Effect of Phosphine Substitution on the Electronic Structure of Cobalt Tricarbonyl Nitrosyl[†]

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The He-I ultraviolet photoelectron spectra of a series of phosphine-substituted organometallic complexes, $Co(CO)_2NOL$ (L = CO, PMe_3, PEt_3, PPr_3, PBu_3, PCy_3, PPh_3, and $P(OMe)_3$) are reported. The first vertical ionization energy of the complexes was found to be 8.75 (CO), 7.85 (PMe_3), 7.69 (PEt_3), 7.47 (PPr_3), 7.49 (PBu_3), 7.71 (PCy_3), 7.58 (PPh_3), and 8.15 eV ($P(OMe)_3$) ± 0.03 eV. Quantum chemical calculations at the HF, DFT (B3LYP), and EOMIP-CCSD levels of theory were employed to interpret both the trends in the series and the most important features of the spectra. Photoelectron spectra of some of the complexes are also reported at He-II photon energy. Intensity changes in the photoelectron bands between He-I and He-II photon energies are discussed on the basis of the orbital compositions.

Introduction

Transition-metal complexes are used as catalysts in numerous reactions of biological and industrial importance. Cobalt tricarbonyl nitrosyl has a particularly important role in organic chemistry,[1−3] chemical vapor deposition,[4−6] and even in nanotechnology.[7,8] Experiments show that phosphine substitution, due to its effect on the electronic structure and its steric demand, may strongly affect the stability and catalytic activity of transition-metal carbonyls.[9−11] Therefore, $Co(CO)_2NOPR_3$ (R = Me, Et, Pr, Bu, Cy, Ph, and OMe) seem to be an ideal set of systems to study the influence of tertiary phosphine substitution on the electronic structure of an organometallic complex.

In recent years, several studies were carried out on the electronic structure of $Co(CO)_3NO$. The first He-I photoelectron spectrum (PES) was published by Hillier et al.[12] They assigned the recorded spectrum using Koopmans' theorem.[22] Later, CI and Xα-SW[13,14] calculations showed the inadequacy of this approximation. The latest theoretical study[14] by Decleva et al. predicts the following order of valence orbitals: $8a_1$, 8e, 7e, 6e, $1a_2$, 5e, 4e, $7a_1$, $6a_1$, 3e, starting with the lowest ionization potential. The order of the first two orbitals is obscured by the fact that these peaks are not resolved in the PES.

However, no photoelectron spectrum of the phosphine derivatives of $Co(CO)_3NO$ has been published. Still, the approximate adiabatic ionization energy of some of the complexes has been known from the EI mass spectrometry studies of Distefano et al.[15]

In the present work, we report the He-I and He-II photoelectron spectra of $Co(CO)_3NO$ as well as EOMIP-CCSD calculations for the parent compound. Because of its high computational cost, EOMIP-CCSD studies of large organometallic complexes are few and far between.[16] It nevertheless proved to be useful and sometimes the only feasible way to get an appropriate assignment of the photoelectron bands.

We changed the R group in a systematic manner and took He-I photoelectron spectra of $Co(CO)_2NOPR_3$ (R = Me, Et, Pr, Bu, Cy, Ph and OMe). In some cases, He-II spectra were also recorded to study the orbital compositions. The obtained photoelectron spectra were compared to each other to see the effect of the change in the alkyl or aryl group in the phosphine ligand.

Experimental Approach

Preparation of the Samples. The synthesis of $Co(CO)_2NOPR_3$ (R = Me, Et, Pr, Bu, Cy, Ph, and OMe) has been previously described by others.[17] The following method was used to synthesize all the samples. At room temperature, 5.0 mmol of the appropriate phosphine was dissolved in 50 mL of tetrahydrofuran (THF), and 5.0 mmol (0.865 g) of $Co(CO)_3NO$ was added to it under an atmosphere of nitrogen. The reaction mixture was stirred for 2−6 h, and then the solvent and the excess of the reactants were removed at reduced pressure. $Co(CO)_2NOPR_3$ (R = Me, Et, Pr, Bu, and OMe) were isolated as dark-red liquids. For R = Cy and Ph, the products were obtained in the form of dark-red solids. The yield was 80% or above in all cases, and the samples were stored under an inert atmosphere at −25 °C. $Co(CO)_3NO$ (Strem Chemicals) and the phosphines (Sigma-Aldrich) were used without further purification.

