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Synthesis and structural characterization of Ti(III) and Mo(III) complexes supported by PNP pincer ligands

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ABSTRACT

New Ti(III) and Mo(III) complexes of formulae [(PNP-Ph)$TiCl_3$], **1**, and [(PNP-^{i}Pr)$MoCl_3$], **2**, where PNP-Ph = *N,N'*-bis(diphenylphosphino)-2,6-diaminopyridine and PNP-^{i}Pr = *N,N'*-bis(diisopropylphosphino)-2,6-diaminopyridine were synthesised, in moderate yields, by reaction of $MCl_3\cdot(THF)_3$ (M = Ti and Mo) with the suitable ligand precursor. The solid-state molecular structures of complexes **1** and **2** were obtained by single-crystal X-ray diffraction. Crystal data for $C_{37}H_{41}Cl_3N_3O_2P_2Ti$ (**1**$\cdot(C_4H_8O)_2$): triclinic, space group P-1 (no. 2), a = 10.0945(4) Å, b = 10.3002(4) Å, c = 18.6233(7) Å, α = 92.412(2)°, β = 91.108(2)°, γ = 101.705(3)°, V = 1893.65(13) Å^3, Z = 2, μ(MoKα) = 0.559 mm^{-1}, D_{calc} = 1.361 g.cm^{-3}, 20760 reflections measured ($2.021 \leq \Theta \leq 27.130$), 8327 unique ($R_{int}$ = 0.0399, R_{sigma} = 0.0414) which were used in all calculations. The final R_1 was 0.0316 (I > σ(I)) and wR_2 was 0.0850 (all data). Crystal data for $C_{17}H_{33}Cl_3MoN_3P_2$ (**2**): tetragonal, space group $I4_1/a$ (no. 88), $a = b$ = 19.468(4) Å, c = 31.711(6) Å, $\alpha = \beta = \gamma$ = 90°, V = 12019(5) Å^3, Z = 16, μ(MoKα) = 0.816 mm^{-1}, D_{calc} = 1.202 g.cm^{-3}, 42367 reflections measured ($2.569 \leq \Theta \leq 25.347$), 5498 unique ($R_{int}$ = 0.1408, R_{sigma} = 0.1293) which were used in all calculations. The final R_1 was 0.1005 (I > σ(I)) and wR_2 was 0.3194 (all data). The coordination geometry around the titanium and molybdenum centers is best described as octahedral, with three donor atoms of the PNP ligand and one chlorine atom occupying the equatorial plane. The axial positions of the octahedron are occupied by the other two chlorido ligands in both complexes. The NH spacer groups in the PNP ligands have an important role in the establishment of hydrogen bonds between the complexes and molecules of the solvent or neighbouring species.

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1. Introduction

Pincer ligands are tridentate chelating species that bind tightly to three adjacent coplanar coordination positions of a metal center, typically in a meridional configuration [1]. The stereochemical parameters of this type of ligands can be easily controlled by modification of the substituents at the donor sites and/or spacers [2,3]. Due to those characteristics, interest in pincer ligands has increased over the last few years as their metal complexes display interesting thermodynamic and kinetic properties [4]. Anionic pincer ligands based on 1,3-disubsituted benzenes were the first to be described and are still the most used pincer structures [5]. More recently, pincer ligands based on 2,6-diaminopyridines have attracted considerable attention because their mid to late transition metal complexes have shown important catalytic applications [6-10]. On the contrary, early transition metal complexes supported by this type of ligand are still much less explored, limited to vanadium species [11,12]. These complexes were found to catalyse the homocoupling of phenylmagnesium bromide in the presence of iodomethane as an oxidising agent, at room temperature, to give phenylbenzene [12]. Although a variety of molybdenum complexes in several oxidation states can be found in the literature [13-25], Mo(III) complexes are scarcely reported [26-28]. In the presence of $CoCp^*_2$ ($Cp^* = \eta^5$-C_5H_5) as a reducing agent and 2,4,6-colidinium trifluoromethanesulfonate as a proton source, complexes of the formula [(R-$PNP^{R'}$)MoI_3] (R = H, Ph, Me, MeO, ferrocenyl, and ruthenocenyl; R' = ^{t}Bu, ^{i}Pr, Ph, and adamantyl) were effective catalysts to produce ammonia from molecular dinitrogen under ambient conditions [28]. Here, we describe the synthesis and structural characterisation of new Ti(III) and Mo(III) complexes supported by PNP pincer ligands based on 2,6-diaminopyridine.

