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Theoretical study of carbon dioxide coordination in palladium complexes†

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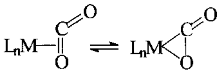
Activation of the relatively inert CO_2 molecule to form higher organic molecules has been a focus of research for many years. Therefore, the coordination of CO_2 to transition metal fragments is of considerable interest. The coordination of CO_2 to transition metals may involve η^1-O, η^1-C, or η^2-C,O bonding. The η^1-C, or η^2-C,O coordination with both early and late transition metal complexes are known. The ancillary ligands on the metal can play a significant role in effecting coordination of CO_2 to the metal center. Here we report a theoretical study of coordination modes of carbon dioxide to palladium complexes. The theoretical geometry and energies of a series of phosphine-substituted palladium carbon dioxide complexes, $(PR_3)_2Pd(CO_2)$, were investigated. The phosphine ligands included PH_3, PMe_3, PCy_3, PMe_2Ph, $PMePh_2$, PPh_3, $P(OCH_3)_3$, $P(CH{=}CH_2)_3$, PF_3, PCl_3, and PBr_3. The electron-rich $(PR_3)_2Pd$ fragments can act as Lewis bases towards the CO_2 molecule. We have examined the phosphine ligand influence on the electron density of the palladium center. In all cases the η^2-C,O bonding mode was lowest in energy. The interaction between metal fragment and CO_2 frontier orbitals will be presented in order to provide an understanding of Pd—CO_2 bonding. Copyright © 2001 John Wiley & Sons, Ltd.

Keywords: theoretical; palladium; carbon dioxide; coordination; orbital interactions

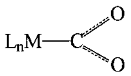
INTRODUCTION

Transition metal CO_2 complexes have drawn much attention because coordination to transition metal complexes is expected to activate the inert CO_2 molecule to undergo subsequent fixation into organic substances. The interaction of CO_2 with transition metal complexes has been extensively studied in the past two decades.[1] This gave rise to a number of transition metal complexes and produced a variety of chemical transformations, including insertion, dimerization, and disproportionation reactions.

The first reports on the coordination of CO_2 to transition metal centers came from Vol'pin *et al.* in 1969[2] and Jolly *et al.* in 1971.[3] At that time, however, the information of the binding mode of the CO_2 ligand was very scarce. The CO_2 molecule is linear with a negative partial charge on the oxygen atoms and a positive partial charge on the carbon center. This polarization allows for different interactions with potential coordination centers in metal complexes. There are three main types of interaction with a mononuclear center: η^2-C,O coordination (**I**), η^1-C coordination (**II**), or η^1-O end-on coordination (**III**). CO_2 can also act as a bridging ligand in bimetallic complexes; however, this mode will not be discussed in this paper.



I



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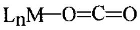

III

Carbon dioxide can act as a π-Lewis acid, particularly if the coordination to the metal occurs via the η^2 side-on mode or via the central carbon in the η^1-C mode. In this case an electron-rich metal fragment donates electrons to the π* lowest unoccupied molecular orbital (LUMO) of the CO_2 ligand, resulting in a bent O—C—O geometry. These two bonding modes were confirmed in the

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structurally characterized complexes Ni$(PCy_3)_2(\eta^2$-$CO_2)$,[4] and Rh$(diars)_2(Cl)(\eta^1$-$CO_2)$.[5] The η^1-O end-on bonding mode will not likely involve the π^* LUMO and should give a linear O—C—O geometry; however, no X-ray data are currently available for this bonding mode. A few reports claim the characterization of stable adducts with η^1-O coordination; one such example involved a gas-phase and matrix isolation study of the $W(CO)_5$(O-CO) complex.[6]

Computational and molecular orbital studies of complexes containing a CO_2 ligand can lead to a better understanding of CO_2 coordination to transition metals and several computational studies have been reported. Recently, a high theoretical level has been used to model the coordination with $(PH_3)_2Ni$, showing strong preference for the η^2-C,O mode.[7] Herein we report the study of the analogous $(PR_3)_2Pd$ fragment and its interaction with CO_2 ($PR_3 = PH_3$, PMe_3, PCy_3, PMe_2Ph, $PMePh_2$, PPh_3, $P(OCH_3)_3$, $P(CH{=}CH_2)_3$, PF_3, PCl_3, and PBr_3).

