cated on the grounds of kinetic, thermodynamic, and structural studies on both natural[1,2,3,46,47] and synthetic ion carriers.[8,9,48]   The rules represented here may thereby be regarded but as preliminary structural

(46) H. Diebler, M. Eigen, G. Ilgenfritz, G. Maass, and R. Winkler, *Pure Appl. Chem.*, **20**, 93 (1969).
(47) V. Prelog, *Pure Appl. Chem.*, **25**, 197 (1971).
(48) W. E. Morf, D. Ammann, E. Pretsch, and W. Simon, *Pure Appl. Chem.*, **36**, 197 (1973).

guidelines toward the attainment of the desired internal cavities. We are currently engaged in further experimental and theoretical studies to validate these rules, as we believe that they may assist in the understanding of natural systems and in the design of new synthetic analogues.

Chemistry of Triosmium Carbonyl Cluster Compounds and Its Implications for Catalysis

RICHARD D. ADAMS

Department of Chemistry, Yale University, New Haven, Connecticut 06511

The subject of catalysis as mediated by transition-metal agents can be separated into two fairly distinct areas known as heterogeneous catalysis and homogeneous catalysis. Heterogeneous catalysis typically takes place under multiphase conditions, and in many systems the chemical transformations occur at exposed metal atoms on the surface of a solid.[1-3] Homogeneous catalysis, on the other hand, takes place in a single phase (usually solution), and in most cases the chemical transformations occur on a single metal atom in a molecular complex.[4,5] Because of these basic physical and chemical differences, the chemistry in these areas has been developed fairly independently. Recently it has been speculated that polynuclear metal complexes containing metal–metal bonds (commonly referred to as cluster compounds)[6] might serve as models for surfaces and that the study of them might help to bring the research in these two areas closer together.[7-9] However, it is also probable that these cluster complexes will prove to have chemical and physical properties that are unique unto themselves, and thus may provide the basis for the development of a new class of transition-metal catalysts.[10,11] For these reasons we have undertaken a study of the chemistry of a series of triosmium carbonyl cluster complexes formed by the addition of a variety of small heteronuclear unsaturated molecules to the cluster complex $H_2Os_3(CO)_{10}$.

The molecule $H_2Os_3(CO)_{10}$ (I) has been shown to contain a triangular cluster of 3 osmium atoms with 10 linear terminal carbonyl ligands.[12] The two hydride ligands bridge one unusually short osmium–osmium internuclear separation. Electronically, the cluster contains 46 electrons, which is 2 fewer than the 48-electron closed-shell configurations characteristic of triangular clusters. Various theories have been advanced to rationalize the bonding in I,[12a,13] but its most important feature is that it does behave chemically as

Scheme I
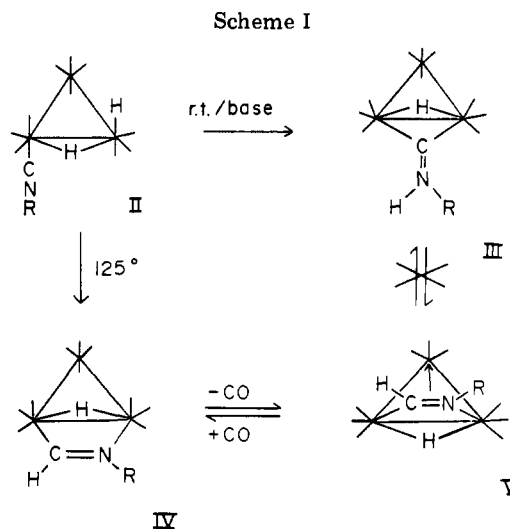
if it were electron deficient. For example, it readily adds donors, L (e.g., CO, phosphines, phosphites, isocyanides, etc.) (eq 1) to form 1:1 adducts that contain the closed-shell 48-electron configuration.[14]

(1) Thomson, S. J.; Webb, G. "Heterogeneous Catalysis"; Wiley: New York, 1968.
(2) Rideal, E. K. "Concepts in Catalysis"; Academic Press: New York, 1968.
(3) Anderson, J. R. "Chemisorption and Reactions on Metallic Films"; Academic Press: New York, 1971; Vol. 1–2.
(4) Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980.
(5) James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973.
(6) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; Chapter 26.
(7) Muetterties, E. L. *Science (Washington, D.C.)* **1977**, *196*, 839.
(8) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1975**, *84*, 959.
(9) Ugo, R. *Catal. Rev.* **1975**, *11*, 225.
(10) Wyman, R. In "Transition Metal Clusters"; Johnson, B. F. G., Ed.; Wiley: New York, 1980; Chapter 8.
(11) Pittman, C. U.; Ryan, R. C. *Chem.-Tech. (Heidelberg)* **1978**, *7*, 170.
(12) (a) Broach, R. W.; Williams, J. M. *Inorg. Chem.* **1979**, *18*, 314. (b) Orpen, A. G.; Rivera, A. V.; Bryan, E. G.; Pippard, D.; Sheldrick, G. M.; Rouse, K. D. *J. Chem. Soc., Chem. Commun.* **1978**, 723.
(13) Raithby, P. In "Transition Metal Clusters"; Johnson, B. F. G., Ed.; Wiley: New York, 1980; Chapter 2.

