(3) (a) P. A. Kilty and W. M. H. Sachtler, *Catal. Rev.*, **10**, 1 (1974); (b) H. H. Voge and C. R. Adams, *Adv. Catal.*, **17**, 151 (1967); (c) G. W. Keulks and J. F. Outlaw, Jr., Proceedings of the Fifth International Conference on Catalysis, J. W. Hightower, Ed., North-Holland Publishing Co., Amsterdam, 1973.
(4) E. P. Kündig, M. Moskovits, and G. A. Ozin, *J. Mol. Struct.*, **14**, 137 (1972).
(5) M. Moskovits and G. A. Ozin, *J. Appl. Spectrosc.*, **26**, 487 (1972).
(6) D. McIntosh and G. A. Ozin, *Inorg. Chem.*, **16**, 51 (1977).
(7) D. McIntosh and G. A. Ozin, *Inorg. Chem.*, **16**, 59 (1977).
(8) D. McIntosh and G. A. Ozin, *Inorg. Chem.*, in press.
(9) M. E. Volpin and I. S. Kolomnikov, *Pure Appl. Chem.*, **33**, 567 (1973).
(10) (a) E. P. Kündig, M. Moskovits, and G. A. Ozin, *Nature (London), Phys. Sci.*, **236**, 69 (1972) **239**, 90 (1972); (b) W. Klotzbücher, D. Singh, and G. A. Ozin, to be published.
(11) H. Huber, D. McIntosh, and G. A. Ozin, submitted.
(12) P. J. Hayward, D. M. Blake, G. Wilkinson, and C. J. Nyman, *J. Am. Chem. Soc.*, **92**, 5873, 1970.
(13) E. P. Kündig, M. Moskovits, and G. A. Ozin, *Angew. Chem., Int. Ed. Engl.*, **14**, 292 (1975).
(14) Labeling experiments using $^{12}CO_2/^{13}CO_2/Ar$ isotopic mixtures confirmed that weak absorptions in the 1600-cm^{-1} region were associated with trace amounts of H_2O rather than coordinated CO_2.
(15) Note, that had I been the carbonate, then both the symmetric and asymmetric ν(C—O) stretching modes should have been observed[12] in the 1250–800 cm^{-1} region.

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Synthesis and Characterization of Reactive Intermediates in the Palladium Atom–Ethylene System, $(C_2H_4)_nPd$ (where n = 1, 2, or 3)

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The cocondensation of Pd atoms with C_2H_4 and C_2H_4/inert gas matrices at 15 K is shown to provide a direct and efficient route to binary palladium ethylene complexes of the form $(C_2H_4)_nPd$ (where n = 1, 2, or 3). The complexes were identified and characterized by infrared and UV–vis spectroscopy coupled with ethylene concentration studies, warm-up experiments, and $^{13}C_2H_4$ and $^{12}C_2H_4/^{13}C_2H_4$ isotopic substitution. Extended Hückel molecular orbital calculations are performed for all three complexes and prove to be a useful aid toward understanding the origin of and observed trends in their UV charge-transfer spectra. Comparisons between the $(C_2H_4)_nPd$ complexes and the analogous $(C_2H_4)_nNi$ complexes are briefly discussed. The suitability of $(C_2H_4)Pd$ as a localized bonding model for the π-complexed form of ethylene chemisorbed onto palladium is also considered.

Introduction

A promising chemical approach which is receiving increasing attention in the field of heterogeneous catalysis[1] involves the use of transition metal atoms for synthesizing localized bonding models of the chemisorbed state.[2] With a careful choice of reaction partners and experimental conditions one can, in principle, design a metal atom–ligand combination to simulate and study almost any adsorbate–adsorbent interaction of catalytic interest.[3,4]

Because olefins are involved in a large number of important heterogeneous catalytic reactions of industrial significance,[5] we chose initially to study the interactions between ethylene and group 8 metal atoms using cryochemical trapping techniques.

In a previous paper[6] we reported that by using Ni atom/C_2H_4 and C_2H_4/Ar matrix cocondensation reactions one can gain a synthetic route to the extremely labile reaction intermediates $(C_2H_4)Ni$ and $(C_2H_4)_2Ni$ as well as the known compound $(C_2H_4)_3Ni$.[7] These complexes were characterized by matrix infrared and UV–vis spectroscopy, coupled with nickel–ethylene concentration studies and warm-up experiments.

In this paper we have extended the technique to palladium atoms to determine whether binary ethylene complexes of palladium, like those of nickel, have an independent existence. By using a combination of ethylene concentration and matrix warm-up experiments, we have been able to definitely identify three $(C_2H_4)_nPd$ complexes, the highest stoichiometry of which is proven from $^{13}C_2H_4$ isotope labeling experiments to be $(C_2H_4)_3Pd$. A previous claim to have synthesized $(C_2H_4)_3Pd$ at 77 K,[7c,d] while effectively demonstrating the existence of a binary Pd/C_2H_4 complex, employed comparative infrared spectroscopic techniques for making a stoichiometric assignment, rather than isotopic labeling. In this paper we will demonstrate that the infrared technique without isotopic substitution is somewhat suspect, in that in a series of complexes $(C_2H_4)_nM$ the infrared peaks shift very little on increasing n or on changing M. On the other hand, we find that the metal-to-ligand charge transfer transitions (MLCT) in the UV spectra of $(C_2H_4)_n$ Pd are quite sensitive to variations in both n and M.

