Stable Osmium Hydrido−Carbene Complexes with CH_2 and Secondary Carbenes CHR as Ligands

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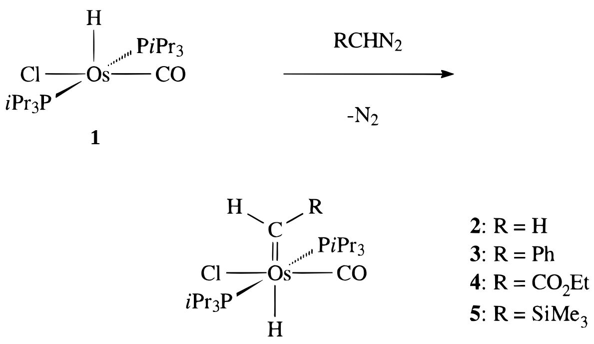
*Summary: The five-coordinate compound [OsHCl(CO)(PiPr$_3$)$_2$] (**1**) reacts with diazoalkanes RCHN$_2$ (R = H, Ph, CO$_2$Et, SiMe$_3$) at room temperature to give instead of the expected insertion product [Os(CH$_2$R)Cl(CO)(PiPr$_3$)$_2$] the isomeric osmium(II) hydrido−carbene complexes [OsHCl(=CHR)(CO)(PiPr$_3$)$_2$] (**2**−**5**) containing the hydrido and the carbene ligands in trans disposition. Treatment of **3** (R = Ph) with HCl in toluene affords the dichloro complex [OsCl$_2$(=CHPh)(CO)(PiPr$_3$)$_2$] (**6**), the molecular structure of which has been determined.*

Hydrido−carbene species are considered to be important intermediates in the reductive polymerization of CO known as the Fischer-Tropsch process.[1] A crucial step of the proposed mechanism is the migration of a metal-bonded hydrogen to a carbene fragment, leading to a metal−alkyl species. According to ab initio calculations, for the model system RuH(=CH$_2$)Cl the conversion to Ru(CH$_3$)Cl proceeds with a rather low barrier of 11.5 kcal/mol and is exothermic by 7.1 kcal/mol.[2]

In continuation of our work on the chemistry of the five-coordinate hydridoosmium(II) complex [OsHCl(CO)(P*i*Pr$_3$)$_2$] (**1**),[3] the observation that terminal alkynes HC≡CR react with **1** to give instead of the expected 1:1 adducts the vinyl derivatives [Os(CH=CHR)Cl(CO)(P*i*Pr$_3$)$_2$][4] prompted us to study also the reactivity of **1** toward CH$_2$N$_2$ and other diazoalkanes. We were interested to find out whether on this route, by insertion of the generated carbene fragment into the Os−H bond, 16-electron alkylosmium(II) compounds of the general composition [Os(CH$_2$R)Cl(CO)(P*i*Pr$_3$)$_2$] would be accessible which, in contrast to the 18-electron alkylosmium(II) complexes [OsH(CH$_2$R)(CO)$_2$(P*i*Pr$_3$)$_2$] (R = H, OMe),[5] are still unknown. Besides this reaction the formation of a formyl complex by migration of the hydride to the carbonyl ligand is also conceivable. This would be related to the behavior observed by Roper et al. for the reaction of CH$_2$N$_2$ with [OsCl(*o*Tol)(CO)(PPh$_3$)$_2$], where the aryl ligand migrates to the CO to give the η^2-acyl complex [OsCl(η^2-C(O)*o*Tol)(=CH$_2$)(PPh$_3$)$_2$].[6]

Scheme 1



The reaction of **1** with a freshly prepared solution of diazomethane in ether proceeds quite rapidly at room temperature and gives, after removal of the solvent, quantitatively a yellow solid which is analyzed as a 1:1 adduct of **1** and CH$_2$.[7] The fact that the hydrido−methylidene complex **2** (Scheme 1) and not the isomeric methyl compound [Os(CH$_3$)Cl(CO)(P*i*Pr$_3$)$_2$] is formed is clearly indicated by the ^{1}H NMR spectrum, which (in C$_6$D$_6$) displays besides the signals for the phosphine ligands a triplet of triplets for the Os−H proton at high field (−4.48 ppm) and two broadened singlets for the CH$_2$ protons at low field (17.9 and 16.9 ppm). The ^{13}C NMR spectrum of **2** exhibits resonances at 285.0 and 182.0 ppm that are assigned to the Os=CH$_2$ and OsCO carbon atoms, respectively.[8]

Substituted diazomethanes such as PhCHN$_2$, EtO$_2$CCHN$_2$, and Me$_3$SiCHN$_2$ behave similarly to CH$_2$N$_2$ and

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(7) Data for **2**: mp 95 °C dec. Anal. Calcd for C$_{20}$H$_{45}$ClOOsP$_2$: C, 40.77; H, 7.70. Found: C, 40.50; H, 8.01.

