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# $\sigma$-Donor and $\pi$-Acceptor Properties of Phosphorus Ligands: An Insight from the Natural Orbitals for Chemical Valence

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The bonding between phosphorus ligands X = $PCl_3$, $PF_3$, $P(OCH_3)_3$, $PH_3$, $PH_2CH_3$, $PH(CH_3)_2$, $P(CH_3)_3$ and the metal-containing fragments $[Ni(CO)_3]$, $[Mo(CO)_5]$, and $[Fe(CO)_4]$ have been studied by Natural Orbitals for Chemical Valence (NOCV). The main attention was paid to estimation of donor ($\Delta q_d$) /acceptor ($\Delta q_{bd}$) properties of X on the basis of NOCV's charge criterion. All ligands X are found to be both $\sigma$-donors and $\pi$-acceptors. The best $\sigma$-donor and $\pi$-acceptor ligands are $P(CH_3)_3$ and $PY_3$ (Y = F,Cl), respectively, in both the nickel and molybdenum complexes. The NOCV contributions to deformation density show that the $\sigma$-component corresponds to the donation from the lone electron pair of phosphorus, enhanced further by a transfer from ancillary halogen atoms (in the case of $PCl_3$ and $PF_3$) to a bonding region and to oxygen atoms of carbonyls. The $\pi$-bonding is due to the electron transfer from the metal into the empty orbital of X, mostly exhibiting phosphorus *3p* character. It was shown that within the molecular orbital framework, the trend for the donor/acceptor strength of X can be explained by the difference in the orbital energies of the orbitals involved in the donation/back-donation. Regarding the influence of the metal fragment on the donor/acceptor properties of X, it was demonstrated that the relative order of the phosphorus ligands remains in general intact. The only exception is the $P(OCH_3)_3$ ligand changing its position in molybdenum series compared to the nickel complexes. However, a change in the metal-containing fragment can influence the magnitude of electron transfer. For the set of phosphorus ligands studied here the effect is much less pronounced than for other ligands studied previously.

## Introduction

The phosphorus ligands belong to one of the most ubiquitous groups in transition metal chemistry. Understanding of the metal−phosphorus bonding is crucial for rationalizing the trends in the energetic stability and reactivity of complexes.[1−8] Information about the nature of the metal−phosphorus bond is also essential for characterizating and tuning the properties of these compounds and potentially design new active catalysts.[1,2] In this respect, a quantitative description of the metal−phosphorus bonding is desirable.

In the 1970s Tolman pointed out that it is very difficult to extract separate information about the donation/back-donation effects solely on an experimental basis in the phosphorus-based compounds.[9,10] Afterward, many attempts have been made in the experimental area to quantitatively assess the donor/acceptor properties of various ligands.[11−22] In these studies the conclusions on donor/acceptor properties were drawn *indirectly*, using spectroscopic and structural data.[17−24]

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On the other hand, numerous theoretical methods have been applied to characterize donor/acceptor properties of phosphorus ligands.[8,14,25−45] Those methods and concepts can be generally grouped into two categories. The methods in the first group offer a quantitative assessment of donor/acceptor properties of an *isolated* ligand, completely neglecting an influence of the metal-containing fragment in a particular complex. The approaches used in this context include molecular electrostatic potential analysis (MEP),[34,46] or the method based on the analysis of the frontier orbital density.[47]

The second group collects approaches in which donor/acceptor properties are extracted on the basis of whole *transition metal-containing complex*. It comprises energy partitioning schemes,[33,35−37,48−52] Charge Decomposition Analysis (CDA),[14,27,28] Constrained Space Orbital Variation (CSOV),[29,30] natural bond-orbital approach[38,48] or quantitative analysis of ligands effect (QALE).[39]

We have recently proposed the *Natural Orbitals for Chemical Valence* (NOCV) that provides the natural orbital representation of the deformation density, leading to a very compact description of bonding in terms of only a few orbitals, localized in the bond region.[42−45,49,51,53,54] It has been shown[42−45,49,51,53,54] that NOCV allows for a separation and quantitative assessment of the contributions to the deformation density from the ligand → metal (donation) and metal → ligand (back-bonding) *electron charge transfers*. Thus, it is possible to directly address the Dewar−Chat−Duncanson model.[55,56]