2. Experimental

2.1. General considerations

The compounds *N,N'*-bis(diphenylphosphino)-2,6-diaminopyridine (PNP-Ph) [29] and *N,N'*-bis(diisopropylphosphino)-2,6-diaminopyridine (PNP-^{i}Pr) [21] were prepared according to the literature.

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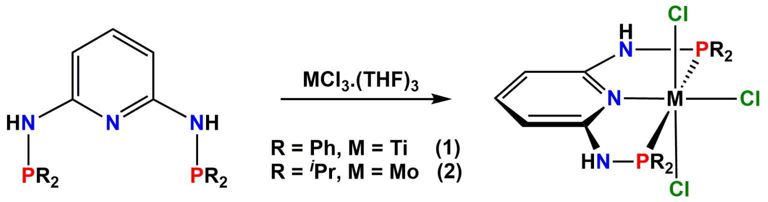

Scheme 1. Synthetic route for the preparation of [(PNP)MCl_3] (M = Ti, **1**, and M = Mo, **2**) complexes.

All other reagents were commercial grade and were used without further purification. All manipulations were performed under an inert atmosphere of dry oxygen-free nitrogen by means of standard Schlenk and glovebox techniques. Solvents were pre-dried using 4 Å molecular sieves and refluxed over sodium benzophenone in an atmosphere of N_2 and collected by distillation. The ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker AVANCE-250 spectrometer at 296 K and referenced to tetramethylsilane and H_3PO_4 (85%), respectively. Elemental analyses (C, H, N) were performed in a Fisons CHNS/O analyser Carlo Erba Instruments EA-1108 equipment at the Laboratório de Análises do Instituto Superior Técnico.

2.2. Synthesis and characterization

2.2.1. N,N'-Bis(diphenylphosphino)-2,6-diaminopyridine, PNP-Ph

A solution of Ph_2PCl (7.20 mL, 38.96 mmol) in toluene (60 mL) was added dropwise to a solution of triethylamine (5.11 mL, 36.66 mmol) and 2,6-diaminopyridine (2.00 g, 18.33 mmol) in the same solvent (100 mL), at 0 °C. The reaction mixture was heated to 50 °C, and the precipitate formed was filtered off. The solvent was removed under vacuum and the remaining oil was recrystallized from toluene/*n*-hexane (1:1). Color: White. Yield: 91%. ^{1}H NMR (250.0 MHz, $CDCl_3$, δ, ppm): 7.51-7.38 (m, 21H, *Py*), 6.55 (dd, *J* = 7.9 Hz, *J* = 1.2, 2H, *Py*), 5.36 (d, *J* = 8.2 Hz, 2H, N*H*). ^{31}P{^{1}H} NMR (101.2 MHz, $CDCl_3$, δ, ppm): 27.9.

