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Triosmium Clusters Formed by Oxidative Addition and Decarbonylation of 2-Formylpyrrole: Crystal Structures of Three Triosmium Clusters Containing Aromatic or Nonaromatic Heterocyclic Ligands Derived from Pyrrole

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The μ-acyl cluster $[\mathrm{Os_3H(\mu_2\text{-}\overline{NHCH{=}CHCH{=}C}CO)(CO)_{10}}]$ (**1**) is formed by oxidative addition of 2-formylpyrrole to $[\mathrm{Os_3(CO)_{10}(MeCN)_2}]$ in refluxing cyclohexane in the same manner as with other aldehydes. The crystals of **1** are trielinic, space group $P\bar{1}$, with cell dimensions a = 14.882 (2) Å, b = 15.626 (4) Å, c = 9.447 (3) Å, α = 107.39 (2)°, β = 97.29 (2)°, γ = 97.84 (2)°, and Z = 4. The structure was refined to R_w = 0.034. The pyrrolylacyl ligand bridges two osmium atoms through the C and O atoms of the original formyl group. Thermal loss of two COs from **1** gives two isomers of the cluster $[\mathrm{Os_3H_2(\mu_3\text{-}C_4H_3N)(CO)_9}]$ (**2** and **3**), isomer **2** converting to **3** thermally. Isomer **2**, $[\mathrm{Os_3H_2(\mu_3\text{-}\overline{NHCH{=}CHC{=}C})(CO)_9}]$, retains the NH bond and is directly related to the *N*-methyl analogue of **2**, $[\mathrm{Os_3H_2(\mu_3\text{-}Me\overline{NCH{=}CHC{=}C})(CO)_9}]$ (**5**), and closely related to the benzyne cluster $[\mathrm{Os_3H_2(C_6H_4)(CO)_9}]$, both of known X-ray structure. Cluster **2** converts to **3** by cleavage of N–H and Os–C bonds and with formation of C–H and Os–N bonds. Crystals of **3** are monoclinic, space group $P2_1/c$, with cell dimensions a = 11.308 (2) Å, b = 12.457 (2) Å, c = 15.384 (3) Å, β = 123.59 (2)°, and Z = 8. The structure was refined to R_w = 0.052. The structure is best defined by a model in which the $\mu_3\text{-}\overline{\mathrm{N{=}CHCH{=}CHC}}$ ligand is coordinated to one Os atom through a N atom and to the other two through a single C atom forming a μ_2-alkylidene bridge. The C_4N ring is formally nonaromatic and is oriented vertically to the metal plane. Another nonaromatic derivative formed as a byproduct along with **2** and **3** in the direct reaction of pyrrole with $[\mathrm{Os_3(CO)_{12}}]$ is the cluster $[\mathrm{Os_3H(\mu\text{-}\overline{N{=}CCH_2CH{=}CH})(CO)_{10}}]$ (**4**). Crystals of **4** are monoclinic, space group $P2/b$, with cell dimensions a = 28.704 (2) Å, b = 14.377 (3) Å, c = 9.304 (3) Å, γ = 94.16 (2)°, and Z = 8. The structure was refined to R_w = 0.064. The stabilization of nonaromatic tautomers of pyrrole by coordination to Os_3 groups in clusters **3** and **4** is discussed.

Introduction

Previously we have shown that 2-formylpyrrole is useful for introducing pyrrole rings into triosmium clusters.[1] The mildest entry into this chemistry is by displacement of the acetonitrile ligands of $[\mathrm{Os_3(CO)_{10}(MeCN)_2}]$ with oxidative addition of 2-formylpyrrole. There is cleavage of the aldehydic C–H bond to give the μ-acyl cluster $[\mathrm{Os_3H(\mu_2\text{-}\overline{NHCH{=}CHCH{=}C}CO)(CO)_{10}}]$ (**1**). The X-ray structure of **1** has confirmed that the initial cleavage is at the aldehyde group rather than at the ring sites which are known to be cleaved in the direct reaction of pyrrole with $[\mathrm{Os_3(CO)_{12}}]$.[1,2] Subsequent thermal decarbonylation of **1** (173 °C, 15 min) gives two isomeric nonacarbonyl derivatives, **2** and **3**, each of which contains a heterocyclic ring triply bridging an Os_3 cluster of atoms. We initially based the structures of these compounds on spectroscopic evidence,[1,2] but this did not uniquely define the structure of **3**. Now we are able to characterize cluster **3** crystallographically and can also unambiguously assign the structure of cluster **2** by comparison with its *N*-methyl analogue, the X-ray structure of which we have already reported.[3] From the direct reaction of pyrrole with $[\mathrm{Os_3(CO)_{12}}]$ which gave isomers **2** and **3** predominantly, we also obtained a small amount of another cluster, $[\mathrm{Os_3H(C_4H_4N)(CO)_{10}}]$ (**4**). Although the stoichiometry of **4** seems to imply that it is a simple oxidative addition product of pyrrole (C_4H_5N) formed by N–H cleavage, there was ^{1}H NMR evidence for a CH_2 group in the ring and hence we proposed that we had stabilized the unstable tautomer of pyrrole, $\overline{\mathrm{N{=}CHCH{=}CHCH_2}}$, by coordination. We are now able to confirm this proposal by reporting its X-ray structure, and, although the ligand is probably $\overline{\mathrm{N{=}CCH_2CH{=}CH}}$ rather than $\overline{\mathrm{N{=}CCH{=}CHCH_2}}$, this is not unquestionable and this structural point will be discussed later.

Almost all of this chemistry seems to be unique to triosmium clusters. For example, there are no other reported examples of the pyrrolic ligands found in compounds **1**–**4**. The only other organometallic compounds of pyrrole and substituted pyrroles seem to be limited to pyrrolyl complexes with M–N σ-bonds or with η^5-coordination as in

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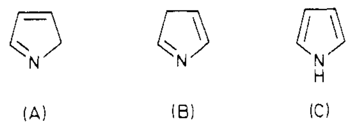


Figure 1. Pyrrole (C) and its less stable tautomers A and B.

azaferrocene and to η^5-pyrrole complexes related to η^6-benzene complexes.[4] For example, *N*-methylpyrrole forms complexes $[Cr(C_4H_4NMe)(CO)_3]$ and $[Fe(C_4H_4NMe)(C_5H_5)]^+$, but the pyrrole ligands are only weakly coordinated in these species.[5-9] The σ-complexes of pyrrole described in this paper are remarkably stable which is fortunate since we have only been able to synthesize them at rather high temperatures. Furthermore the strength of the σ-bonds between Os and the C and N atoms are strong enough to stabilize each of the nonaromatic tautomers A and B of pyrrole (C) (Figure 1).