Experimental Section

Monatomic Pd vapor was generated by directly heating a 0.010 in. ribbon filament of the metal or 0.005 in. Pd ribbon wound on a W support with ac in a furnace similar to that described previously.[8] The palladium (99.99%) was supplied by McKay. Research grade $^{12}C_2H_4$ (99.99%) and Ar (99.99%) were supplied by Matheson of Canada and $^{13}C_2H_4$ (91%) by Prochem. The rate of Pd atom deposition was continuously monitored using a quartz crystal microbalance.[9]

In the infrared experiments, matrices were deposited onto a NaCl or CsI optical plate cooled to 15 K by means of an Air Products Displex closed cycle helium refrigerator. Infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer. UV–vis spectra were recorded on a standard Varian Techtron in the range 190–900 nm, the sample being deposited onto a NaCl optical plate.

Extended Hückel calculations for $(C_2H_4)_{1,2,3}Pd$ were performed on an IBM 7094 computer.

Results and Discussion

Infrared Experiments. When Pd atoms are cocondensed with $^{12}C_2H_4/Ar \simeq 1/10$ mixtures at 15 K (using very low concentrations of Pd to eliminate complications due to cluster formation, Pd/Ar $\simeq 10^{-4}$),[10] aside from infrared absorptions belonging to free ethylene isolated in the Ar matrix (labeled E in all figures), a number of new absorptions were observed in the ν(CH), ν(C═C), $\delta(CH_2)$, and $\rho_w(CH_2)$ regions (Figure 1B) which are clearly associated with ethylene coordinated to palladium. Warm-up experiments performed in the range 10–45 K demonstrate that the set of new absorptions can be ascribed to *two* distinct species labeled III and II in Figure 1B and Table I. Of particular note is the fact that the absorptions labeled III occur at frequencies very close to those

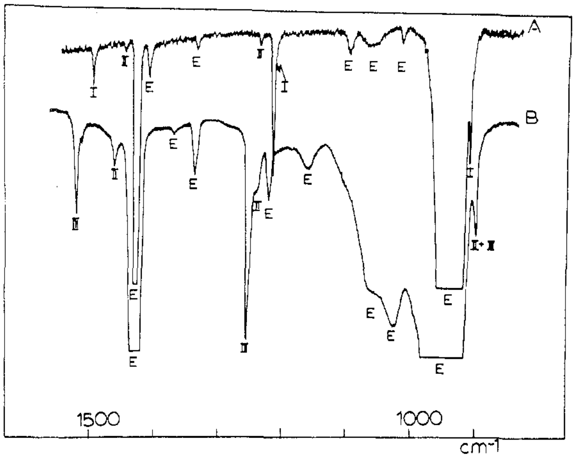


Figure 1. The matrix infrared spectra observed on depositing Pd atoms with (A) $C_2H_4/Xe \simeq 1/100$ and (B) $C_2H_4/Ar \simeq 1/10$ at 15 K ($Pd/\text{inert gas} \simeq 1/10^4$), showing the absorptions of $(C_2H_4)_{1,2,3}Pd$, labeled I, II, and III, respectively. The absorptions associated with free C_2H_4 in the matrix are labeled E.

Table I. The Infrared Spectra and Vibrational Assignments for $(C_2H_4)_nM$ (where M = Ni or Pd and n = 1, 2, or 3)[a]

$(C_2H_4)_3M$ (III)		$(C_2H_4)_2M$ (II)		$(C_2H_4)M$ (I)		Tentative assignment of modes
Ni[c]	Pd[d]	Ni[c]	Pd[d]	Ni[c]	Pd[b,d]	
		2945	2943			
2917	2918			2961	2958	$\nu(CH_2)$
		2885	2888			
1513	1524	1465	1463	1497	1502	$\nu(C{=}C)$
1245	1255	1225	1242	1159	1223	$\delta(CH_2)$
911	904	906	916	901	913	$\rho_w(CH_2)$

[a] Average values quoted in cm^{-1} from the various C_2H_4, Ar, and Xe matrix experiments. [b] A low-frequency mode was observed at about 372 cm^{-1} for $(C_2H_4)_3Pd$ which is tentatively assigned to an asymmetric Pd–ethylene stretching mode. [c] Reference 6. [d] This study.

previously assigned to $(C_2H_4)_3Pd$.[7c,d]

In order to reveal the existence of any lower stoichiometry complexes in the Pd/C_2H_4 system, the rigid matrix $C_2H_4/Xe \simeq 1/100$ was chosen and a typical infrared trace is shown in Figure 1A. The features of special interest under these conditions are the spectroscopic nonobservation of species III and only trace amounts of species II. Aside from free ethylene absorptions, the major new lines occur at frequencies distinct from those of II and III and which, from warm-up experiments, can be associated with a single species labeled I in Figure 1A and Table I.

