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Ethylenepalladium, $(C_2H_4)Pd$, a Localized Bonding Model for the π-Complexed Form of Ethylene Chemisorbed on Palladium

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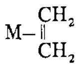
Because of the important role that the group 8 transition metals (Ni, Pd, Pt) play in catalytic reactions of unsaturated hydrocarbons,[1] a major problem has involved an understanding of the nature of the chemisorbed species which form on the active sites of the catalyst surface.

A widely discussed question in organometallic chemistry and heterogeneous catalysis concerns itself with the validity of drawing reasonable chemical representations of those surface species which are involved in surface reactions based on our knowledge of coordination or organometallic complexes.[2,3]

In essence one is inquiring whether or not the chemisorption process on metals (or metal oxides) can be considered as a localized bonding process to a coordinatively unsaturated metal atom (the so-called active site) in a solid surface.

One of the problems that continues to frustrate attempts to answer this question has been the difficulty of obtaining suitable model compounds containing only a single ligand and metal atom of interest. It would appear, however, that by using metal atoms as starting materials in organometallic synthesis,[4] one can obviate the complication of interfering ligands and selectively tailor-make any M–L complex for the specific purpose of comparing its physical and chemical properties with those of $M–L_{ads}$.[5]

In the context of the group 8 transition metals (Ni, Pd, Pt) the results of infrared experiments suggest that ethylene is adsorbed on metal surfaces and supported metals in the form of the σ-bonded $M–CH_2–CH_2–M$ species.[6-8] Very recently infrared evidence has been obtained for the presence of π-bonded species from ethylene chemisorbed on silica-supported Pd and Pt catalysts.[9] These are proposed to coexist with the σ-bonded $M–CH_2–CH_2–M$ species and are found to be more readily removed by hydrogen than the latter.[9] In line with these studies are the results obtained from photoemission experiments,[10] where it is suggested that ethylene is bonded to the surface by means of its π orbital. Interestingly, a recent secondary ion mass spectrometry study[11] of ethylene adsorbed on nickel showed the presence of two distinct types of adsorption, as indicated by the detection of the ions $Ni(C_2H_4)^+$ and $Ni_2(C_2H_4)^+$. These observations supported the idea of a σ-bonded $M–CH_2–CH_2–M$ species and a π-bonded



$$M-\begin{matrix}CH_2\\ \| \\ CH_2\end{matrix}$$

species for ethylene adsorbed on nickel.

In this study we wish to report that we have been successful in generating and stabilizing ethylenepalladium, $(C_2H_4)Pd$, for the first time, using Pd atom/ethylene matrix cocondensation techniques and have obtained its infrared spectrum. We are therefore in a unique position to compare the data with those for the π-bonded form of ethylene chemisorbed on palladium[9] and comment on the usefulness of the localized bonding description of chemisorption[2,3] for a true model reactive intermediate.

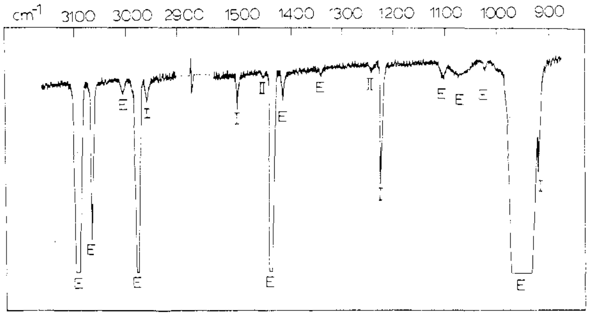


Figure 1. Matrix infrared spectrum observed on depositing Pd atoms with a $C_2H_4/Xe \simeq 1/100$ mixture at 15 K ($Pd/Xe \simeq 1/10^5$) showing the absorptions (I) of $(C_2H_4)Pd$. [The absorptions associated with free C_2H_4 in the matrix are labeled E. II represents a trace amount of $(C_2H_4)_2Pd$.]

