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(Arene)ruthenium(II) Complexes Containing the Monophosphine $RP(CH_2CO_2Me)_2$ or the Deprotonated Unsymmetrical Dianion $[RP(\mathit{C}HCO_2Me)(CH{=}C(OMe)\mathit{O})]^{2-}$ as a Tripodal Chelating Ligand

Jürgen Bank, Olaf Gevert, Werner Wolfsberger, and Helmut Werner*

Institut für Anorganische Chemie der Universität Würzburg,
Am Hubland, D-97074 Würzburg, Germany

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Summary: Reaction of the dichloro compounds $[(mes)RuCl_2\{\eta^1(P)\text{-}RP(CH_2CO_2Me)_2\}]$ *(R = iPr (**3a**), tBu (**3b**); mes = mesitylene =* $C_6H_3Me_3$*-2,4,6) with 2 equiv of* $AgPF_6$ *affords the dicationic P,O,O′-chelated complexes* $[(mes)Ru\{\eta^3(P,O,O')\text{-}RP(CH_2C(OMe){=}O)_2\}](PF_6)_2$ *(**4a,b**) which in* CH_2Cl_2*, in the presence of water, undergo partial hydrolysis to give* $[(mes)Ru\{\eta^2(P,O)\text{-}RP(CH_2C(OMe){=}O)(CH_2CO_2Me)\}\{\eta^1(O)\text{-}O_2PF_2\}]PF_6$ *(**5a,b**). Compounds **4a,b** react with 2 equiv of KOtBu in tBuOH to yield the neutral complexes* $[(mes)Ru\{\eta^3(P,C,O)\text{-}RP(CHCO_2Me)(CH{=}C(OMe)O)\}]$ *(**6a,b**) containing both a five-membered phosphino enolate and a three-membered phosphinomethanide ring. A derivative, **7**, of the novel tripodal chelating system is formed by insertion of PhNCO into the C—H bond of the phosphino enolate unit of **6b**.*

The chemistry of bifunctional phosphines of general composition $R_2P(CH_2)_nY$ and their transition-metal complexes has been an area of active research in recent years.[1] In particular for compounds where Y is OMe, C(=O)R′, or C(=O)OR′, the oxygen donors temporarily are able to protect a vacant coordination site and thus allow the addition of better donor ligands to the metal center under fairly mild conditions. Moreover, with β-phosphino ketones or esters as starting materials, a number of O-metalated (phosphino enolate)metal compounds have been prepared and found to be useful starting materials for C—C coupling reactions with activated alkynes and isocyanates,[2] for the generation of metal acetylides from 1-alkynes,[3] and for reversibly binding carbon dioxide.[4]

In a continuation of our work on the reactivity of phosphino esters $R_2PCH_2CO_2R'$ toward d^6 and d^8 metal centers,[5] we have recently developed a synthetic route to the *trifunctional* phosphines $RP(CH_2CO_2R')_2$ and started to investigate their coordination capabilities.[6] Here we describe the synthesis of (mesitylene)ruthenium(II) complexes containing the potentially tridentate monophosphine $RP(CH_2CO_2Me)_2$ and the remarkable conversion of this molecule to a novel unsymmetrical $\eta^3(P,C,O)$-bonded tripod-type ligand. A first example of isocyanate insertion into one of the C—H bonds of the dianionic ligand will also be reported.

The phosphines **2a,b**, which were prepared according to a recently published method by heating $RP(SiMe_3)_2$ (R = *i*Pr, *t*Bu) with 2 equiv of $ClCH_2CO_2Me$ in benzene,[7] readily react with the dimeric starting material **1** in dichloromethane to afford the mononuclear air-stable dichlororuthenium(II) complexes **3a,b**.[8] Treatment of **3a,b** with 2 equiv of $AgPF_6$ results in the abstraction of both chlorides to yield the dicationic derivatives **4a,b**, in which the intact phosphine behaves as a tridentate bis-chelating ligand.[9] The structural proposal shown in Scheme 1 is supported by the spectroscopic data as well as by conductivity measurements.[9] Since there is only one carbonyl stretching frequency at 1621 cm^{-1} (**4a**) and 1609 cm^{-1} (**4b**) which is lowered by about 110 cm^{-1} compared with the frequency for the monodentate phosphine in **3a,b**, the IR spectra in particular leave no doubt that both ester units are linked to the metal center.