Ultraviolet Photoelectron Spectra. He-I and He-II photoelectron spectra were recorded on a custom-built ATOMKI ESA-32 instrument, which has been described in an earlier paper.[18]

Some of the samples ($Co(CO)_3NO$, R = Me, Et, and OMe), of which the vapor pressure was high enough, were evaporated into the ionization chamber at room temperature, whereas the others with lower vapor pressure (R = Et, Pr, Bu, Ph, and Cy) were introduced into the chamber at elevated temperatures (60−120 °C) using a direct-sample inlet system.

During the measurements, the energy resolution was better than 30 meV. Argon was used as an internal standard and the spectra were calibrated against the Ar $^2P_{3/2}$ peak (IE = 15.759 eV), and the $^2\Sigma^+$ peak of CO could also be used for $Co(CO)_2NOPPh_3$ because the complex suffered partial decomposition at the measurement temperature. The He-II spectra of $Co(CO)_3NO$, $Co(CO)_2NOPMe_3$, and $Co(CO)_2NOP(OMe)_3$ were also recorded. The obtained experimental vertical ionization potentials are collected in Table 1.

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TABLE 1: Experimental Vertical Ionization Potentials of $Co(CO)_2NOL$ (eV)

	L							
band[a]	CO	PMe_3	PEt_3	PPr_3	PBu_3	PCy_3	PPh_3	$P(OMe)_3$
A	8.75−9.11 9.82	7.85−8.30 9.08−9.40	7.69−8.13 9.05	7.47 8.71	7.49−7.82 8.60	7.71 8.87−9.83	7.58 8.86−9.37	8.15−8.56 9.47
B		10.82−11.27	10.33	10.33	10.55	10.57	10.49	10.90
C		11.90−12.90	11.13−11.66	10.83	10.95		11.16−12.27 12.81	11.70−12.34
D	14.14−15.20	13.67−15.08	12.38−13.77	11.56−11.91 13.01−14.19	11.25		13.42 13.81	13.00 13.89

[a] As indicated in Figure 1.

Quantum Chemical Calculations

To help the interpretation of the photoelectron spectra, we carried out quantum chemical calculations to compute the ionization energies of both the parent compound, $Co(CO)_3NO$, and the phosphine substituted complexes at the Hartree−Fock, DFT (B3LYP functional),[19] and EOMIP-CCSD [20] levels of theory. For the HF and B3LYP calculations, the 6-311G** and 6-31++G** basis sets, respectively, were used as implemented in the Gaussian 03[29] program system. At the EOMIP-CCSD level, the pvdz, pvtz (as published by Ahlrichs and co-workers[21]), and 6-311G** basis sets were used for the parent compound only.

To obtain equilibrium geometries, we performed full geometry optimizations at the respective levels of theory, with the exception of the EOMIP-CCSD calculations, where the less-expensive B3LYP/6-31++G** geometries were used.

At the Hartree−Fock level, the ionization potentials are estimated to be the negative of the molecular orbital energies according to Koopmans' theorem.[22] At the DFT level, however, the connection is not straightforward. Although it is known that the highest occupied Kohn−Sham orbital energy corresponds to the first ionization energy if an exact DFT potential is used,[23] the practical use of this theorem and the physical meaning of Kohn−Sham orbitals and orbital energies have been widely debated.[24] However, Baerends and co-workers recently established a connection between the Dyson and the Kohn−Sham orbitals and found that with a near-exact DFT potential the Kohn−Sham orbital energies are indeed good estimates of the ionization energies.[25,26] They have also found that in the case of common approximate hybrid functionals, the highest occupied Kohn−Sham orbital energy does not provide a better estimate of the corresponding ionization energy than the other orbital energies. However, unlike Hartree−Fock orbital energies, which often err in an unsystematic way, Kohn−Sham orbital energies obtained by the broadly used hybrid functionals, for example, B3LYP, tend to underestimate the ionization potentials in a consistent manner for most of the studied molecules.[27] The small standard deviation of the errors in the ionization potentials in a molecule allows for shifting the Kohn−Sham orbital energies so that the HOMO will correspond to the lowest experimental IE, thereby obtaining reliable estimates for the other ionization energies. Thus, we were able to predict the ionization potentials to confirm the assignment of the photoelectron spectra.

