Reactions of Laser-Ablated Palladium and Platinum Atoms with Ethylene: An Infrared Study of the Palladium Complex and Platinum Insertion Product Isolated in Solid Argon

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Reactions of laser-ablated palladium and platinum atoms with ethylene isotopomers have been carried out in excess argon during condensation at 7 K. Infrared spectra show that palladium forms a π complex with ethylene whereas platinum generates an insertion product. Acetylene is a major product, suggesting that H_2 elimination from ethylene is also induced by the metal atom reactions. Product frequencies calculated by DFT are compared with the experimental values.

Introduction

Palladium and platinum are two of the most important metals in catalytic reactions of unsaturated hydrocarbons. The metal complexes not only serve as models for probing the steps in catalytic hydrogenation and oligomerization reactions but also are of great interest from the viewpoint of elucidating the nature of the bonding between the olefinic C═C double bond and a metal center.[1−3] Numerous complexes of Pd and Pt have been reported, and many of them carry very important industrial applications.[2]

Ethylene complexes with metal atoms isolated in inert matrixes have been identified in the infrared spectra.[4−12] Ozin et al. observed four infrared absorptions of a Pd−ethylene complex through the reaction of thermally vaporized Pd atoms with ethylene in excess xenon and argon during condensation.[6,7] The absorptions are rather weak, and the vibrational characteristics are similar to those of the Ni−ethylene complex, which lead to the identification of the π complex. However, Pt complexes of ethylene have received little attention,[13] whereas various platinum complexes with other hydrocarbons or their cations have been identified.[14,15]

Activation of the C−H bond in ethylene by second-row transition-metal atoms, eventually leading to an insertion product, was theoretically investigated by Blomberg et al.[16,17] The coordination energy of Pd to ethylene (−30.7 kcal/mol), forming a π complex, is the largest among those of the second-row transition metals; however, the vinyl hydride product (insertion complex) is not much more stable than the reactants. For the early second-row transition metals, however, the reverse tendency is found.

Matrix isolation of reaction products of laser-ablated Pd atoms and acetylene, including 1:2 and 2:1 π complexes, has recently been carried out in our laboratory.[18] In a similar study of Pt atoms and acetylene, a vinylidene, a C−H insertion, and a π-type complex are identified in the infrared spectrum, but $PtCCH_2$ is the major product.[19] More recently, the reaction of laser-ablated Zr and ethylene has been investigated, and intermediates in the H_2 elimination reaction of Zr and ethylene have been identified in an argon matrix.[20]

Here, we report reactions of laser-ablated Pd and Pt atoms with ethylene in excess argon. The metal−ethylene complexes are characterized through matrix infrared spectra. The vibrational characteristics of the product absorptions are confirmed by isotopic substitution and DFT calculations. Interestingly enough, acetylene is also produced, and other weak reaction products are identified in the infrared spectra.

Experimental and Computational Methods

Laser-ablated palladium and platinum atoms were reacted with C_2H_4, C_2D_4, $^{13}C_2H_4$ (Cambridge Isotope Laboratories, 99%), and CH_2CD_2 (MSD isotopes) in excess argon during condensation at 7 K using a closed-cycle He refrigerator (Air Products HC-2). The methods are described in detail elsewhere.[21−24] Concentrations of gas mixtures range from 0.25 to 5% but in most cases are typically 0.5% in argon. After the reaction, infrared spectra were recorded at a resolution of 0.5 cm^{-1} using a Nicolet 550 spectrometer with a HgCdTe detector. Later, samples were annealed, and more spectra were recorded.

Complementary density functional theory (DFT) calculations were carried out using the Gaussian 98 package,[25] B3LYP density functional, 6-311+G(2d,p) basis sets for C, H, and the LanL2 pseudopotential, and LanL2DZ basis set for Pd and Pt to provide a consistent set of vibrational frequencies for the reaction products. The geometries were fully relaxed during optimization, and the nature of the stationary states is confirmed by vibrational analysis. All of the vibrational frequencies were calculated analytically. In the calculation of the binding energy of a metal complex, the zero-point energy is included.

Results and Discussion

The contrasting chemistry of palladium and platinum is illustrated in their different reaction products with ethylene.

Pd−Ethylene Complex. Figure 1 shows the infrared spectra in the regions of 1000−1550 and 450−1000 cm^{-1} of laser-ablated Pd atoms codeposited with ethylene isotopomers in excess argon at 7 K, and the observed frequencies of the product absorptions indicated with arrows are summarized along with the calculated values in Table 1. The very weak absorptions at 1505.1 cm^{-1} for C_2H_4 shows $^{12}C/^{13}C$ and H/D shifts of −20 and −173 cm^{-1} ($^{12}C/^{13}C$ and H/D isotopic ratios of 1.013 and 1.129). The absorption becomes much stronger in the spectrum of Pd + CH_2CD_2, as shown in Figure 1. The isotopic shifts indicate that the absorptions originate from a vibrational mode