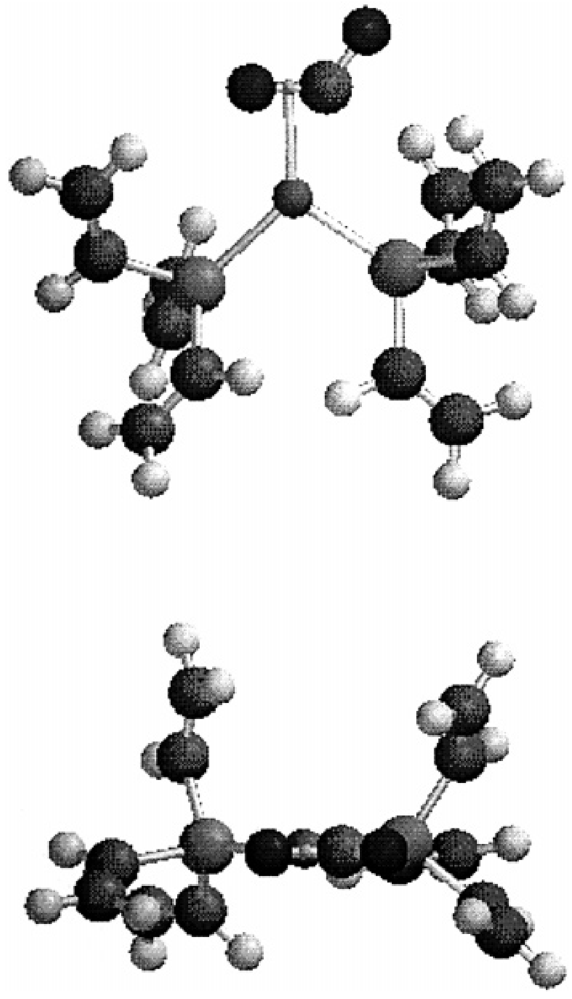

Figure 1 PM3-optimized structure revealing the coordination mode for the CO_2 ligand in the $[PCH{=}CH_2)_3]_2Pd\ (CO_2)$ complex.

COMPUTATIONAL METHODS

The minimal valence basis set of atomic functions was used for all atoms with PM3 and the DN* basis was used in the DFT/SVWN calculations. Relative energies were obtained from geometry optimizations for PM3 calculations and single point energy calculations were used for DFT methods using the PM3 geometries. Starting geometries included tetrahedral phosphorus centers and trigonal planar or square planar palladium centers. The programs PC SPARTAN *Plus* or *Pro* (Wavefunction, Inc.) were employed to perform all theoretical calculations. An energy decomposition analysis was used to calculate a bonding energy (BE) in the $(PH_3)_2Pd(CO_2)$ complexes, Eqns [1]–[3]. The interaction energy (INT) is related to the stabilization energy resulting from the coordination of the distorted CO_2 and $(PH_3)_2Pd$ fragments. The deformation energy (DEF) is the energy required to distort the CO_2 molecule to the bent geometry observed in the coordination complexes.

$$\mathrm{INT} = E[(\mathrm{PH_3})_2\mathrm{Pd(CO_2)}] - E[(\mathrm{PH_3})_2\mathrm{Pd}] - E[\mathrm{CO_2}]_{\mathrm{distort}} \qquad [1]$$

$$\mathrm{DEF} = E[\mathrm{CO_2}]_{\mathrm{distort}} - E[\mathrm{CO_2}]_{\mathrm{linear}} \qquad [2]$$

$$\mathrm{BE} = \mathrm{INT} + \mathrm{DEF} \qquad [3]$$

DISCUSSION

The heats of formation obtained from the PM3 calculations were used to compare the relative stability of the three different bonding modes, η^1-O end-on, η^1-C, or η^2-C,O side-on, of CO_2 to several $(PR_3)_2Pd$ fragments. As anticipated for the electron-rich metal center, the bonding η^2-C,O mode, Fig. 1, was the lowest energy structure for all phosphines studied in this report. Table 1 lists the relative energies for the three different bonding