(8) Selected spectroscopic data for **2**−**5** are as follows. **2**: IR (KBr) ν(CO) 1910, ν(OsH) 1857 cm^{-1}; ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 17.9, 16.9 (both s, br, 1H each, OsCH$_2$), −4.48 (tt, J(PH) = 30, J(HH) = 2 Hz, 1H, OsH); ^{13}C NMR (100.6 MHz, C$_6$D$_6$) δ 285.0 (s, br, OsCH$_2$), 182.0 (t, J(PC) = 8 Hz, CO); ^{31}P NMR (162.0 MHz, C$_6$D$_6$) δ 56.5 (s). **3**: IR (KBr) ν(CO) 1878, ν(OsH) 1830 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 17.45 (m, 1H, OsCH), −4.50 (m, 1H, OsH); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 296.8 (s, br, OsCH), 183.4 (t, J(PC) = 8 Hz, OsCO); ^{31}P NMR (162.0 MHz, CDCl$_3$) δ 47.9 (s). **4**: IR (KBr) ν(CO) 1923, ν(OsH) 1863, ν(CO$_2$) = 1650 cm^{-1}; ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 17.22 (m, 1H, OsCH), −4.95 (dt, J(PH) = 32, J(HH) = 3 Hz, 1H, OsH); ^{13}C NMR (50.3 MHz, CDCl$_3$) δ 267.7 (s, br, OsCH), 179.3 (t, J(PC) = 9 Hz, CO); ^{31}P NMR (81.0 MHz, CDCl$_3$) δ 56.6 (s). **5**: IR (KBr) ν(CO) 1938 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 19.85 (m, 1H, OsCH), 0.16 (s, 9H, SiCH$_3$), −5.62 (dt, J(PH) = 29 Hz, J(HH) = 2 Hz, 1H, OsH); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 327.3 (s, OsCH), 182.6 (t, J(PC) = 8 Hz, OsCO), 0.5 (s, SiCH$_3$); ^{31}P NMR (162.0 MHz, CDCl$_3$) δ 56.5 (s).

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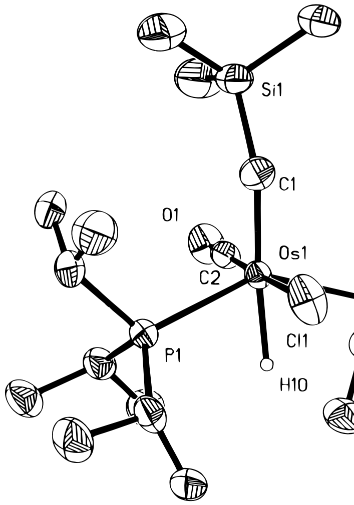
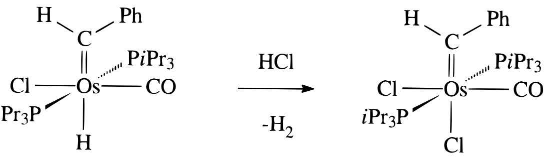


Figure 1. ORTEP diagram of compound **5** (hydrogen atoms besides H10 omitted for clarity). Selected bond distances (Å) and angles (deg): Os−C1, 1.965(5); Os−C2, 1.830(5); Os−P1, 2.403(1); Os−P2, 2.396(1); Os−Cl, 2.514(1); Os−H10, 1.70(4); C1−Si, 1.878(5); C2−O, 1.166(5); P1−Os−P2, 141.38(4); C2−Os−Cl, 177.31(14); C1−Os−C2, 95.3(2); C1−Os−Cl, 82.10(17); C1−Os−P1, 110.42(15); C1−Os−P2, 107.79(15); C1−Os−H10, 168.6(11); C2−Os−P1, 90.44(14); C2−Os−P2, 91.48(15); C2−Os−H10, 96.0(12); P1−Os−Cl, 89.88(4); P2−Os−Cl, 89.93(4); Os−C1−Si, 144.9(3); Os−C2−O, 179.4(4).

