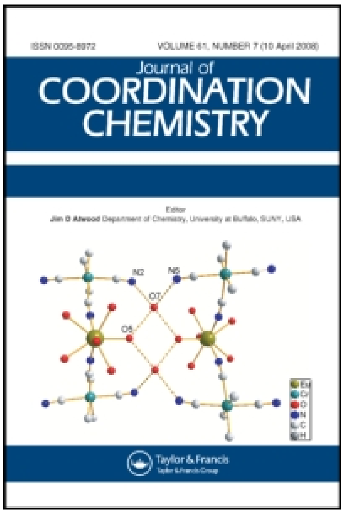

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Xinping Liu[a]; Jin K. Gong[a]; Jeffery W. Seyler[b]
[a] Department of Chemistry, Southeast Missouri State University, Cape Girardeau, MO, USA [b] Department of Chemistry, University of Southern Indiana, Evansville, IN, USA

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THEORETICAL INVESTIGATION OF KETENE BONDING MODES IN BIS(PHOSPHINE) PALLADIUM KETENE COMPLEXES

XINPING LIU[a], JIN K. GONG[a,*] and JEFFERY W. SEYLER[b]

[a]*Department of Chemistry, Southeast Missouri State University, One University Plaza, Cape Girardeau, MO 63701-4799, USA;*
[b]*Department of Chemistry, University of Southern Indiana, Evansville, IN 47712, USA*

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Theoretical studies were carried out on a series of bis(phosphine) palladium ketene complexes $(PR_3)_2Pd(CH_2{=}C{=}O)$, and on the related $CH_2{=}C{=}O$ and $Pd(PR_3)_2$ molecular fragments in order to investigate the electronic structure and the bonding of the ketene ligand to the metal fragment in these complexes. An analysis of the frontier MOs has been performed in order to understand the interactions between the ketene and the metal fragments. The calculated results have shown that the η^2-(C,C) mode is preferred over the η^2-(C,O) mode by 10–15 kcal/mol in bis(phosphine) palladium ketene complexes. The basicity and bulkiness of the phosphine ligands PR_3 have little effect on the bonding mode in $(PR_3)_2Pd(CH_2{=}C{=}O)$ complexes. The most stable structure was calculated to be the η^2-(C,C) square planar geometry with the CH_2 group of ketene out of the molecular plane. Comparison and discussion between the two bonding modes were also presented in this paper.

Keywords: Modeling of ketene bonding; ketene coordination; ketene complexes; palladium ketene complexes

INTRODUCTION

Ketenes $(R_2C{=}C{=}O)$ are reactive organic molecules whose chemistry has been well investigated since the early 1900s.[1–3] Despite the long history of the organic chemistry of ketenes, the first review article of the organometallic chemistry of ketenes by Geoffroy and Bassner was not published until

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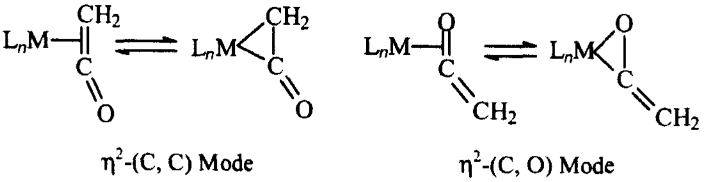
[*] Corresponding author. Tel.: 573 651 2371. Fax: 573 986 6423.
E-mail: jgong@semovm.semo.edu.

1988.[4] Transition metal ketene complexes are important intermediates in catalytic and synthetic processes such as homogeneous and heterogeneous Fischer–Tropsch processes,[5–10] in which catalytic CO activation and C–C bond coupling chemistry are involved. Transition metal ketene complexes have also served as model compounds in carbon dioxide fixation and functionalization processes.

