

Clusters Containing Carbene Ligands. The Formation of a Carbene Ligand by C-H Activation of a π -Complexed Iminium Ligand

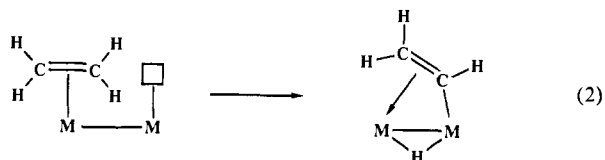
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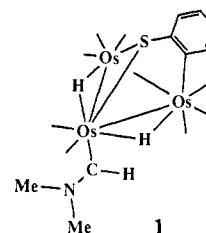
Recently, there has been a flurry of interest in the nature of the activation of olefinic CH bonds by metal complexes.¹⁻⁴ Studies have shown that the barriers to the activation of CH bonds of π -complexed olefins by mononuclear metal complexes are very large.^{2,3} Indeed, evidence has been presented which demonstrates that olefinic CH activation by certain mononuclear metal complexes occurs without precoordination of the olefin, eq 1.²

By contrast olefinic CH activation by polynuclear metal complexes and on surfaces is a relatively facile process.^{5,6} In these cases, it is believed that the activation step is a two-center process, eq 2, in which the olefin is coordinated to one metal atom and the CH cleavage takes place by interaction at a vacant coordination site on a neighboring metal atom.^{5b-c,7}



Iminium ions, $H_2C=NR_2^+$, are isoelectronic to olefins, and they are known to form π -bonded complexes analogous to π -olefin complexes.⁸ In this communication is described the first example of a C-H activation of a π -complexed iminium ion and its conversion into a dialkylaminocarbene ligand.

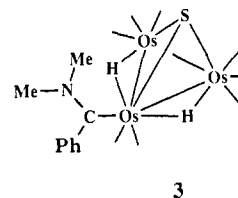
When the compound $Os_3(CO)_8[C(H)NMe_2](\mu-SC_6H_4)(\mu-H)_2$, **1**,⁹ was heated to reflux in $CHCl_3$ solvent for 2 h, it was converted into the new complex $Os_3(CO)_8[\eta^2-Ph(H)C=NMe_2](\mu_3-S)(\mu-H)$,



2, in 20% yield.¹⁰ Compound **2** was characterized by IR and ¹H NMR spectroscopy and by a single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of **2** is shown in Figure 1.^{11,12} Compound **2** consists of a triangular cluster of three osmium atoms with a triply bridging sulfido ligand, eight linear terminal carbonyl ligands, and one bridging hydride ligand. The hydride ligand was not observed crystallographically but is believed to bridge the elongated Os(1)-Os(2) bond. The most interesting ligand in **2** is a $[\eta^2-Ph(H)C=NMe_2]^+$ ligand which is coordinated to Os(1). The Os(1)-C(1) and Os(1)-N distances are the same length, 2.14 (2) and 2.14 (1) Å. The C(1)-N distance at 1.48 (3) Å is similar to a C-N single bond length and indicates that the π -coordination has reduced the C-N double bond character significantly.⁸ A similarly coordinated iminium ligand was recently observed in the complex $Os_3(CO)_7(\mu-CNMe_2)(H_2CNMe_2)(\mu-SPh)(\mu-H)$.^{8a}

The formation of **2** has involved a remarkable shift of the ortho-metalated phenyl ring in **1** to the (dimethylamino)carbene ligand. This included a cleavage of the S-C bond, a shift of one hydride ligand to the ring, and the formation of a C-C bond between the ring and the carbene ligand. The sequence of these events is not yet known. A similar shift of a phenyl ring to a (dimethylamino)carbyne ligand was recently observed for the compound $Os_3(CO)_8(\mu-CNMe_2)(\mu-SPh)(\mu-H)$.⁹

When compound **2** was heated to reflux in heptane solvent for 30 min, the iminium ligand was transformed into a phenyl(dimethylamino)carbene ligand in the product $Os_3(CO)_8[C(Ph)NMe_2](\mu_3-S)(\mu-H)_2$, **3**,⁹ which is formed in a quantitative yield.