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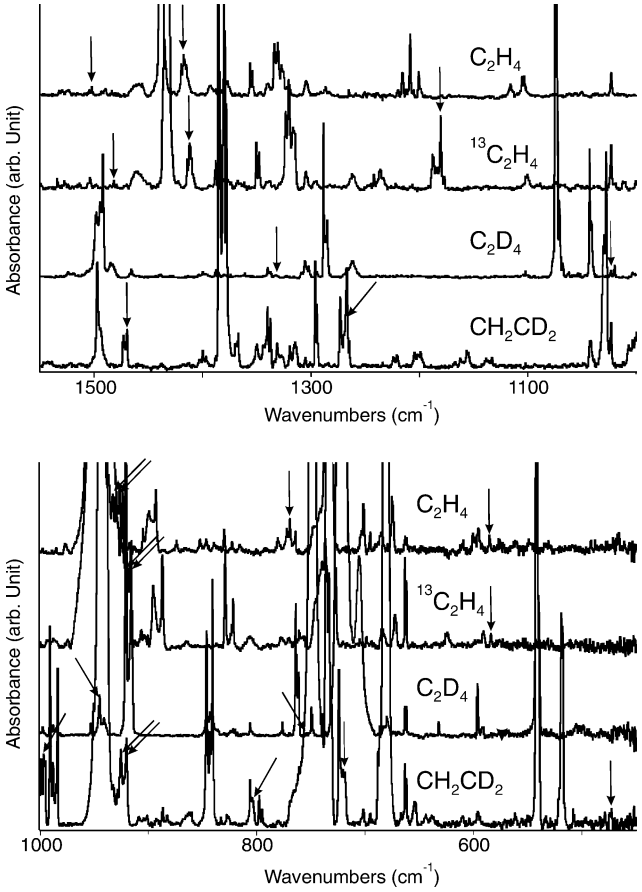

Figure 1. IR spectra in the regions of 1000−1550 and 450−1000 cm^{-1} for laser-ablated Pd atoms codeposited with ethylene isotopomers diluted in argon at 7 K. The product absorptions marked with arrows are believed to arise from the π complex of Pd and ethylene isotopomers.

where the C═C stretching and CH_2 deformation are strongly coupled; therefore, they are attributed to the ν_2 A_1 ν(CC) + $\delta(CH_2)$ mode.

The C═C stretching mode of the π complex is accompanied by a small change in the dipole moment along the C_{2v} molecular axis. As a result, the C═C stretching mode, which is originally IR inactive for ethylene, becomes active in the π complex; however, the intensity is expected to be very low. The weak product absorptions near 1505 cm^{-1} are consistent with the expected vibrational characteristics of the π complex.

The relatively strong absorptions at ~1418 cm^{-1} show very small $^{12}C/^{13}C$ and large H/D shifts of −5 and −365 cm^{-1} ($^{12}C/^{13}C$ and H/D isotopic ratios of 1.003 and 1.385, respectively). They are attributed to the ν_{13} B_2 CH_2 scissoring mode, whereas the absorptions at about 1215 cm^{-1} show a much larger $^{12}C/^{13}C$ shift of −35 cm^{-1} and a smaller H/D shift of −269 cm^{-1} ($^{12}C/^{13}C$ and H/D isotopic ratios of 1.024 and 1.285), indicating that the absorptions originate from a vibrational mode where the C═C stretching and CH_2 deformation are strongly coupled, similar to those of the ν_2 band. They are assigned to the ν_3 A_1 $\delta(CH_2)$ + ν(CC) mode. Strong coupling of the C═C stretching and CH_2 scissoring for the ν_2 and ν_3 modes is a typical characteristic of a metal−ethylene π complex as discussed in previous studies.[6,7] The strongest product absorptions are observed at ~928 cm^{-1} with $^{12}C/^{13}C$ and H/D shifts of −10 and −191 cm^{-1} ($^{12}C/^{13}C$ and H/D isotopic ratios of 1.011 and 1.258), which are attributed to the ν_{14} B_2 CH_2 wagging mode.

Ozin and Power conducted first the reaction of thermally evaporated Pd and ethylene isotopomers (C_2H_4, C_2D_4, and $^{13}C_2H_4$) and observed four bands from each isotopomer.[6,7] The product absorptions were compared with those of the Ni−ethylene complex;[5,10,11] they concluded on the basis of the characteristics of the observed bands that the Pd atom forms a π complex with ethylene. To compensate for the weak infrared absorptions of the metal−ethylene complex, the concentrations of the reactants in their experiments were relatively high.

The π complex has 15 vibrational modes, 12 of which are infrared active except for the 3 A_2 modes. The hydrogen stretching absorptions of the complex are not observed in this study, in part because of the fact that the hydrogen stretching region is dominated by much stronger broad absorptions of ethylene in the matrix spectrum. The frequencies of the ν_2 absorptions (A_1) shown in Table 1 are almost identical to the previously reported value by Ozin and Power (1502 cm^{-1}); however, the ν_3 and ν_{14} absorptions differ by 5−15 cm^{-1} from the previous values.[6,7] The relatively high concentrations of ethylene in argon (up to 10%) used in the previous study might cause frequency shifts due to molecular interactions with the products. In addition, we observe three weaker modes, ν_{10}, ν_{11}, and ν_{13}, not reported by the Ozin group, and we employ the lower-symmetry CH_2CD_2 isotopic precursor molecule, which provides additional vibrational information including the enhancement of the mostly C−C stretching mode intensity.