An a priori assignment on the basis of these results is that *three* complexes have been generated where

$$I \equiv (C_2H_4)Pd$$

$$II \equiv (C_2H_4)_2Pd$$

$$III \equiv (C_2H_4)_3Pd$$

Verification of these tentative assignments stemmed from a series of ten ethylene–inert gas concentration experiments in the range 1/100 to pure ethylene, together with their associated warm-up experiments. In all cases the data agreed with our proposed assignments. Moreover, the parallelism with the analogous nickel data,[6] also shown in Table I, is most striking.

As with the corresponding Ni data,[6] our experiments with Pd atoms in pure C_2H_4 reveal the interesting phenomenon that both $(C_2H_4)_2Pd$ (II) and $(C_2H_4)_3Pd$ (III) form on 15 K deposition. Their relative concentrations as indicated by their integrated infrared absorbances remain roughly constant up to about 60 K. At 70 K, $(C_2H_4)_2Pd$ gradually decays relative to $(C_2H_4)_3Pd$ and at 80 K, as the C_2H_4 matrix gradually sublimes from the cold window, the absorptions of $(C_2H_4)_3Pd$ essentially disappear. Whether or not the $(C_2H_4)_3Pd$ species decomposes at these temperatures or is simply lost into the vacuum system as the matrix breaks up will form the basis of a future quadrupole mass spectroscopic investigation, although it has been reported that $(C_2H_4)_3Pd$ is stable up to 190 K in the absence of a matrix support.[7c,d]

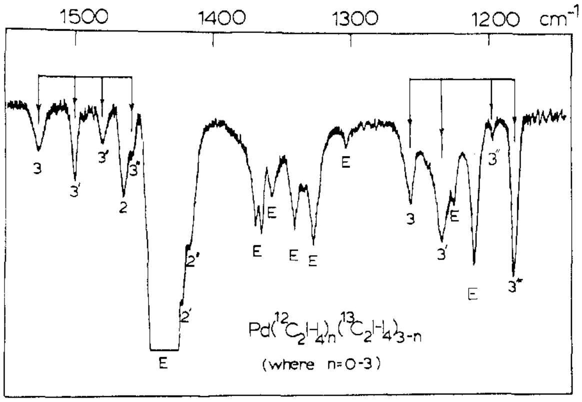


Figure 2. The matrix infrared spectrum observed on depositing Pd atoms with $^{12}C_2H_4/^{13}C_2H_4/Ar \simeq 1/1/10$ at 15 K, showing the isotope patterns in the $\nu(C{=}C)$ stretching and $\delta(CH_2)$ deformational regions of $(^{12}C_2H_4)_n(^{13}C_2H_4)_{3-n}Pd$ (where n = 0–3).

We believe that the coexistence of both $(C_2H_4)_3Pd$ and $(C_2H_4)_2Pd$ in pure C_2H_4 matrices, as in the case of the analogous nickel compounds,[6] may be an artifact relating to the favorable packing requirements of II in the crystal lattice of solid C_2H_4 (space group $D_{2h}{}^{12}$, *Pnnm*), see ref 11.

Having tentatively assigned the highest and lowest stoichiometry compounds in the Pd atom/ethylene system to III and I, respectively, we then examined the corresponding $^{12}C_2H_4/^{13}C_2H_4$ mixed isotopic data in order to verify our proposals.

Unequivocal stoichiometric assignments for III and I were obtained by examining the isotopic patterns in the $\nu(C{=}C)$ stretching (1550–1450 cm^{-1}) and $\delta(CH_2)$ deformational (1300–1000 cm^{-1}) regions under conditions which favored optimum spectral and chemical resolution of III and I. (We are aware that these modes may be highly coupled[25] and a normal coordinate analysis employing infrared and Raman data for the $(C_2H_4)_nPd$ species is underway.[26])

Our best results for species III were obtained with $^{12}C_2H_4/^{13}C_2H_4/Ar \simeq 1/1/10$ mixtures and a typical infrared spectrum is shown in Figure 2. Aside from absorptions associated with free $^{12}C_2H_4$ and $^{13}C_2H_4$ labeled E, a *quartet* isotope pattern can be discerned in the $\nu(C{=}C)$ stretching and $\delta(CH_2)$ deformation regions which, from their frequencies and warm-up behavior, can be ascribed to species III. These values are listed in Table II.

To establish which of these isotope lines are associated with the mixed isotopic molecules $(^{12}C_2H_4)_n(^{13}C_2H_4)_{3-n}Pd$ (where n = 0–3), we separately investigated the corresponding reaction with $^{13}C_2H_4$ and our assignments are displayed in Table II.

It is interesting to note that the "conventional" quartet isotopic pattern of $M(^{12}C^{16}O)_n(^{13}C^{16}O)_{3-n}$ (where n = 0–3),[12] the origin of which is related to the existence of a positive $k_{CO\cdot CO}$ interaction force constant, is *not* observed for III. Instead, one observes an "inverted" quartet isotope pattern for both the $\nu(C{=}C)$ and $\delta(CH_2)$ modes (Table II), which serves to characterize III as a tris(ethylene)palladium complex but with *negative* stretch–stretch and angle interaction force constants.

