

Ph.D. Dissertation

PONGOR CSABA ISTVÁN

Photoelectron spectroscopy and photoionization mass spectrometry of organometallic compounds



Laboratory of Physical Organometallic Chemistry
Eötvös Loránd University
Budapest

Advisor:
Bálint Sztáray, Ph.D.

Consultant:
László Szepes, D.Sc.

Eötvös Loránd University, Budapest
Doctoral School of Chemistry
Head of School: György Inzelt, D.Sc.

Theoretical and Physical Chemistry, Structural Chemistry program
Head of Program: Péter Surján, D.Sc.

— 2011 —

I. Introduction

Organometallic compounds are used as catalysts and reactants in numerous reactions of industrial and biological importance with applications ranging from synthetic chemistry to nanosciences. Therefore it is crucial to understand the electron structure, reaction mechanisms and thermochemistry of these compounds to find new directions in the development of catalysts and precursors. UV photoelectron spectroscopy (UPS)^{1,2,3} and photoelectron photoion coincidence spectroscopy (PEPICO)^{4,5,6,7,8} are useful methods to investigate the electron structure and gas phase ion chemistry of organometallic compounds and complement each other well. Photoelectron spectroscopy gives the opportunity to study the electron structure of compounds. Photoelectron photoion coincidence spectroscopy on the other hand allows the study of mechanisms and energetics of gas phase dissociation reactions. Our task is to better understand how the variation of both ligands and metals affect electron structure, reaction mechanisms and reaction energetics. Conclusions deduced from the electron structure of compounds can be used to predict trends in reaction kinetics, dynamics and thermochemistry. In some cases exactly the opposite is possible, changes in bond dissociation energies within a family of compounds can suggest differences in bonding properties of ligands.

In order to maximize the amount of relevant information a good set of model compounds has to be selected with care. The investigation of families of compounds where ligands and metallic elements are systematically varied is a viable approach to narrow down the infinite number of possibilities. It is of special advantage that the approach especially advantageous as it matches the strategies chemists use when fine tuning catalysts and precursors. Results from these studies can shorten their struggles and perhaps also point to the application of new ligands and molecules. Bond dissociation energies (BDE) and heats of formation are also important as they are readily calculated and used to explain substituent effects. However, measured dissociation energies are rarely available to test the validity of these results, making quantitative results important to theoreticians as well.

Our group has been playing an active role in using UPS and PEPICO techniques to study organometallics. The fundamental goal of this thesis is to show that photoionization techniques are useful tools to study organometallic compounds and that results deduced from the analysis of experimental data can be of interest to theoretical

and applied chemists alike. The objects of our interests were families of compounds that can be conceptually derived from each other by interchanging a heteroatom with a different atom in the same group of the periodic table. It will be shown that this strategy can lead to interesting changes in the physical and chemical properties of these compounds. Three groups of compounds have been investigated: transition metal complexes containing chalcocarbonyl ligands (CO, CS and CSe), transition metal compounds containing phosphine and heavier analogue ligands (PMe₃, PEt₃, AsMe₃, SbMe₃) and trimethyl derivatives of the N group (AsMe₃, SbMe₃ and BiMe₃).

II. Results and discussion

II.1. Donor-acceptor properties of CX (X = O, S, Se) ligands in cyclopentadienyl manganese carbonyl complexes.

The donor-acceptor properties of the chalcocarbonyl (CO, CS, CSe) ligands were studied using photoelectron spectroscopy. HeI and HeII photoelectron spectra of CpMn(CO)₃, CpMn(CO)₂CS and CpMn(CO)₂CSe were recorded. The assignment of the spectra was based on experimental considerations and quantum chemical calculations. Besides *Koopmans'* theorem (at HF/6-311G** level), *Kohn-Sham* orbital energies, at the level of B3LYP/6-311G**, were also used. The analysis of the HeI and HeII spectra of the thio- and selenocarbonyl complex revealed significant differences in both donor and acceptor properties of the CO and CX (X = S, Se) ligands. The photoelectron spectrum and visualization of some relevant *Kohn-Sham* orbitals of CpMn(CO)₂CS can be seen on Figure 1.