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(8) (a) By the procedure described for $[(mes)RuCl_2(PMe_2Ph)]$,[8b] compounds **3a,b** were isolated as red-brown air-stable solids in 90–95% yield. (b) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233–241.

(9) The preparation of **4a** is as follows. A solution of **3a** (243 mg, 0.47 mmol) in 20 mL of CH_2Cl_2 was treated with $AgPF_6$ (240 mg, 0.95 mmol) and stirred for 30 min at room temperature. The solvent was removed, the residue was extracted with 20 mL of acetone, and the extract was brought to dryness in vacuo. An orange solid was obtained, which was repeatedly washed with small amounts of THF and dried: yield 271 mg (78%); mp 157 °C dec; conductivity (in CH_3NO_2) $\Lambda = 108$ $cm^2\ \Omega^{-1}\ mol^{-1}$. Anal. Calcd for $C_{18}H_{29}F_{12}O_4P_3Ru$: C, 29.56; H, 4.00. Found: C, 29.69; H, 4.25. Compound **4b** was prepared analogously: orange solid; yield 80%; mp 167 °C dec; $\Lambda = 116$ $cm^2\ \Omega^{-1}\ mol^{-1}$. Anal. Calcd for $C_{19}H_{31}F_{12}O_4P_3Ru$: C, 30.61; H, 4.19. Found: C, 30.49; H, 4.06.

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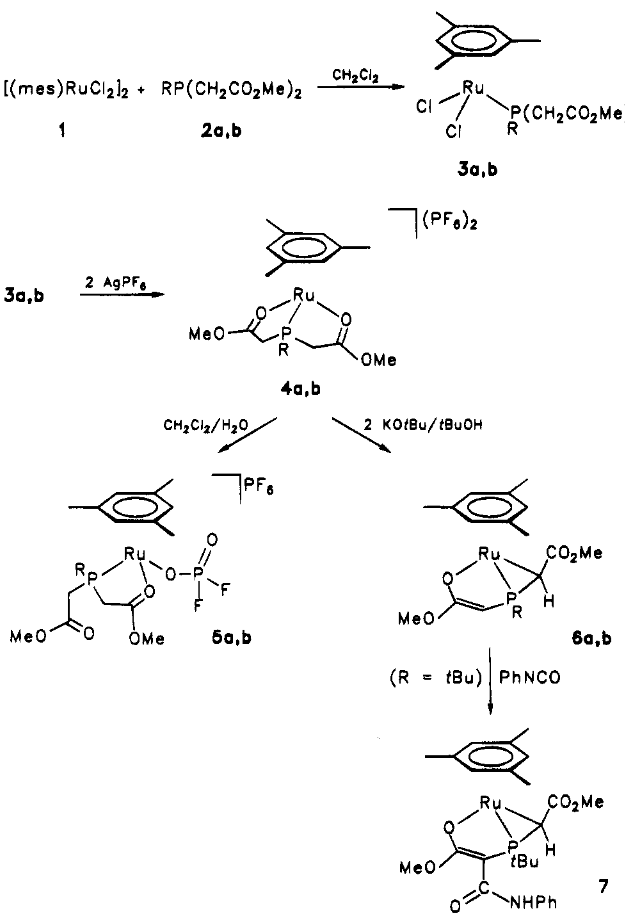
Scheme 1[a]



[a] R = *i*Pr (**a**), *t*Bu (**b**).

In polar solvents such as dichloromethane, in the presence of small amounts of water, partial hydrolysis of the hexafluorophosphate anion of **4a,b** occurs leading to the monocationic (difluorophosphinato)ruthenium(II) complexes **5a,b** in almost quantitative yield.[10] Such a transition-metal-mediated conversion of PF_6^- to $PO_2F_2^-$ is not without precedent[11] and with (arene)ruthenium compounds has been observed in the formation of $[(C_6Me_6Ru)_2(\mu\text{-}O_2PF_2)_3]PF_6$ from $[(C_6Me_6)Ru(acetone)_3](PF_6)_2$.[12] The X-ray structural analysis of **5b** reveals[13] that the phosphino diester is bonded to ruthenium in a $\eta^2(P,O)$ mode, forming one five-membered chelate ring and leaving one CH_2CO_2Me group uncoordinated.