Ketenes are carbonyl analogs of allenes with two perpendicular π bonds. They can be bonded to transition metal complexes in a variety of ways. The two most common bonding modes for mononuclear ketene complexes are the η^2-(C,C) and the η^2-(C,O) coordination to L_nM fragment, as illustrated below:



Early transition metal complexes favor the η^2-(C,O) bonding mode due to the electrophilic property of these metals. Several early transition metal ketene complexes, such as Ti, V, and Zr,[11–13] have been structurally determined by X-ray diffraction. All of the reported structures display η^2-(C,O) geometries. In contrast, the η^2-(C,C) bonding mode is preferred by late transition metal complexes. The η^2-(C,C) mode for Ni, Pd, and Pt has been characterized spectroscopically and reported in the literature,[14–16] however, some exceptions were also found.[17,18] For example, most of the nickel ketene complexes were found to favor the η^2-(C,O) bonding mode. Hofmann *et al.* reported the first η^2-(C,O) bonded nickel ketene complex.[17] We prepared our first η^2-(C,O) bonded nickel ketene complex, $(Cy_3P)_2Ni[\eta^2$-(C,O)–O=C=CH$_2]$,[18] shortly after Hofmann. These discoveries led to a very interesting question. Why does nickel form both η^2-(C,O) and η^2-(C,C) ketene complexes? Some theoretical investigations of ketene binding to Ni and Pt metal complexes have been reported.[18,19] Those computational studies indicate that Ni prefers the η^2-(C,O) bonding mode and Pt prefers the η^2-(C,C) bonding mode. We are interested in investigating palladium ketene complexes. Given its position between Ni and Pt, can palladium form both η^2-(C,O) and η^2-(C,C) ketene complexes? What bonding mode is preferred by palladium ketene complexes? What are the effects of the basicity and the bulkiness of the phosphine ligands PR_3 on the bonding mode? Our theoretical investigations focus on palladium ketene complexes containing a series of phosphine ligands (PR_3), to provide further understanding to the binding modes of palladium ketene complexes.

COMPUTATION METHOD

The calculations reported in this paper have been performed by the PC SPARTAN Pro and PC SPARTAN PLUS programs[20,21] and were done on Windows 98/NT based personal computers. The minimal valence basis set of atomic functions was used for C, H, O, P, and Pd atoms. Specifically, hydrogen was allotted a single function (1s); carbon, oxygen, and phosphorus atoms four functions, *i.e.*, s, p_x, p_y, and p_z; palladium atom nine functions, *i.e.*, d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{yz}, d_{xz}, s, p_x, p_y, and p_z.

The starting geometry of the model molecule $(PH_3)_2Pd(CH_2{=}C{=}O)$ was based on the X-ray determined structure for $[(dtbpm)Ni(\eta^2\text{-}(C,O)\text{-}Ph_2{=}C{=}O)$,[17] dtbpm = bis(di-tert-butylphosphino)methane, together with the experimental geometry of free PH_3.[22] All geometrical parameters of $Pd(PR_3)_2(CH_2{=}C{=}O)$ were optimized in order to compare their relative energies.

RESULTS AND DISCUSSION

Preliminary Investigation of the Two Bonding Modes

We have undertaken a semi-empirical theoretical investigation (PM3 level) on geometries and energies of several phosphine substituted Pd ketene complexes, $(PR_3)_2Pd(CH_2{=}C{=}O)$. The phosphines used in this study are PH_3, $P(CH_3)_3$, $P(OCH_3)_3$, $P(Ph)_3$, $P(CH{=}CH_2)_3$, and PF_3. Complexes of both ketene bonding modes, *i.e.*, η^2-(C,O) or η^2-(C,C), were completely optimized in order to compare their relative energies. The energy differences between the two bonding modes for the different phosphine ligands are shown in Table I.

TABLE I The relative energies between η^2-(C,C) and η^2-(C,O) modes (kcal/mol)

	η^2-*(C,C) mode*	η^2-*(C,O) mode*
$(PH_3)_2Pd(CH_2{=}C{=}O)$	0	10.5
$[P(CH_3)_3]_2Pd(CH_2{=}C{=}O)$	0	10.7
$[P(OCH_3)_3]_2Pd(CH_2{=}C{=}O)$	0	13.7
$[P(CH{=}CH_2)_3]_2Pd(CH_2{=}C{=}O)$	0	10.7
$[P(C_6H_5)_3]_2Pd(CH_2{=}C{=}O)$	0	11.0
$(PF_3)_2Pd(CH_2{=}C{=}O)$	0	10.2

These results indicate that the basicity and bulkiness of the phosphorus ligands have little effect on the preference for the η^2-(C,C) mode over the η^2-(C,O) mode. This may be due to the fact that the phosphorus atom is a strong Lewis base. Even in the $(PF_3)_2Pd$ fragment the Pd has a partial negative charge.