DFT calculations were carried out for the π complex at the B3LYP/6-311+G(2d,p) and LanL2DZ levels. The optimized $^1A_1$

TABLE 1: Observed and B3LYP Calculated Frequencies of the Fundamental Bands of the Pd−Ethylene Complex ($^1A_1$ State)[a]

	Pd(C_2H_4)			C_2H_4		Pd(C_2D_4)		Pd($^{13}C_2H_4$)			Pd(CH_2CD_2)		
description	exptl	calcd	int	calcd	exptl	calcd	int	exptl	calcd	int	exptl	calcd	int
ν_1 A_1 CH_2 s. str.		3114.7	5	3136.6		2279.8	1		3108.1	5		3111.0	8
ν_2 A_1 ν(CC) + $\delta(CH_2)$	**1505.1**,[b] 1502.4	1555.5	1	1686.7	1330.6	1374.5	4	**1485.3**,[b] 1482.4	1533.3	0	1470.0	1520.1	2
ν_3 A_1 $\delta(CH_2)$ + ν(CC)	1216.4, 1208.7	1248.2	7	1379.8	946.5	966.2	2	1188.0, 1180.3	1219.2	7	999.3, 995.5	1018.8	3
ν_4 A_1 CH_2 rock	933.9	940.6	3	973.4		699.7	0	922.4	937.1	3	720.8	733.1	6
ν_5 A_1 PdC_2 s. str.		363.0	7			350.1	7		352.5	7		361.0	6
ν_6 A_2 CH_2 str.		3178.7	0	3193.8		2370.2	0		3165.8	0		2376.5	1
ν_7 A_2 CH_2 rock		1228.6	0	1247.4		984.6	0		1213.6	0		1135.3	0
ν_8 A_2 CH_2 twist.		942.1	0	1057.5		672.9	0		940.7	0	804.4	840.6	1
ν_9 B_1 CH_2 a. str.		3202.2	7	3221.9		2382.6	3		3189.1	7		3190.6	4
ν_{10} B_1 CH_2 rock	769.5	822.6	0	838.4		590.9	0		821.5	0		670.0	0
ν_{11} B_1 PdCH bend	585	558.8	10			404.8	7	584	557.8	10	474	450.9	6
ν_{12} B_2 CH_2 str.		3107.3	10	3124.0		2244.5	4		3102.4	10		2262.5	3
ν_{13} B_2 CH_2 scis.	1420.1, 1417.1	1465.5	7	1478.5	1052.9	1085.0	5	1414.5, 1412.5	1459.8	7	1267.2	1308.6	7
ν_{14} B_2 CH_2 wag	930.1, 926.8	950.2	27	976.2	736.6	765.7	14	920.4, 916.8	940.0	27	925.9, 920.8	946.0	16
ν_{15} B_2 PdC_2 a. str.		353.6	3			318.4	3		343.1	2		330.8	3

[a] Frequencies are in cm^{-1}; calculated intensities are in km/mol. Calculated frequencies listed for C_2H_4 by the Pd(C_2H_4) mode derived therefrom. [b] Bold denotes the surviving matrix site on annealing.

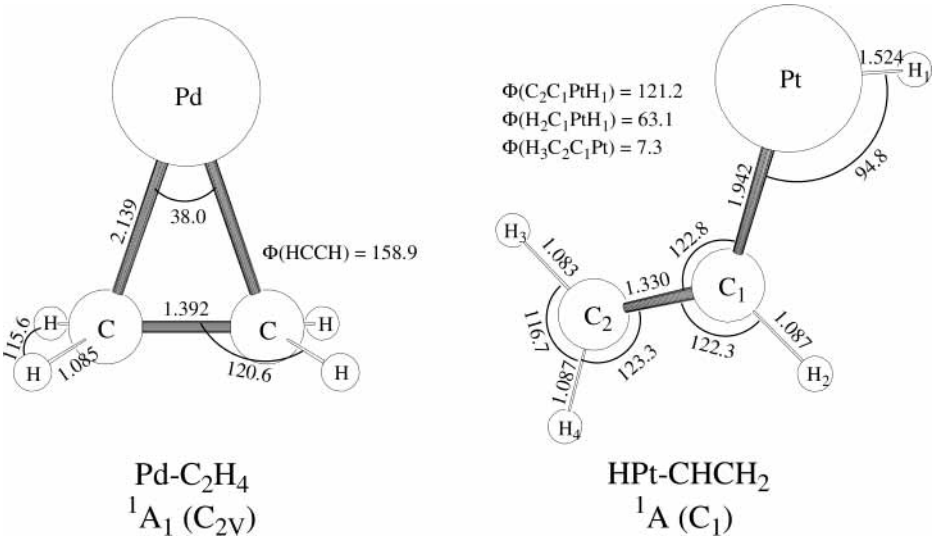

Figure 2. Optimized molecular structures of the π complex of Pd and ethylene and the insertion complex of Pt and ethylene in their ground electronic states. The bond lengths and angles are measured in angstroms and degrees, respectively. Some of the dihedral angles (Φ) are also shown.

