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Vibrational Study of the Metal-Olefin Bond in 1,5-Cyclooctadiene Complexes of Rhodium(I), Palladium(II), and Platinum(II)

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The infrared and Raman spectra of 1,5-cyclooctadiene (C_8H_{12}) ($RhClC_8H_{12}$)₂, $PtCl_2C_8H_{12}$, and $PdCl_2C_8H_{12}$ have been recorded. Assignments are given for bands I and II, for olefinic CH wagging and rocking modes, and for metal-olefin stretching modes. On the basis of the shift in the frequencies of bands I and II and the CH wagging modes and the frequency of the symmetric metal-carbon stretching modes, the total interaction between the metal and olefin is $Rh > Pt > Pd$. The shift of the CH rocking modes and the frequency of the asymmetric metal-carbon modes are consistent with the π interaction going in the order $Pt > Rh > Pd$ with all complexes having extensive π interaction.

Introduction

The nature of the metal-olefin bond proposed by Dewar¹ and later modified by Chatt and Duncanson² is generally accepted. The model consists of two components (σ and π). While this general scheme is accepted, there has been considerable controversy over the extent to which each contribute to the overall strength of the metal-olefin bond and over what factors control the relative strengths.

Vibrational spectroscopy has been shown to be an effective tool for the study of the nature of the metal-olefin bond. Early vibrational work centered on the change in energy of the carbon-carbon double-bond stretching mode [$\nu(C=C)$], the magnitude of which was initially considered to be directly proportional to the strength of the metal-olefin interaction. However, the shift of the $\nu(C=C)$ mode has been shown to also be dependent upon the extent to which this motion couples with an in-plane olefinic C-H wagging mode [$\rho_w(C-H)$]. Indeed, these modes are so strongly coupled that they are referred to as bands I and II,³ and the magnitude of their combined shift is used as a measure of the total ($\sigma + \pi$) metal-olefin interaction.

In order to differentiate between the strengths of the σ and π components one must study vibrational modes whose energies are dependent upon the amount of electron density present in the π component of the metal-olefin bond. One mode of this type can be described as a metal-olefin tilting mode, which involves motions of the olefinic carbon atoms into and out of the region of π -electron density. In a complex containing a minimum amount of π -electron density a motion of this type should occur below $\sim 200\text{ cm}^{-1}$. As the amount of electron density present in the π component increases, the energy of this mode will increase to the point where it occurs in the same energy region as the classical symmetric metal-olefin stretching mode ($400 \approx 500\text{ cm}^{-1}$). In this case it has been described as the antisymmetric metal-olefin stretching mode. Therefore, the relative frequencies of the symmetric and antisymmetric metal-olefin stretching modes of a series of complexes should give information on relative amount of π components of the metal-olefin bonds.

Another vibrational mode of particular interest is the out-of-plane olefinic C-H rocking mode [$\rho_r(C-H)$]. A motion of this type will move the olefinic hydrogen into and out of the region of π -electron density. The energy of this mode should increase as the amount of electron density in the π component increases. Therefore, the extent to which these modes shift up in energy should be a measure of the strength of the π component.

A study of the series of Pt(II) and Pd(II) complexes of cyclopentene performed in our laboratory⁴ revealed that bands I and II shifted to lower wavenumbers to the same extent in both the Pt and the Pd complexes, indicating that the total metal-olefin interaction was approximately the same. This conclusion was supported by the study of the energies of the symmetric metal-olefin stretching mode. However, an examination of the $\rho_r(C-H)$ modes revealed that these modes shifted to a higher energy in the Pt(II) complex than in the Pd(II) complex, indicating that the Pt-cyclopentene bond contained a stronger π component than the Pd-cyclopentene bond. This conclusion was supported by the fact that there were two high-frequency metal-olefin stretching modes in the Pt complex but only one in the Pd complex. This was interpreted as indicating that the antisymmetric metal-olefin stretching mode occurred at a higher energy in the Pt(II) complex than in the Pd(II) complex.

