

## Carbyne(dichloro) and Carbyne(dichloro)hydrido Osmium Complexes from Alkyne Precursors

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The dichloro(dihydrido)osmium(IV) and dichloroosmium(II) compounds **4** and **5**, which contain the hemilabile chelating phosphinoester  $\text{Pr}_2\text{PCH}_2\text{CO}_2\text{Me}$  **2** as ligand, react with alkynols  $\text{HC}\equiv\text{CPh(R)OH}$  ( $\text{R} = \text{Me, Ph}$ ) to give the octahedral carbynedichloroosmium(II) complexes **7** and **8**; the related starting material **6** with  $\text{Pr}_2\text{PCH}_2\text{CH}_2\text{NMe}_2$  **3** as ligand on treatment with  $\text{HC}\equiv\text{CPh}_2\text{OH}$  yields a carbyne(dichloro)hydrido compound, and with  $\text{HC}\equiv\text{CPh}$  a vinylidene osmium(II) derivative.

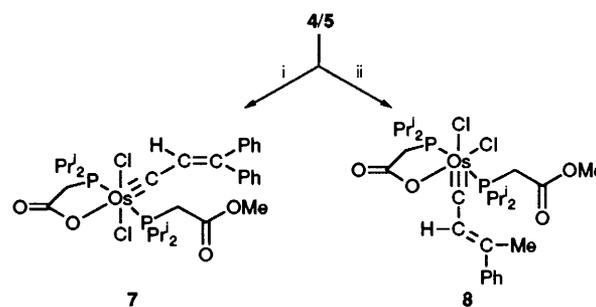
The successful generation of vinylidene and allenylidene ruthenium(II) complexes  $[\text{RuCl}_2(=\text{C}=\text{CHR})\text{L}_2]$  **1** and  $[\text{RuCl}_2(=\text{C}=\text{C}=\text{CRR}')\text{L}_2]$  **2** [ $\text{L} = \text{Pr}_2\text{PCH}_2\text{CH}_2\text{OMe}$ ,  $\text{Pr}_2\text{PCH}_2\text{CO}_2\text{R}$ ,  $\text{Pr}_2\text{PCH}_2\text{C}(\text{O})\text{Me}$ ] from  $[\text{RuCl}_2\text{L}_2]$  and terminal alkynes have prompted us to find out whether analogous osmium compounds are accessible *via* a similar route. In this communication we describe that whereas the reactions of the respective starting materials **4**, **5** and **6** with  $\text{HC}\equiv\text{CPh}$  follow a similar course as those of their ruthenium counterparts, the behaviour of **4**, **5** and **6** towards alkynols  $\text{HC}\equiv\text{CPh(R)OH}$  ( $\text{R} = \text{Me, Ph}$ ) is significantly different. Instead of OH-functionalized vinylidene osmium(II) derivatives, which eventually could be converted to allenylidene complexes,<sup>2,3</sup> carbyne osmium compounds are formed which, depending on the type of the hemilabile phosphine ligand, have not only a different composition but also a different coordination sphere.

The dichloro(dihydrido)complex **1**, the synthesis of which has been described previously,<sup>4</sup> reacts with 3 equiv. of the phosphinoester **2** in hexane at room temperature to give the moderately air-sensitive substitution product **4**.<sup>†</sup> Temperature-dependent NMR measurements reveal that this compound is fluxional in solution on the NMR timescale. If the reaction of **1** with **2** is carried out in a sealed tube, loss of  $\text{H}_2$  occurs immediately and the bis(chelate)osmium(II) complex **5** is formed. The isomer shown in Scheme 1 is one of the five possible stereoisomers having a coordination sphere in which the phosphorus atoms are equivalent.