TABLE 2: Geometrical Parameters and Physical Constants Calculated for Pd and Pt Complexes with Ethylene[a]

parameters	C_2H_4	Pd−C_2H_4	HPt−$CHCH_2$
r(C−C)	1.325	1.392	1.330
r(C−H)	1.084	1.085	1.087, 1.083, 1.087
r(C−M)		2.139	1.942
r(M−H)			1.524
∠CCH	121.7	120.6	122.8, 123.3
∠HCH	116.6	115.6	116.7
∠CMC		38.0	
∠CMH			94.8
Φ(HCCM)		100.6	7.3
Φ(HCMH)			63.1
Φ(HCCH)		0.0, 158.9	2.9, 177.2
Φ(CCMH)			121.2
q(C)[b,c]		−0.19	−0.34, −0.23
q(H)[b,c]		0.10	−0.03, −0.10, −0.10, 0.10
q(M)[b]		0.01	0.23
μ[d]	0.00	0.79	0.81
$\Delta E(\pi)$[e]		30.2	63.5
ΔE(ins)[f]		2.2	55.4

[a] B3LYP bond lengths and angles are measured in angstroms and degrees, respectively. [b] Mulliken atomic charge. [c] The first value is the value of the atom closest to the metal atom. [d] Molecular dipole moment in D. [e] Binding energy for π complex measured in kcal/mol. [f] Binding energy for insertion product measured in kcal/mol.

structure is shown in Figure 2, and the geometrical parameters are listed in Table 2. The calculated frequencies are compared with the observed values in Table 1, showing very good agreement. This result reconfirms the conclusion in earlier studies that Pd forms a π complex with ethylene,[6,7] which is also consistent with the result of the earlier theoretical studies about activation of the C−H bond in ethylene by a second-row transition-metal atom.[16,17] Coordination of the Pd atom to ethylene is energetically very favorable, but C−H insertion is not.

$$Pd + C_2H_4 \rightarrow Pd(C_2H_4)(^1A_1) \qquad (\Delta E = -30 \text{ kcal/mol}) \tag{1}$$

It has been reported that early second-row transition metals form metallacyclopropanes, whereas the late ones form π complexes.[26,27] They are called metallacyclopropanes because the C═C bond is weakened so much upon formation of the

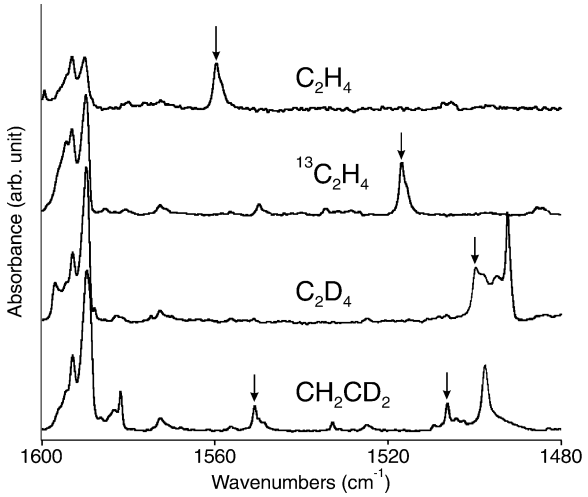

Figure 3. IR spectra in the region of 1480−1600 cm^{-1} for laser-ablated Pt atoms codeposited with Ar/C_2H_4 at 7 K. The absorptions marked with arrows are believed to originate from the C═C stretching mode of the Pt−ethylene insertion product. Note the large $^{12}C/^{13}C$ isotopic shift.

complex that the C═C bond length approaches that of a C−C single bond. As shown in Table 2 and Figure 2, the C═C bond length of the Pd-ethylene complex is 1.39 Å, not much longer than that of a normal C═C bond (1.34 Å), indicating that the complex is a typical metal−ethylene π complex.

Pt−Ethylene Insertion Product. Shown in Figure 3 is the infrared spectra in the range of 1480−1600 cm^{-1} of laser-ablated Pt atoms codeposited with ethylene isotopomers diluted in Ar at 7 K. The absorption at 1559.7 cm^{-1} shows a very large $^{12}C/^{13}C$ shift of −42.8 cm^{-1} and a relatively small H/D shift of −59.9 cm^{-1} ($^{12}C/^{13}C$ and H/D isotopic ratios of 1.028 and 1.040), indicating that it is the C═C stretching absorption of a Pt−C_2H_4 reaction product. It is also notable that the product absorptions, marked with arrows, are quite strong, unlike the ones observed in the Pd + ethylene spectra in the same C═C stretching region.