Experimental Section

Synthesis. Previously reported triosmium clusters were synthesized by the reaction of 2-formylpyrrole with $[Os_3(CO)_{10}(MeCN)_2]$ which gives $[Os_3H(\mu\text{-}\overline{NHCH{=}CHCH{=}C}CO)(CO)_{10}]$ (1) (66%) which can then be converted thermally in refluxing *n*-decane to the isomers $[Os_3H_2(\mu_3\text{-}\overline{NHCH{=}CHC{=}C})(CO)_9]$ (2) (40%) and $[Os_3H_2(\mu_3\text{-}\overline{N{=}CHCH{=}CHC})(CO)_9]$ (3) (30%).[1] The direct reaction of pyrrole with $[Os_3(CO)_{12}]$ in refluxing decane gave **2** (25%), **3** (40%), and $[Os_3H(\overline{N{=}CCH_2CH{=}CH})(CO)_{10}]$ (4) (20%).[1] Yellow crystals of **1**, **3**, and **4** suitable for single-crystal X-ray structure determination were obtained by slow evaporation of solutions of the compounds in dichloromethane–hexane mixtures, relying on the greater rate of evaporation of the chlorinated solvent in which the clusters are more soluble.

Crystal Structure Determinations. Crystals of each compound, **1**, **3**, and **4**, were examined by utilizing similar procedures. The crystal was attached to a glass fiber mounted in a brass pin in a goniometer head and optically centered on an Enraf-Nonius CAD4 diffractometer. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement of 23 reflections ($3 \leq \theta \leq 16°$) for **1**, 23 reflections ($6 \leq \theta \leq 19°$) for **3**, and 24 reflections ($3 \leq \theta \leq 18°$) for **4**. Details of the crystal data parameters for each compound are given in Table I. The lack of systematic absences for **1**, systematic absences $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$, for **3**, and systematic absences $hk0$, $k = 2n + 1$, for **4** indicated the space groups $P\bar{1}$, $P2_1/c$, and $P2/b$, respectively. These were verified by least-squares refinement of the structures. Data were collected at room temperature by using the ω–2θ scan technique. The scan rate varied from 1.3 to 8.3° min^{-1} in ω, and data were collected to a maximum 2θ angle of 40° for **1** and 50° for **3** and **4**. The scan range was calculated by θ scan width = $(0.8 + 0.350 \tan \theta)°$, and backgrounds were measured, using the moving crystal–moving counter technique, at the beginning and end of each scan. As a check on crystal and electronic stability, three representative reflections were measured every 120 min. Although no significant changes were observed, a decay correction was applied to each data set as well as an empirical absorption correction based on a series of ψ scans with relative transmission coefficients of 0.281–0.998 for **1**, 0.295–0.995 for **3**, and 0.634–0.998 for **4**. Lorentz and polarization corrections were also applied to the three data sets.

Structures **1** and **3** were solved by standard Patterson and difference Fourier methods, while **4** was solved by direct methods and difference Fourier synthesis. No attempt was made to locate hydrogen atoms except for the hydridic hydrogens attached to the osmium atom rings; their positions were calculated by using HYDEX[10] and verified by the skeletal geometry of the clusters. For each structure the osmium atoms were refined anisotropically and all other non-hydrogen atoms isotropically. The hydridic hydrogen atoms were included in the final cycle but with fixed position and thermal parameters. The final fractional atomic coordinates are listed in Tables II, III, and IV for compounds **1**, **3**, and **4**, respectively.

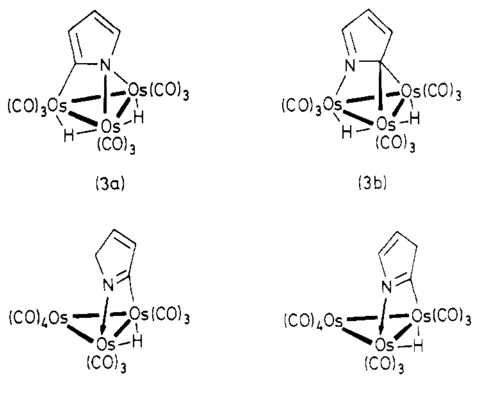
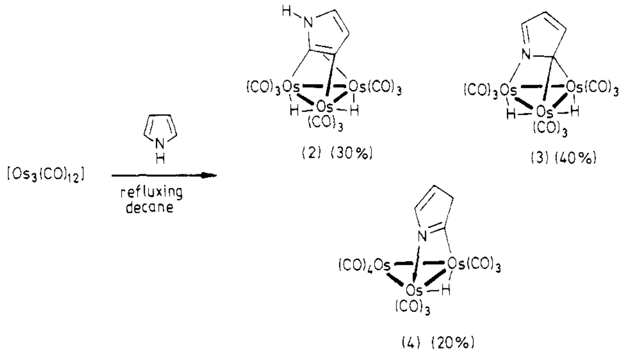


Figure 2. Alternative structures for $[Os_3H_2(C_4H_3N)(CO)_9]$ (3) and for $[Os_3H(C_4H_4N)(CO)_{10}]$ (4) that we were unable to distinguish from our IR and NMR data.

Scheme I



Since the β angle of the monoclinic cell ($P2_1/c$) for compound **3** was quite large, 123.59 (2)°, the cell was transformed to $P2_1/n$ in which the β angle was only 102.31 (2)°, as suggested by one of the reviewers. Subsequent refinement of the atomic parameters using this smaller β-angle cell gave identical results, e.g. R, R_w, B's, and errors, except that as expected the correlation coefficients between refined parameters had become very small. We have reported, however, the original $P2_1/c$ cell results.

Scattering factors were taken from Cromer and Waber.[11] Anomalous dispersion effects were included in F_c: the values of $\Delta f'$ and $\Delta f''$ were those of Cromer.[12] Only those reflections with $I_o > 3\sigma(I_o)$ were included in the least-squares refinements. The highest peaks in the final difference map were positioned near to or within the osmium rings.

All calculations were carried out on a DEC MicroVax computer using the SDP/VAX system of programs.[13] Anisotropic thermal parameters (Tables S1, S2, and S3), structure factors (Tables S4, S5, and S6), and least-squares planes (Tables S7, S8, and S9) have been deposited as supplementary material.