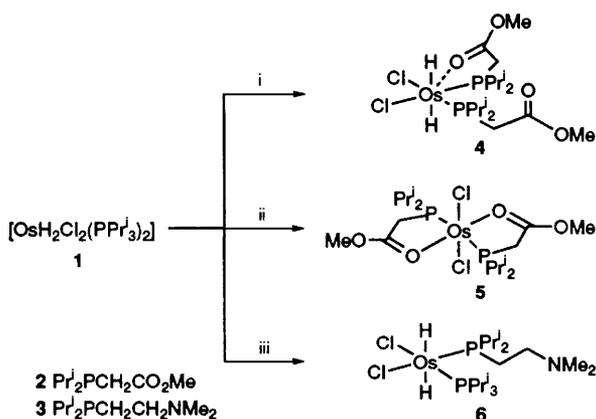
The reaction of **1** with the bulky aminophosphine **3** in benzene at 25 °C yields nearly quantitatively a pale yellow air-sensitive compound **6**, which is the result of the exchange of a single phosphine ligand. Various attempts to prepare a product with two coordinated aminophosphines **3** remained unsuccessful; they led instead to the known aminocarbene complex  $[\text{OsCl}_2\{\kappa^2(\text{C},\text{P})\text{-CHNMeCH}_2\text{CH}_2\text{PPr}_2\}]\{\kappa^2(\text{P},\text{N})\text{-Pr}_2\text{PCH}_2\text{CH}_2\text{NMe}_2\}$ .<sup>5</sup> Whereas both compounds **4** and **5** on treatment with phenylacetylene give the vinylideneosmium(II) derivative  $[\text{OsCl}_2(=\text{C}=\text{CHPh})\{\kappa(\text{P})\text{-Pr}_2\text{PCH}_2\text{CO}_2\text{Me}\}]\{\kappa^2\text{-}(\text{P},\text{O})\text{-Pr}_2\text{PCH}_2\text{C}(\text{O})\text{OMe}\}$ ,<sup>5</sup> the corresponding reactions

of **4** and **5** with alkynols  $\text{HC}\equiv\text{CPh(R)OH}$  ( $\text{R} = \text{Me, Ph}$ ) afford the new carbyne osmium(II) complexes **7** and **8** instead of vinylvinylidene or allenylidene compounds.<sup>3,6</sup> The formation of the vinylcarbyne ligand is accompanied by an ester cleavage which converts one of the phosphinoester units into a phosphinoacetate moiety (Scheme 2). A similar conversion (with elimination of  $\text{MeCl}$ ) has recently been observed on treatment of the iridium(I) complexes *trans*- $[\text{IrCl}(\text{L})\{\kappa(\text{P})\text{-Pr}_2\text{PCH}_2\text{CO}_2\text{Me}\}_2]$  ( $\text{L} = \text{CO}$ ,  $=\text{C}=\text{CHR}$ ) with basic  $\text{Al}_2\text{O}_3$ .<sup>7</sup> Although **7** and **8** have been purified by column chromatography using neutral  $\text{Al}_2\text{O}_3$ , NMR studies reveal that the ester cleavage occurs immediately after the addition of the alkynol to **4** or **5**, respectively.

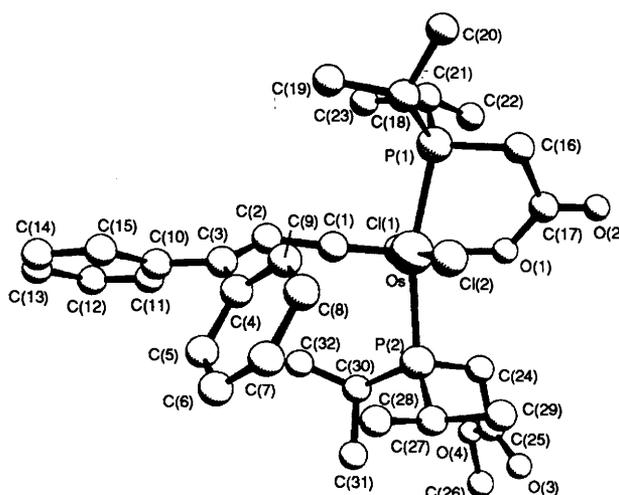
The proposed structures for compounds **7** and **8** with *trans*-disposed phosphine ligands are in accordance with IR and NMR spectroscopic data. However, the considerable differences in the chemical shifts of the  $^1\text{H}$  NMR signals of the protons of the isopropyl groups in **7** and **8** led us to assume that two different isomers with *trans*- $\text{Pr}_2\text{P}$  units are formed. The *E*-configuration at the  $\text{C}=\text{C}$  double bond of **8** was confirmed by