The transformation is believed to have been made possible by a multicenter activation process that utilizes a vacant coordination

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- (10) The principal product of this reaction is $Os_3(CO)_8(\mu-CNMe_2)(\mu-SPh)(\mu-H)_2$, **4**, 60% yield. Under the previously reported conditions compound **2** is not formed.⁹ Compound **2** appears to be formed by a reaction that competes with the transformation of **1** into **4**, because **2** cannot be converted into **4** and vice versa. Compound **2** was isolated in 20% yield by TLC on silica gel as a nearly colorless band that elutes behind **4** with hexane solvent: IR (ν_{CO} , hexane, cm^{-1}) 2083 (m), 2047 (s), 2018 (m), 2002 (s), 1986 (m), 1969 (m), 1956 (w). In $CDCl_3$ solution **2** exists as a mixture of two slowly interconverting isomers in an approximate 3/2 ratio: ¹H NMR (δ , $CDCl_3$) major isomer 7.40-7.45 (m, C_6H_5), 3.78 (s, CH), 3.17 (s, CH_3), 2.89 (s, CH_3), -20.37 (s, OsH); minor isomer 7.40-7.45 (m, C_6H_5), 3.07 (s, CH), 3.45 (s, CH_3), 2.44 (s, CH_3), -20.01 (s, OsH).

- (11) Crystals of **2** were grown by slow evaporation of solutions in CH_2Cl_2 /hexane, 1/1 solvent at $-5^\circ C$. Compound **2** crystallizes in the triclinic crystal system. Space group: $P\bar{1}$, $a = 10.132$ (5) Å, $b = 13.143$ (5) Å, $c = 9.982$ (5) Å, $\alpha = 107.48$ (3)°, $\beta = 116.37$ (3)°, $\gamma = 78.85$ (4)°, $Z = 2$, $\rho_{calcd} = 2.82$ g/cc. The structure was solved by a combination of Patterson and difference Fourier techniques and was refined (2533 reflections) to the final values of the residuals $R = 0.056$ and $R_w = 0.064$. Data were collected on a Rigaku AFC6 diffractometer by using $Mo K\alpha$ radiation. All calculations were done on a Digital Equipment Corp. MICROVAX II computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., College Station, TX. All data were corrected for absorption. Only the osmium and sulfur atoms were refined with anisotropic thermal parameters.

- (12) Selected intramolecular bond distances (Å) and angles (deg) are as follows: Os(1)-Os(2) = 2.925 (1) Å, Os(1)-Os(3) = 2.807 (2), Os(2)-Os(3) = 2.741 (2), Os(1)-C(1) = 2.14 (2), Os(1)-N = 2.14 (1), C(1)-N = 1.48 (3); Os(1)-C(1)-N = 70 (1), Os(1)-N-C(1) = 70 (1).

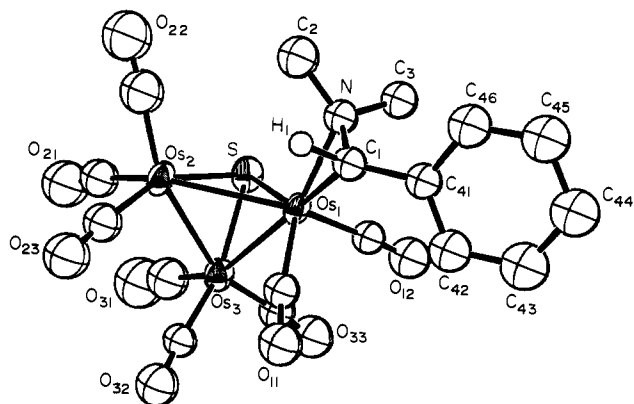
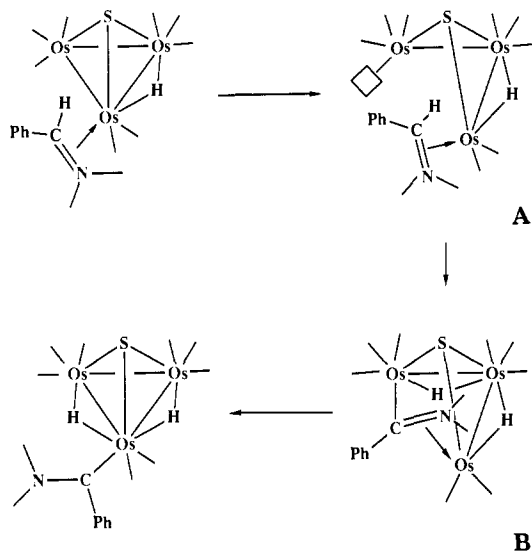