$$I$$
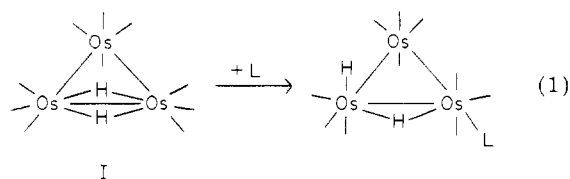
Because of their importance in fuel and energy-related problems, we have been interested in aspects of the hydrogenation of CO and CO_2. In 1976 Muetterties reported that $Os_3(CO)_{12}$ can catalytically and homogeneously hydrogenate CO under mild conditions[15] Unfortunately, the level of activity was very low. In more recent work it has been shown that the activity can be increased in Lewis acid solvents but that fragmentation of the cluster also becomes important.[16]

We did not observe evidence of C–H bond-forming processes in reactions of I with CO and CO_2 under mild conditions and thus focused our attention on small related heteronuclear unsaturated molecules that we felt might serve as reasonable models for CO and CO_2. The molecules which we investigated were isocyanides, nitriles, isocyanates, carbodiimides, isothiocyanates, and carbon disulfide. With these, we have observed a wealth of ligand addition and cluster-based ligand transformation processes that we feel may be of relevance to the development of cluster compounds as catalysts.

Reactions with Isocyanides

The reaction of I with isocyanides proceeds initially as expected, and 1:1 adducts II are formed (Scheme I).[17] These molecules contain one bridging and one terminal hydride ligand in addition to the isocyanide ligand. Interestingly, we have found that one hydride ligand can be readily transferred to the isocyanide ligand, but, depending on the reaction conditions, this transfer can occur in either of two ways.

In donor solvents or nondonor solvents containing a trace of base (e.g., Et_3N), hydrogen is quantitatively transferred to the nitrogen atom at room temperature in a matter of minutes. The product whose general structure III was confirmed crystallographically, contains a *N*-hydrido *N*-alkyliminyl ligand in which the former isocyano carbon atom bridges a pair of metal atoms. Because this transformation is base catalyzed, we believe it takes place via a proton abstraction from II followed by a proton readdition. In the course of this process, a cluster anion of the form $HOs_3(CO)_{10}CNR^-$ is probably formed. Such as anion would probably contain a bridging isocyanide ligand and have a gross structure analogous to the related cluster anions $HRu_3(CO_{11}^{-}$[18] and $HFe_3(CO)_{11}^{-}$.[19] Most importantly, bridging isocyanide ligands are nonlinear as a result of the existence of a lone pair of electrons on the nitrogen atom. If the basicity of the lone pair exceeds that of the solvent, the proton would be returned to the complex at the nitrogen atom.
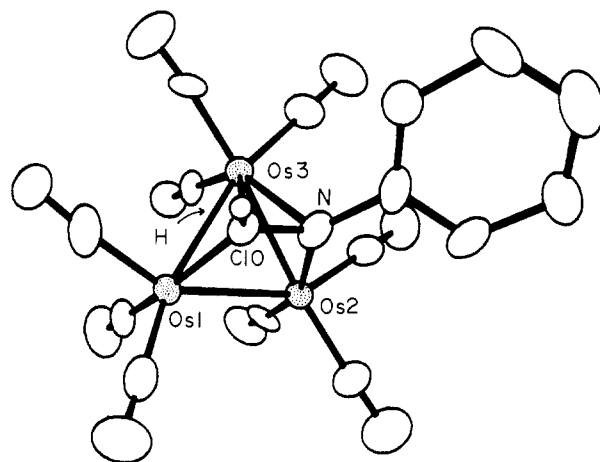
Figure 1. Molecular structure of $HOs_3(CO)_9(\mu\text{-}\eta^2\text{-HC}{=}NPh)$ (I).

When solutions of II are heated in nondonor solvents, one hydride ligand is selectively transferred to the carbon atom of the isocyanide ligand. The products IV and V contain a formimidoyl (HCNR) ligand coordinated to an edge and face of the cluster, respectively. The structure of V, R = Ph (Figure 1), was confirmed crystallographically. The iminyl C–N bond length, 1.415 (11) Å, is close to the length of a carbon–nitrogen single bond. This long length can almost certainly be attributed to a reducing effect produced by the trinuclear coordination.[20] Since the formation of III occurs apparently by a *dissociative* process and since the products IV and V cannot be converted into III and vice versa, we believe that the formation of IV and V must occur by an *intramolecular insertion* type mechanism. Further details remain to be established.