react with the hydrido complex **1** to afford the corresponding carbene complexes **3**−**5** in excellent yield.[9] The reaction of **1** with Me_3SiCHN_2 is rather slow and proceeds possibly via an $Os(N_2CHSiMe_3)$ species as an intermediate. **3**−**5** are microcrystalline, almost air-stable solids which in contrast to **2** can be stored under argon at room temperature for weeks. The methylidene complex **2** is more labile and particularly in solution decomposes slowly to give some unidentified products. The most characteristic features of the spectroscopic data of **3**−**5** are the hydride resonances at −4.5 to −5.6 ppm in the ^1H NMR and the signal of the Os═*C*HR carbon atom at 267−327 ppm in the ^{13}C NMR spectra.[8] Most remarkably, the signal of the OsH proton of **2**−**5** experiences a significant downfield shift by ca. 27 ppm compared to the starting material **1**, which is probably due to the strong *trans* influence of the carbene ligand.

Scheme 2



2 **6**

The molecular structure of **5** is illustrated in Figure 1.[10] The coordination geometry around the metal center is distorted octahedral, with the two phosphines, the CO and the chloride, and the hydride and the CHR unit occupying *trans* positions. The most notable detail is the strong bending of the P−Os−P axis (141.38(4)°) toward the position of the hydride ligand. This bending is more pronounced than in *cis*,*cis*,*trans*-$[OsH(CH_3)(CO)_2(PiPr_3)_2]$[5] and even more than in the five-coordinate compound $[Os(CH{=}CHPh)Cl(CO)(PiPr_3)_2]$, where the P−Os−P bond angle is 167.4(1)°.[4] The Os−C1 distance is 1.965(5) Å and is thus almost identical with that of the osmium nitrosyl-carbene complexes $[Os({=}CH_2)Cl(NO)(PPh_3)_2]$ (1.92(1) Å) and $[Os({=}CF_2)Cl(NO)(PPh_3)_2]$ (1.967(4) Å).[11]

While the $Os{=}CH_2$ compound reacts with a solution of HCl in toluene to give a mixture of products, among which the dihydrogen complex $[OsCl_2(\eta^2\text{-}H_2)(CO)(PiPr_3)_2]$ could be detected by ^1H and ^{31}P NMR spectroscopy,[12]

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[9] A preparative procedure for **3**−**5** is as follows. A solution of **1** (200 mg, 0.35 mmol) in 10 mL of toluene was treated with a 2-fold excess of $RCHN_2$ (R = Ph, $SiMe_3$) dissolved in hexane. An evolution of gas (N_2) was observed. After the reaction mixture was stirred for 30 min (R = Ph, CO_2Et) or 15 h (R = $SiMe_3$) at room temperature, the solvent was removed and the remaining residue repeatedly washed with 1 mL portions of hexane: yield 98% (**3**), 81% (**4**), 79% (**5**). **3**: orange solid; mp 117 °C dec. Anal. Calcd for $C_{26}H_{49}ClOOsP_2$: C, 46.94; H, 7.42. Found: C, 47.34; H, 7.42. **4**: orange solid; mp 133 °C dec. Anal. Calcd for $C_{23}H_{49}ClO_3OsP_2$: C, 41.78; H, 7.47. Found: C, 41.51; H, 7.19. **5**: yellow solid; mp 132 °C dec. Anal. Calcd for $C_{23}H_{53}ClOOsP_2Si$: C, 41.77; H, 8.08. Found: C, 41.32; H, 8.26.