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Table I. Summary of Crystal and Intensity Data

	1	3	4
formula	$C_{15}H_5O_{11}Os_3N$	$C_{13}H_5O_9Os_3N$	$C_{14}H_5O_{10}Os_3N$
MW	945.81	889.79	917.80
descriptn	pale yellow platelet	yellow platelet	dark yellow fragment
system	triclinic	monoclinic	monoclinic
a, Å	14.882 (2)	11.308 (2)	28.725 (4)
b, Å	15.626 (4)	12.457 (2)	14.389 (2)
c, Å	9.447 (3)	15.384 (3)	9.302 (1)
α, deg	107.39 (2)		
β, deg	97.29 (2)	123.59 (2)	
γ, deg	97.84 (2)		94.14 (2)
V, $Å^3$	2043.8	1805.3	3834.5
space group	$P\bar{1}$	$P2_1/c$	$P2/b$
Z	4	4	8
D_{calc}, g cm^{-3}	3.07	3.27	3.18
cryst size, mm^3	0.28 × 0.17 × 0.06	0.17 × 0.10 × 0.01	0.26 × 0.28 × 0.34
μ, cm^{-1} (Mo Kα)	186.8	211.4	199.4
λ(Mo Kα), Å (graphite monochromator)	0.71073	0.71073	0.71073
temp, °C	25 (1)	25 (1)	25 (1)
no. of unique data	3978	3213	7172
no. of data with $I_o > 3\sigma(I_o)$	3484	2340	3463
no. of parameters refined	271	121	256
$R = \sum(\lvert F_o\rvert - \lvert F_c\rvert)/\sum\lvert F_o\rvert$	0.031	0.041	0.058
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.034	0.052	0.064
largest shift/esd	0.01	0.01	0.03
weighting scheme	$1/\sigma(F_o)^2$	$1/\sigma(F_o)^2$	$1/\sigma(F_o)^2$
highest peak in final diff map, e $Å^{-3}$	0.62	0.88	1.82

Results and Discussion

Synthesis of Compounds 1–4. The direct thermal reaction of pyrrole with $[Os_3(CO)_{12}]$ is slow, requiring long times or high temperatures, and we originally reported that in refluxing Decalin (ca. 190 °C) this gave only **2**,[2] but later we showed that the compound that we initially reported as **2** is actually **3**.[1] In a more careful study of the products of the thermal reaction at the slightly cooler conditions of refluxing decane (174 °C), we were able to identify clusters **2**, **3**, and **4** (Scheme I). We had proposed that the clusters **3** and **4** were nonaromatic forms derived from pyrrole, each containing a tetrahedral ring atom, but since these proposals were based on spectroscopy, they were made tentatively.[1] Indeed we could not discriminate spectroscopically between the alternatives **3a** and **3b** with different modes of attachment of the C_4H_3N ring (Figure 2), but we originally preferred **3a** in the belief (now shown to be mistaken) that the nitrogen atom, rather than a carbon atom, would bridge osmium atoms. Likewise we could not be completely sure of the position of the CH_2 group in cluster **4**. We originally proposed structure **4a** on the basis of the ^1H NMR shift for the CH_2 group at δ 4.70 which seemed to place it adjacent to the electronegative nitrogen atom, but we could not be sure that the structure **4b** was not adopted instead (Figure 2).[1]

Later we found that an easier route to compounds **2** and **3** was by the chemistry in Scheme II involving an initial oxidative addition of the formyl group of 2-formylpyrrole to give the acyl complex $[Os_3H(\overline{NHCH{=}CHCH{=}C}CO)(CO)_{10}]$ (**1**) which doubly decarbonylates at higher temperatures to the clusters **2** and **3**.[1]

The X-ray crystal structures of **1**, **3**, and **4** are presented here. We had hoped to determine also the structure of cluster **2**, but were unable to obtain suitable crystals. The *N*-methyl analogue $[Os_3H_2(C_4H_2NMe)(CO)_9]$ (**5**) formed in the direct reaction of *N*-methylpyrrole with $[Os_3(CO)_{12}]$ is directly comparable to **2** spectroscopically,[1] and there can be no doubt that **2** and **5** are isostructural. Since X-ray structures of **5** and its thiophene counterpart are known,[3] we can be sure of the overall structure of **2** without knowing its detailed molecular parameters.

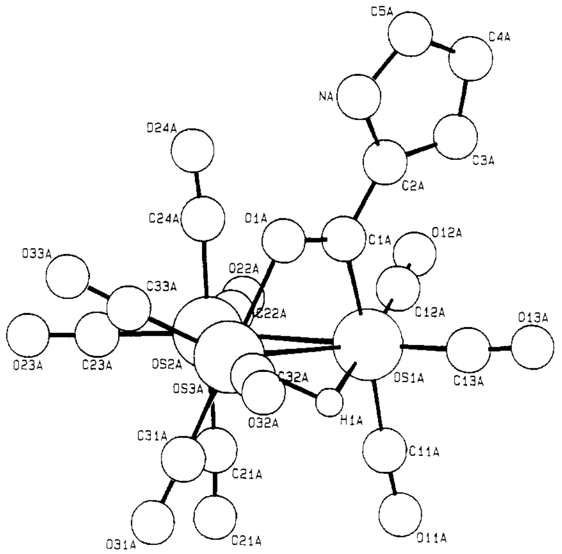
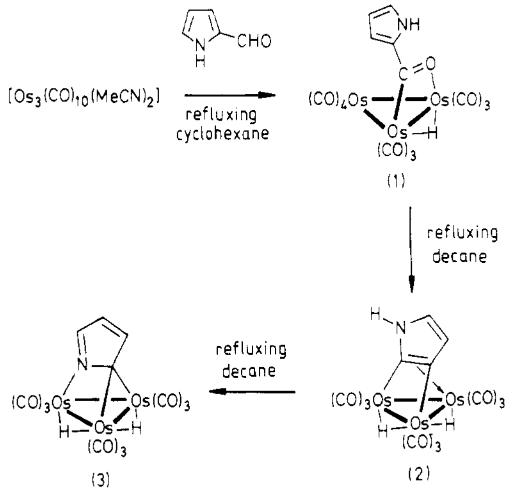


Figure 3. Molecular structure of the acyl cluster $[Os_3H(CO\text{-}C_4H_3NH)(CO)_{10}]$ (**1**, molecule A). The atoms are represented as spheres with sizes proportional to their covalent radii (PLUTO program, SDP/VAX).

Scheme II



Structure of Cluster $[Os_3H(\overline{NHCH{=}CHCH{=}C}CO)(CO)_{10}]$ (1). The molecular structure of cluster **1** is shown in Figure 3 and selected bond lengths and angles in Table V. The compound is as expected for an oxidative addition product of an aldehyde with $[Os_3(CO)_{10}(MeCN)_2]$ and consistent with its IR spectrum around 2000 cm^{-1} which is very similar to those of other clusters of the type $[Os_3H(\mu\text{-}RO)(CO)_{10}]$.[14-16] The ν(CO) (acyl) absorption is at 1425 cm^{-1} consistent with its bridging nature, and ν(NH) is at 3464 cm^{-1}. The role of the pyrrole as a bystander