In a study of a series of norbornadiene complexes of Rh(I), Pt(II), and Pd(II) in our laboratory,⁵ it was observed that the total metal-olefin interaction is ordered as $Rh > Pt > Pd$, whereas the strength of the π component was ordered as $Rh \approx Pt > Pd$. It should be noted that the extent of the π interaction in these complexes appears to be the largest, but the differences in the extent of the π component appear to be the least of those complexes studied in this laboratory.

In order to study the factors influencing the relative strengths of the σ and π components, we decided to investigate a series of complexes of Rh(I), Pt(II), and Pd(II) with cyclooctadiene, since it is a nonconjugated diolefin with three carbon-carbon single bonds between the two olefinic linkages, as opposed to norbornadiene, which has two carbon-carbon single bonds separating the two double bonds.

Experimental Section

The complexes were all prepared and purified by published procedures: ($RhClC_8H_{12}$)₂,⁶ $PtCl_2C_8H_{12}$,⁷ and $PdCl_2C_8H_{12}$.⁸ The purity of all complexes was verified by elemental analysis.

The infrared spectra were recorded on a Perkin-Elmer Model 521 spectrometer. The rhodium and platinum complexes were sampled in the form of cesium chloride pellets while the palladium complex was sampled in Nujol. Uncomplexed cyclooctadiene was sampled as both a thin film as well as in a 0.02-mm cesium bromide solution cell.

The Raman spectra were recorded by using a Jarrell-Ash 25-300 Raman spectrometer equipped with an ITT FW-130 photomultiplier

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Table I. Correlation of the Modes of Cyclooctadiene in the Free State and in Its Complexes^a

C ₈ H ₁₂		(RhClC ₈ H ₁₂) ₂		PtCl ₂ C ₈ H ₁₂		PdCl ₂ C ₈ H ₁₂			
IR	Raman	IR	Raman	IR	Raman	IR	Raman		
1658	1659	1468	1462	1495	1495	1519	1524	a ₁	band I
						1504	1508		
1484	1482	1474	1471	1478	1482	1480	1475		
1446	1444	1446	1440	1455	1452	1450	1449	a ₁	δ(CH ₂)
1432	1428	1430	1428	1435	1430	1430	1435		
1424	1425	1422	1417	1428	1424	1422	1425		
	1398	1368	1365	1379	1380	1390	1387	a ₂	ρ _w (CH)
1357	1352		1361		1363	1382	1383	a ₁	
1322	1220	1327	1318	1342		1342	1338		
1316	1310	1300	1297	1313	1310	1312	1309		
1266	1269	1228	1229	1243	1241	1248	1245	a ₁	band II
1235	1239	1235		1236		1238			
1211	1206	1212	1206	1227	1231	1232	1230	a ₁	
1194	1192	1174	1176	1181	1185	1180	1184		ρ _w (C-H)
	1147		1165		1165		1163	a ₂	
1086	1082	1084		1088		1088		a ₁	
1004	1008	993	998	1029	1028	1010	1011	a ₁	
969	962	958	950	1011	1010	995	992		
908	901	884		910		906			
895	893	865		872		871			ρ _w (C-H)
842	841	828		844		846			
823	824	815	820	832		823			
799	800	876	870	910	904	866	868	a ₁	ρ(C-C-C)
755		794		810		789			ρ _r (CH)
710	707	775	769	782	778	766	762	a ₁	ρ _r (C-H)
653	655	687	690	694	693	679			ρ _r (C-H)

^a Frequencies in cm⁻¹.

tube and Hamner photon-counting electronics. Approximately 400 mW of the 647.1-nm line of a Spectra-Physics Model 164 krypton ion laser was used for irradiation of the complexes. All reported frequencies are good to ±4 cm⁻¹.

It should be noted that the complexes are unstable toward stationary irradiation with laser powers greater than ~100 mW. Therefore a spinning cell was constructed such that samples could be pressed into a groove cut into the face of the cell, while the back was mounted on an electric motor and the cell spun at ~2000 rpm. With this sampling technique the complexes were observed to withstand up to 1200 mW of 514.5-nm radiation.