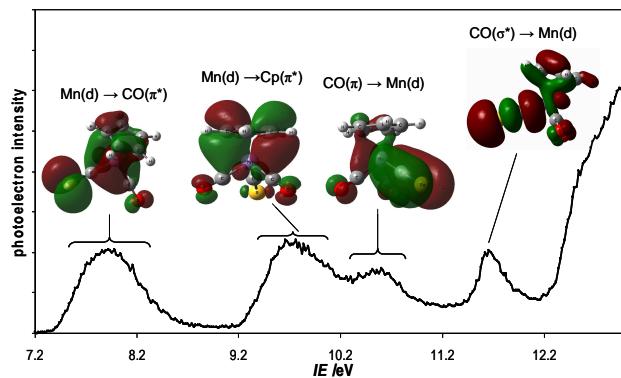


Figure 1. GaussView plots of typical *Kohn-Sham* molecular orbitals assigned to the bands in the HeI photoelectron spectrum of CpMn(CO)₂CS.

Destabilization of the first ionization energy in the chalcocarbonyl complex of about 0.1 eV showed that these ligands are stronger overall electron donors. σ -donor strength was

assessed using the stabilization of the σ^* -donor orbitals in the complexes compared to the free molecules which was 0.51 eV for CS and 0.64 eV for CSe. The trend shows that there is an increasing strength from CO to CSe. The π -donor/acceptor ability of ligands can be ranked using the ΔE_s parameter of Lichtenberger⁹ that is derived from the splitting of the first three ionization energies in half sandwich compounds. ΔE_s for CpM(CO)₂L (where M is a transition metals) complexes are -0.375 where L=CO, -0.3 where L=CS and -0.35 where L=CSe. These results show that the calcocarbonyls are better π -donors as there is firm consensus in the literature that their π -acceptor strength is higher¹⁰. The higher negative ΔE_s value for CSe and the fact that the overall donor strength is almost as large as for CS showed that the CSe is a much stronger π -acceptor than π -donor.

II.2. Photoionization studies of complexes containing phosphine and phosphine analogue ligands

Five new transition metal complexes with phosphine, arsine, and stibine ligands were synthesized. The electronic structure of Co(CO)₂NOL and CpMn(CO)₂L (L=PMe₃, AsMe₃, SbMe₃) complexes were studied with ultraviolet photoelectron spectroscopy and DFT calculations. The assignment of the photoelectron bands was based on the trends in spectral features, on the energy dependence of photoionization cross sections (differences between HeI and HeII spectra, and on DFT calculations of the orbital energies. As an example the photoelectron spectrum and visualization of some relevant Kohn-Sham orbitals of CpMn(CO)₂(PMe₃) can be seen on Figure 2.

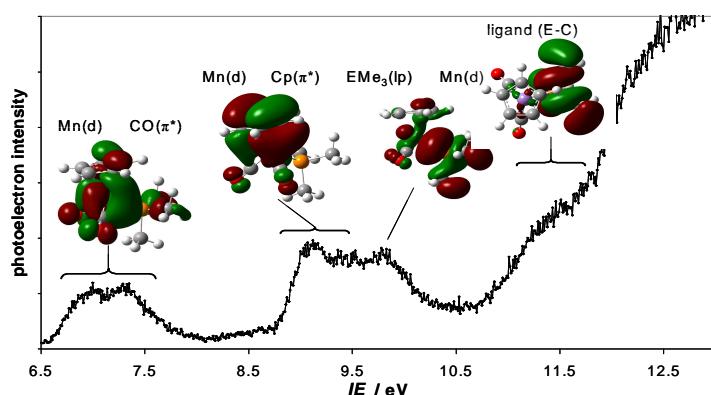


Figure 2. GaussView plots of typical Kohn-Sham molecular orbitals assigned to the bands in the HeI photoelectron spectrum of CpMn(CO)₂(PMe₃).

