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Activation of an Aliphatic C–H Bond at Room Temperature. Conversion on a Cluster of a Stable σ-Bonded Alkyl Group to a μ_2-Alkylidene Ligand. Synthesis and Crystal Structure Determination of $HOs_3(6\text{-}CH_2C_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_9$ and $H_2Os_3(6\text{-}CHC_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_8$[1,2]

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$Os_3(CO)_{10}(MeCN)_2$ reacts with i-Pr-Pyca{Me}[2] in toluene at room temperature to give $HOs_3(6\text{-}CH_2C_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_9$ (1), one of the few examples of a cluster with a metal–σ-alkyl bond. The presence of the latter type of bond was demonstrated by a single-crystal X-ray structure determination. Crystals of $HOs_3(6\text{-}CH_2C_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_9$ (1) are monoclinic of space group $P2_1/a$ with cell constants a = 16.480 (3) Å, b = 14.805 (2) Å, c = 9.459 (1) Å, β = 94.74 (2)°, and Z = 4. A total of 3267 reflections have been used in the refinement, resulting in a final R value of 0.057. Complex 1 is a coordinatively saturated 48e cluster containing a triangular array of osmium atoms [Os(1)–Os(2) = 2.885 (1) Å, Os(2)–Os(3) = 2.971 (1) Å, and Os(1)–Os(3) = 2.905 (1) Å]. The i-Pr-Pyca{Me} ligand has been converted into a monoanionic tridentate ligand that is bonded in a σ,σ-N,N′-chelate (4e) fashion to Os(2) and via a single σ-C-Os interaction [Os(3)–C(6) = 2.22 (2) Å] to the $Os_3(CO)_9$ unit. The most interesting part of the structure is the σ-bonded alkyl moiety that has been formed by C–H activation of the 6-Me substituent on the pyridine and is stabilized by the chelate-bonded α-diimine moiety. The hydride was not located, but from structural features it can be deduced to bridge the Os(2)–Os(3) bond. On thermolysis of 1 in n-nonane at 130 °C CO was eliminated and $H_2Os_3(6\text{-}CHC_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_8$ (2) was formed. Crystals of $H_2Os_3(6\text{-}CHC_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_8$ (2) are monoclinic of space group $P2_1/n$ with cell constants a = 16.284 (1) Å, b = 16.325 (1) Å, c = 8.605 (1) Å, β = 93.80 (1)°, and Z = 4. A total of 3174 reflections have been used in the refinement, resulting in a final R value of 0.051. The X-ray structure determination showed that the σ-bonded alkyl moiety in 1 is converted to an alkylidene ligand which is almost symmetrically bridging an Os–Os bond [Os(1)–C(6) = 2.14 (1) Å and Os(3)–C(6) = 2.18 (1) Å], leaving the geometry of the chelate-bonded α-diimine moiety virtually unchanged. The molecule contains three Os–Os bonds [Os(1)–Os(2) = 2.785 (1) Å, Os(2)–Os(3) = 2.806 (1) Å, and Os(1)–Os(3) = 2.981 (2) Å]. The two hydrides were not located, but structural features indicate that they are bridging the Os(1)–Os(3) and Os(2)–Os(3) bonds.

Introduction

The activation of C–H bonds, especially of aliphatic carbon–hydrogen bonds, by metal clusters is of great interest.[3,4] Alkyl moieties complexed to an array of metal atoms are believed to be key intermediates in hydrocarbon transformations on metal surfaces.[5] Only in recent years progress has been made in the understanding of the factors that influence the reaction routes and their relative rates and mechanisms involving C–H bond activation.

Interesting results have been obtained by studying the synthesis and reactivity of osmium carbonyl alkyl clusters. For example in the alkyl complex $HOs_3(CO)_{10}(Me)$ α-reductive elimination giving $H_2Os_3(CO)_{10}(\mu\text{-}CH_2)$ was observed,[6] whereas the ethyl group in $HOs_3(CO)_{10}(Et)$ underwent α- and β-elimination resulting in $H_2Os_3(CO)_{10}(\mu\text{-}CHMe)$ and $H_2Os_3(CO)_{10}$ together with ethylene.[7] The presence of coordinating atoms attached to the alkyl group may stabilize the metal–alkyl bond.[3,4] This was observed for example in $HOs_3(CO)_{10}(MeCHOMe)$ and $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}SCH_2)$.[8,9]

In the course of our study on the reactivity of α-diimines[10a–c] toward the trinuclear osmium carbonyl cluster $Os_3(CO)_{10}(MeCN)_2$, we recently isolated two isomers of $Os_3(CO)_{10}$(R-Pyca): $Os_3(CO)_{10}$(R-Pyca(4e)) (isomer A), containing a chelating, 4e-donating R-Pyca ligand, and $Os_3(CO)_{10}$(R-Pyca(6e)) (isomer B), containing a 6e-donating R-Pyca ligand (Figure 1).[11a–c] On thermolysis the

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(1) Part 4; for earlier parts see ref 11a–c.

(2) Pyridine-2-carbaldimines, $6\text{-}R^1\text{-}C_5H_3N\text{-}2\text{-}C(H){=}NR$, are abbreviated as R-Pyca{R^1}. When R^1 = H, the abbreviation R-Pyca can be used. 1,4-Disubstituted-1,4-diaza-1,3-dienes, RN=C(H)C(H)=NR, are abbreviated as R-DAB. The number of electrons donated by the ligands to the cluster is indicated in parentheses: i.e., α-diimine(4e) stands for σ,σ-N,N′ chelating, 4e coordinated, for which the coordination mode is also denoted as isomer A; α-diimine(6e) stands for σ-N,μ_2-N′,η^2-C=N′ bridging, 6e coordinated, for which the coordination mode is denoted as isomer B; α-diimine(8e) stands for σ,σ-N,N′-η^2,η^2-C=N,C′=N′ bridging, 8e coordinated.

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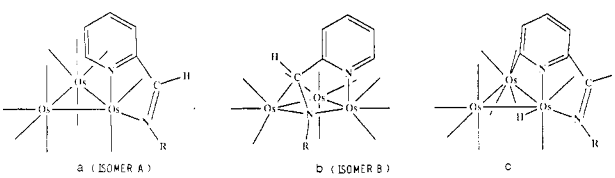

a (ISOMER A) b (ISOMER B) c

Figure 1. Schematic structures of (a) $Os_3(CO)_{10}$(R-Pyca(4e)) (isomer A), (b) $Os_3CO)_{10}$(R-Pyca(6e)) (isomer B), and (c) HOs_3-(C_5H_3N-2-C(H)=NR)$(CO)_9$.

former compound was converted to $HOs_3(C_5H_3N$-2-C-(H)=N-R)$(CO)_9$ in which the R-Pyca ligand is converted to a monoanionic terdentate ligand by ortho-metalation (Figure 1c). Therefore we directed our attention to the study of the effect of replacing the ortho-hydrogen atom of the pyridine ligand by a methyl group.

In this paper we describe the results of this study which show that in the reaction of R-Pyca{Me} with $Os_3(CO)_{10}$-$(MeCN)_2$ at room temperature, the methyl group was activated, resulting in an unique and very stable terminal metal to carbon σ-bond. The osmium–carbon σ-bond of this compound could be reacted further at 130 °C to a μ_2-alkylidene ligand.

Experimental Section

Materials and Apparatus. NMR spectra were obtained on a Bruker AC100 and AC200 spectrometer. IR spectra were recorded with a Perkin-Elmer 283 spectrometer. Field desorption (FD) mass spectra were obtained with a Varian MAT 711 double-focussing mass spectrometer with a combined EI/FD/FI ion source and coupled to spectro system MAT 100 data acquisition unit.[12] Elemental analyses were carried out by the section Elemental Analyses of the Institute of Applied Chemistry, TNO, Zeist, The Netherlands. All preparations were carried out in an atmosphere of purified nitrogen, using carefully dried solvents. The R-Pyca ligands have been prepared by the condensation reaction of 6-methylpyridine-2-carboxaldehyde with the appropriate amine.[13a-c] $Os_3(CO)_{10}(MeCN)_2$ was synthesized by a modified literature procedure.[11a] Silica gel (60 mesh) for column chromatography was activated before use.