2.2.2. N,N'-Bis(diisopropylphosphino)-2,6-diaminopyridine, PNP-^{i}Pr

Triethylamine (4.71 mL, 33.78 mmol) was added to a suspension of 2,6-diaminopyridine (1.82 g, 16.68 mmol) in toluene (100 mL). The mixture was cooled to 0 °C, and $^iPr_2PCl$ (5.35 mL, 33.65 mmol) was added dropwise. Upon further cooling to -70 °C, a 2.5 M solution of *n*-BuLi in hexane (13.51 mL, 33.78 mmol) was slowly added. The solution was allowed to reach room temperature and then stirred overnight at 80 °C. The reaction mixture was filtered, and the solvent was removed under vacuum. The remaining oil was recrystallized from toluene/*n*-hexane (1:1). Color: White. Yield: 97%. ^{1}H NMR (250.0 MHz, $CDCl_3$, δ, ppm): 7.20 (t, *J* = 8.1 Hz, 1H, *Py*), 6.38 (dd, *J* = 8.0 Hz, *J* = 2.1, 2H, *Py*), 4.38 (d, *J* = 10.7 Hz, 2H, N*H*), 1.69 (m, *J* = 7.0, *J* = 1.9 Hz, 4H, C*H*(CH_3)$_2$), 1.05-0.93 (m, 24H, CH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (101.2 MHz, $CDCl_3$, δ, ppm): 49.2.

2.2.3. [(PNP-Ph)$TiCl_3$], 1

A solution of PNP-Ph (250 mg, 0.52 mmol) in THF was added to a suspension of $TiCl_3$·(THF)$_3$ (175 mg, 0.47 mmol) in the same solvent, and the reaction mixture was refluxed overnight. The solvent was evaporated, and the brown solid obtained was washed with small portions of toluene and dried in vacuum. Crystals suitable for single crystal X-ray diffraction were obtained by slow concentration of a THF solution at room temperature using a H-shape glass tube containing the solution of the compound and a small volume of toluene in each side of the tube. Color: Brown. Yield: 55%. Anal. calcd for $C_{29}H_{25}Cl_3N_3P_2Ti$·(C_4H_8O)$_2$·(H_2O)$_2$: C, 54.73; H, 5.59; N, 5.18. Found: C, 54.04; H, 4.75; N, 4.90%.

2.2.4. [(PNP-^{i}Pr)$MoCl_3$], 2

A solution of PNP-^{i}Pr (341 mg, 1.00 mmol) in toluene was added to a suspension of $MoCl_3$·(THF)$_3$ (374 mg, 0.90 mmol) in the same solvent. The reaction mixture was refluxed overnight, providing a green precipitate. The solid was filtered off, washed with small portions of Et_2O, and dried under vacuum. Crystals suitable for single-crystal X-ray diffraction were obtained by slow concentration of a CH_2Cl_2 solution at room temperature using a H-shape glass tube containing the solution of the compound and a small volume of toluene in each side of the tube. Color: Green. Yield: 64%. Anal. calcd for $C_{17}H_{33}Cl_3MoN_3P_2$·(CH_2Cl_2)$_{0.3}$: C, 36.51; H, 5.95; N, 7.38. Found: C, 36.38; H, 6.28; N, 7.36%.

2.3. General procedure for X-ray crystallography

Suitable crystals of compounds **1** and **2** were coated and selected in Fomblin® oil in an inert atmosphere of nitrogen. The crystals were then mounted on a loop external to the glovebox environment and data was collected using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Bruker AXS-KAPPA APEX II diffractometer. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all observed reflections [30]. Absorption corrections were applied using SADABS [31]. The structures were solved by direct methods using SIR97 [32]. Structure refinement was done using SHELXL-2018/3 [33]. These programs are part of the WinGX software package version 2021.3 [34]. Hydrogen atoms bonded to nitrogen were located on the difference map and refined freely. Hydrogen atoms bonded to carbons were inserted in the calculated positions and allowed to refine riding in the parent atom. Compound **2** crystalized with diffuse and disordered solvent molecules that could not be modeled. Therefore, they were removed using the Squeeze/PLATON sequence [35]. A total void of 3774 Å^3 containing 1516 electrons per unit cell was found and fits well for two molecules of dichloromethane (42 electrons) in the asymmetric unit. The poor diffracting power and crystal quality of **2** (as attested by the R_{int} value obtained) precluded the final refinement to lower the corresponding *R* values. Crystallographic and experimental details of data collection and crystal structure determinations for compounds **1** and **2** are available in Table 1. Illustrations of molecular structures were made with ORTEP-3 for Windows [36].

