

Potential models of the interactions between nitrogen-containing heterocycles and the active catalyst sites in heterogeneous hydrodenitrogenation catalysts

A. Eisenstadt, C. M. Giandomenico, M. F. Frederick, and R. M. Laine

Organometallics, **1985**, 4 (11), 2033-2039 • DOI: 10.1021/om00130a018 • Publication Date (Web): 01 May 2002

Downloaded from <http://pubs.acs.org> on April 26, 2009

More About This Article

The permalink <http://dx.doi.org/10.1021/om00130a018> provides access to:

- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article



ACS Publications
High quality. High impact.

Potential Models of the Interactions between Nitrogen-Containing Heterocycles and the Active Catalyst Sites in Heterogeneous Hydrodenitrogenation Catalysts

A. Eisenstadt, C. M. Giandomenico, M. F. Frederick, and R. M. Laine*,[†]

Organometallic Chemistry Program, SRI International, Menlo Park, California 94025, and Nicolet XRD Inc., Fremont, California

Received January 28, 1985

At present, there is no general description of the interactions between nitrogen heterocycles and the active catalyst sites in heterogeneous hydrodenitrogenation (HDN) catalysts that promote hydrogenation and then hydrogenolysis of the C–N bond. We have attempted to model such interactions through studies of the reactions of osmium and ruthenium clusters with common HDN model substrates, including quinoline, pyridine, tetrahydroquinoline (THQ), and piperidine. $\text{Os}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ with quinoline or pyridine lead to complexes of the general formula $\text{M}_3(\mu\text{-H};\mu\text{-Y})(\text{CO})_{10}$ ($\text{M} = \text{Ru}, \text{Os}$; $\text{Y} = \text{C}_9\text{H}_7\text{N}, \text{C}_9\text{H}_8\text{N}, \text{C}_5\text{H}_8\text{N}$) or $\text{M}_3(\mu\text{-H};\mu\text{-Y})_2(\text{CO})_8$ ($\text{M} = \text{Ru}, \text{Os}$; $\text{Y} = \text{C}_5\text{H}_8\text{N}, \text{C}_9\text{H}_8\text{N}$). The reactions of $\text{Os}_3(\text{CO})_{12}$ with aliphatic heterocyclic amines leads to complexes having stoichiometries of $\text{Os}_3(\mu\text{-H};\mu\text{-Y})(\text{CO})_{10}$ ($\text{Y} = \text{C}_5\text{H}_8\text{N}, \text{C}_9\text{H}_8\text{N}, \text{C}_9\text{H}_6\text{N}$), $\text{Os}_3(\mu\text{-H})_2(\mu\text{-Y})(\mu\text{-Y}')(\text{CO})_8$ ($\text{Y} = \text{C}_9\text{H}_8\text{N}, \text{Y}' = \text{C}_9\text{H}_8\text{N}$), or $\text{Os}_3(\mu\text{-H};\mu\text{-Y})_2(\text{CO})_8$ ($\text{Y} = \text{C}_9\text{H}_8\text{N}$), and when the heterocyclic amine is 1,2,3,4-tetrahydroquinoline (THQ), a small amount of free quinoline is also produced. As a general rule, both aliphatic and aromatic nitrogen heterocycles undergo α -metalation during reactions with both homogeneous and heterogeneous metal complexes or particles. In the case of osmium and ruthenium, metalation results in the formation of metallocyclobutenes even when the starting heterocycle is saturated. Thus, activation/dehydrogenation of the N–H and α -C–H bonds of secondary amines occurs readily in the systems described here. Reaction pathways for the formation of the various products and their relationships to hydrogenation and dehydrogenation catalysis are proposed.

Hydrodenitrogenation (HDN) is the catalytic process by which nitrogen is removed as ammonia from petroleum, coal, shale oil, and tar sands during refining to fuels and petrochemical feedstocks. Current HDN technology utilizes heterogeneous transition-metal catalysts, typically sulfides of Co and Mo (CoMo) or Ni and Mo (NiMo) supported on alumina. The process is energy intensive and consumes H_2 in undesirable hydrogenation reactions that reduce the energy yield of the refined product.^{1–5} Consequently, there is an ongoing interest in understanding and improving this process. Recent literature examines HDN catalysis for nitrogen-containing model compounds such as pyridine/piperidine,¹ indole,⁶ or quinoline/tetrahydroquinoline^{2,7,8} and studies of alternative catalyst systems such as unsulfided metal⁹ and those based on rhenium.¹⁰ However, a general description of the interactions between nitrogen heterocycles and the active catalyst sites that promote hydrogenation and then hydrogenolysis of the C–N bond has not yet emerged.

Recently, we reported that the transalkylation of tertiary amines, which involves the catalytic cleavage of C–N bonds, can be catalyzed homogeneously by group 8 metal carbonyls (including Ru, Os, Rh, and Ir).¹¹ We have further demonstrated that these same homogeneous catalysts can mimic the reactions of some heterogeneous catalysts, including the CoMo HDN catalyst with amines.^{12–14} Our group^{15,16} and others^{17,18} have also studied the regioselective hydrogenation of aromatic nitrogen heterocycles (the first step in HDN) by homogeneous group 8–10^{3d} catalysts. Again, no attempt was made to correlate these studies with studies of the physical interactions of typical HDN model compounds with the active catalyst sites for hydrogenation in HDN catalysts. It seems reasonable, in light of our modeling studies, that the stoichiometric reactions of nitrogen heterocycles with transition-metal complexes could provide insight into the

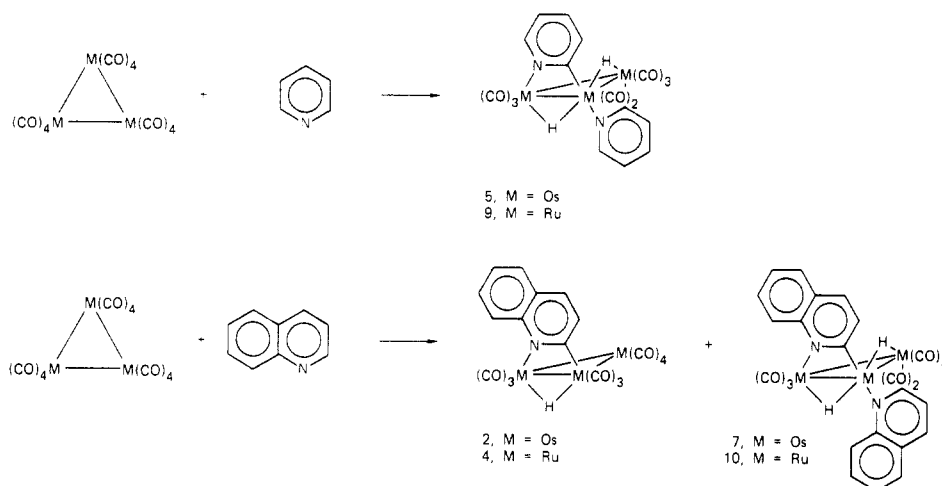
physical, substrate–catalyst interactions that are pertinent to the fundamental hydrogenation and C–N bond cleavage steps of HDN.

