.

Since the 4,5-bis(chalcogenodiphenylphosphinoyl)-1,2,3-triazoles were first discovered several efforts have been made to

explore their coordination chemistry: The 4,5-bis(diphenylphosphinoyl)-1,2,3-triazolate,  $[\text{L}^{\text{T-O2}}]$ , ligates to cobalt(II) and rhodium(I) ions in a  $\kappa^2\text{-N,O}$  chelation mode in the complexes  $[\text{Co}(\text{L}^{\text{T-O2}})_2(\text{py})_2] \cdot 2\text{py}$ ,  $\text{py} = \text{pyridine}$  and  $[\text{Rh}(\text{L}^{\text{T-O2}})(\text{cod})]$ ,  $\text{cod} = \text{cyclooctadiene}$  achieving five-membered metallarings; whereas coordination to uranium(VI) and lanthanum(III) metal centers, being both more oxophilic, exhibited a  $\kappa^2\text{-O,O}$  chelation mode, despite the sterically disfavored seven-membered rings formed in the complexes  $[\text{UO}_2(\text{L}^{\text{T-O2}})_2(\text{dmf})]$  and  $[\text{La}(\text{L}^{\text{T-O2}})_3(\text{dmf})_2]$ ,  $\text{dmf} = \text{dimethylformamide}$  [6]. Interestingly it was reported that the 4,5-bis(diphenylphosphinoyl)-1,2,3-triazolate presents both  $\kappa^2\text{-O,O}$  and  $\kappa^2\text{-N,O}$  chelation modes, in the same coordination sphere, in the complexes  $[\text{Ln}(\kappa^2\text{-O,O-L}^{\text{T-O2}})_2(\kappa^2\text{-O,N-L}^{\text{T-O2}})(\text{dmsO})_2]$ ,  $\text{Ln} = \text{La, Ce}$ ,  $\text{dmsO} = \text{dimethylsulfoxide}$  [7]. Synthesis and reactivity of the sulfur analogue of 4,5-bis(diphenylphosphinoyl)-1,2,3-triazole showed the  $\kappa^2\text{-N,S}$  chelation mode to Pd(II) in the complexes  $[\text{Pd}(\text{L}^{\text{T-S2}})_2]$  and  $[\text{Pd}(\text{L}^{\text{T-S2}})(\text{methallyl})]$  [8]. Although the selenium analogue ( $[\text{L}^{\text{T-Se2}}]\text{H}$ ) was reported in 2003 [9], its coordination chemistry to some transition metals was not reported until 2014: Coordination of  $[\text{L}^{\text{T-Se2}}]$  in the complexes  $[\text{Cu}(\text{L}^{\text{T-Se2}})_2(\text{thf})_2]$  and  $[\text{Zn}_2(\text{L}^{\text{T-Se2}})_4]$  was achieved through nitrogen and selenium atoms ( $\kappa^2\text{-N,Se}$ ) and through both nitrogen and selenium atoms ( $\kappa^3\text{-N,N',Se}$ ) resp.

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rendering, in the latter case, a homoleptic binuclear Zn complex with an unusual molecular structure (referred to as a ‘scorpionate-type complex’) shown in Chart 2. No sulfur scorpionate-type complex was realized when the sulfur triazolate  $K[L^{T-S2}]$  was allowed to react with  $ZnCl_2 \cdot H_2O$ ; instead, the mononuclear complex  $[Zn(L^{T-S2})_2(thf)_2]$  formed [10].

Group 4 metals with 4,5-bis(chalcogenodiphenylphosphinoyl)-1,2,3-triazole ( $[L^{T-E2}]H$ ), E = S and Se have also been investigated showing that monosubstituted (Ti) or disubstituted (Ti, Zr, and Hf) complexes were formed depending on the acidity of the metal center as determined by the ancillary ligands ( $-Cl$  or  $-NR_2$ , R = Me, Et). In all the cases reported the chelation mode of the 4,5-bis(chalcogenodiphenylphosphinoyl)-1,2,3-triazolates was  $\kappa^2-N,E$ ; E = S, Se favoring five-membered rings; and the disubstituted complexes realized a pseudooctahedral geometry [11].