Reactions with Nitriles

In an elegant series of experiments, Kaesz et al. established the nature of the activation and hydrogen reduction of nitrile ligands on the face of an $Fe_3(CO)_9$ cluster.[21] We wondered if the $H_2Os_3(CO)_{10}$ cluster, which contains 10 ancillary carbonyl ligands, could also activate and transfer hydrogen to nitrile ligands. Although I is known to form adducts with benzonitrile, that reaction is readily reversible and, when heated, the adducts revert to the reagents. In hopes of inducing hydrogen transfer, we investigated the reaction of I with the more electron-withdrawing nitrile CF_3CN.[22] CF_3-CN reacts rapidly with I at room temperature and yields two products. Each is the result of the addition of 1 mol of nitrile to the cluster and the transfer one hydride ligand to the nitrile function. The structures of the products, $HOs_3(CO)_{10}[\mu\text{-}\eta^1\text{-N}{=}C(H)CF_3]$ (VI), and $HOs_3(CO)_{10}[\mu\text{-}\eta^2\text{-HN}{=}CCF_3]$ (VII), were established by X-ray crystallographic analyses of their PMe_2Ph derivatives. In VI the hydride ligand was transferred to the carbon atom of the nitrile, and the resultant *C*-hydrido, *C*-trifluoromethyliminyl ligand bridges an edge of the cluster via the nitrogen atom. In

(14) (a) Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1976**, *114*, 313. (b) Shapley, J. R.; Keister, J. B.; Churchill, M. R.; DeBoer, B. G. *J. Am. Chem. Soc.* **1975**, *97*, 4145.

(15) Thomas, M. G.; Beier, B. F.; Muetterties, E. L. *J. Am. Chem. Soc.* **1976**, *98*, 1296.

(16) Choi, H. W.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 2661.

(17) Adams, R. D.; Golembeski, N. M. *J. Am. Chem. Soc.* **1979**, *101*, 2579.

(18) Johnson, B. F. G.; Lewis, J.; Suss, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1356.

(19) Dahl, L. F.; Blount, J. F. *Inorg. Chem.* **1965**, *4*, 1373.

(20) (a) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1976**, *85*, 451. (b) Muetterties, E. L. *Pure Appl. Chem.* **1978**, *50*, 941.

(21) (a) Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7238. (b) Andrews, M. A.; van Buskirk, G.; Knobler, C. B.; Kaesz, H. D. *Ibid.* **1979**, *101*, 7245. (c) Andrews, M. A.; Kaesz, H. D. *Ibid.* **1979**, *101*, 7255. (d) Andrews, M. A.; Knobler, C. B.; Kaesz, H. D. *Ibid.* **1979**, *101*, 7260.

(22) (a) Adams, R. D.; Katahira, D. A.; Yang, Li-Wu *J. Organomet. Chem.* **1981**, *219*, 85. (b) Dawoodi, Z.; Mays, M. J.; Raithby, P. R. *J. Organomet. Chem.* **1981**, *219*, 103.

VI   **VII**
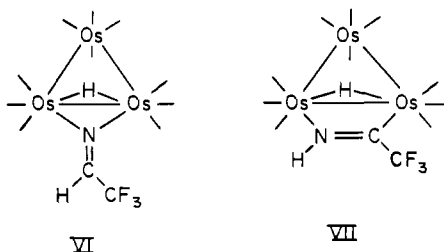
VII the hydride ligand was transferred to the nitrogen atom and the resultant *N*-hydrido, *C*-trifluoromethyl-iminyl ligand bridges an edge of the cluster through both the carbon and nitrogen atoms. Details of the hydrogen-transfer steps are not known, but an isotope labeling study showed that the formation of VI occurred by an *intramolecular* process. Results similar to ours have recently been obtained by Mays et al.[22b] In summary, we observe that the $H_2Os_3(CO)_{10}$ cluster does activate some nitrile molecules and readily transfers hydrogen to the nitrile function. However, unlike the $Fe_3(CO)_9$ system where the reductions apparently occur about a trinuclear site, the reductions by I are, at least in these early stages, confined to the edge of the cluster.

Reactions with Aryl Isocyanates

The reaction of I with *p*-tolyl isocyanate produces an addition, accompanied by a facile hydrogen transfer to the carbon atom, to yield VIII (Figure 2), which contains a *N*-*p*-tolylformamido ligand that bridges an edge of the cluster via its nitrogen and oxygen atoms.[23] The C–N and C–O bond distances in the formamido ligand at 1.33 (1) and 1.27 (1) Å, respectively, are intermediate between single and double bond lengths and imply a π-electron delocalization across the entire three-atom N–C–O unit.

