

donor species during their preparation or, furthermore, in biological fluids, as is the case of immunological reactions, may discourage their use.

No chemical differences were observed when the acidity of the carboxyl-substituted catechol was varied or when the amine-substituted catechol was used as the chelating ligand. Therefore, the series of platinum *o*-catecholates may be an interesting source for an investigation on the only immunological changes in a series of similar metallo antigens.

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Registry No. 1, 73296-00-1; 2, 73296-01-2; 3, 73296-02-3; 4, 73308-29-9; 5, 73296-03-4; 6, 73296-04-5; 7, 73296-05-6; 8,

73296-06-7; 9, 73296-07-8; 10, 73296-08-9; 11, 73296-09-0; 12, 73308-30-2; 13, 73296-10-3; 14, 73296-11-4; 15, 73296-12-5; 16, 73296-13-6; 17, 73296-14-7; 18, 73296-15-8; 19, 73296-16-9; 20, 73296-17-0; 21, 73296-46-5; 22, 73296-47-6; 23, 73296-48-7; 24, 73296-49-8; Pd(1,2-O₂C₆H₃-4-CO₂N(COCH₂CH₂CO))(PPh₃)₂, 73296-50-1; Pd(1,2-O₂C₆H₃-4-CH₂CO₂N(COCH₂CH₂CO))(PPh₃)₂, 73323-94-1; Pd(1,2-O₂C₆H₃-4-CH₂CH₂CO₂N(COCH₂CH₂CO))(PPh₃)₂, 73296-51-2; Pt(1,2-O₂C₆H₃-4-CO₂N(COCH₂CH₂CO))(PPh₃)₂, 73296-52-3; Pt(1,2-O₂C₆H₃-4-CH₂CO₂N(COCH₂CH₂CO))(PPh₃)₂, 73296-53-4; Pt(1,2-O₂C₆H₃-4-CH₂CH₂CO₂N(COCH₂CH₂CO))(PPh₃)₂, 73296-54-5; CH₃CH₂C-H₂NH₂, 107-10-8; PhCH₂NH₂, 100-46-9; NHS, 6066-82-6; 1-[(phenylacetyl)oxy]-2,5-pyrrolidinedione, 23776-85-4; Pt(bpy)Cl₂, 13965-31-6; Pt(COD)Cl₂, 12080-32-9; Pd(PPh₃)₂Cl₂, 15604-37-2; Pt(PPh₃)₂Cl₂, 15604-36-1.

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Reactions of Imines with $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$. Competitive Addition and Abstraction of Hydrogen Atoms to and from an Iminyl Group

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$(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ was found to react with $\text{C}_6\text{H}_5(\text{H})\text{C}=\text{NCH}_3$ in refluxing hexanes solution to produce the compounds $(\mu\text{-H})_2(\mu\text{-N}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_4)\text{Os}_3(\text{CO})_9$, A, and $(\mu\text{-H})(\mu\text{-}\eta^2\text{-C}_6\text{H}_5\text{C}=\text{NCH}_3)\text{Os}_3(\text{CO})_{10}$, B. A has been studied by IR, ¹H NMR, and X-ray crystallographic analyses. Crystal data: space group *Pbca* (*D*_{2h}¹⁵, No. 61; *a* = 13.198 (4), *b* = 21.254 (6), *c* = 15.129 (5) Å, *V* = 4244 (4) Å³, mol wt 943.88; *Z* = 8; ρ_{calcd} = 2.95 g cm⁻³. For 2228 reflections ($F^2 \geq 3.0\sigma(F^2)$), collected by counter techniques, *R*₁ = 0.052 and *R*₂ = 0.057. A contains a triangular cluster of osmium atoms, nine terminal carbonyl ligands, two bridging hydride ligands, and a $\mu\text{-N}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_4$ ligand which bridges an *edge* of the cluster through the nitrogen atom and contains an ortho-metalated phenyl ring. The complex was evidently formed by the addition of one molecule of imine to the cluster, transfer of one hydrogen atom from the cluster to the iminyl group, loss of a carbonyl ligand, and ortho metalation of the phenyl ring. B was apparently formed by addition of the imine to the cluster, abstraction of a hydrogen atom from the iminyl carbon, and loss of H₂ from the cluster.

Introduction

The cluster hydride complex $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ has now been shown to react and transfer hydrogen to a variety of unsaturated small molecules including alkenes,² alkynes,³ carbon disulfide,⁴ isocyanides,⁵ arylisocyanates and isothiocyanates,⁶ ketene,⁷ and methylene.⁸ We have presented evidence that indicates the hydrogen transfer can occur by either intramolecular or dissociative processes.⁵ $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ ^{9,10} and $\text{Os}_3(\text{CO})_{12}$ ^{8,11,12} have also been shown to abstract hydrogen atoms readily from alkyl groups. It appears that there may be a delicate balance between hydrogen addition and hydrogen abstraction reactions in the chemistry of triosmium cluster compounds.

Imines are potential products of isocyanide reductions; thus in connection with our earlier work⁵ we have investigated the

nature of the reaction of imines with $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$. In this paper we wish to present the results of our studies of the reaction of the imine $\text{C}_6\text{H}_5(\text{H})\text{C}=\text{NCH}_3$ with $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$. In this system we have found that both addition and abstraction reactions are important processes.