We also used the infinite-order EOMIP-CCSD method to calculate the ionization energies for the parent molecule. This method has been proven useful before, but in the case of large molecules, the high computational cost often prevents the use of large enough basis sets.

The calculations were carried out using the ACESII [28] and the Gaussian 03[29] quantum-chemical program codes.

Results and Discussion

The He-I and He-II spectra of $Co(CO)_3NO$ and the calculated ionization potentials are shown in Figure 1. The first two bands in the photoelectron spectrum are expected to be due to ionization from molecular orbitals with a strong d character. The calculated contribution of the d atomic orbitals of the metal center is indeed quite substantial in the three uppermost molecular orbitals, and this contribution is decreased in the next two orbitals, in line with the intensity changes between the He-I and He-II photoelectron spectra, that is, the higher the relative intensity of the He-II peak compared to that of the He-I peak, the higher the d contribution. These molecular orbitals can be regarded as π-type bonds formed by the metallic d orbitals and the π^* orbitals of the ligands. Replacing one carbonyl with a strong electron-donor phosphine or phosphite causes the destabilization of these molecular orbitals and a decrease in the ionization potentials. This effect will be discussed later.

A wide Franck−Condon gap separates the first two peaks from a wide band that starts at approximately 13.5 eV. This band consists of several overlapping peaks and is due to ionization from orbitals described as Co−CO, Co−NO bonds, and orbitals localized on the CO and NO ligands.

As mentioned above, HF/6-311G**, B3LYP/6-31++G**, and EOMIP-CCSD calculations were performed for the $Co(CO)_3NO$ molecule in this study. The ionization energies obtained from Hartree−Fock calculations with Koopmans' theorem differ significantly from the experimental ionization energies, as is usually the case with organometallic complexes. Although the DFT orbital energies are lower than the experimental ionization energies by more than 1 eV, the differences between the calculated and the experimental ionization potentials are roughly the same for all of the valence orbitals; therefore, it describes the experimental spectrum more accurately, provided that the orbital energies are shifted by 1.44 eV so that the HOMO orbital energy matches the experimental IE.

The rather expensive EOMIP-CCSD method was found to be the most accurate. For the parent complex, three different basis sets were used: pvdz, pvtz, and 6-311G**. The average difference between the experimental and the calculated IEs that was obtained with the smallest pvdz basis set is about 0.5 eV, whereas the valence triple-ζ 6-311G** basis gives only slightly better results. Calculations with the pvtz basis set of Ahlrichs and co-workers were the most accurate. (Table 3).

The He-I and He-II spectra of $Co(CO)_2NOPMe_3$ and $Co(CO)_2NOP(OMe)_3$ are also shown in Figure 1. Two new peaks can be discerned in the PES of $Co(CO)_2NOPMe_3$ when compared to that of $Co(CO)_3NO$. Calculations and qualitative considerations suggest that these bands are due to removing an electron from the cobalt−phosphorus, and because the phosphorus−methyl bonds are not present in $Co(CO)_3NO$, a wide Franck−