Both the experiments and the calculations show a high *d*-character in the orbitals associated with the lowest-energy bands; these were assigned to metal d-orbitals in back-

bonding type interactions with the π -acceptor ligand (CO, NO) orbitals. In the case of the $\text{CpMn}(\text{CO})_2(\text{EMe}_3)$ complexes (where E=P, As, Sb), the next band is due to the combination on π type orbitals of the cyclopentadienyl ring and d-orbitals of manganese. The subsequent bands were assigned to the ionization of the $\text{E}(\text{lp}) \rightarrow \text{M}(d)$ bond and to the orbitals localized on the EMe_3 ligands. From the photoelectron spectra one might conclude that the overall metal electron density hardly changes from P to Sb. The ionization energy of the $\text{E}(\text{lp}) \rightarrow \text{M}(d)$ bonds shows a decreasing stabilization of the $\text{E}(\text{lp})$ lone pair from P to Sb. This was explained by the increasing s character of the lone pair in the free ligands thus decreasing overlap with the d atomic orbitals (due to steric and electronic reasons).

To further study the impact of substitution on the electronic structure of the parent compounds, *Hirschfeld*^{11,12} and *Voronoi*¹³ charge density analyses were carried out. It revealed that the destabilization of the $\text{M}(d) \rightarrow \text{L}(\pi)$ orbitals is mainly caused by the redistribution of the electron density in the $\text{CpMn}(\text{CO})_2$ and $\text{Co}(\text{CO})_2\text{NO}$ moieties, but the EMe_3 ligands do not donate significant electron density to the metal center. This is especially true for the manganese compounds. Only 10–30% of the increment of the net partial charge on the $\text{CpMn}(\text{CO})_2$ moiety is provided by the EMe_3 ligand, while it is approximately 50% in the cobalt complexes. This in agreement with the higher stabilization of the $\text{E}(\text{lp})$ lone pair in the cobalt complexes derived from the photoelectron spectra. Due to spatial and electronic effects, the Cp ring seems to be an obstacle to the coordination of the EMe_3 ligands to the metal center in the investigated manganese complexes.

Although the stabilization of the lone pair – i.e. the σ donation – decreases from P to Sb, the ionization energies of the metal d orbitals along with the net charge flow from the EMe_3 ligands remain nearly constant. The assumption that this is due to the π acidity of the EMe_3 ligands from P to Sb was probed by determining ΔE_s values as suggested by *Lichtenberger*⁹ and by charge distribution calculations on $d^{10} \text{NiL}_4$ ($\text{L} = \text{CO}$, EMe_3) model complexes. It was found that the back donation from the filled $\text{Ni}(d)$ orbitals to the empty P–C antibonding orbitals is not negligible and it decreases in the following order: $\text{CO} > \text{PMe}_3 > \text{AsMe}_3 > \text{SbMe}_3$.

To investigate the effects of phosphine and phosphine analogue ligands on carbonyl binding the photodegradation mechanism of $\text{LCo}(\text{CO})_2\text{NO}$ ($\text{L}=\text{PMe}_3$, PEt_3 , AsMe_3 , SbMe_3) complexes was also studied using the PEPICO technique. The complicated nature of the ion chemistry of these compounds allowed the modeling of

only the first two carbonyl loss channels. Quantumchemical calculations using the B3LYP functional and several basis sets was used to get a good estimate for the difference of the vertical and adiabatic ionization energy (ΔIE). This was used to determine the adiabatic ionization energies used in the modeling process. Modeling experimental TOF distributions and breakdown diagrams by the *Rice–Ramsperger–Kassel–Marcus* (RRKM) theory¹⁴ yielded bond dissociation energies for the first two carbonyl loss channels (results are summarized in Table 1 and Figure 2).

