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Water-Soluble 3,7-Dimethyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane (dmoPTA) as a Polydentate Ligand: Synthesis of [RuClCp(PPh_3)-μ-dmoPTA-1κP:2$\kappa^2 N,N'$-Co(acac-$\kappa^2 O,O'$)$_2$]·H_2O

Adrián Mena-Cruz,[†] Pablo Lorenzo-Luis,[†] Antonio Romerosa,[*,‡] and Manuel Serrano-Ruiz[‡]

Área de Química Inorgánica, Facultad de Ciencias, Universidad de Almería, Almería, Spain, and Departamento de Química Inorgánica, Facultad de Química, Universidad de La Laguna, La Laguna, Tenerife, Spain

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The dinuclear complex [RuClCp(PPh_3)-μ-dmoPTA-1κP:2$\kappa^2 N,N'$-Co(acac-$\kappa^2 O,O'$)$_2$]·H_2O (**2**; dmoPTA = 3,7-dimethyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane) has been synthesized by reaction of [RuClCp(HdmoPTA)(PPh_3)](OSO_2CF_3) (**1**) with Co(acac)$_2$ in methanol (HdmoPTA = 3,7-H-3,7-dimethyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane). Elemental analysis, IR, NMR, and single-crystal X-ray structure determination have characterized the new complex. This complex is active for the catalytic isomerization of but-1-en-3-ol in acetone better than **1**.

Tertiary water-soluble phosphines have been the most widely used class of hydrosoluble ligands for catalysis in water because of their neutral donating ability, which can effectively stabilize the metal center throughout several catalytic cycles. A variety of hydrosoluble phosphines have appeared throughout the years, and their catalytic potential has been investigated.[1] Our research group has paid special attention to the synthesis of new water-soluble phosphines. We have recently presented the synthetic general procedure for obtaining a family of phosphines containing amino acids[2] and three new PTA derivatives: the dmPTA, dmoPTA, and HdmoPTA (PTA = 1,3,5-triaza-7-phosphaadamantane; dmPTA = *N,N′*-dimethyl-1,3,5-triaza-7-phosphaadamantane; dmoPTA = 3,7-dimethyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane; HdmoPTA = 3,7-H-3,7-dimethyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane).[3] These compounds are easily obtained, being interesting ligands for obtaining new water-soluble complexes useful as catalysts in aqueous homogeneous catalysis. As a result of our initial efforts, the novel complex [RuClCp(HdmoPTA)(PPh_3)](OSO_2CF_3) (**1**) was obtained by the reaction of dmPTA with [RuClCp(PPh_3)$_2$]. In complex **1**, the new ligand HdmoPTA is coordinated by the P atom to the metal.[3] Three conclusions could be extracted from the observed reactivity for HdmoPTA and the analysis of the crystal structure of **1**: (a) the H atom between both CH_3−N atoms can be removed easily using a 0.01 M KOH water solution at room temperature; (b) the two CH_3−N atoms, as tertiary amines, are capable of coordinating to hard atoms; (c) the distance between both CH_3−N atoms [2.702(12) Å] is good enough to suppose that through these atoms the dmoPTA is able to chelate a metal without supporting significant distortion. Therefore, the dmoPTA could be a polydentate ligand through the P and CH_3−N atoms (Scheme 1). To verify this suspicion, we have first studied the reaction of [RuClCp(HdmoPTA)(PPh_3)](OSO_2CF_3) (**1**) with Co(acac)$_2$ (acac = acetylacetonate) in refluxing methanol (see below).

Numerous examples of complexes containing the {Co(acac)$_2$} moiety have been development in recent years because of their actual and potential applications in areas such as bioinorganic chemistry, medicine, high catalytic activity at low cost, antiferromagnetism, and electrochromism and

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[*] To whom correspondence should be addressed. E-mail: romerosa@ual.es.

[†] Universidad de La Laguna.

[‡] Universidad de Almería.

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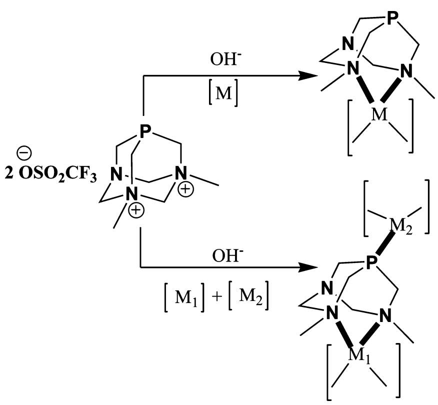
10.1021/ic702239w CCC: $40.75

Scheme 1



as a regulating agent for radical polymerization of poly(vinyl acetate).[4]