Confirmation of the stoichiometry of species I originated from $^{13}C_2H_4/Xe \simeq 1/100$ and $^{12}C_2H_4/^{13}C_2H_4/Xe \simeq 1/1/100$ experiments. The results of these experiments are illustrated

Table II. Infrared Isotopic Substitution Data for $(^{12}C_2H_4)_n(^{13}C_2H_4)_{3-n}Pd$ (where $n = 0–3$)

Obsd freq, cm^{-1}	Mode	Assignments[b]
1524	$\nu(C=C)$	$(^{12}C_2H_4)_3Pd$
1499	$\nu(C=C)$	$(^{13}C_2H_4)_3Pd$
1481	$\nu(C=C)$	$(^{12}C_2H_4)_2(^{13}C_2H_4)Pd$
~1460[a]	$\nu(C=C)$	$(^{12}C_2H_4)(^{13}C_2H_4)_2Pd$
1255[c]	$\delta(CH_2)$	$(^{12}C_2H_4)_3Pd$
1233	$\delta(CH_2)$	$(^{13}C_2H_4)_3Pd$
1196	$\delta(CH_2)$	$(^{12}C_2H_4)_2(^{13}C_2H_4)Pd$
1182	$\delta(CH_2)$	$(^{12}C_2H_4)(^{13}C_2H_4)_2Pd$

[a] Partial overlap of this species with the absorption of $(^{12}C_2H_4)_2Pd$. [b] The frequency ordering and assignments for these isotopic molecules are based on $^{12}C_2H_4/Ar \simeq 1/10$, $^{13}C_2H_4/Ar \simeq 1/10$, and $^{12}C_2H_4/^{13}C_2H_4/Ar \simeq 1/1/10$ experiments and the assumption of a negative $k_{C=C,C=C}$ stretch–stretch interaction force constant. [c] In this frequency range, free ethylene lines occur at 1224 cm^{-1} $(^{12}C_2H_4)$ and 1210 cm^{-1} $(^{13}C_2H_4)$.

Table III. Infrared Isotopic Data for $(^{12}C_2H_4)Pd$ and $(^{13}C_2H_4)Pd$ in Xenon Matrices[a]

Obsd freq, cm^{-1}	Mode	Assignment
2952	$\nu(^{12}CH_2)$	$(^{12}C_2H_4)Pd$
2932	$\nu(^{13}CH_2)$	$(^{13}C_2H_4)Pd$
1502	$\nu(^{12}C=^{12}C)$	$(^{12}C_2H_4)Pd$
1460	$\nu(^{13}C=^{13}C)$	$(^{13}C_2H_4)Pd$
1223	$\delta(^{12}CH_2)$	$(^{12}C_2H_4)Pd$
1193	$\delta(^{13}CH_2)$	$(^{13}C_2H_4)Pd$
913	$\rho_w(^{12}CH_2)$	$(^{12}C_2H_4)Pd$
905	$\rho_w(^{13}CH_2)$	$(^{13}C_2H_4)Pd$

[a] Matrix ratio was $C_2H_4/Xe \simeq 1/100$.

in Table III where it can be seen that the $\nu(C{=}C)$ stretching, $\delta(CH_2)$ deformational regions and $\rho_w(CH_2)$ wagging of I display isotopic *doublets* in the $^{12}C_2H_4/^{13}C_2H_4/Xe \simeq 1/1/100$ experiment, while only *singlets* in the respective $^{12}C_2H_4/Xe$ and $^{13}C_2H_4/Xe$ experiments. These data unequivocally establish I to be monoethylenepalladium.

It was not possible to obtain useful mixed isotopic data for species II for three reasons. First, under no circumstances was it possible to obtain appreciable quantities of II with minimal amounts of I and III. Second, the isotope lines associated with the $\nu(C{=}C)$ stretching mode of II, 1465 cm^{-1}, were overlapped by the intense absorption of free ethylene at roughly 1438 cm^{-1} (see Figure 2). Third, the $\delta(CH_2)$ deformational mode of II never appears as a very intense line and also suffers from band overlap problems. However, having assigned I to $(C_2H_4)Pd$ and III to $(C_2H_4)_3Pd$, one feels confident in assigning II to $(C_2H_4)_2Pd$ by virtue of its concentration and warm-up behavior as well as by comparison with $(C_2H_4)_2Ni$[6] and $(C_2H_4)_2Cu$.[13]

UV–Visible Experiments. Two types of UV–vis study of the Pd atom/ethylene system proved to be most informative. The first involved an ethylene/argon concentration study in the range pure ethylene to 1/200, of which a typical series of spectra are shown in Figure 3A–D, respectively. The spectra are dominated by intense ultraviolet absorptions in the range 200–240 nm. (We note at this point that visible absorptions for 12-, 14-, and 16-electron systems of the type $(C_2H_4)_{1,2,3}Pd$ are not expected if the palladium is formally Pd(0).) With the prior knowledge that $(C_2H_4)Pd$ and $(C_2H_4)_3Pd$ are the dominant species under conditions of high matrix dilution (Figure 3D) and low matrix dilution (Figures 3A and 3B), respectively, one can make the a priori assignment of the three observed ultraviolet transitions of Figure 3 to species I, II, and III as listed in Table IV. These optical spectra indicate that a single, UV–electronic transition can be associated with each of species I to III and that these shift monotonically to higher energies with increasing ethylene stoichiometry.