Trace amounts of a product formed by transfer of hydrogen to the nitrogen atom of the isocyanate are also formed. This latter reaction is enhanced when phosphine ligands occupy the coordination sphere of the cluster. For example, the compound $HOs_3(CO)_9$-$(PMe_2Ph)(\mu\text{-}\eta^2\text{-O}=\!C\!-\!NH\text{-}p\text{-Tol})$ (IX) (Figure 3), was obtained as a principal product from the reaction of $(\mu\text{-H})_2Os_3(CO)_9(PMe_2Ph)$ (X) with *p*-tolyl isocyanate.

X   **XI**
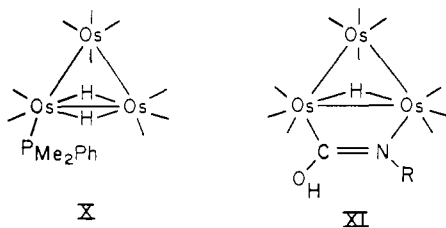
The carboxamido ligand in IX bridges an edge of the cluster via the carbon and oxygen atoms. The mechanism of the hydrogen transfer is not known, but the differences in the product distribution show that the ligand structure of the cluster can dramatically alter the regiochemistry of the hydrogen transfer. Kaesz has found recently that the reactions of I with alkyl isocyanates show evidence of still another mode of hydrogen transfer, namely, transfer of hydrogen to the oxygen atom of the isocyanate XI, and the products of the type IX and XI can be interconverted.[24]

(23) Adams, R. D.; Golembeski, N. M.; Selegue, J. P. *Inorg. Chem.* **1981**, *20*, 1242.

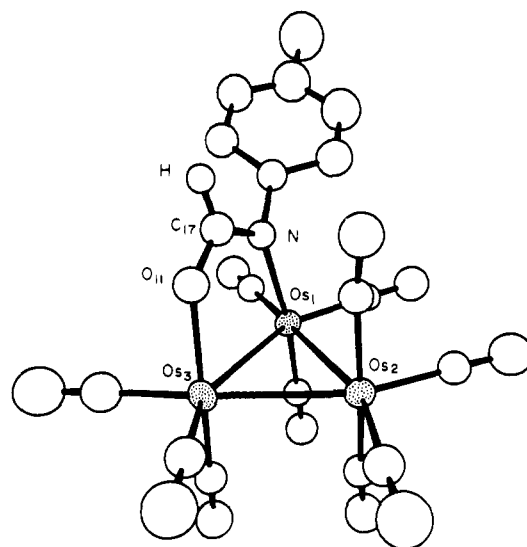(24) Lin, Y. C.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1981**, *103*, 1216.

Figure 2. Molecular structure of $HOs_3(CO)_{10}[\mu\text{-}\eta^2\text{-OC(H)N-}p\text{-tol}]$ (VIII).
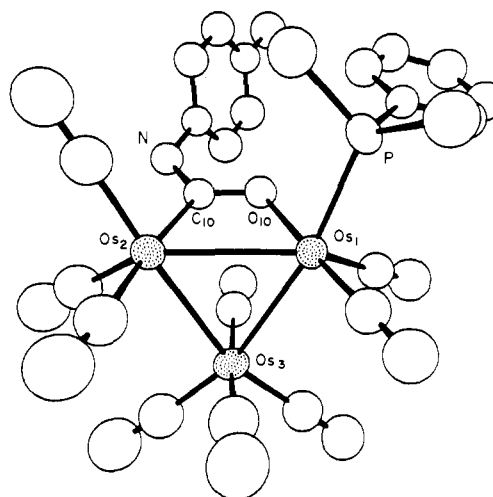
Figure 3. Molecular structure of $HOs_3(CO)_9(PMe_2Ph)(\mu\text{-}\eta^2\text{-}O\!=\!CNH\text{-}p\text{-tol})$ (XI).
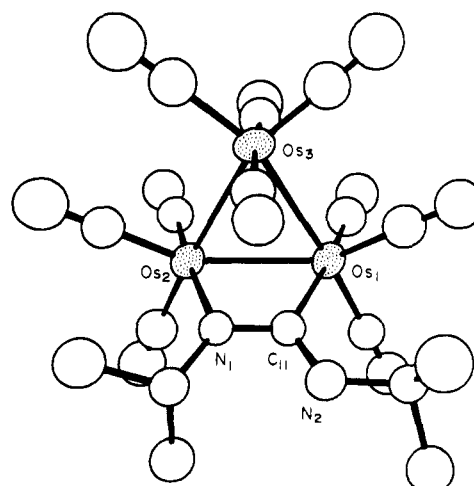
Figure 4. Molecular structure of $HOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-Pr-}i\text{-N}\!=\!CNHPr\text{-}i)$ (XII).