Results and Discussion

Powell and Leedham⁹ report the spectra of the complexes but limit their assignments of cyclooctadiene to bands I and II. Similarly Barna and Butler¹⁰ assign only ν(C=C) in cyclooctadiene. In the tub form, cyclooctadiene possesses C_{2v} symmetry under which the 54 fundamentals are distributed as:

$$\Gamma_{\text{vib}} = 14 a_1 + 14 a_2 + 13 b_1 + 13 b_2$$

In the region below 1700 cm⁻¹, one would expect to find 46 fundamentals but only 32 bands are observed. Thus many of the symmetrically equivalent groups are not coupled vibrationally. Table I gives the IR and Raman spectra between 1700 and 650 cm⁻¹ of C₈H₁₂, (RhClC₈H₁₂)₂, PtCl₂C₈H₁₂, and PdCl₂C₈H₁₂. It should be noted that the number of observed peaks in the rhodium complexes is essentially the same as in free cyclooctadiene and the other complexes, but the rhodium compound has two cyclooctadiene moieties per molecule. This leads to the expected conclusion that the two cyclooctadienes in (RhClC₈H₁₂)₂ are not coupled vibrationally.

Upon complexation, 19 of the C₈H₁₂ bands above 600 cm⁻¹ appear to shift by more than 1%. All of the bands that shift to lower wavenumbers show the greatest shift in the rhodium complex while, with only one exception, all of the bands that shift to a higher frequency shift the most in the platinum complex. There are two types of modes expected to shift to

a lower energy upon complexation due to a lowering of the C=C bond order: skeletal modes and olefinic C—H wagging motions. The more these motions are shifted, the greater is the total interaction. Thus the rhodium complex appears to have the greatest total interaction. There are also two types of modes expected to shift to higher wavenumber due to the electron density in the region between the metal and the carbons (the π bond): the olefinic C—H rockings and those ring-bending modes which become more restricted. The higher the shift of these modes, the more extensive is the π bonding. Thus it would appear that the platinum complex has the most extensive π bonding.

In their investigation, Barna and Butler¹⁰ assign two ν(C=C) modes in free C₈H₁₂: one to a very strong Raman line at 1661 cm⁻¹ and the other to an IR band at 1657 cm⁻¹. In the rhodium complex, they assign four ν(C=C) modes: two in the Raman at 1478 and 1467 cm⁻¹ and two in the IR at 1469 and 1424 cm⁻¹. As mentioned above, however, there appears to be no coupling of the two rings. We agree with the assignment of 1469 cm⁻¹ to band I, but the 1478 and the 1424 cm⁻¹ bands have counterparts in the free cyclooctadiene spectra (see Table I) and are probably CH₂ deformations. The 1467 and 1469 cm⁻¹ bands are probably the same since many of their corresponding IR and Raman frequencies differ. For the same reason we feel there is only one band I in the free ligand. Band II is observed as a strong, polarized Raman peak at 1269 cm⁻¹ in the free ligand and it shifts to lower energy in all three complexes. The assignments of bands I and II in the complexes as well as their percentage shifts are tabulated in Table II. These assignments are essentially in agreement with those of Powell and Leedham.⁹ It will be noted that the ordering in the total shift of bands I and II is Rh > Pt > Pd which is expected to be that of the total interaction.

An examination of the infrared and Raman spectra of free cyclooctadiene and the complexes reveals a band by band correlation of the modes in the free ligand and the complexes can be made. Assignments of the a₁ modes are made on the basis of depolarization ratios obtained from Raman spectra of the free ligand. Due to the complexity of the spectra, no assignments are offered for bands which are essentially un-

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Table II. Assignments and Percentage Shifts of Bands I and II of Cyclooctadiene in the Free State and Its Complexes^a

