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Synthesis of the water-soluble [Rh(Tpms)(CO)(PTA)] compound, the first transition metal complex bearing the 1,3,5-triaza-7-phosphaadamantane (PTA) and the tris(1-pyrazolyl)methanesulfonate (Tpms) ligands

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ABSTRACT

The water-soluble Rh^{I} compound [Rh(Tpms)(CO)(PTA)] (**1**) (Tpms = $O_3SC(pz)_3^-$, PTA = 1,3,5-triaza-7-phosphaadamantane) has been easily prepared in high yield by a single-pot reaction of [{Rh(CO)$_2$(μ-Cl)}$_2$] with PTA and the tris(1-pyrazolyl)methanesulfonate lithium salt Li(Tpms), in a CH_2Cl_2/MeOH solution at room temperature. This synthetic strategy can be easily applied to the preparation of general [Rh(Tpms)(CO)(L)] (L = phosphine) complexes and constitutes a substantial improvement over the previously described procedures. Compound **1** is air stable in the solid state and water-soluble, affording stable solutions under an inert atmosphere. It has been characterized by IR, ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectroscopies, elemental and single crystal X-ray diffraction structural analyses. The solid state structure of **1** has a square-planar geometry with the Tpms ligand coordinating the metal centre in a (κ^2: *N,N*) bipodal mode. The title compound has also been investigated by cyclic voltammetry in CH_3CN, and values of the E_L Lever and P_L Pickett electrochemical parameters (which measure the ligand net electron-donor character) are proposed for the PTA ligand. Complex **1** represents the first example of a transition metal complex bearing both PTA and Tpms (or any other tris(1-pyrazolyl)methane or derivative) ligands.

1. Introduction

The tris(1-pyrazolyl)methanesulfonate species $^-O_3SC(pz)_3$ (Tpms) was designed by analogy with tris(1-pyrazolyl)borate (Tp), both being able to act as monoanionic C_{3v}-symmetrical nitrogen-donor ligands [1–3]. However, unlike the tris(1-pyrazolyl)borate derivatives, insoluble in water and unstable towards hydrolysis, Tpms has a methanesulfonate unit which imparts an increased solubility in polar solvents and a very good stability in aqueous media over a wide range of pH [2]. The tris(1-pyrazolyl)methanesulfonate coordinated as a N_3 tripodal ligand can also be compared to the isoelectronic pentahapto cyclopentadienyl (Cp) ligand [3]. However, as shown recently [4], the Tpms ligand can act not only as a tripodal but also as a bipodal ligand. In the former case, it can exhibit either a N,N,N or a N,N,O coordination, whereas as a bipodal ligand it can coordinate through either N,N or N,O [4,5] (Fig. 1).

Rhodium(I) complexes of formula [Rh(Tpms)(CO)(L)] (L = PPh_3, PMe_3, PCy_3) were prepared for the first time by Klaui et al. [1] and were shown to contain the Tpms ligand coordinated in the N,N bipodal fashion. They were obtained from the dicarbonyl complex [{Rh(CO)$_2$(μ-Cl)}$_2$] and the Tl(Tpms) salt in two steps through the [Rh(Tpms)(CO)$_2$] intermediate formed at a CO pressure of 3–4 atm. As reported in the literature, the [Rh(Tpms)(CO)$_2$] complex catalyses the hydroformylation of *1*-hexene at 60 °C in acetone, but its instability in water has prevented any possible investigation in aqueous media [6]. On the other hand, [Rh(Tpms)(CO)(PMe$_3$)] has been shown to act as a catalyst for both the hydroformylation of *1*-hexene and the carbonylation of benzene [6,7], although the study was also carried out only in non-aqueous solvents for stability reasons. Among the different [Rh(Tpms)(CO)(PR$_3$)] complexes described in the literature [1], only the compound [Rh(Tpms)(CO)(PPh_2PhSO_3K)] was found to be well soluble in aqueous media, its stability in water, however, being limited to the short pH range of 3–4.

In order to overcome these stability problems in aqueous phase, we wondered whether the use of the chemically stable and water-soluble 1,3,5-triaza-7-phosphaadamantane (PTA) ligand instead of the previously reported phosphines [1] could confer a greater stability to the Rh^{I} system. The coordination chemistry of PTA has experienced in the last years a rapid development mainly justified by the search for water-soluble transition metal phosphine complexes [8,9]. They have been shown to possess a good solubility in aqueous media, finding therefore several applications either as catalysts in aqueous phase [9–12], water-soluble antitumor agents [9,13–15] or photoluminescent materials [9,16,17]. Concerning the

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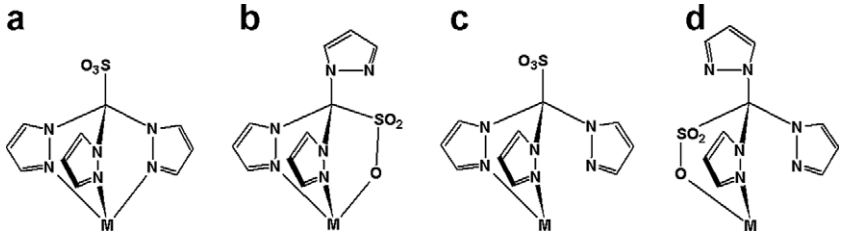


Fig. 1. Possible coordination modes for the Tpms ligand: (a) tripodal N,N,N (κ^3: *N,N,N*); (b) tripodal N,N,O (κ^3: *N,N,O*); (c) bipodal N,N (κ^2: *N,N*); and (d) bipodal N,O (κ^2: *N,O*).

catalytic properties, in particular, it has been shown by some of us that PTA and *N*-alkylated PTA Rh and Ru complexes can act as efficient catalysts for the hydrogenation, hydroformylation and isomerization of alkenes in aqueous systems [8,18,19].