In the present account we will use the NOCV approach in a qualitative and quantitative description of the metal−ligand bonding in selected phosphorus−transition metal complexes. The main goal is to characterize donor/acceptor properties in a series of phosphorus ligands (X = $PCl_3$, $PF_3$, $P(OCH_3)_3$, $PH_3$, $PH_2CH_3$, $PH(CH_3)_2$, $P(CH_3)_3$) in the tetrahedral $Ni(CO)_3X$ systems on the basis of NOCV *charge criterion*. In addition influence of the metal fragment will be investigated by bonding analysis in octahedral $Mo(CO)_5X$ complexes, as well as in the penta-coordinated $Fe(CO)_4X$ systems. The choice of these molybdenum- and iron-based systems in addition facilitates a comparison with earlier theoretical studies based on the other methods/criterions: i.e. *energy decomposition studies* by Frenking[28,50] et. al and Gonzáles-Blanco and Branchadell,[32] *NBO* study by Leyssens,[48] and the *NMR chemical shift* analysis by Ziegler.[33]

## Computational Details

In all the calculations the Amsterdam Density Functional (ADF) program[57−59] was used. The Becke−Perdew exchange-correlation functional[60,61] was applied. A standard double-ζ STO basis with one set of polarization functions was used for main-group elements (H, C, O, F, Cl, P), while a standard triple-ζ basis set was employed for nickel and molybdenum. The *1s* electrons of C, N, O, F as well as the *1s-2p* electrons of P, Cl, and Ni and *1s-3p* for Mo were treated as frozen core. Auxiliary *s, p, d, f,* and *g* STO functions, centered on all nuclei, were used to fit the electron density and obtain accurate Coulomb potentials in each SCF cycle.

The Natural Orbitals for Chemical Valence (NOCV) has been derived from the Nalewajski−Mrozek valence theory.[62−64] The NOCV's, $\psi_i$, are defined as the eigenvectors, $\psi_i = \sum_j^N C_{ij}\chi_j$, that diagonalize the deformation density matrix, $\Delta\mathbf{P}$[42−45,49,51,53,54]

$$\Delta\mathrm{P}C_i = v_i C_i, \quad i = 1...N \tag{1}$$

where $N$ denotes the number of basis functions, $\{\chi_j, j = 1, N\}$, used in the representation for $\mathbf{\Delta P}$.

The deformation density matrix, $\mathbf{\Delta P}$ is defined as:

$$\Delta\mathbf{P} = \mathbf{P} - \mathbf{P}^0 \tag{2}$$

where $\mathbf{P}$ and $\mathbf{P}^0$ correspond to the density matrices of the combined molecule ($\mathbf{P}$) and the considered fragments ($\mathbf{P}^0$). We shall in the following represent $\Delta P$ in a basis of orthogonalized fragment Kohn−Sham (KS) orbitals (OFO). In such a basis the NOCVs are the eigenfunctions of $\Delta P$.[42−45,49,51,53,54]

It follows further[42−45,49,51,53,54] that the deformation density, $\Delta\rho = \rho(\text{molecule}) - \rho^0(\text{fragments})$, can be expressed in the NOCV representation as a sum of pairs of complementary eigenfunctions ($\psi_{-k}$, $\psi_k$) corresponding to the eigenvalues $v_k$ and $-v_k$ with the same absolute value but

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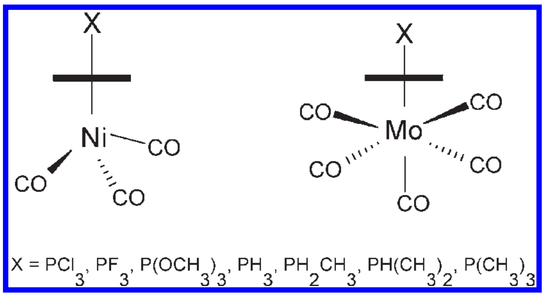

**Figure 1.** Complexes studied in the present work, Ni(CO)$_3$X and Mo(CO)$_5$X with X = PCl$_3$, PF$_3$, P(OCH$_3$)$_3$, PH$_3$, PH$_2$CH$_3$, PH(CH$_3$)$_2$, P(CH$_3$)$_3$. A thick line indicates the way of fragmentation of the complex into the two subsystems.