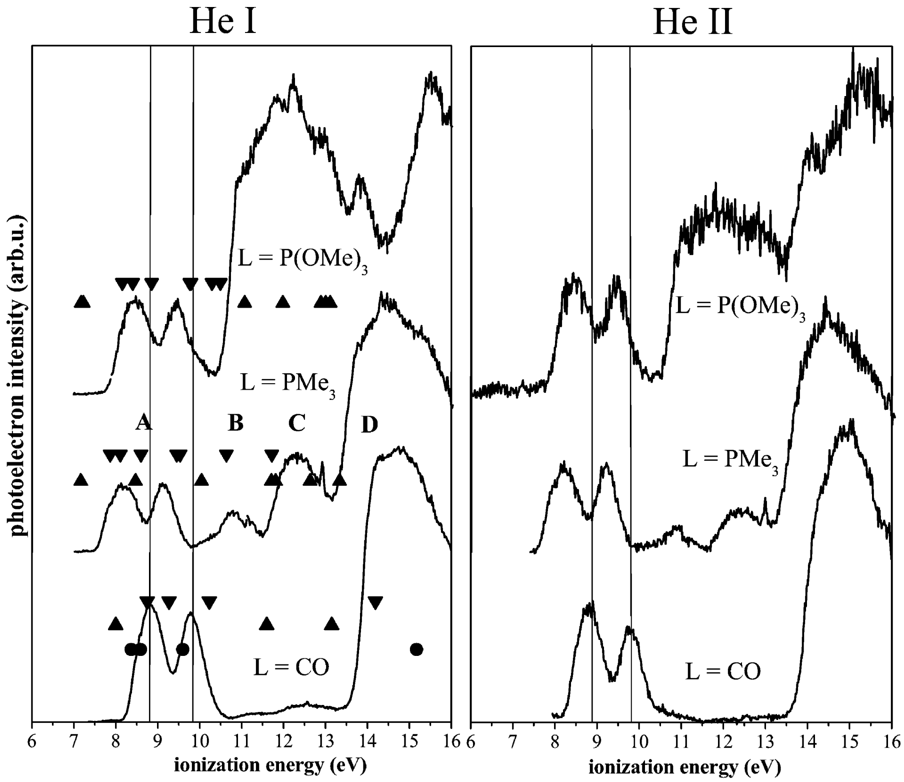

Figure 1. He-I and He-II photoelectron spectra of $Co(CO)_3NO$, $Co(CO)_2NOPMe_3$, and $Co(CO)_2NOP(OMe)_3$. The calculated ionization energies are compared to the obtained spectra. See details in text. (● = ionization energies obtained from EOMIP-CCSD/pvtz calculations, ▲ = ionization energies obtained from HF/6-311G** calculations, and ▼ = ionization energies obtained from DFT studies, shifted so that $-\epsilon$ (HOMO) matches the lowest experimental IE.)

TABLE 2: Stabilization of P_{lp} in the $Co(CO)_2NOL$ Complexes

	L	free ligand	complex[h]
IE(P_{lp}) (eV)	PMe_3	8.60[a]	10.81
	PEt_3	8.31[b]	10.33
	PPr_3	8.16[c]	10.33
	PBu_3	8.00[d]	10.55
	$P(OMe)_3$	9.40[e]	10.90
	PPh_3	7.85[f]	10.49
	PCy_3	7.75[g]	10.57

[a] Ikuta, S.; Kebarle, P.; Bancroft, G. M.; Chan, T.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1982**, *104*, 5899. [b] Weiner, M. A.; Lattman, M. *Inorg. Chem.* **1978**, *17*, 1084. [c] Schmidt, H.; Schweig, A.; Mathey, F.; Müller, G. *Tetrahedron* **1975**, *31*, 1287. [d] Schmidt, H.; Schweig, A.; Mathey, F.; Müller, G. *Tetrahedron* **1975**, *31*, 1287. [e] Cowley, A. H.; Goodman, D. W.; Kuebler, N. A.; Sanchez, M.; Verkade, J. G. *Inorg. Chem.* **1977**, *16*, 854. [f] Distefano, G.; Pignataro, S.; Szepes, L.; Borossay, J. *J. Organomet. Chem.* **1975**, *102*, 313. [g] Daamen, H.; Oskam, A.; Stufkens, D. J.*Inorg. Chim. Acta* **1980**, *38*, 71. [h] Present work.

Condon gap can be found in this region in the spectrum of $Co(CO)_3NO$.