In this contribution we report the synthesis of the new water soluble and water stable [Rh(Tpms)(CO)(PTA)] complex (**1**) obtained in high yield from [{Rh(CO)$_2$(μ-Cl)}$_2$], in a single pot, without the need for isolation of any intermediate. The synthetic strategy presented here, in addition, directly employs Li(Tpms) and PTA without the use of CO and the synthesis of the Tl(Tpms) salt. Moreover, the unprecedented compound **1** is the first transition metal complex bearing both the PTA and Tpms [or any tris(1-pyrazolyl)methane derived] ligands. Compound **1** has been characterized by IR, ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} spectroscopies, ES–MS, cyclic voltammetry, elemental and single crystal X-ray diffraction structural analyses.

2. Experimental

2.1. General materials and experimental procedures

The synthetic work was carried out under an oxygen-free dinitrogen atmosphere, using standard Schlenk techniques. All solvents were dried, degassed and distilled prior to use. [{Rh(CO)$_2$(μ-Cl)}$_2$] (Strem) was used as received. 1,3,5-Triaza-7-phosphaadamantane (PTA) [20] and the lithium salt of tris(1-pyrazolyl)methanesulfonate Li(Tpms) [2] were synthesised in accordance with the literature methods. C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico, Lisbon. Infrared spectra (4000–400 cm^{-1}) were recorded on a Bio-Rad FTS 3000MX instrument in KBr pellets. ^{1}H, ^{13}C and ^{31}P NMR spectra were measured on Bruker 300 and 400 UltraShield™ spectrometers at room and low temperatures. ^{1}H and ^{13}C chemical shifts δ are expressed in ppm relative to Si(Me)$_4$ whereas δ(^{31}P) chemical shifts are relative to 85% H_3PO_4. Coupling constants are in Hz; *abbreviations*: s, singlet; d, doublet; m, complex multiplet; vt, virtual triplet; br, broad. The electrochemical experiments were performed on an EG&G PAR 273A potentiostat/galvanostat connected to a computer through a GPIB interface. Cyclic voltammograms were obtained in a 0.2 M solution of [*n*Bu$_4$N][BF$_4$] in CH_3CN, under N_2, at 25 °C, at a platinum disc working electrode (d = 1 mm) probed by a Luggin capillary connected to a silver wire pseudo-reference electrode. A Pt wire was employed as the counter electrode. The redox potentials of the complex were measured by cyclic voltammetry in the presence of ferrocene as the internal standard, and their values are quoted relative to the NHE by adding 0.245 V [21] to those measured relatively to the SCE by using the [Fe(η^5-C$_5$H$_5$)$_2$]$^{0/+}$ redox couple ($E_{1/2}^{ox}$ = 0.45 V *vs.* SCE, in NCMe [22]) as the internal standard.