opposite signs:

$$\Delta\rho(\mathrm{r}) = \sum_{\mathrm{k}=1}^{N/2} v_{\mathrm{k}}[-\psi_{-\mathrm{k}}^2(\mathrm{r}) + \psi_{\mathrm{k}}^2(\mathrm{r})] = \sum_{\mathrm{k}=1}^{N/2} \Delta\rho_{\mathrm{k}}(\mathrm{r}) \qquad (3)$$

Here the fact that the eigenvalues appear in pairs, where $v_{\mathrm{k}} = -v_{\mathrm{k}}$, is a consequence of $\mathbf{\Delta P}$ being a traceless matrix expressed in an orthonormal (OFO) basis. In eq 3, an eigenvalue $v_{\mathrm{k}}$ corresponds to the fraction of an electron charge that is transferred from the $\psi_{-\mathrm{k}}$ orbital to the $\psi_{\mathrm{k}}$ orbital, when the molecule is formed from the fragments. In our study the donor/acceptor properties of a few typical phosphorus ligands X will be extracted from the results describing the bonding between X and a given metal-based fragment. We will consider subsequently the following metal fragments: Ni(CO)$_3$ and Mo(CO)$_5$, see Figure 1. The complementary pairs of each NOCV define a separate channel for electron charge transfer between the molecular fragments.[42−45,49,51,53,54] The total charge transferred in this channel is given by NOCV eigenvalue as:

$$\Delta q_{\mathrm{k}} = v_{\mathrm{k}} \qquad (4)$$

## Results and Discussion

As we explained in the previous section, donor−acceptor properties of phosphorus ligands can be quantitatively characterized by the NOCV eigenvalues (eq 4). However, visual inspection of the deformation density contributions ($\Delta\rho_\kappa$) is also necessary (eq 3), to identify which orbital pairs correspond to donation, and which correspond to back-bonding. Therefore, we will start the discussion with the NOCV based contributions to the differential density for an example Ni(CO)$_3$−PCl$_3$ complex. We can see from Figure 2a that predominantly three deformation density components characterize the bonding between PCl$_3$ and nickel fragment Ni(CO)$_3$. The first contribution, $\Delta\rho_1$, captures $\sigma$-component of Ni(CO)$_3$−PCl$_3$ bond and it represents the outflow of electron density from the lone pair of phosphorus atoms and the charge accumulation in the bonding region as well as on the oxygen atoms. In addition, the negative $\Delta\rho_1$ contours appears on the chlorine atoms (an outflow from *3p* orbitals) of PCl$_3$. The NOCV eigenvalue $\Delta q_{\mathrm{d}} = 0.47$ can be treated as a direct charge measure of $\sigma$-donor ability of PCl$_3$. The other two components, $\Delta\rho_2$ and $\Delta\rho_3$, clearly indicate the $\pi$-back-bonding character of Ni(CO)$_3$−PCl$_3$ bond, i.e., the electron charge transfer from the metal into the phosphorus ligand. It is also clear from Figure 2a that $\pi$−back-donation is realized by the electron transfer from the metal into the empty orbital

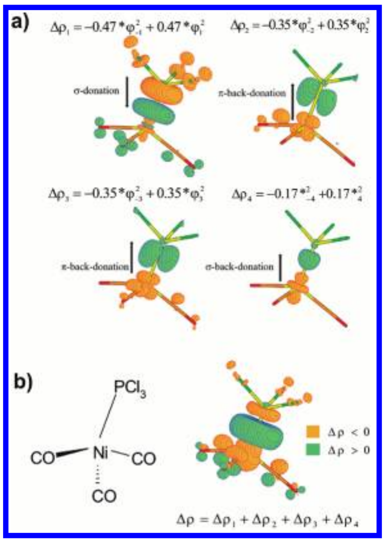

**Figure 2.** Contributions from the pairs of complementary NOCV ($\Delta\rho_1$, $\Delta\rho_2$, $\Delta\rho_3$, $\Delta\rho_4$) to the deformation density $\Delta\rho$ (panel a), and the overall deformation density $\Delta\rho$ (panel b) for Ni(CO)−-PCl$_3$ complex. The contours of $|\Delta\rho| = 0.003$ au are shown.

of PCl$_3$ mostly exhibiting phosphorus *3p* character. It further confirms that it is not *3d*, but *3p* orbital of phosporus that directly participates in the formation of $\pi$-bond, as it was concluded in the previous studies.[28−31,41,52,65−68] The total $\pi$-acceptor ability of PCl$_3$ (eq 5) is given by $\Delta q_{\mathrm{bd}} = 0.35 + 0.35 = 0.70$. The very last contribution, presented in Figure 2a, $\Delta\rho 4$, quantitatively less important, exhibits the $\sigma$-electron transfer from $d_{z2}$ of the metal into the high lying empty orbital of PCl$_3$.