The quantum-chemical calculations indicate a strong d character of the five highest molecular orbitals, whereas the d character of the lower-lying orbitals is less pronounced. This difference in the d contributions, once again, can be compared to the intensity changes between the He-I and He-II spectra of $Co(CO)_2NOPMe_3$. Going from He-I to He-II, photon energy causes an increased intensity of the first two bands compared to those in the 10−13 eV range. The small sharp peak at 12.90 eV is believed to be due to an impurity in the sample.

Hartree−Fock and DFT calculations were performed on this molecule. As usual, Hartree−Fock (Koopmans') calculations do not reproduce the experimental IEs very well. The DFT orbital energies are indeed very low compared to the experimental values, but with a 1.75-eV shift, the overall structure of the photoelectron spectrum is much better reproduced than by using Koopmans' theorem with Hartree−Fock orbital energies.

The He-I and He-II photoelectron spectra of $Co(CO)_2NOP(OMe)_3$ were also recorded. From the comparison of the He-I and He-II spectra, the strong d character of the highest-lying molecular orbitals is again quite clear, and it is in line with the DFT calculations. However, Mulliken population analysis[30] indicates that unlike in the other complexes the contribution of Co(p) atomic orbital is significant in the HOMO and that there is a π-type bond formed between the Co(p), P(p), and O(p) atomic orbitals. The broad band between 10.4 and 13.5 eV consists of several overlapping peaks and could not be sufficiently resolved experimentally. The calculations suggest that the ionization of the oxygen lone pair in the phosphite ligand and the ionization of the Co−P bond are also in this range.

The He-I spectra of $Co(CO)_2NOPR_3$ (R = Me, Et, Pr, and Bu) are compared in Figure 2, and the spectra of R = Cy and Ph are shown in Figure 3.

For the assignment of the He-I spectra of $Co(CO)_2NOPR_3$ (R = Et, Pr, and Bu), analogies to the above-discussed spectra were used. By comparing the photoelectron spectra of $Co(CO)_3NO$ and $Co(CO)_2NOPR_3$ (R = Me, Et, Pr, and Bu) (Figure 2), one can see that the longer the alkyl chain in the phosphine ligand the lower the ionization energy of the first two bands. This indicates a destabilization of the molecular orbitals attributed to back donations from the metal center toward the CO and NO ligands. The bands due to ionizations from the cobalt−phosphorus and phosphorus−alkyl bonds also shift to lower energies. The lone pair of the phosphorus atom is stabilized by 2.0−2.5 eV with respect to the free phosphines, as summarized in Table 2.

TABLE 3: Experimental and Calculated Ionization Potentials of Co(CO)$_2$NOL Complexes (L = CO, PMe$_3$, P(OMe)$_3$)

L = CO

expt	HF 6-311G**	B3LYP 6-31++G**[a]	EOMIP-CCSD pvdz	EOMIP-CCSD 6-311G**	EOMIP-CCSD pvtz	MO character
8.75	8.00	8.75	8.20	8.22	8.37	Co(d)−CO(π)
9.11	11.60	9.27	8.41	8.46	8.59	Co(d)−[CO(π), NO(π)]
9.82	13.15	10.23	9.44	9.55	9.60	Co(d)−[CO(π), NO(π)]
14.14	17.05	14.19	14.96	15.11	15.17	Co(d)−CO(σ)

L = PMe$_3$

expt	HF 6-311G**	B3LYP 6-31++G**[a]	MO character
7.85	7.15	7.85	Co(d)−[CO(π), NO(π), P(p)]
8.07	8.45	8.09	Co(d)−[CO(π), NO(π), P(p)]
8.30	10.02	8.58	Co(d)−[NO(π), P(p)]
9.07	11.68	9.43	Co(d)−[NO(π), P(p)]
9.40	11.78	9.51	Co(d)-CO(π)
10.81	12.60	10.61	Co(d)−[CO(π), NO(π), P(lp)]
11.27	13.30	11.69	P−C bonds

L = P(OMe)$_3$

expt	HF 6-311G**	B3LYP 6-31++G**[a]	MO character
8.15	7.17	8.15	Co(p,d)−[NO(π), CO(π), P(p)−O(p)]
	7.22	8.40	Co(p,d)−[CO(π), NO(π)]
8.56	11.07	8.85	Co(d)−[CO(π), NO(π)]
9.47	11.98	9.76	Co(d)−[CO(π), NO(π)]
	12.89	9.79	Co(d)−[CO(π), NO(π)]
10.94	13.00	10.29	P−O, O−C bonds
	13.11	10.49	Co(p,d)−P(p,s)-O(p)

[a] Shifted so that $-\epsilon$ (HOMO) matches the lowest experimental IE.