Compounds **4a,b** react with 2 equiv of KO*t*Bu in 2-methyl-2-propanol to give the very moisture-sensitive neutral complexes **6a,b** in good yields.[14] Quite unexpectedly, the two $PCHCO_2Me$ units in **6a,b** are not equally bonded to the metal center, which is illustrated by the IR and NMR spectroscopic data. While one chelating moiety forms a five-membered phosphino enolate ring resulting from O-metalation of one $PCHCO_2Me$ unit, the other one constitutes a three-membered phosphinomethanide fragment which is the C-metalation product. We note that complexes with a Ru$\{\eta^2(P,C)\text{-}Me_2PCH_2\}$ moiety but without an arene ligand are well-known[15] and have recently been used for the synthesis of monomeric hydroxo, phenolato, and amido ruthenium derivatives.[16]

The structure of **6a** has been confirmed by an X-ray crystal structure analysis (Figure 1).[17] The five-membered (phosphino enolate)metal unit is nearly planar, with the OCH_3 substituent lying in the ring plane. The electron delocalization within the enolate ring is indicated by the short distances P–C2 and C1–C2 and by the C1–O1 bond length, which is between a C–O single and a C=O double bond. The interatomic bond distances and angles of the three-membered phosphinomethanide–ruthenium fragment are comparable

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(10) The preparation of **5a** was analogous to that described for **4a**, but the reaction mixture was stirred for 12 h at room temperature. Trace amounts of water were introduced from either CH_2Cl_2 or the glass surface. After recrystallization from CH_2Cl_2/OEt_2 (1:5), orange-red crystals were isolated: yield 90%; mp 168 °C dec; $\Lambda = 84\ cm^2\ \Omega^{-1}\ mol^{-1}$. Anal. Calcd for $C_{18}H_{29}F_8O_6P_3Ru$: C, 31.45; H, 4.25. Found: C, 31.37; H, 4.27. IR (CH_2Cl_2): $\nu(C{=}O)_{uncoord}$ 1721, $\nu(C{=}O)_{coord}$ 1609 cm^{-1}. ^{31}P NMR (81.0 MHz, d_6-acetone): δ 50.0 (d, $J(PP) = 4.4$ Hz, iPr$P(CH_2CO_2Me)_2$, −12.7 (ddd, $J(PF) = 970.7$ and 957.6, $J(PP) = 4.4$ Hz, PO_2F_2), −142.7 (sept, $J(PF) = 707.7$ Hz, PF_6^-). Compound **5b** was prepared analogously: orange-red solid; yield 91%; mp 166 °C dec; $\Lambda = 82\ cm^2\ \Omega^{-1}\ mol^{-1}$. Anal. Calcd for $C_{19}H_{31}F_8O_6P_3Ru$: C, 32.53; H, 4.45; Ru, 14.41. Found: C, 32.85; H, 4.46; Ru, 14.77. IR (KBr): $\nu(C{=}O)_{uncoord}$ 1722, $\nu(C{=}O)_{coord}$ 1609 cm^{-1}. ^{31}P NMR (81.0 MHz, d_6-acetone): δ 52.7 (d, $J(PP) = 2.9$ Hz, tBu$P(CH_2CO_2Me)_2$), −13.1 (ddd, $J(PF) = 972.5$ and 963.6, $J(PP) = 2.9$ Hz, PO_2F_2), −142.7 (sept, $J(PF) = 707.7$ Hz, PF_6^-).