Experimental Section

Reactions were performed under a nitrogen atmosphere. Solvents were dried by refluxing over sodium-benzophenone and distilling just prior to use. $\text{H}_2\text{Os}_3(\text{CO})_{10}$ was prepared by the method of Kaesz.¹³ $\text{C}_6\text{H}_5(\text{H})\text{C}=\text{NCH}_3$ was obtained commercially and vacuum distilled prior to use. $\text{Os}_3(\text{CO})_{12}$ was obtained from Strem Chemicals Inc., Newburyport, Mass., and was used without further purification. Infrared spectra were recorded on a Perkin-Elmer 237 spectrometer and were calibrated with polystyrene. ¹H NMR spectra were recorded at the Southern New England High-Field NMR facility operating at 270 MHz. Melting points were obtained on a Thomas-Hoover melting point apparatus and are uncorrected.

Reaction of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ with $\text{C}_6\text{H}_5\text{CH}=\text{NCH}_3$. $\text{H}_2\text{Os}_3(\text{CO})_{10}$ (0.296 g, 0.347 mmol), $\text{C}_6\text{H}_5\text{CH}=\text{NCH}_3$ (0.6 mL), and hexanes (40 mL) were stirred at reflux for 18 h. After being cooled to room temperature, the yellow solution was decanted and the residue (containing largely $\text{Os}_3(\text{CO})_{12}$, 11.6 mg, 4%) was rinsed with ca. 20 mL of benzene. The combined supernatant and washings were chromatographed over silica gel. Hexanes eluted a yellow band which yielded 121.2 mg (36%) of $(\mu\text{-H})(\mu\text{-}\eta^2\text{-C}_6\text{H}_5\text{C}=\text{NCH}_3)\text{Os}_3(\text{CO})_{10}$, B. Benzene eluted a yellow band which gave 42.0 mg (13%) of $(\mu\text{-H})_2(\mu\text{-N}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_4)\text{Os}_3(\text{CO})_9$, A, as yellow crystals. A third band, eluted by THF, gave $\text{Os}_3(\text{CO})_{12}$ (1 mg, 0.33%), benzaldehyde,

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Table I. Experimental Data for X-ray Diffraction Study of $(\mu\text{-H})_2(\mu\text{-N}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_4)\text{Os}_3(\text{CO})_9$

(A) Crystal Parameters at 26 (2) °C	
space group: $Pbca$, No. 61 (D_{2h}^{15})	$V = 4244$ (4) Å ³
$a = 13.198$ (4) Å	$Z = 8$
$b = 21.254$ (6) Å	mol wt 943.88
$c = 15.129$ (5) Å	$\rho_{\text{calcd}} = 2.95$ g cm ⁻³

(B) Measurement of Intensity Data	
radiation: Mo K α , $\lambda = 0.710$ 73 Å	
monochromator: graphite	
takeoff angle: 2.5°	
detector aperture: horizontal, $A + B \tan \theta$ ($A = 3.0$ mm, $B = 1.0$ mm); vertical, 4.0 mm	
cryst-detector distance: 330 mm	
cryst orientation: normal to 111 plane 8.3° for ϕ axis	
rflectns measd: $+h, +k, +l$	
max 2θ : 52°	
scan type: moving crystal-stationary counter	
scan speed (variable): max $\theta = 10^\circ/\text{min}$, min $\theta = 1.2^\circ/\text{min}$	
θ scan width: $0.7^\circ + 0.347 \tan \theta^\circ$ on each side of calcd position	
bkgd: $1/4$ additional scan at each end of scan	
std rflctns: 3 measd after approx each of the 60 data reflections showed only random fluctuation of $\pm 2\%$	
rflectns measd: 4590 including absences	
data used ($F^2 \geq 3.0\sigma(F^2)$): 2228 rflctns	

(C) Treatment of Data	
abs coeff: $\mu = 191.1$ cm ⁻¹	
grid: $8 \times 8 \times 14$	
transmission factors: max 0.130, min 0.0505	
ignorance factor: $p = 0.02$	

and uncharacterized brown products. For A, IR (in CH_2Cl_2) 2115 (m), 2060 (s), 2030 (sh), 2025 (vs), 1975 (w), 1940 (m) cm⁻¹; mp 172–173 °C.

Thermolyses of A and B. Complex A (37.6 mg) and octane (40 mL) were heated to reflux for 24 h. The solvent was removed in vacuo, and the solid residue was dissolved in CDCl_3 and examined by ¹H NMR. The hydride region showed three peaks at δ -11.2 ($\text{H}_2\text{Os}_3(\text{CO})_{10}$), -17.7, and -18.2 (unidentified). No detectable amount of complex B was found.

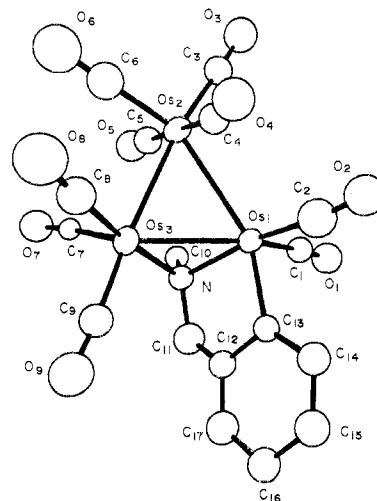
Complex B was recovered unchanged after 42 h in refluxing octane.

Crystallographic Analysis. General Data. All diffraction measurements were performed on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer by using graphite-monochromatized Mo K α radiation. The unit cell was determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index, and least-squares routines. The space group, $Pbca$, was determined from the systematic absences $0kl, k = 2n + 1; h0l, l = 2n + 1$, and $hk0, h = 2n + 1$, observed during data collection.