3. Results and discussion

Treatment of MCl_3·(THF)$_3$ (M = Ti and Mo) with the suitable PNP ligand afforded complexes [(PNP-Ph)$TiCl_3$], **1**, and [(PNP-^{i}Pr)$MoCl_3$], **2**, where PNP-Ph = *N*,*N'*-bis(diphenylphosphino)-2,6-diaminopyridine and PNP-^{i}Pr = *N*,*N'*-bis(diisopropylphosphino)-2,6-diaminopyridine, in moderated yields as shown in Scheme 1.

Table 1. Crystal data and details of structure refinement for compounds **1** and **2.**

Parameter	**1·(C₄H₈O)₂**	**2**
Empirical formula	$C_{37}H_{41}Cl_3N_3O_2P_2Ti$	$C_{17}H_{33}Cl_3MoN_3P_2$
Formula weight	775.89	543.69
Temperature (K)	296(2)	296(2)
Crystal system, space group	Triclinic, *P*-1	Tetragonal, $I4_1/a$
a, (Å)	10.0945(4)	19.468(4)
b, (Å)	10.3002(4)	19.468(4)
c, (Å)	18.6233(7)	31.711(6)
α, (°)	92.412(2)	90
β, (°)	91.108(2)	90
γ, (°)	101.705(3)	90
Volume (Å^3)	1893.65(13)	12019(5)
Z	2	16
ρ_{calc} (g/cm^3)	1.361	1.202
μ (mm^{-1})	0.559	0.816
F(000)	806	4464
Crystal size (mm^3)	0.10 × 0.20 × 0.35	0.20 × 0.20 × 0.20
Θ range for data collection (°)	2.021 to 27.130	2.569 to 25.347
Index ranges	$-12 \le h \le 12$, $-9 \le k \le 13$, $-23 \le l \le 20$	$-23 \le h \le 23$, $-23 \le k \le 23$, $-33 \le l \le 38$
Reflections collected	20760	42367
Independent reflections	8327 [R_{int} = 0.0399, R_{sigma} = 0.0414]	5498 [R_{int} = 0.1408, R_{sigma} = 0.1293]
Data/restraints/parameters	8327/0/441	5498/25/235
Goodness-of-fit on F^2	1.058	1.016
Final R indexes [I≥2σ(I)]	R_1 = 0.0316, wR_2 = 0.0818	R_1 = 0.1005, wR_2 = 0.2728
Final R indexes [all data]	R_1 = 0.0380, wR_2 = 0.0850	R_1 = 0.2049, wR_2 = 0.3194
Largest diff. peak/hole (e Å^{-3})	0.340/-0.374	0.797/-0.428

Table 2. Relevant intermolecular hydrogen bond distances (Å) and angles (°) of compounds **1** and **2**.

Compound	**D-H···A**	**d(D-H)**	**d(H···A)**	**d(D···A)**	**(DĤA)**	**Symmetry operation**
1	N(2)-H(2N)···O(2_$1)	0.84	2.02	2.8574(1)	174	*x*, 1+*y*, *z*
	N(3)-H(3N)···O(1)	0.82	2.05	2.8562(1)	171	1-*x*, 1-*y*, 1-*z*
2	N(2)-H(2N)···Cl(3_$1)	0.86	2.51	3.3523(7)	166	-¼+*y*, ¼-*x*, ¼-*z*
	N(3)-H(3N)···Cl(2_$2)	0.86	2.44	3.2843(7)	168	¾-*y*, ¼+*x*, ¼+*z*