We report here the results of our investigations into the stoichiometric reactions of aromatic and aliphatic nitrogen heterocycles with the hydrogenation and transalkylation catalysts $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Ru}, \text{Os}$). We have isolated osmium complexes containing partially dehydrogenated

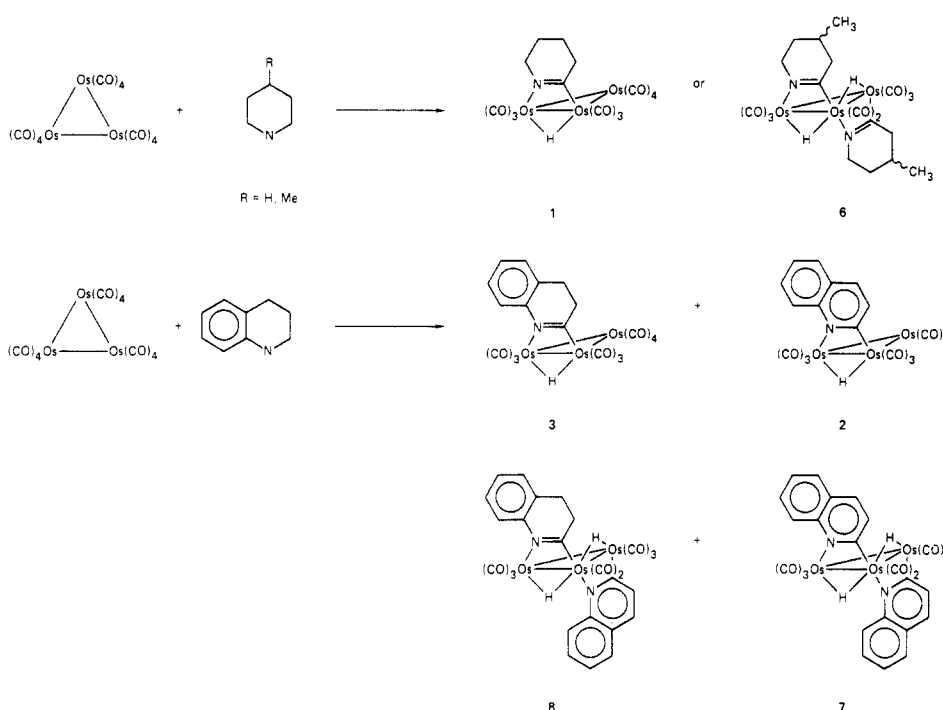
- (1) Sonnemans, J.; Van Den Berg, G. H.; Mars, P. *J. Catal.* **1973**, *31*, 220–230.
- (2) Satterfield, C. N.; Gultekin, S. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 62–68.
- (3) Satterfield, C. N.; Modell, M.; Wikens, J. A. *Ind. Eng. Chem. Process Des. Dev.* **1980**, *19*, 154–160.
- (4) Satterfield, C. N.; Cocchetto, J. F. *AIChE J.* **1975**, *21*, 1107–1111.
- (5) McIlveried, H. G. *Ind. Eng. Chem. Proc. Des. Dev.* **1971**, *10*, 125–130.
- (6) Stern, E. W. *J. Catal.* **1979**, *57*, 390–396.
- (7) Cocchetto, J. F.; Satterfield, C. N. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 49–53.
- (8) Cocchetto, J. F.; Satterfield, C. N. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *21*, 53–61.
- (9) Maier, W. F.; Guttieri, M. J. *J. Org. Chem.* **1984**, *49*, 2875.
- (10) Stern, E. W. *J. Catal.* **1979**, *57*, 390–396.
- (11) (a) Shvo, Y.; Laine, R. M. *J. Chem. Soc. Chem. Commun.* **1980**, 753. (b) Wilson, R. B., Jr.; Laine, R. M. *J. Am. Chem. Soc.* **1985**, *107*, 0000.
- (12) Laine, R. M.; Thomas, D. W.; Cary, L. W.; Buttrill, S. E. *J. Am. Chem. Soc.* **1978**, *100*, 6527–8.
- (13) Laine, R. M.; Thomas, D. W.; Cary, L. W. *J. Am. Chem. Soc.* **1982**, *104*, 1763–1765.
- (14) Shvo, Y.; Thomas, D. W.; Laine, R. M. *J. Am. Chem. Soc.* **1981**, *103*, 2461–2.
- (15) Laine, R. M.; Thomas, D. W.; Cary, L. W. *J. Org. Chem.* **1979**, *44*, 4964–67.
- (16) Giandomenico, C. M.; Eisenstadt, A.; Fredericks, M. F.; Hirschon, A. S.; Laine, R. M. *J. Mol. Catal.*, in press.
- (17) (a) Fish, R. H.; Thormodsen, A. D.; Cremer, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 5243. (b) Fish, R. H.; Thormodsen, A. D. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 292. (c) Fish, R. H.; Thormodsen, A. D. *J. Org. Chem.* **1984**, *49*, 4500.
- (18) Lynch, T. J.; Banah, M.; Kaesz, H. D.; Porter, C. R.; *J. Org. Chem.* **1984**, *49*, 1266–70.
- (19) Yin, C. C.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1975**, 2091–6.

[†] To whom correspondence should be addressed at SRI International.

Scheme I



Scheme II



heterocyclic rings that we believe are related to intermediates in the catalytic hydrogenation of aromatic heterocycles. We find that both the Ru and Os complexes readily activate both aliphatic and aromatic C-H bonds. The X-ray crystal structure of two such osmium complexes containing coordinated quinoline, $\text{Os}_3(\mu\text{-H})(\text{C}_9\text{H}_6\text{N})(\text{CO})_{10}$ and $\text{Os}(\mu\text{-H})_2(\text{C}_9\text{H}_6\text{N})_2(\text{CO})_8$, previously synthesized by Yin and Deeming,²⁰ are reported.