2.2. Synthesis of [Rh(Tpms)(CO)(PTA)] (*1*)

To a solution of [{Rh(CO)$_2$(μ-Cl)}$_2$] (129 mg, 0.331 mmol) in CH_2Cl_2 (8 mL) were added 4 mL of a CH_2Cl_2 solution of PTA (104 mg, 0.662 mmol) and, after 5 min, 4 mL of a Li(Tpms) solution in methanol (199 mg, 0.662 mmol). The reaction mixture was stirred at room temperature for 1 h, a yellow suspension being obtained. The yellow, microcrystalline product **1** was collected by filtration and the filtrate was left in a fridge at ca. 4 °C for 2 days affording **1** as a yellow crystalline solid, which was isolated by filtration, washed with cold methanol (2 × 5 mL) and dried *in vacuo*. Yield 75% (289 mg), based on [{Rh(CO)$_2$(μ-Cl)}$_2$]. Complex **1** is soluble in H_2O ($S_{25\ °C} \approx 12$ mg mL^{-1}), MeCN and MeOH and insoluble in middle- and non-polar solvents like Me_2CO, $CHCl_3$ and CH_2Cl_2, C_6H_6, and Et_2O. Anal. Calc. for **1**, $C_{17}H_{21}N_9O_4PRhS$ (581.35): C, 35.12; N, 21.68; H, 3.64; S, 5.52. Found: C, 35.14; N, 21.35; H, 3.53; S, 5.31. IR (KBr): 3164 (s), 3085 (m), 2934 (m), 2876 (m) ν(CH), 2007 (vs) ν(CO), 1519 (m), 1443 (m), 1415 (s), 1393 (m), 1332 (m), 1267 (m), 1116 (s), 1075 (m), 1060 (m), 1014 (s), 973 (s), 947 (s), 907 (m), 845 (m), 770 (s), 7763 (s), 740 (m), 628 (s), 590 (m), 537 (m), (PTA and Tpms bands) cm^{-1}. ^{1}H NMR (300 MHz, CD_3OD, 25 °C): δ 8.40 (s, br, 3 H, pz-H3,5), 7.85 (d, 3H, $^3J_{HH}$ = 2.08 Hz, pz-H3,5), 6.93 (dd, 3H, $^3J_{HH}$ = 2.08 Hz and 2.83 Hz, pz-H4), 4.60 and 4.54 (2d. 6H, J_{AB} = 13.0 Hz, NC*H*^{A}*H*^{B}N, PTA), 4.17 (s, 6H, PCH_2N, PTA). ^{1}H NMR (300 MHz, CD_3OD, −60 °C): δ 8.97, 7.82, 7.64 (3d, 3H, $^3J_{HH}$ = 2.1 Hz, pz-H3,5), 8.19, 8.16, 8.07 (3d, 3H, $^3J_{HH}$ = 2.1 Hz, pz-H3,5), 6.72, 6.69, 6.48 (3dd (3vt), 3H, $^3J_{HH}$ = 2.1 Hz, pz-H4), 4.56 and 4.50 (2d, 6H, J_{AB}13.0 Hz, NC*H*^{A}*H*^{B}N, PTA), 4.18 (s, 6H, PCH_2N, PTA). ^{31}P{^{1}H} NMR (121.5 MHz, CD_3OD, 25 °C): δ −37.3 (d, $^1J_{Rh-P}$ = 151.1 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, CD_3OD, 25 °C): δ 144.9 (s, 3-C (pz)), 132.9 (s, 5-C (pz)), 107.5 (s, 4-C (pz)), 90.1 (s, C-SO_3), 71.9 (s, NCH_2N), 51.8 (vt, J_{CP} = 16.1 Hz PCH_2N). ^{1}H NMR (400 MHz, D_2O, 25 °C): δ 8.77 (s, br, 1 H, pz-H3,5) 8.11 (s, br, 2H, pz-H3,5), 7.80 (s, br, 1H, pz-H3,5), 7.91 (s, br, 2H, pz-H3,5), 6.70 (s, br, 1H, pz-H4), 6.66 (dd, vt, 2H, $^3J_{HH}$ = 2.3 Hz, pz-H4), 4.59 and 4.56 (2d, 6H, J_{AB} = 13.0 Hz, NC*H*^{A}*H*^{B}N, PTA), 4.19 (s, 6H, PCH_2N, PTA). ^{1}H NMR (400 MHz, D_2O, 80 °C): δ 8.95 (s, br, 3H, pz-H3,5), 8.60 (s, 3H, pz-H3,5), 7.34 (s, 3H, pz-H4), 5.15 and 5.12 (6H, J_{AB} = 12.0 Hz, NC*H*^{A}*H*^{B}N, PTA), 4.75 (s, 6H, PCH_2N, PTA). ^{31}P{^{1}H} NMR (162.0 MHz, D_2O, 25 °C): δ −35.8 (d, $^1J_{Rh-P}$ = 152.0 Hz). Electrochemical data in CH_3CN/0.2 M [*n*Bu$_4$N][BF$_4$]: $E^{ox}_{p/2}$(I) = 0.21 V (*vs.* Fc/Fc$^+$), 0.91 V (*vs.* NHE); $E^{ox}_{p/2}$(II) = 0.70 V (*vs.* Fc/Fc$^+$), 1.40 V (*vs.* NHE); $E^{red}_{p/2}$(III) = −0.65 V (*vs.* Fc/Fc$^-$), 0.05 V (*vs.* NHE).

2.3. Decomposition product of *1* in a solution under air

A D_2O solution of complex **1** in a NMR tube was exposed to air and monitored by ^{31}P{^{1}H} NMR. With time, the gradual replacement of the doublet at δ −35.8 by a singlet at −2.9 ppm was observed, the conversion of **1** being completed in *ca.* 1 week. The solvent was then evaporated *in vacuo* and the yellow residue **2** was washed with water and methanol and dried *in vacuo*. Anal. Calc. for $C_{22}H_{18}N_{12}O_8S_2Rh_2$ (848.4): C, 31.15; N, 19.31; H, 2.13. Found: C, 31.25; N, 18.93; H, 2.04%. IR (KBr): 3190 (w), 3144 (m), 3084 (m), 2934 (m), 2876 (m), 1861 (s), 1416 (m), 1268 (s), 1108 (m), 1056 (m), 764 (m) cm^{-1}. ^{1}H NMR (400 MHz, D_2O, 25 °C): δ 9.18 (dd, $^3J_{HH}$ = 3.3 Hz, $^3J_{RhH}$ = 0.6 Hz, pz-H3), 7.88 (d, $^3J_{HH}$ = 2.5 Hz, pz-H5), 6.83 (dd, $^3J_{HH}$ = 3.3 and 2.5 Hz, pz-H4).

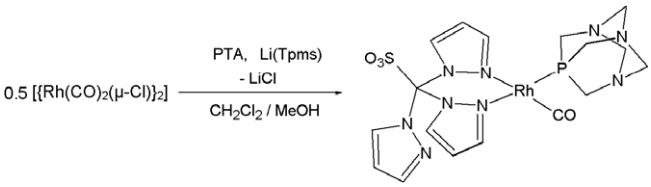
2.4. Refinement details for the X-ray crystal structure analysis of **1**

Single crystals suitable for X-ray analysis were grown from the reaction filtrate (see above) at 4 °C. Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite monochromated Mo Kα radiation. Data were collected at 150 K using omega scans of 0.5° per frame and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all the observed reflections. Absorption corrections were applied using SADABS. Structures were solved by direct methods by using the SHELXS-97 package [23] and refined with SHELXL-97 [24] with the WINGX graphical user interface [25]. All hydrogens were inserted in calculated positions. The selected bond distances (Å) and angles for **1** are given in Table 1, and the crystallographic data summarized in Table 2.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