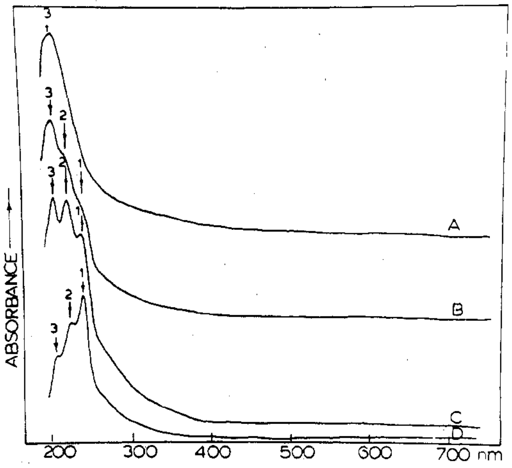


Figure 3. The matrix UV–vis spectra observed on depositing Pd atoms with (A) pure C_2H_4, (B) $C_2H_4/Ar \simeq 1/10$, (C) $C_2H_4/Ar \simeq 1/50$, and (D) $C_2H_4/Ar \simeq 1/200$ mixtures at 15 K, showing $(C_2H_4)_{1,2,3}Pd$, labeled 1, 2, 3, respectively.

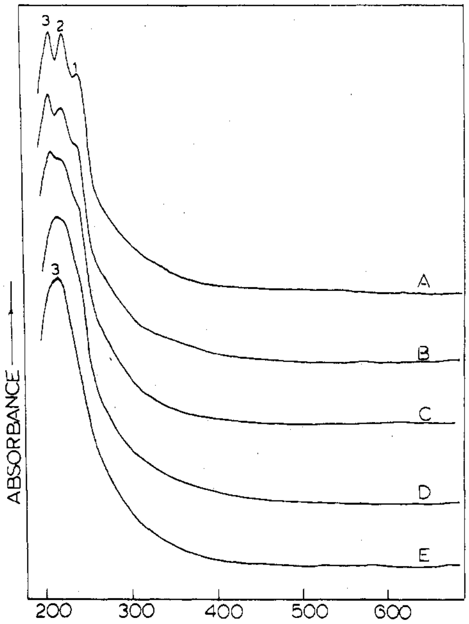


Figure 4. (A) The same as Figure 3C showing the effect of matrix warm-up to (B) 20 K, (C) 30 K, (D) 40 K, and (E) 50 K (same notation as Figure 3).

Table IV. The UV-Vis Spectra of $(C_2H_4)_nM$ (where M = Ni or Pd, n = 1, 2, or 3)

	M = Ni nm	M = Pd nm	Assignment
$(C_2H_4)M$	280	240	MLCT
$(C_2H_4)_2M$	250	221	MLCT
$(C_2H_4)_3M$	236	204	MLCT

Confirmation of these assignments stems from UV–vis warm-up studies of a matrix containing *all* three species on deposition (Figure 4A). Under these conditions, one observes a gradual decrease in the absorbance of the 240-nm band on warming to 20–30 K (Figures 4B and 4C), followed at a different rate by the band at 221 nm. At 45 K (Figure 4E), the major absorbing species corresponds to the band at 204 nm. The warm-up behavior of the three bands at 204, 221, and 240 nm is therefore in accordance with that expected for an assignment to species III, II, and I, respectively.

At this point, the close resemblance of the ultraviolet transitions of $(C_2H_4)_{1,2,3}Pd$ to those observed for $(C_2H_4)_{1,2,3}Ni$[6] shown in Table IV should be noted. First, *one* ultraviolet transition can also be associated with each of the $(C_2H_4)_{1,2,3}Ni$

Table V. Parameters Used in the EHMO Calculations for $(C_2H_4)_nPd$ (where n = 1, 2, or 3)

Orbital	Orbital[a] exponent	H_{ii},[a] eV
Pd 4d	3.400	−8.33
5s	1.570	−7.32
5p	1.570	−2.00
C 2s	1.625	−21.40
2p	1.625	−11.40
H 1s	1.000	−13.60

Bond Distances Used, Å
r(Pd–C) = 2.35
r(C–C) = 1.34
r(C–H) = 1.10

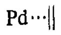
[a] R. Hoffman, *J. Chem. Phys.*, 39, 1397 (1963).

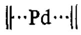
species. Second, these also monotonically *blue* shift, with increasing ethylene stoichiometry. Third, each is *red* shifted with respect to the corresponding $(C_2H_4)_{1,2,3}Pd$ ultraviolet transitions. Fourth, major energy shifts are observed in the ultraviolet spectra of species $(C_2H_4)_nM$ on changing either n from 1 to 3 or M from Ni to Pd; on the other hand, the corresponding relative energy shifts in the infrared are extremely small (Table I).

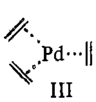
Each of these observations is interesting and carries considerable information regarding the molecular, electronic, and bonding properties of binary, transition metal ethylene complexes.

