

Ruthenium-Stabilized Low-Coordinate Phosphorus Atoms: Structural Evidence for Monomeric Metaphosphonate**

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The metaphosphate anion has attracted steady interest since 1955^[1] in connection with wide applications in phosphorylation reactions.^[2] It has relevance in biochemistry in particular with respect to ATP hydrolysis.^[3] However, despite considerable efforts, monomeric metaphosphates and other dioxophosphoranes are only known as transient species in solution and their existence can be inferred from trapping experiments.^[2–4] Their high reactivity arises from the powerful electrophilic character at the phosphorus center. Several approaches have been tested to stabilize these highly reactive species. Kinetic stabilization by steric protection^[5] proved to be ineffective for dioxophosphorane and led to products that resulted from the insertion of the PO₂ moiety in a neighboring group.^[6] The electrophilicity and the tendency to expand the valence shell were exploited for their stabilization as Lewis salts. This strategy allowed only spectroscopic characterization by ³¹P NMR in a few cases.^[7] Thus, the chemistry of dioxophosphorane suffers from a paucity of information and new approaches to stabilize and enable deeper investigation are highly desirable. This work describes the first isolation and full characterization, including X-ray structural analysis, of stabilized metaphosphonate.

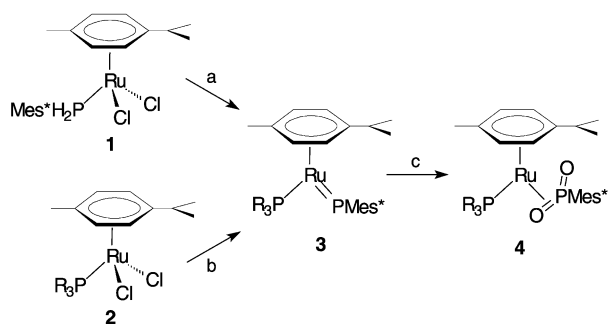
We have developed a novel and successful route to ruthenium-stabilized monomeric metaphosphonate by oxidation of a nucleophilic terminal phosphinidene complex of ruthenium. As recently described by Lammerstma and co-workers, the terminal phosphinidene ruthenium complexes [(η⁶-*p*-cymene)Ru(PR₃)(PMes*)] (**3a**: R = Cy, **3b**: R = Ph^[8]) are formed as dark green solids by the reaction of the primary phosphane complex [(η⁶-*p*-cymene)RuCl₂(PH₂Mes*)] (**1**; *p*-cymene = 4-methyl-*iso*-propylbenzene; Mes* = 2,4,6-tri-*tert*-butylphenyl) with two equivalents of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the presence of PR₃ as a stabilizing ligand (R = Ph, Cy).^[8] Alternatively, treatment of [(η⁶-*p*-cymene)RuCl₂(PR₃)] (**2a**: R = Cy, **2b**: R = Ph) and PH₂Mes* with DBU affords **3** in high yields (Scheme 1).

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Scheme 1. Synthesis of the complexes **3**, **4**: a) PR_3 , DBU, C_7H_8 ; b) PH_2Mes^* , DBU, C_7H_8 ; c) O_2 , Et_2O .

The ^{31}P NMR spectra show a high-field resonance ($\delta = 811$ ppm for **3a** and $\delta = 835$ ppm for **3b**) in the typical region for terminal phosphinidene complexes^[8,9] as well as a signal which corresponds to the PR_3 ligand.^[10] X-ray diffraction study ascertains the structure of **3a**, which compares well with those of $[(\eta^6\text{-}p\text{-cymene})(\text{PPh}_3)\text{Os}(\text{PMe}^*)]$ and $[(\eta^6\text{-benzene})(\text{PPh}_3)\text{Ru}(\text{PMe}^*)]$.^[8] The nucleophilic behavior of the phosphinidene ligand in these complexes arises from a substantial back-donation from the metal. Thus, complexes **3** offer an attractive opportunity to stabilize strong electrophilic phosphorus species such as dioxophosphorane.