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Table II. Fractional Atomic Coordinates for $[Os_3H(\overline{NHCH{=}CHCH{=}C}CO)(CO)_{10}]$ (1)[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Os(1A)	0.32500 (5)	0.22445 (4)	0.18173 (7)	2.66 (2)	Os(1B)	0.06911 (5)	0.76519 (4)	0.11464 (8)	3.02 (2)
Os(2A)	0.30419 (5)	0.30217 (4)	0.48948 (7)	2.55 (2)	Os(2B)	0.13354 (5)	0.77121 (5)	0.41846 (8)	3.11 (2)
Os(3A)	0.41086 (5)	0.16214 (4)	0.41807 (7)	2.73 (2)	Os(3B)	0.15082 (5)	0.61778 (4)	0.17758 (7)	2.81 (2)
O(11A)	0.126 (1)	0.1195 (9)	0.075 (2)	5.8 (3)*	O(11B)	−0.130 (1)	0.759 (1)	0.175 (2)	6.7 (4)*
O(12A)	0.279 (1)	0.4005 (9)	0.148 (1)	5.4 (3)*	O(12B)	0.095 (1)	0.971 (1)	0.224 (2)	6.6 (4)*
O(13A)	0.361 (1)	0.1463 (9)	−0.134 (1)	5.6 (3)*	O(13B)	0.009 (1)	0.740 (1)	−0.216 (2)	6.9 (4)*
O(21A)	0.1279 (9)	0.1594 (9)	0.418 (1)	5.2 (3)*	O(21B)	−0.0588 (9)	0.6676 (8)	0.405 (1)	4.9 (3)*
O(22A)	0.1942 (9)	0.4479 (9)	0.462 (1)	5.2 (3)*	O(22B)	0.090 (1)	0.952 (1)	0.606 (2)	7.6 (4)*
O(23A)	0.3131 (9)	0.3350 (8)	0.823 (1)	4.6 (3)*	O(23B)	0.208 (1)	0.699 (1)	0.666 (2)	6.7 (4)*
O(24A)	0.4921 (9)	0.4335 (9)	0.573 (1)	5.3 (3)*	O(24B)	0.326 (1)	0.8571 (9)	0.394 (1)	5.7 (3)*
O(31A)	0.268 (1)	0.0417 (9)	0.506 (2)	5.9 (3)*	O(31B)	0.018 (1)	0.4935 (9)	0.276 (1)	5.4 (3)*
O(32A)	0.515 (1)	0.0034 (9)	0.317 (2)	6.0 (3)*	O(32B)	0.1601 (9)	0.4606 (8)	−0.099 (1)	4.8 (3)*
O(33A)	0.516 (1)	0.2390 (9)	0.740 (1)	5.3 (3)*	O(33B)	0.3145 (9)	0.5989 (8)	0.385 (1)	4.9 (3)*
O(1A)	0.5071 (7)	0.2507 (7)	0.356 (1)	2.7 (2)*	O(1B)	0.2434 (8)	0.7043 (7)	0.105 (1)	3.3 (2)*
N(A)	0.615 (1)	0.3695 (9)	0.267 (2)	4.0 (3)*	C(3B)	0.244 (2)	0.896 (1)	−0.038 (2)	5.0 (5)*
C(1A)	0.464 (1)	0.277 (1)	0.253 (2)	2.4 (3)*	C(1B)	0.204 (1)	0.767 (1)	0.078 (2)	2.7 (3)*
C(2A)	0.523 (1)	0.339 (1)	0.203 (2)	2.7 (3)*	C(2B)	0.261 (1)	0.825 (1)	0.019 (2)	3.7 (4)*
C(3A)	0.507 (1)	0.376 (1)	0.087 (2)	4.0 (4)*	N(B)	0.350 (1)	0.816 (1)	0.007 (2)	5.0 (3)*
C(4A)	0.589 (1)	0.427 (1)	0.081 (2)	4.6 (4)*	C(4B)	0.386 (2)	0.876 (1)	−0.057 (2)	6.2 (5)*
C(5A)	0.655 (1)	0.424 (1)	0.194 (2)	4.6 (4)*	C(5B)	0.325 (2)	0.925 (2)	−0.088 (3)	6.4 (6)*
C(11A)	0.199 (1)	0.161 (1)	0.121 (2)	4.3 (4)*	C(11B)	−0.056 (1)	0.756 (1)	0.151 (2)	4.6 (4)*
C(12A)	0.297 (1)	0.332 (1)	0.158 (2)	4.1 (4)*	C(12B)	0.085 (1)	0.891 (1)	0.180 (2)	5.0 (5)*
C(13A)	0.343 (1)	0.174 (1)	−0.012 (2)	3.4 (4)*	C(13B)	0.031 (1)	0.748 (1)	−0.087 (2)	5.0 (5)*
C(21A)	0.192 (1)	0.210 (1)	0.439 (2)	3.7 (4)*	C(21B)	0.013 (1)	0.708 (1)	0.412 (2)	4.0 (4)*
C(22A)	0.234 (1)	0.391 (1)	0.469 (2)	3.8 (4)*	C(22B)	0.106 (1)	0.883 (1)	0.529 (2)	4.9 (5)*
C(23A)	0.309 (1)	0.322 (1)	0.695 (2)	2.9 (3)*	C(23B)	0.178 (1)	0.731 (1)	0.573 (2)	4.4 (4)*
C(24A)	0.422 (1)	0.382 (1)	0.534 (2)	3.6 (4)*	C(24B)	0.253 (1)	0.823 (1)	0.403 (2)	4.4 (4)*
C(31A)	0.322 (1)	0.088 (1)	0.470 (2)	3.7 (4)*	C(31B)	0.065 (1)	0.540 (1)	0.238 (2)	3.9 (4)*
C(32A)	0.477 (1)	0.066 (1)	0.352 (2)	3.3 (4)*	C(32B)	0.157 (1)	0.523 (1)	0.006 (2)	2.5 (3)*
C(33A)	0.478 (1)	0.206 (1)	0.617 (2)	3.5 (4)*	C(33B)	0.253 (1)	0.605 (1)	0.306 (2)	4.4 (4)*
H(1A)	0.348	0.120	0.221	4.0*	H(1B)	0.052	0.639	0.062	4.0*

[a] Parameters with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table III. Fractional Atomic Coordinates for $[Os_3H_2(\overline{N{=}CHCH{=}CHC})(CO)_9]$ (3)[a]

atom	*x*	*y*	*z*	*B*, Å^2
Os(1)	0.20623 (5)	0.15596 (5)	0.68965 (4)	2.79 (1)
Os(2)	0.18102 (5)	0.36928 (5)	0.73617 (4)	2.74 (1)
Os(3)	0.43459 (5)	0.23483 (5)	0.87913 (4)	2.85 (1)
O(11)	0.389 (1)	0.090 (1)	0.608 (1)	6.6 (4)*
O(12)	0.212 (1)	−0.068 (1)	0.7731 (8)	5.2 (3)*
O(13)	−0.081 (1)	0.128 (1)	0.482 (1)	6.0 (3)*
O(21)	0.278 (1)	0.567 (1)	0.672 (1)	6.3 (3)*
O(22)	0.141 (1)	0.489 (1)	0.8898 (9)	5.8 (3)*
O(23)	−0.131 (1)	0.389 (1)	0.560 (1)	6.3 (3)*
O(31)	0.606 (1)	0.302 (1)	0.790 (1)	6.5 (3)*
O(32)	0.549 (1)	0.008 (1)	0.924 (1)	6.2 (3)*
O(33)	0.643 (1)	0.327 (1)	1.098 (1)	6.5 (4)*
N	0.262 (1)	0.202 (1)	0.8922 (8)	2.6 (2)*
C(1)	0.142 (1)	0.222 (1)	0.7896 (9)	2.6 (3)*
C(2)	0.018 (1)	0.198 (1)	0.793 (1)	3.6 (3)*
C(3)	0.069 (1)	0.170 (1)	0.895 (1)	3.7 (3)*
C(4)	0.218 (1)	0.174 (1)	0.953 (1)	3.4 (3)*
C(11)	0.320 (2)	0.116 (2)	0.639 (1)	4.9 (4)*
C(12)	0.214 (1)	0.018 (1)	0.742 (1)	3.6 (3)*
C(13)	0.029 (1)	0.134 (1)	0.562 (1)	4.0 (3)*
C(21)	0.241 (2)	0.489 (2)	0.693 (1)	4.5 (4)*
C(22)	0.156 (1)	0.445 (1)	0.829 (1)	3.3 (3)*
C(23)	−0.012 (2)	0.384 (2)	0.629 (1)	4.3 (4)*
C(31)	0.551 (2)	0.273 (2)	0.831 (1)	4.6 (4)*
C(32)	0.507 (2)	0.097 (2)	0.909 (1)	4.3 (4)*
C(33)	0.562 (1)	0.291 (1)	1.015 (1)	3.7 (3)*