Crystal Data. All calculations were performed on a Digital PDP 11/45 computer using the Enraf-Nonius SDP program library. Anomalous dispersion corrections^{14a} were added to the neutral atom scattering factors^{14b} used for all nonhydrogen atoms. Least-squares refinements minimized the function $\sum_{hkl} w(F_o - F_c)^2$ where the weighting factor $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_c^2) = [\sigma(I_{\text{mw}})^2 + (pF_c^2)^2]^{1/2}/Lp$. Crystal data and data collection parameters are listed in Table I.

Crystals of $(\mu\text{-H})_2(\mu\text{-N}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_4)\text{Os}_3(\text{CO})_9$ were grown from solutions in hexanes solvent by cooling to -20 °C. A pyramidal-shaped crystal with dimensions 0.233 mm \times 0.23 mm \times 0.24 mm was mounted in a thin-walled glass capillary. The crystal faces were subsequently identified as 011, 0 $\bar{1}\bar{1}$, 110, $\bar{1}\bar{1}0$, 010, 0 $\bar{1}0$, 101, $\bar{1}0\bar{1}$, and $1\bar{1}0$. Of the 4590 reflections which were measured, 2228 ($F^2 \geq 3.2\sigma(F^2)$) were used in the subsequent structure solution and refinement. The linear absorption coefficient is 191.1 cm⁻¹. The data were corrected for absorption by using the Gaussian integration method.

Structure Solution. The structure was solved by a combination of Patterson and difference Fourier techniques. Full-matrix least-squares refinement using anisotropic thermal parameters for the osmium atoms

**Figure 1.** A perspective ORTEP diagram of $(\mu\text{-H})_2(\mu\text{-N}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_4)(\text{CO})_9$, showing 50% probability ellipsoids.

and isotropic thermal parameters for the remaining nonhydrogen atoms converged to the final residuals $R_1 = 0.052$ and $R_2 = 0.057$. Methylene (H(1) and H(2)) and phenyl (H(14)–H(17)) hydrogen atom positions were calculated by using idealized tetrahedral or planar C_6H_6 geometry. Neither hydride ligands nor methyl group hydrogen atoms were located, and no attempt to place them artificially was made. Comparison of F_o and F_c for intense low-angle data indicated 12 reflections were suffering from extinction effects. These were deleted from the data set. The largest value of the shift/error parameter on the final cycle of refinement was 0.08. The error in an observation of unit weight was 2.71. The largest peaks in a final difference Fourier synthesis were 2.1–2.2 e/Å³ and were clustered about the metal atoms. Final fractional atomic coordinates are listed in Table II. Bond distances and angles with estimated standard deviations determined from the inverse matrix obtained on the final cycle of least-squares refinement are listed in Tables III and IV. A table of final structure factor amplitudes is available (see supplementary material).

Results

$\text{H}_2\text{Os}_3(\text{CO})_{10}$ was found to react with $\text{C}_6\text{H}_5(\text{H})\text{C}=\text{NCH}_3$ in refluxing hexane to produce the compound $(\mu\text{-H})_2(\mu\text{-N}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_4)\text{Os}_3(\text{CO})_9$, A (13% yield), and $(\mu\text{-H})(\mu\text{-}\eta^2\text{-C}_6\text{H}_5\text{C}=\text{NCH}_3)\text{Os}_3(\text{CO})_{10}$, B (36% yield). The ¹H NMR spectrum of A in CDCl_3 showed a methylene resonance at δ 3.99 and an AB quartet, δ 4.52 and 4.29, $J_{\text{AB}} = 15.9$ Hz, of intensity two which indicated the presence of a methylene group with inequivalent protons. The phenyl ring, δ 7.02–7.81, of intensity four suggested that metalation of one of the aromatic C–H bonds had occurred. Metal hydride resonances were observed at -12.50 and -16.04 ppm each with an intensity of one. The details of the molecular structure of A were established crystallographically and are described below.

Complex B has been observed previously as a product of the reaction of $\text{Os}_3(\text{CO})_{12}$ with $\text{C}_6\text{H}_5(\text{H})\text{C}=\text{NCH}_3$ ¹¹ and has been structurally characterized.¹⁵ In this work B was characterized spectroscopically through comparison with authentic material.¹¹

Solutions of A and B have been thermolyzed independently, and there were no spectroscopically detectable quantities of B produced from the solutions of A and vice versa.

Description of the Structure

The molecular structure of $(\mu\text{-H})_2(\mu\text{-N}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_4)\text{Os}_3(\text{CO})_9$ is shown in Figure 1. The molecule consists of a triangular cluster of mutually bonded osmium atoms, nine terminal carbonyl ligands and a $\mu\text{-N}(\text{CH}_3)(\text{CH}_2\text{C}_6\text{H}_4)$ amido ligand. The Os_3 triangle is significantly distorted and has one long bond, $\text{Os}(1)\text{-Os}(2) = 3.117$ (1) Å, one short bond, $\text{Os}(1)\text{-Os}(3) = 2.517$ (1) Å, and one intermediate bond, $\text{Os}(2)\text{-Os}(3) = 2.517$ (1) Å.

(14) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975; Vol. IV: (a) Table 2.3.1, pp 149–150; (b) Table 2.2B, pp 99–101.

