Phosphorus Coordination Chemistry

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

Richard Menye-Biyogo, Fabien Delpech, Annie Castel, Heinz Gornitzka, and Pierre Rivière**

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 PO_2 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 ^{31}P 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 coworkers, the terminal phosphinidene ruthenium complexes [(η^6-*p*-cymene)Ru(PR_3)(PMes*)] (**3a**: R = Cy, **3b**: R = Ph[8]) are formed as dark green solids by the reaction of the primary phosphane complex [(η^6-*p*-cymene)$RuCl_2$(PH_2Mes*)](**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 PR_3 as a stabilizing ligand (R = Ph, Cy).[8] Alternatively, treatment of [(η^6-*p*-cymene)$RuCl_2$(PR_3)] (**2a**: R = Cy, **2b**: R = Ph) and PH_2Mes* with DBU affords **3** in high yields (Scheme 1).

[*] Dr. F. Delpech, P. Rivière, R. Menye-Biyogo, Dr. A. Castel, Dr. H. Gornitzka
Laboratoire d'Hétérochimie Fondamentale et Appliquée, UMR 5069
Université Paul Sabatier
118, Route de Narbonne, 31062 Toulouse Cédex 04 (France)
Fax: (+33) 5–6155–8204
E-mail: delpech@chimie.ups-tlse.fr
riviere@chimie.ups-tlse.fr

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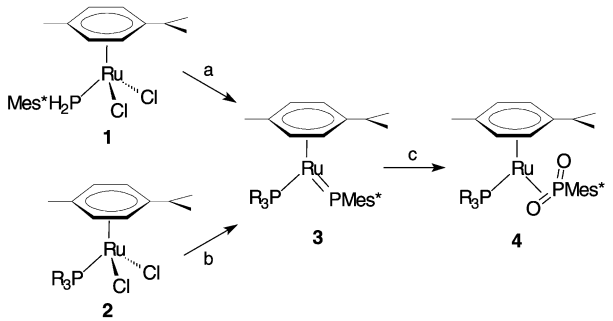


Scheme 1. Synthesis of the complexes **3, 4**: a) PR_3, DBU, C_7H_8; b) PH_2Mes^*, DBU, C_7H_8; c) O_2, Et_2O.

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 [(η^6-*p*-cymene)(PPh_3)Os(PMes*)] and [(η^6-benzene)(PPh_3)Ru(PMes*)].[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 σ^2-λ^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 [(η^6-*p*-cymene)(PR_3)Ru(η^2-OPOMes*)] (**4a**: R = Cy, **4b**: R = 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 P–C(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]

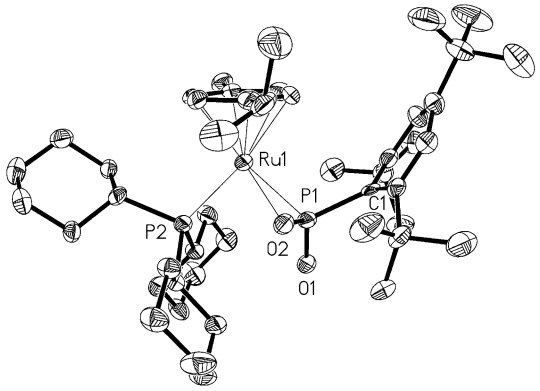


Figure 1. Molecular structure of **4a** (50% thermal ellipsoids; hydrogen atoms and noncoordinated ether molecules are omitted for clarity). Selected bond lengths (Å) and angles (°): Ru1-O2 2.130(4), Ru1-P1 2.2963(17), Ru1-P2 2.3830(17), P1-O1 1.491(5), P1-O2 1.569(4), P1-Ru1-P2 89.91(6), P2-Ru1-O2 87.09(11), 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 ($\approx$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 Ru (dπ) to P=O (π*) 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, O(2)–A = 0.551 Å) of 88.02 ° does not vary significantly than P-M-P (M = Ru, 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 P = O (π*) 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.