Synthesis of $HOs_3(6-CH_2C_5H_3N$-2-C(H)=N-*i*-Pr)$(CO)_9$ (1). *i*-Pr-Pyca{Me} (0.44 mmol) was added to a stirred solution of $Os_3(CO)_{10}(MeCN)_2$ (0.11 mmol) in toluene at -20 °C. The yellow suspension was allowed to come slowly to room temperature and was stirred for 18 h at 20 °C during which the color of the solution turned to deep red. The solvent was evaporated, and the residue was dissolved in 0.5 mL of CH_2Cl_2. By column chromatography the fraction that separated as a red band (eluent hexane/diethyl ether, 1:2) was collected. The solvent was evaporated to 10 mL, and the product precipitated as dark red crystals upon cooling to -20 °C. The solvent was decanted, and the crystals were dried under vacuo. Yield of red 1: 0.055 mmol (50%). IR data (*n*-hexane, cm^{-1}): 2077, 2033, 2008, 1995, 1982, 1975, 1950, 1945. FD-mass: found, *m/e* 987; calcd, *m/e* 986. Elemental Anal. Calcd for $C_{19}H_{15}N_2O_9Os_3$: C, 23.16; H, 1.52; N, 2.84. Found: C, 23.64; H, 1.56; N, 2.73.

Synthesis of $H_2Os_3(6-CHC_5H_3N$-2-C(H)=N-*i*-Pr)$(CO)_8$ (2). $HOs_3(6-CH_2C_5H_3N$-2-C(H)=N-*i*-Pr)$(CO)_9$ (1) (0.11 mmol) was stirred at 130 °C in *n*-nonane while a slow nitrogen stream was passed through the solution. The reaction was continued until IR spectroscopy indicated that the ν(CO) pattern of the starting material was replaced by that of 2, which took about 75 min. The solvent was evaporated, and the residue was dissolved in 0.5 mL of CH_2Cl_2. By column chromatography the fraction that separated as a deep red band (eluent hexane/diethyl ether, 1:1) was collected. The solvent was evaporated to 5 mL, and the product precipitated as dark red crystals upon cooling to -20 °C. The solvent was decanted, and the crystals were dried in vacuo. Yield of red 2: 0.055 mmol (50%). IR data (*n*-hexane, cm^{-1}): 2086, 2053, 2010, 2001, 1993, 1983, 1963, 1936. FD-mass: found, *m/e* 958; calcd, *m/e* 958. Elemental Anal. Calcd for $C_{18}H_{15}N_2O_8Os_3$: C, 22.58; H, 1.57; N, 2.93. Found: C, 22.57; H, 1.45; N, 2.79.

Table I. Fractional Coordinates of the Atoms and Equivalent Isotropic Thermal Parameters of $HOs_3(6-CH_2C_5H_3N$-2-C(H)=N-*i*-Pr)$(CO)_9$ (1)

atom	x	y	z	U_{eq}, Å^2
Os(1)	−0.38054 (7)	0.15434 (7)	0.0753 (1)	0.0276 (5)
Os(2)	−0.32610 (6)	0.28168 (7)	−0.1275 (1)	0.0240 (4)
Os(3)	−0.22179 (7)	0.23767 (7)	0.1347 (1)	0.0269 (5)
N(1)	−0.264 (1)	0.175 (2)	−0.211 (3)	0.03 (1)
N(2)	−0.405 (2)	0.233 (2)	−0.298 (3)	0.04 (2)
C(1)	−0.303 (1)	0.128 (1)	−0.329 (2)	0.011 (9)
C(2)	−0.267 (2)	0.060 (2)	−0.388 (2)	0.04 (2)
C(3)	−0.192 (2)	0.021 (3)	−0.348 (3)	0.05 (2)
C(4)	−0.148 (2)	0.067 (3)	−0.225 (4)	0.06 (2)
C(5)	−0.187 (2)	0.148 (2)	−0.162 (3)	0.03 (1)
C(6)	−0.148 (2)	0.190 (2)	−0.037 (3)	0.04 (2)
C(7)	−0.384 (2)	0.169 (2)	−0.374 (2)	0.04 (1)
C(8)	−0.489 (2)	0.281 (2)	−0.341 (3)	0.04 (1)
C(9)	−0.548 (3)	0.218 (2)	−0.437 (4)	0.07 (2)
C(10)	−0.466 (4)	0.370 (3)	−0.422 (4)	0.08 (3)
C(11)	−0.405 (3)	0.088 (2)	0.245 (4)	0.05 (2)
C(12)	−0.305 (2)	0.063 (2)	0.011 (3)	0.04 (2)
C(13)	−0.432 (2)	0.260 (2)	0.151 (3)	0.04 (1)
C(14)	−0.470 (2)	0.120 (3)	−0.044 (3)	0.04 (2)
C(15)	−0.270 (2)	0.359 (2)	−0.231 (2)	0.04 (2)
C(16)	−0.390 (3)	0.386 (2)	−0.073 (4)	0.06 (2)
C(17)	−0.138 (1)	0.323 (2)	0.189 (3)	0.03 (1)
C(18)	−0.277 (2)	0.275 (2)	0.302 (4)	0.04 (2)
C(19)	−0.178 (2)	0.140 (2)	0.249 (4)	0.05 (2)
O(11)	−0.419 (2)	0.046 (2)	0.336 (2)	0.05 (1)
O(12)	−0.272 (2)	0.002 (2)	−0.012 (3)	0.06 (2)
O(13)	−0.466 (2)	0.318 (2)	0.200 (3)	0.08 (2)
O(14)	−0.528 (2)	0.097 (2)	−0.113 (3)	0.06 (2)
O(15)	−0.234 (2)	0.407 (2)	−0.304 (3)	0.06 (2)
O(16)	−0.432 (2)	0.438 (2)	−0.045 (3)	0.06 (2)
O(17)	−0.092 (1)	0.379 (2)	0.221 (3)	0.06 (2)
O(18)	−0.301 (2)	0.297 (2)	0.400 (2)	0.05 (1)
O(19)	−0.147 (2)	0.078 (2)	0.301 (3)	0.07 (2)

Crystal Structure Determination of $HOs_3(6-CH_2C_5H_3N$-2-C(H)=N-i-Pr)$(CO)_9$(1; $C_{19}H_{15}N_2O_9Os_3$). (1; $C_{19}H_{15}N_2O_9Os_3$). Crystals of the title compound are monoclinic, space group $P2_1/a$, with four molecules in a unit cell of dimensions: a = 16.480 (3) Å, b = 14.805 (2) Å, c = 9.459 (1) Å, β = 94.74 (2)°, V = 2277 Å^3, and d(calcd) = 2.88 g/cm^3. A total of 6642 independent reflections were measured on a Nonius CAD 4 diffractometer, using graphite-monochromated Mo Kα radiation, of which 3375 had intensities below the $2.5\sigma(I)$ level and were treated as unobserved. The osmium positions were derived from an E Fourier synthesis obtained by means of the symbolic addition program set SIMPEL.[14a] The remaining non-hydrogen atoms were derived from a subsequent F_o syntheses. After isotropic block-diagonal least-squares refinement an empirical absorption correction DIFABS was applied.[14b] Subsequent anisotropic refinement converged to R = 0.057 and R_w = 0.109. The anomalous dispersion of osmium was taken into account, and a weighting scheme $\omega = 1/(3.8 + F_o + 0.06F_o^2)$ was applied.[14c] The computer programs used were from the XRAY76 system.[14d] The molecular geometry of 1 with the

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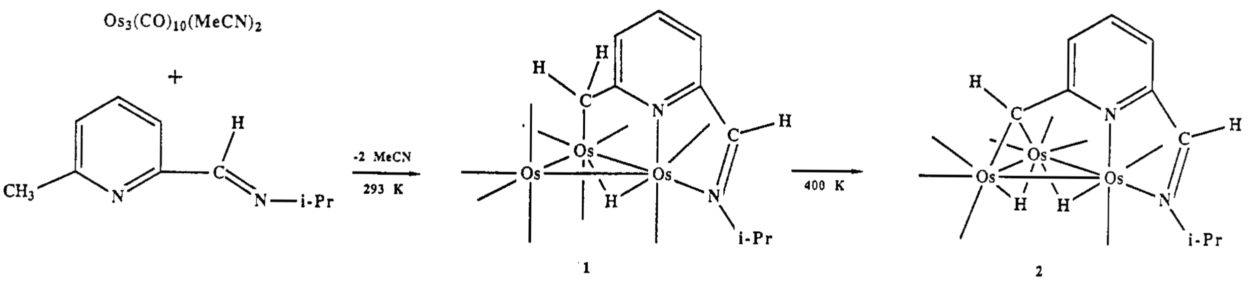
Scheme I. Schematic Structures and Formation of $HOs_3(6\text{-}CH_2C_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_9$ (1) and $H_2Os_3(6\text{-}CHC_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_9$ (2)



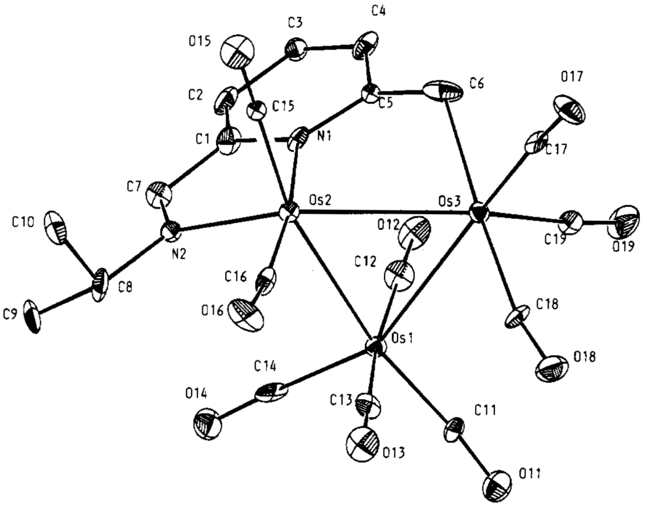


Figure 2. The molecular geometry of $HOs_3(6\text{-}CH_2C_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_9$ (1).