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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $(\mu\text{-H})(\mu\text{-N}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_4)\text{Os}_3(\text{CO})_9$

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> , Å ²	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> , Å ²
Os(1)	0.21467 (7)	-0.06668 (4)	0.04267 (7)	<i>a</i>	C(6)	0.142 (2)	-0.196 (1)	-0.209 (2)	5.0 (7)
Os(2)	0.17150 (8)	-0.12111 (5)	-0.14491 (7)	<i>a</i>	C(7)	0.369 (2)	-0.222 (1)	-0.080 (2)	2.6 (5)
Os(3)	0.27196 (7)	-0.19008 (4)	-0.00336 (7)	<i>a</i>	C(8)	0.176 (2)	-0.252 (1)	-0.023 (2)	4.1 (6)
O(1)	0.277 (1)	0.0687 (9)	0.059 (1)	5.5 (4)	C(9)	0.320 (2)	-0.233 (1)	0.095 (2)	3.8 (6)
O(2)	0.001 (1)	-0.0274 (9)	0.093 (1)	5.1 (5)	C(10)	0.433 (2)	-0.082 (1)	-0.041 (2)	3.1 (5)
O(3)	0.065 (1)	-0.0321 (9)	-0.274 (1)	5.6 (5)	C(11)	0.417 (2)	-0.106 (1)	0.116 (2)	3.5 (5)
O(4)	-0.026 (1)	-0.1432 (10)	-0.044 (2)	5.5 (5)	C(12)	0.347 (2)	-0.104 (1)	0.191 (2)	3.2 (5)
O(5)	0.371 (2)	-0.1113 (9)	-0.252 (2)	5.7 (5)	C(13)	0.250 (2)	-0.078 (1)	0.177 (2)	3.0 (5)
O(6)	0.124 (2)	-0.2417 (11)	-0.246 (2)	7.4 (6)	C(14)	0.181 (2)	-0.071 (1)	0.252 (2)	3.9 (5)
O(7)	0.435 (1)	-0.2426 (10)	-0.126 (1)	5.6 (5)	C(15)	0.215 (2)	-0.088 (1)	0.333 (2)	4.0 (6)
O(8)	0.111 (2)	-0.2902 (10)	-0.035 (2)	6.3 (5)	C(16)	0.307 (2)	-0.115 (1)	0.347 (2)	3.7 (5)
O(9)	0.342 (1)	-0.2635 (10)	0.159 (2)	6.1 (5)	C(17)	0.373 (2)	-0.122 (1)	0.278 (2)	4.0 (6)
N	0.360 (1)	-0.1091 (9)	0.029 (1)	2.8 (4)	H(1) ^b	0.462	-0.074	0.121	6.0
C(1)	0.254 (2)	0.017 (1)	0.047 (2)	3.3 (5)	H(2)	0.455	-0.147	0.125	6.0
C(2)	0.087 (2)	-0.043 (1)	0.068 (2)	5.2 (7)	H(14)	0.111	-0.054	0.243	6.0
C(3)	0.106 (2)	-0.065 (1)	-0.225 (2)	3.9 (5)	H(15)	0.171	-0.080	0.382	6.0
C(4)	0.052 (2)	-0.132 (1)	-0.077 (2)	4.1 (6)	H(16)	0.328	-0.126	0.408	6.0
C(5)	0.294 (2)	-0.114 (1)	-0.211 (2)	4.5 (6)	H(17)	0.439	-0.140	0.287	6.0
		<i>B</i> (1,1)	<i>B</i> (2,2)	<i>B</i> (3,3)	<i>B</i> (1,2)	<i>B</i> (1,3)	<i>B</i> (2,3)		
Os(1)		3.07 (3)	2.61 (3)	2.27 (3)	0.20 (4)	-0.01 (4)	-0.05 (4)		
Os(2)		3.28 (4)	3.41 (4)	2.41 (4)	-0.37 (4)	0.12 (4)	-0.31 (4)		
Os(3)		3.17 (3)	2.35 (3)	3.11 (4)	-0.15 (4)	0.24 (4)	-0.23 (4)		

^a Anisotropic thermal parameters are listed in the second half of the table. The form of the anisotropic temperature factor is $\exp[-1/4 \cdot (B(1,1)h^2a^{*2} + B(2,2)k^2b^{*2} + B(3,3)l^2c^{*2} + B(1,2)hka^*b^* + B(1,3)hla^*c^* + B(2,3)klb^*c^*)]$. ^b Hydrogen atom positions were calculated and not refined.

Table III. Bond Distances (Å) with Estimated Standard Deviations for $(\mu\text{-H})_2(\mu\text{-N}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_4)\text{Os}_3(\text{CO})_9$

Os(1)-Os(2)	3.117 (1)	C(11)-C(12)	1.46 (2)
Os(1)-Os(3)	2.817 (1)	C(12)-C(13)	1.41 (2)
Os(2)-Os(3)	2.914 (1)	C(13)-C(14)	1.46 (2)
Os(1)-C(1)	1.85 (1)	C(14)-C(15)	1.35 (2)
Os(1)-C(2)	1.80 (2)	C(15)-C(16)	1.36 (2)
Os(1)-N	2.13 (1)	C(16)-C(17)	1.36 (2)
Os(1)-C(13)	2.11 (2)	C(17)-C(12)	1.42 (2)
Os(2)-C(3)	1.91 (2)	C(1)-O(1)	1.16 (2)
Os(2)-C(4)	1.89 (2)	C(2)-O(2)	1.24 (2)
Os(2)-C(5)	1.91 (2)	C(3)-O(3)	1.15 (2)
Os(2)-C(6)	1.90 (2)	C(4)-O(4)	1.18 (2)
Os(3)-C(7)	1.86 (1)	C(5)-O(5)	1.19 (2)
Os(3)-C(8)	1.86 (2)	C(6)-O(6)	1.15 (2)
Os(3)-C(9)	1.86 (2)	C(7)-O(7)	1.19 (2)
Os(3)-N	2.13 (1)	C(8)-O(8)	1.19 (2)
N-C(10)	1.54 (2)	C(9)-O(9)	1.20 (2)
N-C(11)	1.52 (2)		