Due to the fact that the donation/back-donation charge transfer channels look qualitatively similar for both types of complexes, i.e., for Ni(CO)$_3$X and Mo(CO)$_5$X, we will not show the corresponding $\Delta\rho_{\mathrm{k}}$ contours. Only the quantitative estimations of donor ($\Delta q_{\mathrm{d}}$)/acceptor ($\Delta q_{\mathrm{bd}}$) abilities of X based on eq 4 will be discussed; they are listed in Table 1.

The results collected in Table 1 demonstrate that the $\sigma$-donor strength decreases in the following order for Ni(CO)$_3$X and Mo(CO)$_5$X complexes:

Ni(CO)$_3$X: **P(CH$_3$)$_3$ = P(OCH$_3$)$_3$ > PH(CH$_3$)$_2$ > PH$_2$(CH$_3$) > PH$_3$ > PCl$_3$ > PF$_3$**

Mo(CO)$_5$X: **P(CH$_3$)$_3$ > PH(CH$_3$)$_2$ > PH$_2$(CH$_3$) > P(OCH$_3$)$_3$ > PH$_3$ > PCl$_3$ > PF$_3$**

We can see from the above sequences that the strongest $\sigma$-donor ligand in the nickel and molybdenum complexes is P(CH$_3$)$_3$, whereas the weakest are PCl$_3$ and PF$_3$ (marked in red above). The same donating strength as for P(CH$_3$)$_3$ was also noted for P(OCH$_3$)$_3$ (marked in brown above) in tetrahedral nickel-based series. We should notice that the changes in *absolute* $\Delta q_{\mathrm{d}}$ are not very large: the difference between the extreme values is only 0.15 for Ni(CO)$_3$X and 0.08 for Mo(CO)$_5$X systems. However, it was shown[49] for other complexes that even a change by 0.1 in the NOCV charge transfer magnitude corresponds to a quite significant change in the bond energies, by ~10−15 kcal/mol, depending on the

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**Table 1.** NOCV-Based Estimation of Donor ($\Delta q_d$) and Acceptor Properties ($\Delta q_{bd}$) of Ligands X in Tetrahedral $Ni(CO)_3-X$ and Octahedral $Mo(CO)_5-X$ Complexes

| | $Ni(CO)_3-X$ | | $Mo(CO)_5-X$ | |
|---|---|---|---|---|
| ligands X | $\Delta q_d$ | $\Delta q_{bd}$ | $\Delta q_d$ | $\Delta q_{bd}$ |
| $P(OCH_3)_3$ | 0.56 | 0.54 | 0.55 | 0.58 |
| $P(CH_3)_3$ | 0.56 | 0.45 | 0.59 | 0.49 |
| $PH(CH_3)_2$ | 0.54 | 0.47 | 0.58 | 0.51 |
| $PH_2CH_3$ | 0.51 | 0.48 | 0.56 | 0.53 |
| $PH_3$ | 0.49 | 0.49 | 0.55 | 0.54 |
| $PCl_3$ | 0.47 | 0.70 | 0.53 | 0.81 |
| $PF_3$ | 0.43 | 0.72 | 0.51 | 0.76 |

complex. Also, it is worth emphasizing that despite these differences in NOCV eigenvalues, the trends that could be intuitively expected are well reproduced for both types of complexes, e.g., an increase in the donor ability with an increase in the number of methyl groups when going from $PH_3$ toward $P(CH_3)_3$. In addition, we observe a minor influence of metal-containing fragment on the *relative* order of $\sigma$-donor ability of X when nickel fragment is replaced by molybdenum-containing species: the order of the ligands remains in general intact. The only exception is $P(OCH_3)_3$ ligand changing its position in molybdenum series compared to the nickel series.