The frequencies are also much higher than those of the CC stretching absorptions expected for a normal metal−ethylene π complex.[6−12] Calculations indicate that the C═C stretching band of the Pt−C_2H_4 π complex would appear below 1500 cm^{-1}

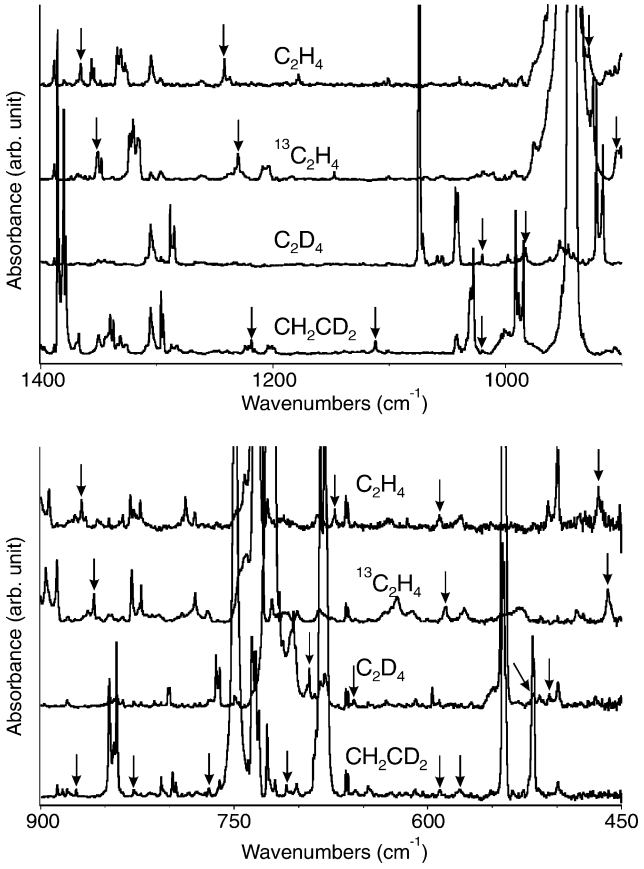

Figure 4. IR spectra in the regions of 950−1400 and 450−900 cm^{-1} for laser-ablated Pt atoms codeposited with ethylene isotopomers diluted in argon at 7 K. The product absorptions marked with arrows are believed to arise from the insertion complexes of Pt and ethylene isotopomers.

with lower absorption intensity. The characteristics of the product absorptions in Figure 3 suggest that they in fact originate from the C═C stretching mode of a C−H insertion product of Pt and ethylene, HPt−$CHCH_2$. The C═C bond becomes polarized upon Pt insertion, yielding a larger change in dipole moment on stretching of the bond, which in turn leads to a stronger absorption than in the π complex. Earlier studies also show that Pt often makes insertion products with hydrocarbons.[14,15,19]

Shown in Figure 4 are the infrared spectra in the regions of 900−1400 and 450−900 cm^{-1} of laser-ablated Pt atoms codeposited with ethylene isotopomers diluted in Ar at 7 K, and the frequencies of the product absorptions marked with arrows are summarized in Table 3. The product bands are, in general, much stronger than those of the π complexes of Pd and ethylene isotopomers.

The product absorption at 1365.6 cm^{-1} show relatively small $^{12}C/^{13}C$ and large H/D shifts of −13.9 and −345.9 cm^{-1} ($^{12}C/^{13}C$ and H/D isotopic ratios of 1.010 and 1.339, respectively). However, the absorption at 1242.1 cm^{-1} shows a similar $^{12}C/^{13}C$ shift of −11.9 cm^{-1} and a little smaller shift of −259.5 cm^{-1} ($^{12}C/^{13}C$ and H/D isotopic ratios of 1.010 and 1.264, respectively). On the basis of the frequencies and the isotopic shifts, the absorptions at 1365.6 and 1242.1 cm^{-1} are assigned to the CH_2 scissoring and the CCH in-plane bending modes, respectively. Another product absorption at 928.0 cm^{-1} with very small $^{12}C/^{13}C$ and very large H/D isotopic shifts of −3.6 and −270.4 cm^{-1} ($^{12}C/^{13}C$ and H/D isotopic ratios of 1.004 and 1.411, respectivley) is assigned to the HCCH out-of-plane bending mode as shown in Table 3.

The observed frequencies are compared with the calculated values for the C−H insertion complex in Table 3, and the agreement is very good. The optimized structure of the singlet insertion product (C_1) is shown in Figure 2, and the geometrical parameters are listed in Table 2. The complex is planar except for the H on platinum. The Pt atom is located slightly above the C_2H_3 molecular plane, and the hydrogen atom bonded to the metal atom is below the plane. Figure 2 also shows that the bond angle ∠CPtH (94.8°) is close to a right angle.

The Pt atom is much heavier than the other atoms in the molecule. Therefore, it is expected from the molecular structure of the insertion complex that the Pt−H stretching mode is almost completely isolated from the other vibrational modes of the complex, resulting in nearly identical metal−hydrogen stretching frequencies regardless of isotopomer. Figure 5 shows the Pt−H and Pt−D stretching regions of the insertion complexes of the ethylene isotopomers. The complexes of C_2H_4, $^{13}C_2H_4$, and CH_2-CD_2 with Pt all have essentially the same Pt−H stretching frequencies, and those of C_2D_4 and CH_2CD_2 also give the same Pt−D stretching frequencies.