C ₈ H ₁₂		(RhClC ₈ H ₁₂) ₂		PtCl ₂ C ₈ H ₁₂		PdCl ₂ C ₈ H ₁₂		
IR	Raman	IR	Raman	IR	Raman	IR	Raman	
1658	1659	1468	1462	1495	1495	1519	1524	band I
		12.0%		9.9%		8.4%		
1266	1269	1228	1229	1243	1241	1248	1245	band II
		3.2%		2.3%		1.9%		
Δ (band I + band II)		15.2%		12.2%		10.3%		

^a Frequencies in cm⁻¹.Table III. Assignments and Percentage Shifts of the Olefinic CH Wagging Modes of Cyclooctadiene in the Free State and in Its Complexes^a

C ₈ H ₁₂		(RhClC ₈ H ₁₂) ₂		PtCl ₂ C ₈ H ₁₂		PdCl ₂ C ₈ H ₁₂	
IR	Raman	IR	Raman	IR	Raman	IR	Raman
	1398	1368	1365	1379	1380	1390	1387
		2.2%		1.4%		0.60%	
1266	1269	1228	1229	1243	1241	1248	1245
		3.0%		1.8%		1.4%	
1194	1192	1171	1176	1181	1185	1180	1184
		1.7%		1.1%		1.1%	
895	983	865	872	871			
		2.8%		2.0%		2.0%	

^a Frequencies in cm⁻¹.

shifted upon complexation. However, the modes that are sensitive to the nature of the bonding, $\rho_r(\text{CH})$ and $\rho_w(\text{CH})$, can be identified and their assignments will be discussed.

The $\rho_w(\text{C—H})$ modes were identified on the basis of their shift upon complexation, and the assignments for these modes are tabulated in Table III. In all cases, the modes decrease in energy the most upon complexation with rhodium, with the observed shift in the platinum complex equal to or greater than the shift in the palladium complex. The largest shift was observed for the a_1 species which is coupled to band I and previously discussed as band II. Bellamy¹¹ reports that cis-disubstituted alkenes characteristically exhibit a $\rho_w(\text{C—H})$ mode at ~ 1405 cm⁻¹. Since the band at 1398 cm⁻¹ in free cyclooctadiene shifts in the order Rh > Pt > Pd and since this mode is not found in the infrared spectrum of free cyclooctadiene, it is assigned to the $\rho_w(\text{C—H})$ mode of a_2 symmetry. Two other bands, at 1194 and 895 cm⁻¹ in free cyclooctadiene, are assigned to $\rho_w(\text{C—H})$ motions.

In the 950–600 cm⁻¹ wavenumber range, the region in which one expects to find the CH rocking modes, several interesting observations can be made. First of all, unlike any other olefins studied, the strongest bands in the Raman spectrum of the free olefin are not bands I or II. Instead, the strongest band is found at 800 cm⁻¹ and the next strongest band occurs at 707 cm⁻¹. Both bands are strongly polarized, with the depolarization ratio for each band less than 0.1. Upon complexation they undergo the largest shifts observed in the cyclooctadiene complexes, shifting up in energy. In the rhodium complex this shift occurs with a reversal in relative intensities. Sverdlov et al.¹² note that a characteristic frequency for an out-of-plane C—H deformation in dialkyl-substituted derivatives of ethylene is 700 cm⁻¹; therefore the 707-cm⁻¹ band is assigned to the a_1 rocking mode. In the complexes it is identified by its intensity and is found at 775, 782, and 766 cm⁻¹ in the rhodium, platinum, and palladium complexes. Another characteristic wavenumber range of $\rho_r(\text{C—H})$ modes is 610–680 cm⁻¹, and in free cyclooctadiene a band is observed at 653 cm⁻¹, which apparently shifts up to 687, 694, and 679 cm⁻¹ in the rhodium,

Table IV. Assignments and Percentage Shifts of the Olefinic CH Rocking Modes of Cyclooctadiene in the Free State and in Its Complexes^a