[10] (a) Crystals were obtained by cooling a saturated solution of **5** in hexane to −20 °C. X-ray structure determination of **5**: data were collected at −80 °C on a Stoe-Siemens-Huber diffractometer with CCD area detector and monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). A semiempirical absorption correction was applied. The structure was solved by Patterson and Fourier methods.[10b] All non-hydrogen atoms were refined anisotropically. The hydrogen atom bonded to Os1 was refined freely, and the hydrogen atom bonded to C1 was refined with a distance restraint and with the displacement parameter set to 120% of the equivalent isotropic U value of C1; the riding model was used for the other hydrogen atoms. Full-matrix least-squares refinement against F^2 with weigthing $w^{-1} = \sigma^2(F_o^2) + (0.0285P)^2$, where $P = (F_o^2 + 2F_c^2)/3$. The R values are defined as $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.[10c] Crystal data for **5**: $C_{23}H_{53}ClOOsP_2Si$, $M_r = 661.33$, monoclinic, $P2_1/n$, $a = 9.101(2)$ Å, $b = 16.847(3)$ Å, $c = 20.226(3)$ Å, $\beta = 93.74(2)°$, $V = 3094.5(10)$ Å^3, $Z = 4$, $D_{calcd} = 1.419$ g cm^{-3}, $F(000) = 1344$, μ(Mo Kα) = 4.361 mm^{-1}, crystal size 0.25 × 0.15 × 0.15 mm, $4.7° \leq 2\theta \leq 50°$; 30 081 reflections measured, 5297 unique reflections ($R_{int} = 0.0568$) and one restraint used for the refinement of 285 parameters, $S = 0.927$, $R1 = 0.0283$ for $I > 2\sigma(I)$, $wR2 = 0.0592$ for all data, maximum/minimum residual density +1.537/−1.017 e Å^{-3}. (b) Sheldrick, G. M. SHELXS-90. *Acta Crystallogr.* **1990**, *A46*, 467. (c) Sheldrick, G. M. SHELXL-96; University of Göttingen, Göttingen, Germany, 1996.

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[13] The preparation of **6** is as follows. A solution of **3** (100 mg, 0.15 mmol) in 5 mL of toluene was treated dropwise with a saturated solution of HCl in toluene until the evolution of gas (H_2) ceased. The solvent was removed, and the red air-stable solid was repeatedly washed with pentane and dried: yield 102 mg (98%); mp 155 °C. Anal. Calcd for $C_{26}H_{48}Cl_2OOsP_2$: C, 44.63; H, 6.91. Found: C, 44.26; H, 6.67. IR (KBr): ν(CO) 1915 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 19.04 (s, 1H, OsCH), 8.28, 7.07 (both m, 5H, C_6H_5), 2.72 (m, 6H, C*H*CH$_3$), 1.25 (dvt, $N = 14.0$ Hz, J(HH) = 7.0 Hz, 18H, CHC*H*$_3$), 1.08 (dvt, $N = 13.6$ Hz, J(HH) = 6.8 Hz, 18H, CHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 278.0 (m, OsCH), 181.0 (t, J(CP) = 8 Hz, CO), 157.2, 132.9, 132.0, 130.3 (all s, C_6H_5), 25.6 (vt, $N = 28.8$ Hz, *C*HCH$_3$), 20.1, 19.4 (both s, CH*C*H$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ 9.3 (s).

[14] (a) Crystals were obtained from toluene/hexane at −20 °C. Crystal data for **6** (from 25 reflections, $10° < \theta < 15°$): monoclinic, space group $P2_1/c$ (No. 14), $a = 11.426(4)$ Å, $b = 16.734(2)$ Å, $c = 32.12(1)$ Å, $\beta = 99.96(2)°$, $V = 6049(3)$ Å^3, $Z = 8$, $D_{calcd} = 1.537$ g cm^{-3}, μ(Mo Kα) = 4.522 mm^{-1}; crystal size 0.23 × 0.15 × 0.13 mm. Solution details: Enraf-Nonius CAD4 diffractometer, Mo Kα radiation (0.710 73 Å), graphite monochromator, Zr filter (factor 15.4), $T = 293(2)$ K, ω/θ scan, maximum $2\theta = 46°$, 8402 reflections measured, 7921 independent, 7897 used for refinement (4507 with $I > 2\sigma(I)$); intensity data corrected for Lorentz and polarization effects, an empirical absorption correction (ψ-scans, minimum transmission 82.84%) was applied, structure solved by direct methods (SHELXS-86);[14b] atomic coordinates and anisotropic thermal parameters refined by full-matrix least squares on F_o^2 (SHELXL-93);[14c] positions of all hydrogen atoms calculated according to idealized geometry and refined as riding atoms; $R = 0.0602$ for $I > 2\sigma(I)$, $wR2 = 0.1425$ for all data reflections;[14d] reflection/parameter ratio 13.14; residual electron density +1.349/−0.997 e Å^{-3}. (b) Sheldrick, G. M. SHELXS-86; University of Göttingen, Göttingen, Germany, 1986. (c) Sheldrick, G. M. SHELXL-93; University of Göttingen, Göttingen, Germany, 1993. (d) $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + 119.2203P$, where $P = (F_o^2 + 2F_c^2)/3$.