[a] Parameters with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

substituent is confirmed by the crystal structure determination.

The unit cell contains two independent molecules, A and B, which have essentially the same geometry; molecule A is shown in Figure 3, and our discussion is based on it. The structure of 1 relates to those established for the μ-acyl clusters $[Os_3H(PhCH_2CO)(CO)_{10}]$[16] and $[Os_3H(C_5H_5FeC_5H_4CO)(CO)_{10}]$[14] formed in a similar way by oxidative addition of phenylethanal and ferrocenylaldehyde. The $\overline{NHCH{=}CHCH{=}C}CO$ ligand is coordinated to the triangular osmium cluster through the acyl carbonyl group and, unlike all other pyrrole derivatives in this paper, the heterocycle is not coordinated. The coordination geometries of Os(1A) and Os(3A) are extremely similar even though they are respectively coordinated to the C(1A) and O(1A) atoms, and although the bond length errors are large, apparent differences suggest that C(1A) exerts a greater trans influence than O(1A); Os(1)–C(1) [2.06 (1) and 2.08 (2) Å] is shorter than Os(3)–O(1) [2.12 (1) and 2.12 (1) Å], and the Os–CO distance trans to C(1) is longer than that trans to O(1), 1.92 (2), 1.92 (2), and 1.85 (2), 1.89 (2) Å, respectively. This has been observed before; for example, the shortest Os–CO bond in $[Os_3(CO)_{10}(CH_2{=}CHCO_2Me)]$ is that trans to the coordinated organic carbonyl group.[17]

Conversion of Cluster $[Os_3H_2(\overline{C{=}CCH{=}CHNH})(CO)_9]$ (2) into $[Os_3H_2(\overline{N{=}CHCH{=}CHC})(CO)_9]$ (3) and Their Structures. One of the more interesting aspects of this work is that the double decarbonylation of 1 give two isomers 2 and 3. Loss of CO from osmium results in transfer of a pyrrolyl group from the acyl carbon to osmium and a second CO loss leads to another oxidative addition (ring C–H cleavage) to give 2, although this is not necessarily correct mechanistically since these steps might occur in the reverse order. This conversion is entirely

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[17] Boyar, E.; Deeming, A. J.; Rothwell, I. P.; Henrick, K.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1437.

Table IV. Fractional Atomic Coordinates for $[Os_3H(\overline{N{=}CCH_2CH{=}C}H)(CO)_{10}]$ (4)[a]

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Os(1A)	0.92020 (4)	0.44329 (9)	0.6698 (1)	3.54 (3)	Os(1B)	0.66144 (4)	0.38167 (8)	1.1707 (1)	3.17 (2)
Os(2A)	0.88862 (4)	0.49846 (8)	0.9489 (1)	2.91 (2)	Os(2B)	0.60038 (4)	0.53057 (8)	1.1693 (1)	3.23 (2)
Os(3A)	0.82444 (4)	0.48525 (8)	0.7044 (1)	3.28 (2)	Os(3B)	0.64818 (4)	0.48187 (9)	1.4321 (1)	3.36 (2)
O(11A)	0.9445 (9)	0.648 (2)	0.604 (3)	7.2 (6)*	O(11B)	0.7496 (8)	0.511 (2)	1.110 (3)	5.2 (5)*
O(12A)	0.9140 (9)	0.382 (2)	0.353 (3)	6.7 (6)*	O(12B)	0.7212 (7)	0.231 (1)	1.279 (2)	4.9 (5)*
O(13A)	1.0222 (9)	0.410 (2)	0.729 (3)	7.2 (6)*	O(13B)	0.6495 (9)	0.330 (2)	0.852 (3)	7.2 (6)*
O(14A)	0.8936 (8)	0.245 (2)	0.761 (3)	5.2 (5)*	O(14B)	0.5734 (8)	0.257 (2)	1.230 (3)	5.9 (5)*
O(21A)	0.9401 (8)	0.689 (2)	0.926 (3)	6.3 (6)*	O(21B)	0.6760 (8)	0.642 (2)	1.004 (3)	6.5 (6)*
O(22A)	0.8505 (8)	0.547 (2)	1.240 (3)	5.6 (5)*	O(22B)	0.544 (1)	0.699 (2)	1.184 (3)	7.7 (7)*
O(23A)	0.9711 (8)	0.406 (2)	1.065 (2)	5.1 (5)*	O(23B)	0.5505 (9)	0.441 (2)	0.911 (3)	7.2 (7)*
O(31A)	0.8420 (9)	0.673 (2)	0.547 (3)	6.7 (6)*	O(31B)	0.7427 (9)	0.593 (2)	1.413 (3)	6.5 (6)*
O(32A)	0.7235 (7)	0.518 (2)	0.779 (3)	5.3 (5)*	O(32B)	0.6243 (9)	0.584 (2)	1.708 (3)	6.8 (6)*
O(33A)	0.8009 (8)	0.375 (2)	0.433 (3)	5.7 (5)*	O(33B)	0.6824 (9)	0.307 (2)	1.570 (3)	7.4 (7)*
N(A)	0.8450 (8)	0.382 (2)	0.953 (3)	4.2 (5)*	N(B)	0.5564 (8)	0.451 (2)	1.309 (3)	3.4 (5)*
C(1A)	0.817 (1)	0.369 (2)	0.841 (3)	3.5 (6)*	C(1B)	0.5789 (9)	0.429 (2)	1.427 (3)	3.3 (6)*
C(2A)	0.784 (1)	0.284 (2)	0.853 (3)	4.0 (6)*	C(2B)	0.544 (1)	0.379 (2)	1.525 (3)	3.9 (6)*
C(3A)	0.796 (1)	0.240 (3)	0.982 (4)	5.5 (8)*	C(3B)	0.501 (1)	0.373 (3)	1.451 (4)	6.3 (9)*
C(4A)	0.834 (1)	0.297 (2)	1.051 (4)	4.6 (7)*	C(4B)	0.5081 (9)	0.419 (2)	1.316 (3)	3.3 (5)*
C(11A)	0.937 (1)	0.565 (2)	0.631 (4)	5.4 (8)*	C(11B)	0.716 (1)	0.469 (2)	1.133 (3)	4.1 (6)*
C(12A)	0.918 (1)	0.407 (3)	0.469 (5)	7 (1)*	C(12B)	0.701 (1)	0.294 (2)	1.240 (4)	4.8 (7)*
C(13A)	0.985 (1)	0.423 (2)	0.709 (4)	4.7 (7)*	C(13B)	0.657 (1)	0.347 (3)	0.972 (5)	7 (1)*
C(14A)	0.901 (1)	0.320 (2)	0.726 (4)	4.7 (7)*	C(14B)	0.608 (1)	0.303 (2)	1.209 (4)	5.3 (8)*
C(21A)	0.921 (1)	0.613 (2)	0.936 (3)	3.8 (6)*	C(21B)	0.647 (1)	0.597 (2)	1.064 (4)	4.5 (7)*
C(22A)	0.864 (1)	0.531 (2)	1.131 (3)	3.9 (6)*	C(22B)	0.566 (1)	0.629 (3)	1.186 (5)	6.7 (9)*
C(23A)	0.942 (1)	0.440 (2)	1.020 (3)	4.1 (6)*	C(23B)	0.570 (1)	0.475 (3)	1.007 (4)	5.9 (8)*
C(31A)	0.836 (1)	0.602 (2)	0.600 (4)	5.3 (8)*	C(31B)	0.709 (1)	0.548 (2)	1.416 (4)	4.8 (7)*
C(32A)	0.762 (1)	0.508 (2)	0.757 (4)	4.3 (6)*	C(32B)	0.632 (1)	0.546 (2)	1.602 (4)	4.8 (7)*
C(33A)	0.809 (1)	0.418 (2)	0.531 (3)	4.2 (6)*	C(33B)	0.672 (1)	0.376 (3)	1.524 (5)	6.5 (9)*