Reactions with Carbodiimides

The reaction of I with dialkylcarbodiimides is similar to that of the reactions with aryl isocyanates; however, only one mode of hydrogen transfer has been observed.[25] This involves hydrogen transfer to the ni-
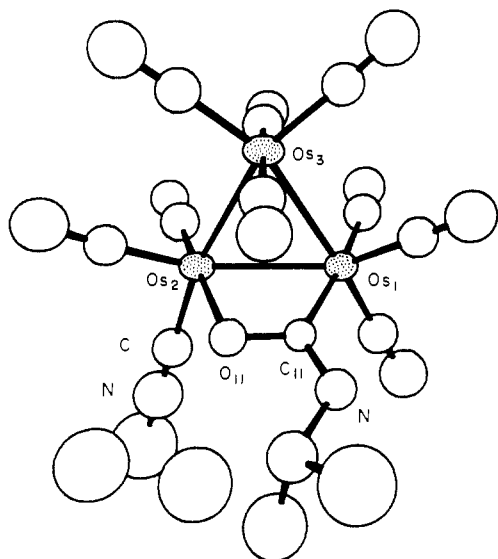
Figure 5. Molecular structure of $HOs_3(CO)_9(CNPr-i)(\mu-\eta^2-O=CNHPr-i)$ (XIII).
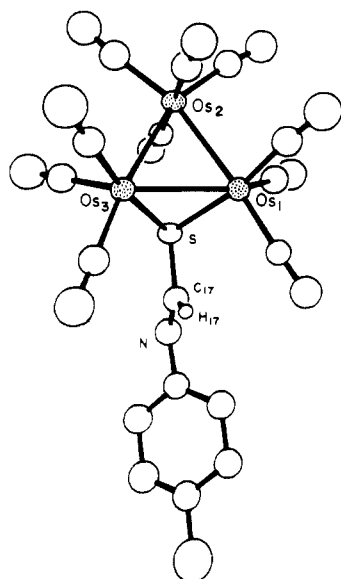
Figure 6. Molecular structure of $HOs_3(CO)_{10}[\mu-\eta^1-SC(H)=N-p-C_6H_4F]$ (XIV).

trogen atom to form the complex $HOs_3(CO)_{10}(\mu-\eta^2-Pr-i-N=CNHPr-i)$ (XII) (Figure 4), which contains an N,N'-diisopropylamidinyl ligand briding an edge of the cluster via one carbon and one nitrogen atom. Unexpectedly, the molecule $HOs_3(CO)_9(CNPr-i)(\mu-\eta^2-O=CNHPr-i)$ (XIII) (Figure 5) was also isolated from this reaction. The formation of XIII appears to have involved the transfer of the HNPr-i group from the amidinyl ligand in XII to the carbon atom of a carbonyl ligand, and the remaining portion of that ligand was converted into an isocyanide ligand. Unfortunately, XII cannot be converted into XIII.

Reactions of Aryl Isothiocyanates

Because of their striking spectroscopic similarities, we initially believed that the products of the reaction of aryl isothiocyanates with I were analogous to VIII. However, an X-ray crystallographic analysis of $HOs_3(CO)_{10}(\mu-\eta^1-SCHN-p-C_6H_4F)$ (XIV) showed an impor-

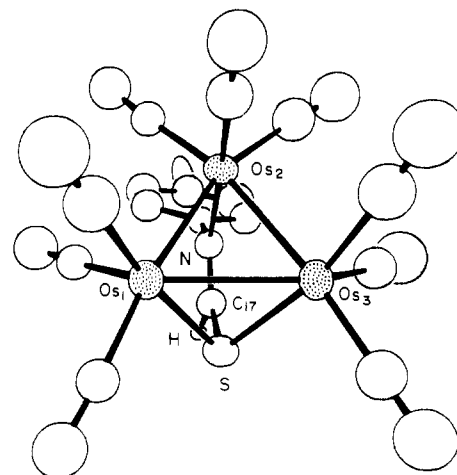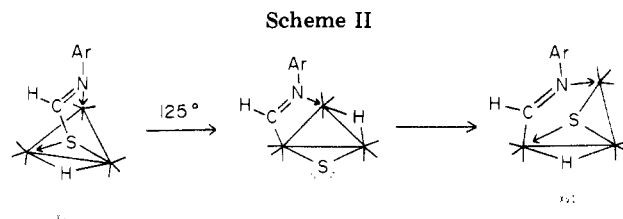(25) Adams, R. D.; Katahira, D. A.; Selegue, J. P. *J. Organomet. Chem.* **1981**, *213*, 259.