Results and Discussion

The reactions of heterocyclic amines with $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Ru}, \text{Os}$) are summarized in Schemes I and II and the physical properties of the products are collected in Table I. All of the heterocyclic amines examined react thermally (125–145 °C) with $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Ru}, \text{Os}$) under N_2 in nonpolar, noncoordinating, anhydrous solvents, forming neutral organometallic complexes. All these compounds are air and moisture stable at room temperature both as

the solid and in solution. Thus, they are readily isolated by chromatography on silica or alumina without decomposition.

Stoichiometry. The thermal reaction of heteroaromatic amines with $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Ru}, \text{Os}$) (Scheme I) in an inert solvent produces complexes with a stoichiometry of $\text{M}_3(\mu\text{-H}; \mu\text{-Y})(\text{CO})_{10}$ ($\text{M} = \text{Ru}, \text{Os}$; $\text{Y} = \text{C}_9\text{H}_6\text{N}$) or $\text{M}_3(\mu\text{-H}; \mu\text{-Y})_2(\text{CO})_8$ ($\text{M} = \text{Ru}, \text{Os}$; $\text{Y} = \text{C}_5\text{H}_4\text{N}, \text{C}_9\text{H}_6\text{N}$). The relative amount of each product obtained depends on the particular amine, metal carbonyl, and reaction conditions. Thus, only bis(pyridine) adducts 5 and 9 are isolated from the thermal reaction of pyridine and the corresponding metal carbonyl. On the other hand, the monoquinoline adducts 2 and 10 are readily isolated when quinoline, which is less basic and bulkier than pyridine, is heated in the presence of the corresponding metal carbonyl. These mono(quinoline) adducts may be converted to bis(quinoline) adducts on prolonged heating in the presence of excess quinoline. In the case of $\text{Ru}_3(\text{CO})_{12}$ the lability of coordinated CO on Ru relative to $\text{Os}_3(\text{CO})_{12}$ can be exploited to influence the relative amounts of mono- and bis(quinoline) adducts obtained. Hence, in a nitrogen atmosphere, the only product is the bis(quinoline) adduct 10, whereas under 1

(20) Cf. Bruce, M. I. In "Comprehensive Organometallic Chemistry: Index of Structures Determined by Diffraction Methods"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 9, pp 1393–5.

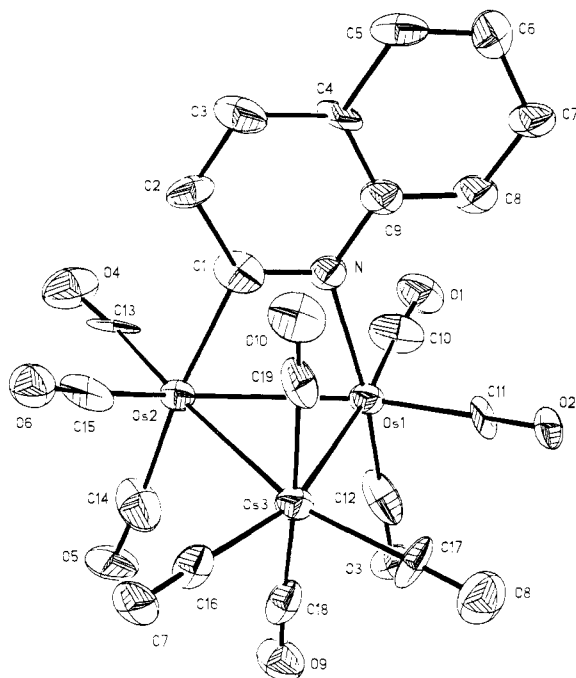


Figure 1. ORTEP diagram of $\text{Os}_3(\mu\text{-H})(\text{C}_9\text{H}_6\text{N})(\text{CO})_{10}$.

atm of CO a 17:1 ratio of the monoquinoline adduct 4 to bis(quinoline) adduct 10 results. On the other hand, even small amounts of CO effectively suppress all reactions of $\text{Os}_3(\text{CO})_{12}$ with quinoline.

The thermal reactions of aliphatic heterocyclic amines with $\text{Os}_3(\text{CO})_{12}$ are summarized in Scheme II. Complexes having stoichiometries of $\text{Os}(\mu\text{-H};\mu\text{-Y})(\text{CO})_{10}$ ($\text{Y} = \text{C}_5\text{H}_8\text{N}$, $\text{C}_9\text{H}_8\text{N}$, $\text{C}_9\text{H}_6\text{N}$), $\text{Os}_3(\mu\text{-H})_2(\mu\text{-Y})(\mu\text{-Y}')(\text{CO})_8$ ($\text{Y} = \text{C}_9\text{H}_8\text{N}$, $\text{Y}' = \text{C}_9\text{H}_6\text{N}$), or $\text{Os}_3(\mu\text{-H};\mu\text{-Y})_2(\text{CO})_8$ ($\text{Y} = \text{C}_6\text{H}_{10}$) are formed, and when the heterocyclic amine is 1,2,3,4-tetrahydroquinoline (THQ), a small amount of free quinoline is also produced. In all complexes, the ligand Y, derived from the starting amine, is partially or completely dehydrogenated. This result is discussed below. The relative amounts of monoamine and diamine adducts formed depends on reaction times. After 3–4 h at 140 °C the monoamine products 2 and 3 predominate, while after 24 h the diamine adduct 8 predominates.

In the absence of catalyst, THQ is not converted to quinoline which confirms that dehydrogenation is promoted by $\text{Os}_3(\text{CO})_{12}$.

