



Molybdenum(VI) complexes supported by chalcogen-based 1,2,3-triazoles



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ABSTRACT

The monosubstituted complex $[\text{MoO}_2\text{Cl}_2\{\kappa^2\text{-O,O'}\text{-}\{4,5\text{-}(\text{P}(\text{O})\text{Ph}_2)_2\text{tzH}\}}]$ (tz = 1,2,3-triazole) (**4**) and $[\text{Mo}(\text{N}^t\text{Bu})_2\{\kappa^2\text{-N,S}\text{-}\{4,5\text{-}(\text{P}(\text{S})\text{Ph}_2)_2\text{tz}\}}_2]$ (**12**), and the disubstituted complexes, $[\text{MoO}(\text{N}^t\text{Bu})\{\kappa^2\text{-O,N}\text{-}\{4,5\text{-}(\text{P}(\text{O})\text{Ph}_2)_2\text{tz}\}}_2]$ (**8**) and $[\text{Mo}(\text{N}^t\text{Bu})_2\{\kappa^2\text{-N,E}\text{-}\{4,5\text{-}(\text{P}(\text{E})\text{Ph}_2)_2\text{tz}\}}_2]$ [E = O(**9**), S(**10**), Se(**11**)] were prepared using the corresponding ligands $[\{4,5\text{-}(\text{P}(\text{E})\text{Ph}_2)_2\text{tzH}\}]$ [E = O(**1**), S(**2**), Se(**3**)] and molybdenum precursors, $\text{MoXYCl}_2(\text{dme})$ (X = Y = O; X = O, Y = N^tBu; X = Y = N^tBu, dme = dimethoxyethane). The disubstituted complexes **4**, **8**, **9** and **11** were obtained regardless of the ligand/metal ratio used in the reaction (1:1 or 2:1). Complexes **8** and **9** exhibit one type of geometric isomer in solution while **10** and **11** show two types of isomers in solution. In these compounds at least one isomer with C₂ symmetry is observed. Complexes **4**, **8**, **9** and **10** were characterized by X-ray diffraction analysis.

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1. Introduction

The coordination chemistry of PXP-type ligands (X = linker) has been widely studied with both main group and transition metals [1]. Indeed, the straightforward oxidation of P(III) to P(V) with oxygen sources (H₂O₂) or elemental chalcogens (S, Se) leads to ancillary ligands with essentially the same backbone structure but differing steric and electronic properties. Consequently, the variability of the donor atoms may give insight to the coordination patterns of the metal centers and the effect of the ligand properties.

In this regard, in the past decade we have studied the coordination properties of metal complexes derived from 4,5-bis(diphenylchalcogenphosphoranyl)-1,2,3-triazole ligands $[\{4,5\text{-}(\text{P}(\text{E})\text{Ph}_2)_2\text{tz}\}]^-$ (tz = 1,2,3-triazole; E = O, S, Se) with hard metal centers. These complexes exhibited unusual structural features and enhanced stability for alkaline and alkaline-earth metals [2–4], as well as interesting chemical properties for Group 13 metal complexes [5,6].

Furthermore, we recently reported on the synthesis and structural characterization of mono- and bichelated group 4 complexes bearing these 4,5-bis(diphenylchalcogenphosphoranyl)-1,2,3-triazole ligands. Controlled hydrolysis reaction on these compounds

showed their ability to assemble (M–O–M)_n cores while retaining the mismatched Ti–Se bonds [7].

Motivated by an interest on the effects of these ligands in the coordination patterns on other hard metals, we focused our attention on oxo and imido molybdenum derivatives. Indeed, oxo-molybdenum complexes containing N,E (E = O, S) bidentate ligands have proven to be efficient in oxygen-transfer reactions [8–10], while bis(imido) molybdenum complexes are important in a number of catalytic processes including imine metathesis [11] and ring opening metathesis polymerization (ROMP) reactions [12].

Herein, we report on the synthesis of oxo and imido molybdenum chalcogen-based 1,2,3-triazole complexes. The multifunctionality of the $[\{4,5\text{-}(\text{P}(\text{E})\text{Ph}_2)_2\text{tz}\}]^-$ ligands with the differing properties of the donor atoms (O, S, Se) make them an interesting type of ligands for the preparation of such molybdenum complexes.