It is apparent that the synergistic effects of the chalcogen, the ring size, and the metal center play a part in the coordination chemistry of the 4,5-bis(chalcogenodiphenylphosphinoyl)-1,2,3-triazolates. In our hands the versatility of the coordination modes of bis(chalcogenodiphenylphosphinoyl) compounds toward transition metals has buttressed the realization of interesting compounds as tetraphenylimidodiphosphate carbonyl rhenium cryptates encasing alkaline metals [12] or molecular hydrogen/oxygen iridium activators containing 4,5-bis(diphenylthiophosphinoyl)-1,2,3-triazolate [13], among others. As an extension of our studies, we focused our attention on the reaction chemistry of potassium 4,5-bis(chalcogenodiphenylphosphinoyl)-1,2,3-triazolates,  $K[L^{T-E2}]$ , E = S, Se towards  $[ReBr(CO)_5]$ .

## 2. Results and discussion

Reaction of equimolar amounts of  $[ReBr(CO)_5]$  **1** and potassium 4,5-bis(chalcogenodiphenylphosphinoyl)-1,2,3-triazolate in boiling toluene afforded the binuclear complexes  $[Re(CO)_3-\mu\{-\kappa^3-N,N',E-L^{T-E2}\}_2]$  (E = S **6**, Se **7**) in 80% and 45% yields, respectively, according to Scheme 1.

Both complexes are white solids soluble in dichloromethane and toluene; in the solid state they are stable for months in air at room temperature. In solution complex **6** is stable for around one week at room temperature and complex **7** decomposes in a few days to give a red solution of unidentified products, both under nitrogen atmosphere.

### 2.1. Spectroscopic characterization of **6** and **7**

The IR spectra in toluene of both **6** and **7** show four strong bands in the  $\nu(CO)$  region corresponding to terminal carbonyl groups in toluene: 2041, 2027, 1938, 1911  $cm^{-1}$  and 2039, 2025, 1937, 1909  $cm^{-1}$ , resp. It is known that binuclear hexacarbonyl complexes containing two  $-M(CO)_3$  moieties may display mainly two conformations of the carbonyl groups of each metal center with respect to one another along the M-M axis: eclipsed, with a  $D_{3h}$  local symmetry of the carbonyl groups, or staggered ( $D_{3d}$  symmetry); both conformers give rise to two IR active bands due to the  $A''_2 + E'$  and the  $A_{2u} + E_u$  modes, respectively [14]. The four-band splitting pattern in **6** and **7** is likely to stem from a decrease in the molecular symmetry caused by the steric requirements of the bound triazolate ligands. X-ray crystallography analysis of **6** and **7** shows that the carbonyl groups of the  $Re(CO)_3$  moieties present an eclipsed fac-carbonyl disposition (see below).

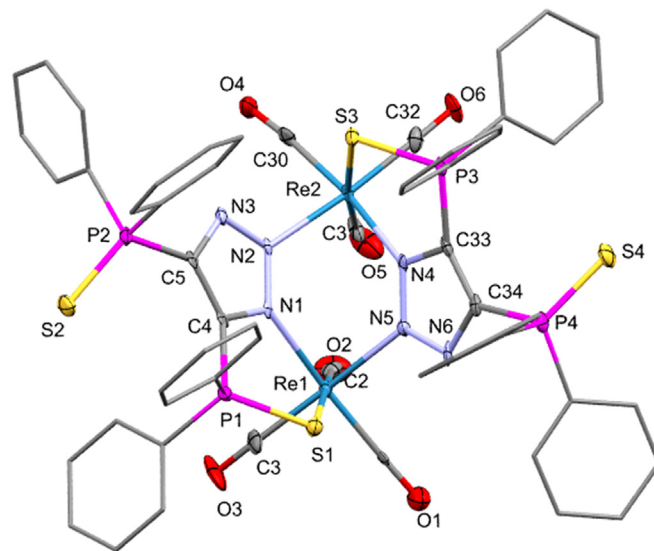
The  $^{31}P\{^1H\}$ -NMR spectra of compounds **6** and **7** exhibit two doublets, each pointing to an asymmetric coordination of the bis(chalcogenodiphenylphosphinoyl)triazolate ligand. Complex **6** signals appear at 48.28 (P-S) and 25.88 (P=Se) ppm with a coupling