Treatment of a CH_2Cl_2 solution of $[\{Rh(CO)_2(\mu\text{-}Cl)\}_2]$ with 2 equiv. of Li(Tpms) and of PTA in CH_2Cl_2/MeOH, at room temperature, afforded (reaction 1) the [Rh(Tpms)(CO)(PTA)] complex (**1**) isolated after 1 h reaction in a high yield (75 %) as a yellow powder. Complex **1** is air stable in the solid state and stable in aqueous solution under an inert atmosphere. It is soluble in H_2O ($S_{22\,°C} \approx 12$ mg mL^{-1}) and in other polar solvents, such as MeCN, Me_2SO and $Me_2C(O)NH_2$, although in the last two solvents it slowly decomposes. It is sparingly soluble in MeOH and EtOH and is insoluble in other middle-, low- or non-polar solvents such as Me_2CO, *n*-PrOH, CH_2Cl_2, $CHCl_3$, Et_2O, CCl_4 or C_6H_6. Analytically pure, bright yellow single crystals suitable for X-ray analysis were obtained upon slow cooling the reaction mixture to +4°C,



(1)

The $^{31}P\{^1H\}$ NMR spectrum exhibits a doublet at δ −37.3 (relative to 85% H_3PO_4) with $^1J_{Rh-P} = 151$ Hz, similar values being also observed [1] for the related [Rh(Tpms)(CO)(L)] compounds [$^1J_{Rh-P} = 148$ (L = PMe_3), 158 (L = PPh_3) or 153 Hz (L = PCy_3)] and for [Rh(acac)(CO)(PTA)] (acac = acetylacetonato, $^1J_{Rh-P} = 172.4$ Hz) [19a]. The ^1H NMR spectrum in CD_3OD is fully consistent with the solid state molecular structure showing two characteristic types of methylene protons for the coordinated PTA. One of them, assigned to the P–CH_2–N moiety, occurs as a singlet at δ 4.17 whereas the other one, corresponding to the N–CH_2–N group, displays an AB spin system centered at 4.57 ppm, attributed to the N–CH_{ax}–N and N–CH_{eq}–N protons, as previously reported [26]. Similarly to other Tpms complexes [1], the ^1H NMR spectrum of **1** at room temperature reveals the presence of three equivalent pyrazolyl rings (three resonances at δ 8.40 (s, br), 7.85 (d) and 6.93 ppm (dd) corresponding to the pyrazolyl protons in positions 3, 5 and 4, respectively), a dynamic and fast pyrazolyl coordination exchange conceivably occurring [1]. However, in accordance with the solid state molecular structure, the pyrazolyl groups become non-equivalent at −60 °C, showing nine resonances on the whole. In contrast to [Rh(Tpms)(CO)(PPh_3)], for which the inequivalence of only one pyrazolyl ring has been reported (total of six resonances), the nine resonance pattern observed herein for **1** is consistent not only with the bipodal N,N (κ^2: *N,N*) coordination mode of the tris(1-pyrazolyl) ligand, but also with the different *trans* influences of PTA and CO to the coordinated pyrazol rings. For the related [Rh(acac)(CO)(L)] (L = P(3-$C_6H_4SO_3Na)_3$, P($CH_2CH_2CN)_3$, P(2-$MeOC_6H_4)_3$, P(4-$MeOC_6H_4)_3$ and P(2,4,6-$MeOC_6H_2)_3$) complexes, the ^1H NMR chemical shifts of the acetylacetonato methyl groups were shown [19a] to highly depend on the ligands in trans positions. In the [Rh(acac)(CO)(PTA)] analogue, on the other hand, no considerable trans influence was revealed, the methyl groups in the acetylacetonato ligand displaying identical ^1H NMR resonances.

Since compound **1** is soluble and stable in aqueous media, its behaviour in D_2O at variable temperature was investigated by ^1H NMR. At 80 °C the ^1H NMR spectrum shows the equivalence of the three pyrazolyl rings (only three resonances at δ 8.95, 8.60 and 7.34 due to the pyrazolyl protons in positions 3, 5 and 4, respectively), as observed in the ^1H NMR spectrum in CD_3OD at room temperature. However, in D_2O at room temperature the pyrazolyl exchange rate becomes comparable to the NMR time scale and the ^1H NMR spectrum of **1** displays in the pyrazole region a pattern of six resonances: three for the uncoordinated pyrazole ring (δ 8.77, 7.80 and 6.70) and three for the other two pyrazole rings that are bound to the metal (δ 8.11, 7.91 and 6.66), with the overall 1:2 intensity ratio. Hence, the pyrazolyl exchange in D_2O is slower than in CD_3OD, and in the latter solvent the equivalence of the pyrazolyl ligands is already observed at room temperature.