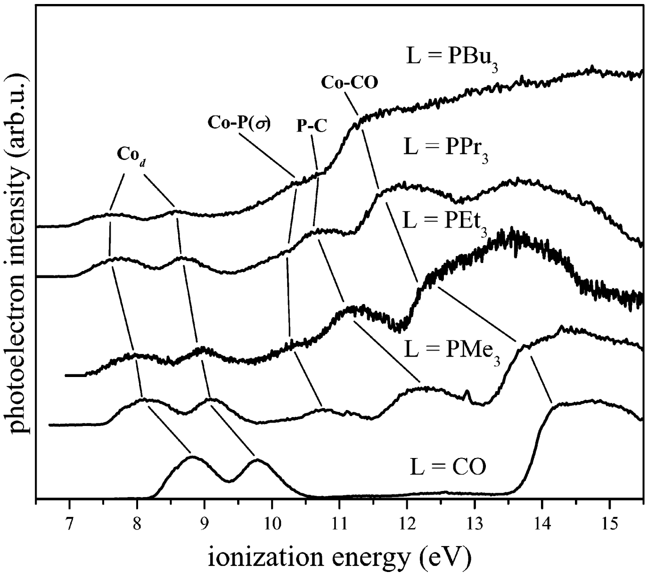

Figure 2. He-I photoelectron spectra of Co(CO)$_3$NO and Co(CO)$_2$NOPR$_3$ (R = Me, Et, Pr, and Bu). Note that the first ionization energies decrease as alkyl chain gets longer.

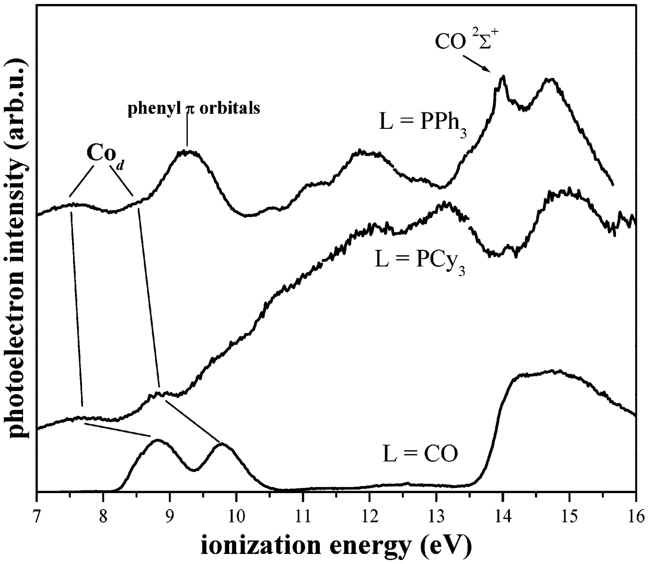

Figure 3. He-I photoelectron spectra of Co(CO)$_3$NO, Co(CO)$_2$NOPPh$_3$, and Co(CO)$_2$NOPCy$_3$. The aromatic PPh$_3$ ligand is a better electron donor than the saturated PCy$_3$ ligand.

In Figure 3, the spectra of Co(CO)$_2$NOPCy$_3$ and Co(CO)$_2$NOPPh$_3$ are compared to that of Co(CO)$_3$NO. From the destabilization of the highest molecular orbitals, one can deduce that the aromatic PPh$_3$ is a better electron donor toward the cobalt center than the saturated PCy$_3$. In the spectrum of Co(CO)$_2$NOPPh$_3$, the band between 9.0 and 10.0 eV can be attributed to the removal of an electron from the π orbitals of the aromatic phenyl groups. This band appears at 9.37 eV, showing a stabilization of approximately 0.2 eV compared to the free triphenylphosphine ligand (IEs of the π orbitals in the free ligand are 9.02 and 9.18 eV).[31] This means that the π orbitals in the aromatic ring are strongly affected by the coordination, and thus, the PPh$_3$ appears to be a better electron donor than the PCy$_3$ ligand with no π orbitals.