The reaction of **1** with Co(acac)$_2$ in methanol[5] led to the new bimetallic complex [RuClCp(PPh$_3$)-μ-dmoPTA-1κP:2$\kappa^2 N,N'$-Co(acac-$\kappa^2 O,O'$)$_2$]·H$_2$O (**2**), which was first characterized by elemental analysis, IR (Figure S1 of the Supporting Information), and NMR spectroscopy. The ^{31}P{^{1}H} NMR spectrum in CD$_3$OD is constituted by two doublets at 52.71 and 51.56 ppm ($^2J_{PP}$ = 41.6 Hz), which had arisen to a field lower than those found in starting complex **1** [δ(PPh$_3$) = 46.00 ppm; δ(HdmoPTA) = −2.93 ppm], while the coupling constant is practically the same ($^2J_{PP}$ = 42.72 Hz). That effect could be justified by considering Co^{II} bonded to dmoPTA through both CH$_3$−N atoms. As expected, the Co^{II} paramagnetic influence on dmoPTA [$\Delta\delta$ (**2**−dmoPTA − **1**−HdmoPTA = −54.49 ppm] is bigger than that on the PPh$_3$ [$\Delta\delta$ (**2**−PPh$_3$ − **1**−PPh$_3$ = 6.71 ppm].[6] Similarly, its ^{1}H and ^{31}C{^{1}H} NMR could only be justified by the Co^{II} paramagnetic effect. An indubitable assignation of the ^{1}H NMR signals was not possible (Figure S2 of the Supporting Information), while the ^{13}C{^{1}H} NMR signals for PPh$_3$ (127.8–136.22 ppm) and Cp (88.24 ppm) were the only ones clearly assigned. It is interesting to point out that the Cp signal is shifted 8.9 ppm to low field with respect to **1**. Powder magnetism measurements of **2** between 2 and 300 K (Figure S3 of the Supporting Information) showed that the values and the shape of the curve are as expected for isolated octahedral Co^{II} ions with some trigonal distortions.[7] Crystals good enough for X-ray diffraction were obtained by slow evaporation from an acetone solution of **2**.[8] A perspective drawing of its crystal structure with atom numbering is depicted in Figure 1. The coordination polyhedron around the Ru atom adopts a highly distorted pseudooctahedral geometry [P1−Ru1−P2 = 99.04(11)°], similar to that observed for piano-stool complexes of the type [RuCpX(L)(L′)]$^{n+}$,[9] such as **1**, recently published by us.[3]

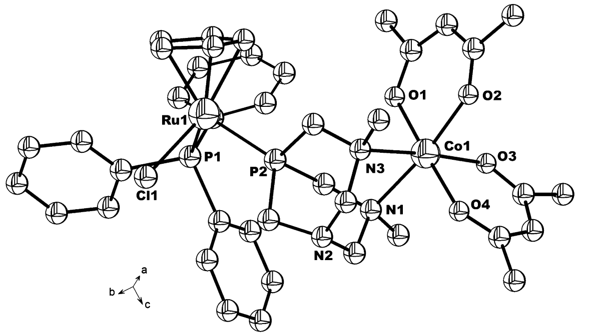


Figure 1. ORTEP diagram of **2**. Ellipsoids are shown at 50% probability. For the sake of clarity, the H atoms were omitted.

No significant differences were found in the rest of the bond distances and angles from those found in similar cyclopentadienyl Ru^{II} complexes.[3,9] The monodentate {RuClCp(PPh$_3$)(dmoPTA-1κP)} entity acts as a bidentate ligand by its CH$_3$−N atoms toward a Co^{II} atom, which

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(4) (a) For example, see: Reeve, T. B.; Cros, J. P.; Gennari, C. *Angew. Chem., Int. Ed.* **2006**, *45*, 2449. (b) Dickie, D. A.; Schatte, G.; Jennings, M. C. *Inorg. Chem.* **2006**, *45*, 1646. (c) Levitin, I. Y.; Yatsimirsky, A. K.; Volpin, M. E. *Organomet. Chem. U.S.S.R.* **1990**, *3*, 442. (d) Debuigne, A.; Caille, J.-R.; Jérôme, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 1101. (e) Rivera, E. F.; Atakan, B.; Kohse-Hoinghaus, K. *J. Phys. IV* **2001**, *11*, Pr3–629. (f) Granquist, C. G. *Handbook of Inorganic Electrochromic Materials*; Elsevier: Amsterdam, The Netherlands, 1995.

(5) Co(acac)$_2$ (0.0858 g, 0.33 mmol) was introduced into a solution of **1** (0.075 g, 0.0095 mmol) in 6 mL of MeOH. The mixture was first stirred at room temperature until dissolution of the reactants was completed and then refluxed for 3.5 h. The solvent was removed until 0.5 mL, and then 5 mL of pentane was added. The obtained pale-brown precipitated was filtered and washed with water (2 × 5 mL). The wet powder was recrystallized in EtOH. Yield: 47.7 mg (∼ 55%). $S_{25°C,H_2O}$ < 1 mg/mL. Elem anal. Calcd for C$_{40}$H$_{52}$N$_3$ClO$_5$P$_2$RuCo (MW = 912.25 g/mol): C, 52.66; H, 5.70; N, 4.60. Found: C, 52.42; H, 5.81; N, 4.47. ^{13}C{^{1}H} NMR (CD$_3$OD): δ (ppm) 88.24 (s, Cp), 127.8–136.22 (m, aromatic, PPh$_3$). ^{31}P{^{1}H} NMR (CD$_3$OD): δ (ppm) 52.71 (d, $^2J_{PP}$ = 41.6 Hz, PPh$_3$), 51.56 (dd, $^2J_{PP}$ = 41.6 Hz, dmoPTA).