As a first step toward understanding these data, an extended Hückel molecular orbital study has been initiated for the $(C_2H_4)_{1,2,3}Pd$ complexes, similar to that previously described for $(C_2H_4)_{2,3}Ni$.[14] The results of these calculations will now be considered together with those of SCF–Xα–SW theory[1] recently applied to $(C_2H_4)M$ (where M = Ni, Pd, or Pt).

Extended Hückel Molecular Orbital Calculations for $(C_2H_4)_nPd$ (where n = 1–3). The calculations have been carried out with the C_{2v}, D_{2h}, and D_{3h} geometries shown below:


I
C_{2v}


II
D_{2h}


III
D_{3h}

The Pd–C bond distance was chosen at 2.35 Å for all three $(C_2H_4)_nPd$ complexes and represents an average of the Pd–olefin–carbon distances found previously in palladium–olefin complexes.[15] The interatomic distances chosen for the coordinated ethylene moiety were identical to those employed by Hoffmann et al.[14] In our EHMO calculations, the 4d, 5s, and 5p orbitals of atomic Pd were used together with Clementi–Roetti[16] orbital exponents, the Cusachs[17] approximation, and unmodified Baranovskii[18] values for the coulomb integrals. The parameters required to reproduce these calculations are listed in Table V.

The resulting orbital energies for all three complexes are depicted in Figure 5 together with the calculated π and π* orbital energies of free ethylene. Generally speaking, the overall features of these energy level schemes are not unlike the EHMO results of Hoffmann et al.[14] for the corresponding nickel complexes (noting that Hoffmann does not report calculations for $(C_2H_4)Ni$) and the SCF–Xα–SW calculations of Messmer et al.[1] for $(C_2H_4)M$ (where M = Ni, Pd, or Pt).

The descriptions of the relevant orbitals depicted in Figure 5 indicate that the Dewar–Chatt–Duncanson[19] description of the palladium–ethylene interaction is an adequate one.

In brief, apart from a group of low-lying CH, CC, and PdC bonding orbitals (Figure 5), the HOMO's for $(C_2H_4)_{1,2,3}Pd$ consist of a cluster of Pd d-like orbitals. In each case, a Pd–C σ-type bonding orbital(s) is found around −13 to −13.5 eV and a Pd–C π-type bonding orbital around −8.8 to −9.0 eV. The antibonding counterpart to the Pd–C π-type orbital is found between −7.75 and −7.50 eV for all three complexes.

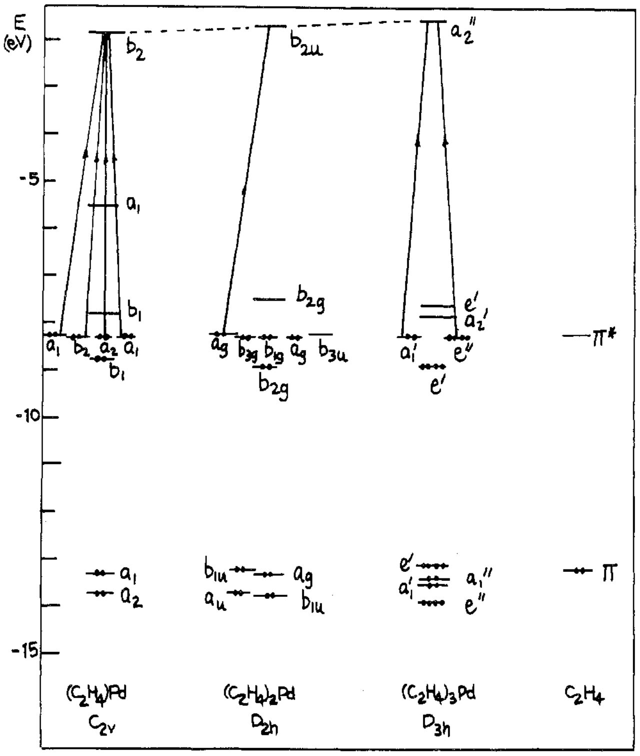


Figure 5. Extended Hückel molecular orbital energy level schemes for C_{2v}, $(C_2H_4)Pd$; D_{2h}, $(C_2H_4)_2Pd$; and D_{3h}, $(C_2H_4)_3Pd$ (see text for notation). Electric dipole and spin-allowed transitions are indicated.

The observation of intense absorptions in the ultraviolet for $(C_2H_4)_{1,2,3}Pd$, which *blue* shift with increasing ethylene coordination number, leads us to believe that the electric dipole and spin allowed electronic transition(s) depicted in Figure 5 are reasonable assignments for the observed bands. In each case they originate from one or more of a group of filled Pd d-like orbitals, which cluster around −8.25 eV for all three complexes. The upper level in each case is best described as an antibonding combination of 4pπ-type atomic orbitals on Pd with symmetry matched $2p_\pi$-type atomic orbitals on carbon. In agreement with the observed UV spectra, these electronic transitions monotonically blue shift on passing from $(C_2H_4)Pd$ to $(C_2H_4)_3Pd$.