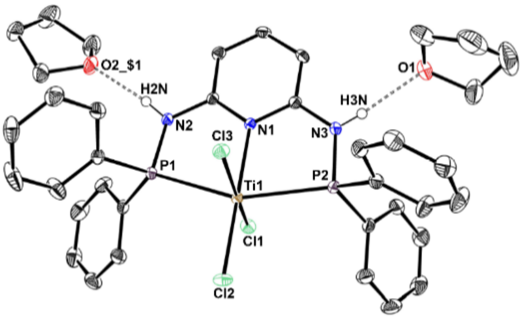

Figure 1. ORTEP diagram of **1** showing thermal ellipsoids at 40% probability level. Selected hydrogen atoms are omitted for clarity. Dashed lines represent hydrogen bonds. Selected bond lengths (Å) and angles (°): Ti(1)-N(1) 2.235(1), Ti(1)-P(1) 2.5487(4), Ti(1)-P(2) 2.5839(5), Ti(1)-Cl(1) 2.3146(4), Ti(1)-Cl(2) 2.3650(4), Ti(1)-Cl(3) 2.3310(4); P(1)-Ti(1)-N(1) 77.63(3), P(2)-Ti(1)-N(1) 76.90(3), P(1)-Ti(1)-Cl(2) 102.62(2), P(2)-Ti(1)-Cl(2) 102.89(2), P(1)-Ti(1)-P(2) 154.37(2), N(1)-Ti(1)-Cl(2) 179.13(3), Cl(1)-Ti(1)-Cl(3) 168.85(2).

Crystals of **1** and **2** suitable for single-crystal X-ray diffraction were obtained by slow concentration of THF and dichloromethane solutions, respectively, at room temperature, using an H-shaped glass tube containing the solution of the compound and toluene in each side of the tube. In these conditions, the evaporation of the solvent is determined by dissolution and diffusion into toluene. Complex **1** crystallized in the triclinic *P*-1 space group, while complex **2** crystallized in the tetragonal $I4_1/a$ space group. ORTEP diagrams of complexes **1** and **2** and the selected bond lengths and angles are shown in Figures 1 and 2, respectively.

The solid-state molecular structures of complexes **1** and **2** determined by single crystal X-ray diffraction show distorted octahedral trivalent titanium and molybdenum centers. The three donor atoms of the PNP ligand and one chloride atom occupy the equatorial plane of both octahedra, which is usually defined as the one containing the donor atoms of the pincer ligand. The P-M-Cl angles are wider than 90°, while the N-M-P and the P-M-P angles are narrower than 90° and 180°, respectively, as a consequence of the chelating nature of the pincer ligand. The axial positions are occupied by two chlorine atoms that define Cl-M-Cl angles that deviate from linearity (168.85(2)° in **1** and 176.7(2)° in **2**) and are contracted toward the pyridine ring. The same pattern is observed for the P-M-P angles (154.37(2)° in **1** and 156.1(1)° in **2**). This feature is also observed in other M(III) complexes (M = V [11,12], Cr [12,37,38], Mo [27], Ru [39], and In [40]) supported by PNP ligands based on 2,6-diaminopyridine. Complex **1** crystallized with two molecules of THF that interact with the NH spacers of the PNP ligand by N-H···O hydrogen bonds with bridging distances of 2.02 and 2.05 Å. Complex **1** is isostructural with vanadium(III) trichlorido $[(PNP-Ph)VCl_3]\cdot(C_4H_8O)_2$ already reported in the literature [11]. Complex **2** shows two hydrogen bonds of the type N-H···Cl established between the amino spacers and the chlorine atoms of neighboring molecules, which are responsible for the molecular assembly. The N(3)-H(3N)···Cl(2) interactions between molecules of **2**, at the supramolecular level, define helicoidal chains that grow along the *a* direction. These chains interact with each other by N(2)-H(2N)···Cl(3) hydrogen bonds with a distance of 2.51 Å, creating a three-dimensional network as shown in Figure 3. Detailed hydrogen bond lengths and angles found in complexes **1** and **2** are shown in Table 2.