(1)-Os(3) = 2.817 (1) Å, and one fairly normal bond, Os(2)-Os(3) = 2.914 (1) Å. The last compares favorably with the distance 2.877 (3) Å which is the average metal-metal bond length in $\text{Os}_3(\text{CO})_{12}$.¹⁶

The nitrogen atom of the amido ligand symmetrically bridges the Os(1)-Os(3) edge of the cluster, Os(1)-N = 2.13 (1) Å and Os(3)-N = 2.13 (1) Å. It is 1.46 (2) Å out of the trismium plane and produces a dihedral angle of 65.9° between the Os(1)-Os(2)-Os(3) and Os(1)-N-Os(3) planes. The shortness of the Os(1)-Os(3) bond can be attributed to the presence of the single bridging atom. Similar shortenings have been observed in the compounds $(\mu\text{-H})(\mu\text{-CHCH}_2\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5)\text{Os}_3(\text{CO})_{10}$,¹⁷ $(\mu\text{-H})(\mu\text{-CHCH}=\text{N}(\text{C}_2\text{H}_5)_2)\text{Os}_3(\text{CO})_{10}$,¹⁸ $(\mu\text{-H})_2(\mu\text{-CH}_2)\text{Os}_3(\text{CO})_{10}$,¹⁹ and $(\mu\text{-H})(\mu\text{-C}=\text{N}(\text{H})(t\text{-C}_4\text{H}_9))\text{Os}_3(\text{CO})_{10}$,²⁰ each of which contains a ligand bridging an Os-Os bond through a single carbon atom. An ortho-metalated phenyl ring is bonded to Os(1) and produces the five-membered chelate ring, Os(1)-N-C(11)-C(12)-C-

Table IV. Bond Angles (Deg) with Estimated Standard Deviations for $(\mu\text{-H})_2(\mu\text{-N}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_4)\text{Os}_3(\text{CO})_9$

Os(2)-Os(1)-Os(3)	58.56 (2)	Os(2)-Os(3)-C(7)	92.1 (5)
Os(1)-Os(2)-Os(3)	55.57 (2)	Os(2)-Os(3)-C(8)	85.7 (5)
Os(1)-Os(3)-Os(2)	65.87 (2)	Os(2)-Os(3)-C(9)	172.5 (5)
Os(2)-Os(1)-C(1)	115.9 (5)	Os(2)-Os(3)-N	90.6 (3)
Os(2)-Os(1)-C(2)	97.3 (7)	C(7)-Os(3)-C(8)	96.1 (7)
Os(2)-Os(1)-C(13)	151.6 (4)	C(7)-Os(3)-C(9)	94.9 (7)
Os(2)-Os(1)-N	85.3 (3)	C(7)-Os(3)-N	93.8 (5)
Os(3)-Os(1)-C(1)	145.6 (5)	C(8)-Os(3)-C(9)	91.0 (7)
Os(3)-Os(1)-C(2)	124.2 (6)	C(8)-Os(3)-N	169.6 (6)
Os(3)-Os(1)-C(13)	94.2 (4)	C(9)-Os(3)-N	91.5 (6)
Os(3)-Os(1)-N	48.7 (3)	Os(1)-N-Os(3)	82.6 (4)
C(1)-Os(1)-C(2)	89.6 (7)	Os(1)-N-C(10)	118.1 (9)
C(1)-Os(1)-C(13)	90.9 (6)	Os(1)-N-C(11)	109.9 (9)
C(1)-Os(1)-N	98.9 (5)	Os(3)-N-C(10)	119.5 (9)
C(2)-Os(1)-C(13)	91.7 (8)	Os(3)-N-C(11)	119.8 (9)
C(2)-Os(1)-N	169.1 (7)	C(10)-N-C(11)	105.8 (11)
C(13)-Os(1)-N	81.3 (5)	N-C(11)-C(12)	111.8 (12)
Os(1)-Os(2)-C(3)	115.2 (5)	C(11)-C(12)-C(17)	124.0 (14)
Os(1)-Os(2)-C(4)	72.6 (5)	C(11)-C(12)-C(13)	118.6 (14)
Os(1)-Os(2)-C(5)	107.2 (5)	C(12)-C(13)-C(14)	119.8 (14)
Os(1)-Os(2)-C(6)	144.3 (6)	C(13)-C(14)-C(15)	118.0 (15)
Os(3)-Os(2)-C(3)	170.8 (5)	C(14)-C(15)-C(16)	122.8 (17)
Os(3)-Os(2)-C(4)	85.4 (5)	C(15)-C(16)-C(17)	120.6 (17)
Os(3)-Os(2)-C(5)	92.2 (5)	C(16)-C(17)-C(12)	121.3 (15)
Os(3)-Os(2)-C(6)	92.7 (6)	Os(1)-C(13)-C(12)	112.5 (11)
C(3)-Os(2)-C(4)	92.4 (7)	Os(1)-C(13)-C(14)	127.1 (11)
C(3)-Os(2)-C(5)	90.2 (7)	Os(1)-C(1)-O(1)	172 (2)
C(3)-Os(2)-C(6)	96.3 (8)	Os(1)-C(2)-O(2)	175 (2)
C(4)-Os(2)-C(5)	177.2 (7)	Os(2)-C(3)-O(3)	178 (2)
C(4)-Os(2)-C(6)	90.5 (8)	Os(2)-C(4)-O(4)	171 (2)
C(5)-Os(2)-C(6)	88.1 (8)	Os(2)-C(5)-O(5)	179 (2)
Os(1)-Os(3)-C(7)	133.1 (4)	Os(2)-C(6)-O(6)	179 (2)
Os(1)-Os(3)-C(8)	121.1 (5)	Os(3)-C(7)-O(7)	176 (1)
Os(1)-Os(3)-C(9)	110.6 (5)	Os(3)-C(8)-O(8)	177 (1)
Os(1)-Os(3)-N	48.6 (3)	Os(3)-C(9)-O(9)	174 (2)