2. Experimental

2.1. General comments

All manipulations were performed under a dry and oxygen-free atmosphere (N₂) using Schlenk-line and glovebox techniques. The solvents were purchased from commercial sources and dried prior to use with an MBraun SPS using Grubb's type columns. Commercially available chemicals were purchased from Sigma–Aldrich and

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used without further purification unless otherwise stated. $[(4,5-(P(E)Ph_2)_2tz)H](tz = 1,2,3\text{-triazole})$ [**E** = O(**1**), S(**2**), Se(**3**)] [13–16], $MoO_2Cl_2(dme)$ ($dme = \text{dimethoxyethane}$) [17], $MoO(N^tBu)Cl_2(dme)$ [18] and $Mo(N^tBu)_2Cl_2(dme)$ [19] were prepared according to the literature procedures. NEt_3 was dried with Na^0 and freshly distilled prior to use. $CDCl_3$ was dried with P_2O_5 , filtered and degassed using a freeze–pump thaw procedure whereas THF was dried upon standing over molecular sieves. The NMR spectra were recorded on a Bruker Avance 300 spectrometer. 1H NMR spectra were referenced to residual protons from the deuterated solvent and 85% H_3PO_4 solution in D_2O was used as an external standard for ^{31}P NMR spectra. Mass spectra (MS) were measured on a Shimadzu GCMS-QP2010 Plus using direct injection and electron impact (EI) ionization technique. IR spectra were recorded on a Bruker Alpha FT-IR spectrometer with an ATR measurement setup (diamond window) under inert atmosphere in a glovebox in the 4000–400 cm^{-1} range. Elemental analyses (C, H, N) were performed on an Elementar MicroVario Cube analyzer. Melting points were measured in sealed glass tubes on a Büchi B-540 melting point apparatus.

2.2. X-ray structure determination

Crystallographic data were collected on a Bruker APEX DUO three-circle diffractometer equipped with an Apex II CCD detector using either $Mo\ K\alpha$ or $Cu\ K\alpha$ Incoatec μS microsources with mirror optic monochromators) at $-173\ ^\circ C$. Suitable crystals were coated with a hydrocarbon oil, picked up with a nylon loop, and immediately mounted in the cold nitrogen stream of the diffractometer. The structures were solved by direct methods ($SHELXS-97$) or using intrinsic phasing [20] and refined by full-matrix least-squares on F^2 [21] using the ShelXle GUI [22]. The hydrogen atoms of the C–H bonds were placed in idealized positions whereas the hydrogen atom from the N–H moiety in **4** was localized from the difference electron density map, and its position was refined with U_{iso} tied to the parent atom with distance restraint. The disordered groups and solvent molecules (**4**·2THF: 2 × THF; **6**·3THF: 1 × THF, H of Me; **7**: 2 × Ph, 3 × THF; **8**·2THF: 2 × THF; **10**·3Toluene: 3 × Toluene) were refined all over two positions (except one THF molecule in **7**, which was refined over three positions) using geometry (SADI, FLAT, SAME) and U_{ij} restraints (SIMU, RIGU, DELU, EADP) implemented in SHELXL [21]. The molecular graphics were prepared using GRETEP, POVray and GIMP [23].

2.2.1. Preparation of $[MoO_2Cl_2\{\kappa^2-O,O'\text{-}[4,5-(P(O)Ph_2)_2tzH]\}]$ (**4**)

NEt_3 (0.36 mL, 0.65 mmol) was added to a solution of the ligand **1** (0.30 g, 0.64 mmol) in THF (15 mL), after 30 min the solution was added dropwise to a solution of $MoO_2Cl_2(dme)$ (0.18 g, 0.64 mmol) in THF (15 mL). The reaction mixture was stirred at ambient temperature for 12 h then filtered through a pad of Celite. The solution was reduced to 5 mL and stored at $-30\ ^\circ C$. Colorless crystals were obtained in 24 h. Yield: 75% (0.22 g, 0.48 mmol). M.p. $245\ ^\circ C$ (dec). IR (ATR): $\tilde{\nu}$ 3271 (N–H), 907 (ν_{as} , MoO_2), 950 (ν_s , MoO_2). 1H NMR (300 MHz, THF- d_8 , $25\ ^\circ C$): δ 7.44 (m, 8H, $m\text{-}C_6H_5$), 7.54 (m, 4H, $p\text{-}C_6H_5$), 7.87 ppm (m, 8H, $o\text{-}C_6H_5$). ^{31}P NMR (121.5 MHz, THF- d_8 , $25\ ^\circ C$): δ 26.5 ppm [P–O(Mo)]. 1H NMR (500 MHz, THF- d_8 , $-50\ ^\circ C$): δ 3.56 (br s, 1H, NH), 7.42 (m, 8H, $m\text{-}C_6H_5$), 7.57 (m, 4H, $p\text{-}C_6H_5$), 7.86 ppm (m, 8H, $o\text{-}C_6H_5$). ^{31}P NMR (202.5 MHz, THF- d_8 , $25\ ^\circ C$): δ 26.8 ppm [P–O(Mo)]. Elemental analysis (%) calc. for $C_{26}H_{21}Cl_2MoN_3O_4P_2$ (668.28): C, 46.73; H, 3.17; N, 6.29. Found: C, 46.79; H, 3.08; N, 6.13.