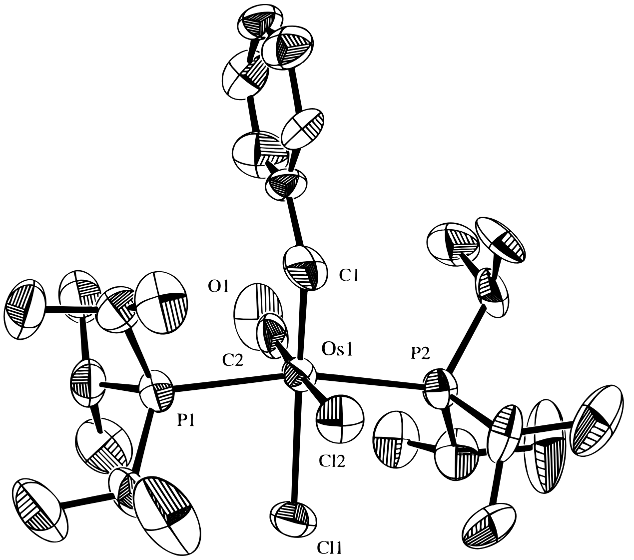

Figure 2. ORTEP diagram of compound **6** (molecule A, hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Os−C1, 1.95(2); Os−C2, 1.85(2); Os−P1, 2.469(5); Os−P2, 2.466(5); Os−Cl1, 2.484(4); Os−Cl2, 2.487(5); C1−C50, 1.46(2); C2−O1, 1.13(2); P1−Os−P2, 167.5(2); C2−Os−Cl2, 176.8(6); C1−Os−C2, 94.6(8); C1−Os−Cl2, 82.7(6); C1−Os−P1, 93.3(5); C1−Os−P2, 99.0(5); C1−Os−Cl1, 169.3(7); C2−Os−P1, 91.3(5); C2−Os−P2, 89.9(5); C2−Os−Cl1, 95.9(6); P1−Os−Cl2, 90.7(2); P2−Os−Cl2, 88.8(2); Os−C1−C50, 139(2); Os−C2−O, 176(2).

the single component **6** is obtained on treatment of the benzylidene complex **3** with HCl under evolution of H_2.[13] The ^{1}H and ^{13}C NMR spectra of **6** both exhibit a low-field signal for the OsC*H* proton and the Os*C*H carbon atom, respectively, leaving no doubt that a derivative of **3** still containing the carbene ligand is formed.

The structural proposal for **6** (see Scheme 2) has been substantiated by X-ray crystallography.[14] There are two independent molecules (A and B) in the asymmetric unit. As shown in Figure 2 for molecule A, the osmium center is octahedrally coordinated with the two phosphines in *trans* positions and the two chloro ligands in a *cis* disposition. In contrast to **5**, the axis P−Os−P of **6** is much less bent, the bond angle P−Os−P being 167.5(2)° for A and 166.3(2)° for B, respectively. While the Os−CO distances of **5** and **6** are virtually the same, the bond length Os−C(carbene) of **6** is slightly shorter than that of **5**, probably due to the replacement of the hydride by the chloride in a *trans* position. The distance Os−C1 in A (1.95(2) Å) is almost identical with the Os−CHPh distance in the bis(triphenylphosphine)osmium(II) complex *cis,cis,trans*-$[OsCl_2({=}CHPh)(CO)(PPh_3)_2]$ (1.94(1) Å),[15] whereas the distance Os−C3 in B (1.89(2) Å) corresponds precisely to the Os−$CHCH_2Ph$ distance of *cis,cis,trans*-$[OsCl_2({=}CHCH_2Ph)(CO)(P\mathit{i}Pr_3)_2]$ (1.887(9) Å).[12] There is no difference in the Os-Cl bond lengths in **6** (in neither A nor B), indicating that the *trans* influences of the carbonyl and the carbene ligands are nearly the same.

Work in progress is mainly designed to find out whether (1) by modifying the reaction conditions the initially formed diazoalkane−osmium complexes can be isolated and (2) starting materials such as $[Os(CH{=}CH_2)Cl(CO)(P\mathit{i}Pr_3)_2]$[4] and $[OsHCl(CO)(PCy_3)_2]$,[16] which are structurally related to **1**, behave similarly toward CH_2N_2 and other diazoalkanes.

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Supporting Information Available: Fully labeled diagrams and tables of crystallographic data, data collection, and solution and refinement details, positional and thermal parameters, and bond distances and angles for **5** and **6** (16 pages). Ordering information is given on any current masthead page.

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