[a] Parameters with an asterisk were refined isotroically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table V. Selected Bond Lengths (Å) and Angles (deg) for the Cluster $[Os_3H(\overline{NHCH{=}CHCH{=}C}CO)(CO)_{10}]$ (1)

	molecule A	molecule B
Os(1)-Os(2)	2.871 (1)	2.878 (1)
Os(1)-Os(3)	2.912 (1)	2.922 (1)
Os(2)-Os(3)	2.846 (1)	2.837 (1)
Os(1)-C(1)	2.06 (1)	2.08 (2)
Os(3)-O(1)	2.12 (1)	2.12 (1)
C(1)-O(1)	1.30 (2)	1.27 (2)
N-C(2)	1.38 (2)	1.42 (2)
N-C(5)	1.37 (3)	1.41 (3)
C(1)-C(2)	1.44 (2)	1.43 (3)
C(2)-C(3)	1.40 (3)	1.37 (3)
C(3)-C(4)	1.38 (3)	1.35 (3)
C(4)-C(5)	1.37 (3)	1.32 (4)
range of Os-CO bond lengths	1.11 (2)-1.17 (2)	1.14 (2)-1.19 (3)
Os(1)-Os(2)-Os(3)	61.24 (2)	61.50 (3)
Os(1)-Os(3)-Os(2)	59.80 (2)	59.94 (2)
Os(2)-Os(1)-Os(3)	58.96 (2)	58.56 (2)
Os(1)-Os(3)-O(1)	68.2 (3)	67.7 (3)
Os(2)-Os(3)-O(1)	89.1 (3)	89.3 (3)
Os(3)-Os(1)-C(1)	66.3 (5)	66.0 (5)
Os(2)-Os(1)-C(1)	87.0 (4)	87.9 (4)
Os(3)-O(1)-C(1)	108.6 (9)	110 (1)
Os(1)-C(1)-O(1)	117 (1)	117 (1)
Os(1)-C(1)—C(2)	130 (1)	130 (1)
O(1)-C(1)-C(2)	113 (1)	113 (1)
range of Os-C-O bond angles	171 (1)-179.6 (8)	173 (2)-179 (2)

equivalent to that of the benzoyl cluster $[Os_3H(PhCO)(CO)_{10}]$ to the benzyne cluster $[Os_3H_2(C_6H_4)(CO)_9]$.[18,19] There is a strong correspondence of IR and NMR data between the pyrrolyne cluster 2 and the benzyne cluster. Unfortunately we could not obtain good single crystals of 2 and have instead determined the X-ray structure of the *N*-methyl substituted analogue $[Os_3H_2(\mu_3\text{-}C_4H_2NMe)(CO)_9]$ (5).[1-3] Clusters 2 and 5 are isostructural since their spectra correspond so closely, and the structure of 5 forms the basis of the depiction of 2 in Schemes I and II.

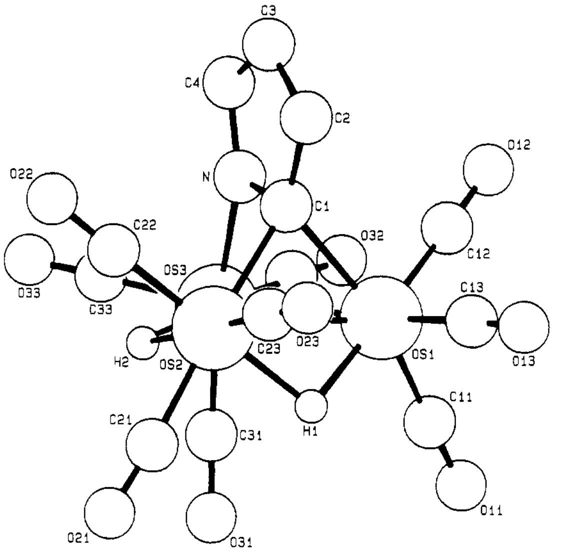

Figure 4. Molecular structure of the cluster $[Os_3H_2(C_4H_3N)(CO)_9]$ (3). The atoms are represented as spheres with sizes proportional to their covalent radii (PLUTO program, SDP/VAX).

Compound 5 is extremely stable thermally and shows no tendency to isomerize at the temperatures at which 2 converts to 3. Therefore the conversion of 2 to 3 depends upon the presence of the NH group and likely involves the transfer of this hydrogen atom. We have shown that this transfer is not an intraligand process since $[Os_3H_2(\overline{C{=}CCH{=}CHN}D)(CO)_9]$ (2-d_1) converts to $[Os_3HD(\overline{N{=}CHCH{=}CHC})(CO)_9]$ (3-d_1).[1] From this result it would seem that a metal hydride transfer to carbon gives the transient species $[Os_3H(\overline{C{=}CHCH{=}CHN}D)(CO)_9]$ fol-

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(18) Azam, K. A.; Deeming, A. J.; Rothwell, I. P. *J. Organomet. Chem.* **1979**, *178*, C20.