In view of the assignment of metal → olefin charge transfer transitions in the 200–300-nm region for platinum–olefin complexes of the type $[(olefin)PtCl_3]^-$, copper halide–norbornene complexes, and silver(I)–benzene and styrene complexes,[20] it would appear to be quite reasonable to describe the observed (and calculated) UV transitions of $(C_2H_4)_{1,2,3}Pd$ as Pd → C_2H_4 charge transfer. A similar description would also seem to be appropriate for $(C_2H_4)_{1,2,3}Ni$.[6,14]

A final point relates to the observed blue shift of the UV transition of $(C_2H_4)_nNi$ on passing to $(C_2H_4)_nPd$. In this context it is worth referring to the results of the more accurate SCF–Xα–SW calculations for $(C_2H_4)Ni$ and $(C_2H_4)Pd$[1] which show that the cluster of filled metal d-like orbitals mentioned earlier (and shown in Figure 5) becomes more stable on passing from $(C_2H_4)Ni$ to $(C_2H_4)Pd$, while the energy of the corresponding, upper recipient orbital remains approximately unchanged. Therefore the absolute value of the metal → ethylene charge transfer energy, according to these Xα calculations, should *blue* shift on passing from $(C_2H_4)Ni$ to $(C_2H_4)Pd$ (presumably a similar conclusion would be arrived at for higher ethylene stoichiometries), consistent with our experimental observations.

Table VI. Infrared Spectroscopic Data for $(C_2H_4)Pd$ and the π-Complexed Form of Ethylene Chemisorbed on Palladium

Approximate description of mode	$(C_2H_4)Pd$,[a] cm^{-1}	$(C_2H_{4ads})Pd$,[b] cm^{-1}	Δ, cm^{-1}
$\nu(CH_2)$	2958	2980	22
$\nu(C{=}C)$	1502	1510	8
$\delta(CH_2)$	1223	Not observed	
$\rho_W(CH_2)$	913	Not observed	

[a] This study. [b] Reference 22.

Monoethylenepalladium, $(C_2H_4)Pd$. A Localized Bonding Model for the π-Complexed Form of Ethylene Chemisorbed on Palladium. The group 8 transition metals (Ni, Pd, Pt) are useful hydrogenation catalysts.[5] Infrared experiments suggest that ethylene is adsorbed on metal surfaces and supported metals in the form of the di-σ-bonded $M-CH_2-CH_2-M$ species.[21] Very recently infrared evidence has been obtained for the presence of π-bonded species from ethylene chemisorbed on silica-supported Pd and Pt catalysts.[22] These are proposed to coexist with the di-σ-bonded $M-CH_2-CH_2-M$ species and are found to be more readily removed by hydrogen than the latter. In line with these studies are the results obtained from photoemission experiments,[23] 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 of ethylene adsorbed on Ni[24] showed the presence of two distinct types of adsorption, as indicated by the detection of the ions $Ni(C_2H_4)^+$ and $Ni_2(C_2H_4)^+$. Of central interest to this discussion is the remarkable similarity between the infrared spectra of $Pd(C_2H_4)$ and $Pd(C_2H_{4\,ads})$[22a] as shown in Table VI. The close correspondence between the observed $\nu(CH_2)$ and $\nu(C{=}C)$ stretching modes strongly suggests that ethylene π bonded to a single palladium atom in $Pd(C_2H_4)$ is an intuitively acceptable localized bonding model for the π-complexed form of C_2H_4 chemisorbed onto Pd.

The small "blue" frequency shift on passing from $Pd(C_2H_4)$ to $Pd(C_2H_{4\,ads})$ 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 $Pd \rightarrow C_2H_4$ charge transfer is marginally less from a Pd surface atom site than from an isolated Pd atom.

Conclusion

The palladium atom–ethylene matrix cocondensation reaction at 15 K has been shown to provide a direct and convenient synthetic route to the reactive intermediates $(C_2H_4)_{1,2}Pd$ as well as the known complex $(C_2H_4)_3Pd$.[7c,d] The $^{12}C_2H_4/^{13}C_2H_4$ isotopic data actually serve to place the original identification of $(C_2H_4)_3Pd$[7c,d] (prepared at 77 K) on a firmer basis.

Of particular interest is the remarkably close resemblance of the infrared spectra of the $(C_2H_4)_nPd$ (where n = 1, 2, or 3) complexes among themselves as well as to the π-complexed form of ethylene chemisorbed onto palladium.[22] Therefore, apart from their inherent chemical and spectroscopic interest, the discovery of the reactive intermediates $(C_2H_4)_nM$ (where n = 1–3, M = Ni or Pd) is significant in that they may serve as valuable "localized bonding" models[2-4] for studying the reactive intermediates and processes involved in olefin oxidations and hydrogenations by supported metal catalysts.[5]

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Registry No. I, 60595-00-8; II, 41582-93-8; III, 57158-85-7; $(^{13}C_2H_4)_3Pd$, 61951-23-3; $(^{12}C_2H_4)_2(^{13}C_2H_4)Pd$, 61951-24-4; $(^{12}C_2H_4)(^{13}C_2H_4)_2Pd$, 61951-25-5; $(^{13}C_2H_4)Pd$, 61951-26-6.