The terminal CO ligand in **1** is easily identified by its characteristic IR stretch (strong and sharp band at 2007 cm^{-1}, in KBr) which is comparable to those observed in the related complexes [Rh(Tpms)(CO)(L)] [1978 (L = PCy_3), 1990 (L = PMe_3) or 1989

Table 1
Selected bond distances (Å) and angles (°) for [Rh(Tpms)(CO)(PTA)] (**1**)

Rh(1)–P(1)	2.2354(8)	P(1)–Rh(1)–N(11)	94.18(7)
Rh(1)–N(11)	2.084(3)	P(1)–Rh(1)–N(21)	174.60(7)
Rh(1)–N(21)	2.099(3)	P(1)–Rh(1)–C(1)	89.40(10)
Rh(1)–C(1)	1.813(4)	N(11)–Rh(1)–C(1)	174.61(15)
S(1)–O(11)	1.440(3)	N(21)–Rh(1)–C(1)	91.23(14)
O(1)–C(1)	1.139(6)	Rh(1)–N(11)–C(11)	131.4(2)

Table 2
Crystal data and refinement parameters for [Rh(Tpms)(CO)(PTA)] (**1**)

Empirical formula	$C_{17}H_{21}N_9O_4PRhS$
Molecular weight	581.38
Crystal size (mm^3)	0.12 × 0.08 × 0.06
Temperature (K)	150(2)
λ (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	10.4470(5)
b (Å)	14.7379(7)
c (Å)	14.8775(7)
α (°)	90
β (°)	108.745(3)
γ (°)	90
V (Å^3)	2169.14(18)
Z	4
ρ_{calc} (Mg/m^3)	1.780
μ(Mo Kα) (mm^{-1})	1.004
F(000)	1176
Number of collected reflections	21 735
Number of unique reflections	5522
$R_{Int.}$	0.0565
Final R_1[a], wR_2[b] ($I \geqslant 2\sigma$)	0.0380, 0.0815
Goodness-of-fit on F^2	1.027

[a] $R_1 = \sum||F_o| - |F_c||/\sum\sum F_o|$.

[b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

(L = PPh_3) cm^{-1}] [1]. Since all these complexes contain the same Tpms ligand, the differences found in the CO stretching vibration must derive from the different effects of the phosphine ligands. Indeed, ν(CO) for such a series of complexes decreases in the order L = PTA > PMe_3 ⩾ PPh_3 > PCy_3, revealing an opposite trend to that found for the cone angle (θ, °) [27] of the respective phosphines, L = PCy_3 (170) > PPh_3 (145) > PMe_3 (134) > PTA (103) [9]. A decrease of the steric hindrance of the phosphine corresponds to an increase of ν(CO), thus to a lowering of π-acceptance of the π^*(CO) orbitals from metal d_π orbitals and/or to an increase of the σ-donation from the weakly antibonding σ-donor orbital of CO to the metal. This behaviour can conceivably be accounted for by the more effective competition of the less bulky phosphines for the available Rh^I π-electron release. This contrasts with the observed [19a] behaviour of the phosphine complexes [Rh(acac)(CO)L] (with the less sterically demanding acetylacetonato ligand in comparison with Tpms), for which ν(CO) increases from the PTA to the PPh_3 complex, PTA thus behaving, as expected, as a weaker π-acceptor than PPh_3. The order of the ^{31}P NMR coordination shift ($\Delta\delta = \delta_{complex} - \delta_{phosphine}$) for the complexes [Rh(Tpms)(CO)(L)] (L = PMe_3 [1,28] ⩾ PTA (this work) > PPh_3 [1,28] > PCy_3 [1,28]) is expected [29,30] to be dependent on both the steric hindrance and π-acceptance of L and does not corroborate any of the above orders of the IR data or cone angles.

A D_2O solution of complex **1** exposed to air was monitored along the time by ^1H, $^{31}P\{^1H\}$ NMR and IR spectroscopies which show the occurrence of a slow decomposition process. The cleavage of the Rh–P bond to form free PTA oxide has been observed, but no evidence for the liberation of Tpms has been revealed. The room temperature ^1H NMR spectra, indeed, showed in the pyrazole region the gradual replacement of the initial six signal pattern by a three resonance pattern (see Section 2), whereas in the PTA region the replacement of the PCH_2N singlet of the coordinated phosphine by the doublet at δ 4.04 ($^2J_{HP}$ = 10.3 Hz) characteristic of free PTA oxide was clearly observed. The $^{31}P\{^1H\}$ NMR spectra, on the other hand, showed the progressive decrease of the original $^{31}P\{^1H\}$ resonance of complex **1**, with the concomitant increase of the free PTA = O singlet, the process being accomplished in a few days. The pale-yellow solid **2** isolated after removing the solvent is insoluble in all common solvents and its IR spectrum shows a strong band at 1861 cm^{-1}, a value similar to that (1845 cm^{-1}) reported [31] for the bridging CO ligands in the dirhodium complex [{HB(pz)$_3$}$_2$Rh$_2$(μ-CO)$_3$] with tris(1-pyrazolyl)borato ligands. Hence, also on account of elemental analysis, the product **2** of decomposition of **1** is tentatively formulated as the dinuclear Rh-Tpms complex with μ-CO ligands [(Tpms)$_2$Rh$_2$(μ-CO)$_2$].