Figure 1. An ORTEP diagram of $\text{Os}_3(\text{CO})_8[\eta^2\text{-Ph}(\text{H})\text{C}=\text{NMe}_2](\mu_3\text{-S})(\mu\text{-H})_2$, 2, showing 50% probability thermal ellipsoids.

Scheme I



site on an adjacent metal atom. Since CO loss was not observed in the transformation, an alternative mode of vacant site formation has been considered. This involves a metal-metal bond cleavage to form an intermediate A as shown in Scheme I. C-H bond cleavage in the iminium ligand would lead to a bridging (η^2 -dimethylamino)carbene ligand,¹³ B, analogous to a σ - π alkenyl ligand, eq 2. A closing of the cluster would lead to the conversion of the bridging carbene into a terminal carbene. We have recently observed a similar transformation of a (μ_3 - η^2 -dimethylamino)-carbene ligand into a terminal carbene ligand.¹⁴

In our recent studies we have discovered several examples of the transformation of tertiary amines into aminocarbene ligands in metal clusters by C-H activation processes. These results provide the first evidence concerning the way in which iminium ligands might be involved in these processes.^{9,15}

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Supplementary Material Available: Tables of crystallographic data, fractional atomic coordinates and thermal parameters, se-

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lected interatomic distances and angles, and anisotropic thermal parameters (7 pages); table of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

The Influence of Surface Atomic Steps on Site-Selective Adsorption Processes. Ethylidyne Formation on Rh{111} and Rh{331}

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Crystal defects such as steps and kinks are considered to be active sites which enhance molecular bond-breaking events in heterogeneous catalytic reactions.¹ In this communication, we present new evidence that suggests that for a class of site-specific reactions, these defects may actually inhibit the desired reaction pathway. Our conclusions are based on studies of CO and C_2H_4 adsorption on Rh{111} and Rh{331} single crystal surfaces at room temperature. These model systems are of interest for several reasons. The Rh{111} surface as depicted at Figure 1a possesses an array of three-fold sites so as to accommodate the observed $c(4 \times 2)$ low energy electron diffraction (LEED)² structure for ethylidyne. The Rh{331} surface, however, is characterized by three rows of a {111} terrace and a {111} single atomic step as shown in Figure 1b. This structure contains only 80% of the number of three-fold sites that are present on Rh{111}. Ethylene undergoes dehydrogenation to CCH_3 (ethylidyne) and presumably requires a three-fold symmetric anchoring position.³ Carbon monoxide, on the other hand, has been observed to bond to a plethora of binding sites, the nature of which are coverage dependent.^{2,4,5} By simultaneously dosing both surfaces with equal amounts of CO or C_2H_4 , we show with use of X-ray photoelectron spectroscopy (XPS) that the coverage of CO on the two crystal surfaces is identical, while the ethylidyne coverage on Rh{331} scales precisely with the number of available active sites. The results suggest that these step defects may then inhibit certain structure-sensitive reactions and that ethylidyne itself may be a novel titrant to determine the number of these sites on polycrystalline surfaces.⁶

Experiments were performed with use of a multitechnique surface analysis system described earlier.⁷ Both the {111} and {331} crystals were affixed to the same sample manipulator and cleaned by using previously developed procedures until no impurity peaks could be observed by XPS. The crystals were then annealed at 1300 K until the characteristic LEED diffraction pattern was observed at room temperature and were subsequently dosed at 300 K with 10 langmuirs⁶ of Matheson Research grade CO or C_2H_4 (at 10^{-7} Torr for 100 s). The C 1s and O 1s peak areas were determined by subtracting the background Rh signal. The pho-

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