2.2.2. Preparation of $[SiMe_3\{\kappa^2-O,O'\text{-}[4,5-(P(O)Ph_2)_2tz]\}]$ (**5**)

1,1,1,3,3,3-Hexametildisilazane (0.52 mL, 0.24 mmol) was added to a solution of **1** (0.75 g, 0.16 mmol) in 25 mL of toluene.

The reaction mixture was placed under reflux during 12 h and then filtered and the volatiles were removed under vacuum. The resulting crude product was washed with hexane giving a white solid. Yield: 60% (0.39 g, 0.32 mmol). M.p. $195\ ^\circ C$. IR (ATR): $\tilde{\nu}$ 1220 ($SiMe_3$), $872\ cm^{-1}$ [P–O(Si)]. 1H NMR (300 MHz, C_6D_6 , $25\ ^\circ C$): δ 0.51 (s, 9H, $SiMe_3$), 7.32 (m, 8H, $m\text{-}C_6H_5$), 7.45 ppm (m, 4H, $p\text{-}C_6H_5$), 7.71 (m, 8H, $o\text{-}C_6H_5$). ^{31}P NMR (121.5 MHz, C_6D_6 , $25\ ^\circ C$): δ 17.5 ppm (P=O). MS(EI): m/z 526 [$M^+ - Me$]. Elemental analysis (%) calcd. for $C_{29}H_{29}MoN_3O_2P_2Si$ (541.59): C, 64.31; N, 5.40; H, 7.76. Found: C, 63.92; H, 5.28; N, 7.50.

2.2.3. Preparation of $[MoO(N^tBu)\{\kappa^2-O,N\text{-}[4,5-(P(O)Ph_2)_2tz]\}]_2$ (**8**)

NEt_3 (1.0 mmol) was added to a solution of **1** (0.306 g, 0.65 mmol) in THF (15 mL), the solution was stirred for 30 min and cooled to $-30\ ^\circ C$ and a solution of $MoO(N^tBu)Cl_2(dme)$ (0.33 mmol) in THF (7 mL) was added dropwise. The solution was stirred at ambient temperature for 12 h and filtered through Celite. All volatile materials were removed under vacuum and the remaining solid was extracted with toluene. The solvent was evaporated under vacuum and the crude product washed with hexanes (3 × 5 mL) giving a brown-greenish solid that was recrystallized from toluene giving yellow crystals. Yield: 70%. M.p. $199\ ^\circ C$ (dec). IR (ATR): $\tilde{\nu}$ 904 (Mo=O), 1118 (P=O), 1025 [P–O(Mo)], $1261\ cm^{-1}$ (Mo=N^tBu). 1H NMR (300 MHz, C_6D_6 , $25\ ^\circ C$): δ 7.78, 8.41, 8.63, 7.53, 7.63 (m, 16H, $o\text{-}C_6H_5$), 7.2–7.5 ppm (m, 16H, $m\text{-}C_6H_5$), 6.74, 6.93 ppm (m, 8H, $p\text{-}C_6H_5$). ^{31}P NMR (121.5 MHz, C_6D_6 , $25\ ^\circ C$): δ 55.2, 55.6 [P–O(Mo)], 29.4, 29.7 ppm (P=O). Elemental analysis (%) calc. for $C_{56}H_{49}MoN_7O_5P_4$ (1119.89): C, 60.06; H, 4.41; N, 8.76. Found: C, 59.89; H, 4.31; N, 8.67.