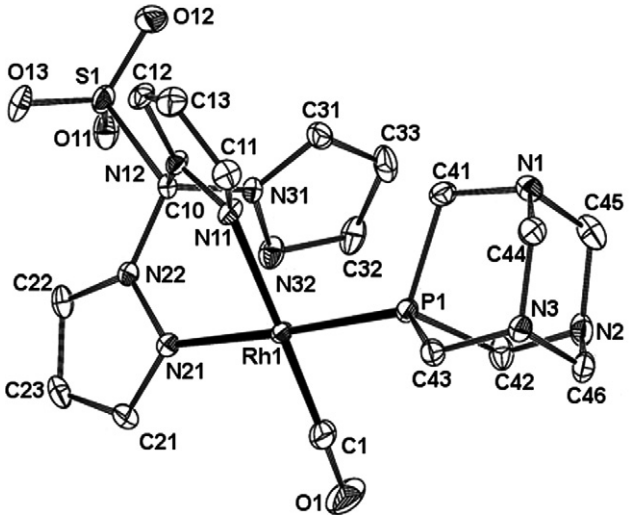


Fig. 2. An ORTEP view of the [Rh(Tpms)(CO)(PTA)] molecule **1**. The ellipsoids are drawn at the 50% probability level and the H atoms are omitted for clarity.

3.2. X-ray crystal structure of *1*

Crystals of compound **1** suitable for X-ray analysis were obtained from slow cooling of a saturated MeOH/CH_2Cl_2 solution at 4 °C. An ORTEP view of complex **1** is shown in Fig. 2, whereas selected bond distances and angles are collected in Tables 1–3. Complex **1** crystallizes in the monoclinic space group $P2_1/c$, and the anionic tris(1-pyrazolyl)methanesulfonate group acts as a bidentate κ^2: *N,N*-ligand, binding the Rh^I atom through the two pyrazolyl nitrogens N11 and N21. The phosphorus P1 and the C1-carbonyl atoms complete the coordination sphere. The C1–P1–N11–N21 moiety is significantly distorted from planarity. The dihedral angle formed by the C1–P1–N11 and the C1–N21–N11 least-square-planes is of 178.13(10)°, with Rh1 lying 0.0667(3) Å above the former plane and 0.0646(3) Å below the latter. The non-coordinated pyrazolyl group points towards the rhodium atom, the distance between Rh1 and N32 being 3.312(3) Å. The difference in the trans influences of the PTA and CO ligands (suggested by low temperature ^1H NMR in CD_3OD, as discussed above) is not clearly reflected in the Rh1–N11 and Rh1–N21 bond lengths since they do not differ significantly (2.084(3) *vs.* 2.099(3) Å). The [Rh(Tpms)(CO)(PPh_3)] analogue [1] also exhibits comparable bond distances of 2.093(3) and 2.100(3) Å, respectively.

Extensive inter-molecular hydrogen bonds are also formed, with *d*(H···A) distances ranging from 2.40 to 2.59 Å. N32 (from a pyrazolyl ring), N1 and N2 (from PTA), as well as the sulfonate and the carbonyl oxygen atoms act as the hydrogen acceptors (Table 3 and Figs. 3 and 4). Additionally, the intra-molecular C22–H22···O11 hydrogen bond provides a further stabilization of the structure.

Table 3
Hydrogen bond geometry (Å, °)

D–H···A	*d*(H···A)	*d*(D···A)	∠(D–H···A)	Symmetry codes
C11–H11···O11	2.44	3.062(4)	122	1/2 + *x*, 1/2 − *y*, 1/2 + *z*
C11–H11···N32	2.52	3.308(4)	140	1/2 + *x*, 1/2 − *y*, 1/2 + *z*
C12–H12···O13	2.57	3.077(4)	114	
C13–H13···O1	2.40	3.227(5)	146	1 + *x*, *y*, *z*
C21–H21···N3	2.49	3.348(4)	150	1/2 − *x*, 1/2 + *y*, 1/2 − *z*
C22–H22···O11	2.54	2.998(4)	110	
C31–H31···N1	2.52	3.460(5)	170	1 − *x*, −*y*, −*z*
C33–H33···O11	2.50	3.421(4)	164	1/2 − *x*, −1/2 + *y*, −1/2 − *z*
C43–H43A···N32	2.60	3.526(4)	156	1/2 + *x*, 1/2 − *y*, 1/2 + *z*
C44–H44A···O12	2.59	3.503(4)	153	1 − *x*, −*y*, −*z*
C46–H46A···O13	2.48	3.468(5)	174	−1/2 + *x*, 1/2 − *y*, 1/2 + *z*

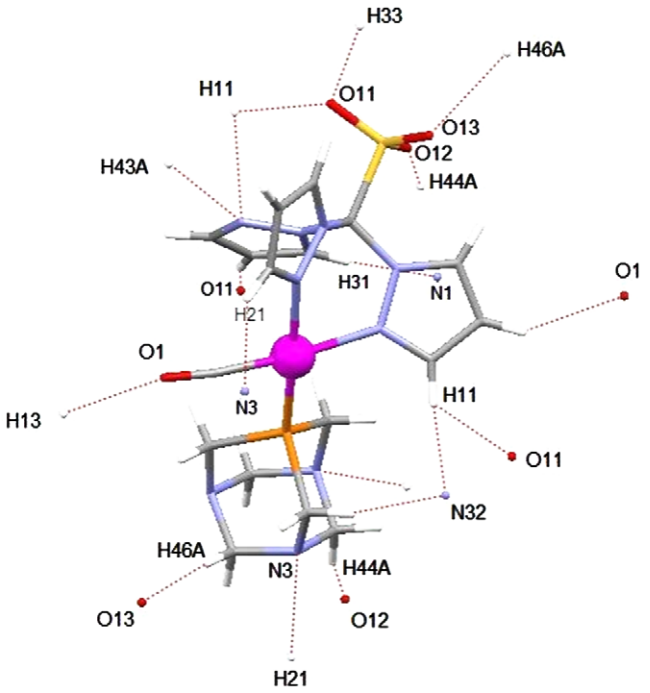


Fig. 3. [Rh(Tpms)(CO)(PTA)] molecule **1** with the inter-molecular hydrogen bonds (dashed lines). Rhodium, purple; phosphorus, orange; nitrogen, blue; oxygen, red; carbon, gray; hydrogen, light gray. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