Figure 7. Molecular structure of $HOs_3(CO)_9[\mu_3-\eta^2-SC(H)=N-p-C_6H_4F]$ (XV).

Scheme II

tant difference (Figure 6).[26] Although the isothiocyanate molecule was added to the cluster and a hydride ligand was transferred to the isocyano carbon atom, the thioformamido ligand was found to bridge an edge of the cluster via the sulfur atom only. In the ligand, the carbon–sulfur distance was found to be very long at 1.782 (12) Å, which is typical of a carbon–sulfur single bond. On the other hand, the carbon–nitrogen distance of 1.279 (12) Å is short and indicative of a carbon–nitrogen double bond. Clearly, the π-electron density that is delocalized in compound VIII is here localized largely between the carbon and nitrogen atoms. We believe that this is a direct consequence of the dinuclear coordination of the sulfur atom, in which the coordination of two lone pairs of electrons from the sulfur atom leads to a greater stabilization of resonance form A than B.
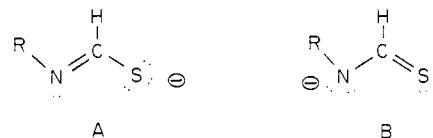
Compound XIV loses 1 mol of CO on photolysis to form $HOs_3(CO)_9[\mu_3-\eta^2-SC(H)=N-p-C_6H_4F]$ (XV) (Figure 7), which contains a triply bridging thioformamido ligand formed through the coordination of the nitrogen atom to the third osmium atom. The carbon–nitrogen and carbon–sulfur distances of the thioformamido ligand in XV show that the π-electron density remains localized between the carbon and nitrogen atoms. When heated, compound XV is transformed into $HOs_3(CO)_9(\mu_3-S)(\mu-\eta^2-HC=N-p-C_6H_4F)$ (XVI) (Figure 8). Compound XVI contains a "open" triangular cluster with only two metal–metal bonds. There is a triply bridging sulfido ligand and a formimidoyl ligand that bridges the open edge of the cluster. It was obviously

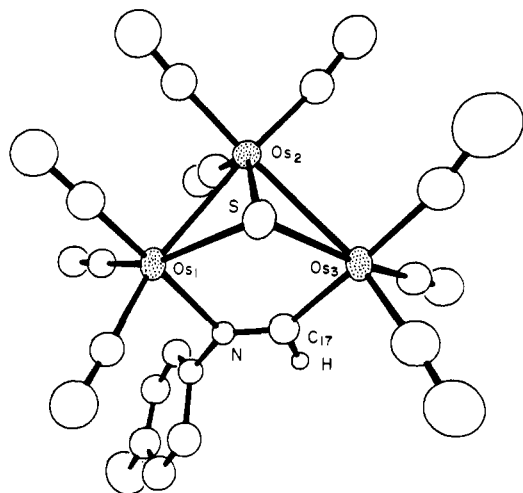(26) Adams, R. D.; Dawoodi, Z. *J. Am. Chem. Soc.* **1981**, *103*, 6510.

Figure 8. Molecular structure of $HOs_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}\eta^2\text{-}HC{=}N\text{-}p\text{-}C_6H_4F)$ (XVI).
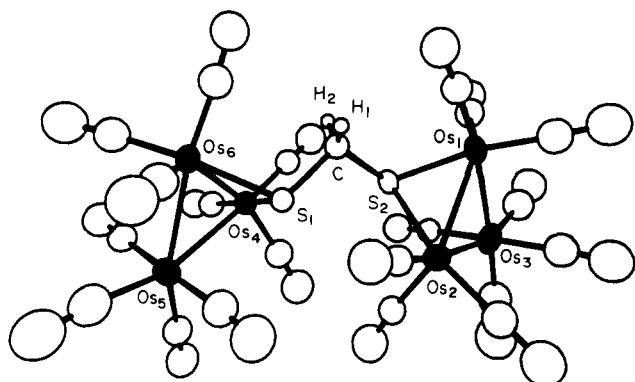
Figure 9. Molecular structure of $(\mu\text{-}S_2CH_2)[HOs_3(CO)_{10}]_2$ (XVII).

formed from XV by cleavage of the carbon–sulfur bond and by formation of a metal–carbon bond (Scheme II). Nucleophilic attack of the sulfido ligand on the third osmium atom induced cleavage of the metal–metal bond. This overall sequence presents, to date, one of the clearest examples of the nature of ligand activation and rearrangement about a trinuclear site. The most important effects are (1) the localization of π-electron density between the carbon and nitrogen atoms, which in turn results in a lowering of the C–S bond order toward one, and (2) the coordination of the nitrogen atom to the third metal atom, which brings the ligand into a position where metal–carbon bond formation is presumably more easily accomplished in conjunction with the carbon–sulfur bond cleavage.