Table II. Bond Distances of the Atoms (Å) with Standard Deviations in Parentheses of $HOs_3(6\text{-}CH_2C_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_9$ (1)

Os(1)–Os(2)	2.885 (1)	N(2)–C(8)	1.58 (3)
Os(1)–Os(3)	2.905 (1)	C(1)–C(2)	1.32 (3)
Os(1)–C(11)	1.95 (3)	C(1)–C(7)	1.50 (3)
Os(1)–C(12)	1.97 (2)	C(2)–C(3)	1.39 (3)
Os(1)–C(13)	1.94 (2)	C(3)–C(4)	1.48 (4)
Os(1)–C(14)	1.85 (2)	C(4)–C(5)	1.51 (3)
Os(2)–Os(3)	2.971 (1)	C(5)–C(6)	1.44 (3)
Os(2)–N(1)	2.07 (2)	C(8)–C(9)	1.58 (4)
Os(2)–N(2)	2.11 (2)	C(8)–C(10)	1.59 (4)
Os(2)–C(15)	1.81 (2)	C(11)–O(11)	1.10 (3)
Os(2)–C(16)	1.96 (3)	C(12)–O(12)	1.09 (3)
Os(3)–C(6)	2.22 (2)	C(13)–O(13)	1.14 (3)
Os(3)–C(17)	1.91 (2)	C(14)–O(14)	1.16 (3)
Os(3)–C(18)	1.97 (2)	C(15)–O(15)	1.18 (3)
Os(3)–C(19)	1.91 (3)	C(16)–O(16)	1.08 (3)
N(1)–C(1)	1.42 (2)	C(17)–O(17)	1.15 (3)
N(1)–C(5)	1.37 (2)	C(18)–O(18)	1.09 (3)
N(2)–C(7)	1.26 (3)	C(19)–O(19)	1.14 (3)

numbering of the atoms is given in Figure 2, which shows an ORTEP drawing of the molecule.[14c] Atomic parameters, bond lengths, and bond angles are given in Tables I, II, and III, respectively. An ORTEP drawing, the anisotropic thermal parameters, and a list of observed and calculated structure factors are included in the supplementary material.

Crystal Structure Determination of $H_2Os_3(6\text{-}CHC_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_8$ (2; $C_{18}H_{15}N_2O_8Os_3$). Crystals of the title compound are monoclinic, space group $P2_1/n$, with four molecules in an unit cell of dimensions: a = 16.284 (1) Å, b = 16.325 (1) Å, c = 8.605 (1) Å, β = 93.80 (1)°, and d(calcd) = 2.78 g/cm^3. A total of 4028 independent reflections were measured on a Nonius CAD 4 diffractometer, using graphite-monochromated Cu radiation, of which 954 had intensities below the $2.5\sigma(I)$ level and were treated as unobserved. The osmium positions were derived from an E^2 Patterson synthesis. A subsequent F_o synthesis revealed the remaining non-hydrogen atoms. After isotropic block-diagonal least-squares refinement an empirical absorption correction DIFABS was applied.[14b] Subsequent anisotropic refinement with unit weights converged to R = 0.051. The anomalous dispersion of osmium was taken into account.[14c] The computer programs were taken from the XRAY76 system.[14d] The molecular geometry of **2** with the numbering of the atoms is given in Figure 3, which shows an ORTEP drawing of the molecule.[14e] Atomic parameters, bond lengths, and bond angles are given in Tables IV, V, and VI, respectively. An ORTEP drawing, the anisotropic thermal parameters, and a list of observed and calculated structure factors are included in the supplementary material.

Table III. Bond Angles of the Atoms (deg) with Standard Deviations in Parentheses of $HOs_3(6\text{-}CH_2C_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_9$ (1)

Os(2)–Os(1)–Os(3)	61.74 (5)	Os(2)–Os(3)–C(18)	109.6 (10)
Os(2)–Os(1)–C(11)	166.5 (8)	Os(2)–Os(3)–C(19)	143.5 (8)
Os(2)–Os(1)–C(12)	90.2 (9)	C(6)–Os(3)–C(17)	89 (1)
Os(2)–Os(1)–C(13)	83.6 (9)	C(6)–Os(3)–C(18)	173.5 (10)
Os(2)–Os(1)–C(14)	92.9 (10)	C(6)–Os(3)–C(19)	88 (1)
Os(3)–Os(1)–C(11)	107 (1)	C(17)–Os(3)–C(18)	88 (1)
Os(3)–Os(1)–C(12)	77 (1)	C(17)–Os(3)–C(19)	97 (1)
Os(3)–Os(1)–C(13)	90.0 (9)	C(18)–Os(3)–C(19)	86 (2)
Os(3)–Os(1)–C(14)	153.3 (7)	Os(2)–N(1)–C(1)	118 (1)
C(11)–Os(1)–C(12)	95 (2)	Os(2)–N(1)–C(5)	124 (1)
C(11)–Os(1)–C(13)	89 (1)	C(1)–N(1)–C(5)	118 (2)
C(11)–Os(1)–C(14)	99 (2)	Os(2)–N(2)–C(7)	121 (2)
C(12)–Os(1)–C(13)	167 (1)	Os(2)–N(2)–C(8)	121 (1)
C(12)–Os(1)–C(14)	97 (2)	C(7)–N(2)–C(8)	118 (2)
C(13)—Os(1)–C(14)	95 (1)	N(1)–C(1)–C(2)	121 (2)
Os(1)–Os(2)–Os(3)	59.46 (4)	N(1)–C(1)–C(7)	111 (2)
Os(1)–Os(2)–N(1)	86.9 (7)	C(2)–C(1)–C(7)	128 (2)
Os(1)–Os(2)–N(2)	94.5 (8)	C(1)–C(2)–C(3)	129 (2)
Os(1)–Os(2)–C(15)	166.9 (6)	C(2)–C(3)–C(4)	113 (3)
Os(1)–Os(2)–C(16)	98 (1)	C(3)–C(4)–C(5)	119 (3)
Os(3)–Os(2)–N(1)	83.2 (7)	N(1)–C(5)–C(4)	121 (2)
Os(3)–Os(2)–N(2)	147.1 (6)	N(1)–C(5)–C(6)	119 (2)
Os(3)–Os(2)–C(15)	107.7 (8)	C(4)–C(5)–C(6)	120 (2)
Os(3)–Os(2)–C(16)	104 (1)	Os(3)–C(6)–C(5)	120 (2)
N(1)–Os(2)–N(2)	75 (1)	N(2)–C(7)–C(1)	115 (2)
N(1)–Os(2)–C(15)	89 (1)	N(2)–(8)–C(9)	112 (3)
N(1)–Os(2)–C(16)	172.8 (10)	N(2)–C(8)–C(10)	105 (3)
N(2)–Os(2)–C(15)	96 (1)	C(9)–C(8)–C(10)	112 (3)
N(2)–Os(2)–C(16)	99 (1)	Os(1)–C(11)–O(11)	176 (2)
C(15)–Os(2)–C(16)	87 (2)	Os(1)–C(12)–O(12)	167 (2)
Os(1)–Os(3)–Os(2)	58.80 (4)	Os(1)–C(13)–O(13)	175 (2)
Os(1)–Os(3)–C(6)	105.2 (7)	Os(1)–C(14)–O(14)	177 (2)
Os(1)–Os(3)–C(17)	162.2 (5)	Os(2)–C(15)–O(15)	177 (2)
Os(1)–Os(3)–C(18)	79 (1)	Os(2)–C(16)–O(16)	173 (2)
Os(1)–Os(3)–C(19)	95 (1)	Os(3)–C(17)–O(17)	175 (1)
Os(2)–Os(3)–C(6)	76.9 (8)	Os(3)–C(18)–O(18)	174 (2)
Os(2)–Os(3)–C(17)	115.8 (7)	Os(3)–C(19)–O(19)	171 (2)

Results

Formation of Products. The overall formation of the complexes of $HOs_3(6\text{-}CH_2C_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_9$ (**1**) and $H_2Os_3(6\text{-}CH\text{-}C_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_8$ (**2**) is shown in Scheme I.