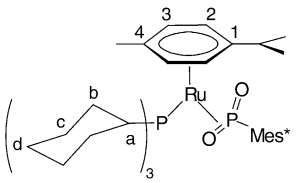
In conclusion, the accessibility of monomeric metaphosphonate relies on its complexation to electron-rich species which reduce electrophilicity. Complexes **4**, in which dioxophosphorane Mes*PO_2 has been generated and stabilized within the coordination sphere of a transition metal, represent the first direct observation of fully characterized monomeric metaphosphonate.

Experimental Section

3a: DBU (0.29 mL; 1.97 mmol) was added to a red slurry of [(η^6-*p*-cymene)(PCy_3)$RuCl_2$] (0.602 g; 1.03 mmol) and Mes*PH_2 (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.



^{31}P NMR (81 MHz, C_6D_6): $\delta = 27.1$ (d, ^2J(P,P) = 45.8 Hz, PCy_3), 40.8 ppm (d, ^2J(P,P) = 45.8 Hz, PO_2Mes*). ^{1}H NMR (200 MHz, C_6D_6): $\delta = 1.05$ (d, ^3J(H,H) = 6.8 Hz, 3H, CH(CH_3)$_2$ *p*-cymene), 1.20 (d, ^3J(H,H) = 6.6 Hz, 3H, CH(CH_3)$_2$ *p*-cymene), 1.29 (m, 12H, C_cH_2), 1.41 (s, 9H, *p*-C(CH_3)$_3$), 1.56 (m, 6H, C_dH_2), 1.81 (s, 3H, CH_3 *p*-cymene), 1.88 (s, 9H, *o*-C(CH_3)$_3$), 1.91 (m, 12H, C_bH_2), 2.14 (s, 9H, *o*-C(CH_3)$_3$), 2.53 (m, 4H, C_aH and $CH(CH_3)_2$ *p*-cymene), 2.95 (s, 1H, C_2H *p*-cymene), 4.17 (s, 1H, C_3H *p*-cymene), 5.40 (s, 2H, C_2H and C_3H *p*-cymene), 7.43 (s, 1H, *m*-Mes*), 7.55 ppm (s, 1H, *m*-Mes*). ^{13}C{^{1}H} NMR (50 MHz, C_6D_6): $\delta = 19.1$ (s, CH_3 *p*-cymene), 20.5 (s, CH(CH_3)$_2$ *p*-cymene), 25.3 (s, CH(CH_3)$_2$ *p*-cymene), 27.3 (s, C_d), 28.4 (d, ^3J(C,P) = 10.2 Hz, C_c), 30.6 (d, ^2J(C,P) = 33.3 Hz, C_b), 31.1 (s, CH(CH_3)$_2$ *p*-cymene), 31.6 (s, *p*-C(CH_3)$_3$), 33.7 (s, *o*-C(CH_3)$_3$), 33.8 (s, *o*-C(CH_3)$_3$), 34.9 (s, *p*-C(CH_3)$_3$), 37.3 (d, ^3J(C,P) = 8.3 Hz, C_a), 39.8 (d, ^3J(C,P) = 2.8 Hz, *o*-C(CH_3)$_3$), 40.7 (d, ^3J(C,P) = 2.8 Hz, *o*-C(CH_3)$_3$), 73.7 (s, C_4 *p*-cymene), 75.2 (d, ^2J(C,P) = 11.1 Hz, C_2 *p*-cymene), 84.6 (d, ^2J(C,P) = 9.2 Hz, C_2 *p*-cymene), 86.3 (s, C_3 *p*-cymene), 93.9 (s, C_3 *p*-cymene), 99.4 (s, C_1 *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**·2Et_2O $C_{54}H_{96}O_4P_2Ru$: 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]

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[15] CCDC 213806 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk). Information about crystal data and structure measurements and refinements are summarized in the Supporting Information.

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