(19) Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1.

Table VI. Selected Bond Lengths (Å) and Angles (deg) for the Cluster $[Os_3H_2(\mu_3\text{-}\overline{N{=}CHCH{=}CHC})(CO)_9]$ (3)

Os(1)-Os(2)	2.8074 (9)	N-C(1)	1.42 (1)
Os(2)-Os(3)	2.9811 (7)	N-C(4)	1.32 (2)
Os(3)-Os(1)	2.7933 (6)	C(1)-C(2)	1.46 (2)
Os(1)-C(1)	2.19 (2)	C(2)-C(3)	1.38 (2)
Os(2)-C(1)	2.15 (2)	C(3)-C(4)	1.40 (2)
Os(3)-N	2.11 (1)		

Range of Os-CO Bond Lengths: 1.85 (2)-1.91 (2)

Os(1)-Os(2)-Os(3)	57.61 (2)	Os(2)-C(1)-N	107.5 (8)
Os(2)-Os(1)-Os(3)	64.32 (2)	Os(1)-C(1)-N	103 (1)
Os(1)-Os(3)-Os(2)	58.07 (2)	Os(2)-C(1)-C(2)	126 (1)
Os(1)-Os(2)-C(1)	50.4 (4)	Os(1)-C(1)-C(2)	130.1 (9)
Os(2)-Os(1)-C(1)	49.1 (4)	Os(3)-N-C(1)	103 (1)
Os(3)-Os(2)-C(1)	63.7 (3)	Os(3)-N-C(4)	147.9 (7)
Os(3)-Os(1)-C(1)	67.0 (3)	N-C(1)-C(2)	106 (1)
Os(2)-Os(3)-N	67.3 (3)	C(1)-C(2)-C(3)	106 (1)
Os(1)-Os(3)-N	70.3 (3)	C(2)-C(3)-C(4)	109 (1)
Os(2)-Os(3)-C(33)	116.1 (5)	C(3)-C(4)-N	110 (1)
Os(1)-Os(3)-C(32)	87.7 (4)	C(4)-N-C(1)	109 (1)

Range of Os-C-O Bond Angles: 171 (1)-179 (2)

lowed by D atom transfer to osmium to give the product. Figure 2 shows two structures we had previously considered for **3** which differ only in the mode of attachment of the C_4H_3N ligand, and we could not discriminate these by NMR data. The single-crystal X-ray structure of **3** is shown in Figure 4, and selected bond lengths and angles are in Table VI. The nitrogen atom is bonded to Os(3) while C(1) bridges Os(1) and Os(2), and hence cluster **3** adopts **3b** in Figure 2. However, to test the possibility of structure **3a**, we attempted to refine the structure after the positions of the metal-bonded carbon and nitrogen atoms were interchanged. This led to a poorer refinement, an enlargement of the thermal ellipsoids for the nitrogen atom, and a contraction of those for carbon, as expected if the supposed carbon atom were actually nitrogen and visa versa. We are confident therefore that the positions of these atoms in Figure 4 are correctly determined.

As expected from the description (**3b**) of cluster **3**, the C_4N ring atoms are closely planar and this plane is perpendicular to the Os_3 plane (dihedral angle 93.0 (4)°). The small tilt from the vertical is toward Os(2), that is, away from the osmium-osmium edge that is not hydride-bridged. The interatomic distances in the ring are all fairly similar although the longer ones do correspond to those represented as single bonds in **3b**. Notably the spiro carbon atom C(1) has the longest ring bonds [1.42 (2) Å to N and 1.46 (2) Å to C(2)]. These distances might indicate residual $p\pi$-$p\pi$ bonding to the spiro atom and that the aromatic character of the ring is not totally quenched in this mode of bonding. The hydride ligands are along the Os(1)-Os(2) and Os(2)-Os(3) edges judged by metal-metal distances and CO positions although these were not located in the structure refinement. Application of the potential minimization program HYDEX confirmed their positions.[10] This method positioned one hydride close to the intersection of the C(12)-Os(1) and Os(22)-Os(2) directions. The hydride ligands exchange (NMR coalescence) which could result from hydride migrations or the interconversion of form **3b** with the less stable form **3a** or from both processes. We have not studied the fluxionality in any detail.

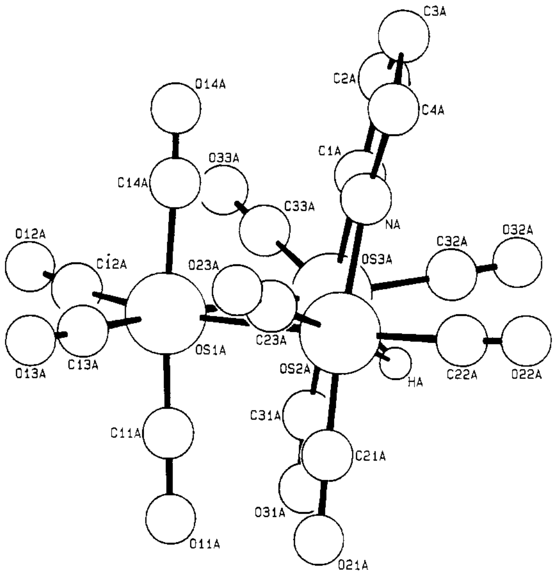

Figure 5. Molecular structure of the cluster $[Os_3H(C_4H_4N)(CO)_{10}]$ (**4**). The atoms are represented as spheres with sizes proportional to their covalent radii (PLUTO program, SDP/VAX).

Table VII. Selected Bond Lengths (Å) and Angles (deg) for the Cluster $[Os_3H(\overline{N{=}CCH_2CH{=}CH})(CO)_{10}]$ (4)

	molecule A	molecule B
Os(1)-Os(2)	2.880 (1)	2.864 (1)
Os(2)-Os(3)	2.925 (1)	2.914 (1)
Os(3)-Os(1)	2.876 (1)	2.865 (1)
Os(2)-N	2.04 (1)	2.09 (1)
Os(3)-C(1)	2.09 (1)	2.05 (1)
N-C(1)	1.35 (1)	1.34 (1)
C(1)-C(2)	1.49 (1)	1.52 (1)
C(2)-C(3)	1.45 (1)	1.50 (2)
C(3)-C(4)	1.44 (1)	1.40 (1)
C(4)-N	1.49 (1)	1.45 (1)
Os(1)-Os(2)-Os(3)	59.40 (1)	59.43 (1)
Os(2)-Os(1)-Os(3)	61.09 (1)	61.11 (1)
Os(1)-Os(3)-Os(2)	59.51 (1)	59.44 (1)
Os(1)-Os(2)-N	88.9 (2)	87.7 (2)
Os(3)-Os(2)-N	67.8 (2)	68.1 (2)
Os(1)-Os(3)-C(1)	86.2 (3)	87.0 (2)
Os(2)-Os(3)-C(1)	67.2 (3)	67.6 (2)
Os(2)-N-C(1)	114.9 (6)	110.4 (6)
Os(3)-C(1)-N	110.5 (6)	114.0 (6)
N-C(1)-C(2)	112.9 (8)	107.5 (8)
C(1)-C(2)-C(3)	104.6 (9)	105.0 (9)
C(2)-C(3)-C(4)	110 (1)	108 (1)
C(3)-C(4)-N	106.0 (9)	107.0 (8)
C(4)-N-C(1)	106.5 (7)	112.3 (7)