The P–Pd–P angle in the optimized structure $(PR_3)_2Pd(CH_2{=}C{=}O)$ lies between 101° and 107°. To provide additional steric factors that may influence the bonding mode, the P–Pd–P angle was varied between 70° and 140° in a model complex, $(PH_3)_2Pd(CH_2{=}C{=}O)$. After constraining the P–Pd–P angle at different degrees before geometry optimization, the energies of the two different bonding modes were calculated. Figure 1 illustrates the curves of the calculated energies as a function of the P–Pd–P angles. The η^2-(C,C) mode (lower curve) is energetically favored over the η^2-(C,O) mode (upper curve) at all calculated P–Pd–P angles for the $Pd(PH_3)_2(CH_2{=}C{=}O)$ model complex.

The minima of the curves occur at 102.7° and 101.9°, for η^2-(C,C) and for η^2-(C,O), respectively. The largest energy difference was found at a P–Pd–P angle of 102°. Considering both electronic and steric factors, these results clearly show that the η^2-(C,C) bonding mode leads to lower energies. These results agree with experimental studies that no η^2-(C,O) mode palladium ketene complex has been found to date.

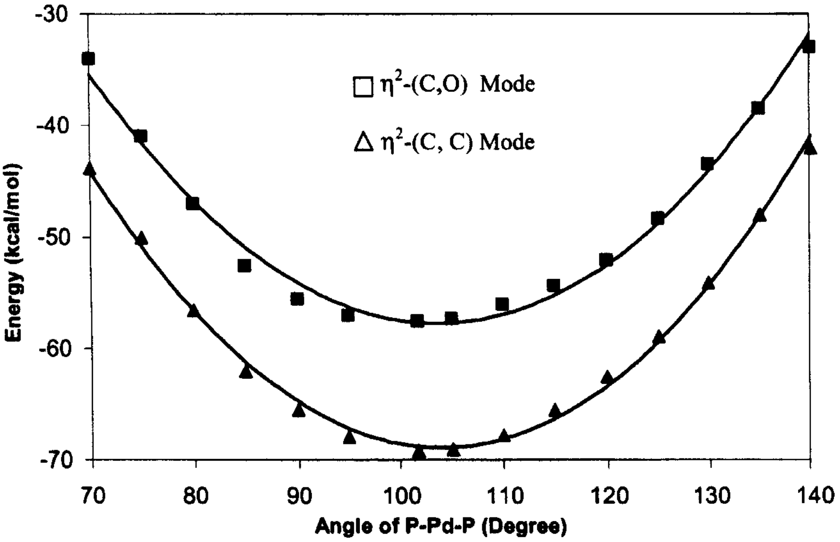


FIGURE 1 Total energy as a function of the P–Pd–P angle (°).

The BE (bond energy) and INT[†] (interaction energy) of the η^2-(C,C) bonding mode for the model molecule, $(PH_3)_2Pd(CH_2{=}C{=}O)$, were calculated to be −98 and −161 kcal/mol, respectively. These values are greater than those of the η^2-(C,O) mode (BE = −87 kcal/mol, INT = −142 kcal/mol). The BE of the η^2-(C,O) mode indicates that the η^2-(C,O) mode may remain in a local minimum. The local minimum of the η^2-(C,O) mode was calculated to have a square planar structure with the ketene CH_2 group in the plane of the $(PH_3)_2Pd(CH_2{=}C{=}O)$ molecule. While the more stable structure was computed to be the η^2-(C,C) mode having a square planar structure with the ketene CH_2 group out of the $(PH_3)_2Pd(CH_2{=}C{=}O)$ molecule plane. The effects of the CH_2 group of ketene will be discussed later. From the above analysis, we may draw a reasonable conclusion that the η^2-(C,C) mode is the preferred coordination mode in the $(PR_3)_2Pd(CH_2{=}C{=}O)$ complexes.

Why Is the η^2-(C,C) Mode Favored?

The preference of the η^2-(C,C) mode over the η^2-(C,O) mode may be understood by examining the interactions of the frontier molecular orbitals between the $Pd(PH_3)_2$ fragment and the unsubstituted ketene. The highest occupied molecular orbital (HOMO) of ketene is a π orbital between the carbon atoms, and a p_z orbital of the oxygen atom, all of which are perpendicular to the ketene plane. The lowest unoccupied molecular orbital (LUMO) is a π^* orbital system that is inside the ketene plane. The HOMO and LUMO of ketene are illustrated in Figures 2 and 3, respectively.