The electron-donor capability and the changes in the electron density around the metal center have been investigated by calculating Mulliken net charges on the metal center and the atoms directly connected to it. The calculated charges are shown in Table 4. The results show that the electron density does not increase on the cobalt atom, whereas it does increase on the ligands connected to the metal center instead. The phosphorus atom bears a large negative charge in the phosphine complexes

TABLE 4: Net Charge on the Metal Center and the Ligands (B3LYP/6-31++G)**

complex	Co	P	N	C (in CO)
$Co(CO)_3NO$	−0.322		−0.098	+0.460
$Co(CO)_2NOPMe_3$	−0.157	−0.316	−0.205	+0.367
$Co(CO)_2NOPEt_3$	−0.166	−0.701	−0.223	+0.293
$Co(CO)_2NOPPr_3$	−0.046	−0.747	−0.213	+0.225
$Co(CO)_2NOPBu_3$	+0.074	−0.799	−0.223	+0.168
$Co(CO)_2NOP(OMe)_3$	−0.692	1.525	−0.180	+0.427

because of the strong electron donation of the alkyl chains. This inductive effect results in an increased electron density on the carbonyl and nitrosyl ligands. Because the highest-energy molecular orbitals in the complex are mainly cobalt d orbitals that interact (back donation) with the antibonding orbitals of the NO and CO ligands, the higher negative charge on these ligands results in the destabilization of these orbitals. However, in the phosphite ligand of the $Co(CO)_2NOP(OMe)_3$ molecule, the phosphorus atom bears a large positive charge because oxygen is a good electron acceptor. The positive charge makes the cobalt atom withdraw electrons from the CO and NO ligands.

Conclusions

The electronic structure of $Co(CO)_3NO$ and a series of its phosphine derivatives has been investigated with ultraviolet photoelectron spectroscopy. The assignment of the spectra was based on qualitative trends in the series of compounds, a set of quantum-chemical calculations, and variable-energy (He-I vs He-II) photoionization. It has been shown that the Hartree−Fock method is inefficient not only for the parent complex but also for its phosphine derivatives. However, the EOMIP-CCSD calculations were more reliable for the parent molecule. Although the ionization potentials are significantly and systematically underestimated by DFT (as was expected because of the DFT local electron correlation treatment), the errors are consistent and a shift in the orbital energies to match the experimental first IE to the HOMO orbital energy results in well-reproduced photoelectron spectra.

The calculations, in agreement with the He-II spectra, showed that the highest-lying orbitals have a strong d character, and they serve the back donation from the metal center toward the CO and NO ligands. These orbitals can be destabilized by increasing the electron-donor capability of the phosphine ligand. By calculating the Mulliken net charges on the cobalt atom and on the atoms directly connected to it, we found that a phosphine ligand with increased electron-donor capability does not entail a more negative cobalt atom but rather more electron-dense nitrosyl and carbonyl ligands. The high negative charge on these ligands destabilizes the high-energy molecular orbitals regarded to be mainly Co d orbitals that interact with the antibonding π^* orbitals of the CO and NO ligands. However, the $P(OMe)_3$ ligand, because of the electronegative oxygen atom, has a much weaker electron-donor ability and can only destabilize these orbitals in a moderate way.

By comparing the ionization energies of $Co(CO)_2NOPPh_3$ and $Co(CO)_2NOPCy_3$, it was established that the triphenylphosphine group is a better electron donor than the saturated tricyclohexylphosphine ligand. This is probably because the aromatic phenyl ring is also affected by the coordination, highlighted by the 0.2 eV stabilization of the phenyl π orbitals in the complex. The saturated PCy_3 ligand has, of course, no occupied π orbitals to help form the Co−P bond.

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