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(14) The preparation of **6a** is as follows. A suspension of **4a** (216 mg, 0.30 mmol) in 15 mL of toluene/*t*BuOH (1:1) was treated with KO*t*Bu (66 mg, 0.60 mmol) and irradiated for 15 min at room temperature in an ultrasonic bath. The solvent was removed, the residue was extracted with 15 mL of diethyl ether, and the extract was brought to dryness in vacuo. A yellow oily material was obtained, which was suspended in 20 mL of hexane and stirred for 12 h at room temperature. A yellow solid was formed, which was repeatedly washed with hexane and dried: yield 78 mg (60%); mp 93 °C dec; MS (70 eV) m/z 439 (M^+). Anal. Calcd for $C_{18}H_{27}O_4PRu$: C, 49.20; H, 6.19. Found: C, 49.23; H, 6.09. IR (C_6H_6): $\nu(OCO)_{ester}$ and $\nu(OCO)_{enolate}$ 1661 cm^{-1} (br). Compound **6b** was prepared analogously: yellow solid; yield 65%; mp 99 °C dec; MS (70 eV) m/z 453 (M^+). Anal. Calcd for $C_{19}H_{29}O_4PRu$: C, 50.32; H, 6.45. Found: C, 49.99; H, 6.37. IR (C_6H_6): $\nu(OCO)_{ester}$ 1687, $\nu(OCO)_{enolate}$ 1646 cm^{-1}. Selected NMR spectroscopic data: **6a**, ^1H NMR (400 MHz, C_6D_6) δ 3.45 (d, $J(PH) = 12.9$ Hz, C*H* of phosphino enolate), 1.67 (s, C*H* of phosphinomethanide), ^{13}C NMR (100.6 MHz, C_6D_6) δ 44.61 (d, $J(PC) = 74.6$ Hz, *C*H of phosphino enolate), 4.90 (d, $J(PC) = 9.8$ Hz, *C*H of phosphinomethanide); **6b**, ^1H NMR (400 MHz, C_6D_6) δ 3.55 (d, $J(PH) = 11.2$ Hz, C*H* of phosphino enolate), 1.69 (d, $J(PH) = 15.3$ Hz, C*H* of phosphinomethanide), ^{13}C NMR (100.6 MHz, d_6-acetone) δ 43.98 (d, $J(PC) = 72.8$ Hz, *C*H of phosphino enolate), −8.72 (d, $J(PC) = 3.3$ Hz, *C*H of phosphinomethanide).

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(17) (a) Crystals were obtained from toluene. Crystal data (from 23 reflections, $10° < \Theta < 16°$): triclinic, space group $P\bar{1}$ (No. 2), $a = 7.913(8)$ Å, $b = 10.195(11)$ Å, $c = 13.48(2)$ Å, $\alpha = 99.47(7)°$, $\beta = 103.91(7)°$, $\gamma = 111.92(5)°$, $V = 939(2)$ Å^3, $Z = 2$, $D_{calcd} = 1.554\ g\ cm^{-3}$, $\mu(Mo\ K\alpha) = 9.25\ cm^{-1}$; crystal size 0.15 × 0.20 × 0.30 mm. Solution details: Enraf-Nonius CAD4 diffractometer, Mo Kα radiation (0.709 30 Å), graphite monochromator, zirconium filter (factor 15.4), $T = 293$ K, ω scan, maximum $2\Theta = 53°$, 3456 reflections measured, 3181 independent, 3181 used for refinement (2784 with $I > 2\sigma(I)$); intensity data corrected for Lorentz and polarization effects; structure solved by direct methods (SHELXS-86);[17b] atomic coordinates and anisotropic thermal parameters refined by full-matrix least squares on F_o^2 (SHELXL-93);[17c] positions of the hydrogen atoms calculated according to ideal geometry and used only in structure factor calculation; $R = 0.028$, $R_w = 0.0681$ for 2784 reflections with $I > 2\sigma(I)$, $R = 0.041$, $R_w = 0.077$ for all 3181 data reflections; reflection/parameter ratio 14.2; residual electron density +0.487/−0.562 e Å^{-3}. (b) Sheldrick, G. M. SHELXS-86; Universität Göttingen, Göttingen, Germany, 1986. (c) Sheldrick, G. M. SHELXL-93; Universität Göttingen, Göttingen, Germany, 1993.