$Os_3(CO)_{10}(MeCN)_2$ reacts with *i*-Pr-Pyca{Me} at room temperature in toluene to give the monohydride complex **1**. Some decomposition was observed when the reaction was started at room temperature which could be avoided

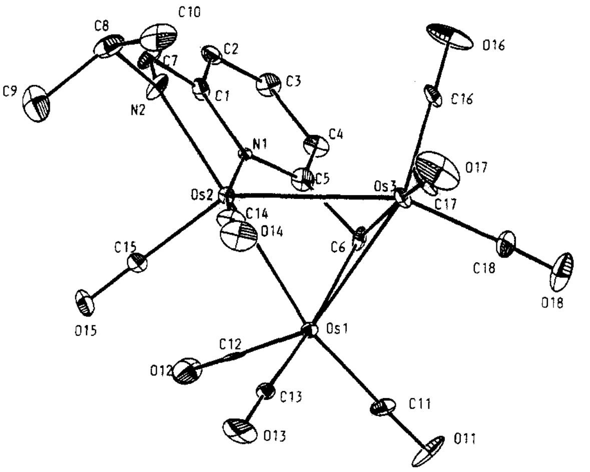


Figure 3. The molecular geometry of $H_2Os_3(6\text{-}CHC_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_9$ (**2**).

Table IV. Fractional Coordinates of the Atoms and Equivalent Isotropic Thermal Parameters of $H_2Os_3(6\text{-}CHC_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_8$ (2)

atom	x	y	z	U_{eq},Å^2
Os(1)	0.95055 (5)	0.68795 (5)	0.48885 (9)	0.0188 (4)
Os(2)	0.88869 (4)	0.80920 (5)	0.67660 (9)	0.0161 (3)
Os(3)	1.01000 (5)	0.68525 (5)	0.80237 (9)	0.0225 (4)
C(1)	1.006 (1)	0.952 (1)	0.686 (2)	0.03 (1)
C(2)	1.077 (1)	0.995 (1)	0.679 (2)	0.03 (1)
C(3)	1.147 (1)	0.957 (1)	0.630 (3)	0.03 (1)
C(4)	1.142 (1)	0.873 (1)	0.599 (2)	0.03 (1)
C(5)	1.067 (1)	0.831 (1)	0.608 (3)	0.03 (1)
C(6)	1.061 (1)	0.739 (1)	0.598 (2)	0.03 (1)
C(7)	0.931 (1)	0.983 (1)	0.756 (3)	0.04 (1)
C(8)	0.804 (1)	0.964 (2)	0.866 (3)	0.05 (2)
C(9)	0.735 (2)	0.975 (2)	0.731 (3)	0.07 (2)
C(10)	0.780 (2)	0.903 (2)	0.989 (3)	0.06 (2)
C(11)	1.008 (1)	0.601 (1)	0.395 (2)	0.03 (1)
C(12)	0.955 (1)	0.757 (1)	0.315 (2)	0.03 (1)
C(13)	0.843 (1)	0.646 (1)	0.437 (2)	0.024 (10)
C(14)	0.801 (1)	0.746 (1)	0.746 (2)	0.03 (1)
C(15)	0.824 (1)	0.837 (1)	0.492 (2)	0.03 (1)
C(16)	1.082 (1)	0.742 (1)	0.947 (2)	0.03 (1)
C(17)	0.941 (1)	0.633 (2)	0.952 (2)	0.05 (1)
C(18)	1.085 (2)	0.593 (1)	0.790 (3)	0.05 (2)
N(1)	1.0019 (8)	0.8704 (9)	0.643 (2)	0.017 (7)
N(2)	0.8751 (9)	0.930 (1)	0.781 (2)	0.033 (10)
O(11)	1.043 (1)	0.550 (1)	0.342 (3)	0.08 (1)
O(12)	0.957 (1)	0.801 (1)	0.211 (2)	0.06 (1)
O(13)	0.780 (1)	0.620 (1)	0.402 (2)	0.07 (1)
O(14)	0.7531 (10)	0.704 (1)	0.787 (2)	0.05 (1)
O(15)	0.7823 (9)	0.850 (1)	0.387 (2)	0.042 (9)
O(16)	1.123 (1)	0.775 (2)	1.034 (3)	0.10 (2)
O(17)	0.902 (2)	0.604 (2)	1.038 (2)	0.09 (2)
O(18)	1.131 (1)	0.544 (1)	0.773 (3)	0.07 (1)

by starting the reaction at −20 °C. Only a very slow reaction was observed when acetonitrile was used as the solvent. The reaction can be viewed as the substitution of two acetonitrile ligands and a carbonyl by two nitrogen donor atoms, an osmium–carbon σ-bond, and a bridging metal hydride atom formed by metalation of the methyl group attached to the pyridine ring. This results in an HOs_3 unit spanned by a new terdentate ligand consisting of a σ-bonded alkyl group attached to a chelate-bonded pyridyl imine moiety.

On thermolysis in *n*-nonane at 130 °C the monohydride complex 1 converted in about 75 min to the dihydride complex 2. In this reaction a carbonyl is eliminated and the σ-bonded alkyl moiety converts to a bridging methylidene ligand with the formation of a second metal–hydride bond. The pyridyl imine part of the ligand remains coordinated in a chelating bonding mode. Complexes 1 and 2 are air-stable, both as solids and in solution. The complexes are sparingly soluble in aliphatic solvents but dissolve readily in more polar solvents. Before the possible reaction routes and the reactivity of the complexes are considered in more detail, the molecular structures and the NMR data of 1 and 2 will be discussed.

Table V. Bond Distances of the Atoms (Å) with Standard Deviations in Parentheses of $H_2Os_3(6\text{-}CH\text{-}C_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_8$ (2)

Os(1)–Os(2)	2.785 (1)	C(2)–C(3)	1.39 (2)
Os(1)–Os(3)	2.806 (1)	C(3)–C(4)	1.40 (2)
Os(1)–C(6)	2.14 (1)	C(4)–C(5)	1.41 (2)
Os(1)–C(11)	1.91 (1)	C(5)–C(6)	1.51 (2)
Os(1)–C(12)	1.88 (1)	C(5)–N(1)	1.29 (2)
Os(1)–C(13)	1.91 (1)	C(7)–N(2)	1.28 (2)
Os(2)–Os(3)	2.981 (2)	C(8)–C(9)	1.57 (3)
Os(2)–C(14)	1.89 (1)	C(8)–C(10)	1.52 (3)
Os(2)–C(15)	1.90 (1)	C(8)–N(2)	1.52 (2)
Os(2)–N(1)	2.133 (10)	C(11)–O(11)	1.12 (2)
Os(2)–N(2)	2.18 (1)	C(12)–O(12)	1.15 (2)
Os(3)–C(6)	2.18 (1)	C(13)–O(13)	1.13 (2)
Os(3)–C(16)	1.89 (1)	C(14)–O(14)	1.11 (2)
Os(3)–C(17)	1.96 (2)	C(15)–O(15)	1.11 (2)
Os(3)–C(18)	1.95 (2)	C(16)–O(16)	1.11 (2)
C(1)–C(2)	1.36 (2)	C(17)–O(17)	1.11 (2)
C(1)–C(7)	1.49 (2)	C(18)–O(18)	1.11 (2)
C(1)–N(1)	1.38 (2)		

Table VI. Bond Angles of the Atoms (deg) with Standard Deviations in Parentheses of $H_2Os_3(6\text{-}CH\text{-}C_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_8$ (2)