Solid-State Structure of Heteroaromatic Amine Adducts. The solid-state structures of the quinoline complexes of $\text{Os}_3(\text{CO})_{12}$ 2 and 7 have been unambiguously assigned by single-crystal X-ray diffraction studies. ORTEP drawings of the mono- and bis(quinoline) complexes are shown in Figures 1 and 2, respectively. Details of the data collection and refinement, and tables of structure factors, atom coordinates and temperature factors, and bond angles and bond distances are provided for each structure in the supplementary tables. The geometry of ligands around the metal triangle in each compound is consistent with that found in structures of the general formula $\text{M}_3(\mu\text{-X};\mu\text{-Y})(\text{CO})_{10}$ and $\text{M}_3(\mu\text{-X};\mu\text{-Y})_2(\text{CO})_8$.²⁰ In each structure the quinoline ligands are coordinated via nitrogen and C-2 to separate osmium atoms of the cluster. The molecular plane containing each quinoline ligand contains an edge of the osmium triangle and is roughly perpendicular to the triangle. The bis(quinoline) adduct 7 (Figure 2) is the lowest symmetry isomer (C_s) of several possible isomers in which the quinoline ligands are situated on opposite faces of the metal triangle. The bridging hydrides are not explicitly found but are assumed to lie along the same edge

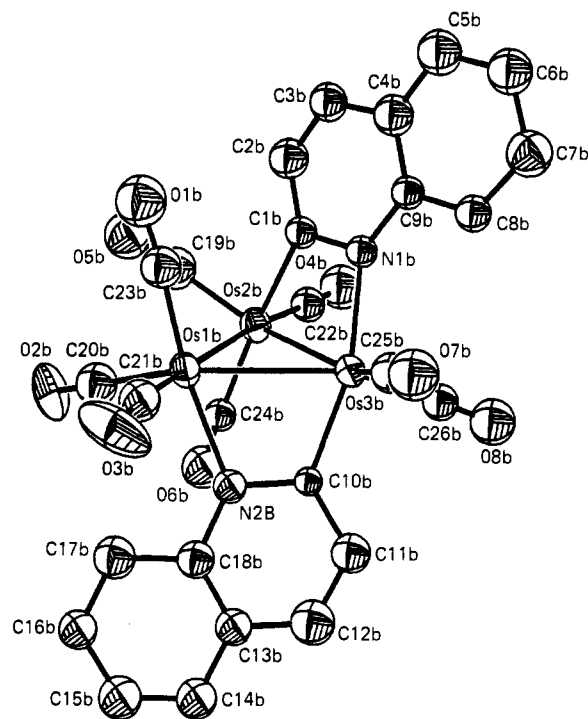


Figure 2. ORTEP diagram of $\text{Os}_3(\mu\text{-H})_2(\text{C}_9\text{H}_6\text{N})_2(\text{CO})_8$.

and opposite to the face containing the quinoline ligand.

The triosmium unit of the monoquinoline adduct 2 is an equilateral triangle within experimental error, with an average Os–Os separation of 2.909 (2) Å. On the other hand, the osmium metal triangle of the bis(quinoline) adduct 7 exhibits two different Os–Os bond lengths. The nonbridged Os–Os separation in this compound is 2.86 Å while the average Os–Os separation along the bridged edges is 2.92 (1) Å.

All of these distances are within bonding range for Os.^{21,22} The internal geometry of the coordinated quinolines in both structures are normal as are the geometries of all of the CO ligands.

Solution Structure of Heteroaromatic Amine Complexes. All the amine complexes that we examined are stable for weeks at room temperature in solution. They do not isomerize, and fluxionality is limited if present at all. Consider the solution-state spectrum of the bis(quinoline) $\text{Os}_3(\text{CO})_{12}$ adduct 7. The hydride region of the ¹H NMR spectrum exhibits two hydride resonances of equal intensity. The ¹³C NMR of 7 reveals that the two quinoline ligands are also inequivalent. This is clearly seen in the aromatic region which consists of six pairs of closely spaced resonance lines and one broadened line, presumably an unresolved pair. The metal-bonded carbons cannot be definitively assigned, but the two resonances at 167.9 and 166.2 ppm that lie between the normal aromatic region and the carbonyl region may be these carbon atoms. The remaining six resonance lines correspond to the eight carbonyl ligands. Two of these lines (180.0 and 177.4 ppm) are more intense than the others and are presumably degenerate. The solid state structure shown in Figure 2 is the only isomer with low enough symmetry to account for these spectra. The degeneracy in the carbonyl resonance lines is probably accidental, although rotation of two pairs of CO ligands would produce the same result. All of the dimeric amine complexes 5–10 exhibit inequivalent hydride and carbon ligand resonances leading us to conclude that

(21) Dahl, L. F. *Ann. N.Y. Acad. Sci.* 1983, 415, 12–15.

(22) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* 1977, 16, 878.

Table I. Spectroscopic Data for Os and Ru Amine Complexes

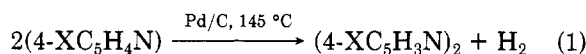
no.	compd	¹ H NMR ^a		¹³ C NMR ^b		IR ^c	MS ^d	elemental analysis					
		aromatic	aliphatic	M-H	>C-M or -C=O			aromatic	aliphatic	C	H	N	Ru
1	H ₂ O ₈ (CO) ₁₀ (C ₃ H ₈ N)	3.40 (m)	-15.3 (s)	191.5	186.0	62.4	2109 (m)	2065 (s)	found	19.20	1.05	1.56	
		2.37 (m)		182.7	178.0	46.7	2064 (s)	2026 (s)	939	19.29	0.97	1.50	
		1.60 (m)		176.8	175.3	23.3	2007 (s)	1997 (m)					
		(2:2:4)		174.9	174.8	19.3	1986 (s)	1973 (w)					
2	H ₂ O ₈ (CO) ₁₀ (C ₃ H ₈ N)	7.9-7.0 (m)		174.5	173.9		2112 (m)	2066 (s)					167-169
				182.3	182.1	146.5	2068 (s)						
				178.3	176.3	130.0	2058 (s)	2028 (s)					
				175.5	175.3	125.4	2018 (s)	2007 (s)					
				174.6	174.1		1990 (s)	1957 (w)					
				173.7	173.6								
				171.3									
3	H ₂ O ₈ (CO) ₁₀ (C ₃ H ₈ N)	7.7-7.0 (m)		187.1	186.0	135.9	2110 (m)	2067 (s)					
				183.4	178.3	132.1	2056 (s)	2029 (s)	987				
				177.6	176.7		2014 (s)	1985 (s)					
				175.3	175.1		1975 (m)	1964 (w)					
				174.2									
4	HRu ₃ (CO) ₁₀ (C ₃ H ₈ N) ^e	8.2-7.4 (m)		202.1	197.7	148.4 ^f	2100 (m)	2060 (s)	found	32.10	1.03	1.93	42.75
				189.0		131.8	2060 (s)	2044 (w)	g	32.03	0.99	1.97	42.56
				126.7	125.6		2023 (s)	2018 (s)					
							2009 (m)	1995 (s)					
							1963 (w)						
5	H ₂ O ₈ (CO) ₈ (C ₃ H ₈ N) ₂	8.13 (dd)		181.0	180.5	155.7 ^h	2087 (m)	2064 (w)	found	29.57	1.50	2.45	256
		7.20 (s)		179.9	179.3	134.0	2063 (s)	2033 (s)	1058	29.66	1.34	2.66	
		6.67 (m)		178.2	177.8	120.5	2007 (s)	1998 (m)					
		(1:2:1)		176.8	176.4		1987 (w)	1977 (s)					
				159.4	158.5		1963 (m)						
6	H ₂ O ₈ (CO) ₈ (C ₃ H ₈ N) ₂	3.42 (m)		181.5	181.1	147.8 ^f	2087 (m)	2066 (s)					
		2.51 (m)		188.7	187.8	138.9	2067 (m)	2033 (s)					
		1.54 (m)		185.3	184.6	132.2	2052 (s)	2033 (s)	1060				
		0.83 (d)		180.2	178.3	129.8	2005 (s)	1976 (m)					
		J = 5.3 Hz		176.5		127.4	1964 (m)						
		(2:1:4:3)				127.0 ^f							
7	H ₂ O ₈ (CO) ₈ (C ₃ H ₈ N) ₂	8.1-7.1 (m)		203.5	201.0	155.3	2087 (m)	2066 (s)					
				196.6	193.3	139.1	2052 (s)	2033 (s)					
				194.8	193.1	133.3	2005 (s)	1976 (m)					
				191.2	186.7	119.8	1964 (m)						
				179.2	176.7								
8	H ₂ O ₈ (CO) ₈ (C ₃ H ₈ N)(C ₃ H ₈ N)	8.1-6.7 (m)		199.9	198.0	147.7	2085 (s)	2079 (s)	g	39.56	2.07	3.55	38.90
				194.7	193.9	136.6	2062 (s)	2043 (s)		39.75	1.79	3.56	38.60
				190.8	187.3	130.1	2013 (s)	1997 (w)					
				187.6	183.9	128.6	1990 (s)	1964 (s)					
				125.3	124.8		1978 (s)	1967 (m)					
9	H ₂ Ru ₃ (CO) ₈ (C ₃ H ₈ N) ₂	8.06 (dd)											
		7.25 (m)											
		6.81 (m)											
		(1:2:1)											
10	H ₂ Ru ₃ (CO) ₈ (C ₃ H ₈ N) ₂	8.3-7.3 (m)											