A natural question that emerges at this point is about the factors determining the trend within $\sigma$-donor ability of X. To answer this question the molecular orbital energies that are directly involved in the $\sigma$-donation transfer are presented in Figure 3a. It is clear from Figure 3a that the strongest $\sigma$-donor ability of $P(CH_3)_3$ can be attributed to the smallest energy difference between the HOMO of ligand (participating in the outflow of electron density) and the LUMO of metal-containing fragments (acting as an acceptor orbital); for this ligand the energy difference is 0.6 eV and 1.16 eV, in molybdenum and nickel systems, respectively. The weakest $\sigma$-donating character of the $PF_3$ ligand is related to the largest orbital energy difference (4.58 eV and 3.58 eV for molybdenum and nickel systems, respectively). Thus, the strength of $\sigma$-donor ability can be in fact related to the electronegativity of X.

Let us turn our discussion to $\pi$-acceptor abilities ($\Delta q_{bd}$) of X extracted from the NOCV eigenvalues (eq 4). The data collected in Table 1 lead to the following orders of $\pi$-acceptor strength for nickel and molybdenum series:

$Ni(CO)_3X$: $PF_3 > PCl_3 \gg P(OCH_3)_3 > PH_3 > PH_2(CH_3) > PH(CH_3)_2 > P(CH_3)_3$

$Mo(CO)_5X$: $PCl_3 > PF_3 \gg P(OCH_3)_3 > PH_3 > PH_2(CH_3) > PH(CH_3)_2 > P(CH_3)_3$

It becomes evident from the above orders and Table 1 that the most effective $\pi$-acceptors are $PF_3$ and $PCl_3$ ($\Delta q_{bd}$ ~0.7 and 0.8 for nickel and molybdenum series, respectively), whereas the remaining species are characterized by significantly lower values of $\Delta q_{bd}$ (~0.5 for both metal series). Similarly to the $\sigma$-components discussed previously, a minor influence of the metal fragment on the relative strength of $\pi$-acceptor ability of X is noted. Among all of the ligands, only $PF_3$ and $PCl_3$ exchanged their relative positions (black and blue in the above orders) when going from the nickel- to the molybdenum-based complexes. We can also see from Figure 3b that $\pi$-acceptor strength of X is related to the molecular orbital energy differences between the orbitals involved in the $\pi$-back-donation, i.e., HOMO of metal-containing fragment (mostly exhibiting either *3d* (Ni) or *4d* (Mo) character) and the LUMO of X. It is clear from Figure 3b that the smaller the energy difference is, the larger $\pi$-acceptor character of X is observed and vice versa. Finally, it turned out that the absolute total charge transfer ($\Delta q_d + \Delta q_{bd}$) is higher (by ~0.1−0.2) for the molybdenum complexes containing halogen atoms compared to those for nickel-based systems.