The HOMO of the $Pd(PH_3)_2$ fragment is of a′ symmetry, which is inside the plane of P–Pd–P. The lowest unoccupied Pd centered molecular orbital (LUMO*) is also of a′ symmetry, which is also inside the plane of P–Pd–P. The HOMO and LUMO* of the $Pd(PH_3)_2$ fragment are illustrated in Figures 4 and 5, respectively.

The interactions between the $Pd(PH_3)_2$ fragment and ketene are most likely to take place among the frontier molecular orbitals. That is, the HOMO of $Pd(PH_3)_2$ donates electrons to the LUMO of ketene (M → L back donation), and the HOMO of ketene donates electrons to the LUMO* of the $Pd(PH_3)_2$ fragment (L → M ligand to metal donation).

[†] The interaction energy (INT) is defined as the stabilization energy of the complexes relative to the distorted fragments. The deformation energy (DEF) is given as the destabilization energy to distort the $CH_2{=}C{=}O$ ligand to its deformed structures in the complexes. The bonding energy (BE) is defined as the sum of INT and DEF. Here, the $Pd(PH_3)_2$ structure was assumed to be fixed. $INT = E[(PH_3)_2Pd(CH_2{=}C{=}O)] - E[(PH_3)_2Pd] - E[CH_2{=}C{=}O]_{dist}$. $DEF = E[CH_2{=}C{=}O]_{dist} - E[CH_2{=}C{=}O]_{opt}$. BE = INT + DEF. The subscripts of "dist" and "opt" refer to the distorted structure and the optimized structure, respectively.

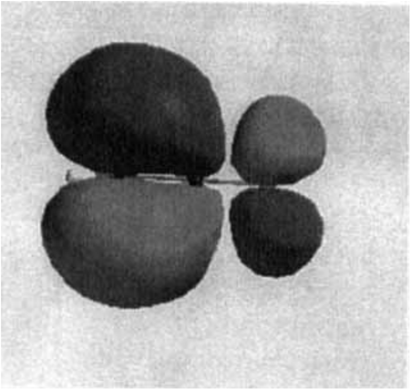


FIGURE 2 (See Colour Plate at back of issue.) HOMO of ketene.

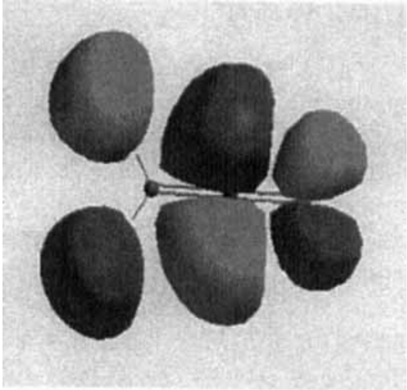


FIGURE 3 (See Colour Plate at back of issue.) LUMO of ketene.

For the two bonding modes of η^2-(C,C) and η^2-(C,O), there are two possible binding interactions between the HOMO of $Pd(PH_3)_2$ and the two LUMOs of ketene. One involves interaction of the HOMO of $Pd(PH_3)_2$ with the π^*_{C-C} orbital, the other is with the π^*_{C-O} orbital. Because the energy of the π^*_{C-C} orbital (0.4 eV) is lower than that of the π^*_{C-O} orbital (1.4 eV) in this case, the π^*_{C-C} orbital is a better electron acceptor than the π^*_{C-C} orbital. Stabilization from the interaction between the HOMO of $Pd(PR_3)_2$ and the π^*_{C-C} orbital of ketene is greater than that from the interaction between the HOMO of $Pd(PR_3)_2$ and the π^*_{C-O} orbital of ketene. Inspection of the symmetry between the HOMO of ketene and the LUMO* of $Pd(PH_3)_2$ fragment, likewise, shows that η^2-(C,C) bonding mode is much preferred due to

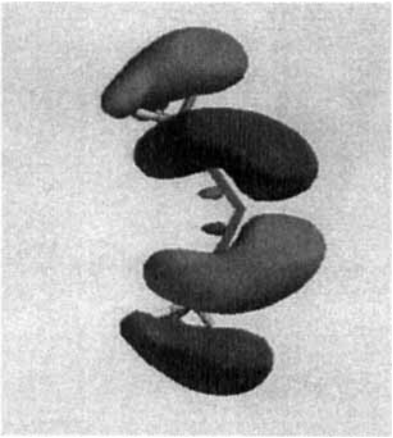


FIGURE 4 (See Colour Plate at back of issue.) HOMO of $Pd(PH_3)_2$.