^a90 MHz in CDCl₃; chemical shift in parts per million relative to Me₄Si; resonance multiplicities are as follows: m = multiplet, d = doublet, s = singlet; integrated resonance ratios are enclosed in parentheses.
^b22.5 MHz in CDCl₃, with 0.04 M Cr(acac)₃; chemical shift in parts per million relative to Me₄Si. ^cIn cyclohexane. ^dParent peak based on most abundant isotope ¹⁸O₈. ^e¹³C NMR without Cr(acac)₃.
^fQuaternary carbon. ^gHigh lability of coordinated CO prevents observation of parent ion. ^hHigh intensity resonance possibly two unresolved carbons. ⁱMixture of four isomers produces multiple closely spaced resonances.

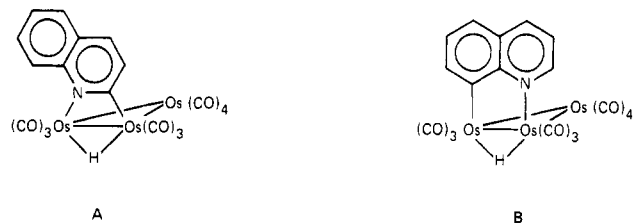
all these complexes have a similar structure.

Structure of Aliphatic and Heterocyclic Amine Adducts. We were not successful in obtaining crystals suitable for single-crystal diffractometry for the aliphatic amine adducts of $\text{Os}_3(\text{CO})_{12}$; however, comparison of the spectroscopic and physical properties of the compounds with those of **2** and **7** and other triosmium clusters containing a metal-bound iminoyl group^{23,24} enable us to assign these structures with certainty. The THQ adduct **3** is a typical monoamine adduct. The ^1H NMR consists of a single metal hydride resonance at -15.07 ppm, which is similar to the shift of -15.15 ppm reported for $\text{Os}_3(\mu\text{-H})(\mu\text{-HC=NPh})(\text{CO})_{10}$,²² and multiplets at 3.60 and 2.68 ppm with equal areas. Resonance lines assignable to THQ N-H or C-H bound to osmium are conspicuously absent. The ^{13}C NMR between 0 and 200 ppm establishes that the THQ carbon bound to osmium lacks hydrogen. This spectrum contains only two strong resonance lines assignable to aliphatic carbons, six lines attributed to aromatic carbons, and 11 resonance lines assignable to carbonyls. These data and the mass spectrum parent ion of 987 fits the formulation shown in structure **3** (Scheme II) in which the THQ coordinated to a decacarbonyltri-osmium unit has undergone oxidative addition of a C-H group and partial dehydrogenation to yield an η^3 -bound iminoyl group. Presumably, one of the 11 carbonyl resonances corresponds to the osmium bound iminoyl carbon. The carbonyl region of the IR spectrum of **3** is similar to that of **2**, suggesting that the disposition of CO groups around the osmium cluster of these two complexes is similar.

C-H Activation. The reactions observed here indicate that a common feature of nitrogen heteroaromatic interactions/reactions with catalysts is nitrogen coordination to metal followed by oxidative addition of the C-H bond α to the nitrogen. While we and others²⁵ observe the formation of metalloazacyclobutenes, still other researchers have observed the formation of metalloazacyclopropenes.²⁶ Furthermore, this feature is common to transition-metal complexes and lanthanide and actinide complexes^{26,27} and also occurs on activated heterogeneous catalysts.²⁸ In fact, this form of C-H activation can be used synthetically for the coupling of pyridines to make novel bipyridyl ligands.²⁹



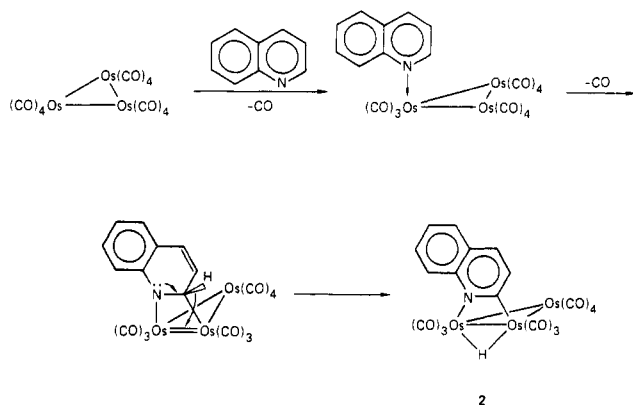
The heteroaromatic amines that we examined metalate exclusively at C-2 even if it is geometrically feasible for other C-H groups to participate.³⁰ This is the case for quinoline, which can metalate as depicted in structures A and B but produces only complexes of type A. This structure was proposed previously by Deeming et al.¹⁹ and is confirmed by single-crystal X-ray diffraction studies of



compounds **2** and **9**. The first step in the quinoline reaction is probably coordination of the nitrogen to metal. It is well-known that N-alkylation of quinoline or pyridine activates both the C-2 and C-4 positions toward nucleophilic attack.³¹ Thus, nitrogen coordination could activate the C-2 position towards reaction with the metal followed by hydride transfer as depicted in Scheme III.