Reactions with CS_2

The reactions of I and X with CS_2 are more complex, but fully explicable in terms of what we have already observed.[27] The reaction of I with CS_2 yields the unusual dicluster product $(\mu\text{-}S_2CH_2)[HOs_3(CO)_{10}]_2$ (XVII) (Figure 9), which contains two trinuclear $HOs_3(CO)_{10}$ clusters linked by a S_2CH_2 ligand. We believe XVII was formed by a reaction in which 2 mol of I combined with 1 mol of CS_2. Each mole of I transferred one hydride ligand to the carbon atom of the CS_2 molecule. Although no intermediates were observed, the reaction is probably a stepwise process, and one could envisage the formation of a transient intermediate analogous to XIV

(27) Adams, R. D.; Golembeski, N. M.; Selegue, J. P. *J. Am. Chem. Soc.* 1981, *103*, 546.
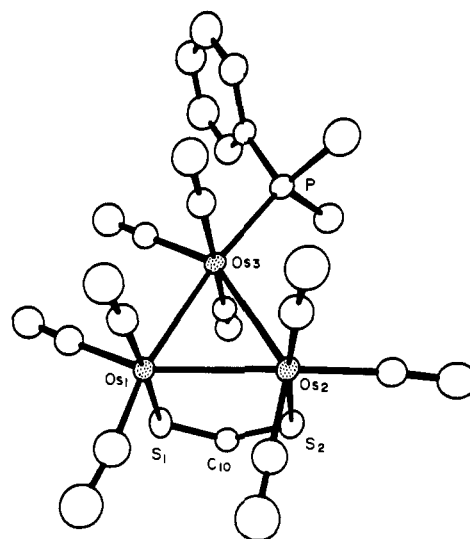
Figure 10. Molecular structure of $HOs_3(CO)_9(PMe_2Ph)(\mu\text{-}\eta^2\text{-}S_2CH)$ (XVIII). Reproduced with permission from *J. Organomet. Chem.* 1980, *195*, 223. Copyright 1980, Elsevier Sequoia SA.
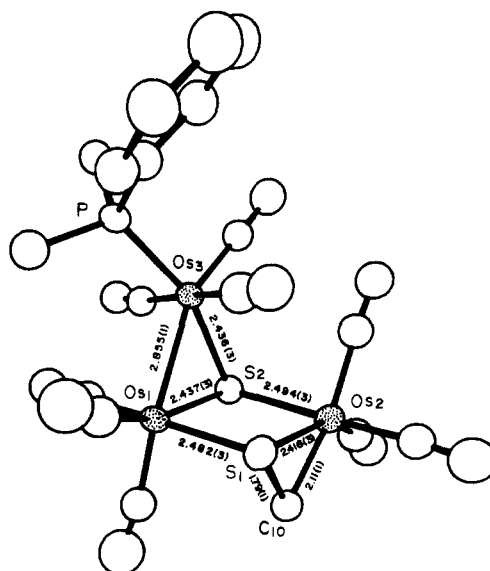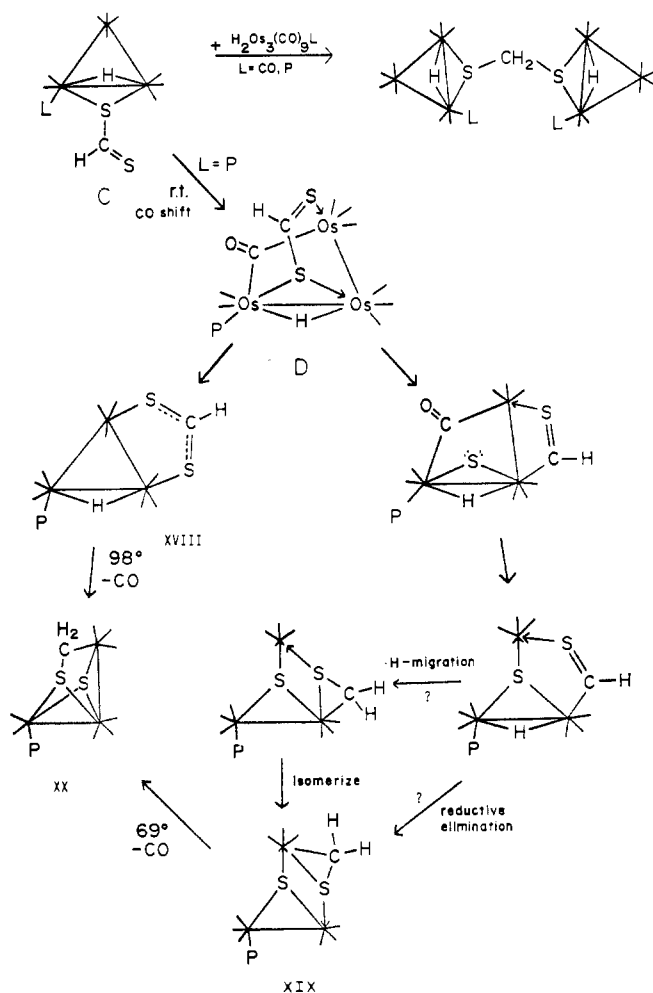
Figure 11. Molecular structure of $Os_3(CO)_9(PMe_2Ph)(\mu\text{-}\eta^2\text{-}S{=}CH_2)$ (XIX).