Table 1. Experimental cobalt–carbonyl bond dissociation energies in complex ions with the following general formula: $\text{LCo}(\text{CO})_3\text{NO}$

Reaction	$\text{L}=\text{PEt}_3$	$\text{L}=\text{PMe}_3$	$\text{L}=\text{AsMe}_3$	$\text{L}=\text{SbMe}_3$
kJ/mol				
First carbonyl loss	89±9	97±12	121±9	123±9
Second carbonyl loss	88±11	85±11	98±9	98 ±8
eV				
First carbonyl loss	0.92±0.09	1.01±0.12	1.25±0.09	1.27±0.09
Second carbonyl loss	0.91±0.11	0.88±0.11	1.02±0.09	1.02±0.08

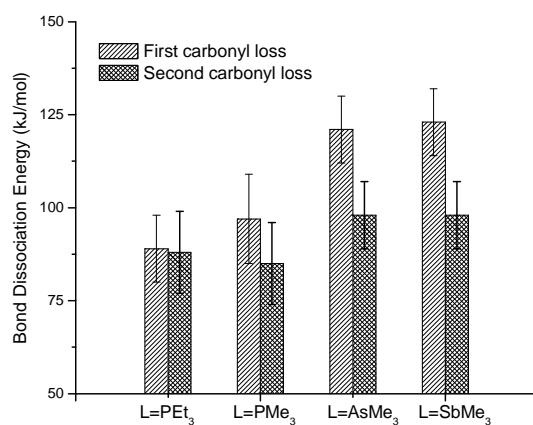


Figure 3. First and second bond dissociation energies of carbonyl loss channels in kJ mol^{-1}

It has been found that the ligands have a strong effect on the metal–carbonyl bond strength. In the complexes containing the arsine and stibine ligand, carbonyl bonding significantly increases compared to the phosphine ligand. Results from the UPS study of these compounds has been used to explain trends in the bond energies of CO in $\text{Co}(\text{CO})_2\text{NOL}$ $\text{L}=\text{PMe}_3$, PEt_3 , As Me_3 , Sb Me_3 complexes. π -acidity of the ligand plays an important role in these trends. The more π -electrons are withdrawn from the cobalt, the

weaker the π back-bonding from the cobalt to the carbonyls, so overall a weaker Co–CO BDE should be observed. Indeed, both the arsine and stibine complexes show markedly stronger Co–CO bonds than the phosphine complex.

II.3. Dissociative photoionization of trimethyl derivatives of As, Sb and Bi

The photoionization/photodissociation mechanism of the trimethylamine to trimethylbismane series was studied by threshold photoelectron photoion spectroscopy (TPEPICO). The slow methyl loss dissociations were modeled with RRKM theory¹⁴ in order to extract the dissociation onsets. The resulting methyl loss onset energies for $\text{As}(\text{CH}_3)_3$, $\text{Sb}(\text{CH}_3)_3$ and $\text{Bi}(\text{CH}_3)_3$ are 10.620 ± 0.041 , 10.068 ± 0.074 and 9.445 ± 0.064 eV, respectively, and the corresponding ionic C–E (E=As, Sb, Bi) bond energies are found to monotonically decrease with the period number of the central atom. The dissociation energetics and dynamics of the three molecules presented here have been compared with previously investigated $\text{N}(\text{CH}_3)_3$ ¹⁵ and $\text{P}(\text{CH}_3)_3$ ¹⁶, thus completing the series from nitrogen to bismuth. *Ab initio* energetics of the reactions have been calculated using composite methods. These calculations strongly suggest that the methyl loss channel in the three higher homologues proceeds via simple homolytic E–CH₃ bond cleavage.