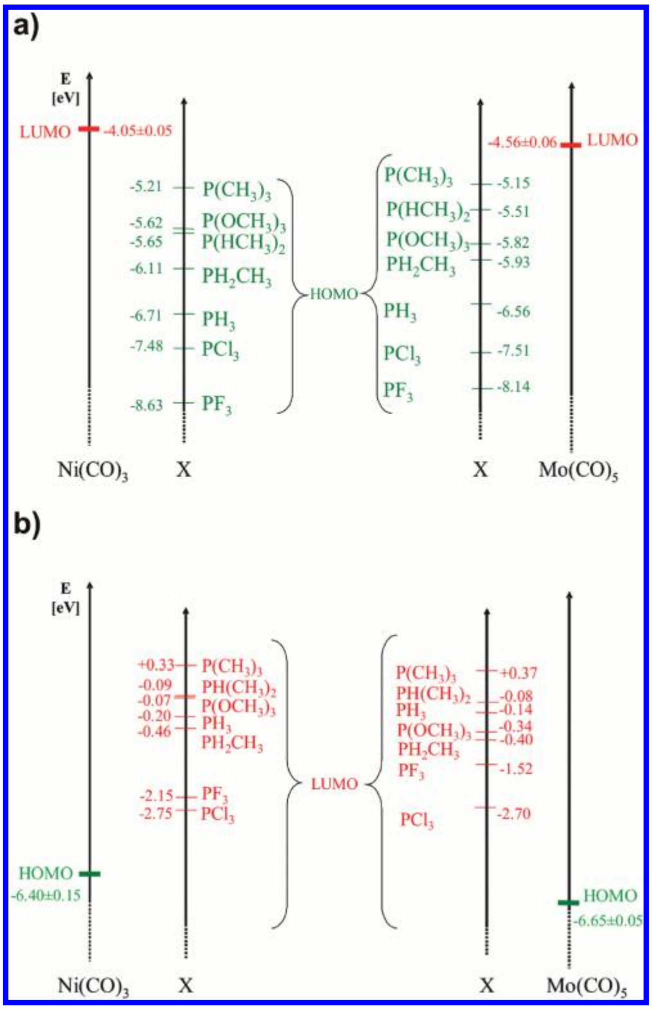

**Figure 3.** (a) HOMO energies of phosphorus ligands (green) and the LUMO of metal-based-fragments (red). (b) Ligand LUMO energies (red) together with the HOMO of metal-containing-fragments (green).

As we have already mentioned, numerous theoretical methods have been applied to characterize donor/acceptor properties of phosphorus ligands.[28,32,33,48,50,52] The choice of the complexes studied in the present work allows for a direct comparison with the earlier theoretical studies.[28,32,33,48,50,52] To facilitate such comparison, it is instructive to discuss not only the quantities characterizing the donor/acceptor character, but as well the ratio of $\sigma$-donor/$\pi$-acceptor strength resulting from those quantities.[48,52] Therefore, in Table 2 we have compared the $\sigma$-donor/$\pi$-acceptor strength obtained from the NOCV eigenvalues and the previous studies.[28,32] For the same reason, we have supplemented the systems reported in Table 1 with the $Fe(CO)_4-X$ complexes with X = $P(CH_3)_3$, $PH_3$, and $PF_3$.

Before we compare our results with those obtained previously by other authors, it is worth emphasizing that a distinctive feature of NOCV approach is that donor/acceptor

**Table 2.** Ratio of $\sigma$-Donor/$\pi$-Acceptor Strength for Selected Phosphorus Ligands Calculated within ETS and NOCV Schemes for Different Metal Complexes: $Mo(CO)_5X$, $Ni(CO)_3X$, and $Fe(CO)_4X$

| Ligands | $Mo(CO)_5$ | $Fe(CO)_4$ | $Mo(CO)_5$ | $Ni(CO)_3$ | $Fe(CO)_4$ |
|---|---|---|---|---|---|
| X | ETS (ref 28) | ETS (ref 32) | NOCV | NOCV | NOCV |
| $P(CH_3)_3$ | 2.62 | 5.82 | 1.20 | 1.24 | 1.48 |
| $PH_3$ | 1.91 | 4.31 | 1.01 | 1.00 | 1.25 |
| $PF_3$ | 0.91 | 2.10 | 0.65 | 0.59 | 0.89 |
| $PCl_3$ | 1.06 | ----- | 0.67 | 0.67 | --- |

properties of ligands are characterized based on the *charge criterion* that originates directly from contributions to the deformation density, i.e., the charge-flow channels between the fragments. The NOCV results lead to the conclusion that the best $\sigma$-donor and $\pi$-acceptor ligands are $P(CH_3)_3$ and $PY_3$ ($Y = F,Cl$), respectively, for all metal series considered. This is in line with the previous energy decomposition studies by Frenking[28] and by González-Blanco,[32] by Leyssens[48] on the basis of second-order perturbative NBO analysis, and by Ziegler[33] on the basis of NMR study. The results presented in Table 2 show that the *ratio* of $\sigma$-donor/$\pi$-acceptor strength of phosphorus species decreases when going from $P(CH_3)_3$ to halogen ligands for both, NOCV-*charge-flows* and the *energy-decomposition-method* (ETS)[28,32] originated data. However, in the latter case the values of the ratio are more pronounced, changing from 2.62 for $Mo(CO)-P(CH_3)_3$ down to 1.06 for $Mo(CO)_5-PCl_3$, and from 5.82 for $Fe(CO)_4-P(CH_3)_3$ down to 2.10 for $Fe(CO)_4-PF_3$. The corresponding NOCV results are 1.20 and 0.67 for $Mo(CO)_5-P(CH_3)_3$ and $Mo(CO)_5-PCl_3$, respectively. Here, it is worth pointing out that the NOCV results obtained for $Ni(CO)_3-P(CH_3)_3$ and $Ni(CO)_3-PCl_3$ are very close (1.24, and 0.67, respectively), showing practically no influence of the metal fragment. However, for $Fe(CO)_4$ fragment the corresponding values are visibly increased (1.48 for $Fe(CO)_4-P(CH_3)_3$ and 0.89 for $Fe(CO)_4-PF_3$). Thus, these examples show that one should be careful with drawing conclusions concerning the metal-fragment influence, as in some cases it can be substantial, and in some can be minor, even for different metals and different coordination numbers. Another important conclusion from a comparison of the donor/acceptor properties based on the energy- and charge-criteria is that the former exhibit much larger differences in the series of complexes. This is in fact similar to a comparison in trends in bond energies and bond orders: it is common that similar bond orders are accompanied by substantially different bond energies.[53,54]