Metalation and dehydrogenation of aliphatic heterocyclic amines occurs when they are heated with $\text{Os}_3(\text{CO})_{12}$ under N_2 . The THQ system is particularly interesting because complete dehydrogenation to quinoline can occur. A plausible sequence of events that accounts for the monoamine adducts and free quinoline formed during the reaction of quinoline and $\text{Os}_3(\text{CO})_{12}$ is depicted in Scheme IV. Initial loss of CO to give a coordinatively unsaturated species followed by coordination of the nitrogen lone pair and then hydrogen transfer could lead to intermediate such as I. Oxidative addition of N-H has been previously observed in the reaction of aniline with $\text{Os}_3(\text{CO})_{12}$.³⁰ Metalation of C-2 could lead to II, from which hydride transfer (pathway A) results in formation of the trapped species **3**. Alternatively, cleavage of the carbon-osmium bond (pathway B) followed by a series of proton transfers leads to an intermediate such as VI and VII. We feel that it is unlikely that direct dehydrogenation of **3** to yield **2** will occur because the hydrogens at C-3 and C-4 are geometrically constrained from interacting with a metal center, and there is no apparent driving force for spontaneous hydrogen transfer. Cleavage of the carbon-osmium bond via pathway B relaxes this constraint. Subsequent hydride transfer (pathway C) leads to trapped intermediates such as **2**, whereas carbon-osmium bond cleavage and dissociation of free quinoline completes the catalytic cycle. Note that pathways C and D together are similar to the reverse

Scheme III



(23) (a) Adams, R. D.; Golembeski, N. M. *Inorg. Chem.* **1978**, *17*, 1969-1973. (b) Adams, R. D.; Golembeski, N. M. *J. Am. Chem. Soc.* **1979**, *101*, 2579-87.

(24) (a) Adams, R. D.; Golembeski, N. M. *J. Am. Chem. Soc.* **1978**, *100*, 4622-23. (b) Adams, R. D.; Dawoodi, Z.; Foust, D. F.; Segmuller, B. E. *J. Am. Chem. Soc.* **1983**, *105*, 831-838.

(25) Nubel, P. O.; Wilson, S. R.; Brown, T. L. *Organometallics* **1983**, *2*, 515-524.

(26) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1-11.

(27) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 267-277.

(28) (a) Morrow, B. A.; Cody, I. A.; Moran, L. E.; Palepu, R. J. *Catal.* **1976**, *44*, 467. (b) Wexler, R. M.; Tsai, M.-C.; Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1984**, *104*, 2034-2036.

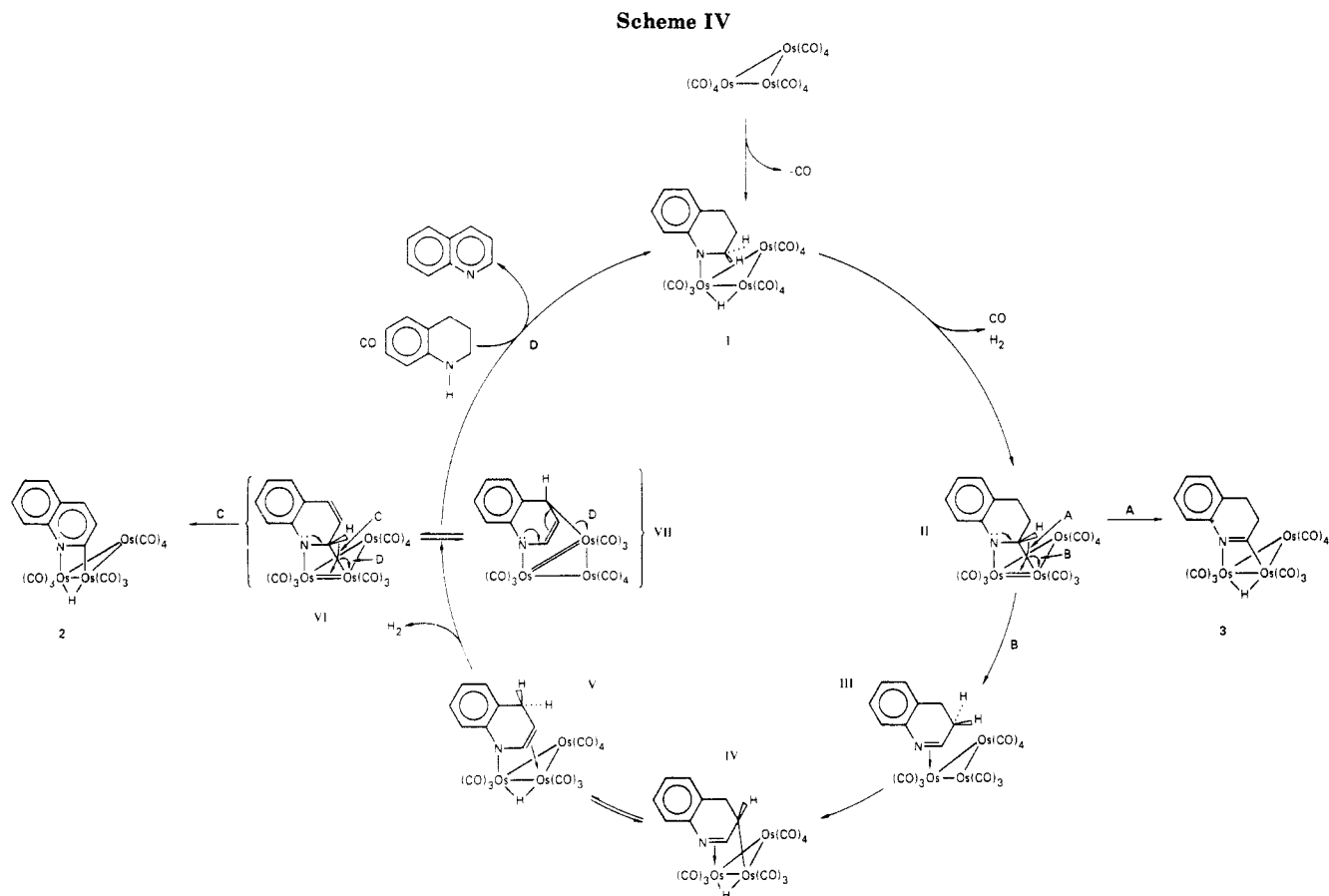
(29) (a) Sprintschink, G.; Sprintschink, H. W.; Kirsch, P. p.; Whitten, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 4947-4954. (b) Rosevear, P. E.; Sasse, W. J. F. *J. Heterocycl. Chem.* **1971**, *8*, 483.