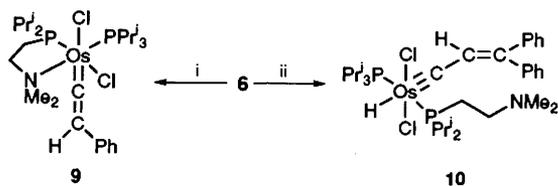
**Scheme 2** Reagents and conditions: i,  $\text{HC}\equiv\text{CPh}_2\text{OH}$  in benzene, reflux, 4 h, 18%; ii,  $\text{HC}\equiv\text{CPh}(\text{Me})\text{OH}$  (racem.) in benzene, reflux, 4 h, 23%



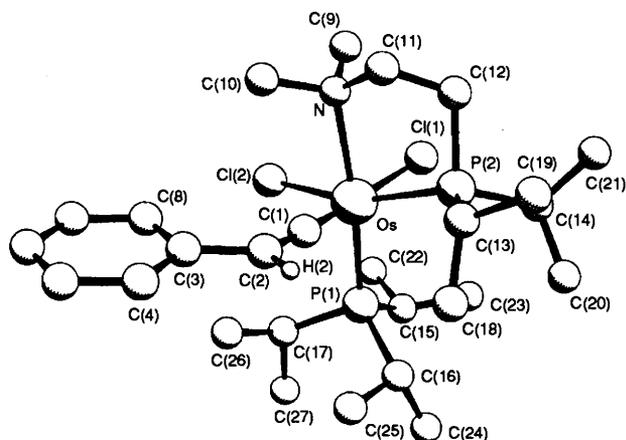
**Scheme 1** Reagents and conditions: i, **2** in hexane, 25 °C, 24 h, 72%; ii, **2** in hexane, 110 °C (sealed tube), 4 h, 90%; iii, **3** in benzene, 25 °C, 3 h, 88%



**Fig. 1** The molecular structure of compound **7**



**Scheme 3** Reagents and conditions: i,  $\text{HC}\equiv\text{CPh}$  in benzene, reflux, 3 h, 82%; ii,  $\text{HC}\equiv\text{CCPh}_2\text{OH}$  in benzene, reflux, 3 h, 11%



**Fig. 2** The molecular structure of compound **9**

NOE measurements. The X-ray structural analysis of **7**<sup>‡</sup> (Fig. 1) reveals a slightly distorted octahedral geometry [bond angles  $\text{Cl}(1)\text{--Os--Cl}(2)$   $168.7(1)^\circ$ ,  $\text{P}(1)\text{--Os--P}(2)$   $165.0(1)^\circ$ ,  $\text{C}(1)\text{--Os--O}(1)$   $173.8(4)^\circ$ ] with the carbyne ligand *trans* to the carboxylate oxygen atom. The  $\text{O}(1)\text{--Os--C}(1)$  unit is almost linear [bond angle  $\text{Os--C}(1)\text{--C}(2)$   $172.0(7)^\circ$ ], and the  $\text{Os--C}(1)$  bond length of  $1.72(1)$  Å is fully consistent with an osmium-carbon triple bond.<sup>8</sup>

Treatment of compound **6** with phenylacetylene in refluxing benzene leads to the formation of the vinylidene osmium(II) complex **9**<sup>‡</sup> (Scheme 3). This is in contrast to the similar reaction of **1** with  $\text{HC}\equiv\text{CPh}$  which gave a carbyne(hydrido) derivative.<sup>9</sup> Surprisingly, in **9** the two phosphine ligands adopt a *cis* arrangement as deduced from spectroscopic data and substantiated by X-ray structure analysis. The SCHAKAL plot (Fig. 2) reveals that the ligand geometry around the metal centre is octahedral with the phenyl ring lying in the [Os, Cl(1), Cl(2), C(1), C(2)] plane. The distances  $\text{Os--C}(1)$  [ $1.82(1)$  Å] and  $\text{C}(1)\text{--C}(2)$  [ $1.31(2)$  Å] of the nearly linear  $\text{Os=C=C}$  unit [bond angle  $\text{Os--C}(1)\text{--C}(2)$   $177(1)^\circ$ ] are almost identical to those of  $[\text{OsCl}_2(\text{C}=\text{CHPh})\{\kappa^2(\text{P},\text{O})\text{--Pr}_i_2\text{PCH}_2\text{C}(\text{O})\text{OMe}\}]$ .<sup>5</sup>

