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## **Electronic Structure of Ni(0) Complexes Containing Ligands with Cumulative Double Bonds**

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## Electronic structure of Ni(0) complexes containing ligands with cumulative double bonds

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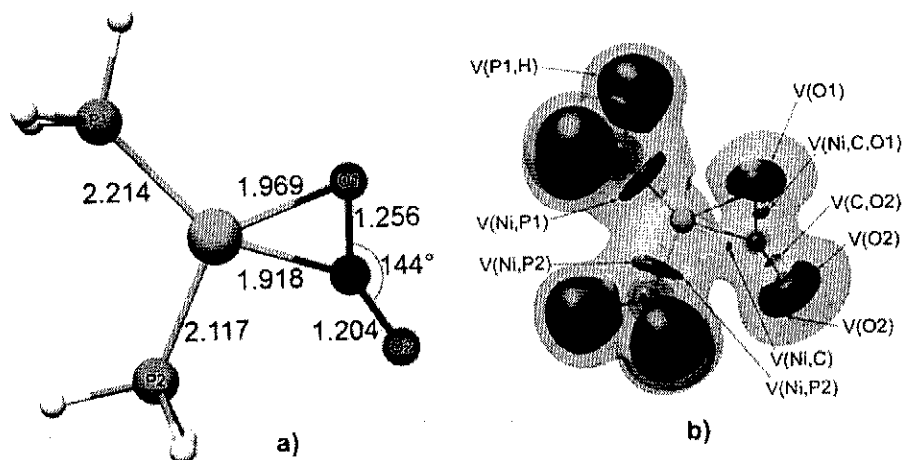
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In our previous study the electronic structure of the Ni(0) complex Ni(PH<sub>3</sub>)<sub>2</sub>(η<sup>2</sup>-CO<sub>2</sub>) (Figure 1) was elucidated within the framework of density functional theory by means of using domain-averaged Fermi hole (DAFH), quantum theory of atoms in molecules (QTAIM), electron localization function (ELF), charge decomposition analysis (CDA), and natural bond orbital (NBO) methods <sup>8</sup>. It was shown, that the carbon dioxide ligand exhibits an unusual coordination behavior due to the highly polarized nature of the O=C bond. According to QTAIM and ELF analyses neither bond path nor V(C,O1) basin was found between Ni and O1. The back-donation from metal to carbon dioxide ligand is influenced by a direct charge transfer from phosphorus to carbon as it was revealed by DAFH and NBO studies.

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<sup>8</sup> T. Kégl, R. Ponec, L. Kollár, *J. Phys. Chem. A*, in press, [dx.doi.org/10.1021/jp201140h](https://doi.org/10.1021/jp201140h)

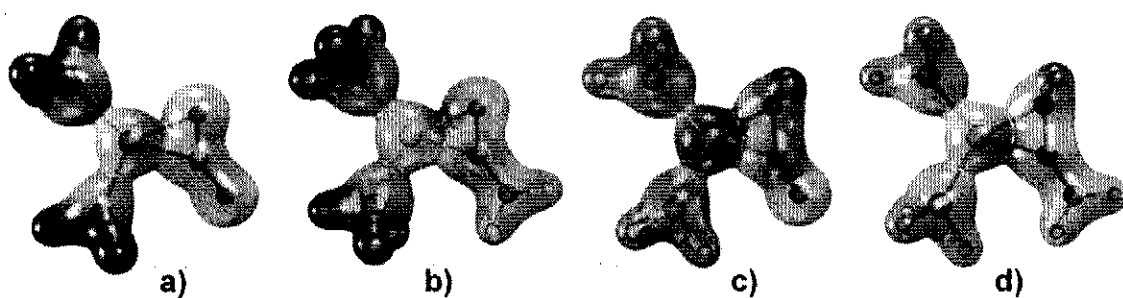


**Figure 1.** (a) Computed structure of  $\text{Ni}(\text{PH}_3)_2(\text{CO}_2)$  at the PBE/PBE/SDD level of theory; (b) ELF = 0.15 (translucent) and ELF = 0.81 (opaque) isosurfaces superimposed for complex  $\text{Ni}(\text{PH}_3)_2(\text{CO}_2)$ . The valence basins are indicated.

The lack of bond path between Ni and O1 can be explained with the high kinetic energy, which overcomes the potential energy. The high kinetic energy is in conjunction with the highly negative electrostatic potential in the Ni-O1 region (Figure 2a).

Further studies on analogous complexes containing ligands with cumulative double bonds, such as  $\text{Ni}(\text{PH}_3)_2[\eta^2-(\text{C},\text{O})-(\text{O}=\text{C}=\text{CH}_2)]$ ,  $\text{Ni}(\text{PH}_3)_2[\eta^2-(\text{C},\text{C})-(\text{O}=\text{C}=\text{CH}_2)]$ ,  $\text{Ni}(\text{PH}_3)_2[\eta^2-(\text{H}_2\text{C}=\text{C}=\text{CH}_2)]$ , show that all complexes possess trisynaptic  $V(\text{Ni},\text{C},\text{O})$  or  $V(\text{Ni},\text{C},\text{C})$  basins in keeping with the  $\pi$ -donor character of the ligand. According to the molecular electrostatic potential maps of complexes depicted in Figure 2 the  $\eta^2-(\text{C},\text{O})$  ketene complex shows the closest resemblance with the  $\eta^2-(\text{C},\text{O})-\text{CO}_2$  complex. ELF studies, however, reveal that this complex features two disynaptic  $V(\text{Ni},\text{O})$  basins very close to the oxygen atom instead of one monosynaptic basin as it was reported for  $\text{Ni}(\text{PH}_3)_2(\text{CO}_2)$ . In the  $\eta^2-(\text{C},\text{C})$  ketene and allene complexes two disynaptic  $V(\text{Ni},\text{C})$  basins can be assigned to the two Ni-C bonds.

Detailed electronic structure studies including DAFH, QTAIM, ELF, CDA, and NBO methods for the four complexes depicted in Figure 2 will be reported.



**Figure 2.** Isodensity surface color-coded by the molecular electrostatic potential for complex a)  $\text{Ni}(\text{PH}_3)_2(\eta^2\text{-CO}_2)$ ; b)  $\text{Ni}(\text{PH}_3)_2[\eta^2\text{-(C,O)-(O=C=CH}_2)]$ ; c)  $\text{Ni}(\text{PH}_3)_2[\eta^2\text{-(C,C)-(O=C=CH}_2)]$ ; d)  $\text{Ni}(\text{PH}_3)_2[\eta^2\text{-(H}_2\text{C=C=CH}_2)]$