C ₈ H ₁₂		(RhClC ₈ H ₁₂) ₂		PtCl ₂ C ₈ H ₁₂		PdCl ₂ C ₈ H ₁₂	
IR	Raman	IR	Raman	IR	Raman	IR	Raman
755		794		810		789	
		-5.2%		-7.3%		-4.5%	
710	707	775	769	782	778	766	762
		-9.2%		-10%		-7.9%	
653	655	687	690	694	693	679	
		-5.2%		-6.3%		-4.0%	

^a Frequencies in cm⁻¹.Table V. Correlation of the Low-Energy Bands of (RhClC₈H₁₂)₂, PtCl₂C₈H₁₂, and PdCl₂C₈H₁₂^a

mode	[RhClC ₈ H ₁₂] ₂		PtCl ₂ C ₈ H ₁₂		PdCl ₂ C ₈ H ₁₂	
	IR	Raman	IR	Raman	IR	Raman
I	573	570	582	579	568	565
II	510	502	510	508	492	490
III	488	480	478	472	455	448
IV	468	465	455	451		402

^a Frequencies in cm⁻¹.

platinum, and palladium complexes, respectively. Another mode assigned to a $\rho_r(\text{C—H})$ motion occurs at 755 cm⁻¹ in free cyclooctadiene and exhibits similar shifts upon complexation. The $\rho_r(\text{C—H})$ assignments are tabulated in Table IV along with the percentage shift upon complexation. It is noted that the ordering of the shifts is always Pt > Rh > Pd which is interpreted as indicative of a greater amount of electron density in the π component of the platinum-olefin bond compared to rhodium, which itself appears to have a stronger π component than the palladium-olefin bond.

One of the skeletal deformations in cyclopentene was assigned⁴ to a strong band at 768 cm⁻¹, and on the basis of its frequency, polarization, and the apparent shift upon complexation the band at 800 cm⁻¹ is assigned to an a_1 skeletal deformation. The large shift could possibly be due to a coupling phenomenon with the a_1 CH rocking mode. Metal-chlorine stretching modes can be identified in these complexes by pressing the chloro compound into a KBr pellet which causes halide replacement in these complexes. In di- μ -chloro-bis(cyclooctadiene)dirhodium(I) only two bands are observed in the Raman which are assigned to $\nu(\text{Rh—Cl})$, thus indicating that the rhodium-chloride bridge is planar and the molecule possesses D_{2h} symmetry. This is in agreement with the vibrational study of Barna and Butler and the X-ray studies of Ibers and Snyder.¹³ The two $\nu(\text{Pt—Cl})$ modes are assigned to bands at 332 and 309 cm⁻¹ whereas the palladium complex exhibits bands at 328 and 293 cm⁻¹ which are assigned to $\nu(\text{Pd—Cl})$.

In the Raman spectrum of free cyclooctadiene, one finds four modes below 500 cm⁻¹ which can be described as skeletal

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twists or torsions. Due to their energetic compatibility with metal-olefin stretching modes, these motions could become mixed together to such an extent as to preclude the assignment of the low-energy ($>600\text{ cm}^{-1}$) region of the complexes as either metal-olefin stretching or "pure" cyclooctadiene. However, due to the nature of these diolefin complexes, one would expect to find four modes attributable to metal-olefin stretching motions.