Table 2. Experimental bond dissociation energies for the mety loss channel of
 AsMe_3 , SbMe_3 , BiMe_3 ,

Reaction	AsMe_3	SbMe_3	BiMe_3
kJ/mol			
Methyl loss	224 ± 11	198 ± 9	132 ± 8
eV			
Methyl loss	2.322 ± 0.12	2.048 ± 0.09	1.365 ± 0.08

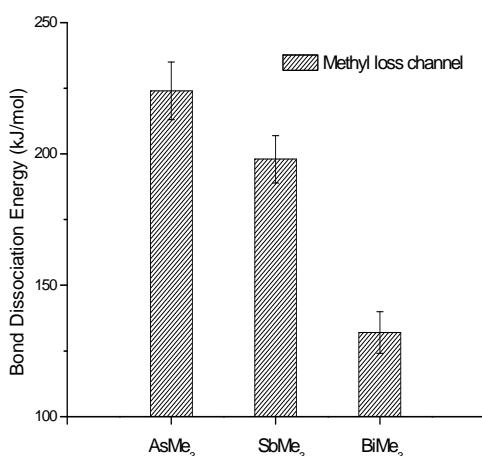


Figure 4. Bond dissociation energies for the methyl

Density functional theory using the B3LYP functional and 6-311++G(d,p) has been also used to calculate bond energies which show that C=E bonds weaken significantly more than C–E single bonds in the N → P → As direction, thus leading to a relative destabilization of the daughter ions. Qualitatively trends can be explained using hybridization of the parent and daughter ions. Products resulting from an H loss in the parent ion are in an σp^2 hybrid state which is energetically more and more disfavored from N to Bi.

III. Conclusions

III.1. Donor-acceptor properties of CX (X = O, S, Se) ligands in cyclopentadienyl manganese carbonyl complexes.

- The net donor character of the thio and selenocarbonyl ligand is stronger than for CO and follow the following trend as shown: CO<CS<CSe.
- The thio and selenocarbonyl ligands proved to be good σ -donors compared to the carbonyl ligand and show the following trend: CO<<CS<CSe.
- All three ligands are strong π -acceptors and this property becomes more evident from oxygen to selenium: CO<CS<CSe

III.2. Photoionization studies of complexes containing phosphine and phosphine analogue ligands

- The σ -donor strength of these ligands changes as follows: PMe₃> As Me₃> SbMe₃.
- The phosphine and phosphine analogue ligands are π -acceptors. The following trends could be determined: CO>>PMe₃ >AsMe₃>SbMe₃.
- Carbonyl binding energies in the gas phase cations have been determined for the first two carbonyl loss channels.

- BDE values in the arsine and stibine complexes increased by more than 0.2 eV giving further proof that these ligands are weaker π -acceptors when compared to phosphines.

III.3. Dissociative photoionization of trimethyl derivatives of As, Sb and Bi

- Adiabatic ionization energies of 8.02 ± 0.05 eV and 8.08 ± 0.05 eV have been determined from the onset of the photoelectron spectrum of AsMe_3 and SbMe_3 respectively.
- Bond dissociation energies of methyl loss channels have been determined using the TPEPICO and show a decreasing trend from As to Bi.
- Taking into account previous studies on NMe_3 and PMe_3 trends in the bond dissociation energies have been explained by using quantumchemical methods. The change in the *s*-character of the lone pairs within the group - besides inducing structural changes- also causes the shift in the stability of possible products ultimately leading to the simplification of the reaction scheme.