(13). The metalated carbon atom C(13) occupies an equatorial coordination site in the plane of the Os_3 triangle. That C(11) is indeed a methylene group is strongly indicated by the ¹H NMR spectrum (vide supra) but also supported by the structure analysis which shows the N-C(11) bond distance at 1.52 (2) Å is very similar to the aliphatic N-C(10) distance of 1.54 (2) Å.

The hydride ligands were not observed crystallographically, but the ¹H NMR spectrum indicated that two are present.

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Table V

Unit Weighted Least-Squares Planes for (μ -H) ₂ (μ -N(CH ₃)CH ₂ C ₆ H ₄)Os ₃ (CO) ₉			
plane	atoms	dist from plane, Å	
1	Os(1)	0.00	
	Os(2)	0.00	
	Os(3)	0.00	
	N ^a	1.46 (2)	
	C(11) ^a	1.72 (2)	
	C(12) ^a	0.58 (2)	
	C(13) ^a	-0.32 (2)	
	2	Os(1)	0.00
		Os(3)	0.00
		N	0.00
C(10) ^a		1.18 (3)	
C(11) ^a		-1.25 (3)	
Os(2) ^a		2.427 (1)	
3		C(12)	-0.01 (2)
		C(13)	0.00 (2)
		C(14)	0.02 (3)
		C(15)	-0.02 (3)
	C(16)	0.01 (3)	
	C(17)	0.01 (3)	
	N ^a	0.44 (2)	
	C(11) ^a	-0.11 (3)	
	4	N	-0.14 (2)
		C(11)	0.16 (2)
C(12)		-0.09 (2)	
C(13)		-0.01 (2)	
Os(1)		0.067 (1)	
C(10) ^a		0.73 (2)	
Os(3) ^a		-2.150 (1)	

Dihedral Angles between Planes

planes	angle, deg	planes	angle, deg
1-2	65.9	2-3	85.1
1-3	54.3	2-4	75.4
1-4	51.9	3-4	9.9

Equations of Planes: $Ax + By + Cz - D = 0$

plane	A	B	C	D
1	0.8859	0.3394	-0.3164	1.8249
2	0.0169	0.2611	-0.9652	-0.9453
3	-0.3683	-0.9147	-0.1661	-0.1426
4	0.3354	0.9421	-0.0003	-0.4517

^a These atoms were not used in the calculation of the plane.

One most probably bridges the Os(1)-Os(3) bond in a conspicuous cavity circumscribed by the carbonyl ligands C(2)-O(2), C(8)-O(8), and C(9)-O(9) and atom C(13) of the metallated ring. Hydride ligands have been found in similar positions in several related molecules.^{17-19,21} The other hydride ligand is probably also a bridging type and most likely straddles the Os(1)-Os(2) bond. This conclusion is based on consideration of the distortions in the Os₃ triangle and carbonyl positions. For example, it is well-known that hydride ligands bridging unsupported metal-metal bonds produce bond lengthening effects of 0.1-0.2 Å.^{21,22} The Os(1)-Os(2) bond distance is 0.203 Å longer than the Os(2)-Os(3) bond and the latter compares favorably with that of a normal osmium-osmium single bond. Furthermore, the equatorial carbonyl ligands on Os(2) exhibit a pronounced bending away from the Os(1)-Os(2) bond. The Os(1)-Os(2)-C(3) angle is 115.2 (5)° while the corresponding angle along the Os(2)-Os(3) bond, Os(3)-Os(2)-C(6), is only 92.7 (6)°. These distortions are very similar to those observed in the molecule (μ -H)(μ -CH₂)Os₃(CO)₁₀ where an analogous arrangement of hydride ligands was confirmed through a neutron diffraction study.¹⁹ Overall, the molecule contains nine linear carbonyl groups

Table VI. Intermolecular Contacts (Å) for (μ -H)₂(μ -N(CH₃)CH₂C₆H₄)Os₃(CO)₉ at Less Than 3.5 Å^a

O(1)···O(1) ^I	3.36	O(3)···C(17) ^V	3.47
O(1)···C(15) ^{II}	3.45	C(3)···O(5) ^V	3.28
O(2)···O(2) ^{III}	3.05	O(4)···O(5) ^V	3.44
O(2)···C(2) ^{III}	3.09	O(4)···O(9) ^{VI}	3.16
O(2)···O(3) ^{III}	3.14	O(4)···C(9) ^{VI}	3.41
O(2)···C(3) ^{III}	3.13	O(5)···O(9) ^{VII}	3.01
O(2)···C(16) ^{IV}	3.29	C(5)···O(9) ^{VII}	3.32
O(2)···C(17) ^{IV}	3.27	O(6)···O(7) ^V	3.16
O(3)···O(5) ^V	3.10	O(6)···O(9) ^{VII}	3.22
O(3)···C(10) ^V	3.47	C(6)···O(9) ^{VII}	3.42
O(3)···C(11) ^{II}	3.39	O(7)···O(8) ^{VIII}	3.43
O(3)···C(12) ^{II}	3.15	O(7)···O(9) ^{VII}	3.49
O(3)···C(13) ^{II}	3.46	O(7)···C(16) ^{VII}	3.49
		O(7)···C(17) ^{VII}	3.32