Formation and Structure of $[Os_3H(\overline{N{=}CCH_2CH{=}CH})(CO)_{10}]$ (4). The molecular structure of cluster **4** is shown in Figure 5, and selected bond lengths and angles are in Table VII. Two independent molecules (A and B) are in the unit cell, but only one is illustrated. The two molecules A and B closely approximate an enantiomeric pair. The structure is similar to structures of other clusters of the general type $[Os_3H(\mu\text{-}X)(CO)_{10}]$ where X is a bridging ligand coordinated through adjacent atoms.[19] Apart from the obvious unsymmetrical nature of the organic ligand, there is an approximate mirror plane through Os(1) and bisecting Os(2) and Os(3). In a very close related structure, that of the imidazolyl complex $[Os_3H(\overline{N{=}CHNHCH{=}C})(CO)_{10}]$,[20,21] the structure refined best with a disordered system involving equal populations of the two possible orientations of the imidazolyl ligand, that is, a molecular with the imidazole bonded through N to one Os atom and through C to another superimposed on another molecule with these atoms reversed. With an ordered

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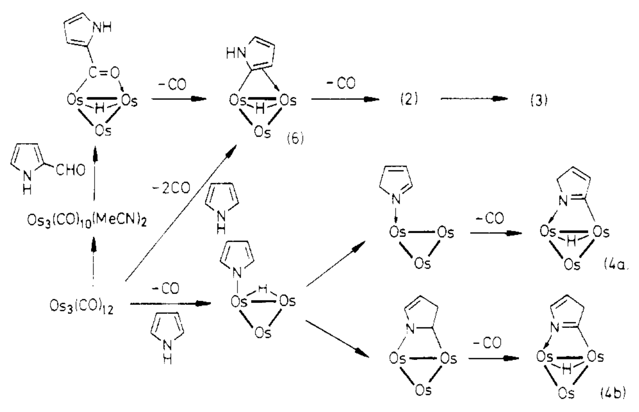
Scheme III



model, the thermal parameters for the osmium-bonded carbon atom were found to be too small. This situation did not arise in the refinement of molecules A and B of **4**. It appears that in this case both molecules are reasonably well ordered, and although it is not possible to make a definitive statement regarding structures **4a** and **4b** from bond distances and their respective esds, it appears as if molecule B adopts the **4a** configuration while molecule A represents a statistical population of both forms, **4a** and **4b**.

Structure **4b** does, however, have some support from analogies we can make with the corresponding chemistry of indole which we find very readily generates (more readily than pyrrole) the analogue of cluster **4** and other clusters containing the same ligand.[22] Only structure **4b** would allow the incorporation of a benzo group across a double C=C bond. Structure **4a** would require the benzo group of indole to span a single C-C bond of the five-membered ring. This would certainly favor the analogue of **4b** for the indole derivative, and probably therefore for the pyrrole compound itself. Such arguments can be dangerous since pyrrole might indeed adopt structure **4a**, but on incorporating the benzo group by using indole, the other isomer might then become the more stable form.

The formation of cluster **4** requires hydrogen atoms to be shifted from the 1- and the 2-positions of pyrrole to the metal atoms to form a hydride and to the 3-position of the ring, respectively. We believe that this process cannot involve the μ,η^2-pyrrolyl cluster $[Os_3H(\mu,\eta^2\text{-}C{=}CHCH{=}CH{=}NH)(CO)_{10}]$ (**6**) (Scheme III), since this is almost certainly the intermediate in the decarbonylation of **1** to give **2** initially and then **3** by isomerization. Cluster **6** closely relates to the known furanyl cluster $[Os_3H(\mu,\eta^2\text{-}C{=}CHCH{=}CHO)(CO)_9]$, which has been shown to convert to the furan analogue of **2**.[23] Cluster **4** was not detected as a product in the decarbonylation of **1** but was only observed to be formed in the direct reaction of $[Os_3(CO)_{12}]$ with pyrrole. Scheme III contains a proposed route for its formation. We believe that **4** is formed as a results of oxidative addition of pyrrole with N-H cleavage in contrast to the C-H cleavage which leads to **2** and **3**. Various hydrogen-transfer reactions could lead to either **4a** or **4b**. Clearly many of the details of this are speculative, and it is possible but we feel unlikely that the unstable tautomers A or B (Figure 1) are in sufficient concentration in equilibrium with pyrrole to react directly and competitively with pyrrole itself.

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Registry No. **1**, 109464-84-8; **2**, 85159-46-2; **3**, 109464-89-3; **4**, 122651-44-9; $[Os_3(CO)_{12}]$, 15696-40-9; $[Os_3(CO)_{10}(MeCN)_2]$, 61817-93-4; pyrrole, 109-97-7; 2-formylpyrrole, 1003-29-8.

Supplementary Material Available: Tables of anisotropic displacement factors and least-squares planes for **1**, **3**, and **4** (8 pages); listings of observed and calculated structure factors (94 pages). Ordering information is given on any current masthead page.

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Carbon-Oxygen Bond Formation on Rhodium Centers. Synthesis, Characterization, Crystal Structure, and Reactions of *trans*-PhORh(CO)$(PPh_3)_2$

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The synthesis of a rhodium phenoxide is reported. The complex *trans*-PhORh(CO)$(PPh_3)_2$ crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with a = 15.794 (3) Å, b = 11.449 (2) Å, c = 20.025 (3) Å, β = 100.220 (13)°, V = 3562 (1) $Å^3$, and Z = 4. Diffraction data (Mo Kα, 2θ = 4.5-50.0°) were collected with a Syntex $P2_1$ diffractometer, and the structure was refined to R_F = 2.8% for 5293 reflections. The structure is isomorphous with the iridium analogue. Important dimensions include Rh-P = 2.337 (1)-2.357 (1) Å, Rh-CO = 1.801 (3) Å, Rh-OPh = 2.044 (2) Å, and Rh-O-C(phenoxide) = 125.52 (19)°. This complex reacts with $Ph_2CHC(O)Cl$ to give the ester $Ph_2CHC(O)OPh$ and with MeI to give anisole, PhOMe. The formation of anisole from the rhodium phenoxide is in contrast to the failure to eliminate ethers from similar iridium complexes and is consistent with the known preference for elimination from second-row (rather than third-row) transition-metal complexes.

Carbon-oxygen bond formation is important in several catalytic reactions.[2-5] A few reports of the stoichiometric formation of esters from reactions of acyl sources with alkoxy complexes have appeared.[6-9] In this paper we show