Os(2)–Os(1)–Os(3)	64.43 (5)	Os(2)–Os(3)–C(18)	155.3 (5)
Os(2)–Os(1)–C(6)	78.1 (5)	C(6)–Os(3)–C(16)	94.6 (9)
Os(2)–Os(1)–C(11)	168.6 (4)	C(6)–Os(3)–C(17)	166.3 (6)
Os(2)–Os(1)–C(12)	94.0 (6)	C(6)–Os(3)–C(18)	89.6 (9)
Os(2)–Os(1)–C(13)	91.7 (6)	C(16)–Os(3)–C(17)	97.9 (10)
Os(3)–Os(1)–C(6)	50.1 (5)	C(16)–Os(3)–C(18)	93 (1)
Os(3)–Os(1)–C(11)	104.3 (6)	C(17)–Os(3)–C(18)	95 (1)
Os(3)–Os(1)–C(12)	138.3 (4)	C(2)–C(1)–C(7)	125 (2)
Os(3)–Os(1)–C(13)	118.2 (5)	C(2)–C(1)–N(1)	121 (1)
C(6)–Os(1)–C(11)	93.1 (9)	C(7)–C(1)–N(1)	114 (1)
C(6)–Os(1)–C(12)	92.3 (9)	C(1)–C(2)–C(3)	120 (2)
C(6)–Os(1)–C(13)	167.0 (6)	C(2)–C(3)–C(4)	117 (2)
C(11)–Os(1)–C(12)	93.6 (9)	C(3)–C(4)–C(5)	120 (2)
C(11)–Os(1)–C(13)	95.9 (9)	C(4)–C(5)–C(6)	122 (1)
C(12)–Os(1)–C(13)	96.5 (9)	C(4)–C(5)–N(1)	120 (2)
Os(1)–Os(2)–Os(3)	58.11 (5)	C(6)–C(5)–N(1)	117 (1)
Os(1)–Os(2)–C(14)	96.0 (7)	Os(1)–C(6)–Os(3)	81.0 (8)
Os(1)–Os(2)–C(15)	83.5 (6)	Os(1)–C(6)–C(5)	118 (1)
Os(1)–Os(2)–N(1)	84.6 (4)	Os(3)–C(6)–C(6)	112 (1)
Os(1)–Os(2)–N(2)	158.5 (3)	C(1)–C(7)–N(2)	117 (2)
Os(3)–Os(2)–C(14)	90.6 (7)	C(9)–C(8)–C(10)	113 (2)
Os(3)–Os(2)–C(15)	141.5 (4)	C(9)–C(8)–N(2)	103 (2)
Os(3)–Os(2)–N(1)	79.0 (4)	C(10)–C(8)–N(2)	110 (2)
Os(3)–Os(2)–N(2)	123.1 (4)	Os(1)–C(11)–O(11)	179 (1)
C(14)–Os(2)–C(15)	90.3 (9)	Os(1)–C(12)–O(12)	178 (1)
C(14)–Os(2)–N(1)	167.5 (6)	Os(1)–C(13)–O(13)	178 (1)
C(14)–Os(2)–N(2)	105.3 (9)	Os(2)–C(14)–O(14)	175 (1)
C(15)–Os(2)–N(1)	102.2 (7)	Os(2)–C(15)–O(15)	175 (1)
C(15)–Os(2)–N(2)	93.6 (8)	Os(3)–C(16)–O(16)	179 (1)
N(1)–Os(2)–N(2)	75.2 (6)	Os(3)–C(17)–O(17)	179 (1)
Os(1)–Os(3)–Os(2)	57.45 (5)	Os(3)–C(18)–O(18)	174 (1)
Os(1)–Os(3)–C(6)	48.9 (4)	Os(2)–N(1)–C(1)	116.2 (10)
Os(1)–Os(3)–C(16)	141.6 (5)	Os(2)–N(1)–C(5)	122 (1)
Os(1)–Os(3)–C(17)	117.5 (6)	C(1)–N(1)–C(5)	121 (1)
Os(1)–Os(3)–C(18)	97.9 (8)	Os(2)–N(2)–C(7)	117 (1)
Os(2)–Os(3)–C(6)	73.3 (5)	Os(2)–N(2)–C(8)	129 (1)
Os(2)–Os(3)–C(16)	105.8 (6)	C(7)–N(2)–C(8)	114 (2)
Os(2)–Os(3)–C(17)	98.0 (7)		

Molecular Geometry of $HOs_3(6\text{-}CH_2C_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_9$ (1). The molecular geometry of 1 together with the atomic numbering is given in Figure 2. In Tables II and III the bond lengths and angles are given.

As shown in the figure the molecule contains a triangular array of osmium atoms. Os(1) is linked to four terminal carbonyl ligands and Os(2) is linked to two carbonyl lig-

Table VII. ^{1}H NMR Data[a]

compd	imine	py	6-CH$_n$-Py[b]	*i*-Pr group	hydride
1	7.42 (s, 1 H)	6.72 (d, 8 Hz, 1 H), 6.48 (dd, 8 Hz, 1 H), 6.28 (d, 8 Hz, 1 H)	2.87 (d, 15 Hz, 1 H), 2.57 (d, 15 Hz, 1 H)	1.19 (d, 6 Hz, 3 H)/ 0.97 (d, 6 Hz, 3 H), 3.96 (sept, 6 Hz, 1 H)	−19.78 (s, 1 H)
2	6.93 (s, 1 H)	6.58 (dd, 8 Hz, 1 H), 6.31 (d, 8 Hz, 1 H), 5.79 (d, 8 Hz, 1 H)	5.22 (s, 1 H)	1.10 (d, 6 Hz, 3 H)/ 0.94 (d, 6 Hz, 3 H), 2.96 (sept, 6 Hz, 1 H)	−10.98 (d, 2 Hz, 1 H), −14.40 (d, 2 Hz, 1 H)

[a] Measured in C$_6$D$_6$ solution. The chemical shifts are given in ppm relative to TMS (multiplicity, coupling, integral); slants separate diastereotopic pairs. Abbreviations: s, singlet; d, doublet; dd, doublet of doublets; sept, septet. [b] Compound **1**, $n = 2$; compound **2**, $n = 1$.

ands and the two nitrogen attoms of the pyridyl imine moiety of the new monoanionic terdentate ligand while Os(3) is linked to three carbonyl ligands and the metalated alkyl group. The Os(2)–Os(3) bond is bridged by a triatomic N(1)–C(5)–C(6) bridge and probably a hydride atom (vide infra). When neglecting the Os(2)–Os(3) bond and assuming that the hydride is bridging the Os(2)–Os(3) bond, all osmium atoms are approximately octahedrally surrounded. The hydride was not located, but its position can be deduced from two structural factors.[15,16a,b] In the first place the angles around the Os(2)–Os(3) bond of both the axial and equatorial carbonyl ligands have increased compared to those of Os$_3$(CO)$_{12}$ [axial Os(2)–Os(3)–C(18) = 109.6 (10)° and Os(3)–Os(2)–C(16) = 104 (1)° and equatorial Os(2)–Os(3)–C(17) = 115.8 (7)° and Os(3)–Os(2)–C(15) = 107.7 (8)°]. Secondly the Os(2)–Os(3) distance of 2.971 (1) Å is significantly longer than the distance between the two nonbridged osmium atoms, Os(1)–Os(2) = 2.885 (1) Å and Os(1)–Os(3) = 2.905 (1) Å. The latter two distances are in the same range as found for the Os–Os single bonds in Os$_3$(CO)$_{12}$ [Os–Os = 2.8771 (27) Å (mean)].[15] The terdentate ligand is coordinated with the pyridine nitrogen atom in an axial position [Os(2)–N(1) = 2.07 (2) Å] while the imine nitrogen atom is equatorially coordinated [Os(2)–N(2) = 2.11 (2) Å]. Within the ligand the imine bond length C(7)–N(2) of 1.26 (3) Å is similar to those in the free α-diimine ligand *c*-Hex-DAB [1.258 (3) Å] and the σ,σ-N,N′-chelating ligand in Os$_3$(CO)$_{10}$(R-DAB(4e)) [1.31 (3) Å].[11a,17]

Within the pyridine ring the C(3)–C(4) and C(4)–C(5) distances of 1.48 (4) and 1.51 (3) Å, respectively, are relatively long when compared to the C(1)–C(2) and C(2)–C(3) distances of 1.32 (2) and 1.39 (3) Å, respectively. The C(5)–C(6) distance [1.44 (3) Å] of the CH$_2$ substituent is rather short whereas the C(1)–C(7) distance [1.50 (3) Å] of the imine substituent is as expected for a normal single bond length.

The most interesting part of the structure is the σ-coordinated alkyl group on Os(3). The Os(3)–C(6) distance of 2.22 (2) Å is slightly longer than the value predicted from addition of the covalent Os and C radii [Os–C(calcd) = 2.211 Å, based upon 0.772 Å, for a tetrahedral C(sp^3)[18] and a r(Os) = 1.439 Å, based upon the average Os–Os distance in Os$_3$(CO)$_{12}$]. Other complexes containing terminal alkyl groups linked to a ligand that is coordinated to one or more osmium atoms are HOs$_3$(C$_8$H$_{12}$O)(CO)$_8$, which contains a complicated trisubstituted η^5-cyclopentadienyl system with one of the substituents coordinated as a terminal alkyl group,[19a] H$_2$Os$_3$(CHC(=O)CH=CEtC(=CHMe)(CO)$_9$,[19b] Os$_3$(μ_3-η^2-SCH$_2$)(CO)$_{10}$,[9] and a whole range of comparable clusters in which one or more carbonyl ligands are replaced by other substituents.[20a–c] The Os–C distances in these examples all amount to about 2.16 Å.