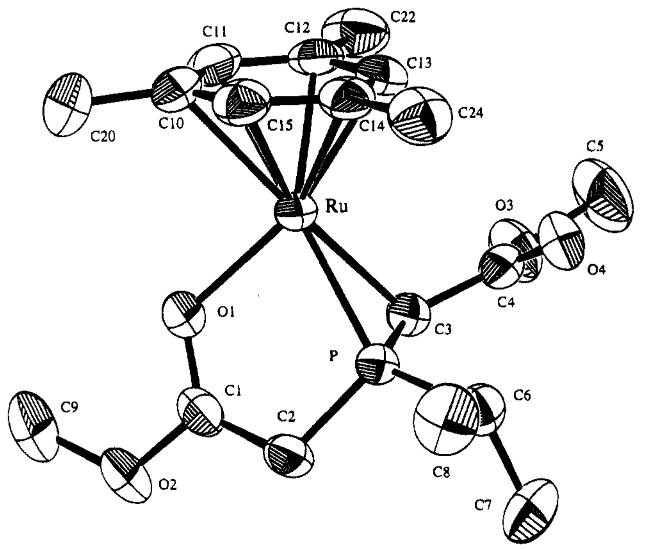

Figure 1. ORTEP diagram of compound **6a** (hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Ru–O1, 2.053(3); Ru–C3, 2.217(4); Ru–P, 2.301(2); O1–C1 1.295(5); C1–O2, 1.323(4); C1–C2, 1.394(5); P–C2, 1.671(4); P–C3, 1.727(4); P–C6, 1.884(4); C3–C4, 1.374(5); O1–Ru–C3, 88.03(14); O1–Ru–P, 80.65(11); C3–Ru–P, 44.91(11); Ru–O1–C1, 116.7(2); Ru–P–C2, 104.2(2); Ru–P–C3, 64.98(13); Ru–P–C6, 138.25(14); Ru–C3–C4, 111.3(3); Ru–C3–P, 70.11(13); O1–C1–C2, 127.7(3); O2–C1–C2, 118.0(3); O1–C1–O2, 114.2(3); C1–C2–P, 110.5(3); C2–P–C3, 106.1(2); C2–P–C6, 112.5(2); C3–P–C6, 119.8(2); P–C3–C4, 118.0(3).

to those found in [Mn(CO)$_4${η^2(*P*,*C*)-Ph$_2$PCH$_2$}],[18a] [C$_5$H$_5$-Mo(CO)$_2${η^2(*P*,*C*)-Ph$_2$PCH$_2$}],[18b] and [(mes)OsCl{η^2(*P*,*C*)-*i*Pr$_2$PCHCO$_2$Me}].[18c]

Preliminary studies on the reactivity of **6a,b** indicate that the novel P,C,O-coordinated tripodal ligand can be transformed into substituted derivatives. Thus, on treatment of **6b** with PhNCO, compound **7** is formed by insertion of the isocyanate into the C–H bond of the phosphino enolate ring.[19,20] Even in the presence of excess PhNCO, no further insertion into the C–H bond of the phosphinomethanide unit and also no enlargement of the RuPC three-membered ring takes place. Work in progress is mainly aimed at further substituting the coordinated P,C,O-tripodal ligand and converting the dianionic unit of **6a,b** or **7** into a tri- or tetrafunctional chiral phosphine.

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Supporting Information Available: Tables of crystallographic data, data collection, and solution and refinement details, positional and thermal parameters, and bond distances and angles for **6a** (6 pages). Ordering information is given on any current masthead page.

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[19] The preparation of **7** is as follows. A solution of **6b** (63 mg, 0.14 mmol) in 10 mL of toluene was treated with PhNCO (33 mg, 0.28 mmol) and stirred for 2 h at room temperature. The solvent was removed and the residue was repeatedly washed with hexane and dried: yield 56 mg (70%); mp 124 °C dec; MS (70 eV) *m/z* 572 (M$^+$). Anal. Calcd for C$_{26}$H$_{34}$NO$_5$PRu: C, 54.54; H, 5.99; N, 2.45. Found: C, 53.96; H, 5.77; N, 2.89. IR (CH$_2$Cl$_2$): ν(NH) 3380, ν(OCO)$_{\text{ester}}$ 1679, ν(OCO)$_{\text{enolate}}$ 1628 cm^{-1}. Selected NMR spectroscopic data: ^{1}H (400 MHz, CDCl$_3$) δ 9.10 (s, N*H*), 1.76 (d, *J*(PH) = 14.8 Hz, C*H* of phosphinomethanide); ^{13}C NMR (100.6 MHz, C$_6$D$_6$) δ 176.15 (d, *J*(PC) = 28.0 Hz, O*C*OMe), 173.94 (s, *C*═O), 165.48 (d, *J*(PC) = 4.9 Hz, *C*O$_2$-Me), 69.30 (d, *J*(PC) = 67.0 Hz, P*C*═C), –3.52 (d, *J*(PC) = 2.8 Hz, P*C*H).

[20] A few other examples of PhNCO insertion reactions into C–H bonds have been described by Braunstein et al.[2a,c]