Table I. Infrared Spectra of $(C_2H_4)Ni$ and $(C_2H_4)Pd$ in Low-Temperature Matrices

Freq, cm⁻¹		Approx description of mode
$(C_2H_4)Ni$[14]	$(C_2H_4)Pd$	
2961	2952	$\nu(CH_2)$
1497	1502	$\nu(C{=}C)^a$
1159	1223	$\delta(CH_2)^a$
901	913	$\rho_w(CH_2)$

[a] These modes are considered to be highly coupled.[17]

Results and Discussion

Our experimental techniques have been described in detail previously.[12] To generate and isolate ethylenepalladium we chose to work in dilute $C_2H_4/Xe \simeq 1/100$ matrices at 15 K using very low concentrations of metal, $Pd/Xe \simeq 1/10^5$.

Under these conditions, experience has proven that metal atom diffusion and aggregation effects are minimized[13] and the lowest stoichiometry mononuclear reaction product predominates.[4]

A typical infrared spectrum obtained using these experimental conditions is shown in Figure 1, where, aside from absorptions belonging to free ethylene isolated in the Xe matrix (labeled E), a number of new absorptions are observed in the $\nu(CH_2)$ (2952 cm⁻¹), $\nu(C{=}C)$ (1502 cm⁻¹), $\delta(CH_2)$ (1223 cm⁻¹) and $\rho_w(CH_2)$ (913 cm⁻¹) regions which are clearly associated with ethylene coordinated to palladium.

On warming of these dilute matrices to 40 K, these four new absorptions gradually decrease in intensity, maintaining approximately the same relative intensities at all times and are hence assigned to a single species I. Concomitant with the disappearance of the absorptions of species I, one observes the growth of new, weak absorptions at 2943, 2918, 2888, 1524, 1463, 1255, 1242, and 904 cm⁻¹ which correspond closely with the major absorptions observed when Pd atoms are cocondensed with *pure* C_2H_4 or *concentrated* C_2H_4/inert gas matrices. Further dilution of the C_2H_4/Xe matrices below 1/100 does not provide any simplification of the infrared spectrum with respect to that observed for species I in Figure 1.

By analogy with the corresponding nickel atom/ethylene matrix cocondensation experiments,[14] which led to the identification of $(C_2H_4)_nNi$ (where n = 1, 2, and 3) we are able to confidently assign species I to the lowest stoichiometry, mononuclear complex, ethylenepalladium, $(C_2H_4)Pd$ (Table I). The details of the higher stiochiometry products $(C_2H_4)_2Pd$ and $(C_2H_4)_3Pd$ will form the subject of another report.[18]

Of central interest to the theme of the present paper is the remarkable similarity between the infrared spectra of $(C_2H_4)Pd$ and $(C_2H_{4_{ads}})$ Pd as shown in Table II. From the close correspondence between the observed $\nu(CH_2)$ and ν-$(C{=}C)$ stretching modes, it is strongly suggested that ethylene π bonded to a single palladium atom in $(C_2H_4)Pd$ is indeed an intuitively acceptable model for the π-complexed form of C_2H_4 chemisorbed onto Pd.[9]

Table II

Approx description of mode	Freq, cm^{-1}		
	$(C_2H_4)Pd$	$(C_2H_{4ads})Pd$[9]	Δ
$\nu(CH_2)$	2952	2980	28
$\nu(C{=}C)$	1502	1510	8
$\delta(CH_2)$	1223	Not obsd	
$\rho_w(CH_2)$	913	Not obsd	

The small "blue" frequency shift on passing from $(C_2H_4)Pd$ to $(C_2H_{4_{ads}})$ Pd implies a slight strengthening of the C—H and C=C bonds of the coordinated ethylene moiety on going from a single Pd atom site to a Pd atom in the metal surface. This might be taken to imply that the extent of Pd → C_2H_4 charge transfer is marginally less from a Pd surface atom site than from an isolated Pd atom. Such a change in electron transfer between metal–ethylene and metal–metal bonds might be taken as evidence in support of photoelectron emission studies[15] which show that alkenes are net electron acceptors from Pt(0) in complexes such as $(Ph_3P)_2Pt(C_2H_4)$ yet net electron donors to surface Pt atoms.[16]

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Electron Transfer in Diazonium Complexes of Ruthenium