(30) Azam, K. A.; Deeming, A. J.; Rothwell, I.; Hursthouse, M. B.; Baker-Dirks, J. D. *J. Chem. Soc. Dalton Trans.* **1981**, 2039-44.

(31) House, H. O. "Modern Synthetic Reactions"; W.A. Benjamin: New York, 1972; pp 2, 74, 75.

(32) (a) Laine, R. M. *Cat. Rev.—Sci. Eng.* **1983**, *25*, 459-474. (b) Laine, R. M. *J. Mol. Cat.* **1983**, *21*, 119-132.

(33) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III \rightarrow 3 and 13.)



of the process by which quinoline and $\text{Os}_3(\text{CO})_{12}$ forms **2** (Scheme III).

The mechanism delineated in Scheme IV can account for the different results observed with THQ and piperidine. Partially dehydrogenated intermediates of THQ such as the hypothetical V have enhanced stability due to delocalization of the nitrogen lone pair into the aromatic ring. Furthermore, the methylene group at C-4 is allylic and benzylic, resulting in enhanced reactivity toward oxidative addition. This driving force is absent in the corresponding piperidine intermediate. Consequently, only partially dehydrogenated products are trapped via pathway A. The catalytic formation of quinoline is also accounted for by Scheme III. Although reasonable amounts of free quinoline are formed initially when THQ is heated in the presence of $\text{Os}_3(\text{CO})_{12}$, the rate of formation falls with time and the turnover number is generally about one. This is anticipated because the catalytic formation of quinoline competes directly with the formation of compounds such as **2**, **3**, and **7**. Compounds **2**, **3**, and **7** contain strong and kinetically stable carbon-osmium bonds; thus, their formation depletes the concentration of catalytically active osmium.

Conclusion

We have observed that the homogeneous hydrogenation and transalkylation catalysts $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Ru}, \text{Os}$) readily dehydrogenate heterocyclic amines, yielding η^3 -iminoyl species. This provides support for the C-N bond cleavage mechanism that we have previously proposed is involved in the transalkylation reaction and HDN. The cornerstone on which these mechanisms are based is the formation of metal-bound iminium species susceptible to nucleophilic attack and/or C-N bond cleavage.

Experimental Section

General Methods. Quinoline, 1,2,3,4-tetrahydroquinoline, pyridine, piperidine, and 4-methylpiperidine were purchased from Aldrich Co. and distilled from CaH_2 or Na under N_2 prior to use. Methylcyclohexane from MCB and *n*-heptane and *n*-octane from Aldrich were purified by washing with acid (H_2SO_4), drying, and distilling. The metal carbonyl $\text{Ru}_3(\text{CO})_{12}$ was purchased from Strem Chemicals. $\text{Os}_3(\text{CO})_{12}$ was prepared by high-pressure reaction of OsO_4 , obtained from Johnson-Matthey, with CO (100 bar) in benzene (at 180 °C for 40 h).

A JEOL FX90Q equipped with a broad-band probe was used to collect ^1H NMR and ^{13}C NMR spectra. The infrared spectra were obtained on a Perkin-Elmer Model 281 infrared spectrometer. Mass spectra were obtained by using an LKB-9000 or a Ribermag R1010C mass spectrometer. Gailbraith Laboratories performed the elemental analyses.

Preparation of $\text{Ru}_3(\mu\text{-H})(\text{C}_9\text{H}_6\text{N})(\text{CO})_{10}$, **4.** A suspension of 0.435 g (0.68 mmol) of $\text{Ru}_3(\text{CO})_{12}$ in 1 mL of quinoline and 25 mL of methylcyclohexane is purged with CO at atmospheric pressure and sealed in a pressure vessel. The sealed vessel is heated to 145 °C for 3 h. After being cooled, the solution is washed with 3 M HCl and then water and dried over Na_2SO_4 . The solvent is removed under reduced pressure, and the residue is chromatographed on neutral alumina, activity grade III, eluting with hexane. The products, in order of elution, are 28 mg of $\text{Ru}_3(\text{CO})_{12}$, 335 mg (69% yield) of **4**, $\text{Ru}_3(\mu\text{-H})(\text{C}_9\text{H}_6\text{N})(\text{CO})_{10}$, and 24 mg (4% yield) at **10**, $\text{Ru}_3(\mu\text{-H})_2(\text{C}_9\text{H}_6\text{N})_2(\text{CO})_8$.

Preparation of $\text{Ru}_3(\mu\text{-H})_2(\text{C}_9\text{H}_6\text{N})_2(\text{CO})_8$, **10.** A suspension of 1.83 g (2.86 mmol) of $\text{Ru}_3(\text{CO})_{12}$ in 2 mL of quinoline and 75 mL of methylcyclohexane is purged with N_2 at atmospheric pressure and sealed in a pressure vessel. The sealed vessel is heated to 130 °C for 2.5 h. After being cooled, the solution is worked up as described above. Two products are isolated: 560 mg (27% yield) of **4**, $\text{Ru}_3(\mu\text{-H})(\text{C}_9\text{H}_6\text{N})(\text{CO})_{10}$, and 1.32 g (59% yield) of **10**, $\text{Ru}_3(\mu\text{-H})_2(\text{C}_9\text{H}_6\text{N})_2(\text{CO})_8$.

Preparation of $\text{Ru}_3(\mu\text{-H})_2(\text{C}_5\text{H}_4\text{N})_2(\text{CO})_8$, **9.** A suspension of 190 mg (0.3 mmol) of $\text{Ru}_3(\text{CO})_{12}$ in 0.6 mL of pyridine and 25 mL of *n*-heptane is purged with CO. The solution is refluxed for 0.5 h. The solution is worked up as described above and yields

104 mg (51% yield) of **9**, $\text{Ru}_3(\mu\text{-H})_2(\text{C}_5\text{H}_4\text{N})_2(\text{CO})_8$.