constant of  $^3J_{P-P} = 3.2$  Hz, while complex **7** signals appear at 29.75 (P-Se) and 17.47 ppm (P=Se) with a coupling constant of  $^3J_{P-P} = 3.0$  Hz, in both cases the signal at lower frequency was assigned to the uncoordinated phosphinoyl moiety; additionally, the  $^{77}Se\{^1H\}$ -NMR spectrum of complex **7** exhibits two doublets: at  $-59.59$  ( $J_{Se-P} = 542$  Hz) assigned to the selenium nucleus of the coordinated phosphinoyl group and at  $-282.74$  ppm ( $J_{Se-P} = 770$  Hz) assigned to the selenium nucleus of the uncoordinated phosphinoyl terminus.

### 2.2. Single crystal X-ray analysis

The structures of **6** and **7** were determined by X-ray crystallography analyses; both complexes are isostructural and crystallize in the monoclinic space group  $P2_1/n$ , complex **6**, and the orthorhombic space group  $P2_12_12_1$ , complex **7**. The molecular structures of both complexes are quite similar, so a general discussion of their structural details is warranted. The molecular structure of **6** is shown in Fig. 1; it comprises two triazolate ligands ligating two  $-Re(CO)_3$  moieties by two nitrogen atoms and one chalcogen atom from each triazolate unit. Such coordination mode of the bis(chalcogenodiphenylphosphinoyl)triazolates with transition metals had not been documented by X-ray crystallography analysis; although it was proposed for the oxygen triazolate analog  $[L^{T-O2}]$  in  $M_2L_3OH$  complexes, M = Co, Ni and Cu [15]. Surprisingly, the coordination mode found in **6** has been reported in complexes of main group metals: Na [16], Sr [17], Al [18]; all of them considered hard' acids according to Pearson's HSAB theory [19].

In the present case such coordination mode allows for the realization of five fused heterocycles with a central  $Re_2N_4$  core.



**Fig. 1.** Molecular structure of **6** including atom-numbering scheme (ORTEP drawing with 50% probability ellipsoids). Phenyl rings' frameworks are drawn as capped sticks without hydrogens for the sake of clarity. Selected bond lengths [Å]: Re(1)-C(2) 1.923(7), Re(1)-C(1) 1.907(7), Re(1)-C(3) 1.933(8), Re(1)-N(5) 2.180(6), Re(1)-N(1) 2.205(5), Re(1)-S(1) 2.5272(18), C(4)-C(5) 1.399(9), N(3)-C(5) 1.349(8), N(2)-N(3) 1.333(7), N(1)-N(2) 1.342(7), N(1)-C(4) 1.350(8), P(1)-S(1) 2.003(3), P(2)-S(2) 1.940(3). Selected bond angles [°]: C(3)-Re(1)-N(5) 178.2(2), C(1)-Re(1)-N(1) 169.5(3), C(2)-Re(1)-S(1) 173.5(2).

The rhenium centers are in distorted octahedral environments bound to three carbonyl groups, two nitrogen atoms and a chalcogen atom. Chalcogen metal coordination rendered the bond distance between P-E (E = S, Se) of the phosphinoyl group longer

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