Compound **6**, like the related dichloro(dihydrido)-osmium(IV) derivative **4**, reacts with the alkynol  $\text{HC}\equiv\text{CCPh}_2\text{OH}$  to yield a vinylcarbyne complex **10**, the composition of which, however, is different from those of the other osmium carbynes **7** and **8**. Since the coordinated aminophosphine, in contrast to the phosphinoester, remains unchanged under the reaction conditions, one hydride ligand is bonded to osmium besides the carbyne, the phosphines and the chlorides. This is confirmed by the  $^1\text{H}$  NMR spectrum in which a doublet-of-doublets at  $\delta -6.72$  is observed. Although all the

carbyne complexes **7**, **8** and **10** are obtained in only moderate yields, their formation is particularly notable insofar as they are barely accessible by other routes.

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## Footnotes

<sup>†</sup> All new compounds gave satisfactory elemental analyses. **4**: colourless crystals, mp  $80^\circ\text{C}$  (decomp.); **5**: orange crystals, mp  $69^\circ\text{C}$  (decomp.); **6**: pale yellow solid, mp  $98^\circ\text{C}$  (decomp.); **7**: dark green air-stable crystals, mp  $162^\circ\text{C}$  (decomp.); **8**: light violet crystals, mp  $131^\circ\text{C}$  (decomp.); **9**: apricot crystals, mp  $170^\circ\text{C}$  (decomp.); **10**: moss-green air-stable crystals, mp  $56^\circ\text{C}$  (decomp.).

<sup>‡</sup> Crystal data for **7**: crystals from acetone-ether;  $\text{C}_{32}\text{H}_{46}\text{Cl}_2\text{O}_4\text{OsP}_2$ ,  $M = 817.8$ ; monoclinic, space group  $P2_1/n$ ,  $a = 10.237(3)$ ,  $b = 11.277(3)$ ,  $c = 29.80(1)$  Å,  $\beta = 91.46(1)^\circ$ ,  $V = 3440(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.58$  g cm<sup>-3</sup>. A crystal of size  $0.25 \times 0.38 \times 0.38$  mm was examined by the  $\omega$ - $\theta$  scan technique using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.70930$  Å). Cell dimensions were obtained from 23 reflections ( $10 < \theta < 14^\circ$ ). 5177 unique data were obtained and 3044 of these with  $F_o > 3\sigma(F_o)$  were used in the refinement;  $R = 0.029$ ,  $R_w = 0.034$ ; reflex-parameter ratio 8.14; residual electron density  $+1.06/-0.51$  e Å<sup>-3</sup>. For **9**: crystals from benzene;  $\text{C}_{27}\text{H}_{51}\text{Cl}_2\text{P}_2\text{NO}$ ,  $M = 712.8$ ; monoclinic, space group  $P2_1/n$ ,  $a = 13.783(6)$ ,  $b = 14.458(4)$ ,  $c = 16.325(7)$  Å,  $\beta = 109.74(2)^\circ$ ,  $V = 3061(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.55$  g cm<sup>-3</sup>. A crystal of size  $0.11 \times 0.2 \times 0.42$  mm was examined by the  $\omega$ - $\theta$  scan technique as for **7**. 4230 unique data were obtained and 2995 of these with  $F_o > 3\sigma(F_o)$  were used in the refinement;  $R = 0.033$ ,  $R_w = 0.040$ ; reflex-parameter ratio 10.1; residual electron density  $+1.16/-0.49$  e Å<sup>-3</sup>. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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