In addition, our NOCV results indicate that halogen ligands are better acceptors than donors. It is not fully consistent with the ETS-based result which revealed $PCl_3$ as slightly better donor than acceptor.[28] On the other hand, our donor/acceptor data are in good agreement with the NMR computational study by Ziegler.[33] Similar lack of quantitative agreement can be observed when comparing donor/acceptor data that comes from CSOV and ETS schemes, as was recently confirmed by Leyssens et al.[48] and Fey et al.[52] Nevertheless, all these decomposition schemes (CSOV, ETS, NOCV) predict consistently $PMe_3$ ligand as better donor and worst acceptor compared to halogen species. In conclusion, it should be emphasized again that different definitions of donor/acceptor strength (resulting from different criteria) can lead to different predictions.

## Concluding Remarks

In the present study the Natural Orbitals for Chemical Valence (NOCV) were used to describe the bond formed between phosphorus ligands X and the metal in the transition-metal complexes. Different metal-containing fragments were considered: $Ni(CO)_3$, $Mo(CO)_5$, and $Fe(CO)_4$. The main goal was to characterize *donor/acceptor* properties of X and to provide a picture of bonding emerging from the decomposition of total deformation density ($\Delta\rho$), both within one theoretical framework. The donor/acceptor properties of the ligands were *quantitatively* described based on the NOCV *charge criterion*. Use of NOCV in addition allows for a *qualitative* depiction of the specific charge transfer channels ($\sigma$ and $\pi$) corresponding to bonding between metal fragment and phosphorus species. Although, bonding of phosphorus ligands X to various metals was extensively studied in the numerous previous works[28,32,33,48,50,52] this is the first analysis that *directly* links the donor/acceptor properties of X to the deformation density components (charge-transfer channels). It should be pointed out that within the NOCV framework it is possible to analyze $\sigma$- and $\pi$-components of the bond not only in highly symmetrical systems, but as well in the complexes without symmetry.[51] In addition, we have shown in the present study how different metal-containing fragments influence the relative donor/acceptor abilities of X.

We found, in line with the other analyses,[28,32,33,48,50,52] that each studied X appeared to be both $\sigma$-donor and $\pi$-acceptor. The NOCV contributions to the deformation density clearly show that the $\sigma$-component corresponds to the donation from the lone electron pair of phosphorus, enhanced further by a transfer from ancillary halogen atoms (in the case of $PCl_3$ and $PF_3$) to a bonding region and to oxygen atoms of carbonyls. The $\pi$-bonding is due to the electron transfer from the metal into the empty orbital of X, mostly exhibiting phosphorus *3p* character.

Concerning a comparison of different ligands, the results demonstrate that the strongest $\sigma$-donating ligand is $P(CH_3)_3$ for all, the nickel, molybdenum, and iron series. On the other hand, the species exhibiting the weakest donation, i.e., $PCl_3$ and $PF_3$, at the same time demonstrate the strongest $\pi$-acceptor character. It was further shown that within the molecular orbital framework, the trend for the donor/acceptor strength of X can be explained by the orbital energy difference between the orbitals involved in the donation and back-donation processes, respectively.

Regarding the influence of the metal-fragment on the donor/acceptor properies of X, it was demonstrated that the relative order of the phosphorus ligands remains in general intact. The only exception is the $P(OCH_3)_3$ ligand changing its position in molybdenum series compared to the nickel complexes. However, a change in the metal-containing fragment can influence the magnitude of electron transfer. For the set of phosphorus ligands studied here the effect is much less pronounced than for other ligands studied previously.[43] However, even small changes in the charge transfer can be reflected by noticeable changes in the bond energies.[49] Therefore, as was also emphasized by other authors,[28] the donor/acceptor properties should always be discussed with respect to a given complex.