Table 1 Comparison of relative energies (kcal mol^{-1}) for the different bonding modes in $(PR_3)_2Pd(CO_2)$ complexes from PM3 calculations

$(PR_3)_2Pd(CO_2)$	η^2-(C,O)	η^1-C	η^1-O
$(PH_3)_2Pd(CO_2)$	0	117	40
$(PMe_3)_2Pd(CO_2)$	0	91	31
$(PMe_2Ph)_2Pd(CO_2)$	0	88	69
$(PMePh_2)_2Pd(CO_2)$	0	87	69
$(PPh_3)_2Pd(CO_2)$	0	88	64
$[P(CHCH_2)_3]_2Pd(CO_2)$	0	85	68
$[P(OMe_3)_3]_2Pd(CO_2)$	0	102	74
$(PF_3)_2Pd(CO_2)$	0	159	118
$(PCl_3)_2Pd(C_2)$	0	66	23
$(PBr_3)_2Pd(CO_2)$	0	58	9

Table 2 Energy decomposition analysis, see text, for the interaction of $(PH_3)_2Pd$ and CO_2 in three different bonding modes

$(PH_3)_2Pd(CO_2)$	η^2-(C,O)	η^1-C	η^1-O
BE	−73	+14	−33
DEF	+57	+37	+1
INT	−130	−23	−34

modes, assigning the lowest energy in each series as 0.0 kcal mol^{-1}. The η^1-C bonding mode was calculated as the least stable complex within each series. It should be mentioned that we did not force a charge transfer complex in modeling these complexes. These results agree with the lack of experimentally isolated η^1-O end-on or η^1-C complexes.

An energy decomposition analysis was performed to determine BEs in the $(PH_3)_2Pd$ complexes. The energy $E_{distort}$ of a distorted, bent CO_2 ligand was included in the evaluation. The BE results, Table 2, show the η^2-C,O mode as the most negative energy at −73.0 kcal mol^{-1} with the η^1-O mode at −33.1 kcal mol^{-1} and the η^1-C mode at +13.9 kcal mol^{-1}. Although the distortion energy is highest for the bent CO_2 in the η^2-C,O coordination, the stabilization energy more than