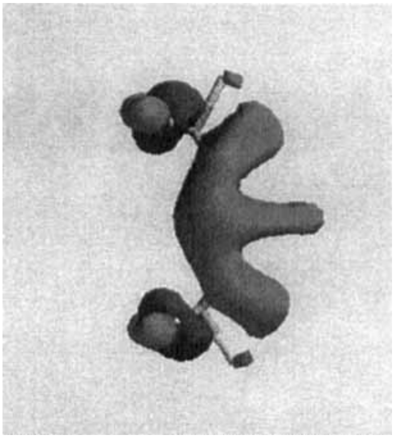


FIGURE 5 (See Colour Plate at back of issue.) LUMO* of $Pd(PH_3)_2$.

the larger overlap of the π_{C-C} orbital with the LUMO* of the $Pd(PH_3)_2$ fragment. This η^2-(C,C) bonding mode leads to lower energy for the Pd ketene complex.

The interactions, HOMO of ketene–LUMO* of $Pd(PH_3)_2$ and LUMO of ketene–HOMO of $Pd(PH_3)_2$, are two-orbital–two-electron interactions, which are stabilizing.[23,24] These interactions are illustrated in Figure 6. In the η^2-(C,C) bonding mode, the stabilizing energy Δ was calculated to be 34 eV, while in the η^2-(C,O) bonding mode, the stabilizing energy Δ was calculated to be only 12 eV.

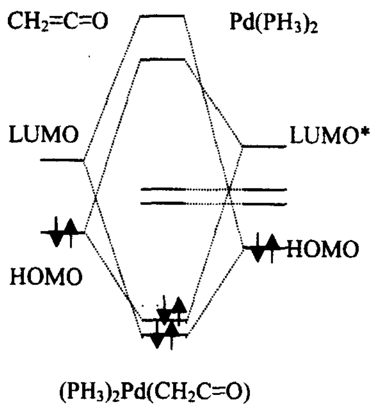


FIGURE 6 Qualitative molecular orbital interaction diagram.

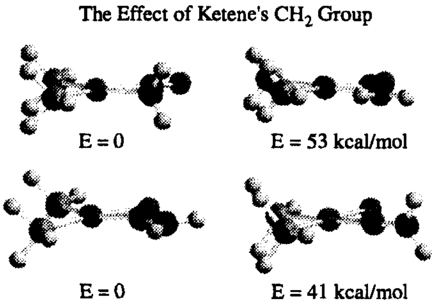


FIGURE 7 (See Colour Plate at back of issue.) The structures for the isomers.

The Effect of Ketene's CH_2 Group

The geometric isomers for the η^2-(C,C) and η^2-(C,O) modes are illustrated in Figure 7. For the η^2-(C,C) mode, $Pd(PH_3)_2(CH_2{=}C{=}O)$ has two isomers with out-plane CH_2 and with in-plane CH_2. The η^2-(C,C) mode with out-plane CH_2 is preferred strongly over the mode with in-plane CH_2 (by 53 kcal/mol). In the η^2-(C,O) complex, the in-plane CH_2 structure is favored strongly over the out-plane CH_2 structure (by 41 kcal/mol).

These preferred structures are consistent with the characteristic of the two LUMOs of ketene, that is, the π^*_{C-O} orbital is in the plane of CH_2 and the π^*_{C-C} orbital is perpendicular to the plane of CH_2. These results in turn confirm that the η^2-(C,C) bonding mode is preferred over the η^2-(C,O) mode.

CONCLUSIONS

The results of our MO studies on the structures and energies of palladium ketene complexes indicate that the η^2-(C,C) bonding mode of the ketene in bis(phosphine) Pd(0) complexes is preferred over the η^2-(C,O) mode by 10–15 kcal/mol. The basicity and the bulkiness of the phosphorus ligands PR_3 have little effect on the bonding mode in the complexes $(PR_3)_2Pd$-$(CH_2{=}C{=}O)$. The most stable structure was calculated to be the η^2-(C,C) square planar structure with the CH_2 perpendicular to the molecular plane. For the η^2-(C,O) square planar structure, a local minimum was computed to be with the CH_2 in the molecular plane.

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