The present results indicate that unlike the Pd atom the Pt atom readily forms an insertion product with ethylene. Calculations are also carried out for a π complex of Pt and ethylene,

TABLE 3: Observed and Calculated Frequencies of the Fundamental Bands of the HPt−$CHCH_2$ Insertion Product (^{1}A State)[a]

										CH_2CD_2					
	C_2H_4			C_2D_4			$^{13}C_2H_4$			HPt−$CHCD_2$			DPt−$CDCH_2$		
description	exptl	calcd	int	exptl	calcd	int	exptl	calcd	int	exptl	calcd	int	exptl	calcd	int
ν_1 CH_2 asym. str.		3202.7	2		2382.7	1		3190.2	3		2272.4	0		3202.1	2
ν_2 C−H str.		3134.4	3		2324.0	1		3124.3	3		3132.0	2		3112.3	2
ν_3 CH_2 symm. str.		3109.0	1		2261.4	1		3102.6	1		2419.8	1		2313.8	1
ν_4 Pt−H str.	2317.7	2419.8	14	1663.0	1716.3	8	2317.7	2419.8	14	2317.7	2382.6	14	1663.0	1716.3	8
ν_5 C═C str.	1559.7	1607.5	44	1499.8	1532.0	48	1516.9	1560.0	38	1506.2	1547.6	52	1550.8	1594.8	41
ν_6 CH_2 scis.	1365.6	1404.4	21	1019.8	1058.7	24	1351.7	1389.4	24	1218.8	1226.0	62	1367.5	1399.1	18
ν_7 CCH IP bend	1242.1	1254.8	59	982.6	996.4	28	1230.2	1242.2	57	1023.0	1037.7	3	1111.9	1123.0	39
ν_8 CH_2 rock		990.3	8	691.9	737.7	5		983.8	9	827.9	851.8	9	785.2	817.4	10
ν_9 HCCH OOP bend	928.0	962.5	24	657.6	707.4	29	924.4	959.3	23	872.5	903.9	17	772.8	801.0	3
ν_{10} CH_2 wag	868.5	914.6	30		748.0	5	858.9	903.8	30	709.7	735.6	22	879.5	919.5	46
ν_{11} CPtH bend	672.0	679.7	33	505.9	505.5	17		674.5	33	590.9	636.9	38	575.0	601.5	17
ν_{12} Pt−C str.	590.9	604.8	10	518.0	552.0	4	586.2	588.7	10		560.2	4		557.0	15
ν_{13} PtCC OOP bend	468	466.1	23		348.1	11	461	463.3	23		381.9	15		385.8	12
ν_{14} PtCC bend		276.2	8		238.3	8		269.9	8		251.3	7		262.8	10
ν_{15} HPtCH distort		198.1	7		143.4	3		197.4	7		195.9	8		143.8	3

[a] Frequencies are measured in cm^{-1}; calculated intensities are measured in km/mol.

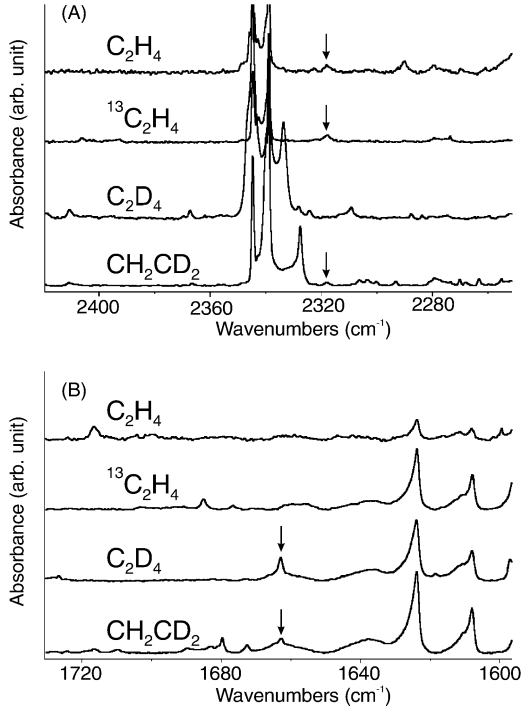

Figure 5. IR spectra in the Pt−H (A) and Pt−D (B) stretching regions for laser-ablated Pt atoms codeposited with ethylene isotopomers diluted in argon at 7 K. Note that the Pt−H stretching frequencies of the complexes of C_2H_4, $^{13}C_2H_4$, and CH_2CD_2 are the same and so are the Pt−D stretching frequencies of the complexes of C_2D_4 and CH_2CD_2.

and with the help of the results, the complex was searched in the infrared spectrum, but there was no trace of the π complex. Table 2 shows that the binding energy of the insertion product relative to the reactants is slightly smaller than that of the π complex at the present level of theory. The absence of absorptions by a π complex of Pt and ethylene remains as an unsolved problem at the moment. A possible explanation is the weak infrared absorption intensities predicted for its fundamental vibrations. Similarly, the π complexes of Zr and Ti atoms with ethylene are not identified, whereas strong absorptions of the insertion products are observed after light irradiation in the matrix infrared spectra.[20,28] Another rationale is that any Pt π complex formed undergoes spontaneous or photoinduced rearrangement to $HPtC_2H_3$.

$$Pt + C_2H_4 \rightarrow HPt{-}CHCH_2(^1A) \qquad (\Delta E = -55 \text{ kcal/mol}) \quad (2)$$