Molecular Geometry of H$_2$Os$_3$(6-CHC$_5$H$_3$N-2-C(H)=N-i-Pr)(CO)$_8$ (2). The molecular geometry of **2** together with the atomic numbering is given in Figure 3. In Tables V and VI the bond lengths and angles are given.

Comparison of Figures 2 and 3 shows that the main differences between **1** and **2** are the σ-bonded alkyl moiety C(6) in **1** versus a bridging alkylidene moiety in **2**, the substitution of one carbonyl ligand on Os(1), and the presence of a second Os–hydride bond in **2**. The alkylidene moiety of the terdentate ligand in **2** is bridging the Os(1)–Os(3) bond with similar bond lengths [Os(1)–C(6) = 2.14 (1) Å and Os(3)–C(6) = 218 (1) Å]. As a result Os(1) and Os(3) are now linked to three terminal carbonyl ligands and Os(2) is linked to two carbonyl ligands and the chelating part of the terdentate ligand. The two hydrogen atoms were not located, but their positions may be deduced from structural factors and by comparing the structure of **2** with that of H$_2$Os$_3$(CO)$_{10}$(μ-CH$_2$) of which a neutron diffraction study was performed.[16a–b,21] One hydrogen atom is bridging the Os(1)–Os(3) bond, probably "below" the Os$_3$ plane opposite to the alkylidene bridge as in H$_2$Os$_3$(CO)$_{10}$(μ-CH$_2$). This is indicated by the large angles of the axial carbonyl ligands on Os(1) and Os(3) around this bond [Os(3)–Os(1)–C(13) = 118.2 (5)° and Os(1)–Os(3)–C(17) = 117.5 (6)°]. Also the angle of the equatorial carbonyl ligand Os(3)–Os(1)–C(11) has increased to 104.3 (6)°. This is not observed for the Os(1)–Os(3)–C(18) angle of 97.9 (8)°. Presumably as a result of the large Os(2)–Os(3)–C(16) angle of 105.8 (6)°, caused by the second hydrogen atom probably bridging the Os(2)–Os(3) bond, C(18) is pushed aside. The hydrogen atom bridging Os(2)–Os(3) is probably in an equatorial position as in H$_2$Os$_3$(CO)$_{10}$(μ-CH$_2$). The second indication that the second hydrogen atom bridges the Os(2)–Os(3) bond and not the Os(1)–Os(2) bond is the observation that the Os(2)–Os(3)–C(16) angle of 105.8 (6)° and the Os(2)–Os(3)–C(17) angle of 98.0 (7)° have increasec compared to the Os(2)–Os(1)–C(12) angle of 94.0 (6)° and the Os(2)–Os(1)–C(13) angle of 91.7 (6)°, respectively.

Finally the nonbridged Os(1)–Os(2) bond of 2.785 (1) Å is in the same range as found for the Os–Os single bonds in Os$_3$(CO)$_{12}$ [Os–Os = 2.8771 (27) Å (mean)]. The Os(2)–Os(3) bond of 2.981 (2) Å is significantly longer due to the bridging hydrogen atom whereas the Os(1)–Os(3) bond of 2.806 (1) Å has not been significantly lengthened by the bridging hydrogen atom due to the alkylidene group bridging the Os(1)–Os(3) bond. When neglecting the Os(1)–Os(3) and Os(2)–Os(3) bonds and assuming that the

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Table VIII. ^{13}C NMR Data[a]

compd	imine	py	6-CH$_n$-Py[b]	*i*-Pr group	carbonyls
1	159.9	170.5, 153.8, 133.8, 128.9, 123.8	-9.0	68.7, 25.9, 23.1	188.8, 183.6, 180.1, 178.5, 178.2
2	163.0	165.5, 155.3, 133.8, 125.1, 120.7	45.4	67.8, 25.9, 24.0	195.6, 190.2, 183.8, 183.7, 181.3, 174.3, 171.1; 169.2

[a] Measured in CD_2Cl_2 solution using an attached proton test pulse sequence. The chemical shifts are given in ppm relative to TMS. [b] Compound 1, $n = 2$; compound 2, $n = 1$.

hydrogen atoms are in the positions as discussed (vide supra), all osmium atoms are approximately octahedrally coordinated. The coordination and bond distances of the chelating part NCCN of the terdentate ligand in 2 is similar to that in 1. The pyridine nitrogen is in an axial position [Os(2)–N(1) = 2.13 (1) Å], and the imine nitrogen is equatorially coordinated [Os(2)–N(2) = 2.18 (1) Å]. The imine bond length C(7)–N(2) or 1.28 (2) Å is as expected for σ-N coordination, and the substituents on the pyridine ring are bonded with normal single-bond lengths [C(1)–C(7) = 1.49 (2) Å and C(5)–C(6) = 1.51 (2) Å]. The internal angle of the bridging alkylidene moiety of the ligand, Os(1)–C(6)–Os(3) of 81.0 (8)°, is within the range of 74–88° given by Herrmann for alkylidene groups bridging a metal–metal bond.[22]

^{1}H and ^{13}C NMR Spectroscopy. The ^{1}H and ^{13}C NMR data of complexes 1 and 2 are listed in Tables VII, and VIII, respectively.

For both complexes 1 and 2 similar resonances are observed for the chelate-bonded moiety of the α-diimine ligand. In the ^{1}H NMR spectra the pyridine protons of both complexes give rise to two doublets and a triplet around 6 ppm. In the ^{13}C NMR spectra the pyridine carbon atoms of both complexes give rise to five separate signals between 120 and 170 ppm. The observed positions for the resonances of the imine protons (around 7 ppm) and the imine carbon atoms (around 160 ppm) are in line with the σ,σ-N,N′-chelating coordination mode.[10,11c,23] In both complexes 1 and 2 two ^{1}H NMR doublets for the *i*-Pr-Me protons and two separate ^{13}C resonances for the *i*-Pr-Me carbons are found which points to a diastereotopicity of the two methyl groups. This is in accordance with the structure as found in the solid state for complex 1 and 2.

The 6-methyl substituent that has reacted to a σ-bonded alkyl moiety in 1 and a bridging alkylidene moiety in 2 gives rise to different ^{1}H and ^{13}C NMR resonances. The observation in the ^{1}H NMR spectrum of 1 of an AX pattern consisting of two doublets of equal intensity at 2.57 and 2.87 ppm with a coupling constant of 15 Hz points to a diastereotopic σ-bonded CH_2 moiety. Similar chemical shifts of 1.69 and 1.34 ppm are found for $Os_3(CO)_{10}(\mu_3,\eta^2\text{-}SCH_2)$[9] and $Os_3(CO)_{10}(Me)(\mu\text{-}I)$,[24] respectively.[25] The ^{13}C NMR resonance at -9.0 ppm for the σ-bonded CH_2 carbon in 1 is within the -59 to +3.4 ppm range characteristic for methyl complexes of Fe, Ru, and Os.[26]

The ^{1}H NMR spectrum of 2 shows a singlet at 5.22 ppm which is assigned to the one proton left on the bridging alkylidene group. This chemical shift is within the 5–11 ppm range given by Herrmann for the ^{1}H NMR chemical shifts of the μ-CHR group [e.g. 6.47/7.75 ppm in $Os_3(CO)_{11}(\mu\text{-}CH_2)$,[27] 9.82 ppm in $Os_3(CO)_{11}(\mu\text{-}CHMe)$,[28] 8.72 ppm in $Os_3(CO)_{11}(\mu\text{-}CHSiMe)$,[28] and 4.35/5.12 ppm in $H_2Os_3(CO)_{10}(\mu\text{-}CH_2)^6$].[22] The ^{13}C NMR signal at 45.4 ppm for the alkylidene carbon in 2 is comparable to the values found for alkylidene carbon atoms in other osmium clusters (e.g. 62.5 ppm for $Os_3(CO)_{11}(\mu\text{-}CH_2)$ and 25.8 ppm for $H_2Os_3(CO)_{10}(\mu\text{-}CH_2)$). These do not fit the 100–210 ppm range given by Herrmann for bridging alkylidene groups.