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Although of recent origin the synthetic chemistry leading to the aryldiazonium–metal (aryldiazenato[1] or aryldiazenido[2]) linkage (M–NNAr) has proven to be extensive and analogies with related metal nitrosyl complexes can be drawn.[1] The synthetic chemistry involved has relied mainly on reactions between diazonium salts and appropriate transition metal complexes. In the net sense the reactions which have been used include substitution (eq 1 and 2), addition or oxidative addition

$$[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^- + ArN_2^+ \xrightarrow[\text{THF}]{} (\eta^5\text{-}C_5H_5)Mo(CO)_2(N_2Ar) + CO \qquad (1)^3$$

$$Fe(CO)_3(PPh_3)_2 + ArN_2^+ \xrightarrow[\text{acetone–benzene}]{} [Fe(CO)_2(PPh_3)_2(N_2Ar)]^+ + CO \qquad (2)^4$$

(eq 3 and 4), and insertion into a metal–hydride bond (eq 5).

$$Ru(PPh_3)_3Cl_2 + ArN_2^+Cl^- \xrightarrow[\text{EtOH–acetone}]{} Ru(PPh_3)_2(N_2Ar)Cl_3 + PPh_3 \qquad (3)^5$$

$$Pt(PPh_3)_3 + ArN_2^+ \xrightarrow[\text{Et}_2\text{O–EtOH}]{} [Pt(N_2Ar)(PPh_3)_3]^+ \qquad (4)^6$$

$$PtHCl(PEt_3)_2 + ArN_2^+ \xrightarrow[\text{EtOH}]{} [PtCl(NHNAr)(PEt_3)_2]^+ \qquad (5)^7$$

Diazonium ions are moderately strong oxidants[8] and net electron-transfer reactions from metal to ArN_2^+ might in certain cases be expected to compete with the synthetically useful reactions mentioned above or to provide pathways for decomposition of M–N_2Ar complexes once formed. As an example of the first kind, $(C_6Me_6)Cr(CO)_2PPh_3$ is known to be oxidized to the monocation by diazonium ions.[9]

We have described the preparations of a series of diazonium complexes of ruthenium by a route not involving diazonium salts. The reactions involve diazotization of primary aromatic amines using a bound nitrosyl group (eq 6).[10] As in metal

$$[Ru(bpy)_2(NO)Cl]^{2+} + ArNH_2 \xrightarrow[\text{CH}_3\text{CN}]{} [Ru(bpy)_2(N_2Ar)Cl]^{2+} + H_2O \qquad (6)$$

nitrosyls, attempts to describe the electronic structure of the M–NNAr group can lead to certain ambiguities as evidenced by the limiting valence bond structures for the Ru–bpy complexes: Ru^{II}–NN^+Ar and Ru^{IV}–NN^-Ar. However, the complexes $[Ru(bpy)_2(N_2Ar)Cl]^{2+}$ have high ν(NN) stretching frequencies (>1980 cm^{-1} in CH_3CN) and chemical reactivity properties similar to those of free ArN_2^+ ions indicating a considerable diazonium ion–ruthenium(II) character in the RuN_2Ar linkage.[10]

From attempts to prepare Ru–bpy–diazonium complexes by direct reactions with ArN_2^+ ions and from the chemical properties of the actual complexes prepared by reaction 6, it is apparent that simple one-electron-transfer processes play an important role in the underlying chemistry. We report here our observations on such processes in some detail since they appear to give general insight into the importance of electron transfer in the formation and stability of metal–diazonium complexes.

Results and Discussion

Electron-Transfer Properties of the Diazonium Complexes. The series of nitrosyl complexes $[Ru(bpy)_2(NO)L]^{n+}$ ($n = 2$, L = N_3, Cl, NO_2; $n = 3$, L = NH_3, py, CH_3CN) are known to undergo reversible one-electron reductions where the oxidizing site in the complex is localized largely at the nitrosyl group (eq 7). $E_{1/2}$ values for the reduction processes, e.g.,

$$[Ru(bpy)_2(NO^+)Cl]^{2+} + e^- \rightarrow [Ru(bpy)_2(\dot{N}O)Cl]^+ \qquad (7)$$

eq 7, fall into the range 0.18–0.56 V in 0.1 M $[N(n\text{-}C_4H_9)_4](PF_6)$–acetonitrile at 22 ± 2 °C vs. the saturated sodium chloride calomel electrode (SSCE).[12] A close similarity has been noted previously between the properties of nitrosyl and related diazonium complexes.[10,13] From their chemical and physical properties, there is clearly considerable