2.2.4. General method for the preparation of $[Mo(N^tBu)_2\{\kappa^2-N,E\text{-}[4,5-(P(E)Ph_2)_2tz]\}]_2$ [**E** = O(**9**), S(**10**), Se(**11**)]

NEt_3 (2.51 mmol) was added to a suspension of the corresponding ligand ${}^{12}E\text{LH}$ (${}^{12}E\text{LH} = 4,5\text{-}[P(E)Ph_2)_2tzH]$; $tz = 1,2,3\text{-triazole}$, $E = O, S, Se$) (0.64 mmol) in THF (15 mL) and was allowed to stir for 30 min. The suspension was cooled to $-30\ ^\circ C$ and a solution of $Mo(N^tBu)_2Cl_2(dme)$ (0.14 g, 0.32 mmol) in THF (10 mL) was added drop-wise. The resulting orange solution was allowed to stir for 4 h at ambient temperature. The solution was then filtered through a pad of Celite and the volatile material was removed under vacuum giving brownish-yellow solids that were recrystallized from cold hexane.

2.2.5. $[Mo(N^tBu)_2\{\kappa^2-N, O\text{-}[4,5-(P(O)Ph_2)_2tz]\}]_2$ (**9**)

Yield: 44% (0.168 g, 0.14 mmol). M.p. $236\ ^\circ C$ (dec). IR (ATR): $\tilde{\nu}$ 879 (P=O), $850\ cm^{-1}$ [P–O(Mo)]. 1H NMR (300 MHz, C_6D_6 , $25\ ^\circ C$): 2.71 [m, 2H, $(CH_2CH_2)_2O$], 3.74 [m, 2H, $(CH_2CH_2)_2O$], 6.85, 7.38 (m, 4H, $p\text{-}C_6H_5$), 7.38, 7.44 (m, 8H, $o\text{-}C_6H_5$), 7.23, 7.53, 7.85, 8.37 ppm (m, 8H, $o\text{-}C_6H_5$). ^{31}P NMR (121.5 MHz, C_6D_6 , $25\ ^\circ C$): δ 26.5 ppm (P=O). HR-MS (ESI⁺, THF): m/z 177.270292 (calcd. 1177.267383) [$M+H$]⁺; m/z 1183.276464 (calcd. 1183.275618) [$M+Li$]⁺. Elemental analysis (%) calc. for $C_{60}H_{58}MoN_8O_4P_4$ (1175.01): C, 61.33; H, 4.98; N, 9.54. Found: C, 61.34; H, 4.80; N, 9.49.

2.2.6. $[Mo(N^tBu)_2\{\kappa^2-N, S\text{-}[4,5-(P(S)Ph_2)_2tz]\}]_2$ (**10**)

Yield: 60% (0.282 g, 0.23 mmol). M.p. $205\ ^\circ C$ (dec). IR (ATR): $\tilde{\nu}$ 709 (P=S), $658\ cm^{-1}$ [P–S(Mo)]. 1H NMR (300 MHz, C_6D_6 , $25\ ^\circ C$): Isomer **10a**: δ 0.87 (s, ^tBu), 6.45, 6.67 (m, 4H, $p\text{-}C_6H_5$), 7.53 (m, 8H, $m\text{-}C_6H_5$), 8.16, 7.98, 7.22 ppm (m, 8H, $o\text{-}C_6H_5$); Isomer **10b**: δ 0.97, 1.03 (s, ^tBu), 6.54, 6.70 (m, 4H, $p\text{-}C_6H_5$), 7.12 (m, 8H, $m\text{-}C_6H_5$), 7.42, 7.51, 8.04, 8.29 ppm (m, 8H, $m\text{-}C_6H_5$). ^{31}P NMR (121.5 MHz, C_6D_6 , $25\ ^\circ C$): Isomer **10a**: δ 29.8 (P=S), 37.2 ppm [P–S(Mo)]; Isomer **10b**: δ 28.3, 30.0 (P=S), 35.4, 39.6 ppm [P–S(Mo)]. Elemental analysis (%) calc. for $C_{60}H_{58}MoN_8P_4S_4$ (1239.27): C, 58.15; H, 4.72; N, 9.04. Found: C, 57.93; H, 4.62; N, 8.89.

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