The resonance of the hydride atom in complex 1 is found as a singlet at -19.78 ppm which indicates that it is in a bridging position.[29] The hydrogen atoms in complex 2 are found at -14.40 and -10.98 ppm, showing a coupling of 2 Hz. Especially the latter chemical shift is at rather low field for a bridging hydride atom. For example, the hydride atoms in $H_2Os_3(CO)_{10}(\mu\text{-}CH_2)$ (for which complex a neutron diffraction study proved that the hydride atoms occupy bridging positions) are found at -20.71 and -15.38 ppm and show a coupling of 1 Hz.

Discussion

Structures. The molecule structure determinations of 1 and 2 show that both are coordinatively saturated 48e clusters containing a triangular array of osmium atoms. In both complexes the α-diimine moiety of the newly formed terdentate ligand ligand chelates one osmium atom while the ligand is further bonded to the $Os_3(CO)_n$ unit (n = 8, 9) by the N(1)–C(5)–C(6) triatomic bridge via the metalated ortho-methyl substituent on the pyridine ring. In this respect 1 and 2 show similar features. Triatomic bridges are a common structural feature in many clusters involving oxygen- and nitrogen-containing ligands.[30]

However, the existence of a σ-bonded alkyl ligand as for 1 has been observed in only a few other osmium clusters [e.g. $HOs_3(CO)_{10}(Me)$, $HOs_3(CO)_{10}(Et)$, $Os_3(CO)_{10}(\mu_3,\eta^2\text{-}SCH_2)$, $Os_3(CO)_{10}(PhSCHMe)$, and $Os_3(CO)_{10}(Me)(\mu\text{-}I)^{24}$].[6,7,9,24,31] The stability of the terminal alkyl group in complex 1 may be enhanced by the metal-coordinated heteroatom attached to it.[3]

Bridging alkylidene groups as in 2 are more common [e.g. $H_2Os_3(CO)_{10}(\mu\text{-}CH_2)$, $Os_3(CO)_{11}(CH_2)$, and $Os_3(CO)_{11}(\mu\text{-}CHMe)$].[6,22,27,28]

Reaction Mechanism. It seems worthwhile to devote some discussion to the formation of the complexes 1 and 2 and to compare it with the isolation, characterization, and reactivity of $Os_3(CO)_{10}$(R-DAB) and $Os_3(CO)_{10}$(R-Pyca{H}).[11a–c] For this comparison the latter two systems will be briefly discussed.[32]

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(24) Morrison, E. D.; Bassner, S. L.; Geoffroy, G. L. *Organometallics* **1986**, *5*, 408.

(25) The observed chemical shifts for the protons of the σ-bonded CH_2 moiety indicate that there is no agostic interaction (which would give rise to an upfield chemical shift). Agostic interactions were observed in the coordinatively unsaturated clusters $HOs_3(CO)_{10}(Me)$ and $HOs_3(CO)_{10}(C_2H_5)$ which showed resonances at about -4 ppm for the σ-bonded alkyl groups: Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726 and ref 6 and 7.

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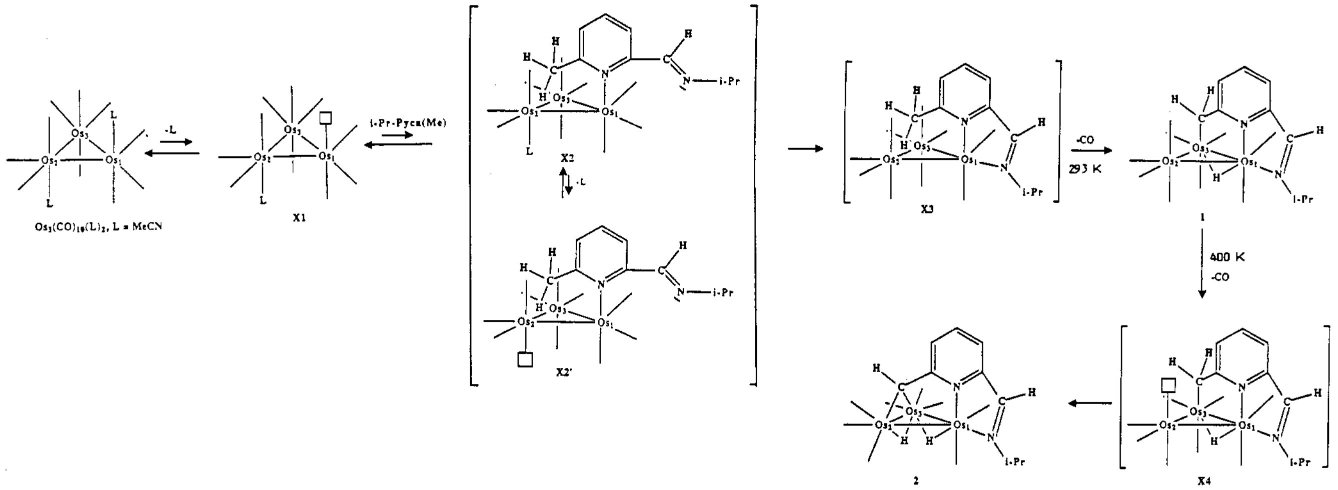
(29) Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1975**, *25*, 145.

(30) Deeming, A. J. *J. Mol. Catal.* **1983**, *21*, 25.

(31) Boyar, E.; Deeming, A. J.; Henrick, K.; McPartlin, M.; Scott, A. *J. Chem. Soc., Dalton Trans.* **1986**, 1431.

(32) Reactions of R-DAB and R-Pyca with $Ru_3(CO)_{12}$ gave cluster breakdown to mono- and dinuclear products (see ref 10a–c). Until now from the reactions of R-DAB and R-Pyca with $Os_3(CO)_{10}(MeCN)_2$ in all cases except one only trinuclear products could be isolated (see ref 11a–c).

Scheme II. Proposed Mechanism for the Formation of $HOs_3(6\text{-}CH_2C_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_9$ (1) and $H_2Os(6\text{-}CHC_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_9$ (2)



In our studies of the reactions of $Os_3(CO)_{10}(MeCN)_2$ and R-DAB two isomers of $Os_3(CO)_{10}$(R-DAB) were isolated. The product ratio depended mainly on the substituent R. Use of small R groups (e.g. c-Pr and *i*-Pr) led predominantly to $Os_3(CO)_{10}$(R-DAB(6e)) (isomer B), containing a bridging, 6e-donating R-DAB ligand. With large R groups (e.g. neo-Pent) the formation of $Os_3(CO)_{10}$(R-DAB(4e)) (isomer A), containing a chelating, 4e-donating R-DAB ligand, was favored. Interestingly with *t*-Bu-DAB no reaction took place. For R = *i*-Pr a solvent effect on the product distribution was observed since the reactions in MeCN and toluene afforded predominantly isomer A and isomer B, respectively. However, in the present case this is of secondary importance.

In the reactions of $Os_3(CO)_{10}(MeCN)_2$ and R-Pyca{H} similar products were isolated. However, for all R groups (i.e. c-Pr, *i*-Pr, *t*-Bu, neo-Pent) the main product was $Os_3(CO)_{10}$(R-Pyca{H}(4e)) (isomer A), whereas $Os_3(CO)_{10}$(R-Pyca{H}(6e)) (isomer B) was isolated only for R = c-Pr and *i*-Pr as a byproduct in minor yield (Figure 1). It is of importance to note that with *t*-Bu-DAB no reaction took place whereas for *t*-Bu-Pyca{H} $Os_3(CO)_{10}$(*t*-Bu-Pyca{H}(4e)) (isomer A) was isolated. Furthermore it was observed that the reactions of $Os_3(CO)_{10}(MeCN)_2$ with the ligands were slower in MeCN than in toluene.

Considering this we proposed the following reaction mechanism. It seemed reasonable to assume that as a first step, as was also proposed by Poë et al., in solution $Os_3(CO)_{10}(MeCN)_2$ dissociates into $Os_3(CO)_{10}$(MeCN) (intermediate X1, Scheme II), with an empty coordination site, and MeCN.[33] In the second step the R-DAB or R-Pyca ligand will get attached to the $Os_3(CO)_{10}$(MeCN) intermediate in a σ-N-coordinated fashion. Because the concentration of $Os_3(CO)_{10}$(MeCN) will be lower in MeCN compared to that in toluene, this scheme explains why the reaction of $Os_3(CO)_{10}(MeCN)_2$ with the ligand is slower in the former solvent. Since with *t*-Bu-DAB no reaction took place and *t*-Bu-Pyca{H} did react, it is most likely that with R-Pyca{H} it is the pyridine nitrogen atom that is σ-N-coordinated and not the imine nitrogen atom. The next sttep with both R-DAB and R-Pyca might then be the attack of the nitrogen lone pair of the noncoordinated end of the ligand on the same osmium atom to which the other end is already coordinated, giving isomer A. Alternatively the π-C=N bond of the noncoordinated end may attack a neighboring osmium atom which gives isomer B.[34]

The observed product distribution in the case of R-DAB is now understandable, since previous studies have shown that larger R groups tend to protect the π-C=N bond of α-diimines against coordination to a metal atom.[10a–c] This results in the formation of isomer A with large R groups and isomer B with small R groups.[35]

For R-Pyca{H} the situation is somewhat different since isomer A was the main product for all R groups. This might be explained by the steric interaction of the hydrogen atom at the 6-position on the pyridine ring and the carbonyl groups on the neighboring osmium atoms. This interaction will hamper the rotation around the Os–N(pyridine) bond, thereby preventing the attack of the π-C=N bond on the neighboring osmium atoms and consequently the formation of isomer B.