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(7) Magnetic susceptibility measurements on polycrystalline samples were carried out in the temperature range 1.9−300 K by means of a Quantum Design SQUID magnetometer operating at 10 000 Oe. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants. Experimental susceptibilities were also corrected for the magnetization of the sample holder.

(8) The structure was determined by direct methods and refined by least-squares procedures on F^2. (a) Altamore, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, G.; Burla, M. C.; Polidori, G.; Camalli, M.; Spagna, R. *Sir 97 Package Program*; **1997**. (b) Sheldrick, G. M. *SHELXL*, version 6.14; Bruker-AXS: Madison, WI, 2003. Crystallographic data were collected at 293(2) K on a Bruker APEX CCD diffractometer (XDIFRACT service of the University of Almería) with Mo Kα radiation (λ = 0.710 69 Å). Crystal data for **2** (CCDC 667604): 0.07 × 0.05 × 0.04 mm^3, monoclinic $P2_1/c$, Z = 4, a = 12.154(5) Å, b = 35.492(5) Å, c = 9.884(5) Å, α = 90°, V = 4082(3) Å^3, $-14 \le h \le 13$, $-35 \le k \le 41$, $-11 \le l \le 11$. Of the 6733 measured independent reflections in the θ range 1.75–24.44°, 3414 have $I_0 > 2\sigma(I_0)$, R1 = 0.0810, wR2 = 0.1468. The function minimized during the refinement was $w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 0.0000P]$, where $P = [(\max(F_o^2) + 2F_c^2)/3]$. The H atoms were refined with isotropic temperature factors. The final Fourier difference maps showed maximum and minimum height peaks of 1.067 and −0.952 e/Å^3.

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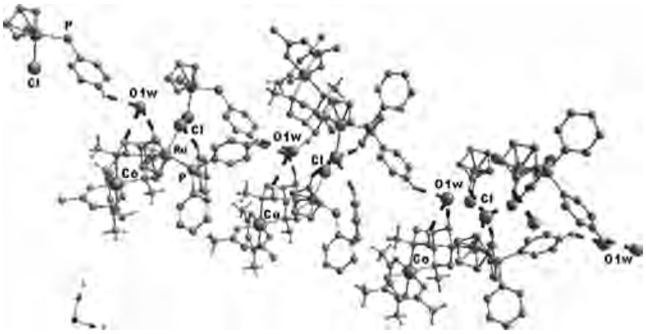

Figure 2. View along the c axis of a packing diagram (section) of **2** through $C_{Cp}-H\cdots Cl$, $C_{PPh_3}-H\cdots Cl$, $C_{dmPTA}-H\cdots O_w$, and $C_{PPh_3}-H\cdots O_w$ interactions (broken lines).

completes its six-coordination geometry with four O atoms from two acac molecules. The ligands bonded to the metal form four stable six-membered chelated rings [2(Co–O–C_3–O)+(Co–N–C–P–C–N)+(Co–N–C–N–C–N)]. The Co atom does not deviate significantly from the mean equatorial plane (0.0163 Å). Rest of the bond distances found are in agreement with those reported for carboxylate- and bpy-containing Co^{II} complexes.[10,11] The values for the dihedral angles between the equatorial plane (N3–N1–O2–O3) and that for the phosphaadamantane bonds (P2–C12–N3–C14) and (P2–C10–N1–C13) are 89.03(36) and 84.97(35)°, respectively. Finally, the heterometallic dinuclear units are interconnected through intermolecular $C-H\cdots Cl$ and $N-H\cdots O_{water}$ interactions (Figure 2; ranging from 2.783 to 2.869 Å and from 2.644 to 2.801 Å, respectively), postulated in the literature as *weak* hydrogen bonds.[12] It is important to stress that only three additional examples for P,N coordination of PTA and its derivatives have been described up to now.[9a,13]

Preliminary tests[14] on the catalytic activity of **1** and **2** in the isomerization of enols to enones show that complex **2** is more active than **1** under similar conditions. A full paper will address the complete catalytic study in due time.

Therefore, the ligand dmoPTA not only is an interesting ligand to obtain heterometallic complexes but could provide a very large variety of new complexes with possible new and interesting properties. An accurate study on the catalytic isomerization of enols by this complex as well as the synthesis of new heterometallic complexes containing the ligand dmoPTA is now in progress.

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Supporting Information Available: Figures S1–S3. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for **2** can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif under CCDC 667604.

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(14) Into a NMR tube was introduced **1** (2.6 mg, 0.032 mmol) or **2** (2.9 mg, 0.032 mmol), 10 equiv of the substrate but-1-en-3-ol (2.8 μL, 0.032 mmol), and 0.6 mL of acetone-d_6. The reaction was checked at room temperature by ^{1}H NMR. At 65 °C, complex **2** catalyzed the isomerization of the substrate to give 3-butanone in 2.5 h, while **1** is not active. The addition of 2.5% water to the reaction increased the activity of **1**, but the reactivity of **2** was even lower.