Other Reaction Products. Whereas Pd and Pt atoms, as described above, form a π complex and an insertion product, respectively, with ethylene during codeposition, various other reaction products are also formed. The observed frequencies listed in Tables 4 and 5 are weaker versions of the products in the reaction of Pd and Pt with acetylene.[18,19] However, a vinylidene complex is identified in the spectrum of Pt and ethylene, which is the major reaction product of Pt and acetylene.[19] Although PdH is observed, we find no evidence for PtH or PtH_2.[29,30] Unfortunately, $Pd(H_2)$ and $Pd(D_2)$ are masked by C_2H_4 and C_2D_4, but Pd(HD) is observed at 804.1 cm^{-1}, and it grows on annealing as found previously.[29]

Among the product absorptions, in both Pd and Pt spectra, the strongest absorptions observed arise from acetylene (Figure 6). Normally, about 20% or more of ethylene is converted to acetylene in the present experiment for both Pd and Pt estimated from the hydrogen stretching absorptions. This result also

TABLE 4: Observed Frequencies (cm^{-1}) of Reaction Products Other than the π Complex of Pd and Ethylene[a]

species	C_2H_4	C_2D_4	$^{13}C_2H_4$		CH_2CD_2	
$Pd(C_2H_2)_2$	3184.2					
$Pd(C_2H_2)$	3163.8					
$Pd(C_2H_2)$	3153.7					
PdH	1952.8				1952.8	
CCH	1845.8					
CCH^+	1820.4					
$Pd(C_2H_2)$	1716.7			1716.7	1649.8	
$Pd(C_2H_2)$	1709.8	1583.1	1651.8	1709.8	1641.8	1583.1
$Pd(C_2H_2)$	1707.4			1707.4	1638.8	
$Pd_2(C_2H_2)$	1572.7	1506.4		1572.7	1521.5	
$Pd_2(C_2H_2)$	1565.8					
$Pd_2(C_2H_2)$	989.6					
$Pd_2(C_2H_2)$	985.7					
Pd(HD)					804.1	
C_xH_y	926.5		916.8			
C_xH_y	893.5		887.5			
C_xH_y	855.5		847.9			
C_xH_y	853.1		845.2			
$Pd(C_2H_2)$	765.8					
$Pd(C_2H_2)$	764.5		756.1			
$Pd(C_2H_2)$	675.4		672.3			
$Pd(C_2H_2)$	674.5		671.5			

[a] Frequencies are all measured in cm^{-1}. Assignments from previous work on reaction of Pd atoms with acetylene.[18]

TABLE 5: Observed Frequencies for Reaction Products Other than the Insertion Complex of Pt and Ethylene[a]

species	C_2H_4	C_2D_4	$^{13}C_2H_4$	CH_2CD_2	
PtCCH	2016.2			2016.2	
$PtCCH^-$	1920.5			1920.5	
CCH	1845.8	1746.5	1785.5	1845.8	1746.5
CCH^+	1724.4		1754.9	1724.4	
$Pt{-}CCH_2$	1716.5	1662.6		1716.5	

[a] Frequencies are all in cm^{-1}. Assignments are assisted by the results of previous work done on the reaction of Pt atoms with acetylene.[19]

indicates that the Pt−acetylene π complexes are not formed as readily as the corresponding Pd−acetylene complexes, which is consistent with our previous results on the reactions of Pd and Pt atoms with acetylene.[18,19] We anticipate that some of the C_2H_2 observed here, and its CCH photolysis product, are produced by VUV photodissociation of C_2H_4 from the ablation plume; however, the large yield of C_2H_2 invites the consideration of additional reaction mechanisms. Furthermore, our CH_2CD_2 experiments give C_2H_2 and C_2D_2 in addition to the dominant CHCD product, although some product scrambling is observed in the VUV photochemistry of CH_2CD_2.[31] Acetylene produced in large quantity suggests that hydrogen is also eliminated from ethylene in the reaction of laser-ablated metal atoms and ethylene, a point advanced earlier for Zr + C_2H_4 reactions.[33] Hydrogen elimination reactions of ethylene by transition-metal atoms have recently drawn broad attention, in particular, the activities of the early second-row transition-metal atoms have been the subject of intense studies.[16,17,26,27,32,33] However, such reactions by the late transition metals have not been closely examined to date.[34]

Figure 7 shows the $Pd(C_2H_2)$ and Pd(CHCD) complexes formed in the reaction of Pd and CH_2CD_2: a weak $Pd(C_2D_2)$ complex band was also observed at 1583.1 cm^{-1}. The frequencies observed here are 0.2−0.3 cm^{-1} higher than those found in the C_2H_2 investigation,[18] which is close enough to confirm that the same complexes are formed.