The correlation of the low-energy region of the complexes is given in Table V. In vibrational studies of Zeise's salt¹³ and cyclopentene complexes of platinum,⁴ the asymmetric stretch, the motion that is particularly sensitive to the π component of the metal-olefin bond, was assigned $\sim 85\text{ cm}^{-1}$ higher than the symmetric stretch. With diolefins, two asymmetric stretching modes are predicted. An examination of Table V reveals that the two highest energy modes in this region (modes I and II) fall at the highest wavenumber in complexes of Pt followed by those of Rh and then Pd. If these modes are indeed associated with in-phase and out-of-phase asymmetric stretching modes, then the extent of the π component goes in the order Pt $>$ Rh $>$ Pd, the same order arrived at from a consideration of the $\rho_r(\text{CH})$ modes. The next two modes of complexes (modes III and IV) are ordered in energy, Rh $>$ Pt $>$ Pd, which is the ordering of the total metal-olefin interaction. This would be the expected ordering of the out-of-phase and in-phase symmetric metal-olefin stretches. Therefore modes I and II are assigned as being associated with the asymmetric metal-olefin stretching or tilting motions where modes III and IV are associated with symmetric metal-olefin stretching motions. This assignment is consistent with the Raman intensities since mode I is the strongest Raman line above 200 cm^{-1} which would imply that it is of a_1 symmetry (the in-phase symmetric stretch). These assignments differ from those of Powell and Leedham in that they preferred to assign the in-phase asymmetric stretch to the 480, 472, and 488 cm^{-1} set in the rhodium, platinum, and palladium complexes and they chose not to discuss the 502, 508, and 490 cm^{-1} correlation at all. Barna and Butler assign this region on the basis of four coupled symmetric olefin modes in a D_{2h} skeleton, ignoring the tilting modes. As mentioned before, we do not feel this is reasonable as it is unlikely they would be coupled and since, on the basis of other data presented, we feel strongly that the tilting modes would also be in this region.

Conclusions

To summarize: the extent of the combined shifts of bands I and II was observed to be Rh $>$ Pt $>$ Pd, which indicates that the total interaction between the metal and the olefin

follows the order Rh $>$ Pt $>$ Pd in agreement with previous work. This conclusion is supported by the observation that the frequencies of the modes associated with the in-phase and out-of-phase symmetric metal-olefin stretching motions are ordered Rh $>$ Pt $>$ Pd. The ordering of the increase in frequency of the out-of-plane olefinic CH modes is observed to be Pt $>$ Rh $>$ Pd. This implies that the extent of the π component is Pt $>$ Rh $>$ Pd. The observation that the frequencies of the bands associated with the symmetric metal-olefin stretching modes follow the order Pt $>$ Rh $>$ Pd supports this conclusion. It should be noted that even though we believe that the π back-bonding is more extensive in Pt(II) than in Pd(II), it is still rather extensive in Pd(II). It is worthwhile to note that these results are similar to those obtained for the corresponding complexes of norbornadiene where the only difference is that the extent of π interaction with Pt and with Rh is about the same.

In monoolefin complexes of these metals the situation is very much different. In the published results of the cyclopentene complexes of Pt(II) and Pd(II), we pointed out that the π back-bonding in Pt appears to be much greater than in Pd. The $[\text{PtCl}_2(\text{C}_5\text{H}_8)]_2$ complex is much more stable, the CH rocking shifts to higher frequency, and the lower frequency metal-carbon stretching is much higher in frequency than in the $[\text{PdCl}_2(\text{C}_5\text{H}_8)]_2$ compound. We were unable to isolate $[\text{RhCl}(\text{C}_5\text{H}_8)_2]_2$. The same can be said for the corresponding ethylene complexes except that the Rh compound can be isolated but it is still unstable.

It appears then that Pt(II) shows extensive π bonding in both mono- and diolefins where Rh(I) and Pd(II) show extensive π bonding to diolefins but much less to monoolefins. One possibility may be the energetic compatibility of the metal orbital and the olefin π^* orbital. Since Pt(II) displays extensive π bonding, it is possible that the Pt(II) d-orbital energy is more compatible with that of the π^* orbital in the monoolefins studied than the lower energies of the d-orbitals in Pd(II) and Rh(I). In the case of a diolefin, however, there are two π^* orbitals which have been calculated to be split by 0.8 eV^{15} in norbornadiene. Thus the lower energy π^* orbital in a diolefin may be lowered sufficiently to interact better with the Pd(II) and Rh(I) orbitals. We are pursuing this possibility with extended Hückel calculations.

Registry No. C_8H_{12} , 111-78-4; $[\text{RhCl}(\text{C}_8\text{H}_{12})_2]_2$, 12092-47-6; $\text{PtCl}_2\text{C}_8\text{H}_{12}$, 12080-32-9; $\text{PdCl}_2\text{C}_8\text{H}_{12}$, 12107-56-1.

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