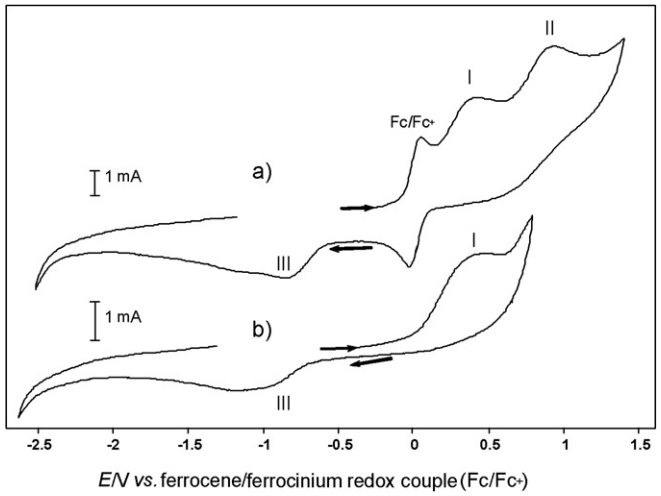


Fig. 5. Cyclic voltammograms of complex **1** (0.86 mM) in a 0.2 M $[Bu_4N][BF_4]$/MeCN solution at a Pt disc (d = 1 mm) electrode. Ferrocene, present in (a), was used as the internal standard. Scan rate = 500 mV s^{-1}.

3.3. Electrochemical behaviour of **1**

The title compound has been investigated by cyclic voltammetry (CV) in MeCN, with 0.2 M $[nBu_4N][BF_4]$ as supporting electrolyte, at a Pt disc electrode. The cyclic voltammogram at 500 mV s^{-1} exhibits a first irreversible oxidation wave (I) at $E^{ox}_{p/2}$ = 0.21 V *vs.* Fc/Fc^+ (0.91 V *vs.* NHE), followed by a second one (II), also irreversible, at $E^{ox}_{p/2}$ = 0.70 V *vs.* Fc/Fc^+ (1.40 V *vs.* NHE) (Fig. 5a). A similar behaviour has been recently reported [32] for the related bis(1-pyrazolylborato)rhodium(I) complexes [Rh(Bp)(CO)L] [L = $P(NC_4H_4)_3$, PPh_3, PCy_3, $P(C_6H_4OMe\text{-}4)_3$] which display, as observed here, two irreversible oxidation processes, the first one at $E^{ox}_{p/2}$ in the range 0.63–0.95 V *vs.* NHE, and the second one at $E^{ox}_{p/2}$ in the range 1.0–1.6 V *vs.* NHE. The strong electrode passivation associated with the oxidation processes prevented any reliable controlled potential electrolysis measurements.

Upon scan reversal following the oxidation waves, cathodic irreversible waves, namely (III) at $E^{red}_{p/2}$ = −0.65 V *vs.* Fc/Fc^+ (0.05 V *vs.* NHE), are also observed, being assigned to the reduction of species formed by chemical reactions following the electron-transfer in the oxidation processes (Fig. 5b) for the case of scan reversal upon the oxidation wave I.

The first oxidation wave I is attributed [32,33] to the metal-centred single-electron Rh^I/Rh^{II} oxidation, and its oxidation potential is expected [34–36] to reflect the net electron-donor abilities of the ligands as measured by the electrochemical E_L ligand parameter (the stronger that character, the lower the E_L value) proposed by Lever [21,37], according to Eq. (2). In this relationship, the redox potential of a hexacoordinate complex (E) is expressed in V *vs.* NHE, $\sum E_L$ is the sum of the E_L values for all the ligands (additive effects), whereas S_M and I_M (slope and intercept, respectively) depend upon the metal and redox couple, the spin state and stereochemistry,

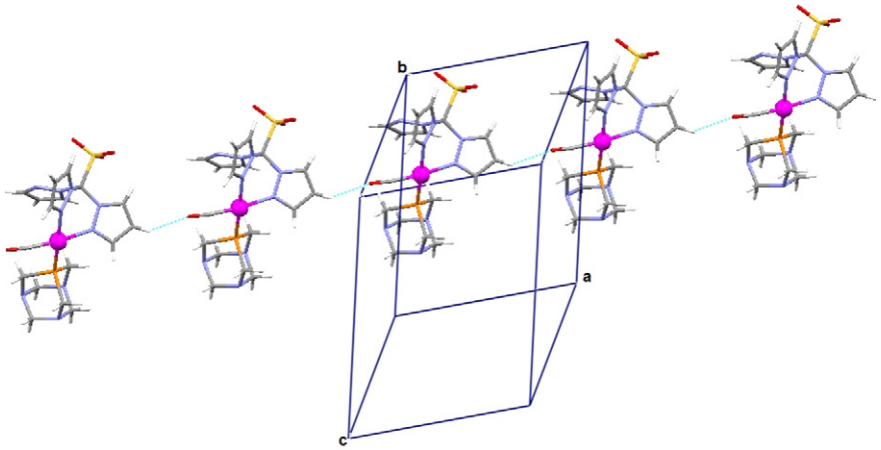


Fig. 4. Fragment of the crystal packing diagram (arbitrary view) and the unit cell of [Rh(Tpms)(CO)(PTA)] molecule **1** showing the shortest C13–H13···O1 inter-molecular hydrogen bonds (dashed lines). Rhodium, purple; phosphorus, orange; nitrogen, blue; oxygen, red; carbon, gray; hydrogen, light gray. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