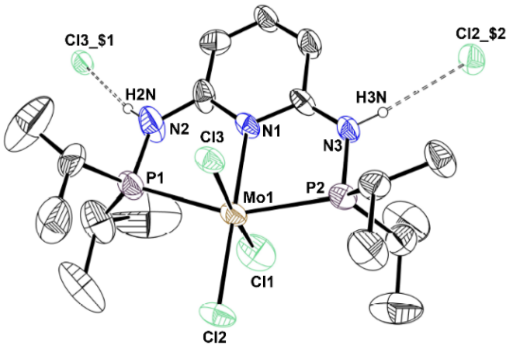

Figure 2. ORTEP diagram of **2** showing thermal ellipsoids at 30% probability level. Selected hydrogen atoms were omitted for clarity. Dashed lines represent hydrogen bonds. Selected bond lengths (Å) and angles (°): Mo(1)-N(1) 2.173(8), Mo(1)-P(1) 2.556(4), Mo(1)-P(2) 2.489(4), Mo(1)-Cl(1) 2.232(5), Mo(1)-Cl(2) 2.421(3), Mo(1)-Cl(3) 2.474(3); P(1)-Mo(1)-N(1) 77.8(3), P(2)-Mo(1)-N(1) 78.7(3), P(1)-Mo(1)-Cl(2) 103.1(1), P(2)-Mo(1)-Cl(2) 100.1(1), P(1)-Mo(1)-P(2) 156.1(1), N(1)-Mo(1)-Cl(2) 176.3(2), Cl(1)-Mo(1)-Cl(3) 176.7(2).

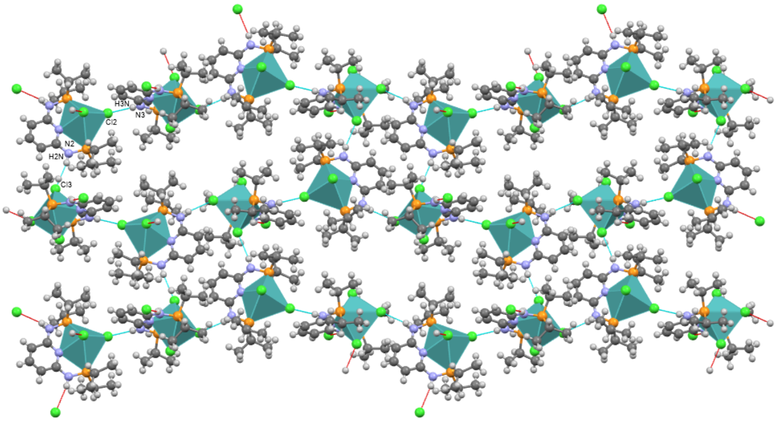

Figure 3. Polyhedral view of the crystal structure of **2** along the *b*-axis showing chains growing in the *a* direction. Dashed blue lines represent hydrogen bonds.

4. Conclusions

[(PNP-Ph)$TiCl_3$] and [(PNP-^{i}Pr)$MoCl_3$] (PNP-Ph = *N*,*N*'-bis(diphenylphosphino)-2,6-diaminopyridine and PNP-^{i}Pr = *N*,*N*'-bis(diisopropylphosphino)-2,6-diaminopyridine) were synthesized and characterized. The solid-state molecular structures of both complexes were determined by single-crystal X-ray diffraction and reveal distorted octahedral geometries. The equatorial planes of the octahedra are occupied by the three donor atoms of the PNP ligands and one chlorine atom. The axial positions are occupied by the other two chlorido ligands. The presence of NH amino spacer groups in PNP ligands plays an important role in the establishment of hydrogen bonds between the complexes and the molecules of the solvent or neighboring species. Such interactions are also responsible for the supramolecular assembly of [(PNP-^{i}Pr)$MoCl_3$] that reveals a three-dimensional network defined by helicoidal chains growing in the *a* direction. To our knowledge, [(PNP-Ph)$TiCl_3$] is the first titanium complex supported by a PNP pincer ligand based on 2,6-diaminopyridine to be described.

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Supporting information

CCDC-2224820 and 2224821 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement

Conflict of interest: The authors declare that they have no conflict of interest.
Ethical approval: All ethical guidelines have been adhered to.
Sample availability: Samples of the compounds are available from the author.

CRediT authorship contribution statement

Conceptualization: Ana Martins; Investigation: Rita Ruivo, Luis Alves; Writing - Original Draft: Luis Alves; Writing - Review and Editing: Luis Alves, Ana Martins; Supervision: Ana Martins; Project Administration: Ana Martins.

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