For the reaction of $Os_3(CO)_{10}(MeCN)_2$ with *i*-Pr-Pyca{Me} we propose that a similar mechanism is operating (Scheme II). Also for this reaction it has been observed that the reaction in MeCN is slower than that in toluene which indicates a reaction via intermediate X1. Secondly it is of interest that in this reaction isomer B is not observed at all. This might be rationalized by the formation of an intermediate with a σ-N-coordinated pyridine nitrogen atom (intermediate X2). X2 will be in equilibrium with X2′, with an empty coordination site, but this is of secondary importance in the present case (vide infra). The large methyl group on the 6-position of the pyridine ring will hinder the rotation around the Os–N(pyridine) bond even more than in the case of R-Pyca{H}, thereby completely preventing the formation of isomer B. Thus the intermediate X2 or X2′ reacts to $Os_3(CO)_{10}$(*i*-Pr-Pyca{Me}(4e)) (intermediate X3), containing a chelating R-Pyca{Me} ligand, by a CO shift from Os(1) to Os(2) with concomitant dissociation of MeCN on Os(2) and formation of a chelating R-Pyca ligand. In the proposed intermediate X3 there is a strong steric interaction between the methyl group on the heterocycle and the $Os_2(CO)_8$ moiety. As a result of this a C–H bond of the methyl group attached to the heterocycle might be activated. The next step in

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[33] Dahlinger, K.; Poë, A. J.; Sayal, P. K.; Sekhar, V. C. *J. Chem. Soc., Dalton Trans.* **1986**, 2145.

[34] The kinetic measurements of substitution reactions of $Os_3(CO)_{10}(MeCN)_2$ with phosphines performed by Poë et al. are in agreement with these findings and further show that the substitution of the second MeCN ligand by a phosphine is much faster. This second step, involving the conversion of the proposed intermediate containing a monodentate coordinated ligand to the product, is probably much faster.

[35] For an explanation of the solvent effect of the reaction with *i*-Pr-DAB, see ref 11a.

the reaction sequence might than be a metalation reaction together with the elimination of a carbonyl ligand to give complex 1.[36,37]

It is of interest to note that the reaction of $Os_3(CO)_{10}(MeCN)_2$ with *i*-Pr-Pyca{Me}, affording complex 1 with a metalated methyl group, proceeds at room temperature. This reaction may be compared with the thermolysis reaction of $Os_3(CO)_{10}$(*i*-Pr-Pyca{H}(4e)) which proceeds at 343 K and afforded $HOs_3(C_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_9$, with an ortho-metalated pyridine ring. The higher temperature needed for the latter reaction to proceed compared to that of the room-temperature metalation reaction that affords complex 1 is remarkable.[38] Even more because it is generally accepted that metal–carbon bonds with aromatic carbon atoms are thermodynamically more stable than those with aliphatic carbon atoms.[3] The lower temperature needed for the reaction of $Os_3(CO)_{10}$(*i*-Pr-Pyca{Me}(4e)) (X3) to complex 1 compared with that needed for the Reaction of $Os_3(CO)_{10}$(*i*-Pr-Pyca{H}(4e)) to $HOs_3(C_5H_3N\text{-}2\text{-}C(H){=}N\text{-}i\text{-}Pr)(CO)_9$ might be explained by the greater steric interference of the methyl group in X3 compared to that of the hydrogen atom in $Os_3(CO)_{10}$(*i*-Pr-Pyca{H}(4e)) with the $Os_2(CO)_8$ moiety, which is an important factor for the activation of C–H bonds.[4,39,40]

At 400 K complex 1 converts to complex 2. For the first step in this reaction we propose that one carbonyl ligand is eliminated, thereby creating a vacant coordination site (see Scheme II, intermediate X4).[22,41a,b] In this coordinatively unsaturated intermediate a considerable interaction between the Os–CH_2–py hydrogen atoms and osmium can be expected.[42] The next step might be the activation of the C–H bond resulting in the oxidative addition reaction that gives complex 2. The geometry and coordination of the chelating part of the ligand is hardly affected in the course of the reaction comparing the structures of 1 and 2.

Conclusions

It is shown that under mild conditions (i.e. 293 K) aliphatic C–H bonds may be easily activated on a transition-metal cluster as demonstrated by the reaction of $Os_3(CO)_{10}(MeCN)_2$ with *i*-Pr-Pyca{Me} which yielded 1, which is one of the few examples of a transition-metal cluster containing a σ-bonded alkyl moiety. The stability of the σ-bonded alkyl moiety may be enhanced when the carbon atom is attached to a ligand that is coordinated to the metal cluster.

It is shown that on thermolysis a second C–H bond of the σ-bonded alkyl moiety is activated and is converted to a μ_2-bridging alkylidene.

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Registry No. 1, 114249-89-7; 2, 114221-39-5; *i*-Pr-Pyca{Me}, 78004-29-2; $Os_3(CO)_{10}(MeCN)_2$, 61817-93-4.

Supplementary Material Available: Listings of anisotropic thermal parameters of the non-hydrogen atoms and ORTEP views of complexes 1 and 2 (4 pages); listings of structure factor amplitudes for 1 and 2 (43 pages). Ordering information is given on any current masthead page.

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(36) Another way of rationalizing the metalation reaction is to view the $Os_2(CO)_8$ fragment isolobal with ethylene that is η^2-coordinated to the $Os(CO)_2$(R-Pyca{Me}) fragment. By rotation of the $Os_2(CO)_8$ fragment the osmium atoms will come within a close distance of the 6-methyl substituent on the pyridine ring which will facilitate the metalation reaction.

(37) The importance of the chelating ligand for the formation of the metal–alkyl bond in complex 1 is also well-illustrated by the reaction of $Os_3(CO)_{10}(C_8H_{14})_2$ with 2-methylpyridine in which the aromatic and not the aliphatic C–H bond is activated: Deeming, A. J.; Peters, R.; Hursthouse, M. B.; Backer-Dirks, J. D. J. *J. Chem. Soc., Dalton Trans.* **1982**, 787. Thus $HOs_3(CO)_{10}(2\text{-}Me\text{-}C_5H_3N)$ is formed in which the heterocycle is ortho-metalated.

(38) In other examples in which activation of aliphatic or aromatic C–H bonds is observed, even higher temperatures are needed. For example $Os_3(CO)_{11}(PMe_3)$ and $Os_3(CO)_{11}(C_5H_5N)$ react to $H_2Os_3(CO)_9(Me_2PCH)$ and $HOs_3(CO)_{10}(C_5H_4N)$ at 151 and 128 °C, respectively (see: Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1973**, 2727. Deeming, A. J. *J. Organomet. Chem.* **1977**, *128*, 63. Johnson, B. F. G.; Lewis, J.; Pippard, D. A. *J. Chem. Soc., Dalton Trans.* **1981**, 407).

(39) Deem, M. L. *Coord. Chem. Rev.* **1986**, *74*, 101.

(40) It should be noted that a close distance between the methyl group and osmium as the only factor might not be sufficient for the metalation reaction to proceed. It is suggested that the failure of most 16e complexes to activate C–H bnds to oxidative addition indicates that the kinetic barrier for C–H activation is of secondary importance (see ref 3). So the driving force of the reaction therefore may be both the relief of the steric interference in the non-metalated product and the stabilization of the metal–carbon bond in complex 1 by the chelating ligand, which are essential factors for metalation to occur (see ref 3 and 39).

(41) (a) Lewis, J.; Johnson, B. F. G. *Gazz. Chim. Ital.* **1979**, *109*, 271. (b) Adams, R. D.; Horvath, I. T. *Prog. Inorg. Chem.* **1985**, *33*, 127.

(42) A similar interaction was observed in the unsaturated clusters $HOs_3(CO)_{10}Me^6$ and $HOs_3(CO)_{10}Et^7$ which were shown to undergo α- and β-reductive elimination reactions.