We observe more $Pd(C_2H_2)$ relative to Pd(CHCD) at medium laser power than the 1:5 distribution of C_2H_2 and CHCD would give if these Pd complexes were formed only from the acetylene

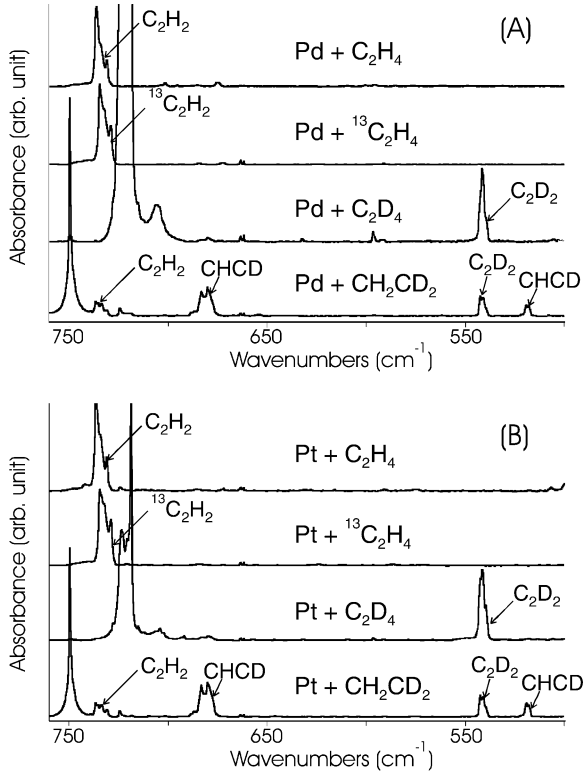

Figure 6. IR spectra in the region of 500−800 m^{-1} for laser-ablated Pd (A) and Pt (B) atoms codeposited with ethylene isotopomers diluted in argon at 7 K. The acetylene Π_u absorptions for the isotopomers are indicated.

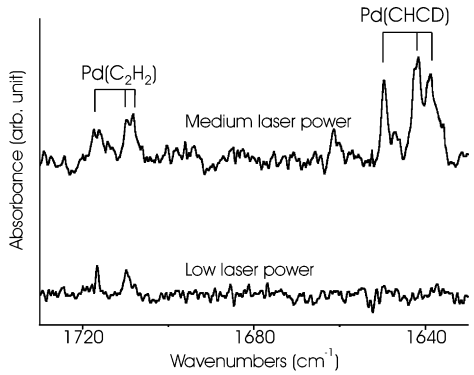

Figure 7. IR spectra in the 1630−1730 cm^{-1} region for laser-ablated Pd codeposited at 7 K with CH_2CD_2 in excess argon using low laser power and medium laser power.

isotopomers. At low laser power, we observe only $Pd(C_2H_2)$. How might we account for this in the reaction of Pd* and CH_2CD_2? This suggests an energized $Pd(CH_2CD_2)$* intermediate, which eliminates the most stable isotopic dihydrogen: this is D_2 (dissociation energy of D_2 is 1.8 kcal/mol higher than that for H_2).[35] In addition, Pd(HD) is observed, which could come from reaction 3b.

$$Pd^* + CH_2CD_2 \rightarrow Pd(CH_2CD_2)^* \rightarrow Pd(C_2H_2) + D_2 \quad (3a)$$

$$Pd^* + CH_2CD_2 \rightarrow Pd(CH_2CD_2)^* \rightarrow Pd(HD) + CHCD \quad (3b)$$

Figure 6 shows the strong π_u absorptions of free acetylene isotopomers, the final products of hydrogen elimination of ethylene isotopomers. It is notable that C_2H_2 and C_2D_2 as well as CHCD are generated as reaction products of hydrogen elimination of CH_2CD_2. The estimated molar ratio between C_2H_2, CHCD, and C_2D_2 produced in the reaction, using the calculated absorption intensities of the π_u bands of the isotopomers, is about 1:5:2, essentially the same for both Pd and Pt. This result is consistent with our previous hydrogen elimination reaction of ethylene by zirconium, an early second-row transition metal.[20] The currently accepted reaction path for the hydrogen elimination reaction does not allow the formation of C_2H_2 or C_2D_2 from CH_2CD_2 because one hydrogen atom is supposed to depart from each carbon atom.[32] This mechanism was proposed for the reaction between thermalized metal atoms and ethylene; our laser-vaporized metal atoms have much higher kinetic and possibly electronic energy. However, the current reaction mechanism has not been tested with CH_2CD_2 in reaction dynamics. Obviously, further studies are needed to examine more closely the details of the hydrogen extraction reaction of ethylene by transition metals.

Conclusions

Reactions of laser-ablated palladium and platinum atoms with ethylene isotopomers have been carried out in excess argon during condensation at 7 K. Evidence shows that the Pd atom forms a π complex with ethylene. The C═C stretching mode, which is originally IR inactive for ethylene, becomes active upon formation of the π complex, but the intensity is still very low. The Pt atom, however, forms an insertion product with ethylene, and the polarized C═C bond results in many strong IR absorptions, particularly the 1559.7 cm^{-1} band, which is the strong C═C stretching mode of the complex as a result of the C−H insertion. This contrasting behavior for Pd and Pt with C_2H_4 is analogous to their reactions with H_2 to form the Pd-(H_2) complex and PtH_2 dihydride.[29,30]

Other reaction products are also generated, especially acetylene, which is the final product of the H_2 elimination reaction of ethylene by metal atoms, and other weak absorptions arise from acetylene complexes. In this context, the π and insertion complexes are in fact reaction intermediates, and the presence of those complexes indicates where high-energy barriers lie in the H_2 elimination reaction path. Finally, C_2H_2 and C_2D_2 are formed along with CHCD in the reactions of CH_2CD_2 with Pd and Pt, which are not allowed in the currently accepted H_2 elimination reaction path, suggesting that the reaction occurs in more than one step or follows a different route.

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