containing a bridging, monohapto dithioformato ligand. Reaction of the uncoordinated sulfur atom in such a species with a second mole of I accompanied by a second hydride shift to the carbon atom would complete the formation of XVII. While mononuclear metal hydride complexes are well-known to react with CS_2 to yield complexes containing dithioformato ligands, we believe that the reduction to a methanedithiolato group as observed in XVII is heretofore unprecedented.

The reaction of X with CS_2 yields two very interesting trinuclear cluster complexes in addition to the expected analogue of XVII. These are $HOs_3(CO)_9(PMe_2Ph)(\mu\text{-}\eta^2\text{-}S_2CH)$ (XVIII) and $Os_3(CO)_9(PMe_2Ph)(\mu\text{-}\eta^2\text{-}S{=}CH_2)$ (XIX). Compound XVIII, shown in Figure 10, contains a dithioformato ligand bridging an edge of the cluster in a form analogous to the formamido ligand in VIII. Unlike compound X each metal atom in XVIII contains three carbonyl ligands. Thus, during its formation one carbonyl ligand was transferred from one metal atom to another. The cluster XIX, shown in Figure 11, is an unusual molecule containing a triply bridging sulfido ligand and a rare di-hapto thioformaldehyde ligand,

Scheme III

Figure 12. Molecular structure of $Os_3(CO)_8(PMe_2Ph)(\mu_3$-$\eta^2$-S$=CH_2$) (XX).

C(10)–S(1), bridging an edge of the cluster. Each metal atom in XIX contains three carbonyl ligands; therefore, as in XVIII, a carbonyl ligand was transferred between two metal atoms during its formation.

Mechanisms that can account for the formation of XVII, XVIII, and XIX are shown in Scheme III. It was observed spectroscopically that the formations of XVIII and XIX are preceded by the formation of an intermediate containing a hydride ligand and a dithioformato ligand. We believe it has the structure C analogous to XIV. This intermediate could add a second mole of cluster at the uncoordinated sulfur atom to form the dicluster complexes containing the methanedithiolate ligand, or, when L is a bulky ligand, react through a unimolecular process in which the uncoordinated sulfur atom attacks the third metal atom. This may induce the carbonyl ligand shift via an intermediate like D from which both XVIII and XIX can be formed.

Interestingly, when compound XIX is heated, it loses 1 mol of carbon monoxide and is converted into Os_3-$(CO)_8(PMe_2Ph)(\mu_3$-S)(μ_3-SCH$_2$) (XX) shown in Figure 12 which contains a triply bridging thioformaldehyde

ligand. The C(10)–S(1) bond distance in the triply bridging thioformaldehyde ligand is 1.869 (6) Å and implies a C–S bond order of only one. Compound XX can be formed by elimination of a carbonyl ligand from metal atom Os(3). The sulfur atom of the thioformaldehyde ligand then shifts to Os(3) from Os(2); however, this simply shifts the ligand deficiency from Os(3) to Os(2). The deficiency is eliminated through the formation of a metal–metal bond between Os(1) and Os(2). Transformations like this could be of importance in the use of clusters for catalysis. Clearly, the opening and closing of the metal–metal bonds have played a key role in the hydrogenation and rearrangement of the CS$_2$ molecule by this cluster.

Summary

The preceding results taken collectively reveal a pattern of ligand transformations influenced by polynuclear ligand coordinations, metal–metal bond cleavages, and facile ligand shifts between metal atoms. Many of these features can have no parallel in the chemistry of mononuclear metal complexes. On the other hand, they may have many similarities to the types of processes that occur at multinuclear metal sites on surfaces. In conclusion, there is considerable reason to expect that cluster compounds do have sufficiently unique chemical properties to allow them to be developed as a new class of reaction catalysts. At the same time they may also serve as viable models for ligand structure, bonding, and reactivity on metal surfaces.