Reaction of THQ with $\text{Os}_3(\text{CO})_{12}$. A suspension of 0.374 g (0.4 mmol) of $\text{Os}_3(\text{CO})_{12}$ in 0.5 mL of THQ and 50 mL of *n*-octane is heated in a sealed vessel under nitrogen for 24 h at 145 °C. After the mixture is cooled, the solvent is removed at reduced pressure and the residue is dissolved in CH_2Cl_2 and filtered. The organic layer is washed with 3% HCl to remove free amine and dried over Na_2SO_4 , and the solvent is removed under reduced pressure. The residue is dried for 8 h at 10^{-3} mm and chromatographed on a silica prep plate (1000 μm thickness) eluting twice with hexanes. Four bands are isolated, containing a total of four compounds. The first band contained 90 mg (22% yield) of **2**, $\text{Os}(\mu\text{-H})(\text{C}_9\text{H}_6\text{N})(\text{CO})_{10}$. The second band contained 20 mg (5% yield) of **3**, $\text{Os}_3(\mu\text{-H})(\text{C}_9\text{H}_6\text{N})(\text{CO})_{10}$. The third band contained 24 mg (6% yield) of **8**, $\text{Os}_3(\mu\text{-H})_2(\text{C}_9\text{H}_6\text{N})(\text{C}_9\text{H}_6\text{N})(\text{CO})_8$, and the final band contained **7**, $\text{Os}_3(\mu\text{-H})_2(\text{C}_9\text{H}_6\text{N})_2(\text{CO})_8$.

Preparation of $\text{Os}_3(\mu\text{-H})_2(\text{C}_5\text{H}_4\text{N})_2(\text{CO})_8$, **5.** A suspension of 0.112 g (0.12 mmol) of $\text{Os}_3(\text{CO})_{12}$ in 0.8 mL (9.9 mmol) of pyridine and 10 mL of *n*-octane is heated in a sealed vessel under 1 atm of H_2 at 145 °C for 15 h. Removal of the solvent and pyridine under reduced pressure followed by chromatography of the residue on neutral alumina (activity grade II) eluting with hexanes yields 0.1 g (88% yield) of **5**, $\text{Os}_3(\mu\text{-H})_2(\text{C}_5\text{H}_4\text{N})(\text{CO})_8$.

Preparation of $\text{Os}_3(\mu\text{-H})(\text{C}_9\text{H}_6\text{N})(\text{CO})_{10}$ and $\text{Os}_3(\mu\text{-H})_2(\text{C}_9\text{H}_6\text{N})_2(\text{CO})_8$. A suspension of 0.32 g (0.35 mmol) of $\text{Os}_3(\text{CO})_{12}$ in 1 mL (8.5 mmol) of quinoline and 20 mL of *n*-octane is heated under N_2 in a sealed vessel at 145 °C for 24 h. The solvent is removed under reduced pressure. The residue is dissolved in CH_2Cl_2 , filtered, and washed with 3% HCl to remove the free quinoline. The organic layer is dried over Na_2SO_4 , and the CH_2Cl_2 is removed under reduced pressure. The resultant crude material is chromatographed on neutral alumina (activity grade II) eluting with hexanes. Two bands are eluted. The first is 84 mg (24% yield) of **2**, $\text{Os}_3(\mu\text{-H})(\text{C}_9\text{H}_6\text{N})(\text{CO})_{10}$, and the second band is 300 mg (82% yield) of **7**, $\text{Os}_3(\mu\text{-H})_2(\text{C}_9\text{H}_6\text{N})_2(\text{CO})_8$.

Preparation of $\text{Os}_3(\mu\text{-H})(\text{C}_5\text{H}_4\text{N})(\text{CO})_{10}$. A suspension of 0.186 g (0.21 mmol) of $\text{Os}_3(\text{CO})_{12}$ in 1 mL (10 mmol) of piperidine and 40 mL of *n*-octane is heated under N_2 in a sealed pressure

vessel at 140 °C for 3.5 h. After the mixture is cooled, the solvent is removed under reduced pressure and the residue is chromatographed on neutral alumina (activity grade III) eluting with petroleum ether or hexane. Two bands are eluted. The first contains 35 mg of a mixture of unidentified products and **1**, $\text{Os}_3(\mu\text{-H})(\text{C}_5\text{H}_8\text{N})(\text{CO})_{10}$, while the second band contains 131 mg (68%) of **1**.

Preparation of $\text{Os}_3(\mu\text{-H})_2(\text{C}_6\text{H}_{10}\text{N})_2(\text{CO})_8$. A suspension of 0.54 g of $\text{Os}_3(\text{CO})_{12}$ in 1 mL of 4-methylpiperidine and 60 mL of *n*-octane is heated under N_2 in a sealed vessel at 135 °C for 24 h. After the mixture is cooled, the solvent is removed under reduced pressure and the residue is chromatographed on neutral alumina (activity grade II) eluting with hexane. Compound **6** (0.34 g, 60% yield) is isolated as a mixture of four isomers that can not be separated by standard chromatographic techniques.

Acknowledgment. This work was supported by the National Science Foundation through Chem. Eng. Grant No. 8-19541. We would like to thank Johnson-Matthey Inc. for the generous loan of osmium without which we could not have undertaken the work reported here. We would also like to thank Professor W. F. Maier for a preprint of ref 9.

Registry No. **1**, 98105-23-8; **2**, 58399-12-5; **3**, 98105-24-9; **4**, 98105-25-0; **5**, 98105-26-1; **6**, 98105-27-2; **7**, 98105-28-3; **8**, 98105-29-4; **9**, 98105-30-7; **10**, 98105-31-8; THQ, 635-46-1; $\text{Os}_3(\text{CO})_{12}$, 15696-40-9; $\text{Ru}_3(\text{CO})_{12}$, 15243-33-1; Os, 7440-04-2; Ru, 7440-18-8; quinoline, 91-22-5; pyridine, 110-86-1; piperidine, 110-89-4; 4-methylpiperidine, 626-58-4.

Supplementary Material Available: Detailed X-ray crystallographic work, including structure factors, temperature factors, bond lengths, and bond angles for the two crystal structures reported in the text (70 pages). Ordering information is given on any current masthead page.