Using similar oxidation route to that reported to generate metaphosphonate from related $\sigma^2\text{-}\lambda^3$ phosphorus in diphosphene,^[11] we obtained the first monomeric stabilized-dioxophosphorane. Indeed, upon oxidation with O_2 , the dark green solution of **3** turned instantly yellow and yielded $[(\eta^6\text{-}p\text{-cymene})(\text{PR}_3)\text{Ru}(\eta^2\text{-OPOMes}^*)]$ (**4a**: $\text{R} = \text{Cy}$, **4b**: $\text{R} = \text{Ph}$) in high yields (Scheme 1). Interestingly, **4** are mildly air-sensitive and the high electrophilicity of dioxophosphorane is thoroughly quenched since no reaction occurs in the presence of any of the typical trapping agents (CH_3OH , PhNH_2). The formulation of **4** was confirmed by spectroscopic studies. Conversion of **3** into **4** was followed by IR spectroscopy and the spectra (nujol) show appearance of two strong and characteristic absorptions (at 1168 cm^{-1} and 907 cm^{-1} ; 1153 cm^{-1} and 925 cm^{-1} for **4a** and **4b** respectively) assigned to asymmetric and symmetric OPO stretches. Although these bands cannot be considered as pure modes (coupling with Ru-P and Ru-O must be present), they are clearly shifted to low frequencies by comparison to the band observed in RPO_2 (1448 cm^{-1} and 1143 cm^{-1})^[12] and indicate a significant weakening of the P=O bond consistent with ligation to ruthenium. Analogous behavior has been reported in the well-documented coordination chemistry of the somewhat related CO_2 ligand.^[13] ^{31}P NMR resonances are in the expected region for four-coordinate phosphorus atoms ($\delta = 40.8$ ppm for PO_2Mes^* and $\delta = 27.1$ ppm for PCy_3 in **4a** and $\delta = 38.5$ ppm for PO_2Mes^* and $\delta = 25.7$ ppm for PPh_3 in **4b**). ^1H NMR spectroscopic data provide additional structural information. ^1H NMR spectra show for the aryl protons of the p -cymene ligand three resonances in a 2:1:1 ratio, which are significantly shifted upfield relative to those of **1-3**. Such a behavior had been previously observed for half-sandwich complexes exposed to magnetic anisotropy cone of phenyl substituent (known as “ β -phenyl effect”).^[14] Consistently, the

proximity between p -cymene and Mes^* moieties results in restricted rotation about the $\text{P-C}(\text{Mes}^*)$ bond as evidenced by the presence of two Mes^* aryl signals in addition to two o -Me resonances. No change is observed in the NMR spectra over the temperature range of 20°C to 100°C . The molecular geometry of **4a** was determined by X-ray crystallographic analysis (Figure 1).^[15]

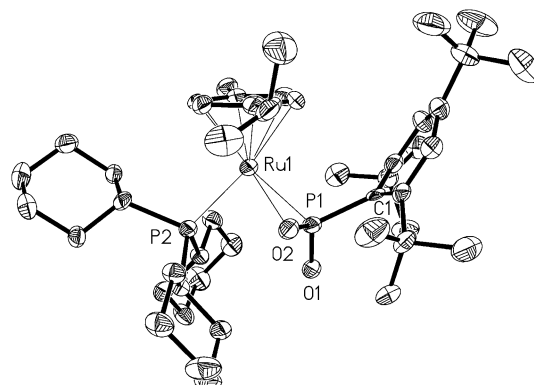


Figure 1. Molecular structure of **4a** (50% thermal ellipsoids; hydrogen atoms and noncoordinated ether molecules are omitted for clarity). Selected bond lengths (Å) and angles ($^\circ$): Ru1-O2 2.130(4), Ru1-P1 2.2963(17), Ru1-P2 2.3830(17), P1-O1 1.491(5), P1-O2 1.569(4), P1-Ru1-P2 89.91(6), P2-Ru1-O2 87.09(11), O1-P1-O2 120.1(2), O1-P1-C1 115.2(3), O2-P1-C1 104.2(3).

The environment around the ruthenium center can be considered as a two-legged piano stool with a P=O bond occupying one of the coordination sites. Complex **4a** features a side-on η^2 -coordinated metaphosphonate, which is unprecedented (Figure 1). The metal-coordinated P(1)-O(2) bond (1.569(4) Å) is longer than the P(1)=O(1) double bond (1.491(5) Å) which is similar to that found in phosphinidene oxide complexes.^[16] However, P(1)-O(2) bond is still shorter than a single P-O bond (≈ 1.63 Å) and indicates significant residual double-bond character. The lengthening of the P=O bond and the planarity of the p -cymene ligand (deviations out the plane from 0.001 to 0.005 Å) in **4** are strong signs of substantial $\text{Ru}(\text{d}\pi)$ to $\text{P=O}(\pi^*)$ back-donation.^[17,18] This bonding mode induces pyramidalization at the P atom with a sum of bond angles of 339° and loss of the planarity for metaphosphonate as observed upon coordination of olefin^[19] or of related bis(imino)- and amino(imino) thiophosphorane^[20] toward a transition metal. Interestingly, the acute P(2)-Ru-A angle (A is the projection of the metal Ru on the P(1)-O(2) bond, $\text{O(2)-A} = 0.551$ Å) of 88.02° does not vary significantly than P-M-P ($\text{M} = \text{Ru}, \text{Os}$) angle in related terminal phosphinidene complexes,^[8] despite the increased steric congestion between the Mes^* group and p -cymene ligand. This unexpected arrangement has its origin in orbital factors. Ab initio calculations performed on monomeric dioxophosphorane have shown that OPO moiety may be described as a four-electron, three-center π system, in which HOMO is mainly localized at the oxygen positions while the LUMO corresponds to $\text{P=O}(\pi^*)$ antibonding orbitals.^[21] Examination of the bonding situation for the metaphosphonate ligand in **4** by using the Dewar–Chatt–Duncanson model

(by analogy with olefin complexes) provides pertinent information. Both donation and back-donation involving the metaphosphonate ligand implicate orbitals that are perpendicular to the plane of the free dioxophosphorane and impose such a face-on orientation for the Mes* group.