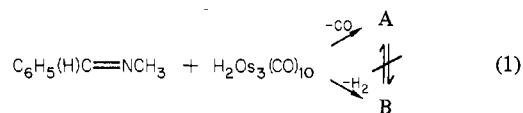
^a Symmetry transforms: (I) $1/2 - x, -y, 1/2 + z$; (II) $1/2 - x, -y, z - 1/2$; (III) $-x, -y, -z$; (IV) $x - 1/2, -y, 1/2 + z$; (V) $x - 1/2, -y, -z$; (VI) $x - 1/2, -y - 1/2, -z$; (VII) $x, -y - 1/2, z - 1/2$; (VIII) $1/2 + x, -y - 1/2, -z$. All esd's ± 0.02 Å.

arranged such that Os(1) has two, Os(2) has four, and Os(3) has three.

The crystal consists of well separated molecules. The shortest intermolecular contacts are between carbonyl oxygen atoms O(5)···O(9) = 3.01 Å and O(2)···O(2) = 3.05 Å (cf. Table VI).

Discussion

Two products, A and B, have been isolated from the reaction of C₆H₅(H)C=NCH₃ with (μ -H)₂Os₃(CO)₁₀. Both products evidently result from the addition of one molecule of imine to one cluster complex. At this point, however, two competing reactions may ensue (see eq 1). In one a hydrogen atom is



transferred to the carbon atom of the imine ligand. The nitrogen atom assumes a bridging position, and after a facile loss of one mole of carbon monoxide, the phenyl ring is ortho-metallated²³ and A is produced. It seems reasonable to expect that an intermediate, possibly (μ -H)[μ -N(CH₃)-CH₂C₆H₅]Os₃(CO)₁₀, C, could form subsequent to hydrogen transfer and prior to decarbonylation and ortho-metallation, but we have not observed it. The analogous species (μ -H)-(μ -N(H)CH₂C₆H₅)Os₃(CO)₁₀, D, has been isolated through the reaction of H₂NCH₂C₆H₅ with Os₃(CO)₁₂.²⁴ However, D is stable and will not yield to ortho-metallation of the phenyl ring. It is not clear why C would readily yield to ortho-metallation, but a form of the *gem*-dimethyl effect could be operative.²⁵ For example, it is known that in cases where H₂NCH₂C₆H₅ will not ortho-metallate, (CH₃)₂NCH₂C₆H₅ will do so rapidly.²⁶ Furthermore, it has been observed that (μ -H)(μ -OCH₂C₆H₅)Os₃(CO)₁₀ ortho-metallates with difficulty²⁴ while the methyl derivatives (μ -H)(μ -OCH(CH₃)C₆H₅)Os₃(CO)₁₀ and (μ -H)(μ -C(CH₃)₂C₆H₅) metalate with ease.²⁷ Alternatively, a hydrogen atom can be abstracted from the iminyl carbon, the cluster loses H₂ and B is produced. Triosmium clusters have been shown to activate aliphatic C-H bonds on several occasions.⁸⁻¹² Deeming et al. have shown that Os₃(CO)₁₂ can activate the C-H bonds of aldehydes⁷ and

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imines.¹¹ The harsher conditions which were required with $\text{Os}_3(\text{CO})_{12}$ are probably due to the need to activate $\text{Os}_3(\text{CO})_{12}$ through loss of CO.

From the stoichiometry of the reactions it seems unlikely that A is produced from B or vice versa and we have shown explicitly that these reactions do not occur by simple thermalolysis. It thus appears that the conditions which promote hydrogen addition to or abstraction from various unsaturated small molecules are not vastly different. In fact, one might be able to exercise a great degree of control over which reaction prevails by introducing small changes in the substituents of the substrate molecule or the ligand structure of the cluster complex.

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Registry No. A, 73193-70-1; B, 63363-66-6; $\text{H}_2\text{Os}_3(\text{CO})_{10}$, 41766-80-7; $\text{C}_6\text{H}_5\text{CH}=\text{NCH}_3$, 622-29-7.

Supplementary Material Available: A table of structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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Reactions of α,β -Unsaturated Imines with $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ Including the Dehydrogenation of an Isopropyl Group