References and Notes

(1) R. P. Messmer, "The Theoretical Basis for Heterogeneous Catalysis", E. Drauglis and R. K. Jaffee, Ed., Plenum Press, New York, N.Y., 1975.
(2) G. A. Ozin, *Acc. Chem. Res.*, **10**, 21 (1977).
(3) R. Ugo, *Catal. Rev.*, **11**, 225 (1975).
(4) E. L. Meutterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975).
(5) (a) G. C. Bond, *Discuss. Faraday Soc.*, **41**, 200 (1966); (b) R. L. Burwell, Jr., "Catalysis Progress in Research", F. Basolo, and R. L. Burwell, Jr., Ed., Plenum Press, New York, N.Y., 1973; (c) J. Kwiatek, "Transition Metals in Catalysis", G. N. Schrauzer, Ed., Marcel Dekker, New York, N.Y., 1971.
(6) H. Huber, G. A. Ozin, and W. J. Power, *J. Am. Chem. Soc.*, **98**, 6508 (1976).
(7) (a) K. Fischer, K. Jonas, and G. Wilke, *Angew. Chem.*, **85**, 620 (1973); *Angew. Chem. Int. Ed. Engl.*, **12**, 565 (1973); (b) E. P. Kündig and G. A. Ozin, "Cryochemistry", M. Moskovits and G. A. Ozin, Ed., Wiley, New York, N.Y., 1976; first communicated at the Merck Symposium, "Metal Atoms in Chemical Synthesis", Darmstadt, May 1974; (c) P. L. Timms, communicated in a paper given at the C.I.C. Meeting, "Chemistry under Extreme Conditions", Toronto, June 1975; (d) R. M. Atkins, R. McKenzie, P. L. Timms, and T. W. Turney, *J. Chem. Soc., Chem. Commun.*, 764 (1975).
(8) E. P. Kündig, M. Moskovits, and G. A. Ozin, *J. Mol. Struct.*, **14**, 137 (1972).
(9) M. Moskovits and G. A. Ozin, *J. Appl. Spectrosc.*, **26**, 487 (1972).
(10) E. P. Kündig, M. Moskovits, and G. A. Ozin, *Angew. Chem., Int. Ed. Engl.*, **14**, 292 (1975).
(11) C. W. Bunn, *Trans. Faraday Soc.*, **40**, 24 (1944), and R. W. G. Wykoff, "Crystal Structures", Vol. 5, Interscience, New York, N.Y., 1966, p 258; W. Press and J. Eckert, *J. Chem. Phys.*, **65**, 4362 (1976).
(12) J. H. Darling and J. S. Ogden, *J. Chem. Soc., Dalton Trans.*, 2496 (1972).
(13) H. Huber, D. McIntosh, and G. A. Ozin, *J. Organomet. Chem.*, **112**, C50 (1976).
(14) N. Rösch and R. Hoffmann, *Inorg. Chem.*, **13**, 2656 (1974).
(15) P. M. Maitlis, "The Organic Chemistry of Palladium", Vol. I, Academic Press, New York, N.Y., 1971.
(16) E. Clementi and P. Roetti, *At. Nucl. Data Tables*, **14**, 445 (1974).
(17) L. C. Cusachs, *J. Chem. Phys.*, **43**, S157 (1965).
(18) A. Baranovskii and A. B. Nikol'skii, *Teor. Eksp. Khim.*, **3**, 527 (1967).
(19) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953); M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C71 (1951).
(20) (a) R. G. Denning, F. R. Hartley, and L. M. Venanzi, *J. Chem. Soc. A*, 1322 (1967); (b) D. J. Trecker, J. P. Henry, and J. E. McKeon, *J. Am. Chem. Soc.*, **87**, 3261 (1965); (c) T. N. Murrel and S. Carter, *J. Chem. Soc.*, 6185 (1964).
(21) (a) B. A. Morrow and N. Sheppard, *J. Phys. Chem.*, **70**, 2406 (1966); *Proc. R. Soc. London, Ser. A*, **311**, 391 (1969); (b) J. Erkelens and Th. Liefkens, *J. Catal.*, **8**, 36 (1967).
(22) (a) J. D. Prentice, A. Lesiunas, and N. Sheppard, *J. Chem. Soc., Chem. Commun.*, 76 (1976); (b) Y. Soma, *ibid.*, 1004 (1976).
(23) J. E. Demuth and D. E. Eastman, *Phys. Rev. Lett.*, **32**, 1123 (1974).
(24) M. Barber, J. C. Vickerman, and J. Wolstenholme, *J. Catal.*, **42**, 48 (1976).
(25) (a) D. C. Andrews, G. Davidson, and D. A. Duce, *J. Organomet. Chem.*, **101**, 113 (1975); (b) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 2519 (1960); (c) J. Hiraishi, *Spectrochim. Acta, Part A*, **25a**, 749 (1969); (d) D. B. Powell, J. G. V. Scott, and N. Sheppard, *ibid.*, **25a**, 327 (1972); (e) M. J. Grogan and K. Nakamoto, *J. Am. Chem. Soc.*, **88**, 5454 (1966).
(26) G. A. Ozin and W. J. Power, in preparation.