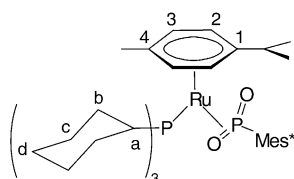
In conclusion, the accessibility of monomeric metaphosphonate relies on its complexation to electron-rich species which reduce electrophilicity. Complexes **4**, in which dioxophosphorane Mes*PO₂ has been generated and stabilized within the coordination sphere of a transition metal, represent the first direct observation of fully characterized monomeric metaphosphonate.

Experimental Section

3a: DBU (0.29 mL; 1.97 mmol) was added to a red slurry of [(η⁶-p-cymene)(PCy₃)RuCl₂] (0.602 g; 1.03 mmol) and Mes*PH₂ (0.274 g; 0.98 mmol) in toluene (10 mL). The mixture was stirred for 1 h at room temperature to afford a dark green solution. The toluene was removed in vacuo and the dark green solid then extracted with pentane (10 mL) and filtered to remove DBU·HCl. Removal of the pentane to a minimal volume and cooling to −25 °C gave 0.780 g of a crystalline solid in 80 % yield.^[10]

4a: A cold (0 °C) ether solution of **3a** (0.166 g; 0.21 mmol) was bubbled with oxygen for 1 min. Removal of the ether to a minimal volume and cooling to −25 °C gave 0.150 g of a yellow crystalline solid in 87 % yield. m.p.: 176 °C.

Atom labeling used in the NMR assignments of **4a** is given below.



³¹P NMR (81 MHz, C₆D₆): δ = 27.1 (d, ²J(P,P) = 45.8 Hz, PCy₃), 40.8 ppm (d, ²J(P,P) = 45.8 Hz, PO₂Mes*). ¹H NMR (200 MHz, C₆D₆): δ = 1.05 (d, ³J(H,H) = 6.8 Hz, 3H, CH(CH₃)₂ p-cymene), 1.20 (d, ³J(H,H) = 6.6 Hz, 3H, CH(CH₃)₂ p-cymene), 1.29 (m, 12H, C₆H₂), 1.41 (s, 9H, p-C(CH₃)₃), 1.56 (m, 6H, C₆H₂), 1.81 (s, 3H, CH₃ p-cymene), 1.88 (s, 9H, o-C(CH₃)₃), 1.91 (m, 12H, C₆H₂), 2.14 (s, 9H, o-C(CH₃)₃), 2.53 (m, 4H, C₆H and CH(CH₃)₂ p-cymene), 2.95 (s, 1H, C₂H p-cymene), 4.17 (s, 1H, C₃H p-cymene), 5.40 (s, 2H, C₂H and C₃H p-cymene), 7.43 (s, 1H, m-Mes*), 7.55 ppm (s, 1H, m-Mes*). ¹³C{¹H} NMR (50 MHz, C₆D₆): δ = 19.1 (s, CH₃ p-cymene), 20.5 (s, CH(CH₃)₂ p-cymene), 25.3 (s, CH(CH₃)₂ p-cymene), 27.3 (s, C₄), 28.4 (d, ³J(C,P) = 10.2 Hz, C₆), 30.6 (d, ²J(C,P) = 33.3 Hz, C₆), 31.1 (s, CH(CH₃)₂ p-cymene), 31.6 (s, p-C(CH₃)₃), 33.7 (s, o-C(CH₃)₃), 33.8 (s, o-C(CH₃)₃), 34.9 (s, p-C(CH₃)₃), 37.3 (d, ³J(C,P) = 8.3 Hz, C₄), 39.8 (d, ³J(C,P) = 2.8 Hz, o-C(CH₃)₃), 40.7 (d, ³J(C,P) = 2.8 Hz, o-C(CH₃)₃), 73.7 (s, C₄ p-cymene), 75.2 (d, ²J(C,P) = 11.1 Hz, C₂ p-cymene), 84.6 (d, ²J(C,P) = 9.2 Hz, C₂ p-cymene), 86.3 (s, C₃ p-cymene), 93.9 (s, C₃ p-cymene), 99.4 (s, C₁ p-cymene), 119.1 (d, ³J(C,P) = 12.9 Hz, m-Mes*), 121.7 (d, ³J(C,P) = 10.2 Hz, m-Mes*), 137.9 (d, ¹J(C,P) = 65.7 Hz, ipso-Mes*), 147.7 (d, ⁴J(C,P) = 3.7 Hz, p-Mes*), 153.6 (s, o-Mes*), 153.9 ppm (s, o-Mes*); IR (nujol): 1168, 907 cm^{−1} (asym and sym OPO); elemental analysis (%) calcd. for **4a**·2Et₂O C₅₄H₉₆O₄P₂Ru: C 66.70, H 9.95; found: C 66.33, H 9.46.

The derivatives **3b** and **4b** were prepared by an analogous method.^[10]

Keywords: coordination modes · P ligands · phosphanes · pi interactions · ruthenium

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