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The unsaturated imine $(\text{CH}_3)_2\text{C}=\text{CHC}(\text{CH}_3)=\text{NC}_6\text{H}_5$ was found to react with $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ to produce the compounds $(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-}(\text{CH}_3)_2\text{CHCC}(\text{CH}_3)=\text{NC}_6\text{H}_5)\text{Os}_3(\text{CO})_9$, A, and $(\mu\text{-H})_2(\mu_3\text{-}\eta^4\text{-CH}_2\text{C}(\text{CH}_3)\text{CC}(\text{CH}_3)=\text{NC}_6\text{H}_5)\text{Os}_3(\text{CO})_8$, B. Both products have been characterized crystallographically by using diffractometer data. For A, the space group is $P2_1/c$ (C_{2h}^2), No. 14, with $a = 14.818$ (5) Å, $b = 9.051$ (5) Å, $c = 20.098$ (6) Å, $\beta = 108.45$ (3)°, $Z = 4$, and $\rho_{\text{calcd}} = 2.59$ g/cm³. The structure was solved by the heavy-atom method and refined to the final residuals $R_1 = 0.058$ and $R_2 = 0.067$. For B, the space group is $P2_1/c$ (C_{2h}^2), No. 14, with $a = 16.060$ (5) Å, $b = 8.820$ (4) Å, $c = 16.809$ (4) Å, $\beta = 93.83$ (2)°, $Z = 4$, and $\rho_{\text{calcd}} = 2.703$ g/cm³. This structure was also solved by the heavy-atom method and refined to the final residuals $R_1 = 0.037$ and $R_2 = 0.041$. A contains a $\mu_3\text{-}\eta^2\text{-}(\text{CH}_3)_2\text{CHCC}(\text{CH}_3)=\text{NC}_6\text{H}_5$ ligand bridging one face of a triangular cluster of osmium atoms. The nitrogen atom is terminally bonded to one osmium atom while the α -carbon serves as a bridge across the two remaining osmium atoms. The hydrogen atom on the α -carbon has been removed, and one has been added to the β -carbon, thus forming an isopropyl group. B contains a $\mu_3\text{-}\eta^4\text{-CH}_2\text{C}(\text{CH}_3)\text{CC}(\text{CH}_3)=\text{NC}_6\text{H}_5$ ligand bridging one face of a triangular cluster of osmium atoms. A terminally coordinated nitrogen atom is again bonded to one osmium atom. The α -carbon bridges the two remaining osmium atoms. The α - and γ -carbon atoms have each lost one hydrogen atom. Together with the β -carbon atom they are bonded in the form of a π -allyl group to one osmium atom. A has been independently converted into B through the dehydrogenation of the isopropyl group.

Introduction

In the preceding paper we examined the reactivity of the cluster complex $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ toward an aliphatic imine.² We found that the cluster reacts with imine groups on a 1:1 basis and can either add or abstract a hydrogen atom to or from the iminyl carbon atom. In further studies we have examined the reactivity of α,β -unsaturated imines with the cluster $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$. With these imines the olefinic group could significantly influence the reactivity of the iminyl group and even participate in the reaction itself. The results of our studies of the reaction of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ with $(\text{CH}_3)_2\text{C}=\text{CHC}(\text{CH}_3)=\text{NC}_6\text{H}_5$ are reported here.

Experimental Section

$\text{Os}_3(\text{CO})_{12}$ was purchased from Strem Chemicals Inc., Newburyport, Mass., and used without further purification. The imine $\text{C}_6\text{H}_5\text{N}=\text{C}(\text{CH}_3)\text{CH}=\text{C}(\text{CH}_3)_2$ ^{3a} was prepared from mesityl oxide

and aniline in the presence of 4A molecular sieves.^{3b} $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ was prepared by the method of Kaesz.^{3c} All reactions were performed under an atmosphere of dry nitrogen. Hexanes solvent was dried by distilling from sodium-benzophenone. Infrared spectra were recorded on a Perkin-Elmer 237 spectrometer and were calibrated with polystyrene. ^1H NMR spectra were recorded on the Southern New England High-Field NMR Facility operating at 270 MHz.

Reaction of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ with $\text{C}_6\text{H}_5\text{N}=\text{C}(\text{CH}_3)\text{CH}=\text{C}(\text{CH}_3)_2$. $\text{H}_2\text{Os}_3(\text{CO})_{10}$ (90 mg, 0.11 mmol), hexanes (25 mL), and $\text{PhN}=\text{C}(\text{CH}_3)\text{CH}=\text{C}(\text{CH}_3)_2$ (0.20 mL, 1.2 mmol) were heated to reflux for 70 h. The yellow supernatant and a 5-mL CH_2Cl_2 washing of a small amount of yellow-brown precipitate were transferred to a grade II neutral alumina column. Elution with hexanes gave a mixture of $\text{Os}_3(\text{CO})_{12}$ and $(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-}(\text{CH}_3)_2\text{CHC}(\text{CH}_3)=\text{NC}_6\text{H}_5)\text{Os}_3(\text{CO})_{10}$, A. Extraction of this mixture with hexanes gave 29.0 mg (27.6%) of pure A, mp 169–740 °C. IR (hexanes): 2100 (m), 2070 (s), 2045 (s), 2010 (s), 2005 (sh), 1995 (m), 1990 (m), 1965 (m), 1960 (sh) cm^{-1} .

Elution of the column with benzene gave a mixture of $\text{Os}_3(\text{CO})_{12}$ and $(\mu\text{-H})_2(\mu_3\text{-}\eta^4\text{-CH}_2\text{C}(\text{CH}_3)\text{CC}(\text{CH}_3)=\text{NC}_6\text{H}_5)\text{Os}_3(\text{CO})_8$, B. Extraction of this mixture with 3:1 hexanes- CH_2Cl_2 gave 43.4 mg (42.5%) of B as yellow crystals, mp 142–143.5 °C. IR (hexanes): 2100 (ms), 2050 (s), 2020 (s), 2000 (s), 1995 (sh), 1980 (ms), 1972 (sh), 1970 (s) cm^{-1} .

Pyrolysis of $(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-}(\text{CH}_3)_2\text{CHC}(\text{CH}_3)=\text{NC}_6\text{H}_5)\text{Os}_3(\text{CO})_{10}$. A. Complex A (31.6 mg, 0.032 mmol) in 25 mL of hexanes was

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