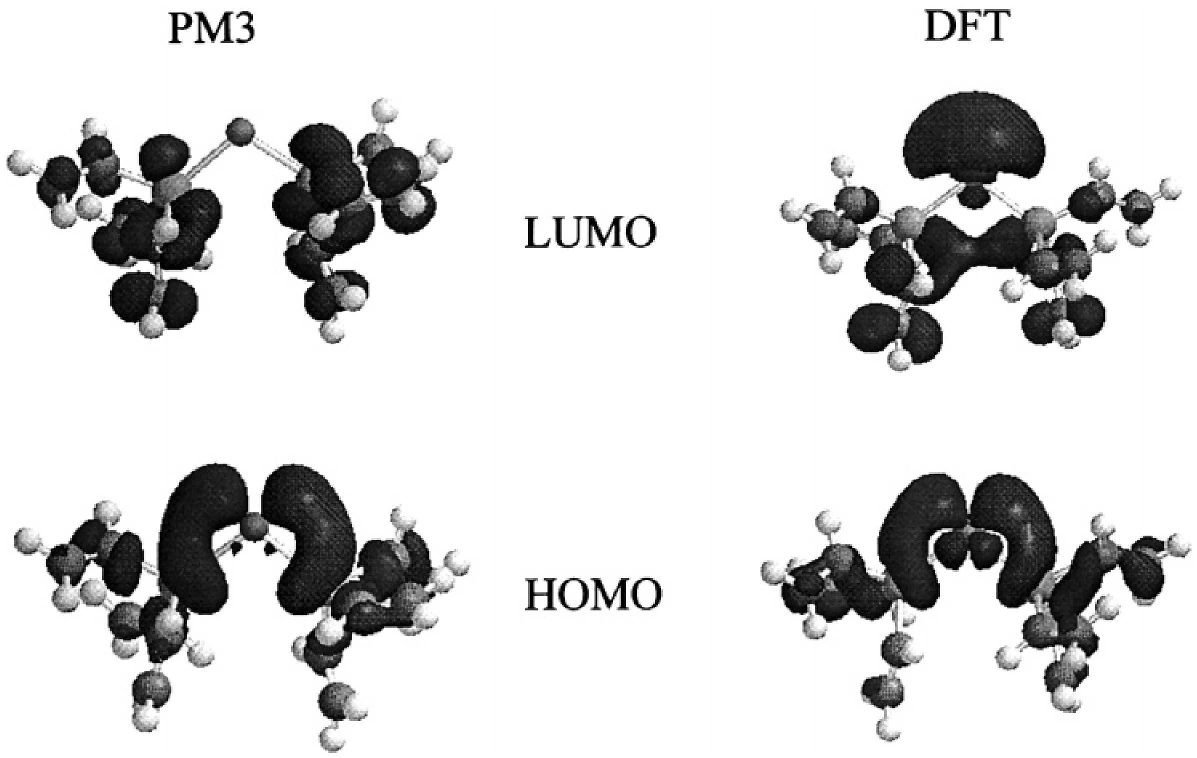

Figure 2 Frontier molecular orbitals for the $[PCH{=}CH_2)_3]_2Pd$ fragment comparing the PM3 and DFT calculations.

compensates. These energies do not rule out equilibria that may exist between bonding modes. The conversion from η^2-C,O to the η^1-O mode in $(PCy_3)_2Pd(CO_2)$ has been illustrated by the coalescence of the ^{31}P NMR signals that exist below 200 K to one signal above 240 K.[8]

To understand the preference for the η^2-C,O side-on bonding, partial charges and frontier molecular orbitals were evaluated. Initial coordination may involve the donation of electron density from CO_2 to a palladium-centered LUMO. The palladium fragment LUMO, Fig. 2, from the PM3 calculations is not of the proper symmetry for a dative σ-bond via donation from the CO_2 ligand. The higher-level DFT calculations did produce an appropriate palladium fragment LUMO of a_1 symmetry. However, the Mulliken partial charge on the palladium center in the $(PR_3)_2Pd$ fragments is negative. This should result in a greater electrostatic repulsion with the partial negative oxygen atoms hindering the formation of η^1-O coordination.

The electron-rich palladium fragments were expected to show metal-to-ligand π-bonding with the CO_2 LUMO, favoring the η^2-C,O side-on coordination. Examination of the highest occupied molecular orbital (HOMO) orbital, Fig. 2, on the C_{2v} palladium fragment reveals a b_2 orbital that is appropriate for π-back-bonding with the C—O π* molecular orbital to form a square planar geometry. The calculated C—O bond orders and the bent geometry agree with this π-bonding. For example, the calculated bond orders are 1.22 and 1.70 and the O—C—O angle is 123.5 ° in the $(PH_3)_2Pd(CO_2)$ complex. Lastly, we evaluated DFT eigen values of the frontier orbitals and have compared the $(PH_3)_2Pd$ energies with the nickel analog. Both palladium and nickel HOMOs are closer to the CO_2 LUMO, <3 eV, than the metal-centered LUMOs are to the π-MO of carbon dioxide, >9 eV. We have found that the orbital energy differences are lower for nickel complexes. This agrees with the relative ease of preparation of the Ni—CO_2 coordination complexes.

CONCLUSION

The most stable bonding mode for $(PR_3)_2Pd(CO_2)$ complexes was calculated to be the η^2-C,O side-on mode. This is supported by frontier MOs from PM3 and DFT calculations where the metal-centered HOMO interacts with the π* LUMO of CO_2. The preference of η^2-side-on mode over the η^1-C and η^1-O modes is independent of the basicity and the bulkiness of the phosphine ligands; however, the relative energy differences do change. The η^2-CO_2 mode is expected in neutral L_nM—CO_2 coordination complexes where M is an electron-rich metal.

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