IV. List of publications

1. **Csaba I. Pongor**, Zsolt Gengeliczki, László Szepes, Frank Axe and Bálint Sztáray, Photoelectron spectra of phosphine analogue complexes of $\text{Co}(\text{CO})_3\text{NO}$ and $\text{CpMn}(\text{CO})_3$, *Organometallics*, 29 (4), 2010, 724–731.
2. Balázs Hornung, Andras Bodi, **Csaba I. Pongor**, Zsolt Gengeliczki, Tomas Baer, Balint Sztaray, Dissociative photoionization of $\text{X}(\text{CH}_3)_3$ ($\text{X} = \text{N, P, As, Sb, Bi}$): mechanism, trends and accurate energetics, *Journal of Physical Chemistry A*, 13(28), **2009**, 8091–8098.
3. **Csaba István Pongor**, László Szepes, Rosemari Basi, Andras Bodi, and Bálint Sztáray. Metal–Carbonyl Bond Energies in Phosphine Analogue Complexes of $\text{Co}(\text{CO})_3\text{NO}$ by Photoelectron Photoion Coincidence Spectroscopy. *Organometallics* (submitted)

Additional articles related to the thesis:

4. Ágnes Révész, **Csaba I. Pongor**, Andras Bodi, Bálint Sztáray, and Tomas Baer, Manganese–Chalcocarbonyl Bond Strengths from Threshold Photoelectron Photoion Coincidence Spectroscopy, *Organometallics*, 25 (26), **2006**, 6061–6067.
5. Zsolt Gengeliczki, **Csaba I. Pongor**, and Bálint Sztáray, Assigning Photoelectron Spectra of Transition Metal Organometallic Complexes on the Basis of Kohn-Sham Orbital Energies, *Organometallics*, 25(10), **2006**, 2553–2560.

V. Literature

-
- ¹ Csákvari, B.; Nagy, A.; Zanathy L.; Szepes L.; *Magyar Kémiai Folyóirat*, **1992**, 98, 10.
- ² Vilesov, F.I.; Kurbatov, B.L.; Terenin, A.N.; *Soviet Physics (Dokl.)*, **1961**, 6, 490.
- ³ Turner, D.W.; Al-Joboury, M.I.; *J. Chem. Phys.*, **1962**, 37, 3007.
- ⁴ Brehm, B.; Puttkamer, E. v. Z.; *Naturforsch. A*, **1967**, 22, 8.
- ⁵ Werner, A. S.; Baer, T.; *J. Chem. Phys.*, **1975**, 62, 2900.
- ⁶ Keister, J. W.; Baer, T.; Evans, M.; Ng, C. Y.; Hsu, C. W.; *J.Phys.Chem.*, **1997**, 101, 1866.
- ⁷ Sztáray, B.; Baer, T.; *Rev. Sci. Instrum.*, **2003**, 74, 3763.
- ⁸ Bodi, A.; Sztaray, B.; Baer, T.; Johnson, M.; Gerber, T.; *Rev. Sci. Instrum.*, **2007**, 78(8), 084102(1–7).
- ⁹ Lichtenberger, D. L.; Gruhn N. E.; Renshaw, S. K.; *J. Mol. Struct.*, **1997**, 405, 79-86.
- ¹⁰ Pruchnik, F. P.; *Organometallic Chemistry of the Transition Elements*, Springer, New York, **1990**.
- ¹¹ Hirshfeld, F. L.; *Theor. Chim. Acta* **1977**, 44, 129.
- ¹² Bultinck, P.; Van Alsenoy, C.; Ayers, P. W.; Dorca, R. C.; *J. Chem. Phys.*, **2007**, 126, 144111.
- ¹³ Fonseca Guerra, C.; Handgraaf, J.W.; Baerends, E.J.; Bickelhaupt, F. M.; *J. Comp. Chem.*, **2004** 25, 189-210.
- ¹⁴ Baer, T.; Hase, W.L.; *Unimolecular Reaction Dynamics: Theory and Experiments*, Oxford University Press, New York, **1996**.
- ¹⁵ Bodi, A.; Sztaray, B.; Baer, T.; *Phys. Chem. Chem. Phys.*, **2006**, 8 (5), 613.
- ¹⁶ Bodi, A.; Kercher, J. P.; Baer, T.; Sztáray, B. *J. Phys. Chem. B*, **2005**, 109, 8393.