$$E = S_M \times \left(\sum E_L\right) + I_M \quad (2)$$

By plotting the $E^{ox}_{p/2}$ (V *vs.* NHE, measured in CH_2Cl_2) *vs.* $\sum E_L$ (V *vs.* NHE) for [Rh(Bp)(CO)(L)] [Bp = bis(pyrazolyl)borate; L = $P(NC_4H_4)_3$, PPh_3, PCy_3, $P(C_6H_4OMe\text{-}4)_3$] [32] and for other tetracoordinate square-planar Rh^I complexes previously described in the literature [33,38], some of us proposed, for such a type of compounds, the relationship expressed by Eq. (3) [32], of the type of Lever's expression (2) in which $S_M = 1.68$ and $I_M = -0.87$ V *vs.* NHE,

$$E^{ox}_{p/2} = 1.68 \times \left(\sum E_L\right) - 0.87 \quad (3)$$

By applying Eq. (3) to the title square-planar Rh^I complex [Rh(Tpms)(CO)(PTA)] (**1**) and taking into account its measured first oxidation potential $E_{p/2}{}^{ox}$ (I) value (0.91 V *vs.* NHE) and the known E_L values for the tris(1-pyrazolyl)methanesulfonate (−0.09 V *vs.* NHE per each coordinated arm [39]) and CO (0.99 V *vs.* NHE [21]) ligands, it was possible to estimate the E_L value for the PTA ligand, *i.e.* 0.25 V *vs.* NHE. This value is comparable (within ±0.05 V) to that (0.34 V) very recently obtained [40] from the values of the first oxidation potential of the tris(pyrazolyl)borate (Tp) Ru^{II} hexacoordinate complexes [Ru(Tp)Cl(PTA)$_2$] and [Ru(Tp)Cl(PPh_3)(PTA)], in NCMe and DMSO, by applying Eq. (2) to the $Ru^{II/III}$ redox couple. Hence, the average E_L value for PTA of 0.32 V (considering that the reported [40] value of 0.34 V is the average of four values) can be obtained. The PTA ligand thus behaves as a moderate net electron-donor, being comparable to pyridine, acetonitrile or PMe_3 (E_L values of 0.25, 0.34 or 0.33 V *vs.* NHE, respectively [21]), but as a considerably more effective electron-donor than *N*-pyrrolyl phosphines such as $P(NC_4H_4)_3$ or $PPh(NC_4H_4)_2$ (corresponding E_L values of 0.69 and 0.60 V *vs.* NHE) [33].

Another electrochemical ligand parameter (P_L) has been proposed by Pickett et al. [41] to measure also the net electron-donor ability of a ligand, and from the linear expression (4), experimentally observed [21] for a considerable number of ligands (except for very strong π-electron acceptors [21,34–36,42]), it was also possible to estimate the still unknown P_L value for the PTA ligand (−0.49 V),

$$P_L = 1.17 \times E_L - 0.86 \quad (4)$$

However, the E_L and P_L values estimated above should be taken cautiously, since they are based on the redox potential of a limited number of complexes, which, moreover, in the case of the Rh^I compound, concerns an irreversible redox process. Hence, the value we have measured (half-peak potential $E_{p/2}{}^{ox}$) is not the thermodynamic one, although it is expected to be closer to the latter than the peak potential ($E_p{}^{ox}$). Further estimates with other suitable compounds (in particular showing reversible oxidation processes) will be required for a better accuracy.

4. Conclusions

We have achieved a rapid, high yield and simple one-pot synthetic procedure to furnish the new water-soluble [Rh(Tpms)(CO)(PTA)] complex (**1**), by using only Li(Tpms), PTA and an accessible Rh^I source as commercially available reagents. With minor adaptations, taking into account solubility differences, this procedure is applicable to other Tpms-Rh^I derivatives bearing different water-soluble phosphines, thus possibly giving a further impulse to the development of Rh-phosphine chemistry and catalysis in aqueous systems. The synthetic method now achieved for such a type of Rh^I complexes is much simpler than that previously used [1], since it does not require the isolation of any intermediate, the use of CO and the synthesis of the Tl(Tpms) salt. Unlike the above reported [Rh(Tpms)(CO)(L)] (L = PMe_3, PPh_3, PCy_3) analogues [1], complex **1** is quite stable in water under an inert atmosphere, constituting therefore a promising catalyst precursor for catalytic reactions in liquid biphasic systems.

Complex **1** is redox active and from the $Rh^{I/II}$ oxidation potential, as measured by cyclic voltammetry, it was possible to estimate the Lever E_L and Pickett P_L electrochemical ligand parameters which show that PTA is a net electron-donor comparable to PMe_3, pyridine or acetonitrile.

The extension of this work to the synthesis of other water-soluble tris(1-pyrazolyl)methanesulfonate-Rh derivatives, as well as the investigation of their catalytic activity in aqueous media, are currently in progress and will be reported elsewhere.

5. Supplementary material

CCDC 677349 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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